JOURNAL OF MATERIALS SCIENCE 25 (1990) 2985–2989

Micromechanism of failure of thermoplastic rubber

NAMITA ROY CHOUDHURY, ANIL K. BHOWMICK*
Rubber Technology Centre, Indian Institute of Technology, Kharagpur 721 302, India

---

The fracture surface morphology of various thermoplastic rubber and rubber vulcanizates based on natural rubber (NR), ethylene propylene diene rubber (EPDM), nitrile rubber (NBR), polyethylene (PE) and polypropylene (PP), namely NR–PE, NR–PP, EPDM–PE, EPDM–PP and NBR–PP, has been studied over a range of blend ratios, levels of interaction, rates, temperatures and modes of testing. The fracture surface changes with changes in blend ratio. Incorporation of a third component like EPDM or chlorinated polyethylene (CPE) to a certain percentage does not change the fracture morphology. Sulphur curing in the NR–PE blend generates a ductile matrix like rubber whereas large fissures are observed for peroxide-cured systems. Modification of both rubber and plastic also changes the surface morphology. The samples tested at various temperatures, rates and modes show similar features on the fracture surface.

---

1. Introduction

The failure of rubber is an ever-exciting subject, especially with the advent of new materials and new techniques to characterize microfeatures. The failure of various rubbers, by using a scanning electron microscopy technique, has been reported in several communications from the same laboratory and the useful features have been summarized by one of the authors in a recent publication [1]. It is interesting to note that the micromechanism of failure could be understood at least qualitatively using the micrographs. For example, the initiation of failure could be identified from micrographs, even in complicated fracture. Deviation of the tear path indicates a higher strength property. Abrasive failure of high-strength rubbers always takes place with the generation of microridges. Quantitative correlation has been attempted using various techniques and materials, but a successful relation in the case of ethylene–propylene diene rubber, natural rubber and polybutadiene has been reported recently by Saha Deuri and Bhowmick [2] with the help of a precut given at the centre of a tensile dumbbell specimen and following the growth of the precut.

Thermoplastic rubber comprising rubber and plastic is of relatively recent origin [3]. The morphology of these rubbers is interesting and the properties seem to be guided by the morphology and strength of individual components and the interfacial adhesion between them. Various technological features of natural rubber–polyolefin systems with and without modification of the components have been described earlier [4–6]. This investigation reports on the micromechanism of failure of thermoplastic rubbers and rubber vulcanizates using natural rubber–polyethylene (NR–PE) and natural rubber–polypropylene (NR–PP), natural rubber–chlorinated polyethylene–polyethylene (NR–CPE–PE), ethylene–propylene–diene rubber–polyethylene and polypropylene (EPDM–PE, EPDM–PP) and nitrile rubber–polypropylene (NBR–PP) systems. The following variables have been taken up for the present investigation:

(i) effect of blend ratio,
(ii) effect of third component,
(iii) effect of dynamic crosslinking,
(iv) effect of chemical modification of component phases,
(v) effect of nature of polymer,
(vi) effect of rate and temperature of testing, and
(vii) effect of mode of fracture, i.e. tensile or fatigue.

2. Experimental procedure

The preparation of the blends and various test specimens has been described in our earlier communications [5–8]. The tensile experiment was carried out at room temperature at 200 mm min^{-1} test speed. The fractured samples were sputter-coated with gold within 24 h of fracture and the surfaces were examined within 48 h of the experiment, using a Philips SEM model 500.

3. Results and discussion

3.1. Effect of blend ratio on fracture surface morphology

The effect of blend ratio on the fracture surface of blends is shown in Figs 1 and 2. The 70:30 NR–PE uncured blend shows a rough surface with a number of small holes only observed at high magnification. The holes indicate fractured rubber particles. The

---

*To whom all correspondence should be addressed.

0022–2461/90 $03.00 + .12

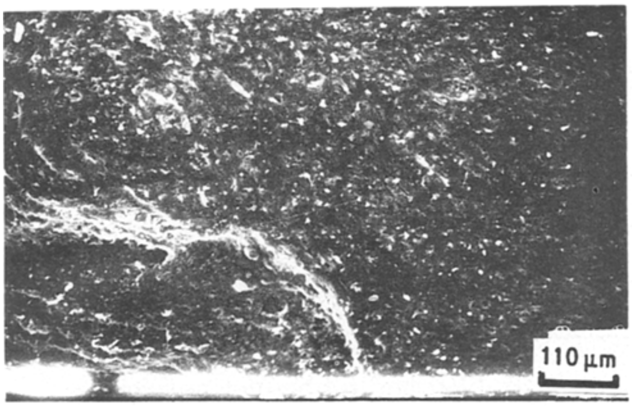

Figure 1 Tensile fractograph of 70 : 30 NR–PE blend.

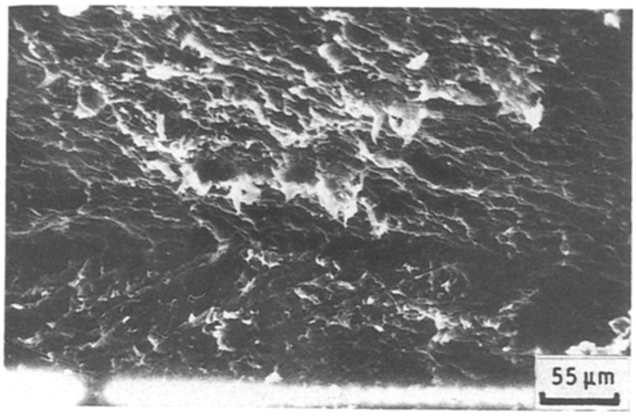

Figure 2 Tensile fractograph of 50 : 50 NR–PE blend.

dimension of the hole is 1.85 μm. With the introduction of more plastic, the fracture surface changes and the deformed rubber particles are fractured leaving behind a regular array of plastic (Fig. 2). At 30 : 70 rubber to plastic ratio the fractured plastic surface shows fatigue markings. The variation observed on the fracture surface is due to variation in the morphology of the rubber–plastic blends which has been discussed earlier [5].

The above surfaces are quite different from tensile-fractured rubber surfaces. Flow lines and tear lines have been observed on the fracture surfaces of rubbers [1]. These are also different from the fractured surface of pure PE which is brittle in nature [9]. The difference becomes more prominent when highly crystalline polypropylene replaces PE. The fracture surface of a 70 : 30 NR–PP blend (Fig. 3) shows an array of plastic, rubber and sheared rubbery regions.

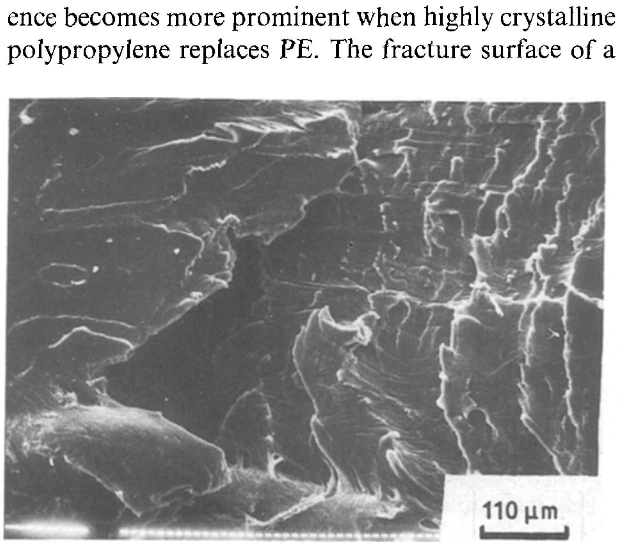

Figure 3 Tensile fractograph of 70 : 30 NR–PP blend.

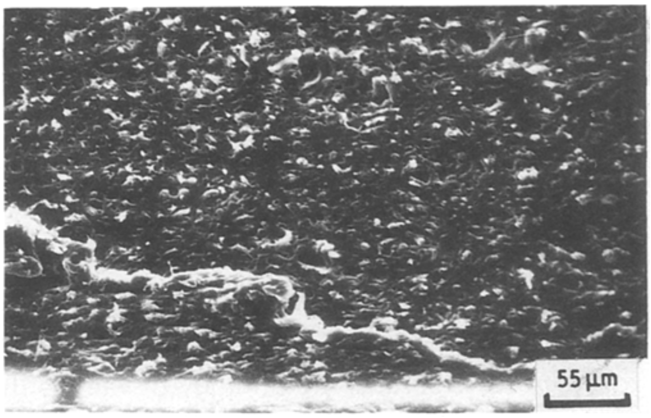

Figure 4 Tensile fractograph of 70 : 20 : 30 NR–EPDM–PE blend.

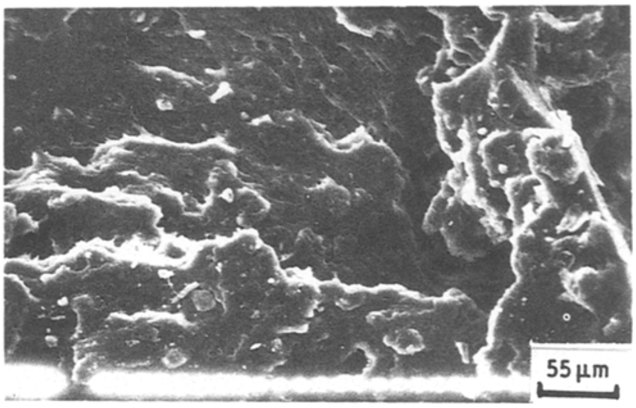

Figure 5 Tensile fractograph of DCP-cured 70 : 20 : 30 NR–CPE–PE blend.

3.2. Effect of addition of third component on fracture surface morphology

It has previously been pointed out that on the introduction of a third component like CPE, EPDM and chlorosulphonated polyethylene (CSPE), the strength of NR–PE composite increases when compared at an equal rubber level [5]. The fractographs are very similar for all 70 : 30 blends containing CPE, EPDM or CSPE as third component. A representative surface of NR–EPDM–PE is shown in Fig. 4, whose features are similar to those of the control (NE–PE). With the increase in plastic content, the fracture surface does

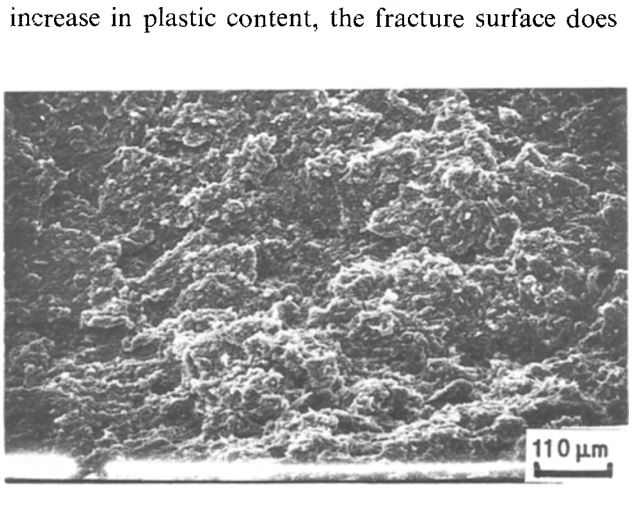

Figure 6 Tensile fractograph of sulphur-cured 70 : 30 NR–PE blend.

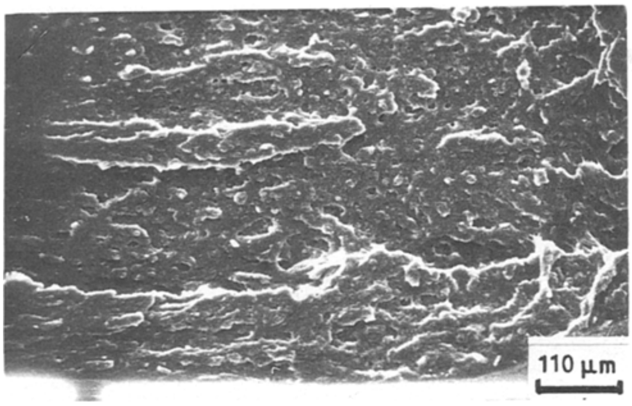

Figure 7 Tensile fractograph of 70 : 20 : 3 : 27 NR–S-EPDM–PE_M–PE blend. (S-EPDM is sulphonated EPDM.)

not change as compared to the control. Since the mechanism of fracture of the NR–third component–PE is similar to that of the control NR–PE at various levels of plastic content, it may be concluded that the variation in strength arises due to the variation in morphology which has been reported before, and variation in the constituents of the phases [5].

The NR–PP blend shows exactly similar behaviour. The fracture surfaces are similar to those of the controls.

3.3. Effect of crosslinking

On curing the rubber phase in the blend the fracture surface shows more rubber-like characteristics. Fractographs of various rubbers have been previously reported by Bhowmick and co-workers [10–12]. The NR–PE system shows flow of the matrix, short tear lines and cracks on the surface. The rubber phase comes out from the matrix during fracture. The addition of a third component causes more flow in the matrix because of the rubbery nature of the third component. A representative photograph is shown in Fig. 5.

The degree of crosslinking was varied by using two different types of crosslinking system, namely sulphur and dicumyl peroxide (DCP). The sulphur system gives a higher strength than the DCP-cured one. The fractograph (Fig. 6) also indicates that the sulphur system makes the matrix more ductile and the large fissures obtained for the DCP-cured system are not observed on the fracture surface. This surface is very similar to the fracture surface of filled rubber as reported earlier [10].

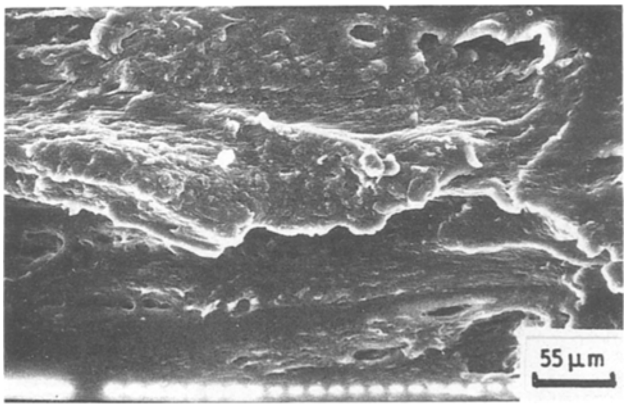

Figure 8 Tensile fractograph of 70 : 20 : 3 : 27 NR–ENR–PP_M–PP blend. (ENR is epoxidized natural rubber.)

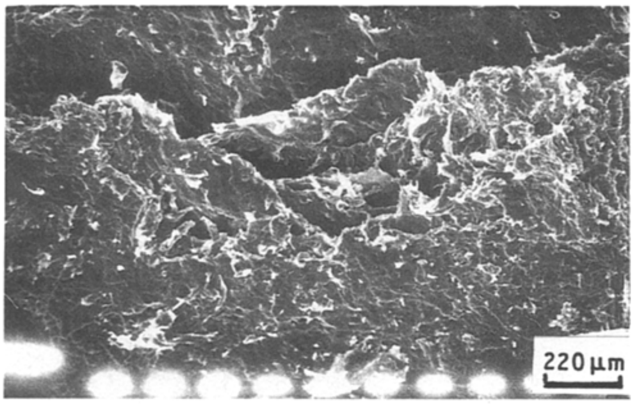

Figure 9 Tensile fractograph of NBR–PP (70 : 30) vulcanizate.

3.4. Effect of chemical modification of component phases on the fracture surface morphology of thermoplastic blends

It has been earlier reported that the chemical modification of plastic and rubber enhances the tensile properties of the composites [6]. The fracture surfaces are reported here. NR(70)–PE_M(3)–PE(27) (where PE_M indicates modified PE) shows a similar fracture surface to NR(70)–PE(30). Even a composition containing 30% modified PE, i.e. NR (70)–PE_M(30), shows similar fracture behaviour. Modification of both rubber and plastic in the blend changes the fracture surface morphology. There are a few flow lines, sometimes deviated, small holes and a few cracks (Fig. 7). It may be mentioned that the composite has 14.4% more strength than the control NR–PE. Generally, the flow of the matrix increases with the use of chemical modifiers, which help the plastic and the rubber to interact intimately.

In polypropylene systems, however, the brittle nature of the fractograph is quite evident even after modification. A representative fractograph using NR–ENR–PP_M–PP is shown in Fig. 8. The strength properties also decrease, due probably to the decrease in crystallinity of PP as reported earlier [7].

3.5. Effect of polymer

The effect of the nature of the polymer on fracture surface morphology could be studied using NR–

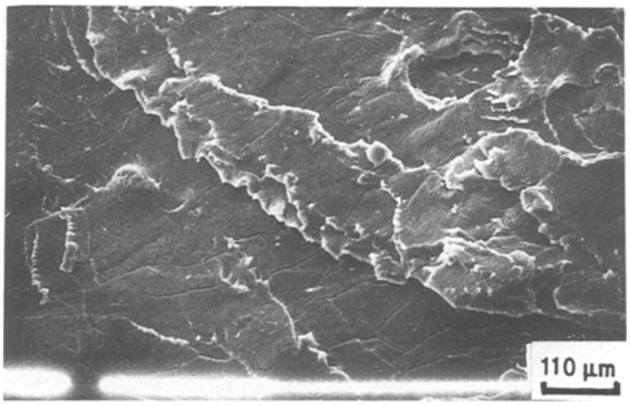

Figure 10 Tensile fractograph of EPDM–PE (70 : 30) vulcanizate.

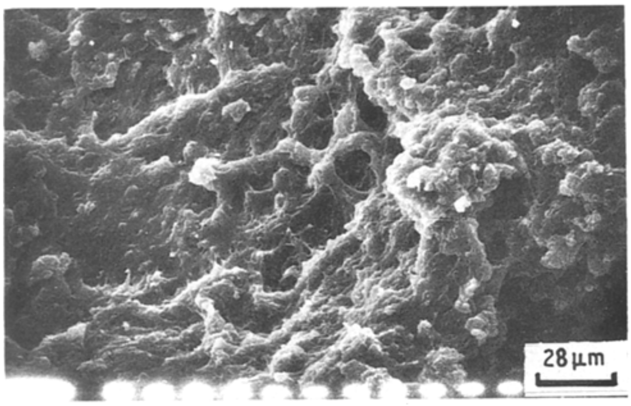

Figure 11 Tensile fractograph of sulphur-cured NR–PE (70 : 30) blend (at 25° C, 500 mm min^{-1}).

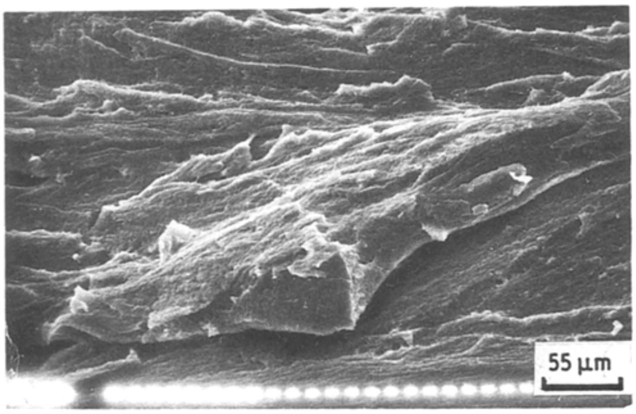

Figure 13 Tensile fractograph of EPDM–PP (70 : 30) vulcanizate (at 25° C, 50 mm min^{-1}).

PP, EPDM–PP, NBR–PP, NR–PE and EPDM–PE (rubber: plastic 70 : 30) systems. It has been observed from the previous fractographs (Figs 3 and 8) that all the samples containing polypropylene as one of the matrix components yield a brittle fracture with very little flow on the surface, which is due to the high crystallinity and hardness of PP. The incorporation of various rubbers in PP generates different fracture surface morphologies as shown in Fig. 3 and Fig. 9. Similarly, the fracture surface of EPDM–PE (Fig. 10) is completely different from that of NR–PE. The deformation of the thermoplastic elastomers depends on the morphology. Differences in morphology give rise to different fracture behaviours and hence variation of the fracture surface morphology.

3.6. Effect of rate and temperature of testing

The effect of temperature and rate of testing on the tensile strength has been reported earlier [8]. It has been observed that at low temperatures and high rates of testing, values of the tensile strength are higher. The fractographs obtained at various temperatures of testing are very similar (Fig. 11), indicating an identical mechanism of crack propagation in these materials at different temperatures. However, the mechanisms of fracture of various materials are different. For example, the sulphur-cured NR–PE (70 : 30) system (Fig. 11) shows more ductile behaviour, which is observed from the flow of the materials, than NBR–PP (70 : 30) vulcanizate (Fig. 12), which shows a brittle nature. The NR–CPE–PE (cured) blend shows an array of one of the components, indicating that a component, presumably rubber, comes out. The EPDM–PE and EPDM–PP (70 : 30) blends show brittle fracture with less flow and deep cracks on the surface. Fig. 13 shows a tensile fractograph of the EPDM–PP system. A change in temperature does not change the mechanism of fracture.

Similar observations are made for testing at low and high rates. The nature of the fracture surface is identical. All the above fractographs indicate that the high or low strength in the material is related to the viscoelasticity of the blends. At high temperature all the composites show low hysteresis and hence low strength.

3.7. Effect of mode of fracture

The fractographs obtained under various failure modes were also examined. It is very surprising that the fractographs of all the samples indicate a similar mechanism of fracture, though subtle differences (for instance in the distance between spacings and the depth of crack lines) exist for test specimens fractured under tensile and fatigue modes. Fig. 14 shows the fatigue failure surface of the sulphur-cured NR–PE system (70 : 30). It has been reported that in rubbers fatigue and tensile fractures generate widely differing morphology [13] and the failure initiation zone and crack propagation zones are clearly distinguishable.

Acknowledgement

The authors thank the Department of Science and Technology, New Delhi for funding the project.

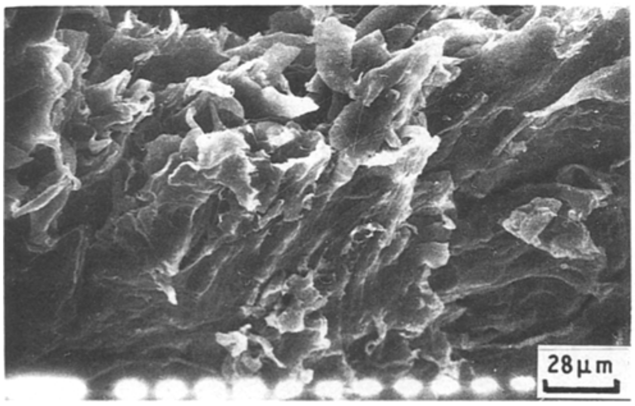

Figure 12 Tensile fractograph of NBR–PP (70 : 30) vulcanizate (at 25° C, 500 mm min^{-1}).

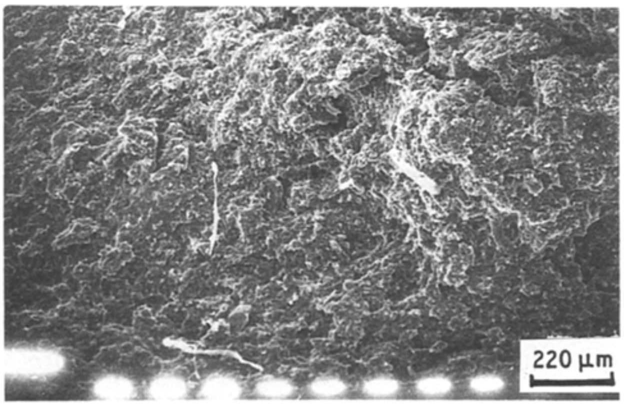

Figure 14 SEM photograph of flexed fracture surface of sulphur-cured NR–PE (70 : 30) blend.

References

1. A. K. BHOWMICK, *Kautschuk Gummi Kunststoffe* **37** (1984) 191.
2. A. SAHA DEURI and A. K. BHOWMICK, *J. Mater. Sci.* **22** (1987) 4299.
3. A. Y. CORAN, in "Handbook of Elastomers – New Development and Technology", edited by A. K. Bhowmick and H. L. Stephens (Dekker, New York, 1988) p. 249.
4. D. J. ELLIOTT and A. J. TINKER, in Proceedings, "Thermoplastic Natural Rubber Blends," International Rubber Conference, Kuala Lumpur, 1985.
5. N. ROY CHOUDHURY and A. K. BHOWMICK, *J. Mater. Sci.* **23** (1988) 2187.
6. *Idem, J. Appl. Polym. Sci.* **38** (1989) 1091.
7. *Idem, J. Adhesion Sci. Technol.* **2** (1988) 167.
8. *Idem, J. Mater. Sci.* **25** (1990) 161.
9. P. I. VINCENT, in "Encyclopedia of Polymer Science and Technology", Vol. 7, edited by N. M. Bikales (Interscience, New York, 1967) p. 292.
10. A. K. BHOWMICK *et al., Rubb. Chem. Technol.* **53** (1980) 327.
11. A. K. BHOWMICK, S. BASU and S. K. DE, *ibid.* **53** (1980) 321.
12. A. SAHA DEURI and A. K. BHOWMICK, *J. Appl. Polym. Sci.* **35** (1988) 327.
13. A. K. BHOWMICK, *J. Mater. Sci. Lett.* **5** (1986) 1042.

Received 14 October 1988
and accepted 24 July 1989