

Nanocomposites with physical crosslinks introduced by core cross-linked star polymers into a like-polymer

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

^a *CRC for Polymers, RMIT University, GPO Box 2476V, Victoria 3001, Australia.*

^b *Institut Montanuniversität Leoben, Franz-Josef-Strasse 18, 8700 Leoben, Austria.*

^c *Polymer Science Group, Chemical & Biomolecular Engineering, University of Melbourne, Victoria 3010, Australia.*

Core cross-linked star (CCS) polymers prepared from a glycol acrylate core with polystyrene (PS) or poly(methyl methacrylate) (PMMA) branches were added as filler to linear PS or PMMA, respectively. Modulated temperature – thermomechanometry (mT-TM) was performed to separate the in-phase and out-of-phase dimension changes, from which the glass transition temperature and linear coefficient of thermal expansion (α) were obtained.

1. Introduction

Core-crosslinked star (CCS) polymers are unique three-dimensional macromolecules that consist of a ‘hard’ crosslinked core surrounded by numerous ‘soft’ linear arms. These polymers are generally synthesized using living radical polymerisation techniques that allow for a high degree of structural control and narrow molecular weight distribution. Despite exhibiting a very high molecular weight, CCS polymers display solubility and viscosity parameters similar to linear and branched polymers of low molecular weight [1]. Despite the wide scale academic and industrial attention star polymers have received, practically no research has been performed regarding structural relaxation, physical ageing, glass transition or thermal expansion properties of CCS polymers and/or blends with linear polymers. These properties can be influenced by fillers and crosslinks, due to the restraints on molecular segmental motion that they impart. CCS polymers can behave in a similar manner, where the arms on the hyperbranched particles can interweave throughout the chains of the matrix polymer. The advantage of CCS-polymer fillers over other types of filler/crosslink is the excellent compatibility and interfacial interaction which occurs, in particular when the polymer matrix and the arms on the CCS polymer are the same material.

Modulated temperature – thermomechanometry (mt-TM) is a novel technique [2] that involves the application of an oscillating temperature to a linear/isothermal underlying heating rate [3]. The modulated temperature program induces a sinusoidal response in specimen dimension change that can be resolved into reversing (in-phase with ΔT) and non-reversing (out-of-phase with ΔT) components. This allows phenomena such as thermal expansion, glass-rubber transition, thermal and structural relaxation, polymer shrinkage and morphological changes to be observed. This is useful for characterization of materials utilized in fields such as packaging, drug delivery and electrical applications.

The aim of this research was to determine the effect of CCS polymers on the relaxation and thermal properties of like-linear polymers. Objectives included observing the influence of CCS concentration and annealing on relaxation, separating the dimension changes of the nanocomposites using mT-TM and determining molecular motions and linear-CCS polymer interaction.

2. Experimental

2.1 CCS Polymer Preparation

Core cross-linked star (CCS) polymers consisting of a poly(ethylene glycol dimethylacrylate) core and PS or PMMA arms were prepared using atom transfer radical polymerisation (ATRP). The initiator (1-bromoethyl)benzene was reacted with styrene to form PS arms, while a 4-toluenesulfonyl chloride initiator was reacted with methyl methacrylate to prepare PMMA arms. The arms were isolated and reacted with ethylene glycol dimethylacrylate to form CCS polymers.

2.2 Nanocomposite Preparation

Preparation of linear-CCS polymer nanocomposites was achieved by dissolution of appropriate amounts of linear and CCS 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. Films for subsequent use were prepared using an IDM heated press. Films were heated to 190 °C, 6 tonne applied, held for 2 min and cooled to ambient. The nomenclature of the nanocomposites is presented in Table 1.

Table 1. Linear-CCS polymer nanocomposite nomenclature

<i>Material number</i>	<i>Linear polymer concentration (%·w/w)</i>	<i>CCS-polymer concentration (%·w/w)</i>
PS-01	100	0
PS-02	90	10
PS-03	70	30
PMMA-01	100	0
PMMA-02	90	10
PMMA-03	70	30

2.3 Modulated Temperature – Thermomechanometry

A TA Instruments Q400EM Thermomechanical Analyser was used to measure the thermal transitions of the nanocomposites. Dimension changes which are in-phase (reversible) and out-of-phase (non-reversible) with the modulated temperature program were separated and analysed. Samples with a height of ~2 mm were heated from 80 to 150 °C at a rate of 0.5 °C·min⁻¹. A sinusoidal modulation with 2 °C amplitude and 180 s period was superimposed on the temperature ramp. Prior to testing, all samples were heated to and maintained at 150 °C for 5 min in order to eliminate any prior thermal history. The samples were cooled at 10 °C·min⁻¹ to 80 °C for testing. In order to study the effects of ageing, samples were cooled from 150 °C to a temperature just below the glass transition temperature (T_g) and held there for 1, 10 or 100 hr before cooling to 80 °C and testing. Annealing temperatures (T_a) of 95 °C and 110 °C were used for the PS-CCS and PMMA-CCS films, respectively. The linear coefficient of thermal expansion (α) was calculated above the T_g using Equation 1;

$$\alpha = \frac{dL}{dT} \cdot \frac{1}{L_0} \quad (1)$$

where dL is the change in dimension, dT is the change in temperature and L_0 is the initial length of the sample.

3. Results and Discussion

3.1 Effect of CCS Polymer Concentration

The reversing and non-reversing curves of the PS-CCS nanocomposites are shown in Figure 1, while the T_g and linear coefficient of thermal expansion (α) data is summarised in Table 2. The reversing (in-phase) curve of pure PS shows an increase in dimension change

(expansion) with temperature, with a single inflection. PS-01 yielded an α value of $403.49 \times 10^{-6} \cdot ^\circ\text{C}$ and T_g of $101 \text{ }^\circ\text{C}$. Incorporation of CCS polymers into the matrix caused α to decrease to 227.68 and $258.73 \times 10^{-6} \cdot ^\circ\text{C}$ for star polymer concentrations of 10 %w/w (PS-02) and 30 %w/w (PS-03), respectively. Conversely, the T_g was observed to increase with CCS concentration, with PS-02 and PS-03 both exhibiting T_g values of $103 \text{ }^\circ\text{C}$, respectively. As shown in Table 2, similar trends were observed for PMMA materials. The non-reversing curves show that shrinkage (reduction in dimension) occurs in all materials at temperatures above the T_g . As CCS polymer content is increased, the gradient of the curves past the T_g decrease. This indicates that shrinkage occurs at a slower rate and over a greater temperature range, suggesting that CCS polymers provide an active role in dimensional stability.

The decrease in thermal expansion and shrinkage and increased T_g suggests that CCS polymers behave in a similar manner to crosslinks. Although the PS or PMMA arms on the CCS polymers are miscible with their respective matrices, they appear to impart restraints on segmental motion of matrix chains and vibrational modes underlying the expansion ability of the polymer. Reducing thermal expansion will cause a subsequent reduction in polymer shrinkage since the latter is dependent on the former. Segmental and vibrational motions can be additionally hindered by the increased matrix viscosity which CCS polymers are known to cause, commonly referred to as the viscosity effect [4]. Furthermore, the observation of a single inflection point in both the reversing and non-reversing curves suggests adequate interfacial interaction between the linear and CCS polymers, with little phase separation.

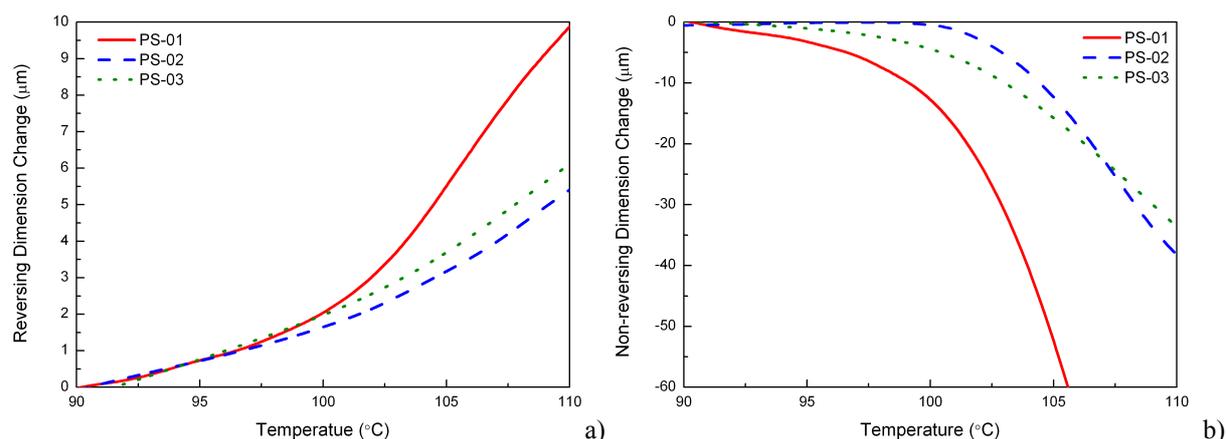


Fig. 1. mT-TM curves of PS-CCS nanocomposites; (a) reversing, (b) non-reversing

Table 2. Glass transition and thermal expansion data of linear-CCS polymer nanocomposites

Material number	T_g ($^\circ\text{C}$)				α ($10^{-6} \cdot ^\circ\text{C}$)			
	No annealing	$t_a = 1 \text{ h}$	$t_a = 10 \text{ h}$	$t_a = 100 \text{ h}$	No annealing	$t_a = 1 \text{ h}$	$t_a = 10 \text{ h}$	$t_a = 100 \text{ h}$
PS-01	101	102	104	105	430.49	1178.75	1190.91	3110.29
PS-02	103	104	105	106	227.68	345.23	670.00	1827.78
PS-03	103	105	106	108	258.73	340.74	512.19	876.89
PMMA-01	120	123	125	126	1296.00	1510.53	2565.08	3904.04
PMMA-02	124	125	125	128	420.83	482.72	830.6	3872.88
PMMA-03	125	126	126	128	390.86	490.68	581.82	3257.14

3.2. Effect of Annealing

Figure 2a shows the reversing curves of the PMMA-01 and PMMA-03 annealed for 1, 10 and 100 h at $110 \text{ }^\circ\text{C}$. Annealing for 1 h produced curves with similar characteristics to their non-annealed counterparts. Increasing the annealing time (t_a) to 10 h caused the gradient of the curves past the T_g to increase, while materials annealed for 100 h produced the steepest curves. This increase in reversing-curve gradient caused the value of α to increase with t_a , as summarised in Table 2. Similarly, the increase in thermal expansion with t_a resulted in an

increase in polymer shrinkage, as shown in Figure 2b. Unannealed PMMA-01 exhibited a T_g of 120 °C. Upon annealing for 1 h, the T_g increased to 123 °C, eventually reaching a maximum value of 126 °C at $t_a = 100$ h. Even after annealing, filled materials (PMMA-02 and PMMA-03) continued to exhibit higher T_g and lower α and shrinkage rates than the pure PMMA films with the same t_a . This suggests CCS polymers continue to behave as crosslinkers, restricting segmental motion during ageing and occupying volume within the composites, reducing space for expansion. Similar trends were observed for PS materials (refer Table 2).

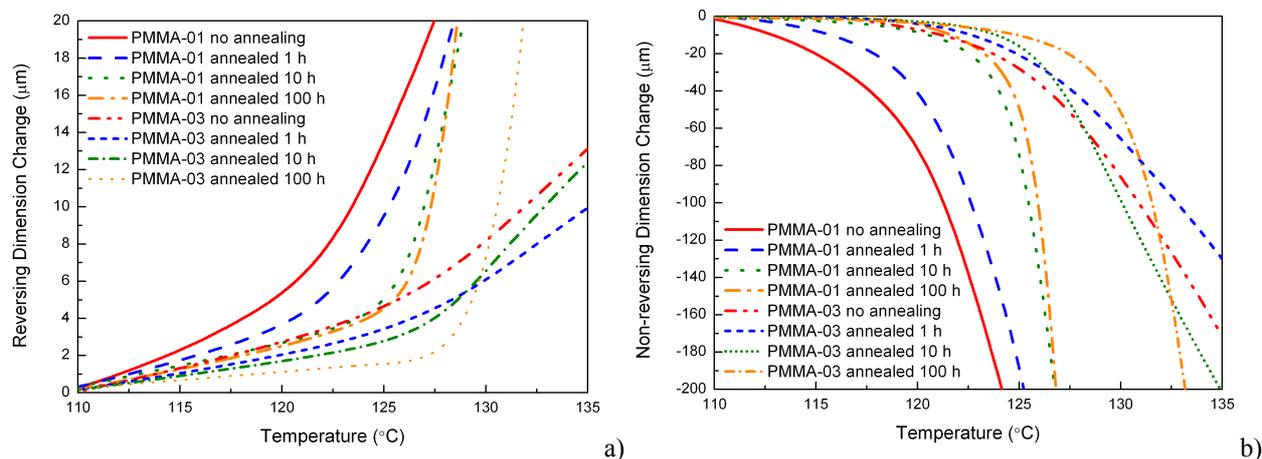


Fig. 2. mT-TM curves of annealed PMMA-CCS nanocomposites; (a) reversing, (b) non-reversing

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, V_F). Above T_g , V_F and mobility are large, allowing polymer chains greater freedom of movement. Upon cooling, both V_F and mobility decrease simultaneously. Furthermore, when a polymer is cooled to below T_g and held for a period of time (annealed), the mobility is small although not zero. As t_a is increased, the V_F and mobility will continue to decrease gradually. This limited mobility hinders polymer chain movement, resulting in increased T_g [5] and above- T_g α and shrinkage [6].

4. Conclusion

Addition of CCS polymers decreased thermal expansion and shrinkage, while an increase in T_g was observed. This suggests that the hyperbranched polymers behave in a similar manner to crosslinks, imparting restrictions on the segmental and vibrational motions of matrix chains. Thermal expansion, shrinkage and T_g increased with t_a , due to reduced free volume and mobility within the nanocomposites. The reversing and non-reversing curves of the materials were successfully separated using mT-TM and suggested good compatibility and interaction between the linear and CCS polymers.

Acknowledgments

The authors acknowledge the financial assistance of the CRC for Polymers.

References

- [1] Wiltshire J T and Qiao G G 2006 *Macromol.* **39** 9018
- [2] Price D M 1998 *J. Therm. Anal.* **51** 231
- [3] Blaine R L 2003 *Proceedings of the 31st NATAS Annual Conference on Thermal Analysis and Applications*
- [4] Ratna D, Varley R, Raman R K S and Simon G P S 2003 *J. Mater. Sci.* **38** 147
- [5] Struik L C E 1978 *Physical Aging in Amorphous Polymers and Other Materials* (Amsterdam: Elsevier) p 799
- [6] Kudryacheva G M, Chinchenko I N, Bakulina G P, Kisilishin V A and Nevskaya T V 1990 *Mech. Compos. Mater.* **25** 564.