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Polymer Vol. 36 No. 12, pp. 2397–2401, 1995

0032-3861/95/$10.00+0.00

Polyethylene toughened by $CaCO_3$ particles*: The interface behaviour and fracture mechanism in high density polyethylene/$CaCO_3$ blends

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(Received 18 December 1992; revised 25 May 1994)

Tensile behaviour and impact force–time curves of high density polyethylene/$CaCO_3$ blends have been investigated. The results showed that there may exist a flexible interfacial area with lower stiffness than the matrix. The concept of yielding in the interfacial area was proposed to explain the fracture mechanism of HDPE/$CaCO_3$ blends. Three types of fracture behaviour were assumed to be dependent on the surface-to-surface interparticle distance: (1) cavitation and crazing; (2) coexistence of cavitation and yielding in the interfacial area; (3) interfacial area yielding and matrix yielding. Based on the results, the interface conditions for brittle–ductile transition and core–shell morphology of $CaCO_3$ particles were discussed.

(Keywords: core–shell morphology; HDPE/$CaCO_3$ blends; fracture mechanism)

INTRODUCTION

Polymer toughened with rigid particles (organic or inorganic) is a new concept for polymer modification. Recently, $CaCO_3$ was successfully used to toughen high density polyethylene (HDPE) in our laboratory[1-5]. There are many factors, such as matrix toughness, particle size, interface adhesion and temperature, which greatly affect the toughening efficiency. It is widely believed that matrix yielding is necessary for polymer toughening. However, the role of interfacial area has not been elucidated clearly for toughening with rigid particles. A quantitative study of the effects of interfacial bonding on rubber-toughened nylon 6 has been carried out by Wu[6]. He has demonstrated that Van der Waals adhesion is sufficient. Nauman and co-workers have shown that the toughness of numerous brittle polymers, such as styrene–acrylonitrile copolymer (SAN), epoxies, polyimides and poly(phenylene ether), have been improved without interfacial bonding between the modifier and matrix[7,8].

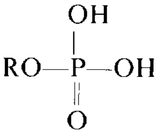
The present paper deals with interface behaviour of high density polyethylene (HDPE)/$CaCO_3$ blends by studying tensile behaviour and impact force–time curves. The core–shell morphology of the $CaCO_3$ particle and its associated fracture mechanism are also discussed.

EXPERIMENTAL

Materials

The HDPE (7000F) used was obtained from Japan (density, $d=0.951\ g\,cm^{-3}$, melt flow index $=0.01$ g per 10 min). Three types of $CaCO_3$ were used as dispersed particles (obtained from Peng conty, Sichuan, China). They had essentially the same chemical composition and were roughly spherical in shape, the average sizes being 6.66, 7.44 and 15.9 μm, respectively.

Phosphate was synthesized in our laboratory with the structure:



$$RO{-}\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle O}{\|}}{P}}{-}OH \qquad (R=C_{12}H_{25}\sim C_{18}H_{37})$$

Sample preparation

$CaCO_3$ was treated with phosphate (1.5 wt%) in a superspeed mixer. The unmodified and modified $CaCO_3$ were mixed with the HDPE by means of a two-roll mill at 150°C for 10 min.

The samples for mechanical measurements were prepared by mould pressing at 180°C under a pressure of $80\ kg\,cm^{-2}$ into sheets 1.0 mm and 4.0 mm thick, which were punched to dumb-bell shape or machined in the form of bars.

Tensile testing

Tensile testing was carried out on a XL-100 Tensile Tester, according to ASTM638M. Speeds of 5 and $50\ mm\,min^{-1}$ were used for modulus and yield stress, and for tensile strength, respectively. The mean value of five measurements was taken.

Impact testing

The notched specimens were tested with a Ceast Izod-type tester made in Italy, according to ASTM256. The impact speed was $3.458\ m\,s^{-1}$ and the force–time

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*Project supported by the National Natural Science Foundation of China

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curves generated during the impact experiment were recorded. The impact speed used in this experiment gave rise to some dynamic oscillation in the force–time curves, but this was negligible except initially, so the force–time signals were treated as smooth traces. Each impact test was repeated at least five times, and the results were averaged.

RESULTS AND DISCUSSION

Modulus

Many equations have been used to explain the modulus of filled materials. Among the most prominent are those developed by Einstein, Kerner and Nielsen[9–11]. These models are as follows:

Einstein:

$$E_c/E_m = (1 + BV_f) \tag{1}$$

Kerner:

$$E_c/E_m = \frac{E_f V_f/[(7-5\nu)E_m + (8-10\nu)E_f] + (1-V_f)/[15(1-\nu)]}{E_m V_f/[(7-5\nu)E_m + (8-10\nu)E_f] + (1-V_f)/[15(1-\nu)]} \tag{2}$$

Nielsen:

$$E_c/E_m = \frac{1 + ABV_f}{1 - B\psi V_f} \tag{3}$$

where

$$A = \frac{7-5\nu}{8-10\nu}$$

$$\psi = 1 + [(11 - \varphi_m)/\varphi_m^2]V_f$$

where E_c is the modulus of the composite, E_m is the modulus of the polymer matrix, V_f is the volume fraction of filler, ν is the Poisson ratio of the polymer and φ_m is the maximum packing fraction of filler. B is a constant parameter accounting for geometry and interface adhesion. Einstein's equation is applicable only for materials filled with low concentrations of non-interactive spheres. If there is no adhesion between the filler and the matrix, $B = 1$, while for excellent adhesion between filler and interphase, $B = 2.5$. For most polymer blends/composites, B lies between 1 and 2.5. Nielsen's modification of Kerner's equation takes into account the filler, interparticle interactions and the relative modulus of the two constituents[12].

For HDPE/CaCO$_3$ blends, $\nu = 0.5$ and $\varphi_m = 0.637$, and the relative tensile modulus (E^c/E^m) *versus* CaCO$_3$ particle volume fraction is shown in *Figure 1*.

It can be seen that for unmodified CaCO$_3$, Einstein modes can well be used to describe the modulus of HDPE/CaCO$_3$ blends with $B = 1.3$. This indicates that the adhesion between HDPE and unmodified CaCO$_3$ is very weak, with just some physical absorption existing at the interfaces. For modified CaCO$_3$ the modulus of the blends is lower than the theoretical value of Einstein. When CaCO$_3$ is treated with phosphate, it reacts to form calcium alkyl phosphate which is deposited on the surface of the filler particle[13]. This provides CaCO$_3$ with a good hydrophobicity and better physical contact between CaCO$_3$ and HDPE is achieved. This may result in recovery of chain mobility of the interfacial layers and change in morphology of the interfacial layers. The interfacial area is composed of calcium alkyl phosphate and an entanglement structure between the molecular chain of HDPE and the large alkyl phosphate group. Softening of the filler–polymer interface has been used to toughen filled polyolefins by several groups[14–16] and it appears to be the best way of improving toughness. Here phosphate can also be considered as a softening agent. Hence a flexible interfacial area having lower stiffness than the matrix may be expected in HDPE/CaCO$_3$ blends. This explains the way the modulus of HDPE/CaCO$_3$ diverges from the Einstein and Nielsen equations.

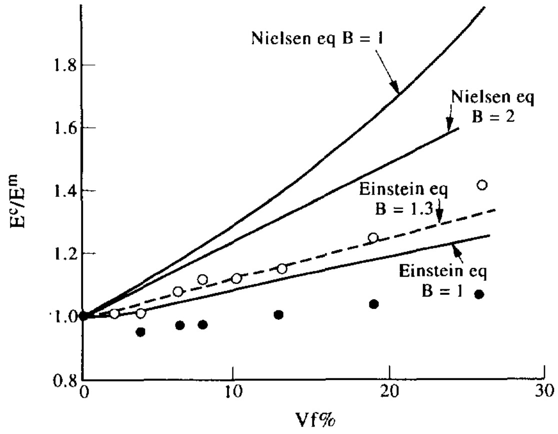

Figure 1 Relative tensile modulus (E^c/E^m) *versus* V_f: (○) HDPE/unmodified CaCO$_3$; (●) HDPE/modified CaCO$_3$

Tensile strength

The lower bound and the upper bound response for the tensile strength of a filled polymer are often represented by the following equations[17,18]:

$$\frac{\sigma_c}{\sigma_m} = 1 - aV_f^b \tag{4}$$

$$\frac{\sigma_c}{\sigma_m} = 1 - aV_f^b + cV_f^d \tag{5}$$

where σ_c is the tensile strength of the filled composite, σ_m is the tensile strength of the polymer, a is a constant related to stress concentrations, V_f is the volume fraction of the filler, b is a constant related to the geometry of the filler, and c and d are constants related to polymer–filler adhesion.

For spherical filler particles having no adhesion to the polymer matrix, $a = 1.21$ and when there is some adhesion, $a < 1.21$; $b = 2/3$ when the sample fails by random fracture and $b = 1$ when the sample fails by planar fracture.

The relative yield stress (σ_y^c/σ_y^m) and relative tensile strength (σ_B^c/σ_B^m) *versus* V_f for HDPE/CaCO$_3$ blends are shown in *Figures 2* and *3*, respectively. It can be seen that both relative yield stress (σ_y^c/σ_y^m) and relative tensile strength (σ_B^c/σ_B^m) for HDPE/modified CaCO$_3$ are higher at $V_f < 16\%$ and lower at $V_f > 16\%$ than those of HDPE/unmodified CaCO$_3$. At $V_f < 16\%$, for unmodified CaCO$_3$, σ_y^c/σ_y^m and σ_B^c/σ_B^m can be described by equation (4) with $a = 1.21$ and $b = 2/3$; for modified CaCO$_3$, $a = 1$,

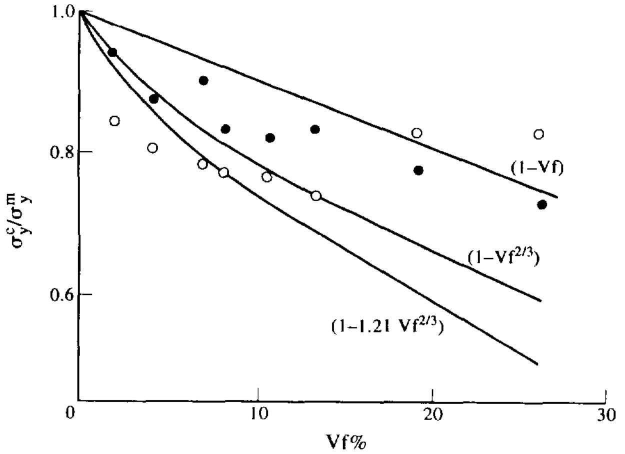

Figure 2 Relative yield stress (σ^c_y/σ^m_y) *versus* V_f: (○) HDPE/unmodified CaCO$_3$; (●) HDPE/modified CaCO$_3$

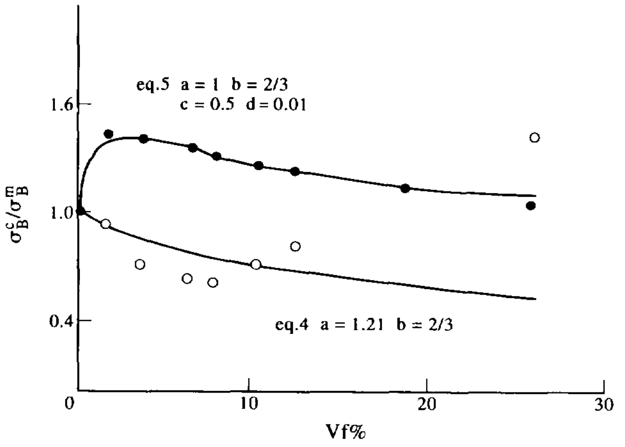

Figure 3 Relative tensile strength (σ^c_B/σ^m_B) *versus* V_f:(○) HDPE/unmodified CaCO$_3$; (●) HDPE/modified CaCO$_3$

$1<b<2/3$. Values of $a=1$, $b=2/3$, $c=0.5$ $d=0.01$ are used for relative tensile strength for equation (5). The selection of values of c and d may have some arbitrariness, but this does not affect the qualitative results of good adhesion between HDPE and modified CaCO$_3$.

At $V_f>16\%$, σ^c_Y and σ^c_B for HDPE/unmodified CaCO$_3$ increase and diverge from equation (4) for $a=1.21$ and $b=2/3$. This is probably due to the fact that the fraction of matrix restrained by unmodified CaCO$_3$ increases as the filler content increases. Both σ^c_Y and σ^c_B for HDPE/modified CaCO$_3$ decrease as the filler content increases. This may be due to the plasticization of phosphate which occurs when the filler content is large.

Now we can conclude that when CaCO$_3$ particles are treated with phosphate, the adhesion between filler and matrix is greatly improved. There exists a flexible interfacial area which has a lower stiffness than the matrix. The stress can uniformly be transferred through the interface and the strength of HDPE is improved.

Force–time curves generated during impact tests

In our previous paper[3], from SEM of fractured surfaces, we divided the impact fracture in HDPE/CaCO$_3$ into three models, i.e. cavitation/crazing, cavitation and shear yielding coexisting, and matrix yielding according to surface-to-surface interparticle distance. However, the conventional measurement of impact strength, leading to the value of the total energy lost by a pendulum breaking a test specimen in a standardized fashion, gives only an overall characterization of the impact behaviour of polymeric materials. In order to obtain more detailed information about the impact process, a Ceast impact tester was used to obtain the force–time curve generated during an impact experiment.

The typical force–time curves for HDPE/modified CaCO$_3$ blends are shown in *Figure 4*. As the CaCO$_3$ content goes from zero to 50 wt%, the fracture mode is brittle up to ~25 wt% CaCO$_3$, then reaches a brittle–ductile transition at ~25–30 wt% CaCO$_3$ and finally becomes completely ductile above 30 wt% CaCO$_3$.

We have reported[3] that when the CaCO$_3$ weight fraction is small (<20–25 wt%), the surface-to-surface interparticle distance (τ) is larger than a critical value (τ_C), i.e. $\tau>\tau_C$. The main way by which the impact energy is dissipated is by cavitation and crazing, and the fracture mode is brittle (*Figures 4A* and *B*). When CaCO$_3$ = 25–30 wt%, $\tau<\tau_C$, and the impact energy is dissipated by cavitation and shear yielding. Above, we infer from the stiffness data that there exists a flexible interfacial area which has a lower modulus than the matrix. The flexible interfacial area is expected to yield prior to the matrix,

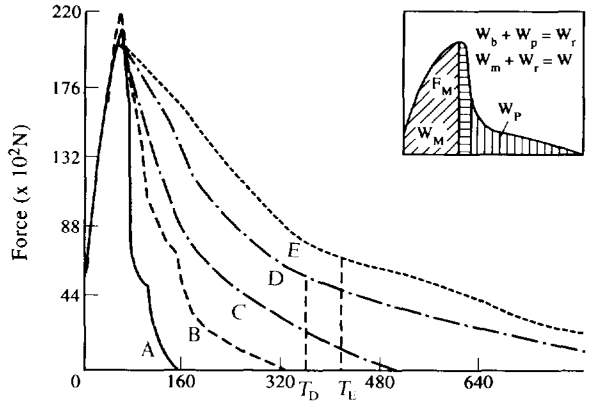

Figure 4 Typical force–time curves generated during impact tests. HPDE/CaCO$_3$: (A) 90/10; (B) 100/0; (C) 75/25; (D) 70/30; (E) 50/50. CaCO$_3$ with a particle size of 6.66 μm and phosphate surface treated

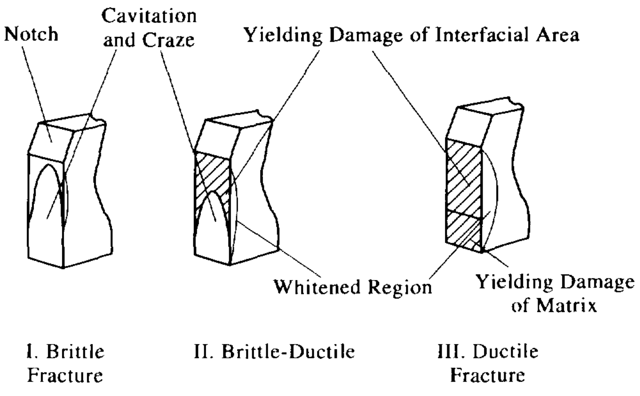

Figure 5 Schematic diagram of the morphology of the notched fracture surfaces

so the shear yielding may be mainly due to yielding of the interface area (*Figure 4C*). As the CaCO$_3$ content increases to 30–50 wt%, τ decreases further, and yielding of the interfacial area may promote matrix yielding. An inflection point (T_D in *Figure 4D* and T_E in *Figure 4E*) can be seen in force–time curves indicating a transition from yielding of the interfacial area to matrix yielding. From this figure we also expect that most of the impact energy may be dissipated by interfacial area yielding rather than matrix yielding. *Figures 5* and *6* show schematic diagrams of the morphology of the notched fracture surfaces and fracture process, respectively. Because it is difficult to tell the difference between interfacial yielding and matrix yielding from SEM more detailed work must be carried out to confirm that interfacial yielding does indeed take place.

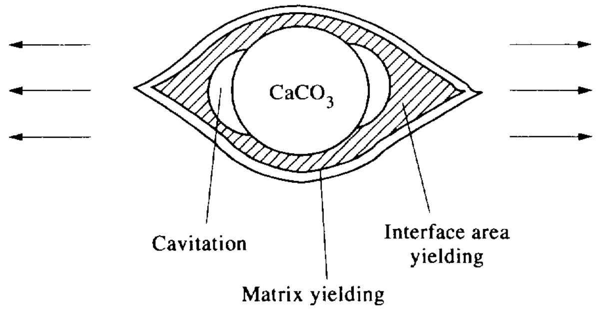

Figure 6 Schematic diagram of the fracture process

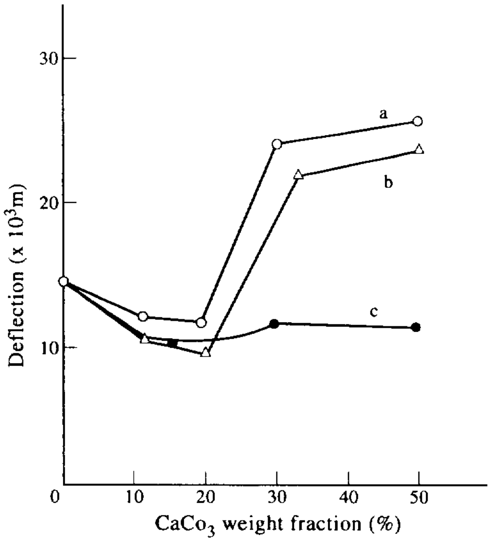

Figure 7 Deflection (X) *versus* V_f in impact tests: (A) 6.66 μm: (B) 7.44 μm; (C) 15.9 μm

If we plot deflection (x) *versus* CaCO$_3$ content, it is very interesting to find that there still exists a sharp transition around a critical weight fraction (w_f) of 22.3% or 25.4%, as shown in *Figures 7A* and *B*, respectively. These values coincide with the onset of the brittle–ductile transition[3]. Beyond the critical content of CaCO$_3$, X reaches a plateau regardless of the CaCO$_3$ particle concentration and size.

Interface conditions of the brittle–ductile transition for HDPE/CaCO$_3$ blends

Previously we have shown that interface adhesion and finer dispersion of particles are necessary to improve the toughness of HDPE/CaCO$_3$ blends, and unmodified CaCO$_3$ cannot be used to toughen HDPE[4]. Here we have shown that yielding of the interfacial area plays a vital role in toughening HDPE. The interface conditions for the brittle–ductile transition of HDPE/CaCO$_3$ blends are: (1) there should be a strong adhesion between the matrix and CaCO$_3$ particle so that the stress is transferred through the interfacial area; and (2) the interfacial area should have a lower stiffness than the matrix and some ability to deform, so that the interfacial area can yield prior to the matrix and induce matrix yielding, whilst maintaining its structural integrity during yielding.

The core–shell model of CaCO$_3$ particle

CaCO$_3$ treated with phosphate can be considered as a core–shell morphology, as shown in *Figure 8*. According to the Tresca or Von Mises criteria, we have:

$$2\tau_{\max} = \max(\sigma_1, \sigma_2, \sigma_3) - \min(\sigma_1, \sigma_2, \sigma_3) \qquad (6)$$

$$\tau_{\mathrm{ocl}} = \frac{1}{3}\sqrt{(\sigma_1-\sigma_2)^2+(\sigma_1-\sigma_3)^2+(\sigma_3-\sigma_1)^2} \qquad (7)$$

where $\tau_{\max}$ and τ_{ocl} are material constants, the critical shear stress and yield stress, respectively, σ_1, σ_2 and σ_3 are principal stresses, which may be written as:

$$\sigma_1 = \frac{1}{2}(\sigma^{rr}+\sigma^{00}) + \frac{1}{2}\sqrt{(\sigma^{rr}-\sigma^{00})^2+4(\tau^{r0})^2} \qquad (8)$$

$$\sigma_2 = \frac{1}{2}(\sigma^{rr}+\sigma^{00}) - \frac{1}{2}\sqrt{(\sigma^{rr}-\sigma^{00})^2+4(\tau^{r0})^2} \qquad (9)$$

$$\sigma_3 = \sigma^{\psi\psi} \qquad (10)$$

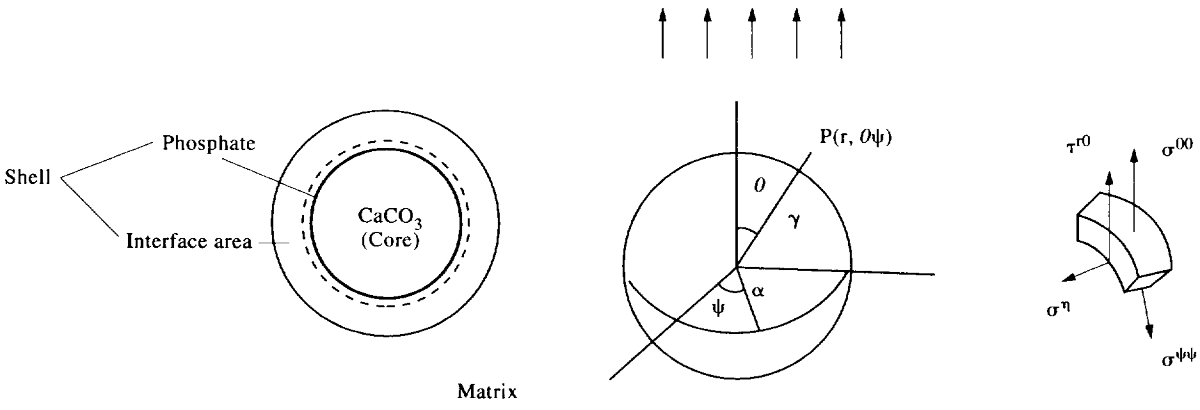

Figure 8 Schematic diagram of core–shell morphology

It has been shown that τ_{max} and τ_{ocl} decay rapidly as the stiffness ratio (G_{matrix}/G_{filler}) increases[19,20]. Therefore, the low shear stress state in the flexible interface area with core–shell morphology ensures the integrity of the interface area and matrix over the entire deformation zone. A schematic representation of the fracture process is shown in *Figure 6*. Here, the most sensitive variable is the thickness of the shell. To obtain a higher modulus than that of the matrix, only a very thin shell is admissible. This requires the adhesion strength to be very strong. The use of a slightly thicker shell lowers the modulus considerably. Hence, a core–shell morphology with very strong interphase adhesion and a very thin shell is necessary to obtain polymeric materials with higher rigidity as well as higher toughness.

CONCLUSIONS

The adhesion between HDPE and CaCO$_3$ can be improved greatly by phosphate treatment. There may exist a flexible interface area, which has a lower stiffness than the matrix. The yielding of the interfacial area plays a vital role in the toughening of HDPE/CaCO$_3$ blends. The three types of fracture behaviour considered were: (1) cavitation and crazing; (2) coexistence of cavitation and interfacial area yielding; (3) interfacial area and matrix yielding. The brittle–ductile transition corresponds to the transition from cavitation-crazing to interfacial area yielding which dissipates larger impact energies.

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