Effect of temperature on thermo-mechanical properties of Macro-Defect-Free cement-polymer composite

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In this work thermo-mechanical properties of MDF cements have been analyzed under complex thermal hystories. In particular the temperature sensitivity of the material has been investigated using dynamical-mechanical analysis. Several tests have been performed to investigate the behaviour of the material from room temperature to 250 °C at a fixed frequency (1 Hz). The viscoelastic behaviour of the composite was then analyzed at different frequencies: it was observed that the material exhibits two main transitions, around 60 °C and 160 °C. For comparison with differential scanning calorimeter analysis the first peak was attributed to the glass transition of the PVAAc while the second one was associated to the melting of the crystalline part of the polymer. In addition, dynamical-mechanical analysis that included complex thermal hystories, were performed both on pure polymer films, and on the MDF cements, confirming that the drop of mechanical properties with temperature is essentially due to the nature of the viscoelastic component. Results obtained are in agreement with the picture of a composite in which a polymeric thermoplastic matrix surrounds partially hydrated cement particles. © *1999 Kluwer Academic Publishers*

1. Introduction

MDF (Macro-Defect-Free) composites have attracted interest since many years after their introduction in 1981 [1, 2]. In these materials, polymer, typically poly(vinyl alcohol acetate) (PVAAc) copolymer, and cement, calcium aluminate cement, undergo high shear mixing and react at low temperature to create a material with distinct characteristics, such as high flexural strength and elastic modulus.

The unique nature of these materials is due to their microstructure that consists of close-packed quasi-unreacted cement particles embedded in a continuous matrix of PVA [3].

Each particle is surrounded by an interphase layer that consists of a nanocomposite region resulting from a fine dispersion of crystalline hydration products embedded in an amorphous organic-mineral matrix [4].

The use of PVAAc in the initial mixture promotes the formation of a highly processable paste at much lower water contents than normal cement pastes (water over cement ratio $w/c = 0.1$ instead of ca. 0.3). Moreover, superior mechanical properties of the hardened cement-polymer composite (flexural strength ∼150 MPa, elastic modulus ∼35 GPa) result from the combination of low water content and mechanically-induced crosslinking reactions which take place between cement and polymer during high shear mixing of the initial paste [2, 5].

The nature of both cement and polymer is very important for the final performance of the composite. The optimum cement-polymer combination consists of calcium-aluminate cement (CAC) and PVAAc [1]. In fact this kind of polymer have significant effects on hydration reactions of the cement and interacts with

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the cement paste producing ionic bonds. In the case of CAC, the normal hydration reactions are strongly modified by PVAAc addition and the polymer reacts with Ca^{2+} and Al^{3+} ions provided by the cement to form calcium acetate and a crosslinked product [6]. Specifically Al^{4+} ions interact with four hydroxyl groups of PVA by an ionic bond.

The chemical structure of MDF composites makes these materials very sensitive to moisture exposure. In particular when MDF composites are immersed in water, the mechanical properties are reduced with increasing water exposure time [7]. Flexural strength of composites drops rapidly to about 40% of the dry value (150 MPa) within 14–21 days of immersion in water, and continues to decrease slowly to 25–30 MPa after longer periods of time.

To improve water resistance of cement-polymer composites several methods have been proposed [8, 9, 10] but no one has completely solved the water sensitivity problem of the material. Drying at higher temperatures it provides only modest increases in wet strength [8]. Besides adding an epoxy-functional silane coupling agent has reduced the initial flexural strength, also in low humidity environments, and has quicken the degradation processes when composites are immersed in water [10]. A significant improvement in moisture absorption and resistance to strength degradation in a 100% relative humidity environment was achieved in organotitanate-modified MDF cement materials [9]. However, a key limitation of this specific crosslinking additive was that partial initiation of this reaction with polymer (PVAAc) occurred during the high shear mixing process. This led to a reduced processing window, and yielded components of lower initial strength relative to the unmodified (standard) MDF cements.

On the contrary to the water sensitivity effect, very little has been published as regards the thermal behaviour. In the literature [11] a few data obtained for CAC-PVAAc composite samples using a torsional pendulum performing dynamic mechanical analysis are reported. It was observed that the dynamic shear modulus shows a discontinuity at 120 °C resembling a sort of glass transition temperature. On the other hand a PVAAc film shows a glass transition temperature (T_g) of about 50 °C.

In this paper the results of several dynamical-mechanical analysis performed on a CAC-PVAAc composite are reported. They have been carried out for detecting the relevant transitions of the material as a function of selected thermal hystories.

2. Experimental
2.1. Materials
The MDF cement-polymer composite characterized by the authors were obtained using the formulation and the process conditions described by Birchall [1] and optimized by Russel [2]. The formulation used for preparing samples of MDF composite is reported in Table I.

CAC, PVAAc and the solution of glycerine and water were pre-blended in a planetary mixer (Hobart) and compounded in a twin-roll mill to form a plastic dough

TABLE I Formulation for MDF composite

Constituent	Parts by weight	Weight (%)	Volume (%)
Calcium aluminate cement (CAC)[a]	100	84.3	65.2
Polyvinyl alcohol/ acetate (PVAc)[b]	7	5.9	12.3
Glycerine	0.7	0.6	1.4
Water	11	9.3	21.1

[a]Secar 71, Lafarge Fondu International.
[b]78.5–81.5% hydrolyzed, Gohsenol KH-17s, Nippon Synthetic Chemical Industry Co. Ltd. Japan.

that was then calendered into a sheet. The obtained paste was pressed in a mold at 80 bar and 80 °C for 10 min and finally cured for 24 h in an oven at 80 °C.

Films of PVAAc were prepared by casting a 10% aqueous solutions in a mold.

2.2. Dynamical-mechanical analysis
A DuPont dynamical-mechanical analyzer, model 983, was used to investigate the properties of the composite under complex thermal hystories. The analysis consists in fixing a low thickness rectangular sample to two arms, one of which is mobile and oscillates at a fixed frequency, while the other one measures the answer of the material and sends informations to the machine. The tested specimens were 50 mm long, 12 mm wide and 1.5 mm thick.

The temperature was scanned from 25 to 250 °C (in some cases 100 °C) at a rate of 1 °C/min. The sample has been tested at frequencies of 0.1, 1, 10 Hz.

2.3. Differential scanning calorimetry
A DuPont differential scanning calorimeter, model 2910, was used to analyzed the thermal properties of PVAAc.

The PVAAc powder was heated first from 25 °C to 150 °C at the rate of 1 °C/min, then quenched and re-heated from 25 °C to 250 °C. In this way performing the first scan it was possible to eliminate volatiles present in the sample that can alterate the value of the glass transition temperature that was calculated esamining the results of the second scan.

3. Results and discussion
Dynamical-mechanical analysis is a technique in which a material is cyclically subjected to repeated small-amplitude strains. The sample, stressed in this way, stores a portion of the imparted energy elastically and dissipates a portion in the form of heat [12]. The quantity E', storage modulus, is a measure of the energy stored elastically, whereas E'', loss modulus, is a measure of the energy lost as heat.

For a viscoelastic material the complex Young's modulus (E^*) is defined as:

$$E^* = E' + iE'' \qquad (1)$$

where the quantity i represents the square root of minus one. Another equation used is:
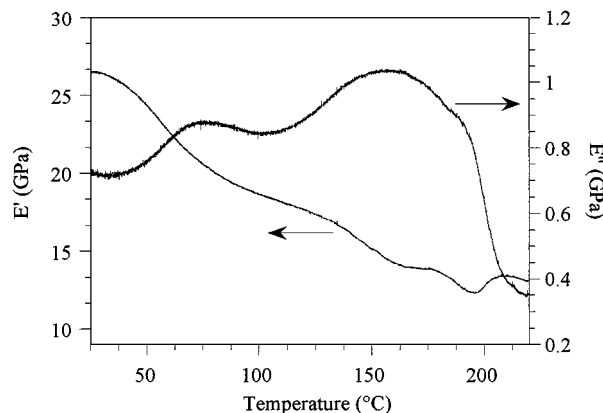
Figure 1 DMA of MDF composite varying temperature from 25 to 250 °C at a heating rate of 1 °C/min and fixing the frequency of the measure at 1 Hz.
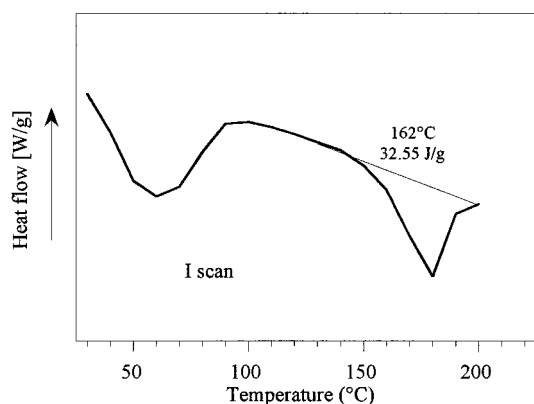

Figure 2 Differential scanning calorimeter analysis of PVAAc Gohsenol KH-17s (I scan).

$$\tan \delta = \frac{E''}{E'} \tag{2}$$

where $\tan \delta$ is called the loss tangent, δ being the angle between the in-phase and out-of-phase components in the cyclic motion.

Fig. 1 shows the result of the dynamical-mechanical analysis fixing the frequency at 1 Hz.

The elastic dynamic modulus (E') curve shows a drop at increasing values of temperature, while the loss factor (E'') curve exhibits two peaks, the first one, not very pronounced at about 60 °C, and the second one, clearly marked, at about 160 °C. The first maximum corresponds to the value of the glass transition temperature of PVAAc as confirmed by data obtained from Differential Scanning Calorimetry (DSC) analysis performed on a PVAAc powder (Figs 2, 3).

The second peak at about 160 °C is due to the melting of the crystalline part of the polymer; infact observing results of the first scan it is evident the presence of an endothermic peak at about 160 °C (corresponding to the melting of the crystalline part) that disappears in the second scan because, after quenching, the polymer has lost its crystalline portion. Dynamical mechanical analysis, in fact, is a good technique to obtain informations about the transitions that occur in a polymer, even if it is not present alone but constitutes the matrix of a composite material. The maxima in the curve of E'' and $\tan \delta$ are often used to measure the T_g [12].
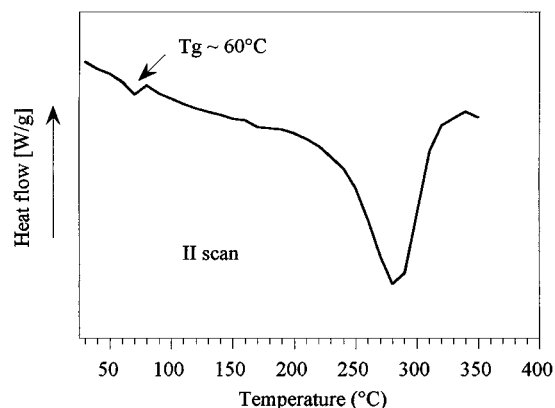

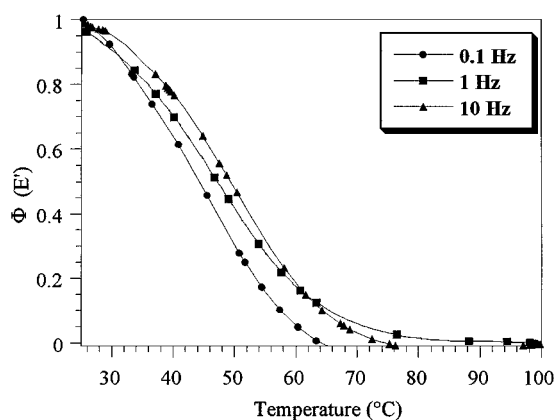*Figure 3* Differential scanning calorimeter analysis of PVAAc Gohsenol KH-17s (II scan).

Figure 4 DMA performed as a function of temperature at various frequencies. ϕ is defined in the text.

Fig. 4 shows the variation of E' at different frequency values varying the temperature from 20 °C to 100 °C. In particular storage modulus data were normalyzed using the following equation:

$$\phi = \frac{E'(T) - E'(T_\infty)}{E'(T_0) - E'(T_\infty)} \tag{3}$$

where the limiting values, i.e. E'_0 and E'_∞, were chosen at $T = 20$ °C and $T = 100$ °C respectively.

It may be seen that, performing the analysis at higher frequency values, the E' curve is shifted towards higher temperatures. In fact for most polymers T_g values are increased about 7 °C for ten fold increase in frequency [12].

The E'' data taken at different frequencies are reported in Fig. 5. Also in this case Equation 3 was used, taking the same temperature range selected for E'. It may be seen that the peak observed at lower temperature is more and more pronounced as the frequency decreases. This is an indication that transitions are more pronounced at lower frequencies while at the same time, the relative peak position shifts towards higher temperatures as the frequency increases.

The broadness of the observed transition is due to different relaxation mechanisms associated with the response of at least two different phases in which the polymer is present in the composite: the bulk polymer and the polymer in the interphase layer.
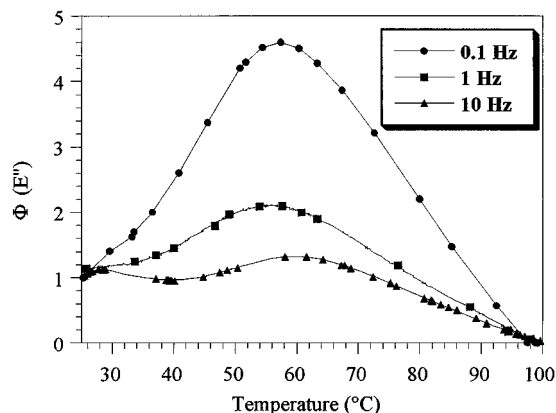
Figure 5 DMA performed as a function of temperature at various frequencies. ϕ is defined in the text.
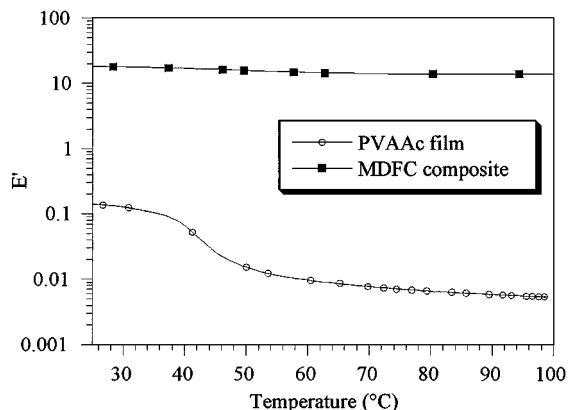

Figure 7 DMA: comparison between the MDF composite and the PVAAc film using a logarithmic scale to plot E'.
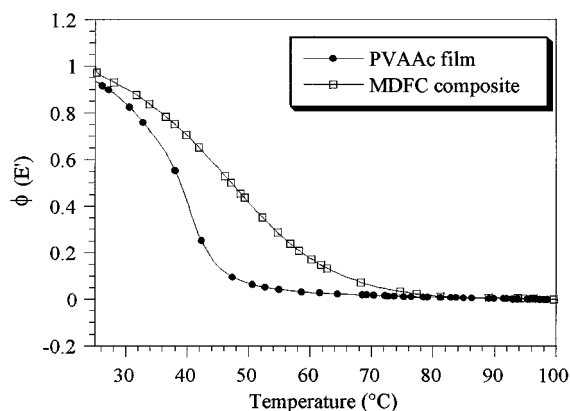

Figure 6 DMA: comparison between MDF composite and PVAAc film.
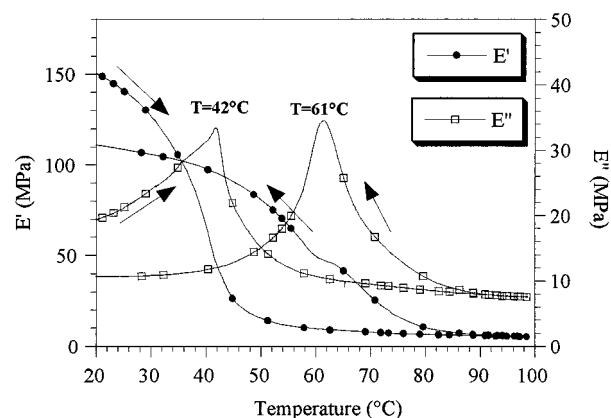

Figure 8 DMA of the PVAAc film at 1 Hz. In a first step the temperature is raised from 20 to 100 °C and then lowered from 100 to 20 °C at rate of 1 °C/min.

The variation of the dynamical-mechanical properties of MDF composite as a function of temperature was compared with those obtained for a PVAAc film. Fig. 6 shows the evolution of E' using Equation 3 both for the PVAAc film and the composite.

The E' curve obtained for PVAAc film shows a clearly marked decrease at increasing values of temperature while the decrease for composite is less pronounced. Such a difference is consistent with the hypothesis that the cement acts as a filler. Again the shift of the transition towards higher temperature is interely related to the "*in-situ*" behaviour of the polymer.

Moreover, it may be noticed that the quantity of water in the composite is lower than that in the plain film, thus E' curve is shifted towards higher values of temperature also because the plasticizing effect of water is accordingly reduced. In fact in the PVAAc film the ratio between water and polymer (w/PVAAc) is 9 while in the composite this value drops to 0.1.

In Fig. 7 are reported the same results of Fig. 6 using the logarithmic scale, as it was done by Russel *et al.* [11]. Reporting the data in this way, it is impossible to observe any drop of E' up to 100 °C for the MDF composite, while, at the same time, the glass transition of PVAAc film is clearly visible.

Further on, the MDF composite and the PVAAc film were both subjected to dynamical mechanical analysis that included complex thermal hystories. The sample were heated (1 °C/min) from 20 to 100 °C and then

cooled (1 °C/min) from 100 to 20 °C. This analysis was performed in order to establish whether the decrease observed for E' was a reversible phenomenon or not. In the case of the PVAAc film, results reported in Fig. 8 show that E' recovers almost completely its original value at room temperature (63%). This is in agreement with the hypothesis that the drop in modulus is due to the glass transition of the polymer, which is typically a reversible phenomenon.

Correspondingly, E'' peaks are located around temperatures were the drop in modulus is observed. However, for the cooling step, the transition occurs at a higher temperature (61 instead of 42 °C). Again, this discrepancy is not surprising for a hydrophilic polymer (like PVAAc) film since heating the film to 100 °C has a drying effect. Subsequently cooled, the sample contains less water, i.e. less plasticizer, and thus undergoes a transition at a higher temperature.

In the case of MDF composite, the same trends are observed (Fig. 9) but E' recovers almost totally (93%) its original value. This can be accounted for by considering that (i) the composite contains less water than the film, and (ii) the water present is strongly bounded.

4. Conclusions

The temperature sensitivity of MDF cements has been investigated utilizing several thermal and mechanical
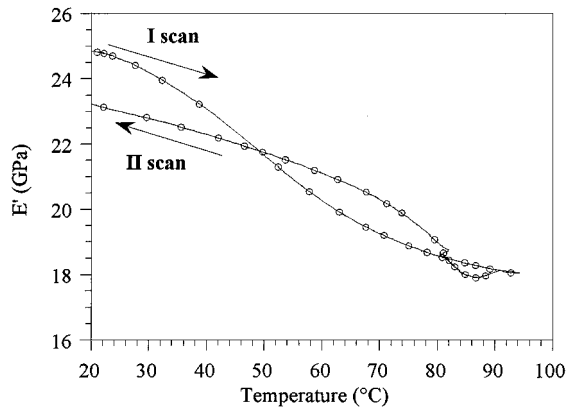
Figure 9 DMA (1 Hz) of MDF cement composite from 20 to 100 °C and then from 100 to 20 °C at a rate of 1 °C/min.

analysis by testing the material from room temperature to 250 °C at different frequencies. The MDF cement-polymer composite studied shows a variation of its properties under increasing temperature conditions typical of those of viscoelastic materials. Contrary to what has been claimed previously [11], this study shows that the MDF composites are sensitive to temperature as far as the mechanical behaviour is concerned. Dynamical mechanical analysis is consistent with the statement that the drop in modulus of MDF composite above room temperature is due to the presence of PVA that shows a typical reversible second order transition (T_g) at ca. 60 °C. The results obtained are in agreement with the picture of a composite in which a polymeric thermoplastic matrix surrounds partially hydrated cement particles. In addition, a deeper dynamical mechanical analysis, highlights a frequency-dependence of mechanical properties of MDF cements that is a typ-ical viscoelastic behaviour of polymer-based composite materials.

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