The anisotropic thermal expansion of 'single-crystal' triblock copolymer films

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Films of polystyrene–polybutadiene–polystyrene triblock copolymer were cast from toluene solutions using the technique of 'roll-casting', which leads to microphase separation of the block copolymer into globally oriented structures that are often termed 'single crystals'. The thermal expansion of unannealed films was found to be dominated by molecular stresses resulting from the casting process. The angular dependence of the thermal expansion coefficient of annealed films, which were free of any preferred molecular orientation, was governed by the supramolecular structure and was found to be in good agreement with theoretical predictions related to traditional composite materials.

(Keywords: block copolymers; roll-casting; thermal expansion coefficient)

INTRODUCTION

Microphase separation of block copolymers into ordered microdomains has been extensively studied both theoretically and experimentally over the years, and the reader is referred to review texts of this topic[1,2]. The literature also contains many accounts of studies in which block copolymers have been treated with the intention of extending the local order of cylindrical or lamellar microdomains to macroscopic samples of global anisotropy, often referred to as 'single crystals'. We have recently reviewed several of these studies, and presented a novel method for casting highly oriented films of block copolymers from solutions subjected to flow[3]. Using this method, termed 'roll-casting', block copolymer solutions were rolled between two co-rotating eccentric cylinders while at the same time the solvent was evaporated at a controlled rate. As the solvent evaporated, the polymer concentration increased, and the block copolymer eventually microphase-separated into globally oriented structures. Depending on the composition of the copolymers used, roll-cast films consisted of uniaxial cylindrical microdomains assembled on a nearly perfect hexagonal lattice or of unidirectional lamellae of alternating composition. Two-dimensional small-angle X-ray scattering (SAXS) and transmission electron microscopy (TEM) indicated the near single-crystal structure of the films.

The initial apparatus used for roll-casting was later modified[4]. The eccentric cylinders were replaced by two counter-rotating adjacent cylinders between which the polymer solution was rolled. In the present study a further modification of the apparatus is presented, in which a third roll is added.

Several studies have appeared in the literature dealing with the properties of oriented block copolymers. However, these have addressed mainly mechanical, optical and diffusive aspects[5–11], whereas relatively little has been published on other anisotropic properties. The present study focuses on the anisotropic thermal expansion of roll-cast films and their directional and angular dependence. The different effects of molecular orientation and supramolecular structure will be demonstrated.

EXPERIMENTAL

Films of a polystyrene–polybutadiene–polystyrene triblock copolymer containing 28 wt% polystyrene were roll-cast from toluene solutions using the apparatus shown schematically in *Figure 1*. The apparatus is a modification of the roll-casting system used in previous work[4]. The main difference between the two systems is the presence of a second nip region obtained by adding a third roll. Whereas in the previous system one of the rolls was made of solid polytetrafluoroethylene (Teflon) to ensure the formation of the polymer film on the other roll, in the present system the two extreme rolls are made of steel wrapped in Teflon sleeves 3 mm thick. The central roll is chrome-plated in order to protect it from scratches, which would later reproduce on the formed films. All three rolls, 90 mm in diameter and 120 mm long, have temperature controlled heating elements running through the axis to allow roll-casting at elevated temperatures. However, this capability of the system was not utilized in the present study. The central roll is fixed and the two extreme rolls are mounted on linear positioning devices so that the gap between two adjacent rolls may be accurately and reproducibly set. All three rolls are connected by a series of gears to a single motor of variable speed. This ensures that the rolls rotate at equal angular velocities at all times.

The experimental procedure by which the films were produced is similar to that described previously[3,4]. Solutions of 40 wt% block copolymer in toluene were poured on the rotating rolls, which were then covered with a transparent enclosure containing a toluene reservoir, used to decrease the rate of solvent evaporation.

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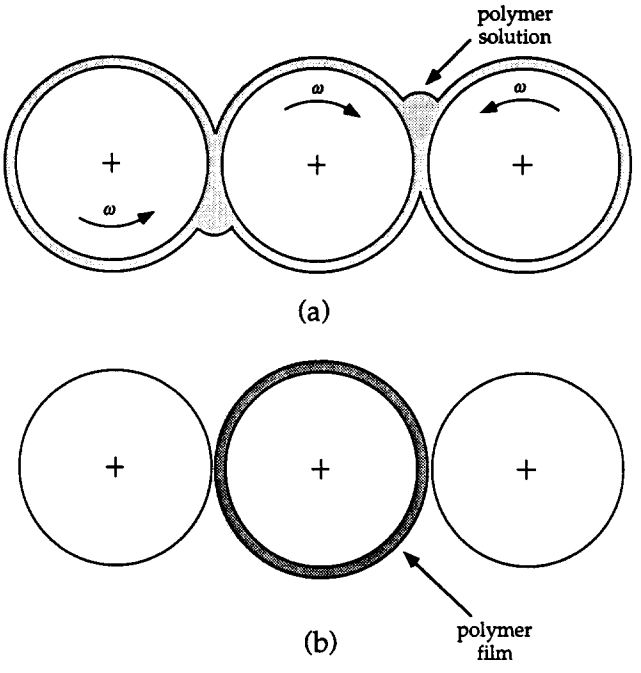

Figure 1 Schematic representation of the roll-casting apparatus: (a) a concentrated solution of block copolymer is processed between three rotating rolls; (b) as the solvent evaporates a highly oriented film of block copolymer is formed on the central roll

Typical runs, performed at 45 rev min^{-1}, lasted about 3 h, during which fresh solution was added periodically, until a film of desired thickness was formed on the central roll. Runs were terminated by first separating the rolls, while still in motion, and only then stopping their rotation.

The material used in this study was a polystyrene–polybutadiene–polystyrene triblock copolymer made by Dexco Polymers (12012 Wickchester, Houston, TX 77079, USA). The molecular weight of each of the polystyrene end blocks was 10 500–10 900, and that of the polybutadiene middle block was 51 000–53 000 (ref. 12). In contrast to other commercial triblock copolymers known to contain various amounts of both diblock and homopolymer, this material is claimed by Dexco Polymers to contain over 99% pure triblock copolymer, and was chosen for this reason.

Non-oriented control samples of the polymer, termed simple-cast films, were quiescently cast from the same solution. The simple-cast and roll-cast films prepared for this study were some 2 mm thick.

All the films produced were dried in a vacuum oven at 50°C for 48 h in order to remove all traces of the solvent. Films receiving only this post-casting treatment will be referred to as 'unannealed'. Some of the films were then annealed for an additional 48 h under vacuum at 120°C, above the glass transition temperature of the polystyrene segments of the block copolymer. These films will be referred to as 'annealed'.

Thermomechanical analysis (t.m.a.) of the films was performed using a DuPont 942 Thermomechanical Analyzer connected to a DuPont Thermal Analyst 2000. The thermomechanical analyser was fitted with a flat-ended quartz probe suitable for expansion measurements.

Small-angle X-ray scattering (SAXS) measurements were performed using a slit-collimation Kratky camera with a linear position-sensitive detector at a sample-to-detector distance of 26.4 cm.

RESULTS AND DISCUSSION

A first series of t.m.a. runs was performed to study the thermal expansion/contraction of roll-cast and simple-cast films, both unannealed and annealed. The changes in the dimensions of the roll-cast films were examined in the three principal directions x, y and z, which are defined schematically in *Figure 2*.

Figure 3 presents the data for the unannealed and annealed simple-cast films. The dashed line indicates the temperature of the films as a function of time. The films were first heated from 25°C at 30°C min^{-1} to 110°C and then maintained isothermally for 15 min, after which they were cooled to room temperature. The solid lines indicate the corresponding changes in the dimensions of the films. Similar behaviour is exhibited by both the unannealed and the annealed simple-cast films: they initially expand by about 2% as a result of the increase in temperature, retain their dimensions when held isothermally at 110°C and contract to within about 0.5% of their original dimensions when cooled back to room temperature.

Figure 4 presents the data for the unannealed roll-cast films. The films were submitted to a temperature cycle

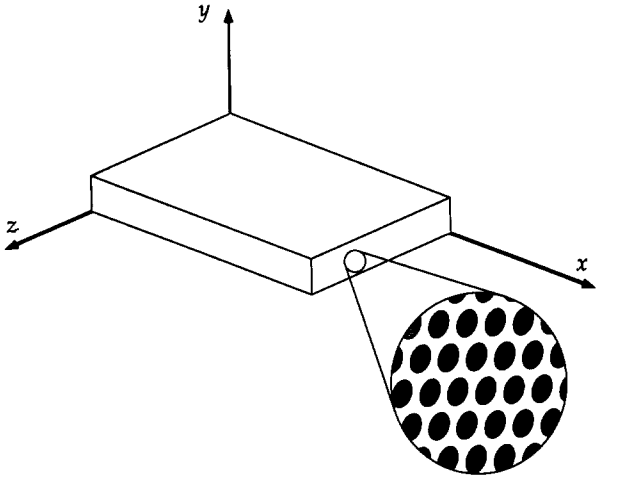

Figure 2 Schematic representation of a roll-cast film identifying the three principal directions referred to in this study. The x direction is the direction of the flow field in which the polystyrene cylinders are aligned

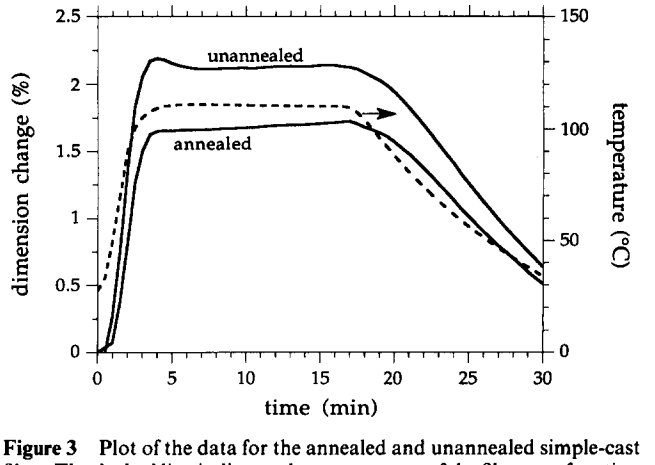

Figure 3 Plot of the data for the annealed and unannealed simple-cast films. The dashed line indicates the temperature of the films as a function of time. The solid lines indicate the corresponding changes in the dimensions of the films

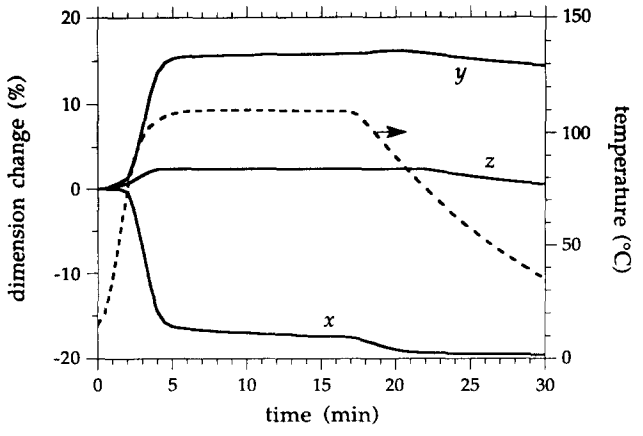

Figure 4 Plot of the data for the unannealed roll-cast films. The dashed line indicates the temperature of the films as a function of time. The solid lines indicate the corresponding changes in the dimensions of the films in the three principal directions

similar to that experienced by the simple-cast films in *Figure 3*. The three solid lines indicate the dimension changes in the x, y and z directions which are identified in *Figure 2*.

Figure 4 clearly shows the anisotropic thermal behaviour of the unannealed roll-cast films. As the temperature is increased, a significant contraction of the films in the x direction is observed, accompanied by a significant expansion in the y direction. The changes in the z direction are much more moderate and are on the order of those observed for the simple-cast films. We also note that in the z direction of the unannealed roll-cast films the dimension changes are more or less reversible (i.e. upon cooling, the films return to their original dimensions). The changes in the x and y directions of the roll-cast films are not reversible and remain even after cooling back to room temperature.

Anisotropic dimension changes were also observed in our previous work[3], in which annealing roll-cast films at 120°C for 70 h resulted in a 14% contraction in the x direction of the films and a 3.8% expansion in the z direction. Measurements, which were conducted using a caliper before and after annealing, were not performed in the y direction. SAXS measurements indicated that the polystyrene cylinders in unannealed roll-cast films were packed closer together than in both simple-cast and annealed roll-cast films. These results were explained by the proposal that during roll-casting not only do the microdomains become oriented in the direction of the flow, but to some extent so do the block copolymer molecules themselves.

The present study provides additional evidence to support this mechanism. The results exhibited in *Figure 4* not only indicate molecular orientation, but also suggest that the molecules are stretched mainly in the xy planes, with very little stretching in the z direction.

This is pictured schematically in *Figure 5* which shows two different views of 'bridge' and 'loop' tie molecules between two polystyrene cylinders in an unannealed roll-cast film. *Figure 5a*, depicting molecules in an xy plane, illustrates how these molecules become stretched in the x direction, whereas tie molecules in the perpendicular xz planes, shown schematically in *Figure 5b*, are relatively stress-free.

This observation may be better understood from the analysis of the velocity profile in the flow field created during roll-casting. A thorough analysis of the flow field has been presented previously[3,4] and will not be repeated here. However, for the purpose of the discussion here it will be pointed out that the velocity profile is not fully developed, and that the velocity in the x direction (v_x) changes both as a function of x and y, i.e. $v_x = f(x, y)$. Since v_x is not a function of z, no molecular orientation is expected to develop in that direction.

When the roll-cast films are annealed above the glass transition temperature of polystyrene, the polystyrene segments regain the mobility lost during solvent evaporation, and the stretched molecules can reconfigure into a less stressed structure, as shown schematically in *Figure 6*. This molecular rearrangement, which is mainly in the xy planes, leads to the irreversible changes in the x and y dimensions (*Figure 4*), and to the changes in the d-spacings detected by SAXS, discussed below.

The presence of molecular orientation in unannealed films based on thermomechanical analysis finds additional support from the results of SAXS measurements. Unannealed and annealed simple-cast and roll-cast films were examined with the path of the X-ray beam normal to the film surface. For the roll-cast films, scattering was measured with the path of the X-ray beam parallel to the y axis and the position-sensitive detector parallel to the z axis.

The d-spacings recorded are summarized in *Table 1*. The fact that annealing the simple-cast films does not affect their d-spacings reflects the absence of processing-related residual stress.

The data for the roll-cast films again indicate that roll-casting leads to a tighter packing of the cylinders relative to simple-cast films. However, whereas in our previous study[3] annealing the roll-cast films resulted in a d-spacing equal to that of annealed simple-cast films, in the present study the annealed roll-cast films exhibit

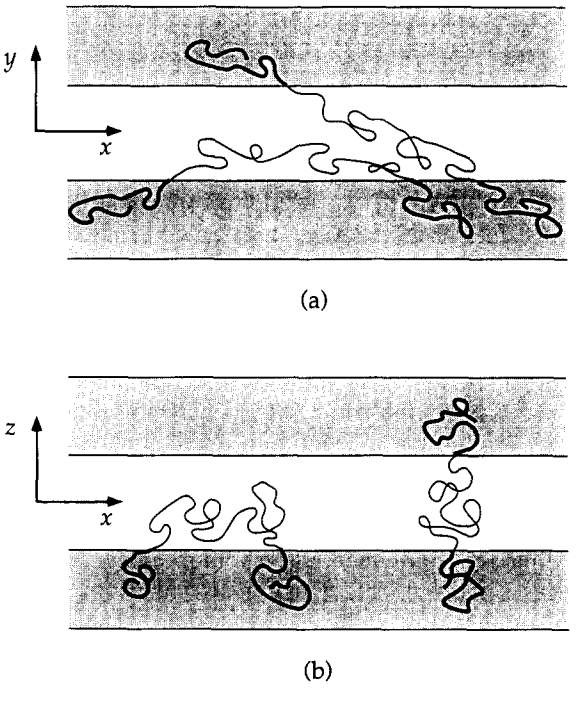

Figure 5 Schematic representation of 'bridge' and 'loop' tie molecules between two polystyrene cylinders in an unannealed roll-cast film: (a) molecules in xy planes become stretched in the x direction; (b) molecules in the perpendicular xz planes are relatively stress-free

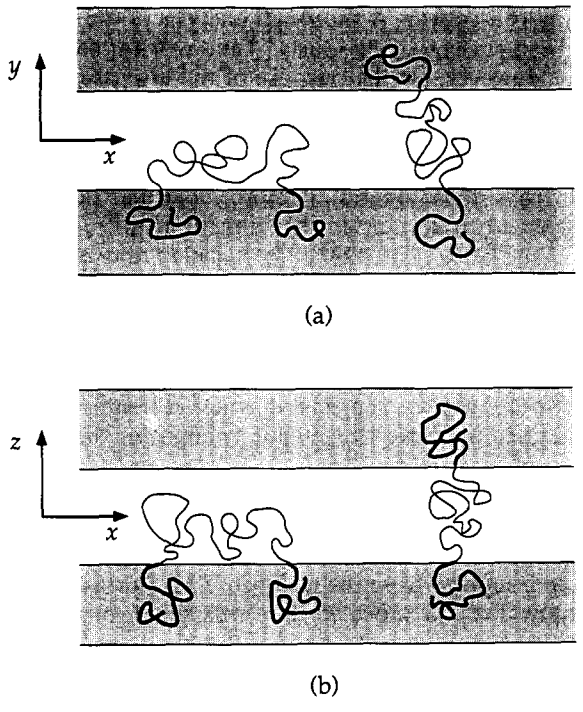

Figure 6 Schematic representation of 'bridge' and 'loop' tie molecules between two polystyrene cylinders in an annealed roll-cast film: (a) *xy* planes—molecules stretched in the *x* direction prior to annealing reconfigure into a less stressed structure resulting in irreversible changes in the *x* and *y* dimensions and in the *d*-spacing; (b) molecules in the *xz* planes are relatively unaffected by the annealing treatment

Table 1 The *d*-spacings recorded by small-angle X-ray scattering for unannealed and annealed simple-cast and roll-cast films

Film	*d*-spacing (Å)
Simple-cast	
Unannealed	270
Annealed	270
Roll-cast	
Unannealed	240
Annealed	260

a spacing somewhat smaller than that of the corresponding annealed simple-cast films (260 Å *versus* 270 Å).

This difference in the results of both studies may be due to differences between the polymers used in both cases. The material used in the earlier study contained, in addition to 71% triblock copolymer (molecular weight 83 000), 27% diblock copolymer (molecular weight half that of the triblock) and 2% homopolystyrene (molecular weight 11 000)[13]. The middle block of a triblock copolymer is tethered to an interface at both ends, which results in additional configurational constraints compared to those imposed on the segments of a diblock molecule which are tethered at only one end. Homopolymer molecules are not tethered at all. The presence of diblock copolymer and homopolymer molecules increases the number of unconstricted chain ends and results in a relative increase in the overall mobility of the system. The nearly 100% pure triblock copolymer in the system used in the present study has a comparatively lower degree of molecular mobility and a reduced ability to disentangle. This could explain the limited extent of structural reconfiguration of the polymer possible during annealing.

We have seen that the thermal behaviour of unannealed roll-cast block copolymer films is dominated by the molecular orientation which differs in the three main directions of the films. We now devote our attention to the influence of the supramolecular structure of the films (i.e. the arrangement of the microphase-separated domains) upon thermal expansion.

Figure 7 exhibits the results of the t.m.a. runs for the annealed roll-cast films. It is evident that annealing the films has resulted in relaxation of the molecular orientation, so that the films now expand upon heating and contract upon cooling back to room temperature in all three directions. The curves for the *y* and *z* directions follow a similar profile, whereas the curve for the *x* direction is somewhat different. This is not surprising, since the annealed films are of axial supramolecular symmetry in the *x* direction.

A second series of t.m.a. runs was performed at a heating rate of 5°C min^{-1} to study the angular dependence of the linear thermal expansion coefficient in the *xz* plane of annealed roll-cast films. It is assumed that annealing the films minimizes any effects of molecular orientation, which according to the first part of this study were not significant in the *xz* planes of the films even prior to annealing.

The linear thermal expansion coefficient α is defined as the temperature-related change in the length of a sample with respect to its initial size L_0:

$$\alpha = \frac{1}{L_0}\left(\frac{\partial L}{\partial T}\right) = \frac{L - L_0}{L_0 \Delta T} \quad (1)$$

Samples were cut from annealed films at angles ranging from 0 to 90° with respect to the direction of orientation, in increments of 15°. The measured angular dependence of the linear thermal expansion coefficient is shown in *Figure 8*. The experimental values of α range from $75 \times 10^{-6}°C^{-1}$ in the *x* direction (0°) to $250 \times 10^{-6}°C^{-1}$ in the *z* direction (90°). These values are quite close to those of pure polystyrene and polybutadiene, respectively.

The angular dependence of the thermal expansion coefficient shown in *Figure 8* is qualitatively similar to that for unidirectional composite materials such as shown by Holliday and Robinson[14] for a polyester/glass fibre system. The roll-cast films of the triblock copolymer studied here may be viewed as nanocomposite materials,

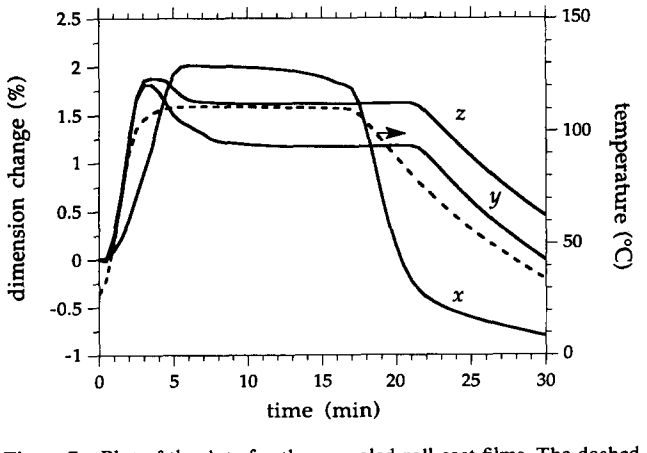

Figure 7 Plot of the data for the annealed roll-cast films. The dashed line indicates the temperature of the films as a function of time. The solid lines indicate the corresponding changes in the dimensions of the films in the three principal directions

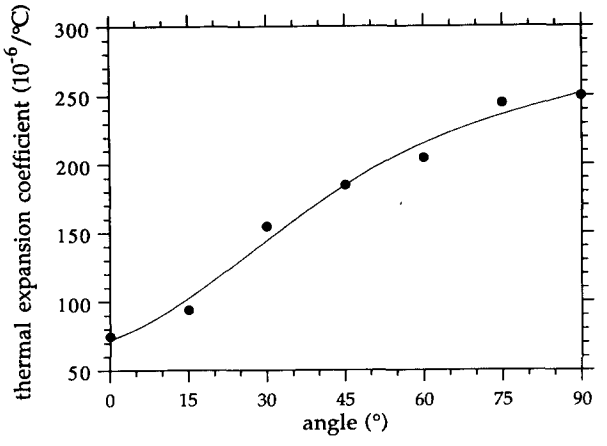

Figure 8 The angular dependence of the linear thermal expansion coefficient in the xz plane of an annealed roll-cast film as determined by t.m.a. at a heating rate of 5°C min^{-1}

in which a polybutadiene matrix is reinforced with unidirectional polystyrene fibres. The values of the thermal expansion coefficients of traditional composite materials in the axial and transverse directions (α_a and α_t, respectively) may be evaluated from the properties of the matrix and filler materials. One approach for doing this, suggested by Schapery[15], was based upon thermoelastic energy principles. This model is applied here to roll-cast films in an attempt to calculate the thermal expansion coefficients in the x and z directions based upon the bulk properties of the two polymers which compose the triblock copolymer.

The equations from Schapery's analysis are:

$$\alpha_a = \frac{1}{E_a}[\alpha_m(1-\phi_f)E_m + \alpha_f\phi_f E_f] \quad (2)$$

$$\alpha_t = (1+\nu_f)\alpha_f\phi_f + (1+\nu_m)\alpha_m(1-\phi_f) - \alpha_a[\nu_f\phi_f + \nu_m(1-\phi_f)] \quad (3)$$

where α is the linear thermal expansion coefficient, E is the module of elasticity and ν is Poisson's ratio; the subscripts m, f, a and t indicate the matrix, filler, and axial and transverse directions, respectively. ϕ_f is the volume fraction of the filler.

The modulus of elasticity of the films in the x (axial) direction to be substituted in equation (2) may also be predicted from composite materials theory[16] using the relation:

$$E_a = E_f\phi_f + E_m(1-\phi_f) \quad (4)$$

Equation (3) was developed for a composite system in which all the fibres have the same mechanical properties, and which is of transverse isotropy (i.e. $\alpha_t = \alpha_z = \alpha_y$). In order to test the validity of the second assumption, the linear thermal expansion coefficient in the y direction of the annealed roll-cast films was also measured. The experimental value found for α_y was 265×10^{-6}°C^{-1}, which is only 6% higher than the value measured in the z direction, making the assumption of transverse isotropy quite reasonable.

Equations (2) to (4) were applied to the block copolymer system in the present study, taking $\phi_f = 0.26$, $\nu_f = 0.38$ and $\nu_m = 0.49$. The values taken for the thermal expansion coefficients and moduli of polystyrene and polybutadiene were $\alpha_f = 75 \times 10^{-6}$°C^{-1}; $E_f = 2 \times 10^3$ MPa (polystyrene), and $\alpha_m = 245 \times 10^{-6}$°C^{-1}; $E_m = 1$ MPa (polybutadiene)[5,17].

The values of the thermal expansion coefficients in the x and z directions as predicted from Schapery's model are 75×10^{-6}°C^{-1} and 260×10^{-6}°C^{-1}, respectively. Almost total agreement is thus found between the calculated and measured values of the thermal expansion coefficient in the axial direction, and there is good agreement between the calculated value of α in the transverse direction and the measured values of both α_y and α_z.

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