# Nylon 6/Ethylene Propylene Rubber (EPM) Blends: Phase Morphology Development during Processing and Comparison with Literature Data

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**ABSTRACT:** The morphology of immiscible blends of nylon 6 and ethylene propylene rubber blends (EPM) was studied. The blends were prepared by melt blending in a twin-screw miniextruder and a Haake Rheocord mixer. The influence of the blend ratio, time of mixing, rotation speed of the rotors, mixing temperature, and quenching of the extruded melt at low temperature on the phase morphology of the blends was quantitatively analyzed. The morphology was examined by scanning electron microscopy (SEM) after preferential extraction of the minor phase. The SEM micrographs were quantitatively analyzed for domain-size measurements. The morphology of the blends indicated that the EPM phase was preferentially dispersed as domains in the continuous nylon matrix up to 40 wt % of its concentration. A cocontinuous morphology was observed at 50 and 60 wt % EPM content followed by a phase inversion beyond 60 wt % of EPM where the nylon phase was dispersed as domains in the continuous EPM phase. The size, shape, and distribution of the domains were evaluated by image analysis as a function of the blend composition. The effect of the time of mixing on the phase morphology was studied up to 20 min for the 30/70 EPM/nylon blend. The most significant domain breakup was observed within the first 3 min of mixing followed by a leveling off up to 15 min. This may be associated with the equilibrium between the domain breakup and coalescence. The influence of rotor speed on the morphology was insignificant at a high rotor speed although a significant effect was observed by changing the rotor speed from 9 to 20 rpm. The influence of high-temperature annealing, repeated cycles of extrusion, the molecular weight of the nylon matrix, and the nature of the mixer type (twin-screw miniextruder versus Haake Rheocord mixer) on the morphology was also investigated in detail. The experimental results were compared with literature data. Finally, the extent of interface adhesion in these blends was analyzed by examination of the fracture-surface morphology. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1405-1429, 1999

**Key words:** morphology development; blends; nylon 6; EPM rubber; coalescence; processing

# **INTRODUCTION**

Thermoplastic elastomers (TPEs) are a relatively new class of materials which combine the excellent processability characteristics of thermoplastics and the physical properties of elastomers. TPEs from blends of rubbers and plastics have attracted much interest in recent years. In these type of blends, the required properties can be easily achieved by the careful selection of the component polymers (rubber and plastic) and their blend ratios.<sup>1,2</sup> However, most of the thermoplastic/rubber blends are immiscible and incompatible. In general, the physical, mechanical,

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Polymer	Source	$M_w$
EPR		
78% ethylene content	Exxon	80,000
Polyamide 6	DSM	15,000
Polyamide 6	DSM	24,000
Polyamide 6	DSM	34,000
Polyamide 6	DSM	44,000

Table IProperties of the ComponentPolymers Used

and rheological properties of immiscible polymer blends depend not only on the constituent polymers but also on the morphologies of the blends. In fact, due to the deformable nature of the minor phase in immiscible polymer blends, a wide range of morphologies (size, shape, and distribution of the dispersed phase) can be obtained during melt processing. Therefore, many studies on the morphology of polymer blends have been performed. The pioneering work on the theoretical investigation of the deformation and breakup of Newtonian droplets in Newtonian media was reported by Taylor.<sup>3,4</sup> He found that the droplet size of the emulsion depends on the interfacial tension and viscosity ratio between the dispersed phase and the continuous phase. The theories of Taylor have been verified by several authors 5-8 and later extended to polymer blends by Wu.<sup>9</sup>

During the melt processing of polymer blends, the final size, shape, and distribution of the dispersed phase are determined by the composition, viscosity ratio, and interfacial tension among the component polymers and the shear rate/shear stress, elasticity ratio, and processing conditions such as time and temperature of mixing, rotation speed of the rotor, and type of mixer. Several investigations have been performed in order to understand the influence of the processing conditions on the morphology and properties of immiscible polymer blends. The most important of these include the studies of Favis and Chalifoux,<sup>10-12</sup> Karger-Kocis and Csikai,<sup>13</sup> Wu,<sup>9</sup> Laokijcharoen and Coran,<sup>14</sup> Scott and Mocosko,<sup>15</sup> Thomas et al.,16-18 and Sundararaj and Macosko.19 Favis and Chalifoux<sup>10-12</sup> undertook a series of investigations in order to understand the how both the size and the shape of the minor phase are controlled during processing. They also analyzed the effect of the morphology on the final properties. Karger-Kocsis and Ciskai<sup>13</sup> reported that for EPDM/polypropylene (PP) blends fine dispersions can be obtained if the ethylene content and the number-average molecular weight of EPDM are low and the viscosity value is near unity.

In the case of ethylene propylene rubber (EPM)/ nylon blends, the particle size of the dispersed EPM phase was found to become larger when the viscosity ratio increases above unity or decreases below unity.<sup>9</sup> The breakup of the domain was reported even when the viscosity ratio was greater than 4. Laokijcharoen and Coran<sup>14</sup> reported on the morphology development in natural rubber (NR)/highdensity polyethylene (HDPE) blends. They ana-

Measurements
Measurements $600 \times 400 \times 800 \text{ mm}^3$ 5 cm³           3.5 cm³           10–360 rpm           107.5 mm           2           350°C           10 min           5 bar           10 min           5 min           Max 51/min
35 W 0.37 kW 5 cm <sup>3</sup> 110/220 222/380 V

Table II Speciations of the DSM Extruder

lyzed the influence of the rotor speed, mixing time, and annealing on the morphology and properties. The morphology development during reactive and nonreactive blending of EPM rubber with two thermoplastic matrices was reported by Scott and Macosko.<sup>15</sup> The influence of the blend ratio and processing conditions on the morphology and properties of various TPEs such as nitrile rubber/HDPE and nitrile rubber/PP was reported by Thomas et al.<sup>16–18</sup> Sundararaj and Macosko<sup>19</sup> reported on the existence of a critical shear rate in polymer blends where a minimum particle size is achieved. This has been explained based on droplet elasticity.

The influence of phase coarsening and coalescence on the morphology of polymer blends is very important since blends are often annealed during fabrication and processing, which leads to coalescence. Interesting studies in this area were reported by Favis,<sup>10</sup> Fortelny and Kovar,<sup>20</sup> Sundararaj and Mocosko,<sup>19</sup> and Thomas et al.<sup>21</sup> Coalescence coarsening was reported by Favis<sup>10</sup> for PC/PP blends at a PC concentration of 23 wt %, where the particle size was found to increase by 75% after annealing for 90 min at 250°C. The effect was reported to be highly dependent on the concentration of the minor phase. Fortelny and Kovar<sup>20</sup> investigated the coalescence behavior in molten PP/EPDM blends and attempted to model the behavior. They reported that the amount of coalescence in blends decreases significantly if the matrix phase viscosity is above a critical value and if the dispersed-phase volume fraction is below a critical value. Sundararaj and Macosko<sup>19</sup> showed that a limiting dispersed-phase size exists at very low concentrations for polymer blends mixed in an internal batch mixer and two types of twin-screw extruders. For uncompatibilized blends, they observed that the final particle size increases with the dispersed-phase concentration due the increased coalescence. The particle-size distribution was also found to broaden at higher concentration due to coalescence.

Nylon 6 is a widely used material in engineering applications. It has superior tensile, tear, and abrasion properties and good chemical resistance. It is extensively used for many applications such as bearings, fishing lines, and ropes and also in the preparation of electrical components. However, nylon has some limitations. It absorbs water in its molded form which causes dimensional changes. It also has poor impact strength and notch sensitivity. These limitations can be alleviated by blending with suitable polymers. Blends of nylon and EPM are a new class of TPEs which combine the excellent processability characteris-



**Figure 1** Haake rheographs of component polymers and blends.

tics and engineering properties of nylon and elastic and the ozone resistance properties of EPM rubber. These blends exhibit excellent impact properties and less water-absorption characteristics. However, they are highly immiscible and incompatible due to the high polarity difference between the component polymers.

The morphology, mechanical performance, and impact properties of these blends have been reported by several authors.<sup>22-25</sup> These include the studies of Martuscelli et al.,<sup>22</sup> Paul et al.,<sup>23</sup> and Gaymans et al.<sup>24,25</sup> Majundar et al. studied the effect of the extruder type on the properties and morphology of nylon 6/EPM-g-Ma blends.<sup>23</sup> However, it is important to mention that almost all these studies are related to blend systems having a very low concentration of the dispersed EPM rubber phase. To our knowledge, to this date, no detailed examination has been made on the morphology development of these TPEs as a function of blend composition, processing conditions (mixing temperature, rotation speed of the rotor, mixing time, and nature of the mixer type, repeated extrusion, quenching, annealing, etc.), and molecular weight of the component polymers.

The main objectives of the present study were to analyze quantitatively the phase morphology development in EPM/nylon 6 TPEs as a function of composition, processing conditions, and molecular weight of the nylon phase. Phase coarsening and coalescence behavior were analyzed as a



(d)





(d)



(e)

(f)

**Figure 2** SEM micrographs showing the morphology of EPM/nylon blends: (a) 10/90 EPM/nylon blend; EPM is dispersed as domains in the continuous nylon matrix. (b) 20/80 EPM/nylon blend; EPM is dispersed as domains in the continuous nylon matrix. (d) 40/60 EPM/nylon blend; EPM is dispersed as domains in the continuous nylon matrix. (e) 50/50 EPM/nylon blend; interpenetrating cocontinuous morphology. (f) 60/40 EPM/nylon blend; interpenetrating cocontinuous morphology. (g) 70/30 EPM/nylon blend; nylon is dispersed as domains in the EPM matrix. (h) 80/20 EPM/nylon blend; nylon is dispersed as domains in the continuous EPM matrix. (i) 90/10 EPM/nylon blend; nylon is dispersed as domains in the continuous EPM matrix.



(g)

(h)



(i) Figure 2 (Continued from the previous page)

function of composition and high-temperature isothermal annealing. The morphology was studied by scanning electron microscopic examination of the preferentially extracted (EPM or nylon depending on the composition) blend samples. The photographs were quantitatively analyzed by image analysis. Finally, the extent of interfacial bonding in these blends was evaluated by the examination of the fracture surfaces by scanning electron microscopy (SEM).

# **EXPERIMENTAL**

### **Materials**

The characteristics of the EPM rubber and different types of nylon 6 used in this study are given in Table I. Both EPM rubber and nylon 6 are commercially available. Nylon 6 of varying molecular weights was received from DSM, Geleen, The Netherlands, as gift samples. EPM rubber was supplied by the Exxon Chemical Co., Belgium, as gift samples. All the nylons were dried at 120°C for 12 h prior to blending.

# **Melt Blending**

Blends were prepared in a corotating twin-screw batch-type miniextruder (DSM) under a nitrogen atmosphere. The specifications of the DSM miniextruder are given in Table II. The mixing time, temperature, and rotor speed were 10 min, 250°C, and 100 rpm, respectively. However, to study the influence of the rotor speed, time of mixing, and temperature on the phase morphology, experiments were performed as a function of rotor speed, time of mixing, and temperature. To study the effect of the mixer type on the morphology, blending was also carried out in Haake Rheocord mixer under a nitrogen atmosphere at a temperature of 250°C and rotor speed of 100 rpm at varying mixing times.

#### **Phase-morphology Studies**

SEM was used to examine the phase morphology of the blends. The samples were fractured under liquid nitrogen and one of the phases was preferentially extracted. For the blend samples having a dispersed EPM phase, this phase was extracted using boiling xylene for 12 h. Also, the EPM phase was extracted in blends having a cocontinuous morphology (50/50 and 60/40 EPM/nylon). When the nylon is the dispersed phase, this phase was removed by using formic acid at ambient temperature for a period of 12 h. The dried samples were sputter-coated with gold prior to SEM examination. A Phillips (XL20 Model) scanning electron microscope operating at 10 kV was used to view the specimens. Several micrographs were taken for each sample. To analyze the extent of interfacial bonding, the fracture surfaces of the samples were analyzed by SEM.

The dispersed-phase size analysis was done using an automatic image analyzing technique which employed IMAGE software. The apparent diameter was measured by scanning the micrographs and individually outlining the particles to calculate their dimensions. Typically, over 400 particles and several fields of view were analyzed. The number-average diameter  $(D_n)$  and weightaverage diameter  $(D_w)$  were calculated from the following relationships:

$$D_n = \sum n_i D_i / \sum n_i \tag{1}$$

$$D_w = \sum n_i D_i^2 / \sum n_i D_i \tag{2}$$

where  $n_i$  is the number of particles within the diameter range *i*.

### **RESULTS AND DISCUSSION**

#### **Rheology of Homopolymers and Blends**

Since the rheological behaviors of the individual component and blends influence the morphological structure, we analyzed the rheological characteristics of the system from the Haake Rheocord torque data. As seen in Figure 1, neat nylon 6 reaches a steady-state torque level after approximately 3 min of mixing at 250°C. Similar results are shown by EPM. Due to the higher viscosity of EPM rubber as compared to nylon 6, EPM shows a higher equilibrium torque value. Interestingly, the blend viscosities are lower than those of the component homopolymers. This is associated with the high interlayer slip between the highly incompatible component polymers. In fact, due to the high-polarity difference, EPM and nylon are highly immiscible and incompatible.

#### Effect of Blend Composition on Phase Morphology

The morphology is a major determinant of the properties of heterogeneous polymer blends. The morphology of heterogeneous polymer blends, in general, depends on the blend composition, interfacial tension between the constituent polymers, viscosity ratio, elasticity ratio, and processing history. The composition dependence of the morphology of heterogeneous polymer blends has been reported extensively in the literature.<sup>16-23</sup> The interesting studies of Denesi and Porter<sup>26</sup> showed that for blends with the same processing history the morphology is determined by the melt-viscosity ratio and composition. When the mixed polymers have similar melt viscosities, the resultant morphology will be a uniform distribution of the minor phase in the major one, no matter which is the minor component. When the components have different melt viscosities, the morphology of the resultant blend depends on whether the minor component has a lower viscosity or higher viscosity than that of the major one. If the minor component has a lower viscosity, this component will be finely dispersed. On the other hand, the minor component will be coarsely dispersed in essentially spherical domains if its viscosity is higher than that of the major one.

The morphology of the blends over the entire range of compositions, that is, from 10/90 to 90/10 EPM/nylon, can be understood from the SEM micrographs given in Figure 2(a–i). For blends having EPM concentrations up to 60 wt %, the rubber phase is extracted by boiling xylene. For other compositions, 70/30, 80/20, and 90/10, the nylon phase was removed by formic acid. The morphology of the blends shows that up to 40 wt % EPM concentration the rubber phase is preferentially dispersed as spherical inclusions in the low-viscosity nylon matrix. An interpenetrating cocontinuous morphology was obtained at 50 and 60 wt % of EPM, followed by a phase inversion beyond



**Figure 3** Effect of EPM concentration on number  $(D_n)$ - and weight  $(D_w)$ -average domain diameter.

60 wt % of the rubber, where the nylon phase is dispersed as spherical inclusions in the continuous EPM phase. The size, shape, and distribution of the domains were quantified by image analysis. In most cases, the domains are spherical in shape. However, a few elliptical and elongated domains also could be seen. The number-  $(D_n)$  and weightaverage  $(D_w)$  domain diameter are plotted as a function of the composition in Figure 3. From Figure 3, it can be seen that both the  $D_n$  and  $D_w$ of the dispersed EPM phase increase with EPM concentration up to 40 wt % and the increase is much sharper above 30 wt % of EPM concentration. The increase in the domain size of the dispersed EPM phase with increasing concentration of EPM is associated with the reagglomeration or coalescence of the dispersed rubber particles. The extent of increase in the particle size  $(D_n)$  from 10 to 20 wt % and 30 to 40 wt % of EPM rubber is 37 and 116%, respectively. This suggests that the phenomenon of coalescence is more predominant at high concentrations of the dispersed EPM phase. However, on the other hand, when nylon is the dispersed phase, the influence of increasing nylon concentration on the coalescence is less predominant as compared to the situation where EPM is the dispersed phase (Fig. 3). This is associated with the high viscosity of the rubber phase



Figure 4 Effect of EPM concentration interfacial area per unit volume.



Figure 5 Particle-size distribution of blends having dispersed EPM phase.

(matrix) which resists the agglomeration of the nylon domains. In fact, when the matrix phase is more viscous, the higher shear forces and, hence, the decreasing collision times along with a more difficult matrix interlayer film drainage between the colliding droplets reduce the coalescence probability. The phenomenon of coalescence at a higher concentration of one of the components was reported by several authors.<sup>16–21,26–28</sup> This is, in general, related to the droplet agglomeration during melt mixing which is well known to be a random process.

It is also important to mention that in polymer blends, depending on the viscosity and elasticity ratio of the component polymers, the amount of coalescence varies. We also estimated the interfacial area per unit volume of each blend composition. This is presented in Figure 4 as a function of the EPM concentration. It is interesting to note that the interfacial area per unit volume decreases sharply when the EPM concentration increases from 30 to 40 wt %. This is associated with the high extent of coalescence in this blend composition as discussed earlier. The polydispersity of the particle-size distribution was found to increase with increase in the dispersed phase (EPM or nylon) concentration, which is evident from Figures 5 and 6. This is also associated with



Figure 6 Particle-size distribution of blends having dispersed nylon phase.



(a)



(b)

**Figure 7** SEM mircrographs of the periphery of the extrudates showing stratification: (a) 20/80 EPM/nylon blend; (b) 10/90 EPM/nylon blend.

coalescence.

To analyze the stratification of the extrudates, if any, we examined the periphery (skin) of the extrudates by SEM. Interestingly, as expected, a stratification phenomenon could be observed with more concentration of the nylon at the periphery. This is shown Figure 7(a,b) and is associated with the migration of the low-viscosity nylon phase toward the periphery of the extrudate encapsulating the high-viscosity EPM phase. This kind of phase segregation during the extrusion of immiscible polymer blends was reported by several authors.<sup>26,29-32</sup> Danesi and Porter<sup>26</sup> studied the influence of the extrusion speed on the stratification of EPM/PP blends; they observed an increased quantity of the lower melt-viscosity polymer at the surface of the extrudates. Yu and Han<sup>29</sup> and Southern and Ballman<sup>30</sup> studied the factors affecting the interface distortion in the two-phase flow of polymer melts. The conclusions of each of these studies were that differences in the shear viscosity between the two melts led to interface distortion with the lower-viscosity melt encapsulating the high-viscosity melt. MacLean<sup>31</sup> and Everage<sup>32</sup> suggested that the reason for encapsulating the high-viscosity fluids by lower-viscosity fluids during the conduit flow is due to the tendency of the multiphase system to take on a phase configuration, giving the lowest rate of viscous dissipation.

### Influence of Rotor Speed on Dispersed-phase Size

Figure 8 shows the dependence of the dispersedphase size on the rotation speed of the rotors for 30/70 EPM/nylon blends. The morphologies of the samples as a function of rotor speed are given in Figure 9(a-d)for 9, 20, 60, and 150 rpm, respectively. The standard deviations in the diameter measurements are given in Table III. In these experiments, the temperature of mixing and the total time of mixing were 250°C and 10 min, respectively. The results illustrate that the most significant breakdown or disintegration of the dispersed phase takes place by increasing the rotor speed from 9 to 20 rpm. Increasing the rpm from 20 to 150 does not have any major influence on the dispersed-phase size although the particle size decreases marginally. If the rpm of the rotor is considered to be proportional to the shear rate, an approximately sevenfold increase in shear rate does not have any major influence on the dispersed-phase size.

The influence of shear stress and shear rate on the phase dimensions has been studied both theoretically and experimentally by many authors. The well-known Taylor's equation<sup>3,4</sup> for Newtonian fluids in shear flow indicates that phase size and shear stress are in inverse dependence. The experimental studies of  $Wu^9$  were in parallel with Taylor's equation where he noted that changing the shear stress resulted in an observable difference in the size of the minor phase. Interestingly, he obtained a master curve by plotting the Weber number versus the viscosity ratio and all his results fit on a single master curve. Mine et al.<sup>33</sup> also reported large differences in the morphology



Figure 8 Effect of rotation speed of the screws on number-average EPM domain diameter for the 30/70 EPM/nylon blend.

on changing shear stress. However, there are many interesting experimental studies in which the authors indicated that varying the shear stress by a factor of 3-4 has little effect on the size of the dispersed phase. These include the studies of Favis<sup>10</sup> and Sundararaj and Macosko.<sup>19</sup> The results of their studies indicate that above a critical shear stress the blends are not sensitive to either shear stress or shear rate. The studies of Favis<sup>10</sup> indicated a decrease of the dispersedphase size for PC/PP blends from 10 to 20 rpm, followed by a leveling off at high rpm. Sundararaj and Macosko<sup>19</sup> reported that there is a critical minimum drop size as the shear rate is varied, and this can be accounted for through the polymer elasticity. When the shear rate is increased, the matrix viscosity decreases and the drop elasticity increases, so that the drop resists the deformation to a greater extent. Consequently, there is an optimum shear rate where the finest dispersion is obtained.

They further suggested that the Taylor limit does not accurately predict the particle size for polymer blends mixed in the batch mixer at low dispersed-phase concentrations. This discrepancy has been explained based on polymer viscoelasticiy. These observations and as well as our present study are important since they are not in parallel with Taylor's predictions. In addition to the polymer viscoelasticity, the deviation from Taylor's theory is also due to the very weak interfacial interactions at the phase boundaries. As a result, the shear stress and shear rate are not continuous at the interface of these highly immiscible blends.

# Influence of Time of Mixing on Dispersed-phase Size

Figure 10(a,-e) shows the morphology of the 30/70 blend mixed for 0.5, 2, 4, 5, and 15 min, respectively. The rotor speed and the mixing temperature were 100 rpm and 250°C, respectively. Figure 11 shows the influence of the dependence of the phase size on the time of mixing. The standard deviation in the diameter measurements is given in Table IV. The results indicate that the most significant domain breakup occurs within the first 3 min of mixing time where melting and the consequent liquefaction take place. Further increase in mixing time up to 15 min does not have any major influence on the particle size, although the smallest particle size was obtained after 10-min mixing. The invariant morphology is due to the rapid reestablishment of equilibrium between domain breakup and coalescence. However, at longer mixing times (> 15 min), the phase dimension increases dramatically. This is associated with the shear-induced phase coarsening. In fact, we observed a strong tendency for coalescence in this system on annealing which is discussed in the coming section. It is also important to consider the possible thermal degradation of the nylon phase at longer mixing times. We observed a drastic reduction in mixing torque at longer mixing times. This is an indication of the possible thermal degradation of the polymer. This will contribute to a decrease in the molecular weight of the nylon matrix phase and finally to a coarser morphology due to rheological reasons.



(b)



(d)

Figure 9 SEM micrographs showing the morphology of 30/70 EPM/nylon blend as a function of screw speed: (a) 9 rpm; (b) 20 rpm; (c) 60 rpm; (d) 150 rpm.

There are several reports in the literature regarding the effect of mixing time on the dispersed-phase size. These include the studies of Karger-Kocsis et al.,<sup>34</sup> Schreiber and Olguin,<sup>35</sup> Favis,<sup>10</sup> Laokijcharoen and Coran,<sup>14</sup> and Scott and Macosko.<sup>15,36</sup> Karger-Kocsis et al.<sup>34</sup> reported on the marginal dependence of the dispersedphase size on the mixing time over a wide range of

	1				
		1	Rotation Speed (rpm	n)	
Parameter	9	20	60	100	150
Domain diameter (µm)	$4.84\pm4.00$	$3.82\pm2.80$	$3.62\pm2.71$	$3.48\pm2.70$	$3.35\pm2.68$

Table III Influence of Rotation Speed on Domain Diameter



(b)



(c)

(d)



(e)

**Figure 10** SEM micrographs showing the morphology of 30/70 EPM/nylon blend as a function of mixing time: (a) 0.5 min; (b) 2 min; (c) 4 min; (d) 5 min; (e) 15 min.

torque ratios. At a very high torque ratio, the very viscous dispersed phase resisted the deformation over a longer time of mixing, and at a low torque ratio where more finer dispersions were generated, it became rather difficult to deform small droplets. The studies of Schreiber and Olguin<sup>35</sup> showed that bulk particle-size reduction takes place very early in the mixing process. The depen-



**Figure 11** Effect of mixing time on the number-average EPM domain diameter for the 30/70 EPM/nylon blend.

dence of the phase size versus the energy input leveled off very rapidly.

Favis<sup>10</sup> studied the effect of the mixing time on the dispersed-phase size up to 20 min at three viscosity ratios for PC/PP blends where PC was dispersed in the PP phase. In this study, the most significant particle-size deformation and disintegration took place within the first 2 min of mixing. After 2 min, very little reduction in the size of the dispersed phase was observed up to 20 min of mixing time, although some phase size/time dependence was observed at an intermediate viscosity ratio. The dispersed-phase morphology as a function of mixing time was investigated for two rubber-modified thermoplastics, namely, aromatic amorphous nylon (Zytel 330)/EPM and polystyrene/EPM, by Scott and Macosko.<sup>15</sup> In this study most of the reduction in the dispersed-phase size was observed at shorter mixing times in conjunction with the melting and softening process. At intermediate mixing times, the morphology consisted of a large number of small particles along with a small number of very large particles in the size distribution. Accoring to Scott and Macosko, the effect of subsequent mixing was primarily to reduce the size

of the largest particles in the size distribution. The very recent studies of Laokijcharoen and Coran<sup>14</sup> also indicated that the major breakdown of the particles occurs at the very beginning of the mixing process. This has been proved to be the same at different rotation speeds of the rotor. These observations including our present study are in agreement with Taylor's theory<sup>3,4</sup> which models the Newtonian drop size using the viscosity ratio,  $\eta_r = \eta_d/\eta_m$ and Weber number, We:

$$We = \eta_m D_{n\gamma} / 2\Gamma \tag{3}$$

where  $\gamma$  is the shear rate,  $\eta_m$  is the matrix phase viscosity,  $D_n$  is the dispersed-phase size, and  $\Gamma$  is the interfacial tension. From this equation, it is clear that there is a critical value of the Weber number, We, below which no particle deformation takes place and, therefore, there exists a critical particle size.

The present study on the mixing behavior of the blends further indicates that the initial melting and liquefaction period is highly important since the final morphology is generated during

	_		Mixing T	ime (min)		
Parameter	0.5	1	5	10	15	20
Domain diameter (µm)	$5.54 \pm 4.60$	$4.86\pm3.70$	$3.75\pm2.35$	$3.48\pm2.70$	$3.73\pm2.80$	$6.10\pm4.60$

 Table IV
 Influence of Mixing Time on Domain Size





(b)

**Figure 12** SEM micrographs showing the morphology of 30/70 EPM/nylon blend at different mixing temperatures: (a) 2608C; (b) 2408C.

this period. This further suggests the importance of the screw design at the melting region of the extruder as indicated by Favis.<sup>10</sup>

# Influence of Mixing Temperature on Dispersed-phase Size

The influence of the mixing temperature on the morphology of 30/70 EPM/nylon blends at two different mixing temperatures is shown in Figures 12(a,b). In Table V, the standard deviation in the diameter measurement is given. Figure 13 shows the influence of the number-average domain diameter on the mixing temperature. It is interesting to note that the lowest domain size is obtained at a temperature of 250°C. As the temperature is increased beyond 250°C, the domain size increases. This may be because at high temperature the viscosity of the nylon matrix decreases sharply and this causes a big mismatch between the viscosities of the two polymers. In addition, since the nylon viscosity decreases, the shear forces involved are too low to cause a particle breakdown. These factors lead to the poor dispersion. Also, at high temperature, there is strong tendency for the melt to undergo phase coarsening, which is discussed below.

# **Coalescence and Phase Coarsening**

Coalescence behavior has been well documented in binary Newtonian mixtures.  $^{37-39}$  It has been reported that the contact time needed for the drop coalescence increases when the matrix viscosity decreases, the drop diameter decreases, and the density difference between the matrix and the drop increases.<sup>38</sup> A three-step mechanism is suggested for the flow-induced coalescence behavior of Newtonian liquid drops as shown in Figure 14.<sup>39</sup> At first, the two drops come closer and rotate in the shear field. The film of the matrix phase between the two drops drains and, consequently, the film thickness decreases to a critical value and, finally, rupture of the interface occurs, leading to coalescence. The modeling of the coalescence behavior in binary Newtonian mixtures has been done using population-balance ideas.<sup>40</sup> The coalescence behavior in viscoelastic polymer systems has not been well understood. Most of the coalescence experiments in polymer blends were

Table V Influence of Mixing Temperature on Domain Size

		Mixing Tem	perature (°C)	
Parameter	230	250	260	270
Domain diameter (µm)	$3.77\pm2.39$	$3.48\pm2.70$	$3.65\pm2.61$	$4.44\pm2.90$



**Figure 13** Effect of mixing temperature on number-average domain diameter for the 30/70 EPM/nylon blend.

made on melt blends and solution-cast blend films.<sup>10,41</sup> Coalescence after mixing is very important since polymer products are often annealed and coalescence may occur during annealing.

Although a polymer matrix will have a high viscosity relative to a Newtonian matrix, drop collision and film drainage in polymer blends will be much different from the Newtonian model due to the different rheological behavior of polymer liquids. Elastic recoil is expected to cause polymer drops to separate during the initial collision step. However, Roland and Bohm<sup>42</sup> reported that increasing the shear rates leads to an increase in the coalescence effect. Coalescence coarsening is believed to represent the late stages of phase separation (McMaster<sup>43</sup>). If high interfacial tension exists between the two phases, there will always



**Figure 14** Idealized depiction of shear-induced coalescence behavior of Newtonian droplets (ref. 37).

be a tendency for the minor phase to minimize its surface-free energy.

Domain ripening for a system of discrete droplets dispersed in a matrix where larger dispersed particles grow at the expense of the smaller ones is referred to as Ostwald ripening. McMaster<sup>43</sup> made a more qualitative analysis by relating the behavior to interfacial tension, the volume fraction of the dispersed phase, and the diffusion coefficient of the matrix. Coalescence in polymer blends without the influence of mechanical stress was modeled by Frotelny and Kovar.<sup>20</sup> Phase coarsening of EPM/PP blends was reported by Jang et al.<sup>44</sup>; they found that, in general, the rate of coalescence increased at longer times. Favis<sup>10</sup> observed coalescence coarsening for PC/PP blends at a 0.23 volume fraction of the PC phase. No coarsening effect was observed at a 0.10 volume fraction of PC. When the matrix and the dispersed phases were inverted, no coalescence could be observed.

In the present study, phase coarsening upon annealing was followed for blends having EPM and nylon as the dispersed phases. The extrudates were annealed for 2 h at a temperature of 260°C. Figure 15(a–f) shows the morphology of the annealed 10/90, 20/80, 30/70, 40/60, 70/30, and 90/10 EPM/nylon blends, respectively. The number- and weight-average domain diameters as a function of the weight percent of the EPM rubber are plotted in Figure 16(a,b), respectively. It can be seen that phase coarsening takes place only at a high concentration of the EPM phase. At low EPM concentration (< 20%), no phase coarsening could be observed. This is in agreement



(b)



(c)

(d)



(e)

(f)

**Figure 15** SEM micrographs showing the morphology of EPM/nylon blends upon annealing at 2608C for 2 h: (a) 10/90 EPM/nylon; (b) 20/80 EPM/nylon blend; (c) 30/70 EPM/nylon blend; (d) 40/60 EPM/nylon blend; (e) 70/30 EPM/nylon blend; (f) 90/10 EPM/nylon blend.



**Figure 16** Effect of EPM concentration on the domain diameter before and after annealing: (a) EPM concentration versus number-average domain diameter; (b) EPM concentration versus weight-average domain diameter.

with the findings of Fortelny and Kovar,<sup>20</sup> who modeled the coalescence behavior in polymer blends. They found that the amount of coalescence in blends decreases significantly if the dispersed-phase volume fraction is below a critical value and if the matrix phase viscosity is above a critical value. For typical particle sizes encountered in polymer blends (about 1  $\mu$ m) and a 0.25 dispersed-phase volume fraction, the model predicts that very little coalescence will occur above a critical matrix phase viscosity of 496 Pa s. In fact, in our system, since the nylon matrix viscosity is low, the EPM coarsening is highly favored. The phase-coarsening behavior of the blends when the nylon phase is dispersed as domains is shown in Table VI. It is seen that phase coarsening could be observed only at a high concentration of the nylon

phase. However, the phase growth was marginal as compared to that of the EPM phase. This is associated with the high viscosity of the EPM

Table VI	<b>Phase Coarsening of Blends (Nylon</b>
as Dispers	sed Phase) upon Annealing
at a Temp	erature of 260°C for 2 h

	Domain Size $D_n$ (µm)		
Blend Composition	Before Annealing	After Annealing	
90/10 EPM/nylon 80/20 EPM/nylon 70/30 EPM/nylon	$\begin{array}{c} 1.43 \pm 0.80 \\ 2.46 \pm 1.01 \\ 2.57 \pm 1.50 \end{array}$	$\begin{array}{c} 1.45\ \pm\ 1.0\\ 2.47\ \pm\ 1.20\\ 3.86\ \pm\ 1.80 \end{array}$	



(b)



(ci)

(cii)



(d)

(e)

**Figure 17** SEM micrographs showing the evolution of morphology as a function annealing time for 30/70 EPM/nylon blend at a temperature of 2708C: (a) morphology after 30-min annealing; (b) morphology after 60-min annealing; (ci) morphology after 90-min annealing; (cii) morphology after 90-min annealing showing elongated domains; (d) morphology after 120-min annealing; (e) morphology of the periphery region (skin) after 30-min annealing.



**Figure 18** Effect of time of isothermal annealing on the number-average EPM domain diameter for the 30/70EPM/nylon blend.

matrix phase. The highly viscous EPM phase reduces the diffusional mobility of the nylon molecules. In addition, the coalescence during mixing is also governed by the interfacial mobility. The high EPM matrix viscosity gives rise to a relatively immobile interface which leads to a longer drainage time for the intervening film.

Phase coarsening has also been followed under isothermal conditions at an annealing temperature of 270°C as a function of time The purpose of this experiment was to follow the evolution of the morphology as a function of time. The morphologies of the 30/70 EPM/nylon blend samples annealed for 30, 60, 90, and 120 min are given in Figure 17(a-c[ci and cii],d), respectively. After annealing, elongated particles also could be seen in some cases [Fig 17(cii)]. The number-average particle diameter is presented as a function of time in Figure 18. It is seen that the numberaverage domain diameter increases as a function of time. The rate of growth is much faster at longer times. This is in agreement with the findings of Jang et al.44 who also observed a slow initial coarsening process followed by a rapid coalescence at longer times. The large coalescence effects seen during annealing of blends containing EPM as the dispersed phase (> 20 wt%) indicate that these blends have a high interfacial mobility. The stratification of the extrudate was also analyzed after annealing. This is shown in Figure 17(e). A high concentration of the nylon phase could be seen at the periphery of the extrudate. The extent of stratification was more severe than that of the unannealed sample (Fig.7). This is due to that during annealing the highly viscous EPM

domains undergo a high extent of coalescence by migrating toward the core of the extrudate.

# Influence of Repeated Extrusion on Dispersed-phase Size

A major complicating factor in the case of an immiscible polymer blend is the intrinsic instability of the morphology in the melt which depends on the shear or elongational stress, viscosity ratio, blend composition, and temperature. In practice, this implies that the phase morphology carefully induced during blending can be completely lost upon further processing. To analyze the stability of the morphology as a function of the extrusion cycle, the 30/70 EPM/nylon blend was subjected to repeated extrusion cycles. For each extrusion, the temperature, rotor speed, and mixing time were 250°C, 100 rpm, and 10 min, respectively. The morphology of the samples is given in Figure 19(a-c) for the second, third, and fourth extrusions, respectively. The number- and weight-average domain diameters are plotted as a function of the extrusion cycle. Both  $D_w$  and  $D_n$ increase with an increasing number of extrusion cycles (Fig. 20). The  $D_w$  values increase at a faster rate. The polydispersity of the particle-size distribution is also found to increase with an increasing number of extrusion cycles.

### Influence of Quenching on Dispersed-phase Size

The quenching of the molten extrudates of the blend immediately after extrusion at a temperature of  $-20^{\circ}$ C was carried out in order to study its

influence on the morphology. The results are presented in Table VII. It can be understood that the morphology of the quenched samples is slightly finer than that of the unquenched samples. However, the effect was marginal with a difference of only 15%. This suggests that ambient cooling of the extrudates does not lead to a high degree of coalescence.

# Influence of the Molecular Weight of the Nylon Matrix on the Dispersed-phase Size

The morphology of the 20/80 and 30/70 EPM/ nylon blends as a function of molecular weight of the nylon matrix phase is given in Figure 21(a-d).

The influence of the molecular weight of nylon 6 on the number- and weight-average diameters for the 20/80 EPM/nylon are presented in Figure 22(a,b), respectively. It can be understood that as the molecular weight of nylon increases a much finer domain size is achieved. The molecular weight effect on the morphology can be explained based on the fact that as the molecular weight of the matrix increases the viscosity of the system increases and this leads to the finer distribution of the minor phase in the major one. The polydispersity was also found to increase with decreasing molecular weight. The influence of the molecular weight of the nylon matrix on the morphology and



(a)



(b)



(c)

**Figure 19** SEM micrographs showing the morphology of 30/70 EPM/nylon blend as a function of repeated extrusion: (a) second extrusion; (b) third extrusion; (c) fourth extrusion.



Figure 20 Effect of extrusion cycle on the number- and weight-average domain diameter for the 30/70 EPM/nylon blend.

properties of various nylon/rubber blends was studied by Paul and coworkers<sup>45</sup>; they observed a decrease in the domain size of the dispersed phase with increasing molecular weight.

### Influence of the Nature of Mixer Type (Twin-screw Extruder Versus Haake Rheocord) on the Dispersed-phase Size

To understand the influence of the nature of the mixer type on the phase morphology, the morphology of the sample blended in the twin extruder was compared with that of the Haake mixer. The rotor speed and the mixing temperature were 100 rpm and 250°C, respectively, in both cases. The morphology of 30/70 EPM/nylon blend was analyzed after 5 and 10 min of mixing time in both cases. The sizes of the dispersed phase after 5-min mixing were 3.75 and 4  $\mu$ m for the twin-screw and Haake Rheocord mixers, respectively. However, after 10 min, the sizes of the dispersed phases were very similar. This suggests that the nature of the mixer type does not have much influence on the morphology of the EPM/ nylon blends.

# Fracture Surface Morphology and Extent of Interface Adhesion

It has already been reported that in the case of immiscible blends composed of a crystalline and an amorphous component, depending on whether the crystalline material is the dispersed phase or the matrix, high-level voiding or good apparent contact, respectively, could be obtained.<sup>46</sup> In view

of this, we examined the fracture-surface morphology of 30/70 and 70/30 EPM/nylon blends. The fracture surfaces of the 30/70 and 70/30 blends are given in Figure 23(a,b), respectively. It is seen that in both cases the extent of the interface adhesion was very poor. In the 30/70 EPM/ nylon blend, the crystallization of the nylon matrix occurs at 180°C. Indeed, during the crystallization of nylon at 180°C, the EPM rubber is much above its glass transition temperature  $(T_{\sigma})$ -308C). Therefore, during the crystallization of the nylon phase, it would be expected to result in the local deformation of the rubbery EPM phase with the likely possibility of microvoiding occurring due to the high immiscibility of the two polymers. The microvoiding could be understood from the fracture surface shown in Figure 23(a). Microvoiding was also observed in the 70/30 EPM/nylon blend, which can be explained based on the contraction of the nylon dispersed phase during crystallization. These observations suggest that compatibilization is essential in these blends to im-

Table VII	Influence of Quenching on the	)
Number-Av	verage Domain Diameter	

	Domain Size, $D_n$ (µm)		
Blend Composition	Ambient Cooling	Quenching	
30/70 EPM/nylon 80/10 EPM/nylon 90/10 EPM/nylon	$\begin{array}{c} 3.48\ \pm\ 2.7\ 2.25\ \pm\ 1.5\ 1.44\ \pm\ 0.80 \end{array}$	$\begin{array}{c} 3.01 \pm 2.2 \ 1.81 \pm 1.4 \ 1.24 \pm 0.79 \end{array}$	



(b)



(c)

(d)

**Figure 21** SEM micrographs showing the morphology of EPM/nylon blend as a function of the molecular weight of the nylon matrix: (a) 20/80 EPM/nylon blend,  $M_w$  15,000; (b) 20/80 EPM/nylon blend,  $M_w$  44,000; (c) 30/70 EPM/nylon blend,  $M_w$  15,000; (d) 30/70 EPM/nylon blend,  $M_w$  34,000.

prove the interfacial adhesion and also for the stabilization of the blend morphology.

# **CONCLUSIONS**

The phase-morphology development during the processing of immiscible EPM/nylon 6 blends was investigated as a function of the composition, rotation speed of the mixer, mixing time and temperature, and quenching and annealing of the blends. The influence of the nature of the mixer type, molecular weight of the nylon phase, and a repeated cycle of extrusion on the morphology was also studied. The morphology of the blends was examined over the entire range of composition. The morphology indicated a two-phase structure in which the high-viscosity EPM phase was dispersed as domains in the continuous lowviscosity nylon matrix up to 40 wt % of the EPM concentration. An interpenetrating cocontinuous morphology was obtained for the 50/50 and 60/40



**Figure 22** Effect of number-average molecular weight of nylon on the EPM domain diameter for the 20/80 EPM/nylon blend: (a) molecular weight versus number-average domain diameter; (b) molecular weight versus weight-average domain diameter.

EPM/nylon compositions. At high EPM concentrations (> 60 wt %), the nylon phase was dispersed as domains in the continuous EPM matrix. The size of the dispersed phase was found to increase with increasing concentration of that phase; this is associated with coalescence. The coalescence behavior was found to be maximum at a 40 wt % dispersed EPM phase. Interestingly, the interfacial area per unit volume of the blend was found to decrease in this blend composition due to the high extent of coalescence.

The size distribution of the domains was also found to increase with increasing coalescence. The cross section of the extrudates indicated stratification phenomena with increased concentration of nylon at the periphery of the extrudate. The influence of mixing time indicated that most of the particle deformation and breakup occurs in the first 3 min of mixing. Extending the time of mixing up to 15 min has little effect on the morphology. However, with longer mixing times (> 15 min), the system showed a strong tendency for shear-induced coalescence. The most significant change in the domain size was observed by increasing the rotor speed from 9 to 20 rpm. However, further increase in the rotor speed had only a marginal effect on the dispersed-phase size. A temperature of 250°C was found to be optimum for the smallest particle size. Isothermal annealing experiments were performed on the blend samples.

Extensive phase coarsening was observed upon isothermal annealing. The coarsening behavior was strongly dependent on the concentration of the dispersed phase, viscosity of the matrix phase, and the duration of annealing. Interestingly, phase coarsening was more prominent at high concentrations of the dispersed EPM phase. The nature of the mixer type (twin-screw extruder versus Haake Rheocord) was found to have



(a)



(b)

**Figure 23** SEM micrographs showing the fracture surfaces: (a) 30/70 EPM/nylon blend; (b) 70/30 EPM/ nylon blend.

no significant effect on the morphology. With the increasing molecular weight of the nylon matrix phase, the size of the dispersed EPM phase was found to decrease. Attempts have been made to compare the experimental results with the literature data. The fracture-surface morphology of the blends indicated a lack of adhesion between the phases as evidenced by the formation of microvoids irrespective of the nature of the dispersed phase (EPM or nylon). Finally, it is important to mention that the present study reveals that compatibilization is essential in these blends to stabilize the blend morphology and to improve the interfacial adhesion. Detailed studies in this direction are in progress in the MSC laboratory.

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