

Annealing and Thermal History Relaxations of Polymer Nanocomposites with Hyperbranched Polymer Particles

S. Spoljaric^a, A. Genovese^a, T. K. Goh^b, G. Qiao^b and R. A. Shanks^a

^a *CRC for Polymers, School of Applied Sciences, RMIT University, Victoria 3000, Australia.*

^b *Chemical & Biomolecular Engineering, University of Melbourne, Victoria 3010, Australia.*

The thermal relaxation of polystyrene-star polymer composites was analysed using differential scanning calorimetry (DSC). Annealing was performed prior to the onset of glass transition at various logarithmically spaced time intervals (1, 10, 100 h). Modulated-temperature DSC (mT-DSC) was performed to separate the glass transition temperature (T_g) inflection as a storage heat capacity (C_p') event and the relaxation enthalpy as a loss heat capacity (C_p'') event.

1. Introduction

Glassy polymers like polystyrene (PS) usually exist in a non-equilibrium state [1]. At temperatures above the T_g , the polymer will be at thermal equilibrium due to the relaxation time being less than 1 s. When the material is cooled below T_g , relaxation times will exponentially increase as the equilibration is retarded with decreasing temperature. The polymer will relax towards equilibrium in a process referred to as physical ageing. Physical ageing of glassy polymers will result in decreased enthalpy and specific volume with time at a rate dependent on temperature. Fillers and crosslinks can influence physical ageing, due to the restraints on molecular segmental motion that they impart. A unique type of filler is a class of hyperbranched polymer referred to as star polymers. They consist of a crosslinked polymer centre with grafted linear polymer branches extending from the core. These branches are usually the same as the matrix polymer to aid with compatibility.

The aim of this research was to determine the effect of hyperbranched particles (HBP) on the relaxation and thermal properties of PS. Objectives included observing the influence of annealing on relaxation, separating the various thermal events of the composites using mT-DSC and determining molecular motions and polymer-filler interaction.

2. Experimental

2.1 Star Polymer Preparation

Core cross-linked star (CCS) polymers consisting of a poly(ethylene glycol dimethylacrylate) (PEGDMA) core and PS arms were prepared using atom transfer radical polymerisation (ATRP). The initiator (1-bromo-ethyl)-benzene was reacted with styrene to form PS arms which are isolated and reacted with ethylene glycol dimethylacrylate to form CCS polymers. A star-like, hyperbranched polymer mixture of linear PS and PEGDMA was also prepared using radical polymerisation. Styrene and divinylbenzene were reacted using azobisisobutyronitrile as catalyst.

2.2 Nanocomposite Preparation

Preparation of PS-star polymer composites was by dissolution of appropriate amounts of PS and star polymer in dichloromethane, followed by rapid precipitation in a large volume of cold methanol. The precipitate was isolated and dried under vacuum (0.05 mm Hg) for at least 10 h. The nomenclature of the nanocomposites is presented in Table 1.



Table 1. PS-Star polymer nanocomposite nomenclature

Sample number	PS concentration (%·w/w)	Star-polymer concentration (%·w/w)
PS-01	100	0
PS-02	90	10
PS-03	70	30
PS-04	-	-

Note: PS-04 is a star-like, hyperbranched polymer mixture of linear PS and PEGDMA.

2.3 Differential Scanning Calorimetry

A Perkin-Elmer Pyris 1 DSC was used to measure the thermal transitions of composites. Measurements were conducted with an ice-water slurry, while a high purity indium standard ($T_m = 156.6\text{ °C}$, $\Delta H_m = 28.45\text{ J}\cdot\text{g}^{-1}$) was used for calibration. A $20\text{ mL}\cdot\text{min}^{-1}$ nitrogen purge through the cell chamber provided an inert atmosphere. Small masses ($\sim 5\text{ mg}$) of film were accurately weighed using a Mettler Toledo MX5 microbalance with internal standard mass calibration. The films were encapsulated in standard $10\text{ }\mu\text{L}$ hermetically sealed aluminium pans, with a matched 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 $20\text{ °C}\cdot\text{min}^{-1}$. The films were subsequently heated to 120 °C at $2\text{ °C}\cdot\text{min}^{-1}$.

The mT-DSC parameters are shown in Table 2. Prior to analysis, samples were heated to 120 °C and held for 5 min to remove prior thermal history, before being cooled to 30 °C at $10\text{ °C}\cdot\text{min}^{-1}$.

Table 2. mT-DSC parameters

$T_1\text{ (°C)}$	$T_2\text{ (°C)}$	$T_3\text{ (°C)}$	Period (s)	$\beta_o\text{ (°C}\cdot\text{min}^{-1})$	$T_{amp}\text{ (°C)}$	$f\text{ (mHz)}$
50	54	52	60	2.0	1.5	16.7

3. Results

3.1 Effect of Hyperbranched Particles and Annealing

The heating endotherms of the star polymer composites are shown in Figure 1a. PS homopolymer (PS-01) displayed a single relaxation endotherm superimposed on the T_g at 102 °C . Incorporation of HBP into the matrix increased the endotherm peak to 105 °C for both 10 and 30 %·w/w samples (PS-02 and PS-03, respectively). The star-like polymer mixture (PS-04) also showed an increased endotherm, at 106 °C . The T_g of the pure PS was observed at 96 °C . Addition of 10 %·w/w star-polymer increased the T_g to 100 °C . Both PS-03 and PS-04 displayed a T_g of 101 °C . Correspondingly, the fictive temperature (T_f) of the composites increased with star-polymer concentration, ranging from 95 °C for pure PS, to 99 °C for PS-03 and 100 °C for PS-04.

The observed increase in glass transition and relaxation behaviour suggests that star-polymers behave in a similar manner to fillers or crosslinks. Although the PS arms on the HBP are miscible with the PS matrix, they appear to impart restraints on segmental motion of matrix chains. Molecular motion can additionally be hindered by the increased matrix viscosity which hyperbranched particles are known to cause, commonly referred to as the viscosity effect [2]. Furthermore, the observations indicate the presence of adequate interfacial interaction between the linear PS matrix and HBP, suggesting little, if any, phase separation.



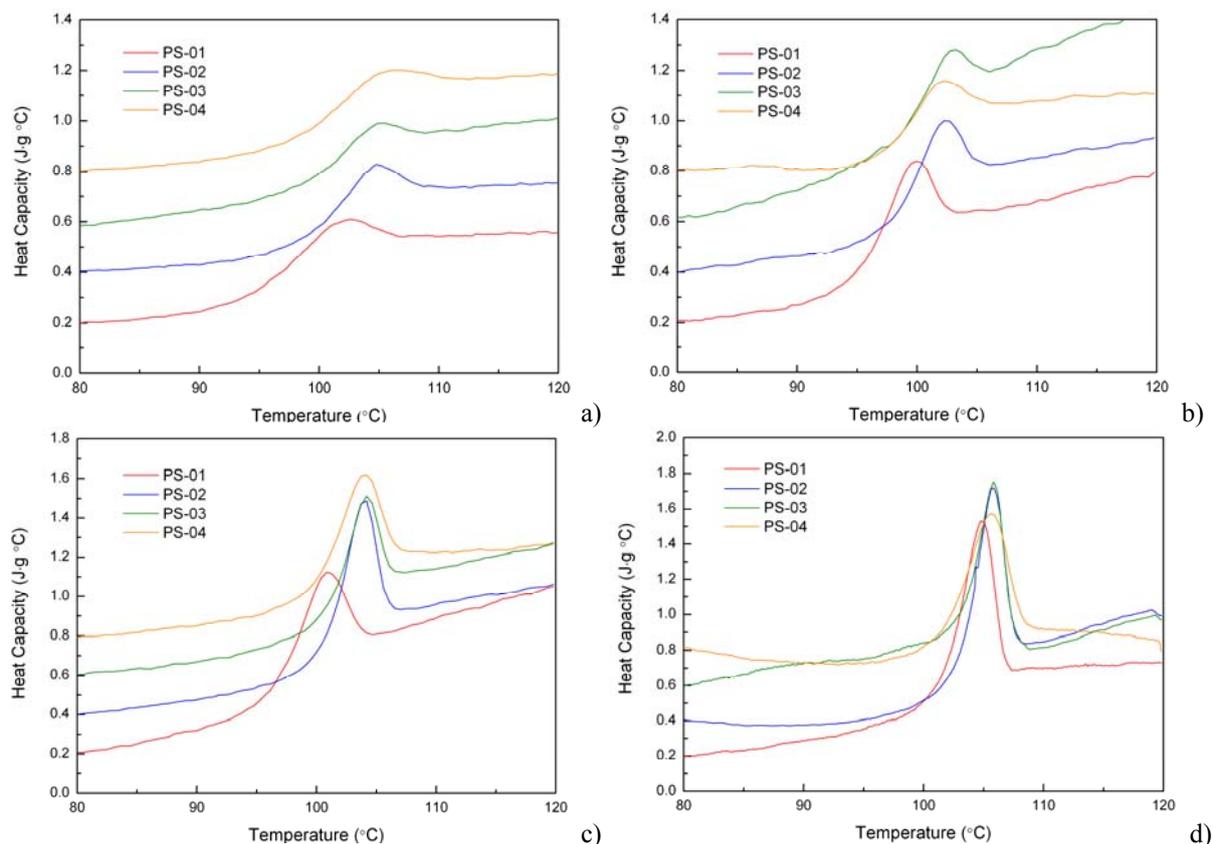


Fig 1. Relaxation endotherms of PS-Star polymer nanocomposites; (a) no annealing, (b) annealed 1 h, (c) annealed 10 h, (d) annealed 100 h.

Fig. 1b, c and d show the relaxation endotherms of the PS-star polymer composites at annealing times (t_a) of 1, 10 and 100 h, respectively. Annealing for 1 h at 95 °C yielded taller, narrower endotherms with a sharper resolution and lower enthalpy than their non-annealed counterparts (Fig. 1a). This resolution continued to increase with t_a , with samples annealed for 100 h producing the tallest peaks. On annealing for 1 h, the endotherm peak of pure PS shifted down to 99 °C. Increasing t_a caused the endotherm peak to shift back towards the non-annealed peak temperature. Similarly, the T_g of PS homopolymer was affected, dropping to 95 °C at 1 h annealing, before gradually returning to 96 °C at 100 h annealing. Samples PS-02, PS-03 and PS-04 showed similar trends to their non-annealed counterparts, exhibiting more pronounced effects in peak shift than the pure PS. This suggests the HBP continue to behave as fillers/crosslinkers, restricting segmental motion during physical ageing.

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). 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.

3.2 Modulated Temperature – Differential Scanning Calorimetry

The total heat capacity (C_p) curves of the PS-HBP nanocomposites are shown in Fig 2a. As with the conventional heating curves, a single, broad glass transition region is observed. To isolate the step change event of the T_g , the reversing (storage) heat capacity (C_p') was



separated from the total C_p (Fig 2b). The T_g is clearly revealed and a shift was observed, confirming that star-polymer particles do influence glass transition behaviour by restricting segmental motion and reducing free volume. The non-reversing heat capacity (total C_p –storage C_p) is shown in Fig 2c, which reveals the enthalpy relaxation of the PS phases. PS-01 and PS-02 exhibited greater endothermic peaks than PS-03 and PS-04, indicating the effect of HBP also reduces the enthalpy relaxation, especially with high HBP content and as a pure star-like mixture (PS-04). This confirms that only the PS matrix and HBP contribute to the glass transition and relaxation behaviour. Furthermore, the single peaks observed in the mT-DSC curves suggest sufficient matrix-filler interaction and little-to-no phase separation.

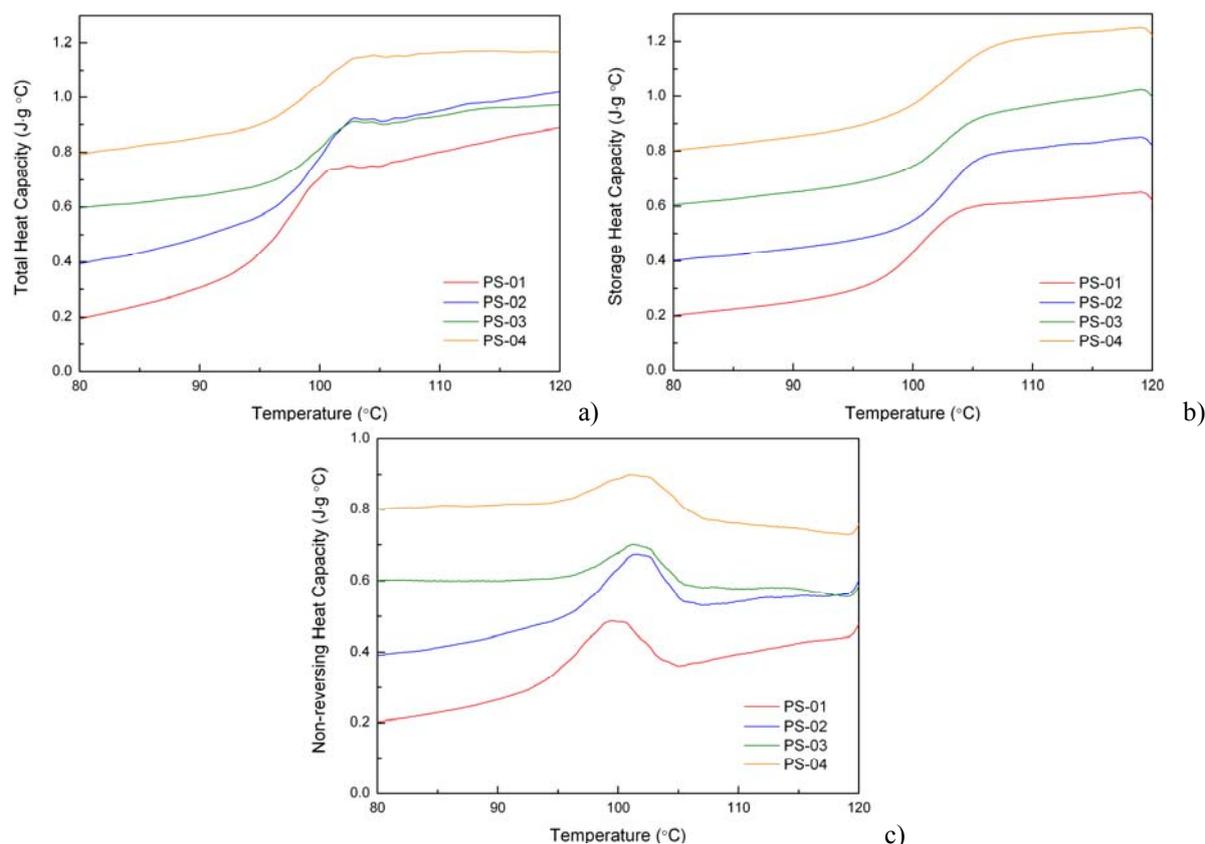


Fig 2. mT-DSC curves of PS-star polymer nanocomposites; (a) total, (b) storage, (c) non-reversing.

4. Conclusion

The presence of HBP increased the endothermic peak, T_g and T_f , suggesting they restrain segmental motion of the matrix chains. Annealing for 1 h shifted endotherms to temperatures lower than non-annealed samples, while increasing t_a moved the peaks back towards their initial location. Annealing for 1 h gives a higher free volume than at equilibrium, while increasing t_a allows the free volume and mobility to slowly decrease. Further analysis using mT-DSC suggested good compatibility between the matrix and HBP. The T_g from the overlapping enthalpy relaxation associated with the transition was successfully separated using mT-DSC.

Acknowledgments

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References

1. Hodge I M and Berens A R 1982 *Macromol.* **15** 762.
2. Ratna D, Varley R, Raman R K S and Simon G P 2003 *J. Mater. Sci.* **38** 147.

