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The effect of boiling water on dynamic mechanical properties of composites

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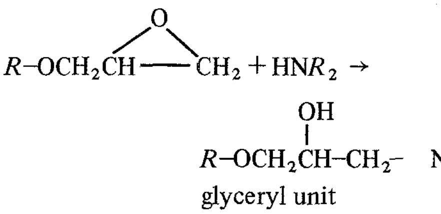
The dynamic mechanical properties of an amine-cured epoxy resin, filled with a range of fillers including glass, carbon, aramid fibres and glass beads, have been determined on a torsion pendulum. The effects of fibre content, orientation and surface treatment on the beta-relaxation near − 50° C at 1 Hz have been studied. For carbon and aramid fibre-filled systems, the maximum value of the loss factor appears to be proportional to the volume-fraction of resin present; however, for glass-filled systems, the observed loss is slightly larger than expected. This difference is not dependent on surface treatment. Composite samples were exposed to boiling water and the dynamic properties determined after periods of immersion of up to 500 h. The change in loss properties may be explained in terms of the formation of a new loss peak near − 30° C. The rate of formation of this loss peak is increased with increasing fibre content and is dependent on the fibre present. It is suggested that this may be caused by the formation of a distinguishable species at the fibre–resin interface formed during the degraditive process. The original dynamic properties of all the systems were recovered on drying the specimens. When systems containing cleaned glass beads are exposed to boiling water, more complex changes are observed. A peak near − 8° C appears initially, but this appears to change to a peak near − 30° C, similar to that observed for fibre-filled systems on prolonged exposure.

1. Introduction

Many studies of the dynamic mechanical properties of amine-cured epoxy resins have been reported [1–7]. A relaxation has been observed near − 50° C at 1 Hz and this is usually referred to as the beta relaxation [1]. It has been shown that this relaxation is related to the presence of the glyceryl unit formed by reaction of the glycidyl unit of the resin with amine [2]:



$$R\text{–OCH}_2\text{CH(O)CH}_2 + \text{HN}R_2 \rightarrow R\text{–OCH}_2\text{CH(OH)–CH}_2\text{–N}R_2 \quad (1)$$

where R is the non-reacting portion of the molecule.

The height of this loss peak is proportional to the concentration of glyceryl units derived from the resin but is not related to glyceryl units from monofunctional glycidyl diluents [3–5]. It may also contain a relaxation related to the diphenyl-propane nucleus in the resin [3].

Other factors which affect the peak-height and position include absorption of water [6, 7], mechanical fatigue [8], and thermal degradation [9]. Studies on the absorption of water by resins and derived composites have shown that, as water is absorbed, the relaxation appears to increase in magnitude and the transition temperature appears to increase [10, 11]. For systems containing clean glass beads, a new relaxation appears near − 8° C which has been associated with free water in the system [11]. Systems containing silane-treated glass beads do not show the appearance of this relaxation. This paper extends these studies to fibre-filled systems.

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2. Experimental procedure

The resin used in this study was the purified diglycidyl ether of 2,2-bis(4′-hydroxyphenyl-)-propane supplied as "Epon" X22 by Shell Chemical (Aust.) Pty Ltd. The curing agent, 1,3-diaminopropane, was laboratory grade material supplied by Koch–Light Laboratories Ltd and was redistilled before use (b.p. 138 to 140° C).

The glass fibre used was continuous E-glass roving (K filament, 20 end)* and was coated with a proprietory, epoxy-compatible, silane size. This is referred to as treated glass. Some fibre was washed repeatedly with chromic acid solution in concentrated sulphuric acid to remove all size and subsequently washed with water and acetone and dried at 150° C and stored over silica gel. This is referred to as cleaned glass.

Carbon fibre used was supplied as Type II, treated fibre† and aramid fibre was supplied as PRD 49 Type III, 20 end continuous roving‡. Soda-glass beads§ were sieved to a size range of 105 to 210 μm and cleaned with the chromic acid solution, as described for the glass fibre.

Some samples were prepared from unfilled resin, and from resin containing liquid water or glass beads. Fibre-reinforced samples were prepared from cleaned and treated glass in axial and circumferential orientations and from carbon and aramid fibres in axial orientation only.

All samples except the water-filled matrix were prepared by premelting the resin and adding a stoichiometric quantity of amine (9.8 wt%). Unfilled and bead-filled systems were cast vertically in teflon-lined copper tubes. Beads were allowed to settle during cure and the test specimens were cut from the bottom of the cured rod, where the glass content was highest. Samples with axially-oriented fibres were prepared by looping an appropriate weight of fibre over a wire, wetting thoroughly in a premixed resin bath and pulling the doubled fibre hank into a teflon-lined copper tube. For circumferentially aligned fibre-filled samples, a filament winding technique was used: the continuous fibre was passed through a resin bath and wound onto a teflon-coated rod. A total of two layers of glass were applied at a helix angle of ± 70°.

All systems except the water-filled matrix were cured for 20 h at 60° C and postcured for 200 min at 150° C. Filament-wound samples, which were not protected externally by a layer of teflon, were postcured under nitrogen to reduce oxidative degradation.

The water-filled sample contained 81 wt% resin, 11 wt% amine and 8 wt% liquid water. The resultant creamy emulsion was cast normally and cured for 20 h at 60° C, but was not postcured. As the amine is partially soluble in water, a 25% excess was added to ensure adequate cure was obtained.

Specimens, as tested, were approximately 120 mm long and rods were 5 mm in diameter; tubes were 5 mm internal diameter and approximately 7 mm in outside diameter. All samples for dynamic testing were fitted with aluminium end-pieces.

Samples with glass-fibre reinforcement were prepared with fibre volume-fractions between 0.19 and 0.34 with axial orientation and between 0.53 and 0.61 with circumferential orientation. Aramid-fibre and carbon-fibre reinforced samples were prepared with fibre volume-fractions between 0.24 and 0.48 with axial orientation only. The single glass-bead-filled sample had a bead-volume ratio of 0.35.

Dynamic mechanical properties were determined using an inverted, free-oscillation torsion pendulum. The accuracy of this instrument has been discussed [12]. The frequency of oscillation was adjusted to remain in the range 0.8 to 1.2 Hz and the temperature range studied was from − 150° C to the glass transition temperature for dry samples or from − 150° C to room temperature for samples exposed to water.

Specimens with fitted end-pieces were exposed to water by immersion in distilled water maintained at a temperature of 98 to 100° C. Samples were removed periodically, the end-pieces cleaned of corrosion products, the samples dried with tissue paper and the dynamic properties determined. They were then returned to the same water bath.

Fibre contents of the axially-aligned fibre-filled systems were calculated from the weight per unit length of the fibre hank used to prepare the sample and the calculated volume of the specimen,

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*Glass Fibre supplied by Australian Fibre Glass Pty Ltd.

†Carbon fibre supplied by Morganite Modmor Ltd.

‡Aramid fibre supplied by E. I. du Pont de Nemours and Co. Inc.

§Soda-glass beads supplied by Catasphere Bead Co.

assuming the density values of the fibres reported in the literature. The fibre contents of glass-filled systems were checked by ignition and found to be in agreement with the calculated values. Glass contents of bead-filled and filament-wound samples were also determined by ignition.

Microscopic examination of cross-sections of samples suggested that void contents were low and fibre distribution was consistent between types of fibre.

To determine the rate of absorption of water, rods 10 to 30 mm in length were dried for 2 h at 150° C and weighed. After immersion for a known period in boiling water, superficial water was removed using absorbent paper and the samples were reweighed.

3. Results

The beta-relaxation in fibre-filled systems is similar to that in the unfilled matrix. The loss peak is unchanged in position, but depressed in magnitude. Fig. 1 shows the dependence of peak height on the volume-fraction of resin present, V_R.

The beta-peak for the water-filled sample occurred at $-55°$ C at a loss tangent of 0.0805. No sign of any peak near -30 or $-8°$ C could be detected.

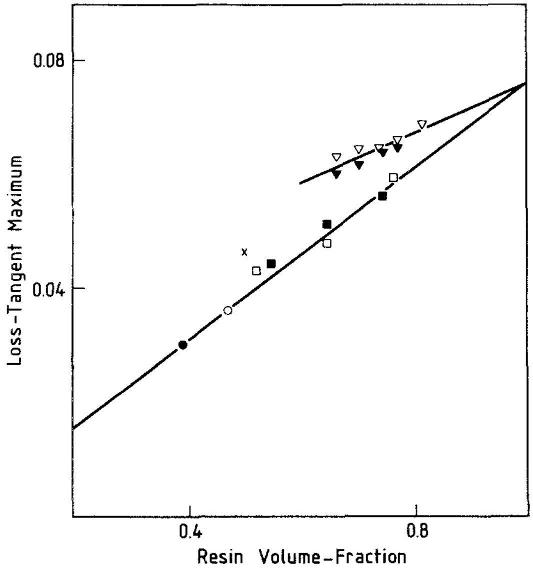

Figure 1 The maximum value of the loss tangent near $-50°$ C for filled systems as a function of the resin volume-fraction. △ cleaned glass fibre, axial orientation; ▾ treated glass fibre, axial orientation; ○ cleaned glass fibre, circumferential orientation; ● treated glass fibre, circumferential orientation; □ aramid fibre, axial orientation; ■ carbon fibre, axial orientation; × glass bead-filled system.

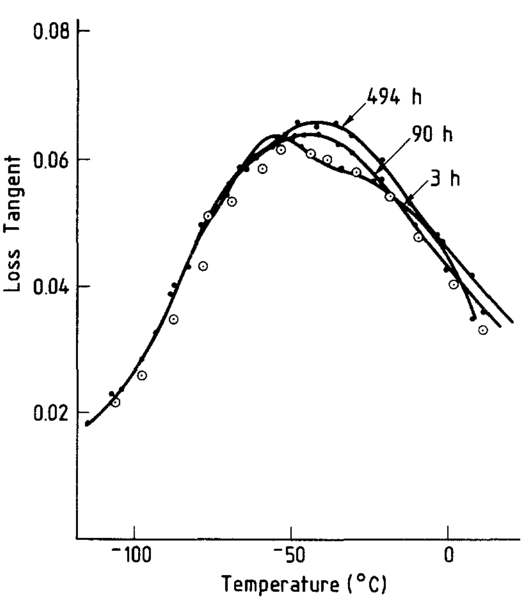

Figure 2 The loss tangent in the region of the beta-relaxation for the system containing axial, treated glass-fibre ($V_R = 0.73$) after exposure to boiling water for the indicated periods. The circled points were obtained after drying following exposure. In this, and successive figures, a few typical, experimental points are shown to indicate scatter. Normally the loss tangent was determined every 5° C.

Exposure of unfilled matrix to boiling water for prolonged periods has little observable effect on the beta-peak. The maximum value of the loss tangent decreases from a value of 0.0725 to 0.070 after exposure for 3500 h.

Results of exposure of composite samples are illustrated in Figs 2 to 6. These show a series of plots of the loss tangent against temperature after successive exposures to water, and after eventual drying under dry nitrogen at 150° C for 2 h for some typical systems.

For samples filled with glass, treated with a silane finish, exposure to boiling water leads to an increase in the maximum loss tangent and a shift of the maximum to higher temperatures, as shown in Fig. 2. For cleaned glass, these changes occur more rapidly and to greater extent, and a peak appears near $-20°$ C, as shown in Fig. 3. The results from filament-wound glass systems are not singificantly different from those from axially-aligned glass fibres; both cleaned and treated cases. The filament-wound specimens, however, become very fragile, especially those based on cleaned glass, and sample failure occurs during dynamic testing after 30 to 100 h. Exposure

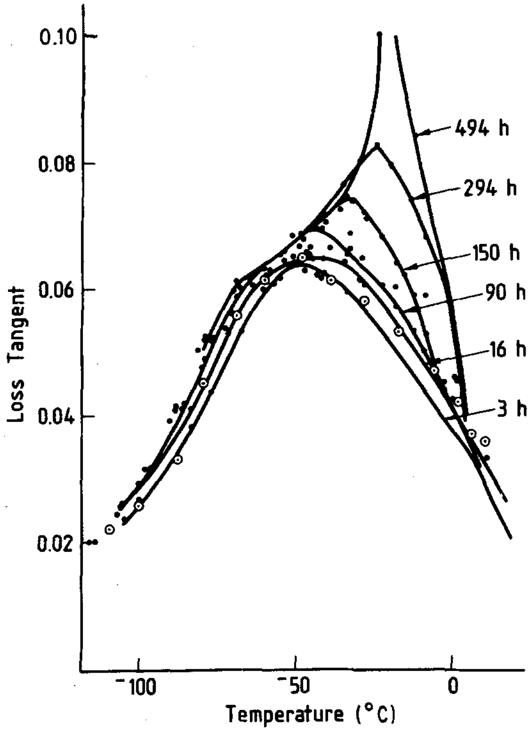

Figure 3 As for Fig. 2 for the system based on axial, cleaned glass-fibre ($V_R = 0.73$).

of axially-aligned carbon fibre composites (Fig. 4) results in peak changes similar to those for treated glass-based samples, whereas results for axially-aligned aramid based samples (Fig. 5) are similar to those for cleaned glass-based samples.

The effect of exposure of composites based on cleaned glass beads over a similar period to the above exposure is illustrated in Fig. 6.

Water absorption rates are very similar in all systems when calculated on the basis of per cent change in weight of the matrix resin, as has been reported for systems filled with glass beads [11]. After 100 h exposure, a weight increase of 3 to 4% was observed. The absorption rate slowly decreased and at 300 h a total weight increase of 5 to 6% was observed.

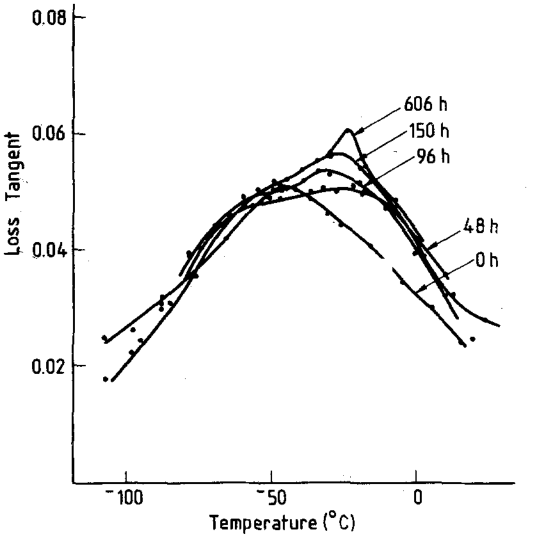

Figure 4 As for Fig. 2 for the system based on axial, carbon-fibre ($V_R = 0.66$).

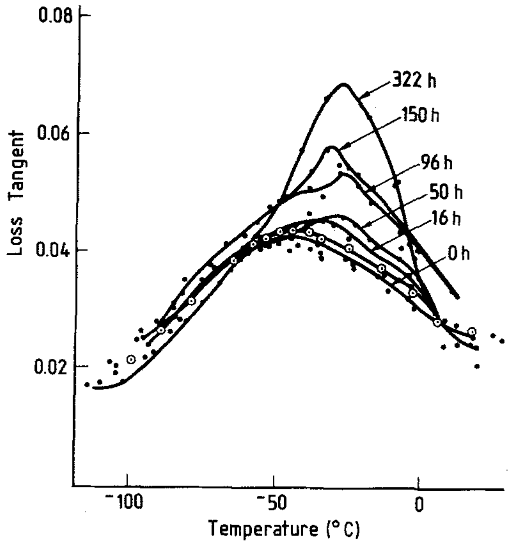

Figure 5 As for Fig. 2 for the system based on axial aramid-fibre ($V_R = 0.66$).

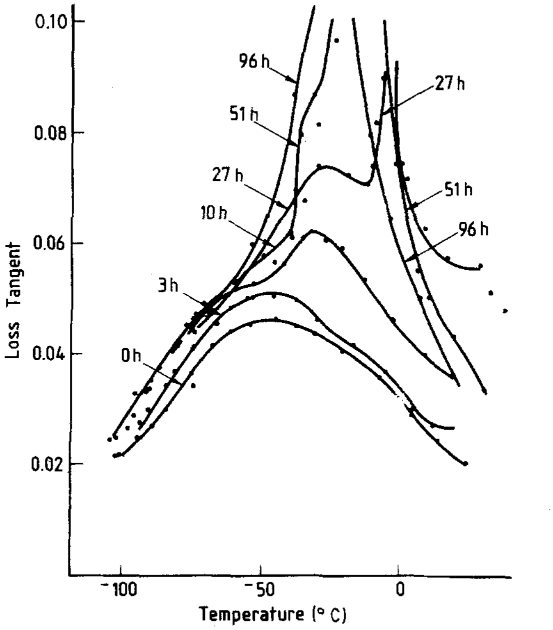

Figure 6 As for Fig. 2 for the system based on glass beads ($V_R = 0.51$).

4. Discussion

4.1. Fibre content and orientation

The fibre content of the specimens appears to affect the maximum value of the loss tangent but not the temperature at which the maximum occurs. The accuracy of determination of this temperature is poor, however. Over the range of fibre contents studied, the maximum value of the loss tangent is approximately proportional to the volume-fraction of resin present. The law of mixtures would suggest such a linear relationship passing through a loss tangent of zero at zero volume-fraction of resin if the fibres do not contribute to the energy loss. This condition appears to hold for systems containing carbon and aramid fibres, but both cleaned and treated glass systems show a positive deviation. This effect could be associated with the high polarity of the glass surface but it is of interest to note that it is not affected significantly by the silane treatment or the cleaning process.

The heights of the beta-peak for filament-wound samples are less reliable than for axially-oriented samples as the outer surface is much less regular due to the winding process, and the resin content varies significantly through the specimen.

4.2. The effect of boiling water on composites

On exposure to boiling water, the loss peak increases in height and moves to a higher temperature. This effect is small in the unfilled samples, even after very long exposures. In the case of treated glass and carbon-fibre filled systems, prolonged exposure causes a shift in the peak to between -20° C and -30° C but the rate of increase of height decreases. This may be associated with the decrease in the rate of absorption of water. For systems based on aramid or cleaned-glass fibres, the peak moves rapidly to -30° C and increases in height dramatically, although water absorption rates are very similar to other fibre-filled specimens. Bead-filled samples showed the formation of the peak near -8° C, as reported earlier. On longer exposure, this system showed the formation of a peak near -30° C, while the peak near -8° C could no longer be detected.

All samples recovered their original loss properties on drying by heating to 150° C for 1 to 2 h.

In general, all loss curves for exposed, filled samples show a higher loss compared to those for exposed, unfilled samples of the same temperature. This is associated with an increase in the temperature of maximum loss and in some cases a new peak near -30° C is resolved. In order to describe these changes quantitatively, attempts were made to resolve the observed curves. It was assumed that an anomalous loss was occurring at all temperatures, independently of the background loss of the bulk resin matrix. A rough estimate of this loss was obtained by use of the relationship:

$$(\tan\delta)_{x,t,T} = (\tan\delta)_{\text{obs},t,T} - V_R(\tan\delta)_{\text{matrix},t,T}, \tag{2}$$

where the loss tangents, $\tan\delta$, for the systems are distinguished by subscripts x for the anomalous loss, obs for the observed loss in the filled system and matrix for the unfilled system. The subscript t refers to the time of exposure of the composite or the unfilled matrix to water and the subscript T refers to the temperature at which the losses were determined. V_R is the volume-fraction of resin in the composite specimen.

This relationship implies several assumptions. First, is that the loss tangent is proportional to V_R at all temperatures. It was shown above that the maximum loss tangent is proportional to V_R and the curves are of similar shape. Second, is that the rate of absorption of water is independent of the presence of the fibre. This was checked experimentally and found to be a reasonable approximation. Third, is that the possible slight effect of the interaction between glass and matrix on the loss tangent could be neglected.

Fig. 7 shows the curves obtained for the resolved, anomalous loss as a function of temperature for the system based on cleaned glass fibre at a resin volume-fraction of 0.73, on exposure to boiling water. A consistent description of these curves and all others obtained is that they show

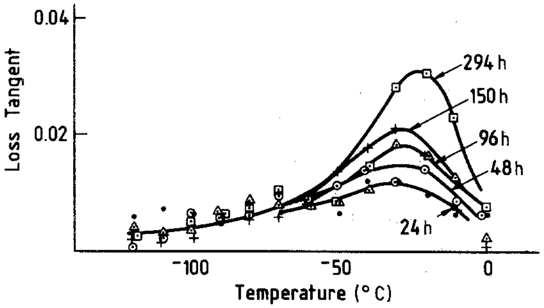

Figure 7 Resolved loss peak for the system based on cleaned glass-fibre ($V_R = 0.73$) after exposure to boiling water for the indicated period.

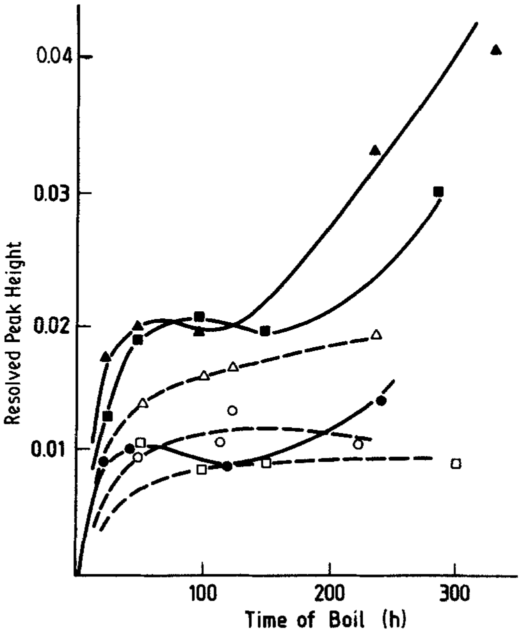

Figure 8 The height of the resolved loss-peak as a function of period of exposure to boiling water. All samples have axial orientation. ● treated glass, $V_R = 0.77$; ○ cleaned glass, $V_R = 0.77$; ■ treated glass, $V_R = 0.73$; □ cleaned glass, $V_R = 0.73$; ▲ treated glass, $V_R = 0.66$; △ cleaned glass, $V_R = 0.66$.

the gradual formation of a peak between − 30 and − 40° C.

Figs 8 and 9 show the variation in height for the resolved loss-peak as a function of exposure time for the systems studied. While there is considerable scatter in the data, the height of the loss peak after a fixed exposure period increases with increasing fibre content. As has been shown earlier [11] and confirmed in the present work, the rate of absorption of moisture is the same for all systems when compared on the basis of the percentage change in weight of the matrix resin. There is no suggestion that the rate of water absorption is increased by increase in fibre content. As the resolved loss appears at approximately the same temperature for all systems, it is probably not associated specifically with the fibre.

A possible mechanism for causing the resolved loss-peak, which is consistent with these observations, would involve the molecular species at the fibre–resin interface. Perhaps, the moisture absorbed at the fibre surface modifies the polar glyceryl entities in the surrounding resin sufficiently to create a distinguishable loss process. The ease of formation of this modified species is greatest for systems based on cleaned glass or aramid fibre and least for systems based on treated glass.

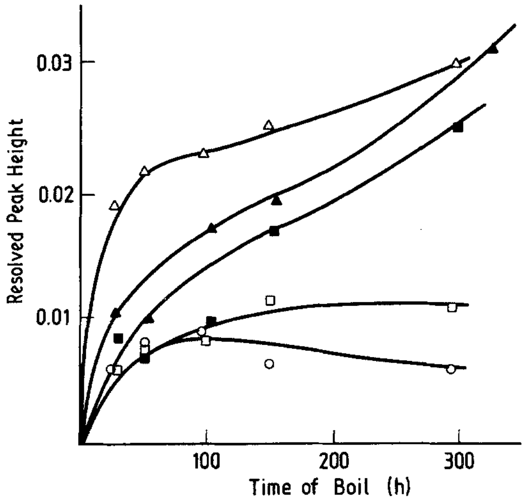

Figure 9 As for Fig. 8. ○ carbon fibre, $V_R = 0.74$; □ carbon fibre, $V_R = 0.64$; △ carbon fibre, $V_R = 0.54$; ■ aramid fibre, $V_R = 0.64$; ▲ aramid fibre, $V_R = 0.52$.

5. Conclusions

The effects of fibrous fillers on the beta-relaxation in an amine-cured epoxy resin have been examined. The peak in loss properties at 1 Hz occurs near − 50° C and this position is independent of the filler. The height is proportional to the resin-fraction in the sample. On exposure to boiling water the peak appears to increase in height and shift to higher temperatures. This observation is best explained by the formation of a new relaxation giving a loss peak near − 30° C. This loss mechanism may be related to reversibly degraded matrix in the interfacial region of the composite.

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