Physical ageing and toughness of diblock copolymers

J. A. DiCorleto[*] **and R. E. Cohen**[†]
Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, USA

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The effects of physical ageing on craze growth behaviour and toughness in a series of polystyrene/polybutadiene (PS/PB) diblock copolymers and diblock/polystyrene blends were studied. Samples with spherical rubber morphology were subjected to one of three thermal histories: quenching, slow cooling or isothermal ageing. Dynamic mechanical spectroscopy revealed significant ageing in the slow cooled and isothermally aged samples. The growth rates of crazes were measured in samples containing volume fractions of polybutadiene ranging from 6% to 18%. No change in craze growth rates occurred following ageing. The rates were successfully modelled using the meniscus instability mechanism with no adjustable parameters for the case of 6% PB. A quantitative analysis was made of the small effect of physical ageing on the thermal stresses that facilitate rubber cavitation and craze growth in the materials with high rubber content. Craze growth measurements on materials with 18% PB supported the analysis in that no change in craze growth rates due to physical ageing was observed. The measured rates for this sample were well described by a cavitation model for craze growth assuming a cavitation stress of 47 MPa. Tensile testing of the aged samples revealed no effect of ageing on the macroscopic toughness of the materials studied here.

(Keywords: rubber-modified polystyrene; block copolymers; toughness; physical ageing)

INTRODUCTION

Rubber-modified polymers may exhibit improved toughness due to their ability to initiate massive amounts of crazing, while retaining the attractive stiffness, processability and density of the glassy matrix. Although properties are improved, it has been shown that the glassy matrix of these materials densifies with time[1]. This phenomenon of densification, termed physical ageing, causes changes that are often detrimental to the physical properties of glassy homopolymers[1]. More recently, it has been shown[2,3] that the glassy matrices of styrene–butadiene–styrene (SBS) and acrylonitrile–butadiene–styrene (ABS) copolymers are also affected. These studies have concentrated on examining the densification and large-scale mechanical properties of the selected copolymers.

The effect of physical ageing on rubber-modified polymers is particularly interesting because of the presence of two phases within the material. In polystyrene-continuous materials, thermal stresses arise from the difference between the thermal expansion coefficients of the glassy and rubbery phases. These stresses play an important role in the craze behaviour[4], and therefore in the toughness, of these materials.

In this paper we examine the effect of physical ageing on the toughness of a series of polystyrene/polybutadiene (PS/PB) diblock copolymers and diblock/polystyrene blends, which have been examined previously in the unaged state[4]. The materials are cast into films having morphologies consisting of rubber spheres (of the order of 100 Å in diameter) within a polystyrene matrix. The experimental approach is three-pronged: dynamic mechanical tests, tensile stress–strain tests and craze growth-rate studies have been conducted. Dynamic mechanical testing was undertaken to document that the imposed thermal histories did affect the relaxation spectrum of the material, i.e. that significant ageing had occurred. Further documentation was done on a macroscopic scale through stress–strain testing. Finally a great deal of attention was given to the examination of the craze velocities in aged materials, based on craze growth models[4] originally developed for unaged block copolymers.

EXPERIMENTAL

The polystyrene/polybutadiene diblock samples were synthesized in this laboratory by means of anionic polymerization as outlined by Bates *et al.*[5] The homopolystyrene was purchased from Pressure Chemical Co. The molecular weights of the polymers used are as shown in *Table 1*.

Films of about 0.5 mm thickness, from which all test specimens were cut, were prepared using a solvent spin-casting apparatus[6]. After casting, samples were removed from the casting cup and further dried and annealed in a vacuum oven at 100°C for 24 h. The morphology of all

Table 1 Molecular weights of polymers used

Sample		M_n (kg mol^{-1}) PS–PB
Diblock	SB4	149–20
	SB5	126–46
	SB11	783–107
Polystyrene	S4	300–0

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[*] Present address: J. J. Thomson Laboratory, University of Reading, Reading RG6 2AF, UK
[†] To whom correspondence should be addressed

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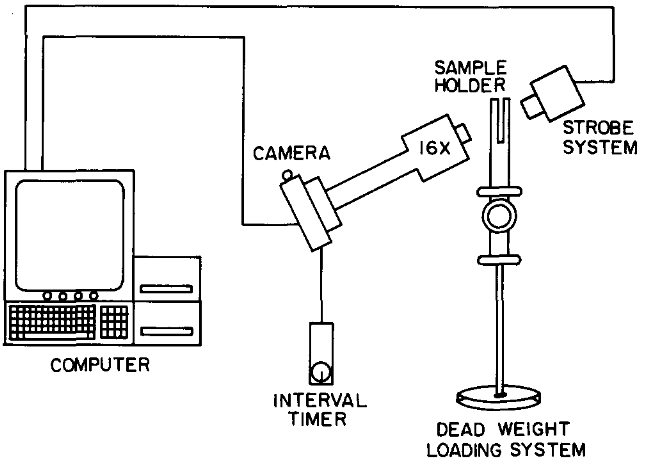

Figure 1 Apparatus for isolated craze growth measurements

films was observed using transmission electron microscopy. The diameter of the rubber domains was measured from the electron micrographs.

Specimens for craze growth and tensile tests were prepared by trimming annealed films with fresh surgical blades using a 'dog-bone' template with a 6.5 mm gauge length. To eliminate nucleation of unwanted crazes at surface imperfections, both surfaces were polished using 0.05 μm CrO slurry on a Microcloth-covered polishing wheel. Polished samples were washed in a dilute detergent solution, rinsed thoroughly and hung vertically in a vacuum oven and annealed for 24 h at 100°C.

The specimens were aged in glass plunger-valved pressure tubes, which were evacuated and filled with argon. The argon environment minimizes oxidative degradation of the polybutadiene. The sample-filled pressure tubes were first placed in a 110°C oil bath for 2 h to erase prior ageing[1]. Samples were then subjected to one of three thermal treatments: quenching, slow cooling, or isothermal ageing. Quenched samples were immediately placed in a liquid-nitrogen bath and removed when boiling ceased. Slow cooled samples were brought to room temperature at a rate of 5°C h^{-1}. To age samples isothermally, the pressure tubes were immediately placed in a second oil bath at 87°C, and later liquid-nitrogen quenched.

Dynamic mechanical properties of the aged and unaged samples were determined using a direct-reading dynamic viscoelastometer, Rheovibron model DDV-II-C. The Rheovibron was operated at a frequency of 11 Hz over the temperature range of 25–120°C. The temperature was raised at 1–2°C $\min^{-1}$.

Stress–strain tests were conducted on a table-top Instron (model 1122). Strain rates of 0.00013 s^{-1} and 0.013 s^{-1} were used. In addition the Instron was fitted with a controlled temperature chamber for sub-ambient testing.

Isolated craze growth experiments were carried out on the apparatus shown in *Figure 1* in the manner outlined by Schwier *et al.*[4]. To ensure controlled nucleation of crazes, the surfaces of aged tensile specimens were indented using a Leitz Microhardness Tester. Photographs of the growing crazes were taken with a specially adapted camera, which allowed it to be fired through the hot shoe by an Apple II computer[7]. The computer simultaneously fired the strobe flash. The time interval between exposures could be varied from 5 s to 30 min, allowing for measurements over three decades of time. The craze lengths were measured from enlarged views of the film negatives.

RESULTS

Dynamic mechanical spectroscopy

The effect of physical ageing on the loss factor, tan δ ($=E''/E'$), is shown in *Figures 2–9* for the series of samples examined. The volume fraction, f, of polybutadiene in the samples ranges from a low of 6% to a high of 18%. The modes of molecular motion that are probed by the tan δ measurement in this region of frequency and temperature are associated with both the polystyrene matrix and the mixed interfacial region between the continuous polystyrene zones and the spherical polybutadiene domains.

In *Figures 2–5*, the effect of cooling rate on tan δ is shown. The level of tan δ is decreased significantly by

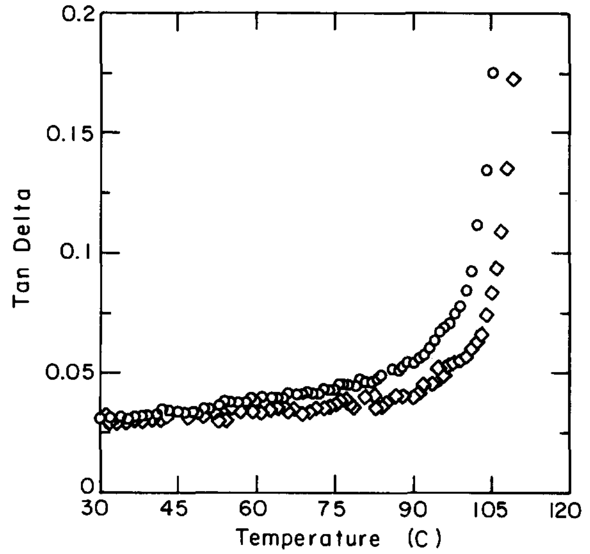

Figure 2 Tan δ as a function of temperature for SB4/S4 blend containing 6 vol% PB: (○) quenched and (◇) slow cooled samples

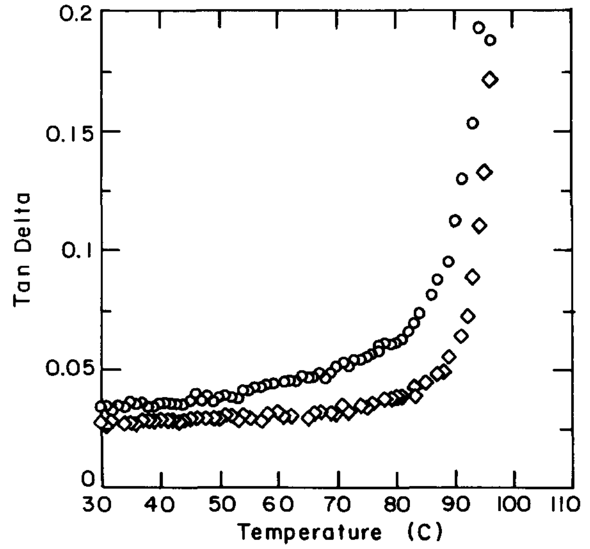

Figure 3 Tan δ as a function of temperature for SB11/S4 blend containing 6 vol% PB: (○) quenched and (◇) slow cooled samples

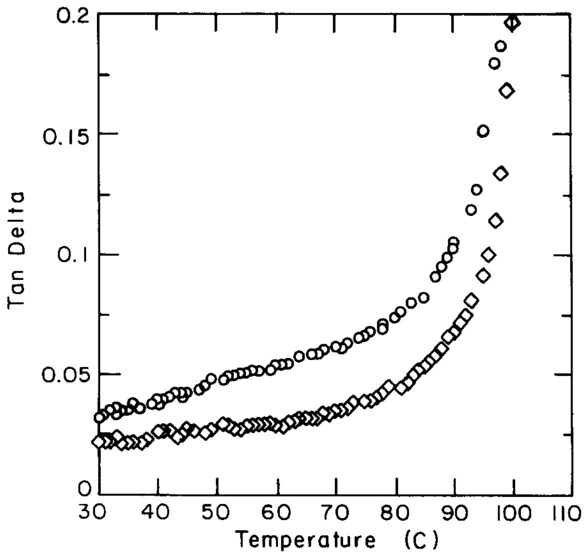

Figure 4 Tan δ as a function of temperature for SB4 containing 14 vol% PB: (○) quenched and (◇) slow cooled samples

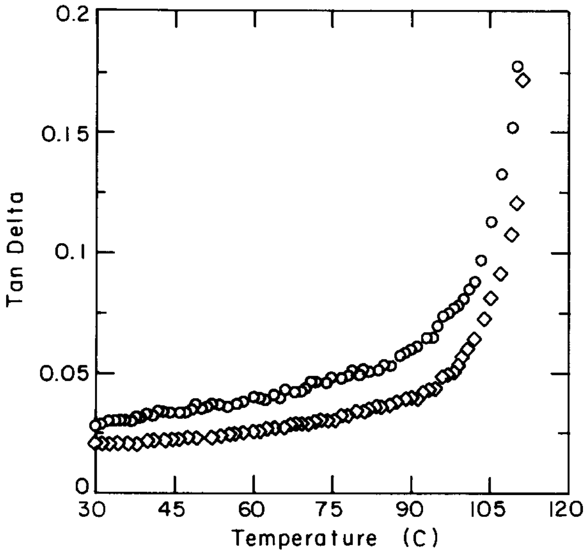

Figure 5 Tan δ as a function of temperature for SB5/S4 blend containing 18 vol% PB: (○) quenched and (◇) slow cooled samples

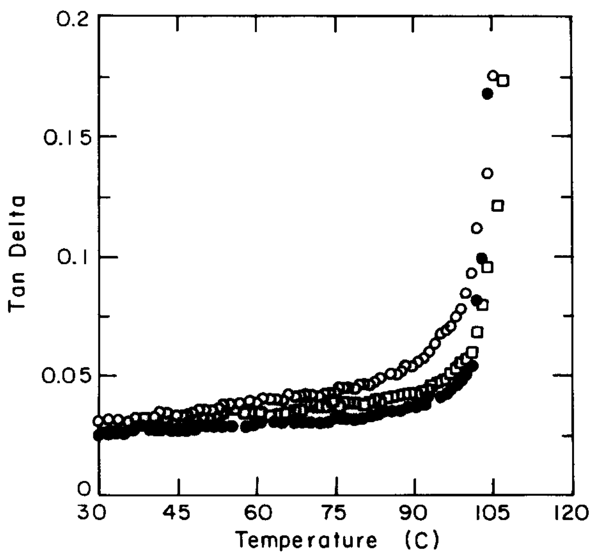

Figure 6 Tan δ as a function of temperature for SB4/S4 blend containing 6 vol% PB: samples were (○) quenched, (□) aged 6 days at 87°C and (●) aged 22 days at 87°C

ageing, beginning at about 50°C and continuing to the softening temperature. The influence of isothermal ageing at 87°C is shown in *Figures 6–9* for the same set of diblock/blends; once again there is a decrease in tan δ with ageing. The figures demonstrate that the shift in tan δ is dependent on the length of time the sample was aged. Prolonged ageing at 87°C (beyond 7–10 days) has little further effect on the tan δ curve as shown in *Figure 6*.

The temperature region over which tan δ is influenced by ageing has been called the β transition of polystyrene[8]. The decrease in tan δ indicates decreases in molecular mobility at a given temperature. A number of researchers[3,8] have correlated decreases in the β transition with decreases in the impact strength and tensile elongation of many polymers including polystyrene copolymers[3].

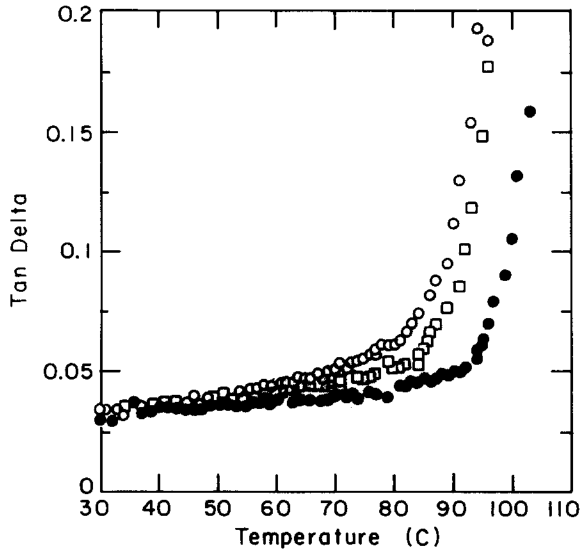

Figure 7 Tan δ as a function of temperature for SB11/S4 blend containing 6 vol% PB: samples were (○) quenched, (□) aged 3 days at 87°C and (●) aged 10 days at 87°C

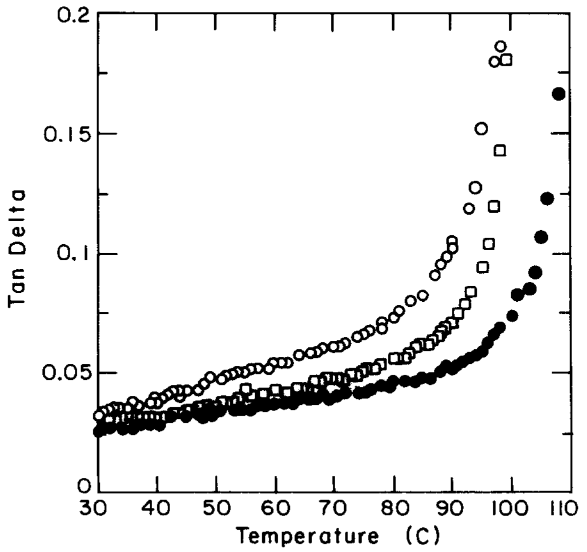

Figure 8 Tan δ as a function of temperature for SB4 containing 14 vol% PB: samples were (○) quenched, (□) aged 3 days at 87°C and (●) aged 10 days at 87°C

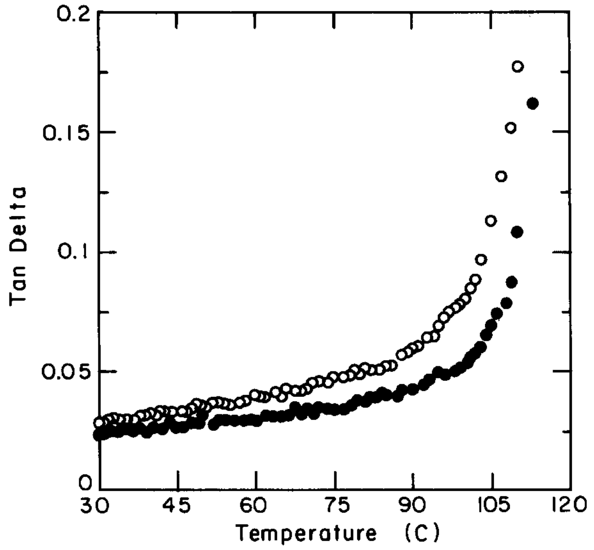

Figure 9 Tan δ as a function of temperature for SB5/S4 blend containing 18 vol% PB: samples were (○) quenched and (●) aged 7 days at 87°C

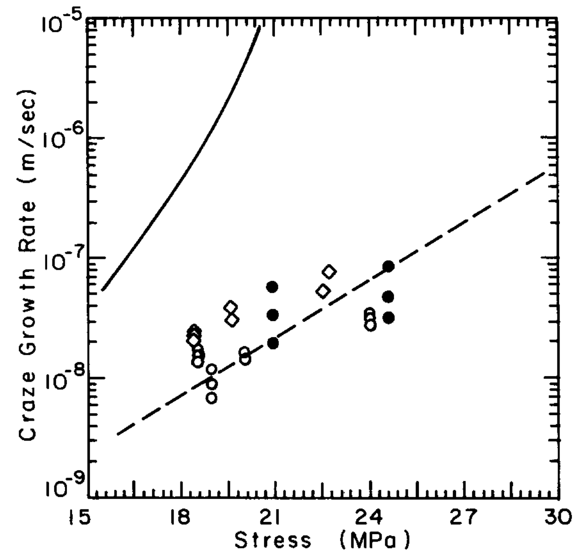

Figure 10 Craze growth rate as a function of applied stress for SB4/S4 blend containing 6 vol% PB: samples were (○) quenched, (◇) slow cooled and (●) aged 6 days at 87°C; (———) cavitation model, (– – –) meniscus model

Craze growth kinetics

Craze growth data for an SB4/S4 blend and an SB11/S4 blend are presented in *Figures 10* and *11*. In both cases the volume per cent of polybutadiene is 6%. The polybutadiene sphere diameter, as determined by transmission electron microscopy, is 120 Å in the case of the SB4/S4 blend, and 250 Å for the SB11/S4 blend. Data for quenched, slow cooled and isothermally aged samples are shown for each blend.

In *Figures 12* and *13* craze growth data for SB4 and an SB5/S4 blend are presented. The volume per cent of rubber is 14% for SB4 and 18% for the SB5/S4 blend. The polybutadiene sphere diameter is 150 Å in the case of SB4 and 200 Å in the case of the SB5/S4 blend. As in the low-rubber-concentration samples, quenched, slow cooled and isothermally aged data are presented.

Also plotted in each figure are the predictions of two different craze growth models, which will be discussed in a later section.

Stress–strain behaviour

Stress–strain results are shown in *Figures 14–23*. Samples were tested at two strain rates, a low rate of 0.00013 s^{-1} and a high rate of 0.013 s^{-1}. In addition, tests were conducted at room temperature (25°C) and at 0°C.

It is clear, upon examination of the data, that neither slow cooling nor isothermal ageing has any significant influence on the flow stress or the overall toughness of these materials. This is true regardless of the strain rate, test temperature or rubber concentration. As would be expected, there is a noticeable increase in the flow stress with increase in strain rate and with decrease in

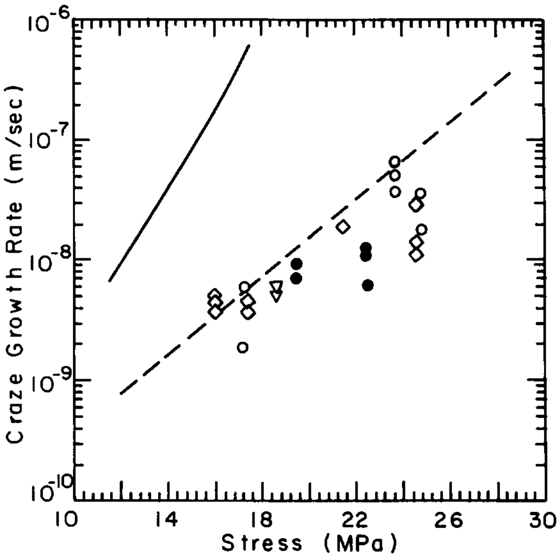

Figure 11 Craze growth rate as a function of applied stress for SB11/S4 blend containing 6 vol% PB: samples were (○) quenched, (◇) slow cooled, (▽) aged 7 days at 87°C and (●) aged 12 days at 87°C; (———) cavitation model, (– – –) meniscus model

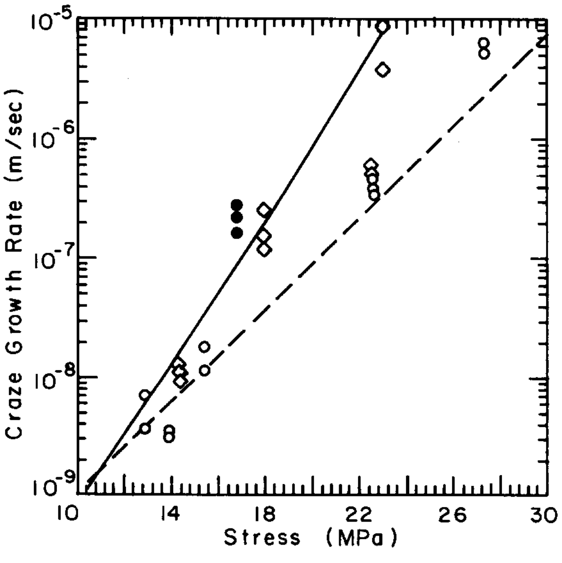

Figure 12 Craze growth rate as a function of applied stress for SB4 containing 14 vol% PB: samples were (○) quenched, (◇) slow cooled and (●) aged 12 days at 87°C; (———) cavitation model, (– – –) meniscus model

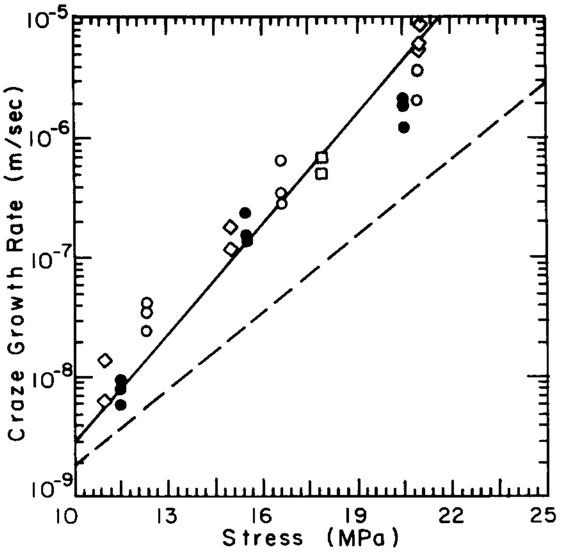

Figure 13 Craze growth rate as a function of applied stress for SB5/S4 blend containing 18 vol% PB: samples were (○) quenched, (◇) slow cooled, (□) aged 5 days at 87°C and (●) aged 7 days at 87°C; (———) cavitation model, (– – –) meniscus model

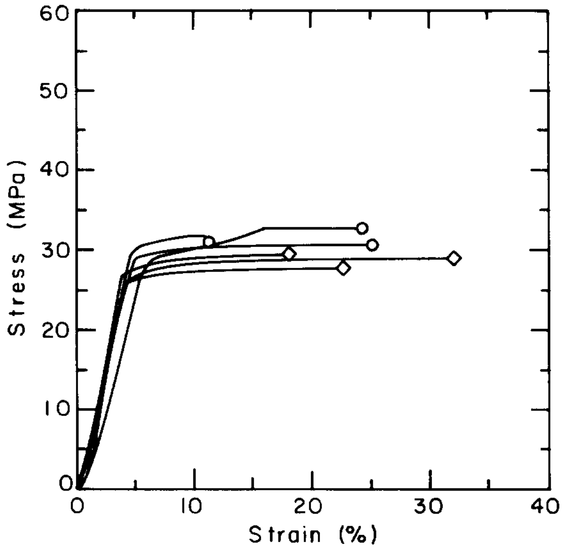

Figure 14 Stress–strain behaviour of SB11/S4 blend containing 6 vol% PB at a strain rate of 0.00013 s^{-1} and 25°C: (○) quenched and (◇) slow cooled samples

temperature for both the low-rubber-concentration (*Figures 14*, *16* and *17*) and high-rubber-concentration (*Figures 19* and *22*) samples. In a similar manner, the modulus increases with increasing strain rate and with decreasing temperature[7].

DISCUSSION

Dynamic mechanical spectroscopy was used to document changes in the material caused by physical ageing. *Figures 2–9* show that the loss factor, tan δ, decreased significantly following slow cooling or isothermal ageing. The amount which tan δ was shifted was not proportional to the concentration of the glassy (and hence aged) phase. The higher-rubber-concentration samples changed in their dynamic mechanical spectra as much as or more than the samples with lower rubber concentrations.

Having established that the samples are significantly aged by imposing various thermal histories, the major thrust of this work is to examine overall toughness, and in particular one component of toughness, the craze growth rate, of physically aged diblock copolymers. In a tensile experiment, toughness (W) is measured by the area under the stress–strain curve. For a high-modulus material, this can be approximated by the product of the flow stress, Y, and the strain to fracture, ε_f (ref. 9):

$$W = Y\varepsilon_f \qquad (1)$$

The strain to fracture is equal to the applied strain rate, $\dot{\varepsilon}$, multiplied by the time to fracture, t_f. Equation (1) can therefore be rewritten as:

$$W = Y\dot{\varepsilon}t_f \qquad (2)$$

For the material used in this study, the primary mode of deformation is crazing[4]. The total dilatational strain

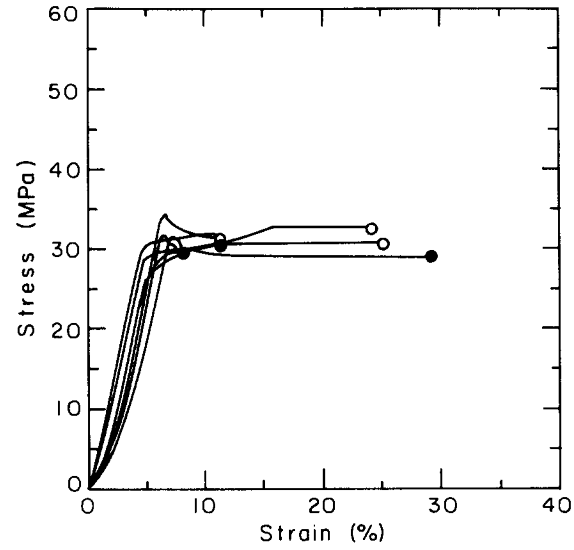

Figure 15 Stress–strain behaviour of SB11/S4 blend containing 6 vol% PB at a strain rate of 0.00013 s^{-1} and 25°C: samples were (○) quenched and (●) aged 7 days at 87°C

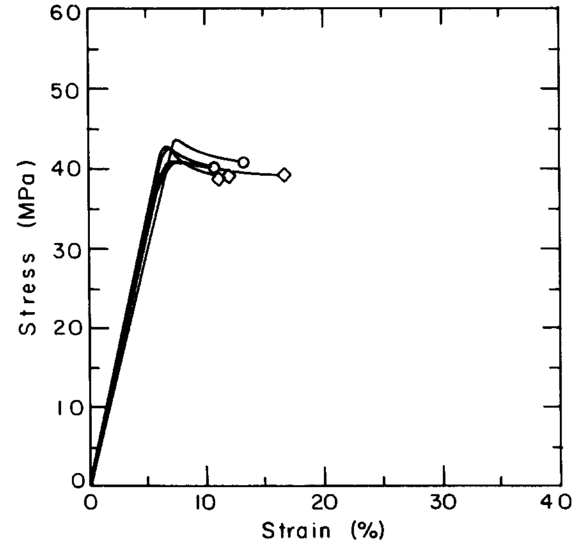

Figure 16 Stress–strain behaviour of SB11/S4 blend containing 6 vol% PB at a strain rate of 0.013 s^{-1} and 25°C: (○) quenched and (◇) slow cooled samples

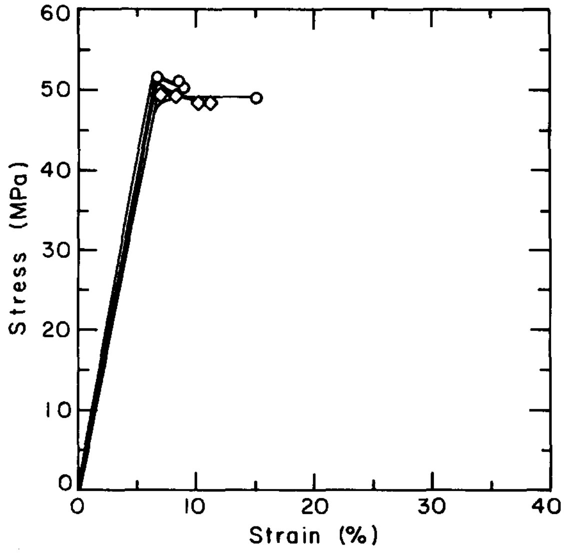

Figure 17 Stress–strain behaviour of SB11/S4 blend containing 6 vol% PB at a strain rate of 0.013 s^{-1} and 0°C: (○) quenched and (◇) slow cooled samples

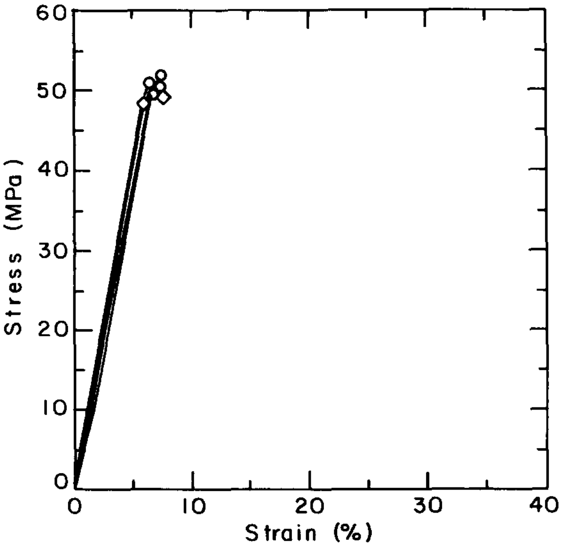

Figure 18 Stress–strain behaviour of SB4/S4 blend containing 6 vol% PB at a strain rate of 0.013 s^{-1} and 0°C: (○) quenched and (◇) slow cooled samples

rate, Φ, must therefore equal the imposed strain rate. The dilatational strain rate can be decomposed into three factors[9]:

$$\Phi = \rho b \dot{a} \tag{3}$$

where ρ is the total active craze-front length per unit volume, b is the typical craze thickness, and $\dot{a}$ is the craze growth rate. Substitution of equation (3) into equation (2) yields the total expression for toughness:

$$W = Y \rho b \dot{a} t_f \tag{4}$$

The craze thickness, b, is a relatively constant material parameter in most polymers. Kramer[10] has shown that mature crazes can thicken by drawing fresh polymer into the craze fibrils; however, this thickening rate is quite small in comparison to the strain generated through the initial craze-tip growth process. We will take craze thickness to be an ageing-independent constant for each of the four separate materials under consideration here. For materials with high rubber volume fraction, the craze thickness is proportional to the polybutadiene sphere diameter, as was suggested by the cavitation model, and equal to twice the sphere diameter[4]. In the case of low rubber volume fractions, b is taken to be equal to that of pure polystyrene[4].

The total active craze-front length is determined by the kinetic balance between crazes initiating and terminating within the material. Because of this, the value of ρ is strongly dependent on the density of initiation sites both on the free surfaces and within the sample. The particles within the diblock material studied here do not act as craze initiators[4,9,11,12]. For a given value of applied stress, ρ can therefore also be considered an ageing-

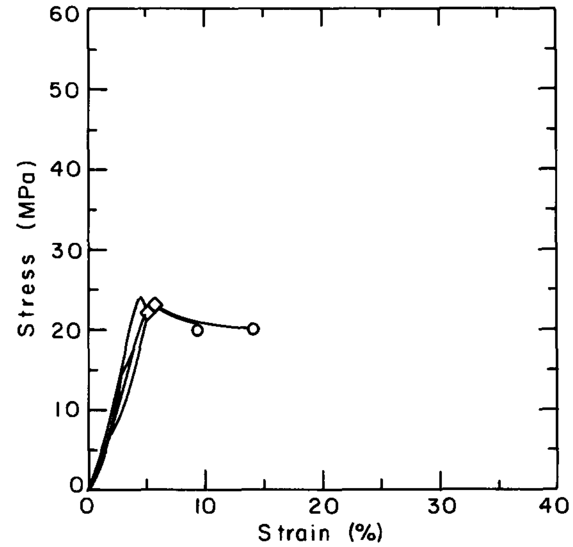

Figure 19 Stress–strain behaviour of SB4 containing 14 vol% PB at a strain rate of 0.00013 s^{-1} and 25°C: (○) quenched and (◇) slow cooled samples

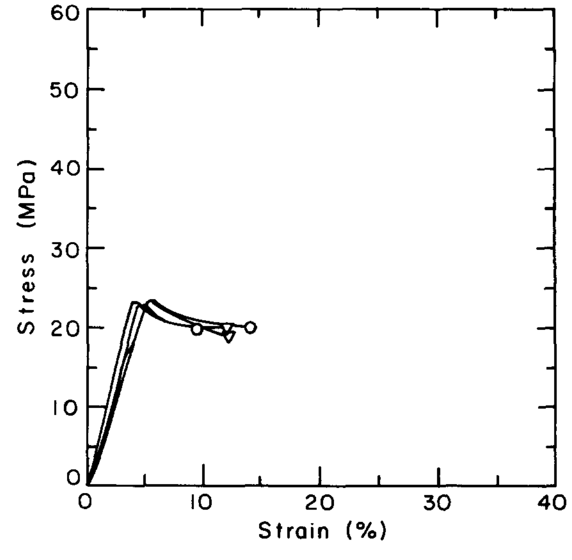

Figure 20 Stress–strain behaviour of SB4 containing 14 vol% PB at a strain rate of 0.00013 s^{-1} and 25°C: samples were (○) quenched and (▽) aged 3 days at 87°C

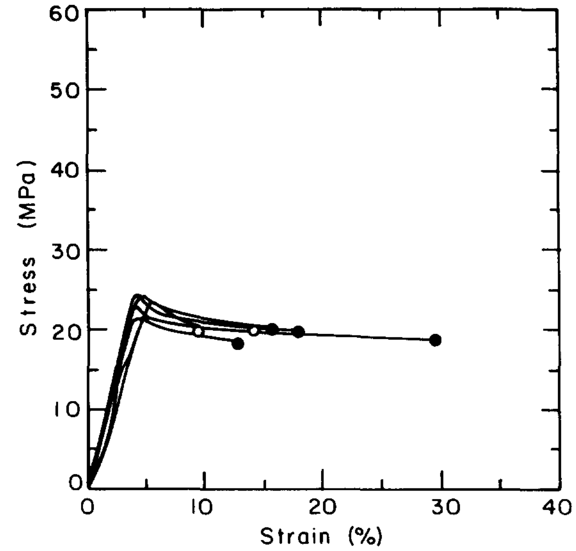

Figure 21 Stress–strain behaviour of SB4 containing 14 vol% PB at a strain rate of 0.00013 s^{-1} and 25°C: samples were (○) quenched and (●) aged 7 days at 87°C

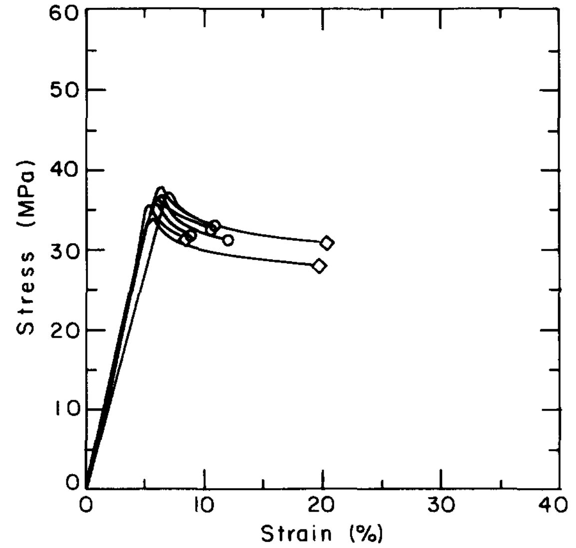

Figure 22 Stress–strain behaviour of SB4 containing 14 vol% PB at a strain rate of 0.013 s^{-1} and 25°C: (○) quenched and (◇) slow cooled samples

independent constant since the extent of surface nucleation of crazes was controlled by the specimen surface preparation procedures used here[7].

The time to fracture for a material is typically the time elapsed before the oldest craze fibrils break down to form a crack. This term is also likely to be independent of ageing since the fibrils in a craze are 'rejuvenated' by the flow process elongating them into their fibrillar form[1]. Thus t_f will be considered constant here for a given material and stress level. The two remaining parameters in the toughness equation are the flow stress and the craze growth rate. For physical ageing to affect the toughness, it must therefore influence either one or both of these terms. *Figures 14–23* clearly show that there is no change in the flow stress following physical ageing. Thus the only manner by which ageing can influence toughness in our materials is through changes in the craze velocity.

Schwier, Argon and Cohen[4] addressed the velocities of crazes in unaged spherical morphology SB block copolymers. At low polybutadiene volume fractions (less than 5%), the craze growth rate was well described using the meniscus instability model put forth by Argon and Salama[13]. This mechanism produces the interconnected passages of a craze by the repeated convolution of the craze-tip interface. The craze growth rate, da/dt, may be written as a function of the applied stress, σ_∞:

$$\frac{da}{dt}=\frac{D_1}{\sigma_\infty}\exp\left\{\frac{-B}{kT}\left[1-\left(\frac{\sigma_\infty\lambda'}{\hat{Y}}\right)^{5/6}\right]\right\} \qquad (5)$$

where a is craze length, t is time, σ_∞ is distant applied stresss, B is activation energy, k is Boltzmann's constant, T is temperature, λ' is craze fibril extension ratio reduced by the effect of orientation hardening and $\hat{Y}$ is athermal flow stress.

The exponential term, which includes λ', the craze fibril extension ratio reduced by the effect of orientation hardening, and $\hat{Y}$, the athermal flow stress, is derived from the inelastic deformation theory of Argon[14]. The pre-exponential term, D_1, is calculated from a number of material parameters, including the polymer surface tension and the exponent of the phenomenological constitutive expression $\sigma=A\dot{\varepsilon}^n$, which describes the plastic flow behaviour of the polymer.

It is clear from examining *Figures 10* and *11* that physical ageing has no effect on the rate of craze growth in those materials which contain low volume fractions of PB. Within experimental error, there is no change in the craze growth rate after slow cooling or isothermally ageing the samples. As would be expected, the data of *Figures 10* and *11* are fit well by the meniscus instability model of Argon and Salama[13], which Schwier *et al.*[4] have shown applies to craze growth in low-rubber-concentration materials of this type. These results are also in agreement with the data collected by Kefalas for pure polystyrene[15]. Kefalas found only a small change in craze growth rates in a limited study on homopolystyrene using a single thermal history for ageing the materials.

In the present study a value of 1.5 × 10^8 m s^{-1} was used for the pre-exponential term, D_1, in the meniscus model.

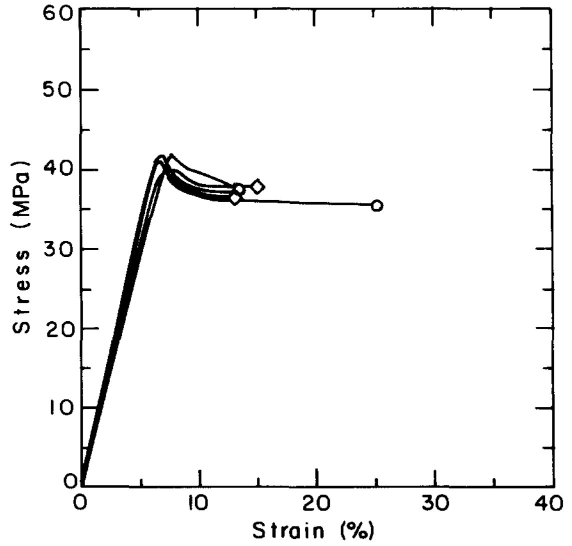

Figure 23 Stress–strain behaviour of SB5/S4 blend containing 18 vol% PB at a strain rate of 0.013 s^{-1} and 0°C: (○) quenched and (◇) slow cooled samples

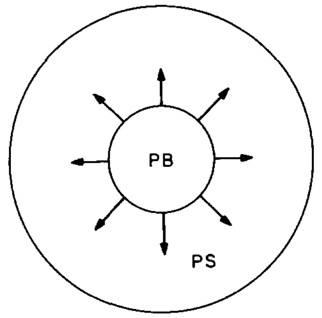

Figure 24 Spherical PB particle under hydrostatic tension due to mismatch between the thermal expansion coefficients of the two phases

This is the value predicted from theory by Argon and Salama[13] and used in their original application of the model to polystyrene. In two later studies on craze growth, Hawkins[16] with polystyrene and Schwier *et al.*[4] with diblock copolymers, D_1 was used as a fitting parameter since the calculated value did not give good agreement with data. The value of D_1 used by Schwier was $2.0 \times 10^7 \mathrm{m\,s^{-1}}$, which is nearly an order of magnitude less than the predicted value used here. Schwier suggested that this discrepancy might in part be due to physical ageing, but the current data indicate clearly that this is not the case.

For materials at higher rubber contents (greater than 11%), Schwier and coworkers[4] were able to model craze growth by assuming that the rate-determining step is the cavitation of the rubber particles. Following cavitation, drawing and fibril formation in the polystyrene matrix occur. This assumption was confirmed with electron microscopy[4,9,12]. The concentrated stresses that cause the rubber to cavitate arise from two contributions. First, and most important, are the thermal stresses induced by the thermal expansion coefficient mismatch between the two phases. The second contribution arises from the local stress concentration that exists ahead of the growing craze tip.

The cavitation model can be expressed in a form similar to the meniscus model:

$$\frac{\mathrm{d}a}{\mathrm{d}t} = D_2 \exp\left\{\frac{-B}{kT}\left[1-\left(\frac{\sigma_\infty \lambda'}{\hat{Y}_\mathrm{c}(1-f)}\right)^{5/6}\right]\right\} \tag{6}$$

with

$$D_2 = \frac{E_\mathrm{c}^2 \varepsilon_\mathrm{m}^2 \delta[1-(1/\theta)]\dot{\varepsilon}_0}{(\sigma_\mathrm{m}-\sigma_\infty)^2 \pi (1-v_\mathrm{c}^2)\varepsilon_\mathrm{cr}} \tag{7}$$

where f is overall sample volume fraction of PB, E_c is Young's modulus (composite), σ_m is stress at which degradation begins, δ is degradation zone half-thickness, θ is ratio of descending to ascending slopes of the degradation traction law[4], $\dot{\varepsilon}_0$ is yield-theory frequency factor, ε_cr is mature craze fibril strain, ε_m is strain at which degradation begins and v_c is Poisson's ratio (composite).

The thermal residual stresses that facilitate cavitation are the direct result of the mismatch between the volumetric thermal expansion coefficients of the two phases. In *Figure 24* a single rubber particle, surrounded by a glassy matrix, is shown in a tensile stress state. Decreases in the volume of the matrix due to physical ageing will cause the 'hole' containing the rubber sphere to contract. Relaxation of the stresses would therefore be proportional to the volume change due to ageing. A second path by which relaxation of the stresses on the particles may occur is through non-linear creep of the glassy matrix.

In order to evaluate the stress relief due to physical ageing, we have considered[7,17] two samples, one that has been quenched from above T_g to room temperature and the other isothermally aged at 87°C for 12 days and then quenched to room temperature. The unaged sample has a 'volumetric thermal expansion coefficient', γ_{PS}, given by:

$$\gamma_{\mathrm{PS}} = \Delta V / \Delta T \tag{8}$$

while the aged sample has an effective thermal expansion coefficient equal to:

$$\gamma_{\mathrm{PS,A}} = (\Delta V + \Delta V')/\Delta T \tag{9}$$

where $\Delta V'$ is equal to the volume change due to ageing. As we have discussed previously[17], the stress at which degradation begins, σ_m, is a function of the thermal stress and the cavitation stress σ_{cav}. The thermal stress, σ_{th}, is calculated from the difference in volumetric expansion coefficients of the polystyrene and polybutadiene[17]. The result of the analysis is that the craze growth rate, at room temperature, is predicted to decrease by no more than 20% upon fully ageing the material at 87°C[17].

The second possibility for time-dependent relief of the thermal stresses on the PB spheres is the effect of non-linear creep of the glassy matrix. The role of PS creep on the stress state of rubber particles has been modelled by Boyce *et al.*[18,19]. They have shown that this mode of relaxation results in a very small decrease in the radial stresses acting on the polybutadiene, although there is a large decrease in the equivalent shear stress, which is related to the deviatoric (non-isotropic) stress state (*Figure 25*).

From both of these analyses, it is clear that neither physical ageing nor non-linear creep of the polystyrene matrix is expected significantly to affect the level of thermal residual stress on the rubber particles; therefore it is also expected that physical ageing should have only a small effect on the rate of craze growth in materials that follow the cavitation model of craze growth.

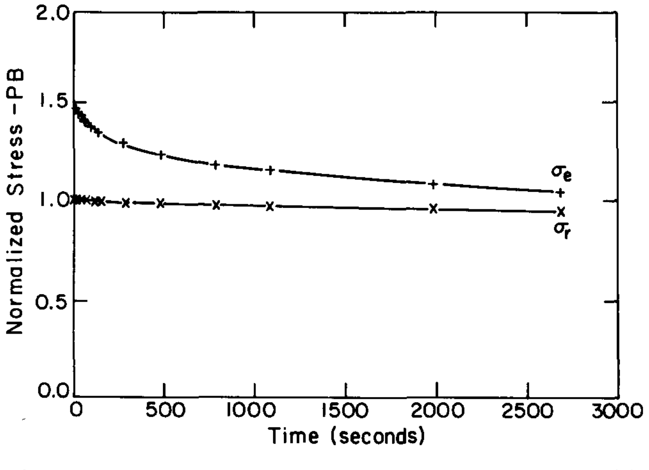

Figure 25 Relaxation of thermal residual stresses due to a PB particle in an infinite PS matrix; σ_r is the radial stress and σ_e is the equivalent shear stress, which is related to the deviatoric (non-isotropic) stress state; stresses are normalized with respect to σ_r at time zero

From *Figures 12* and *13* it is clear that there is no change in craze growth rate due to physical ageing of those materials with high rubber content which are expected to craze via the cavitation mechanism. The slow cooled and isothermally aged samples have rates in good agreement with those for the unaged or quenched samples. This result is in full agreement with the discussion above, which suggested that physical ageing should have little effect on the thermal residual stress and hence on the craze growth rates in these materials.

As discussed previously[7,17], a cavitation stress of 47 MPa was chosen to give the best fit for the data of the SB5/S4 blend (*Figure 13*). In the case where the concentration of rubber was 14% (*Figure 12*), the craze growth rates fell between the predictions of the meniscus and cavitation models. This indicates that neither mode of craze growth is dominant at this volume fraction of polybutadiene. Thus the critical rubber concentration, at which point the cavitation mode of craze growth is dominant, is probably slightly higher than the value of 11% suggested by Schwier[4].

Overall, the picture that emerges is that toughness in these diblock copolymers is not affected by ageing. Toughness in these materials is directly related to the craze growth rate and there is no ageing-induced change in the craze growth rate; nor is there any change in the flow stress or ultimate elongation following ageing. The fact that there is no change in craze growth rates regardless of the mechanism by which the crazes are forming points to the fact that the growing craze front is not sensitive to the physical ageing-induced densification of the material. This can be explained in terms of a rejuvenation of the material immediately ahead of the growing craze tip. It has been shown[1,20] that the application of a stress field to physically aged material causes prior ageing to be erased. The local stress concentration that exists ahead of the growing craze tip due to its crack-like geometry erases the ageing ahead of it so that the material entering the growth zone is, in effect, unaged.

SUMMARY AND CONCLUSIONS

The objective of this work has been to gain an understanding of the interaction between the phenomenon of physical ageing, the thermal residual stresses that exist in polystyrene/polybutadiene diblock copolymers and their craze growth behaviour. The work was based on the existence of newly developed craze growth models[4] for unaged block copolymers.

Craze growth experiments were carried out on diblocks and diblock/polystyrene blends containing volume fractions of polybutadiene ranging from 6% to 18%. At low volume fractions of polybutadiene, i.e. samples containing 6% rubber, there was no change in the craze growth rates following physical ageing. The data for the low-rubber-concentration samples were successfully fitted with the meniscus instability model. A value of 1.5×10^8 m s^{-1} was used for the pre-exponential term, D_1, which is the theoretically predicted value arrived at by Argon and Salama in their original work on polystyrene[13].

Samples containing 14% and 18% polybutadiene were also tested. In these cases there was also no change in craze growth rate following physical ageing. This is in agreement with the analysis done on the relief of the thermal stresses due to physical ageing because the predicted 20% decrease in growth rate[17] is not measurable within experimental error. The craze growth data for the high-rubber blends were well fitted by the cavitation model, assuming a cavitation stress for the polybutadiene of 47 MPa. The agreement of the present data, for high volume fractions of rubber, with the cavitation model is further confirmation of this recently proposed mechanism of craze growth in spherical morphology block copolymers.

Tensile testing of these samples revealed that there was no change in the toughness, i.e. the area under the stress–strain curve, following physical ageing. Tests were done at two strain rates, 0.00013 s^{-1} and 0.013 s^{-1}, and two temperatures, 25°C and 0°C. For all rubber concentrations, the flow stress, elongation to break and modulus were not affected by physical ageing. Because craze initiation occurs only at surface imperfections in these samples, the craze velocity provides the major contribution to their toughness. Since there is no change in craze growth rate, there should be no change in toughness on a macroscopic level, as observed.

The overall picture is that diblock copolymers exhibit toughness that is resistant to physical ageing, even though changes in the relaxation spectrum do occur. In some modes of deformation, for example impact loadings, which have not been investigated here, there may be changes in properties due to physical ageing. While this class of materials does not exhibit the toughness associated with the traditionally ductile polymers, they do possess high yield stresses and elongations to break in the range of 20–40%, which remain unaffected by physical ageing.

In the commercially important rubber-modified high-impact polystyrene (HIPS), where the relatively large rubber/polystyrene particles act as craze initiators, significant changes in the mechanical properties have been documented following physical ageing. As mentioned above, for the diblock copolymers studied, craze initiation is limited to surface flaws, and this is apparently the reason for their resistance to ageing-induced mechanical properties changes; conversely, it is likely that observed ageing-induced reductions in toughness in HIPS-like materials arise from an influence of ageing on the craze-initiation process since it is clear that craze velocities are unaffected by ageing.

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APPENDIX

Nomenclature and parameter values

a	craze length
$\dot{a}$	craze growth rate
B	activation energy for plastic flow of polystyrene (26.0 kcal mol^{-1})

b	mature craze thickness
D_1	pre-exponential term in meniscus instability model ($1.5\times 10^{8}\,\mathrm{m\,s^{-1}}$)
D_2	pre-exponential term in cavitation model
E_c	Young's modulus (composite)
E'	storage modulus
E''	loss modulus
f	volume fraction of polybutadiene
k	Boltzmann's constant
T	temperature
T_β	highest secondary transition temperature
t	time
t_f	time to fracture
V	specific volume
W	toughness as defined by area under a stress–strain curve
Y	flow stress
$\hat{Y}$	athermal flow stress
γ	volumetric thermal expansion coefficient ($\gamma_{PS}=2.0\times 10^{-4}\,\mathrm{K^{-1}}, \gamma_{PB}=7.5\times 10^{-4}\,\mathrm{K^{-1}}$)
δ	degradation zone half-thickness (assumed equal to the rubber particle diameter)
ε_{cr}	mature craze fibril strain ($\varepsilon_{cr}=4.0$)
ε_f	strain to fracture in stress–strain experiment
ε_m	strain at which degradation begins
$\dot{\varepsilon}$	test strain rate
$\dot{\varepsilon}_0$	yield-theory frequency factor ($\dot{\varepsilon}_0=10^{13}\,\mathrm{s^{-1}}$)
θ	ratio of descending to ascending slopes of the degradation traction law
Φ	craze dilatational strain rate
λ'	craze fibril extension ratio reduced by the effect of orientation hardening ($\lambda'=1.853$)
ν_c	Poisson's ratio (composite)
ρ	active craze-front length per unit volume
Ω	stress concentration induced in the rubber domains due to an outside applied tensile stress
σ_{cav}	stress at which polybutadiene cavitates
σ_e	equivalent shear stress
σ_m	stress at which degradation begins
σ_r	radial stress
σ_{th}	thermal stress induced in rubber domains as a result of the thermal expansion coefficient mismatch
σ_∞	distant applied stress

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