Toughening and Reinforcing Polypropylene with Core–Shell Structured Fillers

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ABSTRACT: An elastomer/rigid particle filler with core–shell structure was prepared by twin-screw extruder according to an encapulation model. It was used to toughen and reinforce polypropylene (PP). An original idea of a one-step processing method was adopted in creating PP/polyoctene–ethylene/talc ternary composites. The rheological behavior of PP was changed and the mechanical properties were improved. SEM observation showed that the core–shell structured filler dispersed better in copolypropylene than in homopolypropylene. Two reasons were proposed and proved by the rheology test and SEM observation. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 2397–2403, 1999

Key words: toughening; core–shell structure; polypropylene; composites; filler filled

INTRODUCTION

Recently, rigid particle fillers have been extensively used in creating polymer composites with high strength, high modulus, and low shrinkage.[1,2] However, decreased toughness generally results for the composite.[3] On the other hand, elastomers are generally employed in increasing polymer toughness, but they result in deteriorated stiffness.[4–10] Two-phase composites exhibit only a partial improvement over the matrix material alone, because some selected properties are enhanced at the expense of others. To solve this problem, some nonpolar polyolefin thermoplastics (matrix)/elastomer/filler systems have been investigated.[11–24] But the possible presence of matrix–filler, matrix–rubber, and rubber–filler interfaces in the ternary composites results in a complexity of phase structure[25] and a corresponding variation of the composite properties. According to the theoretical analysis of Matonis and Small,[26] it is doubtful that a mixture of a separately dispersed phase of filler and elastomer, which exhibits two different and distinct responses to the applied load (or deformation), could result in a composite with desirable properties. On the contrary, the encapsulation method is suggested. The proposed model by Matonis and Small[26] is a polyblend of spherical high modulus inclusions encapsulated within a uniform layer of low modulus elastomer and dispersed throughout a suitable matrix. This hypothetical three-phase ordered composite will permit the design of a new material that is stiffer and tougher than the matrix alone. The contribution of the rigid-phase inclusion to the soft-phase shell is to transmit the load from the matrix to the inclusion, which further depends on the interfacial adhesion of the matrix–elastomer and elastomer–filler.

In our earlier work, a kaolin toughened polypropylene (PP) composite,[27] a carbon black filled polyethylene composite,[28] and a PP/ethylene–PP–diene monomer rubber/talc ternary composite[29] were obtained based on the encapsulation model as shown in Figure 1. For all composites, an elastic interlayer that had good interfacial ad-
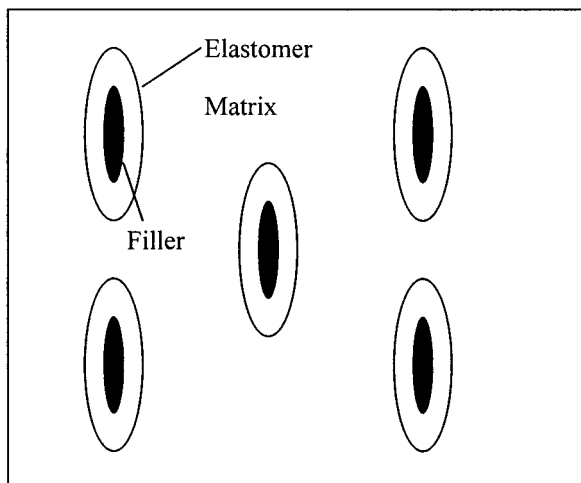
Figure 1 Schematic representation of encapsulation model.

hesion with the inorganic particle was inserted between the filler and matrix.

Based on our earlier works and theoretical analysis, we propose a method to create a core-shell structured filler in advance and then use this filler to toughen and reinforce PP. According to this idea, a talcum powder core/elastomer shell structured filler was prepared using the reactive extrusion technique. The ternary composite was prepared by a twin-screw extruder in our two-step processing method. For the convenience of processing, we proposed an original one-step processing method. Using this method the ternary composite was prepared with an injection modeling machine while it was shaped into the product. It is very convenient and economical for processing because it cuts down on one processing step and the cost.

EXPERIMENTAL

Materials

The polymers used were copolypropylene [PP1340, Yanshan Petro. & Chem. Co, melt flow index

(MFI) 1.06 g/10 min] and homopolypropylene (PP2401, Yanshan Petro. & Chem. Co., MFI 2.45). The inorganic filler used was talcum powder. The elastomer used as the elastic layer around the talcum powder was polyoctene-ethylene (POE). A series of POEs of different MFI values of 0.5, 3.5, 7.7, and 10 were used.

Preparation of Composites

The core–shell structured filler was created from POE (20 wt %), talcum powder (80 wt %), and other additives. The additives we used were dispersants that assure an excellent adhesion between the talc and POE. Directly blended PP/POE/talc without additives was prepared to it compare with core–shell structured filler filled PP. A one-step and a two-step process were adopted to prepare the ternary PP/POE/talc composites. All were extruded and granulated on a Brabender twin-screw extruder (35 mm Φ) at 30 rpm. The barrel temperatures were 180–200°C.

Mechanical Property Testing

The tensile strengths and flexural modulus of the composites were measured on an Instron 1122 at a crosshead rate of 50 and 2 mm/min, respectively. The Izod impact strengths were measured on an XJ-40A impact tester.

Rheology Characterization

The rheological behavior of the ternary composites, PP, and the core–shell structured fillers under different processing methods were characterized by a HAKKE90. The melt temperatures were 180, 190, and 200°C, respectively. Specimens were taken from the mixer at 1, 2, 4, 6, 8, and 10 min.

SEM Observation

The impact fractured surfaces of the composites from different procedures during blending were characterized by a Hitachi S-530 scanning electron microscope.

Table I Mechanical Properties of PP/POE/Filler Ternary Composites with Two Types of Dispersed Phases

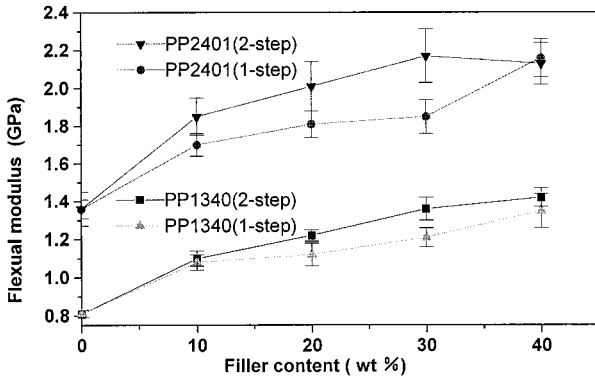|	Directly Blended	Core–Shell Structured Filler
Izod impact strength (J/m)	155 ± 10	222 ± 10
Flexural modulus (GPa)	2.45 ± 0.05	1.64 ± 0.04

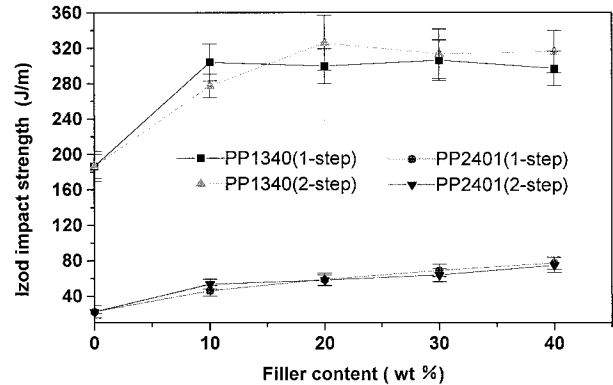**Figure 2** Flexural modulus versus filler content for PP/POE/talc composites.

Figure 3 Izod impact strength versus filler content for PP/POE/talc composites.

RESULTS AND DISCUSSION

Mechanical Properties

Two types of dispersed phases might form when rubber and inorganic filler are blended with a polymer: dispersed rubber and filler or a filler-core/rubber-shell structure. The first type of the dispersed phase was created by directly blending the rubber and filler with PP, while the second type was created when core–shell structured filler was dispersed in the matrix. The mechanical properties of PP/rubber/filler ternary composites largely depend on the morphology of the rubber and filler. Table I shows mechanical properties of ternary composite with these two types of dispersed phases. The notched Izod impact strength of the core–shell structured filler filled PP was greater that of directly blended PP/POE/talc composites. In the flexural modulus the opposite was true. This result coincided with Jancar's theoretical calculation of the modulus of PP/rubber/filler composites.[30] He found that the highest modulus of material corresponded to dispersed phases, and the lowest modulus was corresponded to the core–shell structured phase. The key factor for toughening PP is that the interfacial layer around the talc changes the stress distribution of the matrix near the filler. Due to the redistribution of inner stress, the matrix yield became the dominant damage mechanism. Meanwhile, the core–shell structured filler can initiate the appearance of crazes and stop the development of crazes, which results in a large amount of absorption of the impact energy.

The mechanical properties of the PP/POE/talc ternary composites using the one-step and two-step processes are shown in Figures 2–4. From

the figures one can see that the impact strengths and flexural moduli of the composites were notably enhanced by filling the matrix with core–shell structured fillers. A marked decrease is also observed for the tensile strengths and flexural strengths. The properties as a whole were increased as in our earlier work. We can also see that the tensile strengths and impact strengths of the composites are almost identical with no correspondence with the process we adopted. The values of the flexural moduli of the composites using the two-step process are greater than those of the one-step process. It can be concluded that the dispersion effects of the core–shell structured fillers are better in the two-step process than in the one-step process. This difference is more notable for the composite with a homopolypropylene matrix because of the better compatibility of POE and homopolypropylene.

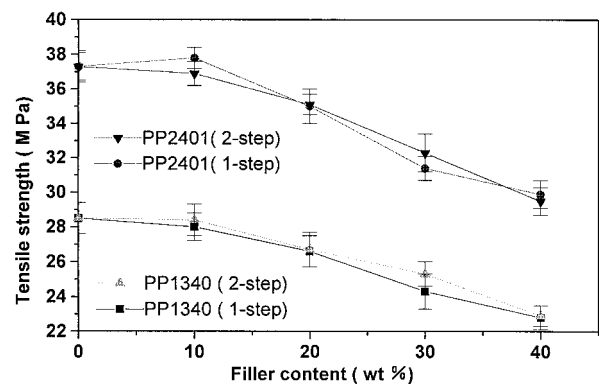Four kinds of POEs with different MFIs (0.5, 3.5, 7.7, and 10) were used to compare the effect of

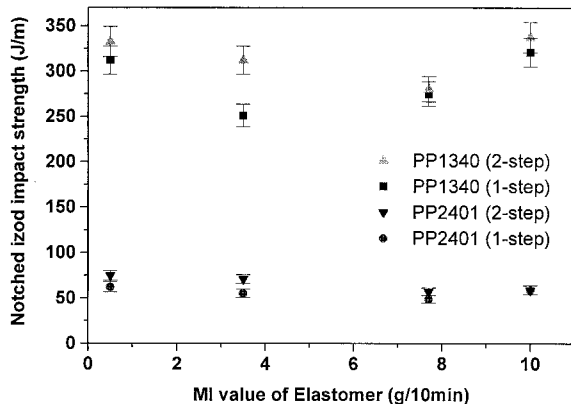**Figure 4** Tensile strength versus filler content for PP/POE/talc composites.

Figure 5   Izod impact strength versus melt flow index value of elastomer for PP/POE/talc composites (40 wt %).

Figure 7   Flexual modulus versus melt flow index value of elastomer for PP/POE/talc composites (40 wt %).

the viscosity of the elastomer on the properties of the PP/POE/talc composites. The results are shown in Figures 5–7. The elastomer MFIs affected the flexural modulus of the ternary composites for copolypropylene and the flexural moduli for copolypropylene and homopropylene. The results showed a trend that the greater the elastomer's MFI the higher the flexural moduli of the composites. This is because the elastomer with the higher MFI dispersed better in the PP matrix, so that assured the dispersal effect of the core–shell structured filler. In addition, the higher the MFI of the elastomer the less the difference of the flexural moduli, especially for copolypropylene. The flexural moduli were almost identical because the elastomer MFI was 10. In the copolypropylene matrix the Izod impact
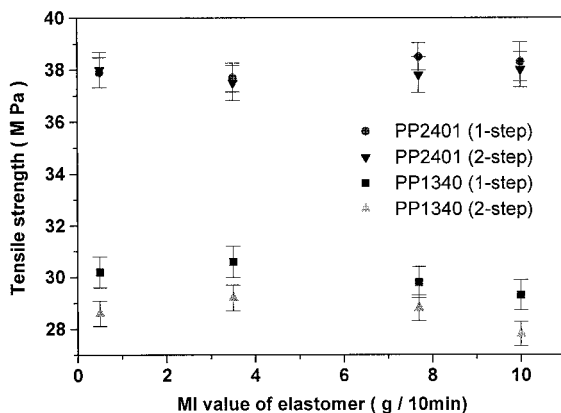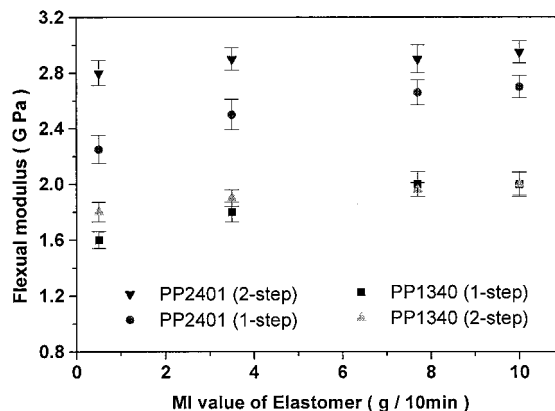
strength was higher for elastomer MFIs of 3.5 and 7.7, but lower for elastomer MFIs of 0.5 and 10. But the elastomer's MFI did not affect the Izod impact strength of homopolypropylene so notably. The reasons are not clear. However, it may have something to do with the following factors: the thickness of the elastic layer, the phase structure of the filler, and the dispersion effect of the filler.

Rheology Characterization

The rheological behavior of PP, core–shell structured fillers, and PP/POE/talc ternary composites are characterized by the curves plotted in Figures 6 and 7. Note that the torque of the ternary composite is between those of PP and the core–shell structured filler. This indicates that the core–shell structured filler can reduce the melting viscosity of PP, while commonly used inorganic fill-
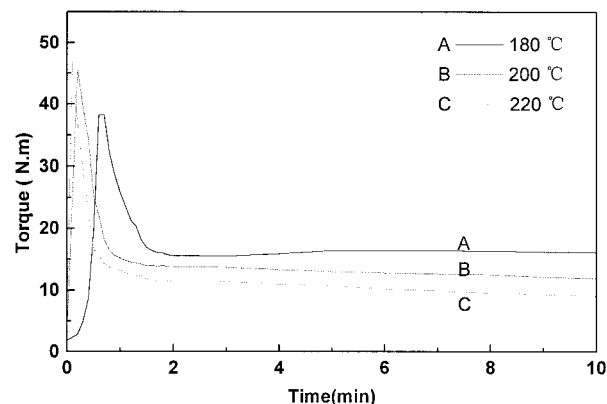

Figure 6   Tensile strength versus melt flow index value of elastomer for PP/POE/talc composites (40 wt %).

Figure 8   Torque versus time for filler filled copolypropylene at different temperatures (40 wt %).
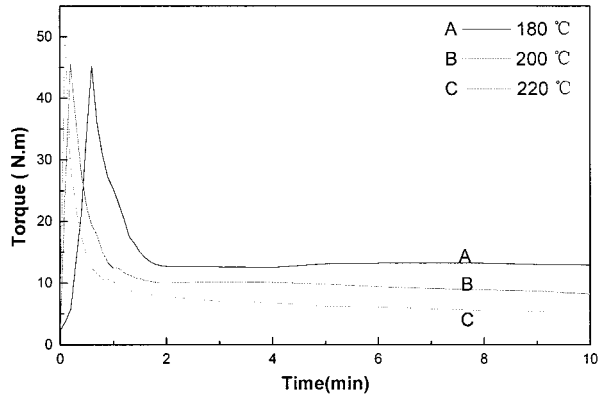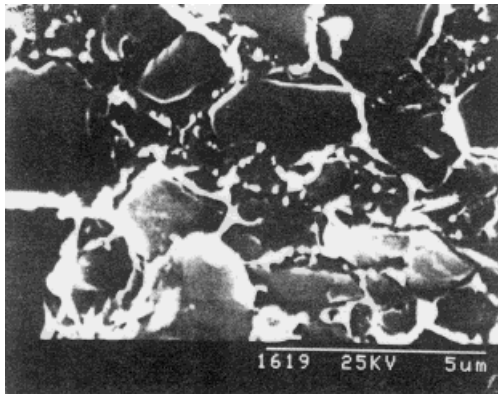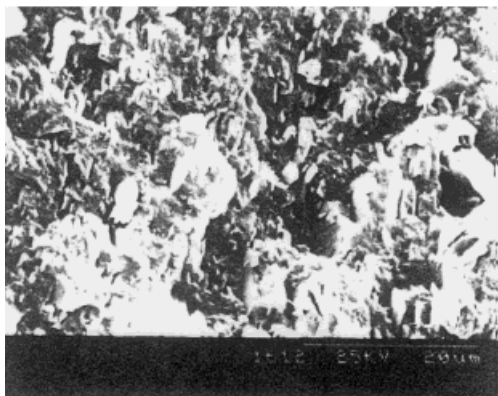
Figure 9 Torque versus time for filler filled homopolypropylene at different temperatures (40 wt %).

ers always enhance the melting viscosity of the matrix. This is because the elastic layer around the talcum powder prevents the direct contagion
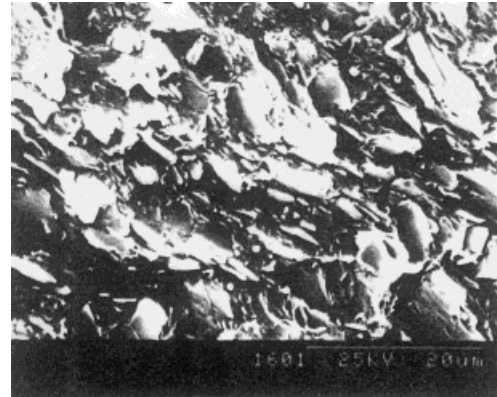

(a)

(b)

Figure 10 SEM photographs of fractured surfaces of homopolypropylene (a) blended 1 min and (b) blended 10 min.

(a)

(b)

Figure 11 SEM photographs of fractured surfaces of comopolypropylene (a) blended 1 min and (b) blended 10 min.
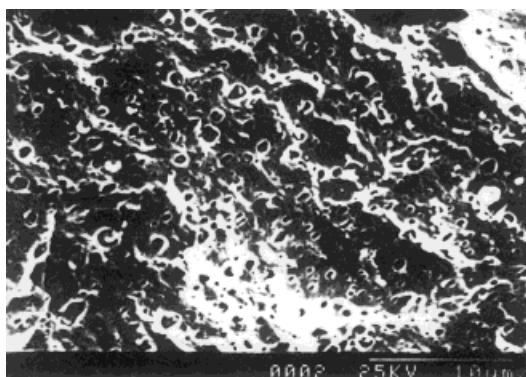
of the talcum powder and the matrix. It can also be seen that the melting viscosity of copolypropylene is greater than that of homopolypropylene. So the viscosity ratio of copolypropylene versus filler is greater than that of homopolypropylene versus filler, which results in a greater dispersion rate of the filler in the matrix copolypropylene. Another phenomena is that the peaks of these curves locate between 0 and 1 min, which means that the dispersal process happens primarily during the first minute. This result is encouraging because it makes one-step processing possible because the shearing effect of the ejector is complete in nearly 1 min.

Figures 8 and 9 show the rheological behavior of the ternary composites at different temperatures. The higher the processing temperature, the lower the composite's torque. Meanwhile, the peaks of the curves appear earlier at a higher
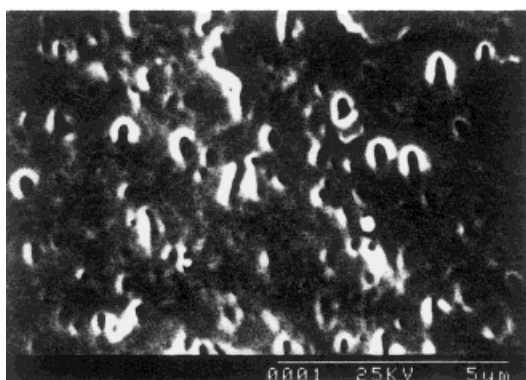
temperature, indicating that the filler disperses more quickly at a higher processing temperature.

Dispersion of Core–Shell Structured Filler

SEM photographs of the impact fracture surface of PP/POE/talc composites are shown in Figures 10 and 11. The dispersion rate of the core–shell structured filler is greater in copolypropylene than in homopolypropylene. This is proved by the rheological characterization test mentioned above. The other reason is that POE is more compatible with copolypropylene than with homopolypropylene, which is proved in the SEM photograph in Figure 12. From these two SEM photographs it can be seen that the diameter of the POE phase is much smaller and more even in the copolypropylene matrix. It is the ethylene chain segment in the copolypropylene and POE that assure the compatibility of the matrix and

Table II   Dispersion Degree of Core–Shell Structured Filler in Matrix

MFI of POE (g/10 min)	PP1340 Matrix		PP2401 Matrix	
	Two Step	One Step	Two Step	One Step
0.5	++	+	++	—
3.5	++	+	++	—
7.7	++	++	++	—
10	++	++	++	—

(++) Well dispersed, (+) even, (—) uneven.

POE rubber. A further experiment in the one-step process indicated that because of these two factors the core–shell structured filler dispersed better in copolypropylene than in homopolypropylene, and the difference could be clearly seen from the surface observation of specimens as is shown in Table II. From the SEM photographs in Figures 10 and 11 the morphology development of the filler in the matrix is obvious. During the first minute the filler is dispersed well in the copolypropylene but not well in the homopolypropylene. To solve this problem in the one-step process, we adopted some methods to enhance the compatibility of the filler and homopropylene. It seems that adding some homopolypropylene when preparing the core–shell structured filler is the best way to improve the compatibility of the filler and matrix, and the effect was satisfactory. Although the flexural modulus was deteriorated slightly, the filler dispersed much better.

(a)

(b)

Figure 12   SEM photographs of fractured surfaces of PP/POE etched with *n*-heptane: (a) homopolypropylene matrix and (b) copolypropylene matrix.

CONCLUSIONS

A core (talcum powder)–shell (POE rubber) structured filler was successfully prepared based on our early works and the encapsulation model.

Using this filler, a ternary PP/POE/talc composite with high toughness and high modulus was created. A one-step process was proposed to prepare the ternary composite and it showed little difference compared to the two-step process.

Rheology characterization and SEM observation indicated that there were two reasons that lead to the different dispersion rates of the filler in homopolypropylene and copolypropylene.

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