Dynamic mechanical properties of poly-2hydroxyethylmethacrylate based composites

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The dynamic–mechanical properties of swollen poly-2-hydroxyethylmethacrylate reinforced with PET net and PP fibrillated films are reported. The results indicate that while the shift factors used for the time-temperature superposition are independent of the fillter content, the tan δ is strongly affected by the reinforcement.

Keywords Composites; dynamic-mechanical properties; poly-2-hydroxyethylmethacrylate; dissipation mechanism; time-temperature superposition principle; filler effect

INTRODUCTION

A great deal of attention has been devoted in the scientific literature to the mechanical and viscoelastic properties of polymeric composites¹ while few papers have been dedicated to the dynamic-mechanical properties of such systems²⁻⁴. Moreover, most of them have dealt with ideally elastic reinforcements in the shape of the fibres or particles such as glass beads, glass fibres, carbon black, mica flakes, etc. In this case the effect of filler on the viscoelastic behaviour of the polymeric matrix is strongly dependent on the bonding mechanism between the two phases⁵⁻⁶.

In recent papers the time-temperature superposition principle has been used to superimpose data obtained in creep and stress relaxation experiments as well as ultimate mechanical properties in flexure and in tension for both unfilled resins and composites⁷. It has been shown that the presence of a filler (both glass fibres or beads) in all cases has no effect on the shift factors used for constructing the master curves.

This report analyses the effect of different reinforcements (polyethylenterephthalate (PET) fibres, tricot PET net and polypropylene (PP) fibrillated films) on the dynamic-mechanical properties of a swollen poly-2-hydroxyethylmethacrylate (PHEMA) matrix.

EXPERIMENTAL

The PHEMA samples were obtained by crosslinking the 2-hydroxyethylmethacrylate (HEMA) monomer using 0.5% by weight ethylenedimethacrylate (EDMA) as the crosslinking agent and 0.1% by weight (referred to HEMA) 2-azoiso-butyronitrile (AIBN) as the initiator, in the presence of 40% diacetin as diluent. The mixture was poured between two glass plates separated by a silicon rubber gasket and crosslinked at 90°C for 1 hour. The PHEMA/PET fibre composites and the PHEMA/PP composites were prepared by filling the space between the glass plates with fibres of commercial PET multifilament yarn (150 dtex/30) or PP fibrillated films oriented at $0/90^{\circ}$ to obtain symmetric and balanced orthotropic laminates. The PHEMA/PET net composites were obtained by using a lamina of an orthotropic tricot PET net. Once the reaction was complete, the samples were immersed for 1

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month in distilled water to eliminate the diacetin and to reach equilibrium swelling. The volume fraction of reinforcement in PHEMA composites has been calculated for PET fibres, PET net and PP films to be 0.03, 0.30 and 0.13 respectively.

The dynamic viscoelastic behaviour has been evaluated by the dynamic viscoelastometer Rheovibron mod. DDV II at the temperatures of 15° (\bullet), 25° (\triangle), 37° (\blacktriangle), 45° (\Box) and 60° C (\bullet) and at the frequencies of 110, 35, 11, 3.5, 0.35 and 1.1×10^{-2} Hz. During the measurements the samples were under 100% relative humidity.

RESULTS AND DISCUSSION

In Figure 1 the storage moduli E' relative to unfilled PHEMA obtained at different temperatures ranging from $T = 15^{\circ}$ C to $T = 60^{\circ}$ C are reported. The data for composites are not shown but show similar behaviour.

These data, for each filler, have been shifted horizontally using a time-temperature superposition procedure, to obtain the master curves shown in *Figure 2* at a reference temperature of 15° C. The presence of the filler increases the modulus and modifies the shape of the curves.



Figure 1 Frequency dependence of storage moduli of pure PHEMA at the temperatures of $15^{\circ}C(\Phi)$, $25^{\circ}C(\Delta)$, $37^{\circ}C(A)$, $45^{\circ}C(\Box)$, $60^{\circ}C(\Box)$



Figure 2 Master curves of storage moduli of PHEMA (a), PHEMA/ PET fibres (b), PHEMA/PP film (c) and PHEMA/PET net (d)



Figure 3 Shift factors a_T versus 1/T. The full circles are data for the unfilled PHEMA

The shift factors used for the superposition procedure are shown in *Figure 3* in an Arrhenius plot. This plot is linear and an activation energy of 10 kcal gmol⁻¹ can be calculated from the slope. The shift factors are independent of the filler content. This implies that, in this region, the temperature dependence of the storage modulus of the polymeric composites is only dependent on the matrix performance, as already found⁷⁻⁸ for other



Figure 4 Frequency dependence of damping factors of PHEMA (a) PHEMA/PET fibres (b), PHEMA/PP film (c) and PHEMA/PET net (d) at the temperatures of 15° C (\bullet), 25° C (\triangle), 37° C (\blacktriangle), 45° C (\Box) and 60° C (\blacksquare)

mechanical properties. The viscoelastic character of the reinforcements does not appear for E' in the range of temperature and frequencies studied and therefore the results obtained are similar to those reported for rigid fillers such as glass or carbon fibres.

In contrast the damping characteristic of the system is filler dependent as indicated in *Figure 4*. In fact all the composite materials tested show a small dependence of tan δ on frequency and temperature while the unfilled PHEMA is strongly dependent on frequency especially at lower temperatures. This indicates that the presence of the filler modifies the dissipation mechanism of the matrix in the composite system so that the tan δ dependence of the composite is similar to that of the reinforcement⁵.

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