Effect of Morphology on Brittle–Ductile Transition of HDPE/CaCO₃ Blends*

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SYNOPSIS

In this paper, the results of a series of investigations of the effect of morphology on the brittle–ductile transition for HDPE/CaCO₃ blends are summarized: (1) It seems the critical ligament thickness increases with increasing matrix toughness; (2) the interphase adhesion is very important for the toughness of HDPE/CaCO₃ blends; (3) small particles are more effective than large ones; (4) CaCO₃ particle aggregation will reduce toughening efficiency; (5) uniform CaCO₃ particle size is more effective than heterogeneous size for the toughening of HDPE. It is expected that a polymer with higher modulus as well as higher toughness will be obtained by appropriately controlling the morphology of HDPE/CaCO₃ blends.
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INTRODUCTION

The rigity and toughness are two key parameters which determine whether a polymer can be used as an engineering material. Thus the toughening of a polymer has always been an important issue in applications of a polymer. So far, the toughening of a polymer is often achieved by modification with rubber. Rubber-reinforced plastics, such as HIPS and ABS, constitute an important class of commercial polymers. But toughening with rubber always lowers the modulus of materials; the application of polymers in engineering is usually limited only by their lower moduli.

Quite recently, we have reported a rather new route to polymer toughening in which polyethylene was successfully toughened with rigid CaCO₃ particles rather than rubber particle.[1–4] This increases not only toughness but modulus, and is very cheap. We expect to obtain polymeric materials with higher rigidity as well as higher toughness in the near future by modification with rigid particles.

In our experiments, we discovered that when sur-face to surface interparticle distance (i.e., matrix ligament thickness, as shown in Fig. 1) reaches a critical value, the sharp brittle–ductile transition in HDPE/CaCO₃ blends occurs, providing that the CaCO₃ particle is smaller than one given size (here is 15.9 μm), as shown in Figure 1.[2,3]

This phenomenon is very similar to that discovered by Wu and Qi through studies on nylon/rubber or PP/rubber blends, respectively.[5,6] The critical matrix ligament thickness may be characteristic of the matrix for a given mode and temperature, and a generalized criterion for polymer toughening. Summarized here are the results of a series of investigations of effect of morphology on the brittle–ductile transition for HDPE/CaCO₃ blends.

HDPE MATRIX TOUGHNESS

As mentioned above, the critical ligament thickness (τ_c) is characteristic of the matrix for given mode and temperature. It is independent of particle concentration and particle size. Several polymer blends, their matrix toughness, and their τ_c's are listed in Table I.

According to Table I, it seems the τ_c increases with increasing matrix toughness. Thus, high matrix toughness should be more effective than a low one.
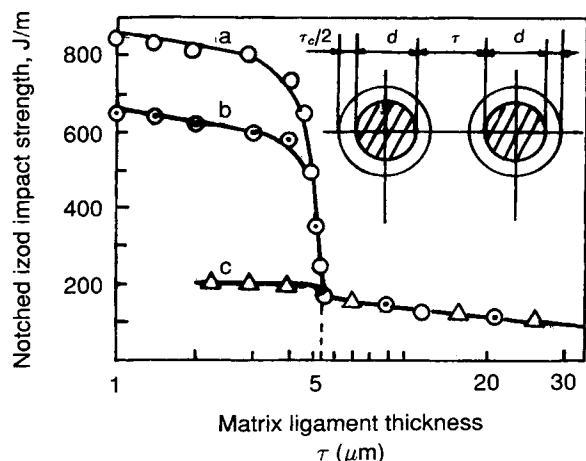
Figure 1   Notched Izod impact strength vs. matrix ligament thickness for HDPE/CaCO₃ blends. CaCO₃ average particle diameter (μm): (a) 6.66; (b) 7.44; (c) 15.9.

This may be due to the fact that the higher the matrix toughness in blends, the easier the plastic deformation induced by particle will be. In Table II is shown the effect of matrix impact strength on toughness of HDPE/CaCO₃ blends (50/50 by weight).[7]

Table II indicates that there exists a critical matrix toughness (here about 42–45 J/m) below which HDPE cannot be toughened detectably by CaCO₃ particles at given particle concentration and average size. That is to say, at the same CaCO₃ concentration and average particle size, the matrix ligament thickness may be smaller than τ_c or larger than τ_c, depending on the matrix toughness. Thus the sharp brittle–ductile transition may occur or not.

INTERPHASE ADHESION

Wu has proposed that van der Waals adhesion is sufficient for toughening in nylon/EPDM blends.

Table I   Several Polymer Blends, Their Matrix Toughness and τ_c[a]

Polymer Blends	Matrix	Notched Izod Impact Strength of Matrix (J/m)	τ_c (μm)
Nylon/EPDM	Nylon	18.6	0.30
PP/EPDM	PP	20.0	0.15
PETG/rubber[b]	PETG	—	0.44
HDPE/CaCO₃	HDPE	180	5.2

[a] See Refs. 3, 5, and 6.
[b] An amorphous copolyester of ethylene glycol, 1,4-cyclohexanedimethanol and terephthalic acid.

Table II   The Effect of Matrix Impact Strength on Toughness of HDPE/CaCO₃ (50/50) Blends

Matrix Notched Izod Impact Strength (J/m)	HDPE/CaCO₃ (50/50) Blends Notched Izod Impact Strength (J/m)	Increase (%)
180.0	850.0	372
162.7	488.3	200
138.8	309.9	119
71.4	224.2	214
44.5	146.7	230
42.7	58.1	38
38.9	50.0	29
29.7	31.7	7

Qi, however, reported that the brittle–ductile transition of PP/EPDM blends only develops readily if the interphase adhesion is improved.[8] Our experimental results showed that the interphase adhesion is important for toughening with CaCO₃ particles.[7] If the CaCO₃ is not treated with a coupling agent, the HDPE/CaCO₃ blends made are very brittle. When CaCO₃ is treated with phosphate, which is hydrophobic, the interphase adhesion between HDPE and CaCO₃ is improved greatly, which makes possible the finer dispersion of CaCO₃ particles. By this method, the ligament thickness is reduced. In Figure 2 is shown the impact strength of HDPE/CaCO₃ (50/50) blends and pure HDPE vs. amount of phosphate. The optimum phosphate amount is found to be about 2% by weight, which may be thought to the amount of phosphate which just covers the surface of CaCO₃ particles. If the amount of phosphate is small (less than 2%), the surface of
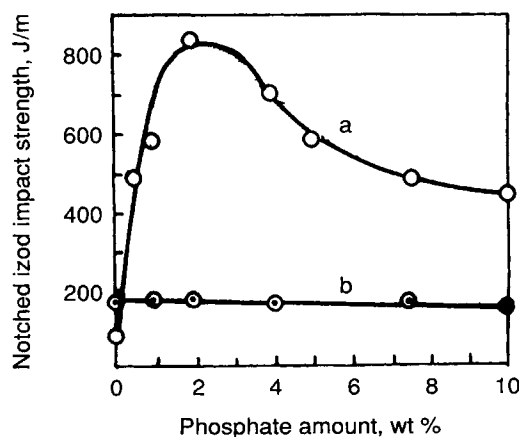

Figure 2   Impact Strength of HDPE/CaCO₃ (50/50) blends and pure HDPE vs. phosphate amount: (a) HDPE/ CaCO₃; CaCO₃ with an average diameter of 6.66 μm was used; (b) pure HDPE.
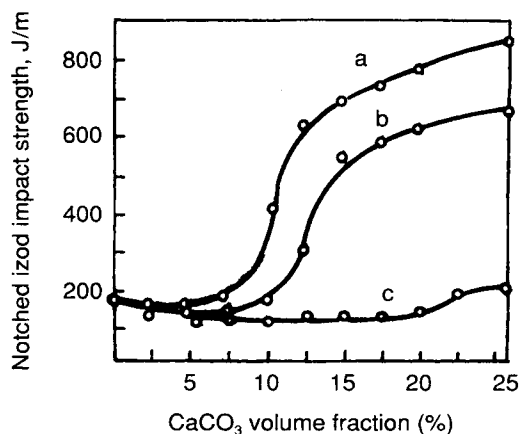
Figure 3 Impact Strength of HDPE/CaCO₃ blends vs. CaCO₃ concentration and size. CaCO₃ average particle diameter (μm): (a) 6.66; (b) 7.44; (c) 15.9.

CaCO₃ particles cannot be covered completely. Thus, the interphase adhesion should be improved with increasing phosphate amount, and the impact strength should increase too. But if the amount of phosphate is increased to more than 2%, the excess phosphate may weaken the impact strength of the matrix.

PARTICLE SIZE

At a given polymer blends, the ligament thickness, calculated by the Equation $\tau = d(k(\pi/6\varphi)^{1/3} - 1)$, will decrease with decreasing particle size. We have reported that, in HDPE/CaCO₃ blends, the smaller the particle size is, the higher the impact strength

and the lower the critical particle concentration will be, as shown in Figure 3. In other words, CaCO₃ particles of large size cannot be used as toughening agents. This can be well understood since the stress field around the large particles is large and thus cracks are propagated rapidly around the particle, leading to the catastrophic break previous to matrix yielding. Is there a lower limit to CaCO₃ particle size? Is there an optimum particle size for the toughness of HDPE/CaCO₃ blends as in the case of toughening with rubber? These questions are somewhat difficult for us to answer because we have yet not obtained CaCO₃ particles with size less than 1 μm.

CaCO₃ PARTICLE AGGREGATION

At a given CaCO₃ particle concentration and average particle size for HDPE/CaCO₃ blends, CaCO₃ particle aggregation will reduce the toughening efficiency. Aggregation forms clusters of particles; the matrix ligament between two clusters cannot yield easily during impact fracture. So the average matrix ligament thickness (τ_a) in aggregated blends is larger than that of well-dispersed blends. Figure 4 shows the micrographs of the fractured surface profiles of HDPE/CaCO₃ (70/30) blends. There is an apparent difference in the fracture surface development. For a well-dispersed blend, HDPE blended with 30 wt % modified CaCO₃ [Fig. 4(a)], a large plastic deformation can be observed, with impact strength of 580 J/m. For a poorly dispersed blend, HDPE blended with 30 wt % unmodified CaCO₃ [Fig.
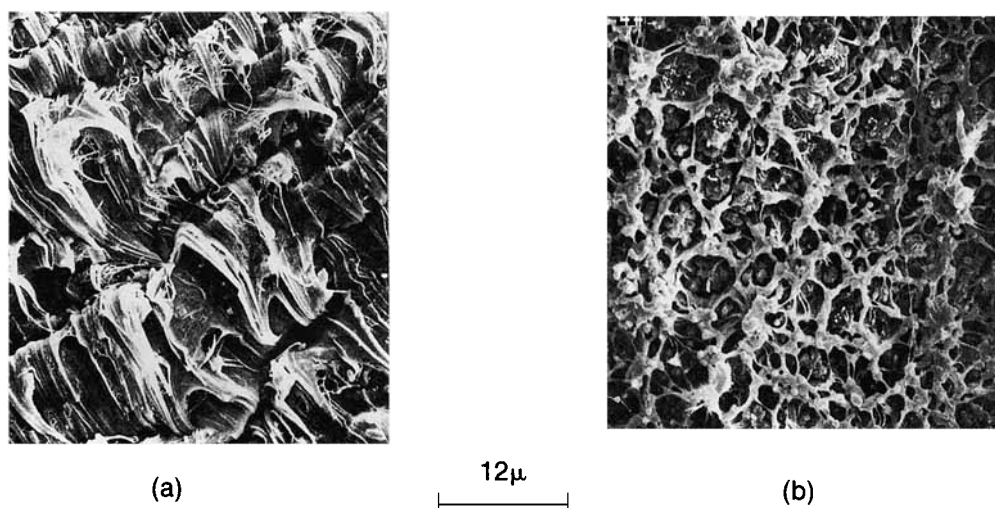

(a)

12μ

(b)

Figure 4 The SEM of fractured surface of specimens after impact testing: (a) HDPE filled with 30 wt % modified CaCO₃; (b) HDPE filled with 30 wt % unmodified CaCO₃ (2500× magnification).

4(b)], we are able to observe agglomerated particles and a very smooth surface, with impact strength of 30 J/m only.

POLYDISPERSITY OF CaCO₃ PARTICLES

In HDPE/CaCO₃ blends, CaCO₃ particles have a range of different sizes. At the same CaCO₃ concentration and average particle size, the effect of size polydispersity can be seen from the ratio of the average matrix ligament in the polydisperse sample $\tau(\sigma_q)$ to that of the monodisperse sample $\tau(1)$[9]

$$\tau(\sigma_q)/\tau(1) = \exp[(\ln \sigma_q)^2]$$

As the size polydispersity increases, the average ligament thickness increases rapidly. Thus uniform CaCO₃ particle size is more effective than heterogeneous sizes for toughening of HDPE/CaCO₃ blends.

CONCLUSION

Though critical matrix ligament thickness is shown to be the most basic factor in toughening of HDPE, there are many factors which affect the brittle–ductile transition greatly. The critical ligament thickness increase with increasing matrix toughness. The interphase adhesion and fine dispersion of CaCO₃

particles are very important for the toughness of HDPE/CaCO₃ blends. Small particles and uniform particle size are more effective than large ones or heterogeneous size.

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