In-Situ Deformation Studies of Rubber Toughened Poly(methyl methacrylate): Influence of Rubber Particle Concentration and Rubber Cross-Linking Density

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ABSTRACT: The deformation behaviour of rubber toughened poly(methyl methacrylate) (PMMA) was studied using real time small angle X-ray scattering (SAXS) with a synchrotron radiation source. The invariant analysis method was used to analyze the influence of rubber particle concentration and rubber cross-linking density on craze concentration quantitatively. It is shown that both rubber particle concentration and the cross-linking density of the rubber layer have a significant effect on craze density. The craze density increases as the concentration of rubber particles increases from 10 wt % up to 30 wt %; thereafter, it decreases as the concentration of rubber particles increases further. For all polymer matrices with different cross-linking densities, a maximum craze concentration appears at ∼30 wt % of rubber particle, which corresponds to a true rubber concentration of about 15 wt %. The influence of cross-linking density on craze concentration is similar to that of rubber particle concentration. As the cross-linking density increases, the craze density first increases and then decreases. The appearance of crazing coincides with the occurrence of the macroscopic yield point of the polymer sample, corresponding to the beginning of plastic deformation. It appears that a sufficient concentration of crazes is needed to achieve an optimum toughness of the PMMA matrix. For the same cross-linking density of the rubber, high toughness requires a sufficient rubber particle concentration which can generate many crazes, while, for a given rubber particle concentration, high toughness is associated with a lower craze density.

Introduction

Rubber toughening of poly(methyl methacrylate) (PMMA) is a frequently used strategy to overcome the normal brittle response to deformation of PMMA. Modern polymerization methods have led to the possibility of preparing rubber particles with a range of different internal morphologies: they may contain several alternating layers of rubber and PMMA, and the properties of the rubber itself can be altered, for instance, by cross-linking. However, an understanding of how changing this structure may affect the subsequent deformation mechanism is somewhat rudimentary, and indeed there is still controversy over what mode of deformation may be most effective. It has long been asserted that the role of the rubber particles is to nucleate a high density of crazes so that a high energy is absorbed before any single craze fails.[1] More recently, it has been demonstrated on the basis of real time X-ray studies using synchrotron radiation that cavitation and shear may both occur before crazing for some toughened styrenic systems, and the two processes combined may contribute more than 50% of the total deformation.[2] Very recently it has been shown that, in a series of model rubber toughened polystyrenes, the impact toughness increases with rubber content, although the amount of crazing itself strongly decreases.[3] Thus, although empirical strategies have been devised to improve performance, it is clear the rationale for these strategies is still muddled.

Small angle X-ray scattering (SAXS) is a useful method for the study of deformation microstructure, and in particular the use of high-intensity synchrotron radiation allows the possibility of an *in-situ* deformation study. In our previous report on the deformation behavior of core shell rubber particles in a PMMA matrix under tensile strain,[4] we have shown that core shell rubber particles (consisting of PMMA core−rubber middle layer−PMMA outer layer) first undergo inhomogeneous deformation (the PMMA core and surrounding rubber layer deform to different extents), followed by progressive debonding or cavitation in the rubber layer beyond the yield point. Recently methods have been developed[5,6] to characterize the amount of crazing which occurs in rubber toughened glassy polymers, using the so-called invariant obtained from SAXS analysis. This invariant analysis is based on the idea that a craze can be effectively modeled within a two phase model and that there are no other scattering sources. However, when core shell particles are used for toughening, the analysis may be affected since the particles themselves can scatter strongly, even in the absence of crazes or cavitation. In our previous paper[7] we have explored the effect of such core shell rubber particles and their deformation on invariant analysis and set up a framework for separating the contribution of the particle form factor from the total X-ray scattering. In this way the contribution of the crazes to the total invariant can correctly be assessed. It is shown that,[7] for a submicron rubber particle system, the scattering from the form factor for core shell rubber particles dominates the SAXS pattern of undeformed samples, and the intensity of this scattering increases as the concentration of rubber particle increases. This scattering needs to be subtracted from the experimental data before the invariant can be quantitatively analyzed for the amount of crazing as deformation proceeds. Subsequent deformation of the core shell rubber particles increases the contribution of the form factor to

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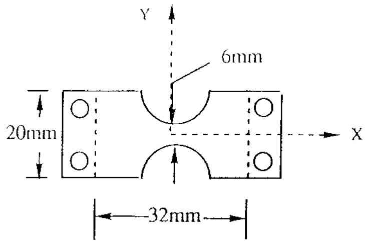

Figure 1. Schematic diagram to show the shape and dimensions of the samples used for this scattering study. The beam impinges at the narrowest point between the two semicircular cuts.

the total invariant, although this effect is fairly minor compared with the contribution due to crazing.

On the basis of this approach, in this paper we will quantitatively study the influence of rubber particle concentration and the cross-linking density of the rubber layer on the formation of crazes using small angle X-ray scattering at the synchrotron radiation source at Daresbury (U.K.). The samples studied here cover four cross-linking densities and five rubber particle concentrations. This set of samples provides an excellent range of samples for systematically studying the influence of rubber particle concentration and cross-linking density on craze formation and the interplay of rubber concentration and cross-linking density on toughening PMMA.

Materials

Model samples of rubber toughened PMMA were supplied by ICI plc with five different concentrations of rubber particles of 10, 20, 30, 40, and 50 wt %. The rubber particles had a three-layer structure: a PMMA core of 80−85 nm radius, a rubber middle layer of 40−50 nm thickness, and a thin outer PMMA layer. The rubber phase therefore only counts for about 50 wt % of the total rubber particle. The toughening particles were prepared by sequential emulsion polymerization, and the rubber layers comprised a copolymer of *n*-butyl acrylate and styrene. The ratio of *n*-butyl acrylate to styrene was 4:1 by weight. Variations in cross-linking within the rubber layer were effected by the use of different levels of addition of allyl methacrylate at levels of 0.5−5% (referred to as cross-linking densities of 0.5−5%) by weight of the total rubber layer mass. The samples were first extruded to ensure proper mixing of the core shell rubber particles and PMMA matrix and then compression molded to about 1.10−1.25 mm thick plaques, which were subsequently machined to an area of 20×50 mm^2. Two circular stress concentrators with a radius of 6 mm were machined opposite to each other in the middle of the sample to ensure that the X-ray beam passed through the region of deformation during tensile testing, as shown in Figure 1. It is important to ensure that there is no damage of the polymer sample during machining. The non-uniform shape means values for precise local strains and stresses are hard to obtain. An extension rate of 0.5 mm/min was used throughout.

Experimental Section

The real time small angle X-ray scattering experiments were carried out on station 2.1 at the Daresbury Synchrotron Radiation Source (U.K.) of the CCLRC. A 2-D multiwire proportional gas-filled detector was used with an effective area of 197×197 mm^2 consisting of 512×512 pixels. As a result, the pixel size of the detector is 0.38×0.38 mm^2. The X-ray wavelength is 1.54 Å. A Miniature Materials Tester (Minimat) tensile testing rig (from Polymer Laboratory) was fitted into the beam line. The extension rate was 0.5 mm/min, and the experiment was carried out at room temperature (i.e. about 20 °C). The sample to detector distance was 875 cm, which covers a q ($q = 4\pi \sin \theta/\lambda$) range from 0.005 to 0.045 Å^{-1}. The beam size on the polymer sample was about 5.5×1.1 mm^2. Two ionization chambers sit in front of and behind the polymer sample, monitoring the changing X-ray intensity during the experiments, which ensures an accurate calibration of scattering intensity in the following data analysis. Since the scattering intensity changes dramatically during the process of deformation, particularly when there is a large amount of crazing in the polymer sample, it is important that the ionization chamber readings are set in their linear regimes during the experiment. The frame time was about 8 s, and there were 20−40 data frames per sample. In order to prevent saturation of the detector, aluminium sheets were placed in front of the detector in order to attenuate the beam. The background scattering and the scattering from a polyethylene standard for each setup of aluminium sheets were also recorded for the following data analysis. The 2-D scattering patterns and the ionization chamber readings as well as the tensile curve from the Minimat were recorded simultaneously. More detailed information about station 2.1 at Daresbury can be found in the paper by Towns-Andrews et al.[8]

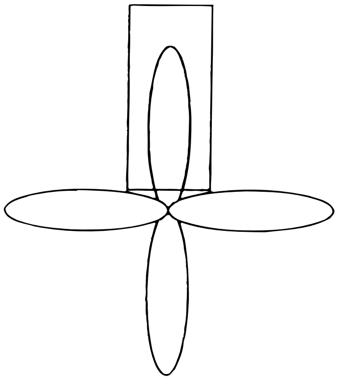

Figure 2. “Ideal” scattering pattern from crazes projected onto a 2-D detector, showing the region of analysis as the box. The tensile axis is horizontal.

Data Analysis

The raw data were first normalized by the ionization chamber readings. This is necessary because the density of the sample is changed during deformation due to crazing, cavitation, and shear yielding of the sample, which leads to a change of absorption of the X-ray beam, as well as the effect of bulk thinning. Moreover, the intensity of the X-ray beam may also change with time. The normalization process will ensure that the changing density during deformation is taken into account. Then, the data were divided by the detector response, followed by subtraction of the background scattering. The q range was calibrated using wet rat-tail collagen as a standard. In this study, the tensile axis is maintained horizontal so that scattering from any crazes that form occurs in the vertical direction (schematically shown in Figure 2).

The craze population can be related to the absolute invariant using a two phase model.[5,6] Since the absolute intensity of scattering cannot be easily obtained, an indirect method was used to analyze the absolute invariant of polymer, using Lupolene as a standard to convert the relative invariant into an absolute one. The relative invariant for the scattering, Q_r, is calculated using the intensity measured by the detector during the experiment and is given by

$$Q_r = \sum_{q_1}^{q_2} I(q) q \Delta q + Q_{\text{tail}}$$

where $I(q)$ is the scattering intensity from crazes at wave vector $\mathbf{q}$, obtained by integrating the intensity along a horizontal line within a rectangle, as shown in Figure 2. In practice this integration is perfomed in two steps, first integrating perpendicular to the streak and then along the streak. This has the effect of slit smearing.[7]

The width of the rectangular area should be sufficiently big that it covers the entire area of the scattering pattern arising from crazes. On the other hand, too large a width may compromise our approximation approach, which uses undeformed scattering to represent the deformed form factor. The practical way is to make sure that the rectangular area covers the scattering from crazes, which can be easily identified by the streak along the meridian. q_1 is the lowest angle in the rectangular area, while q_2 is the highest. Q_{tail} is the relative invariant for the area from q_2 to ∞ and can be calculated using Porod analysis.

According to ref 7, the scattering intensity from crazes in a deformed sample is given by

$$I(q) = I_t(q) - I_u(q)$$

where $I_t(q)$ is the scattering intensity from the sample (integrated along the horizontal line in the rectangular area) at time t and $I_u(q)$ is the scattering intensity for the undeformed sample in the same rectangular area. It is worth noting that $I(q)$ and $I_t(q)$ are functions of time (or, more precisely, functions of the frame number) since the scattering $I_t(q)$ changes during sample deformation.

Porod analysis is applied to calculating Q_{tail} as follows

$$Q_{\text{tail}} = \int_{q_2}^{\infty} I(q) q \, dq = \int_{q_2}^{\infty} \frac{K}{q^3} q \, dq = \frac{K}{q_2}$$

where q_2 is the maximum scattering vector for the area analyzed and K is the Porod constant obtained from a Porod analysis[5,6] using a plot of Iq^3 versus q^3. The relative invariant, Q_r, was converted to the absolute invariant, Q_a, using Lupolene as a standard.

The absolute invariant can be related to the scattering from crazes[6,9] as

$$Q_a = \lambda \sigma_f V_c v_f (1 - v_f) \Delta\rho^2$$

where λ is the wavelength of the X-ray beam (corresponding to 1.54 Å); V_c is the total volume of craze fibrils sampled by the X-ray beam; σ_f is the Thomson scattering factor (=7.9 × 10^{-26} cm^{-2}); v_f is the average volume fraction of the craze, which is about 0.3 according to Schirrer's study;[10] and $\Delta\rho$ is the electron density difference between fibril and void. This can be evaluated as dN_A, where d is the mass density of PMMA (taken as 1.188 g/cm^3)[11] and N_A is the Avogadro constant.

The plastic strain due to crazing is

$$\epsilon_c = \frac{V_c}{V_0}(1 - v_f) = \frac{Q_a}{\lambda \sigma_f V_0 v_f \Delta\rho^2}$$

where V_0 is the total volume of polymer sampled by the X-ray beam.

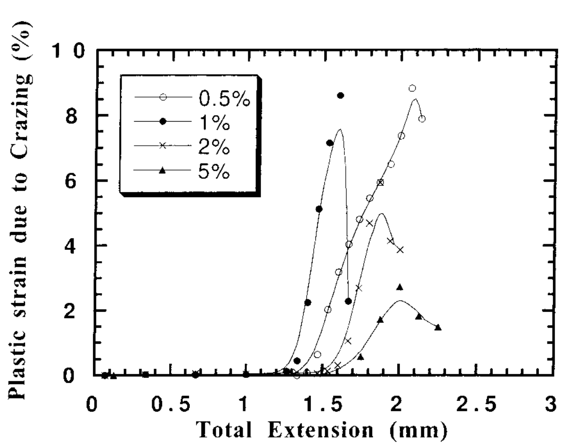

Figure 3. Relation between plastic strain due to crazing and the total extension of the sample. Rubber particle concentration is 30 wt %, and the cross-linking density of the rubber is varied.

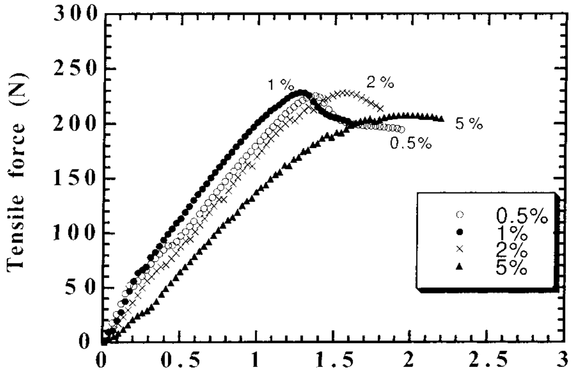

Figure 4. Corresponding tensile curve for the polymer samples shown in Figure 3. The strain rate is 0.5 mm/min.

Results

Figure 3 is the result of invariant analysis for one set of polymer matrices in which the cross-linking density varied from 0.5 to 5% while the concentration of rubber particles was kept constant at 30 wt %. This figure shows the relation between plastic strain due to crazing and the total extension of the sample. The true strain of the sample is difficult to obtain due to its irregular shape. However, the dimensions of the sample and the region (in the middle of the sample) which is sampled by the X-ray beam are the same for all samples examined in this study. As a result, the total extension of the sample can be used indirectly to present the true strain in the region sampled by the X-ray beam.

The onset of crazing for the four samples appears at about 1.3−1.5 mm total extension, and the maximum plastic strain due to crazes decreases with an increase of rubber cross-linking density, as shown in Figure 3. Figure 4 shows the corresponding tensile curves for the same samples. The yield points occur between about 1.3 and 1.5 mm extension. It is interesting to see that the yield points coincide with the onset of crazing for each sample, as shown in Table 1.

Figure 5 shows results from the invariant analysis result for a second set of samples in which the concentration of rubber particles was varied from 10 to 50 wt % while the cross-linking density of the rubber was kept at 2%. It can be seen that the maximum plastic deformation due to crazing first increases and then

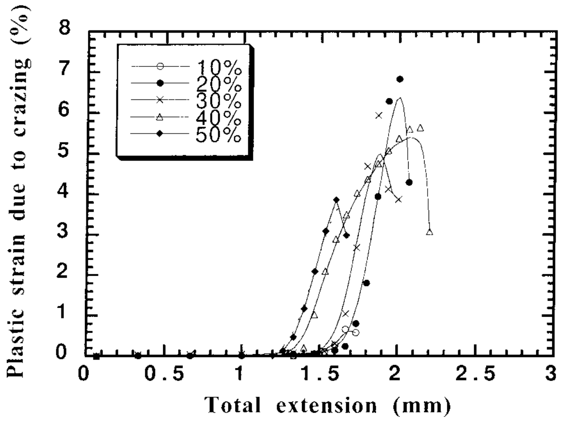

Figure 5. Relation between plastic strain due to crazing and the total extension of the sample. Rubber cross-linking density is kept at 2% while the particle concentration is varied.

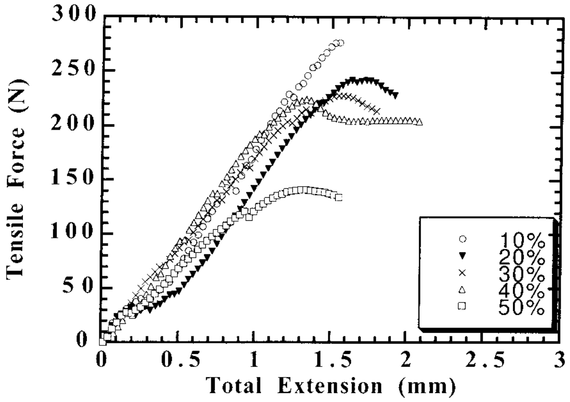

Figure 6. Corresponding tensile curve for the polymer sample shown in Figure 5. The strain rate is 0.5 mm/min.

Table 1. Comparison of the Onset of Crazing with the Yield Point of Polymer Samples (30% Rubber Particle Concentration in All Cases)

cross-linking density of rubber particles (%)	total extension of sample (mm)	
	at onset of crazing	at yield point
0.5	1.2 ± 0.05	1.2 ± 0.05
1	1.2 ± 0.05	1.2 ± 0.05
2	1.4 ± 0.05	1.4 ± 0.05
5	1.5 ± 0.05	1.5 ± 0.05

Table 2. Comparison of the Onset of Crazing with the Yield Point of Polymer Samples (Cross-Linking Density of Rubber Particles, 2% in all Cases)

concn of rubber particles (wt %)	total extension of sample (mm)	
	at onset of crazing	at yield point
10	1.45 ± 0.05	1.45 ± 0.05
20	1.5 ± 0.05	1.6 ± 0.05
30	1.5 ± 0.05	1.5 ± 0.05
40	1.3 ± 0.05	1.3 ± 0.05
50	1.3 ± 0.05	1.3 ± 0.05

decreases as the concentration of the rubber particle increases. The onset of crazing appears in the range of 1.3−1.5 mm total extension. The total extension needed for the onset of crazing decreases as the rubber particle concentration increases. Figure 6 shows the corresponding tensile curves, which again indicate that the yield point coincides with the appearance of crazing, as shown in Table 2.

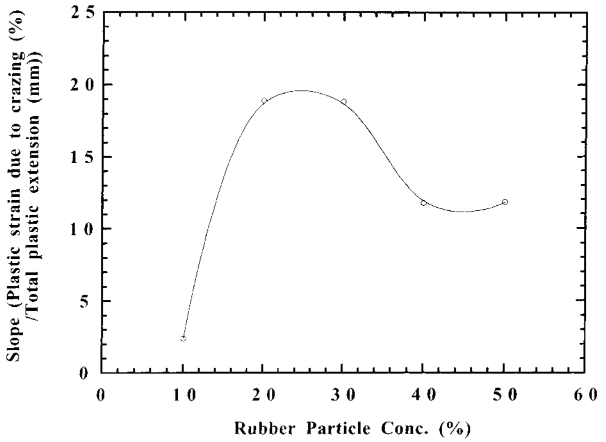

Figure 7. Relation between the propensity for crazing (the slope from Figure 5) and the rubber particle concentration. The cross-linking density is 2%.

By comparing the results of the invariant analysis with the corresponding tensile curves, it can be seen that the maximum strain due to crazing depends strongly on the total achievable extension of the sample. However, the total extension of a sample is influenced not only by its intrinsic structure, such as rubber cross-linking density and rubber particle concentration, but also by the internal morphology (e.g. the distribution of rubber particles in the matrix) and the sample preparation (e.g. the presence of any voiding or damage due to machining). As a result, even for the same cross-linking density and concentration of rubber particles, there is an inherent variability in the total extension measured, and hence this will affect the measured maximum plastic strain due to crazing. In order to avoid this complication, a new parameter is adopted which may represent the influence of cross-linking density and the concentration of rubber particles on crazing more effectively. This parameter is derived from analyzing the initial slope of the crazing plastic strain−extension curve at the point of crazing onset (as in Figures 3 and 5). This slope represents the density of crazes per unit plastic deformation: the higher the slope, the higher the craze density at the same plastic strain. If a sample has a high slope, the polymer matrix has a strong tendency to craze when deformed.

Using this method on the data of Figure 5, we obtain Figure 7. It can be seen from Figure 7 that, for polymer matrices with a 2% rubber cross-linking density, the craze concentration increases with an increase of rubber particle concentration up to 30 wt % and then decreases again as the concentration of rubber particle increases further. This trend is also seen in the polymer matrices with 0.5, 1, and 5% cross-linking densities, as shown in Figure 8. The data in Figure 8 can be replotted to show how cross-linking density affects the craze plastic strain (Figure 9) at different particle concentrations. It can clearly be seen from this figure that the crazing density (for all rubber particle concentrations) increases as the cross-linking density decreases from 5% to 1 or 2% but then falls as the cross-linking density decreases further to 0.5%.

Discussion

Influence of the Rubber Particle Concentration. The plastic strain due to crazing, and hence the craze density in the matrix, depends on the rubber particle concentration. Taking the polymer matrices with 2% cross-linking density as an example, the initial slope of Figure 3, plotted in Figure 7, indicates the rate of increase in craze volume increases with rubber concen-

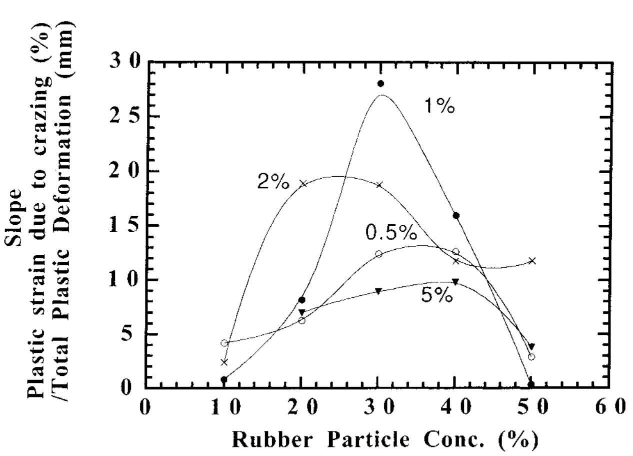

Figure 8. Relation between the propensity for crazing (the slope from Figure 3) and rubber particle concentration for all four rubber cross-linking density sample sets.

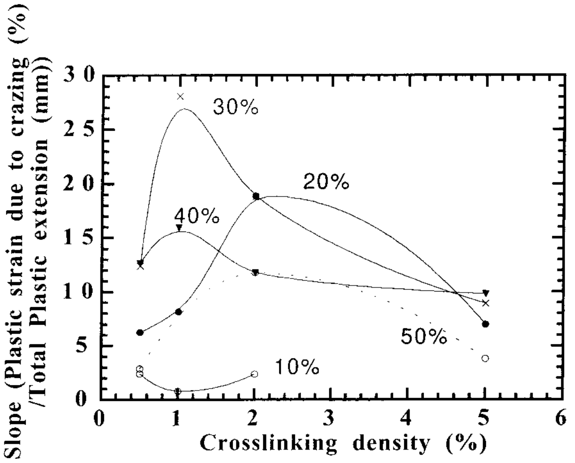

Figure 9. Relation between the propensity for crazing (the slope) and rubber cross-linking density for all five rubber particle concentration sets.

Table 3. Interparticle Distances for Different Particle Concentrations[a]

rubber particle concn (wt %)	interparticle distance (nm)
10	214
20	118
30	72
40	42
50	21

[a] This calculation is done assuming that the particle diameter is 250 nm and the particles have an fcc packing structure (packing efficency of 0.64).

tration up to 30 wt %. After that it decreases. For the other cross-linking densities, a similar relationship exists between the concentration of rubber particles and the propensity for crazing, as shown in Figure 8.

For the same cross-linking density, the influence of rubber particle concentration on crazing would be expected to be through their role as craze initiators. Crazes are initiated at points of maximum triaxial stress concentration, which in rubber toughened systems are usually at the equator of the rubber particles. Therefore the higher the concentration of rubber particles, the higher the concentration of craze nucleation sites. For polymer matrices with 10−30 wt % rubber particle, the particle nucleation mechanism is the dominant force, which leads to an increase of craze concentration as the concentration of rubber particle increases.

However, as the particle density increases, the local stress state will be affected, particularly if shear yield appears or cavitation/debonding occurs, as suggested by our earlier analysis of the form factor scattering.[4] The appearance of a maximum craze concentration at ~30 wt % rubber particles for all polymer matrices regardless of cross-linking density indicates that there is an optimum concentration of rubber particles with regard to craze formation: at low concentrations they are effective as crazing centers and the increase in craze density correlates with particle concentration. However, beyond a certain point, as the volume fraction increases, the particles (more compliant than the matrix) begin to modify the stress field significantly, reducing the overall stress levels sufficiently to suppress craze nucleation.

A study[12] by Gloaguen et al. shows that the yield stress strongly depends on particle volume fraction. It decreases monotonically as the concentration of rubber particle increases. Compared with pure PMMA, a polymer matrix with 45% (v/v) rubber particle has a yield stress of only 40% pure PMMA. More important is that their study shows there is a critical interparticle distance of 50−60 nm (regardless of particle size) which facilitates the formation of shear bands. The interparticle distance here refers to the distance between the outer layers of two neighboring particles (i.e. the gap between particles). In our polymer system, the interparticle distances for different particle concentrations are listed in Table 3. It is interesting to see that the critical interparticle distance suggested by Gloaguen occurs in our system between 30 and 40 wt % rubber particles in our polymer system. Using this concept of a critical interparticle distance provides us with a framework for understanding why polymer matrices exhibit a maximum craze density at 30 wt % regardless of the cross-linking density. For polymer matrices with a rubber particle concentration exceeding 30 wt %, the interparticle distance becomes smaller than the critical distance of 50 nm. The polymer matrices are more susceptible to shear yielding (which will not be detectable in these SAXS experiments), which means the local stress field may reach the critical point for yielding of the matrix before craze initiation. The yielding of the polymer matrix absorbs a large amount of energy and reduces the likelihood of a particle initiating crazing, even though the number of sites which potentially could induce crazing continues to increase.

The aim of incorporating rubber particles into polymer matrices is to improve toughness. High concentrations of rubber particles induce a high craze density, which is a source of energy absorption and hence should improve the toughness. However, crazes also act as weak points which may lead to polymer breakdown. Here, the total extension of the sample before breakdown and the positions of the yield point are used as indirect indicators for assessing the toughness of polymer matrices. In our polymer system, polymer matrices achieve a maximum total extension at about 40 wt % rubber particles, at which level they also exhibit a reasonably high craze density. For low rubber particle concentrations, the matrix is very brittle and essentially no plastic deformation occurs. The craze concentration is very low in this case. This can be seen from the four samples with 10 wt % rubber particles but different cross-linking densities (Figure 9). However, if the rubber particle concentration is too high (i.e. the 50 wt

% sample in this study), the polymer matrices become weak and fail at an early stage of deformation as well. In this case failure may occur by premature breakdown of any cavities which have formed in the rubber particles themselves, without a significant amount of energy being absorbed. Figure 5 shows that the polymer matrix with 10 wt % rubber particle and 50 wt % particle fail at the same extension. However, as will be discussed in the following section where the effect of cross-linking is discussed, for the same concentration of rubber particles a polymer matrix with a low craze density has better properties than one with too high a density.

Influence of the Cross-Linking Density. The influence of the rubber cross-linking density on craze density is, in some respects, similar to that of rubber particle concentration. When the cross-linking density is low, the polymer matrix tends to exhibit plastic deformation and crazing at an early stage of deformation. It is shown in Table 1 that the total extension needed for the onset of crazing increases with an increase in the cross-linking density of the rubber. Moreover, a polymer matrix containing rubber particles with a low cross-linking density also tends to have a higher volume of crazes, although the relation between these two quantities is not a simple linear relationship. Taking the specific case of samples with 30 wt % rubber particle as an example, reducing the cross-linking density leads to a higher contribution to the plastic strain from crazing (see Figure 3). The craze density with the 1% cross-linked sample at its maximum is 4 times that of the 5% cross-linked sample. It is worth noting that since the thickness of the polymer sample varies slightly between samples (ranging between 1.1 and 1.25 mm), the small differences in tensile force between the family of differently cross-linked samples shown in Figure 4 should not be regarded as significant.

Unlike the influence of rubber particle concentration, for which a large population of nucleation sites is the main factor leading to a high craze density, the influence of cross-linking density will be due to the changing characteristics of the rubber phase in response to the deformation, which induces a change in the stress differential at the rubber/PMMA matrix. If the cross-linking density is low, this difference is large, leading to a high craze concentration. As the cross-linking density increases, the difference reduces and more deformation is likely to be borne by the rubber particles themselves rather than the matrix. However, the relation between the cross-linking density and the craze concentration is not a simple linear relation. It exhibits a maximum in terms of crazing strain at about 1−2% cross-linking, as shown in Figure 9. The reason for the fall-off at the lowest cross-linking density is unclear. It may be that at this cross-linking density (0.5%) there is an effect on the internal morphology of the rubber particles which leads to a decrease in crazing. This idea is supported by Figure 10, which is a line trace comparing the X-ray scattering from undeformed samples of 0.5 and 5% cross-linking densities. It can clearly be seen that there is a difference in these two curves, indicating a changing form factor. The rapid decay of the scattering intensity in the 0.5% sample, as opposed to the clear periodic oscillations in the 5% sample, suggests that either the distribution of particle sizes or the regularity of the internal structure is not as good as in the 5% case.

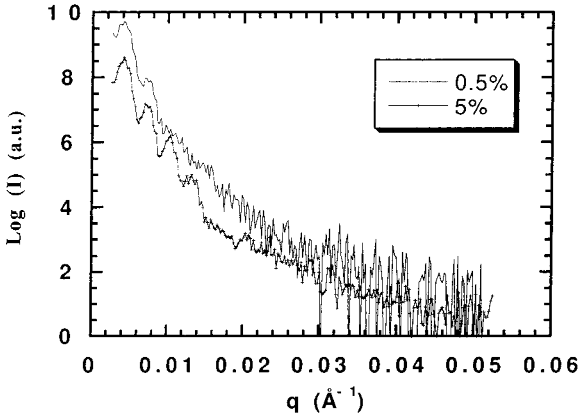

Figure 10. Comparison of X-ray scattering (corresponding to the form factor scattering) for polymer samples with cross-linking densities of 0.5 and 5%, demonstrating the difference in internal structure.

The influence of cross-linking density on craze concentration also depends on the rubber particle concentration. For a polymer matrix with 10 wt % rubber particles, the cross-linking density has no significant effect on craze density, while, with a concentration of rubber particles greater than 20 wt %, the effect of cross-linking density on craze concentration is significant. Calculation[13] has shown that, for an isolated elastic spherical particle in an elastic matrix, the maximum stresses occur at the equator of the rubber particle. Moreover, Broutman and Panizza[14] indicated that, for rubber volume fractions greater than about 0.09, the maximum stress concentration at the particle equator may be appreciably higher than for the case of an isolated particle, which means there is a critical concentration of rubber particles which must be reached before the concentration influences the propensity for craze initiation. This explains why, at low rubber concentrations, cross-linking has no significant effect on craze concentration.

Examining the influence of cross-linking density on the craze concentration and indirectly the resulting toughness of the polymer matrix, it can be seen (Figures 3 and 9) that, for the same concentration of rubber particles, a high cross-linking density may reduce the craze density and increase the total extension of polymer matrix before failure. For example, in polymer matrices with 30 wt % rubber particle concentration, the 5% cross-linking density polymer matrix exhibits the lowest craze density and achieves the highest extension (Figure 4). This is also true for polymer matrices with 20 and 40 wt % rubber particle concentrations. Figure 11 shows the tensile curves for a 40 wt % concentration of rubber particles.

In this paper we only concentrate on investigating the influence of rubber particle concentrations and cross-linking densities on the formation of crazes. Our previous study[4] also revealed that, at the late stage of deformation (after the polymer sample starts to yield), cavitation (or debonding) does appear in rubber particles of this polymer system. When the influence of cross-linking densities and the concentration of rubber particles on the toughness of the polymer matrix is considered, the cavitation of rubber particles should also be taken into consideration since it also serves as a source of energy dissipation. Taking both factors (crazing and cavitation) into account, it is clear that, in order to achieve an improved mechanical strength, the poly-

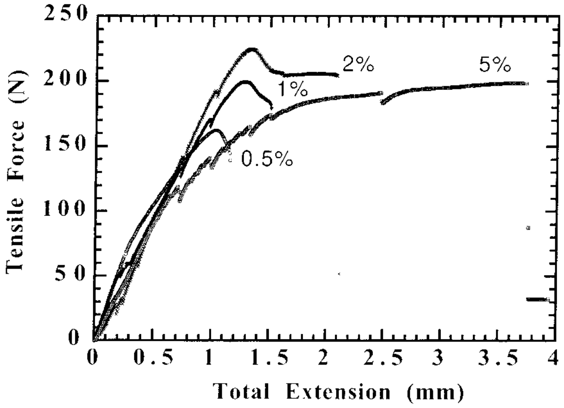

Figure 11. Tensile curves for polymer matrices with 40 wt % rubber particle concentration and different cross-linking densities.

mer matrix should have a reasonable concentration of rubber particles, since rubber particles are a source of cavitation and crazing, both of which absorb energy during deformation, and hence improve the toughness of polymer matrix. (It should be noted that the effect due to cavitation will in general be much less significant than that due to crazing. The importance of cavitation is that it can act as a trigger for subsequent crazing or shear.)

Interplay of Rubber Concentration and Cross-Linking Density. The above discussion demonstrates how the rubber particle concentration and cross-linking density of the rubber particle influence the craze concentration and the toughness of the polymer matrix. For all cross-linking densities, the concentration of the rubber particle should be higher than 20 wt % in order to achieve a reasonable toughness for the polymer matrices. It is worth noting that 20 wt % rubber particles in the matrix only implies about 10 wt % rubber itself, since the rubber particle has a three layer structure. The requirement for a minimum rubber concentration is understandable since the rubber particle not only serves as a location for cavitation but also serves as craze nucleation sites, both processes which absorb energy. However, increasing the concentration of the rubber particle may reduce the yield stress, as shown in Figure 6, and modulus, and too high a rubber loading also appears deleterious, because of coalescence of large flaws such as cavitated particles. As shown in Table 3, for 50 wt % rubber particle concentration, the interparticle distance (the distance between the surface of two particles) is only about 21 nm while the particle size is about 250 nm. Under the conditions studied here, 30−40 wt % rubber particle concentration seems to be the optimum concentration range for polymer matrices.

Cross-linking density influences the craze concentration of the polymer matrix, although it does not have a significant effect on the yield stress, as shown in Figure 6. As a result, manipulating the cross-linking density can be a strategy to control the craze density to achieve a better toughness of polymer matrix, while retaining a high yield stress for the matrix. The interplay of the concentration of the rubber particle and the cross-linking density of rubber provides us with a basis for achieving a better toughness through control of the chemical structure (cross-linking) and morphology (particle concentration).

Finally a note of caution must be sounded regarding the strain rate used. This study has concentrated on revealing mechanisms by using a moderate strain rate, whereas practical applications of rubber toughened PMMA typically involve much faster rates. Care must therefore be taken in extrapolating the understanding gained here to the very different conditions which pertain to impact testing.

Conclusions

Using an improved approach to SAXS invariant analysis for matrices containing core-shell rubber particles, it is found that the craze density increases and then decreases as the concentration of rubber particles in a PMMA matrix increases. The concentration of the rubber particle should be higher than 20 wt % in order to achieve good mechanical properties, at least at low strain rates. An increase of rubber particle concentration leads to a lower yield stress.

Cross-linking density also influences the craze density. By reducing the cross-linking density, the craze density tends to increase and then finally decrease when the cross-linking density is dropped to 0.5%. The final drop of the craze density when the cross-linking density is reduced to 0.5% may be due to a change of internal morphology of the core-shell particles. The change of cross-linking density does not have a significant effect on yield stress.

Crazing is a source of energy absorption and polymer failure. For the same cross-linking density, a reasonable craze concentration is beneficial for toughening PMMA in our polymer system, while for a given concentration of rubber particles, a tougher polymer matrix requires a low craze concentration. The interplay between rubber particle concentration and cross-linking density can provide us with a basis for improving the toughness of polymer matrix.

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