Chemical Industry Co., Ltd., for the sample of the poly(oxyethylene) derivative.

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New Mechanism for Craze Toughening of Glassy Polymers

Introduction. Polystyrene and related homopolymers are brittle materials that typically fail in a tensile test at strains of 5% or less. The failure process occurs by the initiation and propagation of a few large crazes which soon fracture under the relatively high levels of stress. These polymers can be toughened by the addition of a rubbery second phase that forms composite particles, which initiate at relatively low stresses a large volume fraction of crazes that produce substantial plastic strain at relatively low stresses, without apparently initiating failure within the crazes. The crazes are believed to initiate as a result of the stress concentrations caused by the rubber particles, so the rubber acts in an essentially mechanical manner, leaving the properties of the surrounding polymer unchanged. Considerable energy is dissipated in the formation of the polystyrene crazes, producing a relatively tough material that shows "craze plasticity" and failure strains of up to 50%.[1]

In this paper we wish to suggest that a rubbery second phase can promote craze plasticity and toughening by a second entirely different process. A few percent of low molecular weight polybutadiene has been found to reduce the stress to craze polystyrene by a large amount and increase the failure strain up to 20%. The polybutadiene is not thermodynamically compatible with the polystyrene and forms a second phase at concentrations above 0.45%. The polybutadiene is believed to act as an environmental crazing agent and plasticizer whose solubility is enhanced along the craze interfaces and at the craze tip by the hydrostatic tensions that exist in these regions. Most crazes initiate from surface imperfections as in unmodified polystyrene though some may initiate from the larger rubber inclusions. These crazes then propagate in the polystyrene with the inclusion helping to supply the polybutadiene to the craze interfaces. The rubber here is believed to act mainly as a strategically placed low-viscosity plasticizer but is only plasticizing the border regions, the so-called active zone, where craze fibril drawing is taking place.

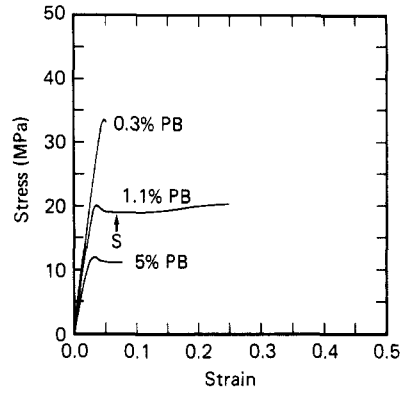

Figure 1. Three representative stress–strain curves of polystyrene containing low M_w PB. The arrow on the 1.1% curve shows where the craze drawing stress, S, was measured. A typical HIPS shows a similar stress–strain curve with S of about 15 MPa.

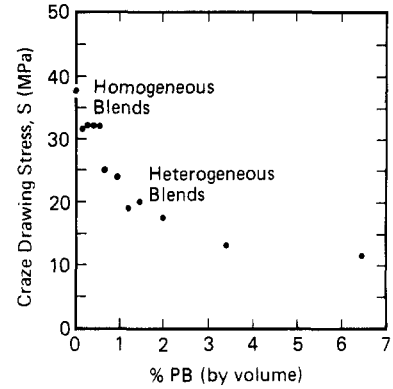

Figure 2. Variation of craze drawing stress with polybutadiene content. For low PB samples the craze yield stress was taken as a good approximation to S.

Experimental Techniques. Blends of polystyrene (PS) (2.7×10^5 M_w, M_w/M_n = 2.4) with polybutadiene (PB) (cis/trans/vinyl ≃ 45/45/10; 2700 M_w) were made by spin casting from toluene solutions in the manner that has been described in detail earlier.[2] Samples with a polybutadiene content of greater than 0.45% were visibly cloudy. They were found by TEM to contain 0.2-μm mean diameter rubber particles. Strips were cut from these samples for tensile testing in an Instron machine at a strain rate of 1.3×10^{-4} s^{-1} at a temperature of 23 °C. The microstructure of the crazes was examined by using small-angle X-ray scattering (SAXS) using the A1 beam line at the Cornell synchrotron source CHESS. The samples were crazed in three-point bending and the scattering from the crazed region in the bent samples was recorded at a camera length of 351 mm using a EG&G PARC OMA diode array detector. Mean fibril diameters were obtained by a Porod analysis of these data in the manner described before.[3] A fibril volume fraction for the crazes of 0.25 was assumed in the analysis for all the materials.

Results and Discussion. Stress–strain curves for several of the samples with different rubber contents are shown in Figure 1, while Figure 2 shows the effect of PB additions on the craze drawing stress of the materials. SAXS curves for two limiting blends are given in Figure 3. It is immediately evident from these results that the addition of a small amount of low molecular weight PB has a strong effect on the crazing properties of the PS

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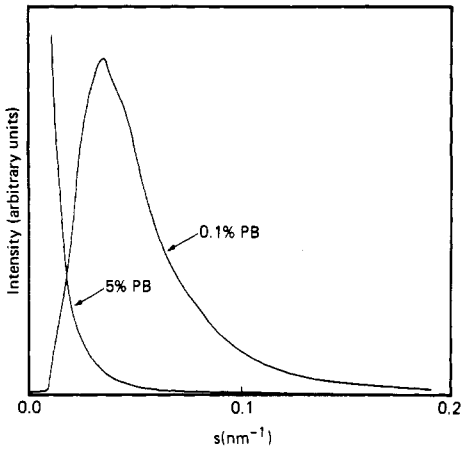

Figure 3. Representative SAXS curves from low and high PB content samples showing the considerable effect of PB content on the craze structures.

Table I

PB concn, wt %	S, MPa	$\bar{D}$, nm	$S\bar{D}$, J m^{-2}
0.1	32	8.7	0.28
0.5	24	9.3	0.22
0.9	17	10.3	0.18
1.2	19	16.4	0.31
1.5	15	17.1	0.26
5.0	11	23.9	0.26

particularly when the PB appears as a separate phase at ca. 0.45 wt %. The data presented in Table I show that the product of craze drawing stress S, with mean craze fibril diameter $\bar{D}$, is constant for these blends. The product $S\bar{D}$ has previously been shown to be constant, independent of crazing temperature or strain rate,[4] for crazes grown in polycarbonate or PMMA. It was also shown to be constant, independent of plasticizer level, when a low molecular weight plasticizer was added to PS.[5] These results have been explained by an extension of the meniscus instability model of crazing[6] to craze width growth.[7] The invariance of $S\bar{D}$ follows directly from this model if the craze surface energy and fibril volume fraction are independent of temperature and plasticizer level. Hence, the fact that $S\bar{D}$ was found to be independent of PB level in the results presented above is evidence that the low molecular weight PB acts by a plasticization mechanism and not just as a craze initiation source or a surface energy modifier. In the experiment referred to earlier[5] where a low molecular weight plasticizer (dibutyl phthalate) was added to polystyrene, a plasticizer concentration of 15% was required to reduce the craze drawing stress by a factor of 2; in contrast only 1.5 wt % is required for the same reduction using low M_w PB most of which is present as separate particles. Apparently not only is the low M_w PB an enormously efficient plasticizer but its efficiency continues to increase when its solubility limit is exceeded. This paradox can be explained by the effects of local stress on equilibrium absorption of an oligomer or low molecular weight polymer into a high molecular weight polymer.

The active zone at the craze–matrix interface, the thin layer from which polymer is drawn into the craze, should be under considerable hydrostatic tension σ. This hydrostatic tension is expected[8] to increase greatly the equilibrium solubility ϕ_s of an oligomeric fluid (partial molecular volume Ω) in the polymer. The hydrostatic tension can be considered as a negative osmotic pressure as long as the fluid itself is not subject to σ, a condition fulfilled in this instance because the PB particles cavitate. From Flory–Huggins theory of polymer–polymer solutions it has been shown that[8]

$$\phi_s = \phi_0 \exp(\sigma\Omega/kT)$$

as long as ϕ_s is small. While the ϕ_0 estimated from either the appearance of PB particles above 0.45 wt % or from the Flory–Huggins parameter (ca. 0.1[9]) for PS–PB is low, the application of even small hydrostatic tension increases it considerably. For example, as the hydrostatic tension σ must be at least $S/3$, for the smallest S observed, 11.3 MPa, σ must be at least 3.7 MPa and this gives $\phi_s/\phi_0 >$ 95, yielding a ϕ_s of greater than 0.4. It seems plausible then that this stress-enhanced absorption is the reason for the apparent high plasticizing efficiency of the PB. It should be noted that, as far as the authors are aware, this strong stress-enhanced sorbtion has not been observed experimentally.

The continued decrease in crazing stress and increase in fibril diameter for PB volume fractions above the solubility limit $\phi_0 = 0.0045$ shows, however, that the PB absorption in the active zone of the growing craze cannot be an equilibrium phenomenon; if it were, there should be no further change in S or $\bar{D}$ for $\phi > \phi_0$. Rather these changes imply that there is a kinetic limitation of the supply of PB molecules to the craze interface away from the PB particle reservoirs. (Exhaustion of these reservoirs cannot be responsible for the relatively high values of S (and low values of $\bar{D}$) at low ϕ's since S is approximately constant with time during the craze growth as shown in Figure 1.) PB molecules must diffuse away from the particle reservoirs along the surface of the polymer in the craze and dissolve in the active zone. The volume fraction in the active zone under these conditions ϕ_{sk} is found from a balance of fluxes to increase strongly as the spacing d between the PB particles decreases. The ϕ_{sk} scales approximately as $1/d^2$ and so increases substantially when ϕ exceeds ϕ_0 if the particle size remains roughly constant as indicated by the electron microscopy results.

Below the solubility limit, however, the PB is distributed uniformly (and immobilized) throughout the glassy PS. Little or no free PB is a available to migrate along the craze surfaces and hence little effect of PB content is predicted in this regime, in agreement with our further observation that only token decreases in S occur at PB contents below the solubility limit.

It is this increase in ϕ_{sk} that is thought to cause the decrease in the crazing stress S observed once the solubility limit is exceeded. Note that there is no specific requirement that the PB concentration be high at the craze tip, since decreasing the plastic resistance of the active zone in the region behind the craze tip will lead to a stress enhancement at the craze tip and a higher craze tip advance rate.

It is also worth pointing out that cross-linked rubber particles as small as 0.2 μm in diameter are not effective craze initiators in PS;[1] the regions of high-stress concentration are too small in volume to allow a craze nucleus to form. Thus the crazes here are expected to initiate, as for pure PS, from surface imperfections primarily. Neither the large drop in crazing stress nor the corresponding large increase in the $\bar{D}$ as the PB volume fraction increases can be due to the simple stress concentration effects of the PB particles. The increase in $\bar{D}$ in particular signifies that the PB must strongly affect the craze widening (fibril drawing) process and not just craze initiation.

We therefore propose that the basic mechanism by which low M_w PB acts to toughen PS is one in which there is a hydrostatic tension-enhanced dissolution of the PB in the active zone along the craze interfaces with the PB diffusing along these interfaces from rubber particle reservoirs. The dissolved PB acts as a plasticizer thus de-

creasing the craze fibril drawing stress. This toughening mechanism should occur in any system where an incompatible low molecular weight rubbery polymer is finely enough dispersed in a glassy polymer matrix. It may even be a factor in normal rubber-toughened polystyrene where there could be a significant low molecular weight sol fraction dissolved in the rubber particles. In this context it is relevant to note that craze fibrils and craze interfaces are stained dark by exposing the samples to OsO_4. This phenomenon has been ascribed to the reaction of OsO_4 with (1) double bonds produced as decay products of the radicals created by the chain scission inherent in the crazing process[10-12] and/or (2) unknown molecular heterogeneities[11] on the surface of fibrils. The first hypothesis does not explain why the craze staining in the PB-modified PS is much stronger than that in crazes in pure PS. The extra staining observed in high-impact polystyrene (HIPS) may then be the staining of the low molecular weight unsaturated rubber fraction which diffuses out from the rubber particles along the craze-matrix interfaces during craze growth.

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Order-Exchange Correlated Two-Dimensional NMR Study of Slow Molecular Motion in Highly Oriented Crystalline Poly(oxymethylene)

Two-dimensional (2D) NMR spectroscopy has become a valuable method for the study of molecular order or dynamic processes such as those resulting from chemical exchange, molecular motion, and spin diffusion.[1-10] In those experiments, the new signals due to molecular order or exchange are introduced by means of an additional spectral frequency dimension. In heterogeneous solids, e.g., glassy polymers, the type and the time scale of molecular motion may depend on the degree of molecular order. Therefore, experiments are desirable which can *correlate* molecular order and dynamics in partially oriented materials. One obvious way to correlate order and exchange for a partially oriented polymer sample is provided by 3D NMR.[11] Recently, we have developed a new rotor synchronized magic angle spinning (MAS) NMR method which can detect the correlation of molecular order and dynamics in partially ordered materials in two dimensions already.[12]

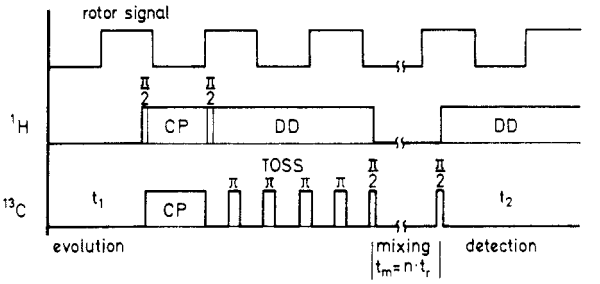

Figure 1. Two-dimension rotor synchronized ^{13}C MAS NMR pulse sequence for the correlation of molecular order and spin exchange.

The technique and the analysis of the sideband patterns are described in ref 12. It is the purpose of this paper to demonstrate its potential in polymer science by giving a preliminary report of a study of the chain mobility in highly oriented poly(oxymethylene) (POM).

The technique is based on three concepts: (i) By synchronization of the data acquisition with the rotor position in MAS-NMR of partially ordered polymers, a 2D sideband pattern can be obtained for each resonance, where the sidebands in the ω_1-dimension reflect the degree of molecular order.[7,8] (ii) Sidebands can be suppressed by applying the TOSS sequence[13-15] (total suppression of spinning sidebands). (iii) When combining TOSS with the exchange experiment,[1a] suppressed sidebands reappear in the presence of ultraslow dynamic processes during the mixing time.[16]

By combination of these three concepts, i.e., rotor-synchronized TOSS with insertion of a mixing time to allow for exchange, a 2D experiment can be designed,[12] where most of the sidebands occur only if the residue giving rise to the signal is involved in *both* molecular order and dynamics.

The pulse scheme for this experiment is given in Figure 1. After the pulse programmer is triggered by the rotor signal, the evolution period t_1 is inserted, being incremented in 16 steps of Δt_1 equal to one-sixteenth of one rotor period t_r. Transverse ^{13}C magnetization is created via cross-polarization (CP). After CP we apply the conventional TOSS pulse sequence consisting of four π-pulses the pulse spacings of which have been tabulated by Dixon.[14] For isotropic samples thereby the total suppression of spinning sidebands is achieved, whereas the sidebands are not suppressed for ordered samples, vide infra. At the point when the acquisition begins in a standard TOSS experiment, the transverse magnetization is stored parallel to the magnetic field by a 90° pulse, and a mixing period of an integral number of rotor periods starts. The remaining transverse magnetization dephases quickly because proton decoupling its turned off during the mixing time t_m. At the end of the mixing period the magnetization is rotated back into the transverse plane of the rotating

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