A New Mechanism of Toughening Glassy Polymers. 1. Experimental Procedures

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ABSTRACT: Normally brittle, high molecular weight polystyrene can be very effectively toughened by blending polybutadiene of 2.76 kg/mol at volume concentrations of a few percent. An increase of toughness by about a factor of 10 above that of homo-PS can be readily achieved with a 1.1% PB-2.76K blend if the precipitated PB pools can be maintained at a size smaller than 0.2 μm. It is proposed that this dramatic effect is the result of a controlled solvent crazing action of the PB-2.76K on the homo-PS when the former becomes soluble into the latter in the fringing layers of the craze borders subjected to negative pressure by the local craze tuft drawing process.

I. Introduction

Many atactic, flexible-chain glassy polymers such as PS, PMMA, and their various modifications have very attractive properties of stiffness and appearance and are relatively easily processed into finished products but suffer from brittleness in the unoriented form.[1] While moderate levels of uniaxial or biaxial orientation can rectify this imbalance, both types of orientation processing limit the range of shapes that can be manufactured and restrict the applicability of manufacturing processes such as injection molding.

Alternative approaches to the alleviation of this brittleness problem have included blending with other less flexible chain homopolymers that are known to undergo plastic flow in tension rather than exhibit crazing.[2] The most widely preferred alternative approach to the alleviation of the brittleness problem of flexible-chain polymers, however, is rubber modification by incorporation of a substantial volume fraction (typically 0.1) of an elastomeric component in the form of a block or graft copolymer. The elastomer undergoes phase separation, while maintaining a high-quality interface between the homopolymer and the precipitated compliant particle phase.[1]

It has now been well established that the inelastic strain in the flexible-chain homopolymers deformed in tension is produced by the dilatational plasticity of crazes, initiated from surface imperfections,[1] and that the brittleness results from the premature fracture of such crazes when the latter, during their growth, encounter inorganic particulate impurities. Thus, the root cause of the brittleness in question is the fracture of craze matter, initiated from the supercritical flaws that result when a growing craze encounters a poorly adhering inorganic dust particle, typically of micron dimensions.[3-5] This undesirable response has a number of important ingredients. The surface imperfections on the average have a relatively low potency to initiate crazes. They can provide, at best, plastic response only in a surface layer. For additional plastic extension the crazes must spread under the prevailing tensile stress into the elastic interior regions of the stressed part at rates governed by the kinetics of craze matter production at the borders between the initiated crazes and the solid homopolymer. The combination of the low volume density of surface-initiated crazes and their growth kinetics is such that the rates of deformation imposed by a testing machine or an impact require a high tensile stress acting across the crazes to match the dilatational craze strain rate against the imposed rates. Finally, the fracture toughness of craze matter is insufficient to cope with the flaws introduced by the micron size, poorly adhering inorganic dust particles present in the solid polymer when these particles become incorporated into a growing craze. Elegant experiments by Yang et al.[5] have demonstrated that elimination of the dust particles, which initiate the final craze fracture, is impractical and is, at best, only marginally effective. Thus, not withstanding the many explanations found in the literature, the principle reason for the effectiveness of high-impact polystyrene (HIPS) or acrylonitrile–butadiene–styrene (ABS) polymers in toughening is the substantial lowering of the craze flow stresses (by more than a factor of 2) that results from the heterogeneous rubbery particles that they contain. The principle function of these particles of adequate compliance[6,7] and size[8] is to initiate a much larger density of active crazes throughout the volume of the solid polymer than what can be generated from surface imperfections. Within the restriction of the normal craze growth kinetics, this then permits the matching of the plastic craze strain rate to the imposed deformation rates under a considerably lower tensile stress for which the flaws due to most of the usual dust particles now become subcritical and the polymer survives long enough to undergo substantially larger strains to fracture.

In the course of investigating the role of heterogeneous particle morphology on their compliance and the resulting craze-initiating potency in a series of blending experiments of PS with low molecular weight PB,[9-11] we had obtained a family of tough heterogeneous polymers with unusually low craze flow stresses. Analysis of the craze-initiating potency of these particle morphologies[6,7] together with the known kinetics of craze growth in PS[12] had led to the conclusion that the observed toughnesses were anomalously large and could not be accounted for by the known factors described above. Experiments on the extraordinary retraction behavior upon unloading of extensively crazed but unfractured samples of some of the blends[13] pointed

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Table I
Characteristics of Components in Blends

component	$\bar{M}_w$, kg/mol	$\bar{M}_n$, kg/mol	$\bar{M}_w/\bar{M}_n$
PB-2.76K	2.76		1.06
PB-6K	6.0		1.06
PB-23.6K	23.6		1.06
PS-3.6K	3.6		1.08
PS HH101	268.0	112.0	2.39
PS-152K	152.0		1.06
PS-300K	300.0		1.06

to other unusual behavior of these materials. We report here the results of additional blending experiments of homo-PS with small-volume fractions of low molecular weight PB (2.76 kg/mol) coupled with a set of in situ SAXS experiments, which together not only clarify the earlier anomalous findings but also establish a new and potentially quite important mechanism of toughening of brittle flexible-chain homopolymers.[14]

II. Experimental Details

II.1. Blending Experiments. The principal homopolymer under consideration was a broad molecular weight distribution, commercial PS known under the trade name of HH-101 obtained from the Monsanto Polymer Products Co. (Springfield, MA). This material had been used in all our previous blending experiments. In addition, two other narrow molecular weight distribution, PS homopolymers with average molecular weights of 3.6 and 300 kg/mol were obtained from Pressure Chemical Co. (Pittsburgh, PA). The properties of these and those of the additional PB components used in the blending studies are listed in Table I together with their abbreviated designations that will be used throughout this paper. The principal PB component used in the blends was a low molecular weight (2.76 kg/mol), anionic solution polymerized material obtained from Polysciences, Inc. (Warrington, PA) with a polydispersity ratio of 1.01. ^{1}H NMR measurements have shown it to be predominantly of 1,4 addition. In addition, two other narrow molecular weight PB components of 6 and 23.6 kg/mol of similar pedigree obtained from the same source were also used in some ternary blends. Solution-blending and spin-casting techniques developed earlier[9,10] were used to prepare films of a thickness in the 0.2–0.7-mm range. Weighed quantities of binary and ternary blend components were dissolved in 100 mL of reagent-grade toluene. After complete dissolution of 5 g of polymer, the solution was filtered through a Millipore PTFE filter of 10-μm pore size into an aluminum spin cup rotating at 3600 rpm. The details of this device and the schedule of material preparation have been discussed in detail earlier.[15] At the completion of the spin casting, the films were vacuum annealed at 100 °C for a period of 24 h. Later it was found, however, that an additional thermal treatment of 12 h at 110 °C was necessary for reducing the residual entrapped solvent in the films of the blends with PB-2.76K in the composition range of 0.2–2.0 wt % PB to negligible levels. Prepared and thermal treated specimens were subsequently maintained in an environment of 55–60% relative humidity.

II.2. Morphology and Testing. The morphology of the blends was examined in a Phillips EM 300 electron microscope. Contrast enhancement between the PB and PS was achieved by staining with a 1% aqueous solution of OsO_4 according to well-established procedures. The microtoming to thicknesses of 500–900 Å was performed with a LKB Model 8800 Ultratome using glass knives (for more details refer to ref 9). An Instron testing machine (Model 1122) was used for the tension and compression tests. Compression samples were prepared by compression molding 2-mm disks cut from the spin-cast films.

II.3. Craze Growth Experiments. A limited number of craze growth rate experiments was carried out on translucent specimens prepared from annealed cast films containing 0.5 wt % PB-2.76K in PS. Details of the sample preparation and measurement procedure have been described elsewhere.[21,22]

II.4. SAXS Experiments. The in situ SAXS experiments were carried out at the A1 beam line of the Cornell University Synchroton source, CHESS. The samples were crazed in three-point bending. The scattered intensity from the crazed regions in the bent samples was recorded at a camera length of 351 mm by using an EG&G PARC OMA diode array detector. Mean fibril diameters of the craze matter were obtained by using a standard Porod analysis from these data in the manner described in detail elsewhere.[16] A fibril volume fraction of 0.25 for the craze was assumed in the analysis for all the samples based on previous experience.[16]

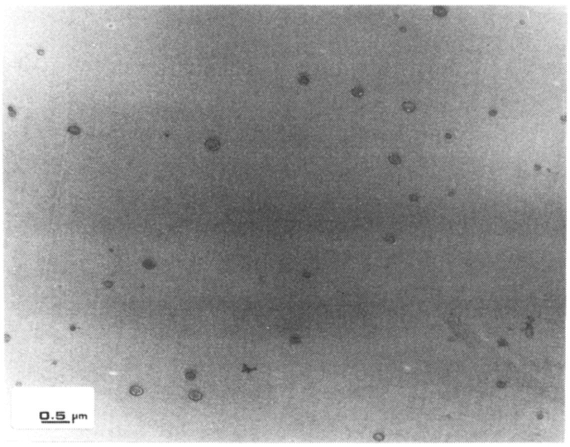

Figure 1. Particles of PB-2.76K in a blend of HH-101 PS with less than 1.1% by weight of PB-2.76K.

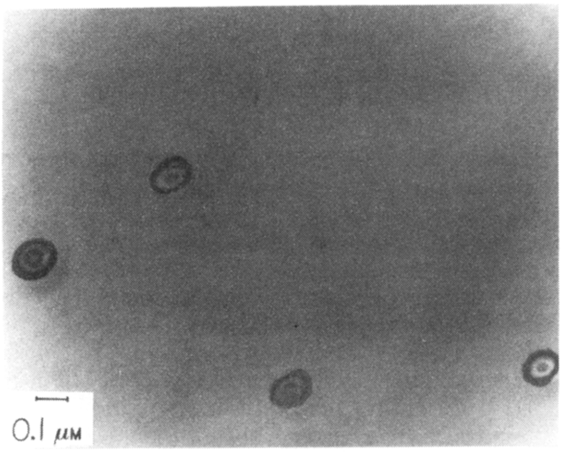

Figure 2. Larger magnification of the small concentric shell PB particles in the blend shown in Figure 1.

III. Experimental Results

III.1. Morphology and Physical Properties of Blends. The majority of the blends that were studied were binary blends of HH-101 PS containing various weight fractions of the PB of the lowest molecular weight of 2.76 kg/mol. Transmission electron microscopy of these blends indicated that those with a weight fraction of PB of less than 4.5×10^{-3} were homogeneous while those with weight fraction above 4.5×10^{-3} showed a precipitated second phase of PB in the form of a finely dispersed set of "particles". The latter were of a diameter of less than 0.2 μm as shown in Figure 1 for weight fractions of less than 1.1% PB-2.76K. This established that the solubility limit of PB-2.76K was at a 4.5×10^{-3} weight fraction. Some of these "particles" showed a concentric shell structure containing 2–3 PS shells of roughly 200-Å thickness separated by intermediate PB shells of similar thickness as shown in Figure 2. There was no known or readily identifiable block copolymer component in the blends to produce such a concentric shell morphology. In other seemingly similar blends "particles" appeared homogeneous. In view of this, no special importance is

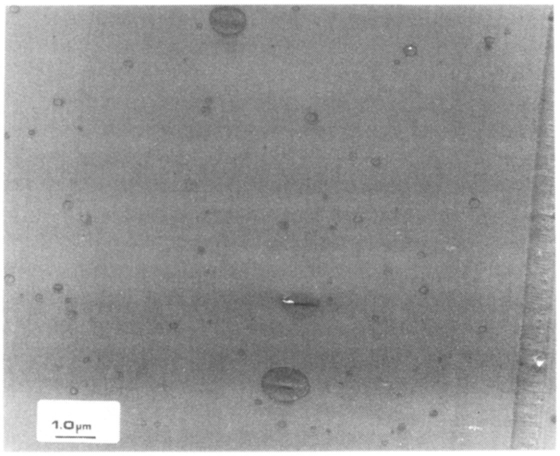

Figure 3. Bimodal distribution of rubbery particles with a family of larger PB-2.76K pools in a blend with more than 1.1% by weight of PB.

associated to the shell structure of those particles that exhibited such a structure. In blends with weight fractions exceeding 10^{-2} and up to 5×10^{-2} a second set of particles appeared having diameters of 1.0 μm or larger as shown in Figure 3. These appeared to be homogeneous pools of pure PB and had apparently formed through aggregation of smaller "particles".

On the basis of the hypothesis that some of the low molecular weight component of the broad-distribution HH-101 PS associates preferentially with the low molecular weight PB-2.76K to form the concentric shell morphology of the particles, additional blends were prepared utilizing only narrow-distribution PS of a molecular weight of either 152 or 300 kg/mol. In both cases it was found indeed that the particles became homogeneous without the concentric shells.

The glass transition temperatures of the binary blends of HH-101 PS containing PB-2.76K were determined from DSC measurements conducted on the individual spin-cast films. When an initial set of experiments showed significant depressions of T_g with small weight fractions of added PB-2.76K, residual solvent was suspected and the specimens were given an additional thermal treatment of 12 h at 110 °C in vacuo as already stated above. The measured change in the T_g in these specimens is shown in Figure 4 and is found to be quite minimal. There is a small depression of about 1 °C in T_g at the solubility limit of 0.45% by weight of PB-2.76K. This small effect completely disappears at a composition of 2% PB. We attribute the elevation of the measured T_g at 5% concentration of PB, above the value for homo-PS to experimental error.

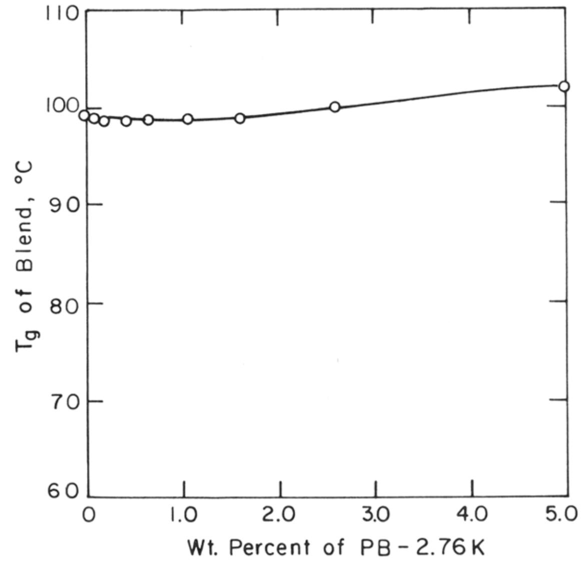

Figure 4. Change in T_g of blends as a function of weight concentration of PB-2.76K.

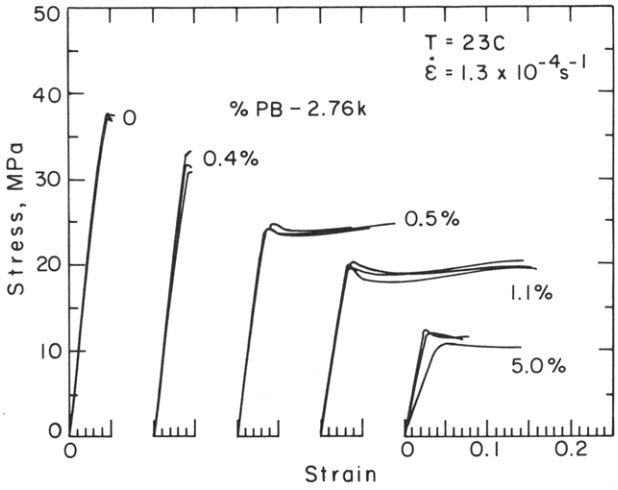

Figure 5. Stress-strain curves of five blends with a systematically increasing weight concentration of PB-2.76K. The two brittle blends are homogeneous.

III.2. Stress–Strain Experiments. Figure 5 shows five stress–strain curves with systematically displaced origins to better show the changing details. The craze yield stress of unmodified HH-101 PS is seen to be between 37 and 38 MPa with a plastic strain to fracture of 1–1.5%. The stress–strain curves for a homogeneous blend with 0.4% of PB-2.76K, just at the border of the solubility limit of the PB, show a slightly reduced modulus and yield stress in the range of 32 MPa with no improvement in strain to fracture. In comparison the stress–strain curves for the first heterogeneous blend with 0.5% of PB-2.76K show a significantly reduced yield strength of around 24 MPa and a greatly increased strain to fracture of around 16%. In the blend with 1.1% of PB-2.76K the yield stress has dropped to 19 MPa and the strain to fracture has increased to 23%. In blends with an increasing weight percent of PB-2.76K, up to 5%, the yield stress continues to decrease monotonically but at a decreasing rate. The strain to fracture, however, decreases also beyond the peak value reached at about 1.1% of PB-2.76K. This decrease in strain to fracture is observed to set in upon the appearance of the larger, micron-sized homogeneous PB particles in the blends. Figures 6 and 7 summarize the monotonic decrease in the yield strength and the rise and fall of the strain to fracture with an increasing weight percent of PB-2.76K. This behavior produces a maximum in tensile toughness of 4.6 MJ/m^3 at about 1.1% of PB-2.76K, which is fully a factor of 8.3 improvement of the tensile toughness of unmodified homo-PS. The change in normalized tensile toughness with the changing weight percent of PB-2.76K is shown in Figure 8. Its behavior parallels closely the behavior of the strain to fracture.

Finally, a few compression experiments were also carried out on small disk-shaped specimens of 2-mm diameter and 2–4-mm height. The results in Figure 9 show that there is a modest decrease in the compressive yield strength over the range of 0–1.5% of PB-2.76K. While this drop is more than what can be attributed to a rule of mixtures effect, it is very much less than the reduction of the craze flow stress in tension. This indicated that the plasticization effect of PB in tension is not global.

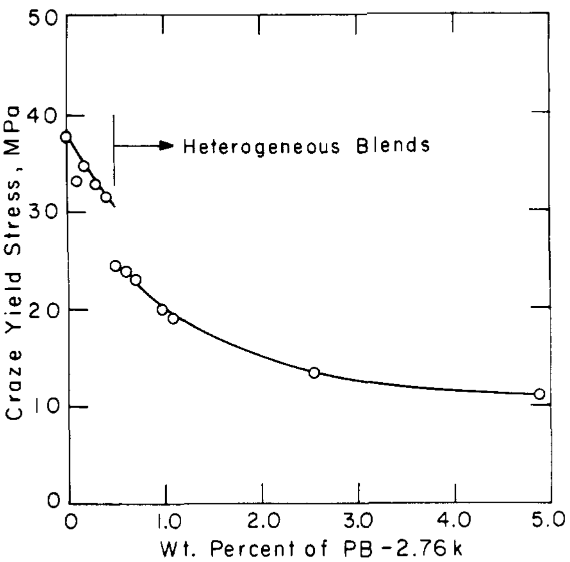

Figure 6. Dependence of craze yield stress on the concentration by weight of PB-2.76K.

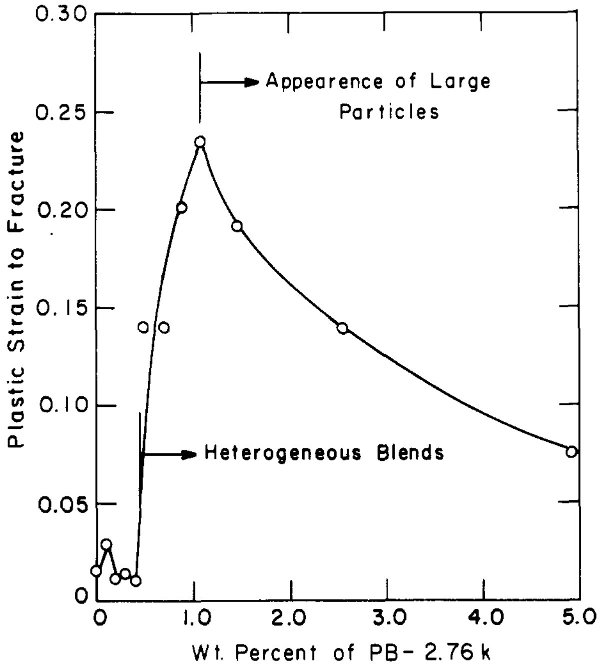

Figure 7. Dependence of the strain to fracture of blends on the concentration by weight of PB-2.76K.

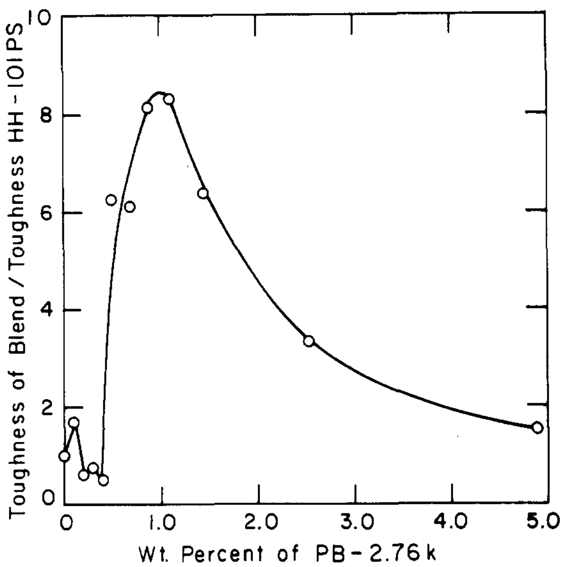

Figure 8. Dependence of the toughness ratio of blends on the concentration by weight of PB-2.76K.

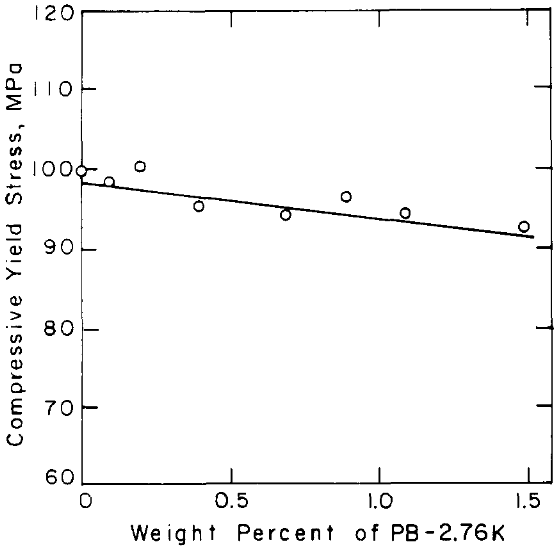

Figure 9. Dependence of compressive yield strength on the concentration by weight of PB-2.76K.

The introduction of the PB-2.76K makes the blends more compliant as expected. The normalized change in the modulus, as determined from the initial slopes of the stress–strain curves, with an increasing weight percent of PB-2.76K is shown in Figure 10. The decrease parallels the monotonic decrease in the craze yield stress and therefore would appear to constitute the well-known behavior of homogeneous glassy polymers.[17,18] We note, however, that the drop in modulus is far in excess of the drop in compressive yield stress shown in Figure 9, which represents a global behavior. This suggests that the modulus determined from the slopes of the stress–strain curves reflects the presence of considerable craze strain in what appears to be elastic behavior.

In order to develop a better understanding of the role of the PB, other blends were prepared containing PB of 6 kg/mol molecular weight at a weight percentage of 1.1 PB, which was the optimum blend of maximum toughness for PB-2.76K. The results are listed in Table II and indicate that the normalized toughness decreases sharply with increasing molecular weight of PB. This trend, if monotonic, suggests that blends of even larger toughness ratios are probably attainable with a PB of a molecular weight of less than 2.76 kg/mol. This possibility is presently under study. From the accompanying paper[19] where we discuss the mechanism of this toughening process it should become clear, however, that while improvements in toughness should indeed be possible with a PB of smaller molecular weight, the toughness cannot increase indefinitely with a decreasing molecular weight, if for no other reason than that very low molecular weight PB will remain in solution in PS to much larger concentrations, and precipitation of the PB into pools is necessary for the toughening effect.

To ascertain the possible role of the concentric spherical shell morphology of the small particles in blends having the optimum weight fraction of PB-2.76K, the tensile properties of additional blends with narrow-distribution homo-PS of molecular weights of 152 and 300 kg/mol in place of the HH-101 PS were also investigated. As mentioned in section III.1 such blends contain only homogeneous rubber particles. The measured toughness

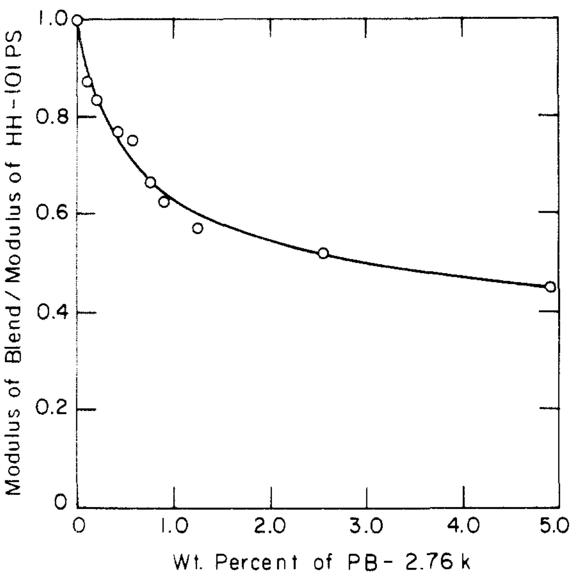

Figure 10. Dependence of the modulus ratio of blends on the concentration by weight of PB-2.76K.

Table II
Dependence of Normalized Tensile Toughness on Molecular Weight of PB in Binary Blends with HH-101 PS, at a Weight Fraction of 0.01

PB mol wt, kg/mol	toughness of blend/ toughness of HH-101 PS
2.76	8.4
6.00	1.2
23.60	2.06

Table III
Dependence of Normalized Tensile Toughness on Molecular Weight of a Narrow-Distribution PS Matrix, in Blends with PB-2.76K, at a Weight Fraction of 1.1–1.2 × 10^{-2}

PS mol wt, kg/mol	toughness of blend/ toughness of HH-101 PS
HH-101	8.40
152	4.30
300	4.45

ratios of these blends are given in Table III and indicate that they are considerably lower than those of blends utilizing the wide-distribution PS. This degraded behavior is primarily a result of lower strains to fracture.

In a final variation of blends to explore the cause of the concentric spherical shell morphology of the particles and their resulting properties, a set of ternary blends was also prepared by using only narrow-distribution components consisting of PS-300 (kg/mol) for the majority matrix phase with equal weight fractions of PB-2.76 (kg/mol) and PS-3.6 (kg/mol) to form the balance. While the morphological studies of these blends were inconclusive, some evidence was found that the introduction of small weight fractions of PS-3.6K into a narrow-distribution matrix of PS-300K restores the somewhat degraded properties of this material in binary blends. Thus, a blend of 0.5% PB-2.76K, 0.5% PS-3.6K, and 99% PS-300K had a somewhat larger flow stress and a somewhat better strain to fracture than the optimum binary blend of 1.1% PB-2.76K in HH-101 PS. In light of the SAXS experiments to be discussed in section III.4 below and the basic toughening model presented in the companion paper,[19] however, we conclude that the above results on the ternary blends are not significant and are within the overall scatter in reproducibility.

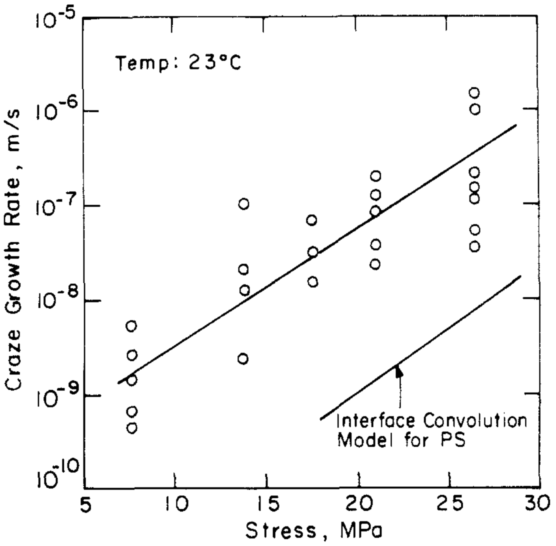

Figure 11. Stress dependence of craze growth rate in a blend of 0.5% PB-2.76K in PS.

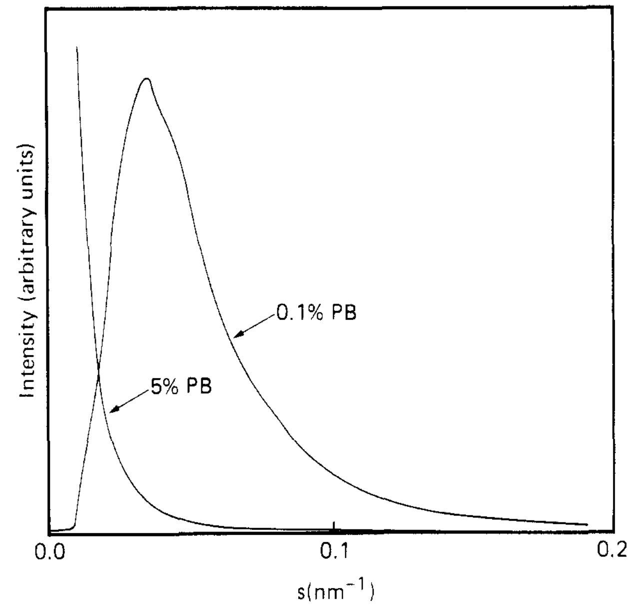

Figure 12. Distribution of scattered X-ray intensity from two crazed samples with concentrations by weight of 0.1% and 5% of PB-2.76K, in SAXS experiments.

III.3. Craze Growth Experiments. Craze growth rate results for a blend containing 0.5% PB-2.76K in polystyrene are presented in Figure 11. For clarity, growth rate data for polystyrene are omitted, but predictions of the interface convolution model[12] for polystyrene are represented by a straight line in the lower right corner. The straight line drawn through the data for the PB-2.76K PS blend signifies that the growth mechanism has not changed, and the growth rate at a given stress for polystyrene has only shifted to lower stresses. For a given growth rate, the shift in stress shown in Figure 11 is indeed close to the drop in craze yield stress shown in Figure 5.

III.4. SAXS Experiments. Figure 12 shows the scattered SAXS intensity from the central, extensively crazed regions of the three-point bend specimens for a 0.1% PB-2.76K (homogeneous) blend and a 5% PB-2.76K (heterogeneous) blend. It is immediately clear from these two typical curves for a homogeneous and a heterogeneous blend that small amounts of low molecular weight PB-2.76K have a strong effect on the morphology of the craze matter and the crazing properties of the PS, particularly when the PB appears as a separate phase above a weight percentage of ca. 0.45%. The results of the conventional Porod analysis of the scattered intensity are shown in Table

Table IV
Results of SAXS Measurements from Crazed Binary Blends of HH-101 PS with PB-2.76 (kg/mol) of Increasing Weight Fractions

PB-2.76K, wt %	σ_c, MPa	$\bar{D}$, nm	$\sigma_c\bar{D}$, J/m^2	homo or hetero blend
0.1	32	8.7	0.28	homo
0.5	24	9.3	0.22	hetero
0.9	17	10.3	0.18	hetero
1.2	19	16.4	0.31	hetero
1.5	15	17.1	0.26	hetero
5.0	11	23.9	0.26	hetero

IV, which indicates that, for the operational assumption that the craze matter volume fraction remains constant at 0.25, the product of the craze flow stress, σ_c, with the mean craze fibril diameter, $\bar{D}$, remains constant in all the blends, within experimental error. As is by now well-known, this result is a signature of the interface convolution (Taylor (meniscus) instability) mechanism of craze matter production at the craze borders.[12,20] The important implications of this finding are discussed in section IV and in much greater detail in the companion paper.[19]

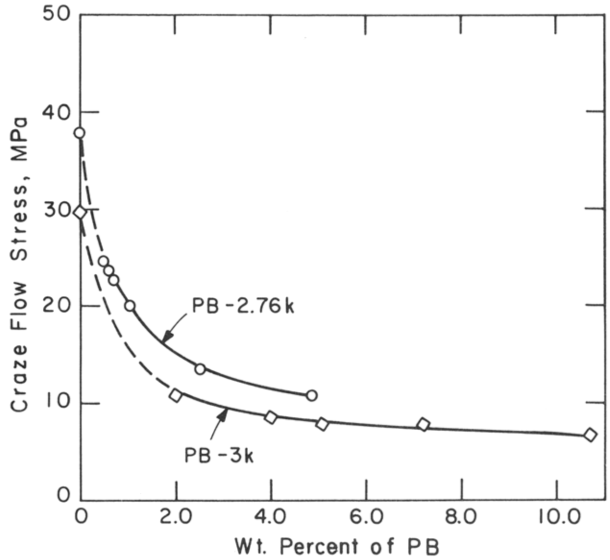

Figure 13. Dependence of craze flow stress on the concentration by weight of PB-2.76K in blends of this investigation (open circles) and of PB-3K in earlier blends (open diamonds) to modify the morphology of KRO-1 particles (from ref 9).

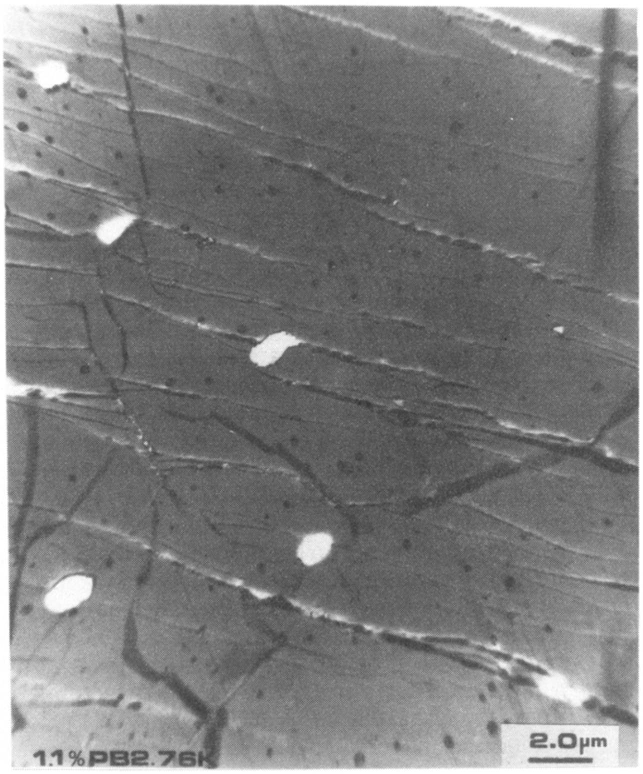

Figure 14. Micrograph of crazes in a strained blend of HH-101PS with 1.1% by weight of PB-2.76K.

IV. Discussion

The present experimental results on the dilute blends of HH-101 PS with low molecular weight PB-2.76K have much in common with the earlier blending results[9,10] in which KRO-1 block copolymer resin at a relatively larger volume fraction of about 0.22 was incorporated into the same homo-PS, both independently and in ternary blends together with a PB of a 3 kg/mol molecular weight. There too the addition of the PB-3K resulted in very substantial reductions in craze flow stress and very large accompanying strains to fracture—of up to nearly 100% for a blend ratio PB-3K/KRO-1 of 0.5. In those experiments, however, the principal and striking result appeared to be a morphological transformation in the particles from the tortuous PB rods in a topologically continuous majority block copolymer phase of PS to concentric spherical shells of PB and PS. While this morphological transformation increased the compliance of the composite particles very significantly and led to a much enhanced potency for craze initiation, it was noted that the improvement in compliance fell far short of an explanation of the very low craze flow stresses at ca. 10 MPa. This conclusion was reached, first, because precise micromechanical models of the elastic properties of the particles[6] could account for a craze initiation stress of no lower than about 28 MPa and, second, because the flow stress indicated clearly that the reduction had to be in the craze growth resistance of the surrounding PS background between the particles rather than be due to an alteration in the initiation condition for crazes.[7,10] Thus, it is now clear that the principal agent responsible for the large reduction in craze flow stress both then and in the present investigation is the low molecular weight PB. This conclusion is made more emphatic by Figure 13 which shows the present results (open circles) and those of the earlier blending experiments (open diamonds) where the craze flow stress has been plotted as a function of only the added PB-3K without regard of the very substantial weight fractions of KRO-1 resin. The two curves parallel each other closely, but the present flow stresses lie considerably above those of the earlier ternary blends. This is not unexpected. In the earlier blends the substantial volume fractions of the concentric spherical shell particles have acted as potent craze-initiating sites throughout the volume, establishing a large active craze front length per unit volume (or active craze interface density per unit vertical length[21] and thereby permitting a match between the imposed deformation rate and the craze strain rate at a considerably lower craze velocity than is possible in the present blends. Figure 14 shows a micrograph of a strained sample of an optimum blend of HH-101PS with 1.1% of PB-2.76K. It demonstrates that the inelastic behavior of the sample was indeed the result of craze plasticity but shows no evidence that the crazes were initiated by the small rubber particles. This is in agreement with expectations from HIPS and observations from the earlier blends that indicated that compliant particles of a diameter of 0.4 μm or smaller cannot initiate crazes.[10,21] Thus, we conclude that in the present blends crazes were initiated from surface imperfections, as in homo-PS, but apparently experienced only little resistance to their growth in the PS matrix—in common with the crazes in the previous blends.

The results of the craze growth and SAXS experiments have confirmed that the crazes grow and widen indeed by the interface convolution mechanism and that the low craze flow stresses result from a low local craze growth resistance. Thus, on the basis of these results and the many earlier observations, we have proposed that in both the present blends as well as in the previous blends containing concentric spherical shell particles the dramatic increase in toughness results from a controlled solvent crazing action of the low molecular weight PB.[14] As is developed in some detail in the companion paper,[19] we propose that when a growing craze taps into the small spherical pools of PB-2.76K, the latter rapidly drains onto the interface of the craze matter with the solid polymer. There, under the action of the local negative pressure in the fringing layer where craze tufts are drawn out of the solid polymer the PB-2.76K rapidly diffuses into this layer affected by the negative pressure. Under the conditions of the experiments discussed here this occurs at a rate several orders of magnitude faster than the rate of advance of a craze in a normal-tension experiment, because of the radically increased solubility, diffusivity, and decreased plastic resistance made possible by the local layer of negative pressure on the craze borders. That low molecular weight PB can be a solvent crazing agent has been verified in separate experiments and will be reported elsewhere.

Apart from the remarkable agreement between the theoretical model and the experimentally determined decrease of the craze flow stress with the increasing weight fraction of PB-2.76K, several other earlier observations are also in agreement with this proposed mechanism. In earlier experiments on crazed heterogeneous blends with concentric spherical shell particles it was observed that, upon unloading, the stretched sample retracts nearly by 90% and that, upon a period of rest, it shows prominent signs of healing and reconversion of craze matter into solid polymer.[13] At room temperature such behavior can only be possible if the effective T_g of the craze matter is only marginally higher than room temperature; i.e., it is extensively plasticized. It must be noted that the pools of PB-2.76K are completely in equilibrium in contact with the homo-PS when no stresses are applied. In fact, under these static conditions, as we have demonstrated earlier,[10,22] the thermal misfit stresses subject the PB to negative pressure and the surrounding cavity walls to a compensating small pressure. This lowers the solubility and diffusivity of the PB-2.76K in PS to negligibly low levels, under normal conditions.

We note that in the previous blending studies[10,11] where the PB-3K had produced a morphological transformation in the KRO-1 resin from a tortuous rubber rod morphology to a concentric spherical shell morphology the PB-3K must have retained its identity in the new spherical shell morphology and at least partially drained onto the interfaces of the crazes emanating from the particles once the latter had initiated crazes. That this was likely to be the case is indicated by the reappearance of the PB-3K in the new morphology as included pools when the blend ratio of PB-3K/KRO-1 exceeded 0.5. Effects similar to this where low molecular weight PB components associate with PB/PS diblock components, mimic the behavior, and acquire the morphology of a new diblock with a higher molecular weight ratio were also found in the blending experiments of Schwier et al.[23] using primarily diblock copolymers.

According to our proposed model the flow stress should monotonically decrease with an increasing weight fraction of low molecular weight PB since all of the PB that is tapped into by crazes will end up being acquired in the fringing layers of crazes, which in turn become stretched out to be converted into craze matter. Thus, if the pools of PB always remained smaller than subcritical flaw sizes for craze matter, the toughness of the blends should also monotonically increase. Unfortunately, as Figure 3 shows, larger pools of PB with diameters in excess of 1 μm begin to appear more regularly in blends with a PB content larger than 1.1%. Since these large particles apparently constitute supercritical flaws in craze matter once their contents are drained onto crazes, fracture ensues and the toughening process is short circuited.

The mechanism of toughening of glassy polymers by controlled solvent crazing is likely to have wide-spread industrial application. It achieves very attractive levels of toughness with rather small additions of rubber resulting in nearly transparent polymers because of the small particle sizes involved. The relatively small volume fractions of rubber also result in only negligibly small levels of stiffness loss. (A patent application has been filed by Gebizlioglu, Cohen, Argon, and Beckham on this new mechanism of toughening.[24])

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References and Notes

(1) Bucknall, C. B. *Toughened Plastics*; Applied Science Publishers: London, 1977.
(2) Wellinghoff, S. T.; Baer, E. *J. Appl. Polym. Sci.* **1978**, *22*, 2025.
(3) Murray, J.; Hull, D. *J. Polym. Sci., Part A-2* **1970**, *8*, 1521.
(4) Doyle, M. J.; Maranci, A.; Orowan, E.; Stork, S. T. *Proc. R. Soc. London* **1972** *A329*, 137.
(5) Yang, C.-M.; Kramer, E. J.; Kuo, C. C.; Phoenix, S. L. *Macromolecules* **1986**, *18*, 2010.
(6) Boyce, M. E.; Argon, A. S.; Parks, D. M. *Polymer* **1987**, *28*, 1680.
(7) Argon, A. S.; Cohen, R. E.; Gebizlioglu, O. S. In *Mechanical Behavior of Materials*. Yan, M. G., et al., Eds.; Pergamon Press: Oxford, 1987; Vol. 1, p 3.
(8) Argon, A. S.; Cohen, R. E.; Gebizlioglu, O. S. In *Toughening of Plastics*; The Plastics and Rubber Institute: London, 1985; p 21-1.
(9) Gebizlioglu, O. S.; Argon, A. S.; Cohen, R. E. *Polymer* **1985**, *26*, 519.
(10) Gebizlioglu, O. S.; Argon, A. S.; Cohen, R. E. *Polymer* **1985**, *26*, 529.
(11) Gebizlioglu, O. S.; Argon, A. S.; Cohen, R. E. In *Multi-Component Polymer Materials*; Paul, D. R., Sperling, L. H., Eds.; American Chemical Society: Washington, DC, 1986; p 259.
(12) Argon, A. S.; Salama, M. M. *Philos. Mag.* **1977**, *36*, 1217.
(13) Gebizlioglu, O. S.; Argon, A. S.; Cohen, R. E., to be published.
(14) Brown, H. R.; Argon, A. S.; Cohen, R. E.; Gebizlioglu, O. S.; Kramer, E. J. *Macromolecules* **1989**, *22*, 1002.
(15) Bates, F. S.; Cohen, R. E.; Argon, A. S. *Macromolecules* **1983**, *16*, 1108.
(16) Brown, H. R. *Mater. Sci. Rep.* **1987**, *2*, 315.
(17) Argon, A. S. *Philos. Mag.* **1973**, *28*, 839.
(18) Argon, A. S.; Bessonov, M. I. *Philos. Mag.* **1977**, *35*, 917.
(19) Argon, A. S.; Brown, H. R.; Cohen, R. E.; Gebizlioglu, O. S.; Kramer, E. J. *Macromolecules*, following paper in this issue.
(20) Kramer, E. J. In *Advances in Polymer Science: Crazing*; Kausch, H. H., Ed.; Springer: Berlin, 1983; Vol. 53/53, p 1.
(21) Piorkowska, E.; Argon, A. S.; Cohen, R. E. *Macromolecules*, in press.
(22) Schwier, C. E.; Argon, A. S.; Cohen, R. E. *Philos. Mag.* **1985**, *52*, 581.
(23) Schwier, C. E.; Argon, A. S.; Cohen, R. E. *Polymer* **1985**, *26*, 1985.
(24) Gebizlioglu, O. S.; Cohen, R. E.; Argon, A. S.; Beckham, H. W. U.S. Letters Patent Application, filed May 4, 1987.

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