Interaction between Ca Ions and Poly(acrylic acid) Chains in Macro-Defect-Free Cements: A Theoretical Study

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Several experimental and theoretical studies have related the peculiar mechanical properties of the macro-defect-free polymer−cement composites with the existence of a *cross-linking* of the polymer chains by Al or Ca ions coming from the hydration reactions of the cement. In the present study, the interaction of Ca ions with the $-COO^-$ groups of one or two poly(acrylic acid) (PAA) chains has been investigated with *first-principles* theoretical methods in order to achieve evidences of PAA cross-linking. The present results show that a stable CaO_4 complex can be formed by a Ca ion and the O atoms belonging to the $-COO^-$ groups of two polymer chains. This implies the existence of a quite efficient cross-linking because a Ca ion becomes anchored to *four* points of *two* PAA chains. The stretching frequencies of several Ca−O and C═O bonds have also been estimated. The achieved results suggest that indirect evidence of the PAA cross-linking could be obtained by infrared spectroscopy measurements.

Introduction

The flexural strength of high-alumina and Portland cements can be increased dramatically by incorporating a polymer component [e.g., poly(vinyl alcohol) (PVA)] in the cement paste 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 modified cements were termed macro-defect-free (MDF) cements by referring to the absence of the relatively large voids or defects which are usually present in cement pastes.[1,3,4] Several experimental studies have since clarified that a “new” composite material is produced by the incorporation of PVA in the cement paste, the microstructure of which is characterized by grains of partially hydrated cement particles embedded in a matrix of polymer.[6,7] Interphase regions coat the individual cement grains. In the case of high-alumina cements, these regions consist of an amorphous phase of $Al(OH)_3$ and PVA, inside of which are dispersed fine crystallites of hydration products. The peculiar mechanical properties of the high-alumina cement MDF materials have also been attributed to chemical reactions occurring between the PVA polymer and the inorganic ions produced by the cement constituents dissolved in water.[3−9] More specifically, 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.[8,9] The cross-linking of the polymer chains could be a *key factor* in the mechanical behavior of the MDF materials. In fact, cross-linking can strengthen the network of the PVA chains around the cement grains as well as favor an intimate mixing of the cement and the polymer. Furthermore, if Al ions may link PVA chains together, they may also link PVA chains to O atoms of the inorganic matrix, thus strengthening the organic−inorganic interfaces. Only indirect evidences of cross-linking have been found by experiments.[6,7,10] Neverthe-

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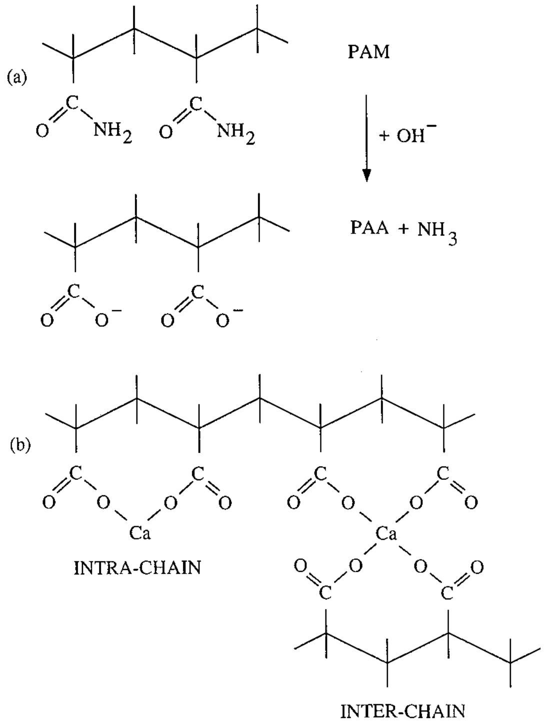

Figure 1. (a) Hydrolysis of the amide functional groups in the PAM chains and formation of PAA chains under anionic form; (b) intrachain and interchain O−Ca−O linkages coming from the interaction of Ca ions with the PAA chains.

less, in the case of high-alumina cement MDF materials, the possibility of cross-linking of PVA chains by Al ions has been strongly supported by the results of a recent theoretical study.[11] In the case of Portland cement MDF materials, the main components of which are calcium silicates and PVA, worse mechanical properties have been observed with respect to the high-alumina MDFs.[3] The different mechanical behavior of these two MDF materials has been accounted for by another theoretical study in terms of a cross-linking of the PVA chains by Ca ions (coming from the hydration of Portland cements) which is weaker than that realized by the Al ions (coming from the hydration of high-alumina cements).[12] The above results have stimulated the investigation of Portland MDFs incorporating polymers different in nature from PVA, e.g., derivatives of poly(acrylic acid).[13−15] Poly(acrylic acid) in anionic form (PAA) may be formed, for instance, by the hydrolysis of the poly(acrylamide) (PAM) functional groups in the presence of hydroxyl ions; see Figure 1a. It has been suggested that the PAA chains chelate to the Ca ions through the carboxylate anions, as sketched in Figure 1b.[13] However, there are no satisfying evidences of cross-linking of the PAA chains by Ca ions.[14,15] Furthermore, there is no information about the *nature* and the *strength* of the Ca−O chemical bonds involved in the PAA cross-linking. This has motivated the present investigation of the interaction of Ca ions with poly(acrylic acid) chains. In particular, in the present study, the Car−Parrinello (CP) method[16,17] has been employed to investigate the equilibrium geometries, the electronic charge distributions, the strength, and the stretching frequencies of several chemical bonds in model systems where a Ca ion is bonded with two or four O atoms of one or two PAA chains, respectively. The present results show that Ca ions actually form chelates with the carboxylate anions of the PAA chains and that an *interchain* O−Ca−O linkage is more stable than an *intrachain* linkage; see Figure 1b. Interestingly, a Ca ion tends to be fourfold-coordinated in a planar CaO_4 complex which involves the O atoms of two PAA chains. Thus, the Ca ion is anchored to *four* points of two PAA chains (two points for each chain). This suggests the existence of a quite efficient PAA cross-linking by Ca ions. In particular, this cross-linking should be more efficient than that realized by the Ca ions in the case of the PVA polymer.[12] The present results suggest, therefore, that derivatives of the PAA polymer can improve the mechanical properties of MDF composites formed by Ca-rich cements. Finally, the stretching frequencies of several Ca−O and C=O bonds have been evaluated. The achieved results suggest that indirect evidence for the PAA cross-linking could be obtained by infrared spectroscopy measurements.

Computational Methods

In the 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.[18,19] The exchange-correlation functional used in the calculations includes gradient corrections to the local density approximation[20,21] in the form proposed by Becke and Perdew.[22,23] 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.[24] 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 PAA chain aligned with one side of the cell. As an example, in the calculations, the fragments of the PAA chains shown in Figure 2d are repeated along the chain axis in order to simulate chains of infinite length. This approach allows us to describe a PAA chain as a system with full translational periodicity in one dimension. The sides of the simulation box (10.06, 7.95, and 12.78 Å) are chosen

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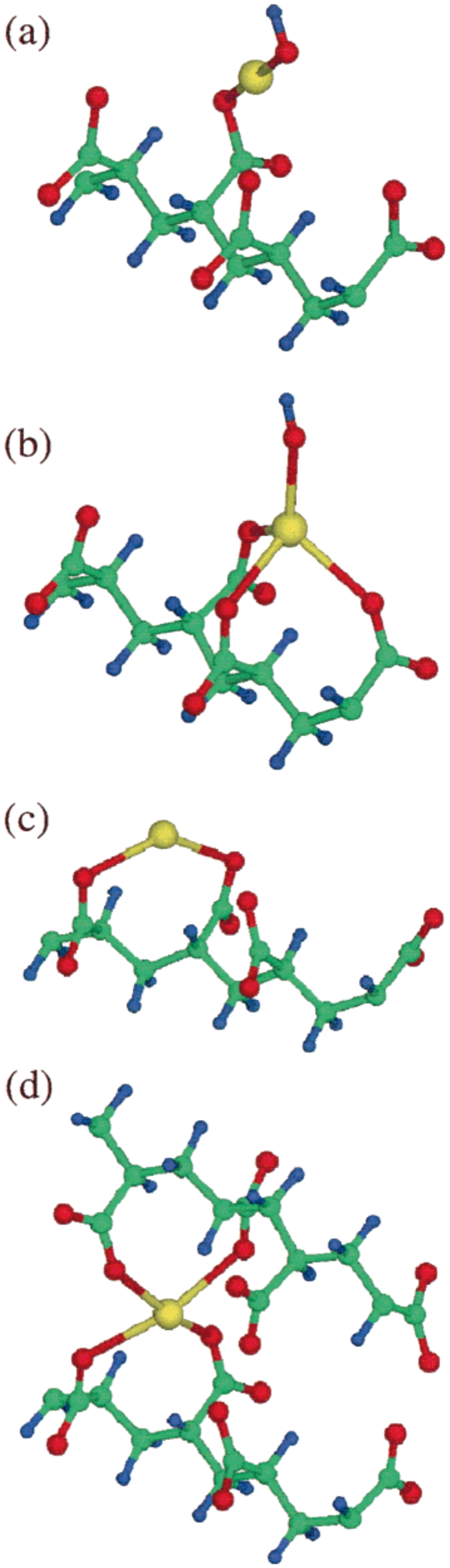

Figure 2. (a and b) Structure of the Ca[PAA]OH^{3-} system at the beginning and at the end of a geometry-optimization procedure, respectively (see text). (c) Intrachain linking in the Ca[PAA]$^{2-}$(two Ox.) system: a Ca ion is bonded to two O atoms of the *same* PAA chain. (d) Interchain cross-linking in the Ca$[PAA]_2^{6-}$ system: a Ca ion is bonded to four O atoms of two PAA chains. The Ca, C, O, and H atoms are identified by the colors yellow, green, red, and blue, respectively.

in order to contain two PAA chains arranged as in Figure 2d. The supercell sizes also minimize possible spurious interactions between the fragments in the supercell and their images. CP calculations have been successfully performed in the investigation of structural and electronic properties of complex organic molecules.[25,26] Notwithstanding, further tests have been performed here in order to verify the convergence of the calculations with respect to the kinetic energy cutoff (which controls the number of plane waves 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.[27] Equilibrium geometries (i.e., bond angles and bond lengths) have been evaluated in the cases of the CaO and $Ca(OH)_2$ molecules and of an isolated PAA chain in anionic form. In the PAA case, a tetrahedral symmetry has been found around the C atoms. The values of 1.10, 1.51, 0.99, and 1.28 Å have been calculated for the C−H, C−C, O−H, and $C=O$ bond lengths, respectively, in good agreement with experimental values.[28] 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.[29] The harmonic approximation has been used to evaluate the stretching frequencies of the Ca−O and $C=O$ bonds. Finally, the geometries of some complexes formed by Ca and hydroxyl ions have been checked by using thoroughly different all-electron theoretical methods involving atomic-orbital basis sets in the Hartree−Fock approximation.[30] In particular, the 3-21G** basis set and the Fletcher and Powell geometry-optimization procedure have been used in the calculations.

Results and Discussion

Calcium and oxygen atoms may give rise to a variety of complicated structures in organic complexes and inorganic compounds where the Ca atom coordinates a different number of O atoms, also in excess of 6.[31−33] In the present work, a preliminary study has been performed of the Ca−O chemical bonds in simple molecules, CaO and $Ca(OH)_2$, and in complexes, $Ca(OH)_4^{2-}$ and $Ca(OH)_6^{4-}$, where a Ca atom has different coordination numbers. All of these systems have been considered as isolated molecules in a gaseous phase. The geometries of the above systems have been optimized by following the atomic forces and by minimizing the total energies. Details of the optimized geometries are given in Table 1. In the case of the CaO molecule, the strength of the

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Table 1. Ca−O Bond Lengths and O−Ca−O Bond Angles in the Optimized Geometries of the Systems Investigated in the Present Work[a]

system	Ca−O (Å)	Ca−O′	O−Ca−O (deg)
CaO	2.36		
$Ca(OH)_2$	2.36		180
$Ca(OH)_4{}^{2-}$(planar)	2.53		90
$Ca(OH)_4{}^{2-}$(tetr.)	2.54		109
$Ca[PAA](OH)^{3-}$	2.50	2.45	114
$Ca[PAA]^{2-}$(two Ox.)	2.43		106
$Ca[PAA]^{2-}$(three Ox.)	2.45	2.48	103
$Ca[PAA]\text{-}(OH)_2{}^{4-}$	2.52	2.55	104
$Ca[PAA]_2{}^{6-}$	2.52		88
$Ca[PAA]_2\text{-}(OH)_2{}^{8-}$	2.64	2.46	

[a] [PAA] stands for a fragment of a PAA chain (see the text). In systems with two or more Ca−O bonds, only the most representative values of the Ca−O bond lengths are reported together with mean values of the O−Ca−O bond angles.

Table 2. Dissociation Energy Values, *D*, Calculated for Reactions Involving Different Molecules and Model Systems Investigated in the Present Work[a]

reaction of dissociation	D	D_b
$CaO \rightarrow Ca + O$	−4.0	
$Ca(OH)_2 \rightarrow Ca^{2+} + 2OH^-$	−16.7	−8.4
$Ca(OH)_4{}^{2-}$(planar) $\rightarrow Ca^{2+} + 4OH^-$	−20.4	−5.1
$Ca(OH)_4{}^{2-}$(tetr.) $\rightarrow Ca^{2+} + 4OH^-$	−20.4	−5.1
$Ca(OH)_6{}^{4-} \rightarrow Ca^{2+} + 6OH^-$	−4.8	−0.8
$Ca(OH)_4{}^{2-} \rightarrow Ca(OH)_2 + 2OH^-$	−3.7	
$Ca(OH)_6{}^{4-} \rightarrow Ca(OH)_2 + 4OH^-$	+11.9	
$Ca[PAA]\text{-}OH^{3-} \rightarrow Ca^{2+} + [PAA]^{4-} + OH^-$	−18.6	−4.6
$Ca[PAA]^{2-}$(two Ox.) $\rightarrow Ca^{2+} + [PAA]^{4-}$	−14.7	−7.3
$Ca[PAA]^{2-}$(three Ox.) $\rightarrow Ca^{2+} + [PAA]^{4-}$	−14.2	−4.7
$Ca[PAA]\text{-}(OH)_2{}^{4-} \rightarrow Ca^{2+} + [PAA]^{4-} + 2OH^-$	−19.2	−4.8
$Ca[PAA]_2{}^{6-} \rightarrow Ca^{2+} + 2[PAA]^{4-}$	−22.4	−5.6
$Ca[PAA]_2(OH)_2{}^{8-} \rightarrow Ca^{2+} + 2[PAA]^{4-} + 2OH^-$	−21.0	−3.5

[a] 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 elecronvolts.

Ca−O bond has been investigated by considering the reaction of dissociation:

$$CaO \rightarrow Ca + O$$

In the case of all of the other systems, hypothetical reactions of dissociation have been considered where the Ca−O bonds are broken by producing Ca^{2+} and negative ions, e.g.,

$$Ca(OH)_4{}^{2-} \rightarrow Ca^{2+} + 4OH^-$$

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

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

There are no experimental counterparts for the above reactions of dissociations. Notwithstanding, these reactions have been considered here because they lead to the formation of similar ionic species, thus permitting a comparison of the strength of the Ca−O bonds formed in different systems; see Table 2. In the case of the CaO molecule, the value of the calculated bond length, 2.36 Å, agrees with the experimental value measured for the Ca−O bond length in the $Ca(OH)_2$ molecule (2.37 Å).[29] The dissociation energy of the Ca−O bond, −4.0 eV (in the present study, endothermic reactions of dissociation are characterized by a negative sign of D), is also in good agreement with the experimental value of −4.2 eV.[28] 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 equal to that found in the CaO molecule. The calculated D value is −16.7 eV. This corresponds to a dissociation energy *per* Ca−O bond, hereafter referred to as D_b, equal to −8.4 eV. In the case of the $Ca(OH)_4{}^{2-}$ complex, two stable configurations have been found with planar and tetrahedral geometries of the CaO_4 fragment, respectively. These two configurations are both characterized by Ca−O bond lengths close to 2.5 Å; they have close total energy values and the same 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

$$Ca(OH)_4{}^{2-} \rightarrow Ca(OH)_2 + 2OH^-$$

turns out to be endothermic, with a D value of −3.7 eV for both configurations, thus confirming their stability. The geometry and the stability of the two $Ca(OH)_4{}^{2-}$ configurations have been checked by using an all-electron quantum-chemistry theoretical method.[30] The achieved results are in very good agreement with the results given by the CP method. In particular, they confirm the stability of both configurations of the $Ca(OH)_4{}^{2-}$ complex and give a value of −4.4 eV for the D value of the above dissociation reaction. The above results are supported by several experimental findings. A planar complex, $Be(OH)_4{}^{2-}$, has been observed in concentrated alkaline solutions.[34] It is also well-known that several O atoms are bonded with a Ca atom in organic complexes such as that formed by Ca ions with EDTA (ethylenediamine tetraacetate), $Ca(EDTA)^{2-}$. The crystal structure of $Ca(EDTA)^{2-}$ is characterized by an intricate network of ligand-bridged coordination complexes where the Ca−O bond lengths range from 2.36 to 2.53 Å, in good agreement with the present results.[32] It may be worth noticing that the Ca−O bonds in the $Ca(OH)_4{}^{2-}$ complex are slightly longer than those formed in the $Ca(OH)_2$ molecule and in the $Ca(EDTA)^{2-}$ complex. This suggests that the presence of two extra electrons in the small $Ca(OH)_4{}^{2-}$ complex induces a slight weakening of the Ca−O bonds. This suggestion is also supported by the larger negative D_b value found for the $Ca(OH)_2$ molecule with respect to that estimated for the $Ca(OH)_4{}^{2-}$ complex.

In the case of the $Ca(OH)_6{}^{4-}$ complex, the CaO_6 fragment 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

$$Ca(OH)_6{}^{4-} \rightarrow Ca(OH)_2 + 4OH^-$$

turns out to be exothermic with a D value of +11.9 eV. This result seems to confirm that the Ca−O bonds are weakened by an excess of electronic charge in small

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complexes formed by a Ca atom fourfold- or sixfold-coordinated by O atoms.

The above results have been taken into account in the investigation of the interaction of Ca ions with PAA chains. Different model systems have been considered, where a Ca atom is bonded to one or more O atoms of one or more PAA chains. The most interesting systems are shown in Figure 2. In these systems, a polymer chain is represented by the $(-CH_2-CH-COO^-)_4$ fragment, hereafter referred to as $[PAA]^{4-}$. This fragment is repeated along the chain axis in order to simulate chains of infinite length. In the first system, $Ca[PAA]OH^{3-}$, a Ca^{2+} ion is bonded to an O atom of the $[PAA]^{4-}$ fragment and to an OH^- group. Parts a and b of Figure 2 show the geometry of this system at the beginning and at the end of the geometry-optimization calculation, respectively. These figures clearly show a tendency of the Ca ion to bind four O atoms. Moreover, in the optimized geometry the Ca−O bonds have almost the same length, thus suggesting the formation of four equivalent bonds; see Table 1. The CaO_4 fragment has an almost tetrahedral configuration similar to that found for one of the configurations of the $Ca(OH)_4{}^{2-}$ complex. A planar configuration of the CaO_4 fragment cannot be achieved in the present case because of the limited displacement ability of the three O atoms belonging to the PAA chain. In a second system, $Ca[PAA]^{2-}$(two Ox.), the Ca ion is bonded to two O atoms belonging to the carboxylate anions of the *same* PAA chain, thus realizing an intrachain O−Ca−O linkage; see Figures 1b and 2c. In this configuration, the Ca−O bonds are slightly longer than those formed in the $Ca(OH)_2$ molecule, while the O−Ca−O bond angle exhibits a strong deviation from the in-line O−Ca−O arrangement found in the molecule; see Table 1. Finally, in the third model system, $Ca[PAA]_2{}^{6-}$, the Ca atom is bonded to four O atoms of *two* PAA chains, thus realizing an interchain O_2-Ca-O_2 linkage; see Figures 1b and 2d. In this system, the relative positions of the two polymer chains have been chosen in order to permit the interaction of the Ca ions with more than two O atoms. At the beginning of the geometry-optimization procedure, the Ca atom is bonded to *two* O atoms only, which belong to different PAA chains. As the geometry of the system is fully relaxed by following the atomic forces, two further O atoms move toward the Ca atom, thus leading to the formation of a CaO_4 fragment. In particular, the carboxylate groups of two $-CH_2-COO^-$ fragments rotate around the C−*C* axis to make one of the two O atoms closer to the Ca ion. In the CaO_4 fragment, the four O atoms are at the same distance from the Ca atom and give rise to an almost planar geometry like that found for one configuration of the $Ca(OH)_4{}^{2-}$ complex; see Table 1 and Figure 2d. In the $Ca[PAA]_2{}^{6-}$ system, a tetrahedral configuration of the CaO_4 fragment cannot be achieved because of the limited displacement ability of the O atoms in the PAA chains. Further model systems have been investigated in order to analyze the effects of OH^- ions and higher coordination numbers of the Ca atom on the stability of the intrachain and interchain linkages. In the case of the intrachain linkage, two further model systems, the $Ca[PAA]^{2-}$(three Ox.) and the $Ca[PAA](OH)_2{}^{4-}$ systems, have been considered. The $Ca[PAA]^{2-}$(three Ox.) system differs from the $Ca[PAA]^{2-}$(two Ox.) system of Figure 2c only for the starting geometry, which is characterized by a Ca ion bonded with three O atoms of the PAA chain instead of two. In this case, the geometry-optimization procedure has found a metastable configuration where the Ca ion forms a distorted trigonal pyramid with the three O atoms of the PAA chain. This configuration is close in energy to that of the $Ca[PAA]^{2-}$(two Ox.) system. The $Ca[PAA](OH)_2{}^{4-}$ system can be derived from the $Ca[PAA]^{2-}$(two Ox.) system of Figure 2c when two OH^- ions are bonded to the Ca ion. The Ca ion is therefore fourfold-coordinated by the two O atoms of the PAA chain and by the two O atoms of the OH^- ions. The optimized geometry of this system corresponds to a distorted tetrahedral geometry of the CaO_4 fragment. Details of the geometries of the above systems are given in Table 1. In the case of the interchain linkage, a $Ca[PAA]_2(OH)_2{}^{8-}$ system has also been investigated, which derives from the $Ca[PAA]_2{}^{6-}$ system of Figure 2d when two OH^- ions are bonded to the Ca ion. Slightly different starting geometries have been considered for the $Ca[PAA]_2(OH)_2{}^{8-}$ system. Moreover, there are no symmetry constraints in the geometry-optimization procedure. This procedure should permit an evolution of the system toward its most stable geometry during the geometry-optimization calculation. In the optimized geometry, the system presents a distorted octahedral configuration for a CaO_6 complex where the four O atoms of the PAA chains form the square basis of the octahedron and the O atoms of the OH^- ions occupy the two remaining vertexes of the octahedron. The CaO_6 fragment is characterized by two short Ca−O(H) bonds and by four longer (and weaker) Ca−O bonds which involve the O atoms of the PAA chains; see Table 1. This geometry should be compared with that of the $Ca[PAA]_2{}^{6-}$ system, where four equivalent Ca−O bonds are formed; see Table 1. The above results indicate that the stronger interaction of the Ca ion with the two OH^- ions weakens the interaction of the Ca ions with the neighboring O atoms of the PAA chains. It is worth noticing that the $Ca[PAA]_2(OH)_2{}^{8-}$ system is metastable with respect to the $Ca[PAA]_2{}^{6-}$ system, as shown by the reaction of dissociation

$$Ca[PAA]_2(OH)_2{}^{8-} \rightarrow Ca[PAA]_2{}^{6-} + 2OH^-$$

which turns out to be exothermic with a *D* value of +1.4 eV.

The nature and the strength of the O−Ca−O chemical bonds formed in the above model systems have then been investigated by analyzing isosurfaces corresponding to the *same value* of the *valence* electronic charge density and dissociation energies corresponding to the reactions shown in Table 2. The isosurfaces corresponding to the $Ca[PAA]OH^{3-}$, $Ca[PAA]^{2-}$(two Ox.), and $Ca[PAA]_2{}^{6-}$ systems are shown in parts a−c of Figure 3, respectively. In all of the systems, a homogeneous distribution of the electronic valence charge on the O atoms neighboring the Ca atom is found. In particular, in the cases of the $Ca[PAA]OH^{3-}$ and $Ca[PAA]_2{}^{6-}$ systems, the shape of the isosurfaces confirms the formation of four equivalent Ca−O bonds. The ionic character of the Ca−O bonds is clearly shown by a piling up of the electronic charge density on the O atoms. Quite

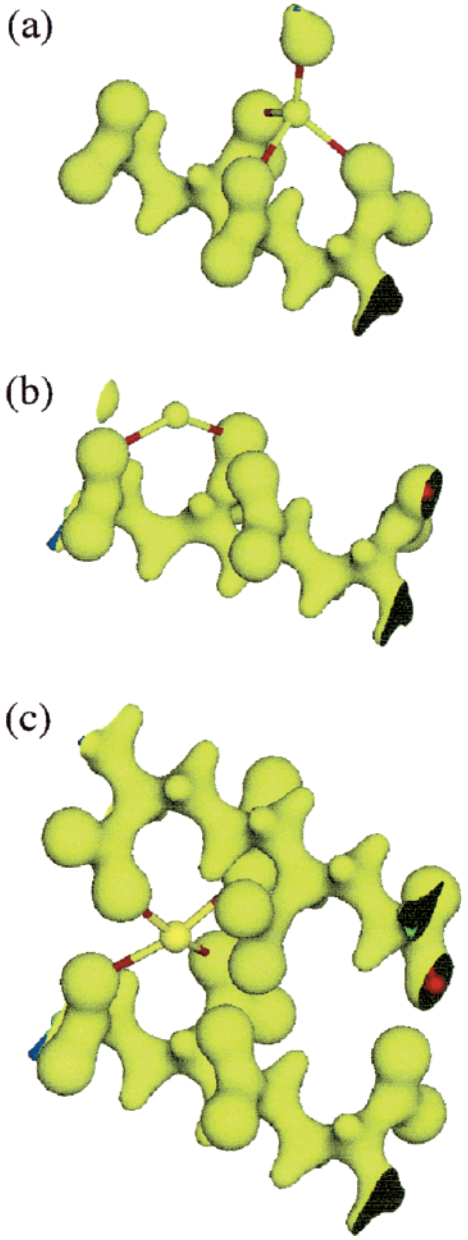

Figure 3. Isosurfaces of the *valence* electronic charge densities calculated for the different Ca−PAA systems investigated in the present study: (a) Ca[PAA]OH^{3-} system as shown in Figure 2b; (b) Ca[PAA]$^{2-}$(two Ox.) system as shown in Figure 2c; (c) Ca[PAA]$_2$$^{6-}$ system as shown in Figure 2d. The isosurfaces correspond to an electron density of 0.14 e/au^3.

similar isosurfaces characterize the other model systems investigated here.

For what concerns the stability of the above Ca−PAA systems, in the case of intrachain linkage, the tendency of the Ca ion to coordinate more than two O atoms, already shown by the evolution of the Ca[PAA]OH^{3-} geometry, is confirmed by the close D values found for the Ca[PAA]$^{2-}$(three Ox.) and Ca[PAA]$^{2-}$(two Ox.) systems; see Table 2. Furthermore, the large negative D value of the Ca[PAA](OH)$_2$$^{4-}$ system shows that a Ca ion may give rise to an intrachain linkage which involves two OH$^-$ ions. This result and the large negative D value found also for the Ca[PAA]OH^{3-} system suggest that the most stable intrachain configurations involve OH$^-$ ions bonded to the Ca ion. On the other hand, an analysis of the D_b values corresponding to the above systems shows that the Ca[PAA]$^{2-}$(two Ox.) system of Figure 2c has the most stable Ca−O bonds; that is, this system is quite stable once it is formed. For what concerns the interchain linkage, the Ca[PAA]$_2$$^{6-}$ system has the larger negative D and D_b values with respect to the Ca[PAA]$_2$(OH)$_2$$^{8-}$ system; see Table 2. This result is accounted for by the differences between the geometries of the two systems discussed above. An overall analysis of the results given in Table 2 shows that the D value corresponding to the Ca[PAA]$_2$$^{6-}$ system is the largest negative value, thus indicating that the formation of this system is favored with respect to the other systems involving PAA chains and the molecular complexes formed by Ca and hydroxyl ions. In particular, the interchain O−Ca−O linkage turns out to be more stable than the intrachain linkage.

Table 3. Calculated and Experimental Values of the Stretching Frequencies of Several Ca−O and C═O Bonds in the Systems Investigated Here (See the Text)

system	bond	n(calc)	n(exp)^b
Ca(OH)$_2$	Ca−O	687	680^b
Ca[PAA]$^{2-}$(two Ox.)	Ca−O	550	
Ca[PAA]$_2$$^{6-}$	Ca−O	540	
Ca[PAA]$_2$$^{6-}$	−C═O(−O−Ca)	1590	1507−1630^c
Ca[PAA]$_2$$^{6-}$	−C═O(−O)$^-$	1412	1416^c

[a] The vibrational frequencies are given in reciprocal centimeters. [b] Values from ref 29. [c] Values from ref 35.

The above results support therefore the existence of a cross-linking of PAA chains by Ca ions. Further support comes from a detailed analysis of the D_b values of Table 2. Although these values indicate that each Ca−O bond formed in the Ca[PAA]$_2$$^{6-}$ system (D_b = −5.6 eV) is weaker than a single Ca−O bond formed in the Ca(OH)$_2$ molecule (D_b = −8.4 eV) or in the Ca[PAA]$^{2-}$ system (D_b = −7.3 eV), the breaking of the cross-link between two polymer chains implies (at least) the breaking of *two* Ca−O bonds because the Ca ion is anchored to *four* points of two PAA chains (two points for each chain). This process requires an energy of −11.2 eV. The present results also suggest that the PAA cross-linking is stronger than the O−Ca−O cross-linking of PVA chains by Ca ions. In fact, in the latter case, a different theoretical study has shown that *only two* Ca−O bonds of an O−Ca−O group can be formed in the cross-linking of two PVA chains; i.e., the Ca ion is anchored to *two* points of two PVA chains (one point for each chain).[12] Furthermore, each Ca−O bond has a D_b value of ∼6 eV, which is close to that found for the Ca−O bonds formed with the PAA chains. Finally, the existence of tetrahedral and planar configurations of the Ca(OH)$_4$$^{2-}$ complex and of similar configurations of the CaO$_4$ fragment in the Ca[PAA]OH^{3-} and Ca[PAA]$_2$$^{6-}$ model systems suggests that the CaO$_4$ atomic arrangement is quite "flexible". It is expected, therefore, that the PAA cross-linking by Ca ions exists even in the presence of local structural deformations, such as those occurring in real materials.

The vibrational frequencies of several Ca−O and C═O bonds have also been evaluated in the Ca[PAA]$^{2-}$(two Ox.) and Ca[PAA]$_2$$^{6-}$ systems, which are characterized by the most different Ca−O atomic arrangements, that is, by the presence of the CaO$_2$ and CaO$_4$ fragments, respectively. The present results are in good agreement with the available experimental results; see Table 3. In the Ca[PAA]$^{2-}$(two Ox.) and Ca[PAA]$_2^{6-}$ systems, the Ca−O stretching frequencies have almost the same value. Thus, these frequencies do not permit one to distinguish between intrachain and interchain linkages. The stretching frequencies of the C═O bonds have been evaluated in different carboxylate groups of the Ca[PAA]$_2^{6-}$ system. In a −COO−Ca− fragment, where an O atom is bonded with a Ca atom, the C═O bond has a stronger double-bond character and a higher stretching frequency than those in a *free* COO$^-$ group. This result agrees with the trends shown by the C═O vibrational frequencies measured in the cases of free acetate ions and metal complexes of carboxylic acids[35] and suggests a way to get indirect evidence for the PAA cross-linking. In fact, the formation of Ca−O bonds should be accompanied by an increase of the stretching frequency of the C═O bonds in the involved carboxylate groups with respect to the C═O frequency in free groups. This result would not enable a discrimination between (interchain) cross-linking and intrachain linking of the PAA chains but, together with an observed improvement of the mechanical properties of the MDF material, could be considered an indirect evidence of cross-linking.

Conclusions

The interaction of Ca ions with the carboxylate anions of one or two PAA chains has been investigated by first-principles theoretical methods. The present results indicate the formation of a stable CaO$_4$ complex which involves the −COO$^-$ groups of two different polymer chains. This gives support to the existence of a quite efficient cross-linking of the PAA chains because the Ca ion is anchored to *four* points of *two* PAA chains. Further, the CaO$_4$ fragment should be flexible enough to permit PAA cross-linking even in the presence of local deformations. The present results also suggest that the PAA cross-linking is more efficient than that realized in the case of the PVA polymer, where a Ca ion is anchored to *two* points of two PVA chains.

Theoretical investigations of the microchemical reactions between the organic and inorganic phases in MDF composites suggest the following relative strengths of the polymer-chain cross-linking: Al−PVA > Ca−PVA and Ca−PAA > Ca−PVA. The different strength of the polymer-chain cross-linking is certainly related to the mechanical properties of MDF materials. However, the above results cannot be *directly* related to the strength of those materials. In fact, other effects must be taken into account, e.g., the effects of processing where cross-linking may have opposite effects on the final mechanical strength of the MDF material.[36]

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