Compatibilizing effect of ethylene-vinyl acetate-acrylic acid copolymer on nylon 6/ethylene-vinyl acetate copolymer blended system: mechanical properties, morphology and rheology

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A polymer blended system of nylon 6 and ethylene-vinyl acetate copolymer (EVA) compatibilized with ethylene-vinyl acetate-acrylic acid ternary copolymer (EVAA) has been studied. EVA is incompatible with nylon 6, however, the combination of the EVA and EVAA results in compatibilized blends with good toughness. The compatibilization of EVAA is achieved by the similar structure with EVA and the reaction between its carboxylic groups and amine groups of nylon 6. The ternary blends were characterized through the mechanical, morphological and rheological property investigations. The dramatic increasing in impact strength and the fine dispersing of EVA in nylon 6 matrix demonstrated a good compatibilizing effect of EVAA on the blends of nylon 6 and EVA. © *2001 Kluwer Academic Publishers*

1. Introduction

Nylon 6 is an important engineering plastic with good performance, which has found wide application in the fields of vehicles, electronic appliances and sophisticated machinery and has been used to replace metal materials in machinery [1]. However, it is brittle, especially when flaws are present and/or in low temperatures, its application is greatly limited [2, 3]. Therefore, the toughening of nylon 6 has attracted a great deal of attentions from both research organizations and industry. A large number of efforts were made to toughen nylon 6 through blending with elastomers. It is well known that elastomers are usually incompatible with nylon 6, the impact strengths of the nylon 6 and elastomer blends are hardly higher than that of pure nylon 6 [4, 5]. For this reason, the compatibilization between nylon 6 and the elastomer components becomes a key in the toughening of nylon 6 [6, 7]. One of the approaches is the reactive extrusion of nylon 6 with a maleic anhydride grafted elastomer. The maleic anhydride group reacts with the amine groups of nylon 6 and thus bridge nylon 6 and elastomer, and results in an improved toughness [8–10]. Generally employed elastomers include ethylene-propylene-diene copolymer (EPDM), styrene-butadiene-styrene block copolymer (SBS), styrene-ethylene-butadiene-styrene block copolymer (SEBS), etc [11–15].

Blending nylon 6 with modified ABS is another possibility. ABS possesses an incomplete core-shell structure with a core of styrene-butadiene copolymer and a shell of styrene-acrylonitrile copolymer. In order to improve the miscibility of nylon 6 and styrene-acrylonitrile copolymer, the common practice is to graft glycidal (math)acrylate onto the shell of ABS, or to graft acrylamide onto nylon 6 chains [16–19]. A core-shell particle was recently developed and employed to toughen nylon 6. The core-shell particles possess a flexible core of poly(butyl acrylate) (PBA) and a glassy shell of poly(methyl methacrylate) (PMMA). Since PMMA and nylon 6 are not miscible, the epoxy resins were employed as the compatibilizer [20–22].

In this paper, a copolymer of ethylene and vinyl acetate was proposed as a novel impact modifier for nylon 6. Ethylene-vinyl acetate copolymer (EVA) is flexible, cheap and easily available. However, it is not compatible with nylon 6. An ethylene-vinyl acetate-acrylic acid copolymer (EVAA) developed by Du Pont was adopted as a compatibilizer of nylon 6/EVA blends. The mechanical properties, morphology and rheological performance of the nylon 6/EVA/EVAA blended systems constitute the content of this paper.

2. Experimental
2.1. Materials

Nylon 6 (commercial grade: 1013B, number average molecular weight: 25,000) was supplied by UCB Chemical Co., Ltd., Japan. EVA, with the content of 24 wt% vinyl acetate, was supplied by Beijing Organic

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Chemical Co., Ltd., China. EVAA (commercial name: Elvaloy) with the content of 13 wt% vinyl acetate and 2.5 wt% acrylic acid, respectively, was purchased from Du Pont Chemical Co., Ltd., USA.

2.2. Preparation of blends
Nylon 6 was dried for 12 h and preserved in an airtight aluminum-polyethylene package before use. Blends of various components were mixed with a WP 35 mm twin-screw extruder (L/D = 35). All the ingredients were tumble-blended and fed through the throat of the extruder. Barrel and die temperature was set from 205 to 240°C, and the rotation speed of screw was set to 180 rpm. The blends passed through a cooling water bath and were palletized. All the extrusion parameters were changed as little as possible from one formulation to another.

2.3. Mechanical properties test
Tensile property was measured with an Instron Universal Testing Machine (Model 1130) according to ASTM D638 at room temperature. Notched Izod impact strength was measured with a SUMITOMO impact tester according to ASTM D256. The thickness of Izod impact specimens was 1/8 inch, and impact energy was 4 J. Five measurements were done for each data point in all mechanical property testing.
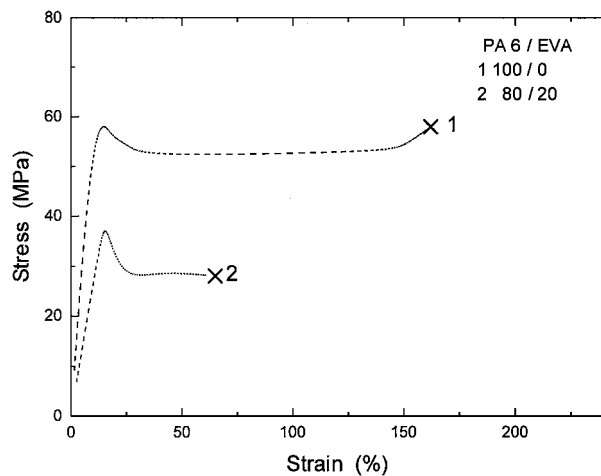
2.4. Scanning electron microscopy observation
The sample bars were fractured in liquid nitrogen. The fractured surface was etched with boiled mixture of toluene and methyl-ethyl-ketone toluene at the ration of 60/40 (wt/wt) for 2 h, then coated with an Au/Pd alloy, and subsequently observed under SEM (Cambridge S250). The photomicrographs of SEM were analyzed with an image analyzer (IBAS 1/2).

Figure 3 Compatibilizing effect of EVAA on notched impact strength of nylon 6/EVA blends.

Figure 1 The stress-strain curves of nylon 6 and nylon 6/EVA binary blend.
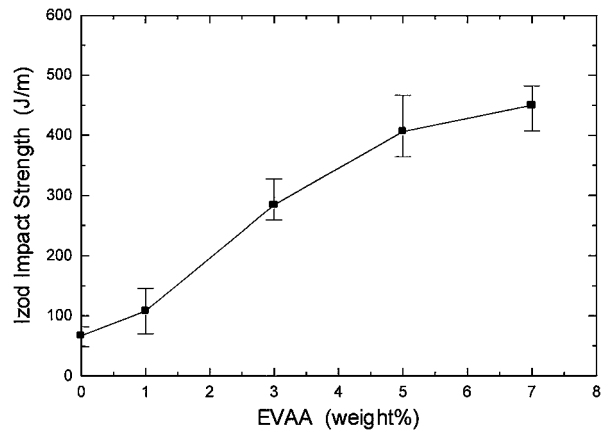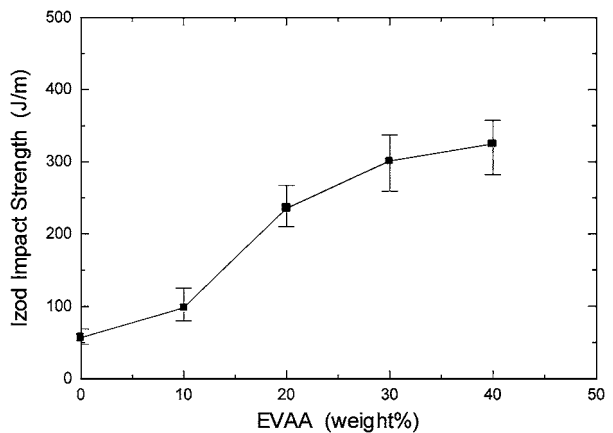

Figure 4 Notched impact strength for nylon 6/EVAA binary blends.

Figure 2 Compatibilizing effect of EVAA on tensile strength and elongation at break of nylon 6/EVA blends.
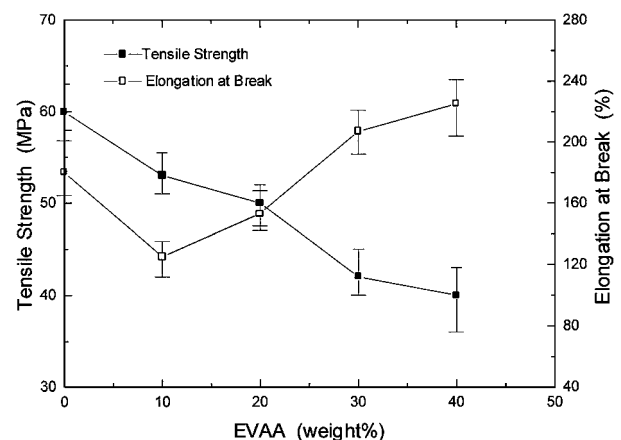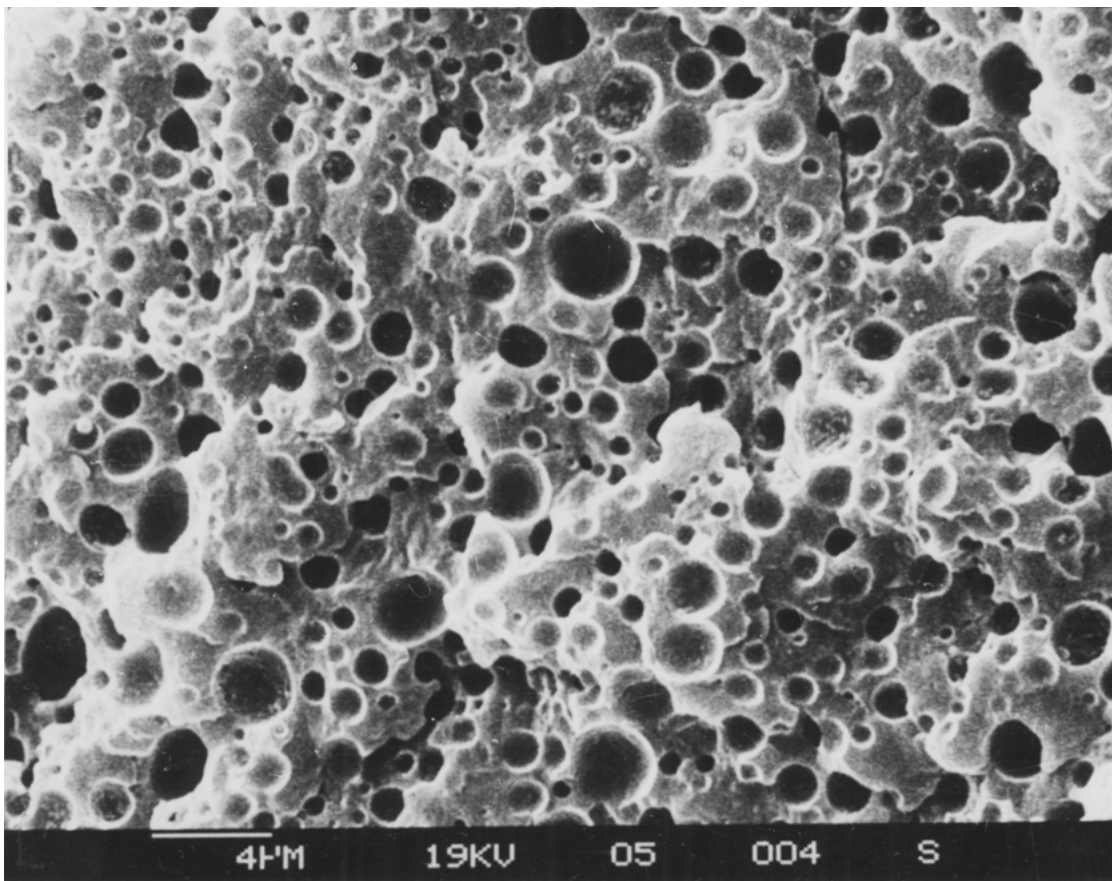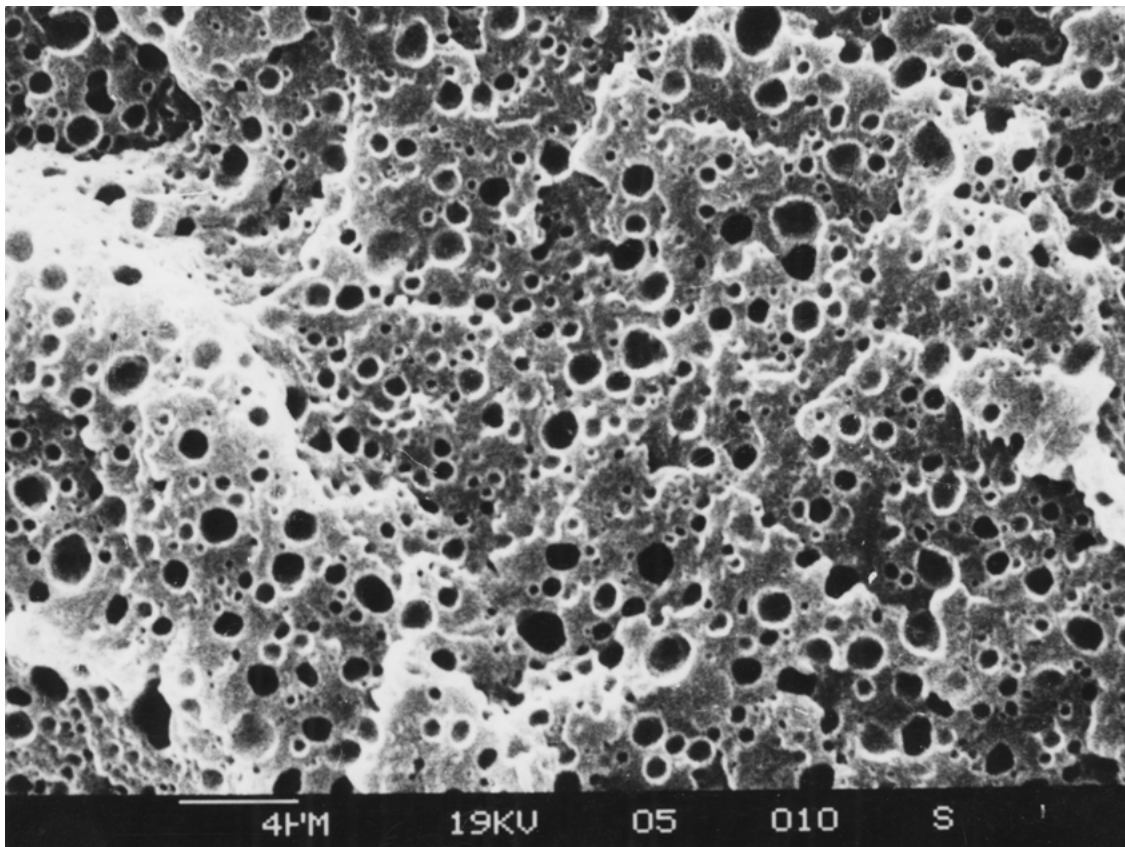

Figure 5 Tensile strength and elongation at break for nylon 6/EVAA binary blends.

(a)

(b)

Figure 6 SEM photographs of the fracture surface of the nylon 6/EVA blends in the ratio of 80/20 (wt/wt) with EVAA content of: (a) 0 wt%, (b) 1 wt%, (c) 3 wt%, (d) 5 wt%, and (e) 7 wt%. (*Continued*)

2.5. Rheological properties measurement

The apparent viscosity at various shear rates were measured with a capillary rheometer (TOYOSEIKI Mode 1B) at 240°C with a capillary with an L/D ratio of 43/1. The melt flow index was measured according to ASTM D1238 at 250°C with a 2,160 g weight.
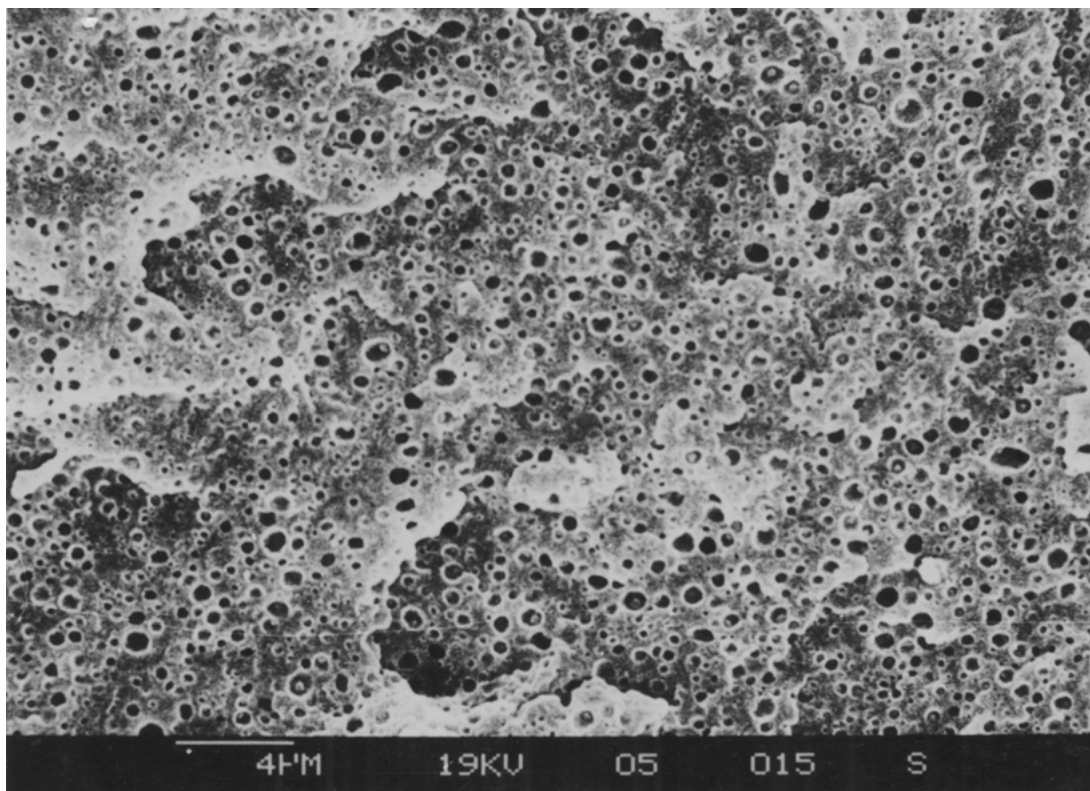
3. Result and discussion

3.1. Mechanical properties

The incompatibility of nylon 6/EVA blends is reflected from the stress-strain curve in Fig. 1. Whereas pure nylon 6 possesses a tensile strength about 70 MPa and an elongation at break over 160%, nylon 6/EVA blend
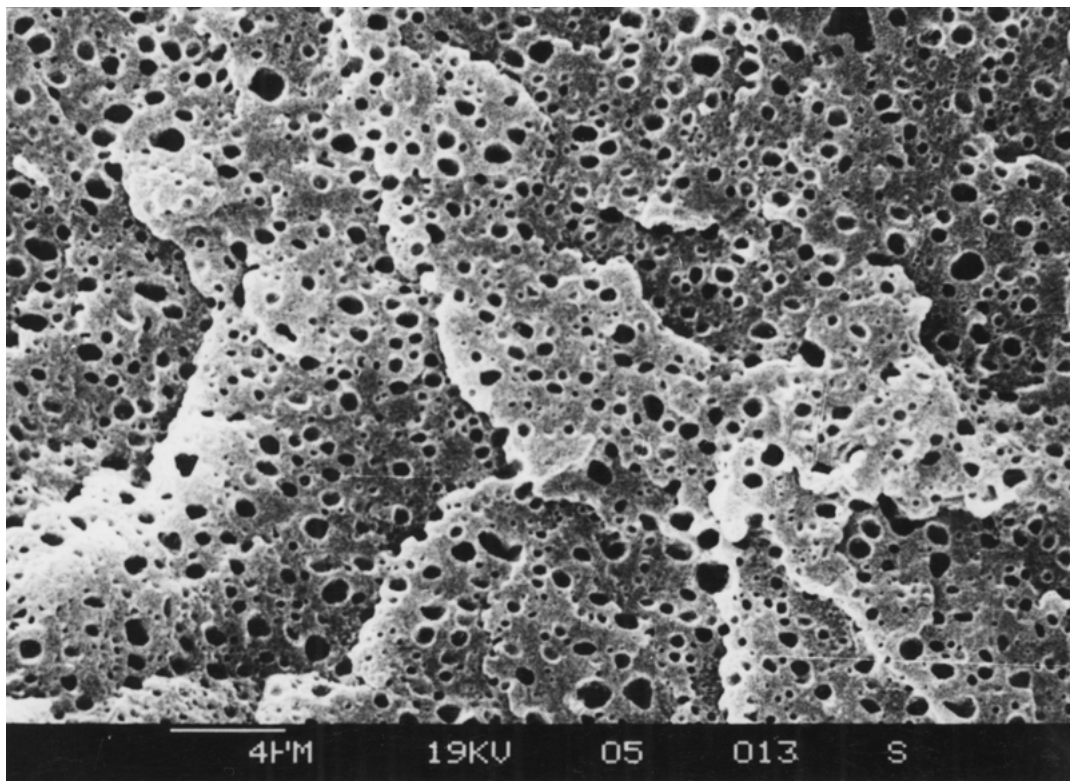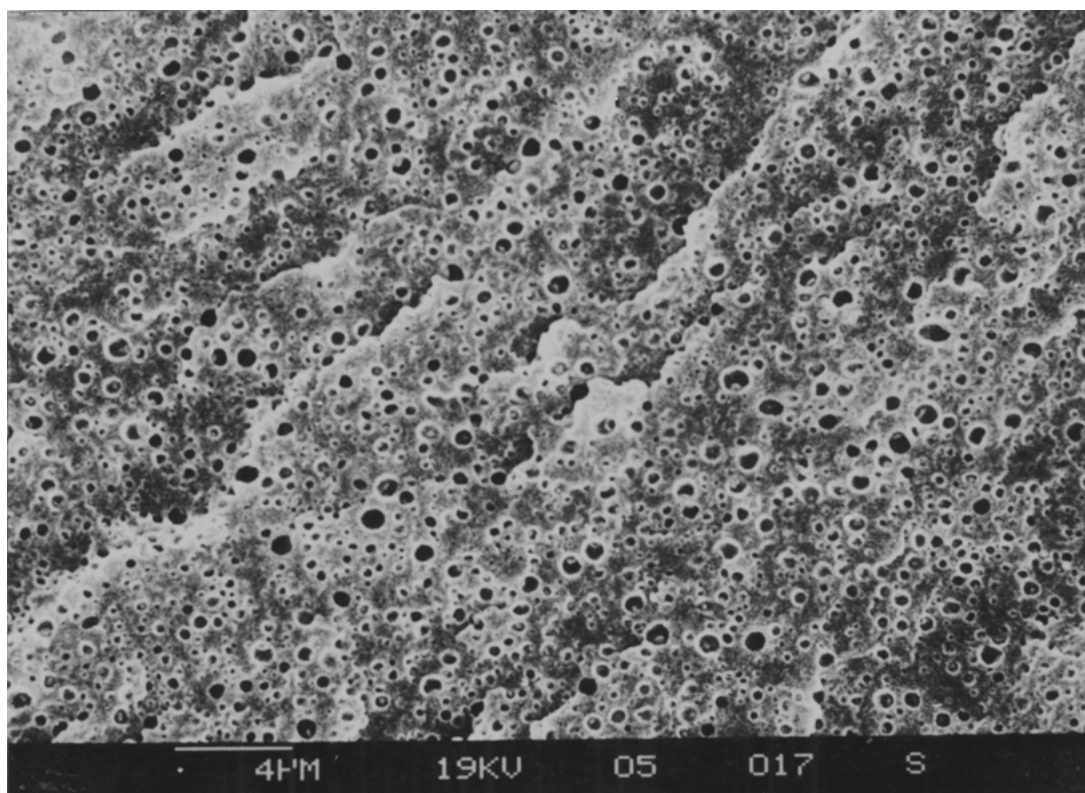
(c)

(d)

Figure 6 (*Continued*).
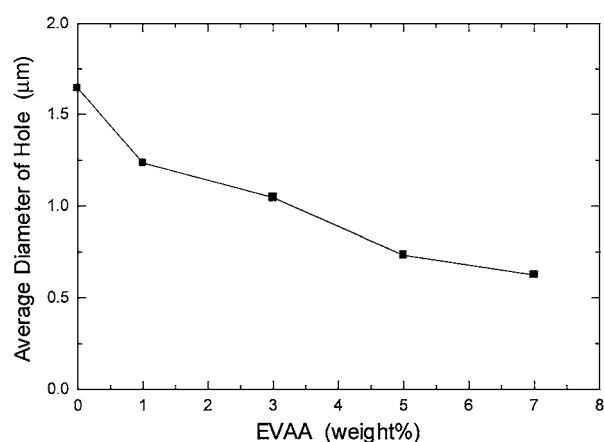
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(e)

Figure 6 (*Continued*).

Figure 7 Average hole size on SEM photographs of the fracture surface.

in the ratio of 80/20 (wt/wt) has only poor values in both cases. The decrease in tensile strength is partially because of the dilution of the hydrogen bonds among nylon 6 by the segments of EVA, and more importantly, partially because of the repulsion between the polar segments of nylon 6 and the non-polar ones of EVA. Also for the latter reason, the elongation at break decreases. The compatibilization, however, can be improved by introducing EVAA, a copolymer of ethylene and acrylic acid. Because of the similarity of chain structure, EVAA is miscible with EVA in all proportions. The acrylic acid can react with amine group of nylon 6, which makes EVAA a good compatibilizer between nylon 6 and EVA. Indeed, as shown in Fig. 2, the tensile properties of nylon 6/EVA blends were significantly improved by introducing EVAA. The elongation at break achieved a high value of 200% when 7 wt% EVAA was added.

In other words, EVAA increased the adhesion at interfaces of different domains, and reduced the repulsion among the segments of nylon 6 and EVA. The latter imparts the former greater mobility. The compatibilization of EVAA also improved the tensile strength of uncompatibilized nylon 6/EVA blend. One may notice in Fig. 2, compared with 40 MPa for uncompatibilized ones, the strength of 54 MPa was achieved. However, because of the incorporation of flexible components that is amorphous, the tensile strength of the blends was still lower than pure nylon 6. The decrease in crystallinity of nylon 6 resulted by blending may also play a role.

A more profound improvement in mechanical properties was seen in toughness in Fig. 3. The notched impact strength for pure nylon 6 is about 47 J/m [1]. Nylon 6/EVA blend at the ration of 80/20 (wt/wt) possesses notched impact strength a little higher than the neat nylon 6. This "a slight higher" contrasts the case for the tensile strength. As seen above, blending with EVA, which is incompatible with nylon 6, results in a decrease of tensile strength, yet causes a slight increase in notched impact strength. One may conclude that the low notched impact strength of nylon 6 is owing to the poor mobility of the segments resulted from the high crystallinity. The introduction of EVA increases the proportion of the amorphous part and increases the mobility of the segments. At the same time, because of the incompatibility, many weak interfaces were produced, through which the cracks may propagate. Two effects thus control the notched impact strength: segment mobility and the weak interface with the former being a little bigger. The compatibilizer, EVAA, constitutes bridges between the two components and makes

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the links stronger. It is seen that sharp increases in notched impact strength were obtained. When 7 wt% of EVAA is introduced, the notched impact strength can be as high as that of 460 J/m.

It is interesting to notice that, as shown by Figs 4 and 5, EVAA itself constitutes a good impact modifier for nylon 6, and the toughening effect is obvious. However, when increasing amount of EVAA was introduced, the blending system underwent a brittle-ductile transition. When the content of EVAA is about 20 wt%, the notched impact strength reached as high as 320 J/m, and the blends became tougher with the increasing amount
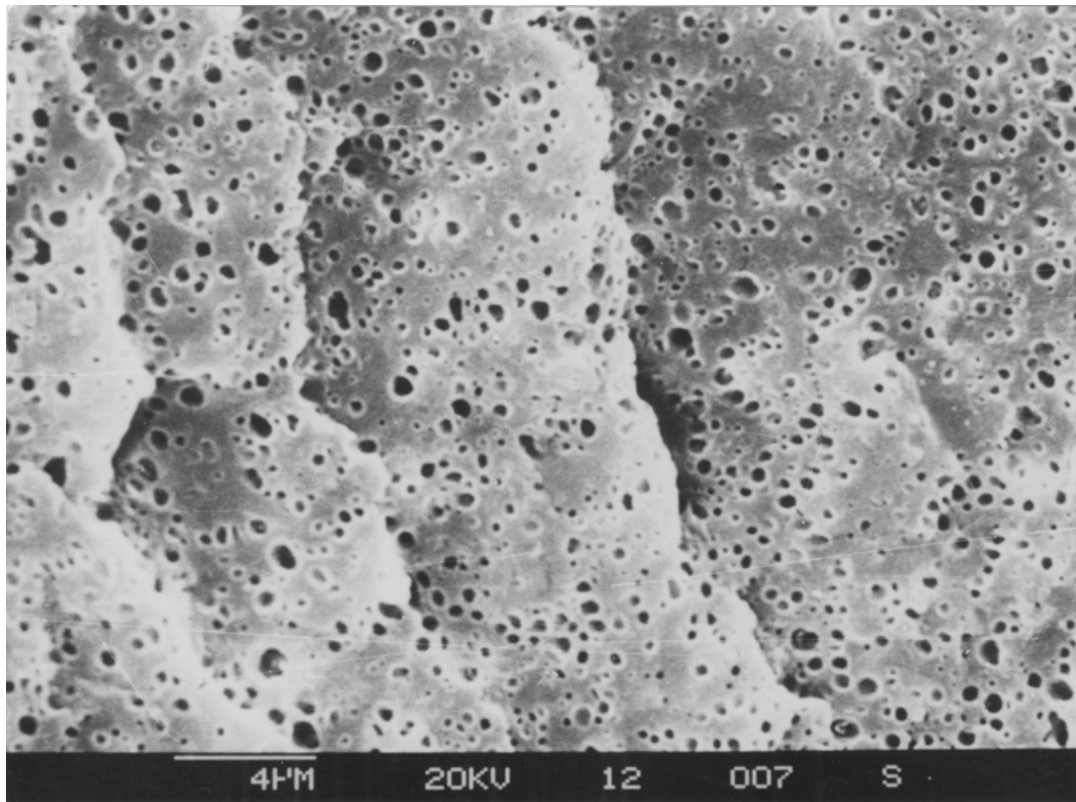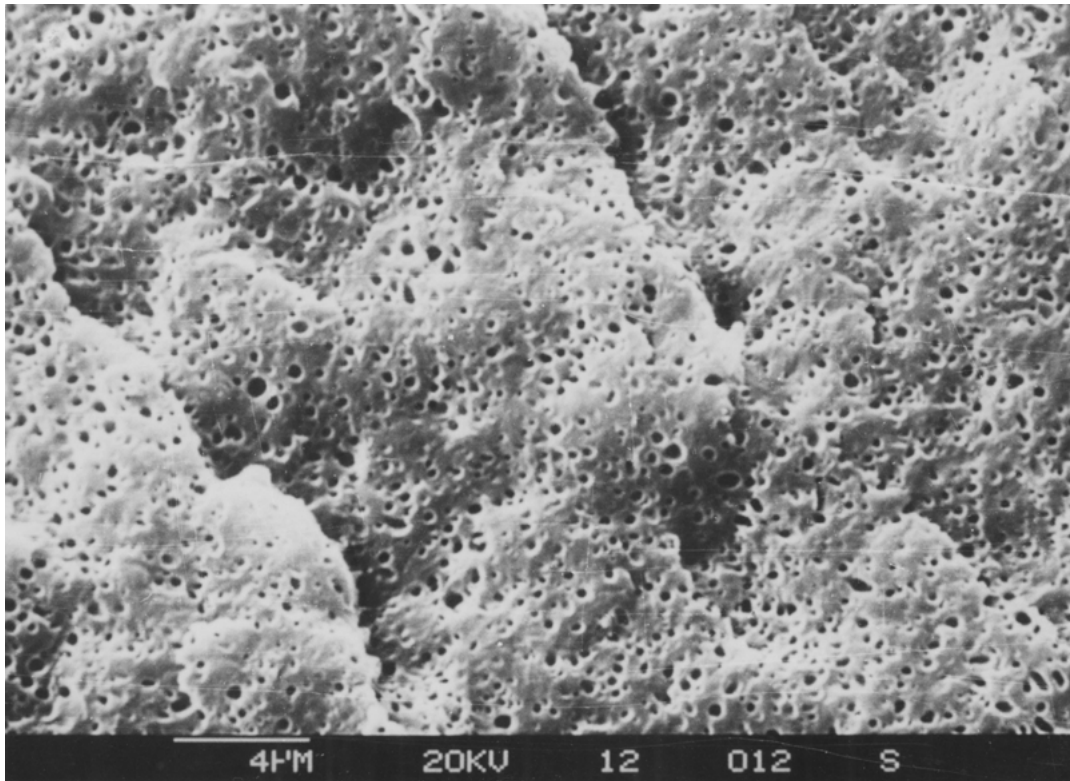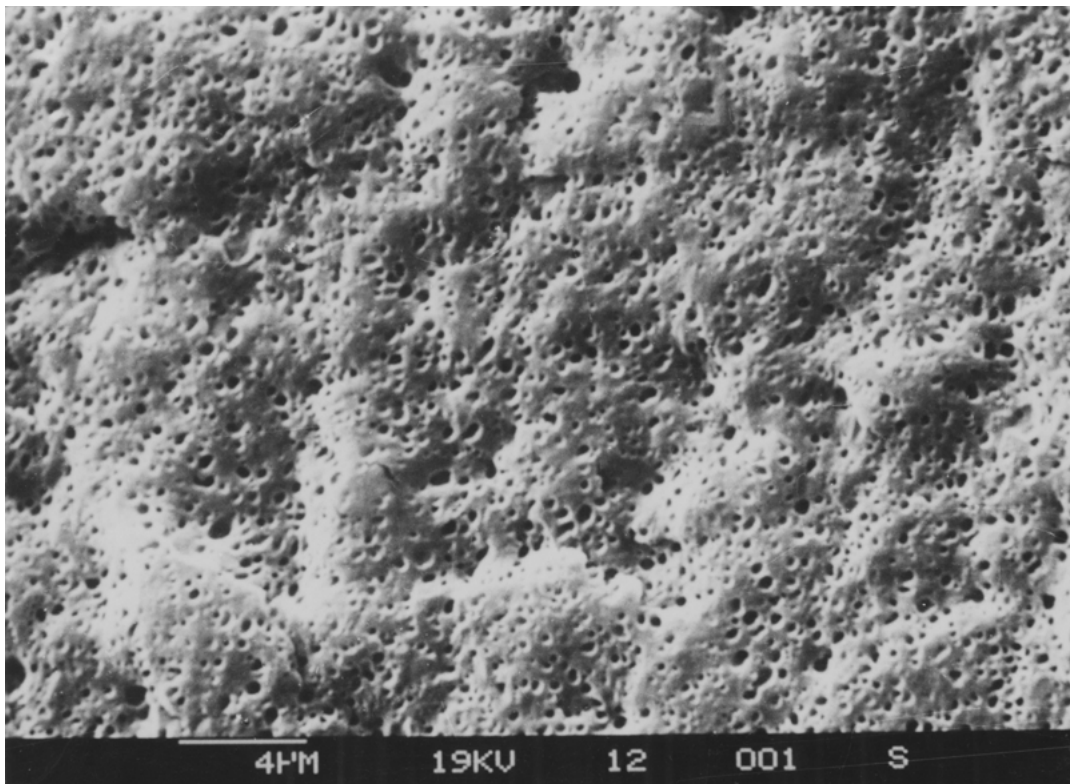

(a)
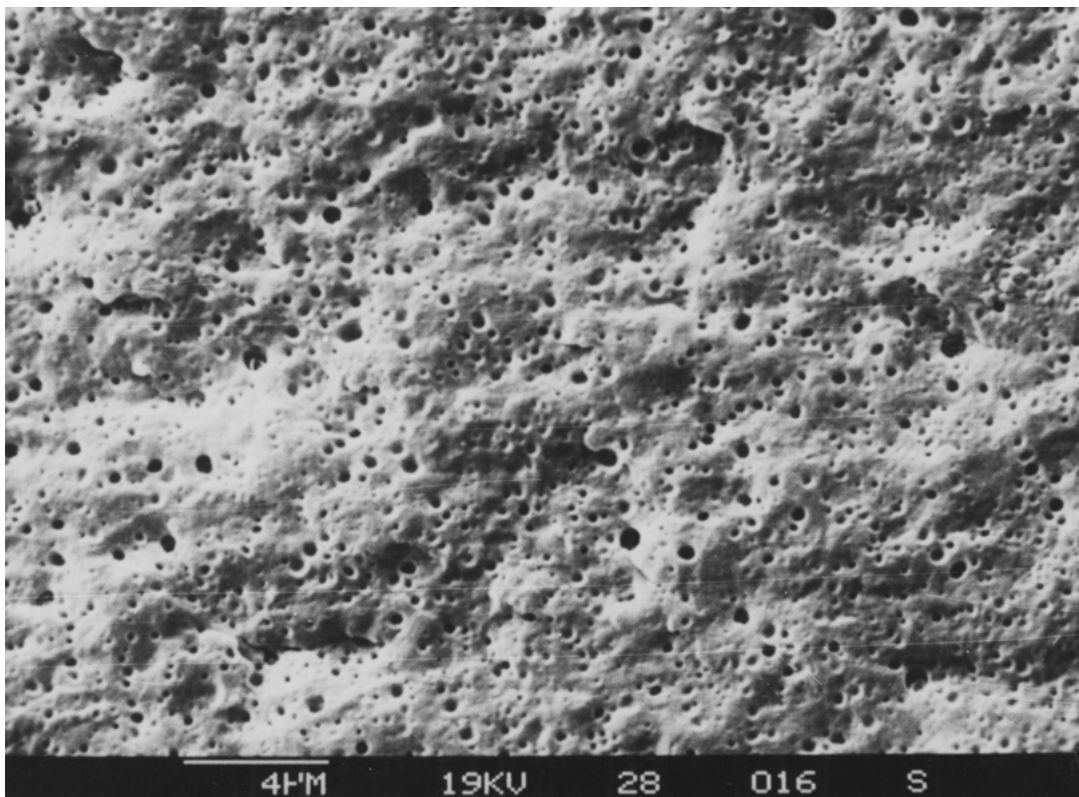
(b)

Figure 8 SEM photographs of the fracture surface of the nylon 6/EVAA blends in the ratio of: (a) 90/10, (b) 80/20, (c) 70/30, and (d) 60/40 (wt/wt). *(Continued)*

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(c)

(d)

Figure 8 (*Continued*).

of EVAA. It can be concluded from the composition of EVAA, which is in fact a modified EVA, that EVAA possesses the rubber nature of EVA and linking acid groups. However, because of its extremely high price, EVAA is more suitable to be used as a compatibilizer that as an impact modifier.

3.2. Morphology

The morphology for various blends was investigated by SEM. All of blending samples were firstly subjected to a brittle fracture at a low temperature, the fracture surface was subsequently etched with a mixture of toluene and methyl-ethyl-ketone to remove the EVA and/or EVAA

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species. The holes left on the fracture surface of nylon 6 matrix reflects the morphology of the domains of the dispersed phase by SEM in Fig. 6. The statistic average diameter of hole was detected from SEM photographs by an image analyzer, and was shown in Fig. 7. Fig. 6a is for the fracture surface of binary blend of nylon 6/EVA at the ration of 80/20 (wt/wt). It is seen the holes are large and non-uniform. The size of EVA domains ranges from 0.5~2.4 μm. It may be concluded that there is a low interface adhesion between the EVA domains and nylon 6 matrix, therefore EVA was not well dispersed. It has been reported that for a nylon 6/elastomer blended system, only when the size of the elastomer particles smaller than 0.7 μm, the blend can be well toughened [23–26]. With the EVA size of 0.5–2.4 μm, not only are the tensile properties poor, but also no toughening can be achieved. The interface adhesion between the two components can be obviously improved by introducing EVAA, as shown by Figs 6 and 7, according to the samples containing 1 wt%, 3 wt% 5 wt% and 7 wt%, respectively. When 1 wt% of EVAA was introduced, the size of holes decreased to under 1.2 μm. As the EVAA content increased, the size of the holes became increasingly smaller and more uniform. When the EVAA content was 7 wt%, the size of the dispersed domains decreased to under 0.4 μm. Such a fine dispersion was attributed to compatibilization and resulted in a well toughening.

Fig. 8 are the microphotographs of nylon 6 and EVAA binary blends. Since EVAA is compatible with nylon 6, and also constitutes an impact modifier for nylon 6, it is intuitive to expect that EVAA is well dispersed in nylon 6 matrix with the domain size independent of its contents. However, Fig. 8 shows that the domain size decreases as the content of EVAA increased. Such a self-dispersing effect is attributed to the reaction between the carboxyl groups of EVAA and the amine groups of nylon 6. The more the EVAA introduced, the larger the amount of links was generated between nylon 6 and EVAA. As a result, the dispersion of EVAA in nylon 6 matrix became finer.

3.3. Rheological behaviors
The viscosity-shear rate relationship for the nylon 6/EVA/EVAA systems are plotted in Fig. 9, and
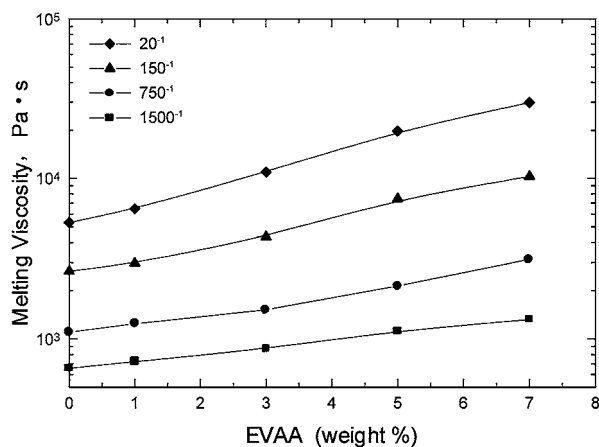
Figure 9 Compatibilizing effect of EVAA on the apparent viscosity of nylon 6/EVA blends.
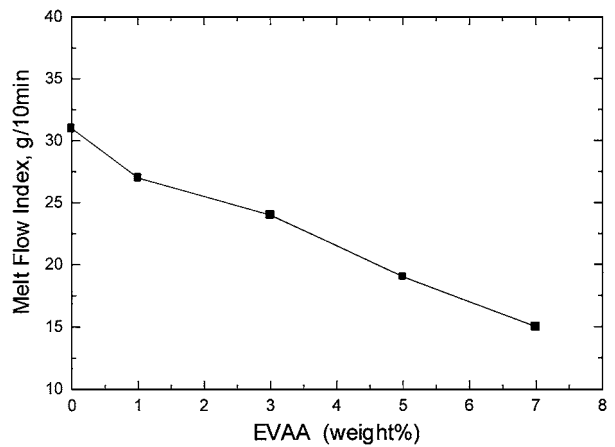
Figure 10 Compatibilizing effect of EVAA on the melt flow index of nylon 6/EVA blends.

compatibilizing effect of EVAA on the melt flow index of blends was shown in Fig. 10. The investigation of the rheological properties would further reveal the interaction and reaction among different components. At least three of phenomenon can be found from Figs 9 and 10 as follows.

(1) The viscosity of Nylon 6/EVA blend without compatibilizer is lower than that of neat nylon 6;

(2) At a certain shear rate, and a constant temperature, the higher the content of EVAA in a blend, the higher the viscosity is;

(3) The higher the shear rate, the less sensitive the viscosity to the content of EVAA in a blend.

The decrease in viscosity by blending EVA with nylon 6 constitutes an evidence of the incompatibility. The resistance to flow of a polymer melt mainly comes from the entanglement of the segments. The chains of nylon 6 are flexible ones, and they entangled seriously when in a melt state. The introduction of EVA, whose segments repulse those of nylon 6, equal to de-entangle the chains at where there are EVA domains. As a result, the viscosity is lowered. However, when EVAA is added, the repulsion between segments of nylon 6 and EVA is partially eliminated. The compatibilization increases the interaction among the segments, and thus increase the viscosity of the system. However, there is a more important mechanism for the increase in viscosity caused by EVAA. The acrylic acid of EVAA reacts with the amine group of nylon 6 as follows:
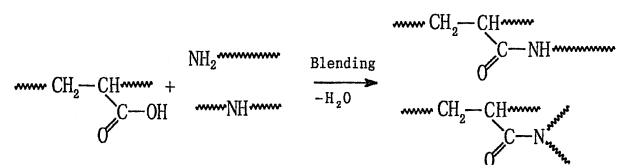
Hydrogen bonding interaction may be also generated between carboxylic acid groups of EVAA and amine groups of nylon 6 as shown in the following scheme:
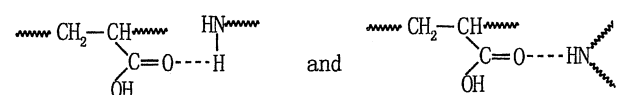
The above reaction and hydrogen bond result in both increases of molecular weight and degree of branch, which constitute the main reasons for the increase of viscosity of the compatibilized blends. The phenomenon (3) above can also be explained by the entanglement of the segments. During the flow of a polymer melt, the chains de-entangled by shear and re-entangled by thermo-motion. If the rate of the former is less than the latter, the viscosity is low. However, when the shear rate is high enough, the rate of de-entanglement is greater than that of entanglement, the viscosity would be much lower. For these reasons, at high shear rates the viscosity increment caused by the compatibilizer is smaller than that at low shear rates.

4. Conclusion

EVAA constituted a good compatibilizer between nylon 6 and EVA. Via the combined toughening of EVA and EVAA, the notched impact strength for nylon 6/EVA blend could be remarkably increased by a factor of chemical reaction between the acrylic acid group and the amine groups of nylon 6. The EVA and EVAA species formed dispersed particles in the matrix of nylon 6. The size of the dispersed phase was controlled by the amount of EVAA. When EVAA content was 7 wt%, the size of the dispersed domains was below 0.4 μm. Such a fine dispersion resulted in a marked toughening. The introduction of EVAA increased the viscosity of nylon 6/EVA blends. However, at high shear rates, the increase in viscosity was less marked than that at low shear rates.

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