

The Effect of Extruder Temperature and Maleated Polypropylene on Polypropylene/Nylon-6,6 Blend: A Small Angle X-ray Scattering Study

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SYNOPSIS

A series of small-angle X-ray scattering measurements were performed to study the polypropylene/nylon-6,6 polymer blends with or without the compatibilizer: maleated polypropylene. The blends were made at various temperatures using a venting conical twin-screw extruder with a constant extruding flow rate. The X-ray scattering results show that the dispersion of nylon-6,6 in polypropylene is improved for temperature above the melting point of nylon-6,6 (265°C) when the compatibilizer involved is not used. As the compatibilizer is incorporated, the dispersion is significantly improved, even at the temperature below 265°C. With the compatibilizer, the dispersed nylon-6,6 particle size and shape in the blends are independent of blending temperature, suggesting that the temperature effect is overwhelmed by the effect of the compatibilizer. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Polymer-polymer blends are one of the most promising areas for developing novel materials with improved properties in a relatively short development time. Polymer blends can be distinguished roughly into two categories: One involves homogeneous polymer alloys, exhibiting intermediate properties of the individual components. The other consists of heterogeneous polymer blends, wherein one polymer is dispersed in the other, which serves as the continuous phase. Normally, these two polymers are immiscible. This type of blend has the advantage of providing additivity of the phase properties. Additionally, it may exhibit new properties due to a particular morphology.¹

To develop such a blend with the desired engineered properties, the dispersed phase often requires good isotropy and, preferably, with small and a monodisperse domain size. This is generally achieved by introducing suitable modifiers into the

blend to interlink the two immiscible components. Varying the physical conditions of blending is another alternative to improve the dispersion. For example, many thermoplastic materials are routinely blended with a rubbery polymer, like polyolefins, at the melting temperature to improve the toughness and the high impact resistance.²

Polypropylene/nylon-6,6 blends is one of the attractive engineering polymer blends for commercial applications.³ In this particular blend, polypropylene provides hydrophobicity, while nylon-6,6 is the hydrophilic component. Due to this dual characteristic, proper blending of them requires optimization of the composition, process temperature, and flow rate as well as the selection of compatibilizers.

A widely used compatibilizer for polyolefin/nylon blends are maleic anhydride-grafted polymers. In this work, we selected the maleated polypropylene that is a commercial product from BP Chemicals (polybond-1000, referred to as PB). It has been shown to be maleated selectively at the chain ends. The chemistry of the anhydride moiety reacting with the amine group is the key step in the blending.⁴ To blend the polypropylene and nylon-6,6, we used a venting conical twin-screw extruder. The experi-

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ment was performed at several temperatures for two series at a constant flow rate.

To characterize the dispersion state of the nylon-6,6 in the blends, small-angle X-ray scattering was applied. The results show that the dispersion of nylon-6,6 depends on the extruding temperature when no compatibilizer is involved. The dispersion is generally poor at the temperature below the melting point of nylon-6,6. It is improved when temperature is higher than or equal to the melting point. As PB is incorporated, the dispersion is significantly enhanced, overwhelming the temperature dependence.

EXPERIMENTAL

Sample Preparation

Polypropylene ($M_w = 552,500$; $M_w/M_n = 7.3$) was obtained from Kodak. Nylon-6,6 (Zytel 101) was obtained from DuPont. Maleated polypropylene (PB, $M_w = 157,800$; $M_n = 43,700$; $M_w/M_n = 3.61$) was obtained from BP Chemicals. All materials were used as received without treatment.

To blend the polymer, samples were first predried at 80°C overnight, weighed and premixed in a plastic bag, and placed in a hopper. They were then extruded in a Brabender extruder, with venting conical twin screws. The blending temperature was controlled using electric heating elements with $\pm 1^\circ\text{C}$ accuracy. A constant flow rate was maintained for all the blendings. The output polymer blends from the extruder were thin films. These polymer films were then cut into 1×2 cm pieces and stacked to make 1 mm-thick samples for small-angle X-ray scattering experiments. Table I gives the compositions, blending temperatures, and the thickness of the polymer blends obtained.

Table I Sample Compositions and Experimental Conditions

Sample	PP/N-6,6/PB	Blending Temp (°C)	Thickness (mm)
C-0	100/0/0	240	0.044
C-1	70/30/0	250	0.040
C-2	70/30/0	270	0.044
S-1	40/30/30	240	0.044
S-2	40/30/30	250	0.049
S-3	40/30/30	265	0.044
S-4	40/30/30	270	0.042

PP = polypropylene; N-6,6 = nylon-6,6; PB = polybond-1000.

Small-angle X-ray Scattering

Small-angle X-ray scattering (SAXS) was performed on a 10 M SAXS instrument at Oak Ridge National Laboratory (ORNL). The X-ray was generated from a Rigaku-Denki rotating anode with a copper target, operating at 4 kW. The $K\alpha$ wavelength of 1.54 Å was selected using a pyrolytic graphite monochromator. Using a series of pinholes, the X-ray beam was collimated to 1 mm² at the sample position. The sample-to-detector distance was set at 5.176 M, which gives a scattering vector Q range from ~ 0.01 to $\sim 0.1 \text{ \AA}^{-1}$. A beam stop of 1.5 cm diameter was located in front of the detector to stop the direct beam. A two-dimensional continuous wire detector was used to detect the scattered photons. The samples were made 1 mm in thickness and loaded into a vacuum chamber with an automatic sampling wheel. Each sample was measured for 1 h to ensure good counting statistics. The raw data were corrected for dark current and background and reduced to the absolute intensity based on a calibrated polyethylene standard of known scattering cross section at the peak position.

RESULTS AND DISCUSSION

Seven samples were investigated in the SAXS experiment: the control sample (polypropylene, C-0 in Table I), the direct blending sample without PB (C-1 and C-2), and four three-component samples (S-1, S-2, S-3, and S-4).

Figure 1(a) is a contour plot of the X-ray spectrum of C-0. Each contour represents the equal-intensity line. Those near the center are the small-angle scattering [see Fig. 1(b)]. One notes that there are two half-circle contours on each side of the center. These are two correlation peaks at the reference angle $\omega = 0^\circ$ (designated). These peaks (P peaks) have preferred orientation (nonsymmetric with respect to the beam center), indicating that the system is not isotropic at 240°C. This preferred orientation may arise from a lamellarlike structure due to a low shear rate in the extrusion. The integrated scattering intensity spectrum, $I(Q)$, along the azimuthal axis (in the direction photons travel) is shown in Figure 1(b), where a broad correlation peak is observed. $Q = (4\pi/\lambda) \sin \sigma/2$ is the scattering vector, where $\lambda = 1.54 \text{ \AA}$ is the X-ray wavelength and θ is the scattering angle.⁵ One should be cautioned here not to analyze the integrated spectrum by treating it as an isotropic system, since the structure may be perturbed by the shear-induced structure. However, the system is a homopolymer used as the continuous

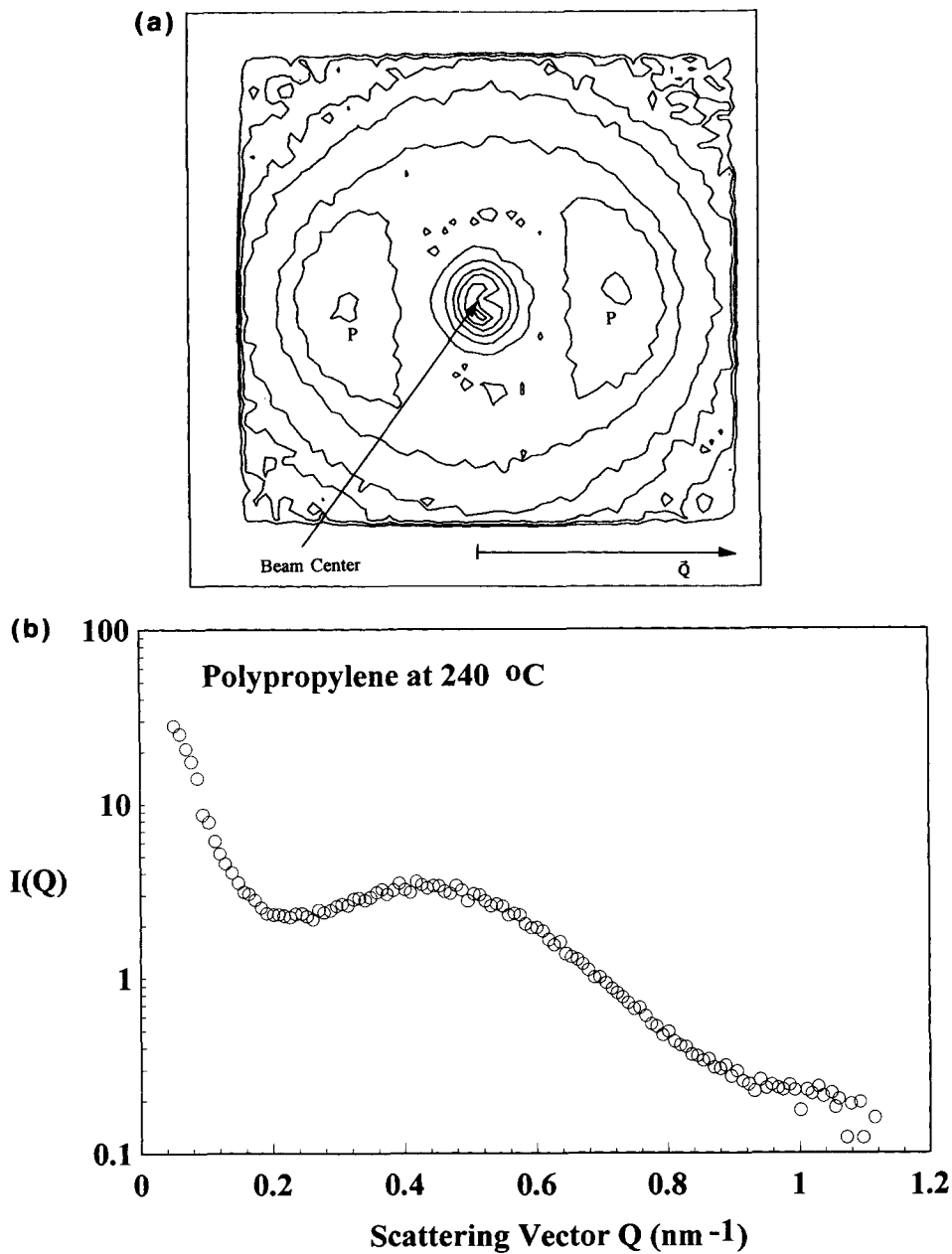


Figure 1 (a) Two-dimensional contour plot of the X-ray scattering spectrum for C-0; the center is the beam stop. The contours around it show that there is small-angle scattering (or there are large objects in the system). Q axis is in the radial direction. It covers a spatial range to 1.2 nm^{-1} . The frame is for presentation purposes. The two half-circle contours indicate that there are two correlation peaks (P peaks in the figure) with preferred orientation (nonsymmetric with respect to the center). (b) The integrated (along azimuthal axis, the direct beam direction) spectrum for (a).

phase in the subsequent blending systems. Thus, C-0 is to be used as the control.

Figure 2 illustrates the two-dimensional spectrum for sample C-1 that was blended at 250°C . As one can see, two more correlation peaks [compared with Fig. 1 (a)] were observed, exhibiting the morphology

of the nylon component. This clear separation of the characteristic peaks directly indicates that these two polymers are incompatible under these blending conditions (temperature and flow rate). As we raise the blending temperature to 270°C (sample C-2), nylon-6,6 melts ($m_p = 265^\circ\text{C}$), and the blend be-

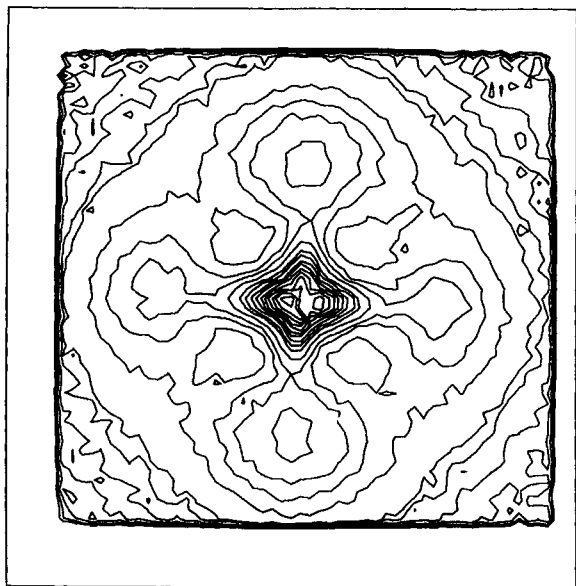


Figure 2 Two-dimensional X-ray scattering spectrum for C-1. The Q range is the same as in Figure 1 (a). Four correlation peaks were observed. Obviously, the two newly added peaks are from the nylon-6,6 component. The distinctive addition of the peaks means that nylon-6,6 does not “dissolve” in polypropylene.

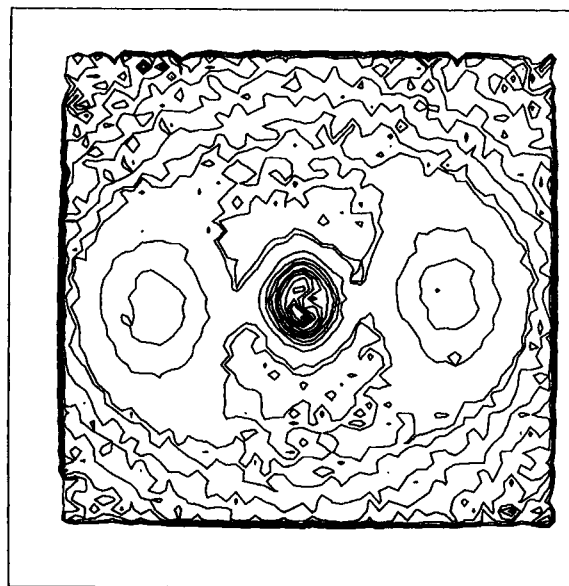


Figure 3 The same as Figure 2 for C-2.

comes more homogeneous, as one can see in Figure 3. The spectrum is similar to the pure polypropylene case [see Fig. 1 (a)], except with a slightly different shearing effect. One notes that the nylon peaks [the extra peaks in Fig. 2 compared with Fig. 1 (a)] com-

pletely disappear at this blending temperature. This is an indication that the nylon-6,6 is “dissolved” into polypropylene and loses its homopolymeric morphology. The morphology of polypropylene remains. Figure 4 shows the integrated spectra for these two cases. One can see the rapid decreasing of the C-2 scattering intensity at almost all scattering angles (the entire Q range). In this case, the observed feature of the blend is mainly from polypropylene.

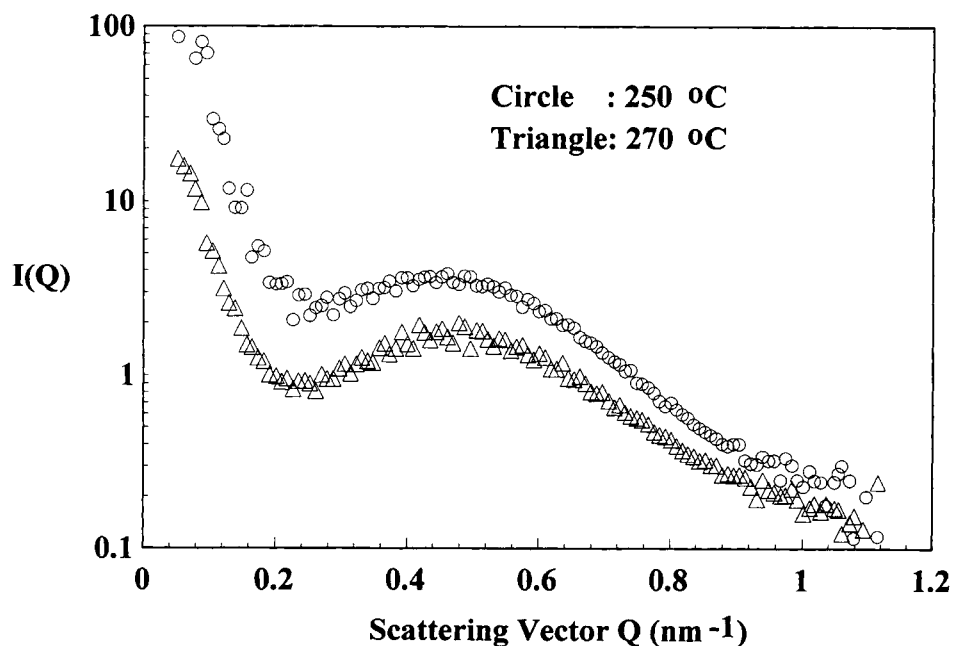


Figure 4 Integrated scattering intensity vs. Q for C-1 and C-2.

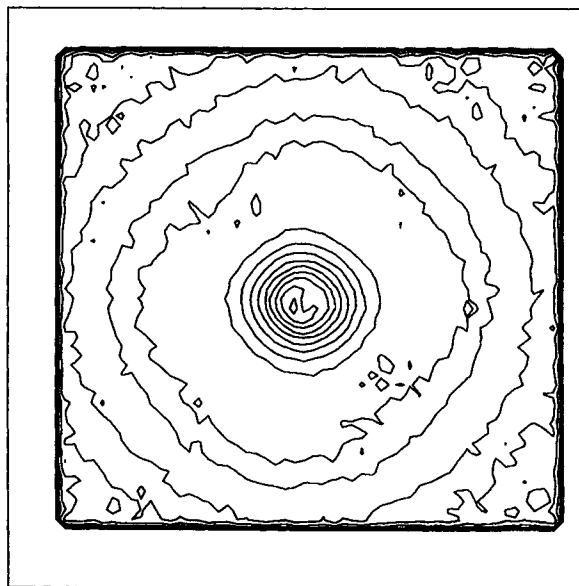


Figure 5 Two-dimensional X-ray scattering spectrum for S-2. The Q range is the same as Figure 1(a). One notes that the preferred orientation nearly disappears, indicating a good dispersion of nylon-6,6.

Although increasing the blending temperature improves the nylon-6,6 dispersion, polypropylene is basically hydrophobic, whereas nylon-6,6 is hydrophilic. Due to this fundamental difference, a good dispersion of nylon-6,6 can be obtained only at a relatively severe blending condition such as high temperature (Fig. 3) if no compatibilizer is used.⁶ It would be easier to disperse nylon-6,6 if a com-

patibilizer is incorporated into the blend. Samples S-1 to S-4 are the three-component systems with 30% maleated polypropylene as the compatibilizer. Figure 5 shows a typical two-dimension spectrum of these systems. This is the case at the 250°C blending temperature. Although the blending temperature is below the melting point of nylon-6,6, it is fairly isotropic as one can see (no preferred orientation is shown), indicating a good dispersion of nylon-6,6. Figure 6 shows the integrated scattering spectra at various blending temperatures (S-1-S-4, see Table I). The main features of the spectra remain nearly the same for all blending temperatures. No appreciable temperature effect was observed, as far as the scattering intensity distribution (or morphology) is concerned. However, these spectra differ from the control sample [Fig. 1(b)] substantially. Figures 7-10 illustrate this point. For all cases, the intensity at the small Q range drastically increases. It is an indication that the nylon-6,6 although "dissolved," forms particles of an average size larger than that of polypropylene. This is because the scattering intensity is proportional to the square of the sizes of the dispersed particles (in this case, the nylon-6,6) when the system is isotropic.⁵

To further characterize the structure of the dispersed nylon-6,6, we analyzed the scattering spectra using the Guinier⁷ and the Porod⁸ analyses. We first examine the Porod region to evaluate approximately the shape of the disperse particles. It has been derived by Porod that $\ln[I(Q)]$ as a function of $\ln(Q)$ should approach to a -4 slope at the large Q value,

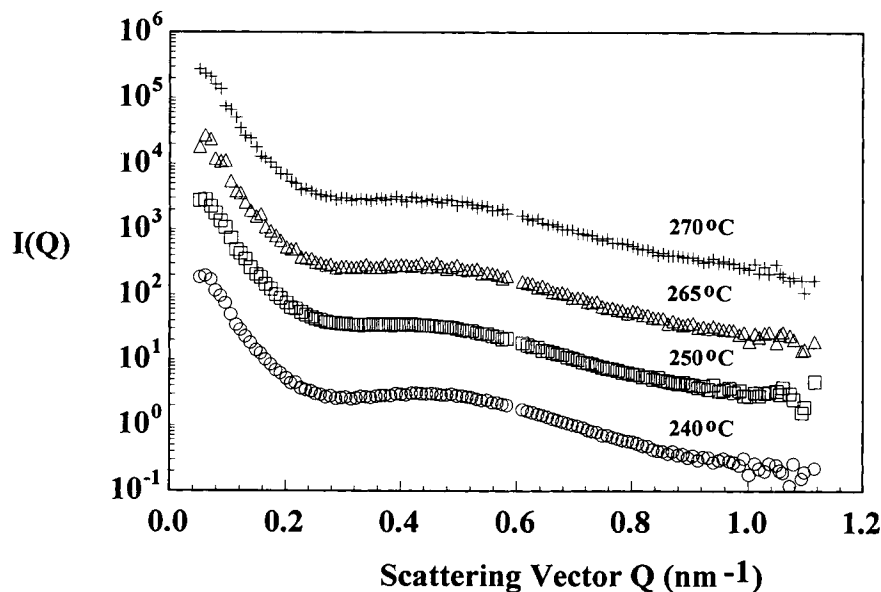


Figure 6 $I(Q)$ vs. Q for S-1 to S-4. Curves are shifted for better representation.

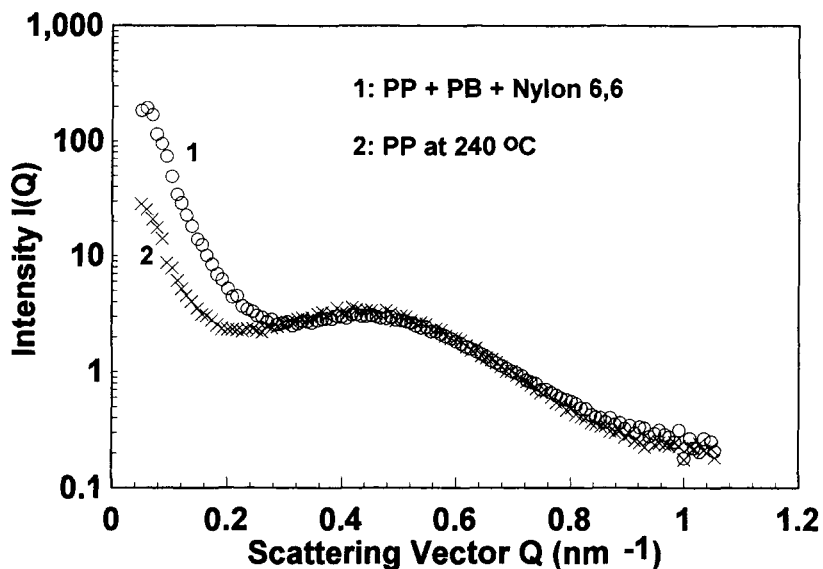


Figure 7 $I(Q)$ vs. Q for S-1 and C-0. The increase at small Q region indicates that the dispersed nylon-6,6 has a particle size much larger than that of polypropylene.

provided that the scatterers have smooth surfaces (or the interface between the scatterers and the continuous phase is smooth, from the photon wavelength point of view) and the particles are spherical in shape. For other smooth particles of different geometry, $I(Q)$ behaves differently. Cylindrical particles have a linear behavior at the "medium" Q range (in this case, approximately from 0.2 to 0.7 nm^{-1}) when the intensity is plotted as $\ln[QI(Q)]$

vs. Q^2 . For a sheetlike particle, $\ln[Q^2I(Q)]$ vs. Q^2 would give show linearity. Figures 11-14 show the Porod analysis and the slopes calculated at the large Q regions. Except for the case of 270°C, the slopes are all close to -4 , which is a slope for a spherical particle. In fact, the sample blended at 270°C gives -3.87 , which is close to -4 as well. Clearly, the blending temperature does not significantly alter the shape of the disperse particles. Knowing that the

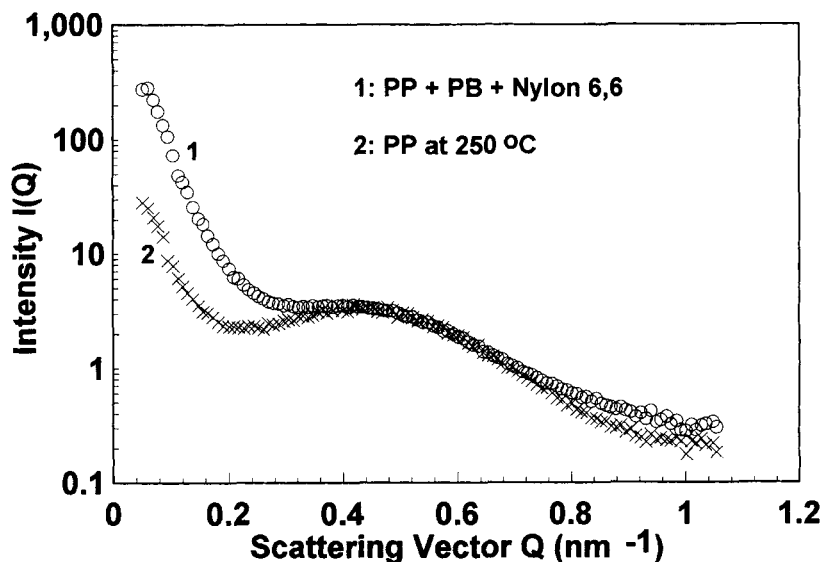


Figure 8 Same plot as Figure 7 for S-2 and C-0.

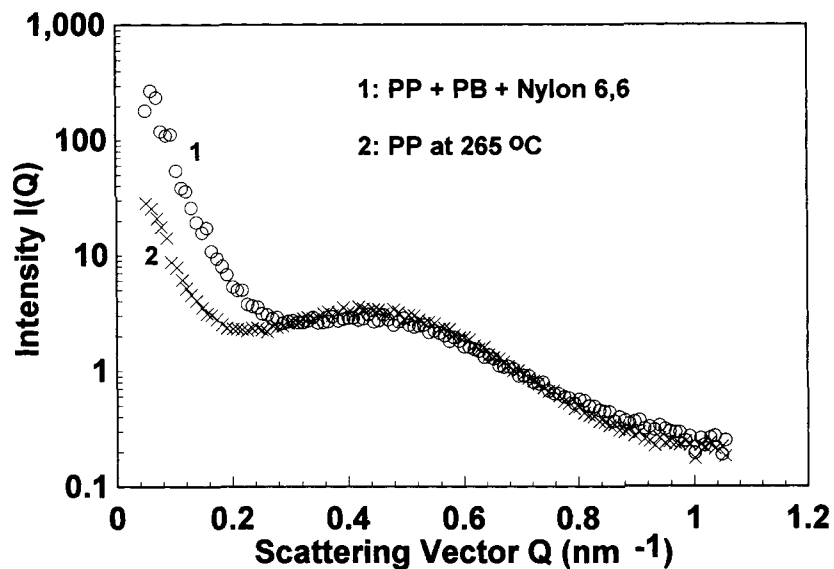


Figure 9 Same plot as Figure 7 for S-3 and C-0.

nylon-6,6 particles are approximately spherical, we can estimate the size by applying the Guinier analysis.⁷ The Guinier analysis is applicable at the small Q region, where the scattering intensity related to the radius of gyration according to

$$\ln[I(Q)] \cong I_0 e^{-1/3 R_g^2 Q^2} \quad QR_g \leq 1 \quad (1)$$

In Figures 15–18, we plot $\ln[I(Q)]$ vs. Q^2 . From the

initial slopes, we obtained the radii of gyration. The radii of gyration so obtained are near 22.5 nm (or ~ 30 nm radius) for all four cases. This indicates that the incorporation of the compatibilizer enhances the dispersion of nylon-6,6 so significantly as to overwhelm the blending temperature effect. No matter whether the blending temperature is below or above the nylon-6,6 melting temperature, the structure of the dispersed nylon-6,6 remains more or less the same.

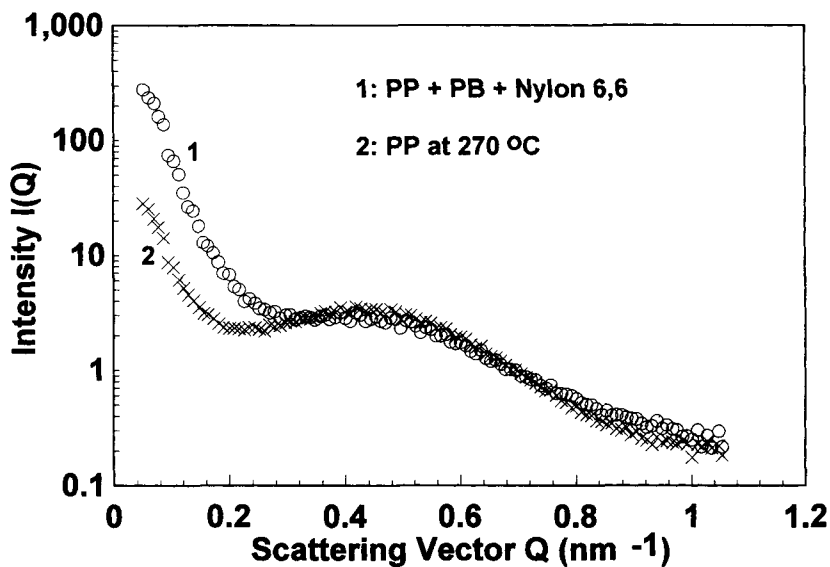


Figure 10 Same plot as Figure 7 for S-4 and C-0.

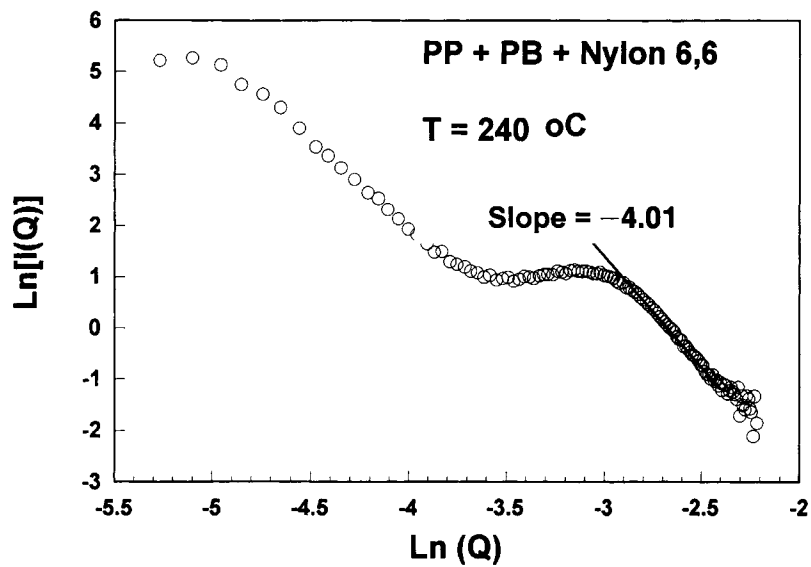


Figure 11 $\ln[I(Q)]$ vs. $\ln Q$ for S-1. The slope at large Q is close to -4 , signifying a nearly spherical particle.

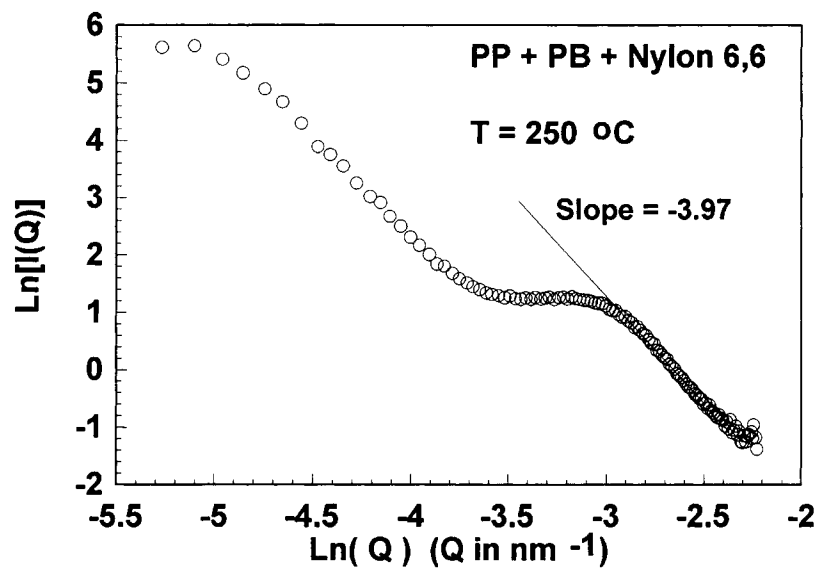


Figure 12 Same plot as Figure 11 for S-2. The slope at large Q is again close to -4 .

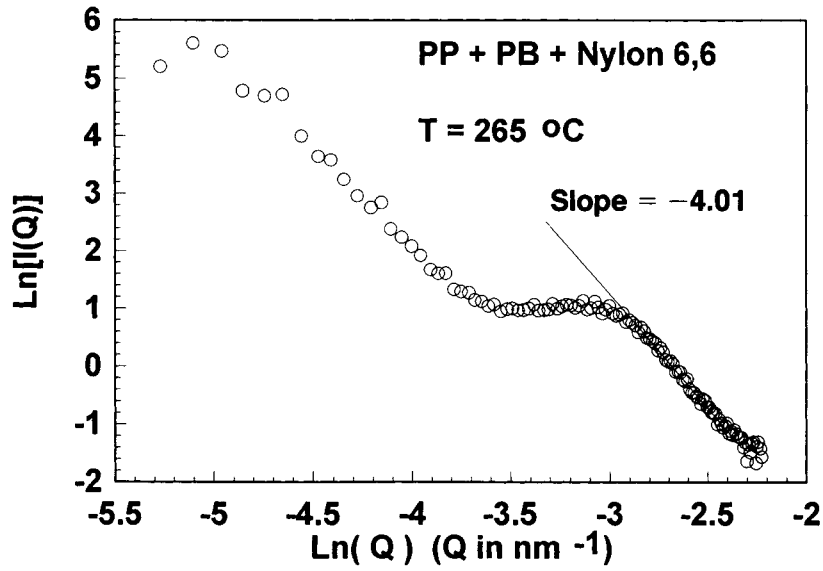


Figure 13 Same plot as Figure 11 for S-3. The slope at large Q is again close to -4 .

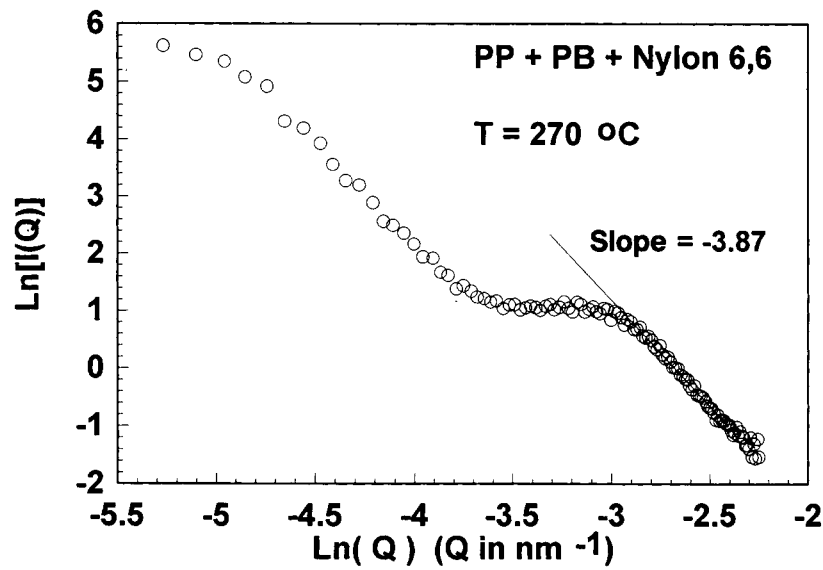


Figure 14 Same plot as Figure 11 for S-4. The slope at large Q is slightly lower (-3.87), but still close to 4 .

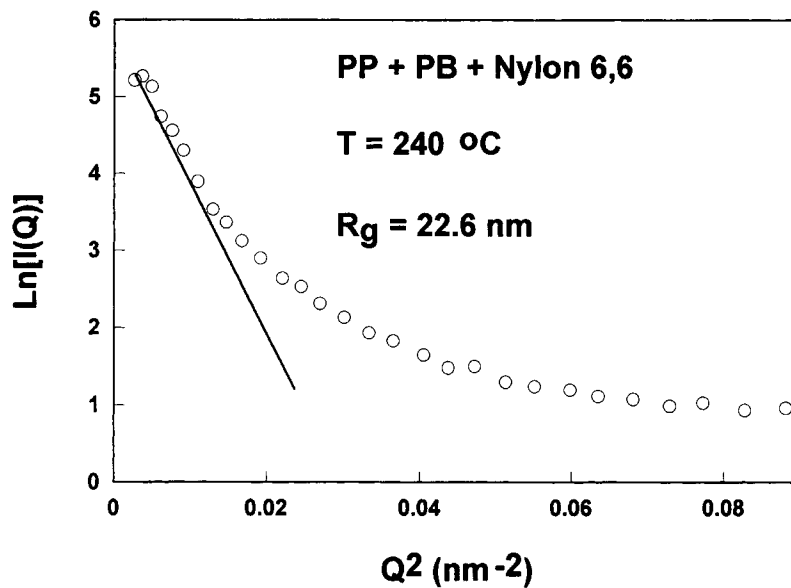


Figure 15 Guinier analysis for S-1. The R_g obtained is about 22.5 nm (22.3 nm).

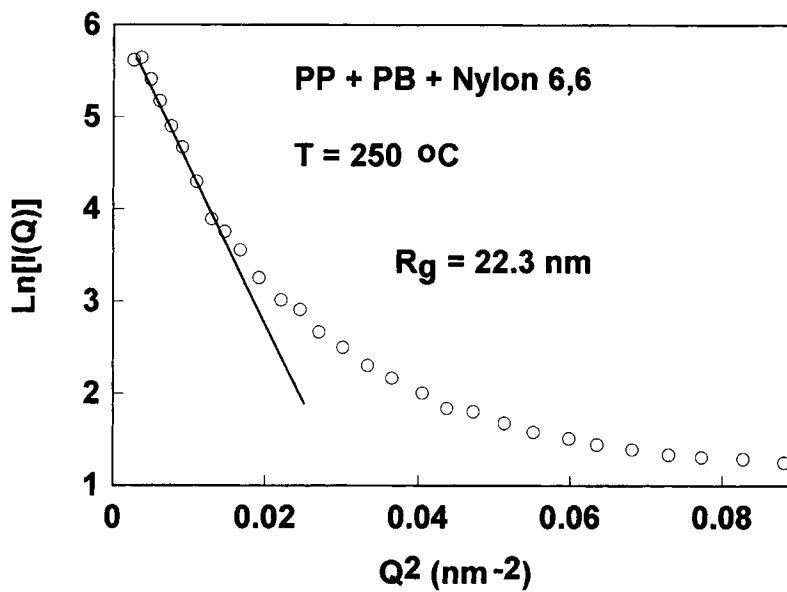


Figure 16 Same plot as Figure 15 for S-2. The R_g obtained is also 22.5 nm (22.8 nm).

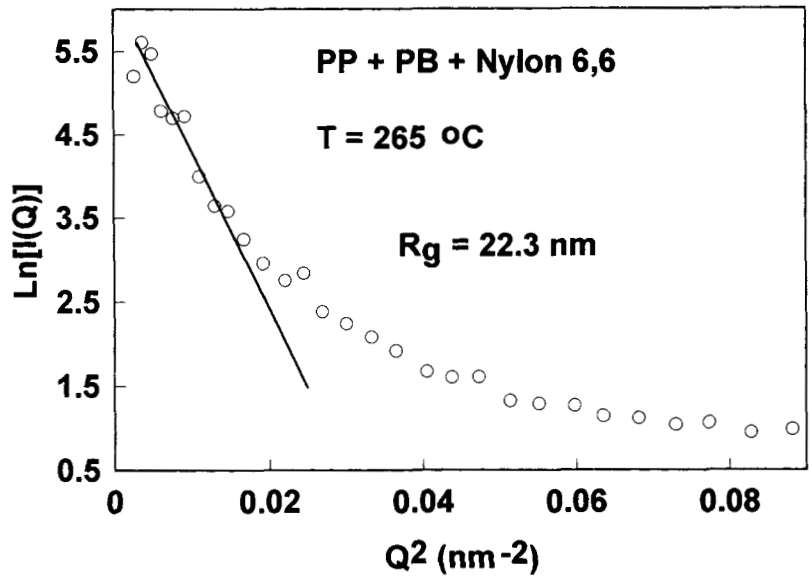


Figure 17 Same plot as Figure 15 for S-3. The R_g obtained is again close to 22.5 nm (22.6 nm).

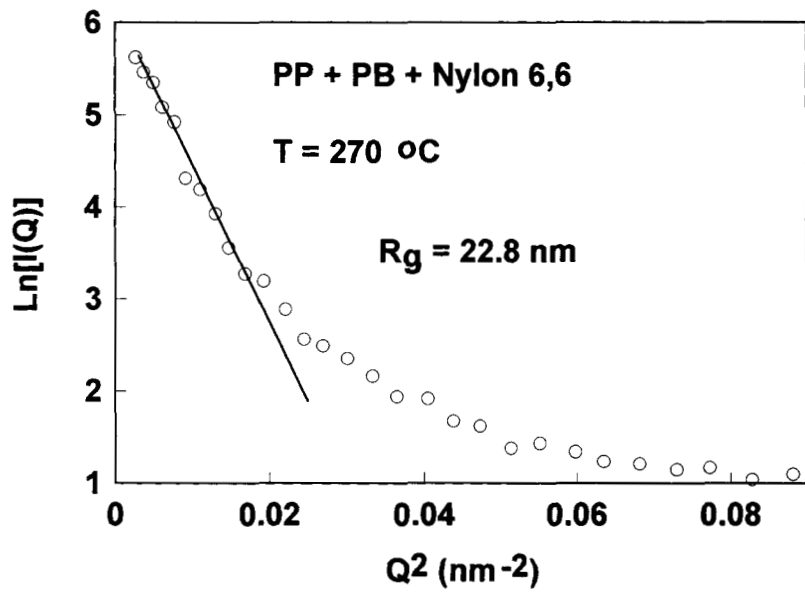


Figure 18 Same plot as Figure 15 for S-4. The R_g obtained is 22.3 nm. The relative constant R_g indicates that the temperature effect in dispersing nylon-6,6 is negligible when the compatibilizer is present.

CONCLUSION

In conclusion, we used a double-screw extruder to blend polypropylene and nylon-6,6 with and without the compatibilizer, maleated polypropylene, at various temperatures. The dispersion and structure of the nylon-6,6 in the blends were analyzed using small-angle X-ray scattering. For direct blending of polypropylene and nylon-6,6 without the compatibilizer, nylon-6,6 does not disperse well unless temperature is raised to 270°C, where nylon-6,6 is melted. As the compatibilizer is incorporated, the dispersion of nylon-6,6 is significantly improved, while the temperature effect becomes ineffective.

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