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Toughening of nylon with epoxidised ethylene propylene diene rubber

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Blends of nylon-6 and epoxidised ethylene propylene diene (eEPDM) rubber were prepared through reactive mixing. It is found that the toughness of nylon-6 can be much improved by this method, and that the particle size of eEPDM is much smaller than that of unexpoxidised EPDM (uEPDM) rubber in a nylon-6 matrix. This indicates that the epoxy group in eEPDM could react with a nylon-6 end group to form a graft copolymer which could act as an interfacial compatibiliser between the nylon-6 and the eEPDM rubber dispersed phase. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: nylon-6; ethylene propylene diene rubber; toughening)

Introduction

Improving the toughness of polymeric materials with epoxidised ethylene propylene diene (eEPDM) rubber is a new method of polymer modification. Recently, eEPDM has been successfully used to toughen poly(butylene terephthalate) (PBT) and polycarbonate (PC) in our laboratory[1,2].

Nylon, like PBT and PC, is a pseudoductile polymer. It has a high crack initiation energy but a low crack propagation energy, and so has a high unnotched but a low notched impact strength. Matrix yielding is the main mechanism of energy dissipation in such super-tough polymer/rubber blends[3,4]. This phenomenon was also observed in PBT/eEPDM and PC/eEPDM blends in our experiments[1,2]. Generally, super-tough nylon is obtained by mixing grafted rubber with a reactive polar group such as maleic anhydride. Now it is expected that super-tough nylon can be obtained by the method of mixing with eEPDM, which, to our knowledge, has not been reported so far.

Experimental

Materials and specimen preparation. The nylon-6 used in this paper was a commercial polymer, manufactured in the Heilongjiang Nylon Plant, Harbin, China. The material was dried at 120°C for 12 h in a vacuum oven to remove absorbed water before melt-processing. The EPDM was also a commercial polymer, EPT 4045 (made in Japan), having a diene component 5-ethylidene-2-norbornene (ENB), a propylene content (C_3) of 35.9 mol%, and a glass transition temperature (T_g) of about −42°C measured by dynamic mechanical analysis.

The eEPDM used in this work was synthesised in our own laboratory. The EPDM was first dissolved in toluene, then epoxidised with performic acid which was formed in situ from formic acid and hydrogen peroxide. The details of its preparation process and characterisation are described elsewhere[5].

The nylon-6/eEPDM blends with different rubber contents were mixed in a Brabender-like apparatus (Rheocoder XSS-300; Shanghai, China) at 230°C for 5 min at a roller speed of 40 rev min^{-1}.

Notched impact tests. The notched Izod impact strength of nylon-6/eEPDM blends were measured by use of an XJU-22 Izod impact tester (Chengde, China) at 25°C. The samples for impact testing were obtained by compression-moulding the nylon-6/eEPDM blends at 230°C, then cutting them into rectangular specimens which were sharply notched with a fresh razor blade. The size of the rectangular specimens was 63.5 mm × 12.7 mm × 3.2 mm.

Morphology. The morphology of the nylon-6/eEPDM blends was characterised by using a scanning electron microscope (model JXA-840; Japan). The test specimens were first cold-fractured in liquid nitrogen, then coated with a thin layer of gold–palladium alloy to avoid charging under the electron beam.

Results and discussion

Reactive blending. In 1985, Wu[6] first proposed the critical interparticle distance (IDc) model. A blend will toughen when the interparticle distance (ID) is smaller than the IDc, and it will be brittle when the ID is greater than the IDc, where the ID is given as

$$\mathrm{ID} = d\left[\left(\frac{\pi}{6V_f}\right)^{1/3} - 1\right] \qquad (1)$$

in which d is the average rubber particle size, and V_f is the rubber volume fraction. The experimental results of Borggreve *et al.*[7] showed that the IDc is about 0.3 μm at 25°C for nylon-6/EPDM blends. From equation (1) it is known that for a given rubber content, in order to obtain ID ≤ IDc, the rubber size d must be smaller than a critical value d_c. From equation (1), we can obtain $d_c = 1.3$ μm for nylon-6/EPDM blends with a 24% weight fraction of EPDM.

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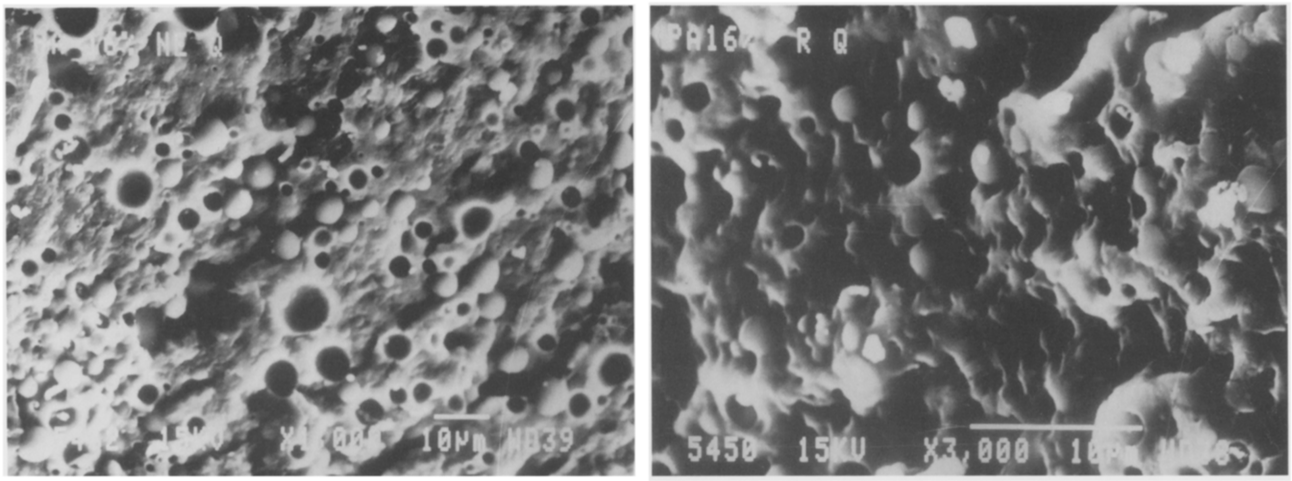
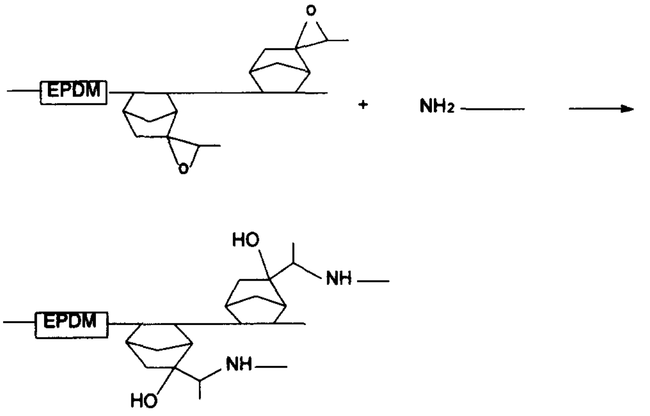


(a) (b)

Figure 1 Scanning electron micrographs of (a) nylon-6/uEPDM and (b) nylon-6/eEPDM. Note the different scales in (a) and (b)



Scheme 1

Because of epoxidation, the epoxy groups, as functionalised sites, can react with the terminal amino group in nylon-6, as shown in *Scheme 1*.

When eEPDM is melt-mixed with the nylon-6 matrix, according to the reactions shown in *Scheme 1*, a graft copolymer (eEPDM–g–nylon-6) is presumably formed in the interface between the rubber domains and the nylon-6 matrix, which can act as an effective compatibiliser, decreasing the interfacial tension. This results in a finer dispersion of the rubber phase. Tang and Huang[8] presented a relationship between the average dispersed particle size and compatibiliser concentration, as shown in equation (2).

$$d = (d_0 - d_s)e^{-KC} + d_s \qquad (2)$$

where d_0 and d_s are the average sizes of the dispersed phase particles when the concentration of the compatibiliser is zero and at saturation, respectively, C is the concentration of the compatibiliser, and K is the rate constant for the change of interfacial tension with concentration of compatibiliser. In equation (2), it is clear that the particle size will rapidly decrease with the concentration of compatibiliser.

Figure 1 shows scanning electron micrographs of cold-fracture surfaces of the nylon-6/unepoxidised UEPDM (84/16) and nylon-6/eEPDM(84/16) blends, from which it can be seen that rubber sizes for the nylon-6/eEPDM blend vary from 0.7 to 2 μm, while the rubber size for the nylon-6/uEPDM blend varies from 2 to 8 μm. As these two blends were melt-mixed under the same conditions (such as the same temperature and roller speed, *etc.*), the different rubber sizes in the nylon-6 matrix must result from the difference between the compatibilities in nylon-6/eEPDM and nylon-6/uEPDM.

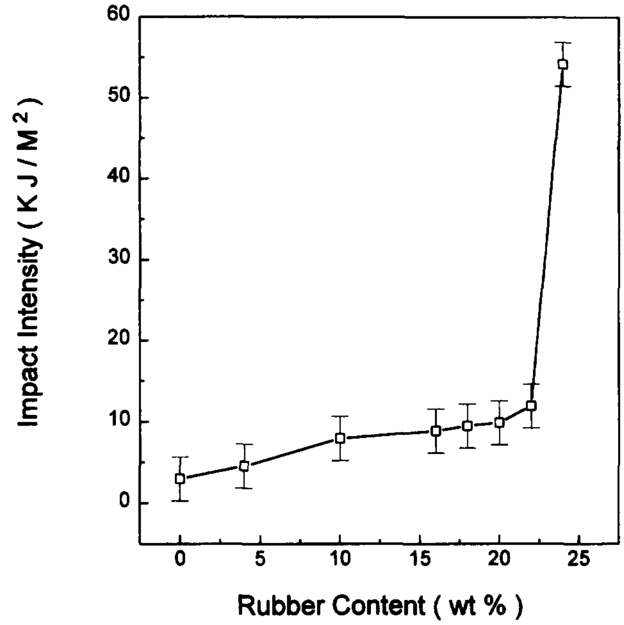


Figure 2 Plot of impact strength *versus* rubber content for nylon-6/eEPDM blends

Impact testing analysis. The mechanical properties of a series of nylon-6/eEPDM blends containing 0–24 wt.% eEPDM were determined. *Figure 2* shows the variation of notched Izod impact strengths for specimens with increasing rubber contents at 25°C. When the rubber content was 24 wt%, the notched Izod impact strength of the nylon-6/eEPDM blends shows a great improvement, with a strength value being about 18 times that of pure nylon-6. Here we would like to emphasise that the colour of the nylon-6/eEPDM blends is fairly white. However, the colour of the general super-tough nylon obtained by mixing with EPDM–g–maleic anhydride is deep yellow.

Conclusions

In nylon-6/EPDM blends, the size of the rubber domains is large and the adhesion between the rubber and plastic phase is poor. Therefore, its toughness cannot be improved greatly at room temperature. However, when epoxidised EPDM is used, its epoxy-containing groups can react with the nylon-6 matrix, forming a graft copolymer EPDM–g–nylon. A finer dispersion of the rubber phase in the matrix is obtained. This will induce local yielding of nylon-6 around the rubber particles, making the toughness of the blend increase greatly when the interparticle distance is smaller than a critical value IDc.

Acknowledgements

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