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**On the Toughness of Thermoplastic Polymer Nanocomposites as 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 systems. 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% each. 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 the nanocomposites containing MWCNT and GR by contrast to those with MMT and BA. Accordingly, the toughness of nanocomposites with homogeneously dispersed and low aspect ratio fillers may be properly determined using the EWF. Results indicated that incorporation of nanofillers may result in an adverse effect between the specific essential and non-essential work of fracture parameters.

1 Introduction

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 [1].

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 deeply double edge notched tensile loaded (DEN-T) specimen in Figure 1.

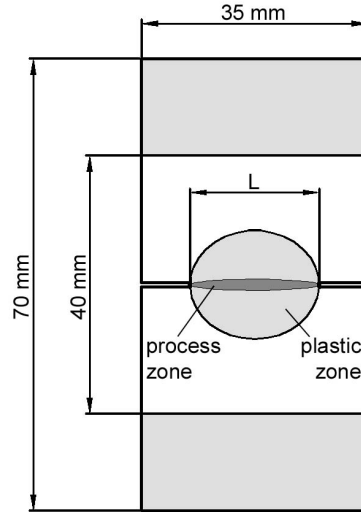


Figure 1. Schematic diagram showing the fracture zones in a DEN-T specimen

The total work of fracture (W_f), calculated from the area of the force-displacement ($F-x$) curves, is given by:

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

Equation 1 can be rewritten into the specific terms (Equations (2) and (3)):

$$W_f = w_e \cdot Lt + \beta w_p \cdot L^2 t \quad (2)$$

$$w_f = w_e + \beta w_p \cdot L \quad (3)$$

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. Its value can be equalled with the resistance to crack initiation. The slope (βw_p) of the linear regression can be treated as a measure of the resistance to crack growth of the material. Detailed information on the EWF testing, data reduction and interpretation can be taken from recent reviews [1,2].

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 [1,3]. 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 following the research philosophy: a) using nanofillers of different aspect ratio and with different dispersibility in polymer melts, and b) choosing such model polymers which satisfy

all the requirements of the EWF use. Accordingly, the following fillers were selected: fibrous multiwall carbon nanotube (MWCNT), platy-type graphene (GR), organophilic-modified montmorillonite (MMT) and quasispherical synthetic boehmite alumina (BA). Unlike MWCNT and GR, hold tightly together by Van der Waals forces, MMT [4], and especially BA [5-6] can be well dispersed in various thermoplastics via melt compounding.

2 Materials and testing methods

Materials and specimen preparation

As matrix materials poly(propylene-*block*-ethylene) (EPBC; Tipplon K499, TVK Nyrt., Tiszaújváros, Hungary) and poly(ethylene terephthalate glycol) (PETG; Eastar Copolyester 6763, Eastman Chemical Company, Kingsport, TN, USA) were selected. These polymers fulfill the most important EWF requirement, namely full ligament yielding prior to crack growth [7-8]. The selected nanofillers were: MWCNT (Baytubes C 150P; Bayer Material Science AG, Leverkusen, Germany), GR (xGnP, XG Sciences Inc., Lansing MI, USA), MMT (Cloisite 30B, Southern Clay Products, Inc., Austin TX, USA) and BA (DisperalP3; Sasol GmbH, Hamburg, Germany). All these fillers were introduced in 1 wt% in the thermoplastics during extrusion melt compounding in a Labtech Scientific type twin-screw extruder (L/D=44; D=26 mm). The granulated nanocomposites were sheeted to a thickness of ca. 0.6mm by compression molding (Collin Teach-Line Platen Press 200E). During processing the recommendations of the suppliers were followed.

DEN-T specimens with the dimension 35 x 70 mm (width x length, cf. Figure 1) 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 [1,8] was adapted:

$$w_f = w_{f,y} + w_{f,n} = (w_{e,y} + \beta^y w_{p,y} \cdot L) + (w_{e,n} + \beta^n w_{p,n} \cdot L) \quad (4)$$

where y and n subscripts denote the yield- and necking/tearing-related terms.

The failure mode of the specimens was inspected in light (LM; Olympus BX51, Hamburg, Germany) and scanning electron microscopes (SEM; JEOL JSM-6380LA, Tokyo, Japan). The conductivity of the test specimens was ensured by coating with an Au/Pd alloy.

3 Results and discussion

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

Modification with GR and MWCNT strongly affected the F-x curves of both PETG and EPBC. Though for the yielding section the self-similarity criterion (i.e. linear transformation results in overlapping of the related curves) fairly holds, this is not at all the case for the necking/tearing part – cf. Figure 2. Accordingly, the w_f vs. L regressions underlayed 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, as well – cf. Tables 1 and 2. Therefore, the EWF conditions were clearly violated when testing GR and MWCNT modified EPBC and PETG nanocomposites. On the other hand, the EWF approach can still be adapted for their yielding-related loading parts of the corresponding F-x curves – cf. Equation 4.

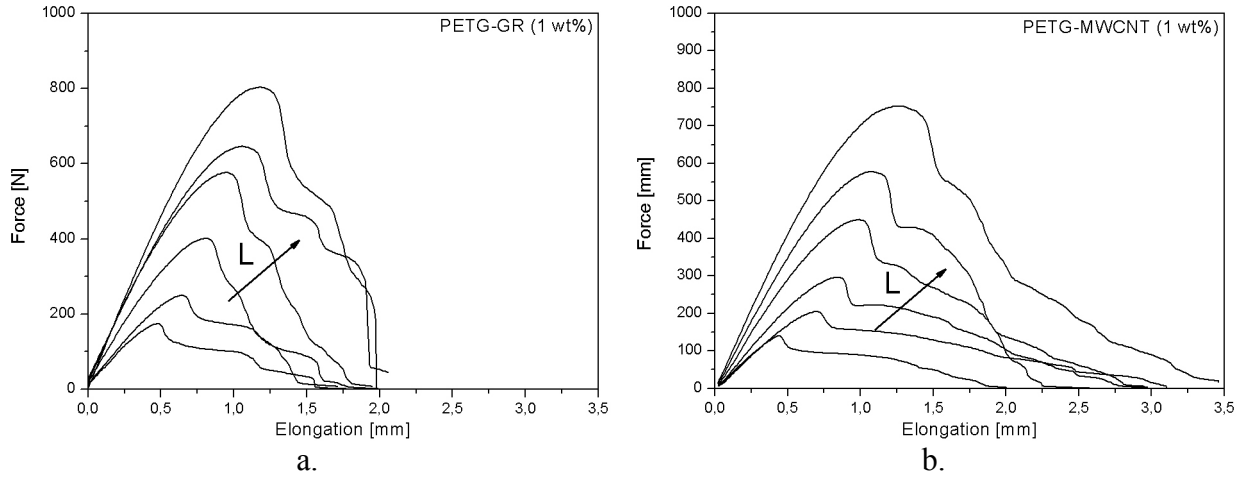


Figure 2. F-x traces as a function of the ligament length (L) measured on DEN-T specimens of PETG-GR (a) and PETG-MWCNT (b). Partitioning between yielding- and necking/tearing-related sections are indicated for the highest ligament specimen

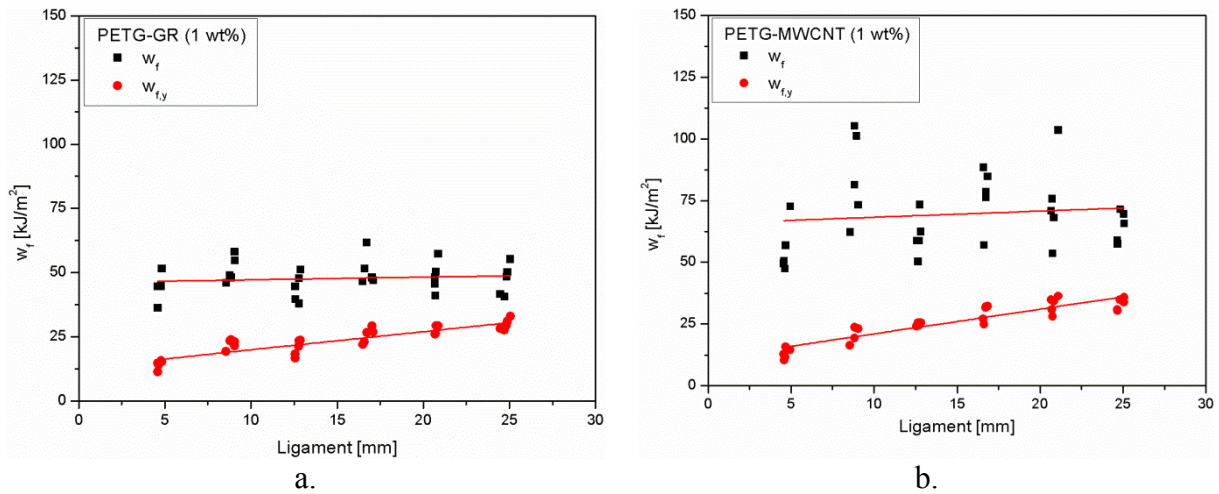


Figure 3. w_f -L traces as a function of the ligament length (L) measured on DEN-T specimens of PETG-GR (a) and PETG-MWCNT (b)

	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
BA	45.0	4.8	0.84	2.7	0.90	0.94
GR	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 (βw_p) 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
BA	51.6	8.3	0.97	9.2	1.12	0.93
GR	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 (βw_p) 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. Moreover, the load drop associated with full ligament yielding [1,8] was also well resolved. This was most helpful to perform the energy partitioning according to Equation 4 – cf. Figure 5.

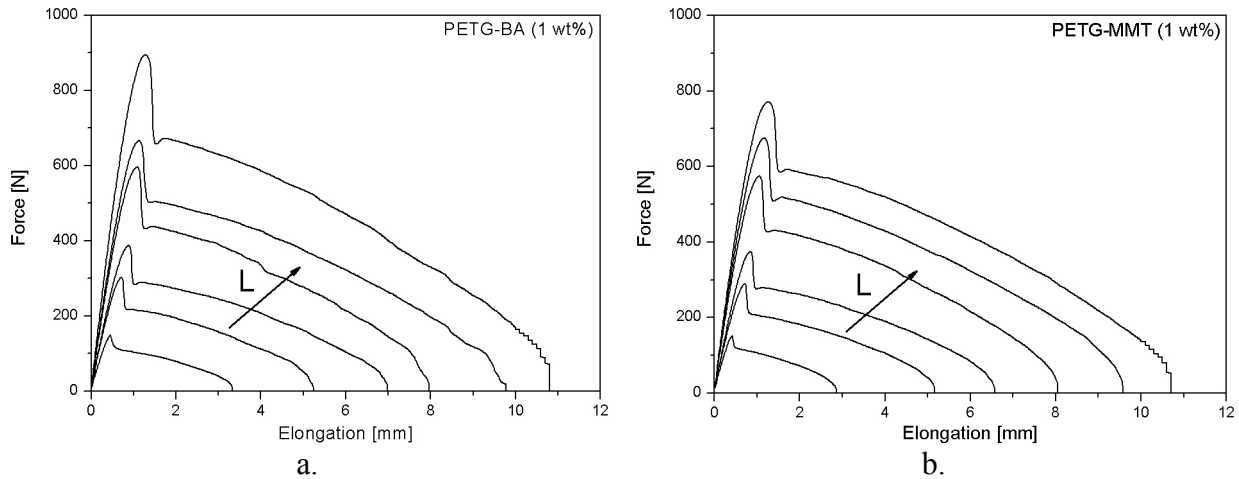


Figure 4. F-x traces as a function of the ligament length (L) measured on DEN-T specimens of PETG-BA (a) and PETG-MMT nanocomposites (b)

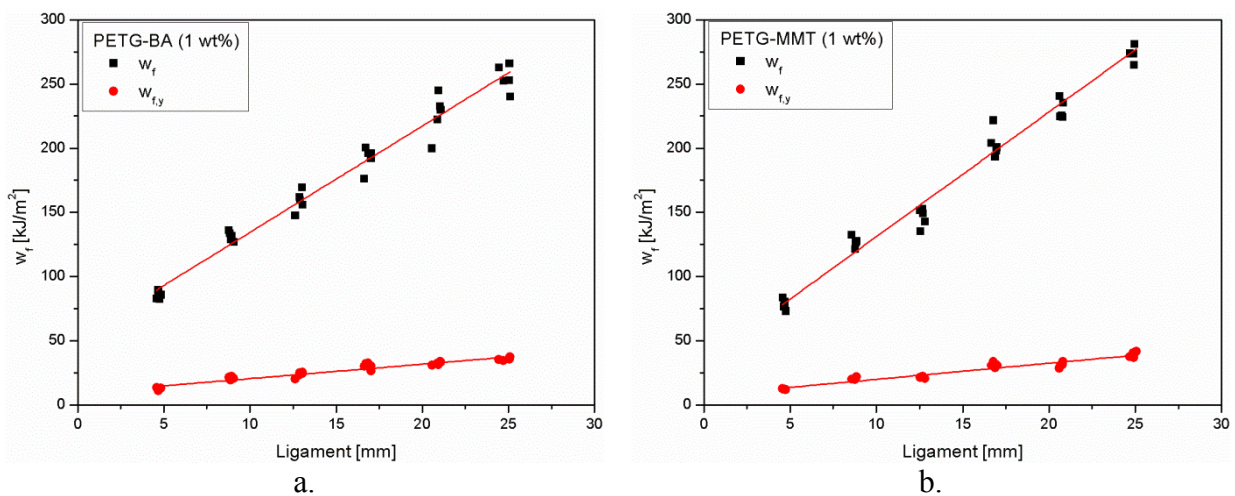


Figure 5. w_f -L traces as a function of the ligament length (L) measured on DEN-T specimens of PETG-BA (a) and PETG-MMT (b)

Note that the load drop is prominent for the PETG (cf. Figure 4) but hardly resolvable for EPBC-based BA and MMT nanocomposites (cf. Figure 6). In case of EPBC instead of instantaneous a delayed yielding occurred which is termed to blunting [1,9]. Further, premature failure in the necking/tearing stage often occurred, especially at high L values – cf. Figure 6a. Nevertheless, the related w_f vs. L traces proved to be fairly linear (cf. Figure 7) with rather high R^2 values – cf. Table 1.

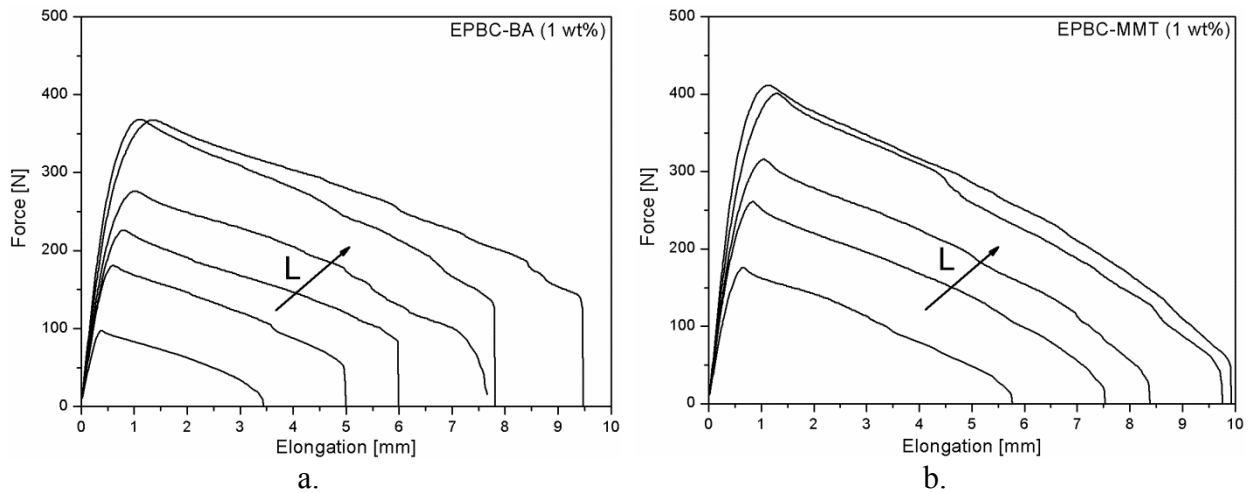


Figure 6. F-x traces as a function of the ligament length (L) measured on DEN-T specimens of EPBC-BA (a) and EPBC-MMT nanocomposites (b).

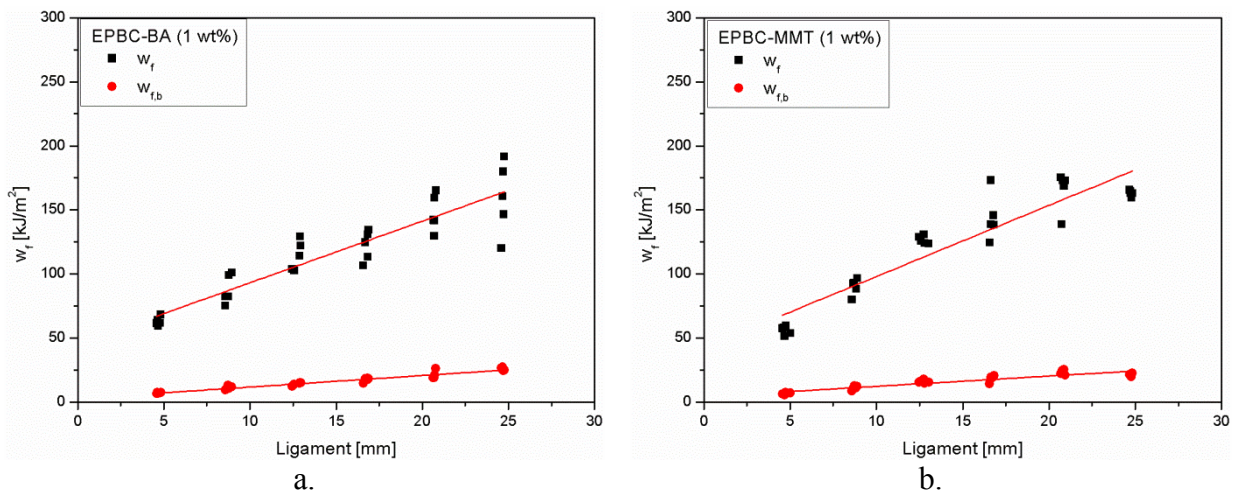


Figure 7. w_f - L traces as a function of the ligament length (L) measured on DEN-T specimens of EPBC-BA (a) and EPBC-MMT (b). Note: $w_{f,b}$ is the blunting-related specific work of fracture calculated by considering the absorbed energy until the maximum load.

Results in Table 1 and 2 suggest that BA nanofiller only slightly affected the specific EWF parameters. This can be traced to the fact that BA does not influence the morphology of either amorphous or semicrystalline polymers markedly [5-6,10]. The scenario is somewhat different for MMT which is prone for the formations intercalated tactoids and may have a large impact on the morphology of semicrystalline systems [4]. This may be the reason for the different changes in the yielding-related terms, i.e. $w_{e,b}$ was enhanced and $\beta'w_{p,y}$ reduced for EPBC/MMT, whereas $w_{e,y}$ was reduced and $\beta'w_{p,y}$ slightly enhanced for PETG/MMT.

Failure

LM pictures were taken from the plastic zone areas of the DEN-T specimens of the neat and modified PETG (cf. Figure 8). One can see that the plastic zone is well developed and quite 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 unstable 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 or decreasing molecular weight in unfilled polymers [1].

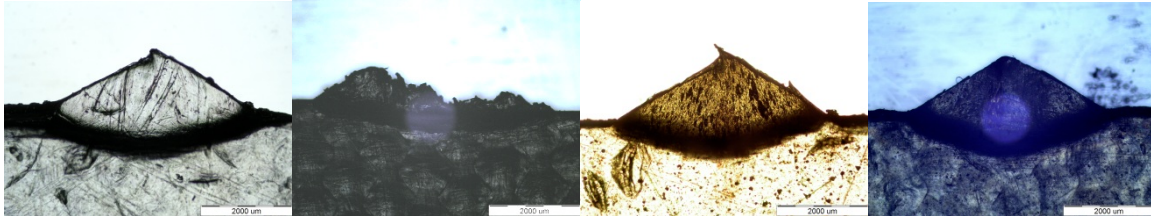


Figure 8. LM pictures taken from the failed DEN-T specimens of the neat PETG, and its nanocomposites containing GR, BA and MMT, respectively (from left to right)

SEM picture taken of the transition zone from the bulk toward the plastic zone of PETG-BA (cf. Figure 9) indicates that the latter was generated by shear yielding. 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. Figure 9B supports that BA particles can be treated as quasispherical ones, in fact.

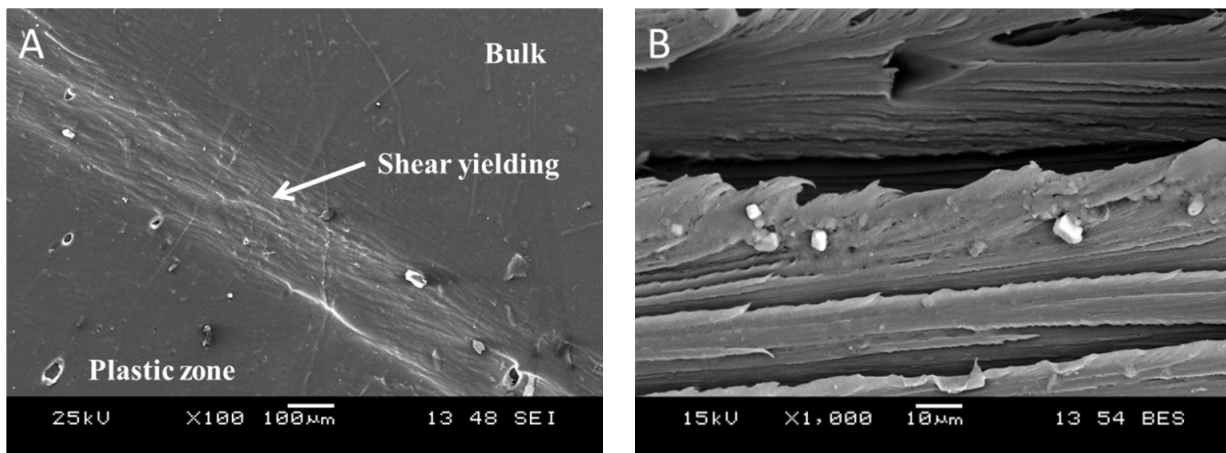


Figure 9. SEM pictures from the surface of the transition between the plastic zone and bulk (A) and from the fracture zone (B) of a DEN-T specimen of PETG-BA

Similar to PETG-BA, the smooth development of the plastic zone in PETG-MMT should be ascribed to the homogeneous distribution of the MMT tactoids (not reported here) which thus have markedly smaller aspect ratios than GR or 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. Figure 10 compares the fracture surfaces (i.e. process zones) of the DENT-specimens with BA, MMT, MWCNT and GR nanofillers. All nanocomposites failed ductilely via voiding/crazing, followed by void/craze growth with extensive fibrillation [11]. Voiding is caused by the filler particles, acting as stress concentrators, and easily detaching from the matrix. The difference in the failure between the nanocomposites is due to the fillers' dispersion. The ductile deformation of the EPBC is less influenced by the

homogeneously and finely dispersed fillers, like BA (cf. Figure 11). By contrast, large aggregates, like GR and MWCNT in Figures 10C and 10D, induce secondary cracking and results in a highly inhomogeneous stress field. This hampers the craze growth with fibrillation the final outcome of which is a premature failure. This is the reason why the DEN-T specimens failed by instable necking/tearing. This manifested in unreliable EWF data – cf. Table 1.

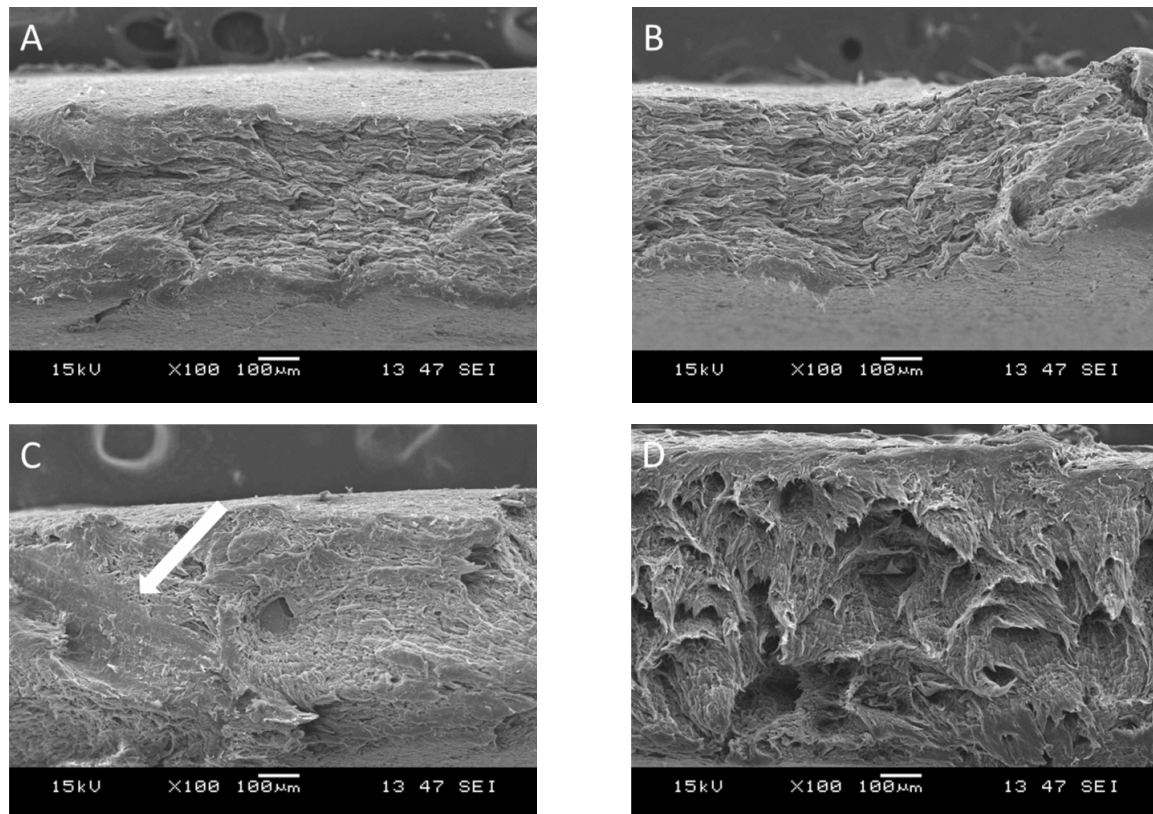


Figure 10. SEM pictures from the fracture zones of DEN-T specimens of EPBC-BA (A), EPBC-MMT (B), EPBC-GR (C) and EPBC-MWCNT (D). Note: secondary cracking is indicated by arrows.

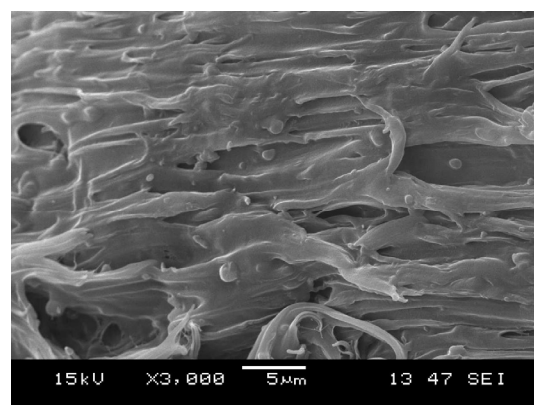


Figure 11. SEM picture from the fracture zone of EPBC-BA

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. This is due to an inhomogeneous stress field created which hampers the full development of shear yielding (PETG) and voiding/crazing (EPBC). As a consequence, the traditional EWF data reduction becomes inapplicable. This problem can be overcome in some cases by the energy partitioning provided that for the yielding section of the load-displacement traces 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 check how the EWF parameters are affected by the nanofillers' inherent (composition, aspect ratio, surface coating...) and dispersion characteristics in the matrices.

Acknowledgements

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