

Characterization of Microstructure and Fracture Behavior of Polypropylene/Elastomer Blends Containing Small Crystal in Elastomeric Phase

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SYNOPSIS

Fracture behavior of polypropylene (PP)/ethylene-propylene-rubber (EPR) blends containing small crystal in elastomeric phase was investigated. Various ethylene- α -olefin copolymers (ECP) were used as crystal components and put into the elastomer phase of the blends. The crystallite size was controlled by changing the composition of the ECP. From thermal analysis and electron microscopic analysis, it was found that the ECP having a smaller crystal had better affinity to EPR and thus the crystal was finely dispersed in the elastomeric phase. The ECP with large crystallite size had poorer affinity to EPR and tended to segregate in the elastomeric phase. Scratch resistance and tensile elongation of blends were measured and it was found that the small crystal drastically improved the above properties while the large crystal deteriorated them. The dispersed small crystal was thought to act as a crosslinking point in the elastomeric phase. The reinforcement of the elastomeric phase by such quasi-crosslinking structure was the possible reason for the improvement of the mechanical properties of the blends. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Polypropylene (PP)/ethylene-propylene-rubber (EPR) blends have been widely used for automobile parts, appliances, and other industrial uses because of their superior mechanical properties and processabilities. Many efforts are still being made to further improve their properties and expand their application fields.

Most of these blends contain 20–40 wt % EPR and it is generally believed that spherical EPR domain is dispersed in continuous PP matrix. On the other hand, Nomura et al. recently proposed a new structural model where PP crystalline lamella is dispersed in an amorphous matrix.^{1–4} Their model was based on transmission electron microscopic analysis. They interpreted the mechanical properties of PP/EPR blends with the above model. The model

was also applied to improve the properties of PP/EPR blends. By putting polyethylene (PE) crystal into the rubber, they could reinforce the amorphous matrix and succeed in improving the stiffness and surface hardness of the blend. Addition of the PE crystal to the elastomeric phase was done by replacing a part of EPR with ethylene copolymer. They concluded that PE crystal with thicker lamella, i.e., with higher melting temperature, was more effective to stiffen the amorphous matrix and to improve the surface hardness of the blend.¹ Although a remarkable effect of PE crystal on properties such as stiffness was revealed, their investigation was limited to small deformation, i.e., elastic deformation region. Its effect on the large deformation fracture behavior was still uncertain.

A scratch formation is one of the fracture phenomena that takes place at material surface. Although the scratch resistance is a very important property in practical use, it has not yet been intensively investigated. Recently, Yokomizo and Fujita developed a method to quantitatively evaluate

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scratch resistance.⁵ From their analysis, it has been shown that scratch resistance depends on both elastic property and fracture strength.

By applying Yokomizo's method, we examined the effect of PE crystallite size on scratch resistance. Its effect on tensile elongation is also studied. The crystal structure existing in the elastomeric phase is analyzed by small angle X-ray scattering (SAXS) and transmission electron microscopy (TEM). The affinity of crystalline ethylene copolymer and EPR is evaluated from the melting behavior of the blends.

The effect of the PE crystal on fracture behavior and its reinforcing mechanism will be discussed together with a new design concept of PP-based polymer blends.

EXPERIMENTAL

Materials

Polypropylene was supplied by Tonen Chemical Corp. The specific gravity was 0.89 and MFR was 40.

EPR was supplied by Japan Synthetic Rubber Co., Ltd. The specific gravity was 0.86. The Mooney viscosity, ML_{1+4} (100°C) was 63 and ethylene content was 78 wt %.

Ethylene- α -olefin copolymers (ECP) with various composition were used to put into the elastomer phase. The PE crystallite size was controlled by changing the copolymer composition. The characteristics of the copolymers are listed in Table I.

EPR/ECP binary blends and PP/EPR/ECP ternary blends were prepared by a 45-mm ϕ twin screw extruder. The binary blends were used for X-ray analysis and thermal analysis. The ternary blends were used for TEM observation, scratch resistance measurement, and tensile elongation measurement.

The composition of binary blends and ternary blends are shown in Tables II(a) and II(b), respectively.

Transmission Electron Microscopic (TEM) Analysis

A 2-mm-thick sheet of PP/EPR/ECP ternary blends was stained with RuO_4 . The stained sheet was ultramicrotomed to prepare a thin film of about 100 nm thickness. TEM analysis of the thin film was carried out by a Hitachi H-7000 at 100 kV.

X-Ray Analysis

Small angle X-ray scattering (SAXS, McScience) measurement was carried out on EPR/ECP binary blends. The long period (L) of ECP crystal was calculated using Bragg's law.

$$L = \lambda/2 \sin \Theta \quad (1)$$

where L is the long period, λ is the wave length of the incident X-ray (0.15418 nm), and Θ is the scattering angle. The crystallite size (d) was obtained from the following equation:

$$d = X_c L \quad (2)$$

where X_c is the crystallinity obtained from equation (3).

Thermal Analysis

Melting behavior of EPR/ECP binary blends was analyzed by a differential scanning calorimeter (DSC7, Perkin-Elmer). A sample was first held at 200°C for 10 minutes and crystallized by decreasing the temperature to -30°C at a rate of 10°C/min. Then it was held at -30°C for 5 min. Finally, the melting behavior was recorded by increasing the temperature to 200°C at a rate of 10°C/min.

From the above measurement, the melting temperature (T_m) and the heat of fusion (ΔH_f) were obtained. The following equation was used to calculate the crystallinity of PE copolymers (X_c) where ΔH_c is the heat of fusion for perfect crystal (=293 J/g).⁶

Table I Characteristics of Ethylene- α -olefin Copolymer (ECP)

ECP (No.)	Density (g/cm ³)	T_c (°C)	T_m (°C)	ΔH_f (J/g)
ECP1	0.89	062	074	085
ECP2	0.91	103	120	116
ECP3	0.92	105	123	125
ECP4	0.95	115	132	219

Table II(a) Weight Composition of EPR/ECP Binary Blends

Exp. No.	EPR	ECP			
		ECP1	ECP2	ECP3	ECP4
B1	75	25			
B2	75		25		
B3	75			25	
B4	90				10

$$X_c = 100\Delta H_f / \Delta H_c \quad (3)$$

Scratch Resistance

Scratch resistance was evaluated by a continuous loading-type scratch intensity tester (Heidon Corp.) and a surface roughness tester (Rank Talor Hobson Corp.). A schematic instrumental setup of the scratch intensity tester is shown in Figure 1. A detailed experimental procedure is described elsewhere⁵; a brief outline is given below.

A scratch needle with a spherical tip is penetrated vertically into a material surface under a constant load. Then the needle is horizontally moved along the material at a constant rate. While a scratch is formed on the material surface, a horizontal scratch force (F_s) is recorded by a transducer equipped with a tester. Scratch resistance is evaluated from the depth of a formed scratch, H , which is measured by the surface roughness tester. A typical scratch profile is shown in Figure 2.

Yokomizo has examined the scratch resistance of several polyolefin polymer alloys and found that H could be described as follows⁵:

$$H [\mu\text{m}] = 0.48d_{\text{max}} [\mu\text{m}] - 1.39 \cdot 10^{-3} \times P_s [\text{kg}/\text{cm}^2] + 15.2 \quad (4)$$

where d_{max} is the penetrated depth of the needle measured by the surface roughness tester. P_s is the

stress generated while scratching, which was obtained from the following equation:

$$P_s = (F_s - F_f) / A \quad (5)$$

F_s and F_f are the scratch force and the frictional force generated while scratching and measured by the scratch tester. A is the cross-sectional area of the formed scratch measured by the surface roughness tester.

Furthermore, they found that the parameters d_{max} and P_s were closely related to elastic property and fracture property, respectively.⁵

We evaluated the scratch resistance with the above method and analyzed the effect of existing ECP crystal on the scratch formation behavior of PP/EPR blends from obtained parameters d_{max} and P_s .

In this study, material surface was scratched by a sapphire needle with 0.05 mm radius tip under a condition of 50 mm/min scratch speed, 30 gf vertical load.

Tensile Elongation

Tensile elongation behavior was examined according to JIS K7113. A 3-mm-thick sheet was injection molded. A dumbbell-shaped specimen (JIS No. 2) was cut out of the sheet. An Instron Model 4302 universal tester was used to examine the tensile

Table II(b) Weight Composition of PP/EPR/ECP Ternary Blends

Exp. No.	PP	EPR	ECP1	ECP2	ECP3	ECP4
T1	67.0	33.0				
T2	67.0	24.8	8.2			
T3	67.0	24.8		8.2		
T4	67.0	24.8			8.2	
T5	67.0	29.7				3.3

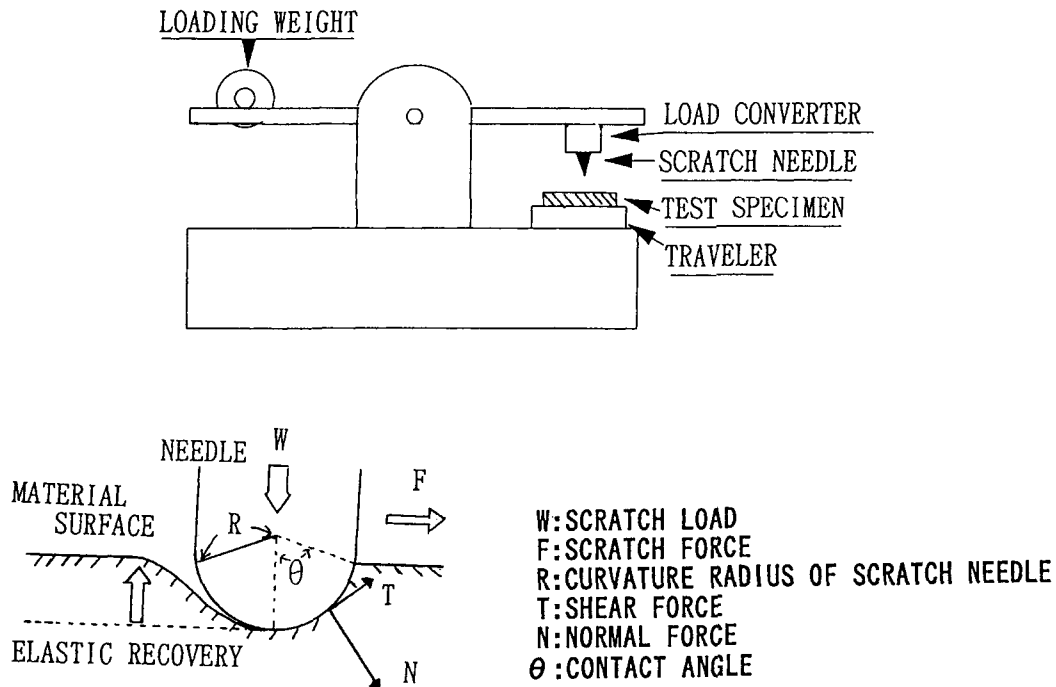


Figure 1 Experimental set-up of the scratch intensity tester.

elongation behavior at room temperature. The crosshead speed was 50 mm/min.

RESULTS AND DISCUSSION

Morphology of PP/EPR/ECP Ternary Blends

The transmission electron micrographs of PP/EPR/ECP ternary blends are shown in Figures 3 and 4. In spite of the difference in the crystallinity of the ECP component, their morphological features are very similar. They consist of two phases: a bright PP phase and a dark EPR/ECP phase. The size of each phase is almost the same and the overall morphology is not affected by the crystallinity of ECP

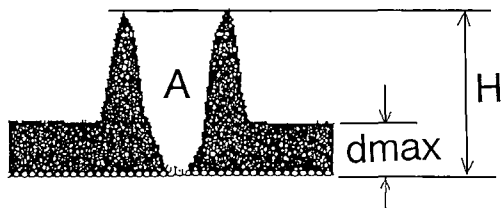


Figure 2 Scratch profile measured by surface roughness tester.

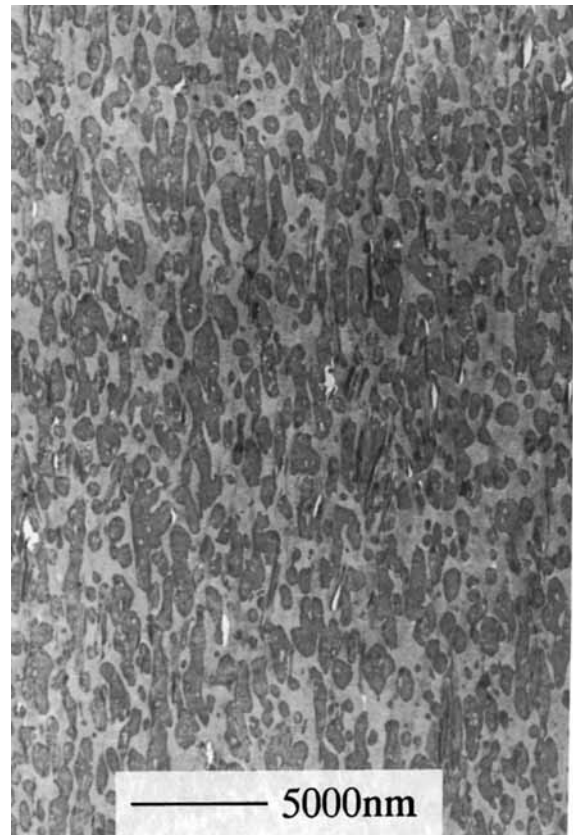


Figure 3 TEM micrograph of PP/EPR/ECP1 ternary blend.

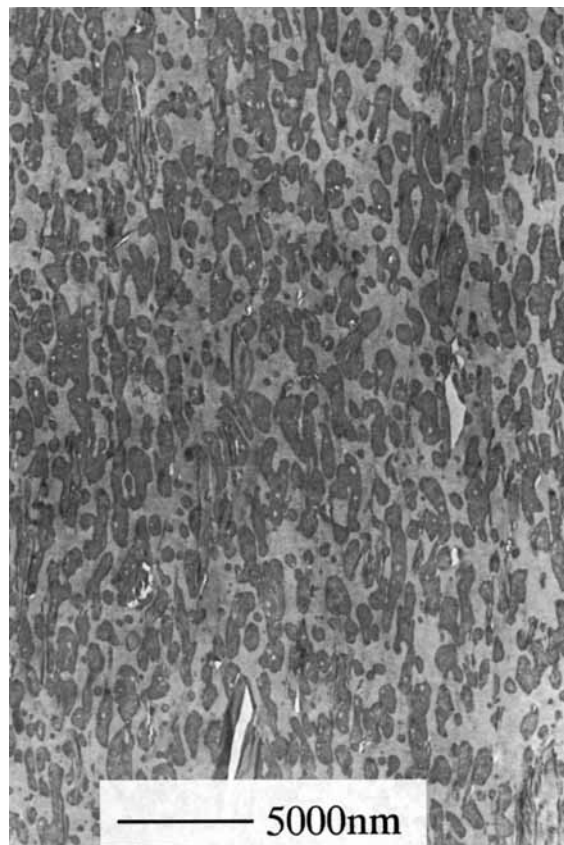


Figure 4 TEM micrograph of PP/EPR/ECP4 ternary blend.

components. It is probably because ECP content was too low compared to EPR content and thus ECP did not affect the whole morphology of the blends.

Figures 5 and 6 show higher magnification TEM micrographs of the above samples. Contrary to the similarity of the whole morphology, a remarkable difference in the elastomeric phase is observed. In the blend containing lower crystallinity ECP (ECP1), the ECP crystal is finely dispersed in the elastomer phase and forms a relatively uniform structure. Although a periodic fine structure is observed inside the elastomeric phase, it is too small for its size to be accurately quantified. On the other hand, in the blend having higher crystallinity ECP (ECP4), ECP is segregated and forms a lamellar structure. Thus the elastomer phase is very inhomogeneous. Observed lamellar thickness in this blend system is 10 to 20 nm.

The above observation showed that the small amount of ECP crystal did not affect the overall morphology while it strongly affected the morphology inside the elastomeric phase.

ECP Crystalline Structure in Elastomeric Phase

The structure of ECP crystal dispersed in the elastomeric phase was analyzed by DSC and SAXS. EPR/ECP binary blends were used for DSC and SAXS measurement to eliminate a strong interfering signal which arises from PP. The results are summarized in Table III. The crystallite size of ECP component varied from 3 nm to 8.5 nm. The thermal property and the crystallinity varies in the same manner as the crystallite size.

The crystallite size (lamellar thickness) of the blend containing ECP4 as a crystalline component is 8.5 nm. It is slightly smaller than that obtained from TEM analysis (10 to 20 nm). There are two possible explanations for the discrepancy between SAXS and TEM results. In TEM analysis, measured lamellar thickness will always be larger than the actual value as long as the observed plane of the microtomed thin section is not exactly aligned to the direction of the lamellar thickness. On the other hand, in SAXS analysis, the measured lamellar thickness will always be smaller than the actual be-

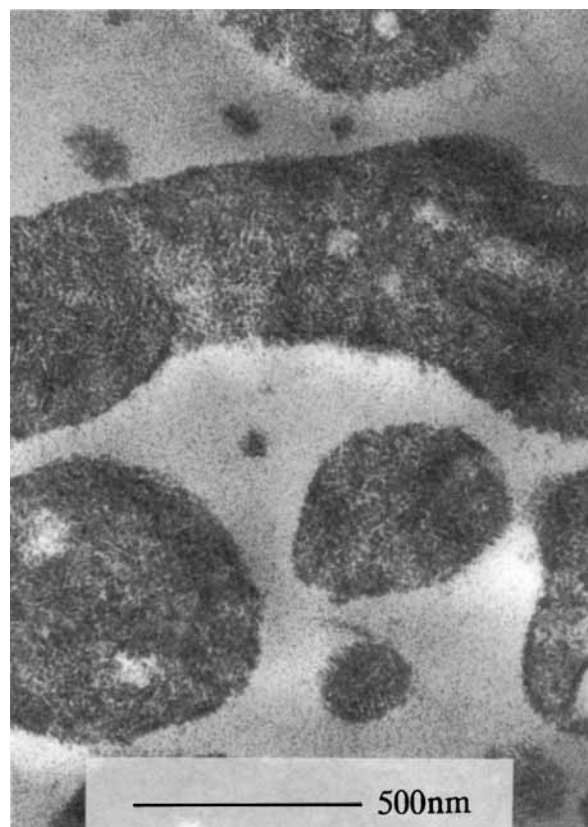


Figure 5 High magnification TEM micrograph of PP/EPR/ECP1 blend.



Figure 6 High magnification TEM micrograph of PP/EPR/ECP4 blend.

cause X_c , which was used to calculate the lamellar thickness in eq. (2), is only an approximation. The X_c used in eq. (2) was the average crystallinity in the elastomeric phase. It is obvious from the TEM photograph (Fig. 6) that the elastomeric phase itself is not homogeneous and therefore the crystallinity of the portion where the crystal lamellar is localized will be higher than the average X_c . Thus the actual lamellar thickness should be a little larger than the calculated value. If these two effects are taken into

account, it can be said that there is a good agreement between TEM and SAXS results.

The dependence of T_m on the composition of EPR/ECP binary blends is shown in Figure 7. If small-crystal ECP (ECP1) is used as a blend component, its T_m begins to decrease at 20 wt % EPR and T_m suppression becomes as much as 5°C at 75 wt % EPR. On the other hand, when ECP with large crystal (ECP4) is used the T_m suppression is much smaller. It is only about 1°C at 80 wt % EPR. The degree of T_m suppression directly reflects the affinity of blend components. Therefore, the affinity of ECP1 and EPR is better than that of ECP4 and EPR.

As a result, ECP with smaller crystallite size (lower melting temperature, lower crystallinity) shows better affinity to EPR and makes the morphology inside the elastomeric phase more uniform.

Effect of ECP Crystal on Scratch Resistance and Tensile Elongation

The effect of ECP crystallite size on the scratch resistance of PP/EPR/ECP ternary blend was examined. The relationship between ECP crystallite size and the scratch depth H is shown in Figure 8. It is obvious that scratch resistance is improved by adding the ECP crystal to the elastomer and that its effect varies with the crystallite size. The scratch resistance is highly improved by addition of a small crystal, but the effect is reduced gradually with increasing crystal size.

As described in the Experimental section, scratch depth H was directly measured by the surface roughness tester. On the other hand, H can be calculated from eq. (1) under given d_{max} and P_s . The relationship between the measured H and the calculated H is shown in Figure 9. A good agreement is seen between them. This fact means that the

Table III Structure of ECP Crystal in Elastomer Phase

Exp. No.	T_c (°C)	T_m (°C)	ΔH_f (J/g)	X_c (%)	d (nm)
EPR	29.0	68.0	29.3	10.0	2.00
B1	44.7	68.2	46.3	15.8	3.02
B2	102.0	120.0	46.9	16.0	3.64
B3	103.0	123.0	58.6	20.0	4.32
B4	114.0	130.0	95.2	32.5	8.46

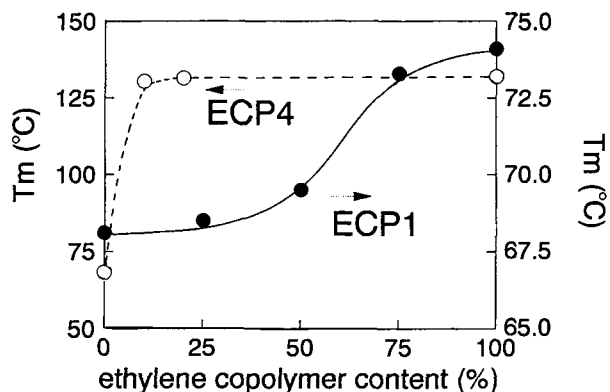


Figure 7 Dependence of T_m on the composition of EPR/ECP blends.

mechanism of the scratch resistance improvement can be investigated by analyzing the two independent parameters d_{max} and P_s .

Figure 10 shows the relationship between ECP crystallite size and d_{max} . It is found that d_{max} of PP/EPR blends is reduced by adding the ECP crystal, but the effect of its size on d_{max} is negligible.

Figure 11 shows the relationship between crystallite size and P_s . Contrary to d_{max} , P_s strongly depends on the size. P_s first increases with increased size, and decreases above 3.0 nm.

From the above result, it is concluded that the change in the scratch resistance of PP/EPR blends is not dominated by the change of d_{max} but by that of P_s . If the size of an added PE crystal is larger than a certain value, it does not work to improve

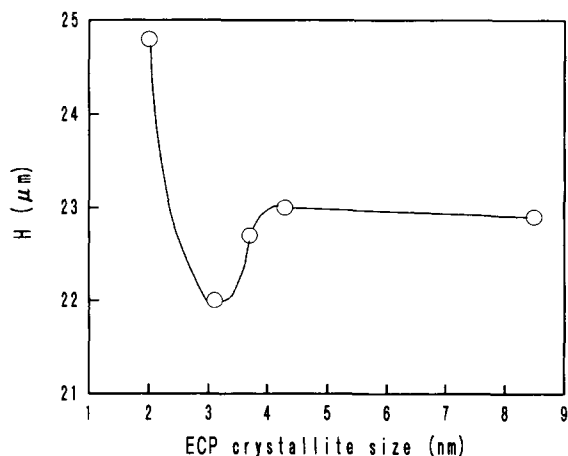


Figure 8 Relationship between ECP crystallite size and scratch depth H .

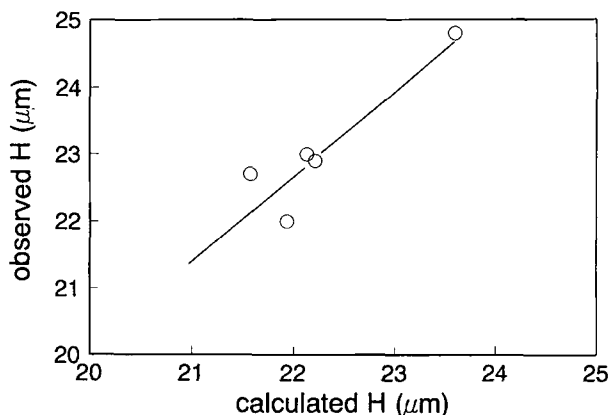


Figure 9 Comparison of calculated H with observed H for PP/EPR/ECP ternary blends.

the fracture property of the material and it deteriorates the scratch resistance.

A relationship between the tensile elongation (E_b) and the crystallite size of added copolymer is shown in Figure 12. Similar to P_s , E_b increases with the addition of small crystal, but it gradually decreases above 3.0 nm.

Origin of Improved Mechanical Properties of Ternary Blends

From DSC and TEM analysis, it was found that ECP with a small crystal had good affinity to EPR and was finely dispersed in EPR phase. On the con-

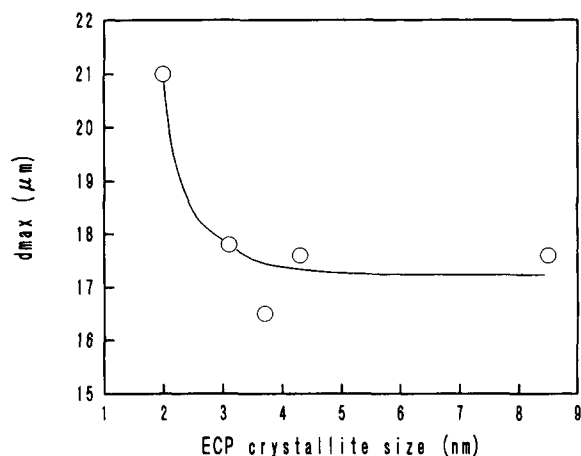


Figure 10 Effect of ECP crystallite size on d_{max} for PP/EPR/ECP ternary blends.

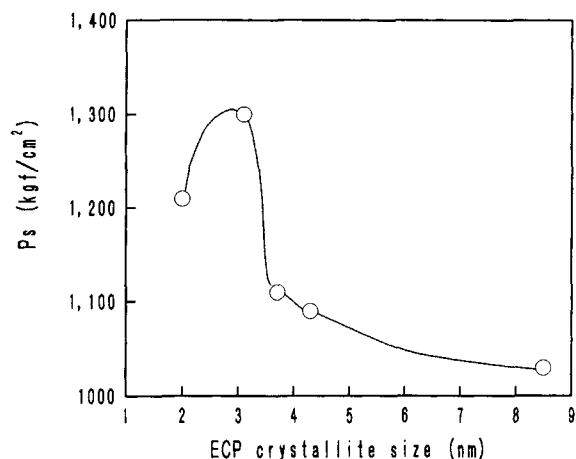


Figure 11 Effect of ECP crystallite size on P_g for PP/EPR/ECP ternary blends.

trary, ECP with a large crystal had poor affinity to EPR and its dispersion in EPR was worse. The overall morphology, such as the shape and average size of the elastomeric phase, was not changed by the crystallite size of added ECP. Therefore the overall morphology cannot explain the difference of the mechanical properties of the blends.

The fracture behavior of the blends was strongly affected by the size of an added crystal. A small crystal made blends more ductile, while a large one made them brittle.

The above results suggest that a small crystal acts as a crosslinking point in EPR phase and reinforces the EPR phase. A network structure formed by these

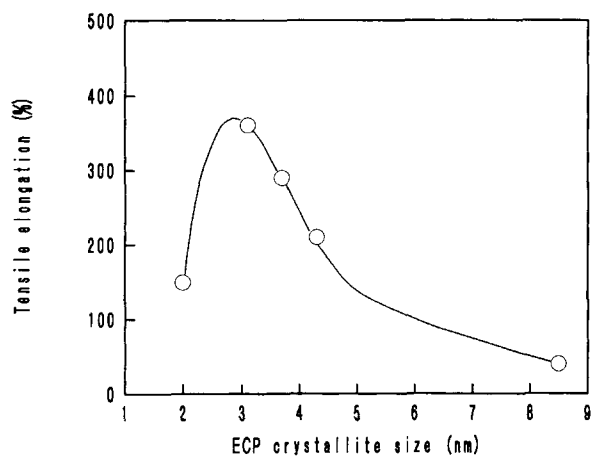


Figure 12 Effect of ECP crystallite size on tensile elongation at break for PP/EPR/ECP ternary blends.

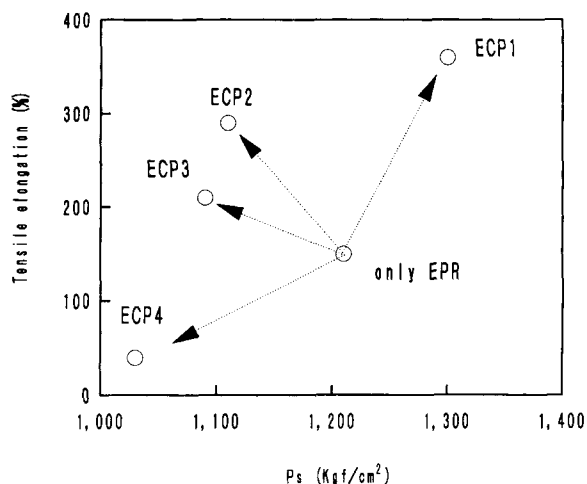


Figure 13 Balance of P_g and E_b of PP/EPR/ECP ternary blends.

crosslinking points is the possible reason for the improvement in the mechanical properties of the blends. As shown in Table III, the original EPR itself contains a small crystal but its crystallinity might be too low to form an effective network structure. By adding ECP, the crystallinity of the elastomeric phase increases and the effectiveness of these crosslinking points is increased; thus the toughness of the blend is improved. If the crystallite size of the added ECP is further increased, the average crystallinity of the elastomeric phase is increased. In the meantime, the affinity of ECP and EPR becomes worse and eventually they tend to segregate each other. As a result, the microstructure becomes as if a rigid filler is put into the elastomeric phase. The large crystal therefore, is considered to act only as a fracture initiator which induces a microcracking or void formation. Consequently a small PE crystal would make PP/EPR blends more ductile, while the large one would make them more brittle.

The scratch resistance/tensile elongation balance of PP/EPR/ethylene copolymer blends is shown in Figure 13. It is obvious that these properties are strongly affected by contained crystallite size. Among these blends, the one with the smallest crystal shows the best property. When a large crystal is contained, either the scratch resistance or the tensile elongation becomes inferior to PP/EPR binary blends.

It is desirable to control the microstructure of the elastomeric phase so that enough of the crosslink point (i.e., small crystal) is dispersed finely and uniformly in the elastomeric phase.

CONCLUSIONS

It was confirmed that the mechanical properties of PP/EPR blends can be improved by adding small crystal to the elastomeric phase. Its effect on the mechanical property was attributed to the formation of a quasi-crosslink structure. It was found that the affinity of crystalline ethylene copolymer and EPR are important in inducing that structure. By applying the above results, the possibility of material design of PP-based polymer blends can be further expanded.

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