ON THE TOUGHNESS OF POLYMER NANOCOMPOSITES ASSESSED BY THE ESSENTIAL WORK OF FRACTURE (EWF) APPROACH

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Abstract
The essential work of fracture (EWF) approach is widely used to determine the plane stress fracture toughness of highly ductile polymers and related composites. To shed light on how the toughness is affected by nanofillers EWF-suited model polymers, viz. amorphous copolyester and polypropylene block copolymer were modified by multiwall carbon nanotube (MWCNT), graphene (GR), boehmite alumina (BA) and organoclay (MMT) in 1 wt.%. EWF tests were performed on deeply double edge notched tensile loaded (DEN-T) specimens under quasistatic loading conditions. Data reduction occurred by energy partitioning between yielding and necking/tearing. The EWF prerequisites were not met with MWCNT and GR. BA affected the EWF parameters at least. Results indicated that incorporation of nanofillers usually enhanced the specific essential work of fracture, however, at cost of the specific non-essential work of fracture parameter. This means that the resistance to crack initiation and to crack propagation can hardly be improved at the same time with nanofillers.

1 Introduction
1.1 EWF method
The essential work of fracture (EWF) concept became very popular to characterize the plane stress toughness of ductile polymers and related systems. The widespread use of the EWF is due to the simple specimens' preparation, easy testing and simple data reduction procedure. Though the EWF method is dominantly used for mode-I type loading, it has been successfully adopted for mode-II and mode-III type deformations, too. Moreover, attempts were also made to deduce plane strain toughness values from EWF tests.
According to the EWF, the total work of fracture (W_f) can be partitioned into two components; i) the essential work of fracture (W_e) consumed in the inner fracture process zone to create new surface, and ii) the non-essential (or plastic) work (W_p) performed in the outer "plastic" deformation zone. The related zones, being surface- and volume-related, respectively, are shown schematically in case of a DEN-T specimen in Figure 1.

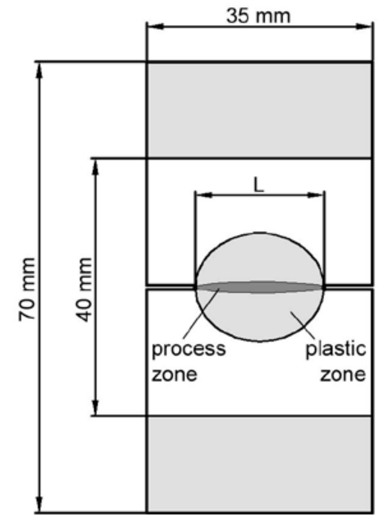


Figure 1. Schematic diagram showing the fracture zones in a DEN-T specimen

1.2. Data reduction

The total work of fracture (W_f), calculated from the area of the force-displacement (F-x) curves (see Figure 1b) is composed of Equation (1):

$$W_f = W_e + W_p \tag{1}$$

Assuming that both zones are within the ligament of the specimen (cf. Figure 1), Equation 1 can be rewritten into the specific terms (Equations (2) and (3)):

$$W_f = w_e \cdot Lt + \beta w_p \cdot L^2 t \tag{2}$$

$$w_f = w_e + \beta w_p \cdot L \tag{3}$$

where L is the ligament length, t is the specimen thickness and β is the shape factor related to the form of the outer plastic dissipation zone. Equation 3 is the base of the data reduction: the specific work of fracture data are determined on specimens with varying ligaments are plotted as a function of the ligament length. w_e is given by the $y(w_f)$-intercept of the linear regression fitted on the w_f *vs.* L data. The slope (βw_p) of the linear regression can be treated as a measure of the resistance to crack growth of the given material. Detailed information on the EWF testing, data reduction and interpretation can be taken from a recent review [1].

1.3 Aims of this work

The easy performance of the EWF test guided researchers to adapt this technique also for systems where it does not work. This happened also in the past when using the EWF for thermoplastic nanocomposites [1]. As a consequence, the published results scatter and do not allow us to make any useful conclusion in respect to the structure-toughness relationships in thermoplastic nanocomposites. This work was foreseen to contribute to this issue by the following research philosophy: a) use of nanofillers with different dispersibility in polymer melts, and b) selecting such model polymers which satisfy all the requirements of the EWF use.

2 Materials and testing methods

2.1. Materials and specimen preparation

As matrix materials poly(propylene-*block*-ethylene) (EPBC; Tipplen K499, TVK Nyrt., Tiszaújváros, Hungary) and polyethylene terephthalate glycol (PETG; Eastar Copolyester 6763, Eastman Chemical Company, Kingsport, TN, USA) were selected which fulfill the most important “EWF requirement”, viz. full ligament yielding prior to crack growth. The selected nanofillers were: MWCNT (Baytubes C 150P), GR (xGnP), BA (Cloisite 30B) and BA (Disperal P3). All these fillers were introduced in 1 wt% in the thermoplastics during extrusion melt compounding in a twin-screw extruder. The granulated nanocomposites were sheeted to a thickness of ca. 0.6 mm by compression molding.

2.2. Testing and data reduction

DEN-T specimens with the dimension 35 x 70 mm^2 (width x length) were subjected to quasistatic loading at 2 mm/min deformation rate at room temperature. The ligament range covered L=5 to 25 mm. At each ligament 5 specimens were tested. During the data reduction the energy partitioning method, recommended by Karger-Kocsis [2] has been followed.

3 Results and discussion

3.1. Load-displacement (F-x) curves and related EWF parameters

Modification with GR and MWCNT strongly affected the F-x curves of both EPBC and PETG. Though for the yielding section the self similarity criterion fairly holds, this is not at all the case for the necking/tearing part – cf. Figure 2. Accordingly, the w_f vs L regressions underlied a large scatter and the related slopes were close to horizontal (i.e. 0) – cf. Figure 3. The correlation coefficients of the linear regressions (R^2) were unacceptably low for both EPBC (0.2-0.45) and PETG (0.77-0.83) – cf. Tables 1 and 2, respectively. As a consequence, the EWF conditions are violated by filling with GR and MWCNT in 1 wt%. On the other hand, the EWF approach can still be adapted for the yielding-related loading part of the F-x curves.

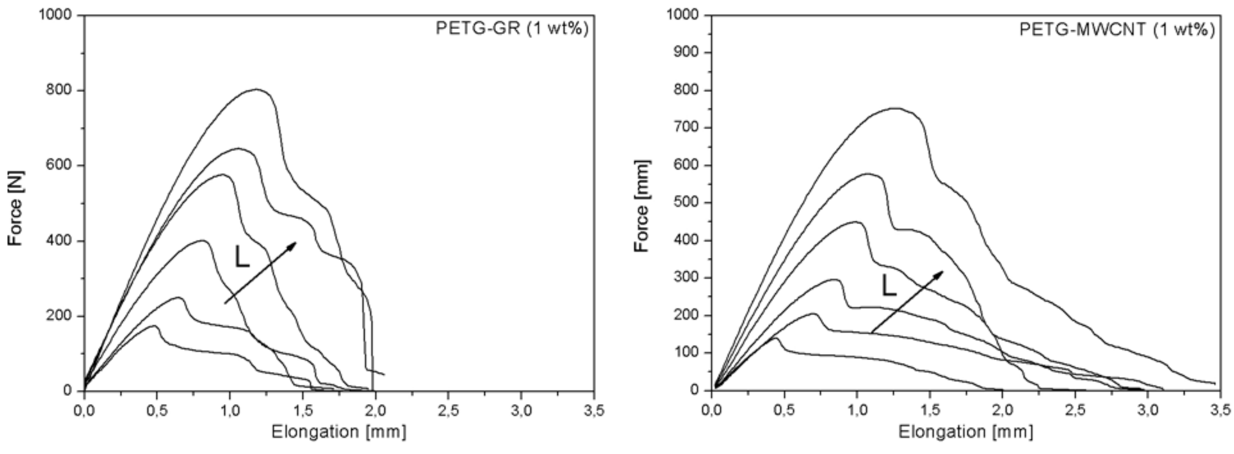


Figure 2. F-x traces as a function of the ligament length (L) measured on DEN-T specimens of PETG-GR (a) and PETG-MWCNT (b).

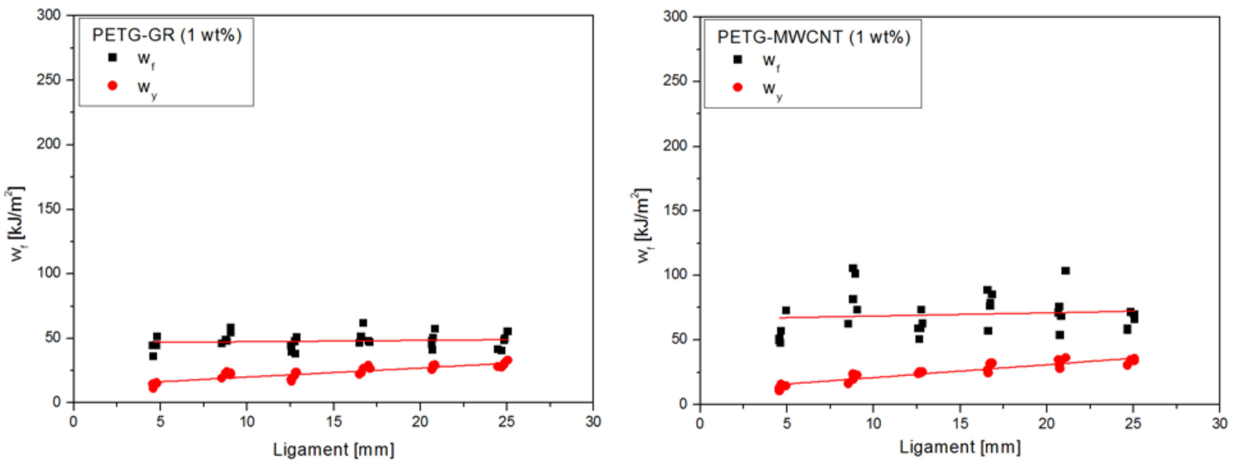


Figure 3. wf-L traces as a function of the ligament length (L) measured on DEN-T specimens of PETG-GR (a) and PETG-MWCNT (b).

	EPBC					
	w_e [kJ/m^2]	**βw_p [MJ/m^3]**	**R^2 [-]**	**$w_{e,y}$ [kJ/m^2]**	**$\beta' w_{p,y}$ [MJ/m^3]**	**R^2 [-]**
Matrix	48.3	6.1	0.91	2.8	0.92	0.93
Bohmite	45.0	4.8	0.84	2.7	0.90	0.94
Graphene	27.6	1.3	0.45	5.4	0.62	0.67
MMT	42.4	5.6	0.87	4.2	0.80	0.85
MWCNT	43.2	0.8	0.20	6.7	0.66	0.73

Table 1. Specific essential (w_e) and non-essential (β_{wp}) work of fracture parameters along with those related to yielding ($w_{e,y}$ and $\beta' w_{p,y}$) for the EPBC-based nanocomposites.

	PETG					
	w_e [kJ/m^2]	**βw_p [MJ/m^3]**	**R^2 [-]**	**$w_{e,y}$ [kJ/m^2]**	**$\beta' w_{p,y}$ [MJ/m^3]**	**R^2 [-]**
Matrix	56.9	8.3	0.96	15.5	0.92	0.87
Bohmite	51.6	8.3	0.97	9.2	1.12	0.93
Graphene	46.1	0.1	0.02	12.8	0.71	0.77
MMT	33.8	9.7	0.97	7.3	1.25	0.94
MWCNT	65.8	0.2	0.02	11.0	1.00	0.83

Table 2. Specific essential (w_e) and non-essential (β_{wp}) work of fracture parameters along with those related to yielding ($w_{e,y}$ and $\beta' w_{p,y}$) for the PETG-based nanocomposites.

By contrast, the EWF could well be applied for the nanocomposites containing BA and MMT. Figure 4 shows that the F-x curves are self similar (i.e. linear transformation results in overlapping of the related curves) and the load drop associated with full ligament yielding is also well resolved. Note that this is prominent for the PETG- (cf. Figure 4) but less developed for EPBC-based BA and MMT nanocomposites (cf. Figure 5). In case of EPBC instead of instantaneous a delayed yielding occurred [3]. The related w_f vs. L traces were linear (cf. Figure 5) with sufficiently high R^2 – cf. Table 1.

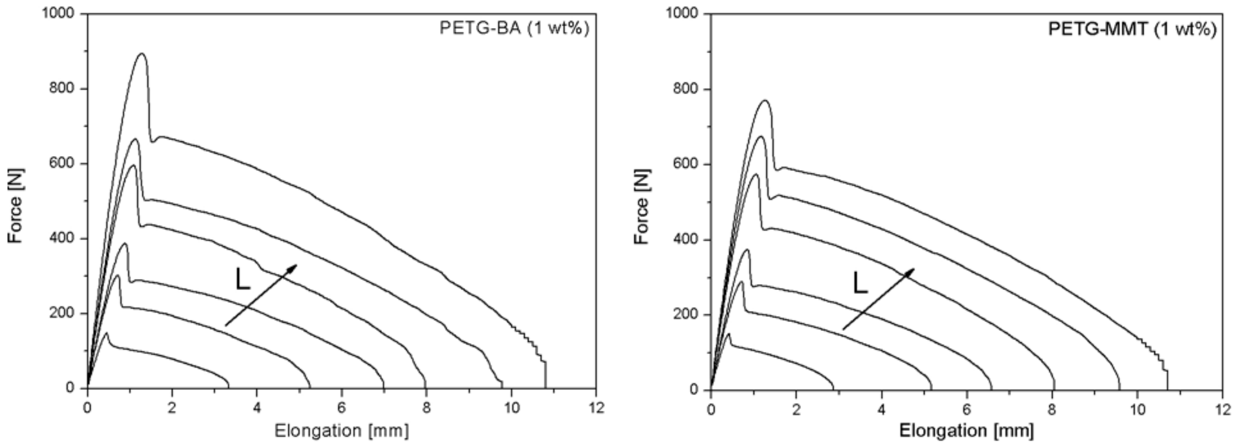


Figure 4. F-x traces as a function of the ligament length (L) measured on DEN-T specimens of PETG-BA (a) and PETG-MMT nanocomposites (b).

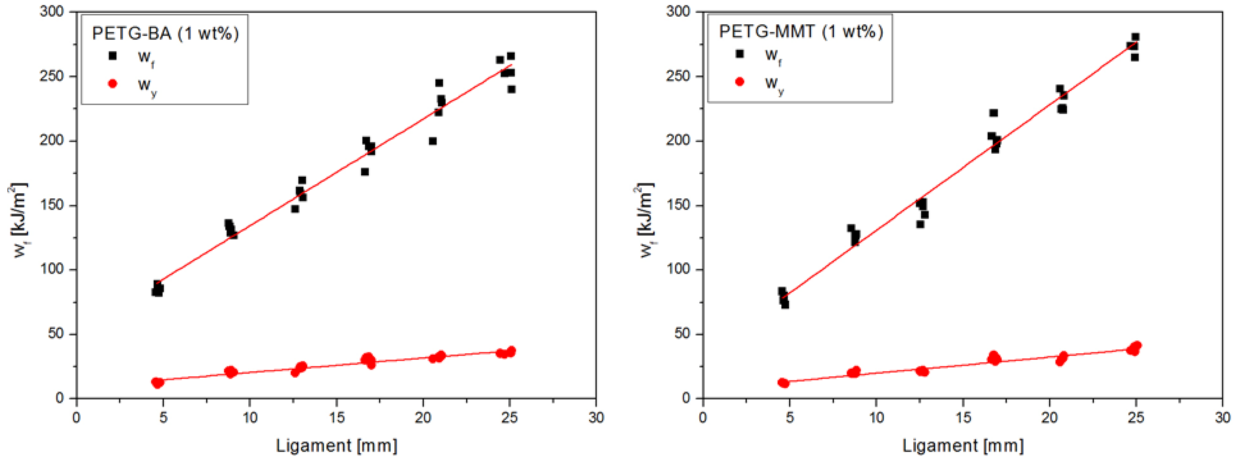


Figure 5. F-x traces as a function of the ligament length (L) measured on DEN-T specimens of EPBC-BA (a) and EPBC-MMT nanocomposites (b).

Results in Table 1 and 2 suggest that both BA and MMT nanofillers only slightly affected the specific EWF parameters. Considering the yielding-related terms it is interesting to note that $w_{e,y}$ was enhanced and $\beta' w_{p,y}$ reduced for EPBC, whereas the opposite happened for PETG.

3.2. Failure mode

Light microscopic (LM) pictures were taken from the plastic zone areas of the DEN-T specimens of the neat and modified PETG (cf. Figure 6). One can see that the plastic zone is well developed for the unmodified and BA- and MMT-filled systems. By contrast, this is not the case for the GR-containing PETG. Though the latter specimen experienced full ligament yielding, the necking/tearing stage became instable most probably due to the inhomogeneous dispersion of the relatively large amount of GR, which in addition has a high aspect ratio. It is noteworthy that unstable fracture in the necking/tearing stage is usually triggered by increasing deformation rate [4] or decreasing molecular weight of amorphous copolyesters [5].

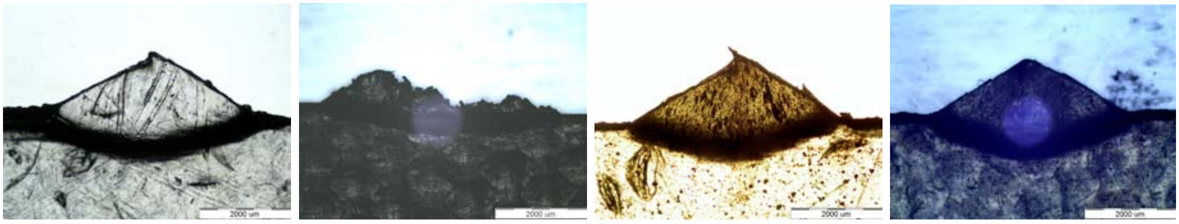
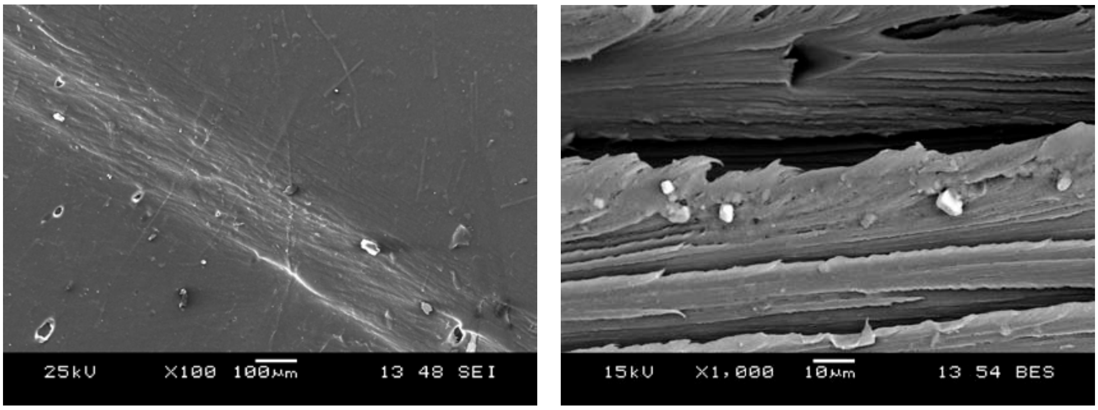


Figure 6. LM pictures taken from the failed DEN-T specimens of the neat PETG, and its nanocomposites containing GR, BA and MMT, respectively (from left to right)

Scanning electron microscopic (SEM) picture taken of the transition zone from the bulk toward the plastic zone of PETG-BA (cf. Figure 7) indicates that shear yielding was responsible for the development of the plastic zone. In the plastic zone some BA-induced voiding can be resolved owing to larger agglomerates. The gross yielding of PETG is, however, not influenced even by larger agglomerates of BA.



a) b)

Figure 7. SEM pictures from the surface of the transition between the plastic zone (bottom left) and bulk (top right) (a) and from the fracture zone (b) of a DEN-T specimen of PETG-BA

Similar to PETG-MMT, the smooth development of the plastic zone in PETG-BA should be ascribed to the homogeneous distribution of these nanofillers which have, in addition, markedly smaller aspect ratios than GR and MWCNT.

The development of the plastic zone and the corresponding failure mode of the EPBC nanocomposites were more complex than those of the PETG-based ones due to the onset of massive crazing.

4 Conclusion

The essential work of fracture (EWF) concept has limited applicability for thermoplastic nanocomposites, even when such polymers are selected as matrices which in unmodified form meet all the necessary requirements (such as the chosen PETG and EPBC). Nanofillers, present in inhomogeneous distribution and possessing large aspect ratio, trigger unstable fracture in the necking/tearing stage due to which the traditional data reduction is inapplicable. This problem can be overcome by energy partitioning provided that for the yielding section of the load-displacement trace the self similarity criterion holds. The toughness of nanocomposites with homogeneously dispersed and low aspect ratio fillers may be properly determined using the EWF. On the other hand, further investigations are needed to derive conclusion on how the EWF parameters are affected by the fillers' inherent and dispersion characteristics.

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