

PP–Elastomer–Filler Hybrids. I. Processing, Microstructure, and Mechanical Properties

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SYNOPSIS

Three-component systems with a polypropylene (PP) matrix consisting of polar elastomer (ethylene–propylene rubber and styrene–ethylene–butylene–styrene grafted with maleic anhydride) or of polar PP (PP grafted with maleic anhydride) and filler were investigated. Three microstructures of PP–elastomer–filler hybrids were obtained by processing control and elastomer or PP modification with the maleic anhydride: fillers and rubber particles were separated in the PP matrix, rubber particles with filler core were distributed in the PP matrix, and mixed microstructures of the first and second. A study of mechanical properties showed that the elastic modulus increased in the first microstructure and impact strength increased in the second microstructure. Mechanisms for the relationships between microstructure, processing, and mechanical properties are discussed. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

One of the most successful outcomes of polymer blends is the low temperature impact improvement of polypropylene (PP) using an elastomer, such as ethylene–propylene (EP) copolymer and styrene–ethylene–butylene–styrene (SEBS) copolymer. However, these elastomers decrease the stiffness of PP significantly. To compensate for this effect of the elastomer, various fillers, such as calcium carbonate, talc, or mica were added to the blends. By the correct addition of elastomer and filler it is possible to obtain a variety of materials with targeted and optimal performance for the specific requirements of different applications. In the three-component PP–elastomer–filler systems, widely differing microstructure and consequently a wide range of properties have attracted increasing interest because of their scientific and commercial importance.

It is well known that the structure and properties of the three-component composites depends on component properties: the characteristics of each component, miscibility, and processing conditions.

For three-component systems such as PP–elastomer–filler, mutual miscibility and adhesion of the components are the crucial factors influencing structure and properties. A designed microstructure can only be obtained by controlled processing conditions with well-controlled interfaces between the various components. Any modification changing this relationship will lead to a significant structure, and consequently, properties change. Figure 1 shows a schematic representation of three microstructures for three-component thermoplastics/elastomer/filler systems: **a** is a separated microstructure where elastomer particles and filler are separated in the polymer matrix, **b** is a core–shell microstructure where elastomer particles with filler core are distributed in the matrix, and **c** is a microstructure of mixed **a** and **b**.

It is seen from Figure 1 that the distribution of filler is the key factor affecting microstructure. Matonis¹ and Matonis and Small² suggested an encapsulation structure to improve both stiffness and toughness. They considered however that such a material would be difficult to obtain in actual practice because very thin layers of elastomer with good adhesion between the components were required. In most of the previous systems the distribution of

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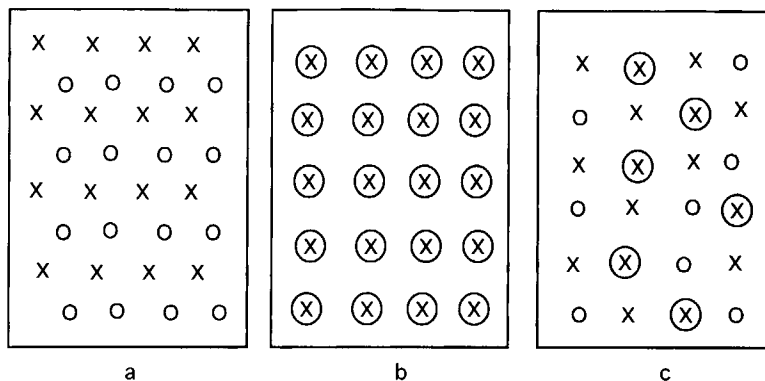


Figure 1 Schematic representation of (X) three microstructures of fillers, and (O) rubber particles in PP matrix: **a**, fillers and rubber particles are separated in PP matrix; **b**, rubber particles with filler core are distributed in PP matrix; and **c**, mixed microstructures of **a** and **b**.

filler was random. There was not a specific attraction for the filler. For example, in the polyvinyl chloride-chlorinated polyethylene-CaCO₃(PVC-CPE-CaCO₃) system, all three components are polar materials, and there are similar surface energies between CaCO₃-PVC and CaCO₃-CPE. During processing the chances of PVC or CPE adsorbing onto CaCO₃ are similar. In the PP-EP-talc system, the adsorption onto talc has no particular preference because both PP and EP are nonpolar materials. This means that controlling processing conditions, such as mixing one polymer with the talc first or blending PP with EP first, to produce a certain microstructure has limitations.

The technique for producing an interlayer on graphite or glass fiber through use of electrostatic forces has been widely reported.³⁻⁵ Peiffer showed that the best impact properties under low temperature⁴ were obtained with an interlayer thickness of approximately 0.2 μm . Kim et al.⁶ observed the effect of the viscosity of the polymer on the morphologies of PP/rubber/CaCO₃ composites.

Recently, various polar functional groups, such as maleic anhydride or acrylic acid, were grafted onto a polymer matrix or elastomer to improve the miscibility and adhesion between polymer and filler, or between polymer matrix and elastomer. For examples, EP or SEBS grafted with maleic anhydride were used to improve the interface with polar polymers, such as polyamide^{7,8}; PP grafted with maleic anhydride or acrylic acid was used to enhance the adhesion between PP and filler.⁹⁻¹¹ More recently, Jancar and Dibenedetto¹² reported ternary composites of PP/EP/filler containing 30 vol % of fillers

[CaCO₃ and Mg(OH)₂]. The effect of elastomer fractions up to 20 vol % on morphology and mechanical properties were reported. The results of Jancar and Dibenedetto showed that both modulus and impact strength with a separation structure were higher than with an encapsulation structure.¹²

In this work various microstructures of three-component PP-elastomer-filler systems containing 15 wt % of talc and different particle sized CaCO₃ were produced by control of processing conditions and use of maleic anhydride grafted PP (MA PP) or elastomer (MA elastomer). Results for the three-component systems of PP-EP (or SEBS-filler) are reported in this article. Mechanical properties of various composites with different microstructures were investigated. The mechanisms of the relationships between the mechanical properties and microstructure are discussed.

EXPERIMENTAL

Materials

The base materials, both polymers and fillers, used in this study are commercially available. Tables I and II list the main characteristics of polymers and fillers. Each material was sourced from the same batch.

Processing and Specimen Preparation

Various components were mixed then extruded with a Haake twin screw extruder (diameter 42 mm, di-

Table I Characteristics of Polymer Materials

Materials	Trade Name	Source	Modification	MFI
PP	LYM-120	ICI		13
MAH-PP	Microlink	Fidene	Grafted MAH (2 wt %)	
EP-1	VM 22	Exxon		11
EP-2	VM 42E	Exxon		2
EP-3	Exxlor-PE805	Exxon		1
MAH-EP-1	Exxlor-PE808	Exxon	Grafted MAH (1.14 wt %)	
MAH-EP-2	Exxlor-1803	Exxon	Grafted MAH (1.14 wt %)	
SEBS-1	Kraton-1652	Shell		
MAH-SEBS-1	Kraton-1901	Shell	Grafted MAH (1.84 wt %)	

ameter : length = 1 : 7) operated at 200°C at 60 rpm. To obtain the designed microstructures two techniques were used: processing control and polymer modification. Table III lists the microstructures controlled by processing and polymer modification. However, to study the effect of processing and polymer modification on the microstructures separately, specimens with different microstructures were also prepared by only one of the techniques.

The test specimens were molded using a Johns-600 injection molding machine with mold temperature of 40°C.

Morphological Characteristics

Undistorted and smooth surfaces were obtained using an ultramicrotome at low temperature with glass knives. The operation conditions were knife angle 48°, knife temperature -130°C, sample temperature -130°C, and sample cross section $\sim 1 \times 1$ mm. The cut surfaces were etched using xylene in a thermostated ultrasonic bath at 20°C for 10 min. The surfaces were examined using a JEOL JSM-840A SEM after coating with gold-palladium alloy. To avoid distortion of the surface the coating was applied for 10 s, then paused for 10 s, then the coating was repeated to a total of 100 s.

Testing of Mechanical Properties

Testing of Impact Strength

The injection-molded bars were notched according to ASTM D-256, using a milling machine. The notch

had an included angle of 45°, a tip radius of 0.25 mm, and a notch depth of 2.5 mm. A Davenport Impact Tester was used for these measurements. Width of the injection-molded specimens was 6 mm. The impact strength, reported in joules/meter of notch, was measured at 23°C.

Testing of Tensile Properties

The specimens were injection molded according to ASTM D-638 (width of narrow section 10 mm, thickness 4 mm, gauge length 80 mm). Tensile tests were performed in accordance with this method on a Lloyd 200 apparatus using a crosshead speed of 50 mm/min. The tests were carried at $20 \pm 2^\circ\text{C}$. All data were recorded and processed using a computer with Lloyd Instruments Software (V. 2.01).

All test bars were left at room temperature (22°C) for 48 h before mechanical testing was performed.

RESULTS AND DISCUSSION

Processing and Microstructure

Various microstructures were obtained by controlling processing conditions and polymer surface modification. Detailed conditions are listed in Table III. To produce materials with separated microstructure, PP grafted with maleic anhydride was used to improve the interface between PP matrix and filler. PP with MAH-PP and talc were extruded first, then mixed PP/MAH-PP/talc was extruded

Table II Characteristics of Fillers

Materials	Trade Name	Source	Particle Size (μm)	Density
Talc	TALC TX	Commercial Minerals	~ 10	2.65
CaCO ₃ -1	OMYACARB1T	OMYA	~ 1.7	2.7
CaCO ₃ -2	O/LITE 95T	OMYA	~ 1	2.7

Table III Microstructure Controlled by Materials and Processing

Microstructure	Materials	Processing
Separated: E and filler are separated	PP/m-PP/E/filler	PP/m-PP/filler were extruded first, then (PP/m-PP/filler)/E are extruded
Core-shell: filler in E particles	PP/m-E/filler	m-E/filler were extruded first, then (m-E/filler)/PP are extruded
Mixed: mixed a and b	PP/m-E/filler or PP/m-PP/R/filler	PP/m-E/filler or PP/m-PP/R/filler were extruded

E, elastomer; m, grafted maleic anhydride.

with EP or SEBS elastomer. This was used to enhance the separation of elastomer particles and filler. Similarly, elastomer grafted with maleic anhydride and two sequential extrusions were used to produce a core-shell structure. It could not be expected that the microstructure of these composites would be exactly separated or core-shell. However, the sequential technique was shown by SEM to successfully provide materials with different microstructures. Further improvement of the interfacial adhesion between polymer and filler can be achieved by surface treatment of the filler. Details of this technique will be discussed in a separate article.

The difference between separated and core-shell microstructure can be observed from cut and etched surfaces. Figure 2 shows the surface cut by a microtome under -130°C and then etched by xylene. Figure 2(a) shows the micrograph of a separated microstructure. It is seen that talc (brighter sheets) and elastomer (dark holes) are separated in the PP matrix. The shape of the elastomer in the separated microstructure is considered to be spherical particles, which is similar to PP-elastomer binary blends. Figure 2(b) shows a micrograph of core-shell microstructure. The core-shell microstructure contains talc particles, and the elastomer is concentrated at

the interface between the PP matrix and talc. When the elastomer was removed most of the talc was also lost from the surface and appeared as dark holes with random shapes. Some isolated talc surrounded by elastomer can still be observed in the core-shell microstructure. Detailed study of morphologies will be discussed in a separate article.

Mechanical Properties

Mechanical properties are significantly different for different composites, especially for different elastomers. To emphasize the effect of microstructure on the mechanical properties, the mechanical properties of different microstructures reported here are relative values compared with mixed microstructures. For example, the moduli of PP/EP-1/talc are separated microstructure 724 MPa, core-shell microstructure 528 MPa, and mixed microstructure 574 MPa. The relative modulus of the separated microstructure is 1.26 and the core-shell microstructure is 0.92.

Effect of Microstructure on Mechanical Properties

Table IV lists the tensile properties of the various three-component blends at room temperature. The

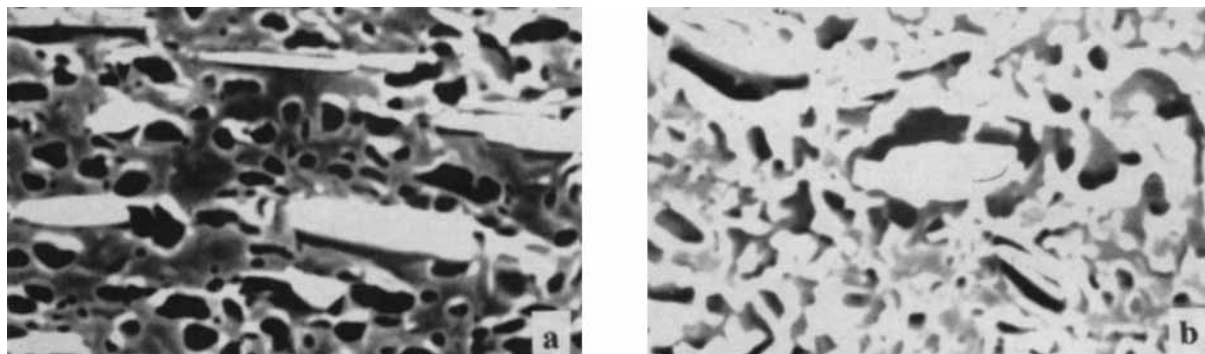


Figure 2 SEM of cut and etched surfaces of different microstructure: **a**, separated microstructure; **b**, core-shell microstructure.

Table IV Relative Tensile Properties of Various Composites with Different Microstructures Compared with Mixed Microstructure

Elastomer	Yield Stress		Modulus		Elongation	
	a	b	a	b	a	b
EP-1	1.02	0.98	1.26	0.92	0.96	1.23
EP-2	1.03	1.00	1.12	0.94	0.97	1.13
EP-3	1.03	0.98	1.07	0.96	—	—
MAH-EP-1	1.02	0.98	1.21	0.96	0.87	1.26
MAH-EP-2	1.08	0.96	1.24	0.93	0.92	1.21
SEBS-1	1.02	0.99	1.14	0.96	—	—
MAH-SEBS-2	1.03	0.97	1.17	0.95	0.91	1.19

All the samples were prepared from a PP/elastomer/talc blend of 60/25/15.

effect of different elastomers on the mechanical properties will not be discussed here. This investigation will focus on the effect of microstructure on mechanical properties.

Elastic Modulus. The elastic modulus of the separation microstructure was clearly higher than that of the core-shell microstructure. The effect of microstructures on the modulus can be explained by the Kerner-Nielsen equations for M , any modulus^{13,14}:

$$M = M_1 \left(\frac{1 + ABV}{1 - B\psi V} \right) \quad (1a)$$

in which

$$A = k_E - 1 \quad (1b)$$

$$B = \frac{M_2/M_1 + 1}{M_2/M_1 - A} \quad (1c)$$

where M , M_1 , and M_2 are moduli of the composite, matrix, and additional component, respectively; V is the fractional component volume; k_E is the Einstein coefficient; and ψ is a factor that depends upon the maximum packing fraction of the filler. The equation can be used directly to estimate the elastic modulus of the three-component system with a separate microstructure:

$$M_c = M_e \left(\frac{1 + A'B'V_f}{1 - B'\psi V_f} \right) \quad (2a)$$

or

$$M_c = M_f \left(\frac{1 + A''B''V_e}{1 - B''\psi V_e} \right) \quad (2b)$$

where M_c , M_e , and M_f are modulus of ternary composite, elastomer and filler, respectively; V_e and V_f are volume fraction of elastomer and filler, respectively; and A' , A'' , B' , and B'' are calculated according to eqs. (1b) and (1c), respectively.

The modulus of the core-shell structure is complicated because of its geometry. Matonis¹ and Matonis and Small² considered that if the elastomer layer was thicker than a certain amount ($R_{\text{filler}}/R_{\text{particle}} < 0.96$), the core-shell inclusion acted principally as an elastomer inclusion with the volume extended by the rigid core. This will result in decreasing the modulus by addition of core-shell particles. However, the decrease of modulus by the core-shell particles compared with pure elastomer was not observed in any experimental work. At the same elastomer content, the modulus of PP/elastomer/filler ternary composite was always lower than that of PP/elastomer binary blends (see Fig. 3). Similar results were reported previously for other ternary systems.^{15,16} Equation (2) provides a useful framework for estimating the elastic modulus but has some well-recognized limitations. The elastic modulus of the core-shell structure cannot be simply predicted by eq. (2), in which V_f was decreased because the filler was covered by elastomer, but M_e must be increased because the elastomer was filled with rigid filler.

Yield Stress. The yield strength was slightly higher for the separated microstructure. Shear yielding in semicrystalline polymers takes place through slip, twinning, and martensitic transformation.¹⁷ The yield behavior of the matrix is affected by an addi-

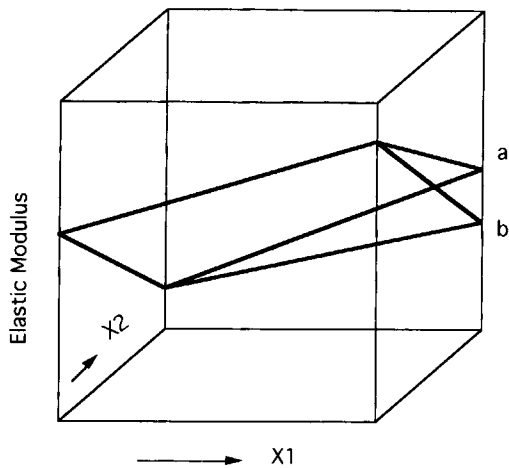


Figure 3 Surface diagram for elastic modulus of PP/elastomer/filler composites. Dependence of modulus on (X_1) filler and (X_2) elastomer concentration and microstructures (**a**, separation; **b**, core-shell).

tional component through influencing its viscoelastic nature. In the general case the effect of additional component on yield strength is similar to that on the modulus that is increased by rigid particles and decreased by elastomer. Our experimental results show that different microstructures seemed to not affect yield strength as much as modulus.

Elongation. Elongation of core-shell microstructure was clearly higher than that of the separated structure. It is well known that the effect of filler and elastomer on the elongation are usually opposite: in most cases, fillers decrease elongation at the yield stress and elastomer increases elongation. There are many examples of increased ultimate elongation

when small amounts of rigid filler (about 5%) are used.¹⁸ In the case of higher filler concentrations, the matrix is restricted in its ability to provide strength between packed particles, and the particles that do not wet and bond well to the matrix cause cavitation. Smaller particles at low concentration are freer to move with the matrix and correspondingly, the matrix is freer to provide strength around them. The viscous drag of small particles with good adhesion to the matrix can then produce an apparent strength improvement and greater tenacity, resulting in higher ultimate elongation. Clearly the materials shown here contain a large amount of filler (15 wt %). Because elongation is one dimension of volume it will vary as the cube root of volume fraction, c , according to an approximation,

$$\epsilon_c = \epsilon_m(1 - c^{1/3}) \tag{3}$$

where ϵ_c and ϵ_m are elongation of the composite and matrix, respectively.

In the core-shell structure the filler was covered by the elastomer and the interface between the filler and polymer (elastomer) was improved. The core-shell particles behave partly like rubber particles. The volume fraction, c , in eq. (3) is expected to be reduced, which will result in an increase in the elongation of the core-shell structure.

Impact Strength. Figure 4 shows the impact strength of the various three-component blends at room temperature (23°C). For a certain formulation, impact strength of core-shell microstructures was always higher than that of microstructure **a**. An important point that should be noted is that through

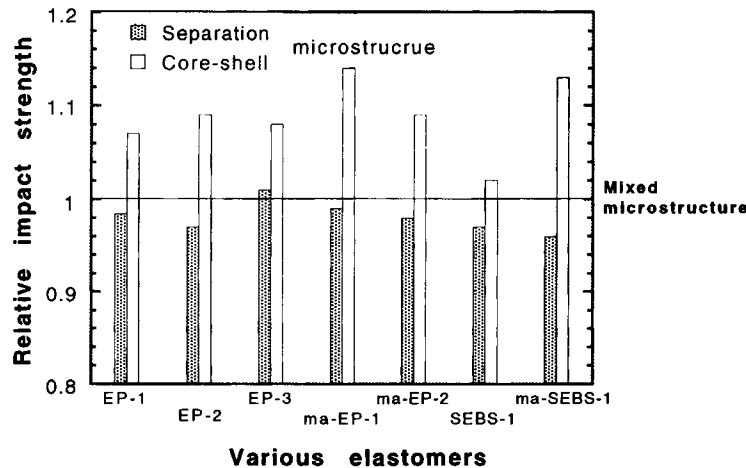


Figure 4 Relative impact strength of different microstructures with various elastomers. All of the samples were prepared from a PP/elastomer/talc blend of 60/25/15.

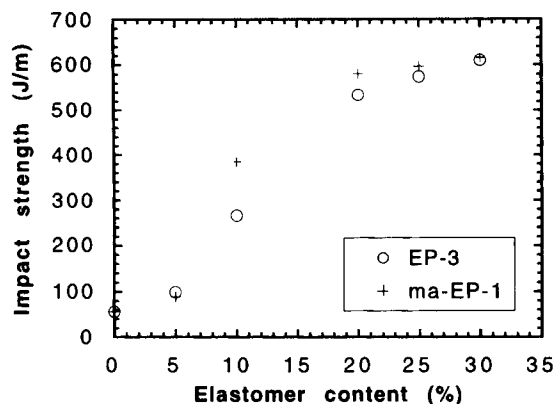


Figure 5 Effect of elastomer content on the impact strength in PP/elastomer binary blends. Both with mixed microstructure c.

the polymer surface modification the difference in mechanical properties between separated or core-shell microstructure is increased.

Brittle-Tough Transition

Figure 5 shows the effect of elastomer on the impact strength of binary blends. Both modified and unmodified elastomer increased impact strength significantly and a brittle-tough transition was observed at about 20 wt % of elastomer. The brittle-tough transition was reported widely and explained by the percolation theory.¹⁸ Modified elastomer only affected impact strength during the transition but did not affect the impact strength before and after the transition.

Figure 6 shows the effect of different microstructures and elastomer content on the impact strength in the PP/elastomer/filler hybrids with 15 wt % talc. It is seen that modified elastomer has higher impact strength than that without modified elastomer, and the core-shell elastomer microstructure always has higher impact strength than the separation microstructure. Comparison of Figures 5 and 6 shows that the toughness improvement with modified elastomer is through increased interfacial adhesion between the elastomer and filler. This is expected because the elastomer modified with maleic anhydride cannot be expected to improve the interface between the PP and elastomer.

In light of the above results, we propose a model to simulate the deformation behavior in the PP/elastomer/filler systems. Figure 7 illustrates a morphological model of microstructure and fracture of PP/elastomer/filler composites. When the elastomer and rigid filler particles are separated in the PP matrix [see Fig. 7(a)], the filler particles tend to produce

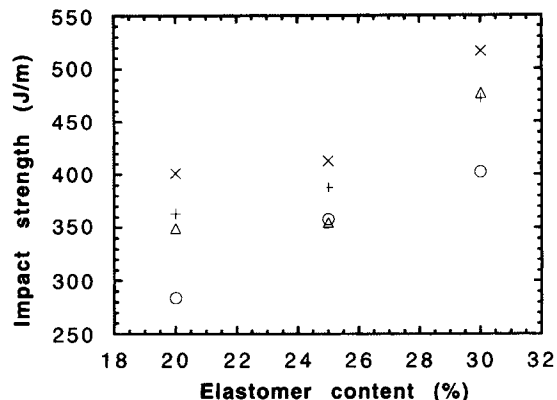


Figure 6 Effect of different microstructures and elastomer content on the impact strength in the system with 15 wt % talc. (×) MAH-EP-1 with core-shell microstructure, (+) MAH-EP-1 with separation microstructure, (Δ) EP-3 with core-shell microstructure, and (○) EP-3 with separation microstructure).

a range of microcracks caused as impact is applied, especially under lower temperatures. Although elastomer particles can stop crack propagation, they will not be fully effective. If the rigid filler particles are covered by elastomer and form a core-shell structure [see Fig. 7(b)], the original microcracks initiated at the filler particles will be prevented and a yielded zone around the elastomer particle, with filler core, will be formed. In this cases the elastomer can be fully effective.

Furthermore, the effect of elastomer on the toughness of PP depends upon the distance between the particles.¹⁹⁻²¹ The filler in the elastomer is expected to decrease the distance between the elastomer particles and make the elastomer more efficient. So far an increase in impact strength by elas-

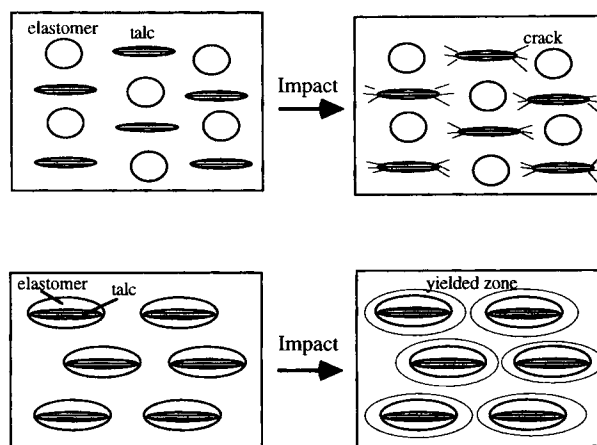


Figure 7 Morphological model of microstructures and fracture of PP/elastomer/filler composites.

Table V Relative Mechanical Properties of Various Microstructures with Different Particle Size of CaCO₃ Compared with Mixed Microstructure

Materials	Microstructure	Modulus	Impact Strength
PP/EP-3/CaCO ₃ -1	a	1.09	0.98
	b	0.97	1.14
PP/EP-3/CaCO ₃ -2	a	1.10	0.99
	b	0.97	1.09
PP/MAH-EP-1/CaCO ₃ -1	a	1.11	0.98
	b	0.98	1.13
PP/MAH-EP-1/CaCO ₃ -2	a	1.08	0.98
	b	0.97	1.13

All the samples were prepared from a PP/elastomer/CaCO₃ blend of 60/25/15.

tomer particles with rigid filler core (in hydride) compared with only the pure elastomer particles (in binary blend) was not observed. The probable explanations are that not all the filler was covered by the elastomer or the elastomer particles with rigid core were not as efficient as pure elastomer particles. Results of the various effects are that impact strength with core-shell microstructure is higher than that with separated microstructure, but still lower than that with only pure elastomer particles.

The mechanisms for increased toughness by different particles can also help to understand the mechanism of toughening by elastomer particles with filler core. The mechanisms for the increased toughness by rubbery particles and rigid particles are different.^{22,23} The elastomer particles greatly enhance the extent of plastic shear deformations in the polymer matrix at the crack tip due to interactions between the stress field ahead of the crack and the rubbery particles.²⁴⁻²⁷ This mechanism may lead to an increase in the fracture energy of one to two orders of magnitude. In the case of rigid particle-filled polymer the main mechanism for increased toughness is crack pinning.^{28,29} The particles act as obstacles that pin the crack and so cause the crack front to divert between the particles. This increase in the linear energy of the crack front is analogous to the line-tension effect in dislocation pinning in metals. Rigid particle fillers typically only increase the value of fracture energy by a factor of two to five. Furthermore, increased toughness by rigid particles has to meet the conditions of small particle size and the number is less than the number of particles that can be fully packed into a matrix. So it is expected that the method of improving microstructure can increase impact strength more than that of simply improving adhesion between polymer matrix and filler.

Effect of Different Particle Sized CaCO₃

Table V gives relative mechanical properties of various microstructures with different particle size CaCO₃. Similar results were found in the PP/elastomer/CaCO₃ systems as in the PP/elastomer/talc systems: separation microstructure increased modulus while core-shell microstructure increased impact strength. However, mechanical properties of different particle size CaCO₃ did not show any significant difference. Examination of the morphologies by SEM also did not reveal any significant difference. The effect of different particles (core) on the mechanical properties will be studied in detail in a future article.

CONCLUSION

The control of microstructure reported in this work promises a breakthrough in the general balance of mechanical properties of PP/elastomer/filler systems. The actual balance of toughness and stiffness of the PP/elastomer/filler ternary composites cannot yet be predicted because of their complex structure involving phase distribution and interfaces. However, the present research led us to develop a model to understand the relationship between processing, microstructure, and mechanical properties. Figures 3 and 8 show the schematic representation of the effect of microstructure on the elastic modulus and impact properties, respectively. In the three-component system, PP/rubber/filler, different microstructures were obtained by controlling processing conditions and polymer surface modification. Separated microstructure increased modulus and core-shell microstructure increased impact strength.

By the correct control of microstructure it is possible to obtain a variety of materials with targeted

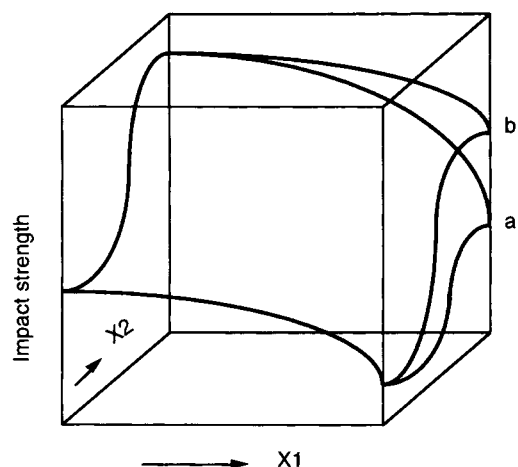


Figure 8 Surface diagram for impact strength of PP/elastomer/filler composites. Dependence of impact strength on (X_1) filler and (X_2) elastomer concentration and microstructures (a separation, b core shell).

and optimal performance for the specific requirements of different applications. For example, it is well known that the influence of rubber on toughness and rheological behavior is contradictory. For a certain formulation with separated microstructure the toughness is expected to increase without affecting flow behavior. Furthermore, the balance between stiffness and toughness is between a cheap filler and an expensive rubber. For a specific hybrid, the cost will be reduced by reducing the content of rubber while retaining the same toughness.

Another advantage of including the polar-group maleic anhydride includes improvement in surface behavior, which is very important in adhesion. Furthermore, it was observed that the elastomer particles in a thermoplastic matrix tend to coarsen because of the difference in surface tensions.^{30,31} Stability of the elastomer particles is expected to increase with a filler core that has good adhesion with the modified elastomer.

The three-component PP/elastomer/filler systems using different particle size CaCO_3 as filler showed similar results.

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