

EFFECT OF PROCESSING METHOD ON THE IMPACT STRENGTH OF POM/TPU/CaCO₃ TERNARY COMPOSITES*

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Abstract Polyoxymethylene (POM)/elastomer/filler ternary composites were prepared, in which thermoplastic polyurethane (TPU) and inorganic filler, namely, CaCO₃, were used to achieve balanced mechanical properties of POM. The dispersion and phase morphology of POM/elastomer/filler composites were found to depend largely on processing method, CaCO₃ content in masterbatch and the filler size. Two processing methods were employed to prepare POM/elastomer/filler ternary composites. One is called the one-step method, in which elastomer and the filler directly melt blended with POM matrix. The other is called the two-step method, in which the elastomer and the filler were mixed to get masterbatch first, which was then melt blended with pure POM of different content. The effect of phase morphology and processing method on impact strength was investigated. It was found that the two-step method results in an increase in impact strength but not for the one-step method. Additionally, the impact strength of POM ternary composites decreases with the increase in the size of CaCO₃ particles.

Keywords: POM/TPU/CaCO₃ composites; Core-shell structure; Impact strength.

INTRODUCTION

Polymer blending or compounding receives increasing interests because it is a relatively easy way to obtain new materials with balanced properties. Generally, an elastomer is used to improve the toughness on sacrifices of the modulus of polymers. Addition of inorganic filler can enhance the stiffness but results in a decrease in toughness. To overcome the drawback resulted by only adding an elastomer or filler, a lot of work has been done on polymer/elastomer/filler ternary system, in which both the elastomer and the filler were used to enhance the toughness and stiffness simultaneously^[1–10]. To achieve the best combination of mechanical properties, the key strategy is to control the dispersion and phase morphology of ternary composites. Concerning the phase morphology of polymer matrix that contains both the elastomer and the filler, there are at least four possible kinds of dispersions, namely, a separated microstructure, a core-shell microstructure, a filler separated together with a core-shell microstructure, and an elastomer separated together with a core-shell microstructure, as shown schematically in Fig. 1. Separated and core-shell microstructures are two morphologies very commonly observed in ternary composites^[11, 12]. Arguments exist on whether separated dispersion or the core-shell microstructure is favorable to toughening. Matonis *et al.*^[1, 2] concluded that the core-shell structure is beneficial to the increase in toughness, and the thinner the elastomer, the stronger is the adhesion between the filler and matrix, and the higher is the toughness. However, it was shown by Yu Long *et al.*^[12] that the modulus can be increased in a condition of separated dispersion while the toughness can be improved in the core-shell microstructure. There are several factors, such as, the composition, processing conditions, adhesion between the filler and the elastomer may affect

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the dispersion and microstructure^[3–10]. Most of these works on toughening mechanism are qualitative in fact and the quantitative relationship between morphology and property has not been established yet so far.

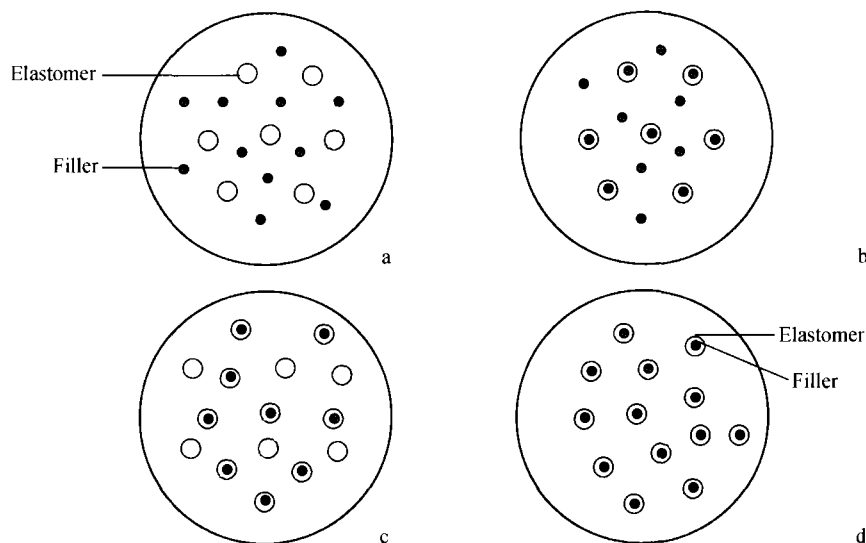


Fig. 1 Schematic diagram of dispersion of elastomer and filler in matrix
a) Separated microstructure; b) Filler separated and core-shell microstructure;
c) Elastomer separated and core-shell microstructure; d) Core-shell microstructure

Polyoxymethylene (POM) is an engineering plastic with good properties, while the low impact toughness, sensitivity to notch and low heat-resistance limit its application. Traditionally, POM is blended with the elastomer to improve the toughness while makes sacrifice on other properties, such as rigidity, modulus *etc.* Inorganic fillers were also used to increase the toughness of POM, yet no remarkable toughness was obtained and even the decomposition of POM caused by inorganic filler was reported^[13]. In order to obtain high performance POM with balanced toughness and modulus, in this work, both the elastomer (TPU) and the filler (nano- CaCO_3) were blended together with POM. By changing the processing method, the ratio of the elastomer to the filler, different phase morphologies were obtained. The effect of phase morphology on the impact strength of obtained POM ternary composites was investigated.

EXPERIMENTAL

Material

The materials used for the preparation of the POM/TPU/ CaCO_3 composites are listed in Table 1. All CaCO_3 were first treated with stearic acid.

Table 1. The physical parameters of raw materials given by the manufacturers

Materials	Density (g/cm^3)	MI (g/10 min)	Diameter (μm)	Brands and manufacturers
POM (M90)	1.40	9.0	—	Yuntian Chemical, Yunnan
TPU	1.20	6.0–12.0	—	Chenguang Chemical Institute, Chengdu
CaCO_3 1	2.70	—	0.08, Particle	Hakuenka DD, Shiraishi kogyo kaisha, LTD.
CaCO_3 2	2.70	—	0.14, Particle	Hakuenka TDD, Shiraishi kogyo kaisha, LTD.
CaCO_3 3	2.70	—	1.0, Particle	Pd-40, Daheng Chemical, Shanghai

Note: All CaCO_3 was treated by stearic acid.

Sample Preparation

Two processing methods were employed to prepare POM/elastomer/filler ternary composites. One is called the one-step method, in which the elastomer and the filler directly were melt blended with POM matrix. The other is called the two-step method, in which the elastomer and the filler were mixed to get masterbatch first, then the

masterbatch was melt blended with pure POM in different content. The blending was conducted in a two-screw extruder at 150–190°C, and injection molding with PS40E5ASE (Japan) at 175–195°C was used to obtain standard specimen for mechanical property tests.

Impact Strength Measurement

The notched impact strength was used to evaluate the toughness of samples. The notched specimens were tested with an I200XJU-2.75 impact tester at room temperature. The impact test for each specimen was repeated at least five times and the results were averaged.

Scanning Electron Microscopy (SEM) Experiments

The morphology of the blends was studied by preferential etching of TPU phase in THF for 2 h. The samples were fractured in the direction perpendicular to flow direction in liquid nitrogen before etching. The etched and cyno-fractured samples were observed with a JEOL JSM-5900LV SEM instrument, using an acceleration voltage of 20 kV, which can show the dispersion of the elastomer and the filler in POM matrix.

RESULTS AND DISCUSSIONS

Processing Method versus Microstructure and Impact Strength

In order to control the dispersion and microstructure of TPU and the filler in POM matrix, two processing methods, namely one-step processing and two-step processing, were used. One expects a separated dispersion of TPU and the filler in POM for one-step processing but a core-shell morphology with the filler covered by TPU for two-step processing. Figure 2 shows the surface of POM/TPU/CaCO₃ ternary composites fractured by liquid nitrogen and etched by THF for 2 h. For one step processing (Fig. 2a), CaCO₃ (brighter particles) and TPU (dark holes) are separately dispersed in the POM matrix. The shape of TPU is spherical and its size is about 0.2–0.4 μm. One also observes the aggregates of CaCO₃ particles with a size of 0.4–0.6 μm. For two-step processing (Fig. 2b), a much better dispersion of CaCO₃ particles with a size of 0.3–0.5 μm is seen. One can not observe much TPU particles in this case. It is most likely that the core-shell microstructure with CaCO₃ particles as the core and TPU as the shell is obtained. This result indicates that one-step processing results mainly in a separated microstructure and two-step processing results mainly in much better dispersion both for TPU and CaCO₃ particles.

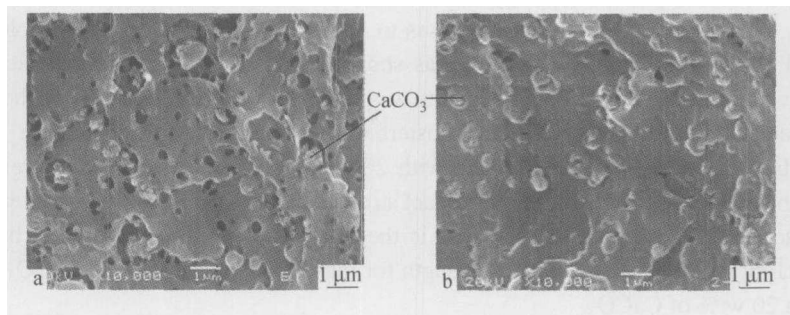


Fig. 2 SEM micrographs of cyno-fractured and etched surface of POM/TPU/CaCO₃ composites

a) One-step processing; b) Two-step processing

The CaCO₃ particle used is 80 nm.

Figure 3 shows the impact strength of POM/TPU/CaCO₃ composites as a function of total content of TPU and CaCO₃ for the two processing methods. The Izod notched impact strength of POM ternary composites prepared by one-step processing method is found to hold constant as a function of TPU and CaCO₃ total content (TPU:CaCO₃ = 80:20 by weight). However, it increases obviously in POM ternary composites prepared by two-step processing method. For example, at total content of 15 wt%, an impact strength of 24 kJ/m² is obtained for two-step prepared composite but only 9 kJ/m² for one-step prepared composite. So in our system, a good dispersion favors the toughness, while the separated microstructure gives no help to impact strength. This result

indicates that the contribution of the elastomer to the impact strength will be cancelled in the presence of rigid filler, if it is dispersed separately in POM matrix. This can be understood as the exposed filler will act as stress concentration, which leads the sample to be fractured in a brittle behavior. However, once the filler is covered by the elastomer with a good dispersion, the stress concentration caused by the filler will be greatly reduced, resulting in a ductile behavior.

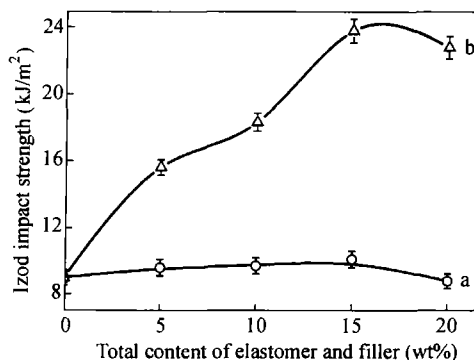


Fig. 3 Izod impact strength of POM/TPU/nano- CaCO_3 ternary composites as an influence of processing method (TPU: CaCO_3 = 80:20)

a) One-step; b) Two-step processing

The CaCO_3 particle used is 80 nm.

Effect of CaCO_3 Content in the Masterbatch on Phase Morphology and Impact Strength

The dispersion and morphology of POM ternary composites can be controlled not only by the processing method but also by the content of the filler in the masterbatch. Figure 4 shows the cyano-fractured and etched surface of POM/TPU/ CaCO_3 ternary composites with different masterbatch composition. It can be seen from these pictures that three kinds of phase morphology are revealed by changing the CaCO_3 content in the masterbatch. When the content of the filler is low (10 wt%), there exists excess TPU which form a phase dispersed in POM, as shown in Fig. 4(a). As the CaCO_3 content increases to 20 wt% in the masterbatch, the content of TPU and CaCO_3 is matchable. One observes mainly a morphology without separated TPU particles (not shown in Fig. 4, but the same as in Fig. 2b). When the CaCO_3 content increases to 30 wt%, one observes a morphology of some fillers which are separated and without covered by TPU, as shown in Fig. 4(b). The Izod impact strength of POM ternary composites with different phase morphologies was investigated and the result is shown in Fig. 5. It is found that the impact strength for all the three masterbatch increases with the increase in total amount of masterbatch, but in different ways. For masterbatch with 20 wt% of CaCO_3 , the impact strength is the highest. Even for masterbatch with 15 wt% of CaCO_3 , the impact strength reaches 24 kJ/m^2 . For masterbatch with 30 wt% of CaCO_3 , the impact strength increases slowly and is the lowest among the three masterbatches. The impact strength is only 16 kJ/m^2 at 30 wt%. The impact strength for masterbatch with 10 wt% CaCO_3 is similar with that for masterbatch with 20 wt% of CaCO_3 .

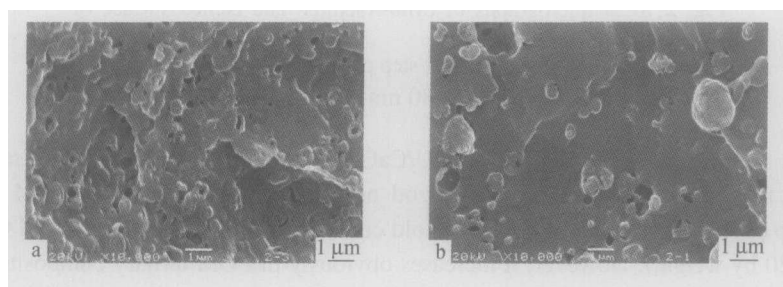


Fig. 4 SEM micrographs of cyano-fractured and etched surface of POM/TPU/ CaCO_3 composites as a function of filler content in masterbatch

TPU: CaCO_3 = a) 90:10; b) 75:25; The CaCO_3 particle used is 80 nm.

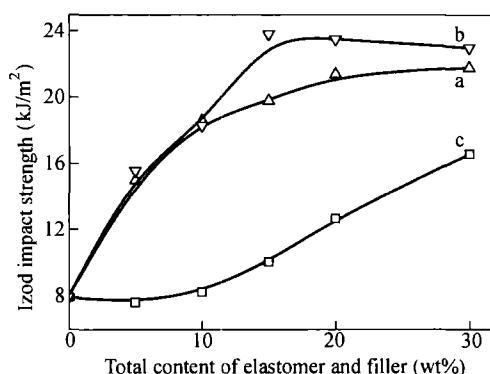


Fig. 5 Izod impact strength of POM/TPU/CaCO₃ ternary composites as a function of CaCO₃ content in masterbatch

TPU:CaCO₃ = a) 90:10; b) 80:20; c) 75:25

Effect of the Size of CaCO₃ on Phase Morphology and Impact Strength

Three kinds of CaCO₃ with different sizes were used to prepare the POM/TPU/CaCO₃ ternary composites by two-step processing method. The content of CaCO₃ in masterbatch was kept constant *i.e.*, 20 wt%. Figure 6 shows the cyano-fractured and etched surface of POM ternary composites with different filler sizes. One always observes a good dispersion for each size of CaCO₃. By increasing the filler size from 80 nm to 1 μm, the total particle size increases. Figure 7 shows the effect of the filler size on the impact strength. It can be found that notched Izod impact strength of POM ternary composites depends largely on the size of CaCO₃ particles. It decreases with the increase of the size of CaCO₃ particles. This result indicates that filler with bigger size cannot be used effectively as a toughening agent for POM.

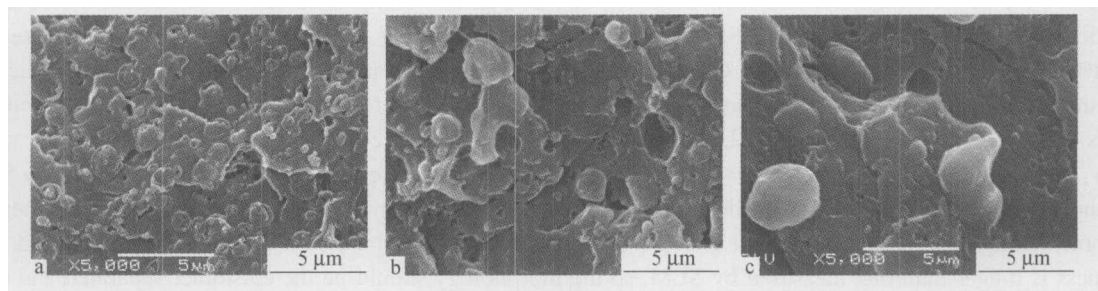


Fig. 6 SEM micrographs of POM/10% TPU/3% CaCO₃ with different filler size

a) 80 nm; b) 140 nm; c) 1 μm

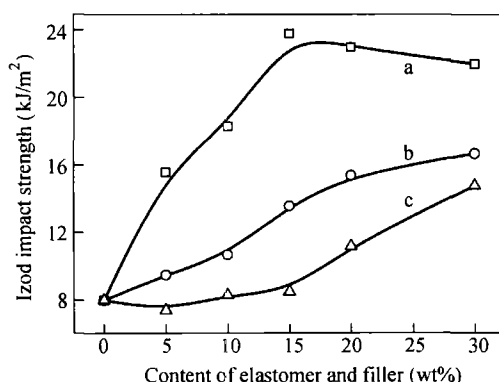


Fig. 7 Izod impact strength of POM/TPU/CaCO₃ ternary composites as a function of CaCO₃ size

a) 80 nm; b) 140 nm; c) 1 μm

Theoretical Calculation

One expects to obtain a core-shell microstructure with CaCO_3 particles covered by TPU elastomer *via* two-step method. Since the experimental observation is not clear-cut, we resort to theoretical calculation. As changing of the content of CaCO_3 in the masterbatch will also cause a change of shell thickness of core-shell particles, the size of CaCO_3 particles will play a role to determine the overall particle size of core-shell microstructure. Presumably, there is only the core-shell microstructure in the system and all the elastomers are used to surround all the fillers, and each core-shell is equal. The phase diameter of core-shell microstructure is shown in Fig. 8. The core diameter and shell thickness are calculated as follows:

$$\frac{(D + 2l)^3 - D^3}{D^3} = \frac{w_2 \rho_1}{w_1 \rho_2} \quad (1)$$

where, D is average diameter of CaCO_3 , l is the elastomer shell thickness, $D + 2l$ is the core-shell particle diameter, w_1 and w_2 are respectively the weight content of filler and elastomer, ρ_1 is the density of CaCO_3 , 2.7 g/cm^3 , and ρ_2 is the density of TPU, 1.2 g/cm^3 .

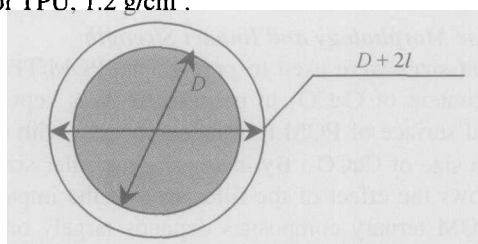


Fig. 8 Schematic diameter of core-shell microstructure

Thus, the particle diameter and shell thickness of POM ternary composites can be calculated by the above equation and compared directly with SEM measurement. This result is listed in Table 2. For composite with 10 wt% TPU and 3 wt% of 80 nm CaCO_3 , the calculated one and SEM measured one are very close, indicating core-shell microstructure is the only morphology in this system. While for the other composites, the calculated values deviate significantly from the SEM measured values. When the content of elastomer is relatively small, *e.g.* $w_1 = 3\%$, $w_2 = 5\%$ or $w_1 = 5\%$, $w_2 = 10\%$, the calculated core diameter is bigger than that measured by SEM, and the morphology should be the filler separated and core-shell microstructure. On the contrary, when the elastomer content is relatively large, *e.g.* $w_1 = 3\%$, $w_2 = 20\%$ or $w_1 = 2\%$, $w_2 = 10\%$, the calculated shell thickness is bigger than that measured by SEM, so the morphology should be the elastomer separated and core-shell with thick shell microstructure. In addition, the effect of core diameter is also listed in the Table 2. It is found that the core-shell particle diameter increases with the increase in filler size. These results are in good agreement with the SEM data.

Table 2. Particle diameter and shell thickness calculated by equation and directly measured by SEM pictures

Size of CaCO_3	w_1	w_2	$D + 2l$ (nm)	D^b (nm)	l^b (nm)	D^a (nm)	l^a (nm)
80 nm	3%	5%	400	260	70	200	90
	3%	10%	360	150	108	160	100
	3%	20%	600	160	280	160	180
	2%	10%	300	80	140	80	120
	5%	10%	750	520	114	300	200
140 nm	3%	10%	1000	550	225	400	120
1 μm	3%	10%	2500	1700	400	1000	80

w_1 : Content of filler; w_2 : Content of elastomer;

^a Directly measured by SEM; ^b Calculated by equation

CONCLUSION

In summary, the dispersion and phase morphologies of POM/elastomer/filler composites depend largely on the processing method, CaCO₃ content in masterbatch and the filler size. The POM ternary composite with good dispersion can be obtained by two-step processing while a separated dispersion of the elastomer and the filler in POM composites can be prepared by one-step processing. The former method results in an increase in impact strength, yet no enhancement of impact strength is seen for the latter method. The impact strength of POM ternary composites decreases with the increase in the size of CaCO₃ particles.

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