Essential Work of Fracture Evaluation of Fracture Behavior of Glass Bead Filled Linear Low-Density Polyethylene

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ABSTRACT: The effect of the glass bead (GB) size and bead content on the fracture behavior of GB-filled linear low-density polyethylene (LLDPE) composites was evaluated by means of the essential work of fracture (EWF). The results indicated the specific EWF (w_e) is lower for the composites than that of pure LLDPE and the obtained w_e values do not show significant differences for the filled samples with different GB diameters. The non-EWF or plastic work (βw_p) also decreased with the addition of GBs, indicating that less energy is absorbed during the fracture process for the composites filled with different diameter GBs. For the composites filled with GBs of different contents, the w_e decreased with increasing GB contents and the βw_p that was higher than that of pure LLDPE at relatively low contents also decreased with the content of GBs. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 1781–1787, 2006

Key words: linear low-density polyethylene; glass beads; composite; fracture

INTRODUCTION

There has recently been increased interest in introducing high modulus glass fillers such as glass fibers[1–4] and glass beads (GBs)[5–7] into tough polymer matrices to consider the cost effectiveness and reinforcing effect on the matrix without reducing the tensile strength and modulus caused by the addition of compliant rubber particles. There are also examples of the toughening effect of rigid inorganic particles, such as GBs and $CaCO_3$, filled into polymers such as high-density polyethylene (HDPE), polypropylene (PP), and so forth in the literature. In these cases, the fracture behavior of the composites was generally evaluated by means of impact tests.

Generally, the fracture behavior occurring at nominal stresses well below the uniaxial yield stress of materials is described with the linear elastic fracture mechanics approach, in which the entire specimen is reasonably assumed to exhibit Hookean elasticity because the area in which energy is dissipated near the crack tip is very small. However, when studying the failure of ductile materials, in which a large plastic zone at the crack tip develops, the energy dissipation is no longer confined to a small local zone near the crack tip. The essential work of fracture (EWF) method has recently gained popularity because of experimental simplicity and it has been used extensively to study the fracture behavior of a wide range of polymeric materials, although the J-integral approach has traditionally been used for fracture toughness evaluation of materials with significant crack tip plasticity.[8–24]

The EWF concept was first developed by Broberg,[24] who proposed that the nonelastic region at the crack tip may be divided into an inner fracture process zone and an outer plastic deformation zone, as shown in Figure 1.

In the EWF test, the following are important correlations:

$$W_f = W_e + W_p \quad (1)$$

$$W_e = w_e\, BL \quad (2)$$

$$W_p = w_p\, \beta B L^2 \quad (3)$$

$$w_f = \frac{W_f}{LB} = w_e + \beta w_p L \quad (4)$$

where L is the ligament length; B is the specimen thickness; W_f is the total work of fracture; w_f is the specific total work of fracture; W_e, the EWF, is essentially a surface energy term whose value is propor-

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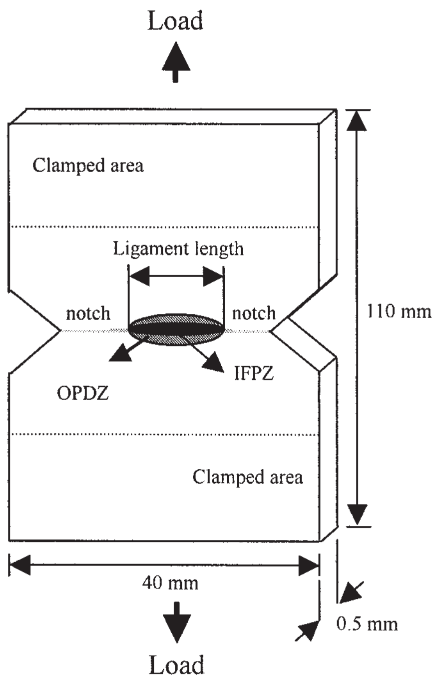

Figure 1 The double-edged notch tension sample used in the EWF test; IFPZ, inner fracture process zone; OPDZ, outer plastic deformation zone.

tional to the ligament area (LB); w_e is the specific EWF; W_p, the non-EWF, is proportional to the volume of the yield zone (BL^2); w_p is the specific non-EWF; and β is a proportionality constant or shape factor associated with the volume of the plastic deformation zone. For a given thickness, the w_e is regarded as a material constant and, provided the term βw_p remains independent of the L, a linear relationship is expected between w_f and L as suggested by eq. (4). The positive intercept of this line with the w_f axis gives w_e, and its slope gives βw_p. The theory background, assumption of analysis, and test procedure of the EWF method were illustrated in the research just mentioned, which is not elaborated on here.

Several studies with the EWF method[18,25–30] have shown that the w_e parameter may be estimated reasonably well via crack-opening displacement (COD) of the advancing crack tip using the following simple relationship:

$$w_e = M\sigma_y \text{COD} \quad (5)$$

where M is a plastic constraint factor whose value for double-edged notch tension (DENT) is 1.15. To obtain the COD, the extension to break values (e_f) were plotted versus the L. A linear dependence exists between the two parameters, that is,

$$e_f = e_o + e_p L \quad (6)$$

The intercept value (e_o) has been identified as the COD of the advancing crack tip[18,25–30] and the slope (e_p) as the plastic contribution to extension. In this work, when recording the load versus displacement curves, the elongation to break was recorded at the same time for calculating the COD.

Mouzakis et al.[6] studied the fracture behavior of hybrid composites consisting of isotactic PP, thermoplastic styrenic elastomer, and GBs by means of postyield fracture mechanics and the EWF theory. However, the effect of the bead size and bead content on the fracture behavior of GB-filled polymers by means of the EWF test was rarely found in the research literature.

In a previous work, we studied the effect of GB size and content on the mechanical properties of GB-filled LLDPE composites. We found the overall mechanical properties of different size GBs in GB-filled LLDPE composites were substantially improved relative to pure LLDPE, demonstrating that in a relative small bead size range, the inorganic spherical particles can effectively increase the mechanical properties of LLDPE. Although the elastic modulus and the elongation to break were almost constant for various filler contents, the tensile strength increased about 30% at low filler content and then remained constant up to 20 wt % filler content and the impact strength exhibited a sharp increase at low filler content and then gradually increased with filler contents increasing to 20 wt %.[31]

The effect of the particle size and filler content on the fracture behavior of GB-filled linear low-density PE (LLDPE) composites were evaluated by the EWF approach in this work.

EXPERIMENTAL

Materials and sample preparation

The LLDPE was a granular material (218W, Sabic Marketing Company) with a melt flow rate measured at standard test conditions as 2.0 g/10 min.

The GBs were hollow beads (Cenospheres) produced by TianXingJian Ltd. (Yibing, P.R.C.). The sizes of the untreated GBs were 5000, 2500, and 1250 mesh, respectively.

The LLDPE and the GBs of different bead sizes with predetermined proportions (mass %) were put into a TSSL-25 corotating twin-screw extruder (length/depth ratio = 23/1, 25-mm diameter, Chengguang Chemical Institute, Chengdu, P.R.C.) to blend them in the molten state of LLDPE with a temperature profile in the range of 160–210°C. Then, they were pelletized after extrusion. After drying to remove the attached moisture during extrusion and pelletizing, the pellets were injection molded into dogbone-shaped tensile samples on a PS40E5ASE precise injection molding machine, with a temperature profile of 170, 190, 220,

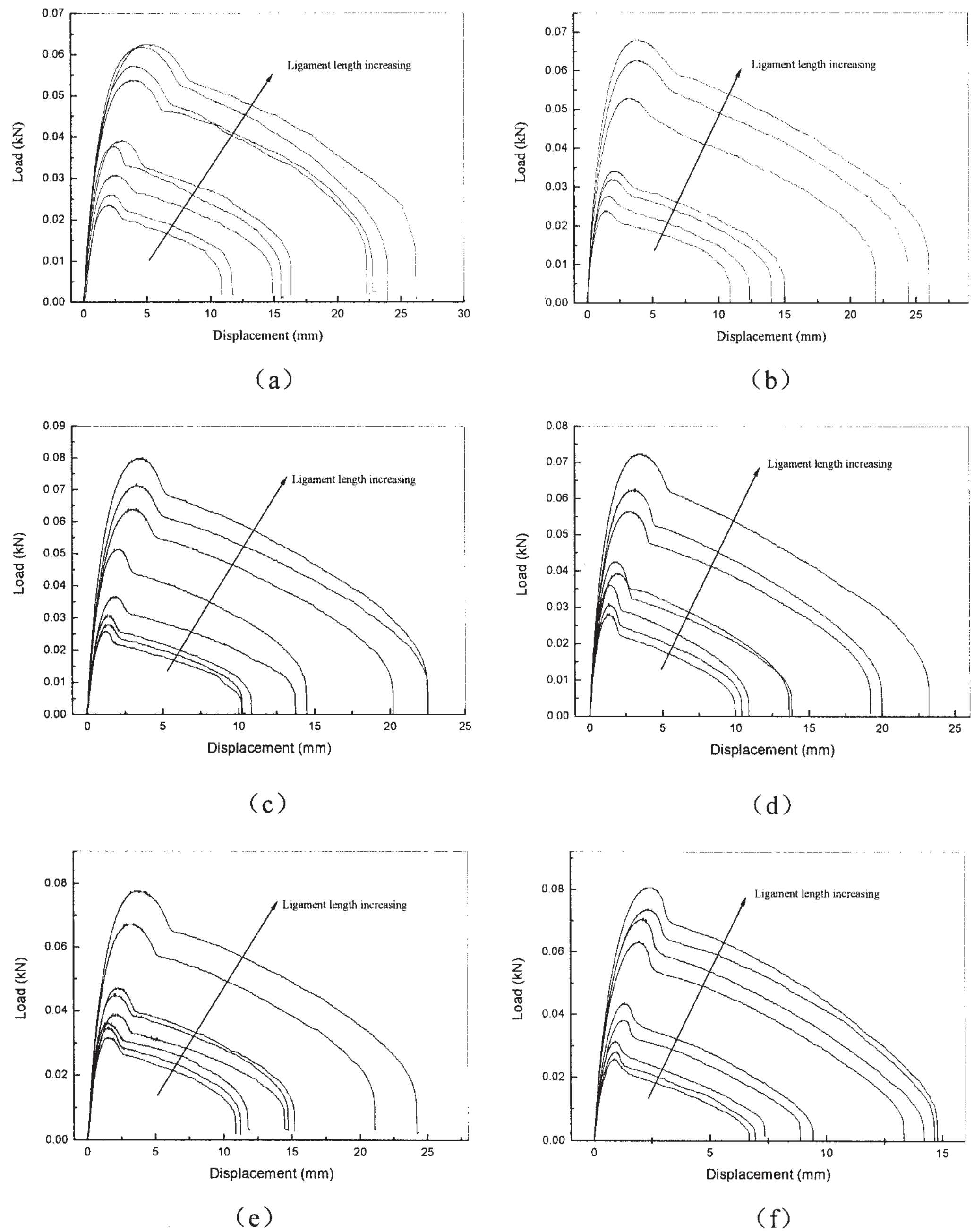

Figure 2 A plot of the load versus displacement of (a) pure LLDPE and (b–f) LLDPE filled with GBs of different sizes: LLDPE with 15 wt % GB content and filled with (b) 1250-, (c) 2500-, and (d) 5000-mesh GBs; and LLDPE filled with 2500-mesh GBs at GB contents of (e) 5 and (f) 40 wt %.

and 220°C from the feeding zone to the nozzle. The injection pressure and the holding pressure were both 56.1 MPa. Then, the obtained dogbone samples were compression molded into sheets of about 0.5-mm thickness at 190°C.

The rectangular (length × width = 110 × 40 mm) DENT specimens seen in Figure 1 (2–13 mm ligaments) were sawn from the compression-molded sheets. Deep blunt notches were induced on both sides of the specimens by a sharp knife. The cut notches were sharpened by a fresh razor blade to produce the sharp precrack that was required. Initial notches were made perpendicularly to the tensile direction with a fresh razor blade, obtaining at least 17 specimens for each set. The ligament lengths and thicknesses were measured before the test using a reading microscope and a Vernier caliper.

Static tensile tests on DENT specimens were performed on an electrical universal tensile testing machine Series IX at 25°C and the crosshead speed was 5 mm/min. Tests were carried out with specimens of the pure LLDPE and GB-filled LLDPE composites. The

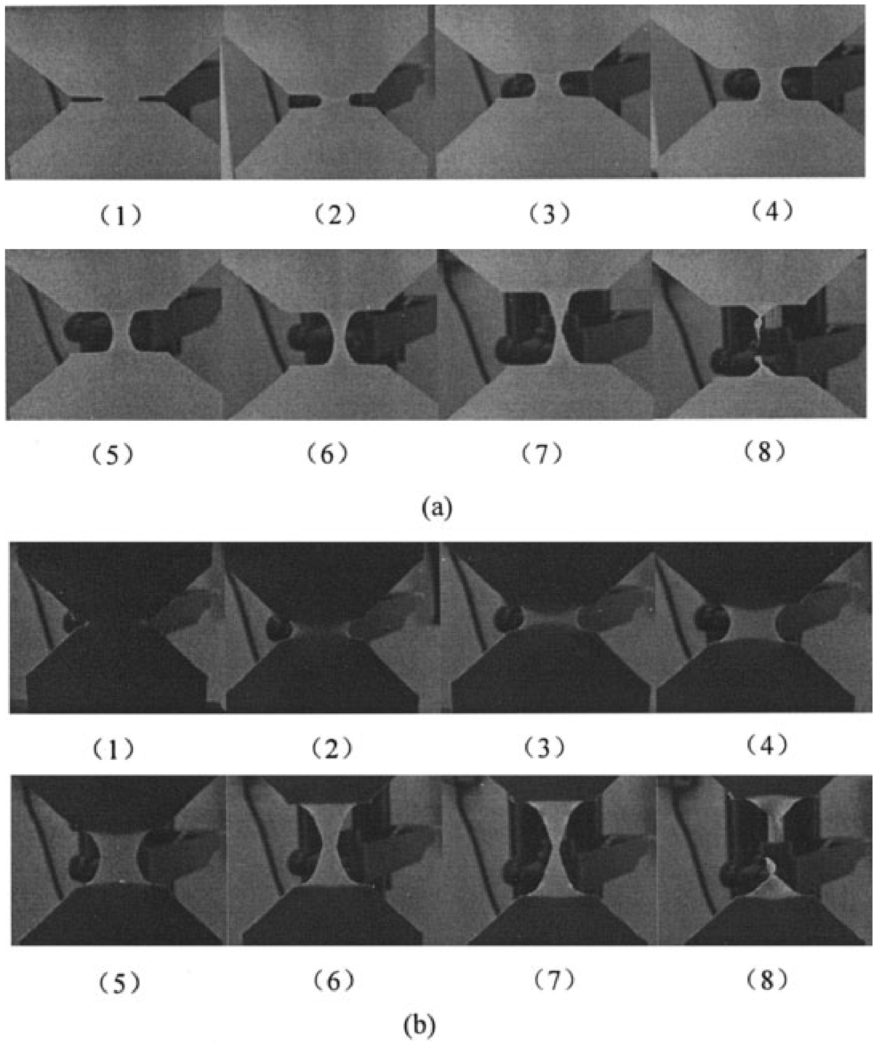

Figure 3 Photomicrographs of the fracture procedure for double-edged notch tension samples of (a) pure LLDPE and (b) GB-filled LLDPE composites. The ligament lengths were (a) 4.548 and (b) 10.372 mm.

load versus displacement curves were recorded, and the absorbed energy until failure was calculated by computer integration of the loading curves.

RESULTS AND DISCUSSION

Stress–strain behaviors

The load displacement curves during DENT tests as a function of the ligament lengths are shown in Figure 2, and the photographs taken during the DENT test for 5000-mesh GB-filled LLDPE composites with different ligament lengths are shown in Figure 3. For pure LLDPE and LLDPE composites filled with GBs of different average diameters and different contents, there was a linear elastic region in the initial stage. Then, two plastic zones were generated at the tip of both cracks, the size of which increased on further loading. The load eventually reached a maximum value, and the two plastic zones continued to propagate. After the peak, a sudden drop in load occurred and the yielded ligament began to form necking. After complete necking of the ligament, the cracks started to grow in a stable manner until final fracture of the specimen. For all materials (pure or filled with GBs with different average diameters or different contents), as the ligament completely yielded before the crack started to propagate, as confirmed from the load displacement plots and from the photographs taken during the test, the prerequisite for the EWF analysis was satisfied.

Effect of GB size

The w_e value was obtained from the linear extrapolation of the w_f versus the ligament length. The slope of the w_f versus the ligament length plot gave the βw_p. The effect of the dimensions (thickness, width, and gauge length), geometry, and test rate on the w_e and

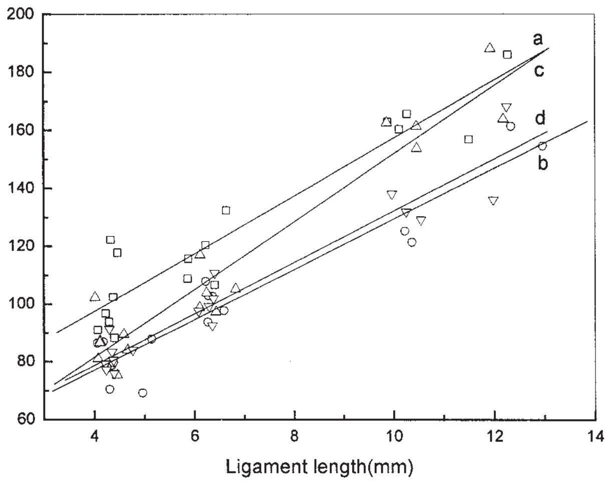

Figure 4 The total specific energy to fracture (w_f) of samples filled with GBs of different average diameters versus the ligament size: (□) pure LLDPE (curve a), (○) LLDPE + 15% 1250-mesh GB (curve b), (△) LLDPE + 15% 2500-mesh GB (curve c), and (▽) LLDPE + 15% 5000-mesh GB (curve d).

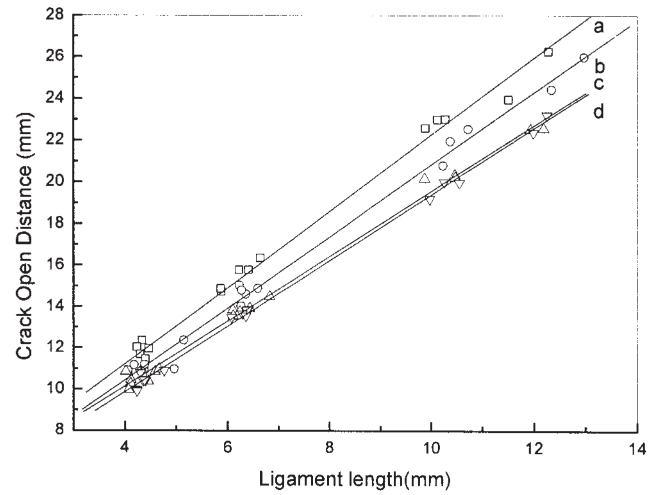

Figure 5 The crack-opening distance of samples filled with GBs of different average diameters versus the ligament size: (□) pure LLDPE (curve a), (○) LLDPE + 15% 1250-mesh GB (curve b), (△) LLDPE + 15% 2500-mesh GB (curve c), and (▽) LLDPE + 15% 5000-mesh GB (curve d).

βw_p values was not considered in this study. Figure 4 shows the plot of w_f of samples filled with GBs of different average diameters against the ligament length and the specific EWF, and the plastic work results are summarized in Table I. From the values listed in Table I it is clear that the specific plane stress fracture toughness is lower for the composites than that of pure LLDPE, indicating that the crack resistance of the composites was lowered with the addition of GBs, which may be caused by the retarded molecular mobility of LLDPE with the addition of GBs. The plastic work, which is the energy dissipated in the process zone, also decreased with the addition of GBs, except for 2500-mesh GBs, indicating that less energy is absorbed during the fracture process for the composites.

In contrast, the obtained values of w_e and βw_p do not show significant differences for the filled materials, which indicates that the effect of the average diameter of GBs on the EWF is relatively small.

The evaluation of the EWF by means of COD was also adopted in this work. To obtain the COD the e_f values were plotted versus the ligament length as shown in Figure 5, and a linear dependence exists between the two parameters as shown in eq. (6).

The e_o has been identified as the COD of the advancing crack tip[18,20–25] and the e_p as the plastic contribution to extension. These parameters are included in Table II.

Similarly, the e_o is lower for the composites than that of pure LLDPE. The e_p also decreased with the addition of GBs but increased with the average GB diameter. In addition, the e_o and e_p do not show much difference for the filled composites.

Effect of GB content

To evaluate the effect of the GB content on the EWF of GB-filled LLDPE, composites with GB concentrations of 5, 10, 15, 20, and 40 wt % were prepared. The plot of w_f versus the ligament length of these samples is recorded in Figure 6, and the EWF results are summarized in Table III. Note that the w_e shows a roughly linear decreasing trend with the increasing of the GB

TABLE I
Fracture Parameters Obtained from EWF Test for Pure LLDPE and Composites of LLDPE and Glass Beads with Different Average Diameters

LLDPE composites	w_e (kJ/m^2)	βw_p (MJ/m^3)	R^2
Pure LLDPE	57.5	9.98	0.910
LLDPE + 15% 1250-mesh GB	42.3	8.72	0.922
LLDPE + 15% 2500-mesh GB	34.7	11.72	0.925
LLDPE + 15% 5000-mesh GB	43.1	8.91	0.910

TABLE II
Fracture Parameters of Extension to Break of Samples Obtained from EWF Test for Pure LLDPE and Composites of LLDPE and Glass Beads with Different Average Diameters

LLDPE composites	e_o	e_p	R^2
Pure LLDPE	3.84	1.84	0.991
LLDPE + 15% 1250-mesh GB	3.51	1.73	0.922
LLDPE + 15% 2500-mesh GB	3.86	1.57	0.994
LLDPE + 15% 5000-mesh GB	3.51	1.59	0.997

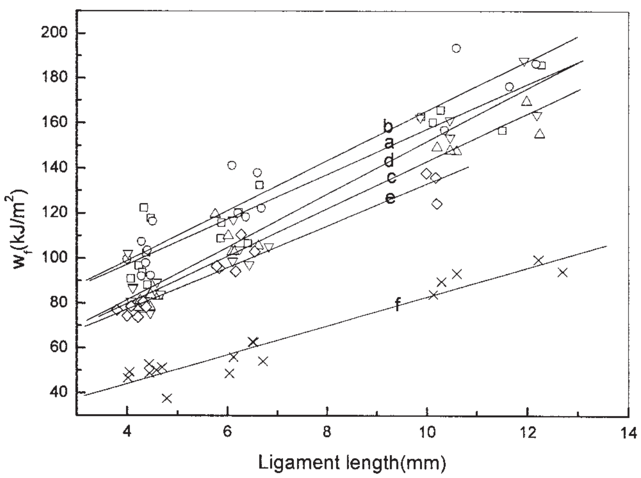

Figure 6 The total specific energy to fracture (w_f) of samples filled with GBs of different contents versus the ligament size. The average diameter of the GBs is 2500 mesh: (□) pure LLDPE (curve a), (○) LLDPE + 5% GB (curve b), (△) LLDPE + 10% GB (curve c), (▽) LLDPE + 15% GB (curve d), (◁) LLDPE + 20% GB (curve e), and (▷) LLDPE + 40% GB (curve f).

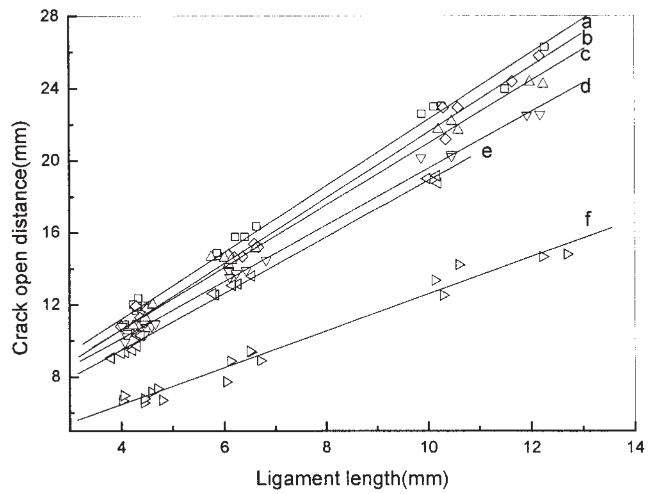

Figure 7 The crack-opening distance of samples filled with GBs of different contents versus the ligament size. The average diameter of the GBs is 2500 mesh: (□) pure LLDPE (curve a), (○) LLDPE + 5% GB (curve b), (△) LLDPE + 10% GB (curve c), (▽) LLDPE + 15% GB (curve d), (◁) LLDPE + 20% GB (curve e), and (▷) LLDPE + 40% GB (curve f).

content. This could also be interpreted from the retarded molecular mobility of LLDPE with the addition of GBs: the retardance of the molecular mobility of LLDPE in the composites increased with the increase of the filler content. At lower content, the plastic work was higher than that of pure LLDPE and then decreased with the content of GBs.

Contrary to the effect of the GB size, the obtained values of w_e and βw_p do show significant differences for the filled materials, which indicates the influence of GB content is somewhat larger than that of the GB size on the EWF and non-EWF.

In addition, the evaluation of the EWF by means of COD was performed and the results are included in Figure 7 and Table IV. In this case, the e_o and e_p for the filled composites were lower than those of pure LLDPE, except for a filler content of 15 wt %. At lower GB content, the e_o increased with the increasing of the filler content, reached a maximum at 15 wt %, and then decreased. This changing trend is somewhat different from that of w_e. However, for e_p, a clear decreasing trend was presented. The results of the COD also indicate a larger influence of the GB content than that of the GB size on the EWF.

CONCLUSION

We found that the w_e was lower for the GB-filled LLDPE composites than that of pure LLDPE, the w_e did not show significant differences for the filled samples with different GB diameters, and the βw_p also decreased with the addition of GBs. For the composites of LLDPE filled with different content GBs, the w_e decreased with the increase of the GB content and the plastic work was higher than that of pure LLDPE at relatively low contents and then also decreased with the content of GBs. Generally speaking, the influence of the GB content was somewhat larger than that of

TABLE III
Fracture Parameters Obtained from EWF Test for Pure LLDPE and Composites of LLDPE and Glass Beads (2500 mesh) with Different Filler Contents

Filler content (wt %)	w_e (kJ/m^2)	βw_p (MJ/m^3)	R^2
0	57.51	9.98	0.828
5	54.85	11.07	0.900
10	37.84	10.52	0.949
15	34.66	11.72	0.922
20	40.22	9.28	0.949
40	18.32	6.47	0.926

TABLE IV
Fracture Parameters of Extension to Break of Samples Obtained from EWF Test for Pure LLDPE and Composites of LLDPE and Glass Beads (2500 mesh) with Different Filler Contents

Filler content (wt %)	e_o	e_p	R^2
0	3.84	1.84	0.991
5	3.35	1.82	0.992
10	3.73	1.72	0.993
15	3.86	1.57	0.994
20	3.25	1.56	0.995
40	2.39	1.02	0.975

the GB size on the fracture behavior of the GB-filled LLDPE composites.

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References

1. Wong, S. C.; Mai, Y. W. Polym Eng Sci 1999, 39, 356.
2. Laura, D. M.; Keskkula, H.; Barlow, J. W.; Paul, D. R. Polymer 2000, 41, 7165.
3. Laura, D. M.; Keskkula, H.; Barlow, J. W.; Paul, D. R. Polymer 2001, 42, 6161.
4. Karger-Kocsis, J. J Polym Eng 1993, 12, 77.
5. Zhang, H.; Berglund, L. A. Polym Eng Sci 1993, 33, 100.
6. Mouzakis, D. E.; Stricker, F.; Mülhaupt, R.; Karger-Kocsis, J. J Mater Sci 1998, 33, 2551.
7. Lee, J.; Yee, A. F. J Mater Sci 2001, 36, 7.
8. Mai, Y. W.; Cotterell, B.; Horlyck, R.; Vigna, G. Polym Eng Sci 1987, 27, 804.
9. Wu, J.; Mai, Y. W.; Cotterell, B. J Mater Sci 1993, 28, 3373.
10. Chan, W. Y. F.; Williams, J. G. Polymer 1994, 35, 1666.
11. Wu, J.; Mai, Y. W. Polym Eng Sci 1996, 36, 2275.
12. Karger-Kocsis, J. Polym Bull 1996, 37, 119.
13. Karger-Kocsis, J.; Czigany, T. Polymer 1996, 37, 2433.
14. Karger-Kocsis, J.; Czigany, T.; Moskala, E. J. Polymer 1997, 38, 4587.
15. Karger-Kocsis, J.; Czigany, T.; Moskala, E. J. Polymer 1998, 39, 3939.
16. European Structural Integrity Society Task Group, Test Protocol for Essential Work of Fracture, Version 5; Les Diablerets, Switzerland, 1998.
17. Ching, E. C. Y.; Li, R. K. Y.; Mai, Y. W. Polym Eng Sci 2000, 40, 310.
18. Mouzakis, D. E.; Karger-Kocsis, J.; Moskala, E. J. J Mater Sci Lett 2000, 19, 1615.
19. Tjong, S. C.; Xu, S. A.; Mai, Y. W. Mater Sci Eng A-Struct 2003, 347, 338.
20. Tjong, S. C.; Xu, S. A.; Mai, Y. W. J Polym Sci Part B: Polym Phys 2002, 40, 1881.
21. Tjong, S. C.; Xu, S. A.; Li, R. K. Y.; Mai, Y. W. Polym Int 2002, 51, 1248.
22. Maspoch, M. L.; Gamez-Perez, J.; Karger-Kocsis, J. Polym Bull 2003, 50, 279.
23. Karger-Kocsis, J.; Barany, T.; Moskala, E. J. Polymer 2003, 44, 5691.
24. Broberg, K. B. Int J Fract 1968, 4, 11.
25. Hashemi, S. Plast Rubber Compos Process Appl 1993, 20, 229.
26. Hashemi, S.; Arkhireyeva, A. J Macromol Sci Phys 2002, 41B, 863.
27. Levita, G. Polym Eng Sci 1996, 36, 2534.
28. Casellas, J. J.; Frontini, P. M.; Carella, J. M. J Appl Polym Sci 1999, 74, 781.
29. Levita, G. J Mater Sci 1996, 31, 1545.
30. Arkhireyeva, A.; Hashemi, S.; Obrien, M. J Mater Sci 1999, 34, 5961.
31. Yang, W.; Shi, W.; Li, Z. M.; Xie, B. H.; Feng, J.; Yang, M. B. J Elastom Plast 2004, 36, 251.