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Cross-Linking of Poly(Vinyl Alcohol) Chains by Ca Ions in Macro-Defect-Free Cements

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In the macro-defect-free cements (MDFs), a *cross-linking* of the polymer chains by Al or Ca ions coming from the hydration reactions of the cement paste may have crucial effects on the mechanical properties achieved by the final materials as well as on the material processing. In the present study, the cross-linking of poly(vinyl alcohol) (PVA) chains by Ca ions has been investigated with *first-principles* theoretical methods and compared with a previously investigated case of cross-linking of poly(acrylic acid) (PAA) chains. The achieved results show the existence of a Ca–PAA cross-linking that is *significantly* more efficient than that realized in the case of the Ca–PVA system. This result implies that the Ca–O bonds involved in the cross-linking of the PVA and PAA chains are affected by the different functional groups present in the two polymer chains and agrees with the improvement of the mechanical properties observed when the PVA polymer is replaced by the PAA polymer in Portland-cement-based MDFs. The achieved results also indicate that the Ca–polymer interactions may have significant effects on the mechanical properties of the above MDFs as well as on their processing.

Introduction

Composite materials with high flexural strength can be produced by incorporating a polymer component, poly(vinyl alcohol) (PVA) or poly(acrylic acid) (PAA), in the paste of high-alumina or Portland cements under high shear and subsequent molding under pressure at 80 °C.^{1–5} The polymer acts as a rheological aid, facilitating particle packing, as well as a filling agent, reducing the material porosity.² These peculiar materials have been termed macro-defect-free cements (MDFs) with reference to the absence of the relatively large voids or defects which are usually present in cement pastes.^{1,3,4} The microstructure of the MDFs is characterized by grains of partially hydrated cement particles embedded in a matrix of polymer.^{6,7} Interphase regions coat the

individual cement grains. These regions generally consist of an amorphous phase formed by the polymer and hydration products of the cement. The peculiar mechanical properties of the MDF materials were initially related to the reduced density of defects in the final cement paste.^{4,5} However, further studies have shown that the mechanical behavior of the interphase regions plays an important role during the fracture of the MDF materials.^{8,9} Moreover, the mechanical strength of the MDFs has been also attributed to chemical reactions occurring between the polymer and the inorganic ions produced by the cement constituents dissolved in water.^{3–7,10–11} As an example, in the case of the high-alumina cement MDFs, the existence of a cross-linking of the PVA chains by Al ions has been suggested, i.e., the formation of O–Al–O bonds where an Al atom is bonded to the O atoms of two different PVA chains.^{10,11} The cross-linking of the polymer chains may have *crucial effects* on the mechanical properties of the MDF

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materials. Metallic ions may link polymer chains together as well as to O atoms of the inorganic matrix, thus strengthening both the network of the polymer chains around the cement grains and the organic-inorganic interfaces. Moreover, cross-linking may favor an intimate mixing of the cement and the polymer as well as the formation of the interphase regions.¹² On the other hand, an excessive networking of the polymer chains induced by cross-linking may damage the interphase regions and hinder the achievement of a workable paste during the material processing. Thus, cross-linking may influence the strength attained by the MDF materials in two different ways: it may strengthen the organic-inorganic interfaces as well as affect the development of the cement-polymer paste, which in turn affects the final microstructure and the mechanical properties of the MDF materials. Despite interest in the potential benefits or drawbacks of cross-linking, only indirect evidences of a linkage of the polymer chains by ions released by the cement have been found by experiments.^{6,7,13} Experimental investigations of cross-linking are difficult due to the complex structure of the MDF materials and a possible interplay between cross-linking and material processing. For instance, in the case of high-alumina cements and PVA, it has been suggested that the cross-linking reactions are induced by the mechanical work performed during the mixing process.¹⁴ On the other hand, in the case of Portland cements and PVA, it is difficult to obtain a workable paste, possibly because of cross-linking effects caused by the Ca ions released by calcium silicates (the main components of Portland cements). The final microstructure and the mechanical properties of the MDFs can be also affected by a postprocessing curing of the MDF materials.¹⁵ In conclusion, the mechanical properties attained by an MDF material are affected by a complex interplay between cross-linking, processing effects, and postprocessing treatments. The above considerations have stimulated a *systematic*, theoretical investigation on the *existence* and the *strength* of the cross-linking of *different* polymer chains by *different* metallic ions. In fact, such an investigation permits the estimation of the *potential* effects of cross-linking on the material properties *by separating* them from the processing or postprocessing effects. In particular, this investigation permits the prediction of the relative strength of different MDF materials, when the processing or postprocessing conditions can be arranged in a way so as to obtain materials with a similar microstructure, i.e., with similar density and type of defects. In this regard, a theoretical estimate of the strength of cross-linking can represent the first step in the understanding of the complex behavior of the MDF materials. Further, the results of a theoretical investigation of cross-linking can give suggestions on possible relationships between cross-linking and material processing. A systematic investigation of the cross-

linking of polymer chains has started with two recent theoretical studies, where the existence and the strength of cross-linking of PVA chains, by Al ions released by high-alumina-cement pastes (Al-PVA),¹⁶ and PAA chains, by Ca ions released by Portland-cement pastes (Ca-PAA),¹⁷ have been investigated. In both cases, the theoretical results support the existence of a cross-linking of polymer chains. The same results indicate that the cross-linking realized by the Al ions is stronger than that realized by the Ca ions. The present study extends the above investigation to the linkage of PVA chains by Ca ions. The Ca-PVA system is of particular interest because it can be compared with the Ca-PAA system, thus permitting to investigate the linkage effects induced by the *same* ion on the chains of two different polymers. The present work is also motivated by experimental studies which suggest an improvement in the mechanical properties of Portland-cement MDFs when the PVA polymer is replaced by the PAA polymer.^{15,18-20}

The same theoretical approach used in the previous studies has been used here. Different model systems have been investigated, where the Ca ions give rise to *intrachain* O-Ca-O linkages (which involve the O atoms of one PVA chain) and *interchain* linkages (which involve the O atoms of two PVA chains). Examples of intrachain and interchain linkages of the PVA chains are given in parts a and b of Figure 1, respectively. The Car-Parrinello method^{21,22} has been employed to investigate the equilibrium geometries, the electronic charge distributions, the strength, and the stretching frequencies of the Ca-O bonds in the selected model systems. The present results show that the interchain linking (i.e., the cross-linking) of PVA chains by Ca ions is significantly less efficient than that realized by the same ions with the PAA chains. It is worth noticing that the Ca ion is bonded to negatively charged O atoms both in the Ca-PVA and Ca-PAA systems. The achieved results indicate therefore that the Ca-O chemical bonding is affected by the two different functional groups, $-O^-$ and $-COO^-$, carried by the PVA and PAA polymer chains, respectively. Moreover, present results agree with the worse mechanical properties shown by the Portland-cement/PVA MDFs with respect to the Portland-cement/PAA MDFs, thus indicating that the Ca-polymer interactions may have significant effects on the mechanical properties attained by these MDFs as well as on the material processing.

The stretching frequencies of several Ca-O bonds have also been evaluated. The achieved results show that the values of the vibrational frequencies corresponding to the intrachain linkages are close to those related to the interchain linkages, thus making an experimental identification of the atomic arrangement

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Table 1. Ca–O Bond Lengths and O–Ca–O Bond Angles in the Optimized Geometries of the Systems Investigated Here Are Given in the Three Leftmost Columns of the Table. Ca–O(C) and Ca–O(H) Identify Bonds Formed by the Ca Ion with the O Atoms of a PVA Chain and of Hydroxyl Groups, Respectively. In Systems with Two or More Ca–O Bonds, Only the Most Representative Bond Lengths Are Reported Together with the Mean Values of the O–Ca–O Bond Angles. Calculated Stretching Frequencies of Some Ca–O(H) and Ca–O(C) Bonds Are Also Given in the Two Rightmost Columns of the Table. The Results Corresponding to Intrachain Linkage and Cross-Linking Are Written in *Italic* and **Bold Characters, Respectively^a**

systems	Ca–O(C) (Å)	Ca–O(H) (Å)	O–Ca–O (deg)	Ca–O(H) (cm ⁻¹)	Ca–O(C) (cm ⁻¹)
Ca(OH) ₂		2.36	180	687 ^a	
Ca(OH) ₄ ²⁻ (planar)		2.53	90		
Ca(OH) ₄ ²⁻ (tetragonal)		2.54	109		
R–(CH–O)–Ca–OH	<i>2.44</i>	<i>2.37</i>	<i>170</i>		
R–(CH–O) ₂ –Ca–(OH) ₂ ²⁻	<i>2.54</i>	<i>2.49</i>	<i>108</i>	<i>492</i>	<i>435</i>
R–(CH–O) ₂ –Ca	<i>2.42</i>		<i>88</i>		
2(R–(CH–O))–Ca	2.43		170		531
2R–(CH–O))–Ca–(OH) ₂ ²⁻	2.50	2.60	90	396	459

^a The corresponding experimental value is 680 cm⁻¹ from ref 35.

realized by the interaction of Ca ions with the PVA chains difficult.

Computational Methods

In the Car-Parrinello (CP) method, the interatomic forces are computed from the instantaneous quantum-mechanical electronic ground state in the Born–Oppenheimer approximation. The electronic ground state corresponding to a given atomic geometry is obtained within the density-functional theory.^{23,24} The exchange-correlation functional used in the calculations includes gradient corrections to the local density approximation^{25,26} in the form proposed by Becke and Perdew.^{27,28} Only the valence electrons are taken into account while the atomic inner cores are frozen. The interaction between the valence electrons and the frozen cores is described by soft first-principle pseudopotentials.²⁹ The single-particle Kohn–Sham wave functions are expanded on a plane-wave basis-set, thus implying the use of periodic boundary conditions (PBC). In the present calculations, the PBC have been applied to a supercell (i.e., the simulation box) containing fragments of a PVA chain aligned with one side of the cell. This approach allows us to describe a PVA chain as a system with full translational periodicity in one dimension. The sides of the simulation box (10.06, 10.06, and 11.85 Å) are chosen in a way so as to contain one or two PVA chains arranged, e.g., as in Figure 2. The supercell sizes also minimize possible, spurious interactions between the fragments in the supercell and their images. To investigate charged systems, a neutralizing background has been added to describe charged supercells. This approach was successful in the investigation of localized charged states in inorganic semiconductors³⁰ and organic molecules.^{31,32} CP calculations have been successfully performed in the investigation of structural and electronic properties of complex organic molecules.^{31,32} Further tests have been performed here and in the theoretical studies cited above,^{16,17} to verify the convergence of the calculations with respect to the kinetic energy cutoff (which controls the number of planewaves used in the calculations) as well as to check the methods in the cases of simple molecules. As far as the kinetic

energy cutoff is concerned, convergence has been achieved by using a value of 22 Ry, in agreement with the results of previous studies.³³ Equilibrium geometries (i.e., bond angles and bond lengths) evaluated in the cases of the CaO and Ca(OH)₂ molecules and isolated PVA chains agree with experiments. In the polymer chains, a tetrahedral symmetry has been found around the C atoms. The values of 1.10, 1.51, and 0.99 Å have been estimated for the C–H, C–C, and O–H bond lengths, respectively, in good agreement with experimental values.³⁴ The value of 2.36 Å found for the Ca–O bond length in the CaO and Ca(OH)₂ molecules is also in good agreement with the experimental value of 2.37 Å.³⁵ Finally, the harmonic approximation has been used to evaluate the stretching frequencies of the Ca–O bonds in several model systems.

Results and Discussion

1. Ca–Hydroxyl Complexes. The model systems investigated in the present study have been chosen by taking into account the general properties of the Ca–O chemical bonds. Calcium and oxygen atoms may give rise to a variety of complicated structures in organic complexes and inorganic compounds where a Ca atom coordinates a different number of O atoms also in excess of six.^{36–38} As an example, in the case of a typical calcium binding ligand, EDTA (ethylenediamine tetraacetate), the Ca(EDTA)²⁻ complex is characterized by a crystal structure where the Ca ion is coordinated 7- or 8-fold by oxygen atoms.³⁷ In the theoretical study of the Ca–PAA system cited above,¹⁷ the Ca–O chemical bonds formed in the Ca(OH)₂ molecule and in the Ca(OH)₄²⁻ and Ca(OH)₆⁴⁻ complexes have been investigated. The results achieved in that study have been taken into account in the present investigation because the interaction of a Ca ion with OH⁻ groups is expected to be similar to the interaction of the same ion with the O⁻ groups of the PVA chain. Some results of the previous study are summarized in the following discussion. The optimized geometries of the above molecule and complexes are given in Table 1. Moreover, the following hypothetical reactions of dissociation have

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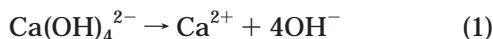
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Table 2. Dissociation Energy Values, D , Calculated for Reactions Involving Different Complexes and Ca–Polymer Systems Investigated in the Present Work. The Four Parts of the Table (from the Top to the Bottom) Show the Results Obtained for: (i) Ca–Hydroxyl Complexes, (ii) Ca–PVA Systems Realizing an Intrachain Linkage, (iii) Ca–PVA Systems Realizing an Interchain Linkage, and (iv) Ca–PAA Systems (from Ref 17). D_b Is the Dissociation Energy Per Ca–O Bond. An Endothermic (Exothermic) Reaction Is Identified by Negative (Positive) Values of D and D_b . All Values Are Given in eV. D and D_b Values Corresponding to Intrachain Linkage and Cross-Linking Are Written in Italic and Bold Characters, Respectively

reaction of dissociation	D	D_b
$\text{Ca(OH)}_2 \rightarrow \text{Ca}^{2+} + 2\text{OH}^-$	-16.7	-8.4
Ca(OH)_4^{2-} (planar) $\rightarrow \text{Ca}^{2+} + 4\text{OH}^-$	-19.8	-4.9
Ca(OH)_4^{2-} (tetragonal) $\rightarrow \text{Ca}^{2+} + 4\text{OH}^-$	-20.4	-5.1
$\text{Ca(OH)}_6^{4-} \rightarrow \text{Ca}^{2+} + 6\text{OH}^-$	-4.8	-0.8
$\text{Ca(OH)}_4^{2-} \rightarrow \text{Ca(OH)}_2 + 2\text{OH}^-$	-3.7	
$\text{Ca(OH)}_6^{4-} \rightarrow \text{Ca(OH)}_2 + 4\text{OH}^-$	+11.9	
$\text{R}-(\text{CH-O})-\text{Ca}-\text{OH} \rightarrow \text{Ca}^{2+} + \text{R}-(\text{CH-O})^- + \text{OH}^-$	-15.4	-7.7
$\text{R}-(\text{CH-O})_2-\text{Ca}-(\text{OH})_2^{2-} \rightarrow \text{Ca}^{2+} + \text{R}-(\text{CH-O})_2^{2-} + 2\text{OH}^-$	-20.1	-5.0
$\text{R}-(\text{CH-O})_2-\text{Ca} \rightarrow \text{Ca}^{2+} + \text{R}-(\text{CH-O})_2^-$	-14.5	-7.2
$2\text{R}-(\text{CH-O})-\text{Ca} \rightarrow \text{Ca}^{2+} + 2\text{R}-(\text{CH-O})^-$	-13.9	-6.9
$2\text{R}-(\text{CH-O})-\text{Ca}-(\text{OH})_2^{2-} \rightarrow \text{Ca}^{2+} + 2\text{R}-(\text{CH-O})^- + 2\text{OH}^-$	-18.8	-4.7
$\text{R}-(\text{CH-COO})_2-\text{Ca}^{2-} \rightarrow \text{Ca}^{2+} + \text{R}-(\text{CH-COO})_4^{4-}$	-14.7	-7.3
$\text{R}-(\text{CH-COO})_2-\text{Ca}-(\text{OH})_2^{4-} \rightarrow \text{Ca}^{2+} + \text{R}-(\text{CH-COO})_4^{4-} + 2\text{OH}^-$	-19.2	-4.8
$2\text{R}-(\text{CH-COO})_2-\text{Ca}^{6-} \rightarrow \text{Ca}^{2+} + 2\text{R}-(\text{CH-COO})_4^{4-}$	-22.4	-5.6
$2\text{R}-(\text{CH-COO})_2-\text{Ca}-(\text{OH})_2^{8-} \rightarrow \text{Ca}^{2+} + 2\text{R}-(\text{CH-COO})_4^{4-} + 2\text{OH}^-$	-21.0	-3.5

been considered where the Ca–O bonds are broken by the production of Ca^{2+} and negative ions, e.g.,



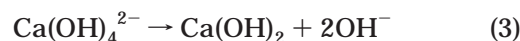
The corresponding dissociation energies (D) have been evaluated by differences of total energies (E) of the involved species, e.g.,

$$D = E[\text{Ca}^{2+}] + 4E[\text{OH}^-] - E[\text{Ca(OH)}_4^{2-}] \quad (2)$$

These reactions have no experimental counterparts. Notwithstanding, they were considered in the previous work and have been considered here because they permit a comparison of the strength of the Ca–O bonds formed in different systems, see Table 2.³⁹

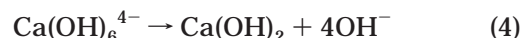
In the Ca(OH)_2 molecule, the atoms of the O–Ca–O fragment show an “in line” geometry with an estimated Ca–O bond length close to the experimental value of 2.37 Å.³⁵ The D value estimated for the dissociation of this molecule is -16.7 eV (in the present study, endothermic reactions of dissociation are characterized by a negative sign of D). This corresponds to a dissociation energy per Ca–O bond, hereafter referred to as D_b , which is equal to -8.4 eV. In the case of the Ca(OH)_4^{2-} complex, the geometry optimization procedure has found two stable configurations with planar and tetrahedral geometries of the CaO_4 fragment, respectively. These two configurations are both characterized by Ca–O bond lengths that are close to 2.5 Å, in good agreement with the experimental results found in the case of the Ca(EDTA)^{2-} complex, where the Ca–O bond lengths range from 2.36 to 2.53 Å.³⁷ The same configurations also have close total energy values and close values for the D and D_b dissociation energies, see Table 2. The stability of the two Ca(OH)_4^{2-} configurations is supported by the D values found for their dissociation in ionic species, which are negative and larger than that

found for the Ca(OH)_2 molecule, see Table 2. Moreover, the reaction of dissociation



results in being endothermic with a D value of -3.7 and -3.1 eV for the tetrahedral and planar configurations, respectively, thus confirming their stability.

In the case of the Ca(OH)_6^{4-} complex, the CaO_6 fragment in the complex has the geometry of a distorted octahedron around the Ca atom. The small D and D_b values corresponding to this complex indicate that it is not stable, see Table 2. As further evidence, the reaction



results in being exothermic with a D value of +11.9 eV.

The above results show that the highest coordination number for a Ca ion bonded to hydroxyl groups is 4. The Ca ion does not reach, therefore, the high coordination numbers that characterize the complexes formed by typical calcium ligands.³⁷ It may be worth noticing that a planar complex, Be(OH)_4^{2-} , has been observed in concentrated alkaline solutions.⁴⁰

2. Ca–PVA Model Systems. In the model systems investigated here, the intrachain and interchain linkages of the polymer chains are realized by a Ca ion which coordinates O atoms belonging to PVA chains and hydroxyl groups. Different atomic arrangements for a Ca ion bonded to the O atoms of two or three PVA chains have been preliminarily analyzed by using a simple molecular-builder program to select configurations compatible with the spatial constraints of the system. This analysis has shown that only two PVA chains may be involved in the binding of a Ca ion, which resulted in being 2-fold coordinated by the O⁻ groups of the polymer chains. Two or four hydroxyl groups were then located next to that Ca ion to increase its coordination number. The geometry of the selected configurations was optimized by performing CP calculations. In the following

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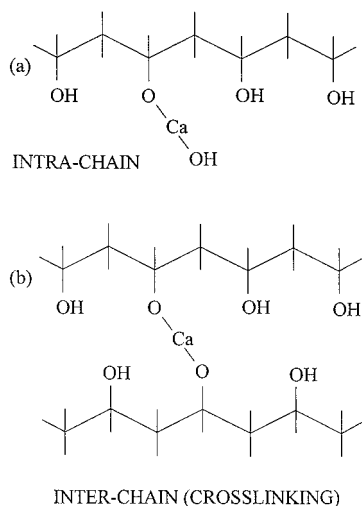


Figure 1. Examples of O–Ca–O linking in the interaction of Ca ions with PVA chains: (a) intrachain linking (the Ca ion is bonded to the O atoms of one PVA chain); (b) interchain linking (the Ca ion is bonded to the O atoms of two PVA chains).

discussion, a fragment of a PVA chain will be designated as $R-(CH-OH)$ or $R-(CH-OH)_2$ depending on the number of $-OH$ groups of the chain (one or two) that are involved in reactions with the Ca ion. Three different model systems have been considered to simulate intrachain linkages, i.e., the bonding of a Ca ion to one PVA chain. In the first Ca–PVA system, the Ca ion is bonded to the O atom of a polymer chain and a hydroxyl group, see Figure 1a. Within the above convention, this system will be designated as $R-(CH-O)-Ca-OH$. The second system, the $R-(CH-O)_2Ca(OH)_2^{2-}$ system, is characterized by a Ca ion bonded to two O atoms of a PVA chain and two hydroxyl groups, see Figure 2a. A third system has also been considered, $R-(CH-O)_2Ca$, where the Ca ion is bonded to two O atoms of a PVA chain. The configuration of this last system can be derived from that of Figure 2a when the two hydroxyl groups are removed. Finally, two more hydroxyl groups have been added to the configuration of Figure 2a, which, however, gives rise to unstable configurations for a 6-fold coordinated Ca ion. The Ca–O bond lengths and the O–Ca–O bond angles found for the optimized geometries of the above systems are given in Table 1. In the $R-(CH-O)-Ca-OH$ system, the O–Ca–O fragment is characterized by an almost linear atomic arrangement with the Ca–O(C) bond slightly longer than the Ca–O(H) bonds formed in the $Ca(OH)_2$ molecule. In the $R-(CH-O)_2Ca(OH)_2^{2-}$ system, the CaO_4 fragment has the geometry of a distorted tetrahedron (the O–Ca–O bond angle formed by the Ca ion and by the two oxygen atoms of the PVA chain is equal to 82°). Moreover, the Ca–O(C) and the Ca–O(H) bond lengths are close to those calculated for the $Ca(OH)_4^{2-}$ complexes. The $R-(CH-O)_2Ca$ system is characterized by an O–Ca–O bond angle of about 90° and by Ca–O bond lengths close to the Ca–O(C) bond lengths found in the $R-(CH-O)-Ca-OH$ system. The interchain linkage of PVA chains by Ca ions has been investigated by considering the $2(R-(CH-O))Ca$ and $2(R-(CH-O))Ca(OH)_2^{2-}$ systems shown in parts b and c of Figure 2, respectively. In the former system, the Ca ion gives rise to an almost linear O–Ca–O atomic arrangement with

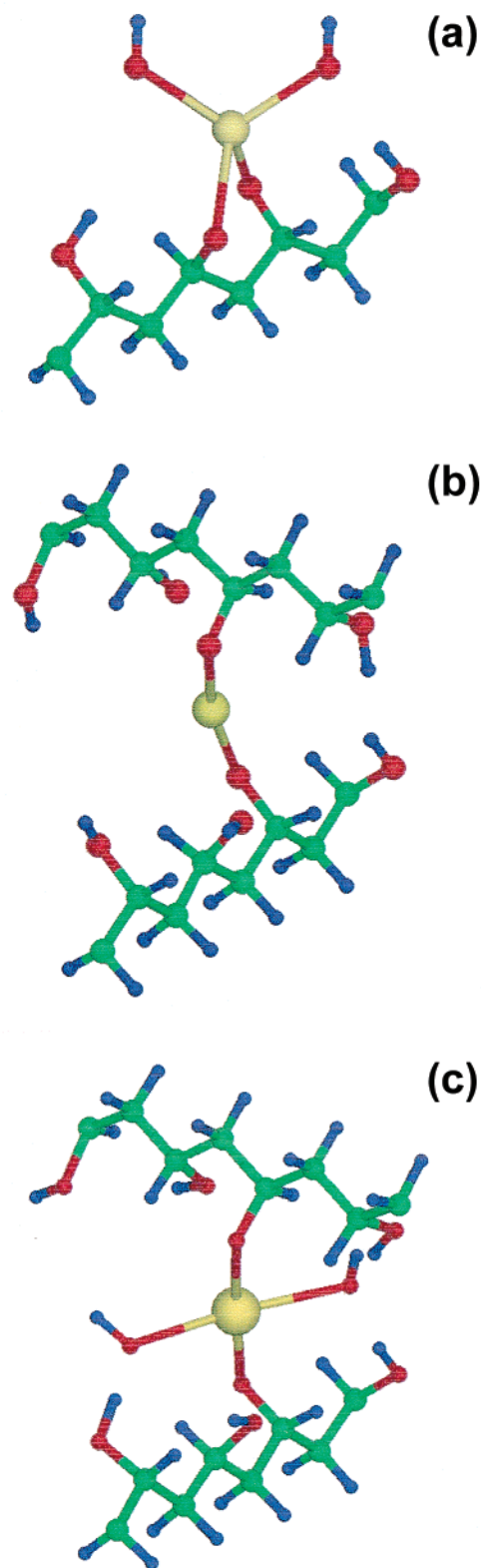


Figure 2. (a) Intrachain linking in the $R-(CH-O)_2Ca(OH)_2^{2-}$ system (see the text): a Ca ion is bonded to two O atoms of the *same* PVA chain and two hydroxyl groups; (b) interchain linking (cross-linking) in the $2(R-(CH-O))Ca$ system: a Ca ion is bonded to two O atoms of two PVA chains; (c) interchain linking (cross-linking) in the $2(R-(CH-O))Ca(OH)_2^{2-}$ system: a Ca ion is bonded to two O atoms of two PVA chains and two hydroxyl groups. The Ca, C, O, and H atoms are identified by the colors yellow, green, red, and blue, respectively.

two O atoms of two different PVA chains. In the latter system, the Ca ion is bonded to two O atoms of two PVA chains and two O atoms of two hydroxyl groups. The $2(\text{R}-(\text{CH}-\text{O}))\text{Ca}(\text{OH})_2^{2-}$ system is characterized by a planar geometry of the CaO_4 fragment and Ca–O bonds that are longer than those formed in the $2(\text{R}-(\text{CH}-\text{O}))\text{Ca}$ system. A third case of interchain linkage has been investigated in a $2(\text{R}-(\text{CH}-\text{O})_2)\text{Ca}$ system where four O atoms of two PVA chains are located close to the Ca ion. However, this system is not stable due to the large distortion of the geometry of the CaO_4 fragment. Further, this system resulted in being higher in energy than the $2(\text{R}-(\text{CH}-\text{O}))\text{Ca}(\text{OH})_2^{2-}$ system, where the formation of a CaO_4 fragment involves the O atoms of two PVA chains and two hydroxyl groups. Finally, the addition of two more hydroxyl groups to the system of Figure 2c does not give rise to stable configurations for a 6-fold coordinated Ca ion. The above results suggest the formation of similar Ca–O bonds in the Ca–PVA systems and in the Ca–hydroxyl complexes. In fact, in the Ca–PVA systems characterized by a 2-fold coordinated Ca ion, the Ca–O(C) bonds are slightly longer than the Ca–O bond in the $\text{Ca}(\text{OH})_2$ molecule. In systems where the Ca ion is 4-fold coordinated, the lengths of the Ca–O(C) bonds are close to those of the Ca–O(H) bonds in the $\text{Ca}(\text{OH})_4^{2-}$ complexes. Further, a 6-fold coordinated Ca ion does not give rise to stable configurations both in the Ca–PVA model systems and in the Ca–hydroxyl complexes.

Present results indicate that the Ca ion is 4-fold coordinated in the above model systems and complexes. This is a rather unusual coordination for a Ca ion that is bonded to O atoms. However, it is worth noticing that the existence of CaO_4 clusters has been reported by an experimental study of the microstructure of a series of superconducting materials.⁴¹

The nature of the O–Ca–O chemical bonds formed in the Ca–PVA model systems has been investigated by analyzing isosurfaces corresponding to a *same value* of the valence electronic charge density. The isosurfaces corresponding to the $\text{R}-(\text{CH}-\text{O})_2\text{Ca}-(\text{OH})_2^{2-}$, $2(\text{R}-(\text{CH}-\text{O}))\text{Ca}$, and $2(\text{R}-(\text{CH}-\text{O}))\text{Ca}-(\text{OH})_2^{2-}$ systems are shown in parts a, b, and c of Figure 3, respectively. All these systems are characterized by a homogeneous distribution of the electronic valence charge on the O atoms neighboring the Ca atom, which supports the formation of similar Ca–O bonds in the case of O atoms belonging to PVA chains or hydroxyl groups. Further, the ionic character of the Ca–O bonds is clearly shown by a piling up of the electronic charge density on the O atoms.

3. Strength of the PVA and PAA Cross-Linking by Ca Ions. The strength of the O–Ca–O chemical bonds formed in the above model systems has been investigated by evaluating the dissociation energies of the reactions reported in Table 2. In the Ca–PVA systems, the *D* value corresponding to the $\text{R}-(\text{CH}-\text{O})_2\text{Ca}-(\text{OH})_2^{2-}$ intrachain system is *close* to the *D* values corresponding to the $\text{Ca}(\text{OH})_4^{2-}$ complexes and *larger* than the values estimated for the interchain systems. Thus, the formation of intrachain systems and Ca–hydroxyl complexes is favored with respect to that of

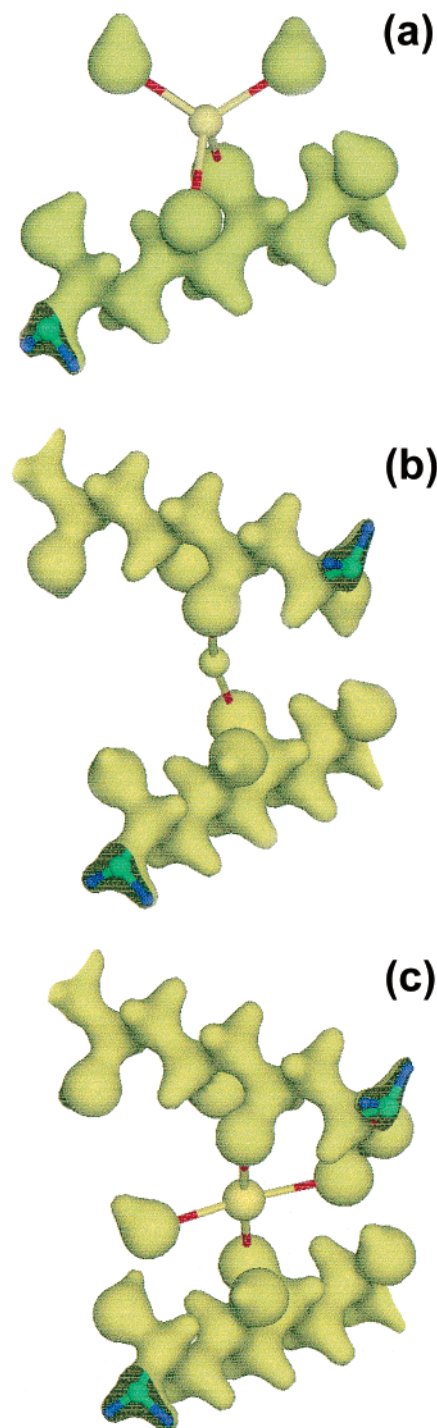


Figure 3. Isosurfaces of the valence electronic charge densities calculated for some Ca–PVA systems investigated in the present study: (a) $\text{R}-(\text{CH}-\text{O})_2\text{Ca}-(\text{OH})_2^{2-}$ system as shown in Figure 2a; (b) $2(\text{R}-(\text{CH}-\text{O}))\text{Ca}$ system as shown in Figure 2b; (c) $2(\text{R}-(\text{CH}-\text{O}))\text{Ca}-(\text{OH})_2^{2-}$ system as shown in Figure 2c. The isosurfaces correspond to an electron density of 0.14 electron charge/(atomic units)³.

interchain systems. Present results have been compared with the results of the theoretical study on the Ca–PAA cross-linking cited above.¹⁷ Some results of that study are reported in the last four rows of Table 2. In the case of the Ca–PAA systems, $\text{R}-(\text{CH}-\text{COO})_4^{4-}$ represents a fragment of a PAA chain carrying four COO^- groups and $\text{R}-(\text{CH}-\text{COO})_2\text{Ca}^{2-}$ represents a model system where only two COO^- groups of the PAA fragment are

(41) Cuvier, S.; Puri, M.; Bear, J.; Kevan, L. *Chem. Mater.* **1991**, *3*, 115.

involved in the formation of bonds with a Ca ion. The $R-(CH-COO)_2-Ca^{2-}$ and the $R-(CH-COO)_2-Ca-(OH)_2^{4-}$ systems give rise to an intrachain linkage; the $2(R-(CH-COO)_2)-Ca^{6-}$ and the $2(R-(CH-COO)_2)-Ca-(OH)_2^{8-}$ systems give rise to an interchain linkage. It has to be noted that in the $2(R-(CH-COO)_2)-Ca^{6-}$ system, *four* O atoms of *two* different PAA chains are bonded to the Ca ion in a CaO_4 fragment. Present and previous results show that the cross-linking of the PVA chains is quite different from that of the PAA chains: (i) In the case of PAA chains, a cross-linking of the polymer chains is favored with respect to intrachain linkages, while an opposite result is found in the case of the PVA chains. (ii) The Ca–O bonds are stronger in the Ca–PAA systems than in the Ca–PVA systems in both the cases of interchain and intrachain linkages. (iii) The Ca–O bonds formed in the Ca–PAA (Ca–PVA) systems are stronger (weaker) than those formed in the Ca–hydroxyl complexes. (iv) In the case of cross-linking of PVA chains, the Ca ion forms *two* Ca–O bonds with the O atoms of two PVA chains (see parts b and c of Figure 2), while in the case of the PAA polymer, the Ca ion forms *four* Ca–O bonds with the O atoms of two polymer chains. This implies that the breaking of the interchain linkage requires the breaking of only one Ca–O bond (i.e., an energy of 4.7 eV) in the case of the PVA chains and two Ca–O bonds (i.e., an energy of 11.2 eV) in the case of the PAA chains. All the above results indicate that a significantly *more efficient* cross-linking has to be expected in the Ca–PAA systems with respect to the Ca–PVA systems. Present results also indicate that the Ca–O bonds involved in the cross-linking of the PVA and PAA chains are affected by the different functional groups, $-O^-$ and $-COO^-$, carried by the two polymer chains, respectively. Finally, the different efficiencies of the cross-linking of the PAA and PVA chains are expected to give appreciable effects on the mechanical properties attained by the Portland–PAA and Portland–PVA MDFs as well as on their processing.

The results of the present and previous studies^{16,17} on the interaction of metallic ions with PVA and PAA chains suggest the following scale of relative strength for the cross-linking of the polymer chains: Al–PVA > Ca–PAA > Ca–PVA.

This scale can be directly related to the different mechanical properties of the corresponding MDF materials (i.e., the MDFs formed by high-alumina cements and PVA, Portland cements and PAA, and Portland cements and PVA, respectively), only if it is assumed that these MDF materials have the same microstructure. Nevertheless, the above scale agrees with the different mechanical properties achieved by the corresponding MDFs, thus suggesting that the characteristics of cross-linking have significant effects on the material properties.

The above comparison of previous results with the present ones confirms the need of a systematic investigation of the ion–polymer interaction. The comparison of the results achieved for the Ca–PAA and Ca–PVA systems (where a same ion interacts with different polymers) shows indeed that a different Ca–O chemical bonding is induced by the different functional groups present in the PAA and PVA chains. On the other hand, a comparison of the results achieved for the Ca–PVA

and Al–PVA systems¹⁶ (where different ions interact with a same polymer) clearly shows that the different chemical properties of Ca and Al lead to different ion–polymer interactions, as expected. Moreover, PVA and Al ions give rise to a strong cross-linking, while the Ca–PVA cross-linking is weaker than the Ca–PAA cross-linking. On the basis of the present results, a theoretical investigation of the Al–PAA system has therefore been started to achieve a complete description of the cross-linking reactions involving the interaction of Al and Ca ions with PVA and PAA polymers.

Finally, the vibrational frequencies of several Ca–O(H) and Ca–O(C) bonds have been evaluated for the $Ca(OH)_2$ molecule in the case of intrachain linkage (i.e., in the most stable $R-(CH-O)_2-Ca-(OH)_2^{2-}$ system) and in the two systems corresponding to an interchain linkage (i.e., in the $2(R-(CH-O))-Ca$ and $2(R-(CH-O))-Ca-(OH)_2^{2-}$ systems); see Table 1. When a Ca ion is bonded to two O atoms of one or two PVA chains and two hydroxyl groups, the Ca–O bonds have similar stretching frequencies in both the cases of intrachain and interchain linkages. More specifically, the values of the Ca–O(H) and Ca–O(C) stretching frequencies are separated by 60 cm^{-1} and are in the range of $390\text{--}500\text{ cm}^{-1}$ in both the $R-(CH-O)_2-Ca-(OH)_2^{2-}$ and in the $2(R-(CH-O))-Ca-(OH)_2^{2-}$ systems. Only the higher value of the Ca–O(C) stretching frequency in the $2(R-(CH-O))-Ca$ system could be helpful to identify a cross-linking configuration of the PVA chains. Therefore, it seems unlikely that experimental measurements can distinguish an intrachain linkage of the PVA chains from an interchain one.

Conclusions

The interaction of Ca ions with one or two PVA chains has been investigated by *first-principles* theoretical methods. The achieved results have been compared with those of a previous theoretical study concerning the interaction of Ca ions with PAA chains. Present results support the existence of a Ca–PAA cross-linking that is *significantly* stronger and more efficient than that realized in the case of the Ca–PVA systems. This result implies that the different characteristics of the Ca–PAA and Ca–PVA linkages are related to the different functional groups present in the PAA and PVA chains and agrees with the improvement of the mechanical properties observed when the PVA polymer is replaced by the PAA polymer in Portland-cement-based MDFs.

The results of the present study also indicate that the Ca–polymer interactions may have significant effects on the mechanical properties attained by the above MDFs as well as on the material processing, which, however, is also affected by kinetic effects not considered in the present study.

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