Binary and Ternary Particulated Composites: UHMWPE/CaCO$_3$/HDPE

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ABSTRACT: A study of the influence of employing ultrahigh molecular weight polyethylene (UHMWPE) on the toughness of CaCO$_3$/high-density polyethylene (HDPE) composites was carried out. Binary and ternary HDPE-based composites with calcium carbonate in the range of 0–40% and UHMWPE in the range of 0–50% were produced by twin-screw extrusion followed by compression molding. From tensile and impact tests, it was found that increasing calcium carbonate content increased tensile modulus, but decreased tensile strength, strain at break, and impact resistance. The addition of UHMWPE helped to increase the strain at break and impact resistance of composites moderately without decreasing modulus or strength. The degree of toughening was found to increase with increasing UHMWPE content, but to decrease as the filler volume fraction was increased. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 75: 1503–1513, 2000

Key words: ultrahigh molecular weight polyethylene; particulate filled composites; tensile; impact

INTRODUCTION

Particulate-filled polymer composite is a subclass of composites that offers desired properties with economical cost. The incorporation of rigid inorganic fillers in the commodity plastics, for example, polypropylene and polyethylene, has caused them to be employed in various engineering applications. When the modulus and/or the strength are increased, the decrease in elongation to break and toughness generally results.[1–4] This is frequently stated to be caused by the incompatibility of the fillers and the matrix resulting in low interfacial adhesion. To improve the adhesion, treatment with coupling agent is the method generally employed to achieve greater adhesion.[5–9] In addition to this method, the polymerization-filling technique has also been developed in which the polymer is polymerized directly onto the inorganic filler surface.[10] Another method is to introduce rubbery inclusion into the composites, which are generally composed of two kinds of structure, core-shell and dispersed structure.[11–14] The core-shell type is comprised of rigid filler as a core and rubbery phase as a shell distributed in the polymeric matrix. Accordingly, mechanical properties of this type of composite is complex and governed by the interplay of the matrix, fillers, and interface of various phases. In the case of dispersed structure, it contains a separately random dispersion of rubbery materials in the matrix of the composite. Although the toughness of particulated composites can be improved by these methods, the reduction of modulus, hardness, and strength of the composites is often observed possibly due to the softening of the material by lower modulus rubbery phase.[11,15–16]

Ultrahigh molecular weight polyethylene (UHMWPE) is an engineering plastic which has

Table I   Composition of Composites

Compositions	% Volume Fraction of $CaCO_3$	% Volume Fraction of HDPE	% Volume Fraction of UHMWPE in HDPE
A0	0	100	0
A10	10	90	0
A20	20	80	0
A30	30	70	0
A40	40	60	0
A0U3	0	97	3
A0U12	0	88	12
A20U3	20	97	3
A20U12	20	88	12
A40U3	40	97	3
A40U12	40	88	12
A40U24	40	76	24
A40U36	40	64	36
A40U50	40	50	50

excellent toughness, high wear strength, and abrasion resistance. Due to its very high molecular mass, the polymer melt hardly flows even above its melting temperature. UHMWPE is, therefore, difficult to process. However, a number of reports showed that UHMWPE was able to blend with other polymers, for example, polyether sulfone, polycarbonate, and even high-density polyethylene, to improve the toughness and slow crack growth resistance of materials.[17–20] The purpose of this study is, therefore, aimed at investigating and exploring the use of UHMWPE as an alternative in toughening highly particulate-filled composites in the system of calcium carbonate and high-density polyethylene (HDPE).

MATERIALS AND METHODS

Materials

Matrix material was HDPE (grade 7000F; Bangkok Polyethylene Co., Ltd., Bangkok, Thailand). Binary composites were composed of HDPE and calcium carbonate powder grade Omega (average particle size 5.53 μm), supplied by Lime Quality Co., Ltd., Bangkok, Thailand. Ternary composites are comprised of binary composites and the addition of UHMWPE (GUR 4150; Hoaest Co., Ltd., Germany).

Sample Preparation

Binary and ternary composites were prepared by mixing raw materials in a corotating twin-screw extruder (Betol BTS40L) producing composites with filler volume fractions ranging from 10 to 40% and UHMWPE volume fraction from 3 to 50% (Table I). The composite pellets were then powderized by a centrifugal mill through a screen mesh of 0.5 mm with the help of liquid nitrogen to prevent oxidation. Sheets of these composites (4 mm) were prepared by compression molding. ISO 527 half-sized tensile specimens were cut from the sheets using a contour cutter. The machined surface was subsequently smoothed by a fine abrasive paper.

Tensile Test

Tensile tests were performed on a universal testing machine (Instron 5583). Dumbbell-shaped tensile specimens (gauge length, 25 mm) were tested according to ISO 527. Tensile modulus was taken as the slope of the initial part of stress–strain curve and yield was determined from the maximum point where the slope of load-elongation curve reached zero. The yield stress was the load at the maximum point divided by the initial cross-sectional area. All tests were carried out at 23°C and 60% relative humidity (RH). The measurements were performed at constant crosshead speeds of 5 mm min^{-1}.

Impact Test

Izod impact test was carried out according to ASTM D256. The test was carried out at 23°C and 60% RH on an instrumented impact tester, Rad-
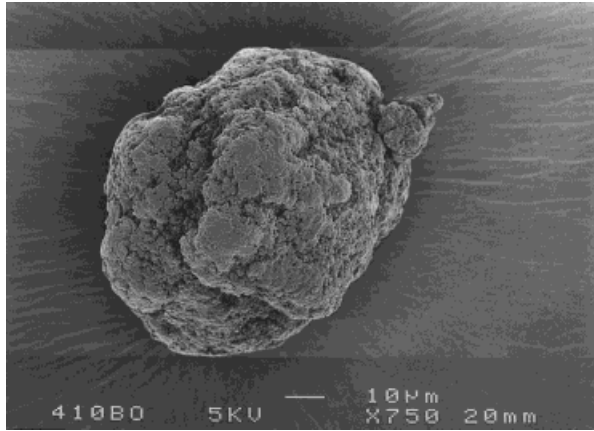
Figure 1 SEM micrograph of as-received UHMWPE particle.

mana ITR-2000, with a notched specimen. The machine employed a pneumatic system to deliver the dynamic force onto the specimens. The impact speeds were constant during the test at a velocity of 3.4 m s^{-1}.

Morphology Observation

Morphology of composites were viewed macroscopically using reflected light microscope (Carl Zeiss, Axiotech) with bright-field mode. Prior to observation, the samples were ground on various grades of silicon carbide paper down to 4000 grit. The specimens were then polished with a napped cloth impregnated with 6-, 3-, and 1-μm diamond paste.

Fractography

Fractured samples of composites were viewed microscopically using a scanning electron microscope (JEOL JSM-5410) at the accelerating voltage of 5 kV. The samples were gold sputtered prior to the observation.

RESULTS

Morphology of Composites

Figure 1 shows the SEM micrograph of as-received particle of UHMWPE before blending. It can be observed that the particle was equiaxed in shape. Figure 2 shows optical micrographs of the polished surface of binary composites, A0, A20, and A40. Calcium carbonate particles appeared darker than the polyethylene matrix and are dis-

persed randomly throughout the matrix. However, in the case of 0.4 filler volume fraction composite, the filler amount was so high that the optical microscope could not distinguish between phases. The optical micrograph, however, appears darker than that of the unfilled polyethylene. Figure 3 illustrates optical micrographs of polished surface of ternary composites, A0U12, A20U12, and A40U12. It can be seen that the
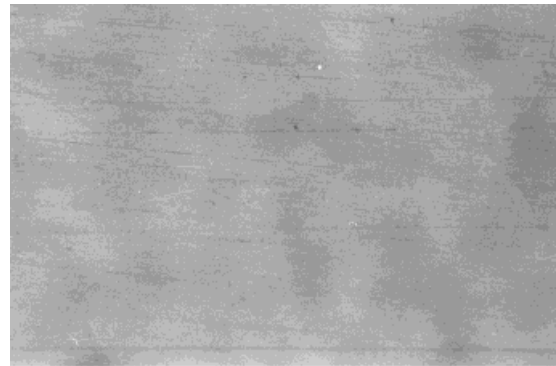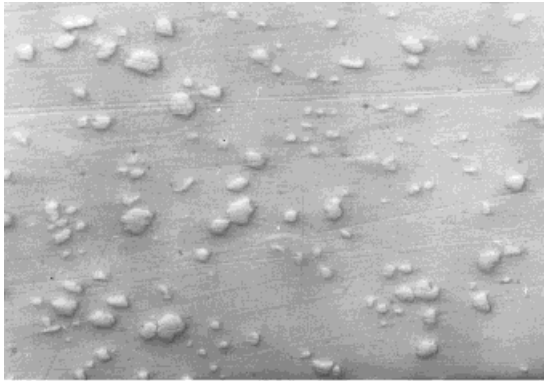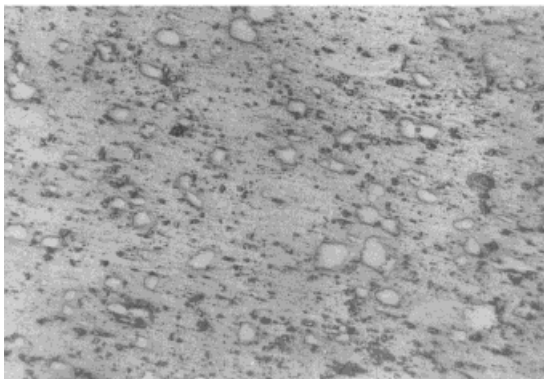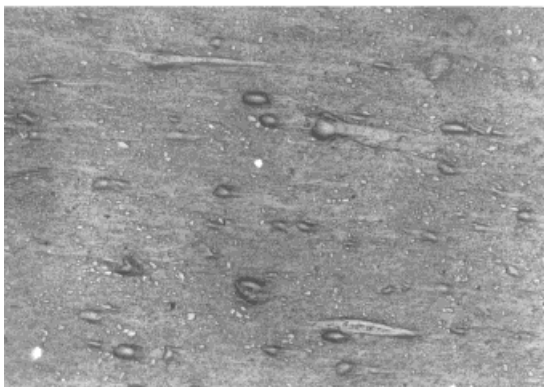

(a)
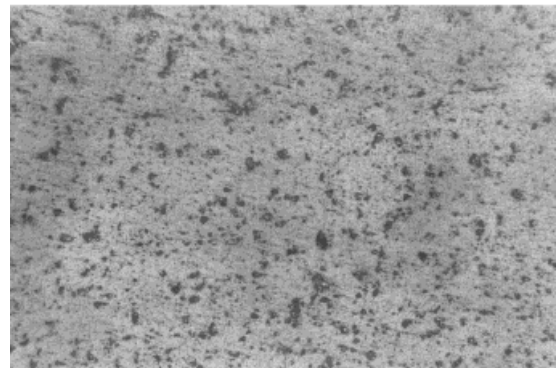
(b)
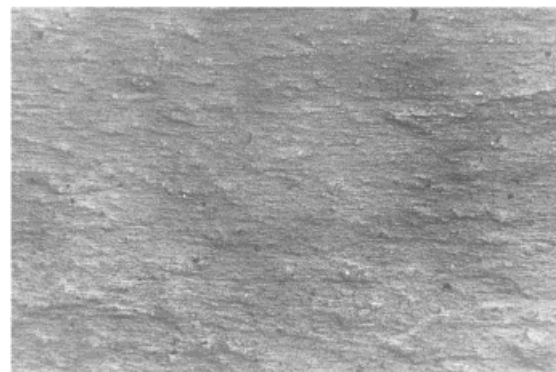
(c)

Figure 2 Optical micrographs of polished surface of binary composites; (a) A0, (b) A20, and (c) A40.

(a)

(b)

(c)

Figure 3   Optical micrographs of polished surface of ternary composites; (a) A0U12, (b) A20U12, and (c) A40U12.

UHMWPE is not miscible with HDPE and each particle is dispersed randomly as an additional phase in the composites.

Mechanical Properties

Figure 4 shows the variation of tensile modulus and tensile strength with $CaCO_3$ content. In gen-eral, the incorporation of $CaCO_3$ particles in polyethylene matrix resulted in the increase in tensile modulus exponentially with an increase in filler concentration. In contrast, the tensile strength decreased as the $CaCO_3$ content increased. The decrease was large at low filler fraction, but leveled off when the filler concentration was greater than approximately 20%. Tensile strain at break and notched Izod impact energy also decreased with increasing filler content (Fig. 5). Figure 6 shows the effect of the addition of UHMWPE on the tensile modulus of ternary composite based on 0.0, 0.2, and 0.4 $CaCO_3$ volume fraction composites. It can be observed that tensile moduli of composites are not significantly affected by the inclusion of UHMWPE. Tensile modulus of ternary composites were all equivalent to the values of binary composites. Figure 7 illustrates the variation of tensile strength of composites with and without UHMWPE fraction. It can be seen that the tensile strength is unchanged by the addition of UHMWPE similarly to the tensile modulus values. In contrast, tensile strain at break of ternary composites increases with increasing UHMWPE content (Fig. 8). However, in the case of unfilled polyethylene and ternary composite without calcium carbonate, the specimen did not break in the tensile test. Therefore, the effect of UHMWPE addition on tensile strain at break for these compositions was not able to be illustrated in this study. Impact studies of the influence of UHMWPE on toughness of composites is shown in Figure 9. It was found that notched Izod impact energy of composites increased with the increase in UHMWPE volume fraction. Nevertheless, 0.4 filler-volume fraction-based composite, A40U3 and A40U12, did not show the increase in the impact energy compared to the one without UHMWPE, A40.

DISCUSSION

The result of incorporating $CaCO_3$ particles into polyethylene matrix is to increase the modulus of the system. This is obviously caused by the increase in the higher modulus filler fraction in the system. Therefore, the greater the $CaCO_3$ concentration, the higher the modulus the composites achieve. The correlation between the increase in modulus and filler volume fraction is observed to be not linear, but a power function. At low filler content, only filler–matrix interaction occurs in the system. However, when the filler content is up
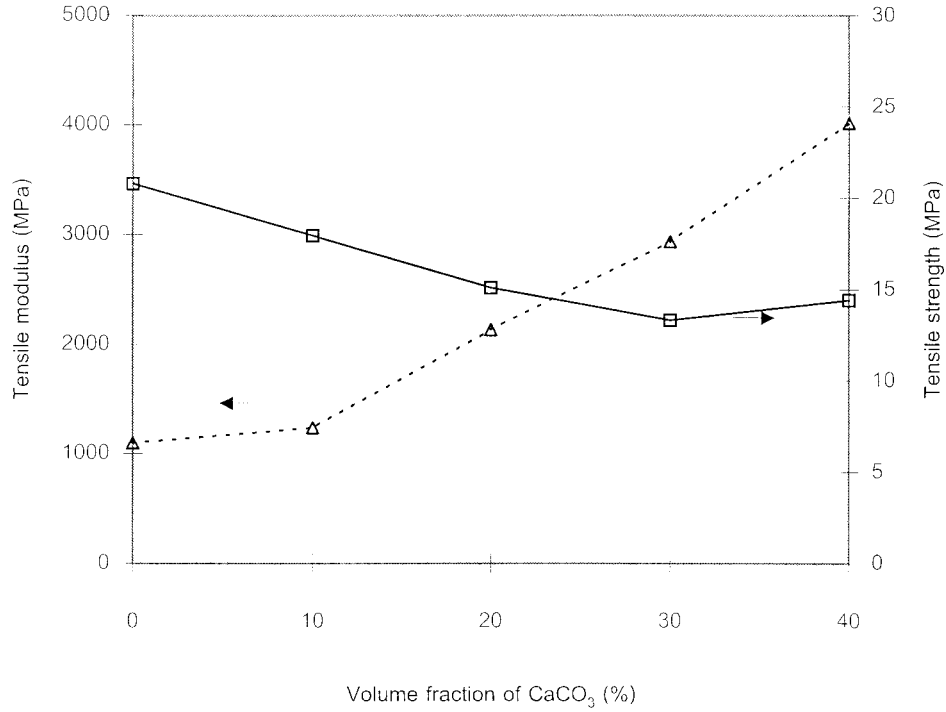
Figure 4   Influence of CaCO$_3$ volume fraction on tensile modulus and tensile strength of composites.
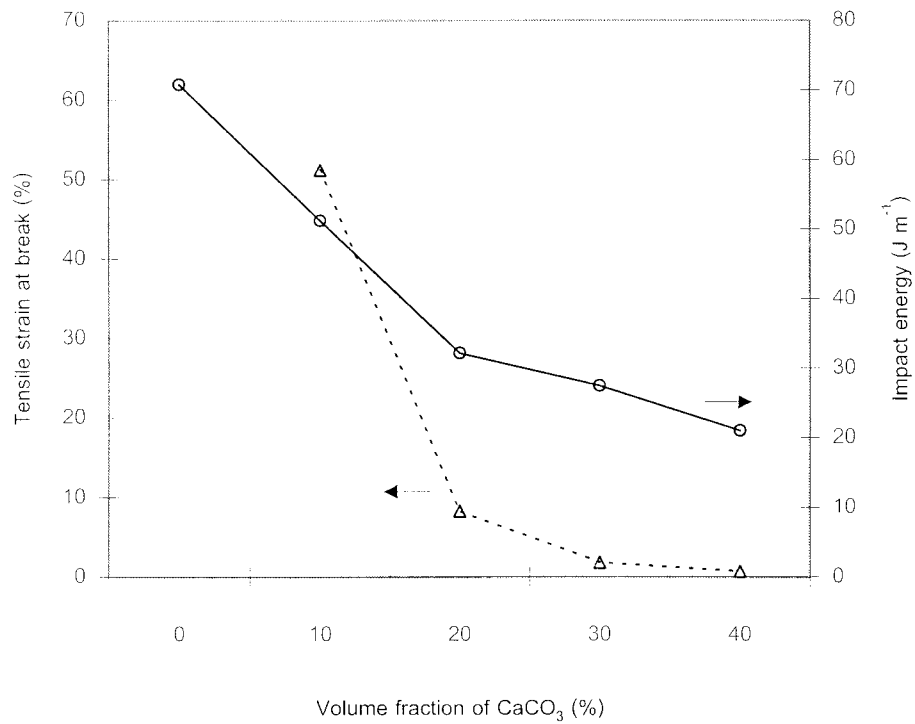

Figure 5   Influence of CaCO$_3$ volume fraction on tensile strain at break and notched Izod impact energy of composites.
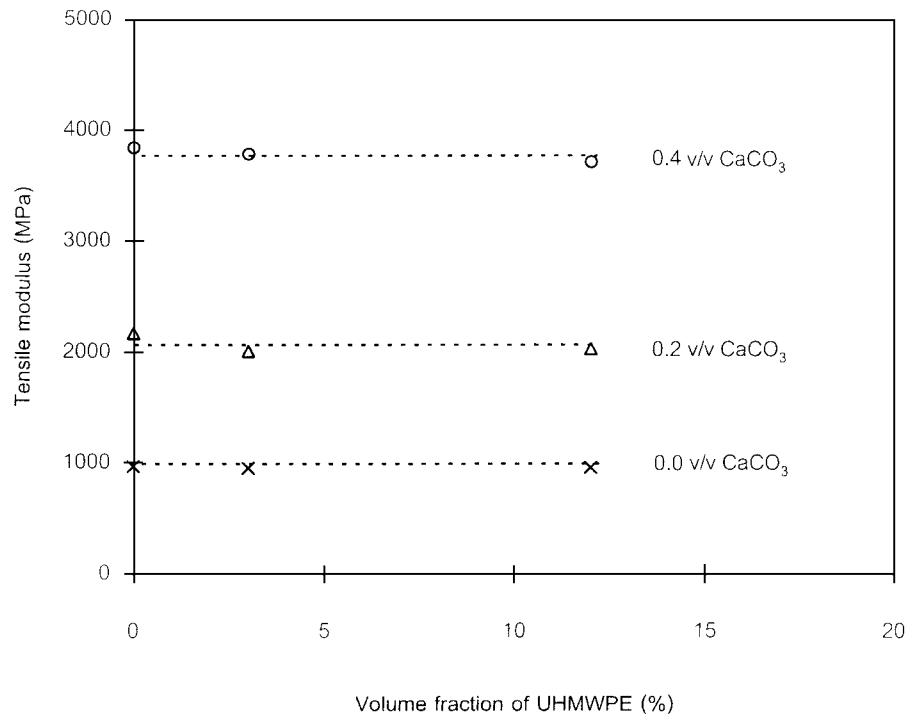
Figure 6   Influence of UHMWPE volume fraction on tensile modulus of 0.0, 0.2, and 0.4 v/v CaCO₃/HDPE-based composites.
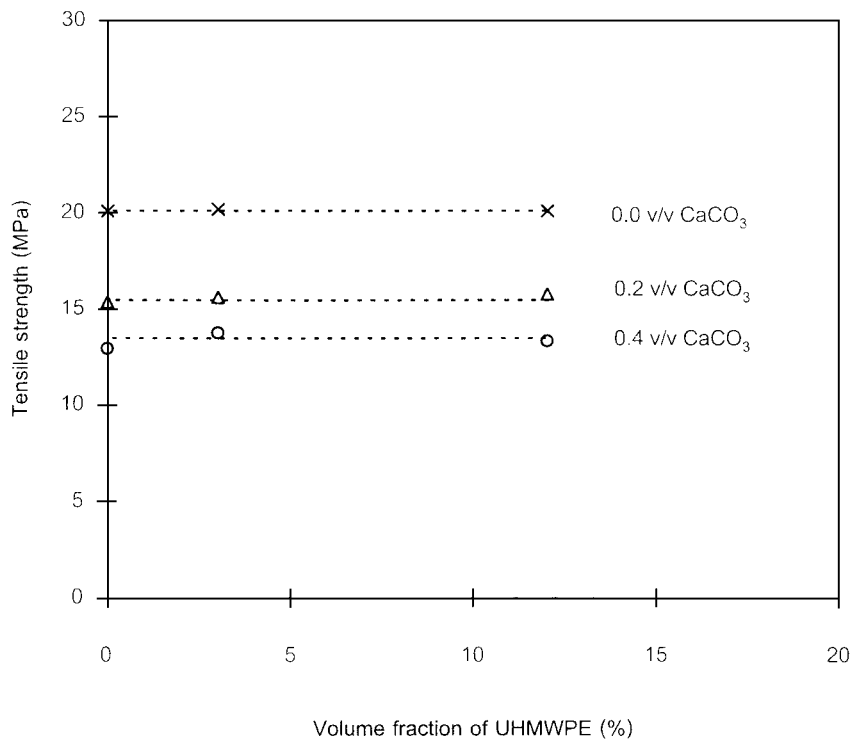

Figure 7   Influence of UHMWPE volume fraction on tensile strength of 0.0, 0.2, and 0.4 v/v CaCO₃/HDPE-based composites.
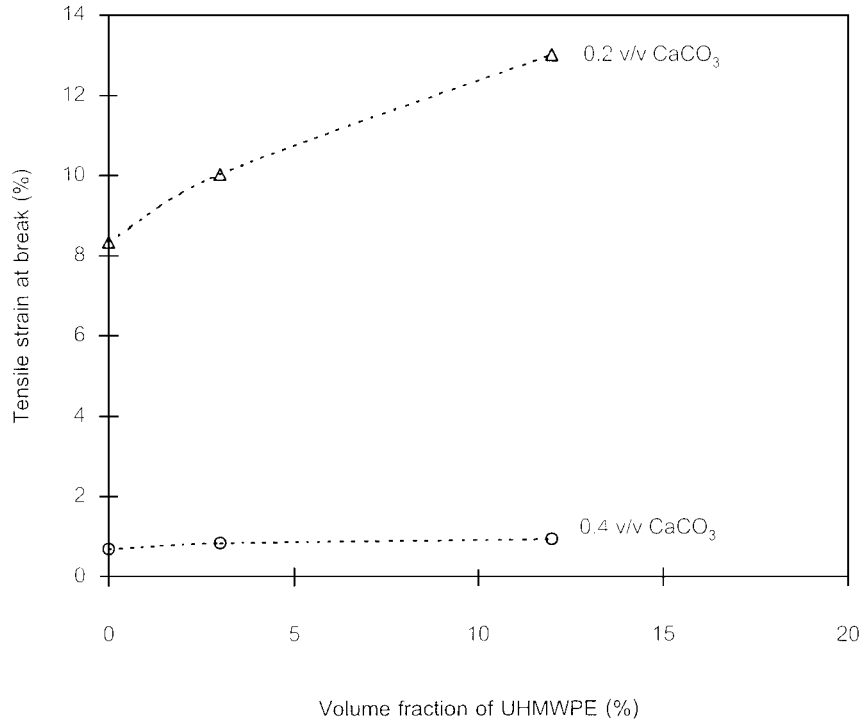
Figure 8   Influence of UHMWPE volume fraction on tensile strain at break of 0.2 and 0.4 v/v CaCO$_3$/HDPE-based composites.
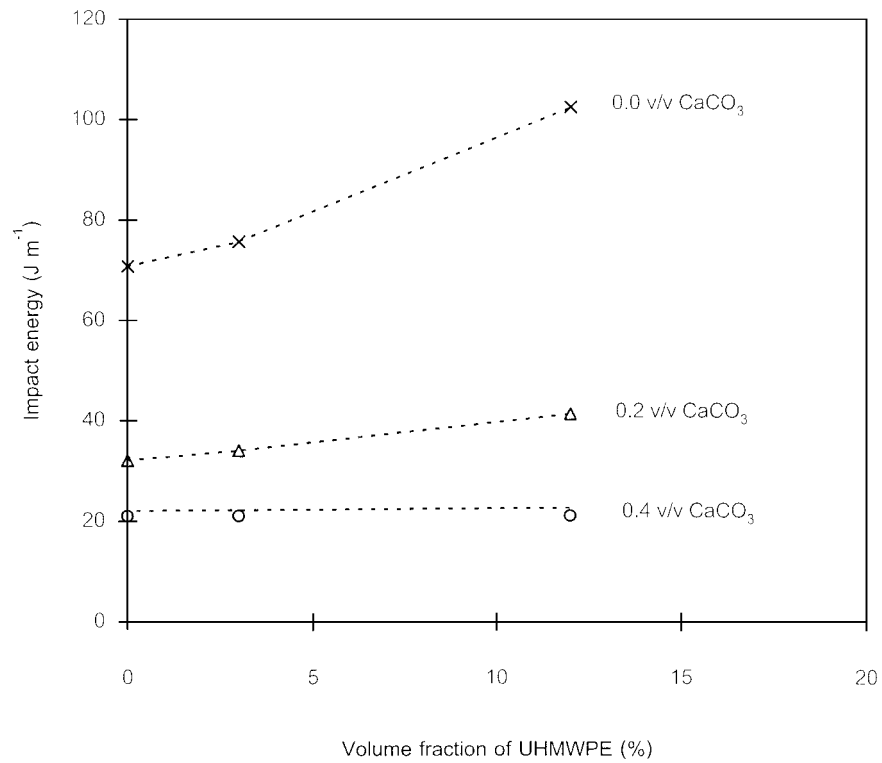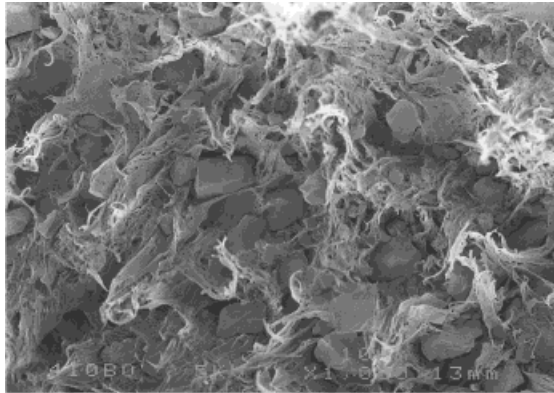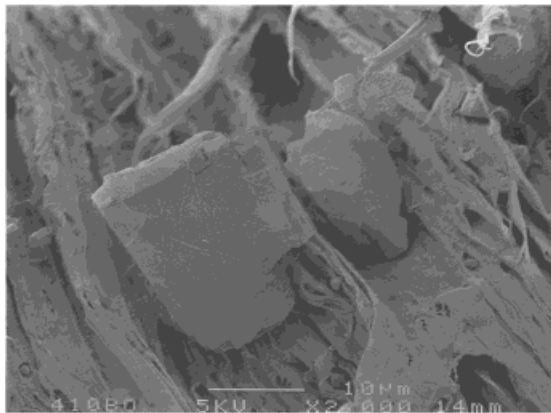

Figure 9   Influence of UHMWPE volume fraction on notched Izod impact energy of 0.0, 0.2, and 0.4 v/v CaCO$_3$/HDPE-based composites.

Figure 10 SEM micrographs of fracture surface of binary composite after tensile test; (a) A20, (b) A20 at higher magnification.

to a certain high filler level, the filler–filler interaction will also play a role in addition to the filler–matrix interaction. Thus, the modulus will not increase proportionally when the filler concentration is high.[21]

The fall of tensile strength, tensile strain at break, and impact energy of composites is obviously due to the presence of fillers. These rigid fillers can act as defects and stress raiser in the composites if the filler is weak or the interface adhesion between fillers and matrix is not strong,[1] which is the case for calcium carbonate–polyethylene composites in the present study. The evidence of weak interface can be clearly observed from the scanning electron microscope micrographs of the fracture surface of the composites after being tested in tension. The micrographs reveal the fibrils of HDPE around calcium carbonate particles and the clean surface of calcium

carbonate particles without the presence of polyethylene layer (Fig. 10). It means that polyethylene debonded completely from calcium carbonate particles by breaking the interface. This results in the decrease in tensile yield stress with increasing filler content, which corresponds to the increase in stress concentration and possible weak points with the increase in calcium carbonate volume fraction. During tensile loading, the interface between polyethylene and calcium carbonate is pulled apart. Then, the fillers debonded from the matrix initiating microcrack with statistically distributed sizes and direction. This debonding changed the recoverable elastic region to irrecoverable plastic region which satisfied the general definition of yielding. Debonding is normally created at a low-stress level and then grows larger, leading to the interruption of load transfer to the matrix. Once the separation is sufficient, the sudden drop of the load is observed, which is a yielding phenomena in load-elongation curve. When the samples were stressed further beyond yield point and the size of the cracks is critically large, these cracks will grow rapidly with successive nucleation and microvoid coalescence, leading to the failure of the whole material at last.

In the case of ternary composites, UHMWPE fraction was observed to exclude from the HDPE/CaCO$_3$ mixture since its high viscosity prevents HDPE or CaCO$_3$ to mix in (Fig. 3). The high elastic behavior and strength of UHMWPE was, therefore, not affected by the presence of filler. This area can, therefore, help in counterforce with respect to the applied force and retard the propagation of the crack. Figure 11 shows the typical
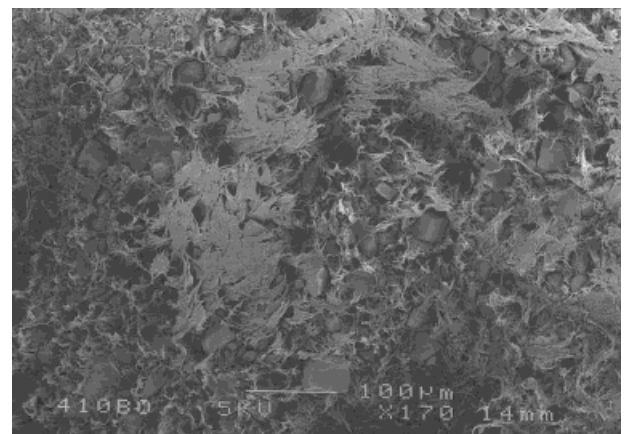

Figure 11 SEM micrograph of fracture surface of ternary composite, A40U36, after tensile test. Fibril extension of UHMWPE is observed.

Table II   A Comparison of Increase in Tensile Strain at Break and Impact Energy of Certain Composites

Based Composite	Volume Fraction of UHMWPE (%)	% Increase in Tensile Strain at Break[a]	% Increase in Izod Impact Energy[a]
0.0 v/v CaCO$_3$	3	N.A.[b]	6.95
	12	N.A.[b]	44.71
0.2 v/v CaCO$_3$	3	20.30	6.21
	12	55.82	21.28
0.4 v/v CaCO$_3$	3	21.44	0.28
	12	34.40	0.57

[a] Compared to 0% volume fraction of UHMWPE.
[b] Specimens did not break in the tests.

fracture surface of ternary particulated composites. It can be seen that, generally, the surface is similar to the fracture surface of binary composite. However, there are areas of larger, coarser, and longer fibril extension of UHMWPE in addition to the normal limited fibril extension around the filler particles. Therefore, UHMWPE does not detach from the HDPE matrix, but rather bonds strongly to the matrix and toughens the composites by its extension. This mechanism is similar to previous investigation by Huang et al., who observed the retardation of the slow crack growth by blending UHMWPE into HDPE. The inclusion of UHMWPE into the binary-particulated composite can, therefore, increase the ductility of the composites resulting in greater strain at break and impact energy compared to the composites without UHMWPE. However, when being compared to rubber, it is not surprising that UHMWPE is less effective than rubber in toughening mechanism. This is due to the fact that UHMWPE is less ductile and elastic. However, this UHMWPE toughening was achieved without a decrease in modulus and strength of the system as normally found in the case of rubber toughening.[11,15,16] It can be seen that both tensile modulus and tensile strength of composites are comparable regardless of the UHMWPE content (Figs. 6 and 7). The independence of modulus and strength on the UHMWPE concentration is due to the fact that the modulus of UHMWPE is on a similar level as that of HDPE and the tensile strength is even greater. Therefore, the incorporation of UHMWPE into HDPE will not deteriorate the stiffness and strength of the whole system, unlike the inclusion of the low-modulus rubbery phase.

The effectiveness of toughening is observed to increase with increasing UHMWPE content, but decrease as the CaCO$_3$ is increased (Table II). In the case of HDPE/UHMWPE blend, A0U0, the effectiveness of toughening is greatest because UHMWPE is in the similar class of polymers as HDPE. Although they are immiscible, the compatibility between phases still exists, providing strong interface adhesion. The applied load is, therefore, able to be transferred effectively, which results in greater ductility of the blend. When calcium carbonate is incorporated in the composites, the area of contact between UHMWPE and HDPE is decreased and substituted by the contact area of CaCO$_3$/HDPE and CaCO$_3$/UHMWPE. As observed previously, the compatibility between CaCO$_3$ and polyethylene is not relatively high. Therefore, the load transfer area in the composites is reduced as a result. The effectiveness of UHMWPE toughening is, therefore, decreased as the calcium carbonate content increases. When the filler concentration is at the highest level in this study, 40%, impact energy is even unchanged by UHMWPE addition, but tensile strain at break is slightly increased. This means that the effectiveness of UHMWPE toughening at high filler-volume fraction is limited. To investigate whether greater concentration of UHMWPE will be able to toughen the 0.4 filler-volume fraction-based composites or not, the content of UHMWPE was then increased further, up to 50%. Figures 12 and 13 show that regardless of the UHMWPE fraction in 0.4 filler-volume fraction-based composite, there is still no apparent effect on the tensile modulus and impact energy as observed previously. However, tensile strain at break and tensile strength increased with increasing UHMWPE content when the UHMWPE volume fraction was beyond 12%. Because the strength of UHMWPE is greater than HDPE, it is possible that a high concentration of UHMWPE incorporated, which substitutes the HDPE fraction will help to coun-
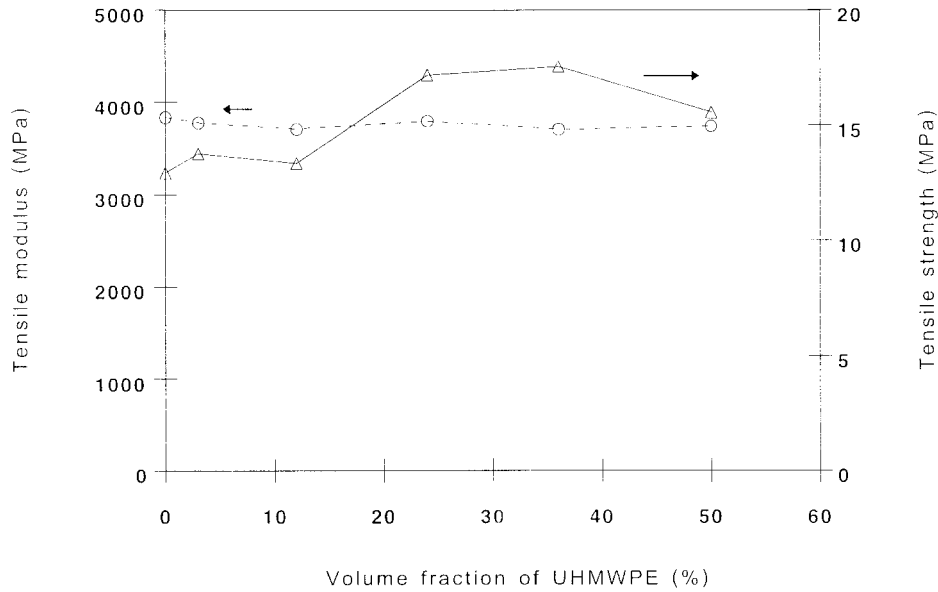
Figure 12 Influence of UHMWPE volume fraction on tensile modulus and tensile strength of 0.4 v/v CaCO$_3$/HDPE-based composites.

terforce the applied load, thus increasing the tensile strength of the composite. The difference trends between tensile strain at break and impact energy data may be due to a combination of the high loading of filler and the difference in the rate of applied force employed in the test.[22] In the case of impact test, dynamic force is delivered to the specimen at the velocity of 3.4 m s^{-1}, whereas the rate of 5 mm min^{-1} (8.3 × 10^{-5} m s^{-1}) is employed in tensile test. The rapid crack propagation in impact condition may not permit UHMWPE to absorb energy effectively as in a comparatively slow tensile test.

CONCLUSIONS

The incorporation of calcium carbonate in HDPE matrix increased the modulus of composites with
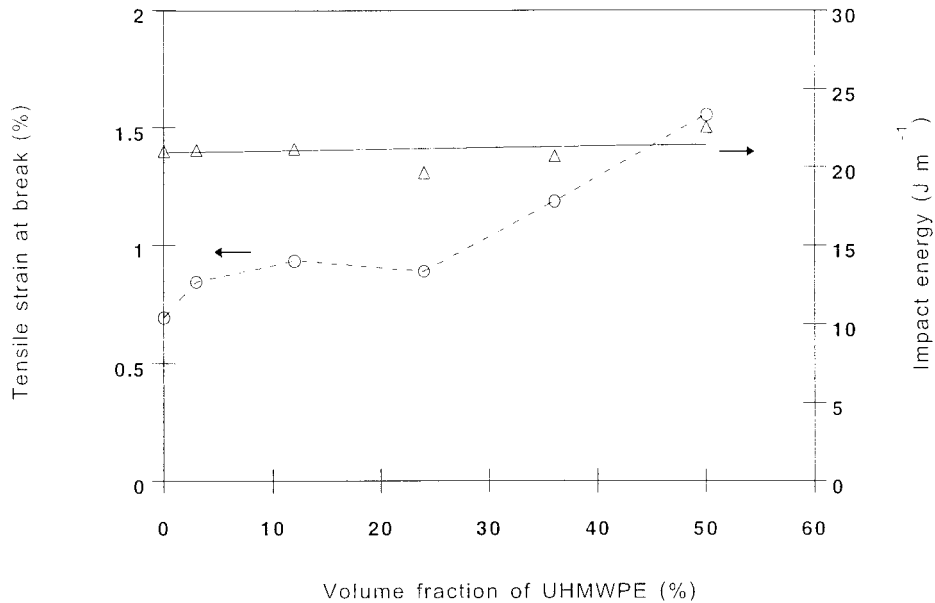
Figure 13 Influence of UHMWPE volume fraction on tensile strain at break and notched Izod impact energy of 0.4 v/v CaCO$_3$/HDPE-based composites.

the reduction in tensile strength, tensile strain at break, and impact resistance. The addition of UHMWPE in the particulate-filled composites increased the ductility of composites by counterforcing the applied load and retarding the crack propagation without a decrease in modulus or tensile strength. The effectiveness of the toughening depended on both UHMWPE and filler content. The greater the concentration of UHMWPE, the higher the degree of toughening of the composites, whereas the increase in filler content decreased the effectiveness.

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