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Dynamic mechanical thermoanalysis of latexes in cement paste

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Abstract

A new approach is proposed to analyze small amounts of polymer in a cement paste by means of a dynamic mechanical thermoanalyser. The polymer-cement ratio is determined from the drop in the storage modulus E' at the glass transition of the polymer. Different calibration curves are determined by analyzing the viscoelastic behaviour of the polymer in the cement from storage or loss moduli and the dissipation factor tanδ. This technique is very sensitive, which makes it possible to calculate a polymer rate accuracy better than ±5%, even in the case of a very porous material, when the polymer rate is lower than 10% by weight.

Keywords: Thermal analysis; Elastic moduli; Mechanical properties; Cement paste; Polymers

Mechanical properties such as flexural strength and toughness of ordinary portland cement (OPC) and calcium aluminate cement (CAC) can be increased by incorporating a polymer component with the cement. When the rate of polymer is higher than 10%, these materials are termed “macro defect-free” (MDF) cements because they allow the porosity of concrete to be significantly reduced.

The two main MDF systems described in the literature are calcium aluminate cement-polyvinyl alcohol and calcium silicate cement-polyacrylamide. Because of the high amount of polymer, these cements are made by calendering, and then a sheet is compression moulded [1,2]. The high mechanical properties of these cements result from the existence of important interactions between the polymer and the cement, such as chelating metal cations, principally Ca^{2+} and Al^{3+} from the cement. Another way to use polymers to reduce porosity is to impregnate hardened cement pastes (PICP) with them.

To characterise viscoelastic behaviour of the polymer in the cement, dynamic mechanical thermoanalysis (DMTA) was used to measure the dynamic response of MDF or PICP using the main relaxation associated with the glass transition of the polymer. In some cases, a decrease in the glass transition temperature (epoxy) accompanied by a diminution of the relaxation amplitude of the polymer in the cement paste has been observed. Whiting and Kline explain this by a dilution of the polymer in the cementing phase [3,4]. On the other hand, for thermoplastics like poly(methylmethacrylate) (PMMA) and poly(ethylene glycol) (PEG) the presence of the cement paste induces specific interactions between the polymer and the cement that involve an increase in the temperature of the glass transition [4]. The mechanical properties of these composites are very interesting, but given the processing difficulties, these materials are not often employed.

Currently, water-soluble polymers at low rates are preferred as plasticizers to reduce the amount of water and improve the rheology of the paste [5,6]. Concerning concrete with sand, the use of aqueous polymer dispersions (styrene-butadiene and acrylic latexes) reduces the porosity that appears at the interface of the sand and the cement paste [7–9]. But analysis of the polymer in the cement paste primarily concerns its influence on mechanical properties, such as compression and flexural strength, and characterization methods for small amounts of polymer are lacking.

The purpose of this study was to analyse a small quantity of an aqueous polymer dispersion in a cement paste by DMTA. The transitions of the water [10–13] and the relaxations of the aqueous polymer dispersion (Tg) were correlated with the amount of polymer used. In particular, the fact that the relaxation of the polymer at its glass transition temperature produces a storage modulus drop was exploited to determine the real polymer rate.

1. Experimental

1.1. Materials

A commercial cement with a high amount of silica (HTS 52,5 PMES CP2, Lafarge Cement, Paris, France) was mixed

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with 15 wt% of silica fume (MST, SEPR, Le Pontet) in order to reduce the production of portlandite [$Ca(OH)_2$]. To keep the water-cement ratio down to 20% by weight, a superplasticizer (Mapfluid, Mapei, Italy, 2.0 wt% with respect to cement) must be added.

The latex used was a styrene-butadiene polymer emulsion (Rhoximat, Rhodia, France) with a solids content of 50 wt% and a glass transition temperature of 0°C, as measured by a differential scanning calorimeter with a heating rate of 20°C/min.

1.2. Mixing procedure

First, while the cement and the silica fume were mixed for 10 min in a mixer (Attritor, Wiener, Amsterdam, Netherlands), half of the plasticizer and a solution of polymer were prepared to get the right water-cement ratio. This solution was then added to the powders and mixed for 2 min. Finally, the other half of the plasticizer was added to reduce the viscosity of the paste and also was mixed during the 2 min. The paste was then cast in a mold ($100 \times 10 \times 10$ mm^3) covered by a release agent.

1.3. Curing procedure

Since this cement contains less than 3% aluminate, hydration and setting were very slow. Because of this fact, the test bars were unmoulded after 3 days and then allowed to cure. Curing was carried out in water at 90°C for 1 day and without water at 90°C during another day.

The specimens were then stocked in a desiccator for at least two weeks before being tested.

1.4. Dynamic mechanical thermoanalysis

A dynamic mechanical thermoanalyser (RSA II, Rheometrics, Piscataway, NJ, USA) was used to measure the dynamic response of these polymer modified cements. The specimen, which measured $50 \times 10 \times 2$ mm^3, was cut with a diamond cutter and polished without water. It was characterized in a three-point flexure test between -150 and 400°C at a fixed frequency between 1 to 10 Hz, with a heating rate of 2°C/min. The storage modulus E', the loss modulus E'' and loss tangent (dissipation) $\tan\delta = E''/E'$ were plotted vs. temperature.

2. Results and discussion

2.1. Analysis of the reference cement paste

The storage modulus E' and the dissipation factor $\tan\delta$ of the cement paste without polymer were measured by the dynamic mechanical analyser at 3 Hz as a function of the temperature. The graphs are shown in Fig. 1.

Two main transitions stand out, which represent a decrease of the storage modulus associated with an internal friction peak on the $\tan\delta$ curve.

The first transition centered between -100 and -40°C shows a large peak on the $\tan\delta$ curve, with a modulus drop of 5 GPa. This transition, observed by Radjy and Richards in hardened cement pastes (HCP), is associated with the water adsorbed near the solid surface. This "adsorbate" transition also exists in other water-adsorbing microporous materials like wood, silica gel, or bentonite clay and the adsorbate $\tan\delta$ peak height for water-saturated HCP depends on the Brunauer-Emmett-Teller (BET) surface area [10,12].

Contrary to these previous studies, however we observed no "capillary" transition near 0°C that is caused by water freezing or melting in the larger capillary pores [11]. Indeed, since we used a plasticizer and only 20% water instead of 45%, there was no capillary porosity in our cement pastes. Above 100°C there was a large drop in the storage modulus, which stabilized after 220°C. This temperature range corresponds to the dehydration of CSH components

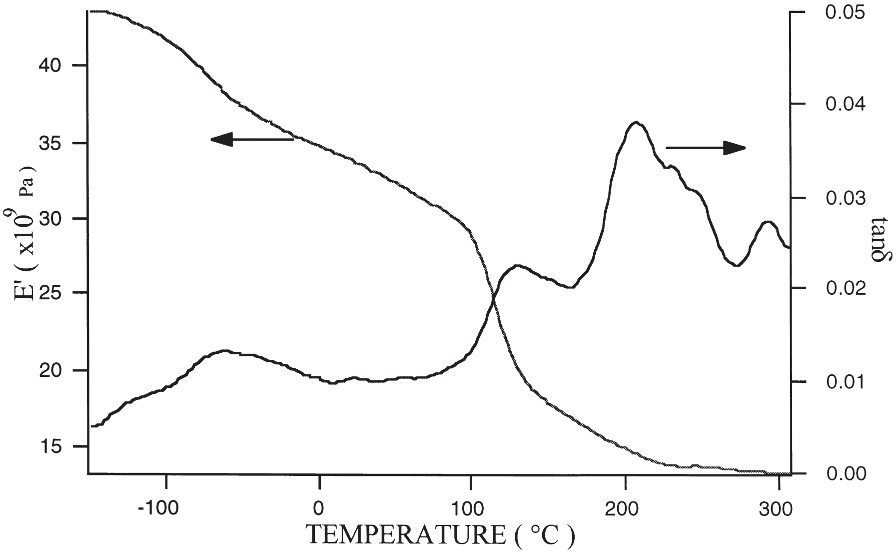

Fig. 1. Storage modulus E' and $\tan\delta$ vs. temperature for a reference cement paste (3 Hz).

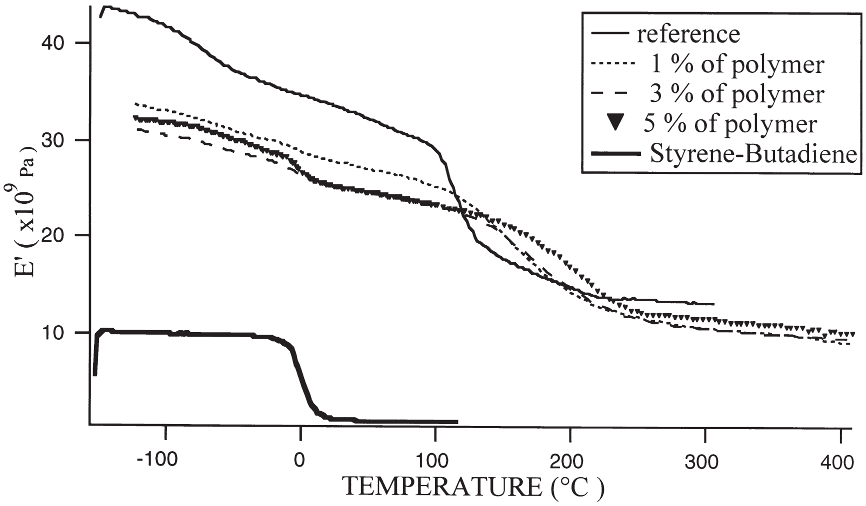

Fig. 2. Storage modulus E' vs. temperature of cement pastes with various amount of polymer (3 Hz).

in cement, which we confirmed with differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) experiments.

2.2. Evidence of the polymer by DMTA

A graph of the storage modulus E' of cement pastes with various amounts of styrene-butadiene emulsion at 3 Hz is shown in Fig. 2 as a function of temperature. Comparing curves of Fig. 2, a new transition appears near 0°C. The amplitude of this relaxation increases with the rate of polymer. Indeed, the analysis by DMTA at 3 Hz of a thin plate of copper covered by the latex gives the glass transition temperature of the polymer at 0°C (“styrene-butadiene” in Fig. 2), as in DSC experiments. So, the new drop in modulus in the cement paste reinforced with the emulsion is really generated by the presence of the polymer. But there is no shift of the glass transition to higher temperatures because the polymer-cement adhesion is not sufficient.

Moreover, the resolution of this technique is greater as the frequency goes down. 3 Hz was therefore used in further experiments to get the best resolution in the shortest time.

2.3. Quantitative determination of polymer rate

2.3.1. Study of the drop in E'

We also noticed that the storage modulus of the polymer-modified cement paste was much smaller than the modulus of the reference cement paste (Fig. 2), because the emulsion involves an increase in the viscosity of the cement paste during mixing, which causes porosity to rise. Indeed, flexural strength and compressive strength are modified by porosity, which can, for instance, result from a high amount of water [14,15]. Fig. 3 confirms that the flexural modulus also

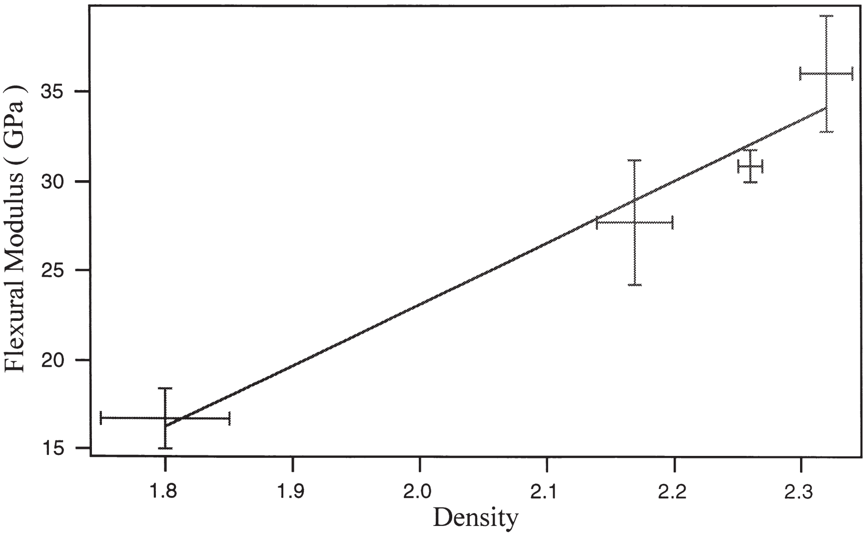

Fig. 3. Flexural modulus of reference cement pastes as a function of density.

Table 1
Influence of normalization with 3% polymer

Specimens	Density	Δ*E*′ (0°C) (GPa)	*E*′ (300°C) (GPa)	Δ *E*′ (0°C)/*E*′ (300°C)
1	2.18	1.50	12.5	0.120
2	2.16	1.40	11.4	0.122
3	2.14	1.35	10.7	0.126
4	2.13	1.30	10.6	0.123
Average	2.15 (± 1%)	1.39 (± 6%)	11.3 (± 8%)	0.123 (± 2%)

depends on porosity, which determines the density of the material. To minimize the effects of the porosity and the geometry of the test bars, when specific mass is greater than 1.8 g/cm^3, the DMTA experiments can be normalized with respect to the modulus at a reference temperature. Indeed, the influence of the porosity on the modulus can be approximated by the formula shown in Eq. (1):

$$Ep(T) = (1-p)\cdot E(T) \tag{1}$$

where *Ep*(*T*) = composite modulus with *p*% porosity; *E*(*T*) = composite modulus without porosity; and *p* = porosity.

So if we divide the temperature-storage modulus by the modulus at a reference temperature, the influence of the porosity is eliminated. The temperature chosen as a reference is 300°C because above 220°C the modulus is constant and the polymer has no effect [see Eq. (2)]:

$$Er(T) = Ep(T)/Ep(Tref) = E(T)/E(Tref) \tag{2}$$

where *Er*(*T*) = relative modulus; *Ep*(*T*) = composite modulus with *p*% of porosity; *E*(*T*) = composite modulus without porosity; and *Tref* = reference temperature (300°C).

In Table 1, experiments with 3% of polymer but different porosities are presented. It was found that normalization reduces uncertainty to ±2%, whereas the drop in the modulus ($\Delta E'$(Tg)) presents a difference of ±6% before normalization. In the same way, the error was found to be greater (±20%) with 1% of styrene-butadiene, because it is more difficult to determine the exact drop in the modulus with a small amount of polymer (Fig. 4).

The influence of the polymer amount on the drop in the normalized storage modulus is presented in Fig. 5. As long as the polymer-cement ratio is less than 10% by weight (i.e., the volume polymer rate is less than 14%), the variation of the drop in the normalized storage modulus can be supposed to be linear. Curve linearity is better if the volume polymer rate is used instead of the polymer-cement weight ratio, because the modulus of composite materials depends on the volume of the different phases. In this way we get a calibration curve that reveals the real rate of styrene-butadiene emulsion in a polymer-reinforced cement paste.

Indeed, the elastic storage modulus E' is a measure of stiffness and is proportional to the amount of energy stored in the material per cycle. As the polymer employed is totally amorphous and the glass transition arises only from the relaxation of the polymer chain segments of this phase, the drop in the modulus is directly associated with the amount of polymer. Dynamic mechanical thermoanalysis is a very sensitive engineering tool to characterize the glass transition temperature of a small amount of latexes in cement paste using the drop in the normalized storage modulus E'.

2.3.2. Study of E″ *and tanδ*

The DMTA technique also gives the variation in the loss modulus *E*″, which characterizes the viscous component of the moduli of the materials under study, and provides the variation in the loss tangent tanδ, which quantifies the phase displacement between the given strain and the measured stress.

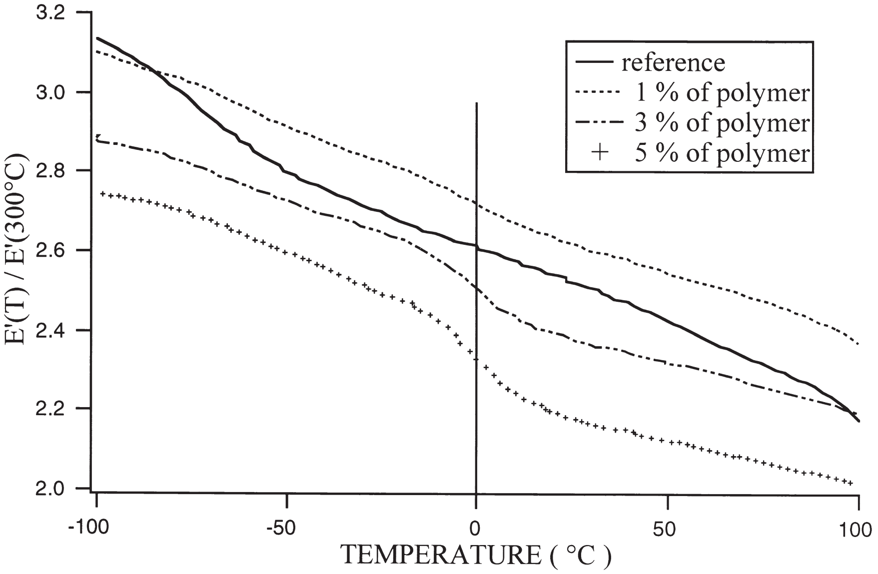

Fig. 4. Normalized storage modulus *E*′ vs. temperature of cement pastes with various amount of polymer (3 Hz).

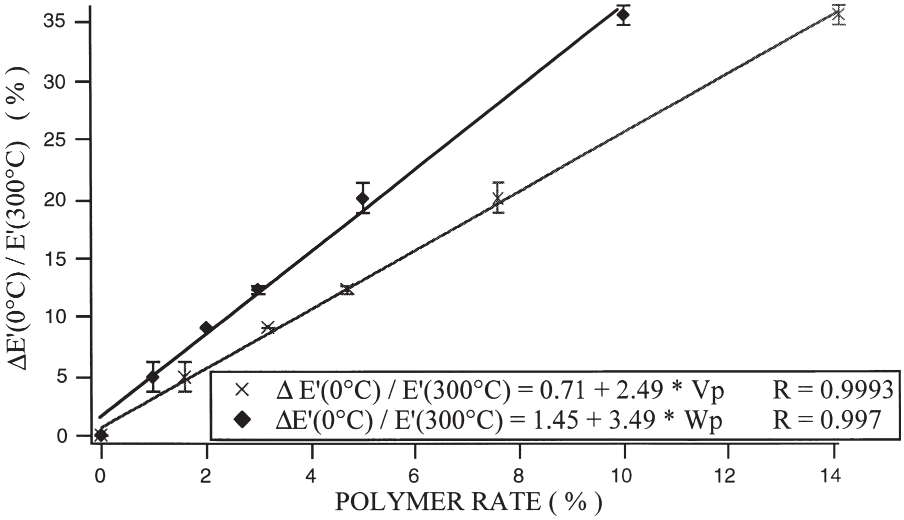

Fig. 5. Normalized storage modulus drop as a function of polymer rate (3 Hz).

The influence of 5% of polymer on these two parameters is shown in the curves of Fig. 6.

First, we noticed that the phase angle was lower than those observed in pure polymer studies. This was due to the fact that cements like ceramics are very rigid materials and the viscous contribution is consequently negligible. Indeed, loss modulus *E*″ represents less than 1% of the storage modulus *E*′. Nevertheless, at the glass transition temperature of the styrene-butadiene copolymer, a high peak is observed on these curves.

The advantage of the tanδ curve is that this parameter is less dependent than the moduli on the geometry of the specimens. Thus, it was not necessary to normalize it. But, as can be seen in Fig. 6, the problem with this parameter is defining the baseline. The amplitude of the peak [height (Δtanδ) and area (Sδ)] must be proportional to the number of entities that relax, and the determination of the baseline fixes the precision of the technique. We calculated that the error from measuring the area and the height of tanδ peak was less than 10%, which is still twice as high as the error calculated with the drop in the storage modulus *E*′. The influence of the volume polymer ratio on the area and the height of tanδ is shown in Fig. 7. We found the area and the height of the tanδ peak to be proportional to the amount of the styrene-butadiene emulsion. This gives two calibration curves, because these parameters are proportional to the amount of energy dissipated per cycle. The analysis of the loss modulus *E*″ (Fig. 8) gives two more calibration curves, but with somewhat lower accuracy (±15%), using the amplitude of the peak (Δ*E*″) and the area under it (*SE*″).

Moreover, as in studies of polymer blends, the study of MDF cements has shown that this technique can be used to

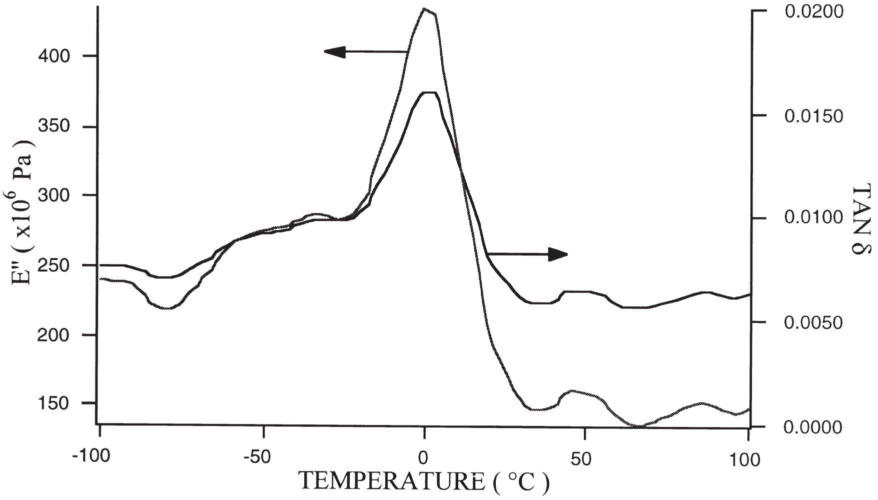

Fig. 6. Loss modulus *E*″ and loss tangent tanδ vs. temperature of a cement paste with 5% polymer (3 Hz).

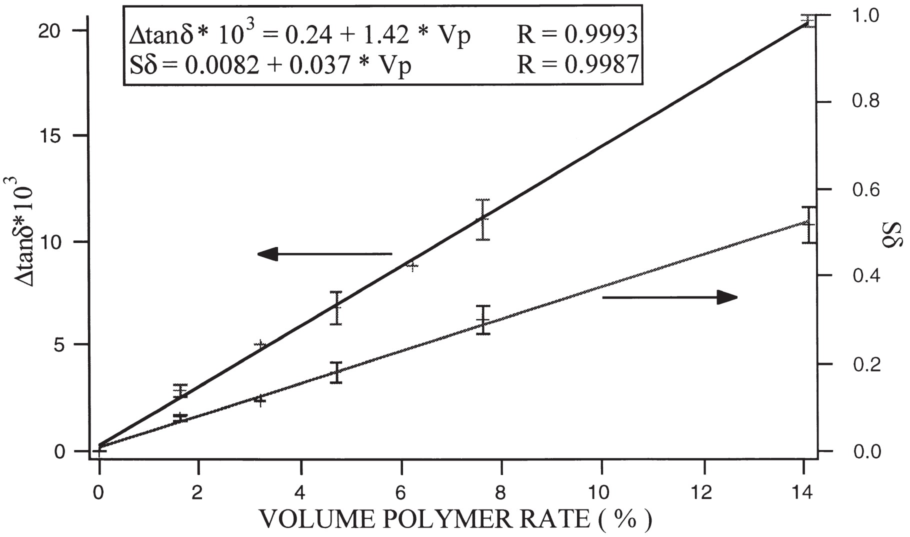

Fig. 7. Influence of volume polymer rate on loss tangent tanδ (3 Hz).

analyse the interactions between the polymer and the cement by looking at the displacement of the glass transition temperature [3,4]. With styrene-butadiene dispersion, polymer-cement adhesion is insufficient to raise the glass transition to higher temperatures. But with acrylic or modified styrene-butadiene dispersions, this technique should be of great interest, if the polymer transition is between −30 to 80°C (i.e., in a temperature range where there is no water relaxation in order to avoid any problem of peak deconvolution).

3. Conclusions

The DMTA technique has been shown to be highly sensitive to detection of the glass transition of a small amount of polymer present in a hardened cement paste. In this study, the analysis of the dynamic modulus of the polymer-modified cement paste allowed a correlation of the fraction of polymer with different parameters, such as the drop in the storage modulus *E′*, the amplitude of the loss modulus *E″* and the dissipation factor tanδ. The analysis of the drop in the storage modulus *E′* seems easier than using tanδ or *E″*, because there is no problem with the line, even if the curves must be normalized to reduce the influence of the porosity and geometry. Moreover, the study of *E′* yields the best resolution with an accuracy of 5%.

Acknowledgments

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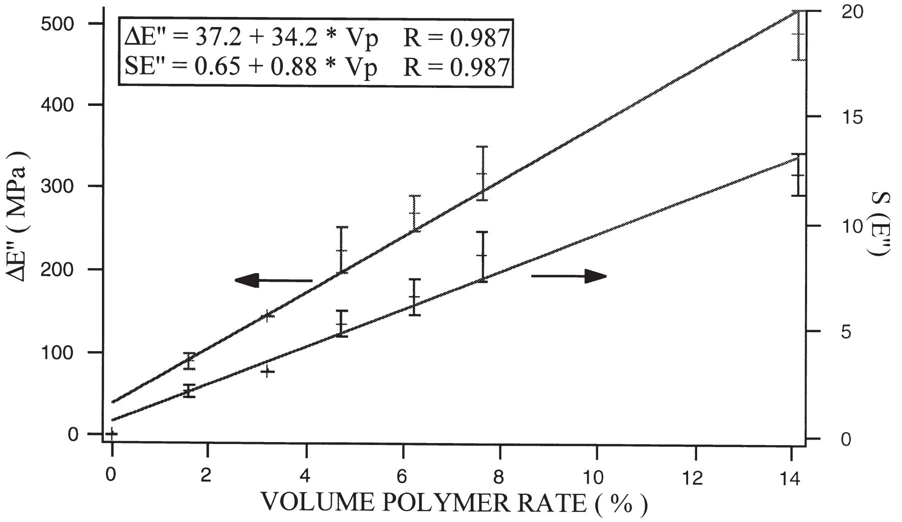

Fig. 8. Influence of volume polymer rate on loss modulus *E″* (3 Hz).

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