

Temperature, Structural and Relaxation Asymmetry Contributions to Physical Ageing of Polymer-Silica Nanocomposites

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Polystyrene and poly(methyl methacrylate)–silica nanocomposites were prepared and analysed using differential scanning calorimetry, in order to determine the influence of nano-particulates on relaxation and thermal properties. Annealing was performed before the onset of glass transition for logarithmically spaced intervals of time (1, 10, 100 h) in order to observe the effect of physical ageing on thermal relaxation.

1. Introduction

The glass transition is a pseudo second order phase transition during which a material in the glassy state transforms on heating into a supercooled liquid. This transition is characterised by the glass transition temperature (T_g), at which sufficient energy is gained for co-ordinated rotation of chain segments. Annealing at temperatures below the glass transition region can influence many properties, including enthalpy, density and creep compliance [1]. During annealing a decrease in enthalpy takes place, which is recovered on reheating to above T_g . This recovery is exhibited as a maximum in the heat capacity at temperatures below or near the upper limit of the glass transition region [2]. In addition, the presence of fillers or crosslinks can further influence relaxation and thermal properties, due to the hindrance of segmental motions and reduction in free volume. The aim of this research was to determine the effect of silica (SiO_2) particles on the relaxation and thermal properties of polystyrene (PS) and poly(methyl methacrylate) (PMMA). Objectives included preparation of the polymer-silica nanocomposites, observing the influence of annealing on relaxation and determining molecular motions and polymer-filler interaction.

2. Sample preparation

2.1 Materials

PS (Austrex 103) was obtained from Polystyrene Australia Pty Ltd, while PMMA was received from Aldrich Chemical Co. Inc., Milwaukee, USA. The fumed silica used was Aerosil R972 (Degussa AG, Frankfurt am Main, Germany). It is a hydrophobic fine powder with a density of $2.2 \text{ g}\cdot\text{cm}^{-3}$, primary particle size of 16 nm and silica content of $\geq 99.8 \text{ \%}\cdot\text{w/w}$.

2.2 Nanocomposite Preparation

PS composites with various fumed silica concentrations (1, 3, 5, 10 and 20 %·w/w) were prepared using a Haake Rheomix 600 Batch Intensive Mixer with Rheocord 90 Control System. Materials were blended using roller-blade type rotors at 50 rpm for 10 min. The mixing temperature was 180 °C to ensure complete polymer melting. Composite films were moulded with a heated press (IDM Instruments Inc., model number: L-0003-1). Films were pressed between platens, heated to 190 °C, held for 2 min and then cooled slowly to ambient. Treated films were stored in sealed plastic bags and kept at ambient conditions.

PMMA- SiO_2 nanocomposites with identical filler concentrations to the PS samples were prepared using solvent dispersion. PMMA was added to dichloromethane and stirred for 1 h at 20 °C, until the polymer completely dissolved. Fumed silica was added to the solution and subjected to ultrasonic disruption (10 min, 20 °C, 20 kHz) to completely disperse the



silica particles throughout the polymer matrix. The polymer solution was rapidly precipitated into a large volume of cold ethanol, before being isolated and dried under vacuum for at least 8 h. Films for subsequent use were prepared using a heated press. The conditions were identical to those used to prepare the PS composites, except the pressing temperature was 160 °C.

2.3 Differential Scanning Calorimetry

A Perkin-Elmer Pyris 1 DSC was used to measure the thermal transitions of composites. Measurements were conducted at ambient with an ice-water slurry, while a high purity indium standard ($T_m = 156.6$ °C, $\Delta H_m = 28.45$ J·g⁻¹) was used for calibration. A 20 mL·min⁻¹ nitrogen purge through the cell chamber provided an inert atmosphere. Small masses (~5 mg) of film were accurately weighed using a Mettler Toledo MX5 microbalance with internal standard mass calibration. The films were encapsulated in standard 10 µL hermetically sealed aluminium pans, with a similar empty pan used as a reference.

Samples were heated to 120 °C to eliminate prior thermal history and held for 5 min prior to cooling to the annealing temperature (T_a), which was 95 °C. Samples were held at T_a for 1, 10 and 100 h before being cooled to 30 °C at 20 °C·min⁻¹. The films were subsequently heated to 120 °C at 2 °C·min⁻¹. All endotherms shown are spaced 0.2 units apart for clarity.

3. Results

3.1 Filler Content and Relaxation

The heating curves of the PS–SiO₂ and PMMA–SiO₂ nanocomposites are shown in Fig 1. PS exhibited a broad relaxation endotherm superimposed on the T_g from ~100 to 110 °C (Fig 1a). On addition of silica, the endotherm remained at 105 °C for 1 %·w/w. Further SiO₂ content caused the endotherm peak temperature to increase slightly, reaching 108 °C at 20 %·w/w. The glass transition behaviour was correspondingly affected by an increase in the heat capacity of the exhibited peaks. The T_g of pure PS was observed at 101 °C. Incorporation of silica resulted in a gradual increase in T_g , ranging from 102 °C at 1 %·w/w to 104 °C at 20 %·w/w. In addition, the fictive temperature (T_f) of the nanocomposites increased with SiO₂ concentration, ranging from 100 °C (pure PS) to 103 °C (20 %·w/w).

PMMA displayed a single relaxation endotherm at 128 °C (Fig 1b). The addition of 1 %·w/w SiO₂ increased the endotherm to 129 °C. The endotherm peak temperature continued to increase with filler concentration, reaching a maximum of 133 °C at 20 %·w/w. Pure PMMA exhibited a T_g of 123 °C. As with the heating endotherm, T_g increased with silica content, ranging from 124 (1 %·w/w) to 129 °C (20 %·w/w). The T_f of pure PMMA was observed at 123 °C. Addition of silica resulted in the T_f remaining at 123 °C for 1 %·w/w. Increasing the filler content raised the T_f , reaching 128 °C at 20 %·w/w.

This shift in glass transition and relaxation behaviour increase as a function of filler concentration has been reported for PMMA–SiO₂ [3, 4] nanocomposites, although the effect of (untreated) SiO₂ on the properties of PS is somewhat unpredictable. The observed behaviour can be attributed to the fumed silica particles occupying and subsequently reducing the total amount of free volume throughout the polymer matrix. As a result, segmental motions of the polymer chains are hindered, causing the observed increase in thermal activation required [5]. Segments of polymer chain can be physical trapped within the silica network, leading to additional geometrical restraints [6]. Furthermore, the restriction of polymer chains indicates sufficient interfacial interaction (in the form of physical bonds) between the polymer matrix and silica filler.



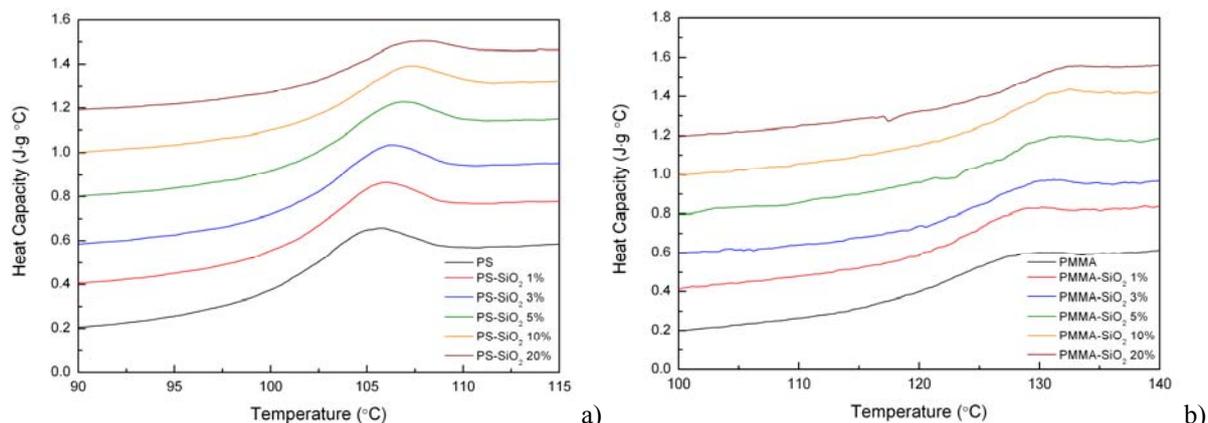


Fig 1. Heating endotherms of (a) PS-SiO₂ and (b) PMMA-SiO₂ nanocomposites

3.2 Effect of Annealing

The annealed relaxation endotherms of the PS-SiO₂ composites are shown in Fig 2. Composites annealed for 1 h at 95 °C displayed taller, narrower endotherms with a sharper resolution and lower enthalpy than their non-annealed counterparts. This resolution continued to increase with increasing annealing time (t_a), the 100 h annealed samples producing the most defined peaks. On annealing for 1 h, the endotherm peak of pure PS shifted to 103 °C. As seen in Fig 2d, increasing t_a caused the endotherm peak to shift back towards the non-annealed peak temperature. The T_g of pure PS was similarly affected, dropping to 98 °C at 1 h annealing, before slightly increasing to 100 °C at 10 h annealing. As seen in Fig 3, PMMA-SiO₂ composites showed similar behaviour to their PS counterparts.

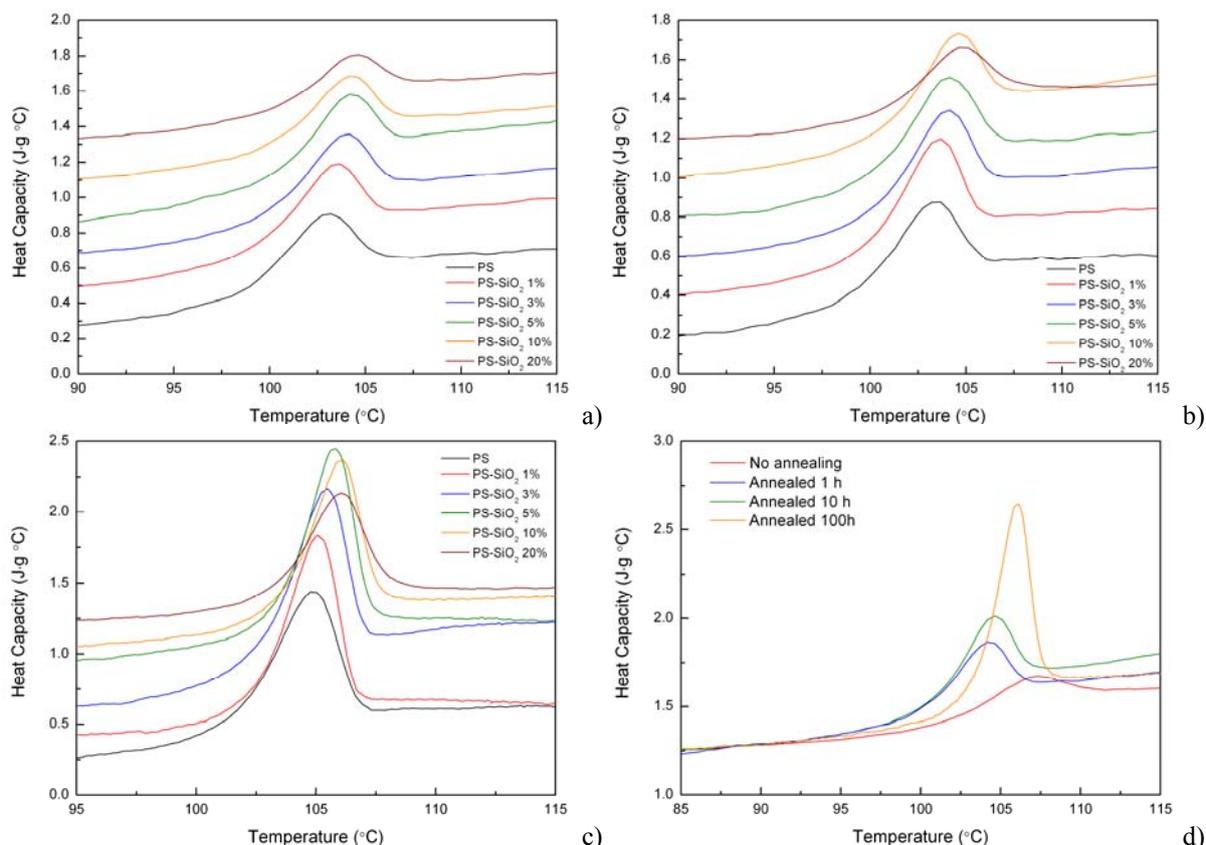


Fig 2. Relaxation endotherms of PS-SiO₂ nanocomposites; (a) annealed 1 h, (b) annealed 10 h, (c) annealed 100 h, (d) PS-SiO₂ 10 % endotherms compared



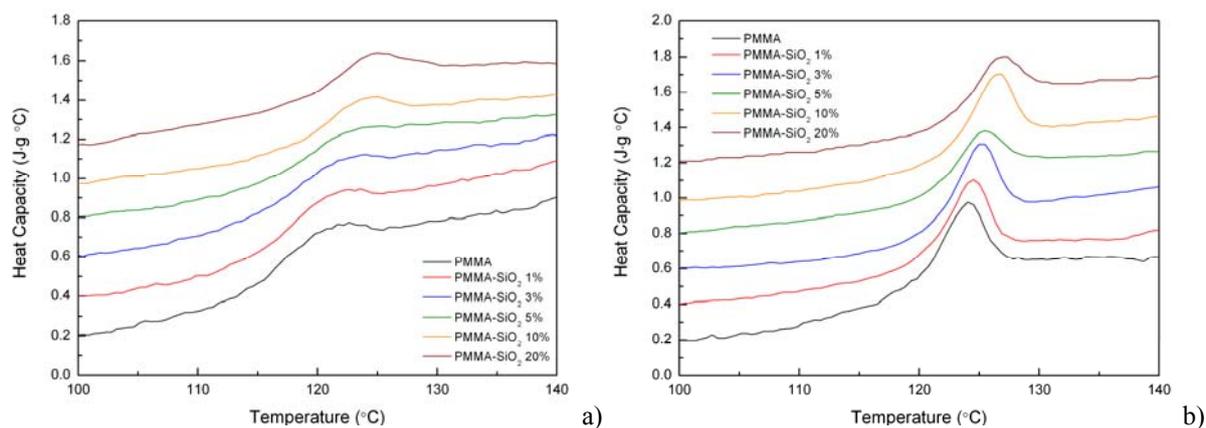


Fig 3. Relaxation endotherms of PMMA-SiO₂ nanocomposites; (a) annealed 1 h, (b) annealed 10 h

Samples containing silica showed similar trends to their non-annealed counterparts, for both the PS and PMMA samples. This suggests the SiO₂ particles continue to restrict segmental motion of the matrix chains during the physical ageing process. Furthermore, it indicates the decreased free volume that SiO₂-filled samples possess is maintained during annealing.

The process of physical ageing is related to the concept of free volume. It states that the transport mobility of particles in a closely packed system primarily depends on the degree of packing (free volume) [7]. Above T_g , the free volume and mobility are large. Upon cooling, both free volume and mobility decrease simultaneously. Furthermore, when a polymer is cooled to below T_g and held for a period of time, the mobility is small although not zero. Due to this reduced mobility, the free volume is greater at this stage than at equilibrium. This increased free volume is responsible for the endotherm peak shift and alteration of polymer properties. As t_a is increased, the free volume and mobility will continue to decrease gradually, shifting the peaks back towards the non-annealed peak location.

4. Conclusion

PS and PMMA-SiO₂ nanocomposites were analysed using DSC. The endotherm peak temperature, T_g and T_f increased as a function of silica concentration, suggesting the presence of SiO₂ reduces free volume and restricts segmental motion. The influence of physical ageing was examined by annealing samples before the T_g for 1, 10 and 100 h. Annealing for 1 h shifted endotherms to lower temperatures, while increasing t_a moved the peaks back towards their initial location. A t_a of 1 h gives a higher free volume than at equilibrium, while increasing t_a allows the free volume and mobility to slowly decrease.

Acknowledgments

We acknowledge the financial support of the CRC for Polymers.

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