

# Particle size distribution in rubber modified polyamides 6

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Particle size and particle-size distribution in rubber-toughened polyamides 6 (PA6) were determined according to the Schwartz-Saltikov method. The quantitative morphological analysis was performed on microtomed samples of binary and ternary blends containing ethylene-propylene random copolymer (EPR) and functionalized EPR rubber (EPR-g-SA). The blends were obtained according to two different methods: concurrent to the hydrolytic polymerization of caprolactam, and simultaneous melt mixing. The formation of an (EPR-g-SA)-g-PA6 copolymer during blending was assumed to occur in the ternary blends. Correlations between particle size, particle size distribution, preparation method, composition and Izod impact strength of such materials were investigated.

## 1. Introduction

The particle-size distribution of the dispersed phase is one of the most important factors in determining the final properties of incompatible polymer-polymer blends and alloys [1]. Generally the mode and state of dispersion of the minor component depends on the composition, blending procedure and processing. Moreover it has been found that the addition of emulsifier and/or compatibilizing agents may drastically reduce the average dimensions of dispersed particles and induce a stronger adhesion with the matrix [2].

In the present paper we report the results of an accurate and thorough morphological analysis carried out in order to determinate size, size distribution and volumetric fraction of rubbery particles dispersed as toughening agents in polyamides 6. An amorphous ethylene-propylene random copolymer (EPR) and a modified EPR (EPR-g-succinic anhydride (EPR-g-SA)) were used as impact modifier of the PA6.

The determination of particle-size distribution and volumetric fraction was performed on samples of blends obtained by two different methods: (a) concurrent with hydrolytic polymerization of  $\epsilon$ -caprolactam, and (b) simultaneous melt mixing of the components. The method of EPR modification, blend preparation, morphology and properties of binary PA6/EPR and ternary PA6/EPR/EPR-g-SA were reported in previous works [3-5]. The formation of an EPR-g-SA-PA6 graft copolymer during blending was assumed to occur in the case of blends containing the functionalized EPR-g-SA rubber.

A detailed and thorough investigation of the mode and state of dispersion of the rubbery phase in such materials was undertaken with the aim of studying: (i) the relationships between particle size, particle size distribution, preparation method and composition of the blends; (ii) the influence, in the ternary blends, of the content of functionalized rubber (EPR-g-SA) on the particle size and particle-size distribution; and (iii)

the correlations between particle size, particle-size distribution and Izod impact strength of the binary and ternary blends.

## 2. Theory

Assuming that the dispersed particles closely approach spherical shape, a mathematical procedure was developed for converting the two-dimensional distribution of particle sections into the corresponding three-dimensional distribution of particle size. The number and the size of the circular traces resulting when the particles are intersected by a random plane can be counted and measured by means of SEM. Then the probable number and size of the spheres that give rise to the observed section distribution can be deduced.

If the spheres in the blends all have the same size (monodispersed system) an extremely simple and general equation applies. It relates the number of particle sections observed per unit area ( $N_A$ ) to the number of spheres per unit volume ( $N_v$ )

$$N_v = N_A/D_j \quad (1)$$

where  $D_j$  is the diameter of spheres. It should be emphasized that  $N_A$  involves the number of particle sections of all sizes per unit area.

When particle sections of only one particular size ( $d_i$ ) are counted, a probability factor must be introduced to account for the arbitrary restriction imposed. Under these conditions Equation 1 becomes

$$N_v = \frac{N_A(i, j)}{p} \frac{1}{D_j} \quad (2)$$

where  $p$  is the probability of the plane intersecting a sphere of diameter  $D_j$  so as to yield sections of size  $d_i$  and  $N_A(i, j)$  is the number of sections of diameter  $d_i$  per unit area obtained from spheres of diameter  $D_j$ . The probability that a random plane intersects a spherical particle between distances  $h_i$  and  $h(i-1)$  from the centre giving rise to circular sections with

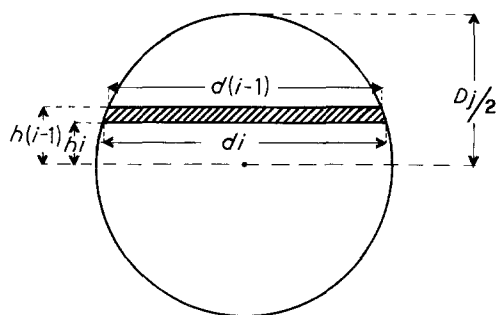


Figure 1 Intersection of a spherical particle by a random plane.

diameters between  $d_i$  and  $d(i-1)$  is equal to the thickness  $h$  of the circular slice divided by the particle radius. This situation is shown in Fig. 1.

$$p = \frac{h}{D_j/2} = \frac{h(i-1) - h_i}{D_j/2} \quad (3)$$

In the case of a polydispersed system of spherical particles intersected by a random plane, some of the observed sections derive from particles of larger sizes. The number of these latter sections must be subtracted from the total number in order to obtain those sections due only to the particles of one size.

The mathematical procedure developed for converting distribution of section diameters into distribution of particle size was made according to the Schwartz-Saltikov methods [6], breaking down the particle size into 15 groups. The basic equation relating the number of particle sections per unit area to the number of particles per unit volume for particles of one diameter was

$$N_A(i, j) = N_v(j) \Delta \{ [j^2 - (i-1)^2]^{1/2} - [(j^2 - i)^2]^{1/2} \} \quad (4)$$

where the first index designates the diameter of the sections, the second one refers to the size of the particles, which form the given sections on the random plane, and  $\Delta$  is the ratio between the observed maximum particle diameter and the number of the fixed groups.

The mathematical corrections, developed for converting the distribution of visible section diameters into distribution of real size of particles yield a shift of the maximum of frequency distributions towards larger particles.

### 3. Experimental details

#### 3.1. Materials

The caprolactam (CL) and aminocaproic acid (ACA) used in this work were FLUKA purum products employed without further purification. The polyamide 6 (PA6) used was SNIAMID ASN 27/S produced by SNIA having a number average molecular weight ( $\overline{M}_n$ ) of  $2.3 \times 10^4$ . Before use, the PA6 was kept under vacuum at  $60^\circ\text{C}$  for 48 h to eliminate the water content stored during industrial washing. Xylene, Carlo Erba, RPE grade was passed over neutral alumina and collected under nitrogen before use.

The ethylene-propylene random copolymer (EPR) was a Dutral CO/054 supplied by Dutral s.p.a. having

TABLE I Compositions of the investigated blends obtained directly during caprolactam polymerization; the preparation method is indicated

Code	PA6 content (wt %)	EPR content (wt %)	EPR-g-SA content (wt %)	Preparation method
A <sub>1</sub>	90	10	0	Solution
A <sub>2</sub>	90	10	0	Bulk
B <sub>2</sub>	80	20	0	Bulk
C <sub>1</sub>	80	18	2	Solution
C <sub>2</sub>	80	18	2	Bulk
D <sub>1</sub>	80	15	5	Solution
D <sub>2</sub>	80	15	5	Bulk

a weight-average molecular weight ( $\overline{M}_w$ ) of  $1.80 \times 10^5$ , and an ethylene content ( $C_2$ ) of 60 mol % and a glass transition temperature ( $T_g$ ) of  $-60^\circ\text{C}$ .

The modified EPR, bearing along its backbone 3 wt % by weight succinic anhydride groups (EPR-g-SA) was prepared following the same procedure already described elsewhere [3].

#### 3.2. Blending

##### 3.2.1. Concurrent blending with caprolactam polymerization

Such blends were obtained directly during caprolactam polymerization via a hydrolytic process. Two different methods of blend preparation were followed: the first (solution method) involved a preliminary dispersion of the rubber in xylene. The second (bulk method) was characterized by the fact that the rubber is directly added to caprolactam and initiator and dispersed by mechanical stirring before polymerization. Further details are reported in a previous paper [4]. The examined blend compositions, together with the preparative method, are indicated in Table I.

##### 3.2.2. Blending by melt mixing

All the binary and ternary blends were prepared in a Brabender-like apparatus (Rheocord E.C. of Haake Inc.) by a simultaneous melt-mixing of all the components at a temperature of  $260 \pm 3^\circ\text{C}$  with a mixing time of 20 min and at a rotation speed of rollers of 32 r.p.m. The examined blend compositions are reported in Table II.

#### 3.3. Specimen preparation and conditioning

The blended materials were compression moulded in a heated press (Wabosh Hydraulic Press) at a temperature of  $260 \pm 5^\circ\text{C}$  and a pressure of  $240 \pm 20 \text{ kg cm}^{-2}$  into 3 mm thick sheets. The samples so obtained were water conditioned before examining following a procedure elsewhere described [3].

TABLE II Compositions of the investigated blends obtained by one-step melt-mixing

Code	PA6 content (wt %)	EPR content (wt %)	EPR-g-SA content (wt %)
A <sub>3</sub>	90	10	0
B <sub>3</sub>	80	20	0
D <sub>3</sub>	80	15	5
E <sub>3</sub>	80	10	10

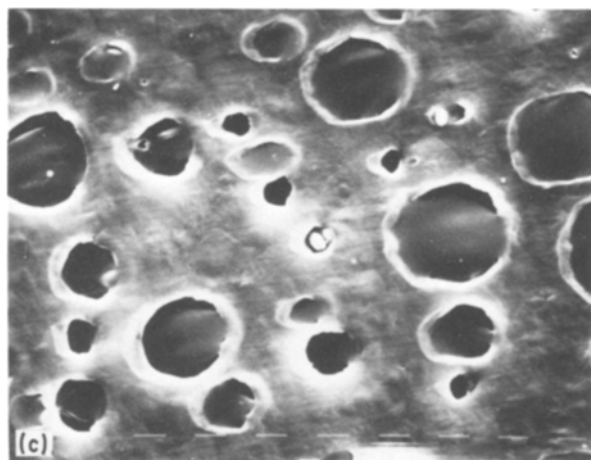
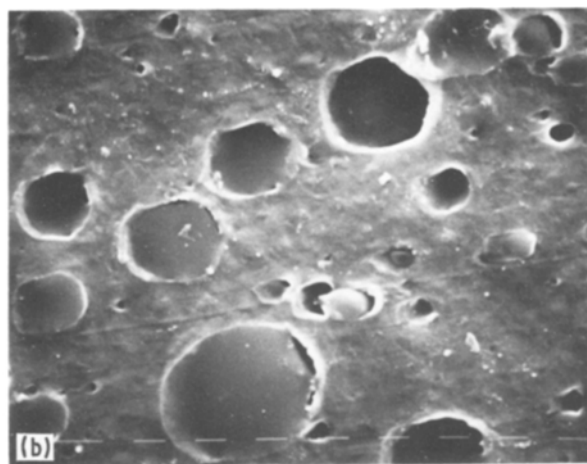
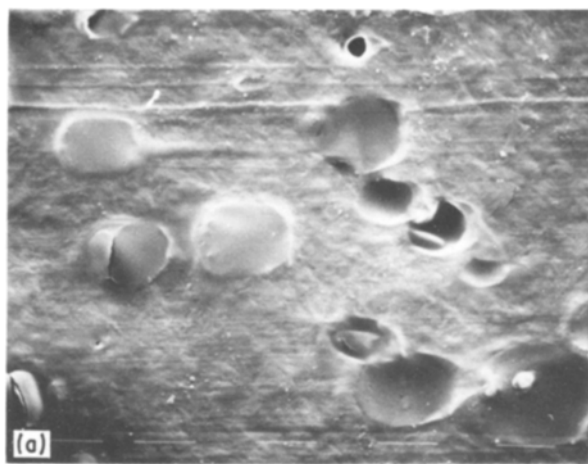


Figure 2 Scanning electron micrographs of microtomed surfaces of: (a) A<sub>1</sub> blend ( $\times 850$ ); (b) A<sub>2</sub> blend ( $\times 435$ ); (c) A<sub>3</sub> blend ( $\times 435$ ). PA6/EPR (90/10).

### 3.4. Techniques

Samples of binary and ternary blends were faced in an ultramicrotome (LKB Ultratome III) at room temperature. The smooth surfaces were coated with gold-palladium by means of a Polaron sputtering and subsequently analysed using a scanning electron microscope (SEM 501 Philips) at suitable magnification. The diameters of the observed particle sections were manually measured on the scanning electron micrographs using a ruler.

## 4. Results and discussion

### 4.1. Particle-size distribution in PA6/EPR binary blends

Typical scanning electron micrographs of microtomed

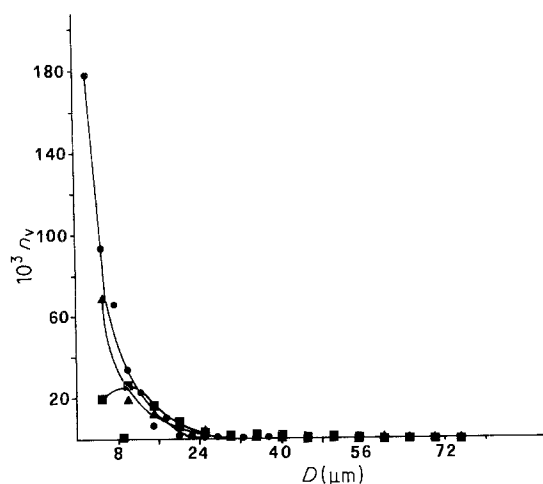


Figure 3 Particle-size distribution curves of (●) A<sub>1</sub>, (▲) A<sub>2</sub>, (■) A<sub>3</sub> blends.

surfaces of A<sub>1</sub>, A<sub>2</sub>, A<sub>3</sub> blends are shown in Fig. 2. The particle-size distribution curves showing the number of particles per unit volume ( $n_v$ ) plotted against particle diameter ( $D$ ) are given in Fig. 3. The EPR particle diameter ( $D$ ), the number and per cent of EPR particles per mm<sup>3</sup> belonging to each group ( $n_v$ ;  $n_v\%$ ) and the total number of EPR particles per mm<sup>3</sup> ( $N_v$ ) are reported in Table III. A comparison of the trends of the curves of Fig. 3 and the data listed in Table III leads to the following conclusions.

1. The total number of dispersed EPR particles per unit volume ( $N_v$ ) is influenced by the blending procedure. The largest value of  $N_v$  is observed in the case of A<sub>1</sub> blend. ( $N_v = 415\,877$ ;  $111\,488$  and  $74\,000$  for A<sub>1</sub>, A<sub>2</sub> and A<sub>3</sub> blends, respectively.)

2. The particle-size distribution curve of A<sub>1</sub> is characterized by a larger presence of particles having dimensions comparatively smaller than those observed for A<sub>2</sub> and A<sub>3</sub> blends. Moreover, in A<sub>1</sub> blend the dispersion of particle size is narrower than in A<sub>2</sub> and A<sub>3</sub> blends. (Most of the EPR domains exhibit a diameter ranging from 2.5 to 17.5  $\mu\text{m}$ .)

3. Particles with almost the same dimensions are found in A<sub>2</sub> and A<sub>3</sub> blends. Nevertheless, the particle-size distribution curves look different. In the region of lowest diameters it can, in fact, be observed that A<sub>2</sub> blend shows  $n_v$  values higher than those of A<sub>3</sub> blend (for  $D = 5.0$ ,  $n_v = 68\,288$  and  $19\,752$  for A<sub>2</sub> and A<sub>3</sub>, respectively).

4. The A<sub>3</sub> blend is characterized by the most homogeneous distribution of particle size.

The values of the volumetric fraction of the rubbery phase, estimated from the particle-size distribution are 16.1%, 17.8%, 16.5% for A<sub>1</sub>, A<sub>2</sub>, A<sub>3</sub> blends, respectively. Such values are in agreement with those calculated on the basis of composition and density of the components (16.6%). Such results strongly support the hysteresis that the particles dispersed do not contain any polyamide inclusions.

The Izod impact behaviour of A<sub>1</sub>, A<sub>2</sub> and A<sub>3</sub> blends, has been studied and the results were reported in previous papers [3, 4]. It was found that A<sub>1</sub> blend shows better impact properties than of A<sub>2</sub> and A<sub>3</sub>

TABLE III Particle diameters ( $D$ ), number and per cent particles per volume unit ( $n_v$  and  $n_v$  %) of  $A_1$ ,  $A_2$  and  $A_3$  blends.  $N_v$  is the total number of particles per volume unit

$A_1$			$A_2$			$A_3$		
$D$ ( $\mu\text{m}$ )	$n_v$	$n_v$ (%)	$D$ ( $\mu\text{m}$ )	$n_v$	$n_v$ (%)	$D$ ( $\mu\text{m}$ )	$n_v$	$n_v$ (%)
2.5	178 056	42.8	5.0	68 288	61.2	5.0	19 752	26.6
5.0	93 389	22.4	10.0	18 316	16.4	10.0	25 918	34.8
7.5	65 820	15.8	15.0	12 102	10.8	15.0	16 197	21.8
10.0	33 512	8.0	20.0	6 575	5.90	20.0	7 051	9.5
12.5	22 556	5.4	25.0	3 452	3.10	25.0	3 127	4.2
15.0	6 380	1.5	30.0	1 185	1.06	30.0	1 255	1.7
17.5	10 246	2.5	35.0	881	0.79	35.0	571	0.77
20.0	1 615	0.39	40.0	284	0.25	40.0	303	0.41
22.5	1 586	0.38	45.0	122	0.11	45.0	60	0.08
25.0	640	0.15	50.0	120	0.11	50.0	26	0.03
27.5	856	0.20	55.0	24	0.02	55.0	27	0.03
30.0	280	0.07	60.0	25	0.02	60.0	30	0.04
32.5	375	0.09	65.0	27	0.02	65.0	42	0.06
35.0	55	0.02	70.0	33	0.03	70.0	16	0.02
37.5	512	0.12	75.0	56	0.05	75.0	26	0.03
$N_v = 415877$			$N_v = 111488$			$N_v = 74000$		

blends. From the above findings one can infer that, in the absence of adhesion or chemical reaction between matrix and dispersed phase, smaller rubbery particles seem to be more effective in generating high local stress concentrations.

Typical scanning electron micrographs of microtomed surfaces of  $B_2$  and  $B_3$  blends are reported in Fig. 4. Particle-size distribution curves are shown in Fig. 5. Looking at the curves and comparing with the data listed in Table IV, it emerges that in  $B_3$  blend a finer dispersion of the EPR copolymer is achieved. The range of the EPR particles which results in such a blend is, in fact, about three times as narrow as that observed in  $B_2$  blend. In  $B_3$  blend most of the EPR particles have a diameter ranging from 2.5 and 20  $\mu\text{m}$  and the largest particles measure 37.5  $\mu\text{m}$ . On the other hand, in  $B_2$  blend, most of the EPR particles exhibit a diameter ranging from 8.4 and 50  $\mu\text{m}$  and the largest particles measure 125  $\mu\text{m}$ . Consequently  $N_v$  for  $B_2$  blend is found to be lower than that calculated for  $B_3$  blend.

By comparing the particle size and the particle-size distribution of the blends, prepared during the hydrolytic polymerization of the CL ( $A_2$  and  $B_2$  blends) it is found that on increasing the EPR content a decrease in the value of  $N_v$  is observed ( $N_v = 111488$  for  $A_2$

and 40452 for  $B_2$ ). Moreover in the case of  $A_2$  blends, a large number of small particles (2.5  $\mu\text{m}$ ) are present.

As far as the blends prepared by melt mixing are concerned ( $A_3$  and  $B_3$  blends) both a decrease in EPR particle size and narrower particle size distribution, enhancing the EPR percentage are observed (compare Figs. 3 and 5, Tables III and IV). From the above it may be concluded that in 20% EPR containing blends, melt mixing seems to be more suitable in dispersing EPR. Such a finding may be accounted for by considering that in the case of preparation of blends concurrently with the hydrolytic polymerization of CL, the stirring of the system becomes less effective thus increasing the EPR content. The volumetric fraction values, estimated from the particle-size distribution are for  $B_2$  and  $B_3$  blends 24% and 27%, respectively. Such values are lower than calculated by composition and density of components (32.9%). Such a discrepancy is account for by the fact that some large EPR agglomerate was not taken into account.

#### 4.2. Particle-size distribution in PA6/EPR/EPR-g-SA ternary blends

Typical scanning electron micrographs of microtomed surfaces of  $C_1$  and  $C_2$  blends are shown in Fig. 6. As shown by the data listed in Table V, a different

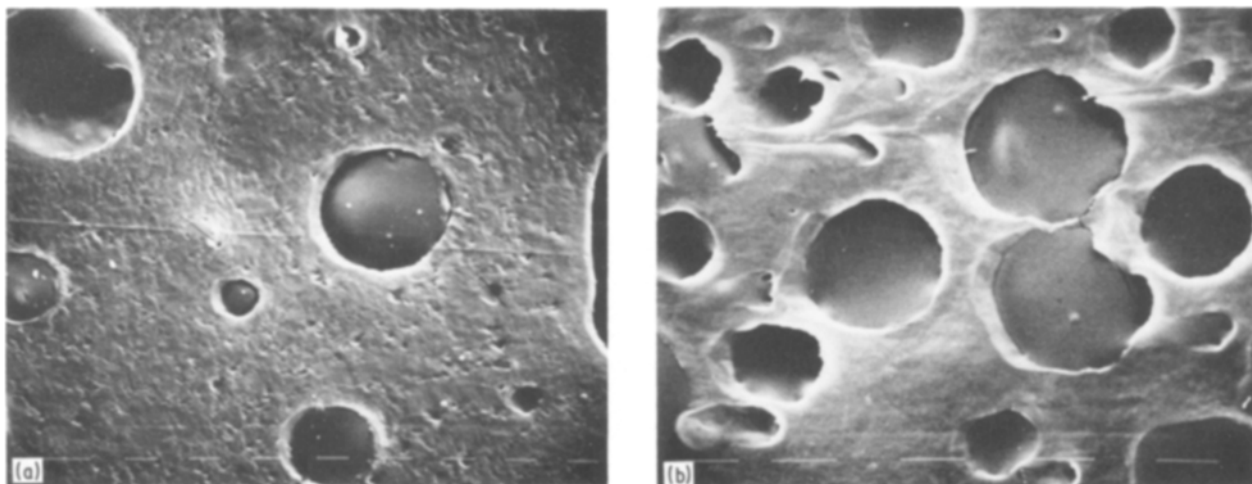


Figure 4 Scanning electron micrographs of microtomed surfaces of: (a)  $B_2$  blend ( $\times 448$ ); (b)  $B_3$  blend ( $\times 875$ ). PA6/EPR (80/20).

TABLE IV Particle diameters ( $D$ ), number and per cent particles per volume unit ( $n_v$  and  $n_v$  %) of  $B_2$  and  $B_3$  blends.  $N_v$  is the total number of particles per volume unit

$B_2$			$B_3$		
$D$ ( $\mu\text{m}$ )	$n_v$	$n_v$ (%)	$D$ ( $\mu\text{m}$ )	$n_v$	$n_v$ (%)
8.4	35 468	87.7	2.5	249 744	43.6
16.7	1 568	3.9	5.0	113 270	19.8
25.1	994	2.4	7.5	75 126	13.1
33.4	427	1.0	10.0	57 974	10.1
41.8	959	2.4	12.5	36 380	6.3
50.1	448	1.1	15.0	14 087	2.5
58.4	154	0.38	17.5	8 788	1.5
66.8	112	0.28	20.0	8 337	1.4
75.2	183	0.45	22.5	3 154	0.55
83.5	54	0.13	25.0	1 944	0.34
91.8	16	0.04	27.5	155	0.03
100.2	18	0.45	30.0	1 181	0.21
108.6	24	0.06	32.5	455	0.08
116.9	10	0.02	35.0	1 210	0.21
125.2	15	0.04	37.5	319	0.06
$N_v = 40\,452$			$N_v = 572\,128$		

particle-size distribution is found in  $C_1$  and  $C_2$  blends. In the case of  $C_1$  the number of total particles per unit volume ( $N_v$ ) is much higher than in  $C_2$  ( $N_v = 1\,608\,636$  for  $C_1$  and only  $24\,077$  for  $C_2$ ). Moreover a large number of dispersed particles with very small dimensions ( $D = 2.5$  and  $5\ \mu\text{m}$ ) is observed in  $C_1$  samples. Finally, in  $C_1$  blend the range of the size of rubbery particles is seen to be about four times narrower than that of  $C_2$  ( $2.5$  to  $37.5\ \mu\text{m}$  for  $C_1$  and  $10$  to  $150\ \mu\text{m}$  for  $C_2$ ). Thus it may be concluded that  $C_1$  samples are characterized by a finer state of dispersion of the rubber component than that observed in the case of  $C_2$  blend, and by a narrower particle-size distribution.

From the above results it appears that the dispersion of the rubbery components in xylene before the polymerization reaction starts is an essential step in order to realize a mixture where the functionalized EPR may act as emulsifier and compatibilizing agent. Contrary to expectations, the addition of functionalized EPR does not yield in  $C_2$  blend a higher degree of dispersion of the rubbery phase than that observed in the binary PA6/EPR  $B_2$  blend prepared according to the same

TABLE V Particle diameters ( $D$ ), number and per cent particles per volume unit ( $n_v$  and  $n_v$  %) of  $C_1$ ,  $C_2$ ,  $D_1$  and  $D_2$  blends.  $N_v$  is the total number of particles per volume unit

$C_1$			$C_2$			$D_1$			$D_2$		
$D$ ( $\mu\text{m}$ )	$n_v$	$n_v$ (%)	$D$ ( $\mu\text{m}$ )	$n_v$	$n_v$ (%)	$D$ ( $\mu\text{m}$ )	$n_v$	$n_v$ (%)	$D$ ( $\mu\text{m}$ )	$n_v$	$n_v$ (%)
2.5	1 276 150	79.3	10.0	16 866	70.1	0.8	7 786 653	51.5	5.0	28 973	50.6
5.0	177 248	11.0	20.0	5 250	21.8	1.6	3 748 684	24.8	10.0	16 886	29.5
7.5	60 023	3.73	30.0	1 019	4.23	2.5	1 673 806	11.1	15.0	5 853	10.2
10.0	49 830	3.10	40.0	387	1.61	3.3	806 393	5.33	20.0	2 920	5.1
12.5	18 058	1.12	50.0	201	0.84	4.2	548 499	3.63	25.0	971	1.70
15.0	11 472	0.71	60.0	103	0.43	5.0	213 067	1.41	30.0	653	1.14
17.5	5 749	0.36	70.0	61	0.25	5.8	81 599	0.54	35.0	653	1.11
20.0	3 149	0.20	80.0	47	0.19	6.6	87 240	0.58	40.0	221	0.39
22.5	2 195	0.14	90.0	39	0.16	7.5	68 730	0.45	45.0	47	0.08
25.0	1 900	0.12	100.0	53	0.22	8.3	41 266	0.27	50.0	12	0.02
27.5	938	0.06	110.0	25	0.10	9.2	17 525	0.12	55.0	12	0.02
30.0	612	0.04	120.0	8	0.03	10.0	13 464	0.09	60.0	12	0.02
32.5	514	0.03	130.0	4	0.02	10.8	18 048	0.12	65.0	13	0.02
35.0	426	0.03	140.0	5	0.02	11.7	10 791	0.07	70.0	17	0.03
37.5	371	0.02	150.0	7	0.03	12.5	9 376	0.06	75.0	26	0.05
$N_v = 1\,608\,636$			$N_v = 24\,077$			$N_v = 15\,125\,144$			$N_v = 57\,252$		

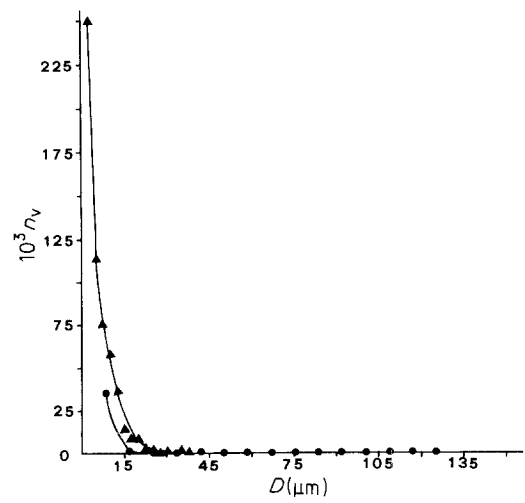


Figure 5 Particle-size distribution curves of (●)  $B_2$  and (▲)  $B_3$  blends.

procedure (compare Tables V and IV). In fact it can be seen that  $N_v$  is for  $B_2$  blend higher than for  $C_2$  ( $N_v = 40\,452$  for  $B_2$  and  $24\,077$  for  $C_2$ ). Furthermore, particles with smaller dimensions are found in large amounts in the case of  $B_2$  blend.

It is likely that the (EPR-g-SA)-g-PA6 graft copolymer, formed during the polymerization, cannot act efficiently as emulsifier. In fact the high reactivity of the anhydride groups probably leads to the formation of a graft copolymer, containing short PA6 branches. This graft copolymer tends to segregate giving rise to the formation of its own phase.

It is interesting to observe that  $C_2$  blends show a better Izod impact behaviour than that of  $C_1$  blend [4]. Such a result indicates that the mode and state of dispersion of the minor component observed for  $C_2$  blend is more suitable in improving toughness than that of  $C_1$  blend, even though in these latter blends a certain degree of adhesion between particle and matrix is observed, on etching the  $C_1$  smoothed surface with boiling xylene vapours (see Fig. 7).

Particle-size distribution curves of  $D_1$  and  $D_2$  blends are shown in Figs. 8 and 9, respectively. It was observed in the case of the blends containing only the 2% functionalized EPR ( $C_1$  and  $C_2$  blend) that a finer

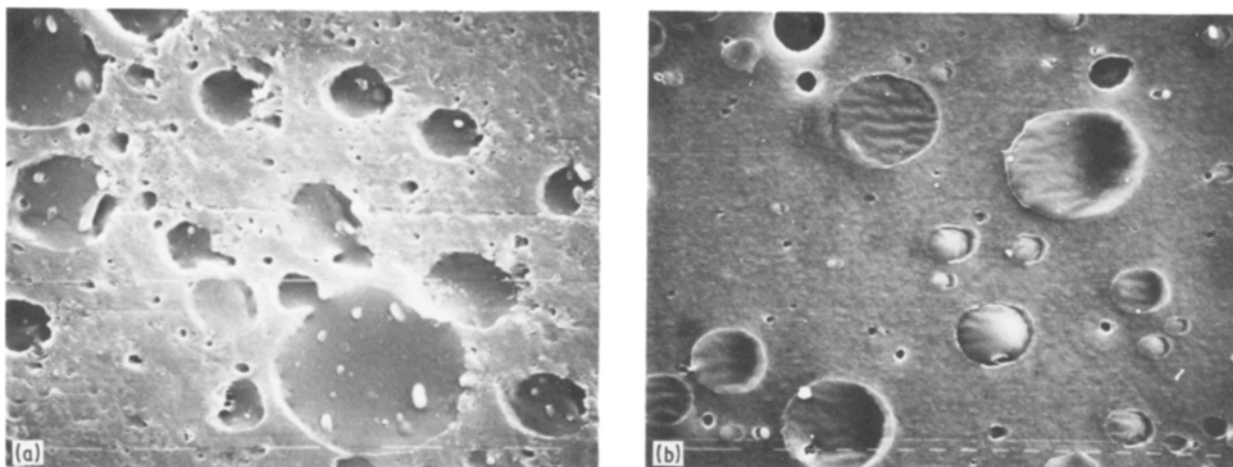


Figure 6 Scanning electron micrographs of microtomed surfaces of: (a)  $C_1$  blend ( $\times 875$ );  $C_2$  blend ( $\times 224$ ). PA6/EPR/EPR-g-SA (80/18/2).

dispersion of the rubbery phase is exhibited by the blend obtained following the solution procedure ( $D_1$  blend). As shown in Fig. 8 and Table V, in such a blend most of the particles have a diameter ranging from 1 to  $5\ \mu\text{m}$ , whereas in  $D_2$  blend it ranges from 5 to  $35\ \mu\text{m}$ . The remarkable higher dispersion degree of the minor components, achieved in  $D_1$  blend, also stands out when comparing  $N_v$  values of  $D_1$  and  $D_2$  blends. In  $D_1$  blend there are about 15 000 000 particles per  $\text{mm}^3$ ; on the other hand, there are only 57 000 particles per  $\text{mm}^3$  counted in  $D_2$  blend.

By comparing the particle-size distribution curve of  $C_2$  and  $D_2$  and of  $C_1$  and  $D_1$  (see Figs 8 and 9) it emerges that the addition of a larger amount of EPR-g-SA (5%) gives rise to a higher dispersion degree of the rubbery phase in the PA6, irrespective of the procedure used. It is, moreover, interesting to observe that a more remarkable improvement in dispersion degree of the minor components results in the blends obtained according to the solution preparative method. This finding suggests that the molecular structure and the amount of (EPR-g-SA)-g-PA6 copolymer, formed during blending, and its capability to act as emulsifier agent, may depend on the mixing conditions. It is likely that the dispersion of the rubbery components in xylene give rise to the formation of a rubber-rubber mixture where the functionalized EPR is finely dispersed. Consequently, during polymerization the

EPR-g-SA molecules have more chance to come into contact with growing PA6 chains.

In the case of  $D_3$  blend, the range of particle diameters is wider than that observed in  $D_1$  but narrower than that of  $D_2$  blend (see Tables V and VI). In  $D_3$  blend most of the particles have diameters lying between 1.25 and  $8.75\ \mu\text{m}$ .

It is to be noted that for the  $B_3$  binary blend, obtained by the same blending method, a higher degree of dispersion of the rubbery phase is achieved (about 5 000 000 particles per  $1\ \text{mm}^3$  blend, whereas there are only 570 000 particles per  $\text{mm}^3$   $B_3$  blend). Such a result indicates that the (EPR-g-SA)-g-PA6 copolymer formed during blending has the capability to act as emulsifier agent, so promoting finer dispersion of the minor components in the PA6.

As far as impact strength is concerned, it appears that, irrespective of the preparation method,  $D_1$  and  $D_2$  blends show the same impact behaviour. Moreover the Izod impact properties of such blends are slightly better than those of  $D_3$  blend obtained by melt mixing [4].

Comparing particle sizes of  $D_3$  blend with the particle size of  $E_3$  blend, containing 10% functionalized EPR, it can be seen that the addition of a greater amount of EPR-g-SA copolymer does not change the range of particle diameters but affects the particle-size distribution. As shown in Fig. 10 the particle-size

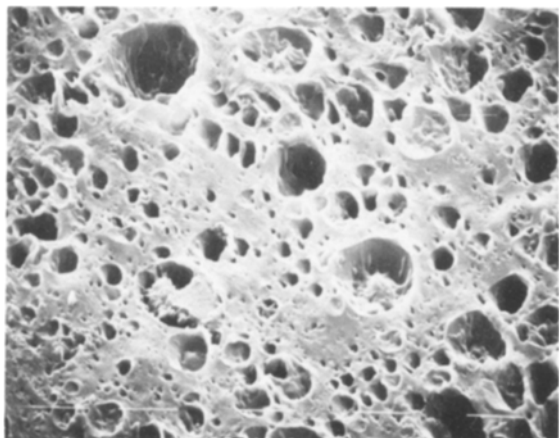


Figure 7 Scanning electron micrographs of  $C_1$  smoothed surfaces etched with boiling xylene vapours ( $\times 810$ ). PA6/EPR/EPR-g-SA (80/18/2).

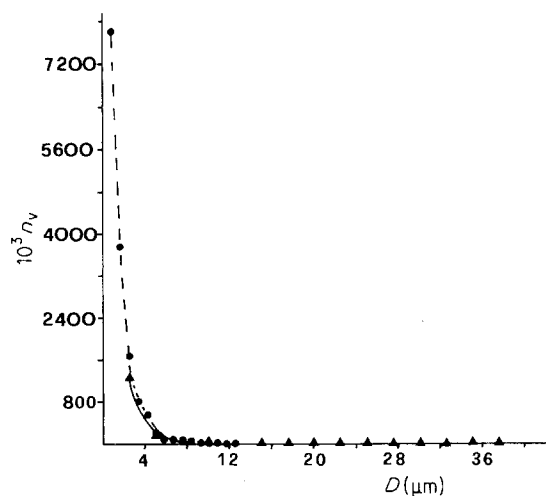


Figure 8 Particle-size distribution curves of ( $\blacktriangle$ )  $C_1$  and ( $\bullet$ )  $D_1$  blends.

TABLE VI Particle diameters ( $D$ ), number and per cent particles per volume unit ( $n_v$  and  $n_v$  %) of  $D_3$  and  $E_3$  blends.  $N_v$  is the total number of particles per volume unit

$D_3$			$E_3$		
$D$ ( $\mu\text{m}$ )	$n_v$	$n_v$ (%)	$D$ ( $\mu\text{m}$ )	$n_v$	$n_v$ (%)
1.25	2 200 997	44.1	1.25	4 386 406	61.0
2.50	1 456 281	29.2	2.50	1 531 899	21.3
3.75	702 189	14.1	3.75	534 685	7.4
5.00	281 299	5.6	5.00	246 324	3.4
6.25	173 894	3.5	6.25	206 369	2.9
7.50	70 296	1.4	7.50	111 488	1.6
8.75	45 279	0.91	8.75	45 705	0.64
10.00	22 630	0.45	10.00	55 112	0.77
11.25	17 209	0.34	11.25	16 149	0.22
12.50	8 819	0.18	12.50	4 660	0.06
13.75	2 188	0.04	13.75	12 850	0.18
15.00	2 526	0.05	15.00	7 399	0.10
16.25	3 462	0.07	16.25	8 407	0.12
17.50	862	0.02	17.50	11 407	0.16
18.75	1 362	0.03	18.75	9 930	0.14
$N_v = 4 989 474$			$N_v = 7 188 796$		

distribution of the rubbery phase in  $E_3$  blend is characterized by a higher number of particles with small dimensions. Moreover, the  $E_3$   $N_v$  values are higher than those of  $D_3$   $N_v$ .

Finally it was found that the Izod impact properties of  $E_3$  blend are better [5] than those observed in  $D_3$  blend, suggesting that the particle-size distribution

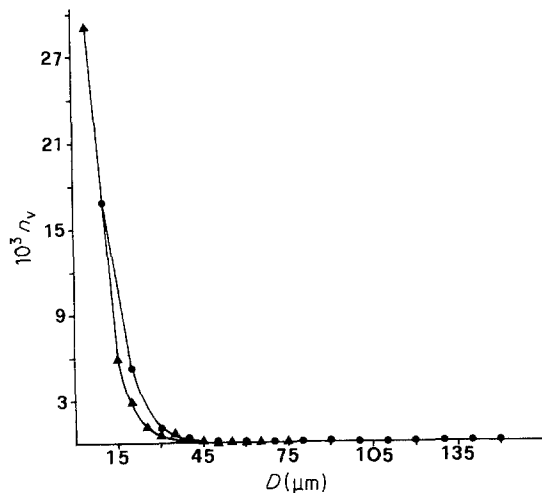


Figure 9 Particle-size distribution curves of (●)  $C_2$  and (▲)  $D_2$  blends.

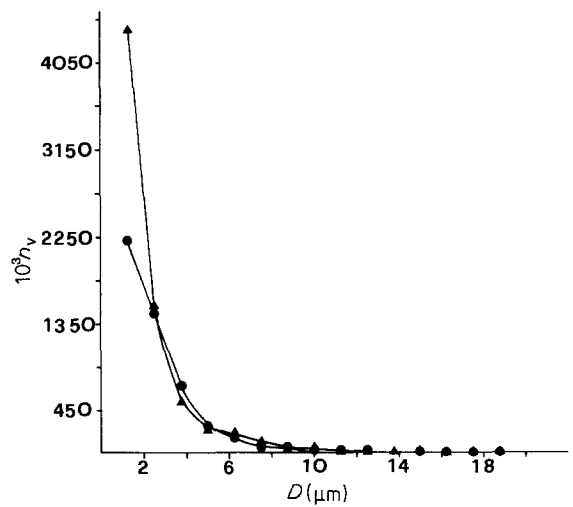


Figure 10 Particle-size distribution curves of (●)  $D_3$  and (▲)  $E_3$  blends.

achieved in  $E_3$  blend is more suitable for inducing toughening characteristics to polyamide.

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