

Mechanical Properties of Organic–Inorganic Polyurethane Elastomers. I. Al(OH)₃–Polyurethane Composites Based on PPG

MUTSUHISA FURUKAWA* and TETSUO YOKOYAMA

Department of Materials Science and Engineering, Faculty of Engineering, Nagasaki University, 1-14 Bunkyo-machi, Nagasaki 852, Japan

SYNOPSIS

Aluminum hydroxide was used as a reactive filler to elastomers prepared from poly(oxypropylene) glycol (PPG), 2,4-tolylene diisocyanate (TDI), and 1,4-butane diol (BD). Mechanical properties, dynamic mechanical properties, and thermal properties were measured. Morphologies were observed by use of X-ray diffraction and scanning electron micrographs. The model reaction of isocyanate and aluminum was also studied. It was found that aluminum hydroxide fillers can be used for cost reduction without any detrimental effects on mechanical properties. Scanning electron micrograph studies of freshly cut surfaces of the aluminum filled elastomers showed that aluminum hydroxide is highly compatible with the elastomer. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Polyurethanes prepared from polyol, diisocyanate, and curing agent are used commercially as coatings, adhesives, foams, castable elastomers, and millable elastomers. Properties of polyurethanes can be varied within a wide range depending on the chemical structures and the molecular weights of the soft segments. Physical and morphological properties of the polyurethane elastomers have been summarized.^{1–4}

Polyurethanes prepared from poly(oxypropylene) glycol (PPG) have poorer properties than those of other polyether glycols based polyurethanes. In order to make PPG based polyurethane elastomers competitive, there is a need to investigate the use of various fillers such as carbon fiber, glass fiber, plastic particles, and inorganic compounds such as silicate and calcium carbonate for their compatibility with polyurethanes.

Polyurethane elastomers have been improved with carbon fiber,⁵ glass fiber,^{6,7} silica,⁸ mica,⁹ and

calcium carbonate,¹⁰ etc. These composites have higher moduli and tensile strengths than the unfilled polyurethanes.

This article reports mechanical properties, thermal properties, and scanning electron micrograph (SEM) studies of the aluminum hydroxide filled polyurethane elastomers based on PPG, 2,4-tolylene diisocyanate (TDI), and 1,4-butane diol (BD).

EXPERIMENTAL

Materials

PPG, having molecular weight $M_n = 988$, was obtained from Sanyo Chemical Industry Co. Ltd. in Japan. Phenylisocyanate (PI) and BD were obtained from Wako Pure Chemical Industries Co. Ltd. TDI was supplied by Nippon Polyurethane Industry Co. Ltd. PPG was dried by passing it through dried nitrogen gas under reduced pressure at 100°C for 12 h. BD, PI, and TDI were freshly distilled prior to use.

Aluminum hydroxide (mean particle size 0.15 μm) from Wako Pure Chemical Industries Ltd. was obtained as a fine white powder.

* To whom correspondence should be addressed.

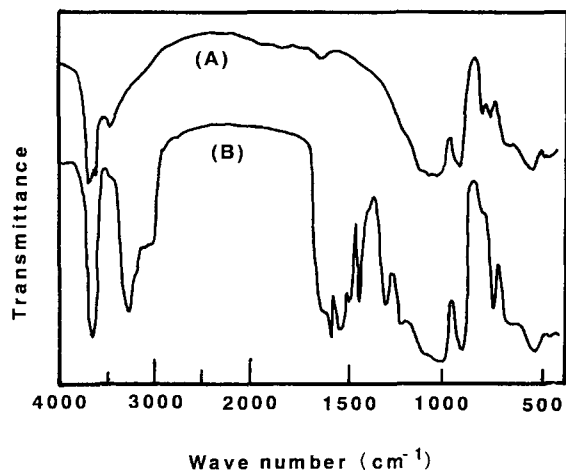


Figure 1 IR spectra of (A) aluminum hydroxide and (B) reaction product of aluminum hydroxide and phenyl isocyanate.

Model Reaction of Aluminum Hydroxide with Phenyl Isocyanate

Aluminum hydroxide (0.26 g) was reacted with PI (4.2 g) in benzene (150 mL) at 80°C for 4 h. Then the reaction mixture was washed with fresh benzene several times and dried under vacuum. The reactant was analyzed by IR spectrometry and X-ray diffraction.

Preparation of Polyurethane Elastomers

Polyurethane elastomers were prepared by the prepolymer method. PPG was weighed into a three-

necked separable flask equipped with a nitrogen inlet, thermometer, and stirrer. The flask was heated to 60°C and was evacuated to degas PPG for 2 h, then was cooled to 45°C. The required amount of TDI was weighed into the flask. The reactants were stirred vigorously under nitrogen atmosphere at 60°C. Small amounts of the reaction mixture were titrated at regular time intervals by the amine-equivalent method in order to check the extent of reaction. When the prepolymer reaction was completed, a molar equivalent of BD was added to the prepolymer and the mixture was stirred vigorously. Then, the resultant viscous liquid was weighed into several disposal cups. The required amount of filler was weighed and put into each cup. The mixture was stirred vigorously and degassed under reduced atmosphere. The viscous liquid was then poured in a heated sheet mold at 90°C, which was treated with silicone release agent. The samples were cured at 90°C for 48 h under a nitrogen atmosphere.

Mechanical Testing

Stress-strain relationships were measured by means of an Instron type tester (Shimadzu Autograph IS 5000). Young's modulus was determined according to the method of Smith and Magnusson¹¹ from stress-strain curves measured at a cross head speed of 10 mm/min (strain rate 0.33 min⁻¹) at 50°C.

The dynamic modulus, E' (storage modulus) and E'' (loss modulus), was measured using a Rheovibron DDV-IIIB (Orientech Ltd., Japan). The measurement were made at a frequency of 110 Hz in a

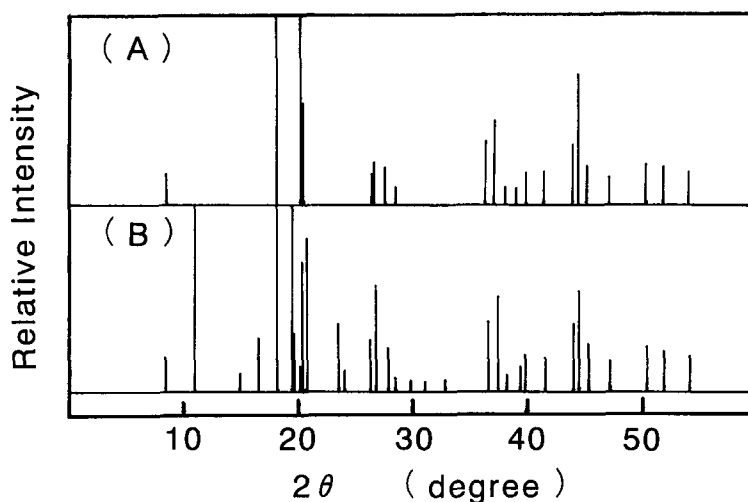


Figure 2 X-ray diffraction profiles of (A) aluminum hydroxide and (B) reaction product of aluminum hydroxide and phenyl isocyanate.

Table I Structure Parameter and Physical Properties

Sample No.	Filler Content (wt %)	Young's Modulus (MPa)	Tensile Strength (MPa)	Elongation at Break	T_g ($^{\circ}$ K)
A-0	0	3.0	8.4	1.39	-35.5
A-1	1	4.1	7.2	1.39	-35.5
A-5	5	4.7	13.0	1.39	-33.0
A-10	10	5.5	14.2	1.37	-37.5
A-15	15	—	—	—	-38.5

temperature range from -160 to 50°C at heating rate of about $2^{\circ}\text{C}/\text{min}$.

Thermal Analysis

Differential scanning calorimetry was carried out with a Rigaku Denki Thermoflex DSC using a sample weight of 20 mg from -100 to 300°C . The heating rate was kept at $10^{\circ}\text{C}/\text{min}$.

X-Ray Diffraction Analysis

Observation of X-ray diffraction patterns was carried out with a Rigaku Denki X-ray instrument ($\text{CuK}\alpha$, Ni filter, 30 kV, 15 mA).

Scanning Electron Microscopy

A JEOL JSTM 100 (JEOL Ltd., Japan) was used. The free surfaces of the freshly cut samples were coated with gold to obtain the photographs.

RESULTS AND DISCUSSION

PI (6.74 mmol/g) was consumed by aluminum hydroxide. IR spectra and X-ray diffraction profiles of aluminum hydroxide and the reaction product are shown in Figures 1 and 2, respectively. In the IR spectrum of aluminum hydroxide, peaks at 3600 and 1100 cm^{-1} were assigned to the hydroxyl group. New peaks in the spectrum of the reaction product appeared at 3300 – 3000 , 1650 , 1600 , 1540 , 1450 , 1300 , and 1210 – 1000 cm^{-1} . The peaks at 3300 , 1650 , 1540 , and 1100 cm^{-1} were assigned to the amide group. The peaks at 1600 , 1420 , 1300 , and 1210 cm^{-1} were assigned to the phenyl group. New diffraction peaks in the X-ray diffraction profile of the reaction product appeared and were not assigned in detail. These results suggest that aluminum hydroxide acts as a reactive filler in polyurethane elastomers.

Polyurethane elastomers were prepared at a reactant ratio of $K = [\text{mole of NCO group}]/[\text{mole of OH group in PPG}] = 2$ and $M = [\text{mole of BD}]/[\text{mole of NCO group in prepolymer}] = 0.3$. Table I shows the structure parameters and physical properties of the polyurethane composites. The polyurethanes prepared have allophanate cross-linked networks. The curing reaction of filled elastomers was faster than that of unfilled elastomer. The unfilled polyurethane was a colorless and transparent rubber and the polyurethane composites were milky rubbers.

Figure 3 shows the relationships of relative Young's modulus, E/E_0 , relative tensile strength σ_b/σ_{b0} , and relative elongation at break, γ_b/γ_{b0} , with filler content. Each relative value is designated as the ratio of the value of the composite to that of the unfilled elastomer. Relative modulus and tensile

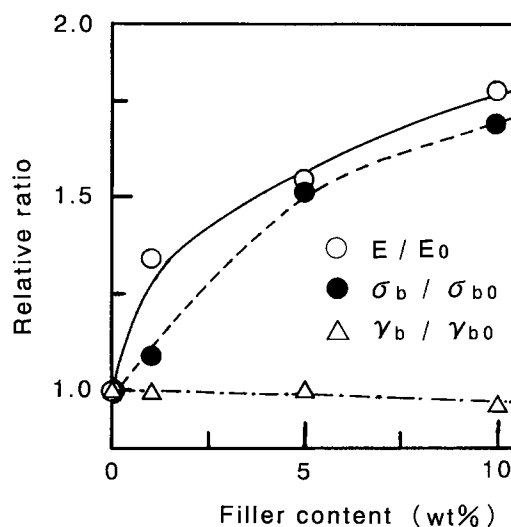


Figure 3 Dependence of relative Young's modulus (E/E_0), relative tensile strength (σ_b/σ_{b0}), and relative elongation at break (γ_b/γ_{b0}) on filler content. (○) E/E_0 ; (●) σ_b/σ_{b0} ; (△) γ_b/γ_{b0} .

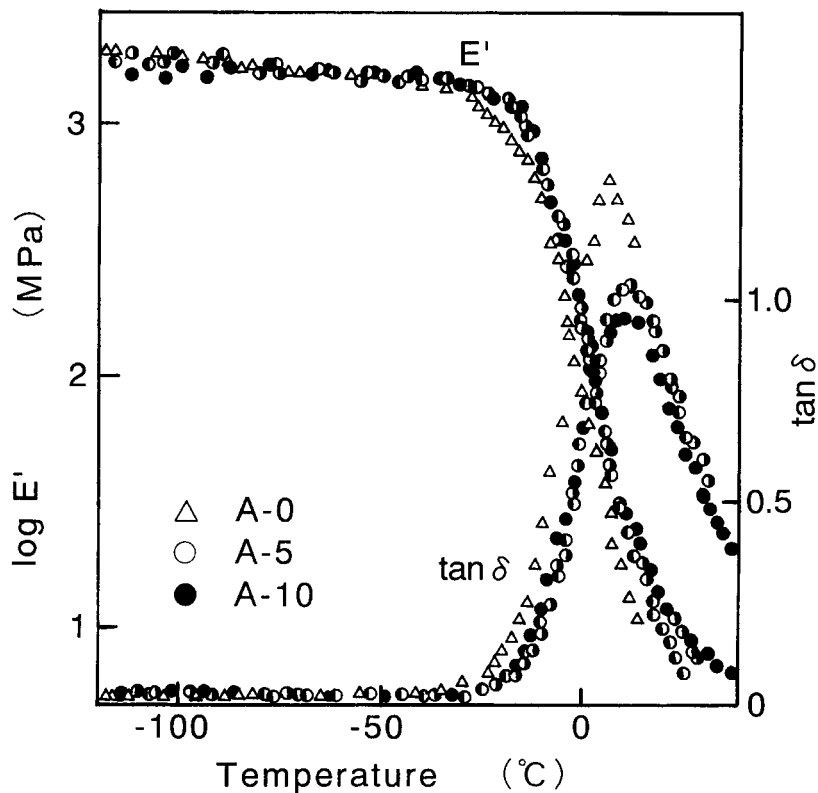


Figure 4 Temperature dependence of dynamic mechanical properties of PPG based polyurethane-aluminum hydroxide composites.

strength of the composites increased with increasing filler content. The elongation of the composites slightly decreased with increasing filler content.

While Young's modulus and tensile strength of the composite elastomer in which the aluminum hydroxide of 10 wt % included was about 1.7-fold those

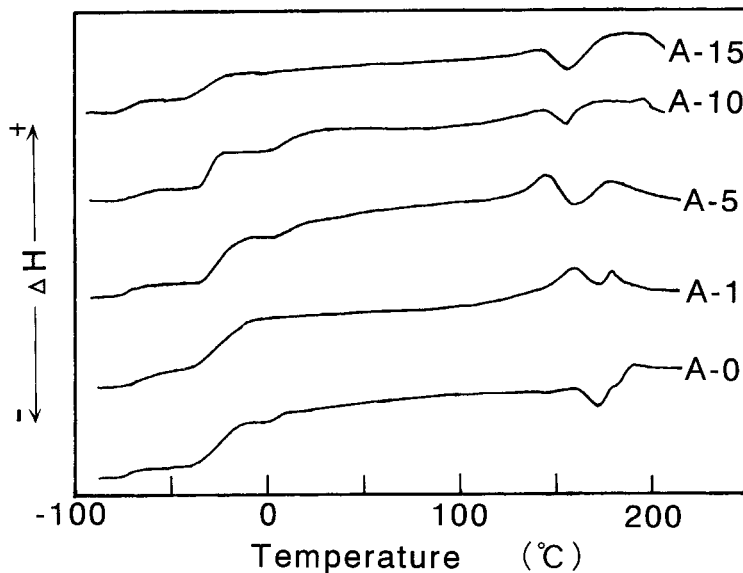


Figure 5 DSC thermograms of PPG based polyurethane-aluminum hydroxide.

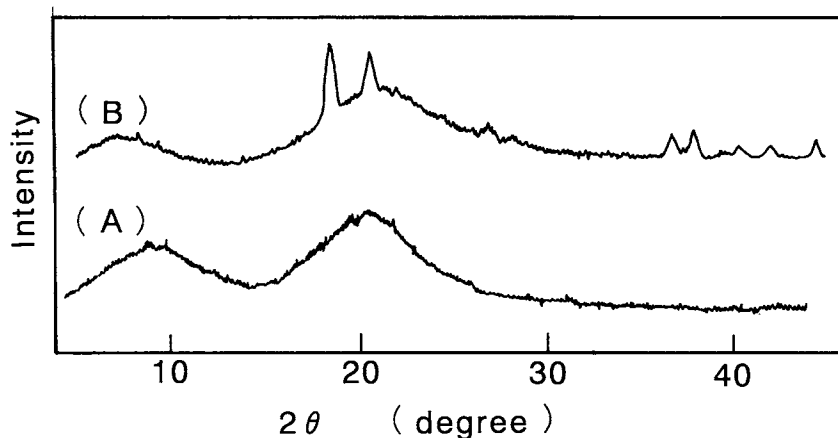


Figure 6 X-ray diffraction profiles of PPG based polyurethane-aluminum hydroxide composite (sample A-15) and unfilled polyurethane (A-0). (A) sample A-15; (B) sample A-0.

of the unfilled elastomer, elongation at break was nearly equal to that of the unfilled elastomer. It is well known that the tensile strength of filled elastomers has a maximum value at some filler content.¹² However, the tensile strength in the range of filler content used in this study increased. These results indicated that PPG based elastomers were significantly reinforced.

The temperature dependence of dynamic modulus, E' (storage modulus) and $\tan \delta$ (loss tangent) of the polyurethanes are shown in Figure 4. The storage modulus of the filled composites in the range of glassy and transition was equal to that of the unfilled elastomer. The rubbery modulus tended to increase and the loss tangent decreased with an increase of filler content.

Figure 5 shows the DSC thermograms of the polyurethanes. The glass-transition temperature (T_g) of the unfilled polyurethane was observed at -35.5°C . Other transitions in the unfilled polyurethane were observed at -75 to -70°C , 163 , and 188°C . Transition at -75 to -70°C was assigned to glass transition of pure soft segments. T_g slightly depended on the filler content, and the range of transition temperatures narrowed with increasing filler content. This result confirmed that fillers that have particle size between 0.1 and $0.5 \mu\text{m}$ did not affect movement of polymer chains in composites. Transitions at 163 and 188°C were assigned to changing morphology or melting of hard segments. The transition temperature observed at 163°C for the unfilled polyurethane decreased and the transition observed at 188°C slightly decreased with an increase of filler content. Decreasing of this tem-

perature may be explained as that the amount of hydrogen bonding between hard segments decreases by the interaction of electron acceptors with aluminum ions.

Figure 6 shows the X-ray diffraction pattern of the composite A-15. The X-ray diffraction pattern of the unfilled polyurethane only had a peak at $2\theta = 20^\circ$ characteristic of the amorphous rubber. The profile of the composite had eight peaks ($2\theta = 18.5, 20.5, 28.8, 37.8, 38.8, 41, 43,$ and 47°) that were assigned to reaction products of aluminum hydroxide with diisocyanate in addition to the peak for amorphous rubber.

Figure 7 shows the SEMs of freshly cut surfaces of the composites. The wetting of aluminum hydroxide by polymer can be seen from these pictures. The aluminum hydroxide particles also seem to be coated with the polymer fairly well.

CONCLUSION

Aluminum hydroxide was reacted with isocyanate groups. Aluminum hydroxide was used as a reactive filler to elastomers prepared from PPG, TDI, and BD. The composites have the same T_g as that of unfilled polyurethane, and higher tensile strength and higher Young's modulus than the unfilled elastomer. These results are attributed to the surface of aluminum hydroxide reacting with isocyanate, and the aluminum hydroxide being very compatible with the elastomer. The composites would be also economically competitive.

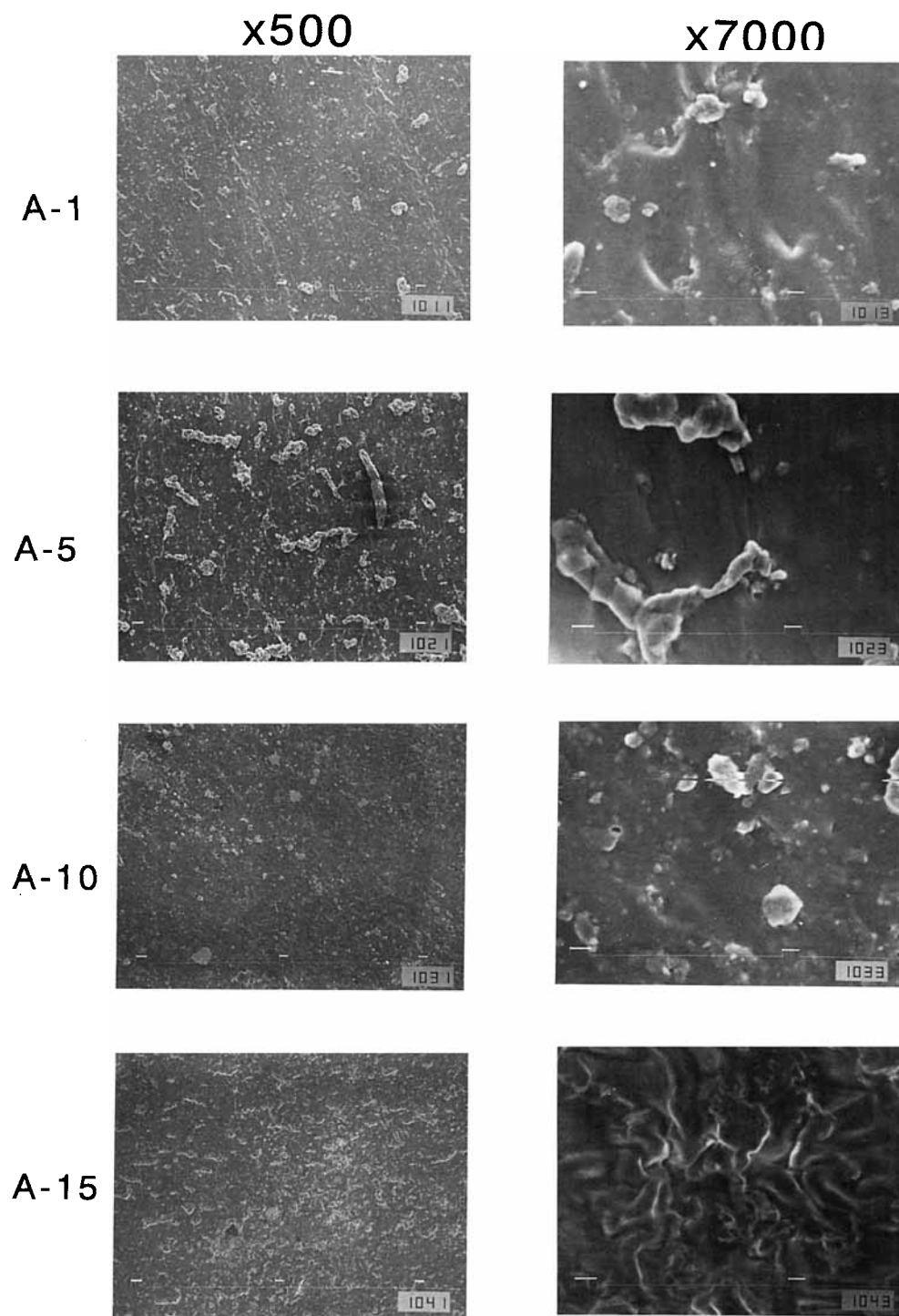


Figure 7 Scanning electronic micrographs of PPG-based polyurethane-aluminum hydroxide composites.

REFERENCES

1. J. H. Saunders and K. C. Frisch, *Polyurethanes, Chemistry and Technology, Part 1 Chemistry*, Interscience, New York, 1962.
2. P. Wright and A. P. C. Cumming, *Solid Polyurethane Elastomers*, Gordon and Beach Science Publisher, New York, 1969.
3. S. L. Cooper, J. C. West, and R. W. Seymour, in *Encyclopedia of Polymer Science and Technology*, Vol. 1, 1976.
4. C. Hepburn, *Polyurethane Elastomers*, Applied Science Publishers, New York, 1992.
5. M. Furukawa, K. Susukida, T. Yokoyama, *J. Soc. Rubber Industry, Jpn.*, **63**(5), 275 (1990).
6. C. H. Chen and C. C. M. Ma, *J. Appl. Polym. Sci.*, **46**, 949 (1992).
7. A. Mateen and A. Shamin, *J. Mater. Sci. Lett.*, **9**, 281 (1990).
8. A. J. Varma, M. D. Deshpande, and V. M. Nadkarni, *Angew Makromol. Chemie*, **132**, 203 (1985).
9. B. Arkless and C. Carreno, *Polym. Mater. Sci. Eng.*, **50**, 440 (1984).
10. K. Chehab and C. L. Beatty, *Polym. Mater. Sci.*, **56**, 449 (1987).
11. T. L. Smith and A. B. Magnusson, *J. Polym. Sci.*, **42**, 391 (1960).
12. Dennis T. H. Wong, and H. L. Williams, *J. Appl. Polym. Sci.*, **28**, 2187 (1983).

Received December 16, 1993

Accepted January 12, 1994