

THE EFFECT OF MATRIX TOUGHNESS ON THE BRITTLE-DUCTILE TRANSITION OF HDPE/CaCO₃ BLENDS*

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ABSTRACT

The effects of HDPE matrix toughness on the brittle-ductile transition of HDPE/CaCO₃ blends are investigated. Not all HDPE can be toughened by CaCO₃ particles. The ability of the matrix to yield plays a fundamental role in determining whether HDPE can be toughened or not. There exists a critical matrix toughness ($I_{sc} \approx 45 \text{ J/m}$) below which HDPE can not be toughened observably by CaCO₃ particle at given average size, and above which the critical matrix ligament thickness (τ_c) is proportional to matrix impact strength.

INTRODUCTION

The brittle — ductile transition is a very important phenomenon for polymer-toughening, especially for toughening of pseudoductile matrices. It has not been noted enough until recently. In many polymer blends, such as Nylon/EPDM, PP/EPDM and HDPE/CaCO₃, a sharp brittle-ductile transition is observed when the average surface-to-surface interparticle distance is smaller than a critical value^[4,5,6]. In other words, the critical condition for brittle-ductile transition is

$$\tau < \tau_c \quad (1)$$

where τ is the surface - to - surface interparticle distance (also termed the matrix ligament thickness, as shown in Fig. 1)

In our previous papers^[1,2,3,4], the brittle — ductile transition, the morphology, percolation model and stress-field overlap of HDPE/CaCO₃ blends were described. It was concluded that toughening with CaCO₃ particles is a new route to polymer modification. Through this way it not only increases the toughness but also the modulus, and the cost is very

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cheap. However, not all polyethylenes can be toughened to a significant extent by CaCO_3 particles. The matrix yielding plays an important role in determining whether the brittle-ductile transition will occur or not at given particle concentration and average size.

Chain structure, phase morphology and toughness relationships in thermoplastic polymers and polymer/rubber blends were discussed by Wu^[7]. According to Wu's result we have:

$$\frac{\sigma_z}{\{\sigma_y\}} \sim \left(\frac{3M_v}{\rho_a} \right)^{\frac{1}{2}} v_e \quad (2)$$

$$\frac{\sigma_z}{\{\sigma_y\}} \sim \left(\frac{\rho_a}{3M_v} \right)^{\frac{1}{2}} C_\infty^{-2} \quad (3)$$

Where v_e is the entanglement density, C_∞ the characteristic ratio of an unperturbed chain, ρ_a the amorphous mass density, M_v the average molecular weight per statistical unit. The mode of fracture mainly depends on the competition between crazing and yielding. When crazing stress σ_z is smaller than yield stress $\{\sigma_y\}$, the polymer will tend to craze-fracture. Otherwise, it will tend to yield-fracture.

Since that C_∞ controls the ductility of matrices, τ_c should correlate with C_∞ for pseudoductile matrices, e. g.

$$\tau_c \sim \frac{1}{C_\infty} \quad (4)$$

On the other hand, I_s (Izod notched impact strength) is also associated with yielding and ductility of matrices, so,

$$\tau_c \sim I_s \quad (5)$$

That is to say, the higher matrix toughness, which tends to yield rather than craze, should correspond to a large τ_c , and it is easy for toughening; while the lower matrix toughness, which tends to craze rather than yield, should correspond to a small τ_c , and it is hard for toughening.

The purpose of this work was to investigate the effect of the matrix toughness on brittle-ductile transition of HDPE/ CaCO_3 blends, and to

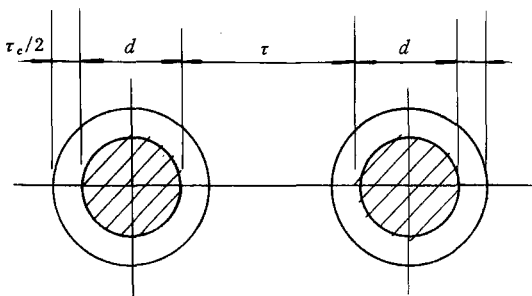


Fig. 1 Schematics of surface to surface inter-particle distance τ . (matrix ligament thickness)

present the relationships between critical matrix ligament thickness and matrix toughness (Impact strength) in HDPE/CaCO₃ blends.

EXPERIMENTAL

1. *Materials*

The high density polyethylene used in this work were HDPE 7000F (high toughness) and HDPE 7008 (low toughness). The manufacturer's description of these HDPE are listed in Table 1.

Table 1 Manufacturer's description of HDPE 7000F and HDPE 7008

HDPE	Manufacturer	Impact/strength (J/M)	MI (g/10min)	ρ
7000F	Mitsui, Japan	180	0.01	0.951
7008	Qilu, China	29.7	8	0.957

CaCO₃ with a size of 7.44 μ m was used as the dispersed particle which came from Peng county, Sichuan, China and were phosphate surface-treated.

2. *Sample preparation*

First the two types of HDPE were mixed by means of two roll mill at 150°C for 10min as the following ratio: HDPE 7000F/HDPE 7008=100/0, 80/20, 70/30, 60/40, 50/50, 30/70, 0/100. In this way various matrices were obtained. Then CaCO₃ and HDPE were mixed by means of 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 80kg/cm² in the sheet form of 4.00mm 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 (the same as AST256), and the mean value of five measurements for each group of samples was taken.

4. *Scanning electron microscopy (SEM)*

Hitachi S-520 Scanning Electron Microscopy was used to observe the surface of fractured bars.

RESULTS AND DISCUSSION

1. *Impact strength and matrix toughness*

The curves of notched Izod impact strength versus matrix toughness are shown in Fig. 2 and Fig. 3.

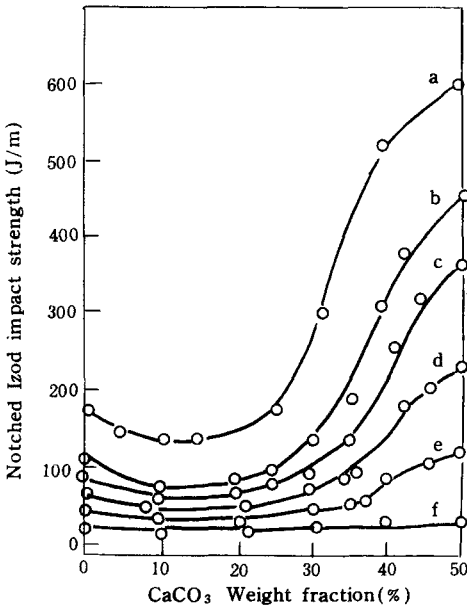


Fig. 2 Notched Izod impact strength vs. matrix toughness for HDPE/CaCO₃ blends. CaCO₃ with a size of 7.44 μm , HDPE7000F/7008: (a)100/0; (b)80/20; (c)70/30; (d)60/40; (e)50/50; (f)30/70

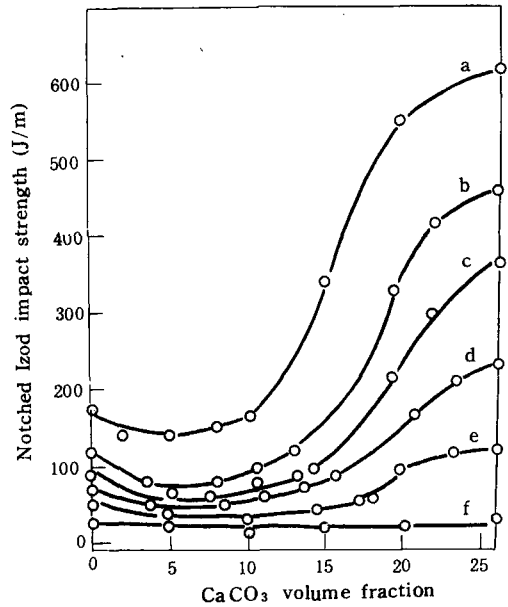


Fig. 3 Notched Izod impact strength vs. matrix toughness for HDPE/CaCO₃ blends. replotted from Fig. 2

For low matrix toughness (HDPE 7008) and HDPE7000F/7008(30/70), no brittle-ductile transitions are observed. As matrix toughness reaches to a critical value, HDPE 7000F/7008 (50/50), the brittle-ductile transition occurs and becomes more sharp as the increasing matrix toughness. Here, we define the occurring of brittle-ductile transition when the impact strength changes from a slightly owing status to observable increasing status. The onset of brittle-ductile transition is considered as the point at which the impact strength reaches to that of original matrix. From Fig. 2 and Fig. 3, the critical CaCO₃ fractions at which the brittle-ductile transition occurred are 37.5 wt% (17.4 vol%), 35 wt% (16 vol%), 32.5 wt% (14.5 vol%), 30 wt% (13.1 vol%), 25 wt% (10.5 vol%) for HDPE7000F/7008=50/50, 60/40, 70/30, 80/20, and 100/0 respectively. High toughness corresponds to low critical value, e.g. brittle-ductile transition is easier to occur.

We can conclude that there exists a critical matrix toughness below which HDPE can not be toughened observably by CaCO₃ at given particle average size. High matrix toughness should be more effective than low ones. At given CaCO₃ concentration and average particle size, the brittle-ductile transition may occur or not, depending on the matrix toughness.

This conclusion explains why the toughened HDPE or PP was not obtained with CaCO₃ particle in some previous studies.

2. Critical matrix ligament thickness (τ_c) and matrix toughness

CaCO₃ particles dispersed in HDPE could be considered as cubic lattice distribution and the dispersion status of CaCO₃ in HDPE has been discussed elsewhere.^[3,8] So Equation (6) can be used to calculate the matrix ligament thickness (surface to surface interparticle distance).

$$\tau = d [(3.14/6V_f)^{1/3} - 1] \quad (6)$$

From Eq(6), the V_f is converted to τ . Fig. 4 shows the Notched Izod impact strength vs. matrix ligament thickness, it can be seen that τ_c increases as the matrix toughness increasing as expected. Table 2 and Fig. 5 show the effect of matrix toughness on τ_c .

Table 2 The effect of matrix toughness on τ_1

HDPE7000F/HDPE7008	Matrix impact strength J/m	V'_f (%)	τ_c (μm)
100/0	180.0	10.5	5.2
80/20	162.7	13.1	4.4
70/30	138.8	14.5	4.0
60/40	71.4	16.0	3.6
50/50	44.5	17.4	3.3
30/70	38.9	—	—
0/100	29.7	—	—

It is interesting to find that τ_c is directly proportional to matrix impact strength. This may be due to that the higher the matrix toughness in blends is, the easier the plastic deformation induced by particle will be. When the content of HDPE 7000 F in matrix is increased, the melting index (MI) decreases observably, resulting in higher shear stress at given melting conditions. This may improve the dispersion of CaCO₃ in the matrix, therefore the toughness. So both the matrix toughness and MI should be considered to explain the impact strength of HDPE/CaCO₃ blends. When the matrix toughness is smaller than 45J/m (50/50) it will tend to craze rather than yield. Within the whole composition of HDPE/CaCO₃ blends, the brittle-ductile transition does not occur for lower matrix toughness.

3. The micrographs of fractured surface

The SEM micrographs of fractured surface of Notched Izod impact

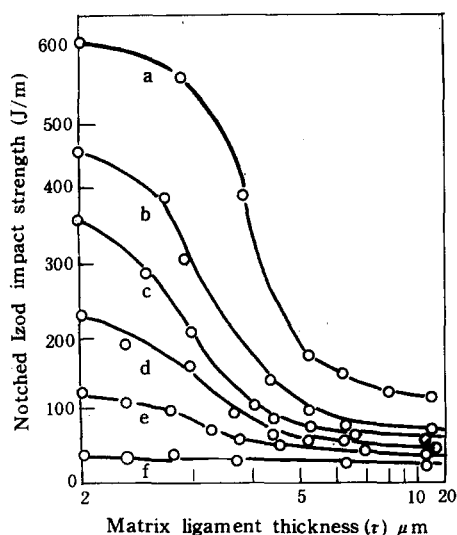


Fig. 4 Notched Izod impact strength vs. matrix ligament thickness for HDPE/CaCO₃ blends

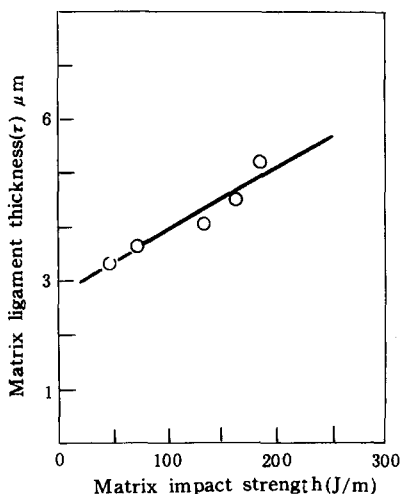


Fig. 5 Matrix toughness vs. critical ligament thickness for HDPE/CaCO₃ blends

samples are shown in Figure 6.

For low matrix toughness the matrix can not be induced to yield even if $\tau < \tau_c$; and the impact energy is mainly dissipated by cavitation-craze (Fig 6 (a)). As increasing matrix toughness, the matrix becomes easier to yield, fibrils are more dense on the fractured surface (Fig. 6(b,c)), the impact energy is mainly dissipated by cavitation and yielding. As the matrix toughness increases furthermore, the yielding propagates and pervades over the entire deformation zone, the impact energy is mainly dissipated by yielding (Fig. 6(d)).

CONCLUSION

The critical matrix ligament thickness τ_c is a characteristic of polymer at given rate, temperature, loading mode, internal stress, and increases with increasing matrix toughness for HDPE/CaCO₃ blends. Not all HDPE can be toughened by CaCO₃ particle. The ability of the matrix to yield plays a fundamental role in determining whether the HDPE can be toughened or not. Matrix toughness exists a critical value ($I_{sc} \approx 45 \text{ J/M}$) below which the criterion for the brittle-ductile transition can not be achieved for HDPE/CaCO₃ blends.

Keywords

Matrix toughness; Critical matrix ligament thickness; HDPE/CaCO₃ blends

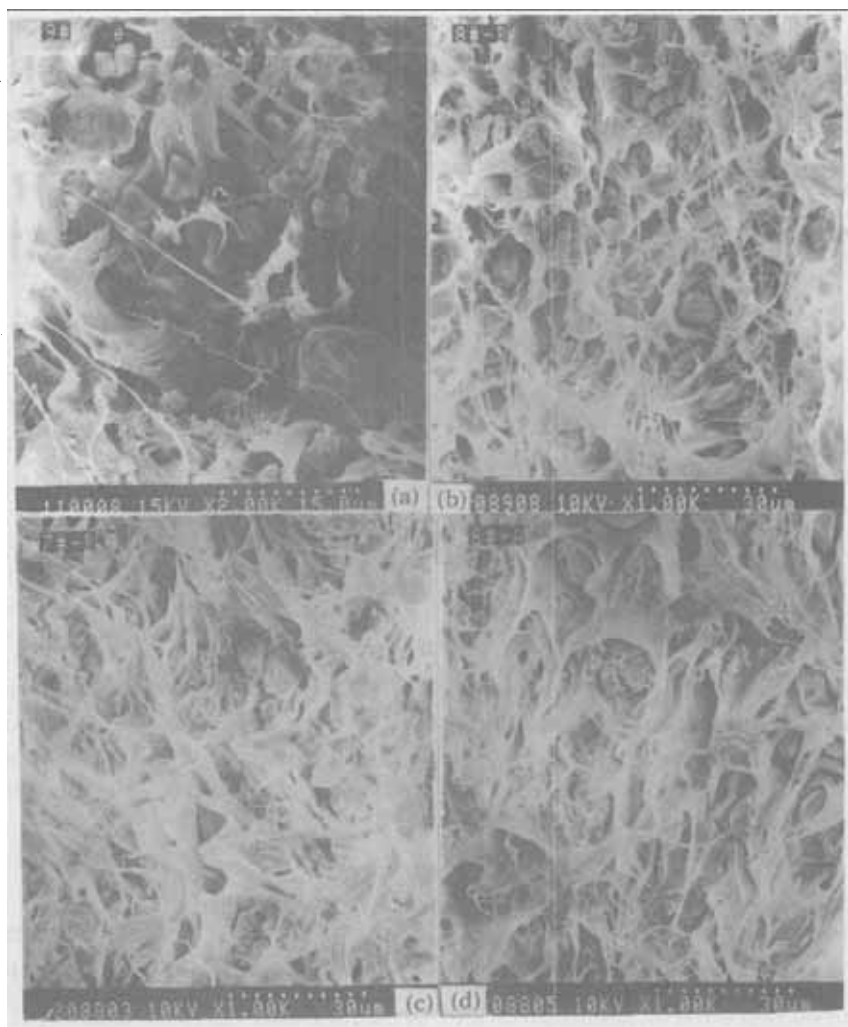


Fig. 6. SEM micrograph of fractured surface for HDPE/CaCO₃ blends, CaCO₃ used are 50 wt%.
HDPE7000F/7008: (a)30/70; (b)70/30; (c)80/20; (d)100/0

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