

# Fracture resistance of polyblends and polyblend matrix composites

## Part III *Role of rubber type and location in nylon 6,6/SAN composites*

S. V. NAIR, A. SUBRAMANIAM

*Department of Mechanical Engineering, University of Massachusetts, Amherst, MA 01003, USA*

L. A. GOETTLER

*Vydyne Tech Center, Monsanto Company, Contonment, FL 32533, USA*

*E-mail: lloyd.a.goettler@solutia.com*

*nair@ecs.umass.edu*

The role of rubber particle type, location and morphology on toughening in blends of nylon 6,6 with styrene acrylonitrile (SAN), with and without fibre reinforcements was examined in this study. The rubber used was ethylene propylene diene monomer (EPDM) rubber and the results were compared to a previous study that used butadiene rubber. The compositions of the blends ranged from pure nylon 6,6 to pure SAN. EPDM rubber was chemically compatibilized with one of the matrix phases rather than grafted, as in the ABS. In order to study the effect of rubber location on fracture behaviour, the approach was to compatibilize EPDM with either the minor phase or the major phase component of the blend. Attention was focused on fracture initiation toughness and fracture propagation toughness, measured through the parameters  $J_{IC}$  and  $J_{SS}$ , respectively.  $J_{SS}$  refers to the steady-state, or plateau value of the material  $R$ -curve and was therefore a measure of total toughness which included the additional component derived from crack extension. The results indicated that EPDM rubber was not as effective a toughening agent as was butadiene in the Acrylonitrile Butadiene Styrene (ABS) system, primarily due to the morphology of EPDM and its interface character with the nylon 6,6 or SAN matrix. It was demonstrated that the embrittlement effects of a second rigid polymer phase can be mitigated by selectively adding rubber to that phase in the alloy or blend. With regard to the role of fibre reinforcement, a strong fibre matrix interface was found to be essential for toughening. Further, the extent of rubber toughening was larger when fibres were present than when fibres were absent, provided the fibre matrix interface was strong. Fibres also, like rubber, enhanced local matrix plasticity as well as reduced the embrittlement effects associated with a second polymer phase.

© 1998 Kluwer Academic Publishers

### 1. Introduction

In the previous two papers [1, 2], the fracture behaviour of nylon 6,6/Acrylonitrile Butadiene Styrene (ABS) blends and fibre-reinforced nylon 6,6/ABS blends was studied. The role of rubber in ABS was isolated by comparing the ABS-containing materials with the corresponding nylon 6,6/styrene acrylonitrile (SAN) polyblends, with and without fibres [2]. By this procedure, it was also possible to understand the role of the rigid SAN phase in the nylon 6,6/ABS alloys and their composites. In ABS, the butadiene rubber was grafted on to the SAN resulting in an optimized microstructure, with rubber particles of around 1  $\mu\text{m}$  size containing occluded SAN within the rubber particles which were spaced around 1–2  $\mu\text{m}$  apart. Furthermore, in this sys-

tem the rubber phase was always contained within the SAN phase. It was shown that while the magnitude of the toughness increase due to rubber was not affected by the presence of the rigid SAN, the SAN caused embrittlement by interface cracking at nylon 6,6/SAN boundaries. Nylon 6,6 likewise caused embrittlement when nylon 6,6 was the minor phase component. Further, the presence of rubber always triggered  $R$ -curve behaviour in the unreinforced materials with the magnitude of toughening associated with the crack propagation stage being substantially larger than that associated with the crack initiation stage. While the presence of fibres also induced  $R$ -curve behaviour it did not follow that the combined presence of rubber and fibres would always result in  $R$ -curve behaviour.

In this work, the role of rubber particle type, location and morphology on toughening in blends of nylon 6,6 with SAN, with and without fibres was examined. For example, there is a need to understand how the fracture resistance changes when rubber is contained within the minor phase component compared to when it is contained within the major phase component. For comparison purposes, we also studied the case when rubber is added without the presence of a second rigid polymer component. Towards the above objectives, fracture behaviour of blends of nylon 6,6 with SAN containing ethylene propylene diene monomer (EPDM) rubber, both with and without reinforcing fibres were studied. The compositions of the blends ranged from pure nylon 6,6 to pure SAN. EPDM rubber was chemically compatibilized with one of the matrix phases rather than grafted, as in the ABS. Also, EPDM could exhibit debonding and cavitation characteristics which are different from those of the butadiene rubber in ABS, because of its different properties. In order to study the effect of rubber location on fracture behaviour, the approach was to compatibilize EPDM with either the minor phase or the major phase component of the blend. As in previous papers, we focus attention on fracture initiation toughness and fracture propagation toughness, measured through the parameters  $J_{IC}$  and  $J_{SS}$ , respectively.  $J_{SS}$  refers to the steady-state, or plateau value of the material  $R$ -curve and is therefore a measure of total toughness which includes the additional component that is derived from crack extension. The results of this study could then be compared to the case when rubber was entirely absent, namely, the nylon 6,6/SAN case discussed in Part II [2].

## 2. Experimental procedure

### 2.1. Materials

The materials used in this study were processed at Monsanto Chemical Company, Springfield, MA. The raw materials used were poly(hexamethylene adipamide) or nylon 6,6, styrene acrylonitrile (SAN), ethylene propylene diene monomer (EPDM) rubber, glass fibres and a maleic anhydride type of nylon 6,6/SAN compatibilizer. In the case of the rubber-modified blends, an attempt was made to vary the microstructures by varying the rubber compatibility. Hence, these blends had, on the one hand, EPDM rubber compatibilized with nylon 6,6 and, on the other, EPDM rubber compatibilized with SAN. In this paper, EPDM rubber compatibilized with nylon 6,6 and SAN, are referred to as EPDM-N and EPDM-S, respectively. The glass fibres used were Star Stran 702, for the nylon 6,6-rich materials, and Star Stran 726, for the SAN-rich materials. Star Stran 702 and 726 are E-type glass fibres, compatible with nylon 6,6 and SAN, respectively, manufactured by Schuller Mats and Reinforcements. The glass fibres were added to the extent of 16 vol% of the total filled polymer. The unreinforced materials included, on the SAN-rich side, 86/14 SAN/EPDM, 20/80 nylon 6,6/SAN with EPDM-S and 20/80 nylon 6,6/SAN with EPDM-N.

On the nylon 6,6-rich side, the materials studied were 80/20 nylon 6,6/rubber, 80/20 nylon 6,6/SAN with EPDM-S and 80/20 nylon 6,6/SAN with EPDM-N. Similar to the case of ABS, the EPDM rubber content was 14% of the total SAN present in the materials, except in the case of nylon 6,6/rubber in which a weight ratio of 80/20 was used. This was done in order to obtain a comparison between this system and the nylon 6,6/ABS system. Glass fibre-reinforced composites were also processed with the above materials as matrices. The appropriate amounts of the different components were compounded together in a 30 mm co-rotating/intermeshing American Leistritz twin-screw extruder. Zone sets varying from 220–260 °C were used, with a vacuum of 28 in. (~71 cm) Hg. The extruded blends were then dried at 80 °C for 18 h in a Conair desiccant bed system. Injection moulding of these blends was carried out using an Engel EC88 machine, with a mould temperature of around 50 °C and an injection pressure of 900–1250 p.s.i. ( $10^3$ p.s.i. = 6.89 Nmm<sup>-2</sup>). Higher moulding temperatures and pressures were used for the fibre-reinforced blends in order to improve flow. Tensile specimens of 1/8 in. (~3 mm) thickness and bend bars of 1/4 in. (~6.4 mm) thickness were made. In order to prevent the effects of moisture, the specimens were first sealed in plastic bags and then in aluminized paper.

### 2.2. Mechanical properties and microstructural evaluation

Tensile tests were carried out in accordance with ASTM D638 on an Instron servohydraulic test machine (model 1321). The fracture initiation toughness,  $J_{IC}$ , was determined using a new protocol proposed by an ASTM task force [3]. The steady state toughness,  $J_{SS}$ , was characterized using pre-cracked three-point bend specimens using a technique discussed in detail previously [1, 2].

Thin sections of the unreinforced SENB samples were cut for transmission electron microscopy (TEM) from the centre parallel to the flow direction. The specimens were cryo-sectioned with a diamond knife and sections were collected on a 400 mesh TEM grid. The microstructures of the materials were examined using a Philips CM12-S TEM operated at 100 kV.

The fracture surfaces of the specimens were examined using a Jeol-JSM5410 scanning electron microscope, after loading SENB specimens at 1 mm min<sup>-1</sup>. The specimens were coated with a thin layer of gold in order to improve conductivity of the surface and prevent electron charging.

## 3. Results and discussion

### 3.1. Microstructures

Rubber compatibility played an important role in determining the microstructures of blends of nylon 6,6 with SAN. This can be seen from the transmission electron micrographs shown in Fig 1–4. SAN is the uniformly grey region, nylon 6,6 the grey region containing “feathery” structures, and EPDM rubber the approximately 0.5 μm thick white phase which contains

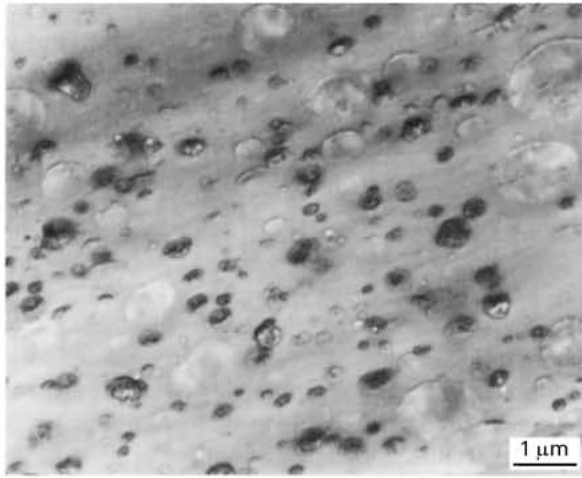


Figure 1 Transmission electron micrograph of 20/80 nylon/SAN with EPDM-S.

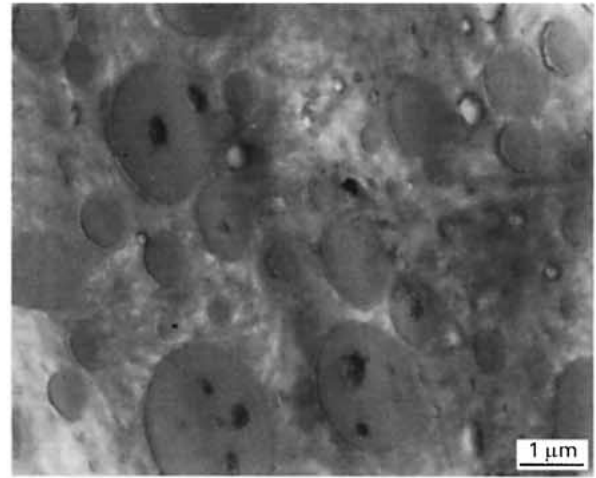


Figure 4 Transmission electron micrograph of 80/20 nylon/SAN with EPDM-N.

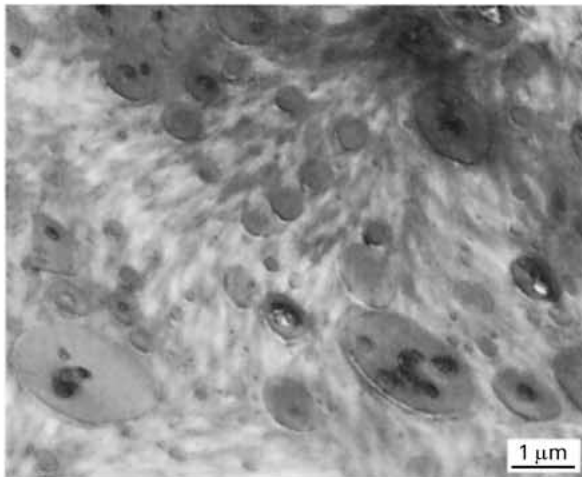


Figure 2 Transmission electron micrograph of 80/20 nylon/SAN with EPDM-S.

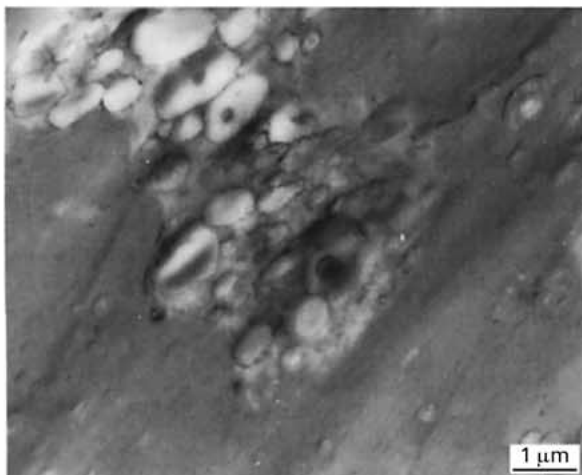


Figure 3 Transmission electron micrograph of 20/80 nylon/SAN with EPDM-N.

dark occlusions when within the SAN. When the rubber was compatibilized with the SAN phase, it was partitioned almost exclusively to the SAN phase. This was true both in the 20/80 nylon 6,6/SAN/EPDM-S

and the 80/20 nylon 6,6/SAN/EPDM-S cases (Figs 1 and 2). When the rubber was compatibilized with the nylon 6,6 phase, it resided predominantly in the nylon 6,6 phase in the case of 20/80 nylon 6,6/SAN/EPDM-N (Fig. 3). But, in the 80/20 nylon 6,6/SAN/EPDM-N blend, the rubber was distributed almost equally to the SAN and nylon 6,6 phases (Fig. 4).

In the SAN-rich materials, the SAN was the continuous phase while the nylon 6,6 was discontinuous. When EPDM-S was used, the rubber was contained in the SAN phase. The rubber particles were very small, non-uniformly shaped particles, varying in size from 0.3–0.5 μm, with an average inter-particle distance of around 0.5 μm or more. The nylon 6,6 particles were mostly oval or circular in shape and were around 0.5–1.5 μm. When Rubber-N was used, most of the rubber particles were contained within the nylon 6,6 phase, so much so, that the nylon 6,6 domains were completely filled with the rubber particles. The rubber particles were non-uniformly shaped in this case also, but were clearly bulkier, of around 1 μm in size. As stated above, the rubber particles were all clustered very close together within the nylon 6,6 domains. The nylon 6,6 particle size was significantly larger and thus there were fewer nylon 6,6 particles compared to when rubber was contained in the SAN major phase.

In the case of the nylon 6,6-rich blends, nylon 6,6 was the continuous phase and the SAN existed as bulky, circular particles. Rubber location did not affect the shape of the SAN particles, but a slight increase in the average SAN particle size was observed when rubber was contained by the SAN. Both in nylon 6,6/SAN/EPDM-N and nylon 6,6/SAN/EPDM-S blends, the rubber particles were non-uniformly shaped and small in size, approximately 0.3–0.5 μm.

In the case of nylon 6,6/EPDM, a more or less optimum microstructure was obtained, with circular rubber particles of around 0.5 μm, separated by distances of around 1–2 μm, on an average (Fig. 5).

The difference in microstructure between the nylon 6,6/ABS system and the nylon 6,6/SAN/EPDM

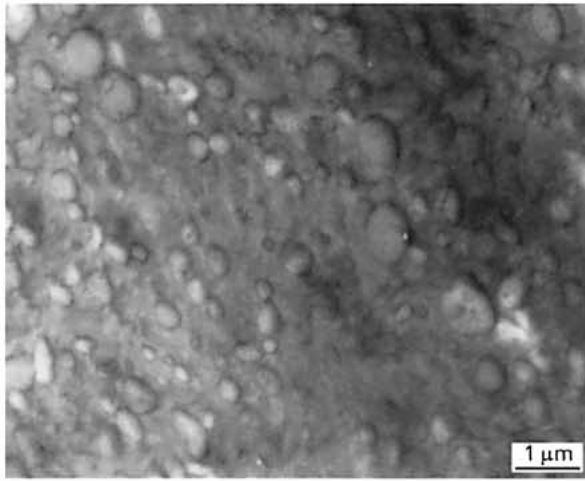


Figure 5 Transmission electron micrograph of 80/20 nylon/EPDM.

system was significant and is believed to play an important role in influencing the fracture behaviour of these blends. In the ABS system, the rubber particles were uniformly shaped and contained occluded SAN phase within them [1]. On average, the particle sizes were around  $1\mu\text{m}$  and the inter-particle distance was between  $1$  and  $2\mu\text{m}$ . In contrast, in the nylon 6,6/SAN/EPDM system, there was greater variability in the morphology of the blends, Figs 1–5. The rubber varied in size from as small as  $0.3\mu\text{m}$  in some blends to as large as  $1\mu\text{m}$  in others. As far as the shape was concerned, the particles were mostly non-uniform, except for the case of nylon 6,6/rubber in which the rubber was well rounded. It can also be observed from the micrographs that the rubber content in the SAN-rich materials was higher than in the nylon 6,6-rich blends. The reason for this, as mentioned earlier, was that the EPDM rubber content was always maintained at 14% by weight of the total SAN present in the materials. Hence a greater SAN content would imply a greater EPDM content. The inner-particle distance depended on the location of rubber. When rubber was contained in the major phase, the particles were well dispersed and separated by around  $1\mu\text{m}$ . When the rubber was contained in the minor phase, the particles were closely spaced within the minor phase, with few/no rubber particles outside.

Another interesting aspect to be noted was that when rubber was contained in the SAN phase, it contained dark-coloured occlusions which are believed to be small SAN particles. But, when the rubber was contained in the nylon 6,6 phase, there were no observable occluded phase particles. Hence when EPDM is within the SAN, the structure is very similar to the ABS, with the SAN containing the rubber and the rubber, in turn, containing occluded SAN. But, the important point is that the EPDM particles were smaller and more irregularly shaped than in the ABS system. Also, the nylon 6,6 was present in the form of elongated fibres in the 20/80 nylon 6,6/ABS. This is not observed in the nylon 6,6/SAN system.

Transmission electron microscopy was not performed in the case of fibre-reinforced blends, due to the difficulty of obtaining thin sections of these mater-

ials by cryotomography. The addition of fibres would not be expected to change the microstructure in terms of where the rubber particles reside. Hence, it could be assumed that the microstructure of all the blends remained the same in this respect. However, the particle sizes of the various phases might undergo a change.

### 3.2. Initiation toughness

#### 3.2.1. Role of rubber

The initiation toughness values of all the unreinforced blends are summarized in Fig. 6. As mentioned in Section 2.1 in the single-phase materials, the rubber was compatibilized with just that phase. Hence, at the end points of the plot, the data points for the minor phase compatibilized rubber and the major phase compatibilized rubber are coincident, because only one matrix phase was present. Comparing with the

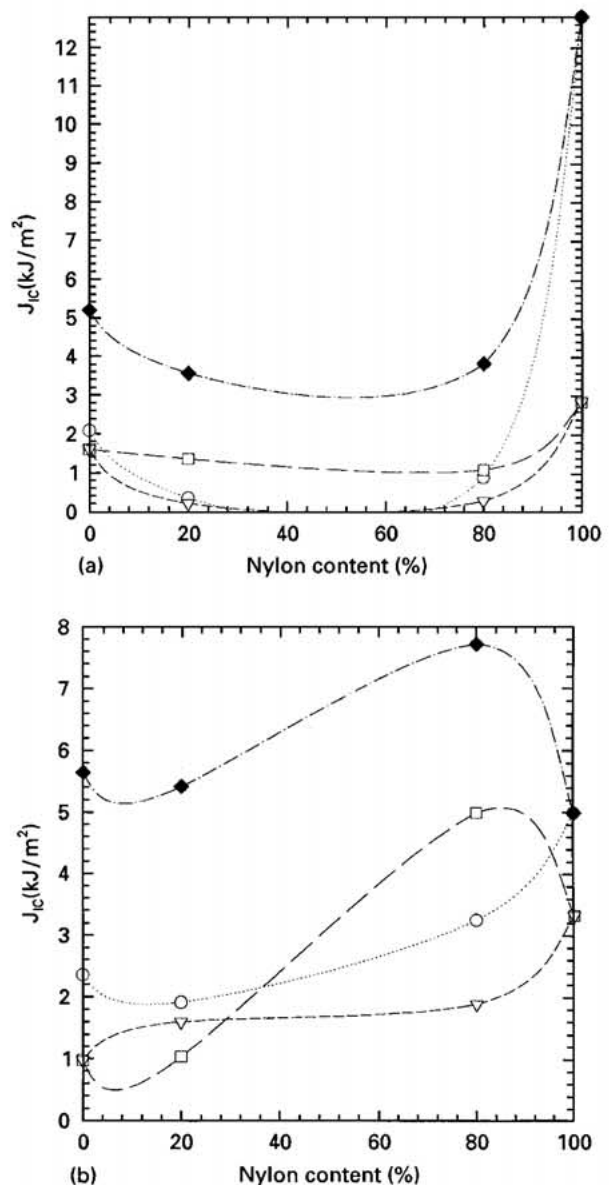


Figure 6 (a)  $J_{ic}$  versus alloy composition for the unreinforced alloys. (b)  $J_{ic}$  versus matrix composition for the fibre-reinforced alloys. (○) No rubber [2], (□) minor phase compatibilized EPDM rubber (▽) major phase compatibilized rubber, (◆) ABS [1].



nylon 6,6/ABS alloys, it is evident that the ABS system had significantly higher values of toughness than the nylon 6,6/SAN/EPDM alloys, at all blend compositions. Evaluation of the fracture surfaces revealed that plasticity associated with failure in the nylon 6,6/SAN/EPDM alloys was lower compared to the nylon 6,6/ABS alloys, that is, the nylon 6,6/SAN/EPDM alloys appeared to fail in a more brittle fashion. This will be discussed in greater detail below.

First, single rigid phase materials containing EPDM rubber, namely, nylon 6,6/EPDM and SAN/EPDM, are considered. As can be seen from the figure, addition of EPDM rubber embrittled both nylon 6,6 and SAN. Whereas the toughness of SAN/rubber was slightly lower than that of pure SAN, nylon 6,6 was significantly embrittled by the addition of rubber. This is in contrast to the nylon 6,6/ABS system, where rubber always played a toughening role and embrittlement was associated invariably with the rigid polymer component. This difference can be understood by examining the fractographs, see Figs. 7a and 8a. It can be seen that the EPDM rubber particles were weakly bonded to both the nylon 6,6 and SAN matrices, as evidenced by the extensive debonding at the rubber/matrix interfaces. In the SAN/EPDM, a limited amount of plasticity was induced by the addition of rubber, as can be seen by comparing the fractograph of SAN/EPDM (Fig. 7a) with that of pure SAN (Fig. 7b). The pure SAN, evidently fractured by a brittle process with no evi-

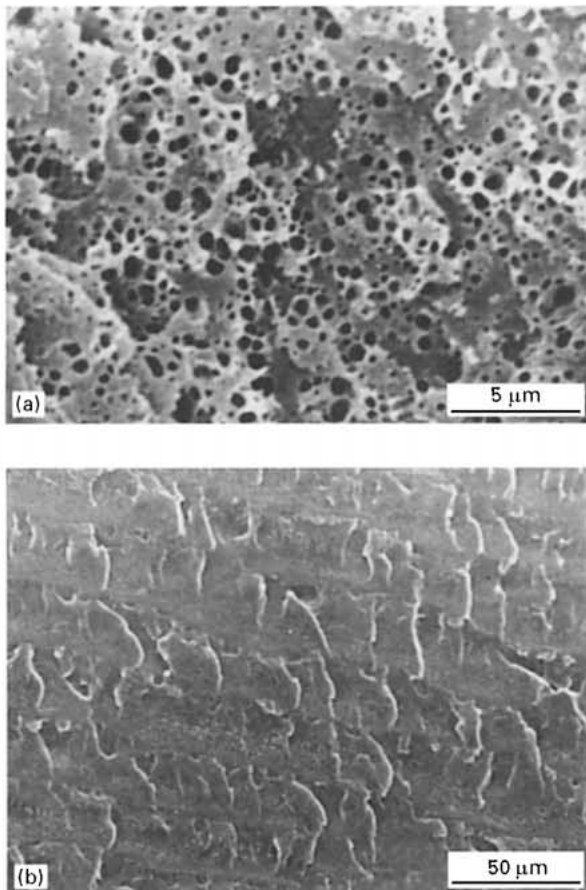


Figure 7 Scanning electron micrographs of the fracture surfaces of (a) SAN/EPDM, and (b) pure SAN.

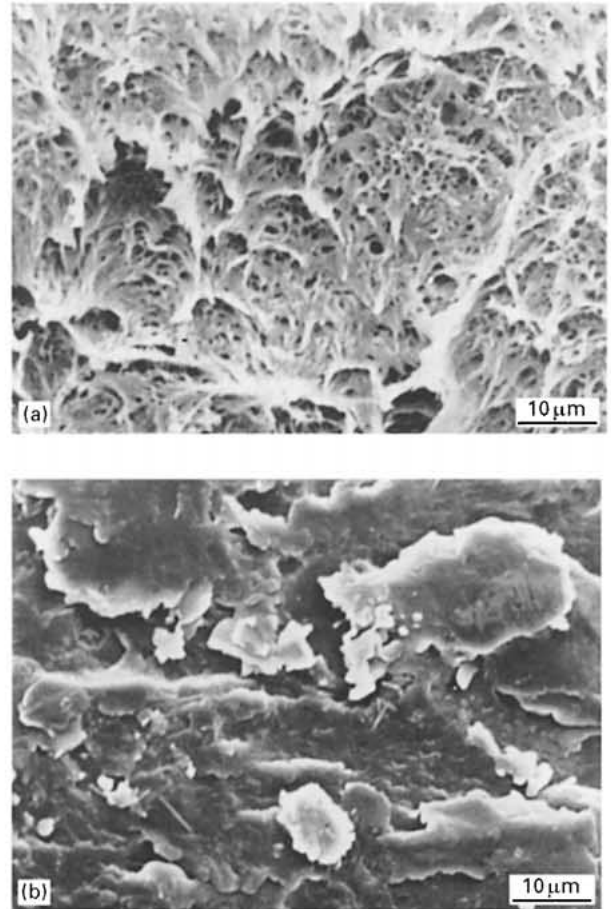


Figure 8 Scanning electron micrographs of the fracture surfaces of (a) nylon/EPDM and (b) pure nylon.

ence of plasticity on the fracture surface. In the SAN/EPDM, however, a certain degree of plasticity was observed around the debonded rubber particles. This, however, did not result in an increase in  $J_{IC}$ , possibly due to the extensive debonding at the EPDM/SAN interface. It is known that for rubber toughening to take place, it is necessary to have a good rubber/matrix bonding, which would then promote cavitation followed by shear yielding of the surrounding matrix phase. However, when the bonding is weak, the rubber particles can debond from the matrix at low values of applied stress. In such a case, the surrounding deviatoric stresses may not be high enough to cause shear yielding. In contrast, in ABS there was extensive plasticity associated with cavitation of the rubber particles [1]. This could be a result of the strong rubber/SAN bonding in this material.

In the nylon 6,6/EPDM, there was a significant amount of plasticity compared to pure nylon 6,6, as qualitatively inferred from the fractographs (Fig. 8a and b). Yet, it was observed that addition of EPDM rubber embrittled nylon 6,6. Again, as can be seen from the fractographs, the EPDM/nylon 6,6 interface was weak and this interface debonded extensively, thus resulting in embrittlement.

Next, 20/80 nylon 6,6/SAN alloys are considered. As was discussed in Part II [2], addition of nylon 6,6 as a minor phase to SAN reduced toughness because of

the embrittlement effect of weak nylon 6,6/SAN interfaces. When EPDM rubber was also added to SAN in addition to nylon 6,6 particles, there was no observed toughening. As was discussed in the microstructures section, the EPDM particles were around 0.5 $\mu\text{m}$  or smaller when within the SAN. Rubber toughening is known to depend on the particle size and at present, the optimum size is considered to be between 0.5 and 5.0  $\mu\text{m}$ . Hence, it is possible that this requirement was not met. Consistent with the lack of toughening, the fracture surface of this material, Fig. 9b, showed a flat surface with little or no plasticity. This lack of toughening when rubber was contained in the major SAN phase was in contrast to the case of the 20/80 nylon 6,6/ABS, wherein a significant amount of toughening was observed. In the latter, rubber particle sizes were 1–2  $\mu\text{m}$ . Furthermore, as was discussed above, the rubber/matrix interface appeared to be significantly stronger than in the EPDM case. Also, the critical cavitation stress could be different in the ABS, because the cavitation could be promoted by the presence of the occluded SAN particles within. Cavitation is necessary to relieve stress triaxiality and promote shear yielding in the surrounding SAN phase.

In contrast to the above when nylon 6,6 was added to SAN, then, rubber was also added but compatibilized so as to be contained within the nylon 6,6 phase there was an improvement in the fracture toughness over that of 20/80 nylon 6,6/SAN. The toughness, however, was still less than pure SAN by itself. Fig. 9a shows that the surrounding SAN exhibited significant plasticity in this case compared to when the rubber phase was contained in SAN.

There are two possible contributions to the increase in toughness where rubber was contained in the minor nylon 6,6 phase. In the first place, as was discussed in the microstructures section, multiple 1  $\mu\text{m}$  size rubber particles were contained in the nylon 6,6 phase. This combined nylon/rubber particle could behave as a toughening agent. Debonding of the internal rubber/nylon 6,6 interfaces would play the role of “internal cavitation” of the nylon 6,6 particle allowing for more shear plasticity in the surrounding SAN. In this way, the weak EPDM/nylon 6,6 interface could be exploited for toughening purposes. The reason that the toughness was still less than SAN is attributed to embrittlement effects due to the debonding at nylon 6,6/SAN interfaces which would result in an embrittlement effect as was shown in our previous study [1,2].

In the 80/20 nylon 6,6/SAN/EPDM system, once again the most favourable situation from the toughness standpoint was when rubber was contained within the minor SAN phase. As discussed above, the combined SAN + rubber particle can provide some degree of toughening such that debonding at SAN/rubber interfaces act as “internal cavitation” so as to provide some plasticity in the surrounding nylon 6,6. However the toughness of this blend was lower than that of nylon 6,6 due to embrittlement effects by debonding at weak nylon 6,6/SAN interfaces. The extensive debonding taking place at the nylon

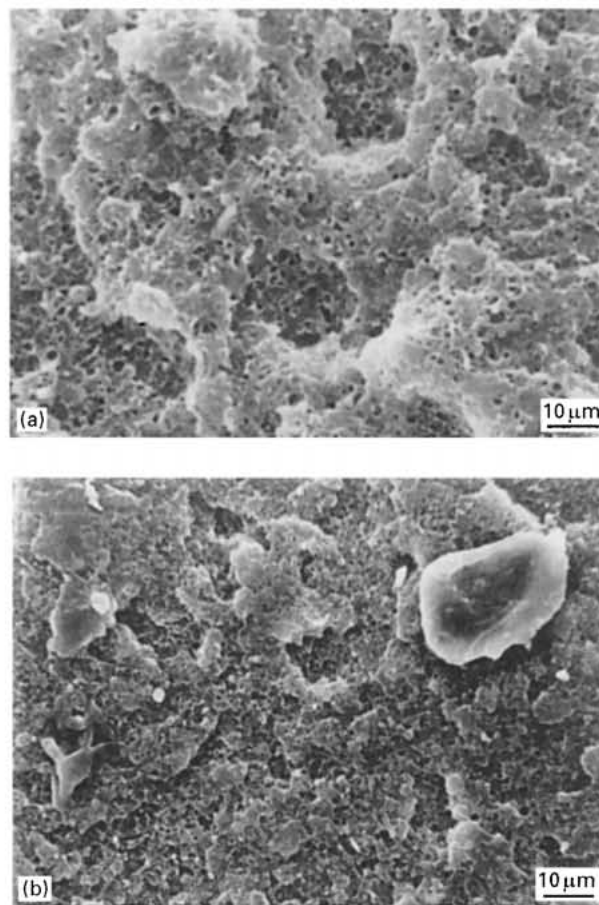


Figure 9 Scanning electron micrograph of the fracture surfaces of (a) 20/80 nylon/SAN with EPDM-N, showing evidence of plastic deformation, and (b) 20/80 nylon/SAN with EPDM-S showing a flat fracture surface.

6,6/SAN interfaces is clearly seen from Fig. 10b. This figure also clearly shows internal debonding within the SAN particle at the SAN/rubber interfaces.

As mentioned in the microstructures section, when EPDM rubber was compatibilized with nylon 6,6 at the 80/20 nylon 6,6/SAN composition, the rubber was distributed in both the nylon 6,6 and the SAN phase. The rubber particle size in the major nylon 6,6 phase was below optimum. Consequently, this rubber could not provide toughening based on established size requirements [4], but instead only contributed to embrittlement by debonding at rubber/nylon 6,6 interfaces just as when only EPDM was added to pure nylon 6,6. Damage formation by debonding at nylon 6,6/SAN interfaces for this material is clearly shown in the fracture surface of Fig. 10a.

It is interesting to compare the toughening in 80/20 nylon 6,6/SAN/EPDM-S wherein rubber was contained within the SAN phase to the toughening in 80/20 nylon 6,6/ABS where also the rubber was contained in the minor SAN phase. Clearly, as seen in Fig. 6, the latter had a significantly higher toughness. This suggests that debonding at SAN/EPDM interfaces within the SAN + rubber particle may not be as effective as internal cavitation of the rubber itself as a mechanism for relieving surrounding triaxial stresses. Another factor is that the rubber particle sizes were small in the EPDM case (0.3–0.5  $\mu\text{m}$ ) compared

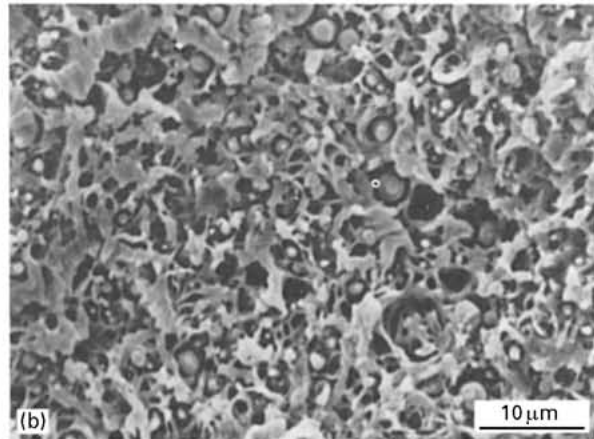
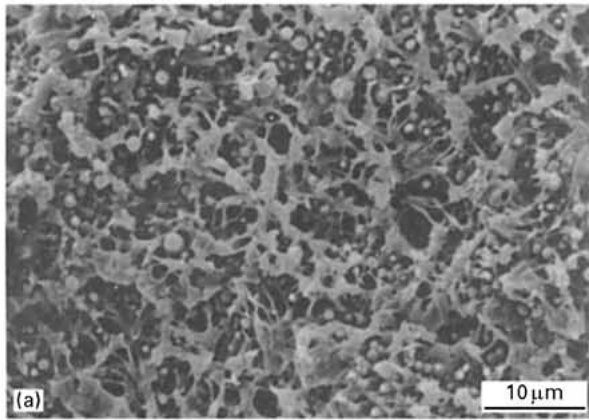


Figure 10 Scanning electron micrographs of the fracture surface of 80/20 nylon/SAN with (a) EPDM-N, and (b) EPDM-S.

to 1 μm in the ABS case, thereby resulting in less than optimum conditions for toughening.

We can summarize the role of rubber particle location on toughening based on the above results. When the rubber particles are located within the minor rigid polymer phase, this combined rigid polymer + rubber particle can act as a toughener, provided the internal rubber particle size is above a critical value. This is in contrast with the case when the rigid polymer phase acts as an embrittling agent when rubber is not present, as shown in the previous part [2]. The ideal situation would be when the rubber particle is contained both in the minor and the major phases. In this way, embrittling effects are minimized and toughening effects are maximized. However, it is critical that the sizes of the rubber particles are sufficiently large and that the rubber/polymer interface is also sufficiently strong.

### 3.2.2. Role of glass fibres

It was shown in Part II [2] that, provided the fibre/matrix interface was strong, there was a possibility of enhancement of plastic deformation in the matrix as the fibres loaded the surrounding matrix in shear. This explained why the fibre-reinforced nylon 6,6/SAN alloys were tougher than the unreinforced nylon 6,6/SAN alloys. The same effect appeared to be operative in the nylon 6,6/SAN/EPDM alloys also. In

other words, when the fibre/matrix interface was strong, the material was toughened when compared to the corresponding unreinforced material. There were three materials in this study which exhibited a weak fibre/matrix interface, as inferred from the clean surfaces of the pulled-out fibres on the fracture surfaces. They were fibre-reinforced SAN/EPDM, fibre-reinforced nylon 6,6/EPDM and fibre-reinforced 20/80 nylon 6,6/SAN/EPDM-N, see Fig. 11 as an example. It shows the clean pulled-out fibres in the last case. In these materials, the addition of fibres had little effect, with the toughness values remaining almost the same.

All other materials had comparatively stronger fibre/matrix interfaces, see Fig. 12a, as an example of a stronger interface, in fibre-reinforced 80/20 nylon 6,6/SAN/EPDM-S. In these materials, the fracture toughness values showed an increase. The increase in the  $J_{1C}$  is attributed to the increased plasticity associated with the fibres combined with diminished degree of debonding at polymer/polymer interfaces. This can be observed by comparing Fig. 10a and b (fracture surfaces of unreinforced 80/20 nylon 6,6/SAN blends with rubber) with Fig. 13a and b (fracture surfaces of

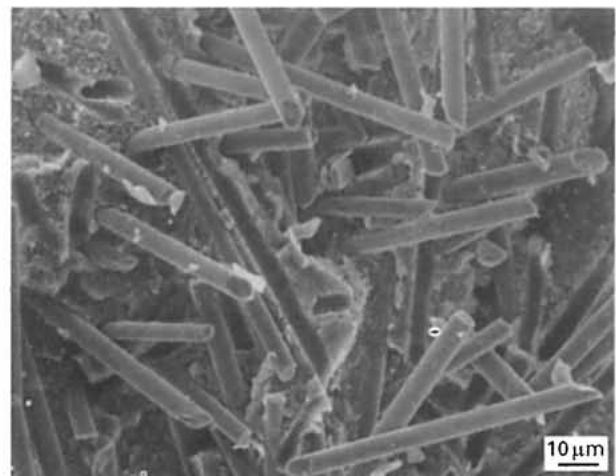


Figure 11 Scanning electron micrograph of the fracture surface of fibre-reinforced nylon/SAN with EPDM-N, showing evidence of a weak fibre/matrix interface.

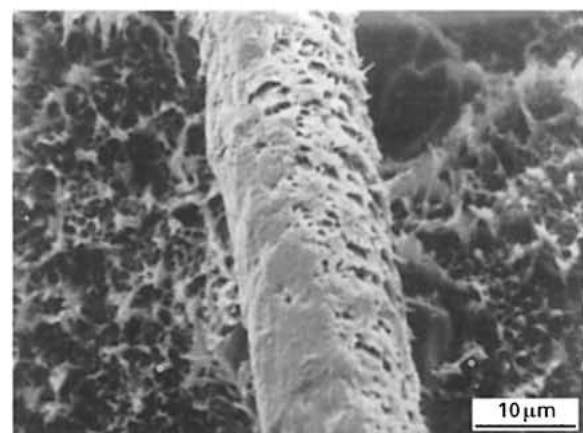


Figure 12 Scanning electron micrograph of the fracture surface of fibre-reinforced 80/20 nylon/SAN with EPDM-S, showing evidence of a strong fibre/matrix interface.



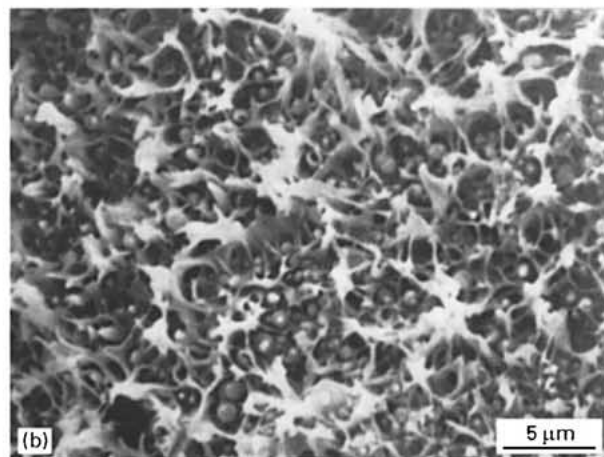
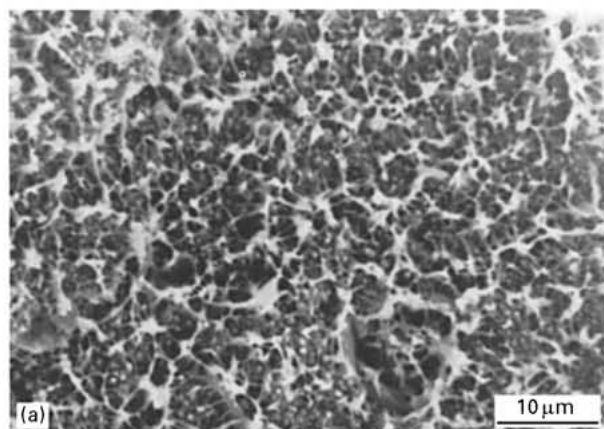


Figure 13 Scanning electron micrographs of the fracture surfaces of the matrix phase of fibre-reinforced 80/20 nylon/SAN with (a) EPDM-N, and (b) EPDM-S, showing evidence of plastic deformation.

fibre-reinforced 80/20 nylon 6,6/SAN blends with rubber). That is, the debonding at the nylon 6,6/SAN and EPDM/matrix interfaces which were observed on the fracture surfaces of the unreinforced materials was largely absent in the presence of fibres. Furthermore, the matrix regions in the composites indicated higher extents of plasticity.

The enhanced plasticity associated with fibres was discussed previously [2] as arising from the higher deviatoric stresses in the vicinity of the fibre/matrix interfaces. By the same token, a higher deviatoric stress component implies also a lower hydrostatic stress component and hence a lower degree of debonding at interfaces. In plastically deforming materials, debonding is sensitive to the level of hydrostatic stresses locally in the matrix. This is a consequence of fibre-induced stress shielding of the matrix discussed in Part I [1] whereby the elongated morphology and high modulus of the fibre result in a greater portion of the applied load to be carried by the fibres. Thus fibres potentially play the dual beneficial role of enhancing plasticity locally while at the same time alleviating embrittlement effects by reducing the tendency for polymer/polymer interfacial debonding.

As was shown above, in the unreinforced materials, a tendency for toughening was shown by 20/80 nylon 6,6/SAN/EPDM-N and 80/20 nylon 6,6/SAN/

EPDM-S, that is, in both cases when rubber was compatibilized with the minor phase component. When these materials were reinforced by fibres, the fibre/matrix interface as mentioned was weak in the 20/80 case but comparatively strong in the 80/20 case. Accordingly, in the 20/80 case the composite had a relatively strong interface in the absence of rubber but a weak interface in the presence of rubber. Therefore, the observed lower toughness of the composite in the presence of rubber is really the consequence of a weakening of the fibre/matrix interface. In contrast, in the 80/20 case, when the fibre/matrix was strong, the extent of rubber toughening was significantly higher in the composite. This is consistent with the results in the previous paper, Part II [2]. It appears that in the presence of the fibres and rubber, plasticity enhancement by shear yielding is greater than when fibres or rubber are present individually. This indicates a positive toughening synergism between rubber and fibres when the fibre/matrix interface is strong, consistent with the previous study.

### 3.3. Propagation toughness

#### 3.3.1. Unreinforced alloys

The results obtained for the propagation toughness of these materials are summarized in Fig. 14. As far as the propagation toughness was concerned, rubber was beneficial in all the blends, in that rubber invariably triggered *R*-curve behaviour and provided substantial increases in the total toughness characterized by  $J_{ss}$ . Hence, in this study also, consistent with the observations made in the previous paper, rubber seemed to play a more important role in the crack growth stage rather than in the initiation stage. As in the initiation stage, it appeared that the presence of rubber in the minor rigid phase was also beneficial to toughening in the crack propagation stage. The highest  $J_{ss}$  values were obtained in the 20/80 nylon 6,6/SAN system wherein the amount of rubber was higher than in the 80/20 nylon 6,6/SAN case. Once again, the higher toughness values could, in general, be correlated with higher levels of plasticity on fracture surfaces. There was no evidence of rubber particle bridging, which has been previously suggested to be a mechanism for providing *R*-curve behaviour.

When rubber was added to pure SAN, *R*-curve behaviour was induced and the total toughness was increased by greater than a factor of four. Comparing the fracture surface of pure SAN, Fig. 7b, with that of SAN/rubber, Fig. 7a, it is evident that whereas the SAN failed in a highly brittle fashion, some plasticity was induced by the rubber, which gives rise to a higher  $J_{ss}$ . As can be seen, there was no evidence of rubber particle bridging. In the 80/20 nylon 6,6/EPDM rubber, the plane strain validity requirement based on the sample thickness [1, 2] was not met, at the  $J_{ss}$  value for this alloy. However, it was clear that *R*-curve behaviour was triggered by rubber although the exact magnitude of crack propagation toughening is not known.

In the polyblends, the rubber-containing materials were clearly higher in  $J_{ss}$  than the corresponding materials without rubber. This was consistent with the



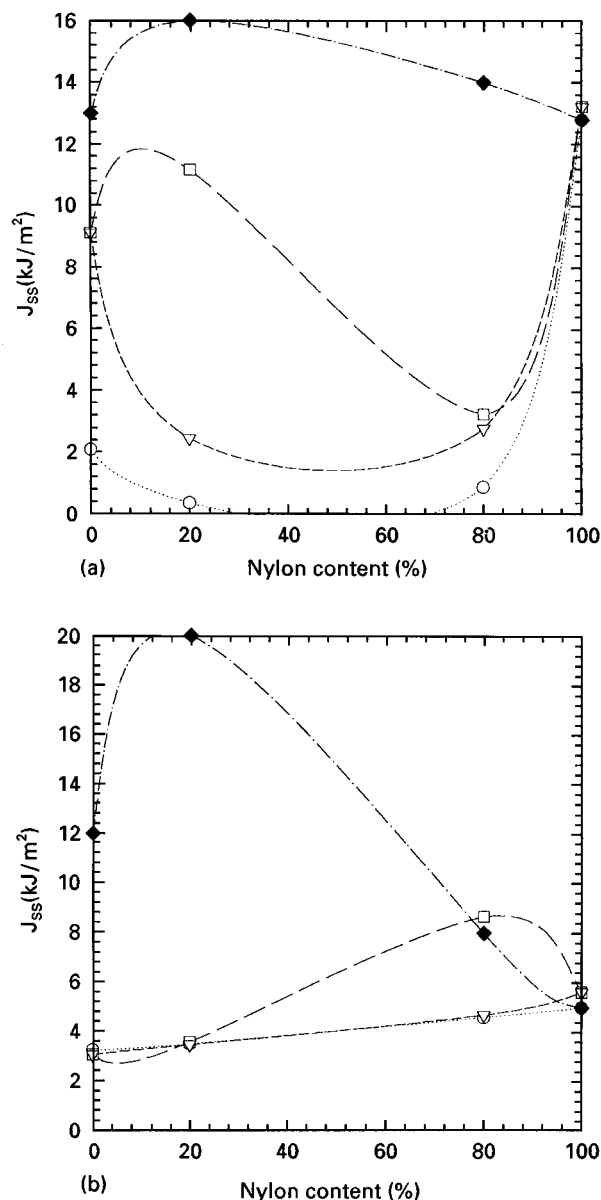


Figure 14 (a)  $J_{ss}$  versus alloy composition for the unreinforced alloys. (b)  $J_{ss}$  versus matrix alloy composition for the fibre-reinforced alloys. (○) No rubber [2], (□) minor phase compatibilized EPDM, (▽) major phase compatibilized EPDM, (◆) ABS [1].

lack of plasticity in the blends in the absence of rubber, as they failed due to extensive debonding at the rigid/rigid interfaces. When rubber was added, plasticity was induced. The material which showed significantly enhanced plasticity (Fig. 9a) was the 20/80 nylon 6,6/SAN with rubber contained in the nylon 6,6. This material, as mentioned, had the highest value of  $J_{ss}$ . When rubber was compatibilized with the SAN, consistent with the flatter fracture surface,  $J_{ss}$  was lowered. In the nylon 6,6-rich blends, as discussed in detail in the initiation toughness results, damage by cracking of nylon 6,6/SAN rigid/rigid interfaces dominated over any matrix (nylon 6,6) plasticity. Although rubber induced the *R*-curve, the quantitative increases in  $J_{ss}$  due to rubber addition were not dramatic, in part because the toughening effects of rubber were counterbalanced by the embrittling effect of the rigid discontinuous second phase (SAN).

### 3.3.2. Fibre-reinforced blends

When fibres were present, *R*-curve behaviour was induced in all materials, even in materials which without fibres did not possess *R*-curve behaviour. These latter materials were the nylon 6,6/SAN materials without rubber. As mentioned above, in the presence of rubber an *R*-curve was present in all the materials. Compared to the unreinforced alloys, fibres contributed to increase in the total toughness when the fibre/matrix interface was strong. As has been discussed [2], this increase is due to the role of fibres in enhancing matrix plasticity. With regard to the role of the EPDM rubber phase on the total toughness of fibre-reinforced composites, it was observed, see Fig. 14, that the EPDM rubber did not contribute to any toughening in the fibre-reinforced SAN-rich alloys. In the fibre-reinforced 80/20 nylon 6,6/SAN alloys, EPDM rubber resulted in substantial toughening when it was contained in the minor SAN phase. The magnitude of this toughening was somewhat larger than when fibres were absent. This again implied, as for the initiation toughness results, that the potential for rubber toughening may be greater in the composites.

### 3.4. Mechanism of rubber/fibre interaction

In the absence of fibres, it was shown that rubber can increase localized plasticity provided the rubber particle/matrix interface was sufficiently strong and the rubber particle size and spacing were suitable. In the presence of a rigid phase, toughness can be maximized by distributing the rubber, ideally, both in the minor as well as the major rigid polymer phases. Rubber in the minor rigid phase alleviated the embrittling effects of the phase, while in the major phase, it can cause shear yielding. Such rubber additions were also shown to trigger *R*-curve behaviour and result in much more toughening in the crack propagation stage.

Fibres by themselves in the absence of rubber cause toughening only when the fibre/matrix interface is strong. Fibres increase deviatoric stresses and thereby enhance matrix plasticity when rubber is present and when the interface is strong. Synergistic interaction can occur with the magnitude of toughening due to rubber greater than when fibres are absent. The mechanism of synergism we propose is that fibres increase deviatoric stresses and thereby enhance rubber-induced plasticity in the vicinity of fibres. That is, shear yielding can occur more readily at rubber particles when fibres are present. Direct evidence of this from TEM studies would be worthwhile to obtain in future studies. Of course, positive synergism of this sort would require that the rubber particle size and spacing, as well as the rubber/matrix interface strength, have all been optimized in the composite. This study does not provide details as to what these optimized values are in the composite when compared to what has already been proposed in unreinforced materials.

Fibres by themselves, like rubber, appeared to always trigger *R*-curve behaviour and thereby generate substantial additional toughening in the crack

wake. In this respect also, fibres behaved similar to rubber. The synergistic interaction between fibres and rubber were also observed in the propagation toughening, namely, that propagation toughening due to rubber can be greater in the presence of fibres when compared to the case when fibres are absent.

A more fundamental insight into toughening resulting from the enhanced plasticity is provided in Part IV [5], wherein we show that toughening is a sum of a crack tip toughness component and a component associated with the crack tip plastic zone.

#### 4. Conclusions

1. EPDM rubber was not as effective a toughening agent as was the butadiene rubber in the ABS system. This is attributed to two main reasons. One, was that the EPDM/matrix interface was much weaker than the rubber/matrix bonding obtained in the ABS system. The other was that the microstructure of the EPDM containing blends appeared not to be optimum, with small, irregularly shaped rubber particles. The better bonding and microstructure in the ABS are attributed to the grafting technique adopted in the manufacture of ABS.

2. In multiphase polymer alloys, the rubber phase could be successfully compatibilized so as to be contained within the major or the minor phase polymer component. One interesting result was that there was a possibility of reducing embrittlement effects due to a second polymer phase by compatibilizing the rubber phase to be contained within that polymer phase. This, in fact, raises the interesting expectation that superior toughness levels could be attained in rigid/rigid polymer alloys by making the rubber reside in both the minor and major phases. The presence of rubber within the minor rigid phase would promote minor phase toughening, thereby counterbalancing the embrittling effects of the minor phase, while the presence of rubber within the major rigid phase would help in shear yielding within that phase. Optimum toughening in this ideal case would require strong polymer/polymer and rubber/polymer interfaces.

3. The toughness values, in general, correlated with qualitatively observed plasticity on fracture surfaces.

This was consistent with the observations of the previous study.

4. The critical role of a strong fibre/matrix interface for toughening was clearly demonstrated in this study. When the interface was strong, fibres toughened the material; whereas when the interface was weak, embrittlement was observed. Also, when the fibre/matrix interface was adequately strong, there was the possibility of synergistic toughening effects between fibres and rubber particles. That is, the extent of rubber toughening was larger when fibres were present than when fibres were absent, in cases where the fibre/matrix interface was strong.

5. In the presence of a strong fibre/matrix interface the role of fibres on fracture resistance of a polymer-polymer blend was two-fold. One, fibres enhanced local matrix plasticity by enhancing the deviatoric stresses and, two, fibres reduced embrittlement effects, essentially because of the lower hydrostatic stresses in the vicinity of fibres and because of matrix stress shielding.

#### Acknowledgements

This project was supported by the National Science Foundation under grant MSS-9201625. The support from Monsanto Chemical Company in terms of raw materials, processing facilities and microscopy is acknowledged. The assistance provided by Mr Larry Gustafson for processing and Dr Dave Alward for the microscopy is also greatly appreciated.

#### References

1. S. V. NAIR, S. C. WONG and L. A. GOETTLER, *J. Mater. Sci.* **32** (1997) 5335-5341.
2. S. V. NAIR, A. SUBRAMANIAM and L. A. GOETTLER, *J. Mater. Sci.* **32** (1997) 5347-5354.
3. "A Testing Protocol for Conducting J-Crack Growth Resistance Curve Tests in Plastics" (1992), ASTM, Philadelphia, USA.
4. S. WU, *Polymer* **26** (1985) 1855.
5. S. V. NAIR, A. SUBRAMANIAM and L. A. GOETTLER, *J. Mater. Sci.*, to be submitted.

*Received 10 October 1996  
and accepted 18 March 1998*