A re-examination of the cavitation model for craze growth in block copolymers with spherical morphology

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A blend of a polystyrene/polybutadiene (PS/PB) diblock copolymer and polystyrene homopolymer was prepared by solution casting to yield a material containing 18 vol% PB and a morphology of PB spheres (200 Å diameter) in a PS matrix. Various thermal histories, including rapid quenching, slow cooling and isothermal ageing, were imposed on specimens of this material; dynamic mechanical tests revealed significant changes in the viscoelastic relaxation spectrum as a function of ageing. Measured craze velocities were compared to the predictions of a rubber particle cavitation model for craze growth in these materials. Using a value of 47 MPa for the cavitation strength of the PB domains, excellent agreement was obtained between the model and all experimental results. Ageing had essentially no effect on craze velocities in this material.

(Keywords: block copolymers; rubber cavitation; crazing mechanisms)

INTRODUCTION

The toughness of many glassy polymers has been improved by modification with rubber, using the methods of blending, grafting and block copolymerization. These rubber-modified polymers are frequently capable of extensive amounts of crazing which results in significant dilatational plasticity. Block copolymers are ideal model materials for studying crazing because of the ease of morphology manipulation; the size as well as the shape of the rubber domains can be controlled.

Recently Schwier, Argon and Cohen[1] proposed a new mechanism of craze growth based on the advance of a cavitation front of thickness equal to the diameter of the spherical rubber domains in the block copolymer morphology. The concentrated stresses that cause the rubber to cavitate arise from two contributions. First, and most important, are thermal stresses induced by the thermal expansion coefficient mismatch between the dispersed rubbery component and the continuous glassy matrix. The second contribution arises from the local stress concentration that exists ahead of the growing craze tip. The model was confirmed through electron microscopy and measurement of craze growth rates on polystyrene/polybutadiene (PS/PB) diblock copolymers containing more than 11 wt% rubber[1].

In this paper this cavitation model for craze growth will be re-examined. In particular, the influence of time-dependent volumetric ageing of the glassy phase on thermal stress and the effect of this change on the crazing behaviour will be addressed. Results of craze growth-rate experiments for aged and unaged samples will be presented and compared with the predictions of the cavitation model.

CRAZE GROWTH BY CAVITATION OF SPHERICAL RUBBER DOMAINS

Schwier, Argon and Cohen[1] addressed the craze growth behaviour of spherical morphology block copolymers over a wide range of rubber concentrations. At low polybutadiene volume fractions ($f < 5\%$), the measured craze growth rates were well described by the meniscus instability mechanism put forth by Argon and Salama[2] for glassy homopolymers. For the materials at high rubber contents ($f > 11\%$), Schwier *et al.*[1] were able to model craze growth by assuming that the rate-determining step is the cavitation of the rubber particles. At intermediate rubber volume fractions ($5\% < f < 11\%$), neither mechanistic model described the craze growth-rate data over the full range of stresses employed, although the two models did bracket the range of observed material response.

In the proposed cavitation mechanism, drawing and fibril formation in the polystyrene matrix occur following the cavitation of a polybutadiene sphere. A quantitative description of the cavitation-controlled craze growth rate, da/dt, in terms of the applied stress, σ_∞, and the degradation stress, σ_m, was presented[1]:

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

with

$$D_2 = \frac{E_c^2 \varepsilon_m^2 \delta[1-(1/\theta)]\dot{\varepsilon}_0}{(\sigma_m - \sigma_\infty)^2 \pi (1-\nu_c^2)\varepsilon_{cr}} \quad (2)$$

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

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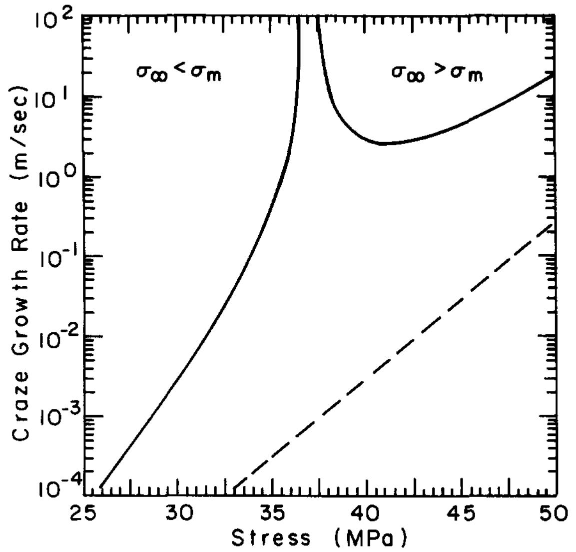

Figure 1 Prediction of the cavitation model (full curves) and the meniscus instability model (broken line) for the dependence of craze velocity on applied stress for a block copolymer containing 18 vol% PB spherical microdomains

degradation traction law[3], $\dot{\varepsilon}_0$ is yield-theory frequency factor, ε_{cr} is mature craze fibril strain, ε_m is strain at which degradation begins and ν_c is Poisson's ratio (composite).

The exponential term arises from the inelastic theory of Argon[3] for glassy polymers, which is used to describe the polymer drawing process in the craze fibrils. Composite material properties, including the athermal yield stress $\hat{Y}$ appropriate to the spherical morphology, were calculated from the pure component properties of Chow[4].

The degradation stress is the point at which the polybutadiene domains reach the critical negative pressure to cavitate under the combined action of the thermal stresses and the stress concentration ahead of the growing craze tip. Thus:

$$\sigma_m = \left(\frac{\sigma_{cav} - \sigma_{th} - \Omega\sigma_\infty}{2\Omega(1+\nu_c)} \right) + \sigma_\infty \qquad (3)$$

where σ_{cav} and σ_{th} are the cavitation and thermal stresses, Ω is the stress concentration induced in the rubber domains by the distant applied stress and ν_c is Poisson's ratio for the diblock copolymer. The thermal stress is calculated from the difference in volumetric expansion coefficients of the polystyrene and polybutadiene:

$$\sigma_{th} = (\gamma_{PS} - \gamma_{PB}) K_{PB} \Delta T / C \qquad (4)$$

where

$$C = 1 + \frac{1}{2(1-f)} \frac{K_{PB}}{K_{PS}} \left(2f + \frac{1+\nu_{PB}}{1-2\nu_{PS}} \right)$$

and where γ_{PS} and γ_{PB} are the volumetric expansion coefficients for polystyrene and polybutadiene, respectively, K_{PS} and K_{PB} are the bulk moduli of the two phases and ΔT is the temperature difference between the test temperature and the matrix glass transition temperature below which thermal stresses can develop.

When the applied stress equals the degradation stress, the value of D_2 and therefore the craze growth rate approach infinity. An infinite craze growth rate would correspond to spontaneous catastrophic failure of the rubber particles throughout the material. In *Figure 1* the craze growth rate for a diblock copolymer calculated from equation (1) is shown as a function of applied stress. The discontinuity that occurs at $\sigma_\infty = \sigma_m$ is apparent. The portion of the curve that occurs for values of $\sigma_\infty > \sigma_m$ has no physical meaning but is included here to show the full range of behaviour of equation (1). Also shown for comparison is the prediction of the meniscus instability mechanism[1,2] of craze growth over the same range of stress.

RELAXATION OF THERMAL RESIDUAL STRESSES

The analysis of Schwier *et al.*[1] showed that over half the stress required to cavitate the polybutadiene particles is provided by the misfit induced by the difference in thermal expansion coefficients of the PB spheres ($\gamma = 7.5 \times 10^{-4}\,K^{-1}$) and the PS matrix ($\gamma = 2.0 \times 10^{-4}\,K^{-1}$) in the range of temperature between the T_g of PS (100°C) and the test temperature (20°C). During this cooling process the PB spheres are constrained from contracting to their equilibrium size by the surrounding glassy matrix, leaving them in a state of triaxial tension (negative pressure). One possible source of relief of these thermal stresses on the PB spheres is through physical ageing of the glassy PS matrix; volumetric contraction[5,6] of the matrix due to ageing will enable the rubber spheres to decrease in size, thereby reducing the level of triaxial tension.

In order to evaluate the amount of stress relief due to physical ageing, consider two samples A and B, where A has been quenched from above room temperature and B has been isothermally aged at 87°C for 12 days and then quenched to room temperature. In *Figure 2* the final volumetric states of these samples, points A and B, are depicted on a volume–temperature curve.

The unaged sample has a volumetric thermal expansion coefficient that is calculated from the volume change over the temperature range and is known from a number of sources[7]. The aged sample is assumed to have

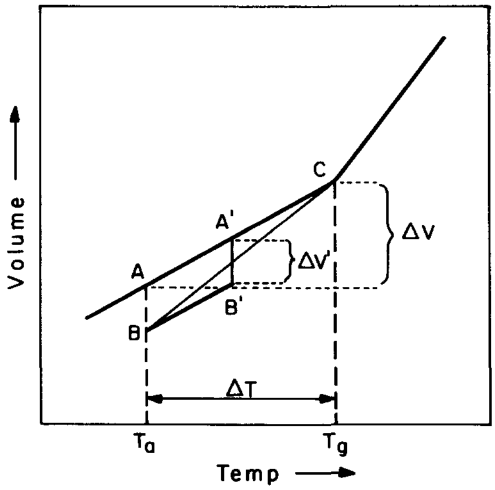

Figure 2 Volume–temperature curve for polystyrene. Point A represents final volumetric state for unaged material, and point B represents final volumetric state for isothermally aged material

Table 1

Specimen	γ_{PS} $\times 10^4$	σ_{th} (MPa)	σ_m (MPa)	Craze velocity ($m\,s^{-1}$) at $\sigma_\infty = 20$ MPa
A (quenched)	2.00	32.6	44.2	5.14×10^{-7}
B (aged)	2.47	29.8	47.1	4.14×10^{-7}

an effective thermal expansion coefficient equal to the slope of the line connecting point B to point C in *Figure 2*: $\alpha_{PS,A} = (\Delta V + \Delta V')/\Delta T$ where $\Delta V'$ is the volume change due to ageing.

To obtain the expected change in craze growth rate due to this ageing-induced stress relief, the thermal expansion coefficient of the aged material is used with equation (4) to obtain the thermal residual stress in the aged sample. The reduced volume change due to ageing ($\Delta V'/V$) is available from the work of Lee[8] and equals 0.00375 for a polystyrene sample aged 12 days at 87°C. In *Table 1* a comparison is made of the thermal and degradation stresses and the corresponding calculated craze growth rate for an unaged and aged sample.

The craze growth rate at room temperature is predicted to decrease by about 20% upon fully ageing the material at 87°C. This amount of change is not statistically significant in craze growth experiments, given the amount of scatter reported by Schwier *et al.*[1] Thus, the somewhat surprising result of the analysis presented here is that craze growth rates, measured on specimens that obey the cavitation model, should be insensitive to various states of physical ageing of the material. The experiments described below were undertaken to examine this prediction.

EXPERIMENTAL

A diblock copolymer/homopolystyrene blend containing 18 vol% polybutadiene was used. The polystyrene/polybutadiene diblock sample (SB5) was synthesized in this laboratory by means of anionic polymerization, as outlined previously[9]. The molecular weight of the PS block was 126 kg mol^{-1} and the molecular weight of the PB block was 46 kg mol^{-1}. The homopolymer of polystyrene (S4) with a molecular weight of 300 kg mol^{-1} was purchased from Pressure Chemical Co. and was solution blended in appropriate amounts with SB11 to obtain the sample containing 18 vol% PB.

Films of about 0.4 mm thickness were prepared using a solvent spin-casting apparatus[10]. Morphology of all films was observed using transmission electron microscopy of osmium-tetroxide-stained ultrathin sections. The diameter of the rubber domains, measured from the electron micrographs, was 200 Å. *Figure 3* shows the spherical morphology of the specimens.

The specimens were aged in glass plunger-valved pressure tubes, which were evacuated and filled with argon to minimize oxidative degradation of the polybutadiene. The sample-filled pressure tubes were then placed in a 110°C oil bath for 2 h to erase prior ageing[6]. Samples were then subjected to one of three thermal treatments: quenching, slow cooling or isothermal ageing. To carry out the quenching process, samples were removed from the oil bath, immediately placed in a liquid-nitrogen bath and removed when boiling ceased. Samples were slow cooled from 110°C 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 for the desired time interval and then liquid-nitrogen quenched.

Dynamic mechanical properties were determined using a direct-reading dynamic viscoelastometer, Rheovibron model DDV-II-C. The Rheovibron was operated at a frequency of 11 Hz while the temperature was raised at a rate of 1–2°C min^{-1}.

Isolated craze growth experiments were carried out in the manner outlined by Schwier *et al.*[1] To ensure controlled initiation of crazes, the surfaces of tensile specimens were indented using a Leitz Microhardness Tester[1]. Photographs of the growing crazes were taken through a microscope at 16 × magnification. Camera and flash were electronically controlled by an Apple II computer. The interval between pictures was systematically varied from 5 s to 30 min. The craze lengths were measured from enlarged views of the film negatives. Plots of these craze lengths vs. time were linear at all levels of applied stress and therefore the craze growth rates, da/dt, were easily obtained from the slopes.

RESULTS

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. The effect of physical ageing on the loss factor, tan δ ($=E''/E'$), is shown in *Figures 4* and *5*. 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 *Figure 4* the effect of cooling rate on tan δ is shown. The level of tan δ is significantly influenced by ageing, beginning in the region of mechanical response at about 50°C and continuing to the softening temperature. The influence of isothermal ageing at 87°C is shown in *Figure 5*; once again there is a significant decrease in tan δ associated with the ageing process.

Craze growth-rate data as a function of applied stress for the SB5/S4 blend are shown in *Figure 6*. Data for quenched, slow cooled and isothermally aged specimens

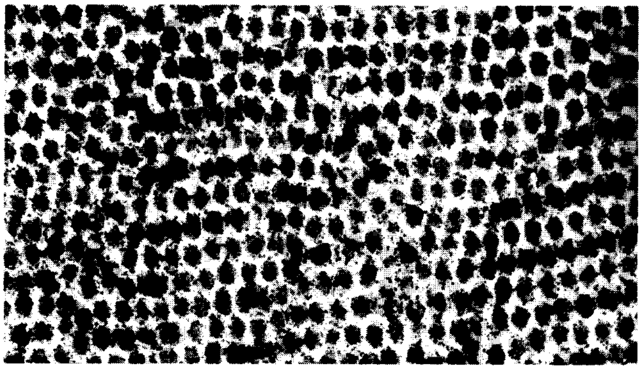

Figure 3 Transmission electron micrograph of an osmium-tetroxide-stained ultrathin section of the diblock/homopolymer blend SB5/S4

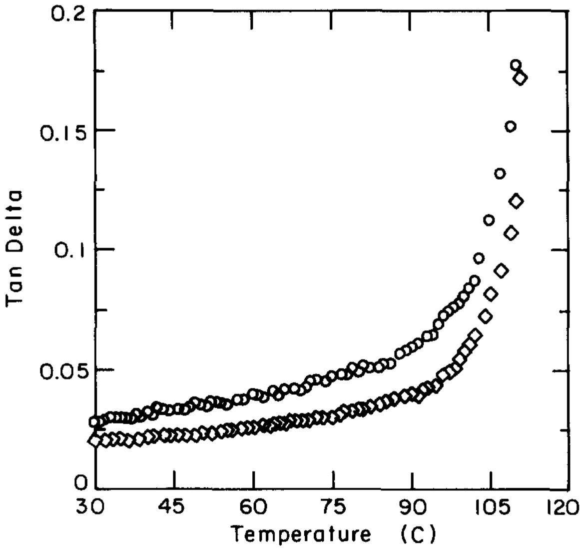

Figure 4 Tan δ as a function of temperature for SB5/S4 blend containing 18 vol% PB: (○) quenched sample and (◇) slow cooled sample

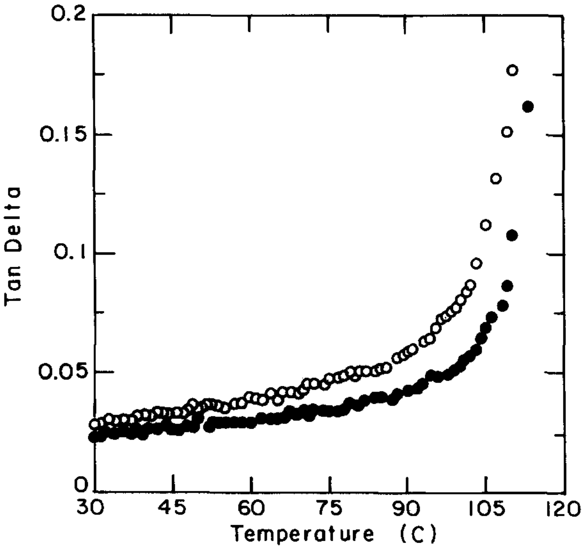

Figure 5 Tan δ as a function of temperature for SB5/S4 blend containing 18 vol% PB: (○) quenched sample and (●) sample aged 7 days at 87°C

are presented. The predictions of the cavitation model and the meniscus model are also included on the graph. Values of the parameters that were used to calculate the model predictions shown in *Figure 6* are provided in the Appendix.

DISCUSSION

It is clear upon examination of *Figure 6* that there is no significant change in craze growth rate due to physical ageing. The slow cooled and isothermally aged samples exhibit rates in good agreement with those for the unaged, or quenched, samples. This result is in full agreement with the predictions of the theoretical analysis presented above, where it was shown that physical ageing should have little effect on the thermal residual stress and hence on the craze growth rates of these materials.

In both the cavitation and meniscus models, all of the parameters except λ' and σ_{cav} can be established theoretically. The term λ' accounts for both the extension ratio λ of the craze fibril and the orientation hardening of the glassy polymer. In this work the value of 1.85, identical to that found by Argon and Salama[2] for pure polystyrene, was used to calculate the model predictions. The intrinsic cavitation strength for a typical rubber such as PB has never been determined, although there has been some work on the expansion of pre-existing flaws[11,12]. Bates *et al.*[10] have shown indirectly that the cavitation stress at −90°C must be greater than 79 MPa. In the work of Schwier *et al.*[1] a value of 60 MPa was chosen as giving the best fit with the data. Here a value of 47 MPa was chosen, the only adjustable parameter required to give excellent agreement with the data. (Larger values of σ_{cav} lower the level of the curve for the cavitation model in *Figure 6*.) This value of 47 MPa is somewhat lower than the 60 MPa chosen by Schwier *et al.*; however, the molecular weight of the rubber blocks in the sample tested here is considerably lower than those with which Schwier worked and may account for the difference in cavitation strength.

The predictions of the meniscus model, which was originally put forth by Argon and Salama[2] for pure polystyrene and which Schwier *et al.*[1] applied to diblock samples containing less than 10 vol% PB, are presented with no adjustable parameters in *Figure 6* for completeness. The craze growth-rate data for the 18 vol% PB sample under consideration here clearly do not follow the meniscus model, as expected.

CONCLUSIONS

We have verified the validity of a previously proposed mechanism of craze growth in certain PS/PB diblock copolymers containing a high volume fraction of spherical PB domains; the mechanism depends upon the cavitation of the rubbery inclusions that occurs at a triaxial stress level of about 47 MPa. Significant ageing of the glassy PS matrix surrounding the PB spheres relieves

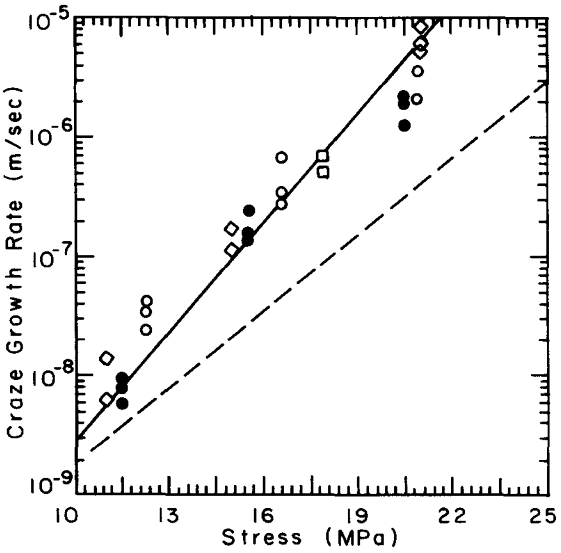

Figure 6 Craze growth rate as a function of applied stress for SB5/S4 blend containing 18 vol% PB: (○) quenched sample, (◇) slow cooled sample, (●) sample isothermally aged 7 days at 87°C and (□) sample isothermally aged 5 days at 87°C; (———) cavitation model and (- - - - -) meniscus model

the thermal residual stresses on these spheres only slightly, so that measured craze velocities are not affected by the ageing process, in keeping with the prediction of the cavitation model. Craze velocity is one factor that influences the toughness of these SB materials[13]; in a forthcoming paper we will examine the effect of ageing on the full set of factors that contribute to the toughness of a series of SB diblock/homopolymer blends covering a range of rubber volume fractions.

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APPENDIX

Nomenclature and parameter values

a	craze length
B	activation energy for PS plastic flow (26.0 kcal mol^{-1})
D_2	cavitation model pre-exponential term
E	Young's modulus ($E_{PS} = 3300$ MPa)
f	volume fraction of PB
K	bulk modulus ($K_{PS} = 3300$ MPa; $K_{PB} = 1940$ MPa)
k	Boltzmann's constant
T	temperature
T_g	glass transition temperature ($T_{g,PS} = 100°C$)
t	time
V	specific volume
$\hat{Y}$	athermal flow stress
γ	volumetric thermal expansion coefficient ($\gamma_{PS} = 2 \times 10^{-4}$ K^{-1}; $\gamma_{PB} = 7.5 \times 10^{-4}$ K^{-1})
δ	degradation zone half-thickness (assumed equal to the rubber particle diameter, 200 Å)
ε_{cr}	mature craze fibril strain ($\varepsilon_{cr} = 4.0$)
ε_m	strain at which degradation begins
$\dot{\varepsilon}_0$	yield-theory frequency factor ($\dot{\varepsilon}_0 = 10^{13}$ s^{-1})
θ	ratio of descending to ascending slopes of the degradation traction law
λ'	craze fibril extension ratio reduced by the effect of orientation hardening ($\lambda' = 1.85$)
ν	Poisson's ratio ($\nu_{PS} = 0.33$)
Ω	stress concentration induced in the rubber domains due to an outside applied tensile stress
σ	stress
σ_{cav}	stress at which polybutadiene cavitates
σ_m	stress at which degradation begins
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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