New Cavitation Mechanism of Rubber Dispersed Polystyrene†

Y. Okamoto,* H. Miyagi, and S. Mitsui

Chiba Research Laboratory, Sumitomo Chemical Company, Ltd., 2-1 Kitasode, Chiba 299-02, Japan

Received June 22, 1993; Revised Manuscript Received September 3, 1993®

ABSTRACT: Cavitation mechanism related with crazing is investigated in high impact polystyrene (PS) with rubber particles of a rubbery core/glassy polymer shell. By transmission electron microscopic work using the annealing effect on craze, we verified that the rubber particles were cavitated after the crazing of PS matrix and that rubber components from rubbery core were sorbed into the crazes. And finite elemental analysis supported that the sorption to craze fibrils would plasticize the craze.

Introduction

Shear yielding, crazing, and cavitation are known as toughening mechanisms of polymers.[1] Cavitation can occur inside of rubber particles or interface between rubber particles and a polymer matrix, and it plays an important role in the toughening of rubber dispersed polymers.[2] Details are not yet known, however, and there are few reports on the cavitation mechanism in brittle matrix, such as polystyrene (PS) matrix.

In 1990, a new toughening model was proposed by Gebizlioglu et al.[3] They examined the mechanism in rubber dispersed polystyrene samples which included low M_w polybutadiene (PB) rubber droplets. They concluded that the liquid PB in these pools acts as a plasticizing agent under the prevailing negative pressures of the craze tip and craze borders to result in a greatly increased propensity for crazing at low stresses, thus avoiding early craze fracture from extrinsic flaws. Furthermore, Argon et al. also provided a theoretical model to express the above phenomenon, and craze flow stress based on the model had shown excellent agreement with experimental measurement.[4]

We recently discovered that cavitation can occur in high impact polystyrene (HIPS) with rubber particles of a rubbery core/rigid polymer shell, and we studied the cavitation mechanism in this system. Here, we provided direct verification of the rubber sorption model by microscopic work using the annealing effect on craze, and we demonstrate by FEM analysis that sorption of rubber components to craze fibrils would plasticize the craze.

Experimental Section

1. Materials. Three types of HIPS were used as base polymers in this study (Table I): (a) that with rubber particles of rubbery core/solid shell (RC-HIPS); (b) that with rubber particles of solid core/rubbery shell (SC-HIPS); (c) that with salami-structure and large rubber particles (L-HIPS).

It is well known that large rubber particles can initiate crazes more easily than core/shell structured submicron rubber particles. Our earlier investigation[5] showed that HIPS with bimodal distribution of rubber particle size (bimodal HIPS) generates long and thick crazes, so we used the following HIPS to study the cavitation mechanism in our system.

Table I. Material Properties of HIPS as Base Polymer for Bimodal HIPS

sample	structure of rubber particles	gel[a] (wt %)	Dp[b] (μm)
RC-HIPS	rubbery core/solid shell	20.0	0.15
SC-HIPS	solid core/ rubbery shell	20.0	0.20
L-HIPS	salami structure	18.0	4.9

[a] Gel: rubber particle phase content in HIPS (wt %). [b] Dp: rubber particle size (μm).

First, we blended RC-HIPS and L-HIPS in a ratio of 70 to 30 wt %, so that it had a bimodal distribution of rubber particle size; we called this RC bimodal HIPS. The same was done with SC-HIPS and we obtained SC bimodal HIPS.

2. Microscopy. To observe the fracture events in these bimodal HIPS. A transmission electron microscope (TEM) was employed. Specimens were prepared from the stress-whitened region caused by impact fracture, and the samples were stained with OsO_4 and microtomed into thin sections.

Results and Discussion

1. Deformation Sequence in RC Bimodal HIPS. In SC bimodal HIPS, we reported earlier the deformation sequence (craze initiation and extension sequence) and the toughening mechanism explained by the energy absorption which was attributed to peculiar craze growth[5].

The same technique was applied to investigate deformation sequence in RC bimodal HIPS, that is, detailed deformation events were observed for a series of samples subjected to different impact energies. These different impact energies were applied by changing the initial hammer angle in the Izod impact test.

Figure 1a–d shows a series of micrographs of the samples described above. In Figure 1a, we can see that the small crazes generate from a salami-structured large rubber particle but no cavitation in the RC rubber particles is yet visible.

In Figure 1b, the number of crazes has increased and they have grown longer. A few cavitations are visible at this stage. The size of the cavitated rubber particles is almost the same as that of other rubber particles.

In Figure 1c, the crazes have further increased in number and length. Many cavitated RC rubber particles can be seen, but only on the lines of matured crazes.

Finally in Figure 1d, the number and lengths of crazes are developed so that we can see a great many cavitated

† Presented at Polymer Blends and Interpenetrating Polymer Networks Symposium of Royal Australian Chemical Institute 9th National Chemistry Convention, Monash University, Melbourne, Australia, Dec 7–9, 1992.

® Abstract published in *Advance ACS Abstracts*, November 1, 1993.

0024-9297/93/2226-6547$04.00/0

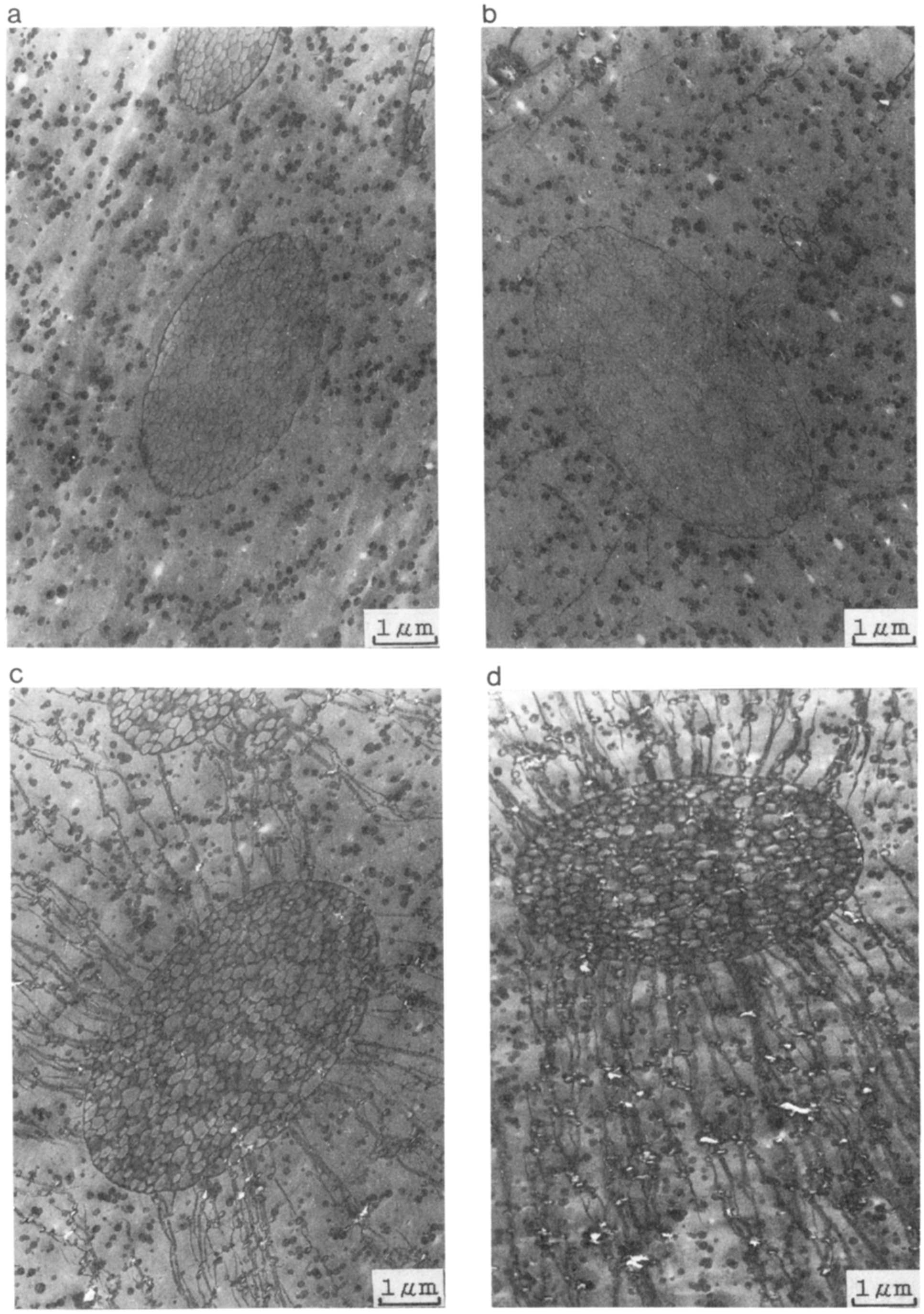

Figure 1. Sequence of plastic deformation in RC bimodal HIPS. Impact energies applied to each specimen were (a) 0.5, (b) 1.2, (c) 4.8, and (d) 10.0 kJ/m^2 in RC bimodal HIPS.

particles; the size and shape of these do not differ much from noncavitated ones.

Parker et al. reported a cavitation mechanism in the PC matrix system[6] (a relatively tougher system than the PS matrix system) in which cavitation occurred first and induced the shear yielding. Here, in contrast, the cavitation mechanism was induced by crazing which occurred first.

To learn more of this cavitation mechanism, we compared the plastic deformation between RC bimodal HIPS and SC bimodal HIPS. These micrographs shown in Figure 1d and Figure 2 are impact-fractured samples obtained for these bimodal HIPS, respectively, and the following differences can be noted: (a) Cavitation is apparent in RC-type rubber particles, but not in SC-type rubber particles. (b) The cavitations occurred inside of the RC-type rubber particles only on the craze lines. (c) There are longer and a larger number of crazes in RC bimodal HIPS.

From these results, it is concluded that: (a) the craze extension mechanism of RC bimodal HIPS and that of SC bimodal HIPS differ somewhat and, (b) there is greater possibility in the RC bimodal system for crazes to extend more and to be more numerous than in the SC bimodal system.

2. Annealing Test of Cavitated Samples. Details of the plastic deformation in RC bimodal HIPS were examined by microscope combined with an annealing test for the impact-fractured sample.

Deformed samples were subjected to different levels of annealing at 110 °C, stained by OsO_4, and observed by TEM.

Generally, rubber particles and crazes in HIPS can be made visible by OsO_4 staining (a) rubber components

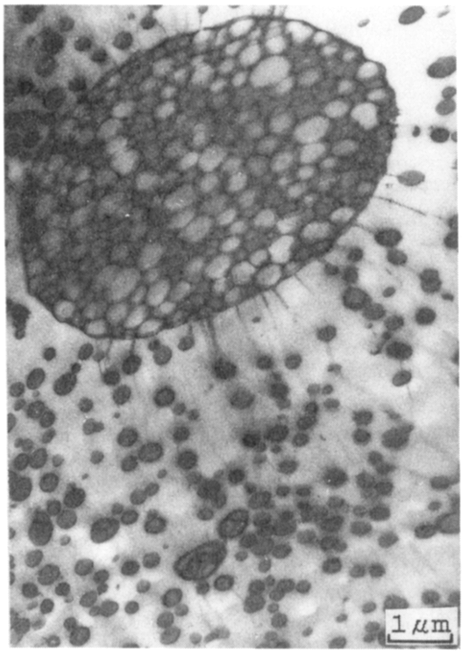

Figure 2. Transmission electron micrographs of fractured sample in SC bimodal HIPS.

because OsO_4 bonds to vinyl groups of rubber components[7] and (b) crazes because OsO_4 is retained in specific microvoids within them.[8]

Crazes can be healed by sufficient annealing, as indicated by the disappearance of the microvoids. We also confirmed that specific gravity of a deformed sample reverts to that of the sample before its deformation by annealing. Hence, if sufficient annealing were done on deformed samples, only the rubber components would be visible.

Impact-fractured samples of RC-bimodal HIPS and SC-bimodal HIPS were annealed for 8 h, respectively, and TEM micrographs are shown in Figure 3a,b. The crazes tend to disappear in both bimodal HIPS, but in RC bimodal HIPS there are many micron spots on the lines of eliminated crazes. These samples were annealed for 36 h (Figures 4a,b). Crazes almost disappeared in SC bimodal HIPS. These results agree well with the fact that crazes can be eliminated by sufficient annealing. In contrast, though in RC bimodal HIPS crazes also tended to disappear, even at this stage stained submicron spots are seen on the lines of the eliminated crazes. Considering the results in SC bimodal HIPS, these micron spots may be rubber components which have been sorbed into crazes.

Thus the following cavitation model was speculated: (a) Crazes are initially generated from large rubber particles. This generation is the same as in our previous investigation that showed occurrence in SC bimodal HIPS. (b) PB rubber sorption into crazes occurs by negative pressure of microvoids in the crazes and results in cavitation of RC rubber particles.

3. FEM Analysis around Rubber Particles. Stress distribution around an RC-type rubber particle was analyzed by the finite element method (FEM) to test our model. FEM model geometry and stress–strain curves as material properties of an RC rubber dispersed model were employed as shown in Figures 5 and 6. The material property data in Figure 6 were taken from our experiments and Polymer Handbook.[9] Unidirectional strain was applied to this FEM model, and stress distribution around the rubber particle was calculated.

On the basis of this model, rubber components sorbed into crazes would plasticize the crazes. Therefore, if rubber components of RC rubber particles were sorbed into crazes, craze initiation stress would be reduced. To express the feature qualitatively by FEM analyses, we calculated the area of the yielding zone. In Figure 7 we have assumed that the three stress–strain curves shown express the different levels of plasticization of the matrix.

The lower the yield stress, the larger the yielding zone. These results are expressed in Figure 8, where the abscissa is yield stress of the matrix and the ordinate is proportional area of the yielding zone in Figure 5. As we expected, the area of the yielding zone increases with decreases in yield stress of the matrix. We therefore conclude that sorption of rubber components into crazes results in enlargement of the yielding zone of the matrix; in other words, the

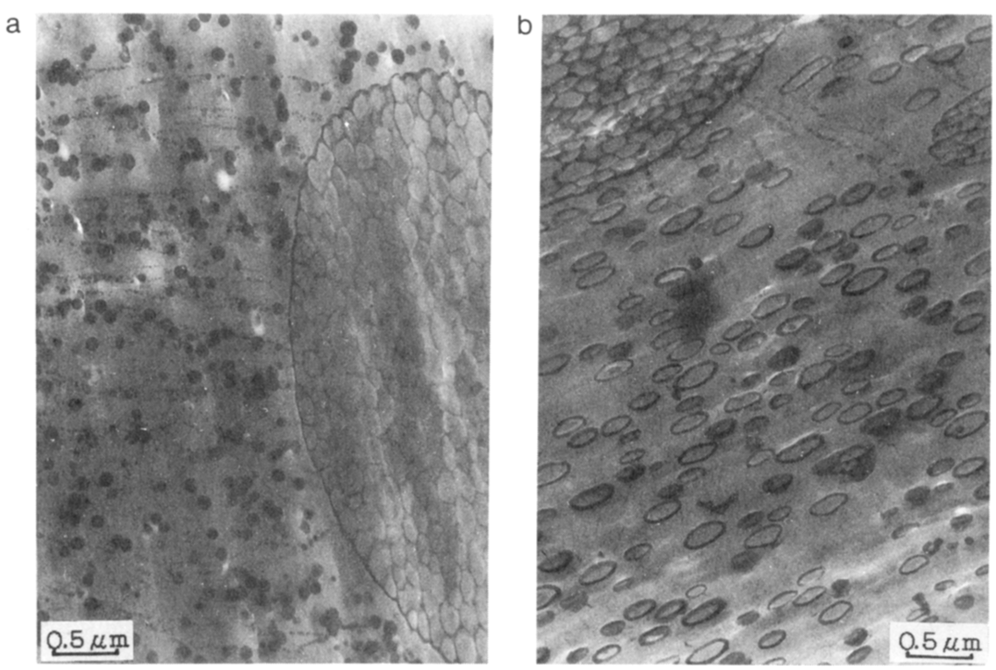

Figure 3. Transmission electron micrographs of fractured samples which were annealed for 8 h after fracture in (a) RC bimodal HIPS and (b) SC bimodal HIPS.

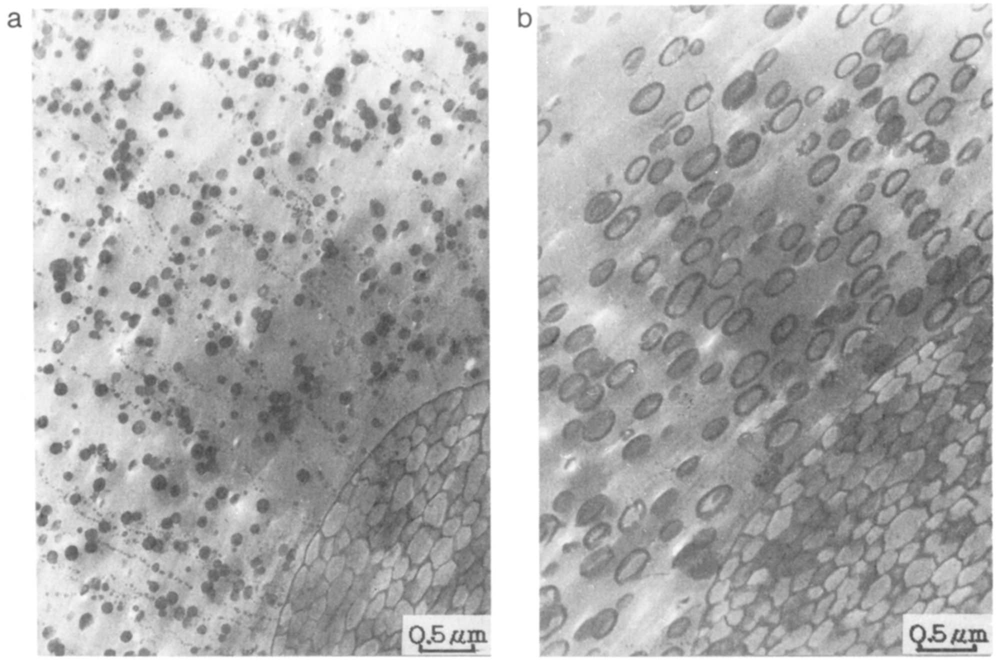

Figure 4. Tranmission electron micrographs of fractured samples which were annealed for 36 h after fracture in (a) RC bimodal HIPS and (b) SC bimodal HIPS.

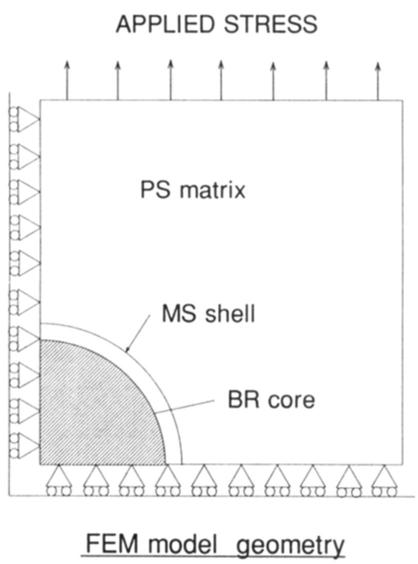

Figure 5. Model geometry for 2D FEM analysis around a rubber particle.

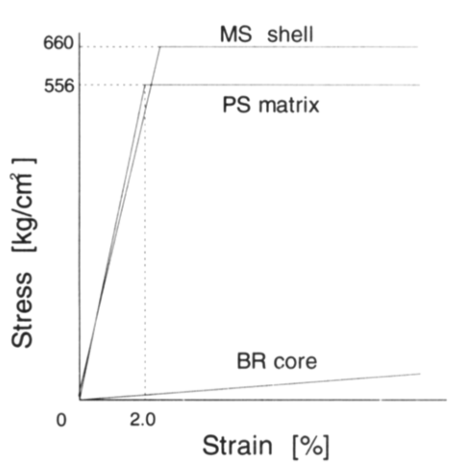

Figure 6. Stress–strain curves used for FEM analysis (for PS matrix and rubber).

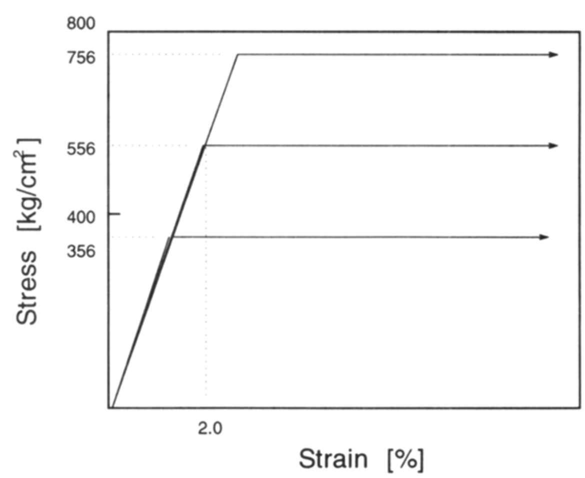

Figure 7. Stress–strain curves to analyze the plasticization effect on yielding zone around a rubber particle.

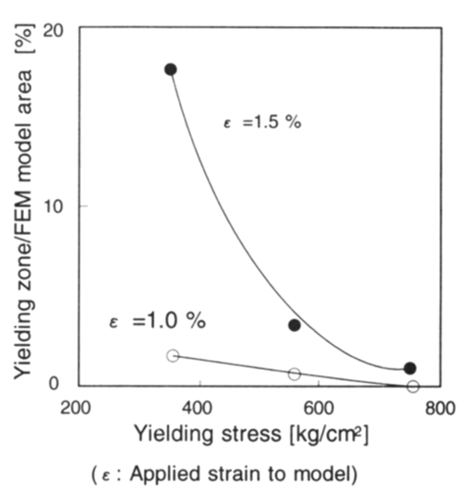

Figure 8. Calculated area of yielding zone.

sorption of rubber components enhances the tendency for crazes to extend and be more numerous. Sorption of rubber components to craze fibrils would thus plasticize the craze and result in a long and thick craze.

Acknowledgment. The authors wish to thanks Prof. Kiyoshi Takahashi of Kyushu University and Dr. Masahiro Kakugo of Sumitomo Chemical Co., Ltd., for their generous support.

References and Notes

(1) Bucknall, C. B. *Toughened Plastics*; Applied Science: London, 1977.
(2) Pearson, R. A.; Yee, A. F. *J. Mater. Sci.* **1986**, *21*, 2475.
(3) Gebizlioglu, O. S.; Beekham, H. W.; Argon, A. S.; Cohen, R. E.; Brown, H. R. *Macromolecules* **1990**, *23*, 3968.
(4) Argon, A. S.; Cohen, R. E.; Gebizlioglu, O. S.; Brown, H. R.; Kramer, K. J. *Macromolecules* **1990**, *23*, 3975.
(5) Okamoto, Y.; Miyagi, H.; Kakugo, M.; Takahashi, K. *Macromolecules* **1991**, *24*, 5639.
(6) Parker, D. S.; Sue, H. J.; Huang, J.; Yee, A. F. *Polymer* **1990**, *31*, 2267.
(7) Kato, A. *Polym. Lett.* **1966**, *4*, 35.
(8) Gebizlioglu, O. S.; Cohen, R. E.; Argon, A. S. *Makromol. Chem.* **1986**, *187*, 431.
(9) Brandrup, J.; Immergut, E. H. *Polymer Handbook*, 3rd ed.; Wiley-Interscience Publication: New York, 1989.