Tensile Test of Poly(vinyl chloride) Filled with Ground Calcium Carbonate Particles

YOSHINOBU NAKAMURA, YUKI FUKUOKA, TAKEO IIDA

Department of Applied Chemistry, Osaka Institute of Technology, 5-16-1, Ohmiya, Asahi-ku, Osaka, 535-8585 Japan

Received 8 October 1997; accepted 12 March 1998

ABSTRACT: The fracture behavior of poly(vinyl chloride) filled with ground calcium carbonate particles during a tensile test was studied. The particles were prepared by crushing natural raw crystalline limestone. For this purpose, 10–50 parts of the particles having two different mean sizes (2 and 8 μm) without further surface treatment were mixed with 100 parts of poly(vinyl chloride) and 3 parts of lead stearate as a stabilizer using a mixing roll. A tensile test was carried out using a dumbbell specimen. As a result, the yield stress decreased with increase in the particle content; however, there was no significant influence of particle size. From scanning electron microscopic observations of the specimen's surfaces during the tensile test, it was found that the particle/matrix interfaces were delaminated and formed voids around the particles when the applied stress approached the yield stress, that is, the particles acted as voids and the matrix around the voids was plastically deformed effectively. These observations appear to be the reason for the decrease of yield stress by the incorporation of the particles. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 311–316, 1998

Key words: polyvinylchloride; calcium carbonate; particulate-filled composite; yield stress; yielding

INTRODUCTION

Poly(vinyl chloride) (PVC) is one of the most widely used polymers, such as in electrical insulators and for plastic moldings and building materials. In many industrial applications, PVC is used as an inorganic particulate-filled composite to improve the mechanical properties, thermal stability, cost, etc. It is well known that the shape, size, and content of filled particles and the adhesion of particle/matrix interfaces strongly affect the mechanical properties and the fracture behavior of composites; however, they are much less studied,[1–3] whereas for an epoxy resin, the effects of the above factors derived from particles on the fracture toughness and mechanical properties of the resin filled with silica or alumina particles have been studied in a series of our investigations.[4–11] As a result, the concept to improve the toughness and mechanical strength for such particulate-filled epoxy systems has been clarified.

Calcium carbonate ($CaCO_3$) particles are widely used as a filler for PVC. In this study, therefore, the fracture behavior during the tensile test of PVC filled with ground $CaCO_3$ particles was investigated fundamentally.

EXPERIMENTAL

Materials

Commercially available PVC (Geon 103 EP, Nippon Zeon Co., Ltd.), lead stearate (Katayama Chemical Industries Co., Ltd.) as a stabilizer for

Correspondence to: Y. Nakamura.

Journal of Applied Polymer Science, Vol. 70, 311–316 (1998)
 CCC 0021-8995/98/020311-06

PVC, and ground $CaCO_3$ particles having two different mean sizes were used. The ground $CaCO_3$ particles were prepared by crushing natural raw crystalline limestone and were sorted by an air separation.

Sample Preparation

PVC [100 parts per hundred parts of resin by weight (phr)], lead stearate (3 phr), and $CaCO_3$ particles (10, 20, 30, and 50 phr) were mixed using a mixing roll at 190 ± 5°C for 15 min. The sheets with about 0.5-mm thickness were prepared by compressing the mixed compounds at 200°C under a pressure of 24.5 MPa for 2 min. The prepared sheets were quenched by a cold press.

Tensile Test

A tensile test was carried out using a dumbbell specimen [Japanese Industrial Standard (JIS) K6301-3 type] with about a 0.5-mm thickness and an Instron universal testing machine (1115 type) with a crosshead rate of 5 mm/min and a chuck distance of 40 mm. The width and length of the neck part of the dumbbell specimen were 5 and 20 mm, respectively. The sides and edges of the specimen were polished using sandpaper no. 800 prior to testing. Yield stress (σ_y) and elongation at specimen break (ε_b) were measured.

Measurement of $CaCO_3$ Particle Size and Void Size

When a particulate-filled composite is drawn, the voids at the polymer/particle interfaces usually form in the case of weak bonding of the interfaces. The tensile test specimen's surfaces after the test were observed by a scanning electron microscope (SEM). The sizes of the filled ground $CaCO_3$ particles and formed voids (the major and minor axes of the void) were measured by image analysis[12–14] using an image processor (TVIP-2000 type, Nippon Avionics) with Image Command 98 software and SEM photographs were obtained.

RESULTS AND DISCUSSION

Figure 1 shows the particle-size-distribution curves of ground $CaCO_3$ particles used in this study. The mean size of the two kinds of the particles used in this study were determined from these data as 2 and 8 μm, respectively. In our article,[15] the precipitated $CaCO_3$ particles, which are bulky coagulated secondary particles consisting of primary spherical units, were mixed with PVC by the same method used in this study. In that case, the mean particle size decreased during the mixing process and the tendency was more remarkable with increase in the particle size and particle content. However, in the case of the ground $CaCO_3$ particles used in this study, no decrease in the particle size during the mixing process was observed.

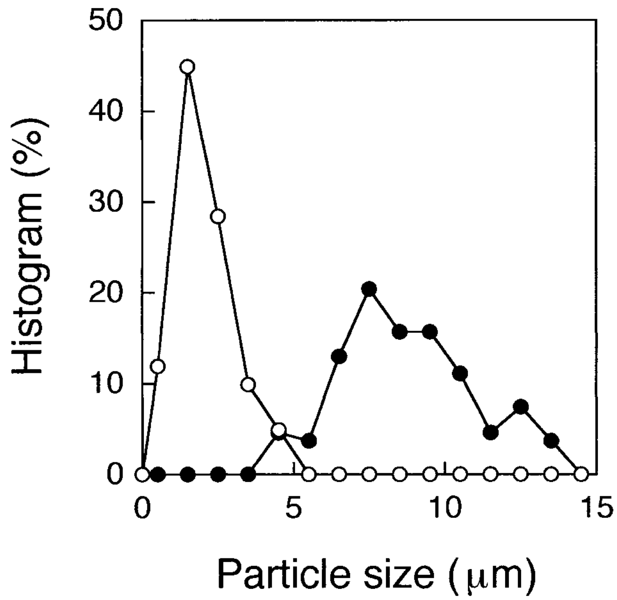

Figure 1 Particle-size distribution curves of ground $CaCO_3$. Mean particle size: (○) 2 μm; (●) 8 μm.

Figure 2 shows the typical stress–strain curve for PVC filled with ground $CaCO_3$ particles obtained in this study. This curve was for the system with a relatively low particle content such as 10 phr. It is representative of a ductile polymer, that is, the stress increased linearly with the strain and it reached the σ_y followed by a slight decrease. Then, it was elongated with almost the same stress and with necking until the ε_b was reached.

Figure 3 shows the effect of the particle content on the σ_y of the PVC filled with ground $CaCO_3$ particles having two different mean sizes measured by the tensile test. The σ_y decreased with increase in the particle content; however, there was no significant influence of the particle size.

Figure 4 shows the effect of the particle content on the ε_b. The ε_b decreased with increase in both particle content and particle size. From these results, it was found that an incorporation of ground $CaCO_3$ particles without further surface treatment decreases the σ_y and ε_b of PVC.

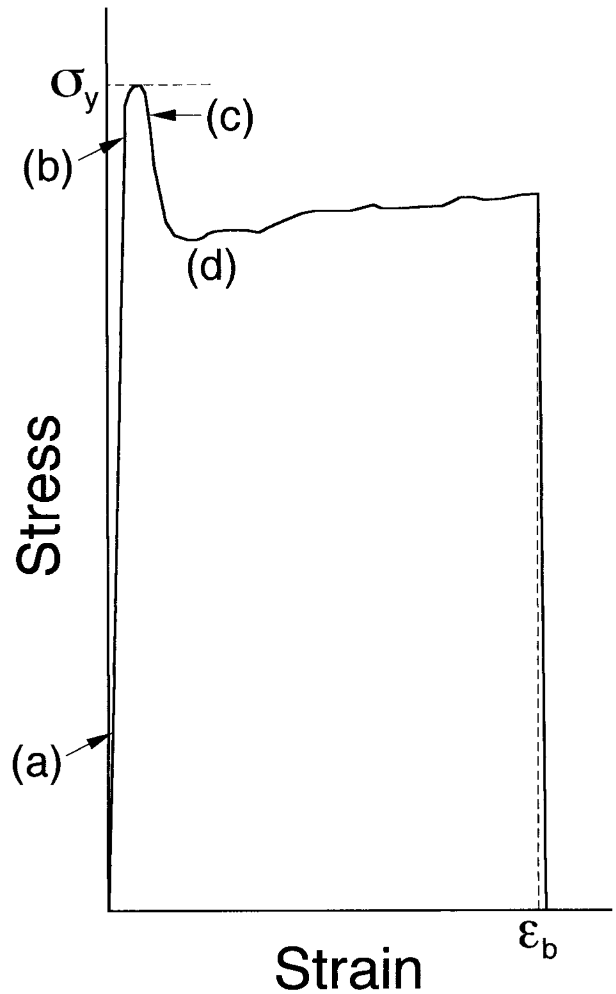

Figure 2 Typical stress–strain curve of PVC filled with ground $CaCO_3$ particles measured by the tensile test. The specimen's surface was observed by SEM during the tensile test at points (a)–(d) and the results are shown in Figure 8.

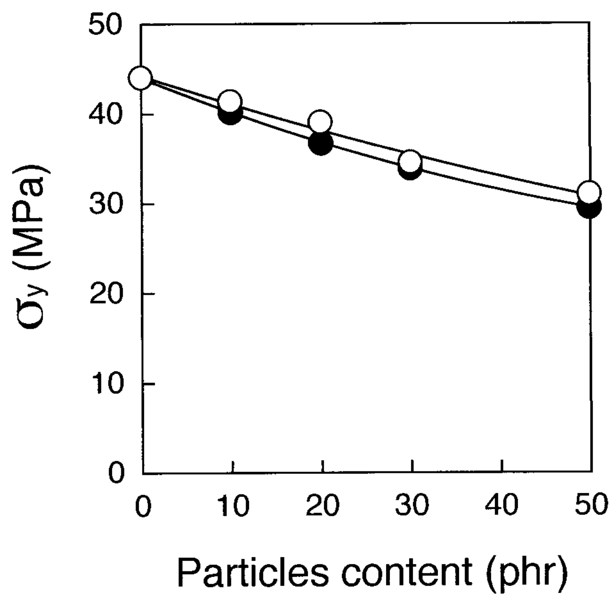

Figure 3 Effect of particle content on σ_y of PVC filled with ground $CaCO_3$ particles. Mean particle size: (○) 2 μm; (●) 8 μm.

Figure 5 shows the surface of the tensile test specimen after the test observed by SEM for the particle size of 8 μm and particle content of 10 phr. The particles were well dispersed in the PVC matrix and the voids formed around the $CaCO_3$ particles were clearly observed. No such void was observed on the specimen's surfaces before the test. Therefore, it is obvious that the voids appeared and were developed during the tensile test. A similar observation was also obtained in the system for a particle size of 2 μm.

Next, the void size and change of size during the tensile test were measured by image analysis using the SEM photographs of the specimen's surfaces after the test, such as in Figure 5. To evaluate the change of the size during the test, the voids were measured in many specimens having different ε_b values after the test. At the moment the specimen broke and was released from the applied stress, the specimen should shrink somewhat in the opposite direction of the tensile. It was already confirmed that the degree of shrink-

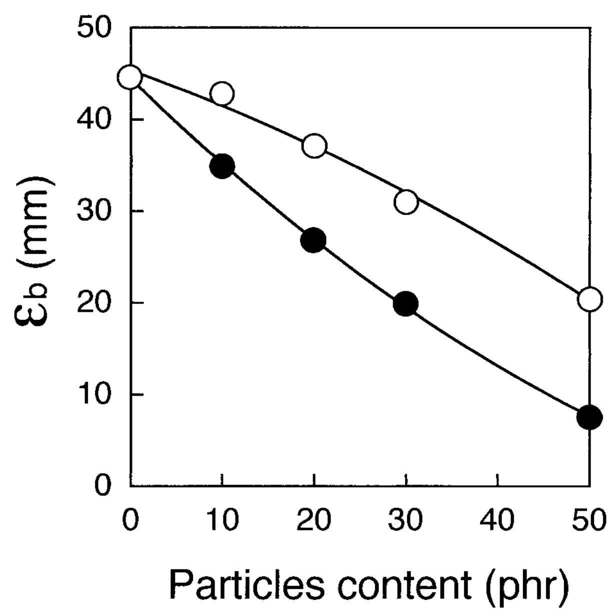

Figure 4 Effect of particle content on ε_b of PVC filled with ground $CaCO_3$ particles. Mean particle size: (○) 2 μm; (●) 8 μm.

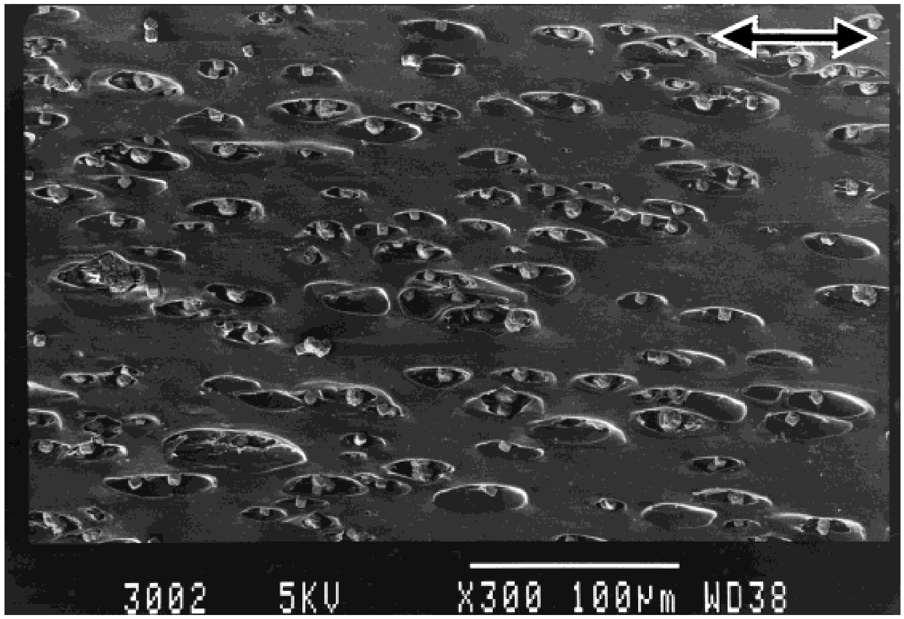

Figure 5 SEM photograph of tensile test specimen's surface after test of PVC filled with ground $CaCO_3$ particles at a particle content of 10 phr and mean size of 8 μm. The ε_b was 36 mm. The arrow indicates the tensile direction.

age was only about 5% of the specimen length in our article.[16] Therefore, it can be said that the void size observed on the specimen's surface after the tensile test as shown in Figure 5 is practically the same as that just developed at the specimen break.

Figure 6 shows the relationship between the major axis of the void and the ε_b. The data in this figure involve those for 10–50 phr. The solid lines were calculated using a method of least squares for the data of each particle size. The major axis of the void was strongly related to the particle size and slightly increased with the ε_b. So, the formation of the void seems to be in the early stage during the tensile test.

Figure 7 shows the relationship between the aspect ratio of the void (the ratio of the major/minor axes) and the ε_b. The increase in the aspect ratio with the ε_b was almost the same level in both particle sizes, namely, the voids develop in almost the same ratio independent of the particle size.

Next, the test was stopped at each of the (a)–(d) points shown in Figure 2, and almost the same point on the surface was observed by SEM to confirm the stage of void formation during the tensile test. However, damage to the PVC matrix by an electron beam occurred during the SEM observation because PVC is an electron beam-degradable polymer. Therefore, the coating of specimen's surface with an evaporating thin Au film repeatedly before each SEM observation was unavoidable.

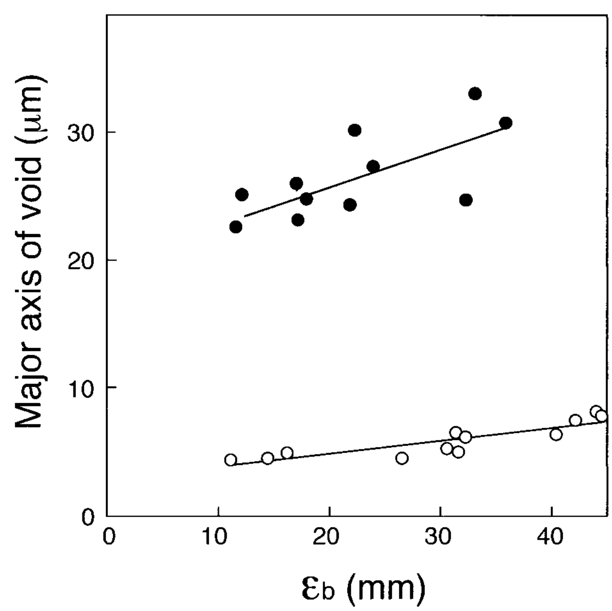

Figure 6 Relationship between the major axis of the void formed around the particles and the ε_b of PVC filled with ground $CaCO_3$ particles at a particle content of 10–50 phr. Mean particle size: (○) 2 μm; (●) 8 μm. The major axis of the void was measured by image analysis using SEM photographs of the tensile test specimen's surface after the test.

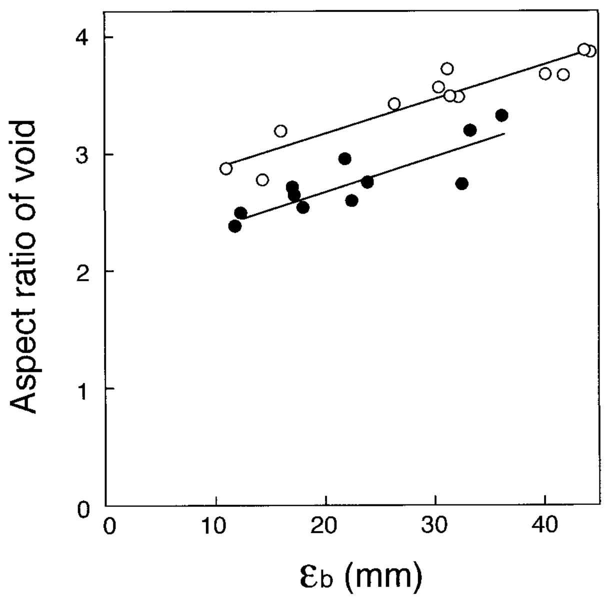

Figure 7 Relationship between aspect ratio of the void formed around the particles and the ε_b of PVC filled with ground $CaCO_3$ particles at a particle content of 10–50 phr. Mean particle size: (○) 2 μm; (●) 8 μm. The aspect ratio of the void was measured by image analysis using SEM photographs of the tensile test specimen's surface after the test.

Figure 8 shows the SEM photographs of the specimen's surfaces during the tensile test for a particle size of 8 μm and a particle content of 10 phr. The photographs (a)–(d) correspond to the (a)–(d) points shown in Figure 2, respectively. The arrow marks in each photograph indicates the tensile direction. At point (a), the specimen's surface was quite same as before the test. At point (b), although many microcracks formed perpendicular to the tensile direction were observed, any change of the surface was observed at this point because the cracks appeared in the evaporating thin Au film on its surface. At Point (c) (just after the σ_y), however, the particle/matrix interfaces had been delaminated and many cracked bands started from the formed voids to the 45° direction of the tensile were clearly observed. In the bands, microcracks of the evaporating thin Au film concentratedly appeared. These bands are termed "shear bands,"[17] in which the matrix of these parts are predominantly plastically deformed (yielded). After point (c), the "stress whitening" that started from some points on the specimen's surface to the 45° direction of the tensile were also observed by the naked eye, whereas in the case of the unfilled PVC system, the stress whitening started from some point at the specimen's edge which seems to have defects. The shear bands that appeared from the voids were more definitely at point (d) than at point (c). In these SEM photographs [Fig. 8 (c,d)], unfortunately, the shape of

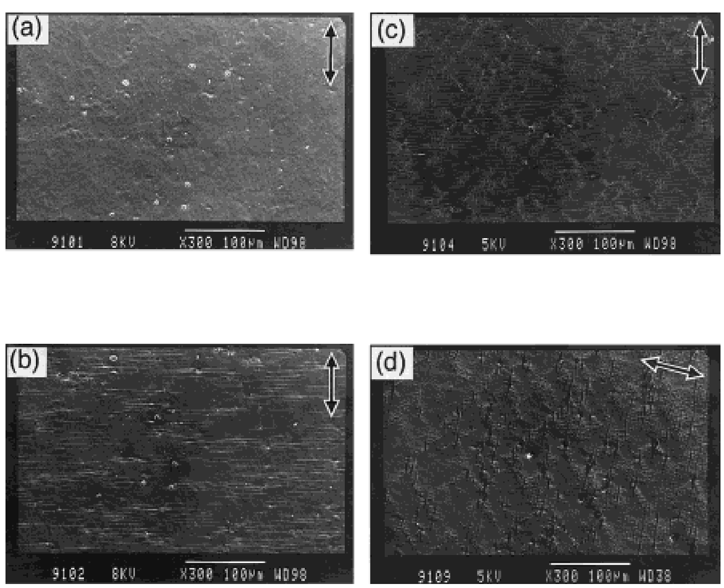

Figure 8 SEM photographs of the tensile test specimen's surface during the test of PVC filled with ground $CaCO_3$ particles at a particle content of 10 phr and mean particle size of 8 μm. The observed points for each SEM photograph during the tensile test are shown in Figure 2. The observed tensile test specimen has an evaporating thin Au film on its surface. The arrow indicates the tensile direction.

the formed voids were not observed so clearly as in Figure 5 because of the existence of the multilayered evaporating thin Au films on its surface. Similar results were obtained in the smaller particle-filled system.

Narisawa et al.[18,19] evaluated the stress field around one stress concentrator in a polymer matrix using a finite element method (FEM) for a void, a soft rubbery particle, and a hard filler particle as a stress concentrator by changing their Young's modulus and Poisson's ratio. According to their FEM evaluation, in the case of a void or a soft rubbery particle, first, the shear yielding starts from the equator of the stress concentrator with increase in the applied stress, and, second, it develops in a 45° direction in a matrix, whereas when a stress concentrator is a hard particle such as an inorganic filler and the adhesion of the interface is complete, first, the shear yielding starts from near the pole at a short distance from the interface of a particle and, second, it develops in the same direction. However, the ability to yield the matrix is lower than in the cases of a void or a soft rubbery particle.

In comparison of our results with their FEM evaluation, when the applied stress approached the σ_y, the particles/PVC matrix interfaces seem to be delaminated and the particles act as voids; thus, the PVC matrix around the voids is effectively plastically deformed. However, the void size increased with particle size as shown in Figure 6. The void seems to act as a defect which initiates the break of the specimen. These observations appear to be the reason why the σ_y decreased with increase in the particle content and the ε_b decreased with increase in both particle content and particle size.

In this study, it was found that the incorporation of ground $CaCO_3$ particles without further surface treatment takes place, yielding the PVC matrix effectively because of their acting as voids by the delamination of their interfaces when the applied stress approached the σ_y. Therefore, their addition decreased the σ_y of the PVC. However, as clarified in our previous articles[4,6] for particulate-filled epoxy resin systems, the ability of forming such localized microdeformation should improve the fracture toughness of the particulate-filled system. This point and the effect of the adhesion of the interface on the properties mentioned in this study will be discussed in our future article.

REFERENCES

1. P. Bataille, S. Boisse, and H. P. Schreiber, *J. Vinyl. Technol.,* **6,** 147 (1984).
2. G. Xue, Q. Fu, J. Ding, S. Jiang, S. Liu, and Y. Xi, *Angew. Makromol. Chem.,* **153,** 89 (1987).
3. F. J. McGarry, J. F. Mandell, and L. Hsueh-Lee, *J. Polym. Sci. Polym. Symp.,* **72,** 83 (1985).
4. Y. Nakamura, M. Yamaguchi, A. Kitayama, M. Okubo, and T. Matsumoto, *Polymer,* **32,** 2221 (1991).
5. Y. Nakamura, M. Yamaguchi, M. Okubo, and T. Matsumoto, *J. Appl. Polym. Sci.,* **44,** 151 (1992).
6. Y. Nakamura, M. Yamaguchi, M. Okubo, and T. Matsumoto, *Polymer,* **33,** 3415 (1992).
7. Y. Nakamura, M. Yamaguchi, M. Okubo, and T. Matsumoto, *J. Appl. Polym. Sci.,* **45,** 1281 (1992).
8. Y. Nakamura, M. Yamaguchi, and M. Okubo, *J. Adhes. Soc. Jpn.,* **29,** 53 (1993).
9. Y. Nakamura, M. Yamaguchi, A. Tanaka, and M. Okubo, *Polymer,* **34,** 3220 (1993).
10. Y. Nakamura, M. Yamaguchi, and M. Okubo, *Polym. Eng. Sci.,* **33,** 279 (1993).
11. M. Ohta, Y. Nakamura, H. Hamada, and Z. Maekawa, *Polym. Polym. Compos.,* **2,** 215 (1994).
12. T. Iida, J. Kawato, S. Tanie, and K. Goto, *J. Appl. Polym. Sci.,* **37,** 1685 (1989).
13. T. Iida, H. Ikeda, Y. Yamashita, and K. Goto, *Kobunshi Ronbunsyu,* **50,** 65 (1993).
14. T. Iida, *J. Adhes. Soc. Jpn.,* **25,** 236 (1989).
15. Y. Nakamura, F. Azuma, and T. Iida, *Polym. Polym. Compos.,* **6,** 7 (1998).
16. Y. Nakamura, A. Ikenaga, M. Sato, and T. Iida, *J. Adhes. Soc. Jpn.,* **34,** 221 (1998).
17. A. J. Kinloch and R. J. Young, *Fracture Behaviour of Polymers,* Elsevier, London, New York, 1983, p. 122.
18. I. Narisawa, T. Kuriyama, and K. Ojima, *Macromol. Chem. Macromol. Symp.,* **41,** 87 (1991).
19. B. Schemer, T. Kuriyama, I. Narisawa, and K. Friedrich, *J. Mater. Sci. Lett.,* **14,** 660 (1995).