**Reconstructing adhesives : an experimental approach to organic palaeolithic technology**
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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).

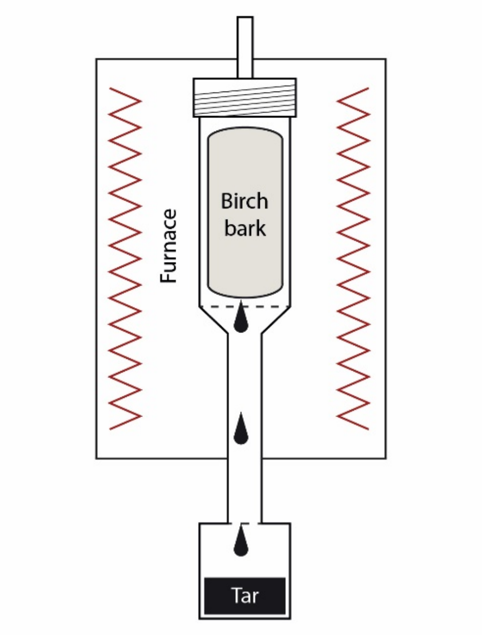


**Fig. 2.** Schematic of tube furnace heating apparatus used to distill birch bark tar. The work-tube and screen to hold the bark are made of stainless steel with a small outlet at the top to relieve pressure in the event that the lower pipe should become blocked. Not to scale.

## 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).

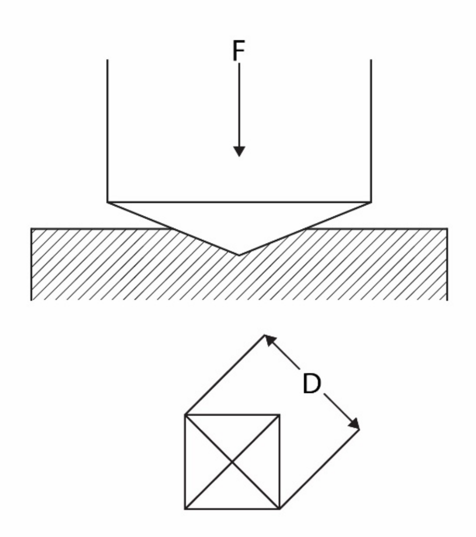


**Fig. 3.** Schematic depicting Vickers hardness method. Shown here is the diamond indenter and substrate (top) and the shape of the indentation and measurement (bottom). Not to scale.

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.

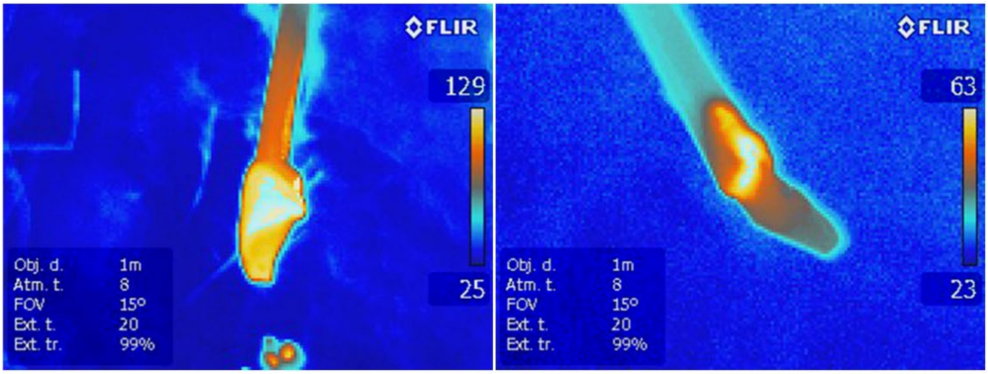


**Fig. 4.** Infrared photographs of a 'pitch stick' used to haft a flint flake to a wooden handle. The resin is held over a fire and warmed until it melts, then it can be 'dabbed' onto the objects to be glued. Photographs are of (left) the pitch stick immediately after heating over a fire before application,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

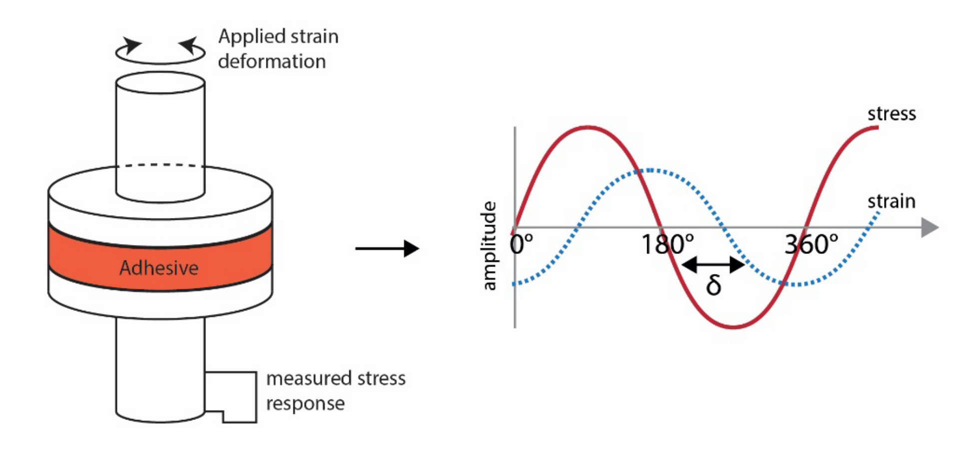


**Fig. 5**. Schematic showing sample and output data from the rheometer. Left: the adhesive sample between the upper and lower plates of the rheometer and the force oscillating about the y-axis (not to scale). Right: the resulting oscillating stress/strain curve. For ideally viscous liquids δ = 90° and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

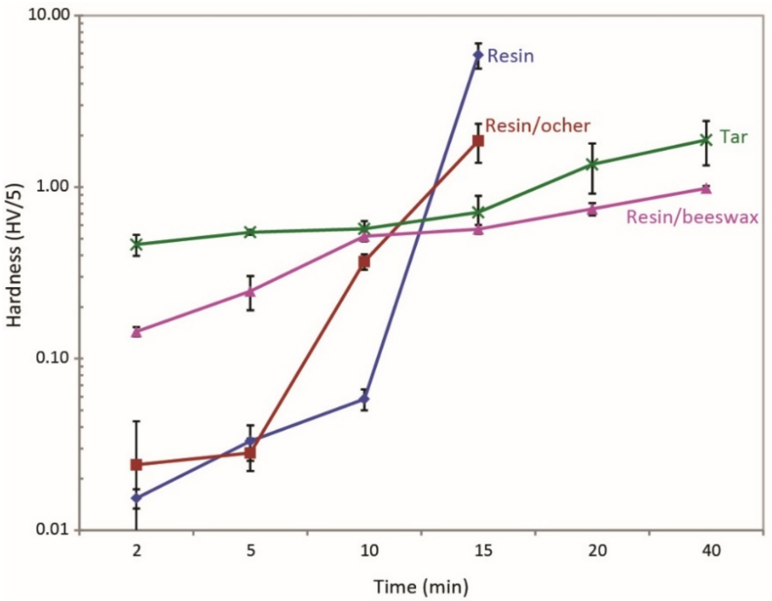


**Fig. 6**. Hardness measurements as a function of heating time. Hardness of resin, resin/ocher, resin/beeswax, and tar adhesives shows that tar is the least affected by prolonged heating.

## 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.

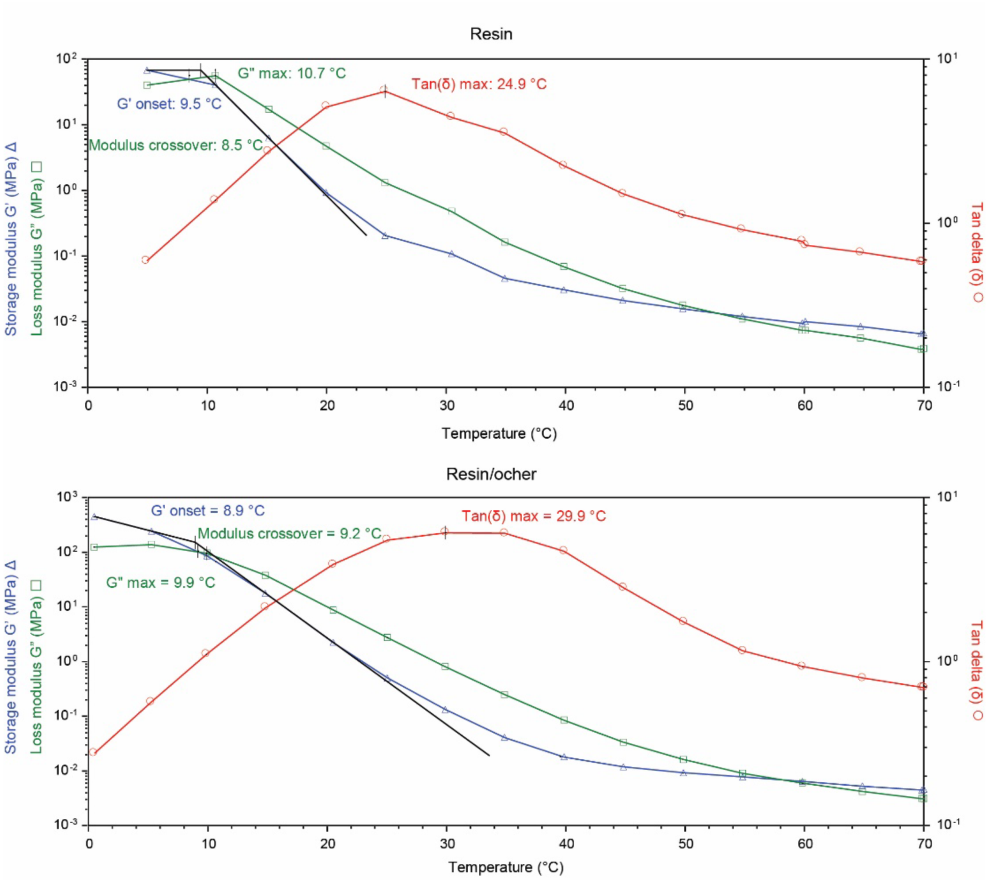


**Fig. 7.** Rheology temperature sweep results. Plot shows the G' onset, G" maximum, modulus crossover, and tan δ maximum of resin (top) and resin/ocher (bottom). Changes are very subtle with the addition of 30 wt.% ocher.

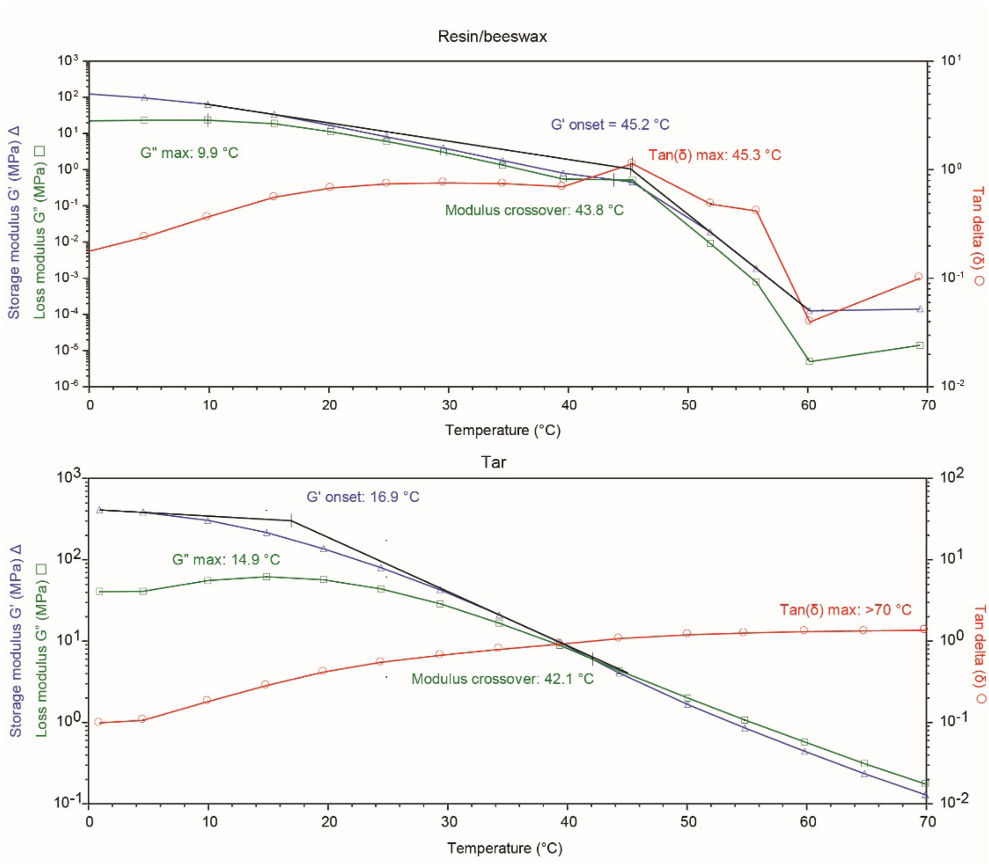


**Fig. 8.** Rheology temperature sweep results. Plot shows the G' onset, G" maximum, modulus crossover, and tan δ maximum of resin/beeswax (top) and birch bark tar (bottom). The addition of beeswax makes resin more closely resemble birch bark tar. After 60 °C, the moduli for beeswax become very low and 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 $T_o$, so a comparison between these materials is more difficult. However, it is clear that the $T_o$ 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. $T_o$ 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.

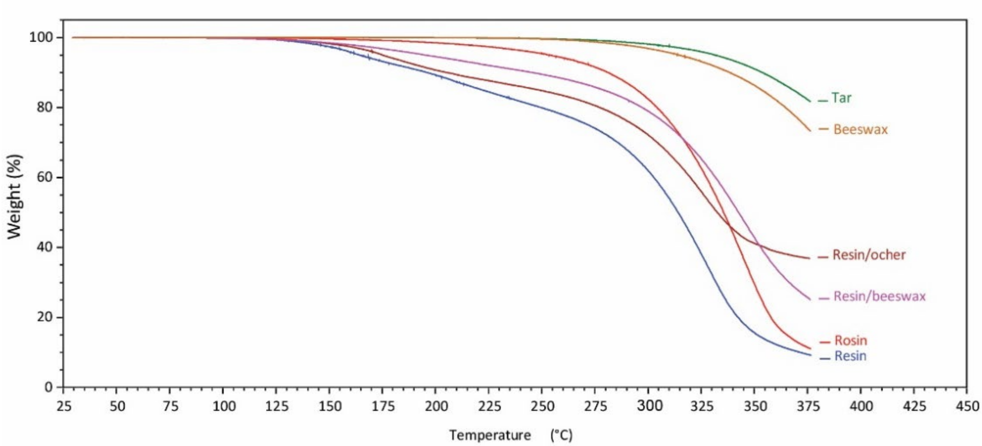


**Fig. 9.** TGA curves. Plot shows the weight loss (%) for tar, resin, resin/ocher, resin/beeswax, beeswax, and rosin during heating from 30 °C to 370 °C.

## 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.