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Physico-chemical effects of hydrothermal ageing of sheet molding compounds between −60 and 250°C

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The term Sheet Molding Compound (SMC) is applied to composites formulated with unsaturated polyester resin (UPE), glass fibers as reinforcement and other additives: thickening agent, low profile agent, inorganic filler ($CaCO_3$), etc. The understanding of the hydrothermal ageing effects of this material is an important factor for its improvement, because this heterogeneous material very easily deteriorates in the presence of humidity. The effect of this kind of ageing is analysed using dynamic mechanical thermal analysis. Our mechanical spectrometry results, show that the hydrothermal ageing produces two types of effects in our model class A SMC samples: firstly, some partially reversible physical effects associated, on the one hand, with the hydrophilisation of the UPE network and, on the other, with the thickening phenomenon (formation of coordinative bonds between the carboxyl groups of the ester linkages and the unsaturated Mg ions). Secondly, some non-reversible chemical modifications due to the partial hydrolysis of the low profile agent (a small amount of PVAc is transformed to PVA and to acetic acid). *© 2001 Kluwer Academic Publishers*

1. Introduction

The SMC is a composite formulated with unsaturated polyester resin (UPE), random glass fiber (25 to 50 mm) and other additives: low-profile agent (PVAc), inorganic filler ($CaCO_3$), thickening agent (MgO), catalyst and mold release agent [1]. This material is widely used in the automotive industry (exterior panels, inner panels, etc.) and the building industry (external panels, doors, etc.), because this composite shows the following advantages: dimensional stability, corrosion and chemical resistance, good thermal stability, low weight, high strength and stiffness, high impact behaviour, surface quality and lower price [2]. Nevertheless, SMCs have a very complex morphology and contain porosity and microvoids as a consequence of the process and shrinkage compensation and they very easily deteriorate in the presence of humidity [3–6]. Water is known to be able to penetrate into the SMC and be one of the most common reasons for ageing. It leads to physico-chemical modifications of the composite, which are observed in the morphology (rearrangement of porosity and microvoids) and in the molecular mobility (modifications on physico-chemical bonds). Indeed, the molecular mobility can be taken as a sensor for the structural evolution at the molecular scale. Thus, the study of water uptake not only allows us to evaluate the SMC's durability, but also to investigate their starting structure.

The objective of this work is the measurement of the influence of hydrothermal ageing on the different molecular relaxations of a model class A SMC, provided by IVECO.

The evolution of tan δ and the real elastic modulus, in the temperature range between −60 and 250°C, for several frequencies is studied by dynamic mechanical thermal analysis (DMTA). The results obtained allow us to distinguish the physical changes which are partially reversible from the non-reversible chemical modifications and to measure the true effect of the hydrothermal ageing on the SMC.

2. Experimental procedure

2.1. Samples and sample preparation

In this study, the model class A SMC is formulated with: 15.36% of UPE (65% in styrene), 12.42% low profile

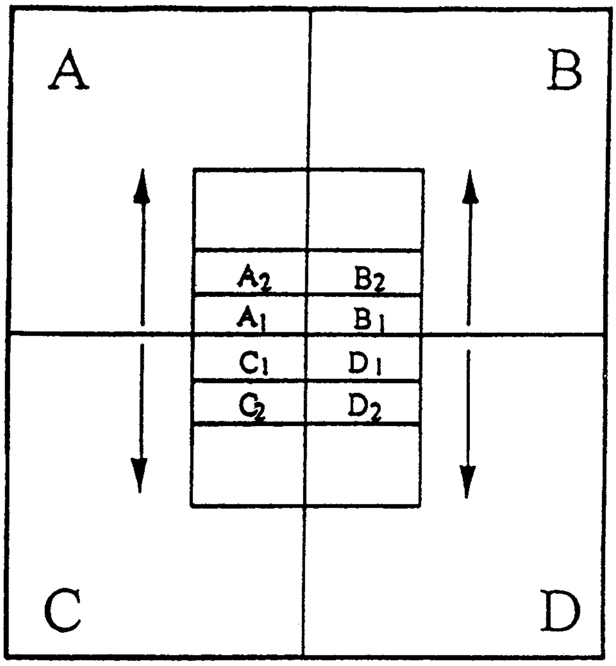

Figure 1 Schematic codification of samples analysed using Dynamic mechanical thermal analysis.

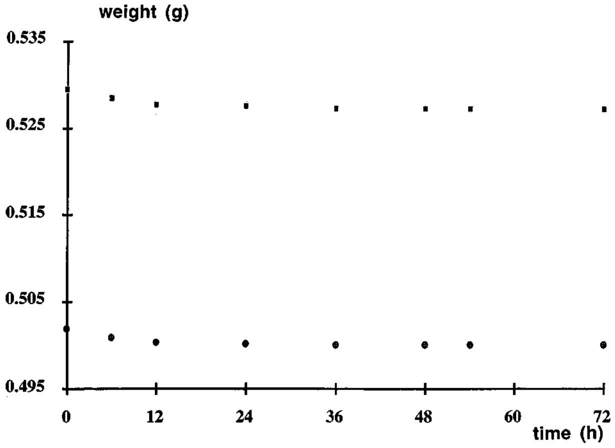

Figure 2 Samples A (▣) and B (◩), dried for 3 days between 68 and 72°C, under vacuum (1 Pa), until constant weight.

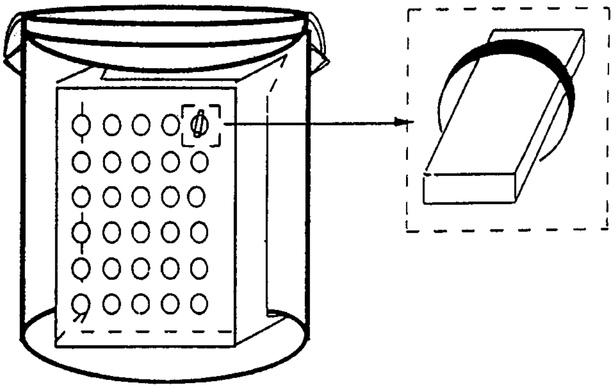

Figure 3 Schematic representation of hydrothermal ageing samples container. Water sorption performed isothermally at 70°C.

agent (PVAc) (40% in styrene), 67.93% $CaCO_3$, 2.36% styrene, 1.93% other additives and 27–28% glass fibers. This SMC provided by IVECO is molded at 150°C under 10 MPa in a conventional press with a molding time of 1 min/mm of thickness. This material is cut in the form of plates (250 × 200 mm, thickness 3 mm), using a diamond saw with water. Next, it is dried under vacuum (1 Pa) at 50°C for three days and stored in closed vessels with silica gel. Due to the heterogeneity in this material, the plate is divided in four blocks A, B, C and D and the samples are cut from the central part [6, 7], as near as possible to each other, in order to minimize the scattering of results (Fig. 1). After cutting, the samples are polished until constant dimensions are obtained ($45 \pm 1 \times 3{,}30 \pm 0{,}05$ mm, thickness $1{,}80 \times 0{,}02$ mm) [8–10], also for reasons of reproducibility of the results. We used a "different sample" for each ageing time and for each reversibility analysis test, about 40 samples (10 samples from each block). The 40 samples are preconditioned by drying for 3 days between 68 and 72°C under vacuum (1 Pa), until they become constant in weight (Fig. 2).

This procedure allows us to eliminate the water absorbed by the sample during the cutting and to obtain "samples" with a behaviour very homogeneous. They are divided into 3 sets: a first set of 4 samples are taken as "reference samples" (a sample from each block), a second set of 15 samples for the hydrothermal ageing test, as aged samples and a third set of 15 samples for the reversibility analysis test, as reversible samples.

2.2. Hydrothermal ageing and reversibility analysis conditions

After preconditioning, the set of 15 samples taken as aged samples, were put in distilled water and placed in thermostatted conditions for hydrothermal ageing. Water sorption was performed isothermally at 70°C. Our hydrothermal ageing procedure is similar to the procedure described by Camino *et al.* [11] and Bigliani *et al.* [12], except that we used a different container (Fig. 3). Our container allows us to ensure that the ageing and the drying on all samples are homogeneous (each whole sample is in contact with the environment). Only some experiments will be described in detail: on samples aged for a few hours (short times), two weeks (middle times) and more than two months (long times). The other experiments made can be easily understood from the analysis of these experiments [13].

The set of 15 samples taken as reversible samples are aged under the same experimental conditions mentioned before and for the same interval of ageing times. After ageing, the samples were dried for 3 days between 68 and 72°C under vacuum (1 Pa), until a constant weight was obtained.

2.3. Dynamic mechanical thermal analysis

Dynamic mechanical measurements were performed using a DMTA MKIII- Rheometrics. The principle is to apply a sinusoidal load on the sample in order to measure the real modulus (E') and tan δ (damping factor). The real (E') and imaginary (E'') moduli represent the elastic and viscous behaviour of the sample, respectively. Their ratio E''/E' defines the loss tan δ or damping factor. Tan δ, E' and E'' are obtained as a function of temperature for the frequencies used (isochronal mode) or as a function of frequency for a fixed temperature (isothermal mode). We determined tan δ, E' and E'' for the 3 sets of samples. They were tested in three-points-bending with a fixed displacement of ±16 mm, in isochronal mode at four frequencies: 1, 3, 5 and 10 Hz with a heating rate of 1°C/min and temperature range between −60 and 250°C. Liquid nitrogen was used to perform low temperature analysis. The flow of nitrogen was maintained until ambient temperatures in order to keep a "homogeneous atmosphere" during the analysis.

3. Results and discussion

3.1. Hydrothermal ageing

Unless otherwise indicated, the exposed DMTA results refer to 1 Hz: Figs 4 to 6, show the curves of tan δ versus temperature of the "reference sample" and the samples aged 1, 4, 400 and 1760 h. In Fig. 4, "reference sample" shows 3 peaks: a very slight shoulder around 25°C [14], wich is possibly associated with a metallic complex, formed between the MgO and the carboxylic groups of the ester linkages [14], a big peak around 50°C, due to the main molecular relaxation of the low profile agent (PVAc) [15, 16] and a broad peak above 150°C, corresponding to the principal relaxation of the UPE network. The shape for the sample aged 1 h is quite different, as the shoulder around 25°C is more marked, and the peak around 50°C is enormously decreased. It is possible to explain in terms of "competition" between the thickening phenomenon (water can be forming coordinative bonds with the carboxyl groups of ester linkages and with the unsaturated Mg ions) (Fig. 7) [17–20] and the hydrolysis of the low profile agent (a small amount of PVAc is transformed to PVA and to acetic acid) [11, 21, 22]. The slight diminution of the level of the broad tan δ peak above 150°C could be associated with the hydrophilisation of the matrix, as a consequence of swelling and plasticization phenomena due to water sorption through microvoids [11, 21]. In the sample aged for 4 h (Fig. 5), the shoulder around 25°C is much more marked, the peak around 50°C is a little decreased and the tan δ peak above 150°C remains. For instance, this behaviour could indicate that the thickening phenomenon is more easily developed than the hydrolysis of PVAc and than the hydrophilisation of the UPE network. Fig. 6 shows the curves of samples aged 400 and 1760 h. They have a different shape, as there are 2 peaks in the low temperature

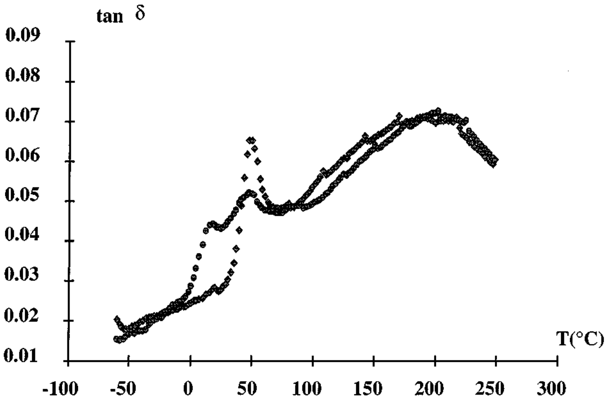

Figure 4 Tan δ versus temperature of the "reference sample" (◆) and the 1 h aged sample (●). Isochronal mode, frequency of 1 Hz and heating rate of 1°C/min.

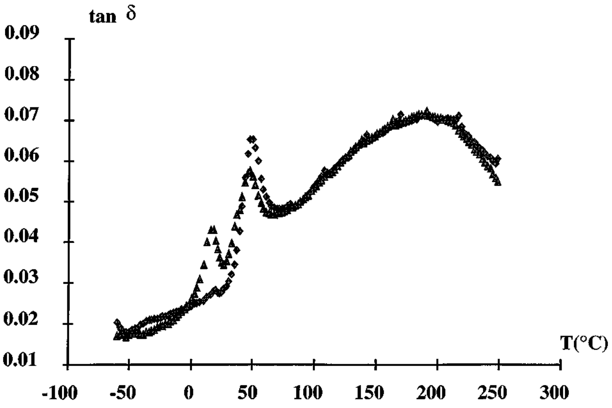

Figure 5 Tan δ versus temperature of the "reference sample" (◆) and the 4 h aged sample (▲). Isochronal mode, frequency of 1 Hz and heating rate of 1°C/min.

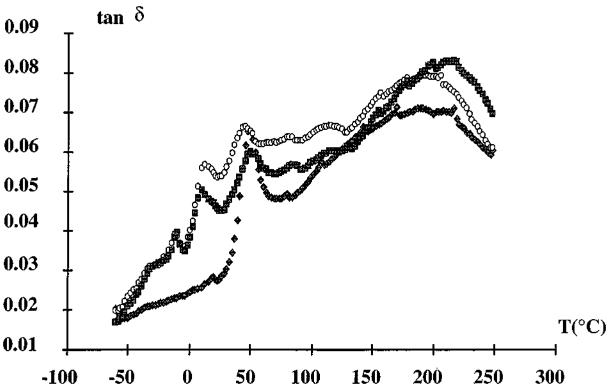

Figure 6 Tan δ versus temperature of the "reference sample" (◆) and the samples aged 400 h (○) and 1760 h (■). Isocronal mode, frequency of 1 Hz and heating rate of 1°C/min.

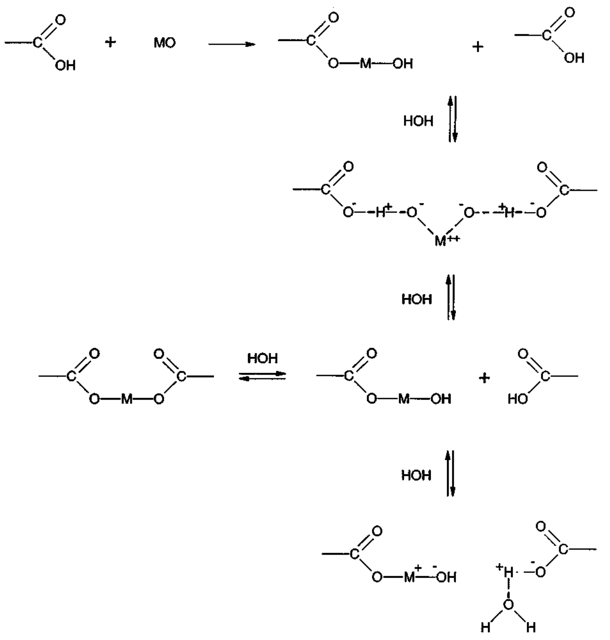

Figure 7 Proposed mechanism of thickening reaction for unsaturated polyester.

zone: a slight shoulder around −30°C, associated with the styrene (rotations of phenylene groups) [23] and, another peak around −5°C, due to secondary relaxation of PVAc [15]. These molecular relaxations are due to local movements (lateral rotation of groups) [24]. Around 80°C, secondary relaxation of the UPE network is observed as a light shoulder. This molecular movement is interpreted in terms of rotation of chain segments (some units of monomers) [24]. The manifestation of all these molecular relaxations types, could be associated with a "plasticization effect" of the material, a result of the augmentation of the local molecular movements, in which the water plays the role of lubricant. In the 400 h aged sample, we observe a significant augmentation of tan δ for a temperature range between 25°C and 175°C. This observation could allows us to think that the hydrolysis of PVAc has a larger influence on the thickening phenomenon [5] and on the hydrophilisation of the UPE network. The PVA and the acetic acid hydrolysis products of PVAc, play a role important in this process of hydrophilisation [11]. On the other hand, in the Fig. 7 is showed the mechanism of thickening proposed by several authors The formation of coordinative bonds have been reported between the Mg ions and the carboxyl groups of ester linkages in the presence of water. This reaction can be partially reversible, if water is removed. Nevertheless, the thickening phenomenon is not well understood yet.

The DMTA also allows us to follow the evolution of the elastic modulus, which complements the results obtained from the curves of tan δ. Figs 8 to 10 show the elastic modulus versus temperature of the "reference sample" and samples aged at 1, 4, 400 and 1760 h. In Fig. 8, the 1 h aged sample shows a remarkable diminution of this parameter. This behaviour allows to confirm that swelling and plasticization, associated with the hydrophilisation of the UPE network begins at short times. For the sample aged 4 h (Fig. 9), the diminution is smaller than the 1 h aged sample. For instance, this observation indicates that the hydrothermal ageing produces: on the one hand, a reinforcement effect on the morphology of the material [6] (modification of ratio and size of microvoids) and on the other, the presence of the thickening phenomenon. Fig. 10 shows the curves of the samples aged 400 and 1760 h. The elastic modulus in the temperature range between −60 and 0°C shows a significant augmentation. It could be explained in terms of the reinforcement effect in relation to ageing times, as a consequence the morphology of microvoids is more modified (ratio and size of microvoids decrease), when the water takes the freezer state. The continuous and important diminution of this parameter observed in the 400 h aged sample, allows us to determine the influence of the hydrolysis of PVAc on the hydrophilisation of UPE network and on the thickening phenomenon.

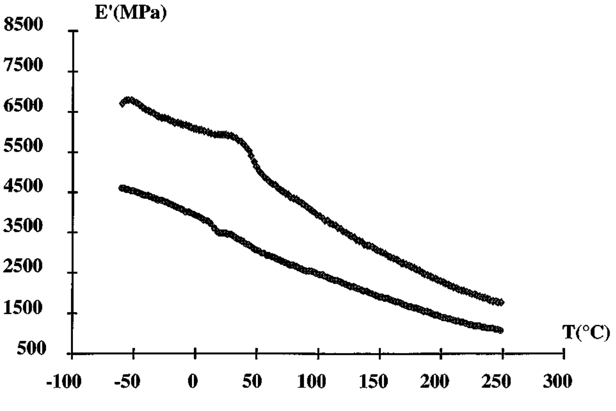

Figure 8 The elastic modulus versus temperature of the "reference sample" (◈) and the 1 h aged sample (◉). Isocronal mode, frequency of 1 Hz and heating rate of 1°C/min.

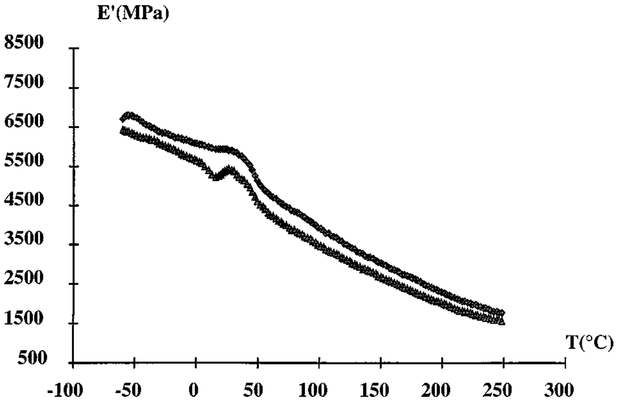

Figure 9 The elastic modulus versus temperature of the "reference sample" (◈) and the 4 h aged sample (▲). Isocronal mode, frequency of 1 Hz and heating rate of 1°C/min.

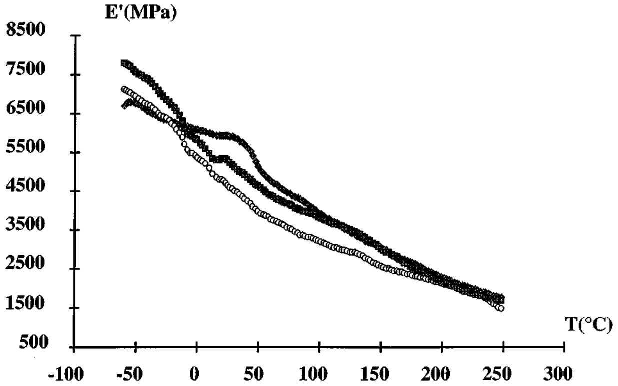

Figure 10 The elastic modulus versus temperature of the "reference sample" (◈) and the samples aged 400 h (◻) and 1760 h (■). Isochronal mode, frequency of 1 Hz and heating rate of 1°C/min.

3.2. Reversibility analysis

We used this procedure to distinguish the physical effects of the hydrophilisation of the matrix and the thickening phenomenon from the chemical modifications due to the hydrolysis of PVAc. Figs 11 to 16 show the evolution of tan δ and the elastic modulus versus temperature for the "reference sample" and the 1, 4, 400 and 1760 h reversible samples. In Fig. 11, the shape of the curves for the "reference sample" and 1 h reversible sample are similar. The slight decrease of tan δ, for the 1 h reversible sample, could confirm that the hydrophilisation of matrix and the "competition" between the thickening phenomenon and the hydrolysis of PVAC, begins at short times. Tan δ for the 4 h reversible sample (Fig. 12) shows an important increase, this discrepancy

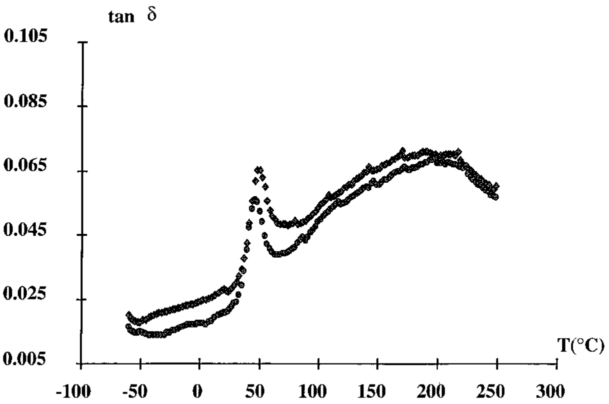

Figure 11 Tan δ versus temperature of the "reference sample" (◈) and the 1 h reversible sample (◪). Isochronal mode, frequency of 1 Hz and heating rate of 1°C/min.

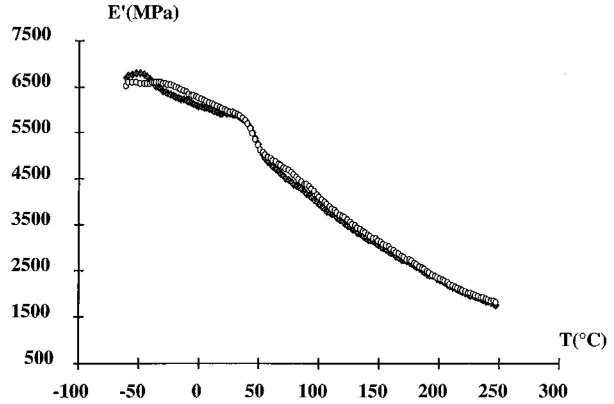

Figure 14 The elastic modulus versus temperature of the "reference sample" (◈) and the 1 h (○) reversible sample. Isochronal mode, frequency of 1 Hz and heating rate of 1°C/min.

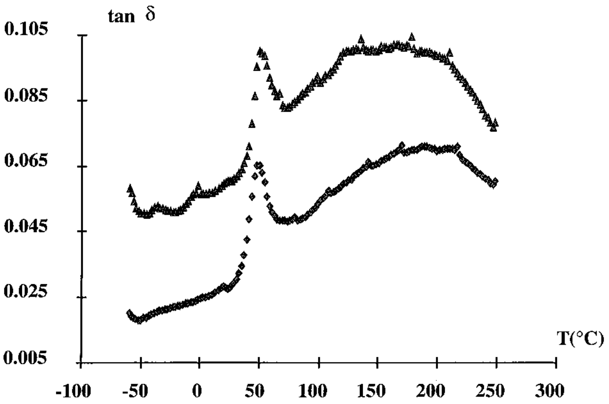

Figure 12 Tan δ versus temperature of the "reference sample" (◈) and the 4 h reversible sample (▲). Isochronal mode, frequency of 1 Hz and heating rate of 1°C/min.

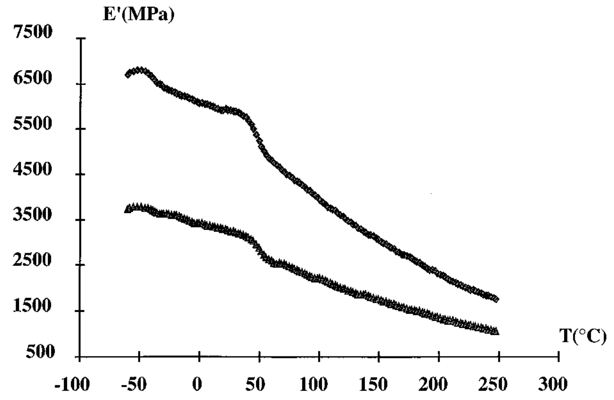

Figure 15 The elastic modulus versus temperature of the "reference sample" (◈) and the 4 h reversible sample (▲). Isochronal mode, frequency of 1 Hz and heating rate of 1°C/min.

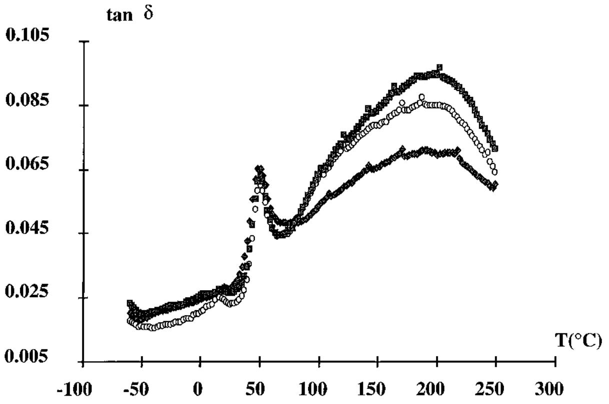

Figure 13 Tan δ versus temperature of the "reference sample" (◈) and the 400 h (○) and 1760 h (■) reversible samples. Isochronal mode, frequency of 1 Hz and heating rate of 1°C/min.

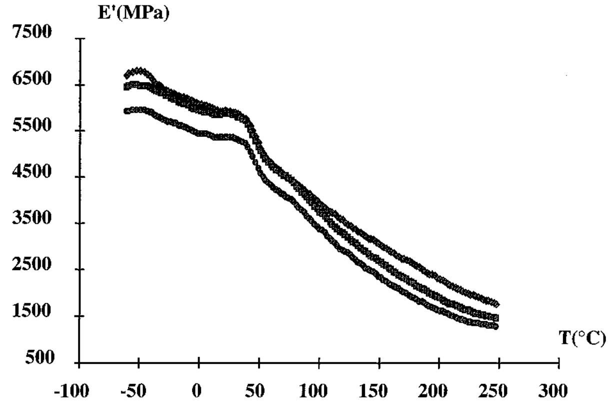

Figure 16 The elastic modulus versus temperature of the "reference sample" (◈) and the 400 h (◪) and 1760 h (■) reversible samples. Isochronal mode, frequency of 1 Hz and heating rate of 1°C/min.

led us to think of a possible heterogeneity in the model class A SMC composition. We have thus determined the percentages of inorganic filler ($CaCO_3$) and glass fiber for the "reference sample" and the aged samples (Table I), using the burning loss test for Glass fiber reinforced polymers (NF T 57-518, Octobre 1987). In comparing the percentages obtained of $CaCO_3$ and glass fiber between the "reference sample" and the aged samples, we can conclude that the material is homogeneous. This behaviour could confirm that the thickening phenomenon is the more remarkable physical effect. In Fig. 13, the peaks in the low temperature zone of the 400 and 1760 h reversible samples disappear, so the physical effects are mainly reversible, since the curve recovers the typical shape when the water is removed. This observation confirms the "plasticization effect" of water on the local movements. The thickening phenomenon is partially reversible, in that the peak is observed at the same temperature, with a slight lowering of tan δ. This result allows us to apply the mechanism of thickening

TABLE I Percentages of $CaCO_3$ and glass fiber. The burning loss test for glass fiber reinforced polymers (NF T 57-518, Octobre 1987)

Sample	Ageing	$CaCO_3$	Glass fibres
	(hr)	(%)	(%)
A17	Non	56.4	26.8
B1	Non	56.6	27.2
C15	Non	55.8	27.7
D16	Non	55.9	27.1
C14	1	56.7	26.9
D4	2	55.9	28.2
A16	3	56.1	27.8
B13	4	55.8	28.5
B15	8	56.7	27.0
C9	12	56.0	27.8
D13	24	56.1	27.5
A1	48	56.1	28.0
A8	400	56.2	27.8
D8	472	56.6	27.1
B8	736	55.6	28.7
C6	952	55.7	28.0
B10	1760	55.6	27.7

reaction refered in to Fig. 7. In addition, the thickening phenomenon has been observed for the first time in this kind of composite. A slight lowering of tan δ around 50°C, indicates some non-reversible chemical modification associated with a partial hydrolysis of PVAc [11, 12]. The continuous and important augmentation of tan δ between 80 and 150°C, allows us to confirm that the ratio of hydrophilisation of the matrix is a function of the hydrolysis of PVAc. In the case of the elastic modulus, the shape of the curves for the "reference sample" and 1 h reversible sample (Fig. 14) is similar. This result confirms that at short times, swelling and plasticization associated with the hydrophilisation of the UPE network are reversible, when the water is removed. With the remarkable diminution of the elastic modulus, observed for the 4 h reversible sample (Fig. 15), we could determine that the hydrophilisation of the matrix is directly influenced by the start of the "competition" between the thickening phenomenon and the hydrolysis of PVAc.

The elastic modulus of the "reference sample" and the 400 and 1760 h reversible samples are presented in Fig. 16. A slight diminution of this parameter in the low temperature zone between −60 and 0°C, shows that the reinforcement effect disappears with departure of water. This observation explains the physical effect in terms of partial reversibility.

The significant diminution of this parameter for the 400 h reversible sample, allows us to confirm that the hydrophilisation of the matrix and the thickening phenomenon are directly influenced by the hydrolysis of PVAc.

4. Conclusion

According to the results obtained, we can conclude that the hydrothermal ageing produces two types of effects on the model class A SMC:

Physical effects of a reversible nature and non-reversible chemical modifications. The physical effects partially reversible at short times, are associated with the hydrophilisation of the UPE network and with the thickening phenomenon as a consequence of coordinative bond formation between the carboxyl groups of the ester linkages and the unsaturated Mg ions. At intermediate times, in the low temperature zone between −60 and 0°C, these effects are associated with local movements (rotation of lateral groups and rotation of chain segments) and with the reinforcement effect, a result of the morphological modification of the ratio and size of microvoids, when water takes the freezer state.

The non-reversible chemical modification associated with a partial hydrolysis of low profile agent is observed at intermediate times, due that a small amount of PVAc is transformed to PVA and to acetic acid.

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