Reconstructing adhesives : an experimental approach to organic palaeolithic technology

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An Experimental Approach to Organic Palaeolithic Technology

Paul R.B. Kozowyk

Reconstructing Adhesives: An Experimental Approach to Organic Palaeolithic Technology
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Layout and cover: Paul R.B. Kozowyk
About the cover: Drops of compound (left), resin (middle), and tar (right) adhesives; incomplete due to the impartial archaeological record and a lack of information on material properties. By combining data from experiments some of the gaps can be filled.
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An Experimental Approach to Organic Palaeolithic Technology

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“But the gum, being organic, has vanished like its organic users.”
John Greenway – Down Among the Wild Men

To my parents, for being stuck with me.

Contents

1. Introduction

The archaeological record of the Palaeolithic, as the name implies, is dominated by the presence of objects made from stone. Decay often limits the preservation of organic remains from the deep past, creating a biased view in the archaeological record. Yet under exceptional circumstances organic materials persist, providing a glimpse of the more unfamiliar materials and technologies of past populations (Hurcombe 2014). The scarcity of organic material, however, creates a problem in itself. Rare finds are often assigned great significance by archaeologists, while by the very nature of their rarity, little is known about the material itself.

As an example, it is widely accepted that the earliest adhesives and the role they played in hafting was an important advancement in the history of technology and in the evolution of the human mind (Ambrose 2001, 2010; Barham 2013; Haidle *et al.* 2015; Lombard 2007; McBrearty and Brooks 2000; Wadley 2010, 2013; Lombard and Wadley 2009; Coolidge and Wynn 2009). Adhesives, sometimes singular finds, have featured in many heated discussions about Neandertal and modern human cognitive and technological abilities (Coolidge and Wynn 2009; Marean 2015; Roebroeks and Soressi 2016; Wragg Sykes 2015; Wadley 2013; Lombard and Wadley 2009), yet our knowledge of the adhesive material itself is comparatively limited. The materials we engage with are an integral part of who we are (Malafouris 2013), and together with the fossil record are our only link to understanding where we came from. To comprehend the material world of the past, we must first therefore directly engage with the materials we want to understand (Ingold 2007). That is the principle aim of this thesis. Throughout the four research articles that follow, I will experimentally reconstruct and analyse aspects of adhesive manufacture, application, use, re-use and decay. By focusing on material properties, aspects fundamental to materiality and how we interact with and are shaped by our environment (Jones 2004), this thesis will answer several pressing questions about the technology and material choices made by Middle to Late Pleistocene humans.

Research context

Much of the research in Palaeolithic archaeology ultimately revolves around discovering what makes us human, and how we got here. Studying Neandertals provides a unique opportunity here. *Homo neanderthalensis* are our closest ancestral relatives, and are the most well researched of all extinct hominin species. They are distinctly human, yet still ‘not us’. Although there was some interbreeding (Prüfer *et al.* 2014), we survived to colonize every continent on Earth, and Neandertals disappeared approximately 40,000 years ago (Higham *et al.* 2014). Palaeolithic research thus often focuses on the behavioural, cognitive, and technological abilities of Neandertals compared with modern humans (Villa and Roebroeks 2014; Villa and Soriano 2010; Wadley 2013; Nowell 2010). At the forefront of this research over the past decade are debates about early fire production and use (Sorensen 2017; Sorensen *et al.* 2018; Dibble *et al.* 2018; Heyes *et al.* 2016; Roebroeks and Villa 2011; Aranguren *et al.* 2018; Stahlschmidt *et al.* 2015; Gowlett 2016), bone tool manufacture (Soressi *et al.* 2013), exploitation of marine resources (Cortés-Sánchez *et al.* 2011; Hardy and Moncel 2011), the presence of ornaments, pigments and symbolic behaviour (Zilhão 2011; Zilhão *et al.* 2010; Jaubert *et al.* 2016; Hoffmann *et al.* 2018a; Hoffmann *et al.* 2018b; Aubert *et al.* 2018; Bonjean *et al.* 2015; Dayet *et al.* 2014; Dayet *et al.* 2019; Roebroeks *et al.* 2012; Finlayson *et al.* 2012; Mellars 2010; Peresani *et al.* 2011), and finally, adhesive production and hafting (Degano *et al.* 2019; Niekus *et al.* 2019; Schmidt *et al.* 2019; Zilhão 2019).

At first glance, adhesives may not seem as significant or relevant to what makes us human as controlling fire or symbolic behaviour. Yet today, adhesives are an integral part of every-day life. They help hold together everything from the shoes we walk on to the electronics we use to communicate. During the Middle and Late Pleistocene, adhesives were used for backing or hafting stone tools – creating a handle to improve prehension and efficiency (Fig. 1). A process which fundamentally altered the way humans made and used tools (Barham 2013). Beyond this, adhesives are a practical material for studying human behaviour for a number of reasons. They come from a range of environmental sources and have different functional roles, as well as unique appearances, colours, tactility, smells and tastes. Differences in adhesive technology are therefore likely to represent decisions made by ancient humans, providing a window onto their behaviour (cf. Sillar and Tite 2000). Adhesives often require the controlled use of fire to produce, undergoing chemical and physical transformations and can also be freely moulded, shaped, combined and re-used. This makes them the first transformative, additive and plastic technology.

It could be argued that other technologies included any one of these aspects. Fire, cooking, heat treating lithics, or altering pigment could be considered transformations. Hafting is an additive technology, and perhaps playing with wet clay could be considered plastic. Whether these all preceded the first use of adhesives is another question. Yet one thing remains certain; they do not individually meet all of the criteria. Transformative metallurgy, or the ability to transform copper ore into bronze by adding tin, is the first time another technology satisfies all three criteria. It is transformative (the molecular structure is altered, creating an entirely new material), additive (a mixture of tin and copper creates bronze, which can also be melted and combined into larger pieces), and plastic (the material can be freely moulded and shaped). Ceramic technology is similar, but is only plastic before it has been fired. Transformative metallurgy is seen as a technological paradigm shift, fundamentally altering the way humans understood and interacted with the materials of their environment (Golden 2010). Adhesives share many of these qualities, yet appear more than 150,000 years before the advent of ceramics and metallurgy.

Fig. 1. Two recreated examples of adhesive hafts. A backing made of pine resin, beeswax and red ochre (left) providing a safer grip for a flint knife. And birch bark tar used to glue a flint spear point to a wooden handle. Both allow the tools to be used more easily, safely, and with greater force.

In 1996, direct evidence of adhesives used by Pleistocene humans was published, (Boëda *et al.* 1996) and its implications and significance summarily discussed (Holdaway 1996). Five years later, a clear case was made for the importance of adhesives in the discussion about Neandertal cognition and technology. Two lumps of tar (also referred to as pitch) found in an open pit mine near Königsaue, Germany were chemically analysed and discovered to have originated from birch bark (Koller *et al.* 2001; Grünberg *et al.* 1999). The intentional production of birch bark tar by Neandertals was seen as a clear sign of their considerable technical abilities (Koller *et al.* 2001). The same year it was suggested that the production of composite tools (containing a handle, stone insert, and binding material) is analogous to grammatical language, in which hierarchical assemblies can be combined or recombined for different functions (Ambrose 2001). Explaining how to make a composite tool was also said to be the equivalent of sharing a recipe or telling a short story, suggesting Neandertals were likely able to speak (Ambrose 2001). Yet at the time this was written, very little was actually known about adhesives during the Palaeolithic. It was unclear how birch bark tar could have been produced, or even discovered, using Neandertal technology. It was also unknown what types of adhesives contemporaneous modern humans in Africa were using, or what these were like to make.

Experimental studies a few years later showed that red ochre, present on a number of Middle Stone Age backed artefacts from Rose Cottage and Sibudu Caves in South Africa, served a functional role by making adhesives stronger and easier to manipulate (Wadley 2005). The distribution patterns of ochre on Howiesons Poort segments also suggests that Middle Stone Age humans were using different adhesive recipes depending on the raw material of the tool (Lombard 2007), corroborating the functional use of ochre.

Further experimental work by Wadley (2010) and Wadley, Hodgskiss and Grant (2009) explored the role of ochre in compound adhesives in greater detail. The research by Wadley put forth the hypothesis that compound adhesive manufacture can be used as a proxy for modern cognition (Wadley 2010, 2013; Wynn 2009). On top of combining different parts of a composite tool, Wadley detailed that manipulating adhesives required mental processes such as forward planning, mental rotation and abstraction. The adhesives needed to be kept in attention and rotated near a fire while the artisan balanced the handle and position of the tool with the consistency of the adhesive and the heat of the fire (Wadley 2010). The addition of disparate materials without adhesive-like characteristics of their own, collected at different times and in different places, to improve and transform the material, balancing properties such as tack and viscosity, point to modern-like levels of cognitive ability (Wadley 2010; Wadley *et al.* 2009; Ambrose 2010).

The discovery of Neandertal associated adhesives from as old as 191,000 years ago (Mazza *et al.* 2006) pushed the discussion about adhesive technology back to the Middle Pleistocene. Further Middle Palaeolithic adhesive finds (Boëda *et al.* 2008b) helped open up comparisons between Neandertal and modern human adhesive and hafting technologies. Villa and Soriano (2010) suggest that the transport and use of sandy balls of a naturally occurring tar-like petroleum substance known as bitumen for hafting Levallois artefacts and the distillation of tar from birch bark are clearly analogous to early modern human technological capacities. Tar production by Neandertals has since been used as evidence of the controlled use of fire and a clear demonstration of their technological and cognitive abilities. Most frequently referenced is the complexity of producing tar without modern fire-resistant containers and the strict control of fire temperatures (Roebroeks and Soressi 2016), often stating that temperatures must be kept between 340 and 400 °C (Zilhão 2011; Roebroeks and Villa 2011; Wragg Sykes 2015). However, claims of the narrow range of temperatures were overzealous, as tar can actually be produced at temperatures above and below what was previously stated (Şensöz 2003; Puchinger *et al.* 2007).

Wragg Sykes (2015) gives the most in-depth look at Neandertal tar technology, providing a possible *chaîne opératoire* of a birch tar hafted tool, and describing the greater cognitive, social and behavioural implications. She concludes that Neandertal tar production is equivalent to early modern human compound adhesive use in southern Africa. Both required advanced cognitive capacities such as enhanced working memory and attendant executive processing (Wragg Sykes 2015). Perhaps even more intriguing, are the effects that the recognition of a fundamental and non-reversible transformation of matter might have had on the way humans understand and engage with the material world (Wragg Sykes 2015). Over evolutionary spans of time these interactions with materiality have the potential to yield new brain structures, influencing the development of the human capacity for conceptual thought (Overmann and Wynn 2019). However, unlike the lithic record, one of the examples used by Overmann and Wynn (2019) to postulate the effects of materiality on human cognition, evidence for early adhesive technology is not so abundant. Further, many of the discussions and arguments given above are based on how Middle Palaeolithic and Middle Stone Age adhesives were produced, and how they behave; empirical information for which is limited in the archaeological record, but can be expanded on thorough experimentation.

Archaeological context

It is important to describe the known archaeological material before proceeding with the methods and aims of this thesis. I have already stated that preservation of adhesives and other organic artefacts from the European Middle Palaeolithic and African Middle Stone Age is rare. Here I will present a brief overview of the relevant archaeological material to help clarify just how scarce securely dated and chemically identified adhesives are (Fig. 2).

Currently, the oldest known adhesives are two approximately 200,000 year old flint flakes containing lumps of birch tar from Italy (Mazza *et al.* 2006). Other securely dated and chemically identified birch bark finds come from Zandmotor, the Netherlands (Niekus *et al.* 2019) and Königsaue, Germany (Koller *et al.* 2001). Similar to the Campitello find, the Zandmotor piece is an unretouched flint flake with a significant portion still encased in birch bark tar. It has been directly dated to approximately 50,000 years ago (Niekus *et al.* 2019). At Königsaue, two lumps of tar were found, no longer adhering to any flint. However, one of these pieces does show impressions of what is thought to be a bifacial knife, a fingerprint, and some wood fibres, suggesting it may have been used as part of a haft. The two Königsaue pieces were also directly dated, providing minimum ages of 43,000 and 48,000 years ago (Koller *et al.* 2001).

Adhesives likely associated with Neandertals, have also been found at sites in Syria, Romania, and Italy. Umm el Tlel, Syria yielded bitumen residues on flint artefacts from approximately 71,000 years ago (Boëda *et al.* 2008b; Bonilauri *et al.* 2007). At the nearby site of Hummal, artefacts containing residues which were also identified as bitumen, dating between approximately 80,000 and 50,000 years ago were found (Hauck *et al.* 2013; Monnier *et al.* 2013). At Gura Cheii-Râşnov Cave, Romania, bitumen residues were identified with potential attribution to a very young Mousterian layer of approximately 30,000 years ago. At Fossellone Cave, Italy, flakes and scrapers with pine resin and possibly beeswax were found dating between 55,000 – 40,000 (Degano *et al.* 2019). At Sant'Agostino Cave, Italy, additional flakes and scrapers were found with pine resin residues dated to approximately 43,000 years ago (Degano *et al.* 2019). Roughly contemporaneous with these last two, but attributed to anatomically modern humans is evidence of a mixture of plant gum and ochre at the Uluzzian site of Grotta del Cavallo, Italy (Sano *et al.* 2019). Although while the materials mentioned above were all identified with gas chromatography mass spectrometry, at Grotta del Cavallo, only Fourier transform infrared spectroscopy was used, making the precise nature of the organic component more tenuous.

Apart from the securely dated and identified adhesives, several more sites contain possible evidence of adhesive use by Neandertals in Palaeolithic Europe. The following examples suggest that adhesive residues may be more widespread than previously indicated, although current thorough analysis of the adhesives themselves remains relatively limited. The site of Inden-Altdorf, Germany contains numerous micro-residues dating to between 128,000 and 114,000 years ago believed to be birch bark tar on the basis of SEM-EDX and optical microscopy (Pawlik and Thissen 2011). At El Sidrón, Spain, indirect evidence of bitumen use has been suggested by the presence of bitumen residues in the dental calculus of one Neandertal individual (Hardy *et al.* 2012). Residues associated with hafting, but not subjected to any chemical analysis have also been found at Starosele (80–40,000 BP), Ukraine (Hardy *et al.* 2001). Numerous other examples of hafting based on microwear, morphology, and impact fractures have been identified (Solecki 1992; Lenoir and Villa 2006; Rots 2009, 2015; Shea 1997; Shea *et al.* 2002), but without the presence of adhesives these will not be discussed further.

Contemporaneous with many of the finds from western Eurasia, are residues identified as belonging to the Middle Stone age at three different sites in South Africa. At Border Cave, artefacts were found to contain a possible tar produced from yellowwood (*Podocarpus*) bark between 43,000 and 40,000 years ago (Villa *et al.* 2012). Alternatively, this material may have been heated and partially pyrolysed yellowwood resin. Diepkloof Rock Shelter yielded one analysed Late Howiesons Poort (60,000–55,000 BP) quartz flake containing resin originating from the yellowwood tree (Charrié-Duhaut *et al.* 2013). At Sibudu, two Howiesons Poort segments contain similar yellowwood resin, dated to between 65,000 and 62,000 years old (Villa *et al.* 2015).

More evidence of potential adhesive use from the African Middle Stone Age has been identified based on the presence of microscopic residues, including ochre and possibly resin from Sibudu and Rose Cottage Cave, South Africa (Gibson *et al.* 2004; Lombard 2006b). Further, hafting inferred from microwear analysis and the presence of ochre has been identified at three sites in Northeast Africa spanning approximately 150,000 years of the Middle Stone Age (Rots *et al.* 2011).

This puts the number of Middle Palaeolithic sites containing securely dated and chemically identified adhesive residues at five from Europe (six if Gura Cheii-Râşnov Cave, Romania, and seven if Grotta del Cavallo, Italy are included). Two Middle Palaeolithic sites from the Levant, and three Middle Stone age sites in Africa meet the same criteria (Fig. 2).

Although preservation makes residues rare, hafting appears to be widespread throughout western Eurasia and Africa during the late-Middle and Late Pleistocene. Among both Neandertal and African human populations, different adhesives and adhesive mixtures were used. Further, tools hafted with adhesives were clearly employed for a wide variety of tasks, including cutting, scraping, piercing, and for projectiles or hunting implements (Hardy 2004; Hardy *et al.* 2001; Lombard 2006b; Rots 2009, 2013; Rots *et al.* 2015). Due to the available varieties, improving our understanding of ancient adhesive materials will greatly aid in our understanding of the technological choices of these past populations. How this is accomplished in this thesis will be the topic of the following section.

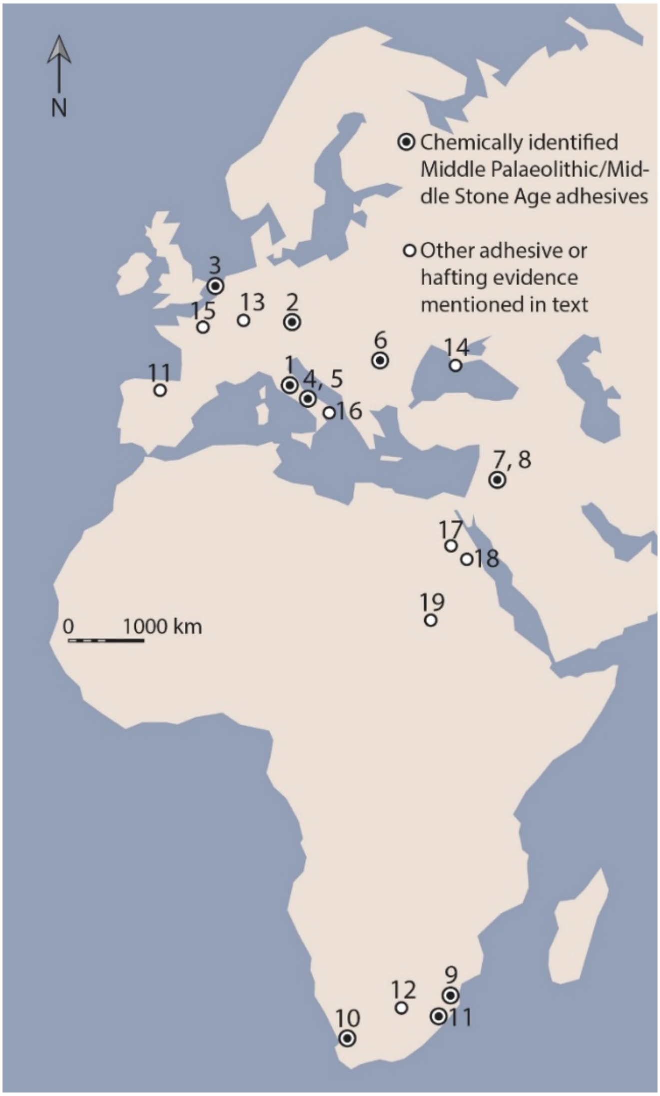

Fig. 2. Map of Africa and western Eurasia showing the location of all known sites containing Middle Palaeolithic or Middle Stone Age adhesives that have been securely chemically identified, and other sites referenced in the text. 1) Campitello Quarry, Italy: birch bark tar, >191 ka. 2) Königsaue, Germany: birch bark tar, ~45 ka. 3) Zandmotor, the Netherlands: birch bark tar, ~50 ka. 4) Fossellone Cave, Italy: pine resin, beeswax, 55–40 ka. 5) Sant'Agostino Cave, Italy: pine resin, ~43 ka. 6) Gura Cheii-Râşnov Cave, Romania: bitumen, ~30 ka. 7) Umm el Tlel, Syria: bitumen, ~71 ka. 8) Hummall, Syria: bitumen, 80–50 ka. 9) Border Cave, South Africa: yellowwood tar or resin, 43–40 ka. 10) Diepkloof Rock Shelter, South Africa: yellowwood resin, 60–55 ka. 11) Sibudu, South Africa: yellowwood resin, ochre, 65–62 ka. 12) Rose Cottage Cave, South Africa: ochre, possible resin, 68–60 ka. 13) Inden-Altdorf, Germany: possible birch bark tar, 128–114 ka. 14) Starosele, Ukraine: hafting residue, 80–40 ka. 15) Biache-St-Vaast: hafting wear traces, ~253 ka. 15) El Sidrón, Spain: bitumen in dental calculus, 51–47 ka. 16) Grotta del Cavallo, Italy: gum, ochre, 45–40 ka. 17) Taramsu, Egypt: hafting wear traces, Nubian. 18) Sodmein Cave, Egypt: hafting wear traces, Nubian. 19) Sai 8-B-11, Sudan: hafting wear traces, <60 ka.

Approach

There are two approaches to improve our understanding of ancient adhesive use. First, archaeologists can seek out new discoveries or explore ways to obtain more information from the archaeological material itself. This provides new data that is helpful in answering *what* materials were Neandertals using for adhesives? Or w*hat* types of tools did they haft with adhesives? The answers to these questions have been, in part, discussed in the previous section, although new finds will undoubtedly create a far more complete picture. When dealing with organic remains from a period as remote as the Middle Palaeolithic, however, there will always be missing and partial information. The second way we can improve our understanding of ancient adhesives is by comparison to ethnographic and experimental references. This approach helps answer questions as to *why* certain adhesives were used for particular tools or tasks.

Using ethnographic analogies has a long history in Palaeolithic Archaeology as a way of bridging the gap between the present and fragmentary archaeological record, and the behaviours of past populations. By combining resources from ethnography, primatology, experimentation and archaeology we are able to interpret the fragments of remaining material to the best of our ability (Atici 2006). Ethnographic analogy and experimental archaeology have long since been used in many prominent Palaeolithic discussions (Binford *et al.* 1988; Binford *et al.* 1985; Dibble and Whittaker 1981; Kuhn 1989). Ethnography has also played a direct part in discussions about ancient adhesives (Sahle 2019; Wadley *et al.* 2015; Binford 1984).

Experimenting with adhesives

Some of the earliest experiments in archaeology were concerned with distinguishing naturally and artificially flaked stones (Evans 1897; Lin *et al.* 2018). Knowledge of flintknapping, and of the processes and fracture mechanics involved, have allowed for a thorough understanding and recreation of the production processes and chaîne opératoires of stone tools (e.g. Rezek *et al.* 2011; Dibble and Rezek 2009; Dibble and Pelcin 1995; Dibble 1997; Soressi and Geneste 2011; Cotterell *et al.* 1985). This has culminated in a level of understanding whereby differences in production sequences can be used to explain the degree of social intimacy between Neandertals and early modern humans in Europe (Roussel *et al.* 2016). No such research history or body of knowledge exists for Palaeolithic adhesives.

That is not to say that there have been no experiments on ancient adhesives. Only that compared with lithics, adhesive experiments are in relative infancy. In the 1980s experimental work explored the role of ochre in Upper Palaeolithic adhesives (Allain and Rigaud 1986; Allain and Rigaurd 1989). Since then a number of studies have investigated other aspects of adhesive production and use. These include testing tar production methods (Piotrowski 1999; Pomstra and Meijer 2010; Osipowicz 2005; Rageot *et al.* 2018; Schenck and Groom 2016; Schmidt *et al.* 2019; Pfeifer and Claussen 2016), re-heating of Australian resins (Parr 1999), the benefits of adding ochre to resin and gum adhesives (Wadley 2005, 2010; Wadley *et al.* 2004), the influence of filler particle size and surface roughness on adhesive performance (Zipkin *et al.* 2014), and the role of fire in the life of an adhesive (Cnuts *et al.* 2017). Additionally, extensive experimental work has been conducted which, although aimed at lithic analysis, particularly impact fractures and wear, makes direct use of adhesives in the tests (Barton and Bergman 1982; Fauvelle *et al.* 2012; Hutchings 2011; Iovita *et al.* 2014; Pétillon *et al.* 2011; Pokines 1998; Schmitt *et al.* 2003; Shea *et al.* 2002; Sisk and Shea 2009; Waguespack *et al.* 2009; Moss and Newcomer 1982; Gaillard *et al.* 2015).

Despite the breadth of these experiments, there remains a number of areas where further research is still necessary. First, although there have been numerous studies into the Palaeolithic distillation of birch bark into tar, very few have been successful in producing useable quantities of tar. Second, the benefits of adding ochre have primarily been tested by actualistic studies, lacking a quantification of specific performance metrics. Third, the re-use of materials is an important aspect of Palaeolithic technologies (Venditti *et al.* 2019; Vaquero 2011) and has been understudied, particularly with regards to Palaeolithic adhesive materials. Fourth, many of the performance experiments that have been described above (with the noted exception of Zipkin *et al.* 2014) test adhesives as part of a complete hafted system. Evidence shows that adhesives were used for a number of different tool types and functional roles (Rots 2013). To test each of these functions and hafting forms poses significant logistical challenges. Experiments that test bulk properties, that is, material properties of the adhesives itself, independent from joint geometries, are therefore more practical for initially comparing materials for a wide range of applications (Petrie 2000). Finally, very little is known about the post depositional decay on different adhesive types, and how this affects what survives to the present. The experiments in this thesis address the issues outlined above and will be explained in greater detail below.

Research Assumptions

There are some limitations and assumptions to both ethnographic and experimental approaches to studying adhesives. Using analogies without considering these assumptions may therefore be misleading and over-stepping. First, as a significant limitation of a purely ethnographic approach, there is no contemporary population that produces birch bark tar using technology similar to that from the Palaeolithic. Specific questions regarding birch tar technology can therefore not be directly addressed. Second is a wider problem which also encompasses some experimental work. When parallel examples do exist between the ethnographic and Palaeolithic record, the cognitive processes of humans operating within a specific cultural context are used to explain past material in a modern-centric way (Garofoli 2016; Lin *et al.* 2018). The line is blurred even further when the population in question did not share the same brain shape or ontogeny as us, as was the case with Neandertals (Hublin *et al.* 2015; Gunz *et al.* 2010; but see also: Ponce de León *et al.* 2016). We are implicitly biased in trying to understand materials and devising experiments to look at aspects which we, today, find significant or important. This is no guarantee that ancient hominins thought about them in the same way as us, or even thought about them consciously at all (cf. Corbey *et al.* 2016).

Other assumptions that are commonly left implicit in experimental archaeology are uniformitarian in nature. Uniformitarian assumptions comprise a significant part of how we study the past and should be stated explicitly (Faith and Lyman 2019; Domínguez-Rodrigo 2008; Lin *et al.* 2018). It seems obvious that natural processes and physical properties, such as fracture mechanics, molecular adhesion, and thermodynamics, operate today as they did in the Palaeolithic (Eren *et al.* 2016; Lin *et al.* 2018). But what of the materials these processes were acting on? It is unlikely that flint is any different now than it was 100,000 or even 3 million years ago. What about the resin from a pine tree, or the tar from birch bark? Perhaps there were slight differences during the Palaeolithic, but these most likely fall well within the range of natural variation among trees today (cf. Holonec *et al.* 2012; O'Connell *et al.* 1988). Species such as pine and birch are still recognizable during the Pleistocene, (Bertran *et al.* 2008; Bigga *et al.* 2015) and the physical principles which govern natural adhesive functional requirements (adhesion, phase/state changes, pyrolysis) remain the same.

Another assumption relates to the material acquisition. Most of the adhesive materials used for the research in this thesis were either commercially purchased, or produced in a laboratory. In this case it was considered that the benefits from controlling variables and using highly replicable materials outweighed the improved likeness to Palaeolithic materials by using naturally sourced ingredients. A similar example would be using glass for lithic flaking experiments (Dibble and Rezek 2009). In attempting to determine fundamental principles of flake shape and size, using natural flint, or naturally sourced resins, introduces too many variables.

As long as archaeologists acknowledge these assumptions, and understand the limits, experimentation is a valuable aid in Palaeolithic archaeology. There are fundamental questions that can be answered and data that can be produced using experiments, which reinforce hypotheses and theories about technologies in ancient societies and peoples (Outram 2008). With a combination of actualistic and laboratory experiments, and careful consideration of the research questions and limitations, experiments can provide a solid framework for studying past behaviour.

Aims

For all of the discussion surrounding Middle Palaeolithic and Middle Stone age adhesives, remarkably little work has been done on the methods of production, and the properties and preservation of the materials themselves. Discussions are often centred on Neandertals or Middle Stone Age humans, and what they did with adhesives, or how adhesives reflect increasing cognitive capacity. Because there is no overview of the material itself, the discussion of the technology is incomplete, lacking a clear empirical base. How can we discuss Neandertal control of fire or technological complexity if we do not understand the temperatures needed to create tar and what techniques were at their disposal? How can we discuss the efficacy of compound adhesives production and its implications for the cognitive capacities of Pleistocene humans without understanding the extent to which different materials and their ratios affect the properties of compound adhesives? And finally, how can we assign significance to the presence of certain adhesive types without knowing how distorted what we find in the archaeological record is due to taphonomic processes?

I will therefore use the material as a starting point for this thesis, exploring the different stages in the lives of different natural adhesives from their first production through to their re-use and the effects of taphonomic decay after being discarded. I will show what influence the materials, their production and properties have on the technological developments of the Middle to Late Pleistocene. This type of empirical information on material properties, gained only through experimentation, is necessary if we wish to further the discussion in any meaningful way. No matter whether we want to test theories against data, or fit data into a coherent story (Hodder 2004, 28), we first need more data to begin with.

Research questions

To address the issues outlined above, this thesis is divided into four independent research papers. These papers will answer the following primary research questions:

1. How was birch tar first discovered and then produced using Palaeolithic technology?
2. How do ingredient ratios influence adhesive performance and the efficacy of compound adhesive production?
3. Why did Neandertals use birch bark tar despite the high investment in time, resources, and production complexity?
4. Is there a preservation bias favouring certain adhesive types in the archaeological record?

Answering the above questions will help resolve some of the broader issues associated with ancient adhesive studies. For example:

a) Different tar production strategies have implications for our understanding of the complexity of Neandertal technology and mastery of pyrotechnology. Knowledge of different potential tar production methods is therefore necessary to understand the range of technologies at their disposal, and also what we should look for in the archaeological record.
b) The suitability of compound adhesives as a proxy for studying complex cognition. Currently, there is little empirical data on the performance of compound adhesives, making comparisons with other materials and ingredients difficult, thus hampering discussions about behaviour and cognition.
c) The material choices made by Neandertals. Without a comparison of adhesives and their relevant material properties it is impossible to assess why certain materials were used and others were not.
d) Finally, how accurately does the archaeological record reflect what was being used in the past. Preservation of organic material is highly dependent on burial conditions. However, there also exists considerable variation among natural adhesive types and it is unknown what effect this has on their preservation.

Thesis outline

Chapter 1 – introduction. The current chapter includes background information on the current state of Palaeolithic adhesive research and archaeological adhesive findings, and states the research questions and assumptions.

Chapter 2 – birch tar production provides an explanation as to how the oldest, and potentially most complex and costly, known adhesive technology was discovered and developed. Without a solid framework for how birch tar can be produced using Palaeolithic technology furthering discussions about the cognitive and technological abilities of Neandertals based on this technology is not possible. By testing the efficiency of three distinct tar production techniques, we created a framework for how Neandertals may have initially recognised birch bark tar, and developed the process into more efficient methods of tar production necessary to produce the large volumes we find associated with individual Neandertal artefacts.

Chapter 3 – adhesive efficacy uses modern internationally recognized materials testing standards (ASTM) to further understand the functional role of ochre and beeswax in resin and gum adhesives. The hypothesis that adhesives can provide a proxy for studying the cognition of Pleistocene humans was first raised based on the identification of ochre hafting residues on Middle Stone Age artefacts from southern Africa (Wadley 2010). However, these tests were primarily field-based actualistic experiments. In order to further substantiate this hypothesis, I conducted a series of lap shear and impact tests following ASTM protocols. The aim of this research was twofold: 1) To test whether ingredient ratios play a significant role in the performance of a Stone Age adhesive, supporting the hypothesis that the Middle Stone Age people who made compound adhesives must have been skilled artisans. 2) To employ modern standardized testing to answer an archaeological question, creating a body of experimental material property data that can be used as a reference for future work. The increase in the use of experimental archaeology to answer questions about the deep past has been increasing, and the ability to conduct replicable and reliable tests is more important than ever before.

Chapter 4 – Use and re-use expands on chapter three by testing a greater number of material qualities that are important for stone tool hafting adhesives. While the lap shear tests in chapter 3 are useful in expediently comparing the static performance of an adhesive, real life applications call for a more dynamic method of testing. Rheology, hardness measurements after differential heating, and thermogravimetric analysis, provide a far more thorough account of Palaeolithic adhesive performance. This chapter also shifts the focus from the African Middle Stone Age, to the European Middle Palaeolithic, with an emphasis on studying birch bark tar – a material used by Neandertals since the Middle Pleistocene. There have been multiple discussions about Neandertal adhesive use, in direct comparison with that of anatomically modern humans in southern Africa, with very little experimental work or understanding of the adhesives themselves and how they compare (cf. Villa and Soriano 2010). This chapter contributes significantly to our understanding of the material properties of Palaeolithic adhesives, and the technological choices associated with making and using different natural adhesive types.

Chapter 5 – preservation represents one of the final stages in the life of an adhesive. Taphonomy plays an important role in all of archaeology, but becomes even more significant the farther back in time one goes, especially when dealing with organic materials. Understanding the role of taphonomy on the life of an adhesive from the Middle to Late Pleistocene is therefore of the utmost importance. This chapter explores the issue of adhesive preservation by leaving replica adhesives and flint flakes, some with wood handles and some without, to weather naturally at two different locations for six months, two years, and three years. The differential preservation of natural adhesives provides an explanation for why we find what we do in the archaeological record. It also greatly increases the scope for future research by suggesting the number of adhesive types used in the past may well have been far greater than what we find today.

Chapter 6 – conclusion. The final chapter synthesizes chapters two to five, summarizing answers to the research questions and describing how they fit into a narrative of early modern human and Neandertal technological choices and abilities, as well as providing scope for future research.

2. Birch tar production

Experimental methods for the Palaeolithic dry distillation of birch bark: implications for the origin and development of Neandertal adhesive technology

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Abstract

The destructive distillation of birch bark to produce tar has recently featured in debates about the technological and cognitive abilities of Neandertals and modern humans. The abilities to precisely control fire temperatures and to manipulate adhesive properties are believed to require advanced mental traits. However, the significance given to adhesive technology in these debates has quickly outgrown our understanding of birch bark tar and its manufacture using aceramic techniques. In this paper, we detail three experimental methods of Palaeolithic tar production ranging from simple to complex. We recorded the fuel, time, materials, temperatures, and tar yield for each method and compared them with the tar known from the Palaeolithic. Our results indicate that it is possible to obtain useful amounts of tar by combining materials and technology already in use by Neandertals. A ceramic container is not required, and temperature need not be as precise as previously thought. However, Neandertals must have been able to recognize certain material properties, such as adhesive tack and viscosity. In this way, they could develop the technology from producing small traces of tar on partially burned bark to techniques capable of manufacturing quantities of tar equal to those found in the archaeological record.

Introduction

The manufacture and use of adhesives for hafting has become a focal point in the debate about the cognitive and technological capabilities of Neandertals and early modern humans (Kozowyk *et al.* 2016; Lombard 2007; Villa and Roebroeks 2014; Wadley 2010; Wynn 2009; Villa and Soriano 2010; Wragg Sykes 2015). Adhesives are one of the earliest transformative technologies known (Wadley 2013) and tar production is at least 200 thousand years old (ka) (Mazza *et al.* 2006). Tar is synthesized from the dry (destructive) distillation of organic material, commonly birch bark (*Betula* sp.) or pine wood (*Pinus* sp.). Tar distillation is thought to be a complicated process requiring forward planning, knowledge of materials and abstraction (Wragg Sykes 2015; Koller *et al.* 2001). The oldest known tar-hafted stone tools were discovered at a Middle Pleistocene site in Italy, during a time when only Neandertals were present in Europe (Mazza *et al.* 2006). Tar lumps and adhesive residues on stone tools were also found at two Neandertal sites in Germany dating to 40-80 ka and ~120 ka respectively (Koller *et al.* 2001; Pawlik and Thissen 2011). Direct evidence for adhesive use in Africa is more numerous but only goes back to ~70 ka (Lombard 2006a, 2007). It has been argued that the innovative nature of compound adhesive manufacture in southern Africa is a proxy for complex cognition (Wadley 2010; Wadley *et al.* 2009). Yet compound adhesives share many similarities to birch bark tar production (Wragg Sykes 2015; Koller *et al.* 2001) and may be equally sensitive to additives or post-production processes (Kozowyk *et al.* 2017a). Tar production in Palaeolithic Europe has in turn been used to argue for similarities between the technological capabilities of Neandertals and their near-modern contemporaries in Africa (Roebroeks and Soressi 2016; Villa and Roebroeks 2014; Wragg Sykes 2015). It is presently unknown why evidence of tar production by modern humans is much younger, but if birch bark is more suitable for making tar than other materials, then the absence of birch in Africa might be one explanation.

In historic and modern periods, tar was produced on an industrial scale using large earth mounds, or in kilns using ceramic or metallic containers. It is unclear how tar was produced during the Pleistocene when ceramic containers are rare or unknown. Previous experimental attempts at tar manufacture using aceramic or Palaeolithic technology often lack detail. Furthermore the resulting tar yield is unknown or too small to be measured (e.g. superficial residues coating a thermocouple (Schenck and Groom 2016)), and are thus not enough to effectively haft a tool (Groom *et al.* 2013; Osipowicz 2005; Pomstra and Meijer 2010; Pfeifer and Claussen 2016; Palmer 2007). The significance birch tar production is given in debates about Neandertal and modern human technology and cognition (cf. Roebroeks and Soressi 2016; Villa and Roebroeks 2014; Wragg Sykes 2015; but see also: Coolidge and Wynn 2009) has therefore outgrown our knowledge of the material and its production processes. We cannot fully understand the cognitive complexities and reconstruct the required degree of innovation associated with tar manufacture if we do not know what production methods were available.

Here we present an experimental study testing the dry distillation of birch bark to produce tar using variations on previously explored potential Palaeolithic techniques: the 'ash mound' (AM) method (Pomstra and Meijer 2010), the 'pit roll' (PR) or cigar roll method (Pawlik 2004; Pawlik and Thissen 2011; Pawlik 1995), and the 'raised structure' (RS) method (Schenck and Groom 2016; Osipowicz 2005; Pfeifer and Claussen 2016; Groom *et al.* 2013; Piotrowski 1999; Surmiński 1997). We assessed these production methods in three ways:

1) Yield – time and fuel spent versus tar quantity obtained,
2) Temperature – required degree of temperature control to successfully produce tar,
3) Complexity – number of individual components (cf. technounits (Oswalt 1976)) and the number of steps (Perreault *et al.* 2013) required to produce tar.

The detailed account of aceramic tar production methods described here provide a new empirical baseline to reconstruct the origin and the evolution of tar technology and its associated cognitive skills through the Pleistocene.

Results

Experimental tar

The tar we produced was a dark brown/black material that varied in consistency somewhat depending on the method. We use the term 'tar' here rather than 'pitch' because our experimental products varied in consistency depending on the method and ambient temperature. Tar more accurately describes the complete material initially produced during destructive distillation, while pitch is generally more solid, and may require further refinement (Collin and Höke 2005). The ash mound produced tar tended to be the hardest, as many of the liquid volatiles can easily escape during production due to the porosity of the ash. The pit roll and raised structure methods produced a softer material. They contained only slight charcoal and soil contamination. All of the experimental tars would be suitable for hafting at the ambient temperature they were produced at (~5 °C), but the pit roll and raised structure tars became somewhat softer at room temperature (Fig. 1).

The tar yield described below uses data from our most successful experimental attempts. This reduces any potential bias that may exist due to our own skills and learning curve. There is very little modern expertise regarding producing birch bark tar aceramically. Our results indicate a starting point, and should not be considered the maximum possible output rate, or be used to directly interpret how long it would take Neandertals to make tar. All the data from our experiments are provided in the Supplementary Information to help reproducibility and explain in detail what the values represent.

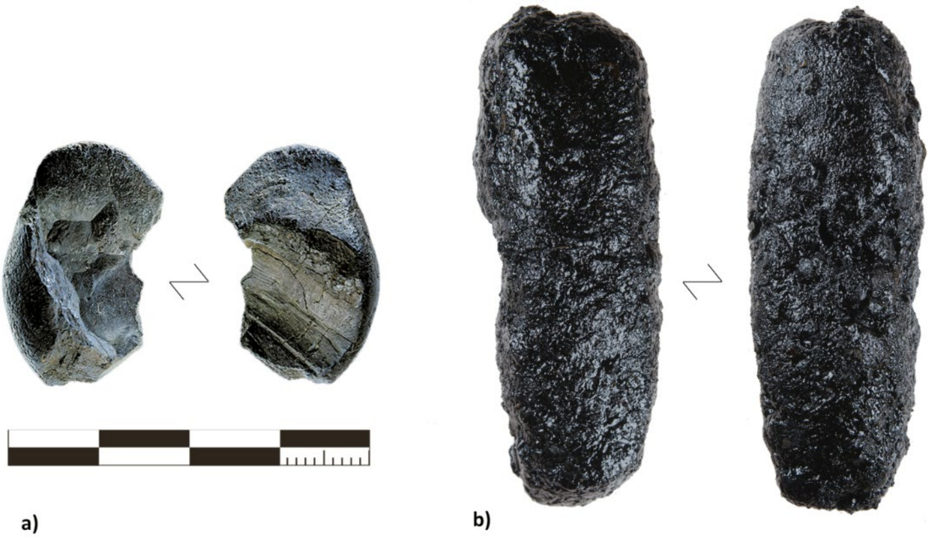

Fig. 1. A) The larger of the two tar lumps found at Königsaue (photo credit: Landesamt für Denkmalpflege und Archäologie Sachsen-Anhalt, Juraj Lipták)

compared with B) the maximum yield of tar produced with the raised structure method (RS 7).

Ash mound

Up to approximately 1.0 g of tar per 100 g of bark was obtained using the ash mound technique. Ambers and ash were placed over a bark roll, tied with fresh wood fiber to keep it tight. No vessel, pit or structure is required using this technique. Tar was collected between the bark layers and could be scraped off (Supplementary Figure S1). However, because the roll was in direct contact with embers from a glowing fire, care needed to be taken to balance the ratio between embers and ash. Ash keeps the oxygen out, but too much will lower the temperature. Likewise, too many embers can raise the temperature and oxygen content and tar will burn before being collected.

Pit roll

Techniques similar to the one described by Pawlik (2004), in which a roll of bark is ignited and placed burning side down into a small pit with a pebble at the bottom to collect the tar, were found to be unsuccessful. The temperature was never high enough or sustained for a long enough period of time to produce tar (Supplementary Fig. S2). The pebble used to collect the tar was blackened due to the burning roll being placed on top, but no tar was found. Rather than placing the burning end in a pit, we were successful when hot embers were placed on top of the bark to provide continuous heat. Pyrolysis oils and tar dripped out of the bottom of the bark roll in small quantities, and in one case (PR11) a considerable amount of tar (1.8 g) was collected in the birch bark vessel placed below the roll (Supplementary Fig. S3). In some experiments tar was also collected from between each layer of bark in a similar manner to the ash mound method. Using the pit roll technique with capping embers and bark container, the maximum tar output was 2.4 g per 100 g of bark.

Raised structure

Here we adapted a method described by Groom and Schenck (2013); a birch bark container is placed in a pit, an organic mesh covers the pit and on the mesh we placed a large loose roll of bark the bark is covered with clay and a fire is lit over the mound (Supplementary Figure S10). This method resulted in the most variable output of tar, but when successful it gave the highest yields by a large margin (Fig. 2). Despite requiring the longest set-up and run-time, as well as using the most firewood, it was the most successful and efficient method. We achieved a maximum tar yield using this technique of 9.6 g per 100 g of bark, or a total of 15.7 g from one attempt.

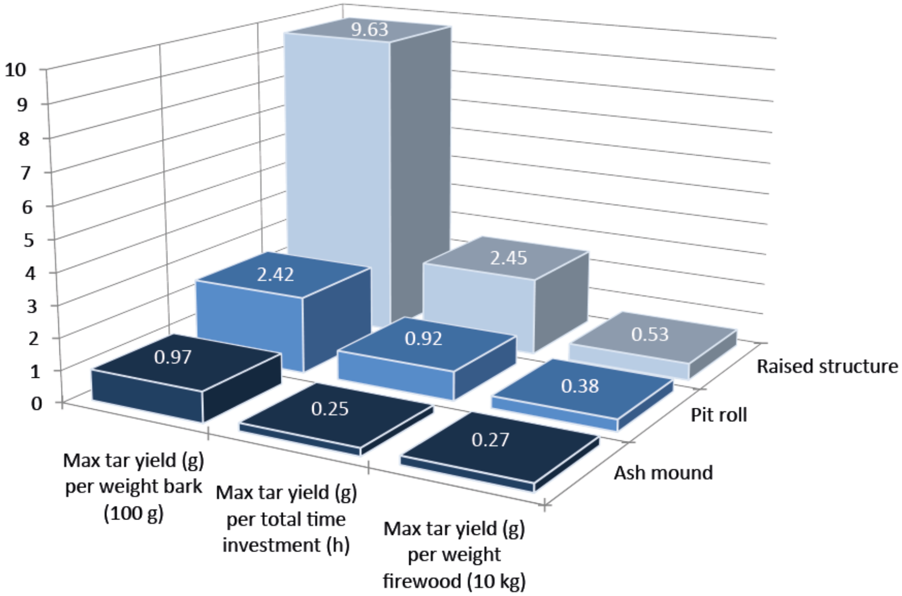

Fig. 2. Maximum tar production efficiency for each method tested. If ash and embers from a fire used for other tasks were utilized then the tar yield/time investment and tar yield/firewood for the ash mound and pit roll method would also increase.

Comparison with archaeological tar

The three largest prehistoric birch bark tar finds are those from the Middle Palaeolithic sites of Campitello Quarry in Italy (Mazza *et al.* 2006), Königsaue in Germany (Grünberg 2002) and the Mesolithic site of Star Carr in England (Aveling and Heron 1998). Using a value of 1.14 g/ml for the density of wood tar (Collin and Höke 2005), the largest volume of birch bark tar found at Campitello Quarry measuring approximately 40 × 32 × 18 mm should weigh a maximum of 14.6 g, not excluding the volume occupied by a ~5 mm thick flake. The smaller residue from Campitello Quarry is less than 20 × 20 mm and only a few mm thick, but this is likely incomplete (Mazza *et al.* 2006). Due to degradation, the values of 1.38 g and 0.87 g given for the tar found at Königsaue (Grünberg 2002) are unlikely to represent the original mass of the lumps. These must have been closer to 5.7 g and 1.7 g given the known density of wood tar (Collin and Höke 2005) and the dimensions of the lumps (Grünberg 2002). The tar finds from Star Carr, described as 'resin cakes', are between 25 mm and 45 mm in diameter and a few mm thick (Aveling and Heron 1998), so were likely originally between 1.5 – 6.5 ml, or 1.7 – 7.5 g.

These volumes are well within the production range of all our methods. For some of the most successful runs, we produced approximately 1.0 g of tar from the ash mound, and 1.8 g of tar from the pit roll. These would therefore need to be repeated only once or twice to produce the smaller lump of tar from Königsaue, and between six and 11 times to produce the tar found at Campitello quarry. If the ash and embers for the ash mound and pit roll methods were obtained from a central hearth used for cooking and/or other purposes, then the efficiency is improved and having to repeat this process would not be much of a drain on fuel resources. Alternatively, our raised structure method produced 15.7 g of tar in one successful attempt, enough to make a 'cake' or lump nearly 45 mm in diameter and 10 mm thick, as large as those found at Star Carr (Aveling and Heron 1998), Campitello Quarry (Mazza *et al.* 2006), or larger than both lumps found at Königsaue combined (Fig. 1). It is also worth considering that our own hands-on practice was limited and improved across time for the pit roll and raised structure techniques (Supplementary Table S1). We in turn expect that with more practice the tar yield will improve further.

If tar was produced on an opportunistic basis, when there was a fire present, when a single tool required repair, or when time was available the plausibility of using simpler low-yield methods increases. It is also possible that the archaeological examples of tar have survived, or more likely have been recognized during excavation, because they are exceptionally large. A tightly fitted haft, or a joint that also contains a binding will require less tar than that found at Campitello. This combined with the ideas that adhesives can be re-used and that it is unlikely a Neandertal would need to haft an entire toolkit at once, further demonstrate the viability of the methods used here.

Depending on the tree species, tar yields using laboratory techniques are in the range of 3.1% (*Quercus cerris*) to 14.3% (*Betula alba*) (Hayek *et al.* 1990), so our yield of 9.6% using the raised structure is comparable even to dry distillation in a lab setting using glass containers. Moreover, our tar is naturally more condensed than lab produced tar which retains all volatiles; if lab produced tar were to be reduced to a semi-solid suitable for hafting, the yield would decrease further and be even closer to what we attained. All of the aceramic methods tested here are therefore viable in terms of yield and what is known from the archaeological record.

Temperature control

During our successful (tar-yielding) experiments there was at least one point for each method (either in the fire, ashes, or bark) that exceeded 400 °C, and another point (in the bottom of the roll or pit) that was less than ~200 °C. Between these two points conditions are suitable for tar production; for birch bark this can be as low as 250-300 °C (Pakdel *et al.* 2002) and over 500 °C (Fagernäs *et al.* 2012; Puchinger *et al.* 2007; Nilsson *et al.* 1999). For the ash mound technique, maximum and minimum temperatures between the inside and outside of the bark roll varied relatively little compared with the other methods (Supplementary Fig. S5). In the raised structures, fire temperatures fluctuated dramatically and reached as high as 900 °C, but the structure kept the birch bark closer to 450 °C or less and the collection vessel below 150 °C (Supplementary Fig. S6, S7). Temperatures for the pit roll technique are intermediate with the hottest temperature in the bark and the coolest temperature in the pit itself. The vessel in the bottom of the pit never reached more than 100 °C (Supplementary Fig. S8). The ability to strictly control temperatures to a narrow range between 340 °C and 370 °C for tar production (Koller *et al.* 2001; Villa and Soriano 2010) is thus not as necessary as previously thought (Fig. 3).

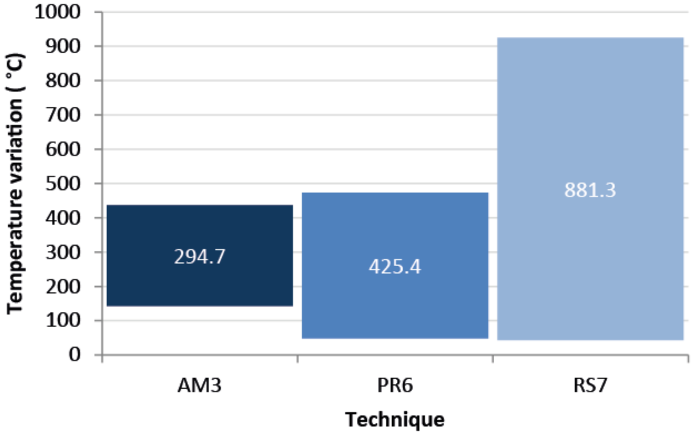

Fig. 3. Display of temperature variation within each method. The temperature inside the bark roll (AM3) and vessel (PR6, RS7) was recorded when the temperature in the heat source (fire and/or embers) for each technique reached its maximum.

The degree of temperature monitoring also appears to vary directly according to the complexity of the structure. Actualistic fire experiments have shown that surface fire temperatures can fluctuate dramatically, while sub-surface temperatures below a fire are more constant (Bentsen 2013). Due to the direct contact that the birch bark roll has with hot embers and oxygen in the ash mound, this method is more similar to a surface fire and the temperature needs to be managed more closely. Here small amounts of ash were added to the mound if it appeared to be smoking too much, and embers were added if it seemed too cold, although this was subjective and relied only on the operator's experience. It was clear during our experiments that the operator with the highest hands-on experience with the ash-mound technique (author DP (Pomstra and Meijer 2010)) produced the most consistent amount of tar (Supplementary Table S1). On the other hand, with the raised structure method, the structure itself manages the temperature by isolating the bark from the fire, thus removing this level of know-how from the equation; all that is needed is to maintain flaming combustion around the structure. This would have required the same level of attention as tending a hearth for purposes such as warmth, light, or cooking. However, because the flames needed to be burning for several hours, this process would have required more effort and attention to collect wood and maintain the fire than the ash mound or pit roll method. As with previous experiments (Schenck and

Groom 2016), it seems that once learned, this method is simple to operate. In terms of required temperature control, the pit roll method falls between the ash mound and the raised structure technique. Just as the sub-surface temperature in an open hearth is lower and more controlled than the surface temperatures (Bentsen 2013), the temperature in the pit is lower and more stable than the ash and embers above the pit. The tar will never burn away completely because the depth of the pit limits the oxygen to such an extent that the temperature begins to decline automatically before getting too hot (Supplementary Fig. S8). Using this method, bark and embers could be put in place, and the process could be left alone without requiring any further intervention or attention. The only significant limitation is that if the embers are too small to begin with they may burn out before much tar is produced.

Complexity

The setup time and the run time of each method increased in the same order as the number of steps and the material diversity. Excluding tools and processes required for fire production, the ash mound is made of the fewest individual components (embers, ash, and birch bark). The pit roll method requires more components (digging stick, vessel, pit, embers, birch bark), and the raised structure method requires yet more components (digging stick, vessel, pit, willow twigs, pebbles, earth, water, fire, and birch bark). If we use the maximum yield obtained for each method (Fig. 2) the results indicate that as the complexity increases so does the amount of tar obtained (Fig. 4).

The required amount of temperature control is also directly associated with the structural complexity of each method. As more complex techniques are employed, the amount of oxygen is reduced and the bark is isolated. The control of heat is thus ‘automated’ by the structure, reducing the practical expertise required to control the temperature while increasing tar yield (Fig. 4). This pattern is repeated in historical and modern tar and charcoal production techniques as well. Internally heated tar pits or mounds (in this case similar to our ash mound) have relatively few separate parts, but require constant care by numerous people to manage the internal environment during the entire firing process (Emrich 2013). The introduction of kilns, although more complex structurally, required less manual or personal management and improved yields (Surmiński 1997; Emrich 2013). The implementation of various modern feed-stock gas furnaces takes this one step further by completely automating the process (Roy *et al.* 1988).

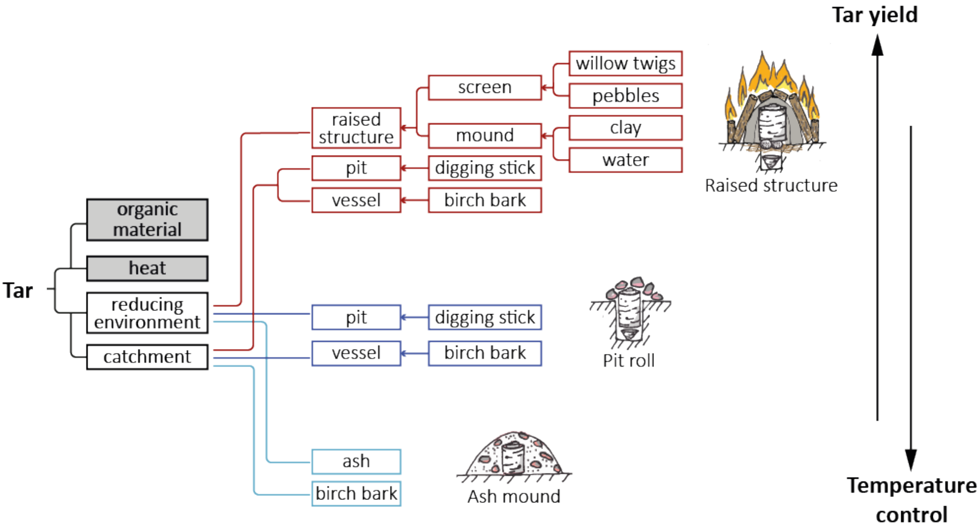

Fig. 4. Depiction of the increase in complexity of each method and the associated increase in tar yield and decrease in required temperature control.

Discussion

It is known that Neandertals were fire users, even if the necessity of fire use and their ability to produce fire on demand has been disputed (Heyes *et al.* 2016; Sandgathe *et al.* 2011; Sorensen 2017). Here, we show that tar can be produced using aceramic technology compatible with a Neandertal context. Enough tar can be produced using low-tech solutions, such as the ash mound with the only prerequisites being the presence of fire and birch bark.

Origin of tar technology

Birch bark is an excellent fire starter (Tilton 2005; Canterbury 2015), tends to roll naturally when peeled off a tree, will curl further on exposure to heat, and is known in the ethnographic record to have been used (rolled) as torches and fire-lights (Lyford 1982; Butler and Hadlock 1957; Oswalt 1976), as well as to have served many other practical purposes (Butler and Hadlock 1957; Croft and Mathewes 2014). Birch bark is known to contain proportionally higher extractives than many other plant resources (Hayek *et al.* 1989; Hayek *et al.* 1990; Hon and Shiraishi 2000), and was also one of the most common trees in Palaeolithic Europe (Helmens 2014; Urban and Bigga 2015). A tightly rolled piece of birch bark simply left in a fire and removed when partially burned, once opened, will sometimes contain small traces of tar inside the roll along the burned edge. Not enough to haft a tool, but enough to recognize a sticky substance. From this point the ash mound is a small step forward. Piling the remnants of a hot fire over the bark is also analogous to some traditional cooking methods using ash (Dea *et al.* 1991; Harney 1951) see also (Henry 2017).

Hafting technology is known from 300-200 ka and may be as old as 500 ka (Wilkins *et al.* 2012). Neandertals are known to have used wood as a resource (Schoch *et al.* 2015; Hardy 2004; Hardy and Moncel 2011), remains of birch bark charcoal have been identified (Harold L. *et al.* 2009; Conard and Adler 1997), and fire use did occur during the middle Pleistocene (Cohen *et al.* 2012; Harold L. *et al.* 2009; Conard and Adler 1997). To produce tar using the ash mound technique would only necessitate the combination of materials and properties already known by Neandertals. It is therefore not surprising that Neandertals discovered how to produce birch bark tar and used it for hafting.

The largest imaginative leap required to use tar for hafting would have been the comprehension of using a sticky substance to hold two objects together. However, early forms of hafting, possibly without adhesives, may predate the discovery of birch bark tar (Rots 2013; Rots *et al.* 2015). Water resistant materials, such as fats, resins, and tars can also be used to protect bindings from moisture (Rots 2010). It is possible that the early function of tar may have been to assist and waterproof the binding on a haft (e.g. sinew, hide, or vegetal fibers), and as the production and quantities of tar improved, it gained the more primary function as a fixative agent or adhesive.

Development of tar technology

We can hypothesize that after having discovered tar while using birch bark close to a fire-place, a major improvement will be placing a bark roll in a depression or pit to limit the oxygen and prevent too much of the tar or bark from burning away. It could have then been observed that pyrolysis products would flow out of the bottom of the bark roll, so a catchment method would improve the yield. Yet, using this method, tar and bark are still lost to combustion. The third major improvement would be to isolate the bark from direct contact with extremely high temperatures and oxygen by building a clay or earthen structure. Placing the bark inside an enclosed structure with the heat source outside reduces the likelihood of tar or pyrolysis products from burning away. Creating a screen to support the bark and raising the bark and structure above ground aids in heat transfer. The pit allows for vessels of non-heat-resistant materials to be used, and prevents the tar from being exposed to excessive heat for a prolonged period. Our own methods are combinations and improvements on previously tried techniques, both historical and experimental, and it is likely that numerous other combinations or variations could exist to fill in the gaps.

The discovery of birch bark tar can be explained through a number of discrete technological steps, rather than requiring any major *eureka* moment or leap of innovation. This also increases the possibility for the independent discovery or re-discovery of this technology throughout the Middle Palaeolithic. To acquire the necessary expertise to produce useable quantities of tar, however, Neandertals must have been able to recognize properties, such as adhesive tack and viscosity. In this way they could develop the technology from small traces of tar on partially burned bark to techniques capable of producing the volumes required to haft a large stone flake.

Possible archaeological traces

Lack of adhesive evidence during the Middle Palaeolithic may be a product of taphonomic or research biases, so understanding what to look for will be beneficial to future studies. Unfortunately traces of early tar production strategies are unlikely to be easily discernible in the archaeological record. The ash mound method leaves virtually no trace, and the only remains from the pit roll method were a small depression less than 10 cm deep by 10 cm in diameter. Although the centre of the bark roll reached high enough temperatures to leave a lasting trace in the soil, the bottom of the pit did not (Aldeias *et al.* 2016; Brodard *et al.* 2016).

One of the most enduring traces could have been the pebbles, yet our experiments showed that their use for collecting or 'condensing' tar is not necessary. We found that in many cases a birch bark vessel was in fact the best option. It was never so hot that a fire-resistant retort was required, and the funnel shape available from a folded circular piece of bark allowed for the collection of greater quantities of tar. Tar removed from these birch bark vessels also contained traces of un-charred bark. The presence of un-charred bark to describe an incomplete production process (Pawlik 2004) must therefore be used with caution as it may in fact come from successful attempts.

If the earliest tar-makers, whether it was at Campitello Quarry, Italy (Mazza *et al.* 2006) and Königsaue, Germany (Koller *et al.* 2001), or at some still undiscovered archaeological site, used simple techniques, such as the ash mound or pit roll method, then it will be difficult to find direct traces of the first tar production strategies. However, the tar lumps themselves may be able to give further insights into the evolution of the used technique. Chemical and microscopic analysis of experimental material alongside archaeological remains may help illuminate which methods were likely used in the past by understanding the formation and thermal degradation of biomarkers (cf. Duce *et al.* 2015; Koller *et al.* 2001) as well as by identifying additives.

Conclusion

While there are many potential methods of producing tar (Pfeifer and Claussen 2016; Pomstra and Meijer 2010; Schenck and Groom 2016; Piotrowski 1999; Surmiński 1997), we have demonstrated that there are at least three successful aceramic solutions, ranging from low to high-tech. A simple bark roll in hot ashes can produce enough tar to haft a small tool, and repeating this process several times (simultaneously) can produce the quantities known from the archaeological record. Our experiments allowed us to develop a tentative framework on how the dry distillation of birch bark may have evolved, beginning with the recognition of small traces of birch bark tar in partially burned bark rolls. Small changes and additions to the production process would have allowed easier regulation of fire temperatures, and improved tar yield efficiency. Such a framework is consistent with the technology and resources available to Neandertals during the Middle Palaeolithic. Given the ephemeral nature of the expected traces, however, it will be difficult to find direct evidence for the evolution of tar production techniques in the sediments of Palaeolithic archaeological sites. Further investigation of the composition and nature of the tar lumps themselves may help in the future to refine the history of the development of tar technology.

Considering that birch bark was available in Europe during the Pleistocene, and that Neandertals are known to have used wood resources and fire, it is now clear that Neandertals could have invented the transformative technology simply by recombining knowledge they already had. Such an invention must have been driven by curiosity and interest in properties like the tack and viscosity of the newly discovered material. Moreover, in order for tar production to become a perennial innovation, Neandertals must have been able to maintain the process of dry distillation as a useful technique for producing adhesives.

Methods

Materials

Birch bark from *Betula pendula* trees was collected in southern England and the Netherlands during August 2016 and prepared into rolls on-site before each experiment in December 2016. Bark from both branches and trunks of trees ranging from approximately 5 cm to 15 cm in diameter was used. Firewood was store-bought kiln dried assorted European hardwoods (*Quercus, Fagus,* and *Fraxinus*) with a moisture content approximately 10-15%. Pollen records show oak (*Quercus*) was present in Europe at times associated with the use of birch bark tar (Helmens 2014; Roucoux *et al.* 2006) and all three of the firewoods used have calorific values comparable to birch. The greatest variation in thermal output of firewood comes from moisture content (Krajnc 2015), which we controlled by using kiln dried woods.

Experiments were conducted under a shelter at the Leiden University experimental house at the Horsterwold in Flevoland, the Netherlands. A weather station (Alecto WS4050) was placed several meters away to record the local ambient temperature, humidity, and wind speed and direction during each experiment. Temperatures during tar production were recorded at several points for each method using thermocouples connected to an Extech SDL200 4 channel temperature meter (Supplementary Fig. S9-S11). Thermocouples were not consulted to guide the experiments; the collected data was only used for analysis after the experiments were complete. A breakdown of the three tar production methods tested is described below.

Aceramic distillation experiments

Three tar production methods were used, and each was tested between 5 and 11 times (Supplementary Table S1). For each experiment, set-up time, run-time, fuel use, temperature curves, technounits (Oswalt 1976), operational steps and tar yield has been recorded. Details and photographs of the remains from each method are available in the Supplementary Information.

Ash mound. A tightly made roll of birch bark was covered in embers and ash from a long-burning fire (Pomstra and Meijer 2010) (Supplementary Fig. S1). The heat from the embers works with the ash and the tightly rolled bark to limit oxygen, inhibiting combustion and encouraging the formation of tar. No vessel was used and the tar was scraped off each consecutive layer of bark as the roll was unwrapped (Pomstra and Meijer 2010).

Pit roll. The pit roll method involved digging a small cylindrical pit, in this case approximately 8 cm deep by 6 cm in diameter to help exclude oxygen. A bark roll (approximately 9 cm long by 5 cm diameter) was placed inside the pit. We tested three principle variations of this method. PR1 and 2 were based on the description given by Pawlik (Pawlik 1995; Pawlik 2004). A pebble was placed in the bottom of a pit, and a roll of birch bark was ignited. The burning end of the bark was then placed into the hole. PR3 and 4 are similar, but with the burning end up to try and encourage longer combustion. PR5-9 had hot embers placed on top of the bark in order to provide additional heat. PR5 contained a pebble in the bottom of the pit, PR6 contained a strip of bark in the bottom of the pit, and PR7-9 used a small birch bark cup tucked in the bottom of the roll to collect any tar or pyrolysis oils that dripped out of the bottom of the bark (Supplementary Fig. S3).

Raised structure. This method was essentially a reproduction of the 'two pot' method (Bacon 2007) without the use of metal or ceramic containers (Supplementary Fig. S4), although we did use a metal container on one attempt. A small pit was dug in the ground (approximately 7 cm deep and 9 cm wide) and a vessel was placed at the bottom of the pit. A screen of green wood (willow, *Salix* sp.) sticks was placed across the top of the pit, pebbles and then a roll of birch bark was placed on top of the screen. Wet earth was placed over the bark to seal the bark inside a dome-like structure. For variations on this and failed attempts see the Supplementary Information Table S1.

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3. Adhesive efficacy

Lap Shear and Impact Testing of Ochre and Beeswax in Experimental Middle Stone Age Compound Adhesives

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Abstract

The production of compound adhesives using disparate ingredients is seen as some of the best evidence of advanced cognition outside of the use of symbolism. Previous field and laboratory testing of adhesives has shown the complexities involved in creating an effective Middle Stone Age glue using Acacia gum. However, it is currently unclear how efficient different adhesive recipes are, how much specific ingredients influence their performance, and how difficult it may have been for those ingredients to be combined to maximum effect. We conducted a series of laboratory-based lap shear and impact tests, following modern adhesion testing standards, to determine the efficacy of compound adhesives, with particular regard to the ingredient ratios. We tested rosin (colophony) and gum adhesives, containing additives of beeswax and ochre in varying ratios. During both lap shear and impact tests compound rosin adhesives performed better than single component rosin adhesives, and pure acacia gum was the strongest. The large difference in performance between each base adhesive and the significant changes in performance that occur due to relatively small changes in ingredient ratios lend further support to the notion that high levels of skill and knowledge were required to consistently produce the most effective adhesives.

Introduction

The creation of multi-component tools was an important advancement in the history of technology, and in the evolution of the human mind (Barham 2013; Ambrose 2001, 2010; Coolidge *et al.* 2016; Lombard 2008; Wadley 2010; Prinsloo *et al.* 2014; Coolidge and Wynn 2009; Conard and Bolus 2003; McBrearty and Brooks 2000). It required the collection and combination of disparate materials in varying forms for different purposes. This is believed to have required mental capabilities analogous to those possessed by modern humans (Ambrose 2010). In addition, many hafted tools were held together with adhesives. Similar to the tool itself, the adhesives may have also been made using a combination of materials for different purposes (Lombard 2008). Prehistoric adhesives were made out of a range of materials (Regert 2004), from bitumen, a naturally occurring tar-like substance, to deciduous plant gums, conifer resins, and tars or pitches produced from the destructive distillation of birch bark and other woods (Boëda *et al.* 2008a; Helwig *et al.* 2014; Regert 2004; Koller *et al.* 2001). The oldest known evidence for compound adhesives comes from the Middle Stone Age in southern Africa and may be as old as 70,000 years (Lombard and Wadley 2009; Delagnes *et al.* 2006). The oldest known single-component adhesives are birch bark pitch made by Neandertals during the Middle Palaeolithic in Europe nearly 200,000 years ago (Mazza *et al.* 2006). The production of complex adhesives is considered to be a potential proxy for cognitive traits such as advanced working memory capacity, chronesthesia (mental time travel), multitasking, abstraction and recursion (Koller *et al.* 2001; Lombard 2008; Wadley 2010; Prinsloo *et al.* 2014; Lombard and Wadley 2009; Coolidge and Wynn 2009; Coolidge *et al.* 2016; Wragg Sykes 2015). A hunter's dependency on reliable weapons would have been a strong incentive to create effective adhesives (Lombard and Wadley 2009), and making optimised adhesive mixtures requires high levels of knowledge of natural resources to estimate ingredient ratios and understand (chemical) reactions and bonds. It also requires controlled use of fire so as not to overheat and damage the adhesive during its manufacture (Koller *et al.* 2001; Lombard 2008; Villa *et al.* 2005). One argument for this hypothesis, that adhesive production requires modern-like cognitive abilities and a detailed understanding of the materials, is that the ratios of compound adhesive ingredients had to be very precise to successfully create glue with optimum adhesive power. This idea has not been tested systematically and the standardised adhesive property tests that we discuss in this paper are a first effort to do so.

Several previous actualistic and laboratory experiments have been conducted using replicated adhesives based on rosin (*Pinus* sp.), beeswax, ochre (Gaillard *et al.* 2015; Allain and Rigaud 1986), and acacia gum (*Acacia karoo* and *Acacia senegal*), (Lombard and Wadley 2009; Villa *et al.* 2005; Zipkin *et al.* 2014). These experiments showed that there are a number of factors that require attention for an effective adhesive to be produced and used. Allowing adhesives to air dry versus drying them near a fire, and the particle size of mineral fillers have recognisable impacts on the performance of adhesives. Our study is aimed at understanding how changing ingredient ratios influence adhesive strength. Different real-life applications of tools also subject adhesives to different load rates, and we will test several adhesive recipes with both impact and lap shear experiments to consider these changes. Laboratory testing is gaining popularity as a means to understand the materials and technologies of past human populations, and the necessity to combine actualistic field experiments with laboratory-based experiments is well understood (Coles 1979; Dibble and Rezek 2009; Marsh and Ferguson 2010; Outram 2008; Zipkin *et al.* 2014). In order to focus on the specific effect of changing ingredient ratios and eliminate other variables as much as possible, we opted to conduct standardised laboratory adhesive tests (ASTM 2010, 2011a), rather than field experiments.

Materials and methods

Adhesive ingredients

We created 20 different adhesive recipes inspired by the archaeological record (Table 1). We experimented on commercially available pine rosin (*Pinus* sp.) and acacia gum (*Acacia senegal*) as our primary adhesives, and beeswax and red ochre powder as primary and secondary additives. All ingredients are store bought (Table in S1 Table) to reduce as much as possible any variation that may exist in material collected from the wild. Pine rosin, otherwise known as colophony, is obtained by removing the volatile turpentine portions from pine resin (Gaillard *et al.* 2011) and was selected to represent adhesives made from conifer resins (Helwig *et al.* 2014; Regert 2004; Charrié-Duhaut *et al.* 2013; Mateos *et al.* 2015). Acacia gum was tested to compare our results with previous experiments (Villa *et al.* 2005; Zipkin *et al.* 2014). We included beeswax as the primary additive to act as a plasticiser. Beeswax may have been used approximately 40,000 years ago with resin as an adhesive (d'Errico *et al.* 2012), and shares many similarities to other lipids, such as animal or vegetable fats, possibly associated with adhesives (Helwig *et al.* 2014; Regert 2004; Lombard 2004; Delagnes *et al.* 2006). The use of beeswax in other experimental hafting projects also points to its possible necessity in producing successful resin-based adhesives (Rots 2008; Villa *et al.* 2005; Gaillard *et al.* 2015; Allain and Rigaud 1986; Iovita *et al.* 2014; Delagnes *et al.* 2006; Pétillon *et al.* 2011; Moss and Newcomer 1982; Barton and Bergman 1982). Red ochre was used as a secondary additive in combination with beeswax because of its association with adhesives and hafting among a number of different sites across Africa, Europe, and North America, and because it has been demonstrated to have positive effects on the properties of adhesives (Allain and Rigaud 1986; Helwig *et al.* 2014; Delagnes *et al.* 2006; Lombard 2008; Villa *et al.* 2005; Gibson *et al.* 2004; Rots *et al.* 2011). This is a natural red iron oxide (α-Fe_2O_3) pigment with a particle size less than 62.5 µm from the Ardennes region, Belgium.

Table 1. Overview of the tested adhesive recipes.

Main Ingredient	mg	Primary Additive	mg	Secondary Additive	mg
pine rosin	250	beeswax	250	none	-
pine rosin	250	beeswax	250	ochre	50
pine rosin	250	beeswax	250	ochre	100
pine rosin	250	beeswax	250	ochre	150
pine rosin	300	beeswax	200	none	-
pine rosin	300	beeswax	200	ochre	50
pine rosin	300	beeswax	200	ochre	100
pine rosin	300	beeswax	200	ochre	150
pine rosin	350	beeswax	150	none	-
pine rosin	350	beeswax	150	ochre	50

pine rosin	350	beeswax	150	ochre	100
pine rosin	350	beeswax	150	ochre	150
pine rosin	400	beeswax	100	none	-
pine rosin	400	beeswax	100	ochre	50
pine rosin	400	beeswax	100	ochre	100
pine rosin	400	beeswax	100	ochre	150
rosin	500	none	-	none	-
acacia gum	350	beeswax	150	none	-
acacia gum	350	beeswax	150	ochre	150
acacia gum	500	none	-	none	-

Adhesive preparation

Due to the difference in material properties, sample preparation varied somewhat between pine rosin and acacia gum adhesives. For pine rosin each ingredient was measured by weight to the nearest one-tenth of a gram and mixed together in an aluminium tray over an electric hot plate. The combined weight of rosin and beeswax in each mixture was 500 mg, and ochre was added to this in 50 mg increments (equalling 10, 20 and 30% increases). During the mixing, temperatures were kept below 140°C to avoid any thermal degradation that may take place at higher temperatures (Norlin 2005; Gaillard *et al.* 2011). Small glass beads with a diameter of 90 to 130 microns (µm) were added 'like a pinch of salt' and thoroughly mixed into the adhesive to ensure the set bondline thickness of each test piece was similar. These beads are often used in commercial adhesive testing in very small portions (about 2 wt%) and have no effect on the performance (Broughton and Gower 2001). The adhesives were constantly stirred for two minutes before use, and again briefly in between each application on every specimen to reduce the sagging of the ingredients. Once the adhesive was completely melted and mixed, both surfaces to be bonded were simultaneously dipped in the adhesive and immediately clamped together.

Sample preparation of acacia gum was done using a method similar to Zipkin *et al.* (Zipkin *et al.* 2014). First, the gum was ground into particles approximately 2 mm in diameter using a mortar and pestle. The appropriate amount of gum was then weighed and mixed with boiling water until it dissolved. It was then further reduced with heat until it reached a more useable consistency. The remaining ingredients were added at this point, following the same procedures used for pine rosin. Finally, unlike rosin, which behaved as a hot melt adhesive and cured as it cooled, the acacia gum required time to air dry. All samples were thus left in the open for six days (following Wadley (Villa *et al.* 2005)).

Lap shear

For all material properties tests, a number of internationally recognised standards have been developed. These ensure replicability regardless of the practitioner or laboratory. One of the most common set of standards are those of ASTM International. Of these standards, lap shear tests are widely used as adhesive joint strength tests because they are easy to conduct and closely resemble the geometry of many practical joints, including one of the most common and versatile stone tool hafting methods, the cleft haft (Barham 2013). Furthermore, cutting, scraping and piercing tools must all withstand some form of shear force, in which adhesives perform best. For example, the vertical downwards force applied during cutting or scraping will create a bending stress and a vertical shear stress, and the horizontal component of the cutting force will create a tension and shear stress at the adhesively bonded joint. A piercing tool will also experience compressive shear forces on impact, and tension shear forces upon removal. As in many lap shear tests, cutting, scraping, and piercing are generally subjected to low load rates; the tool edge is placed on the worked surface, and increasing pressure is applied until there is sufficient force to cut, pierce, or scrape the surface as desired.

The ASTM D1002 test standard was therefore used for the quasi-static shear strength of a single-lap joint. This test measures ‘apparent’ shear strength because true shear strength is difficult to determine with single thin-adherend lap shear specimens, as the eccentricity of force being applied bends the substrate material and introduces peel stresses along the bond termini (Brockmann *et al.* 2009). These additional stresses, however, help to resemble practical joints more closely, as joints in real life applications are rarely subject to perfectly planar shear forces. Due to the relatively weak nature of the adhesives (compared with modern glues) one property of the test standard was changed. We used beech (*Fagus* sp.) plywood instead of aluminium for the substrate material to improve the likelihood of cohesive failures rather than measuring bond strength of the adhesive to aluminium. The wooden test specimens are 4.0 mm × 25.4 mm × 100.0 mm long. The bond overlap was 12.7 mm (Fig 1).

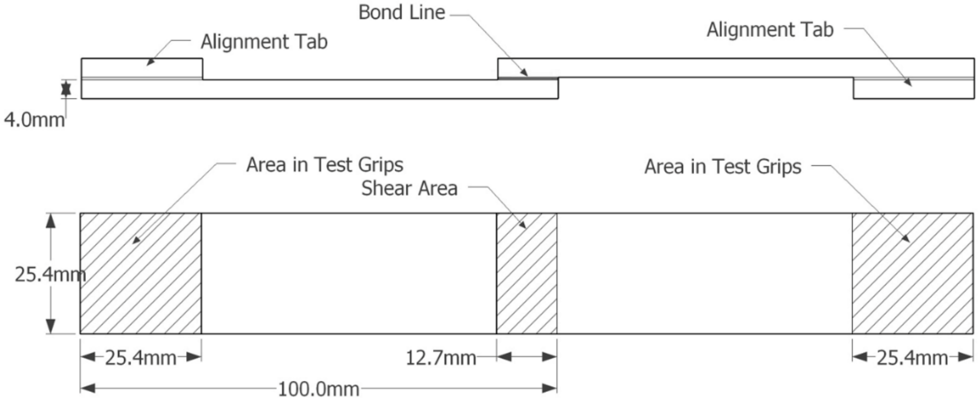

Fig. 1. Schematic of standardised wood lap shear test specimen. Side and top view of test specimen composed of two adherends adhesively bonded together in the centre (bondline).

To ensure maximum adhesion, samples were degreased with acetone, abraded with 100 grit sandpaper, and degreased again prior to the application of the adhesive. Lap shear tests were performed in the Delft Aerospace Structures and Materials Laboratory at the Delft University of Technology using a Zwick-Roell 1455 tensile bench with a 20 kiloNewton (kN) load cell at a rate of 1.3 mm/minute and a preload of 10 N. Specimens were mounted vertically between two clamps, which are then moved apart from one another at a constant speed until bond failure (Fig 2). If the adhesive does not fail completely, tests are ended automatically when the force reaches one-half that of the maximum obtained force. Five individual specimens were tested for each adhesive recipe. Tests were conducted at an ambient air temperature of 21 – 23°C and a relative humidity of 39 – 50%.

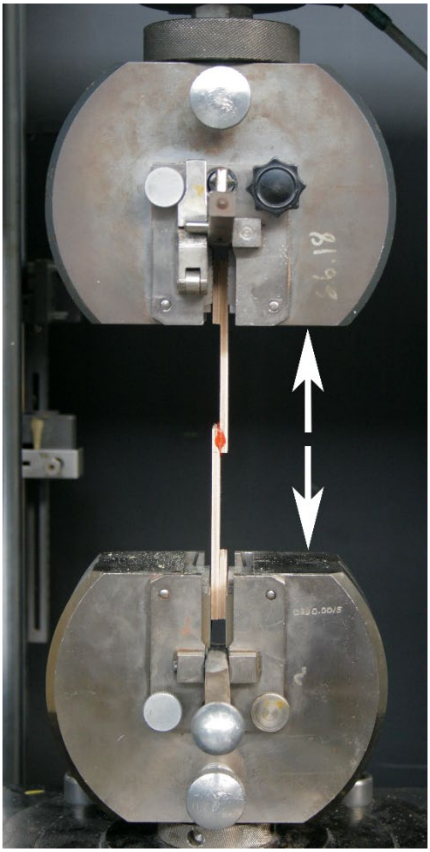

Fig. 2. Sample in lap shear test apparatus. Clamps of a Zwick-Roell 1455 tensile bench containing standard adhesive lap shear test specimen with arrows indicating the applied direction of force.

Data generated from lap shear experiments can be analysed by two means: 1) Inspection of the bonded surfaces after failure can show if the break is adhesive or cohesive, giving essential information on the interaction between the adhesive and adherend. This is especially relevant when comparing substrate materials and adhesion strength. 2) Stress/strain curves generated by the test machine provide data on elastic and plastic deformation, brittle and ductile fracture, the maximum shear force an adhesive can withstand, and the amount a given material can be displaced before failure (Fig 3). The results are given as the maximum recorded force (N) divided by the bonded surface area (mm^2), or Megapascals (MPa), and the displacement in mm. Fracture type can also be determined from the stress/strain curves, by looking at the amount of plastic deformation prior to absolute failure.

Those curves ending abruptly with little to no arch represent brittle fractures, where the material fails catastrophically and without warning (Fig 3). Ductile fractures are shown by the gradual decrease in stress prior to failure (Fig 3). In this study, we are most concerned with the maximum force, as this is the simplest indication of what will make a strong adhesive for many different hafting purposes.

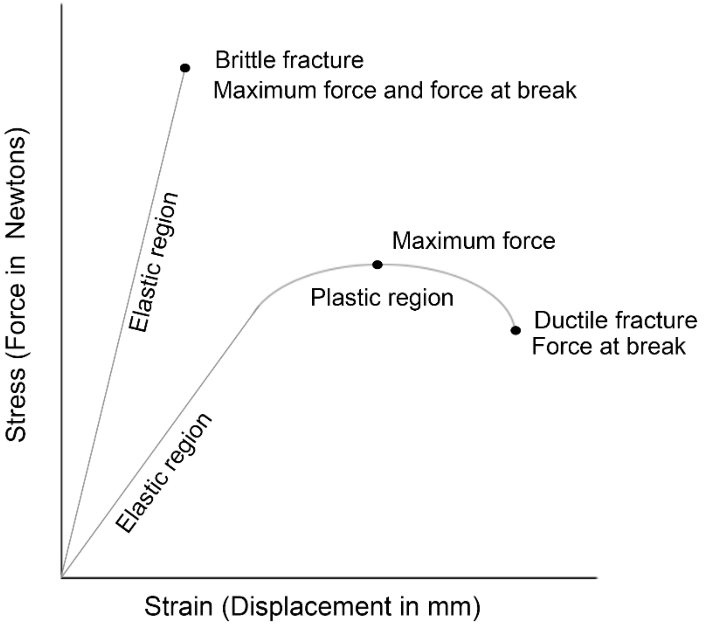

Fig. 3. Idealised example of stress/strain curves. Curves for two different materials displaying brittle and ductile failures. The elastic region is the linear part of the curve, and any displacement along this section is temporary. The plastic region occurs after, and displacement here is permanent.

Impact

Materials often behave differently at high load rates (impact) than they do at low load rates (quasi-static loading as in the lap shear), thus making it difficult to accurately predict how materials behave during high speed impacts based on the data obtained during low load rate tests. For example, it is possible for ductile materials to shatter abruptly under impacts (Callister and Rethwisch 2010). High and low load rates also correspond to different prehistoric tasks; hafted spear points were probably subjected to high load rates, whereas hafted scrapers were subjected to low load rates. The load rate during ASTM D1002 lap shear test is 1.3 mm per minute (2.17 x 10^{-5} metres per second); by comparison the pendulum hammer as described in ASTM D950 impact test strikes the adherend with a velocity of 3.46 metres per second. The latter is faster than the loading speeds estimated by Shea *et al.* (Kafkalidis and Thouless 2002) for stabbing, but slower than those for spear throwing (Shea *et al.* 2002). There are numerous procedures to test the impact resistance of materials. The most common are the Charpy and Izod tests (Callister and Rethwisch 2010), of which ASTM D950 (ASTM 2011a) is a variant. We used this standard as guidelines to determine if some adhesive recipes are better suited to one task over another.

Impact tests were performed using a Zwick 5113 pendulum impact tester in the Department of Advanced Soft Matter at the Delft University of Technology. A pendulum hammer is released from a swing angle of 124.4 degrees and accelerates to a speed of 3.46 m/s before impacting the specimen locked in the clamps. The samples were made from solid pieces of tropical hardwood, and cut to 12.0 mm × 18.0 mm × 55.0 mm. The top 10.0 mm was cut off and adhesively bonded back on with each adhesive, creating a bonded surface area of 216.0 mm^2. The hammer impacted the 18 mm wide face of the sample less than 1 mm from the bondline. Due to test machine differences from those in the standard (ASTM 2011a), a steel reinforcement was placed behind each specimen to ensure the adherend would not break before the adhesive (Fig 4). Impact tests were conducted at an ambient air temperature of 22 – 23°C and a relative humidity of 40 – 49%.

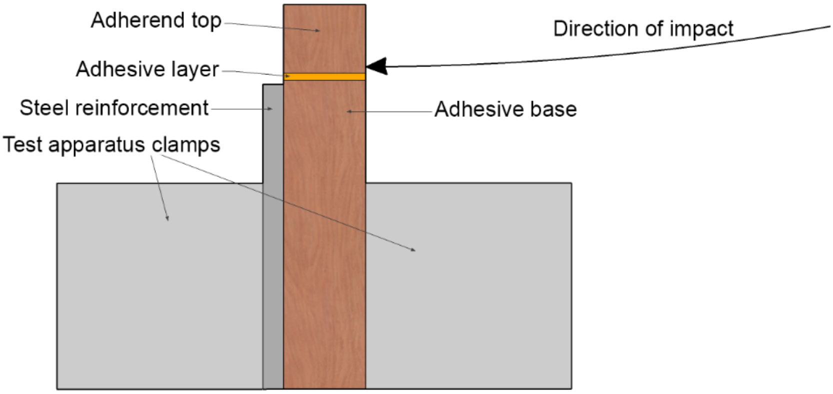

Fig. 4. Cross section of impact test set-up. Cross section showing the direction and point of impact just above the bondline (adhesive layer) and steel reinforcement of the impact specimen.

The absorbed impact energy in Joules (J) is recorded by measuring the difference between the maximum height of the pendulum swing before and after the impact (Sato 2005). The difference in behaviour under impact forces requires a different analysis than that of lap shear tests. The data are recorded as a single measurement of absorbed energy. The greater the energy absorbed, the better the adhesive is at withstanding impacts. Fracture type is thus not measurable, although it is assumed that most adhesives will fail in a brittle manner during impacts (Callister and Rethwisch 2010). Adhesive and cohesive failure type can still be determined by analysing the bonded surfaces after the failure of each joint.

Results

Lap shear

The strength of lap shear tests is recorded as the maximum force over the surface area of the bond. Table 2 displays the maximum, minimum, and mean values for each adhesive recipe. The weakest adhesive is 100% rosin; this material broke under the 10 N pre-load of the test machines and thus could not be accurately recorded. When looking at only adhesives containing rosin and beeswax, the strongest contained 350 mg rosin and 150 mg beeswax (average maximum force (Fmax) = 2.64 MPa). Adding ochre in 50 mg increments to this adhesive further improved the performance. The strongest adhesive using rosin contains 350 mg rosin, 150 mg beeswax and 100 mg red ochre powder (average Fmax = 3.49 MPa). Moreover, when no ochre is present, the 350 mg rosin/150 mg beeswax adhesive becomes significantly weaker than that containing the optimum amount of ochre (P = 0.05, two-tailed t-test). The mean of the next five strongest rosin-beeswax-ochre adhesives all fall within the range of the 350 mg rosin/150 mg beeswax/100 mg ochre mixture. By dividing the maximum force (N) by the total displacement (mm) of two adhesives, an approximation of stiffness (N/m) can then be compared. In the correct proportions (350 mg rosin/150 mg beeswax/100 mg ochre), ochre improves the stiffness of adhesive mixtures. However, with higher beeswax-containing adhesives (200 mg and 250 mg beeswax), adding 100 mg ochre has no measurable effect on stiffness (Fig 5). The weakest rosin adhesive contains 250 mg rosin, 250 mg beeswax and 50 mg ochre (average Fmax = 1.297 MPa). The strongest adhesive overall is made of 100% acacia gum (average Fmax = 5.18 MPa). Beeswax only, and beeswax and ochre combinations reduce the average strength of pure acacia gum to 1.87 MPa and 2.06 MPa, respectively. Adhesive maximum force and displacement at maximum force for each recipe is presented in Fig 6.

Table 2. Overview of lap shear results. Mean maximum force (Fmax), maximum Fmax, minimum Fmax, displacement (DL) at Fmax, and standard deviations (S) of all lap shear tests (n=5 for each recipe). Adhesive recipes are expressed by the mass of each ingredient (mg).

Recipe (mg)	**Mean Fmax Mpa**	**S**	**Maximum Fmax**	**Minimum Fmax**	**Mean DL at Fmax**	**S**
250 rosin/250 beeswax	1.85	0.55	2.78	1.42	1.4	0.2
250 rosin/250 beeswax/50 ochre	1.27	0.15	1.45	1.09	1.2	0.3
250 rosin/250 beeswax/100 ochre	1.56	0.43	1.81	0.96	1.3	0.2
250 rosin/250 beeswax/150 ochre	1.43	0.09	1.58	1.34	1.1	0.1
300 rosin/200 beeswax	2.12	0.43	2.66	1.50	1.4	0.2
300 rosin/200 beeswax/50 ochre	1.91	0.14	2.07	1.74	1.4	0.1
300 rosin/200 beeswax/100 ochre	2.18	0.13	2.28	1.97	1.5	0.2
300 rosin/200 beeswax/150 ochre	2.42	0.20	2.71	2.20	1.5	0.1
350 rosin/150 beeswax	2.64	0.47	3.26	1.97	1.5	0.3

350 rosin/150 beeswax/50 ochre	3.39	0.29	3.44	3.02	1.9	0.1
350 rosin/150 beeswax/100 ochre	3.49	0.67	3.92	2.32	1.6	0.3
350 rosin/150 beeswax/150ochre	2.99	0.68	3.93	2.43	1.5	0.3
400 rosin/100 beeswax	1.59	0.53	2.17	0.71	1.6	0.4
400 rosin/100 beeswax/50 ochre	1.62	0.26	2.01	1.34	1.6	0.5
400 rosin/100 beeswax/100 ochre	3.02	0.87	4.42	2.19	1.8	0.3
400 rosin/100 beeswax/150 ochre	3.17	0.69	3.92	2.16	1.8	0.2
500 rosin	-	-	-	-	-	-
350 acacia gum/150 beeswax	1.87	0.50	2.63	1.40	1.3	0.1
350 acacia gum/150 beeswax/ 150 ochre	2.06	0.61	2.87	1.34	1.4	0.3
500 acacia gum	5.18	0.56	5.94	4.46	2.2	0.2

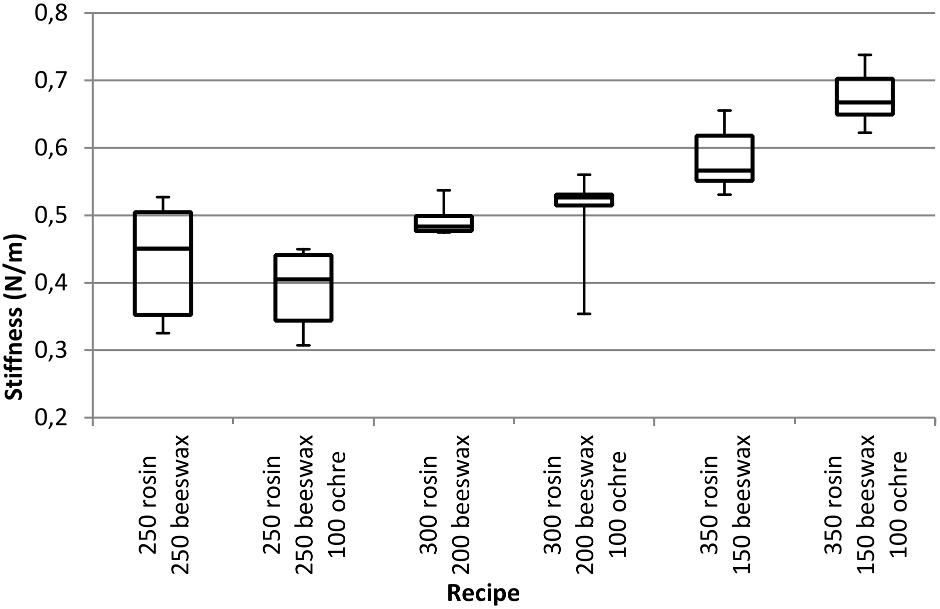

Fig. 5. Relative stiffness of beeswax and beeswax-ochre containing adhesives. Boxplot displaying how the stiffness (N/m) of three different rosin-beeswax adhesives is affected by the addition of 100 mg ochre. Adhesive recipes are expressed by the mass of each ingredient (mg).

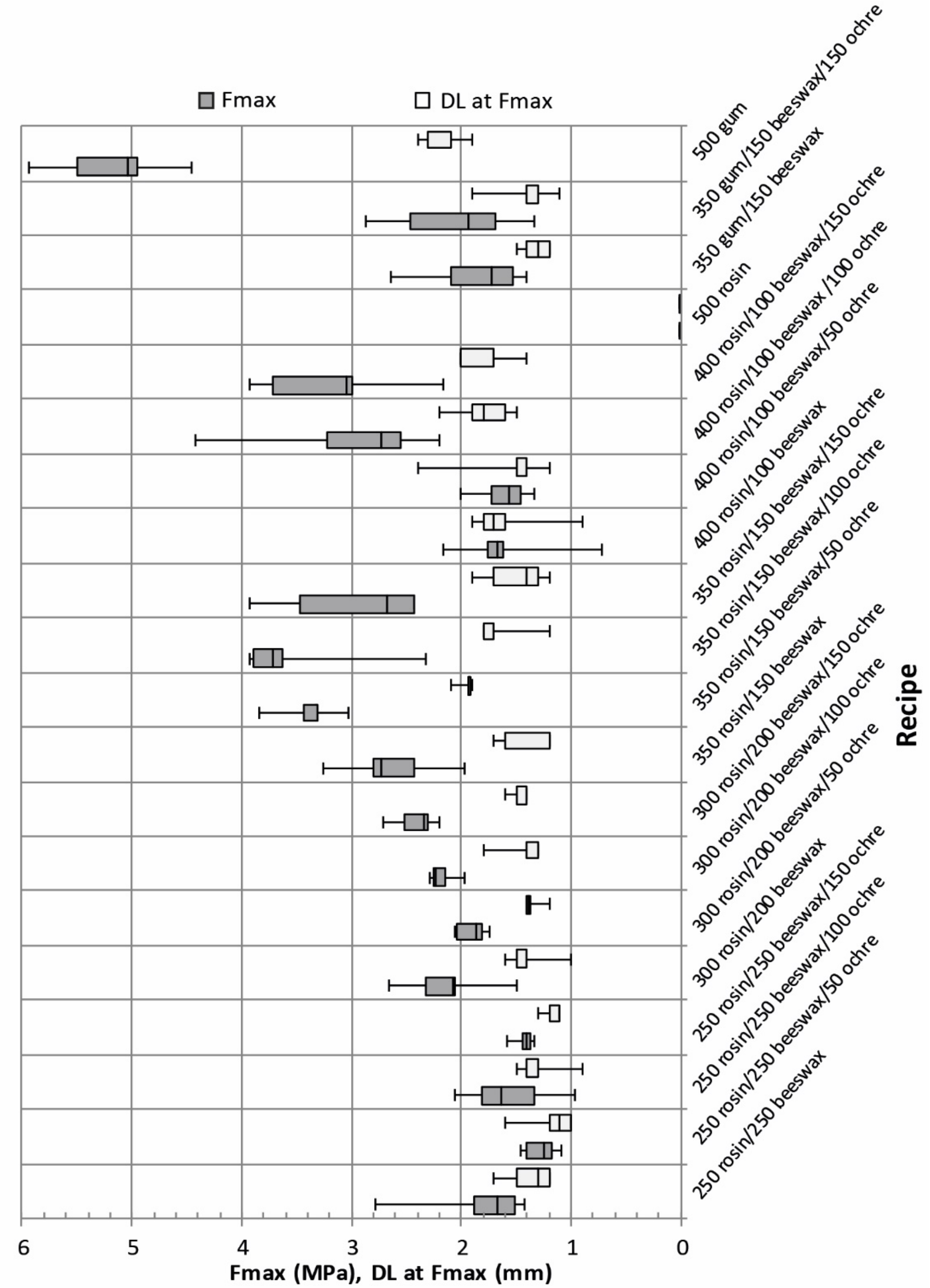

Fig. 6. Lap shear results. Maximum force (Fmax) and displacement at maximum force (DL at Fmax) for each adhesive mixture during lap shear testing. Adhesive recipes are expressed by the mass of each ingredient (mg).

Understanding the failure mode is important for adhesive tests, as it helps indicate which property is being measured. A cohesive failure measures the intermolecular bond strength within the adhesive, while adhesive failures measure the bond between the adhesive and the adherend. With the exception of the 250 mg rosin/250 mg beeswax recipe, which failed adhesively, most other failures were either mixed mode or cohesive (Table 3). However, the classification of failure type on wood lap shear tests proved to be difficult because of the porosity of the wood. Even failures that appeared primarily adhesive still exhibited some evidence of cohesive failure because of the separation of adhesive material with that still present inside the pores of the wooden surface. This was further complicated when ochre was added, as the staining of the wood made it more difficult to separate adhesive failure from cohesive failure. These problems reduced the number of fully diagnostic adhesive failures. Mixed mode failures typically exhibit signs of both cohesive and adhesive failures, and are therefore highly prevalent due to the aforementioned difficulties (Fig 7). There is also a shift among fracture types in rosin adhesives where those ≥350 mg rosin exhibit more brittle fractures and those under <350 mg rosin fail in a ductile manner (Table 3).

Table 3. Overview of failure modes and fracture types from all lap shear tests. Most failures are either cohesive or mixed-mode, suggesting the property being measured was the cohesive strength of the adhesive, and not purely the bond strength to the substrate. Adhesives with <350 mg rosin tend to fail in a ductile manner, while those with ≥350 mg rosin tend to fail in a brittle manner. n=5 for each recipe. Adhesive recipes are expressed by the mass of each ingredient (mg).

Recipe (mg)	Cohesive Failure	Adhesive Failure	Mixed Mode Failure	Brittle Fracture	Ductile Fracture
250 rosin/250 beeswax		5		5	
250 rosin/250 beeswax/50 ochre	3		2		5
250 rosin/250 beeswax/100 ochre	2		3		5
250 rosin/250 beeswax/150 ochre	1		4		5
300 rosin/200 beeswax	5			4	1
300 rosin/200 beeswax/50 ochre	1		4		5
300 rosin/200 beeswax/100 ochre	1		4		5
300 rosin/200 beeswax/150 ochre	3		2		5
350 rosin/150 beeswax	2		3	5	
350 rosin/150 beeswax/50 ochre	2		3	4	1

350 rosin/150 beeswax/100 ochre	3		2	5	
350 rosin/150 beeswax/150ochre		1	4	5	
400 rosin/100 beeswax			5	5	
400 rosin/100 beeswax/50 ochre		3	2	5	
400 rosin/100 beeswax/100 ochre	3		2	5	
400 rosin/100 beeswax/150 ochre			5	5	
500 rosin	-	-	-	-	-
350 acacia gum/150 beeswax	5			5	
350 acacia gum/150 beeswax/ 150 ochre			5	5	
500 acacia gum	5			5	
Total	36	9	50	63	32

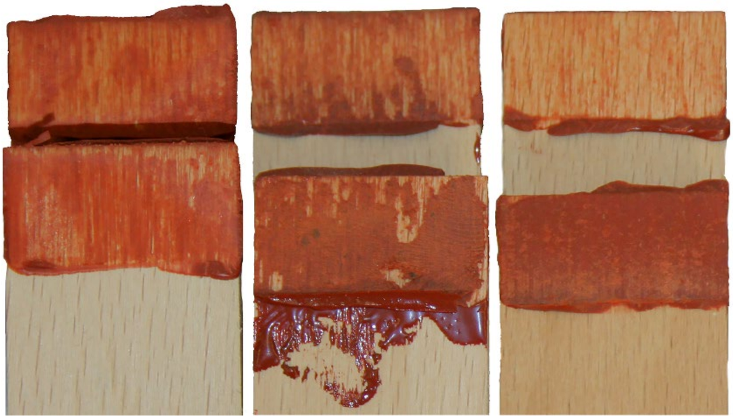

Fig. 7. Example of failure modes through examination of the bonded surfaces after lap shear test completion. Left: cohesive (250 mg rosin/250 mg beeswax/50 mg ochre), the adhesive remains evenly bonded to both sides; middle: mixed-mode (400 mg rosin/100 mg beeswax/100 mg ochre), the adhesive favours one side, but remains bonded to both some areas; right: adhesive failure (400 mg rosin/100 mg beeswax/50 mg ochre), the adhesive remains bonded to one side only.

Impact

The aim of the impact tests was to determine how much each base adhesive was affected by high load rates. Impact resistance is a measure of the adhesive's ability to withstand a rapid application of force. This represents a different practical use of composite tools compared to lap shear tests. Table 4 displays the mean, maximum, minimum and standard deviation of each recipe tested for impact resistance, and Fig 8 shows them in relation to one another. The adhesive consisting of pure rosin was weaker than adhesive mixtures with beeswax and beeswax-ochre (average impact resistance of 0.31 J versus 0.48 J and 0.48 J respectively). One hundred percent acacia gum remained the strongest adhesive and had an average impact resistance of 5.75 J, more than ten times stronger than any rosin adhesive. In addition, the recorded impact resistance for acacia gum was limited in part by the strength of the substrate material and not the adhesive, because in every instance (n=6) the wood specimens broke on or very near the bondline (Fig 9).

Table 4. Overview of impact test results. Mean, maximum, minimum, and standard deviation (S) of impact resistance (J) for each recipe. Adhesive recipes are expressed by the mass of each ingredient (mg).

Recipe (mg)	Mean Impact Resistance	Max Impact Resistance	Min Impact Resistance	S	n
350 rosin/150 beeswax	0.48	0.76	0.33	0.13	8
350 rosin/150 beeswax/150 ochre	0.48	0.54	0.44	0.04	6
500 rosin	0.31	0.44	0.19	0.11	5
500 acacia gum	4.85	6.82	0.36	0.67	6

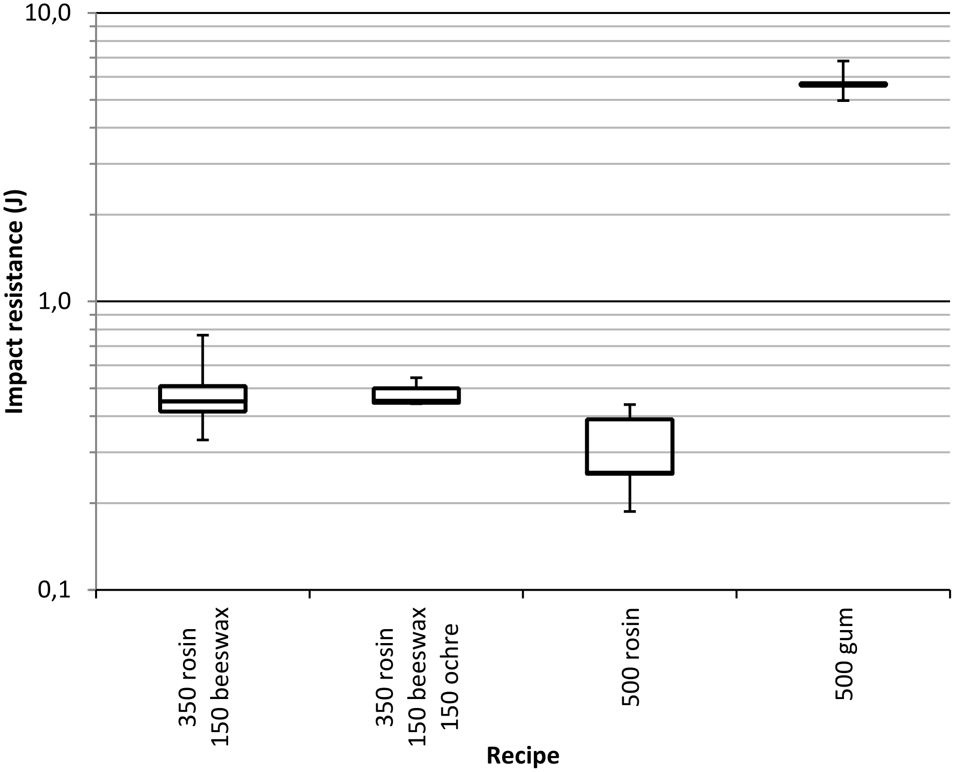

Fig. 8. Impact test results. The logarithmic y-axis represents impact resistance in Joules for each recipe. Adhesive recipes are expressed by the mass of each ingredient (mg).

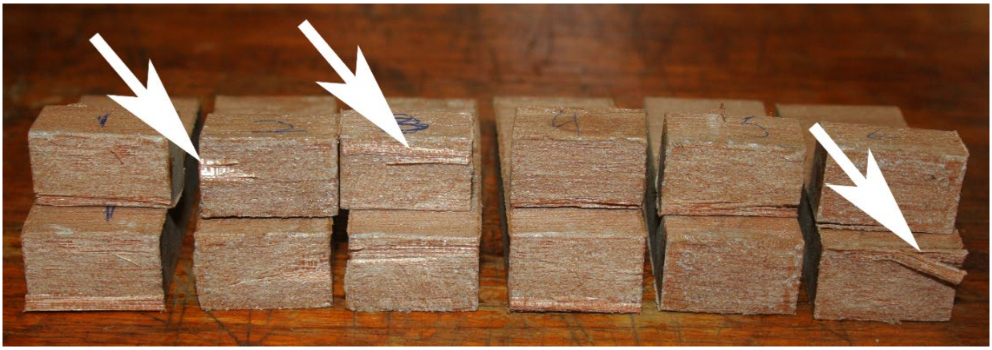

Fig. 9. Photograph showing bonded surfaces of wood adherends with 100% acacia gum after the impact tests. All specimens exhibit some form of substrate failure, though some are more severe than others. The arrows point to areas where the wood failed but the adhesive remained bonded.

During practical use in prehistoric hafting, the adhesive may have acted as more of a plastic to fill spaces and irregularities between the stone insert and the handle, keeping it in place mechanically rather than adhesively. In such cases, measuring the cohesive strength becomes more important. None of the impact tests resulted in adhesive failures. The 350 mg rosin/150 mg beeswax/150 mg ochre adhesive contained one instance of a mixed mode failure, and all the others were cohesive failures, suggesting that the weakest point during impact is the adhesive material itself, and not the bond strength between the two materials.

Discussion

Lap shear experiments with rosin and beeswax performed as expected and support the findings reported in previous studies (Allain and Rigaud 1986; Gaillard *et al.* 2011; Wadley 2005). Beeswax greatly improves the performance by reducing brittleness, and changes of as little as 50 mg (10%) can reveal measurable differences in maximum force and stiffness. However, during the lap shear experiments the optimum ingredient ratio was considerably different to that identified by Gaillard *et al.* (Gaillard *et al.* 2015) under projectile impact experiments. Their results indicate that a ratio of 30% rosin to 70% beeswax is optimum. This difference may be a result from different joint geometries being tested. In our single lap shear joint tests, recipes containing 50% beeswax failed adhesively. If the adhesive was filling an uneven space (e.g. those of Gaillard *et al., p.5* (Gaillard *et al.* 2015)), which would result in more of a mechanical bond holding the flint in place, rather than being between two flat and parallel surfaces, the performance of the higher beeswax content adhesives may improve. This difference compliments the idea that specific adhesive recipes may be required for different tasks, or different haft types, as one type of joint and application of force produces different final results.

The addition of ochre as a third ingredient does not have a one-to-one relationship with performance and does not simply improve each mixture to a certain degree depending on its amount. For example, although it improved the performance in rosin-beeswax mixtures containing ≤30% (150 mg) beeswax, when ochre was added to recipes containing >30% beeswax the resulting adhesive withstood less static force than when no ochre was present. Theoretically, this can be explained by the ratio of rosin to additives. Rosin provides much of the 'tack', holding everything together and sticking to the substrate surfaces, but requires beeswax to prevent it from cracking, and ochre to further stiffen it. Mixtures containing 60% (300 mg) or less rosin are already short on 'tack', and the addition of ochre further reduces the overall amount of rosin, weakening the adhesive even more. However, the ratio of rosin to total weight percentage (wt%) is not the only thing affecting the strength of the adhesive. Ochre was added as an addition to an already blended rosin-beeswax mixture, so 350 mg rosin/150 mg beeswax/100 mg ochre actually contained a smaller rosin-to-total ratio than 300 mg rosin/200 mg beeswax with no ochre, but performed significantly better ($P < 0.01$, two tailed t-test; Fig 10). To summarise, the first step in the process must be correct for the second ingredient to work effectively; add too much beeswax to begin with, and ochre will harm the performance of the adhesive. This suggests that not only is precision required to create the optimum rosin-to-beeswax ratio, but the addition of ochre may require more forward planning if it were to be used efficiently.

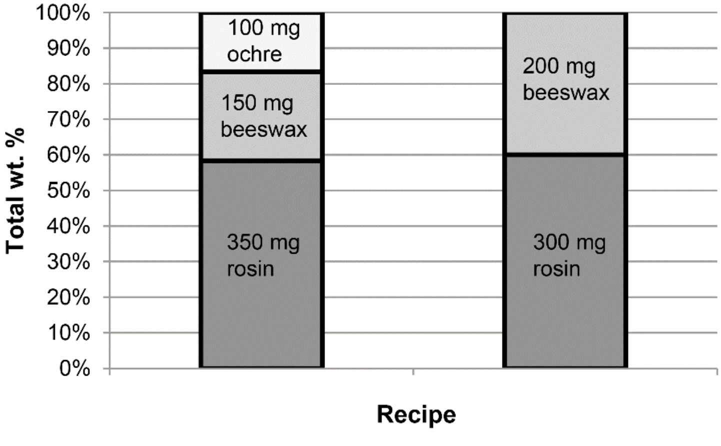

Fig. 10. Comparison of wt% ratios for two different recipes.

As adhesives often play an important part as fillers in a haft, high plastic deformation is a negative trait. We initially hypothesised that adhesives that showed plastic deformation and subsequent warning prior to ductile fractures were beneficial, as preventative measures can often be taken to stop complete failure (Callister and Rethwisch 2010). Ductile fractures also do not result in the same amount of material loss as brittle fractures do, as the latter typically shatters into smaller fragments. In a situation where resources might have been scarce or time-consuming to prepare, preventing absolute failure may have been more important than the maximum strength. However, if an adhesive can withstand a maximum force greater than that which was ever applied to it during use, without undergoing any plastic deformation, then it would remain in its original position after each time it was used. The stone insert would thus be prevented from becoming loose and breaking away from the haft for an extended period of time. Once a material undergoes plastic deformation, however, its shape will be permanently altered. In the context of a hafted stone tool, this may be just enough to create an uneven coverage of either the stone implement, or the wooden handle, creating wiggle room, pressure points, or leverage; all of these can expedite the failure of the haft, and might even necessitate the breaking of the handle or stone insert. Furthermore, tools such as spears would not be very efficient if the point was easily pushed permanently out of alignment. It would therefore be beneficial to determine, through more experimentation, what maximum forces are applied during practical hand-held uses of different tools.

Experimentation by impact testing of pure rosin, rosin-beeswax, and rosin-beeswax-ochre adhesives was conducted to provide a brief comparison of how these recipes perform under different load rates (Girard *et al.* 2014). In general, the performances of the impact tests support those of the lap shear tests. That is, compound rosin adhesives perform better than single component rosin adhesives, and pure acacia gum is the strongest. However, the difference between rosin based adhesives was much less pronounced under impact than lap shear forces. Pure rosin was too brittle and weak to be used in our lap sheer tests, as it broke under the preload of the test machine. However, the performance during impact resistance tests, coupled with examples of resins being used pure from ethnohistoric and archaeological sources (Clark 1975; Helwig *et al.* 2014; Pope 1918) suggests that, although not ideal, pure rosin may still be used successfully for certain applications. For example, if the purpose was to create an adhesive that would shatter on impact thus dislodging the flint point potentially causing more soft tissue damage to the target (Clark 1975; Wadley 2005), pure rosin may be preferable.

Acacia gum does not need any additives and performs exceptionally well under both load types. This is interesting, given previous results from actualistic experiments (Wadley 2005, 2010) in which pure acacia gum was said to be more brittle and weaker than mixtures containing ochre and beeswax. This may result from a different type or origin of the gums used, different environmental conditions, or it may be a result of joint geometry more than adhesive properties. Wadley has shown that pure natural gum adhesives are weak under damp or wet conditions (Wadley 2005). In these situations, additives such as ochre, beeswax or fat may have a different effect on performance. The joints Wadley (Wadley 2005, 2010) used were large balls of adhesive that acted more like a plastic surrounding the stone insert. Our lap shear and impact tests contain only a thin adhesive layer between two flat and well-fitting substrates. Wadley (Wadley 2005) recorded the pure acacia gum adhesives as containing lots of air bubbles and cracks, which crumbled during use. This is less of a problem when the adhesive is applied in a thin layer and clamped. Not only will air bubbles be forced out during clamping and escape a thin layer more easily, the thin layer also reduces the volume of adhesives that may contain large air pockets or defects, thus theoretically reducing the likelihood of weak spots where crack propagation may take place.

The skill required to produce the best adhesive itself is not the only difficult part of creating an efficient haft. Particular adhesives may be better suited to particular joint geometries. The surface preparation and joint assembly must also be accounted for. Surface preparation greatly influences the performance of an adhesive joint (Brockmann *et al.* 2009; Zipkin *et al.* 2014). Any defects along the bondline, particularly near the bond termini, can severely weaken the performance. It follows that if a haft were to be poorly constructed and contained sharp notches, defects, and large spaces 'filled' with adhesive, the strength could be significantly compromised. Although it appears common sense to create smooth edges around a stone tool insert, and we may presently be predisposed to do so for aesthetic reasons, this adds a level of 'folk engineering' to the construction of hafts. Barham (Barham 2013) has already suggested it is likely that the early inventors of hafted tools understood the 'folk physics' of different forces on different tools, such as compression, tension and shear. They would have understood that the haft is the weakest part of the tool, and found ways to improve its strength (Barham 2013). One of these ways was to reduce any point where stresses could concentrate and crack propagation can start. As a consequence, the 'workability' of the material becomes more important in manufacturing a strong haft. A material that is hard to work with, even if stronger than another, may ultimately result in a weaker joint because it contains more defects due to poor application. Lithic standardization and the production of less irregularly shaped artefacts may be another approach to solving this problem. Adhesive performance could be 'improved' by creating a tool that is easier to haft and glue in a clean and smooth manner.

The situations in which acacia gum adhesives broke the wood substrate material during impact tests raise another possibility relating to the addition of ochre and beeswax to some adhesive mixtures. Wooden handles require a considerable investment in time and effort, and it has been suggested that they were re-used (Rots and Van Peer 2006). Stone tools could also be removed from a haft, re-sharpened, and then re-attached (Barham 2013; Pawlik and Thissen 2011; Rots and Van Peer 2006). An adhesive that outlasts both the stone tool and the wooden handle might not be as efficient as one which fails before the other components of the tool. It may be more of an investment to replace a wooden handle than a small amount of adhesive. It is possible that ochre and/or beeswax were added to create a softer and weaker adhesive mixture that would reduce the damage caused to a handle or insert. Furthermore, unlike rosin, which melts easily at low temperatures, dry acacia gum requires crushing and dissolving in hot water before it can be re-used. The addition of beeswax or fat may allow the adhesive to be softened at a lower temperature, facilitating an easy removal of a dull or broken stone insert. More research is required on the effect of additives to specific physical properties of adhesives, such as melting point and tool re-use to validate such hypotheses.

Although the rosin results described above, that ochre as filler and beeswax as a plasticiser can be used to improve the performance of an adhesive, are in agreement with other studies (Allain and Rigaud 1986; Wadley 2010), there is one main difference that should be pointed out relating to *how* ochre improves the performance. Allain and Rigaud (Allain and Rigaud 1986) reported that ochre helps blend resin (rosin) and beeswax, creating a more homogenous mixture. However, it has since been shown that one of the benefits of adhesives made from rosin and beeswax is the natural miscibility of the two ingredients (Girard *et al.* 2014). As a result, they work very well together, specifically because of their ability to blend easily and completely with one another. Acacia gum, although water soluble, has what is known as an 'arabinogalactan protein fraction', which orients oils and makes it naturally able to blend water and lipids. For this reason, acacia gum is employed as an emulsifier to blend ingredients of food-stuffs today, such as water-based drinks with oil-based flavour components (Cunningham 2011; Imam *et al.* 2012; Kennedy *et al.* 2011). It is therefore unlikely that ochre was included to help blend resin or acacia gum with lipid plasticising agents. However, it is still possible that other plant gums potentially collected by MSA humans may not have had this property, and consequently required an ochre-like emulsifying agent.

In a natural setting, the properties of the adhesive ingredients will not be as consistent as our contemporary store-bought counterparts, and the real life applications can vary beyond lap shear and impact test. This is where the 'artisanship' of the tool maker comes in (Wadley 2010). Our results indicate how some specific recipes out-perform others, but to achieve similar results with natural products, many other factors need to be taken into account, understood, and adjusted for. Ochre can vary in quality from one location to another, gum and resin can be affected by exposure time to the air and sun, seasonality and even the previous year's climate (Flindt *et al.* 2005; Hassan *et al.* 2005; Wadley 2010; Mhinzi *et al.* 2008). As shown in our experiments, adhesive efficacy is sensitive to small recipe changes, and this affirms the idea that adhesive manufacturers were ancient artisans [6]. Moreover, it supports the hypothesis that they had the procedural knowledge and cognitive prerequisites necessary for the complex production of compound adhesives, including an understanding of plasticity, consistency, adhesion, and the ability to use abstract reasoning and forward planning. [cf. 6, 8].

Conclusion

Lap shear and impact experiments using different base adhesives and different combinations of additives have successfully shown that changes by as little as 10 wt%. beeswax and ochre can measurably improve performance, but too much will decrease the strength of the adhesive. The addition of beeswax in the correct proportions reduces brittleness, resulting in a stronger adhesive, and ochre can further strengthen the adhesive and will create a stronger and stiffer material, but only in the correct combination with beeswax. Ochre and beeswax improve the impact resistance of pure rosin, but to a lesser degree than they improve lap shear strength. Under the circumstances tested here, pure acacia gum is the strongest adhesive, and unlike rosin it is weakened by the addition of beeswax and ochre. However, the optimum ratio of ingredients is not universal for different base adhesives, or for different tool types and applied forces.

The significant changes that occur in adhesive properties due to small changes in material ratios or manipulations, as demonstrated by the addition of beeswax and ochre to rosin and gum, clearly indicates how intricate adhesive technology is. Rosin-based compound adhesives are challenging to get 'just right', and require precise changes to the ingredients. Considerable technical skill with fire would also be required to melt or dry rosins and gums without burning them (Wadley 2010). Further on-the-spot adjustments to ingredients and ingredient ratios would also be required to compensate for how differently rosin and gum adhesives react to additives. Mental rotation, abstract thinking, forward planning and a detailed understanding of natural adhesive material properties and how they combine would therefore have been required by MSA people to create effective compound adhesives (Wadley 2010, 2005; Wadley *et al.* 2009).

Our results have further demonstrated the wide range of performance properties available from prehistoric adhesives, and their possible suitability for different uses. When the combinative effects of ingredients and additives are considered along with the number of different materials associated with adhesive use and hafting (Ambrose 2010; Charrié-Duhaut *et al.* 2013; Helwig *et al.* 2014; Lombard 2007; Regert 2004), the implied capacity for creative thinking, knowledge, and skill is further increased (confirming Wadley 2010). However, as direct evidence of adhesives from the Middle Palaeolithic and Middle Stone Age is still relatively sparse, additional research will greatly improve our understanding of these materials. Such studies include analysing the preservation qualities, chemical identification and quantification of adhesive components, and more standardized performance testing of different adhesives and joints. All of these research areas will provide additional insight into the purpose of specific materials and material combinations, and will thus contribute to a better understanding of the early humans who used them.

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4. Use and re-use

A new experimental methodology for assessing adhesive properties shows that Neandertals used the most suitable material available

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Abstract

The use of adhesives for hafting stone tools at least 191 ka was a major technological development. Stone tools could be more securely attached to handles, thus improving their efficiency and practicality. To produce functional adhesives required forethought and planning, as well as expertise and knowledge of the resources available in the landscape. This makes adhesives important in discussions about Neandertal and early modern human technological and mental capabilities. However, we currently know very little about how these early adhesive materials behaved under different circumstances, or why certain materials were used and others were not. Here we present the results of controlled laboratory bulk property tests (hardness, rheology and thermogravimetric analysis) on replica Palaeolithic adhesives. We conclude that birch tar is more versatile, has better working properties, and is more reusable than pine resin, the most likely alternative material. Neandertals may therefore have invested more time and resources to produce birch tar because it was the best material available, both functionally and economically, throughout the majority of Europe during the Mid- to Late-Pleistocene. Our results further demonstrate that Neandertals had high levels of technological expertise and knowledge of the natural resources available to them in their environment.

Introduction

Adhesives play a vital role in almost every aspect of modern technology and are studied for many different applications (Keimel 2003; Kinloch 1987; Shields 2013). Yet they are often taken for granted by the general population. Similarly, the archaeological significance of the first use of adhesives was not discussed in detail until relatively recently, owing in part to the limited preservation of organic material from the deep past. The initial discovery of natural adhesives was a major technological development that took place during the mid to late Pleistocene (Koller *et al.* 2001; Mazza *et al.* 2006; Wadley *et al.* 2009; Ambrose 2010; Lombard 2016). Adhesives allowed handles to be securely fixed to stone tools, thus improving efficiency, effectiveness, and greatly aiding the tool users (Barham 2013). Hafting provides greater leverage, allowing more work to be done with less effort, and also facilitates the easier prehension of smaller and sharper stone tools, further benefiting precision tasks. By at least 191 ka Neandertals were producing the first known adhesives by destructively distilling birch bark into tar (Mazza *et al.* 2006). Apart from tar, conifer tree resins used on their own and mixed with ocher and other fillers and plasticizers have been found in southern Africa dating to approximately 60 to 70 ka (Gibson *et al.* 2004; Lombard 2006a; Charrié-Duhaut *et al.* 2013), and in Europe from approximately 55 ka onwards (Bradtmöller *et al.* 2016; Baales *et al.* 2017; Degano *et al.* 2019). Bitumen was also used when it was available (Boëda *et al.* 2008b; Boëda *et al.* 1996; Cârciumaru *et al.* 2012), although natural outcrops are more rare in Europe.

The production of birch tar adhesives during the European Middle Palaeolithic, and of compound adhesives during the African Middle Stone Age are seen as evidence of comparably high levels of cognitive and technological complexity (Wadley 2010; Wadley *et al.* 2009; Wragg Sykes 2015; Villa and Soriano 2010). This is supported by the sensitive nature of resin adhesives to changes in environment and raw materials (Kozowyk *et al.* 2016; Zipkin *et al.* 2014), and further by possible evidence of specific adhesive types being used for specific tasks (Lombard 2007; Wadley *et al.* 2015). Conversely, it has been argued that hafting may not have required anything beyond the already established procedural cognitive abilities of Neandertals (Coolidge and Wynn 2009). It has also been shown how tar production can be discovered and developed through relatively simple steps (Kozowyk *et al.* 2017b). Despite changing perceptions and new discoveries (e.g., Jaubert *et al.* 2016; Aranguren *et al.* 2018), there remains some debate as to whether Neandertals were as technologically or socially adept as contemporaneous modern humans (Gravina *et al.* 2018; Collard *et al.* 2016; Gilpin *et al.* 2016; Coolidge *et al.* 2015).

Considering the importance of these issues and the role adhesives play in discussions about Neandertal technology and cognition, there is currently too little known about the ancient adhesive materials themselves. This makes it difficult to substantiate claims made about the implications of adhesive technology on the development of Neandertals and *Homo sapiens*. Our experiments help fill this gap by providing much needed information on natural adhesive material properties. The data presented here will help elucidate the technological choices made, and the knowledge prehistoric people had of their environment and its resources. For example, does birch tar have superior material properties that might explain why Neandertals went through the trouble of producing it when conifer resins were readily available and commonly used as adhesives (Charrié-Duhaut *et al.* 2013; Helwig *et al.* 2014; Regert 2004)? Likewise, could material properties and availability, rather than technological expertise or cognitive differences, explain adhesive innovation and variation throughout the Middle Palaeolithic?

Unlike lithic studies, which have a long history of experimental research and material analysis (Pelegrin 1991; Tixier 1972; Bordes and Crabtree 1969; Bordes 1947; Pelegrin 2012; Domanski and Webb 1992; Fonseca *et al.* 1971; Dibble 1997; Moore and Perston 2016), research focusing specifically on the material properties of ancient adhesives, rather than the entire haft and delivery system, is comparatively limited. Previous work has demonstrated the sensitivity of compound adhesives to changes in ingredient ratios (Kozowyk *et al.* 2016), how substrate roughness and filler particle size can effect adhesive performance (Zipkin *et al.* 2014), and the effect of combustion features on adhesive deposition and preservation (Cnuts *et al.* 2017). While highly informative, the methods used in these studies are only preliminary, and do not address the full breadth of adhesive properties affecting their use. For example, the lap shear tests used were conducted under a static load and temperature, while the practical application and use of adhesives involve varying temperatures and frequencies. More dynamic testing is therefore required.

There are many aspects of adhesive technology that are vital in the selection of a material, but are not yet well understood for the Palaeolithic. Working properties (the ability to easily manipulate and apply) are an important factor in selecting a material (Petrie 2000). Reusability also has significant implications for the suitability of different adhesives, particularly when resources may be scarce, or production is costly. Limited research has been done focusing on these aspects. Further, many experimental studies focus on projectile use with complete joint geometries (e.g., Fauvelle *et al.* 2012; Gaillard *et al.* 2015; Tomasso *et al.* 2018). This assumes that we know the hafting strategies employed. While still valuable in specific cases, these types of tests only give results applicable to projectiles. Archaeological evidence shows that Neandertals and modern humans were also using adhesives to haft flaked tools for tasks such as chopping, cutting and scraping (Koller *et al.* 2001; Pawlik and Thissen 2011; Hardy *et al.* 2001; Rots *et al.* 2011). As both the joint geometry and the use-type affect the suitability of a particular adhesive, we have used methods that provide bulk material property data, including Vickers hardness, rheology and thermogravimetric analysis (TGA). These take into account changing frequencies and temperatures from different uses, and are not affected by the joint geometry of particular haft types. The data are thus transferable to a wider range of applications.

Materials and methods

Replica adhesive materials

We focused primarily on two types of adhesive: birch bark tar and conifer (pine) resin, as they are of particular interest in discussions about the technological capabilities of Neandertals. Both genera of tree required for these adhesives (*Betula* and *Pinus*) often occur together in pollen records from the Pleistocene (Bigga *et al.* 2015; Dickson 1984), and may have been relatively abundant during periods such as Marine Isotope Stage (MIS) 5a and MIS 7a associated with early archaeological birch tar finds (Helmens 2014; Koller *et al.* 2001; Mazza *et al.* 2006).

Experimental adhesives were reproduced from both birch bark and pine resin. Ocher and beeswax were added to create additional compound resin adhesives

(Table 1). Birch bark was collected from a single mature *Betula pendula* tree in southwestern England in August 2016. Rosin (colophony), ocher and beeswax were purchased from https://www.verfmolendekat.com/en/webshop/ (product numbers 2004247A, 2004215A, 2004087A respectively). The ocher has a particle size of <40 µm, as fine grained (<62.5 µm) particles reportedly perform best (Zipkin *et al.* 2014). Turpentine used was Aquamarijn genuine Portuguese pine turpentine (https://www.ursapaint.nl).

Natural resin is different from birch bark tar as it can be found exuding directly from trees and does not need to be manufactured. Resin is produced by conifers, such as pine (*Pinus*) and spruce (*Picea*), at wounded areas of trees to prevent infection. Fresh resin, sometimes referred to as gum rosin, contains approximately 70-75% rosin, and 20-25% turpentine; the remaining major fractions are water (Fiebach *et al.* 2005). Previously, many archaeological experiments used pure rosin as a base (Gaillard *et al.* 2015; Kozowyk *et al.* 2016; Zipkin *et al.* 2014). This can be purchased commercially at relatively consistent quality levels, making it a good candidate in archaeological experimentation. However, when collected in nature, depending on the age of the resin, the consistency can vary from a clear viscous liquid, to a brittle solid (Fig. 1). For this study, pure rosin was therefore reconstituted with 20 wt. % natural pine turpentine. The resulting material more accurately reflects what is found in nature than pure rosin, and can be consistently reproduced for future experiments.

Fig. 1. Resin dripping from the natural wounds on a tree. Turpentine freezes at -59 °C, so fresh resin is often still soft and sticky at temperatures below 0°C. Older resin at the same location is hard and crumbles easily.

Beeswax improves the hafting qualities of rosin by making it less brittle and easier to work with (Kozowyk *et al.* 2016). Along with ocher, beeswax was used in ancient adhesives, including possible Middle Palaeolithic use at a cave site in Italy (Helwig *et al.* 2014; Wadley 2005; Baales *et al.* 2017; d'Errico *et al.* 2012; Degano *et al.* 2019). Honey producing bees likely inhabited Europe, Africa, and Western Asia by 1 million years ago (Wallberg *et al.* 2014). Beeswax and ocher were therefore included in this study to show how these fillers affect resin, and to better show how a blended and improved compound resin adhesive compares with birch bark tar.

Birch bark tar was produced in a Carbolite GVA 12/300 tube furnace. Inside of which a stainless steel work-tube containing a compartment for holding the birch bark above a screen and funnel that allows the tar to drip out of the bottom of the furnace and into a glass container (Fig. 2). Tar was then reduced to create a more viscous material (Kozowyk *et al.* 2017a). The reduced material is often referred to as pitch. However, we will continue using 'tar' for simplicity and because 'pitch' is also used to refer to gum rosin from conifers. The furnace was programmed to mimic the heating cycle of the most successful raised structure tar production experiment conducted by Kozowyk *et al.* (2017b).

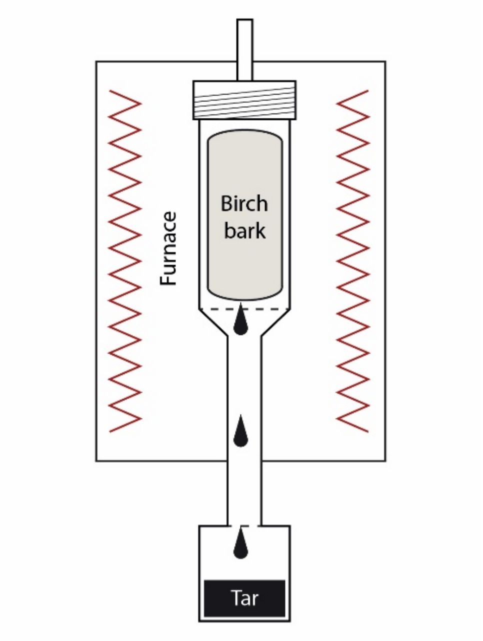

Fig. 2. Schematic of tube furnace heating apparatus used to distill birch bark tar. The work-tube and screen to hold the bark are made of stainless steel with a small outlet at the top to relieve pressure in the event that the lower pipe should become blocked. Not to scale.

Methods

We used three different techniques to show how ancient natural adhesive materials meet the criteria given. Vickers hardness; oscillatory shear rheology; and TGA. For an adhesive to perform well as a stone tool fixative, a number of factors must be met. We consider six criteria as important:

1. It should be readily producible from natural materials available in the environment.
2. It should have good gap filling properties. Stone tools are often irregular shapes that do not form a perfect fit with the haft – adhesives that dry

through evaporation will often shrink excessively. This results in the formation of voids and internal stresses leading to a weak joint (Ebnesajjad 2009). Hot melt adhesives are therefore ideal.

3. It should melt at a low enough temperature to allow for safe application and manipulation by hand.
4. It should be liquid enough to flow and completely cover/bond to the adherend, yet not so much so that it will flow out of the joint before it has set.
5. When cool, it should form a strong and tough solid that can withstand use-forces over a range of temperatures and load rates/frequencies.
6. It should not undergo major physical changes or thermal degradation at melt/application temperatures so that the risk of damaging the material is low and it can be re-used.

Rheology is one of the best methods available for measuring the dynamic properties of an adhesive in both a liquid and solid state. It is therefore the most suitable method for assessing criteria three to six. It is further supported by Vickers hardness tests and TGA to show how exposure to heat during application and re-use affect the materials. These types of tests are often used when studying modern adhesives, and provide information vital in determining the mechanical characteristics of a material (Brockmann *et al.* 2009; Franck 1992; Malkin and Isayev 2006; Mazzeo 2002; Shaw 2011).

Vickers hardness measurements record the resistance to deformation of a material's surface under a controlled load. These were done to expediently record the surface properties of each adhesive before and after continued heating (to simulate re-use or susceptibility to overheating during application). The Vickers method places a diamond shape indenter on the surface of the material and applies a known load (F) for a set amount of time (Fig. 3). Once removed, the volume of the indentation is recorded by measuring the diagonal distance (D) of the diamond impression left in the sample (Fischer-Cripps 2002). Soft materials give large indentations, and hard materials produce smaller indentations. Five measurements were recorded for each adhesive using a Zwick ZHV10 hardness tester with direct mass (5 g) loading of a Vickers diamond pyramid (136°), and the average dimension was used for each material (ASTM 2011b).

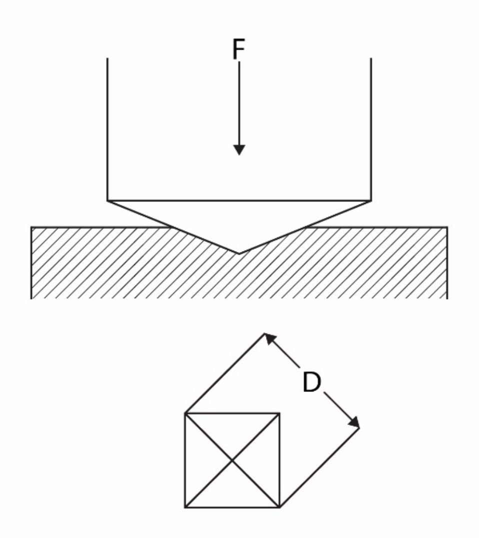

Fig. 3. Schematic depicting Vickers hardness method. Shown here is the diamond indenter and substrate (top) and the shape of the indentation and measurement (bottom). Not to scale.

To understand at what temperature tar and resin adhesives may have been heated to during practical applications, field experiments were first conducted where adhesive 'pitch sticks' (e.g. Gibby 1999) were created, one using birch bark tar, and another with a mixture of 70% rosin and 30% beeswax. These were then heated over an open fire and used to fix a flint flake to a wooden handle. Photographs taken with an FLIR E30 infrared camera shows that during application the adhesives are heated to between approximately 60 and 130 °C (Fig. 4). Therefore, adhesives for the hardness experiments were heated on an electric hot plate at 130 °C. This simulates the hottest temperatures likely attained when applying adhesives in the field using an open fire. Five measurements were recorded for each material after heating for 2 min to ensure an even mixture of each adhesive, and then for 5, 10, 15, 20 and 40 subsequent minutes. Ambient temperature during tests was approximately 22 °C and 65% relative humidity.

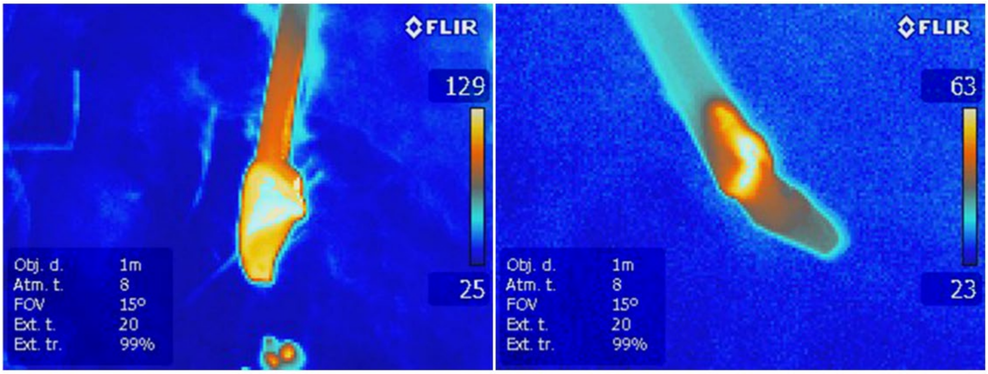

Fig. 4. Infrared photographs of a 'pitch stick' used to haft a flint flake to a wooden handle. The resin is held over a fire and warmed until it melts, then it can be 'dabbed' onto the objects to be glued. Photographs are of (left) the pitch stick immediately after heating over a fire before application, and (right) finished adhesive holding a flint blade (approx. 3 cm long) to the end of a wooden handle.

Oscillatory shear rheology studies the flow and deformation of materials (Menard 1999). How adhesives flow at different temperatures and frequencies is vital for determining their suitability for certain applications. This is especially important for the macroscopic mechanical behaviour of soft materials, such as birch tar, pine resin, and most polymeric materials and melts, because many of them are viscoelastic. The degree of viscous and elastic responses of a material will also change depending on the temperature and frequency of the applied load. High temperatures or low frequencies typically elicit a viscous response, while low temperatures or high frequencies elicit an elastic response. Hot melt adhesives must easily flow during application to create a strong bond with the substrate, and then cool into a tough solid for use (Marin *et al.* 1991). The speed at which the adhesive cools and sets must be fast enough so that it will not flow out of the joint assembly before hardening, yet slow enough to provide the user enough working time to apply it correctly. Measuring these properties is a highly informative way of understanding adhesive characteristics, and rheology is one of the best techniques for doing so.

Oscillatory shear rheology is a form of torsional dynamic mechanical thermal analysis where a cylindrical sample is placed between two parallel plates. The top plate is sinusoidally oscillated about its axis at a fixed strain rate, and the resulting torsional stress is recorded while varying the frequency and temperature (Fig. 5). When a sinusoidal deformation is applied to a perfectly elastic solid, the stress and strain are in phase ($\delta = 0$), and all of the energy of deformation is recoverable in the form of a spring. In a purely viscous material, the phase angle (δ) is exactly 90° because all of the energy is lost to heat (Duncan and Price 2002).

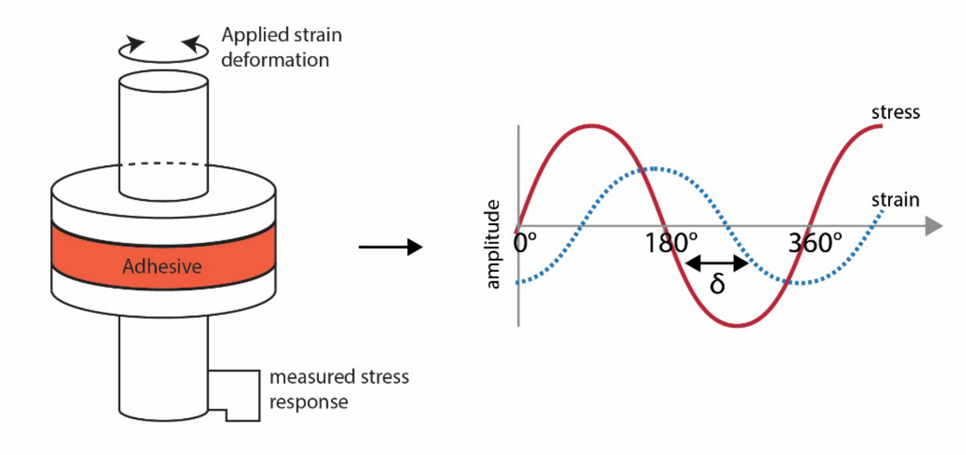

Fig. 5. Schematic showing sample and output data from the rheometer. Left: the adhesive sample between the upper and lower plates of the rheometer and the force oscillating about the y-axis (not to scale). Right: the resulting oscillating stress/strain curve. For ideally viscous liquids δ = 90° and ideally elastic solids δ = 0°.

When a sinusoidal deformation is applied in shear to a viscoelastic material, such as a hot-melt adhesive, the complex shear modulus (G*, the ratio of stress to strain under vibratory shear conditions) can be calculated:

$$G * = G' + iG$$

Where G' is the in phase (elastic) storage modulus, and G" is the out of phase (viscous) loss modulus. The ratio G"/G' gives the mechanical intrinsic damping or loss factor (tan δ) which can be calculated:

$$\tan \delta = \frac{G''}{G'}$$

For adhesive systems, a high value of the storage modulus helps to effectively distribute stress. This generally results in improved impact and peel properties. To enhance the tack of an adhesive, tan δ should be greater than unity, thus G" > G'. For more detailed information see Menard (1999), Hon (2003) and Malkin and Isayev (2006).

In practical terms, G' indicates the solid portion of the material, and is a measure of the hardness and elasticity of the adhesive at a certain temperature. G" represents the liquid portion and gives a sense of the plasticity (non-recoverable deformation) of the adhesive. If G’ is greater than G”, the material is more solid than liquid. When G’ is less than G” (tan δ > 1), the liquid portion dominates, and the adhesive is more fluid-like and can be considered ‘open’. This is when the adhesive will flow and wet the substrate surface, providing a bond between adhesive and adherend (Petrie 2000). Tan δ represents the relationship between the G’ and G”; when tan δ < 1, lower values indicate higher cohesive strength (more cross-links) (Franck, 1992). Modern general purpose hot melt adhesives will often have a G’ at room temperature (25 °C) of about 50 to 500 MPa, and a tan δ value of between 0.1 to 0.3 (Franck 1992). In general, the adhesive should become soft and malleable enough to mould into shape and adhere to the stone tool, yet not so soft that it will flow out of the joint. Ideally, the adhesives should also melt at a temperature that is high enough that it will not melt under normal ambient/environmental conditions, yet low enough so as not to burn the user or cause thermal degradation to the adhesive.

Rheological experiments were conducted using a HAAKE MARS III rheometer with a temperature controlled test chamber and a plate diameter of 8mm and a gap of ~2 mm. The gap changes slightly depending on thermal expansion and flow of the sample. Cylindrical samples of birch tar, resin, resin/ocher, and resin/beeswax 8 mm in diameter and ~2 mm thick were produced to match. To reduce irregularities in the sample size or surfaces, and to relieve internal stresses, the samples were positioned inside the plates of the apparatus and were heated to 40 °C for five min before the tests began. A temperature sweep was conducted from 0 to 70 °C in 5 °C steps. The temperature then dwelled at 70°C for 30 min, and cooled to 25°C for a final measurement. Pure rosin (colophony) was one exception and had a start and end temperature of 30 °C as it would shatter before the test could be completed at lower temperatures. 0.1% strain was applied at each temperature at frequencies increasing logarithmically in 12 steps from 0.1 Hz to 10 Hz. The relatively low level of strain applied prevented catastrophic failures of more brittle materials. These frequencies and temperatures provide a range attainable during practical application and use of hand held stone tools. For example, experiments have shown that hide scraping gestures can have a frequency of approximately 1Hz (Pfleging *et al.* 2015). High frequencies more closely resemble impact or high load rate applications, and low frequencies focus on shear resistance. Each temperature and frequency point was recorded in triplicate and the average value was used. Data analysis and interpretation was conducted using the HAAKE RheoWin software. Modulus crossover and onset points for rheology and TGA were calculated using a linear/cubic spline interpolation technique in TA instruments Trios software v4.3.1 (TA Instruments, New Castle).

Thermogravimetric analysis (TGA) continually measures a sample's mass as a function of increasing temperature over time. Changes in the mass of the sample can indicate physical phenomena including phase changes, thermal decomposition, and absorption and desorption (Coats and Redfern 1963). For the purpose of studying ancient hot-melt adhesives, it is important to understand at what temperatures thermal decomposition begins. This will show which temperature the adhesive can withstand, influencing the ease at which they can be safely heated or re-used without any adverse effects as a result of decomposition. A Perkin Elmer Thermogravimetric analyser TGA 4000 was used to heat each sample (~10-30 mg) in turn from 30°C to 400°C at a rate of 10°C/min under a constant 20.0 ml/min nitrogen flow.

Complete data recorded for each experiment can be found in the supplementary online material, uploaded as a Mendeley Dataset (SOM; doi:10.17632/z69zs69mpg.1).

Results

Hardness

The mean values for each sample are shown in table 2. After 20 min of heating, the resin and resin/ocher mixtures cracked under the indentor and no further accurate measurements could be taken. Final hardness measurements for resin and resin/ocher therefore occur at 15 min. Resin/beeswax and tar adhesives were continually heated with no such problems until 40 min. After 15 min of heating, the resin and resin/ocher adhesives increased in hardness by nearly 3 orders of magnitude (1000×), whereas in the same amount of time, resin/beeswax increased by 2.3×, and tar by only 1.3× (Fig. 6). Beeswax therefore improves the properties of resin adhesives twofold: by hardening soft fresh resin, and also preventing over-heated resin becoming catastrophically brittle.

The variability in hardness between fresh resin and heated resin shown in this paper suggests that there is a 'sweet spot' where resin can perform adequately, especially considering some joints may also have been bound with plant or animal fibers. This is attested by archaeological and ethnographic evidence (Helwig *et al.* 2014; Pope 1918). However, birch bark tar proved to be the least affected, and was more able to withstand prolonged exposure to contact with a 130 °C surface.

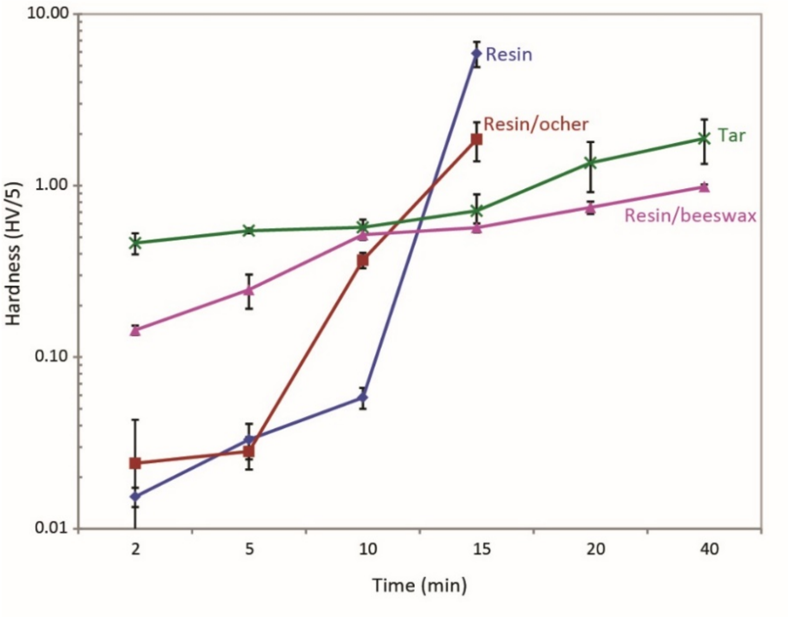

Fig. 6. Hardness measurements as a function of heating time. Hardness of resin, resin/ocher, resin/beeswax, and tar adhesives shows that tar is the least affected by prolonged heating.

Oscillatory shear rheology

The rheological properties of an adhesive are highly dependent on both the temperature and frequency of the tests conducted. Therefore there are a number of important results to examine. The materials tested here will be considered more suitable as a prehistoric adhesive used for hafting stone tools if they have:

1. High G' at the working temperature at which the adhesives are used (25 °C), indicating improved impact and peel properties.
2. Low tan δ (when tan δ < 1) at 25 °C, indicating improved cohesive strength during use.

3. A high temperature G’/G” crossover, so that the material remains primarily elastic at use temperatures.
4. A small change to G* before and after heating to 70°C and holding for 30 min, indicating low levels of degradation at application temperatures.
5. Finally, the comparison of traits at different frequencies will provide an indication of how an adhesive behaves during different uses or tasks. Low frequencies tend to indicate behaviour during application processes and low load rates, and high frequencies indicate behaviour during high load rate applications such as impact resistance.
6.

At room temperature and 1 Hz, the resin tested has a G’ of 0.21 MPa, G” of 1.31 MPa and tan δ of 6.37. Under the same conditions, resin/ocher G’= 0.50, G” = 2.76, tan δ = 5.52; resin/beeswax G’= 8.14, G”= 6.01, tan δ = 0.734; and tar G’= 79.85, G”= 43.91, tan δ = 0.55 (Figs. 7 and 8). Rosin could not be measured at 25 °C because the sample shattered before the test could be completed, but values for 30 °C can be found in Table 3. At 1 Hz the G’/G” crossover for each adhesive is: rosin = 50.7, resin = 8.50, resin ocher = 9.16, resin/beeswax = 43.81, tar = 42.08. Rosin/beeswax could not be tested because at any temperature lower than 25°C it failed and slipped on the plates. Higher clamping pressure would normally solve this problem, but with these relatively weak materials it will either shatter the adhesive, or press it out from between the apparatus plates.

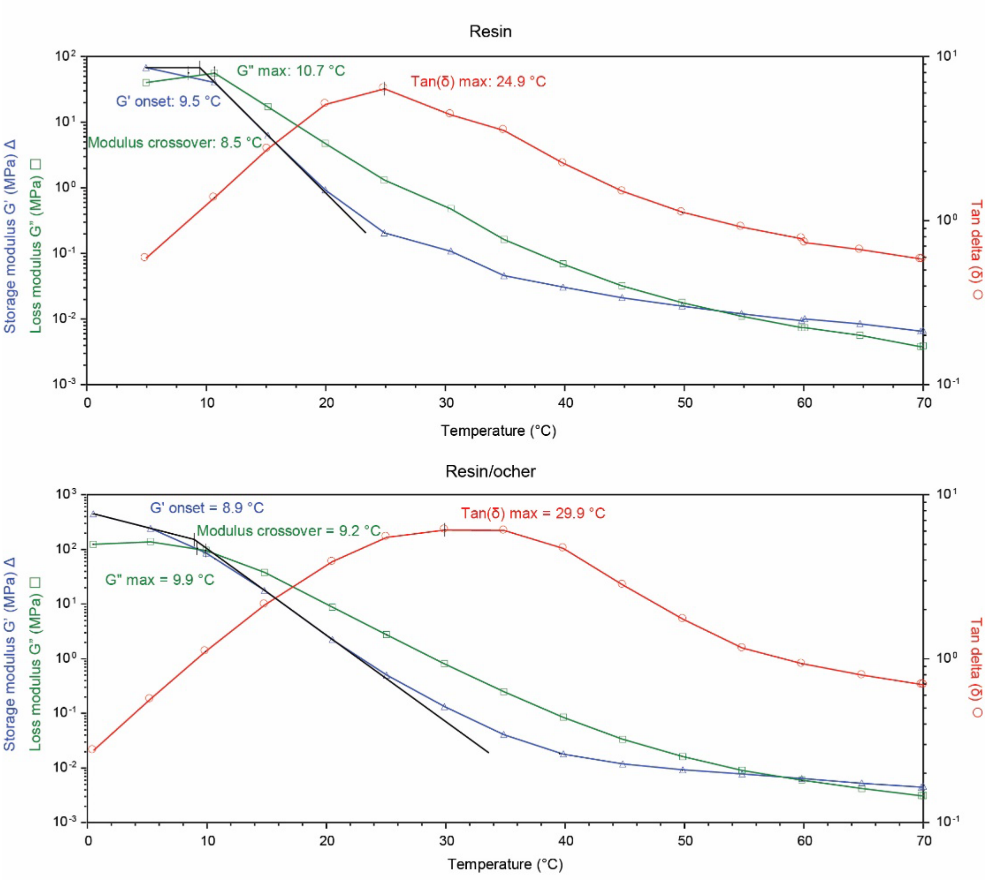

Fig. 7. Rheology temperature sweep results. Plot shows the G’ onset, G” maximum, modulus crossover, and tan δ maximum of resin (top) and resin/ocher (bottom). Changes are very subtle with the addition of 30 wt.% ocher.

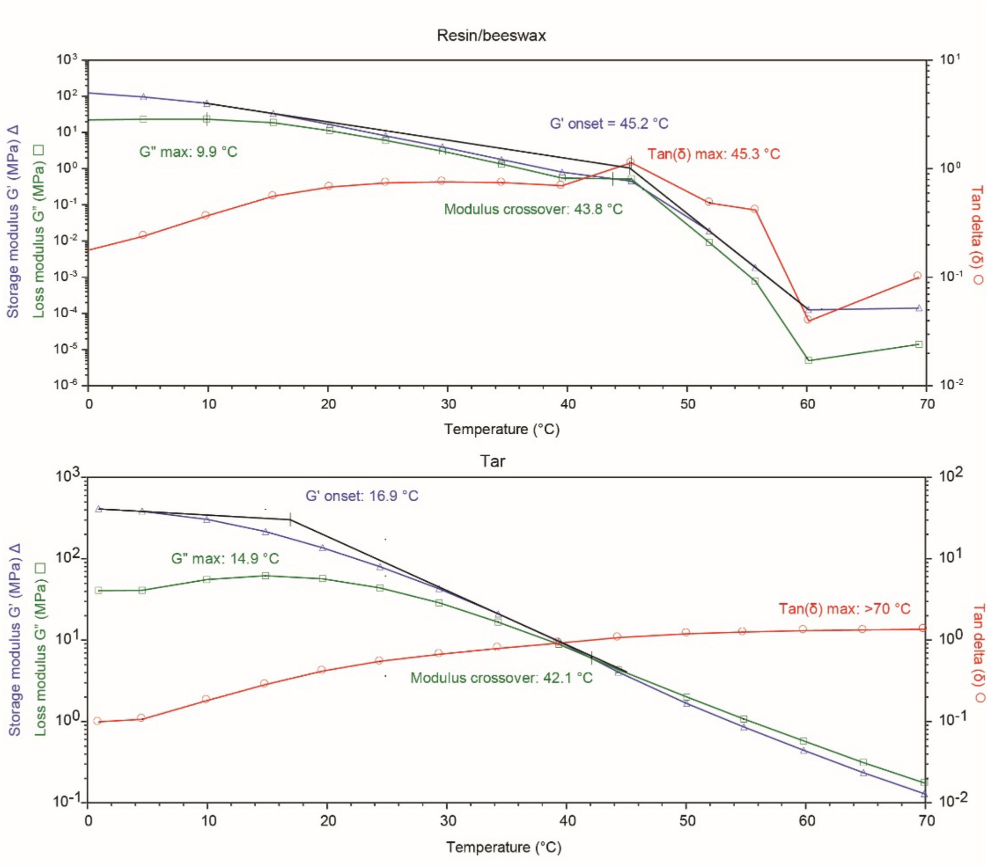

Fig. 8. Rheology temperature sweep results. Plot shows the G' onset, G" maximum, modulus crossover, and tan δ maximum of resin/beeswax (top) and birch bark tar (bottom). The addition of beeswax makes resin more closely resemble birch bark tar. After 60 °C, the moduli for beeswax become very low and less reliable, possibly resulting from the material melting and separating from the upper plate of the rheometer.

Complex shear modulus (G*) values, which represent the overall stiffness of the materials, changed more for resin based adhesives than it did for tar after 30 min at 70 °C (Table 3). G* for resin increased from 2.44 MPa to 12.71 MPa, resin/ocher from 2.80 MPa to 17.04 MPa, resin/beeswax from 10.12 MPa to 37.69 MPa, and tar from 175.49 MPa to 181.94 MPa. This could not be measured for rosin and rosin/beeswax because the samples failed during testing at 25°C before (rosin) and after (rosin/beeswax) heating to 70° C. Resin failed during testing at 0 °C, but was successful at 5 °C. Low temperature characteristics (at 5 °C) of resin, resin/ocher, resin/beeswax, and tar are shown in Table 4.

At low temperatures (0–5 °C), resin shows a lower G* and higher tan δ than any of the measured materials. The high tan δ suggests it has a weaker cohesive strength than the other adhesives. It is therefore not surprising that it failed (brittle fracture) before the tests could be completed at 0 °C. Resin/ocher is stiffer than resin/beeswax, but with a tan δ of 0.57 compared to 0.24, it still shows less cohesive strength. Resin/beeswax and tar both have a tan δ between 0.1 and 0.3 and G' between 50 and 500 MPa, so even at lower temperatures, they fall within the range suggested for modern hot melt adhesives (Franck, 1992).

At higher frequencies (10 Hz) and low temperatures (5 °C) resin has a G' of 84.14 MPa and tan δ of 0.29. For resin/ocher under the same circumstances G' = 480.00 MPa and tan δ = 0.21; resin/beeswax G' = 130.64 MPa and tan δ = 0.17; tar G' = 427.60 MPa and tan δ = 0.06. Under these conditions, resin does have qualities comparable to the other adhesives at warmer temperatures or lower frequencies. However, the cohesive strength, as indicated from the tan δ value of tar, is still higher than any of the others.

Thermogravimetric analysis

Here we used the temperature where resin had lost 20% of its mass as a point of comparison with the other adhesives because the resin adhesive consisted of 80% rosin and 20% turpentine, and the pure rosin adhesive is too brittle to function well as an adhesive at room temperature. This occurred at 250 °C after a time of 24.58 min. At this temperature, pure rosin decreased to 95.48% of its original mass, beeswax to 99.60%, and tar to 99.70%. A mixture of resin/beeswax had decreased to 89.55%. A comparison of the mass curves (Fig. 9) shows that resin begins to lose mass above 100–150 °C, this is a gradual slope as the turpentine fraction is evaporated, until around 275 °C, the curve begins to fall more rapidly (as with that of pure rosin). Resin/ocher behaves similarly to resin; only the overall mass loss over the temperature range 30–375 °C is smaller because of the 30% ocher content. Tar does not reach 80% of its original mass until over 375 °C. Another comparison is to look at the extrapolated onset temperature (T_o) of each material. This is the intersection of the extrapolated baseline and a tangential line drawn from the slope of the weight loss curve, denoting when weight loss begins (Earnest 1988). Tar and beeswax were not heated to a high enough temperature to accurately determine their T_0, so a comparison between these materials is more difficult. However, it is clear that the T_0 of tar and beeswax occurs at a higher temperature than pure rosin, and at a much higher temperature than resin, showing tar and beeswax to be the least affected by temperatures under 300 °C. T_0 for each adhesive is approximately 301 °C for rosin; 146 °C and 293 °C for resin; 152 °C and 295 °C for resin/ocher; 149 °C and 307 °C for resin/beeswax; 333 °C for beeswax; and 333 °C for tar. The primary onset temperature for resin, resin/ocher, and resin/beeswax corresponds with one another and can be attributed to the evaporation of the primary turpentine components starting at ~150 °C (Mirov 1961). The secondary onset temperature for resin, resin/ocher, and resin/beeswax corresponds with the onset temperature for the thermal degradation of rosin at around 300 °C.

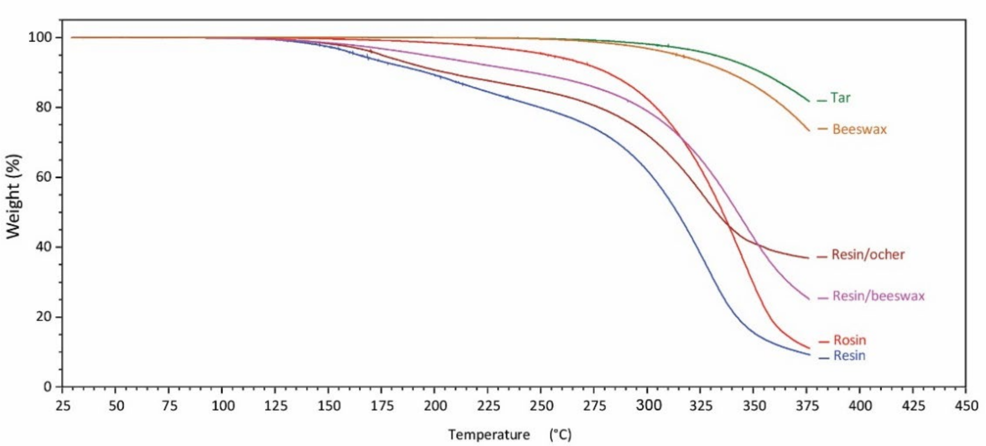

Fig. 9. TGA curves. Plot shows the weight loss (%) for tar, resin, resin/ocher, resin/beeswax, beeswax, and rosin during heating from 30 °C to 370 °C.

Summary of results

Tar has a higher cohesive strength between 0 and 25 °C (indicated by lower tan δ values) and is stiffer (indicated by a higher G*) with better impact and peel resistance (indicated by a higher G’) than resin adhesives. Resin adhesives are often brittle at low temperatures or high frequencies and soft at higher temperatures or lower frequencies, limiting their range of use. Further rheological and TGA measurements show that birch bark tar is the least affected by exposure to high temperatures. After maintaining a temperature of 70 °C for 30 min, for example, the rheological properties of tar changed very little, while resin based adhesives became stiffer. Likewise, tar loses very little mass until over 300 °C and resin begins to lose its turpentine portion between 100 and 150 °C, making it more brittle. Hardness results also support this. Birch tar is therefore a more versatile and suitable material for use as a Palaeolithic adhesive.

Discussion

Until approximately two decades ago, Neandertals were commonly seen as technologically and behaviourally inferior to their anatomically modern human counterparts. The capacity for regular innovation and symbolic thought, for example, were often seen as uniquely modern human traits (Mellars 2005; Klein 2008; Villa and Roebroeks 2014). Since then, this viewpoint has shifted with the discovery and documentation of such finds as wooden spears (Thieme 1997), early adhesives (Mazza *et al.* 2006; Koller *et al.* 2001), exploitation of marine resources (Cortés-Sánchez *et al.* 2011), and potentially symbolic or decorative items and pigments (Soressi and d'Errico 2007; Zilhão *et al.* 2010; Peresani *et al.* 2011; Roebroeks *et al.* 2012). This pattern of discoveries has continued with specialized bone tools (Soressi *et al.* 2013), evidence for planned hunting strategies (Schoch *et al.* 2015), traces of fire production (Sorensen *et al.* 2018) and wooden tools treated or manufactured with fire (Aranguren *et al.* 2018). The finds mentioned above all point to a more advanced technological repertoire than was previously imagined.

In addition to using fire to process wooden implements, Neandertals were also selectively choosing certain tree or animal species, elements, and size ranges for particular tools (Mallye *et al.* 2012; Daujeard *et al.* 2014; Rougier *et al.* 2016; Aranguren *et al.* 2018). Neandertals were likely deliberately selecting Manganese dioxide at Pech-de-l’Azé I due to its beneficial use in fire starting by reducing the auto-ignition temperature of wood (Heyes *et al.* 2016). At Le Moustier, there is evidence Neandertals developed specific technology, adapted to the size and density of the raw material, for processing similar Manganese rich rocks (Pitarch Martí *et al.* 2019). At Poggetti Vecchi, Italy, Boxwood, (*Buxus sempervirens*), the hardest and densest of all European woods, was likely chosen based on its favorable material properties. The laborious task of working such a hard material was lessened by using fire to partially char the material (Aranguren *et al.* 2018). Could Neandertals have had a similar approach and skillset with regards to adhesives, finding solutions to a costly production in order to use a more suitable material? This possibility can be explored by considering what makes a successful stone tool hafting adhesive. Using the criteria first given in the methods section above, a successful material should be readily available in the environment, have good gap filling properties, have melt characteristics suitable for application by hand, form a tough solid when cool, and not undergo major thermal degradation during application.

To date, Middle Palaeolithic adhesives that are securely chemically identified as birch bark tar can be attributed to MIS 7 and MIS 5a (Koller *et al.* 2001; Mazza *et al.* 2006). European pollen records show that both *Betula* and *Pinus* were often prevalent species at these times (Helmens 2014; Tzedakis *et al.* 2004; De Beaulieu *et al.* 2001). Pollen analysis of the layers containing the tar pieces from Königsaue also show an abundance of *Betula* and *Pinus* (Mania 1999). It is possible to discover birch bark tar through relatively simple processes (Kozowyk *et al.* 2017b), although it may still have been a greater time and resource investment than collecting fresh conifer resin. Wherever there are conifers, such as spruce and pine, sticky resin can be found naturally exuding from wounds in the trees. Evidence shows that Neandertals collected and used this resin, possibly with beeswax, at two cave sites in central Italy at approximately 40-55 ka (Degano *et al.* 2019). Beeswax was likely available throughout many of the temperate and warmer periods of the Pleistocene, although its availability remains unknown. Beeswax has also been shown to create a strong adhesive when mixed with rosin (Gaillard *et al.* 2015), and was used in the more recent past (Regert 2004; Baales *et al.* 2017). Both birch bark and pine resin would therefore have been similarly available to Neandertals, and it is clear that they were using these materials. Beeswax was also accessible, but may have been so to a lesser degree.

Unlike other natural adhesives, including plant gums and animal glues, resin and tar are thermoplastic materials which gain strength through solidification/crystallization. They operate as hot melt adhesives and must be applied in a molten state. An added value of these types of hot melts is that they show very good gap-filling properties. There may be some shrinkage as the material cools, but much less so than with a water-based material, such as gum or hide glue, which dry through evaporation. In general, because of the high hydrocarbon nature of tar and resin materials, they also show a low surface tension and wet most surfaces moderately well, thus providing good adhesion.

Both resin and tar adhesives can flow at temperatures below what may cause burning or discomfort to human skin (Lawrence and Bull 1976). Resin and resin/beeswax adhesives become more highly fluid at lower temperatures than birch tar, and tar retains more of its structure at higher temperatures, so is less likely to flow out of the joint assembly before fully solidifying. Finally, of the materials tested, birch tar is the least affected by prolonged exposure to higher temperatures, and maintains the highest rigidity and cohesive strength at use temperatures.

Although it is a greater investment to produce tar, once made, the material outperforms pine resin adhesives in every regard. Birch tar has properties favourable for improved workability, thus being easier to handle and apply. It also has the highest cohesive strength and is a more economical material to use because of the ability to reheat and re-use it with little detrimental effects on performance. Out of the materials available in Europe during the Middle Palaeolithic, birch tar was the best option. This also explains why birch tar technology continued long after the demise of Neandertals.

However, this does not preclude other natural adhesives from being used. Evidence shows that Neandertals were using resin (Degano *et al.* 2019) and Mousterian tools were hafted with bitumen, although in Southwest Asia this is not reliable evidence that they were made by Neandertals (Villa and Soriano 2010). Indirect evidence also suggests bitumen was used at El Sidrón, Spain (Hardy *et al.* 2012). However, bitumen may have varying material properties depending on the source, thus requiring different preparation. It is possible this was not as complex as distilling tar or combining desperate ingredients to form a compound adhesive. Further testing would be of interest here to see if bitumen quality is consistent, or if different sources provide bitumen with different material properties.

In environments without birch, such as Africa or parts of Asia, there may be no plant alternative that is as easily and effectively distilled into tar. In such environments, materials including resin, latex, and gum have been used (Helwig *et al.* 2014; Dickson 1981; Powell *et al.* 2013; Wadley *et al.* 2015; Sahle 2019). Weaker materials can also be selectively employed with the intention that the adhesive fails. For example, to dislodge a projectile point inside of a prey to increase hemorrhaging (Campbell 1999). However, this only benefits projectiles, and is not applicable to the hafting of flakes, knives and scrapers, which make up the majority of known chemically identified Neandertal adhesives. Past experiments have also shown that some of these materials can only be reheated once or twice (Parr 1999), making them less reusable than birch bark tar. Due to the poor preservation of organic remains, we likely have a fragmented account of adhesive use during the Palaeolithic. Further archaeological discoveries will add to the number of ancient adhesive types that should be tested in the future. In turn, this will provide a more complete understanding of how adhesive technology relates to different tool uses and environmental constraints.

The selectivity of birch bark tar over other materials shows that by as early as approximately 191 ka Neandertals had already found the best adhesive material and stuck with it. By distilling birch bark to produce tar, Neandertals demonstrated their knowledge of material properties and their use of technology and abilities to go beyond simply using what was immediately available to them. The superiority of birch tar can be further attested to by reliance on the material during the Middle and Upper Palaeolithic, and throughout the Mesolithic, Neolithic, and Iron Ages (Aveling and Heron 1998; Leito *et al.* 2011; Ribechini *et al.* 2011; Urem-Kotsou *et al.* 2002; Regert *et al.* 2003; Aveling and Heron 1999; Van Gijn and Boon 2006; Dinnis *et al.* 2009). It is possible that the technology, known and used by Neandertals was recognized as superior and adopted by early modern humans arriving in Europe. Alternatively, once modern humans came into contact with birch, they could have discovered tar independently in the same way as Neandertals; by recognizing the black and sticky material inside a half-burnt roll of bark (Kozowyk *et al.* 2017b). Although the prehistoric methods of distilling tar from bark have been lost, processing extractives from birch bark still continues to this day (Krasutsky 2006).

Conclusions

Evidence of hafting adhesives plays an important part in discussions about the technological and cognitive capabilities of Neandertals and early modern humans.

Adhesives from archaeological contexts have been used to imply complex cognition, and the controlled use of fire (Wragg Sykes 2015; Roebroeks and Villa 2011; Wadley 2010). However, without more detailed information on the material properties, it has been difficult to further expand this research. We know very little about how the first natural adhesives behaved under different circumstances. This limits our understanding of why certain materials were used in the past and others were not. Based on our results, Neandertals would have produced birch tar because it is better suited to hafting stone tools than pine resin, the most likely alternative. Birch tar remains stronger over a range of temperatures and for a wider array of uses. It has better working properties, making it easier to apply successfully, and is more reusable than pine resin based compound adhesives. Birch tar was therefore the best adhesive material available throughout most of Europe during the Middle Palaeolithic. Neandertals likely invested more time and resources to produce birch tar, instead of using less versatile but easier to source alternatives. This reaffirms the technical abilities of Neandertals by showing yet another instance of them functioning on the allied principles of both technological flexibility and choices based on material properties.

5. Preservation

Understanding preservation and identification biases of ancient adhesives through experimentation

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Abstract

Adhesive production is one of the earliest forms of transformative technology, predating ceramics and metallurgy by over 150,000 years. The study of adhesive use by Neandertals and early modern humans currently plays a significant role in debates about human technological and cognitive evolution. Depending on the type of adhesive used, different production sequences were required. These can vary in complexity, and would have needed different knowledge, expertise, and resources to manufacture. However, our knowledge of this important technological development is severely hampered by poorly understood taphonomic processes, which affect the preservation and identification of adhesive materials, and leads to a research bias. Here we present the results from a three year field preservation experiment. Flint flakes hafted and non-hafted with replica adhesives were left to weather naturally on and below the surface at two locations with different soils and climatic conditions. Differential preservation was recorded on a variety of natural adhesives by digitally measuring the surface area of each residue before and after the elapsed time. Residues were further assessed and photographed using metallographic optical microscopy. Results show that certain adhesives preserve to a significantly higher degree than others, while some materials may be more easily overlooked or visually misdiagnosed. We must therefore be aware of both taphonomic and identification biases when discussing ancient adhesive technology. This research provides a first look that will help us understand the disparities between which adhesives were used in the past, and what we find in the archaeological record today.

Introduction

Adhesives and hafting have recently become the focus of intense study within the field of Palaeolithic Archaeology. Compound adhesive production by Middle Stone Age humans in southern Africa, and hafting composite tools in general, is seen as evidence of complex cognition implying modern thinking earlier than previously thought (Lombard 2007; Wadley 2005, 2010; Wadley *et al.* 2009; Wadley *et al.* 2004; Wynn 2009; Barham 2013). The production of birch bark tar by Neandertals has also featured in discussions about their technological knowledge and abilities, including their use and control of fire (Kozowyk *et al.* 2017b; Roebroeks and Soressi 2016; Villa and Soriano 2010; Wragg Sykes 2015; Roebroeks and Villa 2011; Niekus *et al.* 2019). A range of experimental work has provided further background knowledge on the material properties and the effects of fire on adhesive residues (Kozowyk *et al.* 2016; Kozowyk *et al.* 2017a; Zipkin *et al.* 2014; Cnuts *et al.* 2017). Advances in chemical analyses have improved our ability to accurately identify adhesive types based on smaller and smaller residues (Hayes *et al.* 2019; Monnier *et al.* 2017; Monnier *et al.* 2013; Cnuts *et al.* 2018; Monnier *et al.* 2018). However, for all of this work, there is still a limited number of well identified and analysed adhesive residues on archaeological material of Palaeolithic origin.

Currently, both securely dated and chemically identified Middle Palaeolithic hafting adhesives include material from just seven locations: Campitello Quarry, Fossellone and Sant'Agostino caves, Italy; Königsaue, Germany; Zandmotor, the Netherlands, and Hummal, and Um el Tlel, Syria (Boëda *et al.* 2008a; Hauck *et al.* 2013; Koller *et al.* 2001; Mazza *et al.* 2006; Degano *et al.* 2019; Niekus *et al.* 2019). Further evidence of Middle Palaeolithic hafting adhesives have been found, or inferred from use-wear, at a number of other sites (Cârciumaru *et al.* 2012; Pawlik and Thissen 2011; Hardy and Kay 1999; Rots 2009, 2013). However, precise chemical identification of residues is uncommon. Adhesive remains from the Middle Stone Age in Africa are similarly rare, and include Diepkloof Rock Shelter (Charrié-Duhaut *et al.* 2013), Sibudu (Villa *et al.* 2015) and Border Caves (Villa *et al.* 2012). Many of these also lack secure chemical identification of organic remains, and instead are inferred based on the presence of use-wear and/or inorganic residues, such as ochre, which is believed to have been a component of compound adhesives to improve strength (Kozowyk *et al.* 2016).

The limited number of adhesive finds from the Middle Palaeolithic and Middle Stone Age is problematic because of the significance adhesive production is given in discussions about Neandertal and early modern human technological and cognitive capabilities. The period from approximately 300,000 to 30,000 years ago was highly significant in human evolution. It is when *Homo sapiens* emerged, interbred with, and ultimately replaced two other hominin species (Galway-Witham and Stringer 2018). The same time period saw what is believe to be the first evidence of behavioural modernity (D'Errico 2003; Nowell 2010). Several significant technological developments also took place during this time period. Prepared core technologies, such as the Levallois technique, became more widespread and allowed the production of smaller and sharper flakes of pre-determined shape, also improving efficiency of raw material use, and creating more uniform thickness (Lycett and Eren 2013). Further, the production and habitual use of fire by Neandertals is believed to have first occurred during the late-middle Pleistocene (Roebroeks and Villa 2011; Sorensen *et al.* 2018). Fire provided light and heat necessary for cooking, giving warmth, and improving the properties of lithics (Sorensen 2017; Clark and Harris 1985; Wadley and Prinsloo 2014).

Flakes with a more uniform thickness are better suited to hafting, and the use of fire is a necessity for producing birch bark tar and mixing some compound adhesives (Kozowyk *et al.* 2017b; Wadley 2005). Together, these technological changes go hand-in-hand with the development of adhesives and hafting, and provided an advantage to the prehistoric users over simple single-component hand held tools and naturally weak or brittle adhesives such as pure pine resin (Barham 2013; Kozowyk and Poulis 2019). However, the direct correlation between adhesives and other contemporaneous technological advances is still unclear. For example, were adhesive technology integrated with the earliest hafting, or did its use come later, after hafting was already well established? Uncertainties here are largely due to the poor preservation of organic materials in the Palaeolithic record. Further to this, the taphonomic impact on different adhesive types is as of yet unknown. The sensitivity of organic remains to these taphonomic processes combined with the highly variable nature of both natural adhesive materials and environmental conditions, means that there is a high possibility of bias in the archaeological record. In addition, the successful discovery and identification of these materials is also minimized because knowledge about what environmental circumstances they survive best in is limited.

To address these issues, we have conducted a series of field preservation experiments. Flint flakes hafted with replica adhesives were left to weather naturally on and below the surface at the Leiden University Material Culture Studies experimental house at Horsterwold, the Netherlands; and the Forensic Anthropology Research Facility (FARF), Texas. Materials tested include pine tar, birch tar, pine resin, beeswax, acacia gum, hide glue, bone glue, and mixtures containing ochre and/or beeswax. We tested the influence of time, temperature, precipitation, soil pH, the influence of sediment cover, and adhesive types on residue preservation. Preservation was recorded by digitally measuring the surface area of each adhesive residue before and after the elapsed time. Micro-residues were further assessed by stereo and metallographic microscopy and assigned a 'preservation index' score of between 0 and 5 (cf. Langejans 2010; Monnier and May 2019).

Materials

Organic remains in archaeology are broken down by three main forces: physical, chemical, and biological. The different properties of natural adhesives would suggest that they have highly variable preservation qualities, and some are much more likely to survive in the archaeological record than others. A number of adhesive materials and recipes have been tested here. These include materials that are known to have been used during the Middle Palaeolithic in Europe; birch (*Betula)* bark tar, and pine (*Pinus*) resin (Degano *et al.* 2019; Mazza *et al.* 2006). Secondly, materials demonstrated by the Middle Stone Age in southern Africa, including compound adhesives of conifer resin, beeswax, and ochre, were investigated (Charrié-Duhaut *et al.* 2013; Lombard 2006a; Villa *et al.* 2015; Villa *et al.* 2012). Third, we included some materials that would have been present and readily accessible, but that have never been chemically identified in the Pleistocene archaeological record, such as acacia gum. Last, hide and bone glue were studied, as these are materials that are known to have been used in historical times, but are not common in pre-history, although the technology required to produce them did exist.

Tar

Tar is a dark viscous liquid material obtained from the pyrolysis or gasification of biomass. The term ‘pitch’ is commonly used to refer to materials made from the pyrolysis of woody materials, and more accurately represents such material that is solid at room temperature (Betts 2000). However, pitch is also sometimes used to refer to pine wood extractives such as gum rosin (Langenheim 2003), and to heated/treated pine resin (Odegaard *et al.* 2014). So to avoid confusion, for the purpose of this paper we will use the term ‘tar’ throughout to refer to material produced from the pyrolysis of plant materials, whether solid or liquid at room temperature.

The oldest known adhesives ever recovered (>191 ka) come from Campitello Quarry in central Italy, and have been chemically identified using GC-MS as being birch bark tar (Mazza *et al.* 2006). Two more lumps of birch bark tar have been found at the open-pit mine of Königsaue, Germany. These have been chemically identified using GC-MS and are minimally dated to approximately 40,000 years ago (Koller *et al.* 2001). A single lump of birch tar adhering to a flint flake has also been found from the Dutch North Sea. This piece has been chemically identified by py-GC-MS and directly AMS 14C dated to approximately 50 ka (Niekus *et al.* 2019). Black residues have been identified on a number of flint tools from Inden-Altdorf, Germany, and Sterosele, Ukraine. Although no chemical analysis has been done, they are believed to be birch bark tar (Hardy and Kay 1999; Pawlik and Thissen 2011). Birch tar adhesives have also been identified at a number of Mesolithic and Neolithic sites (Aveling and Heron 1998, 1999; Urem-Kotsou *et al.* 2002; Van Gijn and Boon 2006; Regert 2004), making it the most commonly identified prehistoric adhesive in Europe.

Despite the apparent bias in favour of birch bark as a material to make adhesives from during prehistory, tar can be produced from any organic material by the same process. Pine has been identified in the Greek Neolithic (Mitkidou *et al.* 2008), and in historic times, pine wood was a primary source of biomass for tar production (Kunnas 2007). It was produced on an industrial scale in Scandinavia and Finland for use as caulking in ships and waterproofing or preserving wood on church roofs (Connan and Nissenbaum 2003; Egenberg *et al.* 2003; Kunnas 2007), and is still being manufactured today for a number of different purposes (Kurt *et al.* 2008; Lopez *et al.* 2010; Paghdal and Schwartz 2009). Both birch and pine species of trees were present together from the end of MIS 6 until MIS 1 and the beginning of the Holocene (Helmens 2014). Although pine tar has been used for water-proofing and protecting wood, birch bark tar is well known for its anti-microbial and anti-bacterial qualities (Baumgartner *et al.* 2012; Yogeeswari and Sriram 2005). Early birch tar may even have been used as a treatment for toothache (Aveling and Heron 1999; Van Gijn and Boon 2006). These properties may result in better preservation, and thus a bias in the archaeological record.

To make tar for our experiments we used a modified gas pottery kiln with an apparatus to allow the heating of wood or bark in an oxygen reducing environment. A 1000 mL metal container with a sealable lid was filled with 193.0 g of pine (*Pinus sylvestris*) wood and another with 110.0 g of birch (*Betula pendula*) bark. After 2-3 hours between 350 and 405 °C the pine wood produced 55.5 g of extractives and the birch bark produced 40.8 g of extractives. These were reduced over a hot plate to remove the volatile portion and produce a material with a consistency that was solid at room temperature (cf. Kozowyk *et al.* 2017a). After this, 14.5 g of wood tar remained (7.5 % yield by weight) and 17.55 g of birch tar remained (16.0 % yield by weight).

Resin

Resins are a form of plant exudate present in the resin canals and excreted at points of injury to help prevent infection and biological damage in trees (Sjöström 1981). They are made primarily of monoterpenes and resin acids (Silvestre and Gandini 2011). Unlike tar, which must be chemically transformed from a material that does not resemble the finished product, resin occurs naturally in a sticky form. Resin is also commonly found in archaeology associated with hafting. The oldest chemically identified adhesive for hafting from the Middle Stone Age is a conifer resin from the yellowwood (*Podocarpus*) tree (Charrié-Duhaut *et al.* 2013). Pine resin has also been identified in a Middle Palaeolithic context in Italy (Degano *et al.* 2019).

Today, resin is most commonly harvested from various pine species by cutting V-shaped notches in the trunk and collecting the resin (or oleoresin) as it flows from the tree as a clear viscous fluid. Resins harvested from pine are often refined further to produce rosin*,* also referred to as colophony (Fiebach et al. 2005). Rosin is a brittle, glassy, transparent solid that is non-volatile and insoluble in water (Coppen and Hone 1995) and is obtained by removing the volatile turpentine or pine oil portions that may be present in resin (Gaillard *et al.* 2011).

If, as would be the case during prehistory, the method of extraction was collecting resin from a wounded tree, as opposed to chemically extracting it from pine wood, it could be found in a range of different consistencies. When fresh, oleoresin contains approximately 68% rosin, 20% turpentine, and 12% water (Gidvani 1946). It is sticky to the touch, but also very soft. As the turpentine and water evaporate, the ratio of rosin increases and the material becomes harder and more brittle. In order to improve replicability, and to avoid un-controllable variables, we are using store bought pine *rosin* for our experiments. However, when referring to archaeological material we will continue to use the term *resin*, as it is unknown whether prehistoric people were using it in a fresh, more ‘resinous’ state, distilling it into rosin, or collecting it when it was already dry and brittle. It is generally accepted that pure rosin makes a poor and brittle adhesive, and requires additives or plasticisers to make it useable (Gaillard *et al.* 2015). However, there are examples where resin may have been used without any additives, or where it may have been advantageous to have a brittle material (Wadley *et al.* 2015; Ellis 1997; Nelson 1997). The state of the resin when collected, may have influenced the necessity to add plasticisers or mineral additives to alter the physical properties – such as increasing stiffness and reducing drying time of resin with ochre, or improving plasticity and workability of rosin with beeswax or fat (Wadley 2005, 2010).

The rosin in this study was heated over an electric hotplate, and applied in a molten state to the flint and haft. For compound adhesives 30 wt.% beeswax was melted and mixed in, and 20 wt.% ochre was then added, as this was determined to be the optimum ratio in adhesive shear tests (Kozowyk *et al.* 2016).

Gum

Gums are similar to resins in that they are plant exudates formed within a tree and excreted at points of damage in order to aid healing and inhibit infection (Coppen 1995). Visually and physically, gums can be almost indistinguishable from resins. They are both exuded from trees as a transparent, sticky viscous liquid, and they both harden and become more brittle as they dry on exposure to the air and sun. Gums differ in that they are composed primarily of sugars and are water-soluble (Langenheim 2003). Archaeological experimentation has shown that acacia gum (also known as Gum Arabic) can be used as a successful adhesive but that the properties can be highly variable, and often require additives such as ochre to improve the workability and alter the performance (Wadley 2005; Zipkin *et al.* 2014). Gums have been used as adhesives in more recent times (Mason *et al.* 1891) and would have been available to ancient humans living in southern Africa. Gum exuding trees are widespread, with acacia alone being present throughout Africa, Arabia, portions of Iran, India, Australia, southern United States and Central America (Mantell 1954). Possible evidence of gum adhesives on Uluzzian backed segments has recently been identified at Grotta del Cavallo, Italy (Sano *et al.* 2019). The absence of any identified gum adhesives from the Pleistocene is then unlikely to be due to economic, technological, performance, or environmental factors. The solubility in water and sugar-rich chemistry of gums suggest another alternative. They are much more chemically and biologically susceptible to degradation than resins and tars. To apply our store bought acacia gum adhesive, we first crushed and then re-constituted it with water until a thick, sticky paste. Then we applied it, and left the gum to air dry.

Animal glues

Animal glues represent a different form of adhesives than plant exudates and tars. They are produced by removing the collagen from organic animal remains, namely animal or fish bones, or animal hides, and converting it through hydrolysis into a natural polymer. This requires a considerable investment in time and energy, but is otherwise not an overly complicated process (Pearson 2003). Collagen extract is collected by boiling the animal remains in water for a prolonged period; through a process of denaturation, the collagen is converted into gelatin (Schellmann 2007). Hide and bone glue today are primarily made of bovine hides, and a mix of bones from cattle and pigs (Schellmann 2007). The earliest recognized use of hide based glues occurs in ancient Egypt and Mesopotamia, where it was likely employed for a range of purposes including fastening wood together, applying ebony and ivory inlay, to fasten woven fabric to wood, and to glue gold foil to plaster (Moorey 1999; Lucas and Harris 2012). No finds are known elsewhere, with the exception of a rare Neolithic find from Switzerland, where it was used in a composite bow (Bleicher *et al.* 2015). Animal glue use has also been documented among Native Americans in North America for tasks such as gluing feathers to arrow shafts or composite bow manufacture (Mason 1894; Campbell 1999). Until the advent of synthetic polymer glues in the 1950's and 1960's, animal glues were the material of choice for woodworking, carpentry, book binding, paper making, and many other tasks (Pearson 2003; Duhamel du Monceau 1771; Hull and Bangert 1952; Keystone 1934). To be used, animal glues are soaked in warm water and heated to just below boiling temperature. The virtual monopoly animal glues had over all other types of natural adhesives in the last several centuries raises the question of why it was not used more often in the deep past? Was it unknown prior to the Neolithic? Was it unnecessary to invest so much time in manufacture when natural and 'ready to use' plant adhesives would work? Or does the water soluble nature disfavour preservation in European prehistory outside of truly exceptional circumstances?

To obtain insight into this question, hide and bone glue adhesives were prepared using methods still employed in some traditional and furniture and musical instrument manufacturing today (Joyce 1987; James 2011). Water is added to the dried adhesive pellets, which become gel-like. Then they are heated inside a second pot of water, to avoid over-heating, until the adhesive liquefies. Once liquid, it can be applied to the haft and flint flake and left to dry.

Beeswax

Beeswax is a natural wax produced from a number of different types of bees, one of the most common being *Apis mellifera*. It consists primarily of hydrocarbons

(14%), monoesters (35%), diesters (14%), free acids (12%), and many other components, although these amounts vary slightly depending on the species of bee and the wax's origin (Tulloch 1980).

Beeswax is used as a component in compound adhesives containing resins and possibly gums (Sano *et al.* 2019). At low temperatures beeswax is brittle, but at room temperature it becomes relatively soft and so is frequently mixed with resin to act as a plasticizer and soften the otherwise brittle material (Kozowyk *et al.* 2016; Gaillard *et al.* 2015). The oldest identified beeswax use comes from Border Cave, South Africa and dates to approximately 44 ka (Wadley *et al.* 2015). Beeswax may also have been used at Fossellone Cave (Degano *et al.* 2019) and Grotta del Cavallo, Italy (Sano *et al.* 2019). More modern beeswax was found on a Final Palaeolithic barbed point from Bergkamen, Germany (Baales *et al.* 2017), and it is likely that by the Neolithic the honeybee was being widely exploited (Roffet-Salque *et al.* 2015; Van Gijn and Boon 2006). For our experiments, we used commercially available pure beeswax and applied it to the flint in the same manner as the resin adhesives.

Ochre

Ochre is a general term often used to refer to natural clay earth pigments obtaining their colour from different iron oxides, but may be broadened further to include any mineral substance containing iron oxide (Rifkin 2011). Ochre, like beeswax, is used primarily as an additive in compound adhesives. On its own, ochre has no adhesive qualities, so its use in hafting has raised some debate over a possible symbolic or technical nature (Wadley 2010). Ochre has been shown to improve the performance and ease of use of resin based adhesives (Kozowyk *et al.* 2016; Wadley 2005). However, it is also possible that other clay-like sediment without the iron oxide component of ochre may serve a similar function (Zipkin *et al.* 2014). Ochre has been identified in many instances with a direct correlation to hafting, dating back to the Middle Stone Age, so its use is unambiguous, regardless of its purpose (Lombard 2006a; Villa *et al.* 2015; Helwig *et al.* 2014; Allain and Rigaurd 1989; Bradtmöller *et al.* 2016; Shaham *et al.* 2010; Dickson 1981; Sano *et al.* 2019).

The significance of ochre in debates about symbolism (Hovers *et al.* 2003) and the technical knowledge or skill of early modern humans makes it necessary to better understand taphonomic processes affecting ochre containing adhesives. The relatively high proportion of ochre-hafting relationships in the current literature raises some questions about its abundance in prehistory. Was ochre frequently and actively sought out as an ingredient in adhesives? Or is the high number of documented cases due to research and taphonomic biases? Ochre may have some anti-bacterial/microbial properties that help reduce the biological decay of hides (Rifkin 2011). Does this lead to an increase in preservation of residues over non-ochre containing adhesives? Does the distinctively red appearance of ochre simply mean that it is identified by archaeologists more frequently? It must also be noticed that the presence of ochre is not necessarily linked with adhesive use. It may also be added for symbolic reasons (cf. Rifkin 2015). The purpose of including ochre in gum and resin adhesives in this study is to determine if its presence improves the successful identification of hafting residues either by increasing visibility, or by providing some form of biological protection.

With the exception of pine tar and birch bark tar, all adhesive materials were purchased from https://www.verfmolendekat.com/en/webshop/. The ochre used in this study is pre-ground to a fine particle size (<62.5 µm) as this has been reported to produce a strong adhesive (Zipkin *et al.* 2014).

Methods

Flint flakes hafted with replica adhesives were left to weather naturally on and 10 cm below the surface at the Leiden University Material Culture Studies experimental house at Horsterwold, the Netherlands and the Forensic Anthropology Research Facility (FARF), USA. Differential preservation was recorded by digitally measuring the surface area of each adhesive residue before and after the elapsed time. We opted for field experiments because they mimic real situations when artefacts are discarded and include a combination of biological, chemical and physical decay.

Field preservation

Adhesives are known to have been used for hafting in Europe as far south as Italy and north as the North Sea (Mazza et al. 2006; Niekus et al. 2019), as well as throughout Africa (Lombard 2006; Rots et al. 2011) and the Levant (Boëda et al. 2008). The range of burial environments in which archaeologists might find adhesive residues is therefore vast. For this study, field preservation experiments were conducted at two highly different locations in order to reflect as broad of a spectrum of potential burial environments as possible. While the locations are not intended to replicate any specific archaeological site, results will provide information on whether burial environment or adhesive type has a greater effect on the preservation potential of residues. Variation in burial environment will also help illuminate any potential differences that might exist between adhesive types. Objects on the surface at the Horsterwold Experimental House, the Netherlands.

1. Objects buried 10 cm below the surface at the Horsterwold Experimental House.
2. Objects on the surface at FARF, USA.
3. Objects buried 10 cm below the surface at FARF, USA.

A total of 160 10 mm diameter pine wood dowels were notched and joined with 10 different replica adhesives to Rijkholt flint flakes in a cleft haft. Half of the hafted samples were removed after 0.5 years (n=20) and the other half after 2 years (n=20) at FARF, and 0.5 years (n=20) and 3 years (n=20) at Horsterwold. At the Horsterwold location, a further 28 samples were made by applying adhesives to the surfaces of larger flint flakes, without using hafts. Of these, 14 were buried for 3 years, and 14 were left on the surface for 3 years. Each material and location was tested in duplicate. Once excavated and collected after the elapsed time, the objects were lightly rinsed with distilled water to clear away excessive sediment, and left to dry for several days before being photographed, measured, and observed with an optical microscope.

Environmental conditions

Climate conditions at FARF near San Marco, Texas and Horsterwold near Zeewolde in Flevoland were taken from 'World Weather Online' https://www.worldweatheronline.com. Monthly conditions are recorded for maximum, minimum and average temperature, rainfall and rain days, humidity, and UV index for the period of April 2016 to May 2019. The area of the facilities in Texas experiences a wide variation in temperatures and conditions, indicating a humid sub-tropical climate. The temperature is hot, with humid summers and short cool winters and significant rainfall variation throughout the year. During the course of these experiments FARF experienced several storms with flash flooding and heavy rainfall. The climate conditions at Horsterwold, the Netherlands are milder, with cool summers and temperate winters. Rainfall is fairly evenly distributed throughout the year. Below is a comparison of the monthly temperatures and precipitation during the period of July 2016 – July 2017, when experiments were active at both locations (Fig X).

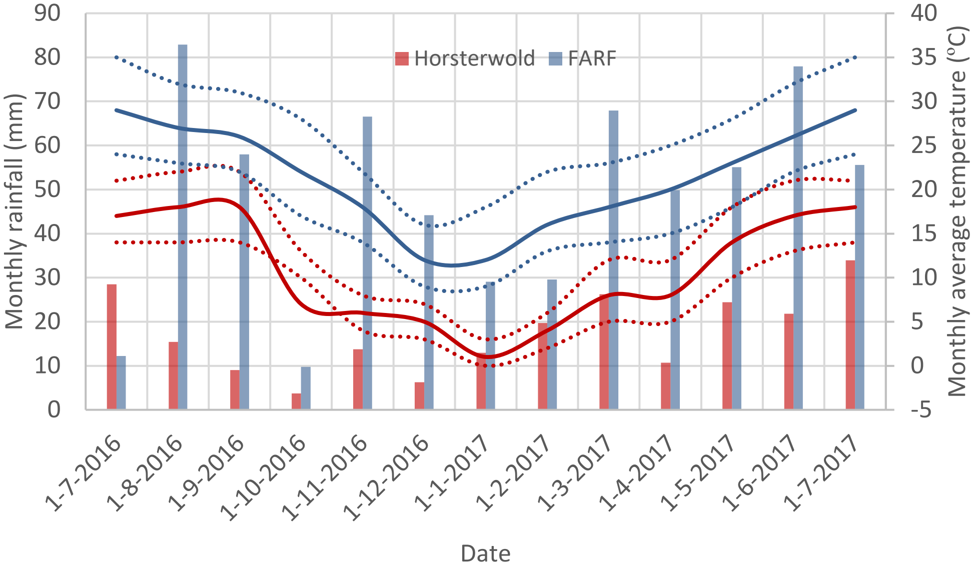

Fig. 1. Monthly average weather for Horsterwold and FARF. Bars = monthly rainfall, solid lines = average monthly temperature, dotted lines = max and min monthly temperatures.

Soil samples were taken from approximately one meter away to measure the soil pH levels. Analysis was done using an Accumet AB150 pH/mV (cf. cf. ASTM 2019). Soil pH from two Horsterwold samples are 7.44 and 7.46. Horsterwold soil is a mixture of fine loamy sand and clay from reworked Pleistocene sands. The immediate location was dredged from the nearby area to create a small artificial island on which the experiments took place. Vegetation at Horsterwold is primarily a deciduous woodland with thick grass growing near the sample locations. Soil pH from two FARF samples are 6.41 and 6.33. The soil at FARF is shallow stony clay over hardened limestone, providing limited storage for water and a high inorganic carbon content reducing plant growth (Carson 2000).

Macroscopic assessment and optical microscopy

In order to quantify the residue preservation a 'preservation index' from one to five was used (Langejans 2010; Monnier and May 2019). Different materials will preserve in different ways, so the scoring used in this paper is unique to adhesives, but provides a simple comparative tool to understand the relative preservation of different residues (Table 1).

Table 1. Preservation index of adhesive residues, after (Langejans 2010).

Preservation index					
5	**4**	**3**	**2**	**1**	**0**
Situation just after use. Thick residue adhering to the flint over >90% of the original covered surface.	Abundant presence of macro-residues over <90% of the original covered surface.	Small traces of macro-residues or considerable discolouration or staining left from the adhesive.	Few deposits left, difficult to see macroscopically. Only slight discolouration or staining on the flint surface.	The occasional residue left. Visible microscopically, usually in flake scars or protected surfaces on the flint.	No observed residues left.

Preservation was further recorded for macro-residues by photographing and digitally measuring the surface area of each adhesive residue before and after the elapsed time. This was done with the measurement tool in Adobe Photoshop CC 2018 19.1.5. Due to the variety in colours, contamination with soil, and translucency of some adhesives, automatic measurements could only be conducted for some red residues from the ochre containing adhesives. This also precluded the use of image measurement software such as ImageJ. However, a test automatic measurement using the histogram setting in Photoshop on one red ochre-containing adhesive gave a result within 2% of the manual measurements. On objects where no clear residues were visible macroscopically, the flint surface was scanned under a metallographic microscope at 40x magnification, and any potential residues were recorded.

Results

The results are first divided into two main categories based on the location of the experiment. Those conducted at Horsterwold in the Netherlands, and those conducted at FARF in the USA. They are then further divided into those experiments left to weather on the surface, and those buried 10 cm underground. Six month experiments are summarily discussed to understand the initial decay. Due to the short duration they are not further elaborated on as we consider the long-term preservation to be most relevant for archaeological remains. At the Horsterwold location, a total of seven objects were not recovered from all surface experiments and two objects were not recovered from all buried experiments. This suggests that the surface samples were more easily disturbed by physical activity and may have been moved by water flow, or animal and plant activity. A total of 13 FARF samples were not recovered due to several extreme flash floods which took place during the allotted time.

Horsterwold Results

Surface

After a period of half a year, the distinction between water soluble and non-water soluble materials is immediately apparent (Table 2). Acacia gum, hide glue, and bone glue, all have a preservation index of zero. Acacia gum with ochre has a preservation index of 3, because there were traces of ochre found across the hafted surface. At the other end of the scale, pine tar, birch tar, beeswax, and resin/beeswax/ochre all received scores of 5 because large amounts of residues remained nearly completely resembling the adhesive when it was freshly applied. Pine resin, and pine resin/beeswax received scores of 4 and 4.5, as slightly less residue remained. Recording the precise surface area of residues remaining shows a slight hierarchy of preservation potential of the non-water soluble adhesives. Resin/beeswax/ochre and birch bark tar both preserved to around 100%. Further, these remains spread out to take up a larger surface area than when deposited. On average, beeswax remained over 96% of the original surface area, pine tar over 93%, resin/beeswax over 92% and resin over 79% of the original surface.

Table 2. Results of 0.5 year Horsterwold surface experiments. Surface area was recorded when visible staining occurred, although these could not obtain a score higher than 3 if no physical residues were present.

Adhesive	Object type	Preservation index	% Residue remaining	Staining?
acacia gum	hafted	0		
acacia gum	hafted	Missing		
acacia gum/ochre	hafted	Missing		
acacia gum/ochre	hafted	3	73	Y
beeswax	hafted	5	96	
beeswax	hafted	5	95	
birch tar	hafted	5	101	
birch tar	hafted	5	99	
bone glue	hafted	0		
bone glue	hafted	0		
hide glue	hafted	0		
hide glue	hafted	0		
pine resin	hafted	4	80	
pine resin	hafted	4	77	
pine resin/beeswax	hafted	5	97	
pine resin/beeswax	hafted	4	87	
pine resin/beeswax/ochre	hafted	5	102	
pine resin/beeswax/ochre	hafted	5	108	
pine tar	hafted	5	91	
pine tar	hafted	5	94	

After three years, the difference between water soluble (gum, hide and bone glue) and non-water soluble (resin, beeswax, tars) is still a clear distinguishing factor between adhesive types, as would be expected. While many of the non-water soluble adhesives in the hafted objects still preserved to a relatively high degree, often with

>75% of the original residue remaining, differences in the amount of remaining surface area are more apparent than after half a year.

The preservation indices on non-hafted flint flakes are lower than hafted flakes (Table 3). Pine tar scored an average index of 4.5 when hafted and 2 when left on the surface of a non-hafted flake. Birch tar lowered slightly from an average index of 5 to 4.5. Pine resin remained the same, and pine resin/beeswax/ochre scored 5 while hafted and 4 on non-hafted flakes. Acacia gum/ochre scored 3 while hafted, and an average of 1 when non-hafted (Table 3).

Table 3. Results of 3 year Horsterwold surface experiments. Surface area was recorded when visible staining occurred, although these could not obtain a score higher than 3 if no physical residues were present.

Adhesive	Object type	Preservation index	% Residue remaining	Staining
acacia gum	hafted	Missing		
acacia gum	hafted	Missing		
acacia gum	non-hafted flake	0		
acacia gum	non-hafted flake	1	1	
acacia gum/ochre	hafted	Missing		
acacia gum/ochre	hafted	3	17	Y
acacia gum/ochre	non-hafted flake	0		
acacia gum/ochre	non-hafted flake	2		
beeswax	hafted	4	84	
beeswax	hafted	4	76	
birch tar	hafted	5	99	
birch tar	hafted	5	98	
birch tar	non-hafted flake	4	49	
birch tar	non-hafted flake	5	99	
bone glue	hafted	1	41	
bone glue	hafted	0		
hide glue	hafted	3	55	Y
hide glue	hafted	2	25	Y
hide glue	non-hafted flake	0		
hide glue	non-hafted flake	1		
pine resin	hafted	Missing		
pine resin	hafted	4	85	
pine resin	non-hafted flake	4	10	
pine resin	non-hafted flake	4	17	

pine resin/beeswax	hafted	4	84	
pine resin/beeswax	hafted	4	84	
pine resin/beeswax/ochre	hafted	Missing		
pine resin/beeswax/ochre	hafted	5	96	
pine resin/beeswax/ochre	non-hafted flake	4	69	
pine resin/beeswax/ochre	non-hafted flake	4	77	
pine tar	hafted	5	91	
pine tar	hafted	4	86	
pine tar	non-hafted flake	3	59	Y
pine tar	non-hafted flake	1		

Buried

After a period of half a year, results of the buried samples were similar to those on the surface (Table 4). With the exception of one bone glue sample, which showed very small trace residues (score of 1), acacia gum, hide glue, and bone glue, all have a preservation index of zero. Acacia gum with ochre has an average preservation index of 3.5, because there were substantial traces of ochre found across the hafted surface. Pine tar, birch tar, pine resin, beeswax, resin/beeswax, and resin/beeswax/ochre all received scores of 5 because large amounts of residues remained, nearly completely resembling the adhesive when it was freshly applied.

Table 4. Results of 0.5 year Horsterwold buried experiments. Surface area was recorded when visible staining occurred, although these could not obtain a score higher than 3 if no physical residues were present.

Adhesive	Object type	Preservation index	% Residue remaining	Staining?
acacia gum	hafted	0		
acacia gum	hafted	0		
acacia gum/ochre	hafted	3	4	Y
acacia gum/ochre	hafted	4	16	
beeswax	hafted	4	89	
beeswax	hafted	5	95	
birch tar	hafted	5	98	
birch tar	hafted	5	100	
bone glue	hafted	1		
bone glue	hafted	0		

hide glue	hafted	0		
hide glue	hafted	0		
pine resin	hafted	5	96	
pine resin	hafted	5	101	
pine resin/beeswax	hafted	5	93	
pine resin/beeswax	hafted	5	94	
pine resin/beeswax/ochre	hafted	Missing		
pine resin/beeswax/ochre	hafted	5	105	
pine tar	hafted	5	97	
pine tar	hafted	5	103	

After three years birch tar appeared almost unaltered, and in two cases spread out to cover a larger surface area than when it was first applied, with an average preservation index of 5 for both hafted and non-hafted flakes (Table 5). Pine tar, on the other hand, appeared more heavily degraded (preservation index of 4.5 for hafted flakes and 3.5 for non-hafted flakes). Although much of the residues were still there, the colour had become more brown, and the surface was cracked and flaking. On the buried samples, there was still a slight difference between adhesives used with a hafted flake, and adhesives which were on a non-hafted flint flake. The non-hafted flakes preserved residues to a slightly lower degree. As with the other experiments, almost no residues were identified securely from the water-soluble adhesives. One exception being the acacia gum and ochre adhesives, which left some slight staining and discolouration over the hafted area, giving an average score of 2 for hafted flakes and 1.5 for non-hafted flakes. It is unlikely much of the organic gum preserved, however, it does provide a clear indication of the region of the tool that was hafted.

Table 5. Results of three year Horsterwold buried experiments. Surface area was recorded when visible staining occurred, although these could not obtain a score higher than 3 if no physical residues were present.

Adhesive	**Object type**	**Preservation index**	**% Residue remaining**	**Staining**
acacia gum	hafted	0		
acacia gum	hafted	0		
acacia gum	non-hafted flake	0		
acacia gum	non-hafted flake	1		
acacia gum/ochre	hafted	2	48	Y

acacia gum/ochre	hafted	2	67	Y
acacia gum/ochre	non-hafted flake	1		
acacia gum/ochre	non-hafted flake	2		
beeswax	hafted	4	44	
beeswax	hafted	4	52	
birch tar	hafted	5	98	
birch tar	hafted	5	112	
birch tar	non-hafted flake	5	98	
birch tar	non-hafted flake	5	104	
bone glue	hafted	0		
bone glue	hafted	0	25	
hide glue	hafted	Missing		
hide glue	hafted	0		
hide glue	non-hafted flake	1		
hide glue	non-hafted flake	0		
pine resin	hafted	5	91	
pine resin	hafted	4	84	
pine resin	non-hafted flake	4	21	
pine resin	non-hafted flake	4	13	
pine resin/beeswax	hafted	5	97	
pine resin/beeswax	hafted	5	92	
pine resin/beeswax/ochre	hafted	4	88	
pine resin/beeswax/ochre	hafted	5	92	
pine resin/beeswax/ochre	non-hafted flake	4	56	
pine resin/beeswax/ochre	non-hafted flake	4	64	
pine tar	hafted	4	88	
pine tar	hafted	5	91	
pine tar	non-hafted flake	4	12	
pine tar	non-hafted flake	3	100	Y

On average, the preservation index of the buried experiments does not differ much from the surface experiments, although the non-water soluble adhesives appears to have preserved slightly better when buried (Fig. 2). The average preservation index for hafted adhesives is higher than non-hafted samples for non-water soluble adhesives. For example, buried birch tar = 5, surface birch tar = 4.5; buried pine tar = 3.5, surface pine tar = 2; and buried acacia gum/ochre = 2 while surface acacia gum/ochre =1.5. Scores for resin/beeswax/ochre and resin are equal for buried and surface samples (Fig. 3). Comparisons are more difficult with water soluble adhesives, because preservation is so poor that accurate identification with optical microscopy is problematic. However, it is clear that the addition of ochre greatly increases visual identification potential of organic adhesive residues.

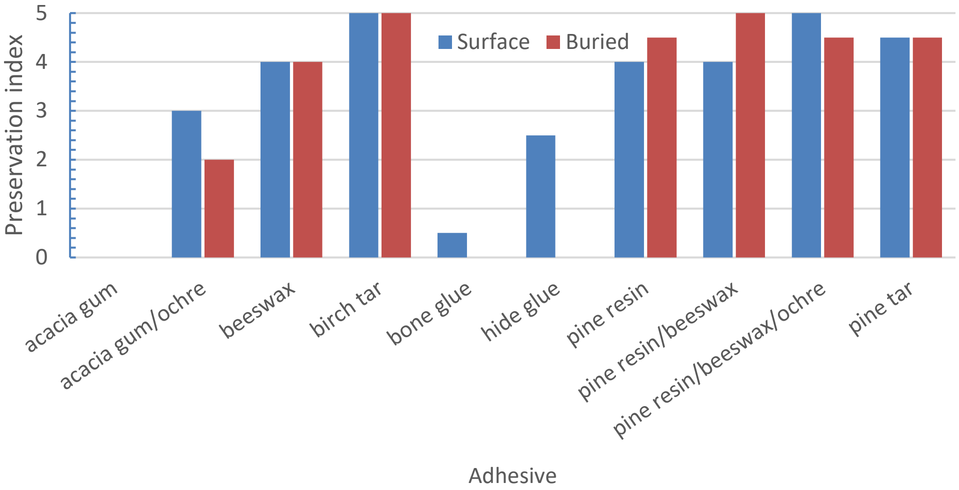

Fig. 2. Average preservation index of adhesives on hafted flint flakes after three years at Horsterwold.

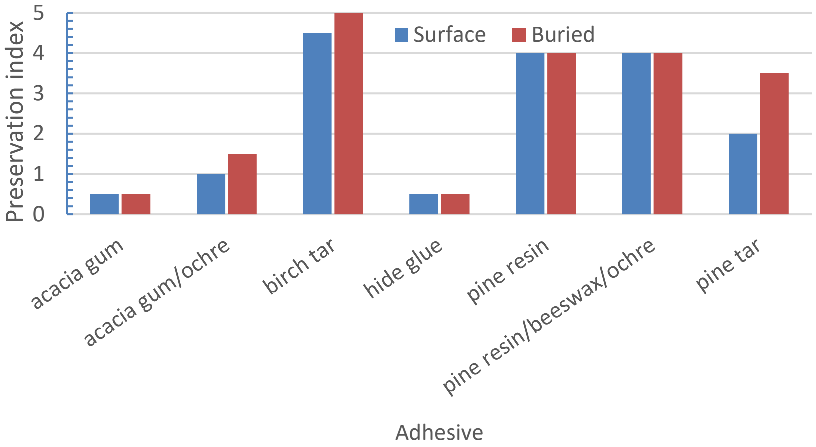

Fig. 3. Average preservation index of adhesives on non-hafted flint flakes after three years at Horsterwold.

FARF Results

Surface

After half a year on the surface at FARF, patterns of preservation reflect those at Horsterwold, however no non-hafted flint flakes were tested here, so comparisons with these cannot be made. Birch bark tar preserves the best, and acacia gum, hide glue, and bone glue preserve poorly (Table 6). However, already after six months there is a greater disparity among the preservation of adhesives than at Horsterwold. Birch tar, and resin/beeswax/ochre were the only adhesives with a preservation index of 5 after half a year on the surface. The next best preserved were resin/beeswax (4), and then pine resin (4), and pine tar (3.5). Acacia gum/ochre scored the same as beeswax (3), because it was easily identifiable and a large portion of the original surface area was stained red.

After a total of two years, the surface residues at FARF changed very little. Birch bark tar still appeared fresh, and spread out to cover a slightly larger surface area than when first applied (score of 5). Resin/beeswax/ochre has the second highest preservation index (4.5), followed by resin/beeswax (4), resin (4), beeswax (3), acacia gum/ochre (3), hide glue (2), bone glue (1), and acacia gum (1; Table 6).

Table 6. Two year surface preservation experiment results from FARF. Surface area was recorded when visible staining occurred, although these could not obtain a score higher than 3 if no physical residues were present.

Adhesive	Preservation index	% Residue remaining	Staining?
pine tar	Missing		
pine tar	Missing		
birch tar	5	106	
birch tar	5	114	
acacia gum	1		
acacia gum	1		
pine resin	4	73	
pine resin	4	74	
beeswax	3	11	Y
beeswax	3	2	Y
acacia gum/ochre	3	52	Y

acacia gum/ochre	3	45	Y
pine resin/beeswax	4	65	
pine resin/beeswax	Missing		
pine resin/beeswax/ochre	5	97	
pine resin/beeswax/ochre	4	90	
hide glue	2		
hide glue	2		
bone glue	1		
bone glue	1		

Buried

After half a year at FARF the buried samples preserved to a slightly higher degree than the surface experiments (Table 7). Birch tar preserved the best, however, in these experiments one of the pine tar samples, as well as pine resin, resin/beeswax, and resin/beeswax/ochre also all scored a preservation of 5. In order of decreasing preservation index, the remaining buried adhesives were acacia gum/ochre, hide glue, bone glue, and acacia gum.

After two years, the preservation index remained slightly higher for adhesives that were buried compared to adhesives that were left on the surface, although fewer samples were recovered from the experiments with buried adhesives, so the difference is minor. Birch tar preserved the best (5), appearing almost unchanged since its application. Resin/beeswax/ochre preserved similarly well (5), and resin/beeswax (4.5) preserved third best. They were followed by pine resin (4), beeswax (3.5), pine tar (3), acacia gum/ochre (3), hide glue (2), and finally acacia gum (1). Bone glue samples were not recovered from this location (Fig. 4).

Table 7. Two year buried preservation experiment results from FARF. Surface area was recorded when visible staining occurred, although these could not obtain a score higher than 3 if no physical residues were present.

Adhesive	Preservation index	% Residue remaining	Staining?
acacia gum	1		
acacia gum	Missing		
acacia gum/ochre	3	29	Y
acacia gum/ochre	3	44	Y

beeswax	4	54	
beeswax	3	5	Y
birch tar	Missing		
birch tar	5	106	
bone glue	Missing		
bone glue	Missing		
hide glue	2		
hide glue	Missing		
pine resin	Missing		
pine resin	4	5	
pine resin/beeswax	4	63	
pine resin/beeswax	5	90	
pine resin/beeswax/ochre	Missing		
pine resin/beeswax/ochre	5	90	
pine tar	3	56	Y
pine tar	Missing		

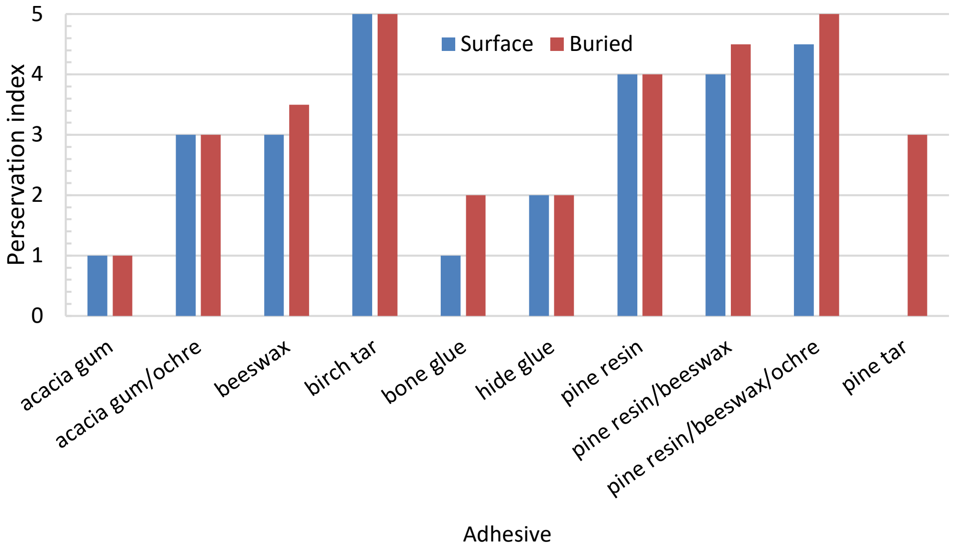

Fig. 4. Average preservation index of adhesives on hafted flint after two years at FARF. Surface pine tar samples were not recovered.

Discussion

Discussion of results

Overall, the preservation of adhesive residues is determined primarily by the type of adhesive, and then to a lesser extent by the presence of a haft and by the environment. Adhesives on hafted flakes preserve better than on non-hafted flakes, and appear to preserve similarly at both Horsterwold and FARF. Being on the surface or buried has little effect on preservation. Adhesives that are non-water soluble preserve better than water soluble adhesives. Birch tar preserves exceptionally well, often appearing similar or spreading out to a larger area than when first applied (Fig. 6). Pine resin preserves surprisingly well given resin's brittle nature. For example, on non-hafted flakes, pine resin had a preservation index of 4 for both buried and surface samples, while pine tar had a preservation index of 3.5 and 2 respectively. A combination of beeswax and resin preserves significantly better than beeswax on its own (two-tailed t-test with independent means for all hafted samples: $t=3.18$, $p=<0.01$). The difference between resin and resin/beeswax is less clear based on the amount of residue remaining, however, many of the pure resin adhesives were more fragile and prone to losing pieces during handling. The addition of ochre, likely improves the preservation of resin/beeswax adhesives. Ochre has no recognizable protective properties when added to acacia gum, however, only that it often remains highly visible while the gum disappears. After two years, ochre can also move and be deposited on areas not originally covered by the adhesive (Fig. 5).

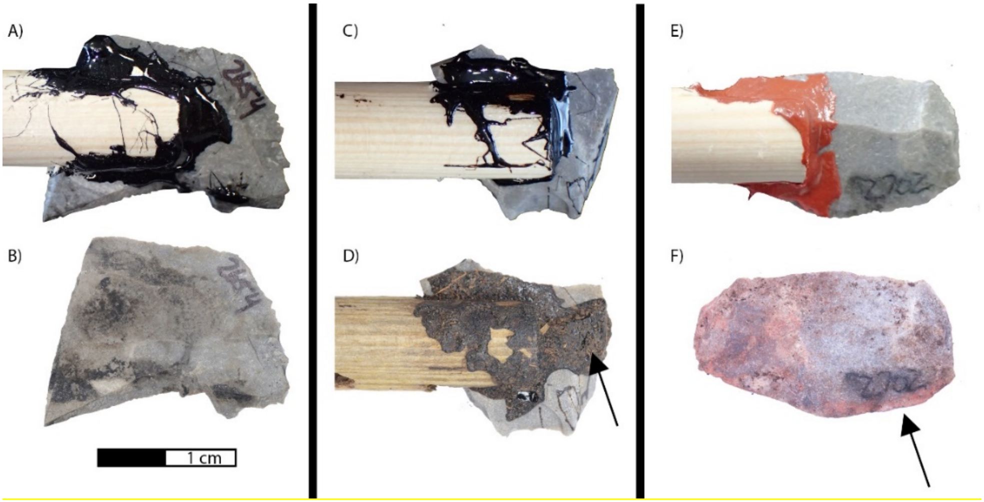

Fig. 5. Image showing spreading of adhesive residues after deposition. Residues before and after of pine tar buried at FARF for six months (A, B); birch tar buried at FARF for six months (C, D); gum/ochre from the surface at FARF for two years (E, F) Arrows point to portions of adhesive residue that have expanded over areas of the flake not originally covered by adhesive.

When looking at only those adhesives which had the highest preservation potentials, it is helpful to directly compare the percentage of adhesive residue remaining (Fig. 6). When considering all hafted adhesives, buried and surface from both locations, birch bark tar falls well outside of the range of standard error of the other adhesives, and preserves to a significantly higher degree than resin/beeswax/ochre (two-tailed t-test with independent means: $t=4.12$, $p=<0.01$) or pine tar ($t=3.55$, $p=<0.01$). Among the other materials, the difference is not so pronounced. However, resin/beeswax/ochre preserved more consistently well than the others. It also clear that beeswax on its own does not survive as well as some of the other materials.

Several adhesives that preserved relatively well on hafted tools appear to have survived to a lesser degree on non-hafted flakes. Likewise, in the single instance where birch bark tar preserved poorly (49% residue remaining), it was on a non-hafted flake on the surface. As the wooden handles appear to have offered some protection, when tools are removed from hafts, either accidentally or intentionally, the likelihood that residues will preserve is further decreased. This has potentially significant ramifications for determining how many tools were hafted in an assemblage, as any tool that was removed from a haft during its use life is less likely to preserve evidence of the adhesive used. Unfortunately movement of many of the surface samples by heavy rainfall meant that we were unable to determine whether preservation was affected by the residue being on the upper or lower side of the tool.

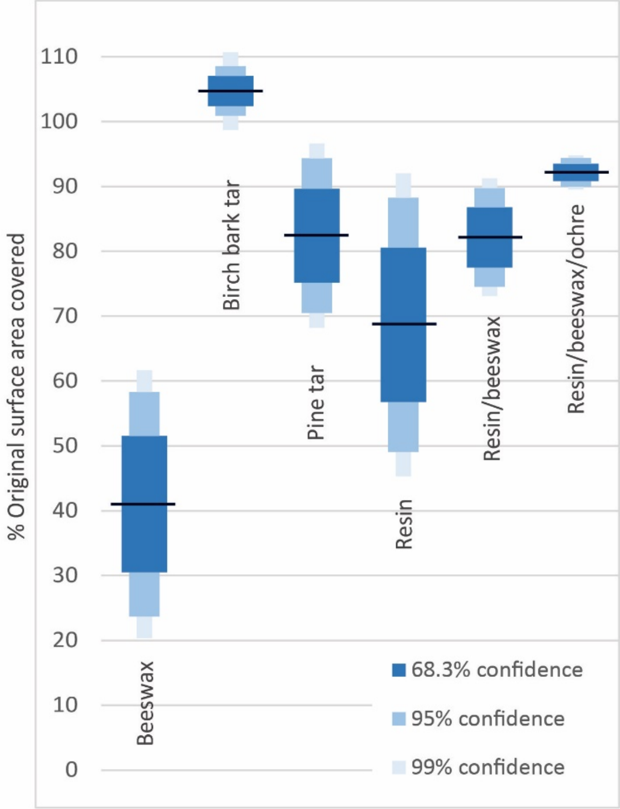

Fig. 6. Bullet graph displaying the error ranges for beeswax, birch tar, pine tar, resin, and resin/beeswax, resin/beeswax/ochre adhesives. Birch tar falls well outside the 99% confidence interval of the other adhesives.

Environmental factors influencing adhesive preservation.

After three years at Horsterwold, preservation of hafted non-water soluble adhesives was slightly better than after two years at FARF. The pattern appears reversed for water soluble adhesives, but this may be attributed to difficulties in the accurate identification of the micro-remains of these materials. The increased decay at FARF is therefore likely due to the environment.

Rates of decay are highly influenced by temperature (Hollesen and Matthiesen 2015). Further, many of the adhesive materials tested also significantly soften at temperatures of around 40 °C (Kozowyk and Poulis 2019). Chemical weathering is also limited in the absence of water, which carries away bi-products of decomposition (Chesworth 1992; Langejans 2010). A combination of hot and humid temperatures and heavy rainfall at FARF will therefore lead to increased biological decay, as well as increased mechanical decay and erosion. On the other hand, although pH levels are close to neutral, they are slightly more alkaline at Horsterwold and acidic at FARF. Microbial biomass increases with pH between 6 and 8 (Aciego Pietri and Brookes 2008), suggesting microbial activity might be higher at Horsterwold. Soil at both locations consists of clay, yet there is more sand at Horsterwold, which has two potential contrasting effects. Firstly, studies have shown that microbial biomass is most concentrated in finer-grained silt and clay soil fractio A combination of beeswax and resin preserves significantly ns (Sessitsch et al. 2001). Secondly, larger grain size increases the flow of water (Allison and Bottjer 2010) , which facilitates decay. As the differences in pH and soil grain size are relatively small between both locations, the greatest difference in preservation most likely comes from the hotter temperatures, and heavier rainfall at FARF.

Current studies on residue preservation and diagenesis are relatively few and have often been conducted under field conditions (Cnuts et al. 2017; Langejans 2010; Monnier and May 2019). Future research should be conducted in a laboratory setting focusing on isolated variables, such as pH level, UV exposure or freeze-thaw cycles, (e.g. Braadbaart et al. 2009) to reach a better understanding of how specific burial conditions and environmental factors effect different adhesive types. Additionally, by exposing experimental residues to artificial accelerated aging conditions, archaeologists will be able to gain a more accurate understanding of the decomposition curves of these materials.

Archaeological comparisons

Despite only being in the ground for two and three years, the preservation indices assigned to the adhesives studied here match our predictions and align well with what is known from the archaeological record. The oldest known archaeological adhesives are birch bark tar (Mazza *et al.* 2006), which are approximately 150,000 years older than resin adhesives (Charrié-Duhaut *et al.* 2013; Degano *et al.* 2019). Results here show that birch bark tar preserves considerably better than any other adhesive tested, so it is not surprising that the oldest known adhesives are of this material. Birch tar is a highly suitable material to haft stone tools with and may have been preferred because of its re-usability, workability, and cohesive strength. Birch tar also has known anti-bacterial properties (Yogeeswari and Sriram 2005) and is more able to withstand both high and low frequency forces at a range of different temperatures (Kozowyk and Poulis 2019). These properties support the high preservation index of birch bark tar. However, there are specific circumstances where a strong adhesive is not necessary, such as for hunting implements that are intended to dislodge in their prey (Wadley *et al.* 2015). Adhesives such as pine resin were also likely obtained more easily than investing in producing birch bark tar. Resin adhesives may well have been employed as early as birch bark tar, but simply does not preserve as well.

The adhesives with the second highest preservation index are also what we find archaeologically from the Middle Palaeolithic and Middle Stone Age, only these are found considerably later than the oldest known birch bark tar (Charrié-Duhaut *et al.* 2013; Degano *et al.* 2019). These include compound adhesives of resin, beeswax, and ochre. A mixture of all three of these ingredients was the strongest potential resin-based adhesive according to an earlier study (Kozowyk *et al.* 2016), so it most likely resists physical decay better than resin or beeswax do individually.

Resin-based adhesives have also been identified from the Middle Stone Age, but may be under-represented compared to compound adhesives because of preservation and identification biases. For example, discolouration of a residue may lead to misidentification (cf. Baales *et al.* 2017). The presence of iron oxide also significantly improves visibility of residues. However, ochre does not necessarily indicate of the presence of a hafting adhesive, as it can also be used for aesthetic or symbolic reasons. Decayed resin and tar adhesives can sometimes appear visually similar to sediment, or to mineral deposits, especially when only in trace amounts (Croft *et al.* 2018). Traces of manganese, for example, frequently occurs in sediment and can closely resemble small specks of tar. Adhesives can also be mixed with sand, soil or clay, as a filler (Dickson 1981; Rots 2008), thus making the visual identification of trace residues even more difficult. However, the presence of red ochre on lithics makes residues more visible.

Pine tar was used extensively in historic times, but its use in the Palaeolithic is less clear. The disparity between birch bark tar, and pine wood tar during the Palaeolithic, is unlikely to be caused by environmental or resource constraints, as birch and pine occur together throughout much of the Pleistocene in Europe (Bigga *et al.* 2015). During the Iron Age, birch bark was also utilized specifically to make tar in an environment where pine was more common (Rageot *et al.* 2016). The use of birch bark tar, and its survival in the archaeological record must therefore be due to technological or taphonomic reasons. Birch bark has been proven to be a very suitable material for producing tar by relatively simple processes (Kozowyk *et al.* 2017b; Schmidt *et al.* 2019). Whether pine tar can also be produced by similar methods is to be tested. Yields in our experimental production here (using a laboratory kiln) were considerably higher for birch bark than for pine wood, which suggests it is a better candidate for simple production methods. However, resin-rich fatwood might significantly increase the yield efficiency of pine, although harvesting fatwood might be more exhaustive than collecting birch bark. One explanation for the absence of pine tar during the Palaeolithic, and even for the predominant use of birch tar during the Neolithic (Regert 2004) is that pine tar does not preserve as well as birch bark tar. The clearest example of this is with the non-hafted flakes from Horsterwold – birch tar appeared as new, even after three years, and pine tar was almost entirely removed, leaving only small fragments and some discolouration of the flint.

From the late Middle Stone Age in southern Africa, there exists several sites where hafting adhesives have been inferred from the presence of ochre residues. Experiments here shown that when ochre-loaded adhesives (in this case acacia gum) degrade, they often leave a visible ochre staining. A similar pattern might also form given enough time with the resin/beeswax/ochre adhesives. However, two issues are of concern here: 1) If the adhesive was loaded with clay or a mixture with lower concentrations of iron oxide, instead of bright red ochre, the visual identification of hafting residues would be easily overlooked. 2) As was shown with some of the experimental samples here, the adhesive residue after recovery is not always present in the same position as when it was originally applied. If the presence of ochre residue is to be used to infer hafting based on its location, then it should be considered that the residues are not all in their original position.

Lombard (2007) showed that micro-residues on tools made from quartz had fewer ochre residues than tools made of hornfels and dolerite. She suggests that this may be the result of a known choice to apply different adhesive recipes for different hafting requirements. However, it is also mentioned that during replication (Lombard and Wadley 2007), residues do not adhere to quartz to the same degree as other course and more porous materials. Differential preservation on various lithic raw materials or in different environments might also explain these differences. Preservation is clearly something that needs to be considered in these situations. More controlled experiments testing the same residues on different lithic raw materials would provide useful information.

The preservation of gum adhesives without ochre, and of hide or bone glue in the archaeological record is exceptionally rare. Under extremely dry conditions, or waterlogged sites, hide glue may preserve for long periods of time. For example, the oldest animal glues in Europe come from a waterlogged site in Switzerland dated by dendrochronology of the bow wood they were used on to a little over 3100 B.C. (Bleicher *et al.* 2015), and the oldest known animal based glue currently come from a cave site in Israel and date to between ca. 8200 –7300 cal. BC (Solazzo *et al.* 2016). Both sites used in this study, Horsterwold and FARF receive a considerable amount of precipitation, but are not waterlogged.

Acacia and other plant gums are polysaccharides with high water solubility and low viscosity (Daoub *et al.* 2016). Until recently, no plant gums have been identified from prehistory. This is likely due to their poor preservation as most plant polysaccharides are rapidly decomposed in soil, sometimes within 6-8 weeks (Martin 1971). However, FTIR anaylsis from Grotta del Cavallo, Italy suggests Uluzzian backed pieces may have been hafted with a mixture of gum, ochre and beeswax (Sano *et al.* 2019). Unfortunately, many of the spectral peaks used to identify gum by the authors also occur in other materials. Polysaccharides also make up 75% of the dry weight of plants (Tseng 1997), further complicating the accurate identification of gum residues. Combination with beeswax and ochre may help inhibit the biological decay of gums adhesives. More specific experiments would need to be conducted to explore this particular combination. If the identification by Sano et al. is correct, however, it highlights the importance of chemically analyzing hafting residues, because organic material may be embedded in inorganic remains, even if not microscopically visible. Indeed, there are numerous examples highlighting the visual ambiguity of many micro-residues (Monnier *et al.* 2013; Monnier *et al.* 2012; Pedergnana *et al.* 2016; Croft *et al.* 2016). That the visual identification of three types of known adhesive residues in this study (gum, hide and bone glue) was impossible after just six months of natural exposure further supports this.

In addition to birch bark tar being the oldest known archaeological adhesive, residues of this material also survive in the largest pieces. Whether this has more to do with how much of the material was initially used is unknown, but samples from Campitello Quarry, Italy and Zandmotor, the Netherlands both have tar likely covering more than 30% of the tool's surface area. In the case of Campitello Quarry, this is an estimate, because the exact size of the flake is unknown. The second object from Campitello Quarry has approximately 25% of one side covered in birch bark tar. The tar from ; Königsaue, Germany, although no tool is available for reference, preserved so well that a finger-print is visible on its surface, suggesting very little, if any, degradation occurred (Koller et al. 2001). Measurements from backed pieces where macro-residues survive from Diepkloof Rock Shelter, South Africa show that the resin adhesives covered on average approximately 28% of the tool surfaces (Fig. 2 1-5; Charrié-Duhaut et al. 2013). Tools from Fossellone Cave, Italy show that the resin and beeswax residue covered approximately 23% of the tool surface, while two tools with resin only averaged residue on approximately 5% of the tool surface (Fig. 2 A, D, E; Degano et al. 2019). Though these measurements must be interpreted with caution as they are taken from selected figures in the literature that showed clearly the residue and both sides of the tools, and we do not know how much of the tools were originally covered by adhesive. However, they give an indication as to how little adhesive residues may degrade under certain circumstances. Birch bark tar, and some resin and resin/beeswax adhesives appear fairly similar after 3 years as they do after 50,000 years. That some adhesives were significantly affected after only 6 months to 3 years, both buried and on the surface, also suggests that if decay is going to happen, it may occur relatively quickly after deposition, regardless of rapid burial by sediment (cf. Barton 2009).

Conclusion

Adhesives provide a unique window onto past technologies and human behaviour. The selection and use of different hafting materials may be the result of environmental constraints, production complexity, physical or material properties, the intended function, or possibly even socio-cultural or economic factors (Wadley *et al.* 2004; Berdan *et al.* 2009; Kozowyk and Poulis 2019; Kozowyk *et al.* 2017b). It is the variation in adhesive properties that can give so much information about the past that also directly effects how likely the materials will survive to be analysed by archaeologists in the first place.

The research presented here provides a first-look at preservation qualities of natural adhesives and how this affects the archaeological record. The findings clearly show that birch bark tar preserves better than any other adhesive material tested. Compound ochre and beeswax-containing adhesives preserve second best, followed by compound resin-beeswax adhesives and then other single component adhesives. Ochre also greatly aids in the recognition of potential hafting residues due to its colour.

Archaeologists' understanding of Palaeolithic adhesive use is changing rapidly. We now know that Neandertal chose to invest considerable amounts of birch bark tar to use small and simple flakes (Niekus *et al.* 2019). Previously, these types of lithics would not warrant residue analysis, unless as a random control sample to test against such 'likely' hafted pieces as backed bladelets, microliths, or possible projectile points. We also know that as well as birch bark tar, Neandertals were using bitumen, resin, and possibly beeswax (Boëda *et al.* 2008b; Degano *et al.* 2019). Adhesives by southern African humans are equally as diverse, but none are as old as the bitumen or birch bark tar finds. Adhesive technology in the deep past was likely more varied than we currently have evidence for. It is important to remain open to the possibility that a wider variety of adhesive types will be found on even more types of stone tools and flakes. And finally, to remember that the life of an adhesive does not end after it is discarded. It remains fluid and can migrate across surfaces, change colour, or disappear entirely.

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6. Conclusion

The aim of this dissertation has been to use experimental archaeology to answer several main questions about the properties, production, efficacy, re-use, and finally decay of adhesives used by Neandertals and early modern humans during the Middle to Late Pleistocene. Below I will outline how my results answer the questions proposed in the introduction, and provide new insights into a significant technological development made by Pleistocene humans.

The story so far

Twenty years ago, little was known about adhesive technology in the Middle Palaeolithic and Middle Stone Age. With the exception of a small number of bitumen traces on stone tools from the Levant, there was no clear evidence showing what materials were being used. The last two decades have seen studies on ancient adhesives develop considerably. Through collaborations with chemists and other specialists archaeologists have been able to identify many more adhesive residues. We now know that both Neandertals and Middle Stone Age humans were using a range of natural adhesive materials, including different resins, compound adhesives, bitumen, and birch bark tar. Adhesive use dates back into the Middle Pleistocene, and the mental capacity to use adhesives for hafting may even have stemmed from the common ancestors of Neandertals and anatomically modern humans (Niekus *et al.* 2019). We also know that during the Middle and Late Pleistocene, humans were using adhesives for a number of different hafting-related tasks. These include not only the stereotypical spear or projectile point, but also scrapers, knives, and even seemingly random flakes (Degano *et al.* 2019; Niekus *et al.* 2019; Mazza *et al.* 2006).

What we did not know before the experiments conducted for this thesis, was the conditions required to invent and develop birch bark tar technology among Neandertals. Nor did we know why this material appears to have been favoured throughout much of prehistory, despite the presumed complexity of its production. It was also unclear how much of an effect ingredient ratios had on the performance of compound adhesives, making it difficult to gauge the level of knowledge or skill required for Middle Stone Age humans to successfully make and use this material. And finally, the potential for preservation biases hampered our ability to give an accurate representation of the range of adhesive technology in the past.

It is now possible to answer these questions, and fit them into a coherent story about Pleistocene adhesive technology. Adhesive technology likely began with single component materials such as bitumen or resin. These are adhesives that naturally occur with a sticky consistency, and require little further manipulation to use. However, birch bark tar and compound adhesives preserve better than others and archaeologists are more likely to find these types of materials from old dates. The earliest adhesives may have been used to provide a backing on simple stone flakes (cf. Niekus *et al.* 2019). Alternatively, they could have been added to an already existing composite tool haft to help strengthen the joint, or protect plant or animal bindings that are sensitive to moisture (Kozowyk *et al.* 2017a; Rots 2008).

With a combination of pyrotechnology, birch bark, and knowledge of some form of simple adhesive use, it is possible that Neandertals could have discovered (and re-discovered) tar accidentally and recognized its potential. Birch is well suited for the accidental discovery of tar, as it has many uses and was relatively abundant during much of the Late Pleistocene (Helmens 2014). Birch bark is waterproof, an excellent fire-starter, and has a high extractive content (Šiman *et al.* 2016; Harkin and Rowe 1971; Bacon 2007; Hordyjewska *et al.* 2019; Miranda *et al.* 2013), giving a relatively high yield of tar, more than twice that of pine wood, from a lightweight raw material.

Although three methods of producing tar from birch bark were tested in Chapter 2, it was hypothesized that other alternatives may have existed, thus providing even more basic starting points for the discovery of birch bark tar. Recently, experiments showing a method of tar production through condensation proved a simpler technique was possible (Schmidt *et al.* 2019). The condensation technique fits well within the developmental model of tar production, outlined in Chapter 2, being simpler than the ash mound method, but also producing significantly less tar.

In order to produce enough tar to use, a level of intentionality would likely have been required. Whether this was using the simplest method and gathering large amounts of raw materials, continually repeating the process, possibly among different individuals, and then combining all of the tar collected, or using a more complex method with multiple working parts. To make tar on demand, Neandertals needed to understand that with the right fuel (birch bark) and fire, tar can be formed. Then, given the right circumstances, it can be collected, and with the right application, it can be a beneficial addition to a tool. While condensed birch tar can be gathered after a small fire, the circumstances under which this is a regular occurrence need to be tested more thoroughly. Tar adhesives become brittle when heated at excessively high temperatures (Kozowyk *et al.* 2017a). A fire burning a combination of fuels other than birch bark (cf. Allué *et al.* 2017; Pop *et al.* 2016), may therefore burn away any tar condensing on nearby rocks before it could be collected.

It has been stated that the process of producing birch tar through the simplest method of condensation may be within cognitive grasp of nonhuman great apes (Schmidt *et al.* 2019). However, there is more to producing tar, even with the condensation method than simply "bringing 2 objects in close proximity and [the] gathering of a resource" (Schmidt *et al.* 2019, 4); one of those two objects needs to be on fire and a third object is needed to scrape or collect the tar. Further, there is more to adhesive use than only producing the material. Once collected, the tar is moulded to suit a particular task, and possibly joined with a fourth object and a fifth if a composite haft is used.

It is the combination of producing a new material with entirely new physical properties, and then shaping it and joining it with yet more objects which is of the greatest significance. This creation and combination would have influenced the way humans saw and interacted with the environment, in a manner akin to the technological paradigm shift most often ascribed to metallurgy (Wragg Sykes 2015; Golden 2010). Finally, manipulating and handling such a plastic material, would likely have helped mould our plastic minds (cf. Overmann and Wynn 2019).

After birch bark tar was first discovered, the technology was either maintained for hundreds of thousands of years, or rediscovered often enough to have been found in a number of different environments and times throughout the Palaeolithic. The loss and rediscovery of birch bark tar technology might explain the significant temporal gap between the Campitello tar and the Zandmotor and Königsaue tars. However, this may also be the result of the sparse archaeological record. If birch tar did not have any more beneficial properties than simpler adhesives, the technology might not have perpetrated through time. Instead, birch tar proved to be tougher, easier to work with, and better suited to re-use. The last point here is of particular significance for harsh environments where resources are scarce. Although initially requiring a higher investment, Neandertals could have produced birch bark tar and then curated and re-used it, carrying enough with them for whatever task arose. For example, large birch trees were relatively scarce in the environment at the time the Zandmotor tar was made and used around 50,000 years ago (Niekus *et al.* 2019). The ability to produce tar efficiently is therefore important, but perhaps more so is the ability to re-use the material.

The properties of birch bark might make it unique among plant resources in its ability to form significant quantities of tar from aceramic production processes. For example, birch bark tends to curl into a roll, more so when heated, thus limiting oxygen in the center of the roll and facilitating pyrolysis. Alternatively, it may burn with a smoke denser in tar particulates which can condense on nearby rocks than other barks or wood. To explore this further, more experiments testing the suitability of other plant materials for creating tar through aceramic methods are necessary.

Birch tar is the oldest known adhesive, but it was not the only natural material used in the past. In environments entirely devoid of birch, Middle Stone Age humans in southern Africa found other solutions for creating strong and re-usable adhesives. The addition of plasticizers and fillers, such as beeswax and ochre to resin creates a compound adhesive that approaches birch tar in terms of workability, performance and reusability.

The first compound adhesives could have occurred through contamination with the surroundings (soil, sand, ochre, charcoal) and a recombination of other materials and technologies used by Middle Stone Age humans. Through repeated use it would have become apparent that adhesives with the right amount of contamination are either easier to manipulate, or better suited to particular applications or use on stone tools made of specific raw materials. Old and brittle resin adhesives become softer when mixed with a plasticizer such as beeswax or fat, for example. However, it is not as simple as improving the properties by only adding a new ingredient. The results from Chapter 3 show that in order to make optimal compound adhesives, Middle Stone Age humans would have needed to carefully balance the ingredients and their ratios, as well as consider raw materials, surface roughness, and the particle size of fillers (Zipkin *et al.* 2014; Wadley 2010). Early compound adhesive users likely had a clear understanding of the effects of mixing different materials, and were able to successfully modify the properties of natural adhesives by combining disparate ingredients in specific ratios. Compound adhesive technology therefore helps show that Middle Stone Age humans had an increased capacity for creative thinking, knowledge, and skill, supporting the hypothesis that compound adhesives can be used as a suitable proxy for complex cognition (Wadley 2010).

Such evidence for the use of highly suitable materials, whether birch tar or compound resin based mixtures, suggests that Pleistocene humans, both Neandertals and anatomically modern humans, were aware of how to create some of the best adhesives from the materials available in their environments. The recent discovery of resin and potential beeswax adhesives made and used by Neandertals at the sites of Fossellone and Sant'Agostino caves (Degano *et al.* 2019) further highlights the similar capacities of Neandertals and anatomically modern humans for adhesive technology.

Beyond birch tar and compound adhesives, materials more prone to excessive degradation can survive in the archaeological record under exceptional circumstances. These include gum adhesives and animal glues (Sano *et al.* 2019; Bleicher *et al.* 2015). It is therefore possible that adhesive technology during the Pleistocene was more diverse than we currently have evidence for, leaving an abundance of further research opportunities.

Future directions

Through the experimental study of material properties and methods of production this thesis provides the foundation from which to study ancient adhesives. Research is ongoing that will help further improve our knowledge of adhesive materials and technology. However, there are a number of important questions and areas of study that remain relatively unexplored, and should not be overlooked.

It is clear that environmental constraints played an important role in the selection of adhesive materials. In order to better gauge material choices made by past populations, it is essential that we understand the environmental context of the finds. Questions associated with this topic are: How common were the trees associated with adhesives, both in the immediate locale, as well as the greater area, and how available were fillers and plasticizers, such as ochre and beeswax, in the environment? Access to certain additives may also influence the primary ingredient choice. Likewise, there are known differences in quality and quantity of plant exudates of different species, plant ages, and geographic locations. It will be necessary to expand our experimental datasets to include other prominent materials; *Prunus* gum, spruce resin, and bitumen have all been used as natural adhesives and sealants in the past, yet little systematic experimental work has tested the properties of these materials.

The recent debate about the complexity of tar production by Neandertals clearly highlights the need for more research on this topic (Schmidt *et al.* 2019; Niekus *et al.* 2019; Kozowyk *et al.* 2020; Schmidt *et al.* 2020). Similar to the work used for comparing production techniques and levels of re-use on Neolithic tars (Rageot *et al.* 2018), experiments exploring adhesives from different birch types, different regions/climates, and subjected to different regimes of re-use and degradation experiments will provide additional valuable information, necessary for future Palaeolithic research. For example, current studies on residue preservation and diagenesis are relatively limited and have often been conducted under field conditions (Cnuts *et al.* 2017; Monnier and May 2019). To reach a better understanding of how specific burial conditions effect different adhesive types, it is necessary to conduct laboratory-based experiments focusing on isolated variables, such as pH level, UV exposure or freeze-thaw cycles, (e.g., Braadbaart *et al.* 2009). This would allow archaeologists to understand which specific conditions are most significant with regards to certain adhesive materials and environments. Further, chemical analysis of such experimental samples would provide more insight into how archaeological adhesives change through time, thus facilitating more accurate identification of degraded material.

There are a number of ephemeral qualities of natural adhesive that are difficult to empirically test for, but may still have had a significant implications for the selection and use of such materials in the past. Aspects such as the colour of birch bark, or the smell of fresh pine resin may have been important criteria to early adhesive makers. A detailed ethnographic review would help to illuminate any potential non-technological reasons for the selection of certain materials. However, ethnographic results would still need to be tested against experimental and archaeological data before making conclusions about the deep past. If there can be no practical or economic benefit to using certain materials, then we may more reliably be able to attribute it to cosmological ideas.

Finally, it is necessary to expand the archaeological dataset. For experimental work to be of value, it must be comparable with archaeological material. Uniform methods of analysis will provide more accurate and comparable data from site to site. Common methods of analysis, such as gas chromatography mass spectrometry are not always possible due to sample size or material curation requirements. Better analytical techniques are continually being developed that require smaller samples, or that are non-destructive, circumventing sampling issues and further helping to elucidate preservation and research biases. New non-destructive methods that can be done *in-situ* also allow general characterization of residues that was previously not possible. As awareness is increasing regarding the importance of adhesives and residues from the Palaeolithic, more archaeological material will no doubt come to light, illuminating the significant gaps that currently exist between known Middle Palaeolithic adhesive finds. Increasing knowledge of how to handle and store residues, and where and what to look for is therefore of paramount importance. This will better equip archaeologists for finding and analyzing future residues, while ensuring research biases about the types of adhesive or tools used with adhesives are kept to a minimum.

Final remarks

The experiments conducted for this thesis have provided an explanation for how the earliest known adhesive technology developed, and why ancient humans chose to continue transforming birch bark into tar, making the first ‘synthetic’ material in the process. I have shown how precise Middle Stone Age humans needed to be with their ingredients to create strong compound adhesives, supporting hypotheses about what this means for their cognitive capacities. And finally, differential preservation creates a biased view, yet suggests that the past was far more diverse than we currently have evidence for. The recent increase in publications containing new Palaeolithic and Stone Age adhesive residues attests to this. Although we will never recreate the exact adhesives of the past, by using controlled and well formulated experiments to understand the relevant material properties, archaeologists can fill in the gaps and paint a clearer picture of what life was like for our distant ancestors.

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Appendix

Chapter 2. Supplementary information

Experimental methods for the Palaeolithic dry distillation of birch bark: implications for the origin and development of Neandertal adhesive technology

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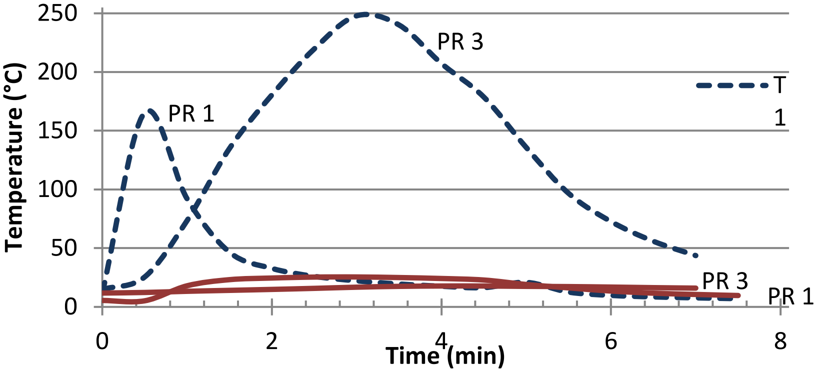
Supplementary Table S1. Recorded data for each attempt.

Exp.	Fire prep time (min)	Set-up time (min)	Run time (min)	Firewood (kg)	Bark before (g)	Bark after (g)	Tar yield (g)	Tar yield efficiency (%)	Ambient temp (°C)	RH (%)	Wind speed (Km/h), direction	Notes
AM 1	120	17	32	10.30	88.00	33.10	0.31	0.35	5.2	91	1.1, SE	
AM 2	180	10	19	7.10	98.00	62.54	0.59	0.60	5.6	92	2.5, S	Firewood added to ash and embers from previous fire
AM 3	210	10	30	3.90	107.00	49.72	1.04	0.97	5.5	92	1.1, SE	Firewood added to ash and embers from previous fire
AM 4	310	10	28	2.90	120.00	54.13	0.18	0.15	4.7	96	0.0, -	Firewood added to ash and embers from previous fire
AM 5 Demo	300	10	36	N/A	53.00	20.45	0.36	0.68	1.2	97	0.0, -	Firewood not recorded
Mean:				**6.05**	**93.20**	**43.99**	**0.50**	**0.53**	**4.4**	**93**		
PR 1	10	22	5	1.00	32.00	30.00	N/A	N/A	5.5	6	3.0, SW	Unsuccessful
PR 2	10	10	5	1.00	30.00	29.00	N/A	N/A	5.5	6	3.0, SW	Unsuccessful
PR 3	10	10	8	1.00	50.00	51.24	N/A	N/A	5.4	6	3.6, SW	Unsuccessful
PR 4	10	5	4	1.00	47.00	43.65	N/A	N/A	5.4	6	3.6, SW	Unsuccessful
PR 5	60	14	30	4.00	52.00	32.67	0.13	0.25	5.0	67	0.0, -	
PR 6	60	15	33	4.00	45.00	26.71	1.53	3.40	2.5	67	0.0, -	High soil contamination in sample
PR 7	60	15	30	4.00	48.00	23.34	0.80	1.67	6.2	75	1.1, SE	High soil contamination in sample
PR 8	60	15	40	4.00	63.00	44.32	0.11	0.17	6.5	73	2.5, S	

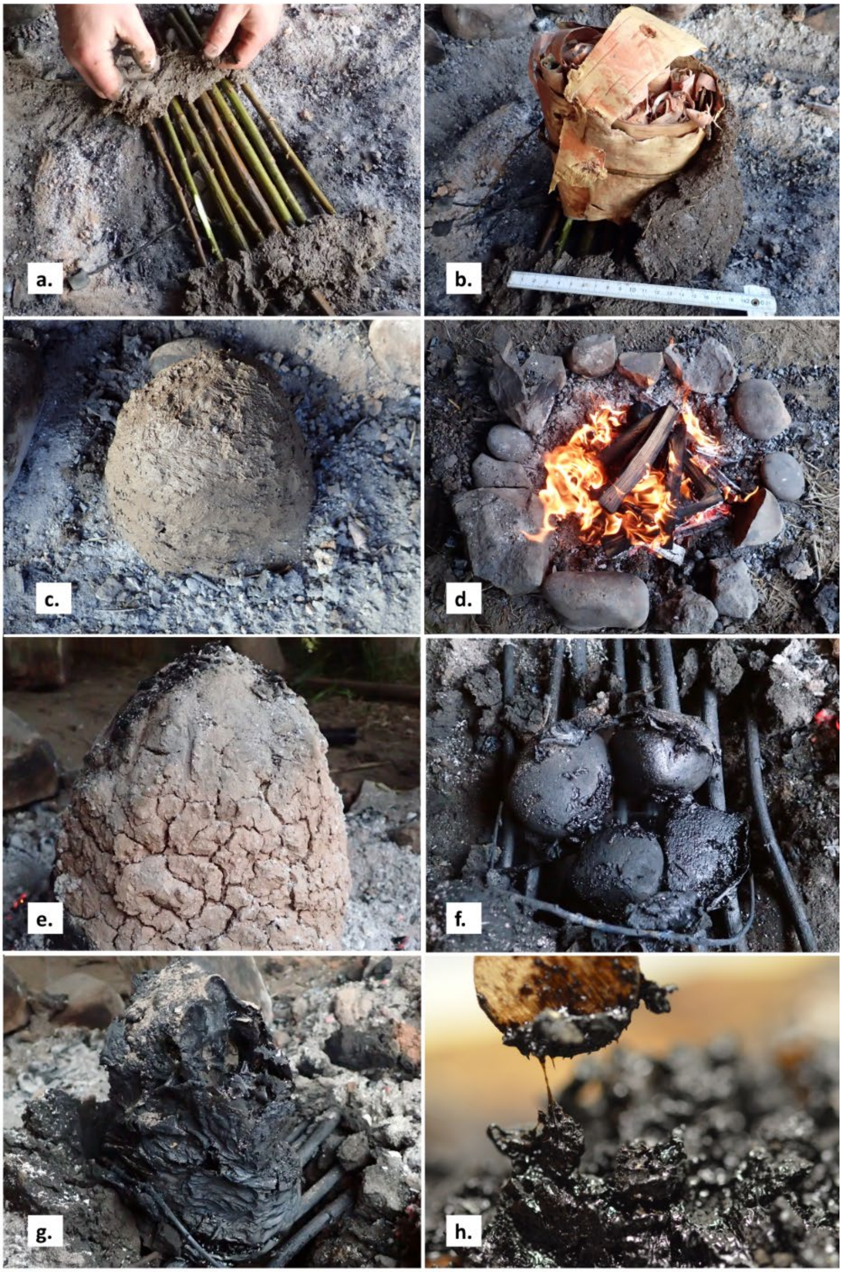
PR 9	60	15	58	4.00	50.00	33.38	0.12	0.24	5.4	79	0.0, -	
PR 10	60	15	41	4.00	62.00	28.03	0.15	0.24	10.6	88	1.1, SE	
PR 11	60	15	40	4.00	73.00	33.41	1.77	2.42	11.2	82	1.1, SE	
Mean:				**4.00**	**56.14**	**31.69**	**0.66**	**1.17**	**6.7**	**90**		
RS 1	10	45	150	7.50	85.00	78.46	N/A	N/A	3.8	99	0.0, -	Unsuccessful - some tar soaked into wood vessel (not enough bark)
RS 2	10	15	165	8.80	88.00	47.34	N/A	N/A	5.4	96	0.0, -	Unsuccessful - some tar soaked into wood vessel (not enough bark)
RS 3	10	20	180	10.70	52.00		N/A	N/A	5.5	92	0.0, -	Unsuccessful - some tar soaked into wood vessel (not enough bark)
RS 4	7	21	230	11.20	52.00	34.31	5.52	10.62	3.0	96	0.0, -	Metal vessel
RS 5	8	22	235	11.20	57.00	39.90	N/A	N/A	3.0	96	2.5, NW	Unsuccessful - some tar soaked into wood vessel (not enough bark)
RS 6	10	25	210	13.00	55.00	6.89	0.17	0.31	5.4	71	2.2, S	Likely not enough bark
RS 7	20	25	340	29.50	163.00	35.00	15.70	9.63	1.2	97	0.0, -	
RS 8	10	57	376	23.90	194.00	38.00	1.86	0.96	8.3	94	0.0, -	Shell vessel - high soil contamination
Mean:				**15.22**	**93.25**	**39.99**	**5.81**	**6.23**	**4.4**	**92**		

Supplementary Figure S1. Photographs of ash mound method. A) Birch bark roll; b) Birch bark roll placed in embers and ash; c) Birch bark roll covered in pile of embers and ash; d) Unwrapping birch bark roll to expose tar which is then scraped off using a stick or flint flake.

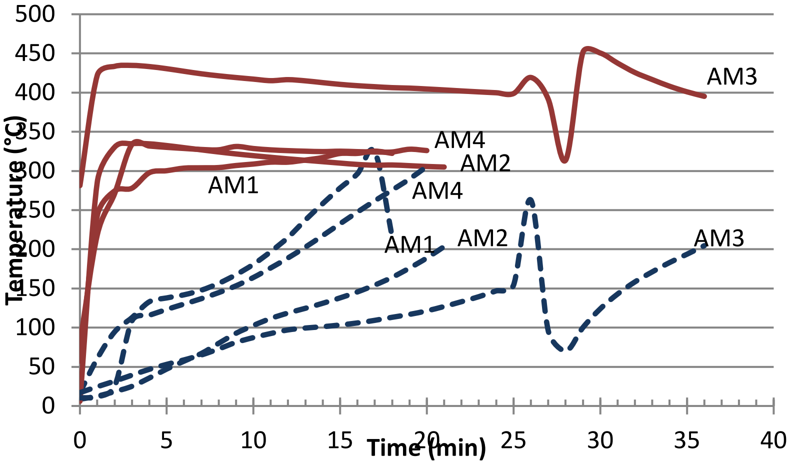


Supplementary Figure S2. Temperature curves of pit roll methods PR1 and PR3 using a pebble and no additional heat source. Temperature was not sustained high enough or long enough to produce tar. T1 = thermocouple in the middle of the bark roll; T2 = thermocouple in the pit below the bark roll.

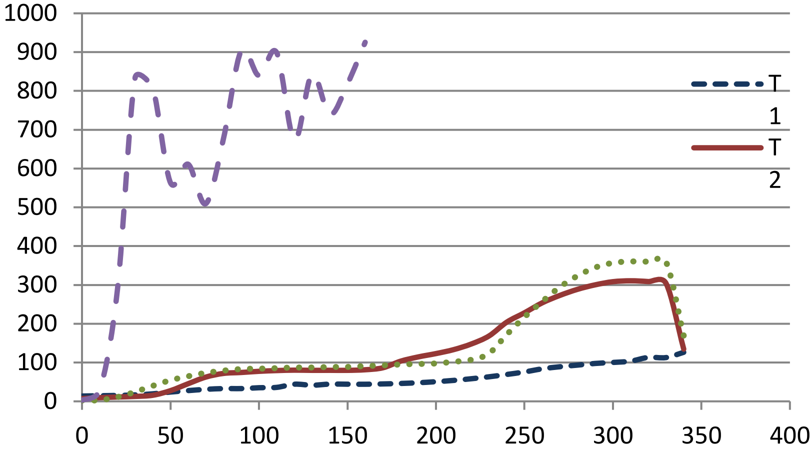
Supplementary Figure S3. Photographs of pit roll method. a) Birch bark roll, pit, and birch bark vessel; b) birch bark placed in pit with hot embers covering everything (flames sometimes occur near the start); c) embers smouldering over the birch bark in pit; d) embers are removed to reveal charred bark (on the top half); e) bark is unrolled to expose more tar, some of which has dripped out of the bottom of the roll and into the vessel in the bottom of the pit; f) birch bark vessel from the bottom of the pit with birch bark tar.



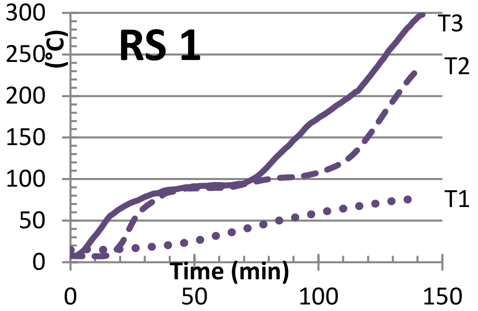
Supplementary Figure S4. Photographs of raised structure method. a) Twigs laid over pit containing birch bark vessel; b) and c) large roll of bark covered in wet clayish soil; d) fire lit all around raised structure; e) structure after firing; f) and g) structure removed to expose pebbles, charred twigs, and charred bark; h) resulting tar scraped from vessel at room temperature.

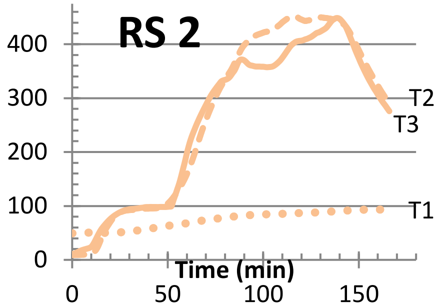


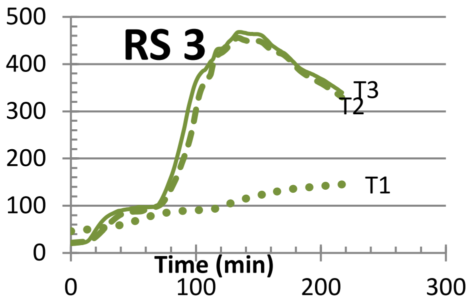
Supplementary Figure S5. Temperature curves for ash mound methods AM1-AM4. The temperature fluctuation of AM3 between 25 and 30 minutes occurred when we removed the bark roll from the ash/embers and placed it back in the fire. T1 = thermocouple in the middle of the bark roll; T2 = thermocouple in the ash/embers outside the bark roll.

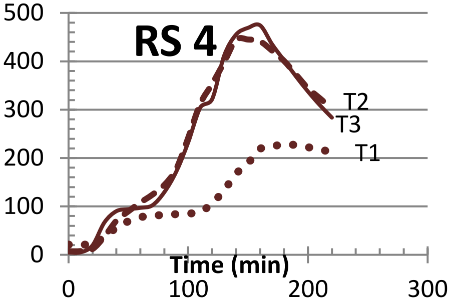


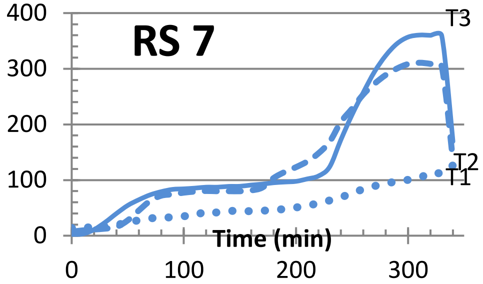
Supplementary Figure S6. Temperature curve for Raised structure RS7. Temperatures inside the earth structure remain below 100 °C until the water has evaporated and then begin to climb between ~175-225 min. Fire temperatures fluctuate dramatically from very early on. In this experiment the fire thermocouple was removed at 170 min due to time constraints on the equipment, but the fire was continually fed until ~325 min. T1 = thermocouple in the vessel in the pit; T2 = thermocouple in the middle of the bark roll; T3 = thermocouple outside the bark roll but inside the earth structure; T4 = thermocouple in the fire.

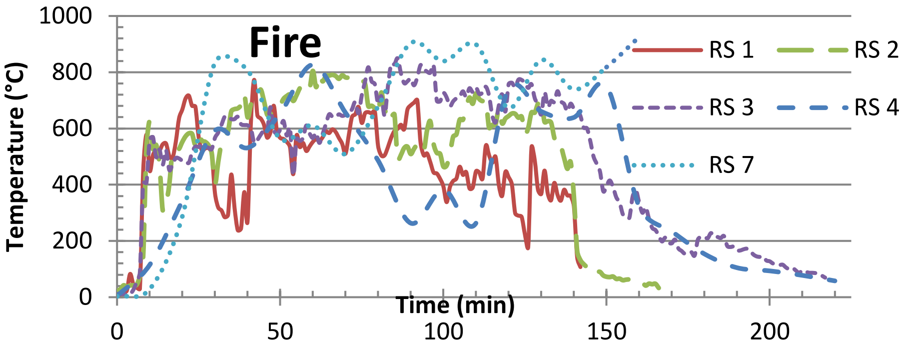

RS 1
(°C)
300
250
200
150
100
50
0
T3
T2
T1
Time (min)
0
50
100
150


RS 2
400
300
200
100
0
T2
T3
T1
Time (min)
0
50
100
150

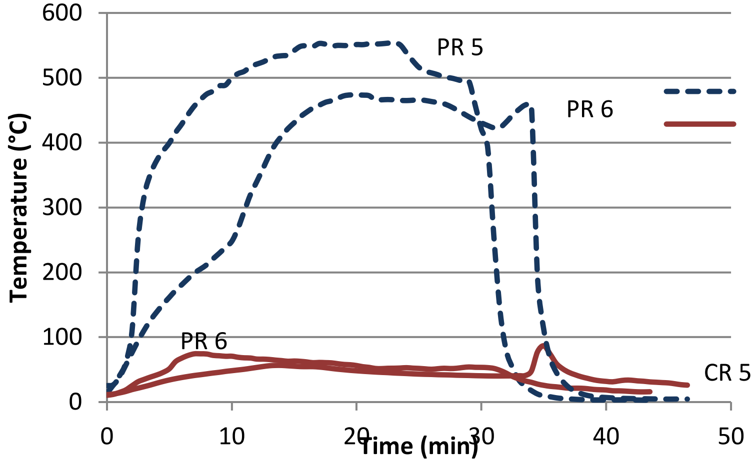

RS 3
500
400
300
200
100
0
T3
T2
T1
Time (min)
0
100
200
300

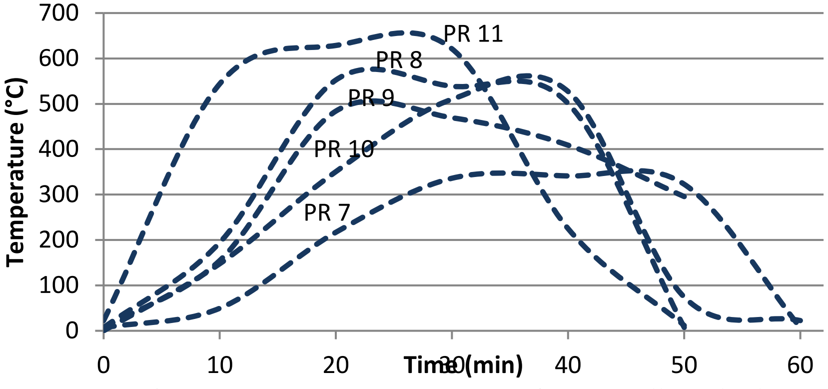

RS 4
500
400
300
200
100
0
T2
T3
T1
Time (min)
0
100
200
300


RS 7
400
300
200
100
0
T3
T2
T1
Time (min)
0
100
200
300

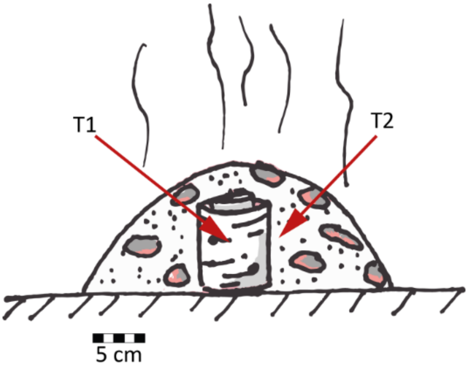

Fire
Temperature (°C)
1000
800
600
400
200
0
RS 1
RS 2
RS 3
RS 4
RS 7
Time (min)
0
50
100
150
200

Supplementary Figure S7 (previous). Temperature curves of raised structure experiments. RS 1-4 T1= vessel, T2=inside middle of roll, T3=outside middle of roll. RS 7 T1=vessel, T2=inside bottom of roll, T3=inside top of roll. The first 50-80 minutes is spent evaporating the moisture from the earth mound, seen by the plateau in temperature for the first part of the curve. In RS7 the larger structure took nearly 200 minutes to dry before heat inside began to climb over 100 °C. Highly fluctuating fire temperatures and steady internal temperatures indicate automatic thermo-regulation by the clay structure and pit.

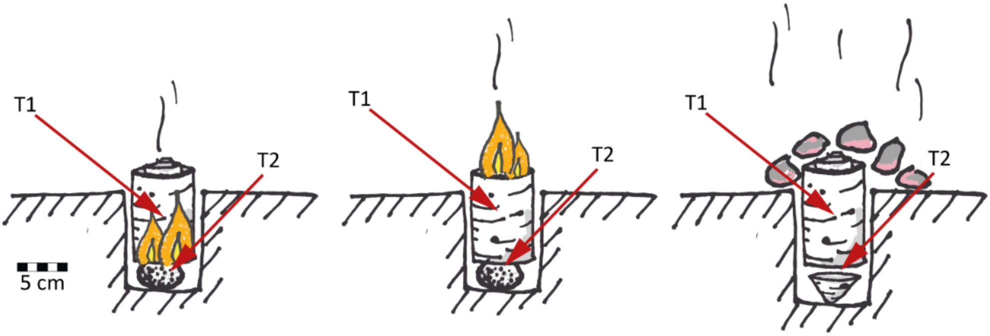




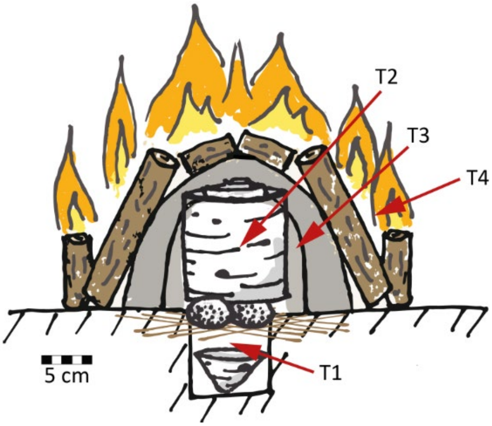
Supplementary Figure S8. Temperature curves for Pit Roll methods PR5, PR6 (top) and PR7-PR11 (bottom). T2 was not recorded for PR7-PR11.Temperatures increase steadily as the embers burn their way through the birch bark, and then decrease as they burn out in the pit. T1 = thermocouple in the middle of the bark roll; T2 = thermocouple in the birch bark vessel in the pit.



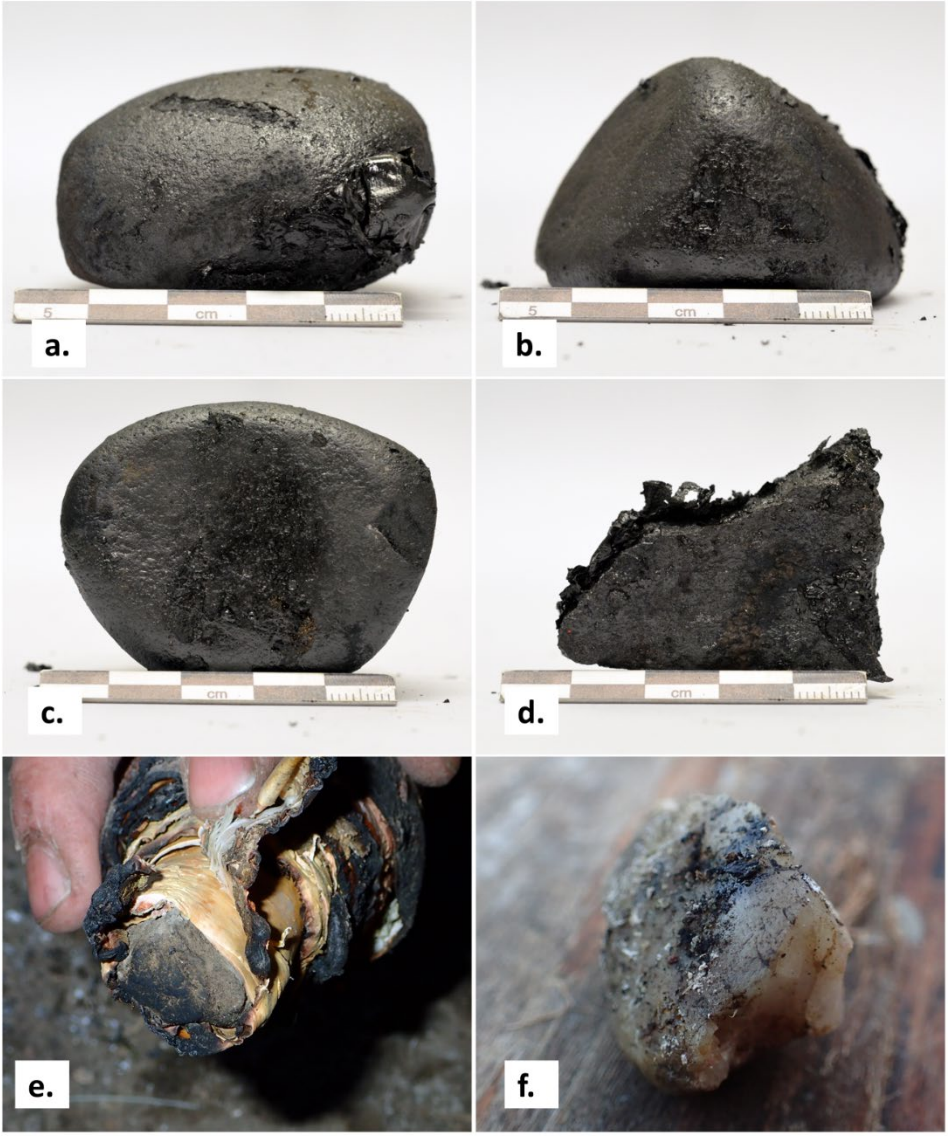
Supplementary Figure S9. Drawing of ash mound method with arrows depicting thermocouple placement. Scale is approximate.



Supplementary Figure S10. Drawing of pit roll methods PR1, PR2 (left); PR3, PR4 (middle), and PR 5-11 (right). Arrows depict thermocouple placement for each method. Scale is approximate.



Supplementary Figure S11. Drawing of ash mound method RS7 with arrows showing thermocouple locations. Earlier attempts did not include pebbles under the bark, and used a wooden cup and a metal container as the vessel instead of a birch bark cup shown here. Scale is approximate.



Supplementary Figure S12. Photographs of pebbles used in experiments. a-d) Pebbles used in raised structure; e) and f) pebbles used in pit rolls PR1-PR4. Some charring occurred on the pit roll pebble turning it black, and traces of pyrolysis products appeared on the other side, but only in very small quantities that could not be removed from the pebble or used for hafting in any way.

Supplementary Figure S13. Photographs of the remains of various methods and products. a) Some tar from the ash mound method that is highly contaminated with traces of un-charred birch bark; b) tar from the RS7 vessel containing very few contaminants; c) lump of tar from RS8 (using a shell vessel) heavily contaminated in soil. It holds its form, but has very little tack due to the over-saturation of particles; d) remains of bark roll from PR 3 and PR 4. Only slight charring at the end that was ignited and the rest is unchanged; e) remains of bark from successful PR experiment contains much more charred bark; f) bark remains from raised structure RS7. The bark is highly charred and does not resemble birch bark macroscopically.

Supplementary Figure S14. Tar from RS 4 (left) and RS 7 (right). RS 4 used a metal container to collect the tar. Temperatures were higher in the metal container (refer above to Fig. S13), but the tar collected remained more liquid than that from RS 7. Suggesting some of the more liquid portion of tar is lost to the earth pit walls, or to the organic vessel.

Notes and comments on aceramic tar production

The following section details our methods, experiences and decisions during the experiments. We included information on: 1) birch bark, 2) fire maintenance, 3) container material and 4) failed attempts and future directions. This information will increase the reproducibility of our work and hopefully spark more much needed research into aceramic tar production.

Bark

Our bark was collected from fresh *Betula pendula* trees, felled the day prior to peeling the bark (August 2016). The bark was used in the experiments five months later (December 2016). Additionally, a small portion (~10%) of bark was collected from trees that had died naturally one year before the experiments. The bark was combined, and selected at random for each experiment. We have seen no evidence to suggest that aged or fresh bark produces more or less tar, but our experiments are unlikely to be consistent enough to see a statistically significant impact regarding the age of the bark.

However, we noticed one difference regarding bark choice between the methods. Thicker and sturdier bark is easier to work with in the ash mount method than thin bark. In this method the bark is unrolled and tar is scraped from the inner surfaces. Thin bark tears easily and it is difficult to unroll thin layers particularly when they are sticky with tar. For the other methods, where tar drips from the bottom of the roll and is collected in a separate container, this is less important, and thinner pieces of bark could be utilised without any detrimental effects. It is currently unknown whether there is a difference in extractive content or quality between thinner and thicker bark remains.

Fire maintenance

For each experimental attempt we had one member conducting the experiment and one or two members recording the information. The data logger recorded temperatures during the experiments, and these were evaluated after each experiment. The temperature and time recordings can be found in Supplementary Figures S5-S8. Below we detail our (at times subjective) decision making, when determining the best methods.

Ash mound

Prior to beginning tar manufacture with the ash mound, a suitable bed of coals and ash was first produced. The time required for this is available in Supplementary Table S1 under 'fire prep time'. This began at 120 minutes for the first attempt, and we added firewood for between 20 and 40 minutes between each successive ash mound attempt. In this way we could utilize the coals of the previous fire. We maintained a flaming fire until we judged there to be enough ash and embers to cover the small roll of birch bark (approximately 6 cm diameter and 10 cm long). No temperature management was conducted up to this point. When the bark roll was placed in the hearth and surrounded with ash and embers, we judged, based on prior experiences, how hot it should be by moving more or less embers over the bark. When too hot, the bark began to smoke, and black smoke indicated that the bark and tar was burning more completely. As this was undesirable, we would remove some embers and/or add ash. The temperature was judged too low if we did not hear any crackling and did not observe any smoke. In these instances we added glowing embers. We stopped these experiments after approximately 20 minutes; the stop time was relatively constant for the ash mound experiments with the exception of AM3. This decision was based on DP's previous experiences and our own experience with how much bark remained and tar had been produced in the prior experiment. In most cases, although we had to manipulate the ashes and embers to some degree, once we thought there was a good temperature inside the mound, our required attention would decrease, and although we checked it fairly frequently (every few minutes) we rarely had to change anything else.

Pit roll

We had no previous experience using the pit roll method, other than what had been mentioned in the literature. After trying it as described (Pawlik 2004), it was clear that this method would not work. The bark was extinguished very rapidly and no tar was produced. We hypothesised that in order to prevent the bark from being extinguished we needed to provide an external heat source, as in the ash mound method. To this end, embers were placed on top of the roll of bark and pit. In order to get suitable embers, a flaming fire only needed to be burning for a short time (see Supplementary Table S1). Once these embers were in place, the pit was left alone and required very little further attention, and no further management. However, if the embers were too small to begin with, then the heat provided was not sufficient to produce much tar. The amount of attention required is difficult to quantify objectively, however. We were learning and improving upon this technique and were recording information, thus our attention was relatively high. Had we been more experienced, and not been interested in the experimental aspects, very little attention would be required. Based on our ash mound experience we stopped the experiments after approximately 30-40 minutes. It was also possible to see how much of the bark roll had burned under the embers, and to see when the embers began to die down. As the thermocouple readings corroborate, around this time the temperatures in the pits also began to decline. The pebble in the bottom of the pit showed us that in some cases tar dripped from the bottom of the roll, but this failed to capture anything, so we placed a small container to catch the tar better. In theory this method could be put in place, and left unattended indefinitely. When the operator returns, the embers would have extinguished and the container could be extracted and tar collected. The only downside being that soil contamination is difficult to control in the small pit, and may be worse if the process was left unattended for a longer period.

Raised structure

Regarding the raised structure method, we had previous experience using similar techniques (PK and GL). Prior we used a metal collection vessel under a muddy structure and in another experiment we used metal containers in the 'two-pot-method' (see Piotrowski 1999; Palmer 2007; Bacon 2007) for details of the two-pot and similar methods). From these experiments we knew that the fire needs to run for approximately one hour to dry the 2-3 cm thick muddy structure (longer when the structure is thicker) and one additional hour to make tar. The fires in the experiments here ran for about 2.5-6 hours, depending on how thick or large our structure was.

During the raised structure attempts, the only aim was to maintain a flaming fire all around the structure. When a part of the fire began to burn out, fresh firewood was added to maintain a flame. As the thermocouple was only placed at a single point on this circular fire, temperature logger readings could not help us determine when to place more firewood (for example on the opposite side of the structure). In these experiments the fire was stoked with new wood approximately once every 20-30 minutes, as with a standard campfire, but at the start it was loaded heavily with smaller wood. We perceived this as less demanding than the ash roll method because the temperature of the bark could never be too high (the structure was insulating the bark), and if the fire was diminished it was very simple to replenish it with more wood. Moreover, the span between re-fueling equaled the total length of the ash mound method, so we could load the fire with wood and then leave it for 20 minutes with minimal attention.

The mound structure itself was made of the earth present in our surroundings with no further alterations. This is a mixture of predominantly clay and earth/soil. We had some problems with the structure cracking, therefore perhaps adding a temper to the clay would help, however it is not completely necessary. Pure sand may be too porous to seal the bark completely, and it may also absorb many of the volatiles that would otherwise condense in the container and form part of the tar. There is likely room for considerable variation in raised structure mound material and consistency. Poor quality material (more porous or more prone to cracking when heated) may need to be thicker, however this will then take longer to heat. Supplementary Figure 6 shows that for RS7 it took approximately 200 minutes to evaporate the moisture from the structure before heating of the internal chamber began. On this attempt we knew we had more bark and a larger structure than before, and thus we left it for as long as possible.

Container material

Despite birch bark being a highly flammable material, we have shown that it survives well in a pit below the fire. This means that a heat resistant retort is not necessary. One important aspect however, is that when only small quantities of tar are produced, the container should be made from non-porous material. There are many possible containers available that would likely be suitable for collecting tar using these methods, including bone, shell, and eggshell. We used birch bark because it minimises the operational steps of each method, ensuring we did not add unnecessary complexity to the production process.

Failed attempts and future directions

It was clear that the early pit roll methods (PR1-PR4) failed because there was not enough heat for a long enough period of time. With the exception of PR6 (which could not be measured accurately due to high soil contamination), PR11 was the most successful, and also the hottest. This method may possibly be improved by creating a larger roll and/or placing more embers on top.

The first three raised structure attempts were unsuccessful, but we observed that tar was absorbed into our wooden container. Therefore we ran one experiment using a metal container underneath the earthen mound (RS4). This attempt was successful, and showed that we were indeed producing tar, but had previously failed to capture it. For RS5 and RS6 we changed the container to birch bark, which had proved successful in the pit roll methods. Although tar had clearly dripped onto the wooden screen, we still failed to collect a sizable amount. We determined that we needed more bark to ensure that enough tar would be produced to drip through the screen and collect in the vessel. In RS7 we combined our prior experiences and in this successful attempt we produced approximately 16 g tar. During RS7 we also added stones on top of our wood screen. This was done in an attempt to raise the bark higher in the structure (and thus make it hotter), and also to potentially mimic the metal container, which may reflect heat back up, rather than allowing it to dissipate into the cool pit below.

We attempted to duplicate our results in RS8, using a shell container. This method was, however, less successful for a number of reasons. The mud structure appeared to crack more than RS7, and smoke could be seen coming from inside the structure. The smoke indicated that tar volatiles were escaping, and that oxygen may have been present in the structure, leading to combustion rather than distillation. Despite this, tar was still produced and dripped again onto the wood screen, and into the shell. However, the small and shallow shape of the shell meant it easily filled with soil when we removed the structure. There was also a small crack in the shell, and some tar was found on the underside. All of these aspects combined made it difficult to collect enough tar (likely much of it was disposed of as soil contamination) during this attempt.

There are several potential areas of improvement with the raised structure to ensure a higher success rate, and all of these will lead to increasing complexity. 1) Lining the collection pit with clay or mud to prevent or limit soil contamination during removal. 2) Creating a better mixture for the structure material, such as including more clay, dung, straw etc. to reduce the chances of it cracking when drying. 3) Allowing the structure time to dry before igniting the fire. This would reduce the amount of firewood needed to heat the bark inside the structure. 4) Larger quantities of bark may also help. Perhaps it will not improve the efficiency (tar/bark ratio), but it will ensure enough tar is produced to be captured effectively.

Chapter 3. Supplementary information

Lap Shear and Impact Testing of Ochre and Beeswax in Experimental Middle Stone Age Compound Adhesives

Authors: P.R.B. Kozowyk, G.H.J. Langejans, J.A. Poulis

Adhesive/additive details

Material	Supplier	Particle size
Pine rosin (colophonium)	Verfmolen De Kat*	N/A
Acacia gum (Arabische gom brokjes)	Verfmolen De Kat*	N/A
Beeswax (bijenwas korrels)	Verfmolen De Kat*	N/A
Red ochre (Luyckse rode oker)	Verfmolen De Kat*	<62.5 µm

* Kalverringdijk 29, 1509BT Zaandam, NL.
Tel: +31(0)75 621 0477
http://www.verfmolendekat.com/webshop/

Chapter 4. Supplementary information

A new experimental methodology for assessing adhesive properties shows that Neandertals used the most suitable material available

Authors: P.R.B. Kozowyk, J.A. Poulis

All supplementary data for this chapter can be downloaded online from Mendeley Data, v1http://dx.doi.org/10.17632/z69zs69mpg.1

Kozowyk, Paul (2019), “Supplementary Online Material: A new experimental methodology for assessing adhesive properties shows that Neandertals used the most suitable material available”

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Summary

The first use of birch tar adhesives by Neandertals over 191,000 years ago marked a significant technological development. The ability to produce entirely new materials through transformative processes was unlike anything that had been done before. In southern Africa, during the Middle Stone Age, humans made compound adhesives by combining disparate ingredients, a task which is believed to have required modern-like levels of cognition. However, for all of the significance given to ancient adhesives in discussions about Neandertal and modern human technological and cognitive capabilities, our knowledge of the material itself is limited.

Throughout the four independent research articles that comprise this thesis, I use a combination of laboratory and field experiments to systematically study adhesive production and material properties. The results of these experiments provide empirical data that will answer several questions necessary to improve our understanding of this important technology. How did Neandertals first develop birch tar technology? Why does birch tar appear to have been used so often during the Palaeolithic, despite its relative complexity and high production investment? To what degree do ingredient ratios affect the performance and efficacy of compound adhesives? And finally, how much does the present archaeological record reflect what adhesives were actually used in the past?

Experimental production methods show that birch tar could have been discovered and developed through a number of discrete steps using already existing Neandertal technology. Rheology, hardness, and thermogravimetric experiments suggest that Neandertals continued to use birch tar as an adhesive, despite its high production costs, because it was the most suitable material that was available to them. Compared with pine resin, the most common alternative, birch tar has higher cohesive strength, and better workability and re-useability.

In the absence of birch, suitable adhesives were produced in a different way by Middle Stone Age humans; by adding disparate ingredients in specific ratios. Lap shear and impact tests following modern materials testing standards show how small changes to ingredient ratios significantly affect adhesive performance. This supports

the hypothesis that compound adhesives are a suitable proxy for complex cognition in the Middle Stone Age.

Finally, the differential preservation of natural adhesives further explains why we find what we do in the archaeological record. The most commonly identified archaeological adhesives, made of birch tar or compound resin-based mixtures, tend to preserve the best. However, there are many other types of natural adhesives, and in exceptional circumstances some that are more prone to degradation can also survive. Further archaeological research will help determine the full extent of ancient adhesive technology.

This thesis provides the first comprehensive study of Middle Palaeolithic and Middle Stone Age adhesives, providing new insight into the material choices and technological capabilities of Neandertals and Middle Stone Age humans. Finally, as awareness for the importance of Palaeolithic adhesive residues continues to increase, and more discoveries are made, new questions and materials that need to be tested are constantly being brought to light.

Samenvatting

Meer dan 191.000 jaar geleden maakten Neanderthalers voor het eerst gebruik van berkenteerlijmen. Deze ontdekking wordt gekenmerkt als een belangrijke technologische ontwikkeling. Het was tot dan toe ongeëvenaard om volledig nieuwe materialen te produceren door middel van een transformatieproces. Tijdens de Middensteentijd, maakten mensen in Zuid-Afrika composiet lijmen door verschillende ingrediënten te combineren; een activiteit waarvan wordt aangenomen dat deze een (soort van) modern denkvermogen vereiste. Echter, onze materiaalkennis van prehistorische lijmen is zeer beperkt en dat is een probleem gezien het belang en de betekenis die aan oude lijmsoorten wordt gegeven in discussies over de capaciteiten van Neanderthalers en de moderne mens.

In de vier onafhankelijke onderzoeksartikelen, die de kern van dit proefschrift vormen, gebruik ik een combinatie van laboratorium- en veldexperimenten om de productie van lijm en de materiaaleigenschappen van lijm systematisch te bestuderen. De resultaten van deze experimenten leveren de empirische gegevens die nodig zijn om vragen omtrent deze belangrijke technologie te beantwoorden. Hoe hebben Neanderthalers voor het eerst de berkenteer technologie ontwikkeld? Waarom lijkt berkenteer tijdens het Paleolithicum zo vaak te zijn gebruikt, ondanks de relatieve complexiteit en hoge productie-investeringen? In welke mate beïnvloeden ingrediënten verhoudingen de prestaties van samengestelde lijmsoorten? En ten slotte, in hoeverre is het archeologische bestand een afspiegeling van hetgeen wat daadwerkelijk in het verleden is gebruikt?

Experimenten met verschillende productiemethoden tonen aan dat berkenteer ontdekt en ontwikkeld had kunnen worden via een aantal afzonderlijke stappen, bouwend op bestaande Neanderthaler-technologie. Reologie, hardheid en thermogravimetrische experimenten laten zien dat Neanderthalers, ondanks de hoge productiekosten, berkenteer als lijm gebruikten, omdat dit voor hen het meest geschikte beschikbare materiaal was. In vergelijking met dennenhars, het meest voorkomende alternatief, heeft berkenteer een hogere cohesie sterkte en een betere bewerkbaarheid en herbruikbaarheid.

In situaties zonder berk produceerden Middensteentijd mensen uit zuidelijk Afrika bruikbare lijmen op een andere manier; door bijvoorbeeld verschillende ingrediënten te mengen. Moderne industriële afschuif (shear)- en impact-testen laten zien hoe de lijmprestaties sterk beïnvloed worden door kleine veranderingen in ingrediëntverhoudingen. Deze resultaten steunen de hypothese dat resten van composietlijmen een geschikte proxy zijn voor complexe cognitie in de Middensteentijd.

Tot slot verklaren de verschillende preservatie eigenschappen van de natuurlijke lijmen welk percentage er bewaard blijft en wat vervolgens terug te vinden is in het archeologisch bestand. De meest geïdentificeerde archeologische lijmen, gemaakt van berkenteer of mengsels op basis van hars, preserveren ook het best. Er zijn echter veel andere soorten natuurlijke lijmen die veel vatbaarder zijn voor degradatie, maar die in uitzonderlijke omstandigheden bewaard kunnen zijn. Om de volledige omvang van deze technologie te bepalen, is meer onderzoek naar archeologische lijmen nodig.

Reflecterend op de onderzoeksvragen kan gesteld worden dat berkenteer ook eenvoudig te maken en te ontdekken is. Echter, deze simpele methoden hebben een lage opbrengst vergeleken met complexere technieken. Doordat berkenteer sterk en goed recyclebaar is en omdat de productie investering meevalt bij de opbrengst, was berkenteer waarschijnlijk voor prehistorische mensen een geprefereerde lijmsoort. In gebieden zonder berk werden composietlijmen gemaakt waarbij de verhoudingen van de ingrediënten erg nauw kwamen. Lijmonderzoek lijkt dus een geschikte manier om het technologisch-kunnen van Neanderthalers en mensen in kaart te brengen. Maar, het archeologisch bestand is niet overal een goede afspiegeling van prehistorisch gebruik; sommige lijmsoorten preserveren beter dan anderen.

Dit proefschrift is de eerste uitgebreide studie naar de materiaal eigenschappen van het Midden Paleolithicum en Middensteentijd lijmen.

Hoewel prehistorische lijmen nooit exact kunnen worden nagemaakt, kunnen archeologen wel relevante materiaaleigenschappen doorgronden. Door middel van goed geformuleerde experimenten kunnen de kennisgaten opgevuld worden, om zo nieuwe inzichten in de materiaalkeuzes en technologische competenties van prehistorische moderne mensen en Neanderthalers te schetsen.

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Curriculum Vitae

Paul Robert Barnard Kozowyk was born in Calgary, Canada on June 21st, 1987. He obtained a bachelor's degree with distinction in Anthropology from the University of Victoria, Canada in 2009. After this, he worked and travelled through more than 40 countries before settling and pursuing an academic career in Leiden, the Netherlands. In 2015 Paul graduated *cum laude*, with a Master of Science in Material Culture Studies from Leiden University. For his master's research on Stone Age and Palaeolithic adhesives, he won the European Society for the Study of Human Evolution's student poster prize, and tied for second place for the Leiden University Master's Thesis Award.

Paul continued studying ancient adhesives and was awarded a grant later in 2015 from the Dutch Research School of Archaeology to further pursue his research. For this he collaborated with the Adhesion Institute at the Delft University of Technology, designing and conducting many experiments in the Delft Aerospace Structures and Materials Laboratory. During this period, Paul authored and co-authored two additional peer reviewed articles, and presented his research at a number of international conferences and workshops. Paul has made replica birch tar hafted tools for a special display at the Rijksmuseum van Oudheden, Leiden, and his photographs and research have appeared in numerous books, newspapers, magazines, and websites.

Currently, Paul is finishing publications based on his experimental data, and will be joining the Ancient Adhesives research team of Dr. Geeske Langejans at the Delft University of Technology.