Effect of Both Uncoated and Coated Calcium Carbonate on Fracture Toughness of HDPE/CaCO$_3$ Nanocomposites

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ABSTRACT: The main goal of this research is to investigate the effect of nano-CaCO$_3$ coated with different content of stearic acid on fracture toughness of HDPE/CaCO$_3$ nanocomposite. For this purpose, HDPE/10 vol % CaCO$_3$ nanocomposites were made using a twin-screw mixer–single-screw extruder. Nanocomposite standard samples were prepared via injection molding method. Three-point bending tests and microscopic evaluations were performed. The results of fracture toughness test showed that the addition of uncoated nano-CaCO$_3$ to HDPE causes to decrease fracture toughness, but it can be increased slightly as stearic acid content added. Also the results showed that the stress whitening zone width depends strongly on both CaCO$_3$ and stearic acid content. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 3688–3694, 2007

Key words: nanocomposite; calcium carbonate; HDPE; surfactant; fracture toughness

INTRODUCTION

The demand market of high-density polyethylene (HDPE) is increasing because of its vast applications, especially for automotive and industrial applications. But its applications have been limited compared to its potential, since its mechanical properties are not high enough for some industrial applications.

To improve the physical and mechanical properties of HDPE, addition of filler, rigid particles, and even elastomer to HDPE is very common. One of the most important filler, which is added to PE, is CaCO$_3$. It can be widely used as filler for almost all polymers. It is inexpensive and can be used at high loading. It is available in different grades: dry processed, wet, or water ground, and can be easily surface treated. Precipitated calcium carbonate (PCC) can be produced in all three crystal modification of CaCO$_3$ and in a wide variety of particle sizes and shapes, including plates and acicular forms. However, only the calcite form with a rhombohedric cell and low aspect ratio has found much commercial application in polymers.

According to author's knowledge, there are some approaches on HDPE composites.[1–20] The first approach paid attention to dependency of mechanical properties of composite on filler particle size.[1–13]

The results showed that tensile behavior of filler-reinforced polyethylene can be increased as the filler size decreased.[1–7] Also it is reported that whenever the secondary phase with nanosize is used, excellent increasing in thermal and mechanical properties can be observed.[8–12] The second approach focused on role of filler size on rheological properties of HDPE/CaCO$_3$ composites.[13–16] The results of this approach showed that carbonate calcium has a big significant effect on rheological behavior of HDPE.[16] Also it is observed that decreasing particle size can act as a barrier during processing of polymer.[17–19] The third approach concentrated on the effect of surface treatment on tensile properties of HDPE/CaCO$_3$ nanocomposites.[17–19] To improve toughness, it is necessary to obtain a sufficient particle matrix adhesion. And so, using optimum amount of surfactant, such as stearic acid (SA) or other fatty acid, can be a good way to make an uniform dispersion with suitable adhesion. Recently, a few papers have reported toughening of polyethylene and polypropylene with small CaCO$_3$ particles coated with SA.[2,5,7,16,20] For example, Lazzeri et al.[16] studied the effect of SA on the mechanical properties of HDPE/CaCO$_3$ nanocomposites. The results showed that the addition of 10 vol % nanosized CaCO$_3$ to HDPE causes to decrease both Young's modulus and yield stress of the composite, but does not change the tendency of the material to neck and draw. The addition of coated nanosized CaCO$_3$ could compensate decreasing of the tensile properties, compared to the uncoated PCC.[16]

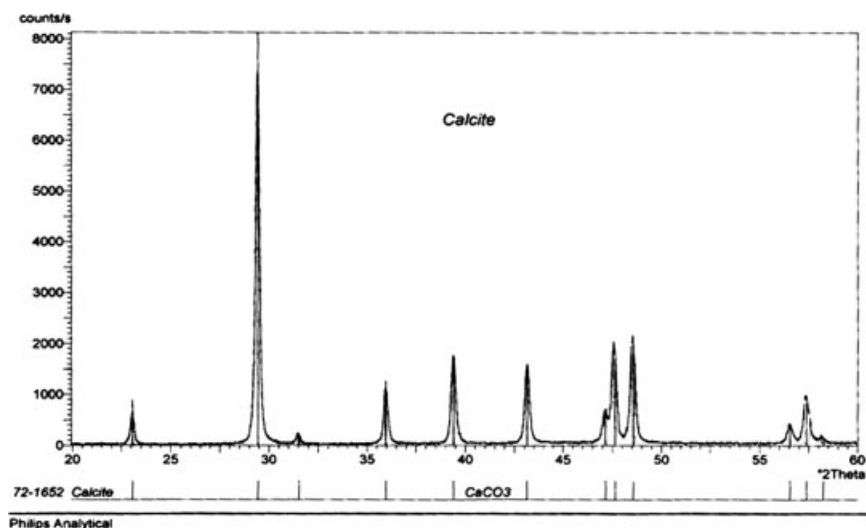*Correspondence to:* S. M. Zebarjad (zebarjad@ferdowsi.um.ac.ir).

Figure 1 XRD spectrum of CaCO₃.

In spite of importance of fracture toughness of polymer nanocomposites, there are a few papers which are concentrated on nanocomposites fracture toughness.[21–24] Nissel et al.[21] studied the effect of nanoparticles on interfacial fracture toughness and dynamics. They showed that the addition of small amount of nanoparticles can drastically reduce the interfacial fracture toughness between polymers.

Dependency of fracture toughness of a commercial epoxy on organoclay has been investigated by Weiping et al.[22] The results showed that fracture toughness of the nanocomposite increased by 1.7 times as organoclay content increased to 1 wt %. Investigation on fracture mechanism of epoxy-silica nanocomposites produced by dispersing silica-organosol particles showed that the addition of silica nanoparticles up to 10 wt % brings about a considerable enhancement in fracture toughness and an increase in the critical crack length for the onset of crack propagation.[23]

Since there is no evidence of any paper, which is focused on role of surfactant on fracture toughness of HDPE nanocomposite, it is decided to clarify the subject which is still under debate. Thus, the main goal of this research is to find out the effect of both untreated and treated CaCO₃ with different content of SA on fracture toughness of HDPE/CaCO₃ nanocomposites.

EXPERIMENTAL

Material

High-density polyethylene (HDPE) Eltex B4020 from Solvay Polyolefins, Rosignano, Italy, was used. The filler particles were SOCAL® PCC obtained from Solvay SBU Advanced Functional Minerals, Salin de Giraud, France. The purity of used powder was

determined using XRD method. Figure 1 shows the spectrum of used nano-CaCO₃ with calcite structure.

Since the main goal of the current research was to investigate role of surface treatment on performance of CaCO₃, three kinds of CaCO₃ with different SA content were employed. Figures 2 and 3 show the scanning electron and transmission electron micrographs taken from the nanoparticles used, respectively. As it can be seen, the morphology of used particles is irregular, and the average particle size is about 70 nm. The specifications of materials used are shown in Table I. Just for simplicity, the coated nano-CaCO₃ is coded as illustrated in Table I.

Sample preparation

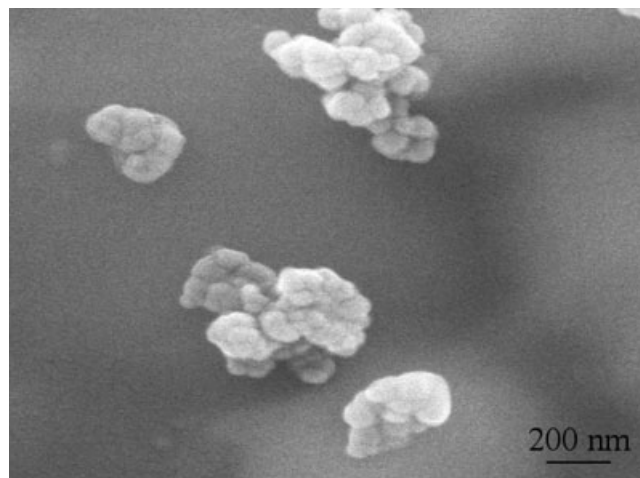Before mixing, PCC powders were dried under vacuum for a minimum of 8 h. Oven-dried PCC powders

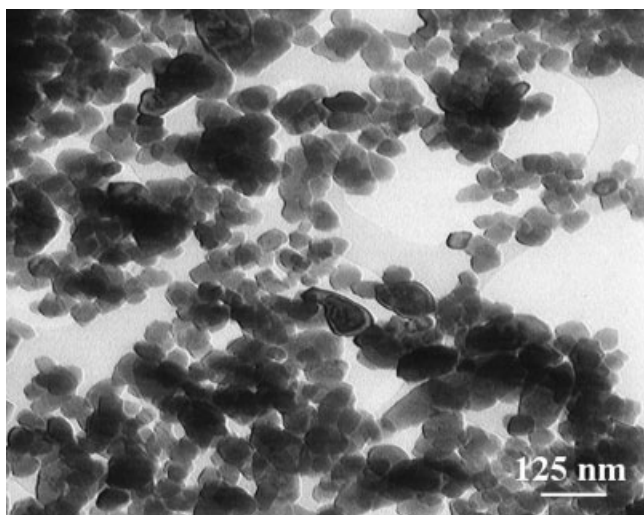**Figure 2** Scanning electron micrograph of the nano-CaCO₃ powder.

Figure 3 Transmission electron micrographs of the nano-CaCO₃.

and HDPE pellets were first mechanically mixed to achieve HDPE/10 vol % CaCO₃ nanocomposites. The mixed HDPE and CaCO₃ were extruded at two stage processing unit composed by a twin screw noninter-meshing corotating mixture (Comac Plast, Milano) and a MV45 single-screw extruder (Comac Plast, Milano). The temperature in different zones of extruder was kept constant from 160 to 200°C. The fracture toughness standard specimens were made using injection molding method. The nanocomposites are coded as shown in Table II.

Three point bending test

Three point bending tests were carried out according to ASTM 5045 standard. The dimensions of all samples including HDPE and its nanocomposites were chosen $280 \times 12 \times 6$ mm^3. To produce a precrack, a razor blade, which had been chilled at low temperature, was used. The chilled razor blade was used to avoid plastic deformation during making a precrack. Triple bending test were carried out with a Zwick tensile machine at a strain rate of 0.4 min^{-1}. Three samples for each type of material were tested at room temperature.

TABLE I
Specifications of PCC Powders

Material	Nominal SA/PCC weight ratio (gram acid/ kilogram PCC)	MOT measured by gravimetry (gram acid/ kilogram PCC)	SA surface concentration (mg/m²)
PCC00	0	0	0
PCC20	20	23.7	1.48
PCC40	38	40.7	2.14

TABLE II
Specification of the Nanocomposites

Material	PCC volume content (%)	Nominal SA/PCC weight ratio (gram acid/kilogram PCC)
Pure HDPE	–	–
PCC100	10	0
PCC120	10	20
PCC140	10	40

Microscopic evaluation

Transmission electron microscope (TEM LEO 912AB (120 kV) with line resolution of 3 Å was performed for observing the nanoparticles. Also to clarify the role of uncoated and coated CaCO₃ particles on fracture mechanism of HDPE nanocomposite, both optical and scanning electron microscopes were used. The stress whiting zone (SWZ) in front of precrack was measured directly by polarized light. An LEO1450VP scanning electron microscope with tungsten filament and 20 V accelerating voltage was used to study the fracture surface of selected samples. The specimens were coated, via a sputter coater with a thin layer of Pt, before microscopic evaluation to avoid charge built up.

RESULTS AND DISCUSSION

A few words must be devoted to the fracture toughness values presented in this work. Considering the yield stress data measured for these materials, KC on our materials including neat HDPE and its nanocomposites does not meet the size limitations for plane strain fracture parameter given by test protocol (1990 testing protocol approved by European Structural Integrity Society (ESIS)). As a matter of fact, the thickness of the sample used is much lower than the real thickness for determination of plane fracture toughness. Thus, one may conclude that the fracture toughness measurements for all the nanocomposites (including unfilled HDPE) cannot satisfy the LEFM requirements. This is similar to what proposed by Zebarjad et al.[25] during determination of fracture toughness of PP and its blend and what reported by Hooley and Moore[26] In fact, they showed that plane strain fracture toughness of PE can be achieved at room temperature if the sample thickness is more than 255 mm.[26] The simple fact that the injection machine necessary to mold such thick samples does not yet exist, it means it would be absurd to compare hypothetical fracture results obtained on samples of such thickness.

Figure 4 shows the load-displacement curves of HDPE and its nanocomposites. The values of fracture toughness can be achieved by using the maximum
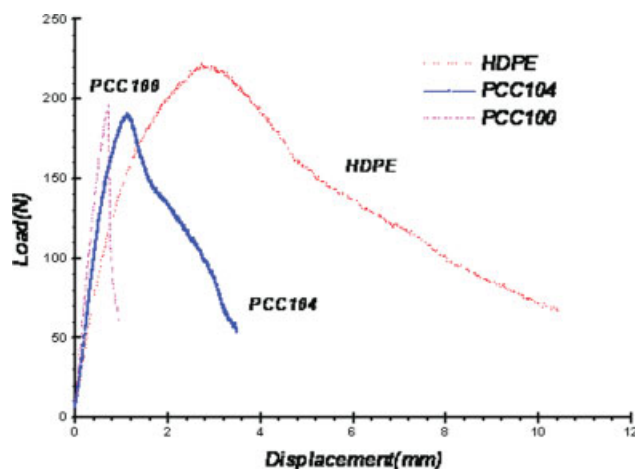
Figure 4 Load-displacement curves of HDPE and its nanocomposites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

load, shown in the Figure 4. As it can be seen, the load-displacement diagram for neat HDPE does not seem linear. Although its deviation is not so much and can be attributed to the accuracy of used equipments but just for checking for neat HDPE, J-testing was performed according to the ESIS protocol, ((European Structural Integrity Society), Recommendation for Determining the Fracture Resistance of Ductile materials, 1991)[27] and J_{IC} at room temperature was measured. The corresponding K_{IC} value was calculated by using the following formula: $K_{IC} = (E \times J_{IC})^{1/2}$ where E is the Young's modulus. The result showed that there is no any significant difference between J-integral method and stress intensity factor method and the fracture toughness achieved for neat HDPE from load-displacement-diagram is valid.

SA content and fracture toughness

Figure 5 illustrates variation of fracture toughness of pure HDPE and its nanocomposites versus SA content. As seen, the addition of 10 vol % CaCO₃ to HDPE make a decrease in its fracture toughness of about 37%. The true reason of this drop can be attributed to the fact that the tendency of uncoated CaCO₃ to agglomeration is so much. In fact, agglomeration is a well-known phenomenon and its probability increases with decreasing particle size. The occurrence and extent of agglomeration are determined by the relative magnitude of the forces, which either bind together the particles or try to separate them. Hornsby[28] listed mechanical interlocking, electrostatic forces, van der Waals forces, liquid and solid bridging as the principle adhesive forces between particles. Among these forces, the effect of mechanical interlocking and electrostatic forces are greater than that of the others.

Since during processing of HDPE nanocomposite, there is no any agent to prevent agglomeration of uncoated nano-CaCO₃, thus the nanoparticles aggregate and act like a big particle. Besides, the nanoparticles tend to decrease their surface contact with matrix by agglomeration. These are why the uncoated PCC particles tend to aggregate.

Although the agglomerated particles can play as stress concentrator points, but in this system, the number of stress concentrators is very low. Therefore, there is a little consumed energy for crack initiation. In summary, the role of agglomerated particle on stress concentrator can be divided into two parts. The first is decreasing of stress concentrator points and the second is increasing the value of stress concentration, i.e., the debonding around a big particle can happen at lower stress rather than the smaller particles. In addition, since there is no any chemical bond between particles and matrix, debonding can occur easily.

Similar to what proposed for crack initiation, crack propagation can be influenced by both particle size and chemical bonding between particles and matrix. Because of lack of chemical bonding between matrix–filler and high stress in front of agglomerated particles, crack propagates easily. This is why fracture toughness of pure HDPE is higher than that of PCC100.

Comparison of fracture toughness of uncoated and coated HDPE/10 vol % CaCO₃ nanocomposite shows that the value of the property depends strongly on SA content. As a matter of fact, the addition of about 4 wt % SA causes to promote fracture toughness of about 20%. The reason can be referred to the effect of SA on preventing the agglomeration of particles and reduce driving force for initiation and propagation of crack due to decreasing agglomerated particle. The experimental results showed that the number of agglomerated particles bigger than 1 μm/250 mm² decreases from 9 For PCC100 to 4 For PCC104 (Fig. 6).
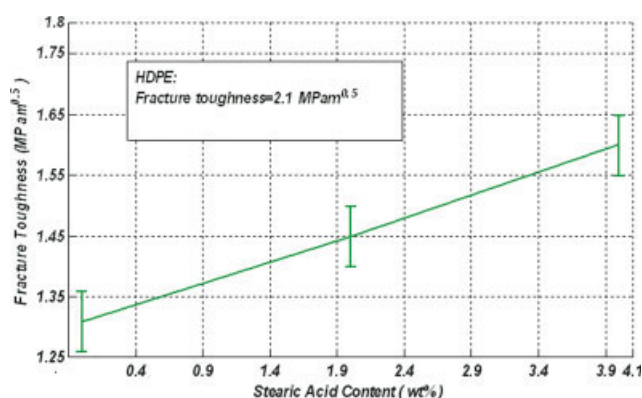

Figure 5 Dependency of fracture toughness of HDPE/10 vol % CaCO₃ on stearic acid content. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
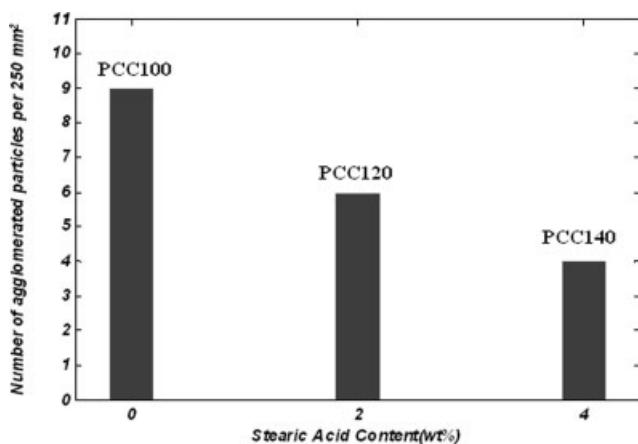
Figure 6 Number of agglomerated particles bigger than 1 μm/250 mm^2 as a function of stearic acid content.
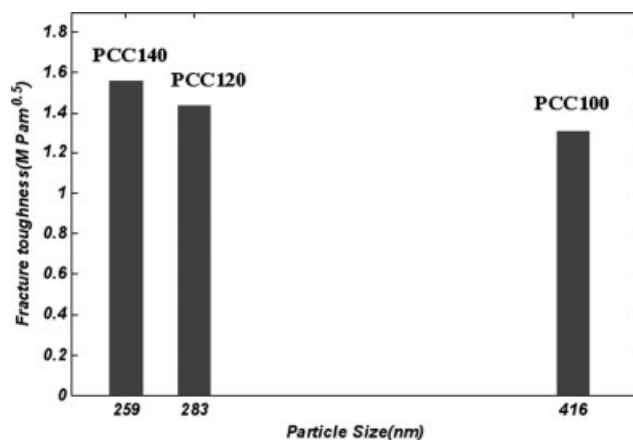

Figure 7 The effect of average particle size on fracture toughness.

It is clear that the interface area between polymer and filler increases as the number of agglomerated particles decreases. All particles behave like stress concentrator points and crack initiation will happen in the polymer–filler interface. Since the consumed energy due to crack initiation increases as the SA content increases, it can be concluded that the debonding and deformation stress need for PCC140 is higher than those of other materials. Besides, lack of chemical bonding between matrix, SA, and CaCO$_3$ results in decreasing of interfacial adhesion between HDPE and uncoated PCC, so interfaces are much weaker than those of coated PCC. In fact SA layer can act as a barrier against crack propagation and increases the consumed energy due to crack propagation (Fig. 5).

The fracture toughness versus average particle size of HDPE nanocomposites are shown in Figure 7 It can be observed that an increase in particle size corresponds with the decreasing fracture toughness.

Debonding stress and fracture toughness

In heterogeneous polymer systems, and especially in composites, basic deformation mechanism is debonding. Debonding is especially important in polyethylene (PE) composites, because of low polarity and low free energy of polymer. Interfacial adhesion is weak and separation of matrix–filler interface can be happened rapidly.

Pukanszky and Voros[29] developed a debonding stress model using the following equation:

$$\sigma^D = -C_1\sigma^T + [(C_2 W_{mf})/R]^{0.5} \qquad (1)$$

where σ^D and σ^T are debonding and thermal stress, respectively, C_1, C_2, and R are constants containing component properties, geometrical parameter, and radius of particle size. W_{mf} is the reversible work of adhesion. As it can be predicted using eq. (1),

debonding stress relates on particle size inversely and debonding stress will be raised as particle size decreases. On the other hand, good adhesive between particle and matrix results in decreasing of debonding points and increasing of fracture toughness. With this regard, addition of SA causes an increase in adhesion interface between particles and matrix, so that the higher fracture toughness of PCC140 can be expected.

Some investigators believed that debonding happened because of thermal stress.[29–33] Indeed, thermal stress appears during deformation and cooling or heating the polymer.[30] Sahebian et al.[32] showed that thermal expansion of HDPE and its nanocomposites depends strongly on both coated and uncoated CaCO$_3$, SA content, and even heating rate. The details of mentioned study illustrated that thermal expansion coefficient of HDPE/10 vol % CaCO$_3$
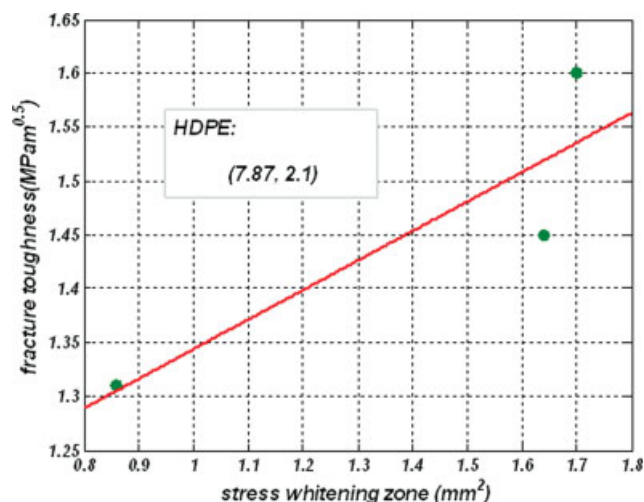

Figure 8 Variation of fracture toughness versus stress whitening zone. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
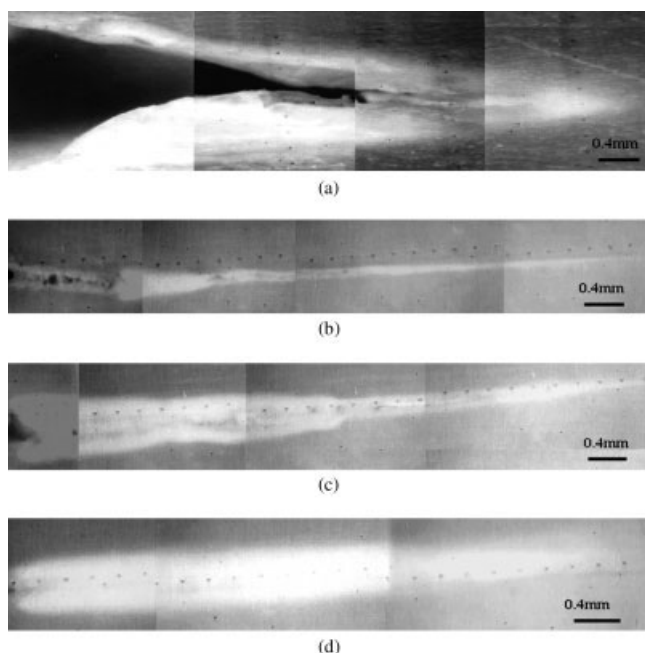
Figure 9 Optical micrographs under cross polarized light, taken from the polished surface of (a) HDPE, (b) PCC100, (c) PCC120, and (d) PCC140.

decreased as SA content increased.[32] With regard to what proposed by Sahebian et al.[32] and eq. (2), it may be concluded that the debonding stress increases as the SA content increases because of its role on bulk thermal expansion. This is because thermal expansion of composite depends on interfacial bonding between particles and matrix and it can be influenced by SA.

Stress whitening zone and fracture toughness

Investigators believed that the fracture energy consumes for many processes such as shear yielding or crazing of matrix, debonding of particles and matrix and stress whitening zone.[25,33-38] Since the scientists who studied fracture behavior of the materials believe that the main part of fracture energy is due to making plastic zone or stress whitening zone in front of precrack, the current research has been concentrated on this subject.

Figure 8 points out the effect of SWZ on fracture toughness for the materials. As it is seen, the addition of 10 vol % uncoated nanosized CaCO$_3$ causes to decrease the area of plastic zone in front of precrack of HDPE drastically. The experimental data indicated that, for compensation this variation, the
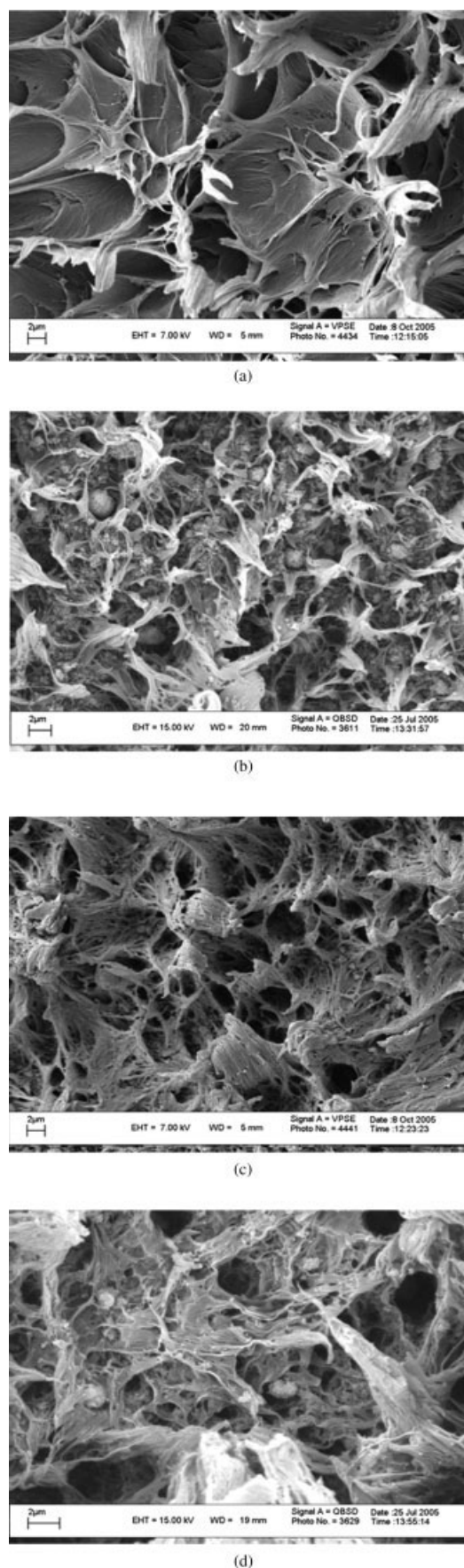

Figure 10 Scanning electron micrographs taken from the fracture surface after three-point bending test of (a) pure HDPE, (b) PCC100, (c) PCC120, and (d) PCC140 at different magnifications (In all micrographs [2 μm]).

addition of coated $CaCO_3$ to HDPE can be useful. It can be observed that the SWZ area increased gradually as the SA content increased from 2 to 4 wt %.

Figures 9(a–d) show optical micrographs in front of precrack taken from the polished surface of HDPE, PCC100, PCC 120, and PCC 140, respectively. It is worth noting to observe plastic zone in front of precrack crosspolarized light was used. Looking at in more details on Figure 9 shows that the SWZ in front of precrack depends strongly on SA content. Since almost all fracture energy consumes inside of SWZ, it may be concluded that the consumed energy increased as the SA increased.

Fracture surface and fracture toughness

For further clarification of the fracture mechanism of HDPE nanocomposites, scanning electron microscopy was employed. Figures 10(a–d) show the fracture surface of HDPE, PCC100, PCC120, and PCC140 nanocomposites, respectively. In PCC100 nanocomposites, some big agglomerated particles can be observed because of the high surface energy of the particles. Plus it can be seen that distribution of particles are not uniform. Also there are some voids induced by different elastic parameters between filler and matrix. Unlike PCC100 the fracture surface of coated nanocomposite is similar to dimple structure. Thus, the higher consumed energy rather than uncoated nanocomposite can be referred to dimple structure.

CONCLUSIONS

To investigate the role of SA content on fracture toughness, a series of HDPE/10 vol % PCC nanocomposites with different SA content were prepared. Three-point bending test and microscopic evaluation were carried out. The results of current study may be summarized as follows:

1. Addition of 10 vol % $CaCO_3$ to HDPE caused a reduction in fracture toughness of its nanocomposites.
2. The number of agglomerated particles reduced as the SA content increased.
3. At constant volume percent of $CaCO_3$, increasing SA promoted fracture toughness of nanocomposite.
4. The variation of stress whitening zone in front of precrack in HDPE depended on both coated and uncoated PCC.

References

1. Chisholm, N.; Mahfuz, H.; Rangari, V. K.; Ashfaq, A.; Jeelani, S. Compos Struct 2005, 67, 115.
2. Wilbrink, M. W. L.; Argon, A. S.; Cohen, R. E.; Weinberg, M. Polymer 2001, 42, 10155.
3. Dali, G.; Argon, A. S.; Cohen, R. E Polymer 1995, 36, 2173.
4. Margolina, A.; Wu, S. Polymer 1988, 29, 2170.
5. Thio, Y. S.; Argon, A. S.; Cohen, R. E.; Weinberg, M. Polymer 2002, 43, 3661.
6. Borggreve, R. J. M.; Gaymans, R. J.; Schuijer, J. Polymer 1987, 28, 1489.
7. Bartczak, Z.; Argon, A. S.; Cohen, R. E.; Weinberg, M. Polymer 1999, 40, 2347.
8. Xiaoqing, G.; Lang, L.; Quangui, G.; Jingli, S.; Gengtai, Z. Mater Lett 2005, 59, 3062.
9. Farhana, P.; Yuanxin, Z.; Vijaya, K.; Rangari, S. J Mater Sci Eng 2005, 405, 246.
10. Berber, S.; Kwon, Y. K.; Tománek, D. Phys Rev Lett 2000, 84, 4613.
11. Hone, J.; Whitney, M.; Zettl, A. Synth Metals 1999, 103, 2498.
12. Bose, S.; Mahanwar, P. A. J Minerals Mater Charact Eng 2004, 3, 23.
13. Bliznakov, E. D.; White, C. C.; Shaw, M. J Appl Polym Sci 2000, 77, 3220.
14. Oberdisse, J.; El Harrak, A.; Carrot, G.; Jestin, J.; Boueé, F. Polymer 2005, 46, 6695.
15. da Silva, A. L. N.; Rocha, M. C. G.; Moraes, M. A. R.; Valente, C. A. R.; Coutinho, F. M. B. Polymer 2002, 21, 57.
16. Lazzeri, A.; Zebarjad, S. M.; Pracella, M.; Cavalier, K.; Rosa, R. Polymer 2005, 46, 827.
17. Zuiderduin, W. C. J.; Westzaan, C.; Huétink, J.; Gaymans, R. J. Polymer 2003, 44, 261.
18. Fu, Q.; Wang, G. Polym Eng Sci 1992, 32, 94.
19. Levita, G.; Marchetti, L.; Lazzeri, A. Polym Compos 1989, 10, 39.
20. Osman, M. A.; Suter, U. W. Chem Mater 2002, 14, 4408.
21. Nissel, J.; HS; DSR; Woodmere, N. Y. Third International Symposium on Interfaces in Polymer Composites and Laminates with Particular Focus at the Nanoscale. Savannah, Georgia, 7–8 Dec. 2004.
22. Weiping, L.; Suong, V.; Martin Pugh, H. Compos Sci Technol 2005, 65, 2364.
23. Ragosta, G.; Abbate M.; Musto, P.; Scarinzi, G.; Mascia, L. Polymer 2005, 46, 10506.
24. Sue, H. J.; Gam, K. T.; Bestaoui, N.; Clearfield, A.; Miyamoto, M.; Miyatake, N. Acta Mater 2004, 52, 2239.
25. Zebarjad, S. M.; Bagheri, R.; Seyed Reihani, S. M.; Lazzeri, A. J Appl Polym Sci 2003, 90, 3767.
26. Moore, G. D. R.; Hooley, C. J. Plast Rubber Process Appl 1981, 1, 121.
27. ESIS (European Structural Integrity Society). A Linear Elastic Fracture Mechanics Standard for Determining Kc and Gc for Plastics, 1990.
28. Hornsby, R.; Premphet, K. J. J Appl Polym Sci 1998, 70, 587.
29. Pukánszky, B.; Vörös, G. Compos Interf 1993, 5, 411.
30. Renner, K.; Min Soo, Y.; János, M.; Hyoung, J. C.; Pukánszky, B. Eur Polym J 2005, 41, 2520.
31. Dieter, G. E. Mechanical Metallurgy; McGraw-Hill: New York, 1986.
32. Sahebian, S.; Sherafat, Z.; Zebarjad, S. M.; Sajjadi, S. A. Ninth Annual Meeting of Iranian Society of Metallurgical Engineers, 15–16 Nov. 2005, Shiraz University, Shiraz, Iran.
33. Wang, Y.; Lu, J.; Wang, G. J Appl Polym Sci 1997, 64, 1275.
34. Badran, B. M.; Galeski, A.; Kryszewski, M. J Appl Polym Sci 1982, 27, 3669.
35. Zebarjad, S. M.; Lazzeri, A.; Bagheri, R.; Frunchi, M. J Mater Sci Lett 2002, 21, 1007.
36. Zebarjad, S. M.; Bagheri, R.; Lazzeri, A. Plast Rubber Compos 2003, 32, 439.
37. Zebarjad, S. M. Mater Design 2003, 24, 531.
38. Zebarjad, S. M.; Bagheri, R.; Serajzadeh, S.; Lazzeri, A. Mater Design 2003, 24, 105.