Chem. Mater. **2001,** *13,* 4335−4341

Macrodefect-Free Cements: The Effect of Chemical Composition on Microstructure

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Received March 8, 2001. Revised Manuscript Received August 21, 2001

The mechanical properties and microstructures of three macrodefect-free (MDF) composites, prepared from Portland and high or medium alumina cements, were evaluated. Transmission electron microscopy shows that the interface between cement grains and the polymeric matrix is porous in the case of alumina cements and pore free in the case of Portland. The analyses of the ions present in the polymeric matrix were performed by energy dispersive X-ray spectrometry, and surface free energy of the materials was estimated through dynamic contact angle measurements by using a Wilhelmy microbalance. The results suggest that Fe^{3+} and Al^{3+} ions interact differently with the polymeric matrix. This fact is also supported by dynamic mechanical thermal tests. When Portland cement is used, the microstructure of the MDF composite does not show any interphase region.

Introduction

Macrodefect-free (MDF) cements are composites obtained by calendering cement pastes containing a water-soluble polymer, that is poly(vinyl alcohol) (PVA).[1−4] This acts as a rheological aid, favoring the packing of cement particles and the reduction of residual macroporosity during high shear mixing. The properties of MDF cements are strictly dependent on the manufacturing parameters and their microstructures. The metallic ions derived from the hydration of cement are known to promote the formation of cross-link bonds once they have diffused into the polymer matrix. Therefore, the improvement in strength that is typically displayed by these materials can also be regarded as a consequence of the chemical reactivity between polymer and cement. According to previous studies,[5,6] the MDF composites, prepared by using high alumina cement, are comparatively stronger than those prepared from Portland cements, and aluminum ion is a better cross-linking agent than calcium ion. Recently, further indirect evidence was obtained, from theoretical evaluations by using ab initio methods, of the energies released during the “complexation” reactions among an Al^{3+} ion and one [Al−PVA(I)] or two [Al−PVA(II)] PVA backbones.[7] The Al−PVA(II) model has been proven to be more stable, even when geometrically distorted as under the application of torsion or bending stresses. Accordingly, the higher theoretical stability of the Al−PVA(II) model with respect to the model I supports the role of these ions in determining the properties of MDF cements.

The use of less expensive and more commonly used cements rather than high alumina cements is advisable and seemingly possible. However, the mechanical properties of MDF prepared with Portland cement will already be lower than those prepared with high alumina cements, due to the high reactivity of tricalcium silicate.[5,6] Therefore, an interesting goal is to determine how the behavior of the MDF composites is modified by the use of cements with lower alumina content and containing a certain percentage of Fe^{3+} ions. Similar to Al^{3+} ions, Fe^{3+} ions could also interact with the polymer matrix. To better investigate the microstructure and its effect on the properties of these materials, a broad characterization using microscopic, mechanical, and surface analyses was carried out on three MDF cements with different contents of aluminum and iron oxides. Since all of the materials have been processed under similar conditions, any differences existing in their properties should be the consequence of the chemical interactions between the cement ions and polymer which occur during the MDF cement processing procedure.

Experimental Section

The materials were a high alumina (Secar 71, Lafarge) cement, a low alumina high iron (Electroland, Cementos Molins) cement, and a Portland (Italbianco) cement whose compositions are listed in Table 1. An 80 mol % hydrolyzed poly(vinyl alcohol)/acetate (PVA/Ac) copolymer was used (Nippon Gohsei Gohsenol KH-17s). The samples were prepared

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10.1021/cm010197+ CCC: $20.00

Table 1. Cement Composition (wt % Oxides)

	Secar 71	Electroland	Portland
Al_2O_3	69−71	40−42	2.5−3.5
CaO	27−29	38−40	65−69
SiO_2	0.8	1.5−3	21−23
Fe_2O_3	0.3	15−17	0−3

Table 2. Compositions of MDF Cements (g of components)

	MDF-S	MDF-E	MDF-P
cement	1000	1000	1000
PVA Gohsenol (7%)	70	70	70
solvent glycerol (6%)	120	120	150
addition			1 ($CaCl_2$)

Table 3. Processing Parameters

mixing time	3 min
calendering time	3.5 min
molding pressure	80 bar (100 bar[a])
molding time	10 min
molding temperature	80 °C (35 °C[a])
curing time	24 h at the r.t.

[a] Sample MDF-P.

according to the specifications reported in Tables 2 and 3, so that three kinds of MDF cements were obtained, which were code-named MDF-S, MDF-E, and MDF-P, respectively. The formulation of MDF-P required a higher amount of water to obtain a workable paste, and its curing stage had to be slightly modified.

Transmission electron microscope (TEM) specimens were prepared by the mechanical thinning of 500 μm thick slices of material down to 100 μm. Final thinning was carried out using a GATAN ion mill. To reduce any possible heating effect from ion bombardment, a cryogenic, liquid nitrogen cooled sample holder was used. Observations were conducted with a Philips 400T instrument operated at 120 kV and equipped with an energy dispersive X-ray spectroscopy (EDXS) system, employed for qualitative and semiquantitative analyses.

An evaluation of the roughness, R_a, of the samples was made using a Dektak3 device on both calendered faces, with the application of the default numerical filters on collected data.

Advancing and receding contact angles were measured by the Wilhelmy technique[8,9] using a Gibertini microbalance (model TDS) at a speed of 105 μm s^{-1} at 23 ± 2 °C. MilliQ water was distilled on the spot, RPE ethylene glycol and synthesis grade α-bromonaphthalene (by Merck Bracco, Milan Italy) were used as received. MDF samples were produced without using any kind of antisticking agents; in fact, even traces of these silicon- or fluorine-containing substances can induce a significant increase in the advancing contact angles.

Dynamical mechanical analyses (DMA) were performed on solid samples by using a PL-DMTA MkII instrument of Polymer Laboratories in bending configuration in two subsequent scans. Storage modulus (E') and loss modulus (E'') were measured at a frequency of 1 Hz, from 0 up to 120 °C in the first scan and up to 160 °C in the second one, with a heating rate of 3 °C min^{-1}.

Flexural strengths and Young's moduli were determined, on samples with dimensions 40 × 40 × 160 mm, by three-point flexural tests using an universal machine (Instron) with a loading rate of 1 mm min^{-1} at room temperature.

Results

1. TEM Observations and EDXS Analyses. As previously reported,[1,2] the microstructure of calcium aluminate MDF materials, as revealed by TEM observations, consists of cement grains embedded in a PVA matrix. It was also observed that the individual grains of cement are coated by an interphase region, which is responsible for mechanical behavior in a dry and wet environment. Gülgün et al.[10] found, in the case of MDF-S, a correlation between the thickness of this porous interlayer and the mixing time, evidencing a degradation of the PVA matrix as a consequence of mechanically induced cross-linking reactions. Tan et al.[11] pointed out that the interphase zone was the result of a reaction among free radical oligomers and cements, derived from the mechanical cleavage of polymer chains, which is caused by the mechanical energy stored in the material during the prolonged mixing of the MDF paste. For this study and with the aim to compare the properties of different MDF cements, the same processing parameters were adopted for all the samples. The mixing time of 3 min was long enough to produce homogeneous composites and a limited degradation.

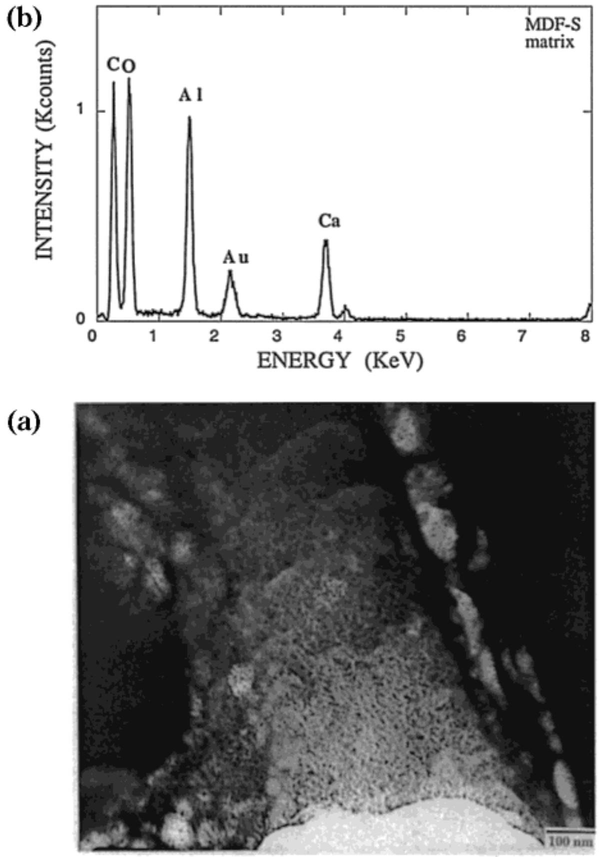

Figure 1. TEM micrograph of the MDF-S sample and EDXS spectrum of the polymeric matrix.

In Figure 1a, a detail of the interfacial zone in the sample MDF-S is seen, displaying a porous layer that is about 100 nm thick, beside which the polymer matrix appears uniform and continuous. Figure 2a shows the polymer−grain interface in the MDF-E sample, which is characterized by a thicker porous layer. Moreover, big particles of Fe_2O_3 were found to be homogeneously dispersed. In contrast, the MDF-P sample (Figure 3a) does not show any interphase and the polymer is

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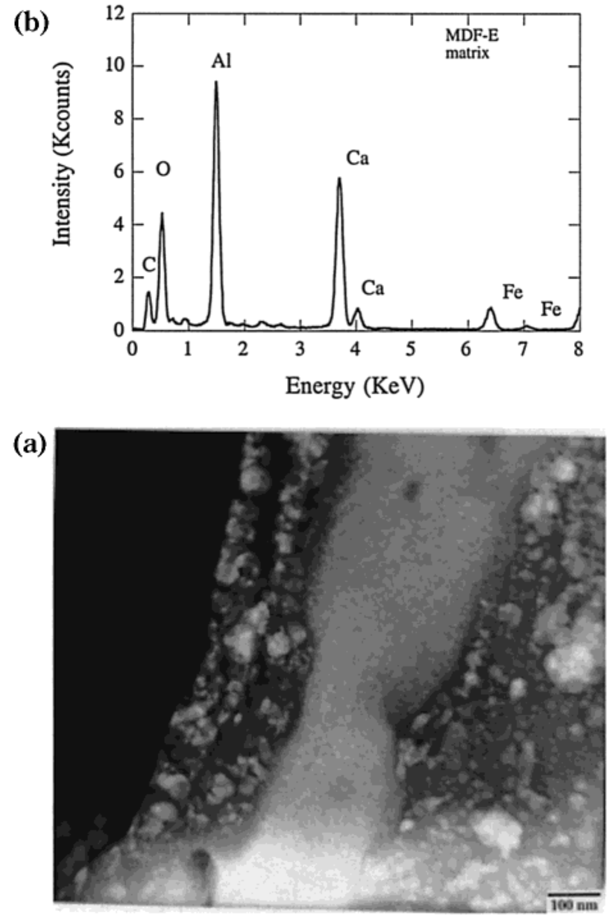

Figure 2. TEM micrograph of the MDF-E sample and EDXS spectrum of the polymeric matrix.

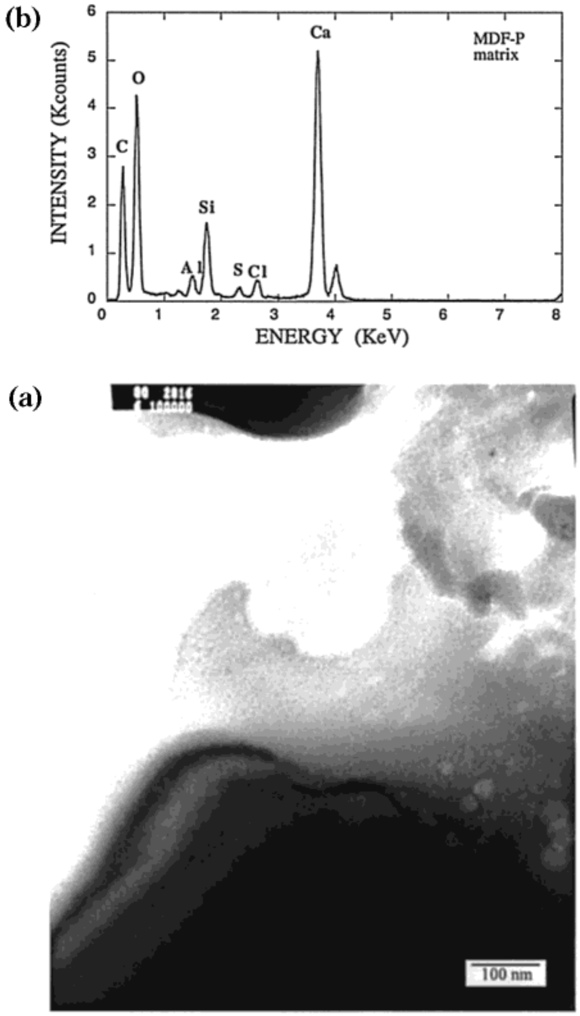

Figure 3. TEM micrograph of the MDF-P sample and EDXS spectrum of the polymeric matrix.

continuous and wets the grains very well. Beside the absence of interfacial porosity, the presence of small precipitates in the PVA matrix is worth noting. These precipitates are microcrystalline grains containing Ca, C, and O, as deduced from EDXS analyses, probably derived by the carbonation of $Ca(OH)_2$ from the hydration of tricalcium silicates.

EDXS analyses were conducted with the primary aim to check for the presence of the original constituents of the cement grains present in the polymeric matrix as a consequence of the thermomechanical processes of forming. In actuality, all the cations, like Al, Si, Ca, and Fe, present to different extents in the different cements were found in the matrix, as can be clearly seen from the EDXS spectra of the three materials displayed in part b of Figures 1, 2, and 3.

To characterize the relationship between the matrix and the corresponding cement composition, a comparison of ratios between integrated intensities of the characteristic lines and nominal ion concentrations in the starting cements was made. This approach was preferred to an evaluation of the ion concentrations, which is unavoidably troublesome and unpredictably affected by matrix effects.

For MDF-S and MDF-P materials, it turned out that the ratios of the experimental EDXS peak intensities are comparable to the corresponding ratios of the nominal concentrations (for instance, the Al/Ca intensity ratio is 1.9 vs 1.8 and 0.04 vs 0.03, respectively). This indicates that comparable diffusive fluxes from the cement grains toward the matrix occurred during the manufacturing, owing to the high reactivity of the calcium aluminate phases in Portland (CA_3) and in the high alumina content (CA_2 more than CA) cements.

In the MDF-E material, the situation is slightly more complex. The experimental intensity ratio Al/Ca is larger than the corresponding ratio for nominal concentrations: 1.8 vs 0.8. The opposite occurs for the Fe/Ca ratios: 0.12 vs 0.24, although in the matrix surrounding the ferrite grains the values are 1.3 and 0.21, respectively. Therefore, in the MDF-E material, a comparatively faster diffusion of Al as compared to Fe ions can be inferred. This is due to a faster dissolution of the calcium aluminate phase (CA) than of the ferrite.

The main microstructural difference observed in the samples is with regard to their porosity, which can be attributed not only to the mechanical work (the same in all cases) but also to the different chemical compositions of the cement samples. According to previous studies, calcium silicate is known to give insoluble hydrate silicate and Ca^{2+} and OH^-, which causes the pH to increase.[5,6] In this case, the PVA/Ac copolymer hydrolyses and rapidly forms cross-links with Ca^{2+}; the paste mixes with difficulty. As a consequence, the radical processes induced by high shear mixing, which

Table 4. Average Values of Roughness

	MDF-S/a	MDF-S/b	MDF-E/a	MDF-E/b
R_a (μm)	0.11	0.09	0.12	0.08

Table 5. Contact Angles of Some Liquids on MDF Samples (deg)[a]

	water		α-bromonaphthalene		ethylene glycol	
	adv	rec	adv	rec	adv	rec
MDF-E	89	22	40	13	68	21
MDF-S	68	18	42	21	54	n.a.

[a] The standard deviation is about 1−2°.

Table 6. Surface Tensions and Its Components (mJ m^{-2})

sample	total	LW[a]	acid[a]	base[a]
MDF-E	35.7 ± 0.9	34.8 ± 0.4	0.1 ± 0.4	1.4 ± 0.4
MDF-S	34.9 ± 1.1	33.7 ± 0.2	0.04 ± 1	7.9 ± 0.9

[a] See Appendix.

are supposed to provide a porous interphase, cannot take place. With aluminous cements, the paste develops an interphase because it is workable during mixing.

2. Roughness and Contact Angle Measurements. A mean of five roughness measurements on each face gave the results listed in Table 4, showing only slight differences of R_a for the two sides of the MDF-S and MDF-E samples. In all cases, R_a values in the 0.08−0.12 μm range were measured. Greater values of roughness would have affected the results of the contact angle measurements, especially the difference between the advancing and receding contact angles, or the so-called hysteresis.[12,13] Moreover, the samples have the same roughness on corresponding faces (produced by the calendering process); for these reasons, we believe that all of the measured differences of the values of the contact angles substantially depend on the chemical arrangement at the surface of the samples.

As shown in Table 5, the advancing contact angles are above zero and in some cases are equal to 90° and even more. The MDF-E material appears significantly more hydrophobic than MDF-S in water. Very high (above 100°) and especially constant values were measured for MDF-P cement. Therefore, an accidental presence of impurities was suspected and could not be excluded definitively.

On the contrary, the receding contact angles were found to be very low and in some cases their value was about zero. This hysteresis is an indication of the heterogeneity of the surface, made by a patchwork of hydrophobic and hydrophilic domains. Particularly, when ethylene glycol was used as a solvent, the mean value of the receding angles was zero, which is a value corresponding to the presence of significant adsorption/absorption of liquid. For this reason, the advancing portion of the run has been used only for the calculation of the surface free energy components. Moreover, to reduce the absorption caused by the capillarity effect, an immersion speed larger than usual was used. Because of the low viscosity of the testing liquids, the capillary number[14] was low and the meniscus shape can be considered to be substantially equivalent to the static one, as happens in the most common cases.

The determination of surface free energy and its components can be performed on the basis of contact angle measurements (see Appendix). The surface free energies were evaluated using an autodeveloped calculation program, SurfTen,[15] based on the so-called surface free energy acid−base theory proposed by van Oss−Chaudury−Good.[16−18] In recent years, the limits of this theory have been debated. The most important issue is that the van Oss−Chaudury−Good theory yields an overestimation of the basic components. To eliminate this problem, a new reference scale for evaluating acid−base strength has been recently proposed and used in this study. Accordingly, the reference values are $\gamma^{LW} = 26.3$ mN m^{-1}, $\gamma^{+} = 48.5$ mN m^{-1}, and $\gamma^{-} = 11.2$ mN m^{-1} for water at 20 °C.[18] However, an absolute scale does not exist and the direct comparison of acidic and basic components of surface free energy is not allowed, but only a relative comparison among the components of the same type is used.[19,20]

As we can see in Table 6, although the total and dispersive values are quite similar, meaning the hydrophobic behavior is predominant for both MDF composites, the basic (hydrophilic) component differs significantly. The dispersive component for the MDF composites shows a value of about 35−36 mN m^{-1}, which is typical of a "polyethylene-like" backbone.[21] Therefore, it can be conceived that the MDF surface is partly made of the most hydrophobic portion of the polymer backbones. In both cases, the calculated standard deviations are larger than that in the case of the acidic component, which is negligible. Instead, the comparison between the two basic components suggests that the presence of iron in the formulation of MDF cement could be responsible for the decrease of the basic component. It is possible to conclude that although the MDF surface displays a general hydrophobic pattern, similar to polyethylene, in the case of the MDF-S samples, a significant number of basic groups (e.g., OH functionalities) emerge at the surface. In fact, it is widely accepted that for thermodynamic reasons (the minimization of surface interfacial energy), the most hydrophobic components of a material are preferentially localized at the outer surface.[22] Instead, for MDF-E, the number of polar/basic groups is lower and, consequently, the hydrophobicity appears greater and does not decrease during the immersion in water. By the repetition of the immersions in water (see Figure 4), the advancing contact angles decrease for both samples but to a much lower extent in the MDF-E

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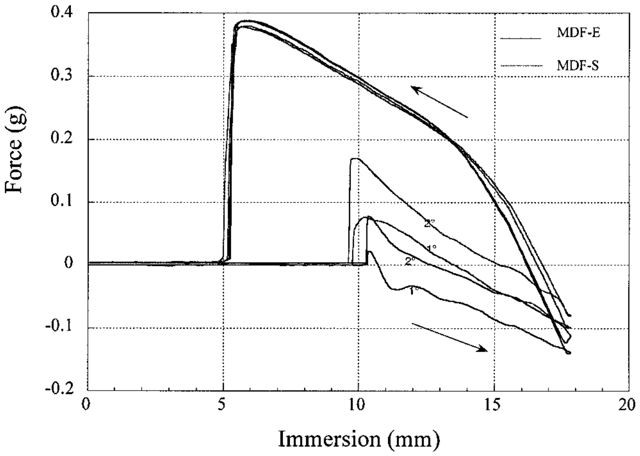

Figure 4. Advancing and receding curves for MDF-E (black) and MDF-S (red) after first and second immersion in water.

Table 7. Flexural Strength, Elastic Modulus (*E*), and K_{IC} of MDF Samples

	MDF-S	MDF-E	MDF-P	MDF-P (10 wt % silica fume)
flexural strength (MPa)	133 ± 7	114 ± 6	32 ± 3	43 ± 3
E (GPa)	32 ± 4	27 ± 3	16 ± 3	22 ± 3
K_{IC} (MPa·m$^{1/2}$)	1.32	1.22	0.89	1.01

sample, confirming its more pronounced hydrophobic properties.

3. Mechanical Properties. Table 7 lists the flexural strength, elastic modulus (*E*), and K_{IC} of the MDF composites. The composition of the cement seems to have a significant effect on the mechanical properties of the MDF composites; the flexural strength decreases as the alumina content is reduced and calcia and silica contents are increased. In the comparison of the mechanical properties of the three composites, the differences can be attributed to cross-link bonds, although other effects have to be taken into account. As far as the MDF-P composites are concerned, it has been already found that, not having formed an interphase, they are relatively weak.[5,6] The lower charge of the calcium ion could partially account for the lack of strong and stable interactions between calcium ions and PVA chains, but the mechanical properties depend more on the amount of process-induced defects.

Dynamical mechanical analyses, a very powerful technique for determining the glass transition and thermal behavior of massive materials, were performed on the MDF samples. The temperature of the glass transition (T_g), if present, was deduced from the inflection of the storage modulus curve and from the corresponding peaks in the curve of the loss modulus. As reported by Alfani et al.,[23] the presence of the polymer phase determines the thermal behavior of the MDF-S composite. In fact, the DMA curve of that sample shows a first wide inflection at 55 °C, like the pure PVA/Ac copolymer, and a smaller one at 120 °C. The MDF-E sample has only a sharp glass transition at 105 °C (see Figure 5). Its *E*′ value at room temperature is slightly lower than that for MDF-S, confirming the differences in elastic modulus already recorded in the static tests. After the sample was cooled, a complete recovery of the mechanical properties was observed. In the second scan, MDF-S exhibits a slight decrease in the glass transition temperature at 50 and 105 °C, respectively, whereas the T_g of MDF-E increases to 135 °C, as an effect of further stiffening. Last, the MDF-P showed a constant decrease in the *E*′ modulus but more slowly than MDF-S and without a real glass transition in the temperature range of 25−160 °C. Similar behavior is retained after a second heating of the same sample. This is partially due to the homogeneous dispersion of microcrystalline calcium carbonate as seen by TEM observations.

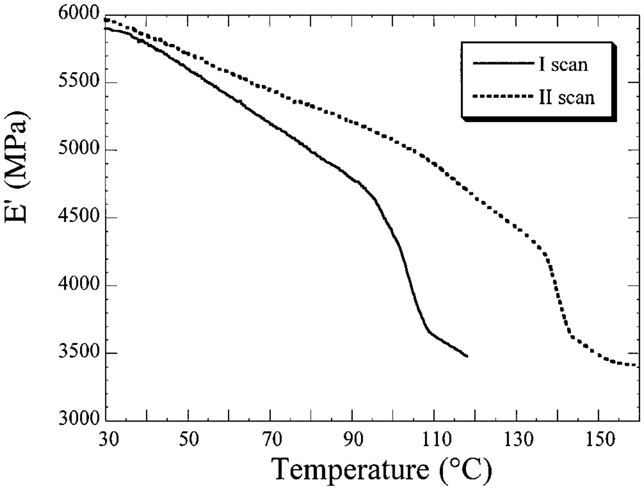

Figure 5. DMA curves (I, II scan) of MDF-E sample.

The different features of the polymeric matrix were revealed also by separately dipping pieces of MDF-S, MDF-E, and MDF−P of similar geometry for 24 h in 1 M HCl. This procedure was used as an accelerated test in a wet environment. After removal, the MDF-S sample showed a remarkable swelling and a rubbery behavior. The MDF-P became uniformly rigid and shrank, because the reaction of $Ca(OH)_2$ with acid drives the silicates to be hydrolyzed and consumed. The MDF-E appeared quite unchanged and slightly flexible. When DMA was performed again after drying, a general worsening of properties was observed and MDF-P and MDF-S even broke during the measurements. Only MDF-E remained intact and exhibited an *E*′ value as high as 2 GPa at room temperature.

Discussion and Conclusions

The inorganic materials have “high energy” surfaces, and for this reason, the contact angles of common liquids on them should be zero. (However, this is not strictly true when impurities have been absorbed from the environment.) The surface free energy of the MDF material is lower than that of conventional cements, because of the presence of the polymeric component, and the measured contact angles are higher than zero.

In the structure of pure crystalline PVA, many hydrogen bonds are formed between adjacent backbones. Moreover, the −OH groups of the same backbone, but pointing outward, are perpendicular.[24] Pure PVA

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is water soluble and many liquids cause it to swell, so contact angle measurements on this polymer have been made using a few, mainly dispersive liquids.[25,26] When the PVA polymer is modified with hydrophobic groups, its properties are drastically changed, so that it is possible to measure its surface properties using water and other nondispersive liquids.[27,28] In fact, the hydrophobic portion of the backbone is exposed to air and high contact angles can be measured. Moreover, PVA is known to form complexes with metallic ions in an aqueous solution,[29] the stability constants of which are in agreement with the so-called Irving−William's series and the hard−soft acid−base (HSAB) theory by Klopman and others.[30,31] The interactions between PVA chains and the metal ions in the MDF composites should be in agreement with this theory too. Both Fe^{3+} and Al^{3+} ions can be considered as Lewis acids with different hardness and softness values. The hexaaquo complex formed by the reaction of Fe^{3+} with water, a hard base, is less acidic than the aluminum complex.[32] In other words, the bond between the oxygen and hydrogen is modified by the different properties of aluminum and iron ions; iron increases the strength of the bond and decreases the ability to donate hydrogen ions. Actually, the degree of hardness−softness of calcium ions is very similar to that of Fe^{3+}.[30] Anyway, the characteristic lifetime for the exchange of water molecules in aqueous complexes is 10^9 times greater for aluminum than for calcium ions.[32]

When MDF is prepared using an high iron, low alumina cement rather than a high alumina one, there is a reduction of the basic groups on the surface of the composite and in the polymer. As the acidic functions cannot be changed significantly, the reduction of the number of the hydroxyl groups exposed to the environment could be the effect of their interaction with iron ions. In fact, at equilibrium, the polymeric chain conformation in a MDF composite (a portion of which is shown in Figure 6 as an example) requires that the hydrophobic hydrocarbon groups of PVA be exposed outward, whereas the basic hydroxyl groups are involved in cross-linking with the metallic ions, as already proposed.[7] So the amount of free OH protruding outward depends on the strength and density of these cross-linking bonds. According to Klopman,[30] Fe^{3+} is supposed to be softer than Al^{3+}; in other words, O−Fe bonds have a slightly more covalent character and higher strength, so that they make the surface less basic and more hydrophobic. Actually, it is likely that only a low percentage of ions present in the MDF interact with the PVA. However, this percentage has to be much higher for iron than for aluminum ions.

The bulk properties of MDF materials are also influenced by the chemical interaction between the cement ions and the polymer. Concerning the thermal behavior of MDF-E, the recorded increase of the T_g value, with respect to that of the MDF-S, may be ascribed to the cross-links, but a modification of the polymeric phase should also be taken into account. In a previous study on the dynamic mechanical characterization of phosphazene-grafted copolymers containing PVA/Ac, a significant increase in the temperature of the glass transition was obtained by the elimination of the acetate copolymer.[33] On the other hand, the PVA/Ac, used for the preparation of the MDF composites, exhibits a glass inflection at 58 °C, a temperature lower than pure PVA which shows a glass transition at 85 °C,[34] so it can be inferred that the acetate copolymer lowers the T_g value. Since the presence of acetate groups, although small, was evidenced by IR analyses (performed in FTIR-ATR mode)[35] only in MDF-S, it can be concluded that the ferrite phase of MDF-E slowly releases iron ions, which, due to their coordination ability, can favor acetate hydrolysis and also form stable complexes with hydrolyzed PVA. The cross-link density and the covalent character increase further upon heating; so the polymeric phase of MDF-E is always less deformable than that of MDF-S. This more accentuated glassy behavior can favor the growth of microflaws and defects, thereby determining the poorer mechanical properties of MDF-E composites.

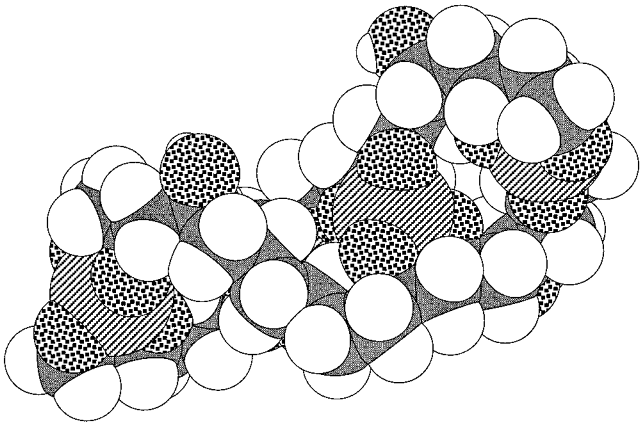

Figure 6. Conformation at the equilibrium of a portion of two PVA chains linked by metallic ions.

Acknowledgment. We are grateful to C. Migliaresi, L. Fambri, and S. Siboni for the helpful discussion. We acknowledge the Italian CNR project "Cementi MDF" for the financial support.

Appendix

For the process of adhesion of two different surfaces, γ_i and γ_s, thermodynamics provides us with the Young−Dupré equation

$$\Delta G^{a}_{si} = \gamma_{si} - \gamma_i - \gamma_s = -\gamma_i(1 + \cos\theta_i) \qquad (1)$$

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which expresses the free energy of adhesion ΔG^{a}_{si} (or "work of adhesion") by means of surface tension of liquid i, γ_i, and the contact angle at the interface among liquid, solid, and vacuum or vapor, θ_i. On the other hand, according to van Oss−Chaudury−Good[16] and Fowkes,[36] the surface energy of a solid or a liquid is the sum of different contributions, $\gamma_s = \gamma_s^{LW} + \gamma_s^{AB}$ and $\gamma_i = \gamma_i^{LW} + \gamma_i^{AB}$ (where the suffixes LW and AB indicate the Lifshitz dispersion and the Lewis acid−base interaction components, respectively). Assuming the validity of a slightly modified Berthelot geometric mean rule, van Oss−Chaudury−Good wrote: $\gamma_s = \gamma_s^{LW} + \gamma_s^{AB} = \gamma_s^{LW} + 2(\gamma_s^{+}\gamma_s^{-})^{1/2}$, where the new parameters (γ_i^{+} = acid component and γ_i^{-} = basic component) have value only in the context of this expression.

Thus, the free energy of adhesion can be expressed by: $\gamma_{si} - \gamma_i - \gamma_s = -\gamma_i(1 + \cos\theta_i) = -2(\gamma_i^{LW}\gamma_s^{LW})^{1/2} + (\gamma_i^{+}\gamma_s^{-})^{1/2} + (\gamma_s^{+}\gamma_i^{-})^{1/2}$, where θ_i is the contact angle between the i and s phases. All acid−base strength evaluations require a reference scale and the definition of the values of both acidic and basic components for a reference material. The constants γ_i^{LW}, γ_i^{+}, and γ_i^{-} have been tabulated at 20 °C, based on the hypothesis that for water at 20 °C, $\gamma_i^{+} = \gamma_i^{-}$. Thus, if we know θ_i for two or three solvents characterized by different polar, dispersive and LW, and acid and base components (usually water, methylene iodide or α-bromonaphthalene, and glycerol, ethylene glycol, or formamide), we will have, correspondingly, a system of three equations in three unknowns, whose resolution allows the parameters γ_s^{LW}, γ_s^{+}, and γ_s^{-} of the solid surface to be obtained.

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