

# Morphological study on the effect of elastomeric impact modifiers in polypropylene systems

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The morphological effect of elastomeric impact modifiers has been studied in polypropylene systems by wide-angle and small-angle X-ray diffractometry, small-angle light scattering, light and electron microscopy and differential scanning calorimetry. It was established that the incorporation of an impact modifier altered the superstructure of the polypropylene matrix by decreasing the average size of spherulites through which the impact strength of the composite may be influenced. The changes in the mechanical and thermal properties are probably caused by the interphase between the amorphous elastomeric modifier and the polypropylene spherulites. The particle size of the dispersed elastomer is of vital importance in toughening of the amorphous polymer while in the crystalline resin, the changes in the superstructure also seem to be very important. Above  $T_g$ , the amorphous impact modifier acts as an energy absorber which markedly influences the crazing susceptibility of the polypropylene matrix.

## INTRODUCTION

Easy processing and extended applicability of polypropylene (PP) has stimulated heavy investment in the PP industry all over the world. In order to avoid an oversupply, the manufacturers endeavour not only to research the new applications but also to replace other polymers by PP through the improvement of some unfavourable properties of PP. In some fields PP is intended to compete with HDPE, ABS or high-impact polystyrene, and to this end the impact strength of PP needs to be enhanced especially at low temperatures.

The glass transition temperature of the amorphous PP is observed in the range of  $0^\circ$  to  $-15^\circ\text{C}$  depending on the test method used. Since this temperature is too high, efforts were made to reduce the  $T_g$  of the amorphous PP by its large-scale copolymerization with ethylene into high-impact random or block copolymers. Applications of plasticizers did not prove satisfactory in this respect because of migration phenomena. A third possibility of reducing the glass transition temperature is the incorporation of an amorphous material of suitably low  $T_g$  (mainly rubberlike ones) into the homopolymer product (formation of a polymer blend). In addition to the suitable  $T_g$ , the modifier should have a mechanical spectroscopical absorption band in the proper temperature range at the frequency of the working load. The wide-spread low-frequency test methods permit an approximate consideration of  $T_g$  of the additive.

In increasing the impact strength, not only the glass transition temperature of the amorphous phase of PP should be used. Another essential characteristic of a high-impact system is its crazing ability. A lot of energy is absorbed by the formation of crazes, without any macroscopic fracture. It is well known that impact grade polystyrene and ABS are

produced by incorporation of elastomeric particles into the amorphous polymer matrix *via* solution or emulsion polymerization. In these cases, a proper selection of the particle size or particle size distribution of the elastomer may lead to a limited degree of crazing since the size of the elastomeric particles acting as stress concentrator keeps a barrier to the extension of crazing. Toughening of amorphous plastics has been thoroughly investigated and reviewed<sup>1-2</sup>; the effects of impact modifiers in a crystalline resin such as PP have been less so.

The impact strength of PP can be favourably influenced by its physical blending with various elastomers such as ethylene-propylene copolymer (EPM), ethylene-propylene-diene terpolymer (EPDM), styrene-butadiene (or isoprene)-styrene block copolymer (SBS or SIS elastomer), butyl rubber etc. Macroscopic properties of blends with these impact modifiers were extensively investigated and reviewed<sup>3-5</sup>. The effects of these high-impact additives on the morphological characteristics of PP have come to the fore only recently<sup>6-7</sup> and the authors have called attention principally to the analogies with the amorphous high-impact systems (i.e. particle size and its distribution of the elastomer).

The present paper aims to interpret the effects of the impact modifiers on the crystal structure of PP using various test methods.

## EXPERIMENTAL

Two commercial grade PP homopolymers (Daplen DM 55 by Chemie Linz A. G. and Pro-fax 6523 by Hercules Inc.) were modified. The blending technique was detailed pre-

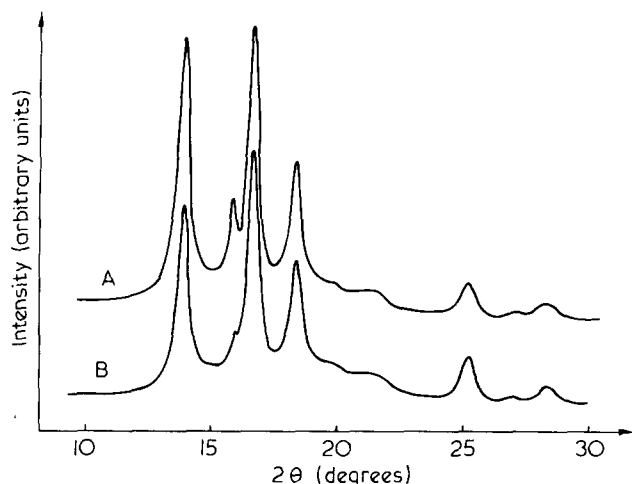


Figure 1 WAXS diffractograms of polypropylenes (A) unmodified and (B) impact modified by blending with 10% of EPM

viously<sup>8-9</sup> where it was established that the highest increment in the impact strength was achieved by EPM and EPDM products, moderate effects were obtained by SBS and SIS thermoplastic rubbers (TR) and by the butyl rubber while polybutadiene, polyisoprene, and polyisobutylene did not increase the impact strength of PP considerably. Accordingly, the present investigations involved the impact modifier systems representing the total series of efficiency as follows:

EPM copolymer (commercial grade, Dutral Co 054 by Montedison), SBS block copolymer (commercial grade, TR 1102 by Shell), and polyisoprene (commercial grade, Cariflex IR 305 by Shell).

Blends were prepared by extrusion and the test specimens were then injection moulded.

Wide-angle X-ray scattering (WAXS) was performed by a Phillips Micro 111 equipment (40 kV, 20 mA) using Ni-filtered  $\text{CuK}_\alpha$  radiation. In small-angle X-ray scattering (SAXS), the Phillips Micro Müller 111 generator was used at 20 kV, 40 mA with a Rigaku-Denki small-angle chamber. The SAXS patterns were recorded in step-scanning regime (at a scanning rate of 0.5'/100 sec) using Ni-filtered radiation.

Small-angle light scattering (SALS) patterns were obtained using a He-Ne gas laser (Hungarian Optical Works) light source. Since the specimens had appropriately smooth surfaces, elimination of the diffuse scattering by the immersion technique was not necessary. For  $H_v$  patterns, the typical exposure time was about 5 sec.

Sections of several  $\mu\text{m}$  in thickness were cut off perpendicularly to the plane of a 2 mm thick injection moulded sheet. The sections were embedded in immersion oil and tested between crossed Nicols by a Polmi A light microscope (LM).

Scanning electron microscopy (SEM) was carried out by a Cambridge Stereoscan S-4 10 equipment. Both the surface of a mechanical fracture and the effect of the chemical etching were studied. Etching was performed by xylene vapour for 20 sec followed by vacuum metallizing the surface by gold.

D.s.c. traces were recorded by a Perkin-Elmer d.s.c. 2 equipment at a heating rate of 20°C/min.

## RESULTS AND DISCUSSION

### Wide-angle X-ray diffractometry

It can be established from the diffractograms that the in-

corporation of the impact modifier leads to an essential change in the structure of PP (see Figure 1). The intensity of the peak at  $2\theta = 16^\circ$ , which corresponds to the 300 reflection of the hexagonal phase<sup>10</sup>, decreases markedly with increasing concentration of the impact modifier. By virtue of the incorporation of the impact modifier, the proportion of the monoclinic and hexagonal phases alters in the PP samples studied. The proportion of these two phases, existing generally together, depends on the moulding conditions and the way of nucleation. Since the former was maintained constant during the preparation of samples, the effect of the impact modifier on the nucleation was suggested then confirmed by the LM and DSC results.

The unit cells calculated from the diffraction band at  $14^\circ$  are between 160 and 165 Å in a wide range of the concentration (0 to 40%) of the impact modifier.

### Small-angle X-ray scattering

It can be stated from the small-angle X-ray diffractograms that the average long period on the one-dimensional sandwich model increases slightly with the concentration of the amorphous impact modifier. This relation is shown in Figure 2 by the curves of the unmodified PP and the system containing 40% of EPM. Values of the long period determined by the Bragg equation were 163 and 184 Å for the unmodified PP and the system containing 40% of the high-impact additive, respectively. Numerical values of the long period were obtained from the Bragg spacing of SAXS curves, though the Tsvankin-Buchanan model<sup>11-12</sup> is widely used as providing more reliable results, since the results were treated only qualitatively. A slight increase in the average long period (i.e. the sum of the average crystallite size and the average interlamellar amorphous region) does not seem to be significant in association with the incorporation of the impact modifier. In several cases the intensity peak assigned to the long period was not observed i.e. no repeating units were present in the systems. A scattering along the direction of irradiation (see Figure 2) is much more characteristic to the

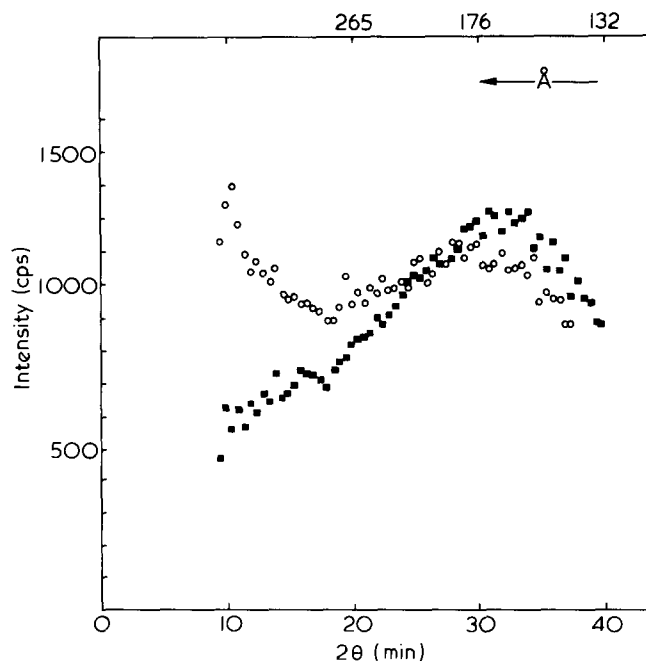
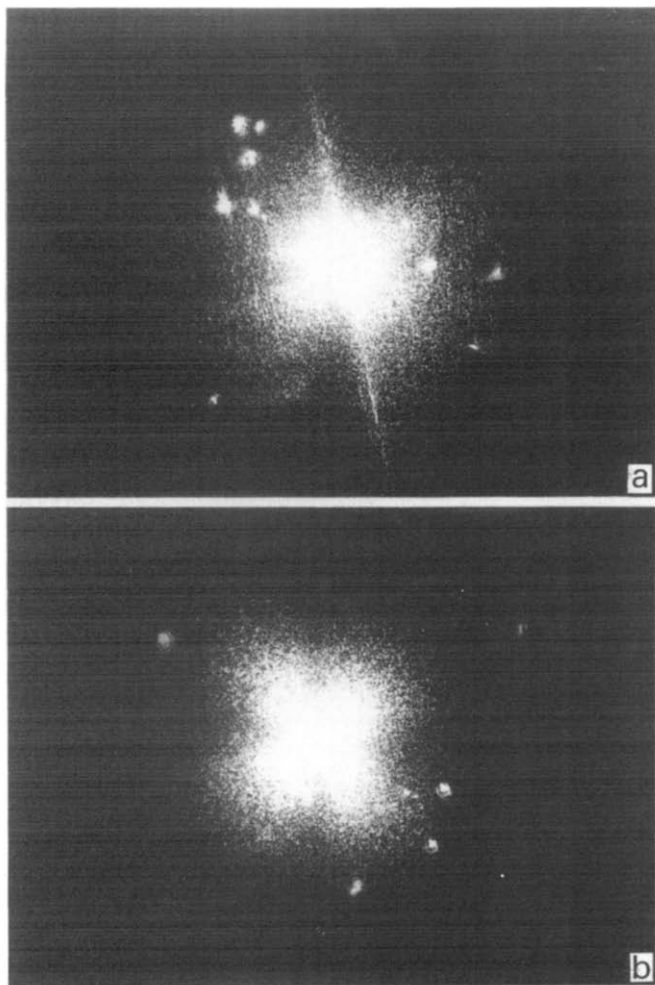


Figure 2 SAXS diffractograms of polypropylene (■) and its blend with 40% of EPM (○)



**Figure 3** Light scattering patterns of polypropylenes (a) unmodified and (b) impact modified by 20% of EPM in  $H_v$  polarization

sample supplemented by the elastomer indicating the presence of  $56\text{\AA}$  scattering centres according to the Guinier equation<sup>13</sup>. It suggests that the incorporated elastomer is present in form of particles.

The SAXS results suggest that much more considerable changes are expected in the lamellar spherulite structure. Analogous results were obtained by this technique for the crystalline blends containing poly( $\epsilon$ -caprolactone) and poly(vinylchloride)<sup>14</sup>.

#### Light scattering

SAXS results indicate a lamellar structure including crystalline lamellae of PP and amorphous ones containing PP and elastomer, the latter dispersed in the amorphous phase.

The small-angle light scattering (SALS) was used as an adequate method for studying the spherulitic structure. Three types of polarization can be applied: vertically polarized incident light and horizontally polarized scattered light ( $H_v$ ), both the incident and the scattered light are vertically polarized ( $V_v$ ), and both are horizontally polarized ( $H_h$ ). Lobe-and-streak patterns in  $H_v$  polarization proved to be usually most characteristic. Such records are presented in *Figure 3* for the unmodified and high-impact PP. The latter one contained 20% of EPM.

The spherulite sizes determined by the Stein method<sup>15</sup> were  $4.3$  and  $3.4\ \mu\text{m}$  for the unmodified PP and for the system containing 20% of EPM respectively. *Figure 3* indicates

that the incorporation of the elastomer alters the initial spherulitic morphology. The same effect, i.e. a decrease in the spherulite radius, was detected by SALS in the superstructure of binary mixtures of high and low molecular weight polyethylenes<sup>16</sup>. The size reduction and change in spherulitic types by the addition of the modifier were also confirmed by the light microscopic investigations (see below). The decrease in the spherulite size with increasing elastomer content indicates an increasing rate of nucleation. The elastomer acts as a nucleating agent which is reflected in the possibility and extent of undercooling (cf d.s.c. measurements).

#### Light microscopy

According to the above results, it appeared that the structural interpretation of the increase in the impact strength of a polymer blend is involved in the supercrystalline structure. Polar optical methods are suitable for its study since they can reveal the spherulitic structure and its change in PP.

It is well known that the isotactic PP has several crystal modifications. Padden and Keith<sup>17</sup> classified the PP spherulites into four types. The Types I and II are formed at about the same growing rate, while Types III and IV grow faster by about 20%. Turner-Jones *et al.*<sup>18</sup> studied the unit cells of modifications of PP superstructure in detail and concluded that Types I and II spherulites had  $\alpha$ -form crystallinity (monoclinic), while Types III and IV were categorized as the  $\beta$ -form (hexagonal). This concurs with the results of Keith *et al.*<sup>19</sup> and is supported by Samuels and Yee<sup>10</sup>. According to the results of d.s.c. measurements<sup>20</sup>, the  $\alpha$ -form has higher stability than the  $\beta$ -form of the PP. The unit cells of the  $\beta$ -form are packed less densely than those of the  $\alpha$ -form. This fact promotes the crystallization of the molecular chains in the  $\beta$ -modification<sup>20</sup>.

Photomicrograms of sections cut perpendicularly to the plane of injection moulded sheets were recorded through polarizing optics and shown in *Figures 4, 5* and *6* for blends containing EPM, SBS and polyisoprene respectively.

Structures damaged or deficient in different extent can well be distinguished from the regular (well developed) spherulites in the micrograms, the former ones correspond to the monoclinic spherulites Type I, while the latter ones are  $\beta$ -form spherulites Type III. Unmodified PP has a regular structure with quite ordered spherulitic texture. The extent of the spherulites Type I increases with increasing concentration of the impact modifier, in accord with the SALS results. It means that the impact modifier is an effective nucleating agent for producing  $\alpha$ -type spherulites. In the  $\alpha$ -form spherulitic structure, however, some spherulites Type III are also observed (see *Figure 4b, c* and *d*); their amount decreases as the concentration of the impact modifier is increased. Studying PP-EPDM systems, Thamm<sup>6</sup> reported that big spherulites are formed at the knit-line of injection moulded specimens. The decrease of the  $\beta$ -form spherulites is supported by the WAXS results too.

Not only the spherulitic structure but also the size of spherulites is changed markedly by the incorporation of the impact modifier. The average spherulite size of a sample containing 5% of EPM additive is about the half of that of the original PP. This spherulite size decreases only slightly by the additional incorporation of the impact modifier. Light microscopic studies of samples modified by SBS as a moderate impact modifier provided similar results except that big spherulites Type III were not observed, in contrast with the samples modified by EPM. For the blends con-

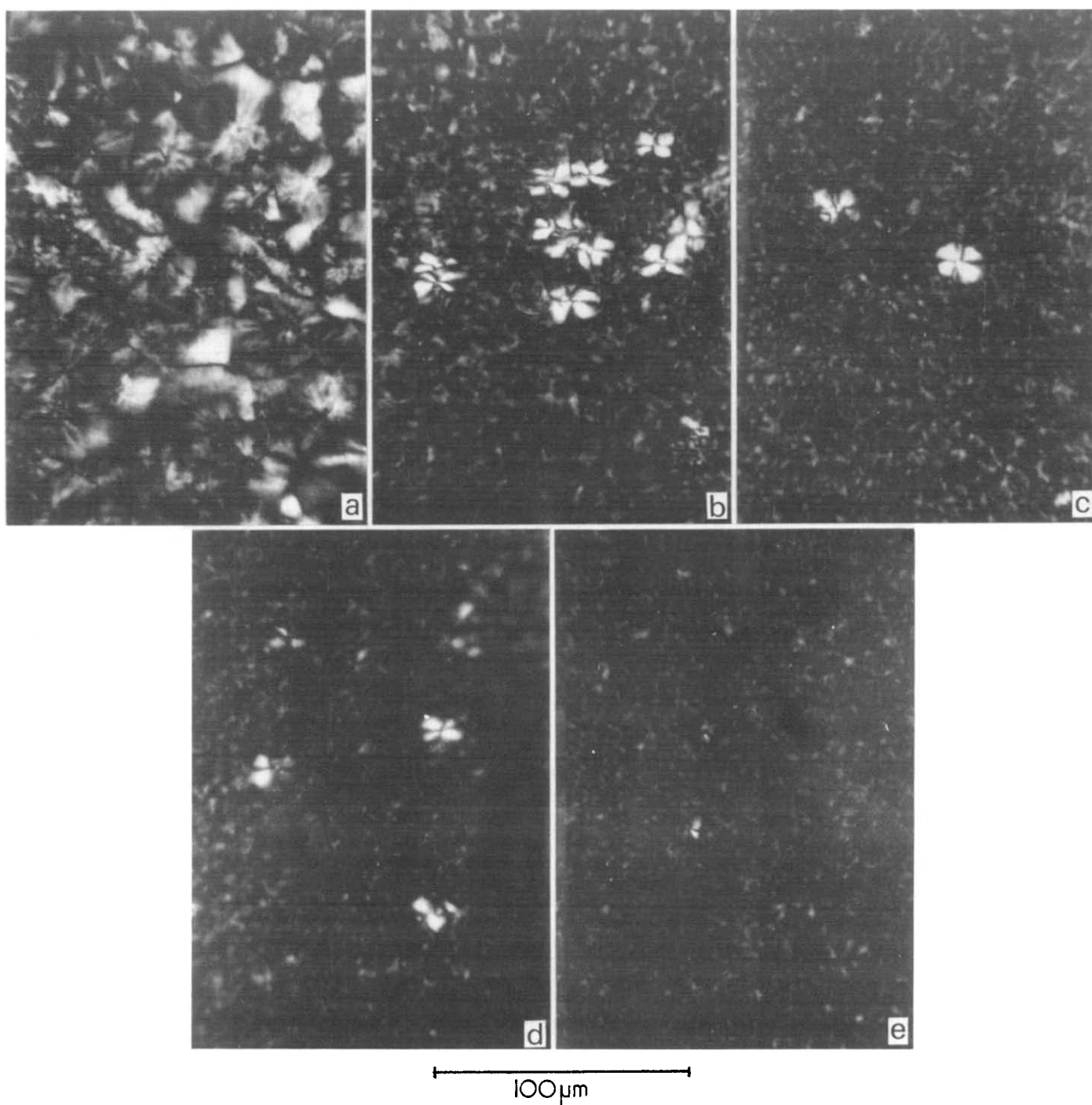


Figure 4 Polarizing light micrograms of PP-EPM blends. EPM contents: 0% (a), 5% (b), 10% (c), 20% (d), 40% (e)

taining polyisoprene, changes in the initial spherulite size are considerably smaller than for either the excellent high-impact EPM or the more moderate SBS. Spherulite sizes determined by light microscopy are shown in Table 1 together with the impact strengths of the blends measured by a Dynstat apparatus according to DIN 53 453 at  $-15^{\circ}\text{C}$ .

It was proved by the microscopic data that the incorporation of impact modifiers, resulting principally in  $\alpha$ -form spherulites, reduced the average spherulite size in PP. The efficiency of the impact modifiers can be associated with the changes in the spherulite size caused by their incorporation (see Table 1). It can be established that the impact strength of the compounds increases with the reduction of the spherulite size. This increase depends on the type of the elastomer used as a function of the compatibility of PP with the elastomer additive. The significance of compatibility appears

in the adhesion of the elastomeric amorphous phase to the spherulites. The strength of adhesion depends on the types of the impact modifier. Thus such a system may be interpreted by a model where the spherulites are completely or partially separated from each other (at higher or lower concentrations of the modifier respectively) and the amorphous layers adhered to the interface of the individual spherulites in which the elastomeric particles are dispersed, acting as stress concentrator sites, similarly to the elastomer particles in toughening the amorphous plastics.

#### Scanning electron microscopy

Test samples were prepared by breaking the polymer blends at the temperature of liquid nitrogen then gold was evaporated onto the broken surface. SEM records on the broken sur-

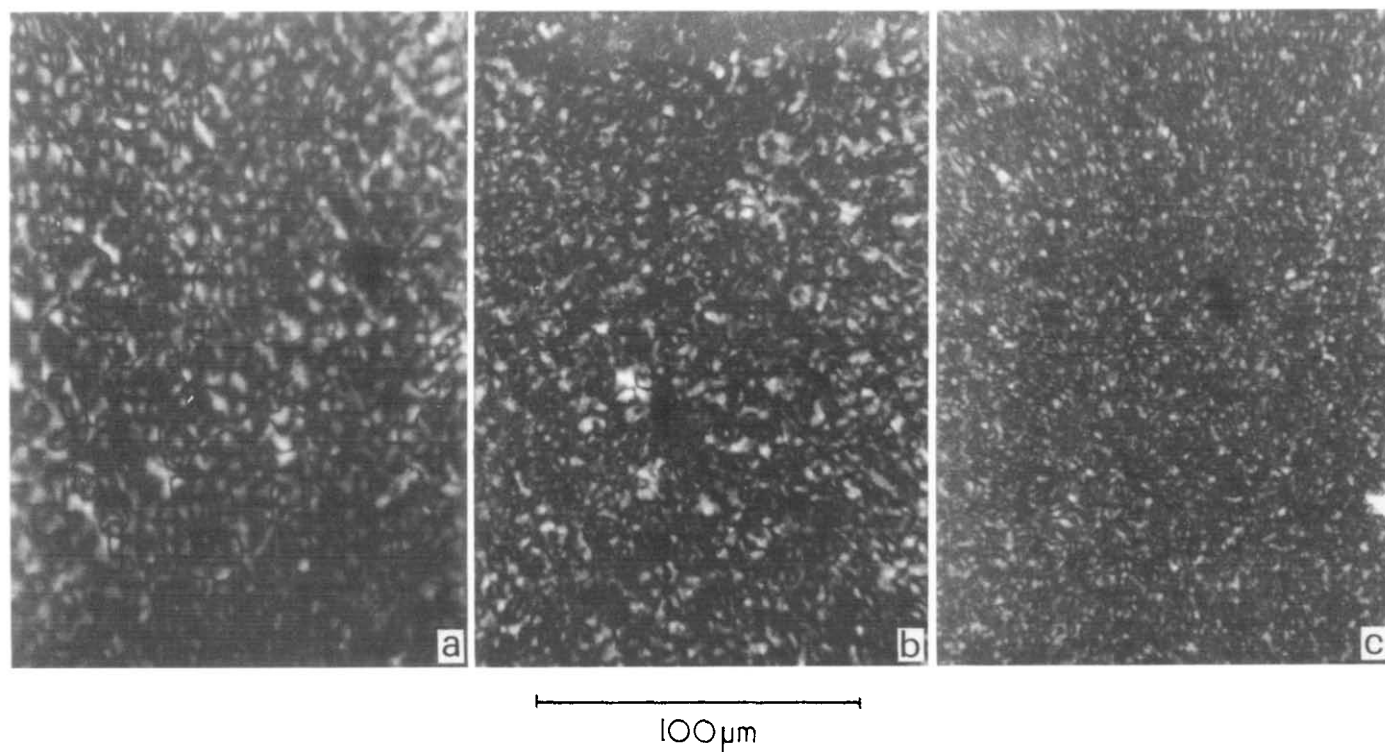


Figure 5 Polarizing light micrograms of PP-SBS blends. SBS contents: 0% (a), 5% (b), 10% (c)

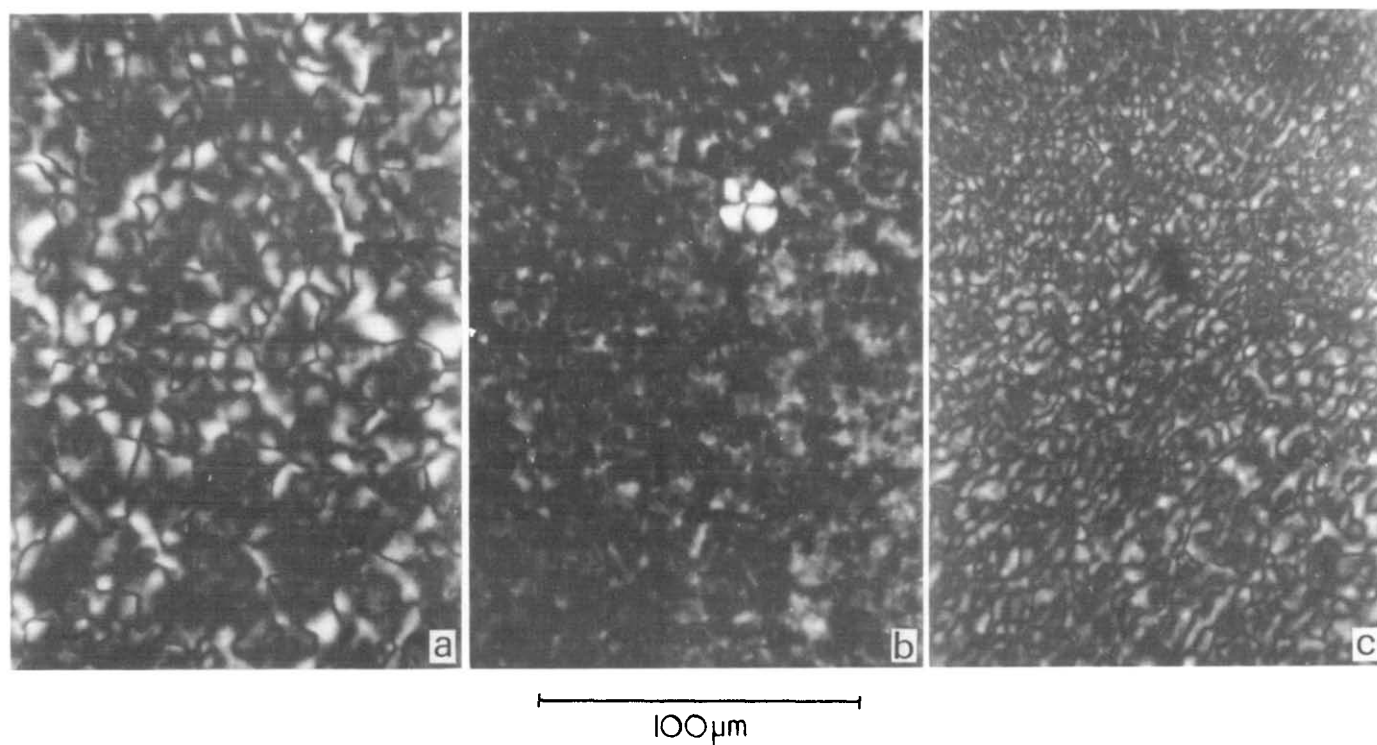


Figure 6 Polarizing light micrograms of PP-polyisoprene blends. Polyisoprene contents: 0% (a), 5% (b), 10% (c).

faces of EPM-modified samples are shown in *Figure 7*. The discernible changes in the texture of the broken surfaces are rather difficult to be brought into connection with changes in the spherulite structure. It may be due to the fact that, at this low temperature, not only the adherence between the impact modifier and PP is impaired but also the amorphous phase crazes or breaks below the glass transition temperature of the additive. Above this temperature, the humps and hollows of the broken surface can be applied for determination

of the particle size of the dispersed impact modifier<sup>6</sup>. Its distribution is quite broad, the particle size of elastomer is in the range of 0.05 to 3 $\mu\text{m}$ <sup>21</sup>.

By chemical etching of the broken surface using xylene vapour, an internal globular structure becomes discernible which may inform about the spherulitic structure and its changes. Chemical etching might influence the spherulitic structure by a secondary crystallization due to the etching solvent. The solvent enhances the mobility of the polymer chains by inter-



position to the interchain forces and stimulates the rearrangement into the crystalline state<sup>22</sup>. It was reported for PP that the spherulitic structure and crystalline particle size was changed by chemical etching<sup>23</sup>. We obtained similar results. It appears more reasonable to apply physical etching (such as ionic etching<sup>24</sup>) excluding the interference of the solvent.

#### Differential scanning calorimetry

It was concluded from the light microscopic results that the average spherulite size decreased by the addition of the

**Table 1** Spherulite sizes determined by light microscopy and impact strengths of polymer blends containing impact modifiers

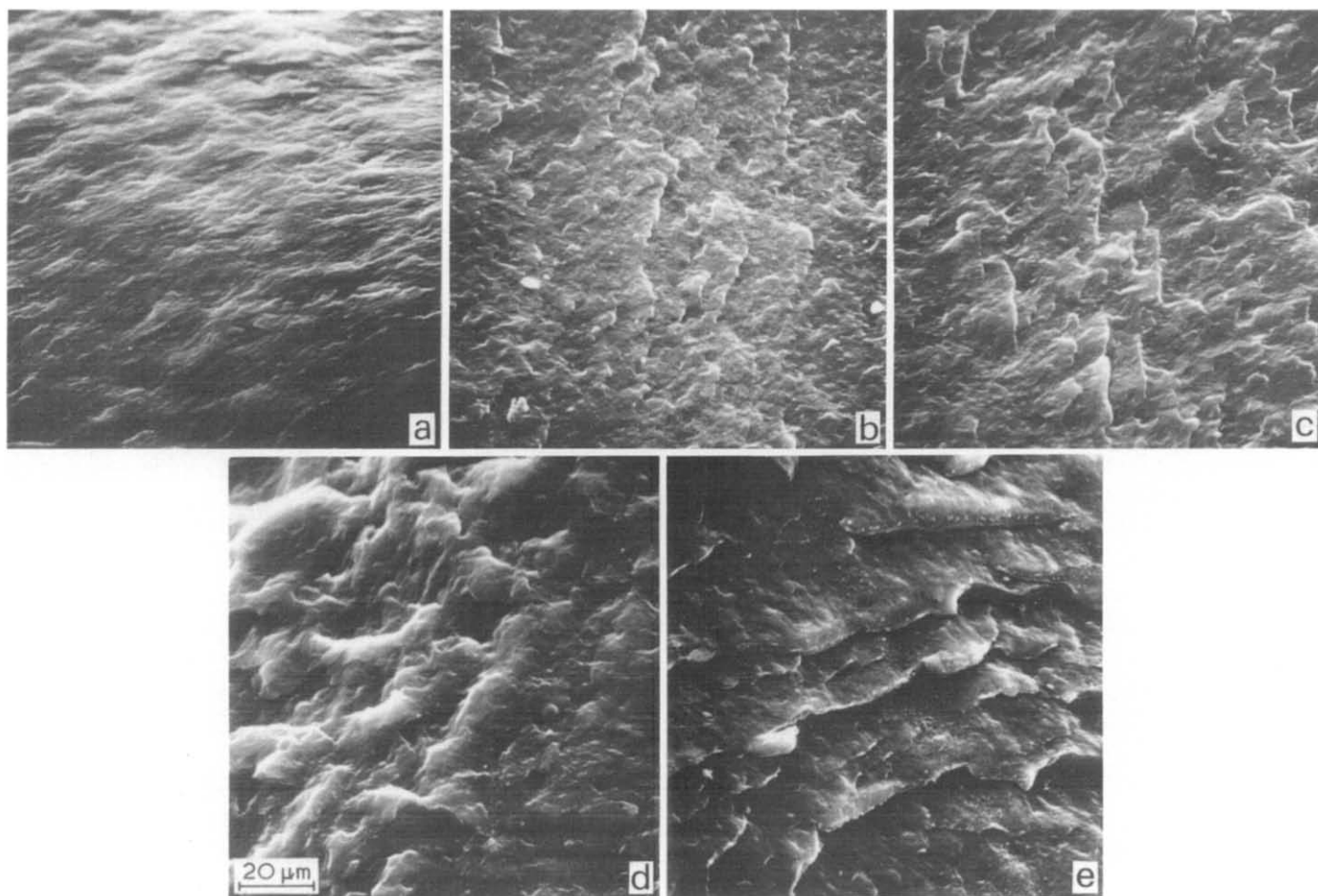
Sample composition		Spherulite sizes ( $\mu\text{m}$ )		Impact strength at $-15^\circ\text{C}$ ( $\text{kJ/m}^2$ )
Polymer	Modifier	Type I	Type III	
PP Daplen DM 55	None	15	19 <sup>a</sup>	3.8
	5% EPM	8.5	19	19.1
	10% EPM	7.5	14	23.2
	20% EPM	6	15	31.6
	40% EPM	5	13	37.8
PP Daplen DM 55	5% Polyisoprene	12	19	4.0
	10% Polyisoprene	9.5	— <sup>a</sup>	4.1
PP Pro-fax 6523	None	12	— <sup>a</sup>	4.0
	5% SBS	8	— <sup>a</sup>	5.9
	10% SBS	4.5	— <sup>a</sup>	15.0

<sup>a</sup> No such a Type spherulite was observed in the investigated region

modifier (see *Table 1*). As a consequence, of the presence of smaller spherulites having lower heat capacity, the melting range of the polymer blend should shift to lower temperatures. It follows from the SAXS patterns that the crystalline proportion of the blends determined by d.s.c. is reduced by the increasing concentration of the impact modifier. D.s.c. results actually proved this assumption. By increasing the concentration of the impact modifier, the melting peak of the polymer blend shifted to lower temperatures while the crystallization peak of the blends shifted to higher temperatures. As a resultant of these two effects, the extent of undercooling decreases (see *Table 2*).

Further evidence was obtained from the d.s.c. measurements that the superstructure was changed by the incorporation of an impact modifier resulting in the formation of tiny  $\alpha$ -form spherulites. The impact modifier acts simultaneously as a  $\alpha$ -nucleating agent decreasing the degree of undercooling which is an important factor of the PP processing<sup>25</sup>. The formation of  $\alpha$ -form spherulites was supported by d.s.c. records showing a single endothermic melting peak at a temperature corresponding to the  $\alpha$ -form spherulites<sup>20</sup> (see *Table 2*).

Morphological studies of PP-based polymer blends with impact modifiers revealed that superstructure of PP was affected by the addition of the modifiers. Polar optical results showed that the incorporation of the additives reduced the average size of spherulites, inhibited the formation of the less stable  $\beta$ -form. A relation can be established between the impact strength and the average spherulite size but impact strengths depend on the type of the impact modifier in con-



**Figure 7** Scanning electron micrograms of broken surfaces of PP-EPM blends. EPM contents: 0% (a), 5% (b), 10% (c), 20% (d), 40% (e)

Table 2 Evaluation of d.s.c. records of PP systems containing impact modifiers

Sample	Melting peak °C	Crystallization peak °C	Degree of under-cooling °C
PP/Daplen DM 55/	164.5	104	60.5
+5% EPM	162	105	57
+10% EPM	161.5	107	54.5
+20% EPM	160.5	107	53.5
+40% EPM	160	117.5	42.5
PP/Daplen DM 55/			
+5% Polyisoprene	163.5	103.5	60.5
+10% Polyisoprene	161.5	105	56.5
PP/Pro-fax 6523/	161.5	104	57.5
+5% SBS	160.5	105	55.5
+10% SBS	160.5	106	54.5

Note: Data in the Table are mean values of several measurements

nection with its compatibility with the polymer. The incorporation of the impact modifier favours the formation of the  $\alpha$ -form spherulites Type I. SEM records suggest that the additives influence the crazing susceptibility and mechanisms as shown in the records of broken surfaces. Changes in the superstructure of PP were supported by the d.s.c. measurements where the melting peaks of blends containing higher amount of additive shifted towards lower temperatures; it can be explained by the formation of smaller spherulites. The thermograms have a single melting peak each at the temperature characteristic to the  $\alpha$ -form spherulites. At the same time, the elastomeric additive acts as a  $\alpha$ -nucleating agent by decreasing the capability for undercooling of the blend. WAXS records suggest that the proportion of the  $\beta$ -phase decreases by increasing the concentration of the impact modifier. SAXS results gave account of a slight increase in the average long periods at low concentrations of the impact modifier while, at higher concentrations, the reflection peak corresponding to the long period disappears. The scattering in the direction of the irradiation reflects to the dispersity of the elastomeric modifier.

For high-impact PP systems (prepared by physical blending) it can be accepted as an informative model that a 'dispersed' spherulitic structure is disjoined by amorphous layers in which elastomer particles are dispersed. It is an analogous picture with the known structure of thermoplastic rubbers where polystyrene regions are embedded into a polybutadiene matrix. The spherulites act as barriers of propagation of crazing while the impact modifier in the amorphous part is the absorber of the mechanical action and the regulator of the crazes.

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