

# Characterization of Polymer Blends and Alloys by Constrained Profile-Analysis of X-Ray Diffraction Scans

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## Synopsis

The composition of polymer blends and alloys and the crystallinity and crystallite size/perfection of each of the components are determined by X-ray diffraction (XRD) methods. A profile-fitting procedure is used to resolve the XRD scan into crystalline and amorphous peaks corresponding to each of the polymers. The procedure uses templates derived from the XRD scans of the homopolymers as constraints. The usefulness of this method for studying the influence of blending and grafting is illustrated by analyzing the data from two-component blends with and without the graft copolymer compatibilizer.

## INTRODUCTION

The recent activity in multicomponent polymer systems obtained by combining two or more polymers at different levels of structure and morphology, such as block and graft copolymers, alloys, blends, and laminates, has motivated us to apply X-ray diffraction (XRD) methods for analyzing these new materials. Such analysis can reveal the composition, crystallinity, crystallite size, and crystalline perfection of each of the components. This information will be useful in understanding the influence of one component on the other, especially if the polymers have some degree of mutual interaction. These techniques are also important in the characterization of fiber reinforced composites.<sup>1,2</sup> In contrast to the analysis of the XRD scans from individual polymers, the analysis of the scans from the blends is not straightforward, because of the overlap of the amorphous halos from the various components present. In this report we illustrate a method in which diffraction scans of each of the components are first defined by a set of parameters, which are then used as constraints in analyzing the XRD scans from polymer blends and alloys.

## EXPERIMENTAL

### Methods

The intensity of the X-rays scattered from a sample can be considered a superposition of the intensities from each of the components in the sample. Thus, if  $A_t$  is the total intensity (integrated over a suitable angular range, e.g.,  $5-90^\circ 2\theta$ ), then

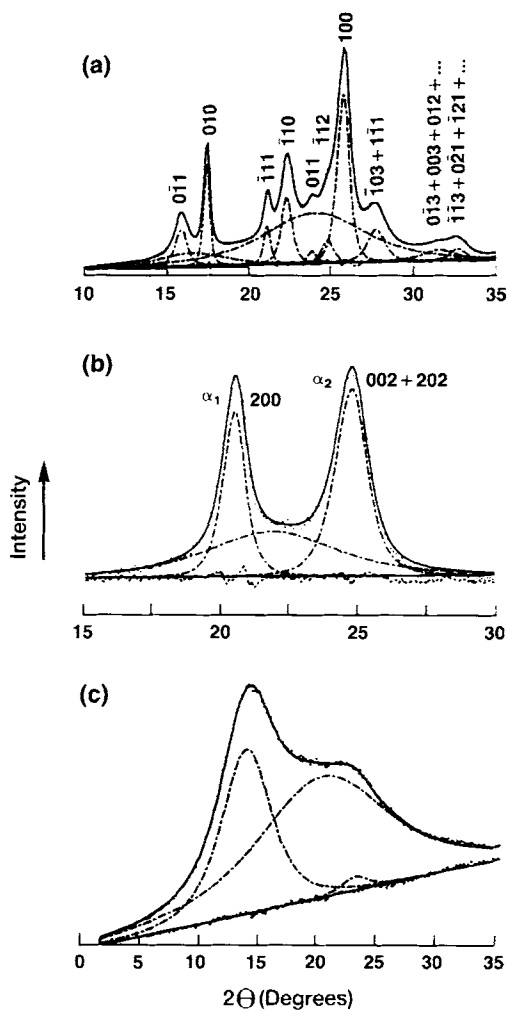


Fig. 1. Analysis of the diffractometer scans to be used as templates. (a) PET (b) Nylon 6 (c) PPE.

In these and the following figures, intensity along the  $y$ -axis is on a linear scale, and is in arbitrary units. The dots are the observed data points, the peaks in dashed lines are the resolved components, the full lines are the sum of the components (this should overlap the observed data points for a perfect fit), and the dashed lines over the baseline (shown by the full line) represent the difference between the observed intensities and the calculated values.

$$A_i = A_1 + A_2 + \dots$$

where  $A_1, A_2, \dots$  refer to the intensity contributions from different polymer species in the sample. The intensities from each of the polymer components can be further written as

$$A_i = A_i^c + A_i^a$$

where  $A_i^c$  and  $A_i^a$  are the contributions from the crystalline and the amorphous

TABLE I  
Profile Parameters for the Templates (Fig. 1)<sup>a</sup>

PET (CI = 49%)												
	Am-1	Am-2	011	010	111	110	011	112	100	103 + 111	Mix.	Mix.
2θ	16.62	24.04	15.92	17.46	21.16	22.36	23.89	24.82	25.73	27.72	31.54	32.67
I(0)	91	350	254	716	267	466	88	157	1170	234	75	82
FWHM	4.55	7.15	0.86	0.43	0.48	0.78	0.57	0.82	0.85	1.24	2.50	1.18

Nylon 6 (CI = 64%)								
	Am.	Alpha		Gamma		PPE (amorphous)		
		200 α1	002 + 202 α2	001 γ1	200 + 201 γ2	Am-1	Am-2	Am-3
2θ	21.83	20.43	24.67	—	—	14.16	20.62	23.41
I(0)	783	2922	3338	—	—	14353	10603	1202
FWHM	5.49	0.98	1.39	—	—	5.05	13.01	2.58

<sup>a</sup> 2θ (CuK<sub>α</sub>) and full-width at half-maximum (FWHM) are in degrees. The peak-height I(0) is in arbitrary units.

regions, respectively, of the *i*th component. By resolving the observed XRD profile into crystalline and amorphous peaks arising from each of the components, we can determine the crystallinity of each of the components in the form of a crystalline index (CI) defined as

$$CI_i = 100A_i^c / (A_i^c + A_i^a)$$

An apparent crystallite size (ACS), which is a measure of both the size of the crystallites and the degree of crystalline perfection (designated CSP), is determined from the full-width at half-maximum  $\Delta(2\theta)$  (FWHM) of the crystalline peaks using the Scherrer equation

$$ACS = 0.9\lambda[\Delta(2\theta) \cos \theta]^{-1}$$

where  $\lambda$  is the wavelength (1.542 Å) and  $2\theta$  is the position of the peak maximum.

The diffractometer scans were fitted using the procedures described elsewhere.<sup>3</sup> The amorphous templates and the crystalline peak positions for semicrystalline polymers were derived from analysis of diffractometer scans from annealed samples of homopolymers. These data for each of the homopolymers were then used in fitting the diffractometer scans from the blend or the alloy. The baselines drawn in our figures are based on diffractometer scans (not shown) obtained from 5 to 100° 2θ.

The profile fitting program "SHADOW" written by Howard<sup>4</sup> was used after modifying the program to fit several amorphous peaks of different shapes. We used modified Lorentzian peak shapes for the amorphous and crystalline peaks. The details of the methods are described in our earlier publication.<sup>3</sup>

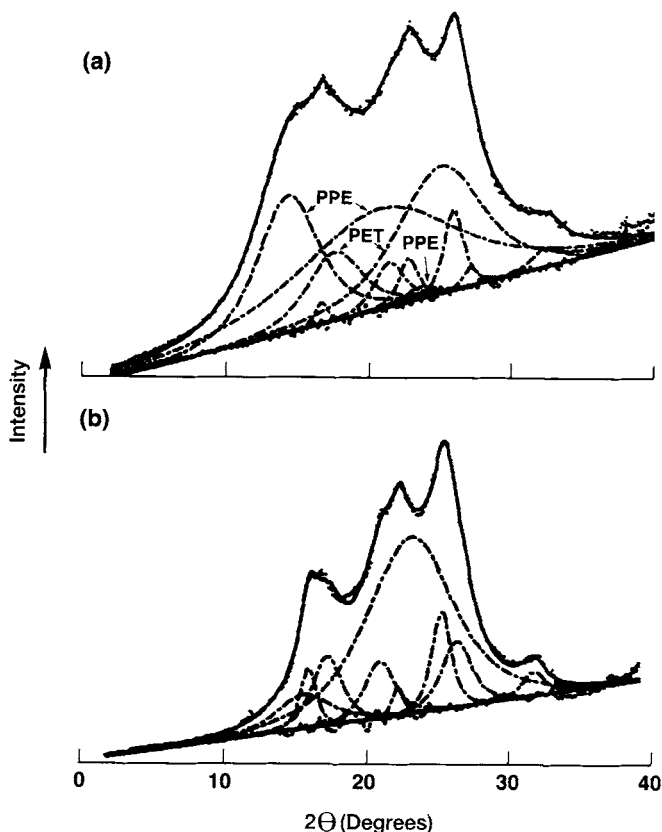


Fig. 2. Profile fitting of the diffractometer scan from annealed specimens of (a) blend of PET and PPE and (b) PET.

XRD scans used in this report were obtained on a Philips APD3600 diffractometer in the parafocus mode using  $\text{Cu K}\alpha$  radiation. Results from blends of PET [poly(ethylene terephthalate)] and PPE [poly(2,6-dimethyl-*p*-phenylene ether)], the blends and alloys (graft copolymer compatibilized) of nylon 6 and PPE will be reported here.

### Materials

PPE powder was dry-blended with 40% PET (0.7 IV) pellets and extruded on a 1 in. single screw extruder at 290°C. The resulting pellets were injection molded into standard test bars on a small Arburg injection molding machine using a mold temperature of 93°C.

PPE powder was dry blended with a grafting agent (fumaric acid) then extruded and pelletized on a 1 in. single screw extruder at 300°C. The resulting functionalized PPE was dry blended with 40% nylon 6 then reextruded at 275°C to form a graft copolymer enriched blend. A control blend comprised of 40% nylon 6 and 60% unfunctionalized PPE was prepared in a similar fashion in

TABLE II  
Profile Parameters for a Blend of PET and PPE (Fig. 2)<sup>a</sup>

PET-PPE blend (annealed)											
	PET								PPE		
	Am-1	Am-2	0 $\bar{1}1$ + 010	$\bar{1}11$	$\bar{1}10$	011 + $\bar{1}12$ + 100	$\bar{1}03$ + $\bar{1}\bar{1}1$	Mix.	Am-1	Am-2	Am-3
$2\theta$	17.30	24.89	16.56	21.47	22.66	25.86	27.03	32.43	14.25	20.70	23.49
$I(0)$	3520	6557	1086	2266	2238	4136	935	970	7003	5174	587
FWHM	4.55	7.15	1.02	2.50	1.58	1.62	1.25	2.50	5.05	13.01	2.58

PET (annealed)									
	Am-1	Am-2	0 $\bar{1}1$	010	$\bar{1}11$	$\bar{1}10$	011 + $\bar{1}12$ + 100	$\bar{1}03$ + $\bar{1}\bar{1}1$	Mix.
$2\theta$	16.09	23.51	16.41	17.73	21.42	22.71	25.74	26.82	32.25
$I(0)$	2192	11434	3868	4461	3658	1887	6284	4244	1543
FWHM	4.55	7.15	1.33	2.50	2.50	0.92	1.63	2.50	1.93

<sup>a</sup>  $2\theta$  (CuK $\alpha$ ) and full-width at half-maximum (FWHM) are in degrees. The peak-height  $I(0)$  is in arbitrary units.

one pass on the single screw extruder. Both blends were injection-molded into standard test bars using a mold temperature of 93°C.

Further details of sample preparation are given in Ref. 5.

## RESULTS AND DISCUSSION

In some multicomponent polymer systems, the diffraction peaks from the various components are well separated, e.g., a blend or a laminate of polyethylene and a fluoropolymer. In such instances, non-linear least-squares procedure can readily resolve the various amorphous and crystalline peaks. But if the scattering profiles from the components in the blend overlap, such as in PET-PPE, PE-N6, and in many carbon-filled or carbon-fiber-reinforced polymers, then such analysis may not provide meaningful results. In this report we illustrate a

TABLE III  
Results of Profile Analysis of PET-PPE Blends

Sample	CI (%)	CSP (Å) 25.7° peak
PET		
Unannealed	31	35
Annealed	36	50
PET/PPE		
Unannealed (44 : 56)	21	50
Annealed (44 : 56)	25	55

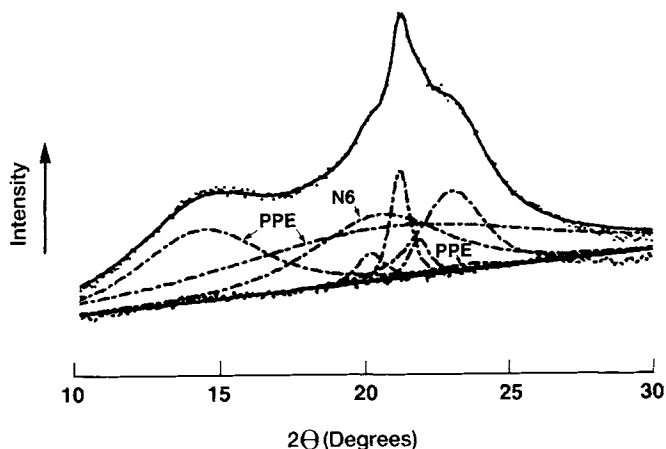


Fig. 3. Profile-fitted diffractometer scans from a blend of nylon 6 and PPE.

method in which the problem of amorphous peak-overlap is overcome by imposing suitable constraints during the profile analysis.

In analyzing the XRD scans in which the diffraction peaks from the various components in the polymer severely overlap each other, we first analyze the scattering from homopolymers. The amorphous scattering derived from these analyses are used as templates in profile fitting the diffraction scans from composites. Figure 1 shows the profile analysis of the scans from PET, nylon 6, and PPE, and the various peak parameters are given in Table I. While nylon 6 could be fitted with one amorphous halo, it was necessary to use more than one amorphous peak in describing the amorphous component in PET and PPE. The choice of the number of peaks may not have any physical significance, but it is a matter of practical convenience. We note, however, that the  $23.4^\circ$  peak in PPE could be the second order diffraction line of the intense  $14.2^\circ$  peak.

Figure 2a shows the XRD scans from a blend of PET and PPE resolved into crystalline and amorphous components of the individual polymers. The results

TABLE IV  
Profile Parameters for Nylon-PPE Blends (Fig. 3)<sup>a</sup>

	Nylon 6							
	Am.	Alpha		Gamma		PPE		
		200	002 + 202	001	200 + 20 $\bar{1}$	Am-1	Am-2	Am-3
$2\theta$	20.51	20.20	23.04	21.24	21.91	14.31	20.77	23.55
$I(0)$	2454	1042	3035	4047	1350	2663	1967	223
FWHM	5.05	1.14	2.50	0.78	0.85	5.05	13.01	2.58

<sup>a</sup>  $2\theta$  ( $\text{CuK}\alpha$ ) and full-width at half-maximum (FWHM) are in degrees. The peak-height  $I(0)$  is in arbitrary units.

TABLE V  
Results of Profile Analysis of Nylon 6-PPE Blend and Alloy

Parameter	Blend	Alloy
Nominal nylon 6/PPE	40/60	40/60
Calculated nylon 6/PPE	40/60	36/64
CI of nylon 6	49	42
$\alpha/\gamma$ ratio of nylon 6	67/33	70/30
Average CS/CP (A)		
$\alpha_1$	75	55
$\gamma_1$	115	105

of the analysis are shown in Table II. In profile-fitting the scans in Figure 2(a), the ratio of the heights of the three amorphous peaks of PPE was kept constant, while the relative heights of the two amorphous halos of PET were allowed to vary. The agreement between the calculated and the observed data was not satisfactory when the relative heights of the amorphous halos of PET was held constant. The rationale for varying the heights of the two amorphous halos independently in PET will be discussed elsewhere.<sup>6</sup> Our preliminary findings suggest that the relative heights of the two amorphous peaks might depend on the order along two different directions, and the degree of this 2-dimensional order in the amorphous regions might vary from sample to sample. To a first approximation, the integrated intensities can be considered a measure of the weight fraction of the component. Therefore, ratios of the total intensity from each of the components are a measure of the fraction of each of the phases. The ratios of PET to PPE calculated from the XRD data are in good agreement with the nominal value of 40 : 60 (Table III). Having separated the scattering from each of the polymer phases, we can then estimate the crystallinity and the crystallite sizes of each of the crystalline phases. Thus, it is possible to characterize one polymer in the presence of another polymer.

The usefulness of such profile analysis of XRD scans from blends is demonstrated in Table III, in which we compare the crystallinity and crystallite sizes of a PET-PPE blend with those of nonblended PET. The XRD scans from the nonblended PET samples were analyzed by methods described in our earlier paper,<sup>3</sup> and a representative scan is given in Figure 2(b). The results in Table III indicate that the PPE reduces the CI in the blend relative to that of nonblended PET. Further, in contrast to non-blended samples, and CSP in the blend does not increase significantly upon annealing (130°C, overnight). These XRD results suggest that the mechanical properties after heat aging of the blend would be superior to those nonblended PET.

An application of the profile-fitting procedure to understand the influence of different methods of preparing multicomponent polymer systems is illustrated with examples from blends and alloys and PPE and nylon 6. In analyzing the scans from these polymer mixtures, in addition to restraining the amorphous halo, it was necessary to ensure that the intensity ratios of the various crystalline peaks are similar to those found in homopolymers. In particular, we required that the intensities of the  $\alpha_2$  and the  $\gamma_1$  peaks of nylon 6 be higher than those

of the  $\alpha_1$  and the  $\gamma_2$  peaks, respectively.<sup>3</sup> A typical profile-fitted result is shown in Figure 3, and the results of our analysis are given in Table IV and Table V. If we assume that the intensities are proportional to the weight fraction of the components, the calculated ratio of nylon 6 to PPE is 40 : 60 in the blend and 36 : 64 in the alloy containing the graft copolymer. These values are in agreement with the nominal values of 40 : 60. In addition to determining the fraction of PPE and nylon 6 and the crystallinity of nylon 6 in these two samples, we can follow the changes in the crystallite sizes and the phase composition of nylon 6.

Nylon 6 exists in two crystalline forms,  $\alpha$  and  $\gamma$ . The thermodynamically stable  $\alpha$  form can be obtained by slow crystallization or annealing. The results of our analysis can be used to determine the ratio of  $\alpha$  to  $\gamma$ . In general, the  $\alpha$  to  $\gamma$  ratio can be related to the thermal/processing history of nylon 6. This  $\alpha$  to  $\gamma$  ratio is  $\sim 70 : 30$  for both the blend and the alloy. The results in Table V show that the crystallinity and the crystallite size of nylon 6 are in general smaller in the alloy containing the graft copolymer than in the blend. This implies that the growth of the crystallites is inhibited in the grafted material compared to that in the blend. Lower crystallinity and smaller or imperfect crystallites may contribute towards improved fracture toughness of the alloy compared to that of the blend. This is in addition to the beneficial role of the graft copolymer in improving the interfacial strength between the semicrystalline nylon 6 domains and the amorphous PPE. We further speculate that the crystallite size is lower in the alloy because of the insertion of the nylon 6 blocks of the PPE/nylon 6 copolymer into the crystalline lamellae. If this were the case, then the interfacial strength between the crystalline lamellae of nylon 6 and the amorphous PPE would be higher as well. Measurements using spectroscopic and neutron scattering methods are necessary to verify this hypothesis.

## CONCLUSION

We have described a procedure for analyzing the X-ray diffraction scans from blends and alloys. We have also demonstrated how these results can be used to characterize the structural features of the individual polymer components, and to understand their contribution to the properties of the blends and alloys.

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