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PP/elastomer/calcium carbonate composites: effect of elastomer and calcium carbonate contents on the deformation and impact behavior

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The morphology and mechanical behavior of ternary polypropylene/ethylene-octene copolymer/calcium carbonate composites have been investigated as a function of elastomer and filler contents. A separate dispersion of phases was observed. Increasing concentration of EOC and $CaCO_3$ promotes a decrease of matrix ligament thickness between elastomer particles resulting in a huge increase of the toughness. The stiff filler used in this study provided the unusual additional benefit of substantially increasing in Young's and flexural modulus of the composites. © *2002 Kluwer Academic Publishers*

1. Introduction

Ternary polypropylene (PP) composites containing an elastomer to improve the toughness and a filler to increase stiffness are of increasing industrial and academic interest because balanced mechanical properties can be achieved. Numerous studies have been carried out on such and similar systems in preceding years [1–6]. Various elastomers and fillers have been used in ternary polypropylene composites. EPDM and EPR have been mostly used as elastomers. The fillers include calcium carbonate [7], talc [8], $BaSO_4$ [9], etc.

In PP/elastomer/filler composites, two types of phase structures can be formed: (1) elastomer and filler particles are separately dispersed in the PP matrix; (2) elastomer encapsulates filler particles forming core-shell inclusions. Kolarik and co-workers [10–11] carried out extensive investigations on the phase structure of PP/elastomer/filler systems. They found that surface treatment of filler resulted in a separate dispersion of phases, and encapsulation occurred when untreated filler was used. Incorporating grated PP with carboxyl groups accounts for a complete de-encapsulation and for a strong matrix-filler adhesion, whereas using functionalized elastomer resulted in a core-shell structure [12]. Although much effort has been put into the determination of phase structure-property correlations in multicomponent systems, contradictory results were reported. Matonis [13–14] suggested an encapsulation structure to improve both stiff and toughness. Scott *et al.* [15] carried out Izod impact tests combined with infrared analysis to determine the extent of embedding and its effect on impact resistance. Composites with a core-shell structure produced slightly increased impact strength and modulus. Kolarik and Jancar [11] studied the effect of functionalized components on phase structure and mechanical properties. They found composites with separately dispersed filler and elastomer achieved with the aid of filler surface treatment had higher tensile impact strength than composites with core-shell particles. In another study, the results showed that while stiffness of PP/EPR/$BaSO_4$ systems was basically determined by the extent of embedding, the correlation of toughness and structure is much more complex

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depending on numerous factors (adhesion, embedding, particle size, elastomer properties, etc.) [9].

The deformation and impact behaviour of PP-elastomer blends has been studied extensively [16–19]. However, the results do not help to explain the relationship between structure and impact toughness in such three-component systems. In this paper, ethylene-octene copolymer (EOC) and stearic acid treated calcium carbonate were chosen to obtain separate dispersion. The goal of the present study is to investigate the effect of elastomer and filler contents on the deformation and impact behaviour of ternary PP composites.

2. Experimental

2.1. Materials

The base material for the composites was a polypropylene homopolymer 1300 [melt flow rate (MFR) = 1.1 g/10 min] supplied by Yanshan Chemical. The elastomer used was a ethylene-octene copolymer (Engage 8180, Dupont-Dow Chemical) consisting of 28 wt% octene with a MFR of 0.5 g/10 min. The filler used was stearic acid treated calcium carbonate (Supercoat, Ecc International) with a median diameter 1 μm.

2.2. Specimen preparation

Altogether 22 composites and reference systems were investigated; their composition is complied in Table I. The composites were prepared in a co-rotating twin screw extruder with an L/D ratio of 32 and screw diameter of 25 mm (TSSJ-25/32, China). The extrusion conditions were 220°C and 180 rpm. The extrudates were pelletized and the resulting pellets of the composites were moulded in a Nissei PS40E5ASE machine into dump-bell-shaped tensile bars (GB1040 Type II specimens, $150 \times 10 \times 4$ mm^3) and rectangular bars ($150 \times 10 \times 4$ mm^3). Flexural test bars were sectioned from the center of the dumb-bell-shaped specimens (GB9341, $80 \times 10 \times 4$ mm^3). Impact tests were performed on the gate end of the rectangular bars (GB1843, $63.5 \times 10 \times 4$ mm^3). A single-edge 45° V-shaped notch (tip radius 0.25 mm, depth 2 mm) was milled in the bars.

TABLE I Composition of the investigated composites and reference compounds (wt%)

Abbreviation	PP1300	Engage 8180	$CaCO_3$ 1 μm
A1	95	5	–
A2	90	10	–
A3	85	15	–
A4	80	20	–
A5	75	25	–
A6	70	30	–
A7	60	40	–
B1	90	–	10
B2	80	–	20
B3	70	–	30
B4	60	–	40
C1	90	5	5
C2	85	5	10
C3	75	5	20
C4	65	5	30
C5	55	5	40
D1	85	10	5
D2	80	10	10
D3	75	10	15
D4	70	10	20
D5	60	10	30
D6	50	10	40

2.3. Mechanical properties

The tensile and flexural properties were studied at room temperature using a Shimadzu AG-10TA tensile tester. The tensile and flexural tests were performed at 50 mm/min and 2 mm/min crosshead speeds respectively. Notched Izod impact strength was determined at a rate of 3.5 m/s. The values of the mechanical properties were calculated as averages over measurements on at least five samples.

2.4. Scanning electron microscopy (SEM)

The phase structures of the composites were analyzed by a scanning electron microscope (X-650, Hitachi). The samples taken from the center of the injection-molded bars were cryo-fractured in liquid nitrogen. The fractured surfaces were etched by n-heptane at 50°C for 5 min in order to remove the elastomer particles from the composites. The SEM (JSM-5900LV, JEOL) was also used to study the morphology of deformation of the fracture surfaces of the Izod samples. The fracture surfaces were coated with gold and examined by SEM.

3. Results and discussion

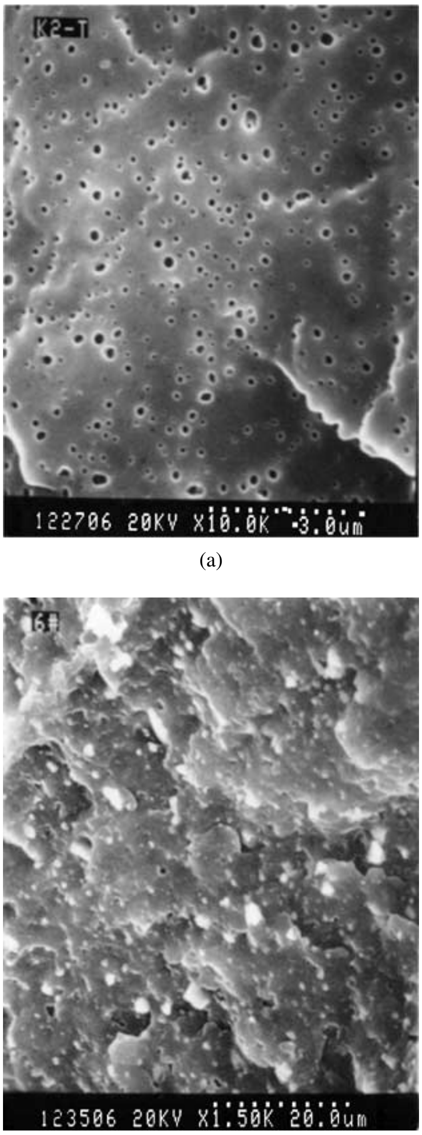
3.1. Morphology

SEM observations demonstrated that the PP/EOC blends investigated exhibit distinct phase separation of components (see Fig. 1a). PP constitutes a continuous matrix in which the elastomer inclusions are dispersed. The dispersion of elastomer particles is quite fine and uniform in size. The diameter of the elastomer inclusions was in the range of 0.1–0.5 μm. Fig. 1b shows that the dispersion of $CaCO_3$ particles with stearic acid treated surfaces was very good with concentration of 5–40 wt% (1.8–18.3 vol%) without aggregation of particles.

Fig. 2 revealed the microstructure of PP/EOC/$CaCO_3$ where EOC and $CaCO_3$ particles were dispersed separately in the PP matrix. Comparing 2a with 2b, an increase of EOC content in the composites did not change this structure, but increased the number density of dispersed EOC particles in the PP matrix. Similarly, the number density of EOC particles with increasing $CaCO_3$ content was found to become larger (comparing Fig. 2b with 2c and 2d).

3.2. Tensile and flexural properties

Table IIa shows the results of tensile and flexural tests on the series of PP modified with EOC and $CaCO_3$, respectively. The data demonstrated that the incorporation of elastomer into PP causes a decrease in the Young's modulus, yield stress, flexural modulus and flexural strength. Similarly, the yield stress is also reduced by $CaCO_3$, which is a result of poor interfacial adhesion between matrix and filler. Apparently surface



(a)

(b)

Figure 1 Cryogenic fractured and etched surfaces of binary systems. (a) A2 (90/10) and (b) B2 (80/20).

treatment with stearic acid does not improve adhesion but merely serves the purpose of random dispersal of particles. However, a substantial increase in the modulus and the flexural strength is achieved for iPP/$CaCO_3$. For instance, the composite with 20 wt% (7.7 vol%) $CaCO_3$ has an increase in Young's modulus by 37%, flexural strength by 17% and flexural modulus by 32%, relative to the unmodified iPP.

Analogous mechanical data obtained from iPP/EOC/$CaCO_3$ composites are presented in Table IIb. These data show that the effect of filler and elastomer on the yield stress is approximately additive, indicating that EOC and $CaCO_3$ contribute to the yield stress of iPP separately. This suggested that no interaction between EOC and $CaCO_3$ in the ternary systems agrees well with the SEM observations in which the phase structure of the ternary composites was of a separate dispersion. Comparing composites C and D, the modulus is decreased by rising elastomer content. However, increasing $CaCO_3$ content can improve the modulus of composites. Thus, the modulus of D6 and D7 remain still higher than that of the neat iPP.

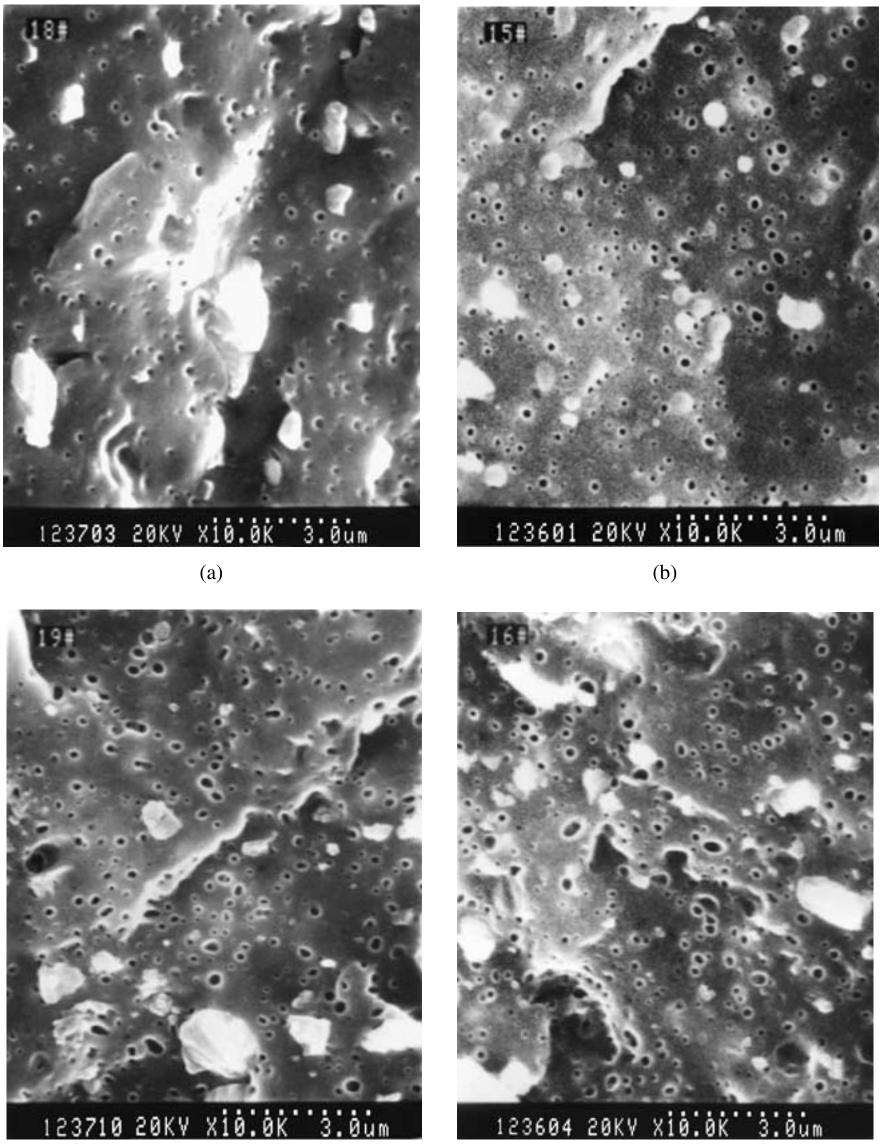
TABLE II The tensile and flexural properties of the investigated composites and reference compounds

Code	Young's modulus (MPa)	Yield stress (MPa)	Flexural modulus (MPa)	Flexural strength (MPa)
(a) Binary system				
iPP	1664	36.8	1660	44.1
A1	1484	32.7	1537	41.7
A2	1304	31.9	1407	39.2
A3	1154	28.1	1201	35.4
A4	1049	26.4	992	31.0
A5	840	24.4	856	28.3
A6	661	22.1	633	24.8
A7	338	17.7	328	18.4
B1	1898	34.8	1848	48.3
B2	2284	33.1	2185	51.8
B3	2521	30.6	2433	51.7
B4	2947	28.4	2748	50.9
(b) Ternary system				
C1	1628	30.8	1514	38.4
C2	1711	29.9	1601	40.5
C3	1823	28.0	1707	43.0
C4	2133	26.0	1974	43.2
C5	2400	23.3	2181	41.5
D1	1400	29.5	1418	37.2
D2	1460	28.0	1472	39.4
D3	1555	26.7	1510	39.8
D4	1611	25.9	1555	40.8
D5	1786	23.9	1683	39.6
D6	1989	21.7	1739	37.3

3.3. Toughness

Fig. 3 presents the notched Izod impact energies (I_s)at room temperature of PP/EOC/$CaCO_3$ composites as a function of the concentration of filler. Fig. 3 demonstrated that the values of I_s of composites C1-5 are in the same range or slightly lower than that of PP/EOC blend A1 with increasing $CaCO_3$. In contrast, an impressive jump of the Izod impact energy I_s for composites D1-6 was observed. It can be seen that when $CaCO_3$ concentration is low (D1), the resulting toughness of the modified polymer is no better than that of blend A2, which has the same weight fraction of EOC (10 wt%). However, there is an obvious transition in toughness from 40.9 kJ/m^2 (A2) to 63.5 kJ/m^2 (D3) when $CaCO_3$ concentration increases from 5 to 15 wt%. Further increase of filler concentration causes only slight improvement of the impact energy. For $CaCO_3$ concentration approaching 40 wt%, a slight decrease of impact energy develops.

Considering the large difference between EOC and $CaCO_3$ density, the weight fraction of compositions of the blends and composites systems were converted into the volume fraction to analyze the effect of EOC and $CaCO_3$ on the impact energy, respectively. Fig. 4 compares the impact energy of binary systems with the ternary systems as a function of total volume fraction of elastomer and filler. It can be observed that modification of PP with EOC or $CaCO_3$ leads to an improvement in toughness to different degrees. While modification with $CaCO_3$ particles into PP increases I_s by merely 110% compared to the neat PP, modification with EOC causes a huge increase of I_s by more than 800%. The same trend can be observed for two types of ternary



(a) (b)

(c) (d)

Figure 2 Cryogenic fractured and etched surfaces of ternary systems. (a) C3 (75/5/20), (b) D2 (80/10/10), (c) D4 (70/10/20) and (d) D5 (60/10/30).

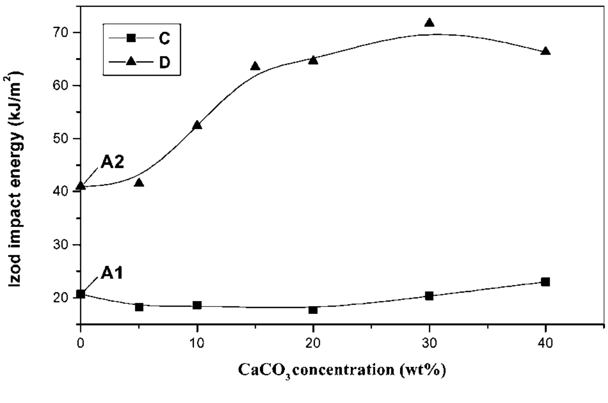


Figure 3 The dependence of notched Izod impact energy on the weight concentration of filler for the ternary systems.

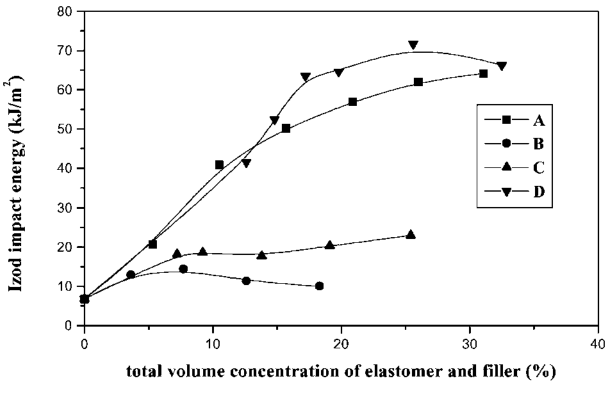
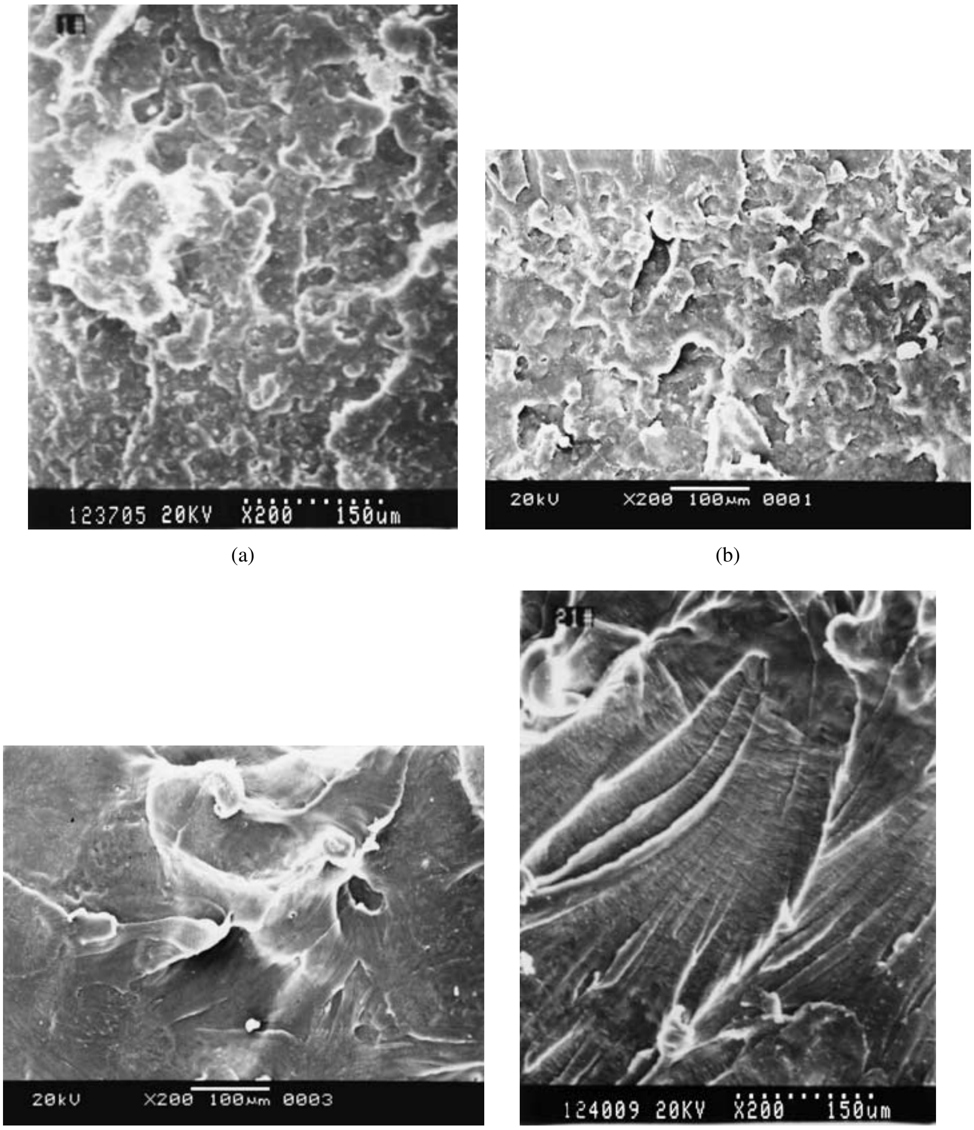


Figure 4 The dependence of notched Izod impact energy on the total volume fraction of elastomer and filler, comparing the binary systems with the ternary systems.

composites C and D. The behavior of composite D is very similar to that of the PP/EOC blend. Moreover, for composition in the 0.14–0.33 vol. fraction range, I_s of composites D is higher than that of blends A. Composite D5 had impact energy approximately 950% higher than that of the neat PP. From this figure, one can notice a correlation between the matrix properties and the toughening effect of $CaCO_3$ particles. Incorporation of $CaCO_3$ into brittle matrix, including the neat PP and PP/EOC blend with low elastomer concentration (5–7 vol%), results in a small improvement in toughness. However, the toughening effect of $CaCO_3$ in a relatively ductile matrix containing 10–14 vol%



(a) (b)

(c) (d)

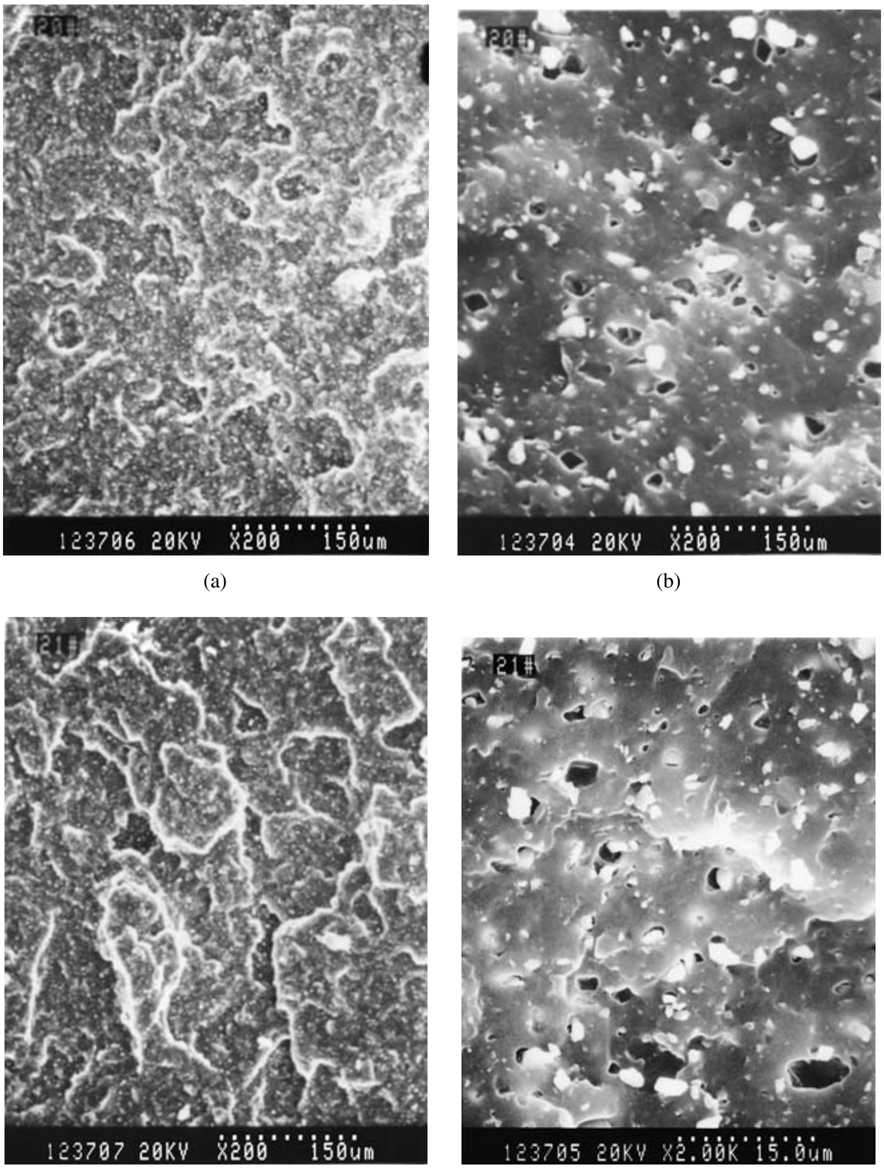
Figure 5 SEM micrographs of the fracture surfaces of Izod samples of iPP and iPP/EOC blends: (a) iPP, (b) A1, (c) A2, (d) A4.

elastomer is in the same range or slightly higher than that of EOC in blend A. Comparative examination of the samples after the impact test also revealed that the specimens of the neat PP, blend A1, composites B and C broke nearly completely, while those of blend A2-7 and composites D did not break completely (30–50% of the cross-section remaining unbroken) and bent instead to allow the pendulum to swing by. Neat PP did not whiten, blend A1 and composites B and C were whitened on the fracture surface, whereas in blends A2-7 and composites D the stress-whitened zone developed beneath the crack flanks and ahead of the crack tip. Hence, one can conclude that the toughening effect of $CaCO_3$ on brittle matrix is small, whereas in a relatively ductile matrix, incorporation of $CaCO_3$ causes a huge improvement in toughness.

3.4. Morphology of fracture surfaces and plastic deformation zone

To investigate the deformation-induced morphology changes during the Izod tests, the fracture surfaces were observed using SEM. Figs 5–7 show SEM micrographs of fracture surfaces of samples of neat PP, A1, A2, A4, B2, C3 and D4. The micrograph in Fig. 5a demonstrated that in plain PP, the fracture surface is macroscopically smooth with only irregular features, resembling those typical for brittle failure. And the fracture of blend A1 with 5 wt% EOC is semi-brittle with little plastic deformation observable on the fracture surface (see Fig. 5b). On the other hand, fracture surfaces of the blends with increasing elastomer content (10–40 wt%), exhibiting high impact energy, show extensive plastic deformation of the matrix accompanying crack propagation. In this range of EOC concentration, a characteristic feature of the fracture surface is the formation of regular striations oriented perpendicular to the direction of crack propagation (from left to right on the micrograph). Such striations were reported earlier by several authors in rubber modified Nylon 6,6 [20] and HDPE [21–22], and were explained in detail by Muratoglu *et al.* [20].

Fig. 6 illustrates the morphology of the fracture surfaces of composites B and C. Since the morphologies within the deformation zone in composites B and C look very similar, we limit the presentation here to representative micrographs of B2 and C3. We recall, that composites B and C exhibit impact energy only slightly



(a) (b)

(c) (d)

Figure 6 SEM micrographs of the fracture surfaces of Izod samples of composites B and C: (a) B2, (b) B2 under higher magnification, (c) C3, (d) C3 under higher magnification.

higher than that of neat PP, much lower than that of blends A and composites D with the same total volume fraction of elastomer and filler (see Fig. 4). Fig. 6a and c show a similar type of morphology observed in neat PP. The fracture surfaces were rather smooth. Fig. 6b and d show more detailed views of the morphology at larger magnification. There is little plastic deformation and no striation observable on the fracture surfaces. However, the debonding of filler particles from the matrix was observed. This suggests that the cavitation formation by debonding is of little effect on energy absorption.

Fig. 7 presents micrograph of the fracture surface of composites D4 (80.2/12.1/7.7 vol%). This micrograph shows extensive plastic deformation, similar to A4 (79.1/20.9 vol%) with similar volume fraction of iPP.

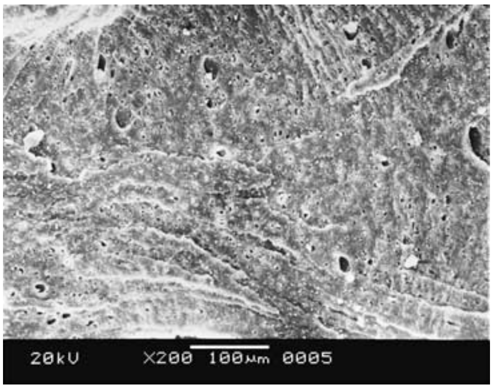


Figure 7 SEM micrograph of the fracture surface of Izod sample of D4.

3.5. The toughening mechanism

As shown by comparison of A, B, C and D, the contribution of the filler to improve the impact energy is smaller than that of elastomer. The microviods formed by the debonding of the filler from the matrix absorbed far less deformation or fracture energy than matrix yield. This suggests that the key to the toughening effect is how to make the matrix yield.

It seems to be appropriate to discuss here the possible reason for the different microdeformation processes between composites C and D based on Wu's percolation theory [23], as well as on the explanation of improved impact energy in semi-crystalline polymers by Bartczak *et al.* [21–22]. Wu [24] was first to propose and to demonstrate experimentally, for rubber-modified Nylon 6,6, that toughness of such systems depends neither on rubber inclusion size nor on rubber concentration alone, but correlates with the thickness L of the matrix ligament between rubber particles. When L is smaller than a certain critical value, L_c, a sharp brittle-tough transition occurs. This critical value is independent of rubber volume fraction and particle size, and is the property of the matrix alone for a given mode, temperature and rate of deformation. He proposed that this distance is the key parameter determining whether a blend will be brittle or tough. In our work, the relation between the toughness and the thickness of the matrix ligament between elastomer particles seems to agree with Wu. In composite C with low elastomer content, elatomer particles are far apart even when much $CaCO_3$ was incorporated, so the stress field around a particle is only slightly or not affected by the presence of other particles. In composites D, increasing EOC content results in an increase of the number density of EOC particles in the matrix and a corresponding decrease of the average thickness L of the matrix ligaments between elastomer particles. At the same time, increasing $CaCO_3$ content in composites D promotes the further decreasing of L. Consequently, when the particles are sufficiently close, the field around neighboring particles will interact considerably resulting in enhanced shear yielding which is observed on the fracture surface of D4 (Fig. 7).

The results presented above prove that in PP/elastomer/filler system, the main factor determining impact resistance is the thickness of the matrix ligaments between elastomer particles, which is effected by the content of the elastomer and the filler, provided that the elastomer and the filler disperse separately in the matrix. It is worth noting that although the debonding of the filler from the matrix absorbs little energy during fracture, the $CaCO_3$ particles can shield crack propagation.

4. Conclusions

A study aimed at investigating effect of EOC and $CaCO_3$ contents on phase morphology and properties of iPP/EOC/$CaCO_3$ composites was performed. The following is to be remarked:

- SEM analysis performed on injection moulded samples showed that EOC and $CaCO_3$ particles with stearic acid treatment dispersed separately in PP matrix.
- Observation of the fracture surfaces revealed that matrix yield absorbed most of the energy during fracture. When the thickness of the matrix ligaments between adjacent elastomer particles is decreased to some degree, the stress fields around neighboring particles interact considerably which results in a toughness jump from 6.8 kJ/m^2 for the neat iPP to 71.7 kJ/m^2 for composite D5 (60/10/30).
- Comparison of experimental results of the ternary systems with those of the binary systems has demonstrated that the same volume fraction of elastomer and filler in composites D as that in blend A achieves the same level of toughness increase. And the use of $CaCO_3$ particles as toughness promoting agents improves the Young's and flexural modulus above that of the neat matrix and well above the reduced Young's and flexural moduli of the elastomer-modified products.

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