# **Dispersivity of Rubbers in Thermoplastic Polymers**

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Received 7 July 1998; accepted 16 November 1998

**ABSTRACT:** The main factors influencing the dispersivity of rubbers (nitrile and ethylene-propylene) in nylon 6 (PA-6) and polypropylene (PP) are investigated. On the basis of an equation, describing the influence of interfacial tension and viscosity ratio of disperse and matrix phases on the average size of dispersed phase particles, analysis of dispergation process in researched blended systems has been conducted. The limits of applicability of a given equation were established. It was shown that the best dispersivity of rubbers in the PA matrix is observed in that case when the viscosity values of initial components of a blend are close to each other. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1563–1567, 1999

**Key words:** nylon 6; polypropylene and rubbers blends; dispersivity and phase structure; viscosity ratio; size of disperse phase particles

## INTRODUCTION

Morphology of polymer blends on the base of thermodynamically immiscible components is basically determined by the following factors: (1) blending conditions, (2) mode of specimen cooling, (3) interfacial interaction, and (4) the viscosity ratio of components.<sup>1</sup> In spite of the great number of publications on this subject, the creation of blends on the base of amorphous-crystalline polymers (isotactic PP, nylon 6, and others) and rubbers for the purpose of preparation of impactand cold-resistant materials is of particular interest. A main problem is, in this case, reception of a material with a required structure.<sup>2</sup> It was found by Wu<sup>3</sup> that for the manufacturing of impactresistant PA-6-rubber blends, the following three conditions are necessary: (1) strong adhesion between the PA-matrix and the rubber phase; (2) optimal size of rubber particles; (3) the distances between rubber particles should be less critical ones. So, for PA-6-maleinized EPR blends, it was shown by Gaymans et al.<sup>4</sup> that the critical size of rubber particles has the order of  $0.1-0.2 \ \mu m$ . However, the question of what depends on the size of disperse phase, first of all, is insufficiently explored elsewhere.<sup>5</sup>

Therefore, in order to find out the main factors influencing the dispersivity, in the present work, we studied a phase structure of polymer blends on the base of PA-6, isotactic PP, and rubbers of various natures [butadiene-nitrile (NBR) and ethylene-propylene (EPR)] by introducing the compounds in them, changing both the viscosity of rubber and the interfacial interaction. At the same time, a type of the blending equipment was varied.

## EXPERIMENTAL PART

## Materials

In this work, the following materials were used.

1. PA-6 of the injection-molding grade 210/ 310 (PA-1) (density, 1.14 g/cm<sup>3</sup>; melt flow index (MFI), 2.3 g/10 min at T = 235 °C and p = 12N; molecular weight, ~ 25,000; melting temperature, 225°C; degree of crystallinity, ~ 50%) and PA-6 of the Aku-

Correspondence to: A. O. Baranov. Journal of Applied Polymer Science, Vol. 73, 1563–1567 (1999)

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lon V-64 trademark (PA-2) (MFI, 2.6 g/10 min at T = 235°C; p, 12N).

- 2. Isotactic PP of the 21030-10 trademark (density, 0.907 g/cm<sup>3</sup>; MFI, 1.0 g/10 min at T = 190°C; p = 21.6N; weight-average molecular weight, 350,000; melting temperature, 165°C; degree of crystallinity, ~ 55%).
- 3. EPR of the Dutral-CO-043 trademark (density, 0.865 g/cm<sup>3</sup>; MFI, 2.2 g/10 min at  $T = 190^{\circ}$ C; p, 21.6N; glass transition temperature,  $-51^{\circ}$ C; propylene contents, 45%).
- Butadiene-nitrile rubber (NBR) of SKN-40 trademark (density, 0.986 g/cm<sup>3</sup>; contents of bonded (nonreactive) acrylonitrile, 36– 40%; glass transition temperature, -32°C; viscosity on Mooney at 100°C (4 min), ~ 85.
- 5. Liquid carboxylated nitrile rubber (LCNR) (molecular weight, 3300; acrylonitrile contents, 15.6 wt %; contents of carboxylic groups,  $\sim 2.25$  wt %; inherent viscosity at 27°C, 1200 Poise).
- 6. Block copolymer of nylon 6 and polybutadiene (PA-PB) (number-averaged molecular weight, 28,400; intrinsic viscosity in cresol, 0.95; molecular weight of butadiene block with terminal carboxylic groups, 3200; contents of 1,2-links of less than 20%).
- 7. Phenolic resin (molecular weight, 500; contents of hydroxylic and phenolic groups,  $\sim 19.0 \text{ wt } \%$ , CH<sub>2</sub>OH groups,  $\sim 11.0 \text{ wt } \%$ , nitrogen,  $\sim 2.4 \text{ wt } \%$ ; the Ubbelohde droplet drop temperature, 85°C.

Due to their high water absorption, initial PA-6 were previously dried in a vacuum thermocabinet at 100°C for 4-6 h.

## **Blend Preparation**

The blending of polymers and rubbers (at a ratio of components of 90/10) was conducted in the melt state in internal-type Brabender mixer or in twinscrew Berstorff extruder (diameter of screw D = 25 mm, ratio L/D = 23) at different rotor (screw) rotation speeds and temperatures of 200 and 240°C.

### **Techniques**

The study of blend structure was carried out by using a JEOL JSM-35C scanning electron microscope. The liquid nitrogen cryogenically fractured

surfaces of various blended samples were investigated. Subsequently, these fractured surfaces were rinsed in acetone or heptane (depending on nature of rubber) during one day. Values of the number-averaged size of rubber particles ( $\alpha_n$ ) calculated from histograms, averaging several micrographs. The measurements were done at different directions (planes of cutting) within the rubber particles.

Simultaneously with the study of phase structure and morphology of blends, the analysis of rheological properties of initial components of blends has been conducted using an INSTRON-1196 capillary viscosimeter of constant flow rate at temperatures (240 and 200°C), corresponding to the temperatures of blend receiving. The flow curves (dependencies of shear stress and apparent shear viscosity  $\eta_{app}$  on effective shear rate on capillary wall  $\dot{\gamma}_w$ ) were measured at various constant speeds of piston movement with use of a die with entrance cone angle of 90° and relation of capillary length to its diameter l/d = 30.

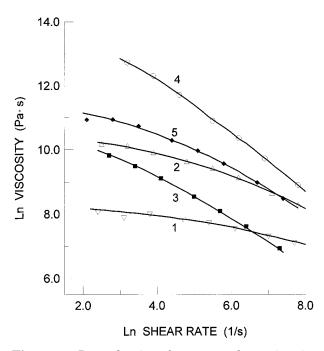
# **RESULTS AND DISCUSSION**

The size and the form of disperse phase in polymer blends are the important factors, determining mechanical characteristics of material. In the work of Wu,<sup>5</sup> the influences of various parameters to the size of disperse phase in polymer mixtures of nylon 6,6 and PET with EPR were investigated. It was shown that the number-averaged size  $\alpha_n$  of disperse phase (EPR) can be evaluated with reasonably good accuracy by the following equation:

$$\alpha_n = 4(\eta_d / \eta_m)^{\pm 0.84} \gamma_{12} / (\dot{\gamma}_w \eta_m).$$
(1)

Mark plus if  $\eta_d/\eta_m > 1$  and minus if  $\eta_d/\eta_m < 1$  undertakes here ( $\gamma_{12}$  is the interfacial tension,  $\dot{\gamma}_w$  is the shear rate,  $\eta_d$  is the viscosity of disperse phase,  $\eta_m$  is the viscosity of matrix).

From equation (1), it is seen that the degree of dispersion of one polymer in another at melt blending is governed first of all by rheological properties of initial components. Therefore, dependencies of apparent shear viscosity  $\eta_{\rm app}$  of researched polymers on shear rate  $\dot{\gamma}_w$  (Fig. 1) were measured. As it would be expected, <sup>6</sup> values of  $\eta_{\rm app}$  steady decreases with the growth  $\dot{\gamma}_w$ , and the slope ( $\Delta \ln \eta_{\rm app}$ )/( $\Delta \ln \dot{\gamma}_w$ ) depends on the type of polymer. The dependence of viscosity on shear rate is described by the following empirical formula<sup>6</sup>:



**Figure 1** Dependencies of apparent shear viscosity  $\eta_{app}$  on the effective shear rate  $\dot{\gamma}_{iv}$  at 240°C for (1) PA-1, (2) PA-2, (3) PP, and (4) NBR, and at 200°C for (5) EPR.

$$\eta_{\rm app} = \eta_0 \dot{\gamma}_w^{n-1} \tag{2}$$

where *n* is the flow index, which n < 1 for the abnormally viscous liquids and n = 1 for Newtonian liquids. From the plots (Fig. 1), the flow indexes in the range of approximately of  $3.0 \leq \text{Ln}$   $\dot{\gamma}_w \leq 7.5$  were calculated and are listed in Table I. It is possible to see that at given temperatures and shear rates, the rheological behavior of nylon 6 is closest to Newtonian liquid behavior, whereas the other materials have pronounced viscoelastic properties.

Quite naturally, at the high values of  $\dot{\gamma}_w$ , the values of  $\eta_{app}$  differ from each other to a smaller degree than at the small  $\dot{\gamma}_w$  values. As follows from formula (1), the growing similarity of values  $\eta_{\rm app}$  of initial components should result in an improvement of dispersiability of one polymer in other. However, the value  $\ln \dot{\gamma}_w = 7$  corresponds to the rotor (screw) rotation speed of blending equipment  $N = 10^4$  rpm, which is practically unenforceable on the available equipment. Usually, the blending is carried out at N = 80-200rpm, which corresponds to Ln  $\dot{\gamma}_w = 2.1 - 3.0.^{5,7}$  In this case, the difference between the values for  $\eta_{\rm app}$  is rather essential, and the limited degree of dispergation must not be significant. Really, in the case of the PA-1–NBR (90/10) blend, for which distinction of viscosities is highest  $(\eta_d/\eta_m = 10)$ ,

dispersion of rubber phase is nonuniform, and the average size of rubber particles is  $\alpha_n = 4 \ \mu m$  [Fig. 2(a)], with the interfacial interaction of polar PA-6 and NBR being maximal among chosen materials.

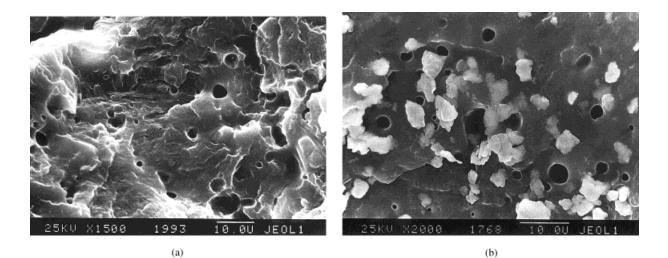
The degree of dispergation did not practically depend on the blending equipment. The influences of shear speed (N), duration, and temperature of blending (T) were investigated. It was found that the optimum conditions of blend preparation from the point of view of their phase structure are as follows: (a) by blending in the mixer Brabender, T = 230 °C and N = 80 rpm during 10 min; (b) by blending in twin-screw Berstorff extruder, T = 240 °C and N = 100 rpm during 10 min. Hence, if viscosities of initial components of a polymer blend differ considerably, neither intensive interfacial interaction, nor the use of more efficient blending equipment (a twinscrew extruder) allows for improvement of the state and degree of dispersion of one polymer in another.

It was possible to reduce the viscosity of rubber (NBR) by the introduction in it of a liquid nitrile rubber with contents up to about 30 wt %. It appears that the reduction of rubber viscosity in 10 times, that is, up to  $\eta_d/\eta_m = 10$ , does not change a degree of dispergation of rubber in nylon 6 by blending on the twin-screw extruder. This result is not described by equation (1); if the interfacial tension, shear rate, and viscosity of matrix (PA-6) do not change practically, the size of the disperse phase should decrease 5-7 times due to such a change of  $\eta_d/\eta_m$ . The validity of the assumption about a permanence of interfacial tension in the PA-1-NBR system by introducing the liquid nitrile rubber was confirmed by calculations of interfacial tension change  $(\Delta \gamma)$  as a result of addition of LCNR, under the following formula<sup>8,9</sup>:

$$\Delta \gamma = \gamma_{\rm PA-NBR} - \gamma_{\rm PA-(NBR+LCNR)} \tag{3}$$

Table IThe Values of Flow Index n in Formula(2) for Initial Blend Components

Polymer	n	
	At 240°C	At 200°C
PA-1	0.80	_
PA-2	0.72	_
PP	0.34	0.39
NBR	0.21	_
EPR	—	0.47



25KU X5400 2147 1.00 JEOL1 25KU X10000 1770 1.00 JEOL1

**Figure 2** Scanning electron micrographs of the fractured surfaces of 90/10 blends: (a) PA-1–NBR, received by blending in a Berstorff extruder; (b) PA-1–NBR + 2% of PA–PB, received by blending in a Berstorff extruder; (c) PA-1–EPR, received by blending in a mixer Brabender; (d) PA-2–EPR, received by blending in a Brabender mixer.

where

$$\gamma_{\mathrm{PA-NBR}} = \gamma_{\mathrm{PA}} + \gamma_{\mathrm{NBR}} - 2\Phi_{\mathrm{PA-NBR}}(\gamma_{\mathrm{PA}}\gamma_{\mathrm{NBR}})^{1/2}$$

(c)

 $\gamma_{\text{PA}-(\text{NBR}+\text{LCNR})} = \gamma_{\text{PA}} + \gamma_{\text{NBR}+\text{LCNR}}$ 

$$-2\Phi_{\mathrm{PA-(NBR+LCNR)}}(\gamma_{\mathrm{PA}}\gamma_{\mathrm{NBR+LCNR}})^{1/2}$$

$$\Phi_{\rm PA-NBR} = \frac{4(\nu_{\rm PA}\nu_{\rm NBR})^{1/3}}{(\nu_{\rm PA}^{1/3} + \nu_{\rm NBR}^{1/3})^2}$$

 $\Phi_{PA-(NBR+LCNR)}$ 

$$=\frac{4\nu_{\rm PA}^{1/3}[w_{\rm LCNR}\nu_{\rm LCNR}+(1-w_{\rm LCNR})\nu_{\rm NBR}]^{1/3}}{\{\nu_{\rm PA}^{1/3}+[w_{\rm LCNR}\nu_{\rm LCNR}+(1-w_{\rm LCNR})\nu_{\rm NBR}]^{1/3}\}^2}$$

Here,  $\gamma_{\text{PA-NBR}}$  and  $\gamma_{\text{PA-(NBR+LCNR)}}$  are interfacial tensions for nylon 6–NBR and nylon 6–(NBR + LCNR) systems;  $\Phi_{\text{PA-NBR}}$  and  $\Phi_{\text{PA-(NBR+LCNR)}}$ , the corresponding interaction parameters;  $\gamma_{\text{PA}}$ ,  $\gamma_{\text{NBR}}$ , and  $\gamma_{\text{NBR+LCNR}}$ , the surface tensions of nylon 6, NBR, and NBR modified by introduction of LCNR, respectively;  $\nu_{\text{PA}}$ ,  $\nu_{\text{NBR}}$ , and  $\nu_{\text{LCNR}}$ , the molar volumes of appropriate components; and  $w_{\text{LCNR}} = 0.3$ , the weight fraction of LCNR in the rubber phase.

(d)

It was found that for the given system,  $\Phi_{PA-NBR} \cong \Phi_{PA-(NBR+LCNR)} \approx 0.990$ . On the basis of conducted calculations, it is established that in addition to NBR  $\sim$  30 wt % of LCNR, the interfacial tension of the PA-1–NBR system practically does not change or even decrease slightly (from

3.7 up to 3.2 mN/m). It seems that formula (1) has restrictions of applicability, and at  $\eta_d/\eta_m > 10-20$ , the use of equation (1) is incorrect. Really, if considering Figure 10 in the work of Wu,<sup>5</sup> it is possible to notice that equation (1) is not correct at the high values  $\eta_d/\eta_m$ . This could be attributed to the change of deformation and fracture character of disperse phase in a melt.<sup>1</sup>

Introduction of PA–PB blockcopolymer, improving interfacial interaction of nylon 6 with NBR results in reduction of the size of disperse phase particles ( $\alpha_n = 3 \ \mu m$ ) [Fig. 2(b)]. The replacement of NBR in the blend on EPR, which has the worse interfacial interaction with nylon 6, results in a decrease of the value of  $\alpha_n$  up to 0.5  $\mu m$  [Fig. 2(c)]. Thus, the change of size  $\alpha_n$  of disperse rubber particles is qualitatively described reasonably well by formula (1) for the values  $\eta_d/\eta_m \sim 10$ . The smallest size of the rubber phase ( $\alpha_n = 0.2 \ \mu m$ ) is observed for PA-2–EPR blend at  $\eta_d/\eta_m \sim 1$  [Fig. 2(d)].

Thus, from the presented experimental results, it follows that the best dispersivity (the smallest size of disperse rubber phase) is observed in that case when the viscosity values of PA-matrix  $(\eta_m)$ and rubber  $(\eta_d)$  are close to each other  $(\eta_d/\eta_m \sim 1)$ . At  $\eta_d/\eta_m = 10$ , the modification of nylon 6 with the purpose of increasing the interfacial tension  $\gamma_{12}$  improves the dispersivity of the rubber phase to a smaller degree. The change of speed of shear deformations (use of a twin-screw extruder) does not largely influence the phase structure of blends if the viscosities of initial components are essentially distinguished.

Applicability of equation (1) in the case of blending of incompatible polymers (PP and NBR) is also considered. The chemical structure of these polymers varies strongly, and the interfacial interaction is very weak. For change of interfacial interaction character, PP, was modified by various oligomers of the resolic type (RO). The modification of PP by means of RO was conducted as follows: at 180-190°C in PP, 2 wt % of RO was added and carefully hashed, then  $SnCl_2$  was added. The infrared (IR) spectra of initial and modified PP after its extraction by o-dichlorobenzene and acetone appeared to be identical, indicating the absence of deep changes in the structure of PP. Evidently, in this case, the RO transforms to a finely dispersed phase. However, it was also observed that the dispersion of NBR in PP depends on the nature of the modifier of the phenolic type used. The detailed discussion of these results is outside the scope of the present work. It is noteworthy only that the most efficient agent

was chosen. By blending the modified PP and NBR, it was found that the dispersity of the rubber phase is slightly improved, and it is due to the essential difference in the viscosities of these two components. For reduction of the rubber viscosity, a low-molecular-weight LCNR was added. As the rheological measurements of viscosity have shown, the given way of reduction of the melt viscosity of the rubber is rather effective. At the introduction in initial rubber of 25 phr LCNR, the rubber viscosity almost coincides with the viscosity of PP at 190°C.

Then, the modified PP and NBR were mixed in temperature-speed conditions, similar to those described above, at an optimum ratio of components (75/25). It was found that in the Brabender mixer, the average size of rubber phase is  $\alpha_n = 10$  $\mu$ m; in the twin-screw extruder,  $\alpha_n = 1 \mu$ m, which is less on the order. Hence, in this case, the type of the blending equipment appreciably influences the dispersity of rubber phase, although the shear speed value (N) was practically the same. It is also necessary here to emphasize that the experimentally observable reduction of  $\alpha_n$  does not follow from formula (1). At the same time, the influence of PP modification and the reduction of rubber viscosity on dispersity is qualitatively described by the model of deformation and fracture of disperse phase, incorporated in basis of equation (1).

Thus, in summary, it can be concluded that equation (1) has limited applicability. It does not describe the size of disperse phase  $\alpha_n$  for large viscosity ratios of components  $\eta_d/\eta_m$  and it depends on the type of blending equipment.

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