

The effects of phase morphology and adhesion between phases on fracture of ethylene-vinylalcohol copolymer/nylon 6/12 copolymer blends

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The effects of phase morphology and the adhesion between phases of ethylene-vinylalcohol copolymer (EVOH)/nylon 6/12 copolymer blends on the fracture properties were estimated. Films of the blends which were obtained by extrusion processing showed different phase morphologies depending on the composition of the nylon 6/12 copolymer. The morphology of the partially miscible blend (EVOH and nylon 6_f-nylon12_{1-f} where $f=0.8$) was needle-like in appearance. On the other hand the immiscible blend (EVOH and nylon 6_f-nylon12_{1-f} where $f=0.5$) had equiaxed particles of nylon 6/12. The plastic deformation of films of the blends was observed using transmission electron microscopy. Deformation zones were observed for both blends but extensive debonding of particle interfaces was observed in the immiscible blend system. These observations are reinforced by our measurements of the interfacial fracture energy, G_c , between EVOH and nylon 6_f-nylon12_{1-f} made using a double cantilever beam test. G_c decreases monotonically as $1-f$ increases. The fracture toughness of the partially miscible blend film measured at low temperature (-80°C) was higher than that of EVOH alone and there was fractographic evidence of a larger crack tip plastic deformation zone. In contrast, the fracture toughness of the immiscible blend was lower than that of EVOH and there was fractographic evidence of extensive debonding of the second phase nylon particles. This result suggests that it is important to have good adhesion between phases to achieve the optimum fracture toughness of these polymer blends. © 1998 Chapman & Hall

1. Introduction

Recently the applications of ethylene-vinylalcohol copolymer (EVOH) have expanded beyond its primary use as a gas (O_2 and CO_2) barrier polymer to include its use as an aroma or solvent barrier polymer. As these applications become more diverse the mechanical properties of EVOH have to be improved. This is because its modulus and toughness values are not satisfactory for some applications.

Polymer blending is the most useful technique to enhance the mechanical properties without decreasing the performance of the matrix. Blends of EVOH with other homopolymers, for example polyethylene, polypropylene, nylon 6, nylon 6-12, nylon12 and polyethylene-terephthalate, have been studied [1–3]. Among these, the blend of EVOH with nylon 6 had

a good miscibility and its mechanical properties were interesting [1]. A hydrogen bonded interaction between $-\text{OH}$ and $-\text{NH}-$ makes the blend miscible in the melt [2] and the modulus decreases as desired with small additions of nylon 6 [1]. However, the processing of such blends with nylon6 is not practical because a gel forms due to the reaction between $-\text{OH}$ and $-\text{NH}_2$ under the extrusion conditions. Blends with nylon 6-12 or nylon12 showed phase separation on an unacceptably large scale [3]. In addition their mechanical properties were not improved.

Binary blends between random copolymers have the possibility of optimizing the miscibility of blends by controlling the composition of both random copolymers. Recently many nylon random copolymers have become commercially available [4]. Nylon

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6_f-nylon12_{1-f} random copolymers can be expected to improve the processability of blends for EVOH because of the lower melting point and lower miscibility of nylon 6_f-nylon12_{1-f} with EVOH. Some of these random copolymers are recommended to be blended with EVOH [1]. However, the detailed effects of the phase morphology and the adhesion between phases on the mechanical properties of the blend are unknown.

In this study EVOH which contained 32 mol % of ethylene was chosen for blends with nylon 6_f-nylon12_{1-f} where *f* could be varied from 0 to 1. Extruded films of blends of EVOH (80 wt %) with random copolymers of nylon 6_f-nylon12_{1-f} with two different compositions, *f* = 0.8 and *f* = 0.5, were prepared. The polymer phase morphology, the adhesion between phases and the fracture toughness of these blends were investigated.

2. Experimental procedures

2.1. Materials

The EVOH and nylon 6_f-nylon12_{1-f} copolymers used in this study are listed in Table I. Blend films with a thickness between 85–100 μm were prepared by extrusion processing using a die temperature of 235 °C from chips preblended at the same extrusion temperature.

2.2. Electron microscopy

Thin films, 1 to 2 μm thick, of EVOH and blends of EVOH and nylon 6_f-nylon12_{1-f} copolymer were obtained by microtoming. The thin films were bonded to a ductile Cu grid (1 × 1 mm grid squares) with cyanoacrylate adhesive. The grid was deformed at room temperature. The deformed films were stained with OsO₄ vapour which preferentially stains the nylon rich phase and were then observed by transmission electron microscopy under tension. The procedures for handling the films follow those described previously for solvent cast films [5].

2.3. Measurement of the adhesion between EVOH and nylon 6-nylon12 copolymer

The adhesion between EVOH and nylon 6/12 copolymer, as represented by the interfacial fracture toughness, *G_c*, was measured using a razor blade and a double cantilever beam (DCB). This DCB method

TABLE I Polymer sample

Polymer	No.	Manufacturer
EVOH (Et = 0.32)	F101	Kuraray
Nylon (f = 1.00)	CM1017	Toray
Nylon (f = 0.80)	CR-9	EMS
Nylon (f = 0.50)	CA-6E	EMS
Nylon (f = 0.50)	CF-6S	EMS
Nylon (f = 0.75)	7125U	Ube Industry

Et: Ethylene mole fraction in EVOH.

f: Nylon 6 mole fraction in nylon 6_f-nylon12_{1-f}.

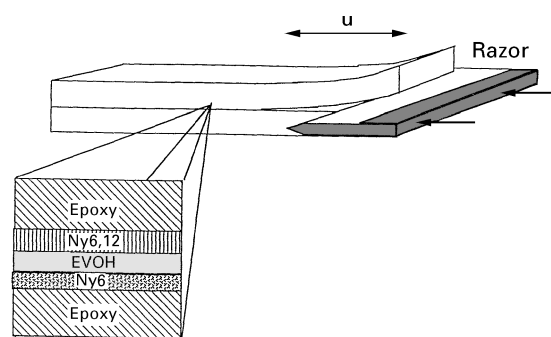


Figure 1 Schematic of the experiment to measure the interfacial fracture energy *G_c*.

has been developed [6] to measure *G_c*, the interfacial fracture energy, for the interface between two of glassy polymers [7–9] or glassy polymer and glass [10]. However, it has not previously been applied to semi-crystalline polymers because these materials are not transparent and they thus do not allow the crack length to be determined optically. In this investigation a new variation of the DCB method is introduced. The beams were produced from an epoxy which consists of a stoichiometric mixture of the diglycidyl ether of bisphenol A and triethylenetetramine that are transparent (similar slabs of EVOH and nylon 6_f-nylon 12_{1-f} are opaque). To ensure flat surfaces the epoxy slabs were cast in moulds constructed from glass sheets sandwiched around a 1.5 mm thick teflon spacer. The glass was coated with a self-assembled monolayer formed from octadecyltrichlorosilane to serve as a mould release. Further details of the procedure are given by Norton [11]. In order to obtain good adhesion between the epoxy and nylon a two step curing procedure was applied. After precuring the epoxy at 50 °C for 2 h nylon 6_f-nylon12_{1-f} copolymer was spun cast on each epoxy slab from a 5 wt % solution of the polymer in 1,1,1,3,3,3-hexafluoro-2-propanol. Then the slabs were cured at 130 °C for 2 h. A film of EVOH was then inserted between two nylon copolymer coated epoxy slabs. The sandwich was welded in a hot press (at 235 °C for 3 min) under just enough pressure to bring the surfaces into good contact. Then the sandwich was rapidly cooled by setting it on a metal slab. After annealing at 70 °C for 1 h to crystallize the nylon 6_f-nylon12_{1-f} copolymer layer, the slab sandwich was cut into strips of 7 mm in width.

The sandwich layer structure of the double cantilever beam specimen is shown in Fig. 1.

A razor blade was inserted at the interface and driven at constant rate of $1 \times 10^{-5} \text{ m s}^{-1}$. The fracture energy *G_c* was computed from the length, *a*, of the measured steady state crack ahead of the razor blade using the formula given by Creton *et al.* [12].

2.4. Measurement of the fracture toughness of films of the blends

The critical stress intensity factor, (*K_{Ic}*), of sample films were measured using a specimen with a single-edge-notched geometry at a testing temperature of –80 °C. The dimensions of the strips between

the grips of the tensile machine were 50 mm in length by 25 mm width. The notch, 1–8 mm long, was cut into one side of the strip with a fresh razor blade at -40°C . The K_{Ic} values were calculated using linear elastic fracture mechanics techniques which give

$$K = \beta\sigma(\pi a)^{1/2} \quad (1)$$

where the geometry factor β is given by

$$\beta = 1.12 - 0.23(a/w) + 10.56(a/w)^2 - 21.74(a/w)^3 + 30.42(a/w)^4$$

and where σ is the tensile stress based on the un-notched area and w is the strip width [13]. The Young's modulus of a sample film was measured at -80°C in tension so that the critical strain-energy release rate (G_{Ic}) could be computed from K_{Ic} .

3. Results and discussion

3.1. Morphology of blend films

The blend of EVOH (80 wt %) and nylon 6_f-nylon12_{1-f} where $f = 0.8$ (20 wt %) seems to be on the edge of miscibility. Fig. 2 (a and b) shows cross-sections of this blend observed by transmission electron microscopy (TEM). Obviously this blend is a partially miscible blend which consists of a matrix of an EVOH rich phase and particles of a nylon 6_f-nylon12_{1-f} rich

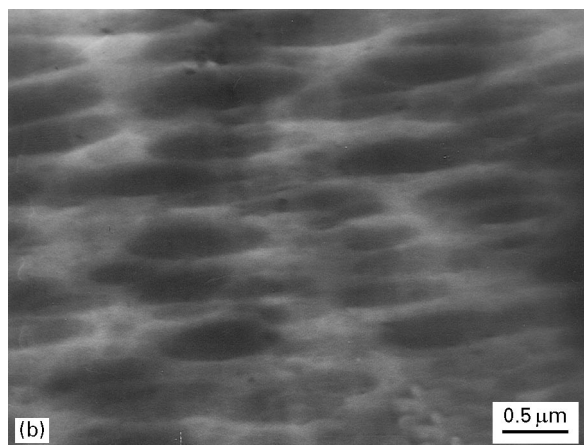
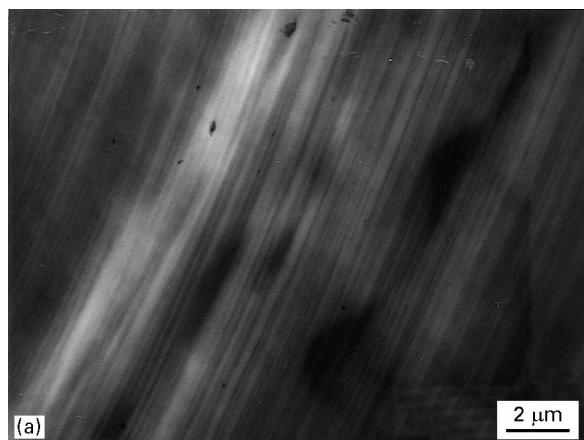


Figure 2 Transmission electron micrographs of the blend of EVOH (80 wt %) and nylon 6_f-nylon12_{1-f} where $f = 0.8$ (20 wt %); (a) section parallel to the machine direction and (b) section transverse to the machine direction.

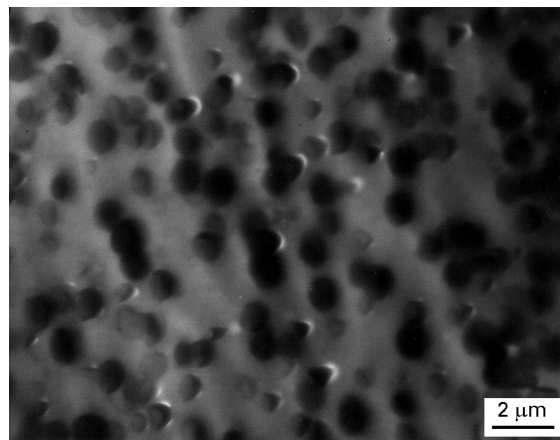


Figure 3 Transmission electron micrograph of the blend of EVOH (80 wt %) and nylon 6_f-nylon12_{1-f} where $f = 0.5$ (20 wt %). Section parallel to the machine direction.

phase where $f = 0.8$. The nylon rich phase particles are needle-like and are oriented in the machine direction. The lateral dimensions of these needles are less than 1 μm . In contrast the blend of EVOH (80 wt %) and nylon 6_f-nylon12_{1-f} where $f = 0.5$ (20 wt %) appears to be strongly phase separated. Fig. 3 shows a cross-section of this blend parallel to the machine direction. The particles of nylon are equiaxed and relatively large (approximately 1 μm diameter) in comparison to the much smaller needles of the partially miscible blend.

3.2. Observation of deformed thin films using TEM

Thin films of these blends were deformed on Cu grids and examined by TEM. The TEM method is very useful for estimating the adhesion between phases of polymer blends [5, 14]. This method will also give us some information on fracture mechanisms under the plane stress conditions which prevail in these thin films. Fig. 4 (a–c) shows the deformation structure of thin films of the blends compared with that of a thin film of EVOH. At room temperature these thin films deformed by shear deformation through the thickness of the film and formed plane stress deformation zones. While the partially miscible blend deformed without the interface between the phases debonding, the blend of EVOH (80 wt %) and nylon 6_f-nylon12_{1-f} where $f = 0.5$ (20 wt %) had debonding at the interface between the particles and the EVOH matrix. This result suggests that the blend of EVOH and nylon 6_f-nylon12_{1-f} where $f = 0.5$ (20 wt %) is strongly immiscible, in agreement with the TEM observations of the particle morphology in the undeformed films (Fig. 3), with a large Flory interaction parameter, χ , that produces a narrow interface between phases across which there is little entanglement and thus minimal stress transfer.

3.3. Interfacial fracture energy between EVOH and nylon 6-nylon12 copolymers

In order to quantify the adhesion between the EVOH and the nylon copolymer phases, the DCB test was

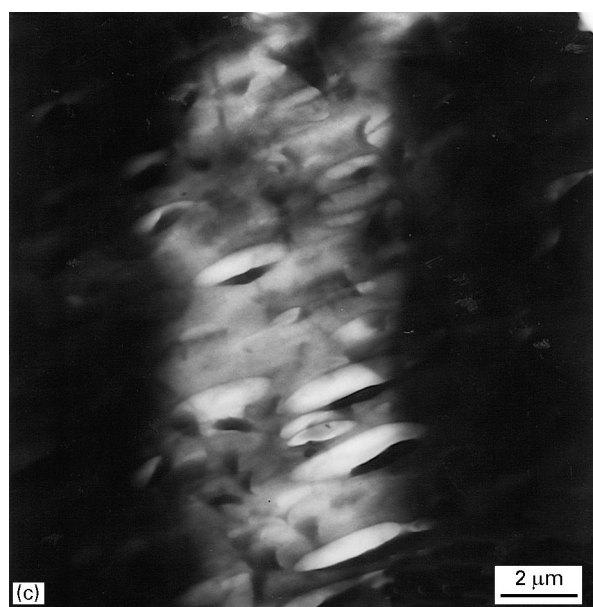
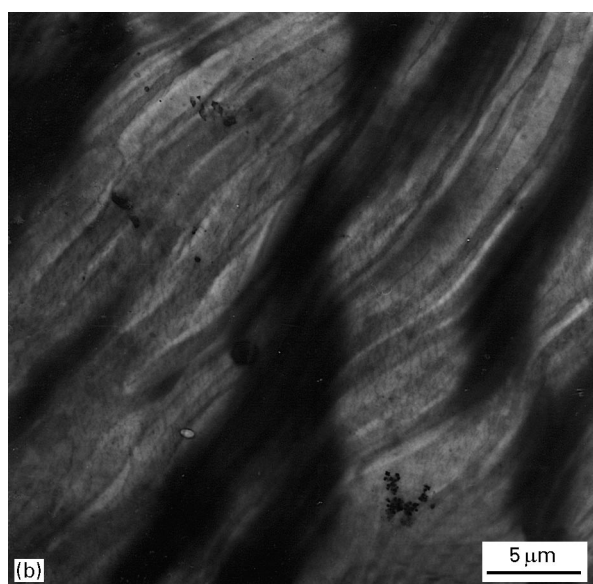
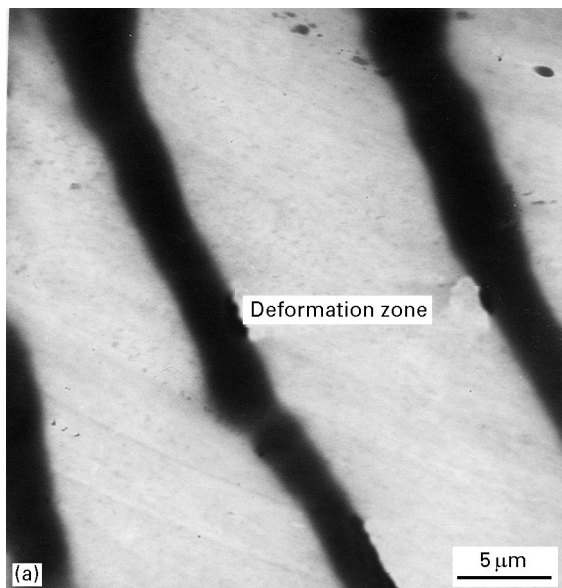


Figure 4 Transmission electron micrographs of deformed thin films of (a) EVOH, (b) blend of EVOH (80 wt %) and nylon 6_f -nylon 12_{1-f} where $f = 0.8$ (20 wt %), (c) blend of EVOH (80 wt %) and nylon 6_f -nylon 12_{1-f} where $f = 0.5$ (20 wt %).

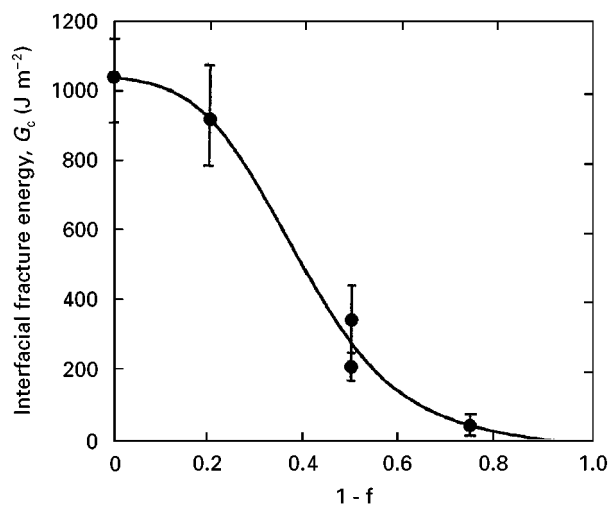


Figure 5 Interfacial fracture energy G_c versus $1 - f$ where f is the fraction of nylon 6 in the nylon 6-nylon12 copolymer.

carried out to measure the fracture energy, G_c , of the interface. Fig. 5 shows the effect of the composition f of nylon 6_f -nylon 12_{1-f} copolymers on the interfacial fracture energy. We find that G_c decreases monotonically as $1 - f$ increases. For $G_c > 600 J m^{-2}$ ($1 - f < 0.3$) the interface fractured in a stick-slip manner, and this mode of fracture results in a larger scatter for these points. From these results it is clear that the interface in the partially miscible blend ($f = 0.8$) has good adhesion. The value of G_c for the interface between EVOH and nylon 6_f -nylon 12_{1-f} with $f = 0.5$ is smaller by a factor of approximately three. The decrease in G_c observed from $f = 0.8$ to $f = 0.5$ is consistent with the TEM observations that interfaces of particles in the $f = 0.8$ blend survive plastic deformation while those in the $f = 0.5$ blend show extensive debonding. The monotonic decrease in G_c with $1 - f$ suggests that the Flory parameter, χ , increases monotonically with $1 - f$. Given that the EVOH is vinyl-alcohol rich (68 mol %), such a monotonic increase in χ as the non polar nylon12 content of the copolymer is increased is not unreasonable.

3.4. Fracture toughness of blend films at low temperature

EVOH is not a brittle polymer at room temperature. However, the toughness of EVOH at low temperature is generally lower than that of the nylons. We have investigated whether blending the nylon 6_f -nylon 12_{1-f} copolymers with EVOH leads to improved fracture toughness of the blends at low temperatures. A temperature ($-80^\circ C$) below the ductile-brittle transition of EVOH was chosen as the temperature at which the fracture toughness was measured. Table II shows the critical stress intensity factors (K_{Ic}) and critical strain energy release rates (G_{Ic}) of EVOH and the blends of EVOH and the two nylon 6_f -nylon 12_{1-f} copolymers. K_{Ic} was measured using a single edge notch sample geometry (strip width w) and did not depend on crack length a as long as $0.10 < a/w < 0.20$. The fracture toughness of the partially miscible blend ($f = 0.8$) was higher than that of

TABLE II Fracture toughness of extruded films

Sample	Critical stress intensity factor K_{Ic} (MPa m ^{1/2})	Young's modulus E (MPa)	Critical strain energy G_{Ic} (kJ m ⁻²)
EVOH	4.0	9906	1.6
Partially miscible blend	4.7	7854	2.9
Immiscible blend	3.2	7979	1.3

Partially miscible blend: EVOH (80 wt %)/nylon 6_r-nylon12_{1-f} where $f = 0.8$ (20 wt %).

Immiscible blend: EVOH (80 wt %)/nylon 6_r-nylon12_{1-f} where $f = 0.5$ (20 wt %).

EVOH, while that of the immiscible blend ($f = 0.5$) was lower. From these results it is speculated that fracture toughness of blend films are related to the adhesion of their interface between phases. Both the Young's moduli are smaller than that of EVOH. This suggests that blending of nylon 6_r-nylon12_{1-f} with EVOH is effective in softening the sample.

3.5. Fracture surface of the films

The reason for the lower fracture toughness of the immiscible blend is apparent from examination the

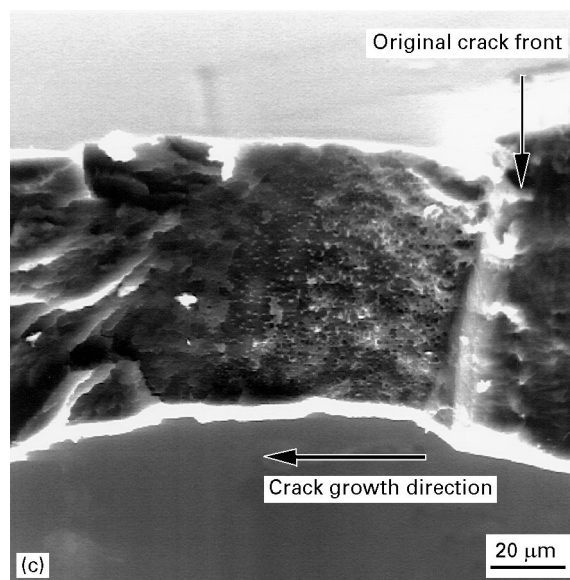
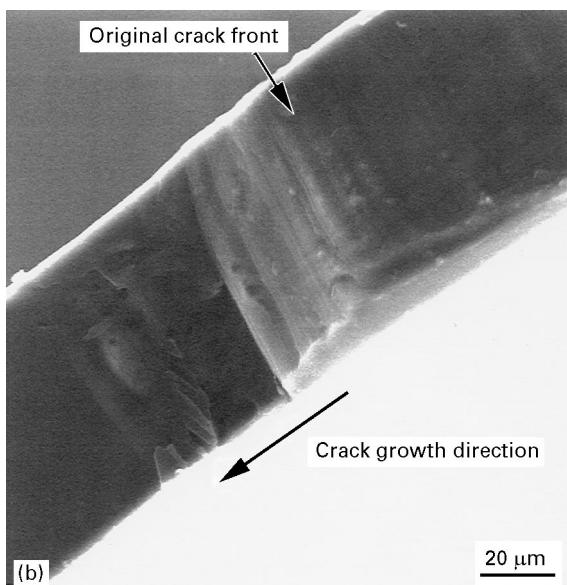
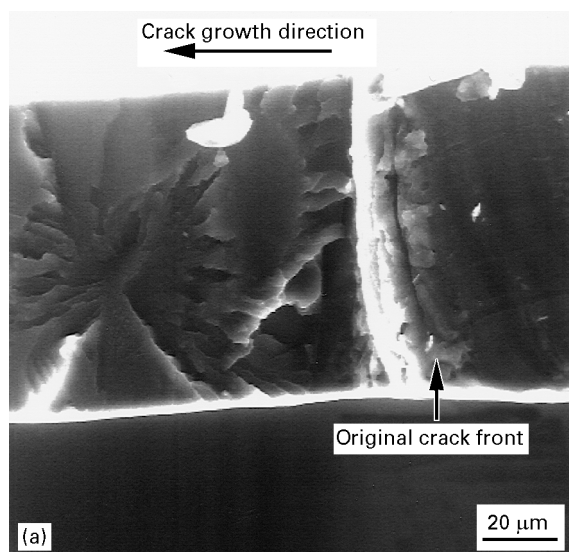


Figure 6 Fracture surfaces of polymers after fracture at -80°C . (a) EVOH, (b) blend of EVOH (80 wt %) with nylon 6_r-nylon12_{1-f} where $f = 0.8$, (c) blend of EVOH (80 wt %) with nylon 6_r-nylon12_{1-f} where $f = 0.5$.

fracture surfaces of the specimens. Fig. 6(a-c) shows the fracture surfaces in the vicinity of the original crack front that were produced by the fracture at -80°C . On the fracture surface of the partially miscible blend there is fractographic evidence of a larger crack tip plastic deformation zone than for EVOH. In contrast the fracture surface of the immiscible blend ($f = 0.5$) shows fractographic evidence of extensive debonding of the second phase nylon particles. This extensive debonding apparently weakens the plastic zone immediately ahead of the crack tip and leads to premature failure of this zone and thus a lower fracture toughness value.

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