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Cooperative toughening and cooperative compatibilization: the nylon 6/ethylene-*co*-vinyl acetate/ethylene-*co*-acrylic acid blends

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Abstract

A polymer blend consisting of nylon 6 and ethylene–vinyl acetate copolymer (EVA) was compatibilized with an ethylene–acrylic acid copolymer (EAA). Neither EVA nor EAA are compatible with nylon 6; however, the combination of the two resulted in a toughened nylon 6. The compatibilization was revealed by the dramatic increase in impact strength, and the smaller particle size and finer dispersion of EVA in the nylon 6 matrix in the presence of EAA. The degree of toughening was evaluated through its effect on the mechanical, morphological and rheological properties, by changing the proportion of the components in the nylon 6/EVA/EAA blends. Because EAA is a compatibilizer for nylon 6/EVA and EVA a compatibilizer for nylon 6/EAA, both the toughening and the compatibilization are cooperative. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Nylon 6; Ethylene–vinyl acetate copolymer; Ethylene–acrylic acid copolymer

1. Introduction

The blending with suitable elastomeric materials has become one of the important means for the improvement of the toughness of a brittle plastic. There is general agreement that the elastomer particle size and the elastomer–matrix adhesion are the important factors that determine the toughness of the plastic/elastomer blends [1–3]. These two factors are, however, inter-related, since changing one of them changes the other one also. Therefore, when studying the two factors, they must be carefully controlled.

The toughening of nylon 6 with elastomers has attracted a great deal of attention [4–6]. However, the hydrocarbon elastomers do not have sufficient affinity for the polar polymer molecules such as nylon 6 [7,8]. This difficulty was avoided by incorporating functional groups into the elastomer that can react with the amine groups of nylon 6 [9,10]. The functional groups provided the adhesion needed and dramatically increased the dispersion of the elastomer resulting in improved toughness [11–13]. Among the hydrocarbon elastomers employed one can list the ethylene–propylene–diene copolymer (EPDM), the styrene–butadiene–styrene block copolymer (SBS), the styrene–ethylene–butadiene–styrene block copolymer (SEBS), etc. [14–17].

The blending with core-shell particles provided another pathway for the toughening of nylon 6. ABS possesses a core of styrene–butadiene copolymer and an incomplete shell of styrene–acrylonitrile copolymer. To improve the adhesion between nylon 6 and the styrene–acrylonitrile copolymer, the common practice was to graft glycidal methacrylate onto the shell of ABS, or acrylamide onto the nylon 6 chains [18–21]. Particles with the flexible core of poly(butyl acrylate) (PBA) and the glassy shell of poly(methyl methacrylate) (PMMA) were recently employed to toughen nylon 6. Since PMMA and nylon 6 are not miscible, epoxy resins were used as compatibilizers [22–25].

In this paper, results are presented regarding the toughening of nylon 6 by a copolymer of ethylene and vinyl acetate, which is suggested as a novel impact modifier of nylon 6. While the ethylene–vinyl acetate copolymer (EVA) is a flexible and easily available compound, it is not compatible with nylon 6. An ethylene–acrylic acid copolymer (EAA) developed by Du Pont was therefore employed by us as a compatibilizer of the nylon 6/EVA blends. The goal of this paper is to examine the mechanical properties, morphology and rheological behavior of the ternary system nylon 6/EVA/EAA. It will be shown that EAA is a compatibilizer for nylon 6/EVA, and that EVA is a compatibilizer for nylon 6/EAA. Hence EAA and EVA are cooperative compatibilizers and tougheners of nylon 6.

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2. Experimental

2.1. Materials

Nylon 6 (commercial grade: 1013B, number average molecular weight: 25,000) was supplied by UCB Chemical, Japan. The ethylene–vinyl acetate copolymer (EVA), with a content of 24 wt% vinyl acetate, was supplied by Beijing Organic Chemical, China. The ethylene–acrylic acid (EAA) (commercial name: Nucrel) copolymer with a content of 3.5 wt% acrylic acid was purchased from Du Pont Chemical, USA.

2.2. Preparation of the blends

Nylon 6 was dried for 12 h and kept in an airtight aluminum-polyethylene package before use. The blends were mixed using a WP 35 mm twin-screw extruder ($L/D = 35$). All the ingredients were tumble-blended and fed through the throat of an extruder. The barrel and die temperatures were increased from 205 to 240°C, and the rotation speed of the screw was 180 rpm. The blends passed through a cooling water bath and were finally pelletized. The extrusion parameters were changed very little from one composition to another.

2.3. Mechanical properties test

The tensile properties were determined at room temperature with an Instron Universal Testing Machine (Model 1130) according to the ASTM D638. The notched Izod impact strength was determined with a SUMITOMO impact tester according to the ASTM D256. The thickness of the Izod impact specimens was 1/8 in. Five determinations were carried out for each data point.

2.4. Scanning electron microscopy

The sample bars were fractured in liquid nitrogen. The fractured surface was etched for 2 h with a boiling mixture of toluene and methyl-ethyl-ketone at a weight ratio of 60/40, then coated with an Au/Pd alloy, and subsequently subjected to observation under a scanning electron microscope (Cambridge S250). The micrographs of SEM were analyzed with an image analyzer (IBAS 1/2).

2.5. Rheological measurements

The torque of the blend samples was determined with a Brabender mixer (Plasti-Corder model PLE 330) at 240°C for 20 min, and recorded as a function of time. The apparent viscosities at various shear rates were determined with a capillary rheometer possessing a capillary with an L/D ratio of 43/1 (TOYOSEIKI Mode 1B) at 240°C The melt flow index was determined according to ASTM D1238 at 250°C.

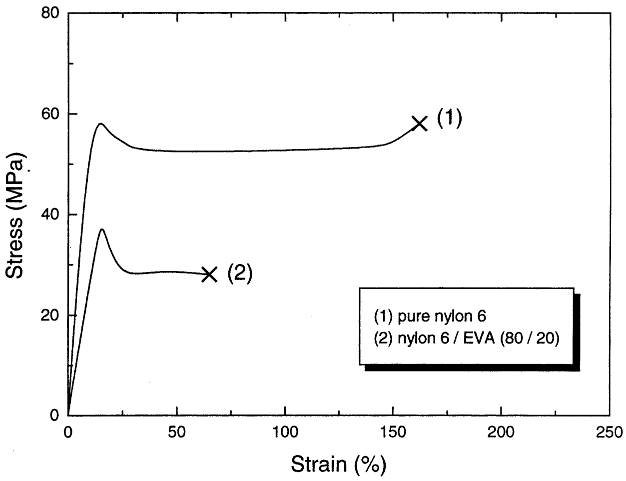


Fig. 1. The stress–strain curves of nylon 6 and nylon 6/EVA (80/20 weight ratio) binary blend.

3. Results and discussion

3.1. Mechanical property

The incompatibility of the nylon 6/EVA blends is reflected in the stress–strain curves of Fig. 1. While the pure nylon 6 possesses a tensile strength of about 60 MPa and an elongation at break of over 160%, the nylon 6/EVA blend at a weight ratio of 80/20 provided lower values for both properties. The decrease in tensile strength occurred partly because of the weakening of the inter- and intra-hydrogen bonding of the nylon 6 molecules by the segments of EVA, and more importantly, because of the incompatibility between the polar segments of nylon 6 and the non-polar ones of EVA. For the latter reason, the elongation at break also decreased. The compatibility could be, however, improved by adding EAA, a copolymer of ethylene and acrylic acid, to the system. Because of the similarity of the chain structures, EAA and EVA are miscible in all proportions. The acrylic acid moieties generated H-bonds and/or reacted with the amine groups of nylon 6, which became thus compatibilized with EVA. Indeed, as shown in Fig. 2, the tensile strengths of nylon 6/EVA blends were improved by the addition of EAA, and the elongation at break became as large as 200% when a sufficiently large amount of EAA was added. This suggests that adhesion occurred between the segments of EVA and those of EAA grafted on nylon. Fig. 2 shows that the tensile strength increased from 40 MPa for the uncompatibilized to 54 MPa for compatibilized blends.

A high improvement in mechanical properties was achieved regarding the toughness (Fig. 3). The notched impact strength of pure nylon 6 is about 19 J/m [26,27], while the nylon 6/EVA blend possessed at a weight ratio of 80/20 a notched impact strength of about 60 J/m. Although EVA alone increased the toughness of nylon 6 by a factor of 3, which represents a moderate improvement,

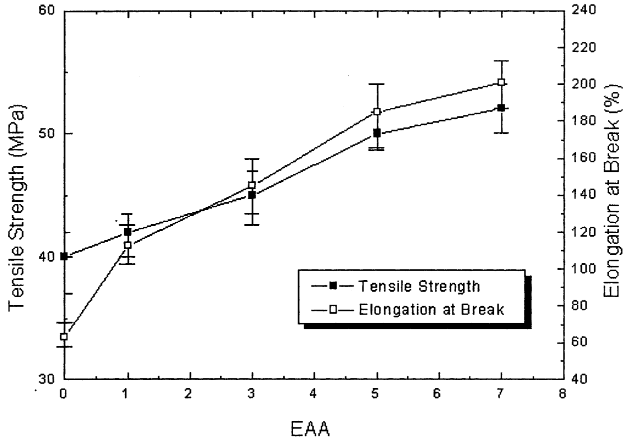


Fig. 2. The effect of EAA content [g/(100 g nylon6 + EVA)] on the tensile strength and elongation at break of nylon 6/EVA/EAA ternary blends (weight ratio nylon 6/EVA = 80/20).

the blend behaved as a brittle material at impact. Because of incompatibility, EVA could not be finely dispersed in the nylon 6 matrix, resulting only in a moderate toughening. However, the compatibilizer, EAA, generated bridges between the two components and decreased the particle size of EVA (more details later). Major increases in the notched impact strengths were obtained as a result of compatibilization. For a sufficiently large amount of EAA, the sample achieved the high notched impact strength of 520 J/m, which represents a tough behavior. Wu [27] found that for the nylon 6/SEBS-g-maleic anhydride system the tough–brittle transition was very sharp, the impact strength increasing sharply from below 200 to above 500 J/m as the particle size became smaller than a threshold value. It is interesting to notice that in the present system the tough–brittle transition was rather a gradual one. The toughness increased with increasing content of compatibilizer (Fig. 3) and the impact behavior of the sample changed from brittle to semi-tough to fully tough.

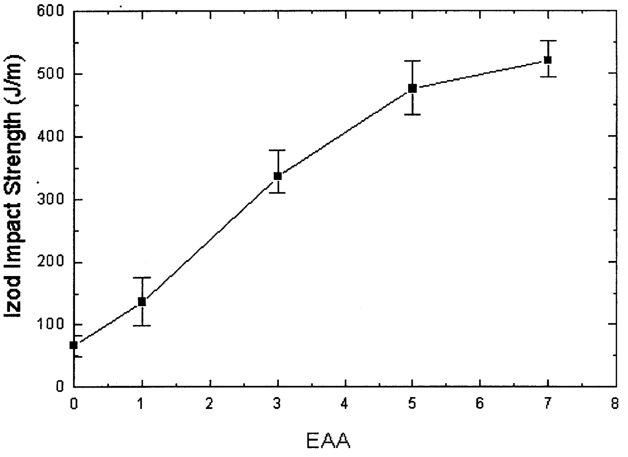


Fig. 3. The effect of EAA content [g/(100 g nylon6 + EVA)] on the notched impact strength of nylon 6/EVA/EAA ternary blends (weight ratio nylon 6/EVA = 80/20).

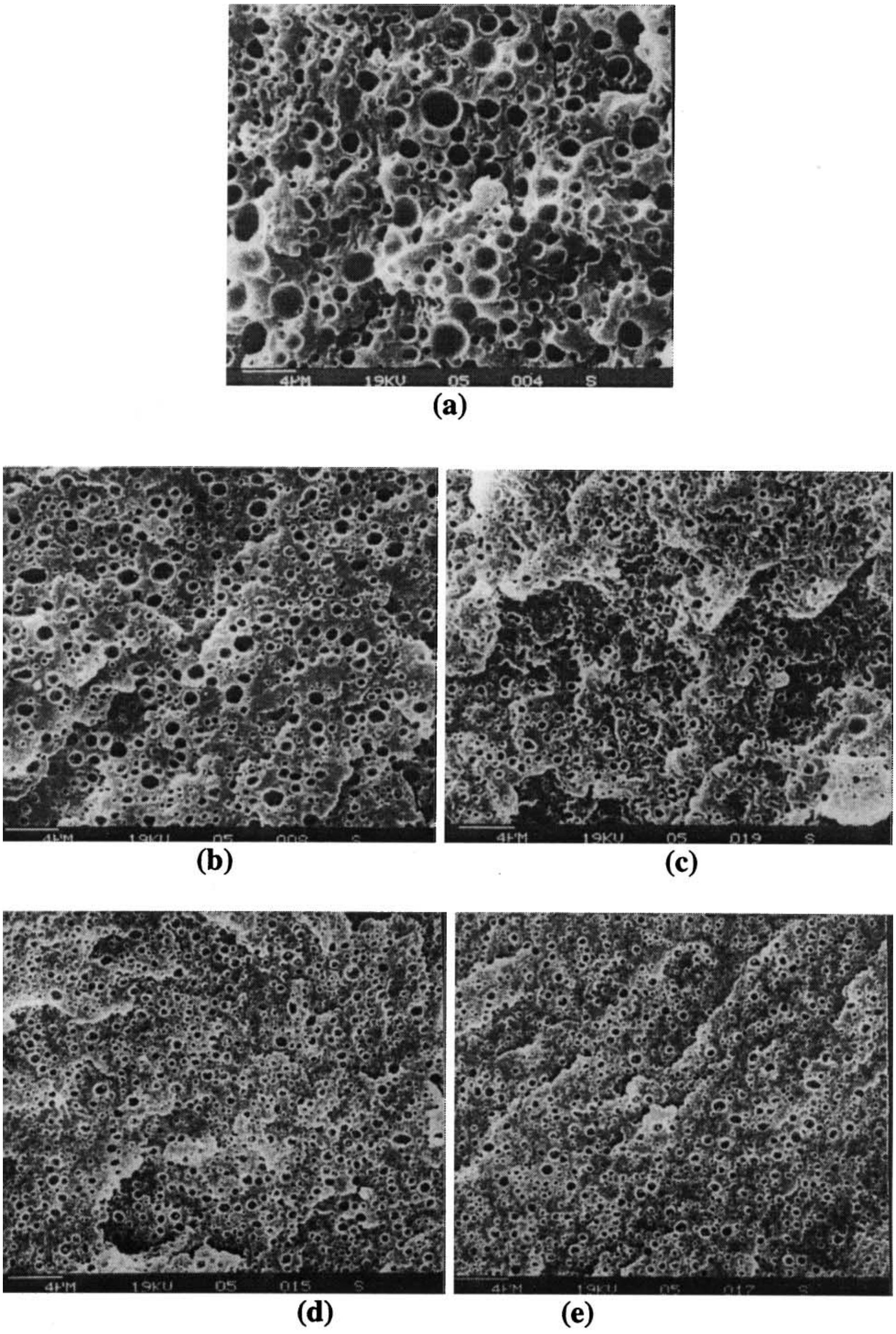
3.2. Morphology

The morphology of the blends was investigated by scanning electron microscopy (SEM). All the samples were first subjected to brittle fracture at low temperature, and the fractured surface was etched with a mixture of toluene and methyl-ethyl-ketone to remove the EVA and/or EAA species. The holes left on the fractured surface of the nylon 6 matrix reflect the morphology of the dispersed phase (Fig. 4). The average diameter of the holes, determined from the SEM micrographs using an image analyzer, is plotted in Fig. 5. Fig. 4(a) presents the fractured surface of a nylon 6/EVA blend at a weight ratio of 80/20 and shows that the holes are large and non-uniform, ranging from 0.5 to 2.4 μm. It is now accepted that for a nylon 6/elastomer blend to be well toughened, the size of the elastomer particles should be smaller than 0.7 μm [13–27]. For non-uniform EVA sizes of 0.5–2.4 μm, the tensile properties were poor, and only a moderate toughening could be achieved. As shown in Figs. 4 and 5, the interaction between the two components was improved by introducing EAA. For 1 wt% EAA, the size of the holes decreased under 1.2 μm. As the EAA content increased, the size of the holes became increasingly smaller and more uniform. For an EAA content of 7 g/(100 g nylon + EVA), the size of the dispersed domains decreased under 0.4 μm. Such a fine dispersion can be attributed to the compatibilization and resulted in a well-toughened blend.

It is of interest to examine the morphology of the nylon 6/EAA blends (Fig. 6). Because the acrylic acid moieties of EAA can react with the amine groups of nylon 6, it was expected the two to be compatible and that EAA would be well dispersed in the nylon 6 matrix. However, the micrographs of Fig. 6 indicate poor dispersions, the sizes of the EAA domains being as large as 1–2 μm and non-uniform. The mechanical properties of the blends, which are presented in Fig. 7, also indicate that these two components are not compatible. Although a reaction can occur between the acrylic acid moieties and the amine groups, the polyethylene segments of the EAA were strongly repulsed by nylon 6, resulting in phase segregation. When EVA was added to the system, a well-toughened nylon 6/EAA blend was obtained. This happened probably because the segments of poly(vinyl acetate) have a polarity between those of polyethylene and nylon 6.

3.3. Rheological behavior

In Fig. 8 the mixing torque of the melt is plotted against the mixing time for systems with various compositions. The pure nylon 6 exhibited a low torque, and the torque of the blend of nylon 6/EVA was even lower. When, however, the compatibilizer EAA was introduced into the system, the torque increased. Indeed, as shown by Fig. 8, the greater the content of EAA, the higher was the torque. The decrease of the torque when EVA was blended with nylon 6 constitutes



(a)

(b) **(c)**

(d) **(e)**

Fig. 4. SEM micrographs of the fractured surface of the nylon 6/EVA blends (80/20 weight ratio) with EAA contents [g/(100 g nylon 6 + EVA)]: (a) 0, (b) 1, (c) 3, (d) 5, (e) 7.

evidence for incompatibility. Besides the volume of the chain, the resistance to the flow of a polymer melt is mainly due to the entanglement of its molecules. The chains of nylon 6 are flexible, and they are entangled in the melt. The introduction of EVA disentangled some nylon 6 chains and, as a result, the torque was lowered. However, when EAA was added, nylon 6 and EVA were compatibilized. This increased the interaction among the segments, and thus the torque was increased. However, there is another mechanism for the increase of the torque caused by EAA that involves the reaction between the acrylic acid moieties of EAA and the amine groups of nylon 6. This reaction increased the molecular weight and the degree of branching, and both increased the torque of the compatibilized blends. Similar changes occurred in the melt flow index of the blends (Fig. 9).

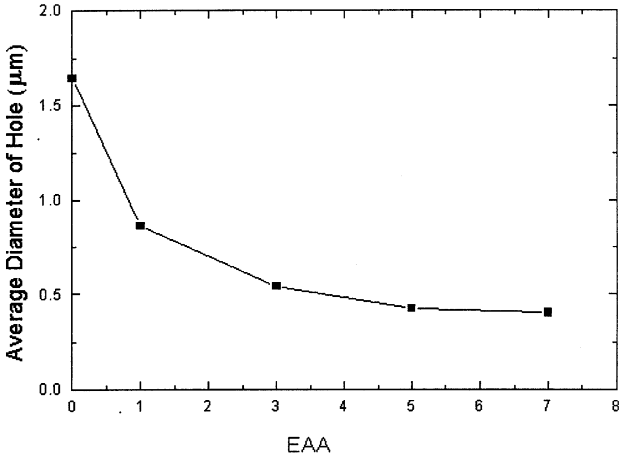


Fig. 5. Average hole size on SEM micrographs of the fractured surface vs. EAA content [g/(100 g nylon 6 + EVA)]. Weight ratio nylon 6/EVA = 80/20.

The melt viscosity at various shear rates is plotted in Fig. 10 as a function of the EAA content. It was found that the melt viscosity of nylon 6/EVA blend without comaptibilizer was lower than that of pure nylon 6; however, the greater the EAA content, the higher became the viscosity. The change in the melt viscosity confirms the explanation provided in the preceding paragraph for the changes in the torque. Fig. 10 also shows that the higher the shear rate, the lower was the viscosity. This can be considered to be a result of increased disentanglement of the chains with increasing shear rate.

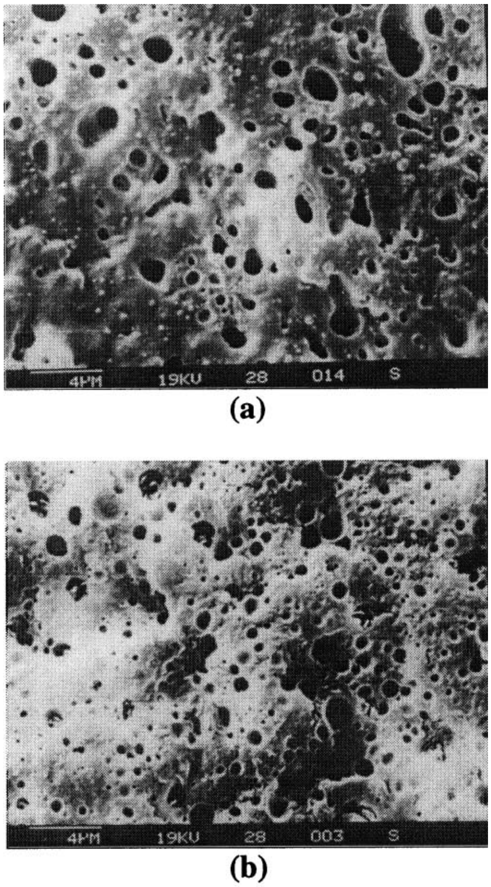


Fig. 6. SEM micrographs of the fractured surface of the nylon 6/EAA binary blends for the weight ratios of: (a) 90/10, and (b) 80/20.

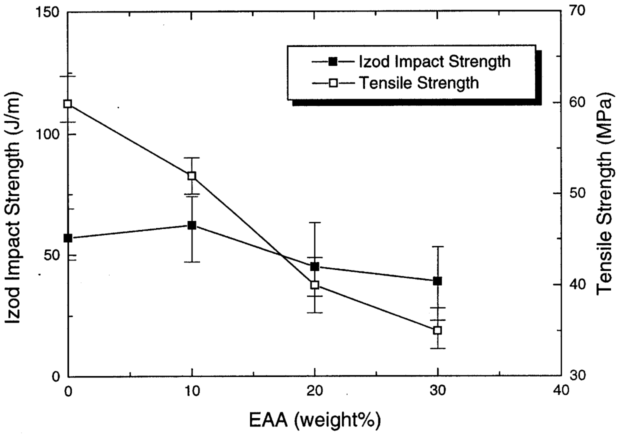


Fig. 7. Tensile strength and notched impact strength of nylon/EAA binary blends.

4. Conclusion

EAA, a copolymer of ethylene and acrylic acid, constitutes a good compatibilizer for the nylon 6/Ethylene–vinyl acetate copolymer (EVA) blend, and EVA a good compatibilizer for the nylon 6/EAA blend. The toughening of nylon/EVA by EAA and of nylon 6/EAA by EVA provides a notched impact strength of nylon 6/EVA/EAA one order of magnitude higher than that of pure nylon 6. The size of the disperse phase of EVA was dependent on the amount of

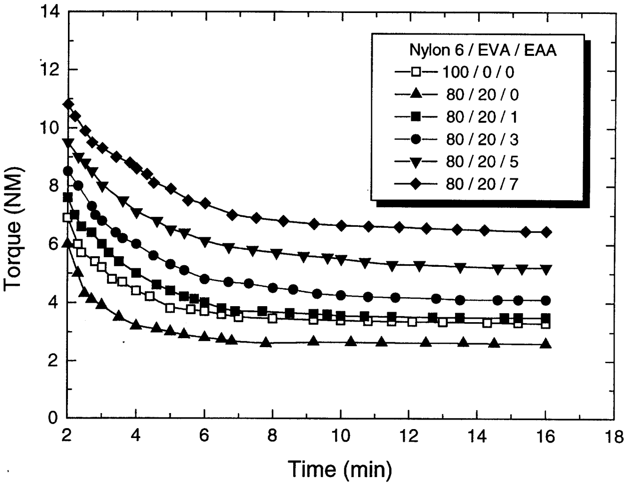


Fig. 8. The mixing torque vs. mixing time for nylon 6 and its blends for various EAA contents [g/(100 g nylon 6 + EVA)], weight ratio nylon nylon 6/EVA = 80/20.

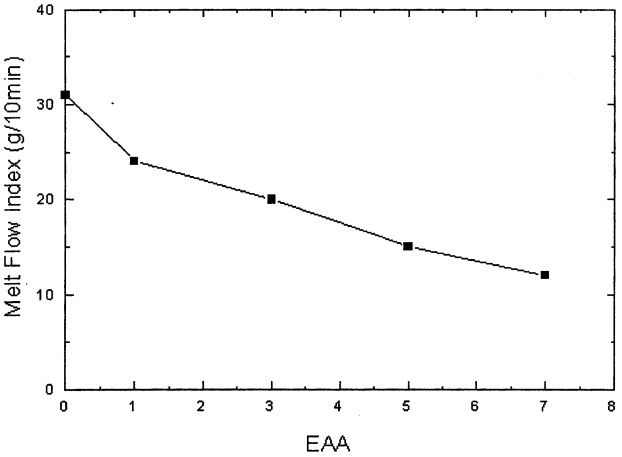


Fig. 9. The effect of EAA content [g/(100 g nylon6 + EVA)] on the melt flow index of nylon 6/EVA/EAA ternary blends (wt ratio nylon 6/EVA = 80/20).

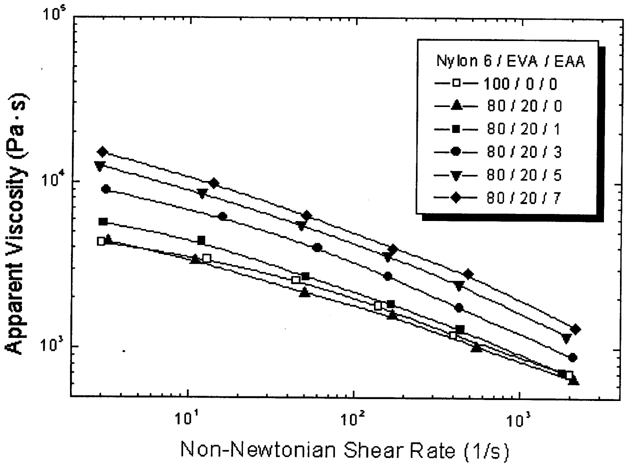


Fig. 10. The effect of EAA content [g/(100 g nylon6 + EVA)]on the melt viscosity of nylon 6/EVA/EAA ternary blends (weight ratio nylon 6/EVA = 80/20).

EAA. When the EAA content was sufficiently high, the size of the dispersed domains of EVA was below 0.4 μm. Such a fine dispersion resulted in a well-toughened blend.

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