Crazing in polystyrene–polybutadiene diblock copolymers containing cylindrical polybutadiene domains

C. E. Schwier*, A. S. Argon and R. E. Cohen
Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA
(*Received 3 December 1984; revised 28 May 1985*)

Polystyrene–polybutadiene diblock copolymers exhibiting morphologies of cylindrical rubbery domains in a glassy matrix were studied in tensile stress–strain experiments. The various contributions of rubber volume fraction, overall copolymer molecular weight, and blending of diblock copolymers with homopolymers were examined. Transmission electron microscopy revealed a novel internal structure of the crazes in certain samples; inspection of the micrographs of these crazes suggests that the craze matter forms by a two-step process: cavitation in the rubbery domains followed by necking and drawing of the topologically continuous polystyrene matrix.

(Keywords: polystyrene–polybutadiene diblock copolymers; crazing; fracture in block copolymers)

INTRODUCTION

The various relationships between molecular structure and macroscopic properties such as toughness in commercial rubber-toughened polymers (e.g. HIPS, ABS), have been investigated for many years and continue to be an active area of interest[1]. These investigations are often hindered by the lack of ability to independently control the molecular and morphological parameters which are strongly inter-related in products obtained from typical industrial synthesis procedures. Because of these difficulties, there has been a trend toward the use of model materials such as block copolymers with controlled microstructures for investigations of this type. Through synthesis, polymer blending and processing, many parameters on a molecular and morphological scale (e.g. microdomain shape, size and spacing) can be altered independently. Nevertheless, good correlations between microstructural features and important macroscopic properties such as toughness have not yet been fully developed, largely owing to the complexity of the toughening mechanisms.

The aim of the work presented here was to identify the toughening mechanisms in a model set of PS/PB diblock copolymers with rod morphology and their blends with homopolymers through stress–strain experiments and transmission electron microscopy of the deformed materials.

EXPERIMENTAL

Polymer synthesis and characterization

The diblock copolymers and most of the narrow molecular weight distribution homopolymers used in this work were synthesized in this laboratory using conventional techniques of homogeneous anionic polymerization.

Details of the synthesis procedures appear elsewhere[2]. Molecular weights and polydispersity were determined for the polystyrene block of the copolymers and for the homopolymers using high pressure size exclusion chromatography (h.p.s.e.c.). Diblock copolymer compositions were determined via u.v. absorption analyses and these values agreed very well in every case with the synthesis stoichiometry. Diblock copolymer molecular weights were then calculated from the combined h.p.s.e.c. and u.v. absorption results; the associated polydispersity index was determined directly by h.p.s.e.c. Characterization results are summarized in *Table 1*; sample designations are the same as in previous publications[2,3].

Sample preparation

Polymer films were prepared using high temperature, inert atmosphere, solvent spin casting[3]. Dilute polymer solutions (about 5% weight) were injected through 10 μm filters into the casting cup which was fitted with a Mylar liner. Nitrogen purging through the caster insured an inert environment and removed the solvent. The casting cup was enclosed in a temperature chamber controlled to 1°C accuracy. Uniform cast films were between 0.5 and 1.0 mm in thickness, depending on the amount of polymer charged to the caster.

The casting rate is a function of the nitrogen flow rate, casting temperature and solvent vapour pressure. Typical casting conditions, optimized by trial and error, are listed in *Table 2* below for two solvent systems.

The cast films were further dried and annealed at 100°C in a vacuum oven, and subsequently stored under vacuum at room temperature in the absence of light.

Transmission electron microscopy

Morphology of the cast films and internal structure of crazes were observed with transmission electron microscopy. Samples of each cast film and various heavily crazed specimens were prepared for microscopy by staining in a 1% aqueous solution of osmium tetroxide for several days

---

* Present address: Monsanto Polymer Products Co., Springfield, Massachusetts, USA

0032-3861/85/121985-09$03.00

Table 1 Designations, molecular weights and molecular weight ratios of the pure di-block copolymers and homopolymers investigated

Sample[a]	M_n (kg/mol) PS–PB	M_w/M_n	Wt % PB
SB2	77–21	1.06	0.217
SB3	85–45	1.07	0.317
SB4	149–20	1.07	0.118
SB5	126–46	1.06	0.242
SB6	122–66	1.07	0.329
SB7	560–59	1.11	0.096
SB8	400–120	1.10	0.230
SB10	600–260	1.20	0.230
SBd3	380–46	1.10	0.106
S2	116–0	1.05	
BO[b]	0–3	1.10	

[a] Abbreviations: S = polystyrene; B = polybutadiene; Bd = perdeutero-polybutadiene; SB, SBd = diblock copolymer

[b] Pressure Chemical Co.

Table 2 Schedule for solvent spin casting

	Toluene (b.p. = 110°C)			THF (b.p. = 67°C) and MEK (b.p. = 80°C)			
Time (days)	1	2	3	1	2	3	4
Temperature (°C)	65	80	100	40	65	80	100
N_2 flow rate (SCFH)	0.1	0.1	1.0	0.1	0.1	1.0	1.0

to enhance absorption contrast between the PB and PS phases. Crazed specimens were stained in the deformed state by use of a stainless steel jig. Ultra-thin sections suitable for transmission electron microscopy were cut on a LKB microtome using fresh glass knives. Morphology and domain size were observed in 300–700 Å thick sections to prevent phase overlap; internal craze structure was observed in 0.1–1.0 μm thick sections to preserve the craze structure. The orientation of the cutting knife to the crazed sample was chosen to minimize interaction between crazes and the knife and to generally minimize microtoming artifacts[4]. The electron microscope, a Philips EM 200, was operated at 60 or 80 kV and calibrated with a diffraction grating carbon replica (21 600 lines cm^{-1}). Typical micrographs of the various samples appear in *Figure 1*.

Tensile testing

Specimens for tensile testing were trimmed from the annealed cast films with fresh surgical blades using a 'dog-bone'-shaped template. Specimens were then annealed (at 100°C) for 24 h, slow cooled (20°C h^{-1}) and tested within two days on an Instron tensile tester (Model 1122). Stress–strain curves were calculated[4] based on a gauge length of 0.63 cm. Actual initial grip separation was 1.90 cm.

RESULTS

Craze flow behaviour

Stress–strain experiments conducted on various diblock copolymers showed the expected behaviour of increasing toughness as either rubber volume fraction or copolymer molecular weight increased (see *Figures 2a–c* and *3a–d*). There is also a steady and expected decline in the tensile modulus and yield stress as the rubber content increases. As the overall molecular weight increases, however, there appears to be a relatively sharp transition from brittle to tough behaviour (SB5 vs. SB8). While only the two parameters of copolymer molecular weight and rubber content appear to have been investigated, on a molecular and morphological scale certain other features

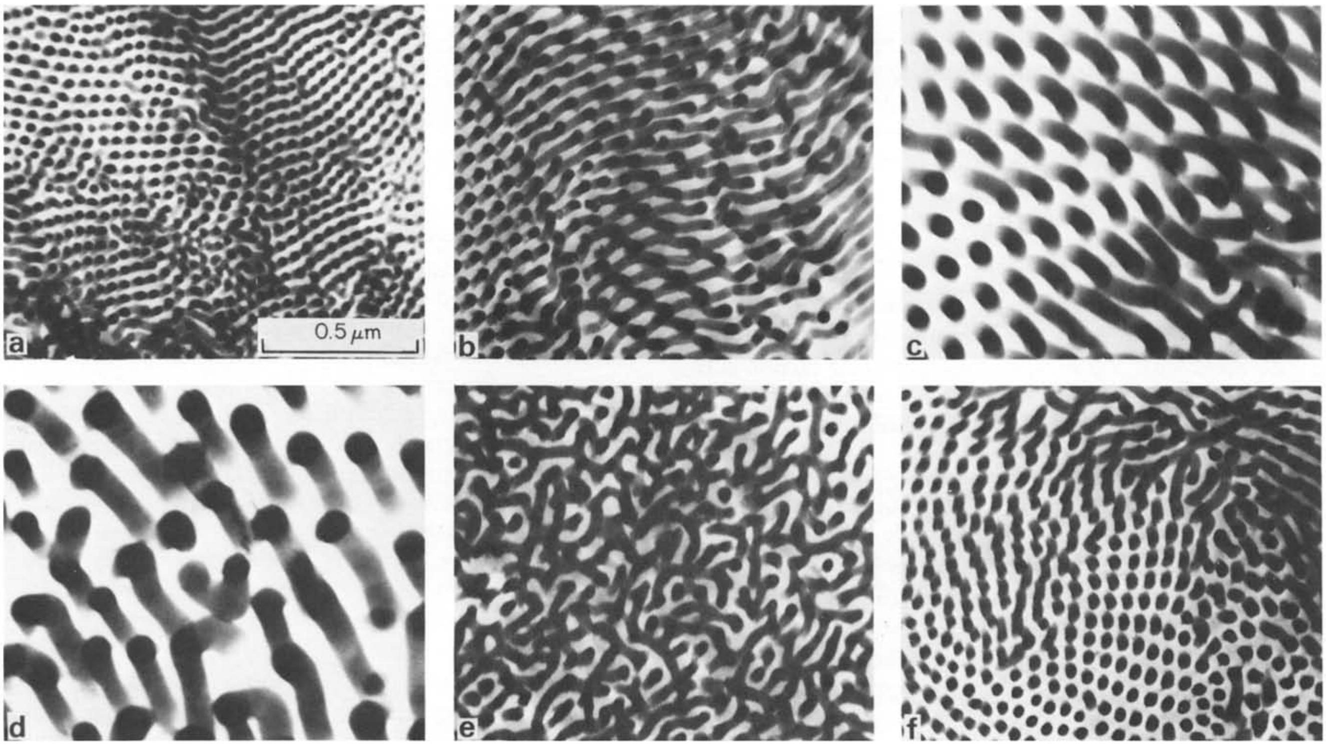

Figure 1 Transmission electron micrographs of cylindrical morphologies (dark regions are PB stained with OsO_4). Materials cast from toluene: (a) SB2; (b) SB5; (c) SB8; (d) SB10. Blends of SB3, SB5 and SB7: (e) cast from toluene; (f) cast from MEK/THF

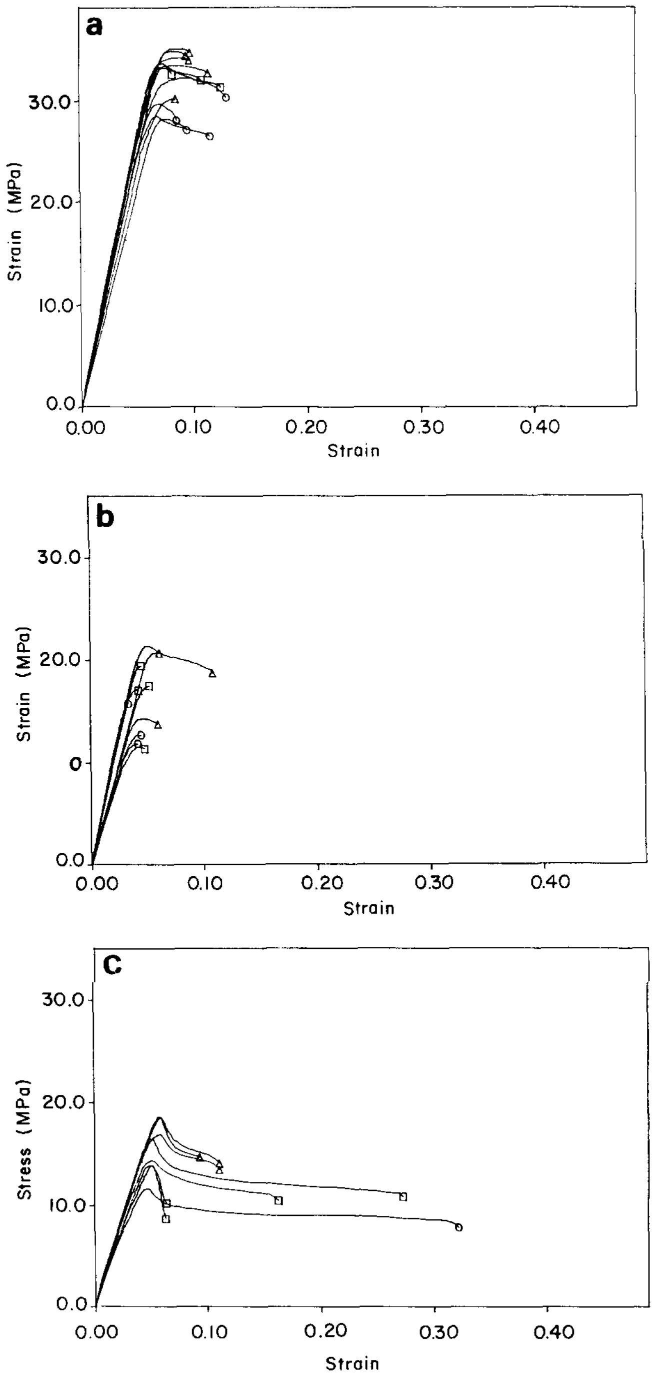

Figure 2 Stress–strain response of three PS/PB diblock copolymers with rod morphology, and increasing weight of PB blocks, at three different strain rates: (a) SB4 13% rod phase; (b) SB5 23% rod phase; (c) SB6 33% rod phase. (○): 0.00013 s^{-1}; (□): 0.0013 s^{-1}; (△) 0.013 s^{-1}

have also been altered and must be noted. Specifically, in pure block copolymers as the volume fraction of rubber increases, the polybutadiene block molecular weight also increases simultaneously, as does the PB cylinder diameter, if during this process the polystyrene molecular weight remains constant. The PB cylinder diameter and inter-cylinder spacings increase at a constant ratio if the overall molecular weight of the block copolymer is increased at a constant molecular weight ratio of PB to PS.

Effect of homopolymer blends

Homopolymer blending is one way of isolating the effect of the block molecular weight on toughness. A blend

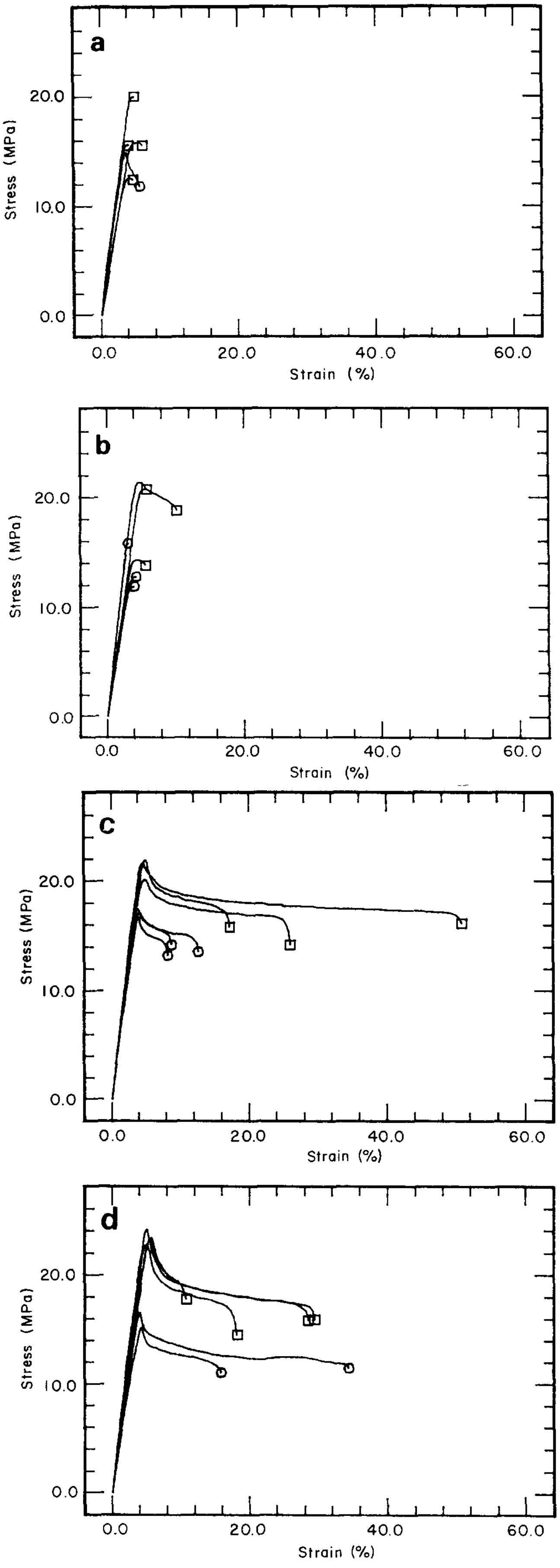

Figure 3 Stress–strain response of four PS/PB diblock copolymers with rod morphology with a nominal weight fraction of PB rods of 0.23 but increasing molecular weight of block components, at two different strain rates: (a) SB2, (b) SB5, (c) SB8, (d) SB10. (□): 0.013 s^{-1}; (○): 0.00013 s^{-1}

of SBd3 with BO was prepared to contrast with SB8. Both of these materials have essentially the same block polystyrene molecular weight of ≈ 400000, weight fraction polybutadiene of ≈ 0.23, and straight rod morphology. The film prepared from the blend can be thought of as the result of snipping the polybutadiene chains in the rubber domains of the SB8 film into many shorter chains. The polystyrene is still connected to the rubber domain but via a much shorter polybutadiene block and a substantial amount of rubber in the domains exists as homopolymer.

The sample containing polybutadiene homopolymer is clearly less tough than the pure diblock, as is clear from *Figure 4*, suggesting that the polybutadiene molecular weight is a significant factor in controlling toughness. But there are some additional anomalies which cannot be easily explained, for example, the strain rate dependence of the toughness. The pure diblock exhibits the unexpected behaviour of high strains to fracture at higher strain rates whereas the blend shows the opposite and more typical behaviour of reduced strains to fracture at higher strain rates.

Effect of crosslinking polybutadiene domains

Another simple way to alter the polybutadiene molecular weight is to crosslink the prepared films with an electron beam. Crosslinking was accomplished with 3 MeV electrons from a Van de Graaf particle accelerator at dosages of 10 or 40 Mrad.

When specimens prepared from irradiated films of SB2 and SB5 were tested they showed improved toughness as is shown in *Figures 5a* and *b*. Since pure polystyrene when irradiated at these doses has unchanged stress–strain behaviour and since all microstructural dimensions and morphology are unchanged, the improved properties can be attributed to the crosslinking of the polybutadiene phase. The crosslinking reaction of polybutadiene has been studied by Basheer and Dole[5] but quantitative details of the chemical changes in the polybutadiene domains are still difficult to ascertain, in part due to the possibility of shielding effects of the polystyrene[5,6]. Specifically, the number of crosslinks, and the average and distribution of molecular weight between crosslinks are unknown. Also the effect of irradiation on the adhesion of the rubber domains to the matrix through grafting reactions in the interfacial zone is unknown. The mechanics of the crazing process is also expected to be altered, first due to significant modulus changes in the rubber phase as a result of heavy crosslinking, and second due to changes in cohesion in the PB phase. As shown in *Figure 5*, very high dosages of irradiation are required to achieve improved properties.

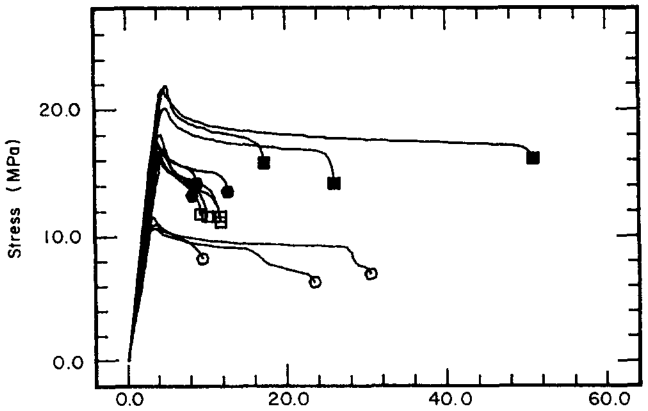

Figure 4 Stress–strain response of a diblock with homopolymer blending, compared with a pure diblock of similar morphology and weight fraction of PB. SBd3/B3=(□): 0.013 s^{-1}; (○) 0.00013 s^{-1}; SB8=(■): 0.013 s^{-1}; (●): 0.00013 s^{-1}

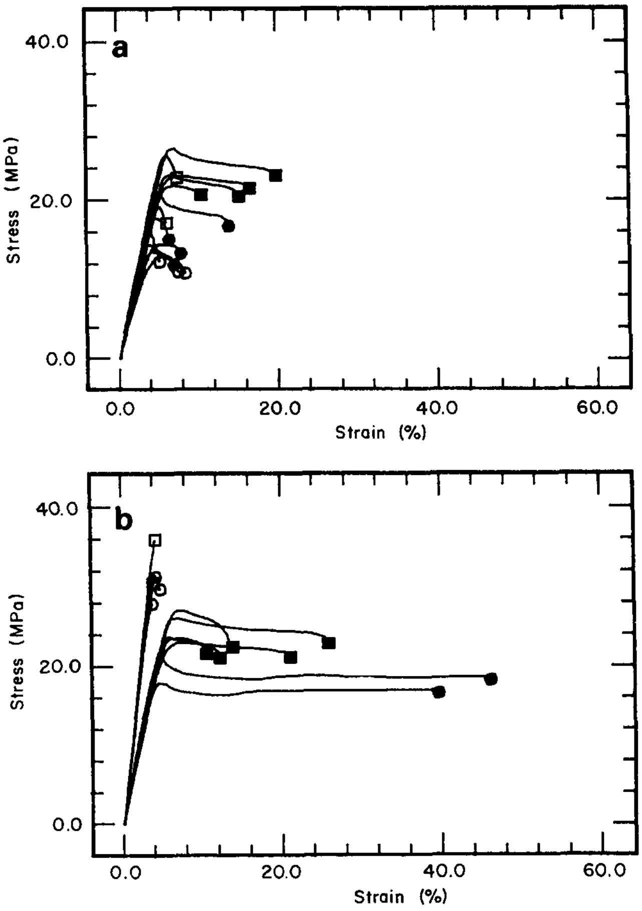

Figure 5 Effect of irradiation crosslinking of PB on stress–strain response: (a) effect of dosage; 10 Mrad=(□): 0.013 s^{-1}; (○): 0.00013 s^{-1}; 40 Mrad=(■): 0.013 s^{-1}; (●): 0.00013 s^{-1}; (b) effect of molecular weight at constant dosage (40 Mrad), S2, pure PS is unaffected; SB5, shows a substantial improvement. SB5=(□): 0.013 s^{-1}; (○): 0.00013 s^{-1}; SB2=(■): 0.013 s^{-1}; (●): 0.00013 s^{-1}

Effect of diblock blending

A blend consisting of 25% SB3, 50% SB5 and 25% SB7 by weight was prepared to investigate the effect of polystyrene molecular weight on toughness. The polybutadiene block molecular weight of these three polymers is nearly identical (≈ 52000) and the blend consists of 23% rubber by weight. The polystyrene block molecular weights vary from 85 kg mol^{-1} to 560 kg mol^{-1}. The number average molecular weight of the polystyrene blocks is slightly higher than the polystyrene block in SB5 but the weight average molecular weight is almost twice that value ($\bar{M}_n = 143$ kg mol^{-1}, $\bar{M}_w = 243$ kg mol^{-1}).

This blend of diblocks, cast from a toluene solution, resulted in a very tough material as shown in *Figure 6a*. However, it is important to note that this material no longer had the straight cylinder morphology typical of pure diblocks cast from toluene, shown in *Figures 1a–d*. Instead a morphology consisting of topologically interconnected rods appeared in the toluene cast diblock blend, as shown in *Figure 1e*. This effect of polydispersity on block copolymer morphology has been documented by Kraus *et al.*[7], and apparently is used by Phillips Petroleum in commercial K-Resins to achieve lamellar morphologies in polystyrene-rich block copolymers. The microstructure of the diblock blend under consideration here can be forced into a straight cylindrical morphology by casting from a suitable solvent, in this case a mixture of 80% THF, 20% MEK by volume. The resulting film had the conventional cylindrical morphology of *Figure 1f*, but was brittle as is clear from *Figure 6b*. Not only does this point out the sensitivity of toughness to details of the morphology, but it also indicates that the polystyrene molecular weight is not by itself the controlling parameter in the toughness of the blends. Provided that certain favourable conditions exist, such as an interconnected cylindrical morphology as in *Figure 1e*, the polystyrene phase is able to deform, form stable crazes, and absorb significant amounts of deformation work before final fracture is initiated in some crazes.

The effect of morphology on physical properties in block copolymers has been studied extensively, especially in the case of systems with continuous or co-continuous rubber phases[8,9]. In general, large changes in properties could be explained in terms of the elasticity of the topologically continuous rubber phase with a hard filler. These concepts do not apply to the present materials because they have topologically continuous polystyrene phases; and the dominant large deformation processes are inelastic and involve yielding and large strain drawing of the polystyrene phase in the process of producing a large volume fraction of craze matter. Discovering how these processes are affected by changes in morphology is difficult but several observations are possible. The test specimens viewed through a light microscope show significant differences between the crazing behaviour of the interconnected cylinder and the straight cylinder morphologies as shown in *Figures 7a* and *b*. The dense, uniform crazes of the interconnected cylinder morphology appear to be very thin and lie in planes normal to the principal applied stress. In contrast, the crazes in the straight cylinder morphology are non-uniform, thick bands of deformation which do not necessarily lie in planes normal to the applied stress. They have a feathery appearance which seems to be a result of its anisotropic morphology. Whereas both morphologies exhibit isotropic behaviour on a macroscopic scale, only the interconnected cylinder microstructure maintains this isotropy down to a scale of typical craze structures (≈2000 Å). The local anisotropy in the straight cylinder morphology of randomly misoriented anisotropic cells appears to have a strong effect on the growth of crazes and also on the craze structure as we discuss below.

Electron microscopy of craze matter

The crazes observed in block copolymer materials with cylindrical morphology are considerably different than typical crazes in homopolymers[10]. *Figure 8a* shows a craze in homopolystyrene, while *Figure 8b* shows that crazes in the diblock materials are more than two orders of magnitude thicker than in homopolystyrene and are not as planar. As noted above, this is a consequence of the anisotropic cell arrangement of the straight cylindrical morphology. Craze growth in block copolymer materials depends on the polybutadiene cylinder orientation. This results in crazes growing preferentially through regions of certain morphological orientation in which the cylinder axes are transversely oriented to the principal strain direction, in contrast to the more expected craze growth along planes normal to the maximum principal stress in an isotropic polymer. Crazes in the cylindrical morphology copolymers also apparently thicken to consume the regions of desired orientation.

A higher-magnification view of the diblock craze matter in *Figure 9* shows that craze fibril diameter and void fraction are similar to those in homopolymer crazes. A much more important observation, however, is the correspondence between the inter-fibril spacing in the 'fishnet' craze structure and the inter-cylinder spacing in the bulk material. Thus the craze matter is apparently formed through the cavitation of the rubber domains and subsequent necking and drawing in the continuous polystyrene matrix. *Figure 9* shows the result of this process for the idealized case of cavitation in the rubber, in three rows of a hexagonally packed cylindrical morphology. The phenomenon of craze growth through rubber cavitation has been observed in other diblock systems (*Figure 10a–d*) and in the lamellar morphology of commercial K-Resin materials[11].

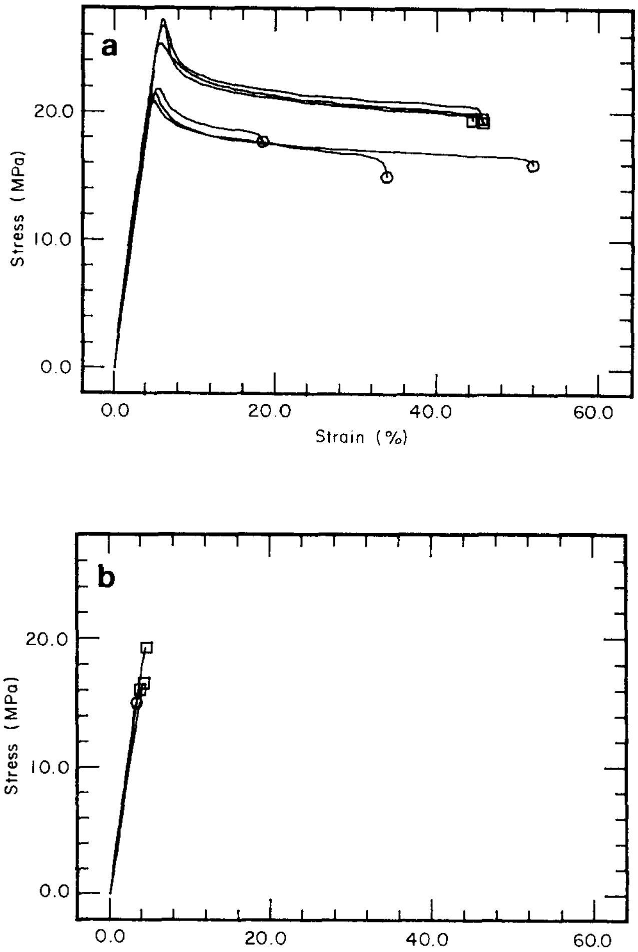

Figure 6 Effect of topological connectivity of PB phase on stress–strain response in a block copolymer blend of SB7 (25%), SB5 (50%), SB3 (25%) with 0.23 weight fraction of PB; (a) cast from a toluene solution with a tortuous morphology shown in *Figure 1e*; (□): 0.026 s^{-1}; (○): 0.00026 s^{-1}; (b) cast from a 80% THF, 20% MEK solution with straight rod morphology; (□): 0.013 s^{-1}; (○): 0.00013 s^{-1}

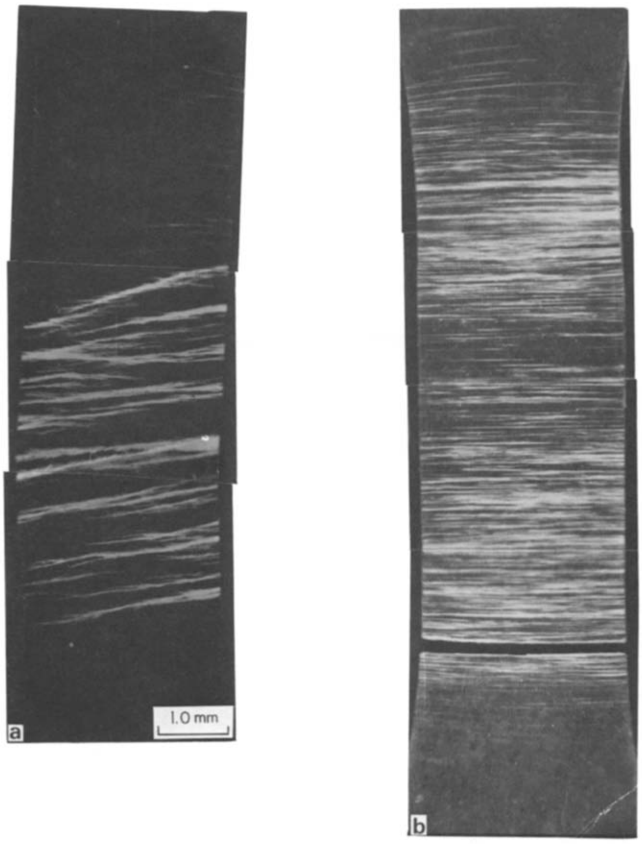

Figure 7 Effect of 'bulk' morphology on craze distribution: (a) straight cylinders (see *Figure 6b*); (b) interconnected cylinders with a tortuous morphology (see *Figure 6a*)

The important quantitative implications of crazing via a mechanism of systematic cavitation in the rubber domains will be discussed in detail in a subsequent paper on block copolymers containing spherical morphologies[12]. The qualitative results shown here, however, clearly demonstrate the importance of the rubber domains in controlling the crazing behaviour and hence the toughness of block copolymer materials in the cylindrical morphologies.

DISCUSSION

The aim of this investigation was to understand how various molecular and morphological parameters affect the toughness of polystyrene/polybutadiene systems. An advantage of the microphase separated block copolymer systems is the ease of controlling these parameters such as block molecular weights, polydispersity, microdomain shape, size and spacing. No simple single correlation could be obtained between the toughness as measured in a stress–strain experiment and any of the molecular parameters that could be independently investigated. The same difficulty was encountered by Kawai *et al.*[13] for the polystyrene/polyvinyl–isoprene system. Experiments reported here, however, indicate the important role played by the rubber domains: the domain shape, orientation, crosslink density and molecular weight, all of which have a strong effect on the toughness.

Several such features are apparent from the experiments. Since at constant molecular weight of PS an increase in the block molecular weight of PB increases the volume fraction of PB, in the envisioned model of craze growth of drawing of the cellular PS carcass after cavitation of the PB, the craze flow stress should decrease monotonically with decreasing PS fraction. Such a decrease is present in *Figures 2a–2c*, but is not linear with the fraction of PS. The calculated nominal stress in the PS phase for the lowest volume fraction of 0.13 is 35% higher than that for the higher volume fractions of 0.23 and 0.33, and of the same order as that for homopolystyrene. In corresponding experiments on block copolymers with

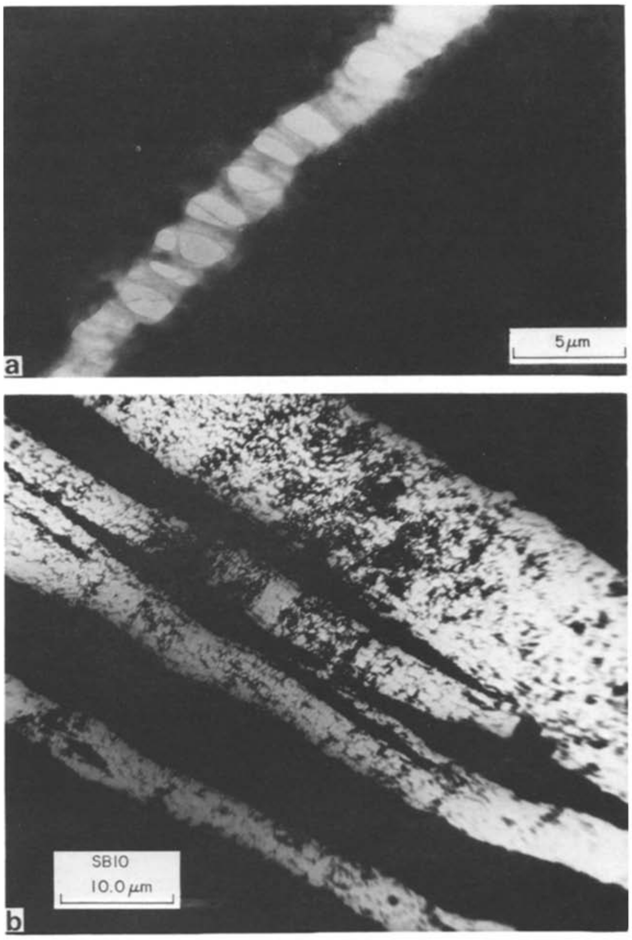

Figure 8 Effect of 'bulk' morphology on the craze matter structure: (a) craze in homopolystyrene [10]; (b) PS/PB diblock with straight rod morphology

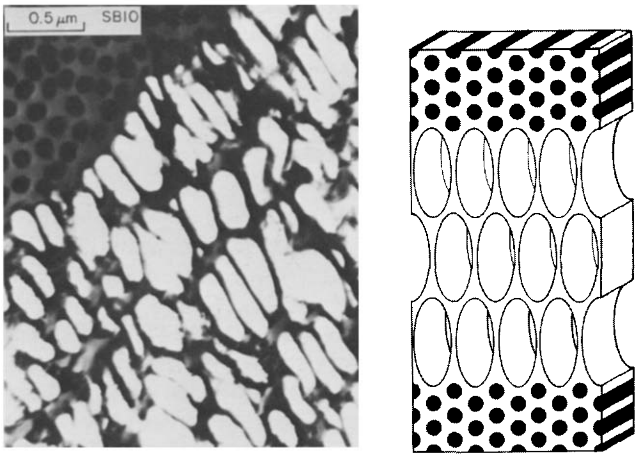

Figure 9 Cellular cavitation mode of craze matter production in a morphology consisting of straight rods of PB. Sketch depicts systematic plastic drawing of PS carcass to form craze matter after cavitation occurs in PB rod phase

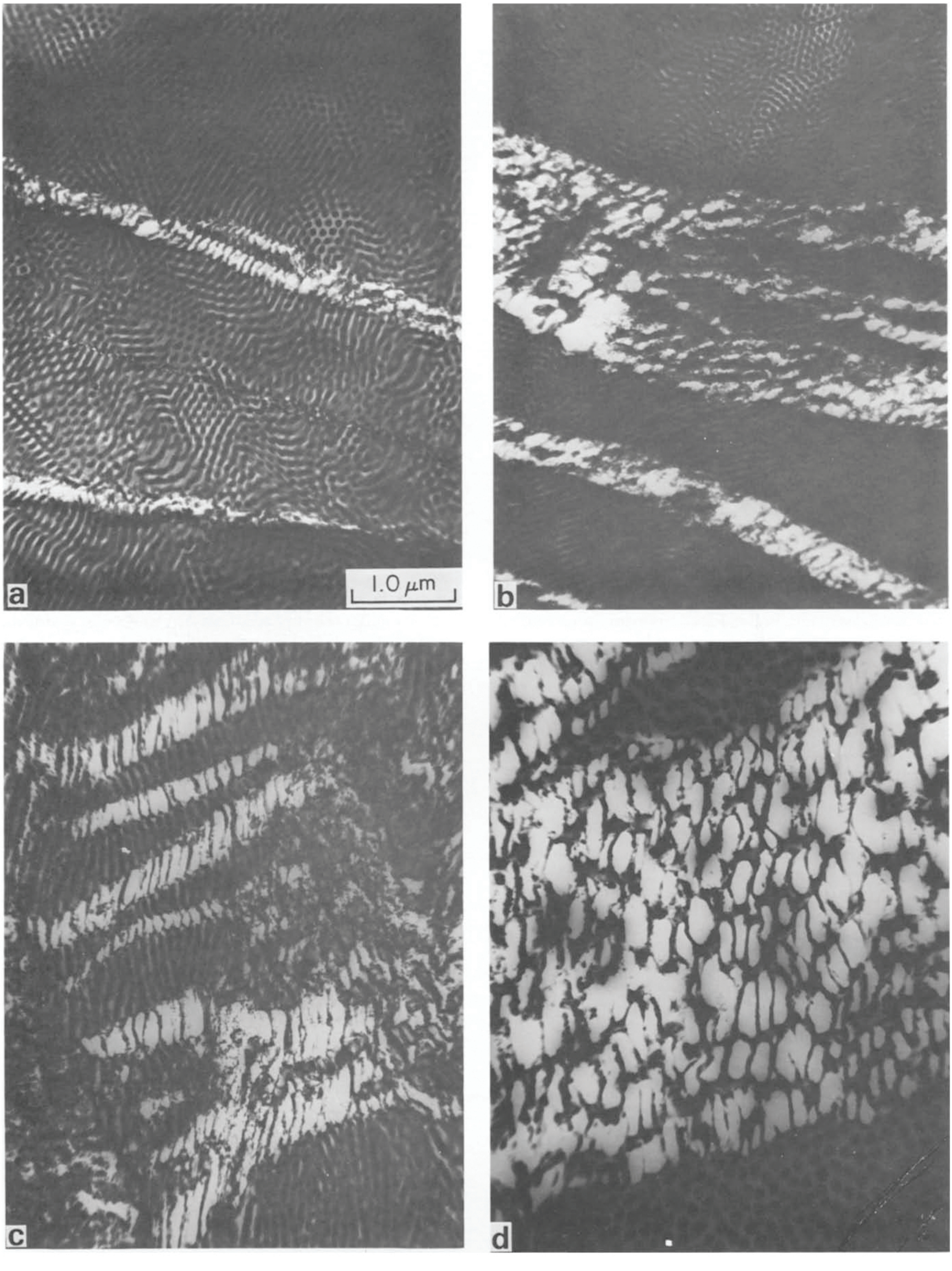

Figure 10 Transmission electron microscopy of craze structure formed by the PB phase cavitation mechanism in several diblocks: (a) SB5; (b) SB6; (c) SB8; (d) SB10

spherical morphology Schwier *et al.*[12] have found indirect evidence that while crazes grow by a repeated cavitation mechanism in block copolymers with a high volume fraction of rubber, they revert to the growth mode by interface convolution in those with low volume fraction of rubber. The evidence here on the levels of the craze flow stresses suggests a similar two-mode behaviour.

In the series of experiments of *Figures 3a–d* the weight fraction of rubber remains relatively constant (see *Table 1*) but the overall molecular weight increases systematically. As expected there is little change in the levels of craze flow stresses but the strains to fracture at constant strain rate increase systematically. This is a direct indication that in this series of materials there is little change in the mechanism of craze growth but that increased molecular weight results in increased mechanical stability of craze matter under stress, and gradually increasing strains to fracture as the earliest-formed crazes continue to support the applied stress for longer periods of time.

A different dimension of the behaviour is represented by the blending experiment of *Figure 4*. Both the SBd3/BO blend and SB8 samples have the same PS molecular weight, and the same weight fraction of 0.23 of PB which suggests that in both cases crazes were growing by the repeated cavitation mode. The craze flow stress of the blend, however, is considerably lower than that of the pure diblock, which indicates that the craze advance is made easier in the blend due to the decreased average molecular weight of the PB. This is attributed to a lower cavitational strength in this PB component, in agreement with the observations of Schwier *et al.*[12] and the measurements of Bates *et al.*[3]. The seemingly inverted behaviour of the dependence of the strain to fracture on strain rate between the blend and the pure diblock is a distortion of an expected regular response of increased time to fracture of craze matter with decreasing stress. Thus, in the SB8 pure diblock the overall time to fracture increases from 20.8 s to 564 s as the stress drops from 18 to 15 MPa while in the blend SBd3/BO it increases from 6.15 s to 1490 s as the stress drops from 14 MPa to 10 MPa. Nevertheless, if the stability of the craze matter were governed only by the molecular weight of the PS and the average size of the PB rods, which are nearly identical in these two cases, the times to fracture of craze matter under the same stress in the two materials should be the same. This is not at all the case, as the times to fracture in the blend are very much shorter for the same stress level than in the pure diblock. A contributing cause to this may be the larger variation in PB cylinder radii in the blend than in the pure diblock, resulting in a probably larger density of structural flaws in the craze matter of the former.

Similar trends are also evident in the irradiated samples shown in the series of experiments of *Figure 5*. Both of the samples of SB2 and SB5 have similar weight fractions of PB. There is no significant difference in the craze flow stresses between the differently irradiated samples. The increased strain to fracture in the SB2 shown in *Figure 5a* with increasing dosage of irradiation suggests that the PB which is the primary beneficiary of such crosslinking continues to transfer the stress to the PS carcass. Comparison of the results between the SB2 and SB5 polymers with the same dosage of irradiation, however, indicates that the beneficial crosslinking effect of irradiation is accentuated with increased molecular weight of the starting polymer.

Finally, the increased toughness due to increased tortuosity of the PB phase in the diblock blends is most dramatic. The more tortuous morphology does not only have a very substantial strain to fracture but also a significantly higher flow stress than the corresponding straight rod morphology version. Assuming that there is no contribution to this altered behaviour from the different solvents used in preparing these different morphologies, the topologically quasi-randomized nature of the orientations of the cylindrical rubbery phase must make it both more difficult to cavitate the PB phase and to bring about the eventual breakdown of the craze matter tufts. The exact nature of this process is not clear.

The inability of previous investigators to develop fundamental relationships between molecular parameters and toughness in HIPS and other heterogeneous polymer systems stems from two problems. First, the various molecular and morphological parameters of interest are difficult to control independently due to the synthesis procedures used, in which simultaneous changes occur in many parameters. This problem is not encountered in the block copolymer systems reported here. Second, a high value of toughness, as we have elaborated above, is the successful combination of several mechanisms working in concert. For materials in which the primary energy absorption mode is crazing, optimal toughness is achieved with massive craze initiation at a relatively high stress, rapid craze growth, and termination or stabilization of crazes without undergoing breakdown into cracks under the applied stress. Any molecular parameter can affect each of these processes in various ways leading to conflicting results when only a single integrated property, such as toughness, is investigated. Thus not only control over molecular and morphological structure is necessary, but a more fundamental approach to the question of toughness is needed. In order to understand the large deformation behaviour of these heterogeneous systems, each step of the toughening process, i.e., initiation, growth, termination and stability of crazes, must be understood independently. It is the second aspect, craze growth, that has made interpretation of the stress–strain behaviour of diblock copolymers with cylindrical morphology difficult. More definitive interpretations have been developed by Schwier *et al.*[12] for diblocks with spherical PB domain morphology where relatively unique modelling can be performed. Nevertheless, many qualitative conclusions can be obtained from the data, which are also in accord with the quantitative trends in the spherical morphology polymers.

As mentioned above, the important role of the rubber domains was demonstrated most clearly in the transmission electron microscopy of craze matter. The important ramifications of these observations can be summarized as follows.

(1) The observations suggest a mechanism for craze growth consisting of the cavitation of rubber domains under the peak tractions at the craze tip, with subsequent necking and drawing in the topologically continuous polystyrene carcass. The random distribution of locally aligned rod domains permits relatively ready widening of the craze by drawing out of polystyrene from the craze flanks. Ideally, this mechanism of craze growth could be modelled, but the random distribution of domain orientations in the straight cylindrical morphology makes such modelling complicated.

(2) The role of various polybutadiene molecular and morphological parameters can be better understood in the light of a mechanistic view of the crazing process. The mechanism of craze growth suggests the importance of various rubber domain features that include: the cavitation strength of PB and the strength of its interface with PS; alterations in the local stress field as influenced by domain orientation; level of thermal negative pressure inside the rubbery cylinders; and finally, the stability of the rubber phase as influenced by rubber crosslinking and molecular weight.

(3) The mechanism of craze growth suggests the ability to control the craze structure on the scale of a few hundred Ångstroms. Ideally the craze fibril diameter and spacing between fibrils could be controlled by fixing the rubber domain size and spacing. These morphological features are easily controlled in block copolymer systems. The possibility exists for finding an optimal craze structure and for preparing a block copolymer system which will craze with that structure.

(4) The rate of craze growth and the craze matter stability are probably the processes most strongly affected by the microphase separated nature of the block copolymer systems. The rubber domains showed no evidence of either initiating or terminating crazes which is expected due to their very small size.

ACKNOWLEDGEMENTS

This research has been supported by the NSF/MRL Program under Grant No. DMR 81-19295, through the Center for Materials Science and Engineering at M.I.T., and by a pre-doctoral fellowship to CES, from the Michelin Foundation. We are grateful to Dr F. Bates for the synthesis of most of the materials used in this investigation. We are also grateful to Drs F. Bates and O. S. Gebizlioglu for many useful discussions.

REFERENCES

1 Bucknall, C. B. 'Toughened Polymers', Applied Science Publishers, London, 1977

2 Bates, F. S., Berney, C. V. and Cohen, R. E. *Macromolecules* 1983, **16**, 1101

3 Bates, F. S., Cohen, R. E. and Argon, A. S. *Macromolecules* 1983, **16**, 1108

4 Schwier, C. E., Sc.D. Thesis, MIT Department of Chemical Engineering, 1983

5 Basheer, R. and Dole, M. *Makromol. Chem.* 1982, **183**, 2141

6 Samuels, S. L. and Wilkes, G. L. *Polymer Engineering Sci.* 1983, **13**, 280

7 Kraus, G., Fodor, L. M. and Rollman, K. W. *Advances in Chemistry Series* 1979, **176**, 277

8 Estes, G. M., Cooper, S. L. and Tobolsky, A. V. *J. Macromol. Sci.-Revs. Macromol Chem.* 1970, **C4**(2), 313

9 Shen, M. and Kawai, H. *Am. Inst. Chem. Eng. J.* 1973, **24**, 1

10 Argon, A. S. and Salama, M. M. *Phil. Mag.* 1977, **36**, 1217

11 Argon, A. S., Cohen, R. E., Jang, B. Z. and Vander Sande, J. B. *J. Polym. Sci., Phys.* 1981, **19**, 253

12 Schwier, C. E., Argon, A. S. and Cohen, R. E. *Phil. Mag.*, in the press

13 Kawai, H., Hashimoto, T., Miyoshi, K., Uno, H. and Fujimura, M. *J. Macromol. Sci., Phys.* 1980, **B17**(3), 427