Polyethylene Toughened by $CaCO_3$ Particle*: Brittle–Ductile Transition of $CaCO_3$-Toughened HDPE

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SYNOPSIS

The dependencies of the notched Izod impact toughness of HDPE/$CaCO_3$ blends on $CaCO_3$ particle concentration and particle size are analyzed. It was found that the notched Izod impact strength (S) of HDPE/$CaCO_3$ blends depends discontinuously on $CaCO_3$ particle concentration. A brittle–ductile transition occurs when the $CaCO_3$ volume fraction (V_f) increases to a critical value (V_f'). Furthermore, a brittle–ductile transition master curve can be constructed by taking the matrix ligament thickness (L) into account as a parameter instead of V_f. The results show that the critical matrix ligament thickness (L_c) is a single parameter for the transition and $L_c = 5.2$ μm for HDPE/$CaCO_3$ blends. The impact strength, however, varies considerably with $CaCO_3$ particle size, which shows that $CaCO_3$ particle size is another dominating parameter for the toughness of HDPE/$CaCO_3$ blends.

INTRODUCTION

Toughening of polymeric materials is often achieved by modification with rubber. This method, however, lowers the modulus of materials. Rigid inorganic toughening is a rather new route to plastic modification.[1-4] Compared with rubber-toughening, the toughening with rigid inorganic particles increases not only toughness but also modulus, and it is very cheap.

In this paper, we investigated the effects of $CaCO_3$ particle concentration and size on the impact strength of HDPE/$CaCO_3$ blends. The toughening mechanism of HDPE/$CaCO_3$ blends has been discussed from the point of view of Wu's criterion on brittle-ductile transitions.[5,6]

EXPERIMENTAL

1. Materials

The high-density polyethylene (HDPE) 7000F used in this study came from Japan with d = 0.951 g/cm^3 and MI = 0.01 g/10 min. Three types of $CaCO_3$ were used as the dispersed particle, which came from Peng county, Sichuan, China, and were phosphate surface-treated. They have essentially the same chemical composition and are of roughly spherical shape. The average sizes were 6.66, 7.44 and 15.9 μm, respectively.

2. Sample Preparation

$CaCO_3$ and HDPE were mixed in a two-roll mill at 150°C for 10 min. The samples for impact testing were prepared by mold pressing at 180°C under pressure of 80 kg/cm^2 in the form of a sheet of 4.0 mm in thickness, then machined in the form of bars.

3. Impact Testing

Notched specimens were tested with an IZOD UJ-40 Impact Tester according to Chinese Standard GB-1843-80. Testing was carried out at 25°C or at −14°C, and the mean value of 10 measurements for each group of samples was taken.

4. Scanning Electron Microscopy (SEM)

A Hitachi S-520 scanning electron microscope was used to observe the $CaCO_3$ particle size, the surface-

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to-surface interparticle distance in the ligament thickness, and the fracture morphology.

RESULTS AND DISCUSSION

1. Impact Strength and Brittle–Ductile Transition

The curves of notched Izod impact strength vs. the $CaCO_3$ weight fraction (W_f) at 25°C are shown in Figure 1. A definite brittle–ductile transition can be observed in Figure 1, at a critical weight fraction (W'_f) of 22.3, 25.4, and 45.0% for curves a ($\bar{d}n$ = 6.66 μm), b ($\bar{d}n$ = 7.44 μm), and c ($\bar{d}n$ = 15.9 μm), respectively.

The relationships between $CaCO_3$ volume fraction (V_f) and W_f are as follows:

$$V_f = \rho_m \cdot W_f / [(\rho_m - \rho_c) \cdot W_f + \rho_c] \qquad (1)$$

where ρ_m is the density of HDPE, $\rho_m = 0.951\ g/cm^3$, ρ_c is the density of $CaCO_3$, and $\rho_c = 2.7\ g/cm^3$. Through eq. (1), the W_f can be rewritten into V_f. Figure 2 shows the S vs. V_f, from which the V'_f of 9.3% ($\bar{d}n$ = 6.66 μm), 10.7% ($\bar{d}n$ = 7.44 μm), and 22.3% ($\bar{d}n$ = 15.9 μm) is obtained.

Figures 3 and 4 show the curves of impact strength of HDPE/$CaCO_3$ blends (6.66 μm) vs. the $CaCO_3$ weight fraction or volume fraction at low temperature: −14°C. A brittle–ductile transition occurred at the same critical weight fraction and critical volume fraction as that at 25°C for $\bar{d}n$ = 6.66 μm.

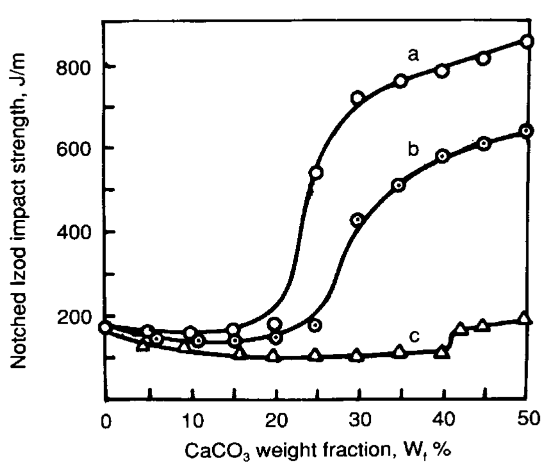


Figure 1 Notched Izod impact strength vs. $CaCO_3$ weight fraction for HDPE/$CaCO_3$ blends: (a) ($\bar{d}n$ = 6.66 μm); (b) ($\bar{d}n$ = 7.44 μm); (c) ($\bar{d}n$ = 15.9 μm).

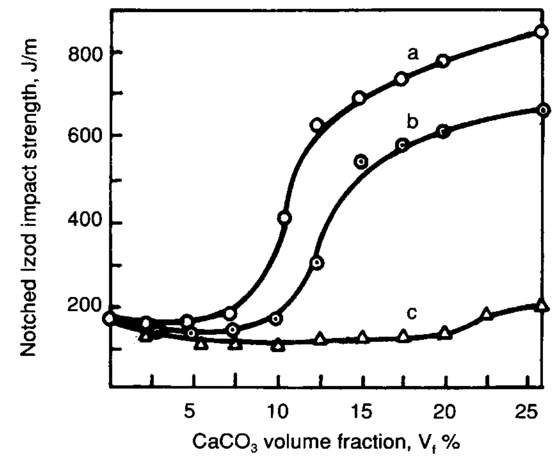


Figure 2 Notched Izod impact strength vs. $CaCO_3$ volume fraction for HDPE/$CaCO_3$ blends, replotted from Figure 1.

2. Critical Matrix Ligament Thickness (L_c)

According to Wu's criterion for the brittle–ductile transition of nylon-6/EPDM blends,[5,6] the critical matrix ligament thickness (L_c) is only one parameter that dominates the transition. To test if Wu's criterion can be used for the HDPE/$CaCO_3$ blends, eq. (2) is used to convert the V_f into L:

$$L = \bar{d}n[(3.14/6V_f)^{1/3} - 1] \qquad (2)$$

It is interesting to find that instead of the three curves in Figure 2 a single brittle–ductile transition

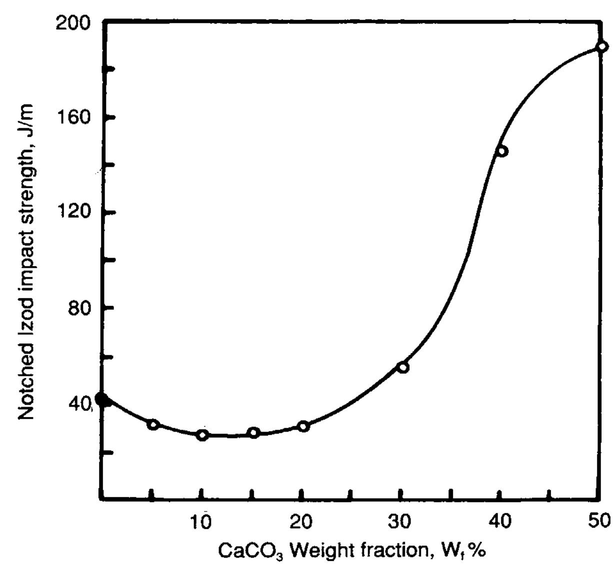


Figure 3 Notched Izod impact strength vs. $CaCO_3$ weight fraction for HDPE/$CaCO_3$ blends at −14°C, $CaCO_3$ with a size of 6.66 μm.

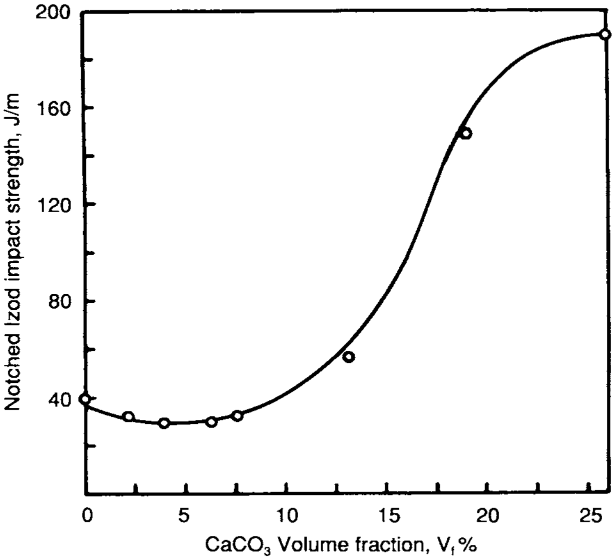


Figure 4 Notched Izod impact strength vs. $CaCO_3$ volume fraction for HDPE/$CaCO_3$ blends at −14°C, replotted from Figure 3.

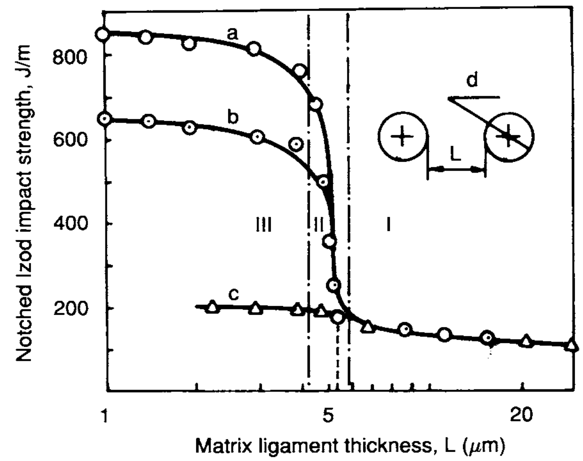


Figure 5 A single-transition master curve for HDPE/$CaCO_3$ blends. Replotted from Figure 2 using matrix ligament thickness L instead of V_f: (a) ($\bar{d}n$ = 6.66 μm); (b) ($\bar{d}n$ = 7.44 μm); (c) ($\bar{d}n$ = 15.9 μm).

master curve can be constructed as shown in Figure 5. This result proves that Wu's criterion can also be used in HDPE/$CaCO_3$ blends; the critical matrix ligament thickness (L_c) for HDPE/$CaCO_3$ blends is 5.2 μm.

The impact strength, however, varies considerably with $CaCO_3$ size, which shows that particle size is another dominating parameter for the toughness of HDPE/$CaCO_3$ blends. It seems that the smaller the $CaCO_3$ particle size the higher the impact strength and the lower the critical volume fraction (V'_f), will be. In other words, $CaCO_3$ particles of large size cannot be used as a toughening agent. This can be well understood since the stress field around the large particles are large and thus cracks are propagated rapidly around the particle, leading to the catastrophic break previous to matrix yielding.

To verify the critical matrix ligament thickness (L_c), the surface-to-surface interparticle distance was measured by SEM. $CaCO_3$ of size 7.44 μm was used and the results are shown in Table I.

A good agreement exists between the value calculated by eq. (2) with that measured by SEM. The ligament appears to form a bridge from which the toughening with rubber and rigid particles may well be related.

There are many factors, such as matrix toughness, interphase adesion, and particle aggregation, that affect the brittle–ductile transition. This aspect, outside the scope of the present paper, will be discussed in detail elsewhere.

3. Impact Fracture Model in HDPE/$CaCO_3$ Blends

To understand the impact fracture model in HDPE/$CaCO_3$ blends, we divided Figure 5 into three regions, e.g., the brittle region (I), the transition region

Table I Surface-to-Surface Interparticle Distance in HDPE/$CaCO_3$ Blends ($CaCO_3$ of Size 7.44 μm Was Used).

		Interparticle Distance (μm)		
$CaCO_3$ (wt %)	Concentration (vol %)	Measured by SEM	Calculated by Eq. (2)	S (J/m)
10	3.8	9.4–10.0	10.4	106
20	8.1	6.0–6.5	6.4	110
30	13.1	4.5–4.9	4.4	430
40	19.0	2.8–3.3	3.0	615

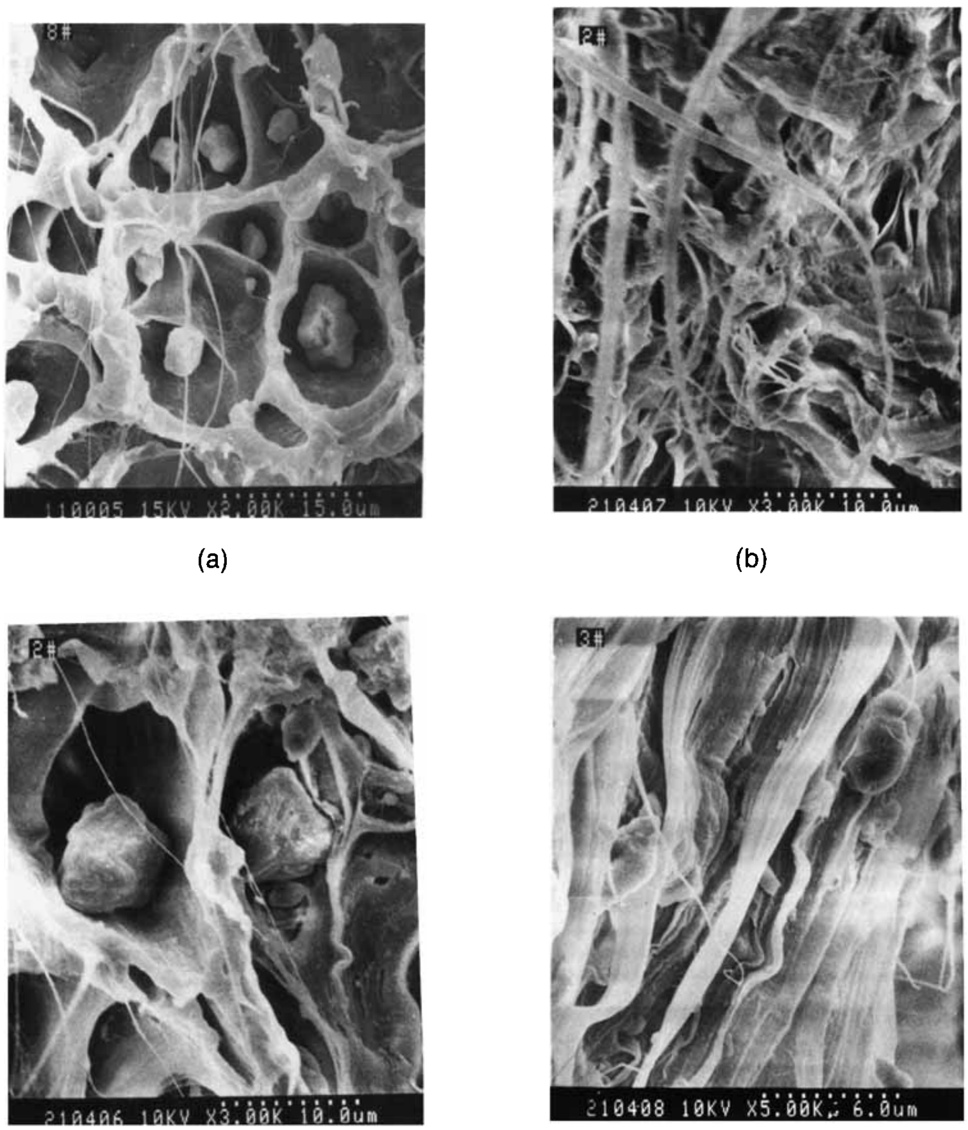
(II), and the ductile region (III). The micrographs of the fractured surfaces in these regions were carefully studied.

Cavitation and Craze in Region I

In region I, $L > L_c$, the impact strength of HDPE/$CaCO_3$ blends is smaller than 200 J/m, and a brittle behavior is observed. Figure 6(a) shows the $CaCO_3$ particle-induced cavitation, which presumably acted as a stress concentrator. The main way by which the impact energy is dissipated is cavitation-craze, so the energy dissipation is very low.

Cavitation and Shear Yielding Coexist in Region II

In region II (brittle–ductile transition region), $L < L_c$, the impact strength is obviously improved, and S varies from 250 to 450 J/m. Two kinds of fracture characteristics can be observed in the fracture surface, which are shown in Figure 6(b) and (c), respectively. At the bases of the notch, we can observe many sticks and a large plastic deformation [Fig. 6(b)]. However, far from the bases of the notch, there exists cavitation where the $CaCO_3$ particles are dislodged from the matrix during impact fracture [Fig. 6(c)]; it is still a brittle fracture. Therefore



(a) (b)

(c) (d)

Figure 6 SEM micrograph for fracture surfaces of the notched Izod impact at 25°C: (a) brittle fracture surface for HDPE/$CaCO_3$ = 90/10; (b, c) fracture surface for HDPE/$CaCO_3$ = 75/25; (d) ductile fracture for HDPE/$CaCO_3$ = 50/50.

in the transition region, cavitation and shear yielding coexist: Shear yielding can absorb a lot of impact energy and the toughness is increased considerably.

Matrix Yielding in Region III

In region III, as L decreases further, the impact strength reaches 850 J/m, about four times that of pure HDPE, namely, ultra-toughness HDPE blends, as shown in Figure 6(d). Matrix yielding becomes larger and larger, fibrils are denser, shear yielding propagates and pervades over the entrive deformation zone, a lot of energy is dissipated, and ultra-toughening materials can be obtained.

Therefore, we can conclude that the brittle–ductile transition corresponds to the transition of cavitation-craze fracture to shear yielding, which dissipates the most of impact energy. This has been explained by the percolating process of "spherical stress" volume in the random lattice.[7]

CONCLUSION

The notched Izod impact strength of HDPE/$CaCO_3$ blends occurs via a brittle–ductile transition when the $CaCO_3$ volume fraction reaches a critical value V_f'. A brittle–ductile transition master curve can be constructed by using the matrix ligament thickness, $L_c = 5.2$ μm for HDPE/$CaCO_3$ blends. The particle size greatly affects the toughness of HDPE/$CaCO_3$ blends. The brittle–ductile transition corresponds to the transition of cavitation-craze fracture to shear-yielding fracture.

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