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Effects of mixed contents of carbon nanoreinforcements on the impact resistance of epoxy-based nanocomposites

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Abstract. The impact behavior of epoxy-based nanocomposites reinforced with carbon nano tube (CNT), carbon nano fiber (CNF) and mixed contents of these nanoparticles was investigated using Izod impact test. The results showed that while the impact strength of nanocomposites containing 1 wt% of CNT and 1 wt% of CNF increased 19% and 13% respectively, addition of mixed contents of these nanofillers (0.5-0.5 wt%) demonstrated higher improvement (21%) in the impact resistance. The trend of the results is explained on the basis of different fracture mechanisms of nanocomposites. Furthermore, the fracture surface of specimens and the dispersion state of nanoenhancers have been studied using scanning electron microscopy (SEM) photographs.

Keywords: nano-structures; resins; impact behavior; mechanical testing

1. Introduction

Polymer based composites are widely utilized in different industries due to their satisfactory mechanical properties and lower weight. Among different polymer materials, epoxy resin has attracted much attention with regards to its favorite features such as high specific strength and flexibility (Wetzel *et al.* 2003). However, the inherent brittle characteristics of epoxy resins make them vulnerable to micro crack initiation and consequently, restrict its applications. Therefore, many research studies have been performed to toughen the epoxy resin using various methods (see for example Lee 2001, Deng *et al.* 2008, Mimura 2001, Chen *et al.* 2013, Hsieh *et al.* 2010, Johnsen *et al.* 2007, Liang and Pearson 2010, Wang *et al.* 2013), for instance the application of nanoparticles as reinforcements. Previous studies have shown that the addition of nanoreinforcements could lead to remarkable increase in the toughness of epoxy resins (see for example Kinloch and Taylor 2006, Miyagawa and Drzal 2005, Geng *et al.* 2008, Fidelus *et al.* 2005, Bortz *et al.* 2011, Ayatollahi *et al.* 2011).

Carbon nanofillers such as CNT and CNF are two common reinforcements in epoxy-based nanocomposites. Several researchers investigated the influence of these carbon nanoparticles on different properties of nanocomposites such as mechanical, electrical, tribological and etc. (Ma *et*

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al. 2010, Al-Saleh and Sundararaj 2011, Roy *et al.* 2012). With regards to toughening characteristics, static and dynamic fracture toughness values are key parameters in evaluating the effects of nanoenhancers on toughening properties of nanocomposites. It has been shown in previous studies that separate addition of CNT and CNF to the epoxy resin could result in decent enhancement for both static and dynamic fracture toughness (see for example Ayatollahi *et al.* 2011, Shadlou *et al.* 2013, Ayatollahi *et al.* 2011, Laurenzi *et al.* 2013, Liu and Wagner 2005).

Although there are numerous papers dealing with the impact resistance of nanocomposites reinforced with CNT or CNF, the influence of hybrid contents of these nanoparticles on dynamic fracture energy of nanocomposites has been scarcely studied in the past. Sui et.al, were the only researchers who investigated the effect of mixed content of CNT and CNF on the basic mechanical properties of epoxy-based nanocomposites but not on impact properties (Sui *et al.* 2009). Their results showed that the flexural strength and the fracture strain of the epoxy composites with mixed content of 0.3 wt% CNF and 0.2 wt% CNT increased by 45% and 64%, respectively. Meanwhile, mixed contents of these nanofillers might influence the impact resistance of epoxy significantly and lead to reasonable enhancement of toughening properties.

The main aim of this article is to study the impact resistance of epoxy-based nanocomposites reinforced with CNT, CNF and combinations of these particles. The fracture surfaces of specimens are investigated using scanning electron microscopy (SEM) photographs and the effects of different possible mechanisms involved in the mechanical properties of nanocomposites are discussed.

2. Experiments

2.1 Material

The epoxy resin ML-506 (Bisphenol F) was chosen due to its low viscosity and extensive industrial applications. Because of its low viscosity, the dispersion of additives in epoxy becomes easier. In addition, HA-11 (triethylenetetramine) was chosen as curing agent. The CNT particles supplied by Nanostructured and Amorphous Materials Inc were functionalized multi walled carbon nanotubes (MWCNTs) with diameters between 10 and 20 nm, lengths between 10 and 30 μm, a carbon purity of 95% and mass density of 200 g/m^2. Also CNFs with diameters in the range of 20-80 nm, lengths larger than 30 μm and density of 0.06 g/m^3 were purchased from Group Antolin (Spain).

2.2 Manufacturing

Two types of epoxy-based nanocomposites were prepared by adding MWCNT and CNF separately with different percent weight contents of 0.1, 0.5 and 1 wt.%. The preparation procedure is described below.

First, epoxy was mixed with the desired contents of MWCNTs or CNFs and stirred for 5 min at 1000 rpm. Then, the mixtures containing 0.1, 0.5 and 1 wt.% of nanoparticles were sonicated for 55 min, 60 min and 70 min, respectively. Afterwards, the hardener was added gradually (i.e., drop by drop) while the mixture was being stirred at 150 rpm to prevent the creation of bubbles. Next, the solution was degassed for 12 min in vacuum and casted into impact test shaped mold.

Based on the experimental results obtained for single nanoparticle nanocomposites, three

Table 1 Detailed compositions of different types of nanocomposites

Type of nanocomposites	Carbon nano-tube (wt.%)	Carbon nano-fiber (wt.%)	Total particle loading (wt.%)
Neat Epoxy	0	0	0
0.1%CNT/EP	0.1	0	0.1
0.5%CNT/EP	0.5	0	0.5
1%CNT/EP	1	0	1
0.1%CNF/EP	0	0.1	0.1

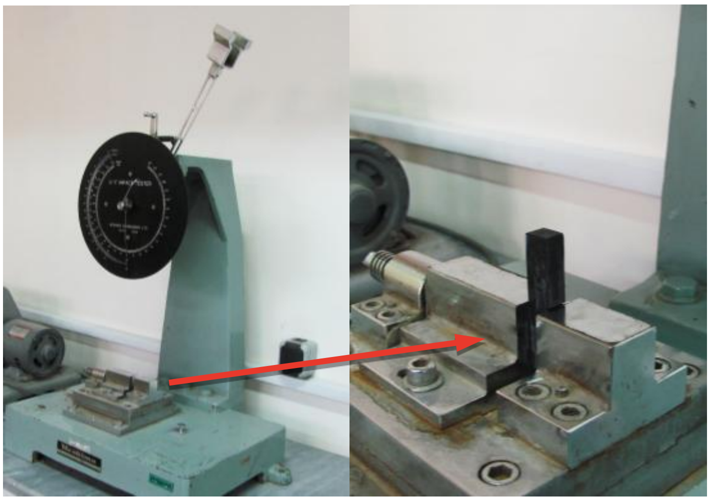


Fig. 1 Experimental set-up for the Izod tests

different mixed contents of MWCNTs and CNF with total content of 1 wt% were selected in preparing hybrid nanocomposites. These three mixed contents were 0.5-0.5, 0.7-0.3 and 0.3-0.7 wt% of MWCNT and CNF, respectively. The procedure of producing hybrid nanocomposites was similar to that of each single nanoparticle nanocomposite. General compositions of all produced specimens are shown in Table 1.

2.3 Test method

The Izod impact strength was measured for neat epoxy and reinforced nanocomposites at room temperature. Izod impact specimens according to ASTM D256-10 standard were tested with a 500 g pendulum (Fig. 1). The dimensions of the notched Izod impact specimens were 63.5 mm (length) ×12.7 mm (width)×10 mm (thickness) with a notch depth of 2.5 mm. Each specimen was held as a vertical cantilever beam and was impacted by a single swing of the pendulum. Therefore, the crack propagated from the tip of the notch. Three samples for each type of nanocomposites were tested and the average results for impact energy were recorded.

2.4 Scanning electron microscopy

After the mechanical tests, the fracture surfaces of the neat epoxy and the nanocomposites were

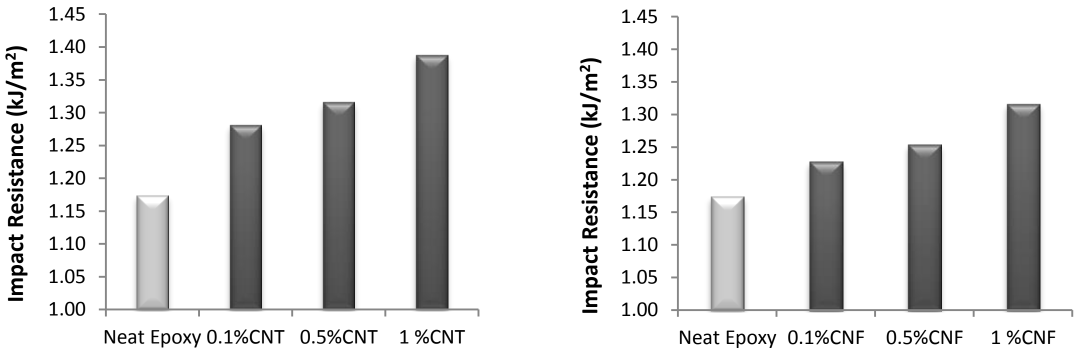


Fig. 2 Impact resistance of (a) MWCNT-epoxy and (b) CNF-epoxy nanocomposites

examined using scanning electron microscopy (SEM) (Tescan VEGA-II SBU) and information related to the dispersion state of MWCNT and CNFs and also the fracture mechanisms was extracted.

3. Results

3.1 Single nanoparticle

Fig. 2 shows the experimental results obtained for the impact energy of nanocomposites reinforced with MWCNT and CNF. As it can be seen, for both types of nanocomposites, there is an incremental trend in the results and the highest enhancement was obtained in nanocomposites containing 1 wt.% of reinforcements within the range considered for particle contents. According to Fig. 2(a), the absorbing energy capacity increases about 10%, 13% and 19% for nanocomposites reinforced with 0.1, 0.5 and 1 wt.% of functionalized MWCNT, respectively. In Fig. 2(b), the impact resistance for the same contents of CNF shows 5%, 8% and 13% improvement relative to the neat epoxy. Therefore, the increase in the fracture resistance of nanocomposites reinforced with MWCNT is relatively higher than the CNF-epoxy nanocomposites.

3.2 Mixed nanoparticles

Fig. 3 shows the results of fracture energy for nanocomposites filled with hybrid contents of MWCNT and CNF. The results of 1 wt.% of MWCNT and CNF are also added to this figure to compare the effects of mixed contents of nanoparticles with those of the individual nanoenhancers. The results show that the fracture energy of nanocomposite with mixed content of 0.5-0.5 wt.% for each nanoparticle exhibits highest improvement of about 21% relative to the neat epoxy. Furthermore, the values of fracture energy for hybrid nanocomposites with 0.7-0.3 and 0.3-0.7 wt.% of MWCNT and CNF have shown enhancement relative to the epoxy resin. However, their enhancement are lower than the improvement in the fracture energies of nanocomposites containing 1 wt % of each nanofiller individually.

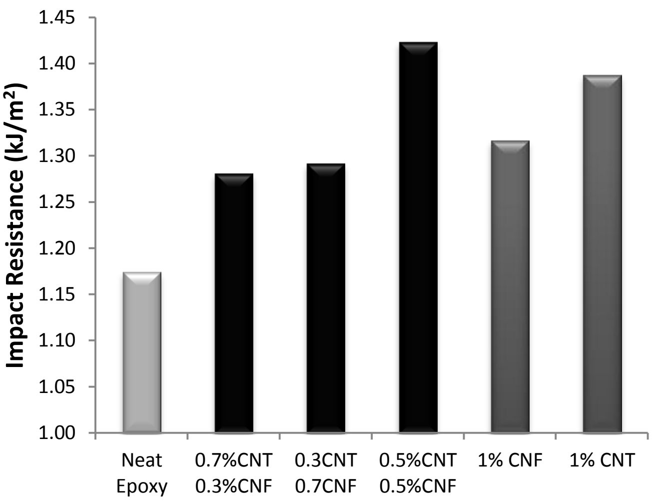
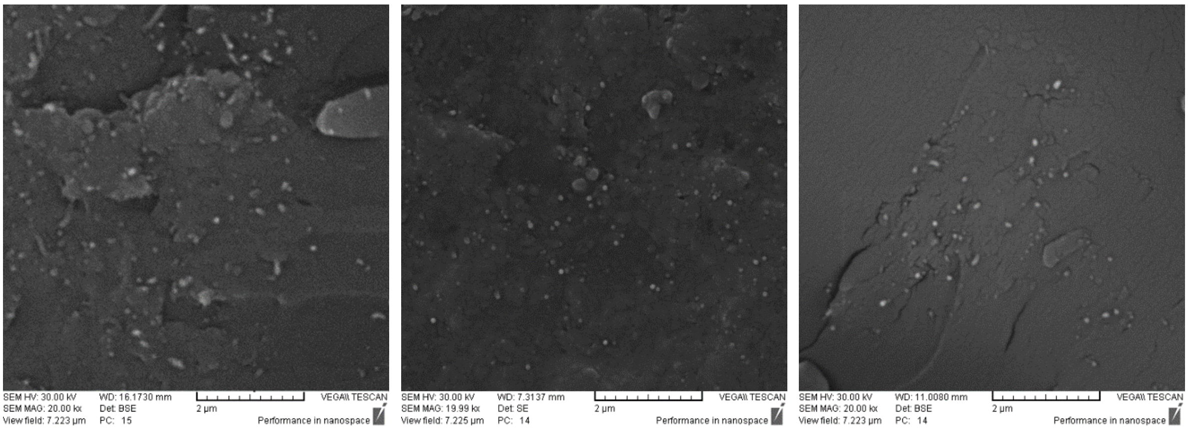


Fig. 3 Impact resistance of nanocomposites reinforced with mixed contents of MWCNT and CNF



(a) (b) (c)

Fig. 4 SEM images showing the dispersion state of nanocomposites containing (a) 0.5wt%MWCNT-0.5wt%CNF (b) 1wt%MWCNT and (c) 1wt% CNF

4. Discussion

In order to justify the trend of experimental results, several micromechanisms that affect the enhancement in the mechanical properties of nanocomposites could be addressed. Generally, the strength and the length of interfacial regions between the nanoparticles and the polymer matrix play a significant role in the performance of different micromechanisms of nanoreinforcements. It is well known that several factors such as surface chemistries (Hirsch and Vostrowsky 2005), geometry (Luo *et al.* 2007) and dispersion state (Ma *et al.* 2010, Song and Youn 2005) of nanofillers influence the interfacial features. Surface chemistries of nanoparticles might be altered using chemical functionalization methods and geometry effects of nanoreinforcements have been

Table 2 Geometrical characteristics of nanoenhancers

Particle	Diameter range (nm)	Length range (μm)	Aspect ratio (L/d)
MWCNT	10-20	10-30	1333
CNF	20-80	30	600

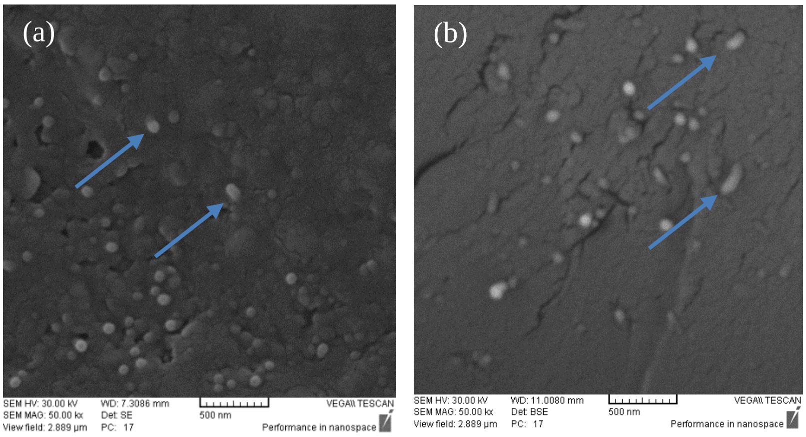


Fig. 5 SEM images showing pulled out nanofillers in the nanocomposites (a) 1 wt% CNT (b) 1wt% CNF

investigated in previous studies (Alishahi *et al.* 2013). Although the presence of agglomerated particles is inevitable, achieving a uniform dispersion state of nanoenhancers could led to remarkable improvement of the fracture energy. The SEM photographs presented in Fig. 4 demonstrate the reasonable dispersion of MWCNT and CNF in different types of nanocomposites suggesting relatively appropriate strength of interfacial regions. This might be one of the reasons for increasing the impact energy in all types of nanocomposites.

In addition to the strength of interface area, the length of this region can affect the dissipating energy mechanisms in nanocomposites. In fact, a longer interface area causes longer crack growth path in this region and consequently, more energy might be absorbed during crack propagation. The effect of nanoparticle aspect ratio on the tensile strength, impact behavior and fatigue behavior of nanocomposites has been investigated by several researchers (Zhang *et al.* 2008, Zhang and Zhang 2007, Ayatollahi *et al.* 2011). They have shown that, in general, with increasing the aspect ratio of nanofillers, the mechanical properties of nanocomposites are improved.

Table 2, shows the geometrical characteristics of nanoparticles used in this study. As it is obvious, the aspect ratio of MWCNT is much higher than CNF particles (more than twice). These characteristics might lead to formation of a longer interface area between the MWCNT and epoxy, and as a result, the impact energy of these nanocomposites takes higher values (see Fig. 2).

In regards to the fracture mechanisms, crack deflection (Zhao *et al.* 2008) and crack pinning (Wetzel *et al.* 2006) are two of the main micromechanisms in nano-reinforcements. On the basis of crack deflection hypothesis, nanoparticles can act as local stopper in the path of crack propagation and then, the crack growth deviates from its initial direction and has to pass over a longer distance. Therefore, the fracture energy increases during crack propagation which results in higher impact resistance of nanocomposites. As an efficient mechanism in the fracture behavior of nanocomposites containing high aspect ratio particles such as MWCNT and CNF, one can name crack bridging (Seshadri and Saigal 2007). Crack bridging phenomenon is related to a situation where the nanofillers are aligned normal to the crack faces and hence, generates higher resistance against crack propagation. According to the data reported in Table 2, MWCNT nanoparticles have higher aspect ratios which demonstrate higher potential for crack bridging in these types of nanoenhancers relative to the CNF nanoparticles. It is noteworthy that another involving mechanism in the fracture of nanocomposites is fiber pull out (Wagner *et al.* 2013) which has deteriorating effects on the fracture parameters.

In order to inspect the pull out mechanisms more precisely, high magnification pictures were also taken from the fracture surfaces. Fig. 5 shows a number of nanofillers that are pulled out of the epoxy matrix. However, some physical features of nanofibers such as waviness can retard the pull out phenomenon and hence increase the fracture energy. This is particularly more important when the aspect ratio of nanoparticles is higher (e.g., in the case of CNT) (Ayatollahi *et al.* 2011).

As illustrated in Fig. 3, hybrid contents of nanocomposites showed reasonable improvements in the impact resistance of epoxy. In order to explain the trend of results, assuming an ideal condition where both CNT and CNF are considered as a tube with diameter d and length L (see Table 2), the approximate number of nanoreinforcements in each type of nanocomposites can be calculated for a test sample. Table 3 demonstrates the calculated numbers of nanoparticles for different nanocomposites. As it can be seen, due to the physical and geometrical characteristics of these particles, the number of MWCNTs in 1 wt.% epoxy-MWCNT nanocomposites is several times the number of CNFs in a sample with the same content of CNF. Additionally, as previously discussed, the aspect ratio of MWCNT is much more than the CNF value. Considering both factors (i.e., number of nanoparticles and aspect ratio), one can conclude that the reinforcement effect of CNT is relatively higher than CNF. This could be easily seen in the experimental results where nanocomposites containing 1 wt.% of MWCNT have a higher impact resistance in comparison with 1 wt% CNF nanocomposites.

Meanwhile, as shown in Table 3, the number of CNT is dominant in all types of mixed content nanocomposites, even if the weight percent of MWCNT is much lower than CNF (for instances, 0.3-0.7 wt% of MWCNT-CNF). Therefore, it can be expected that the results of hybrid contents of MWCNT and CNF nanocomposites will be similar to MWCNT nanocomposites. This assumption is in a relatively good agreement with the experimental results of Fig. 3. While the impact energy of 0.5-0.5 wt% of MWCNT-CNF nanocomposites is near to that of 1 wt.% of MWCNT, the results of other mixed contents (0.3-0.7 and 0.7-0.3 wt% of MWCNT-CNF) are in the same range of nanocomposites reinforced with 0.5 wt% of MWCNT. However, it should be noted that the impact resistance of mixed contents as 0.3-0.7 and 0.7-0.3 wt.% of MWCNT-CNF decreased in comparison with 1 wt.% of MWCNT or 1 wt.% of CNF epoxy nanocomposites. The possible existence of agglomerated particles and the influence of interaction between these two types of

Table 3 Weight and number of nanoparticles in different types of nanocomposites for each test sample

Type of nanocomposites	Weight (g)		Number of nanoparticles	
	CNT	CNF	CNT	CNF
1% CNT	8.06E-02	0	1.71E+13	0
1% CNF	0	8.06E-02	0	2.99E+12
0.5%CNT-0.5%CNF	4.03E-02	4.03E-02	8.55E+12	1.50E+12
0.7%CNT-0.3%CNF	5.64E-02	2.42E-02	1.20E+13	8.98E+11
0.3%CNT-0.7%CNF	2.42E-02	5.64E-02	5.13E+12	2.09E+12

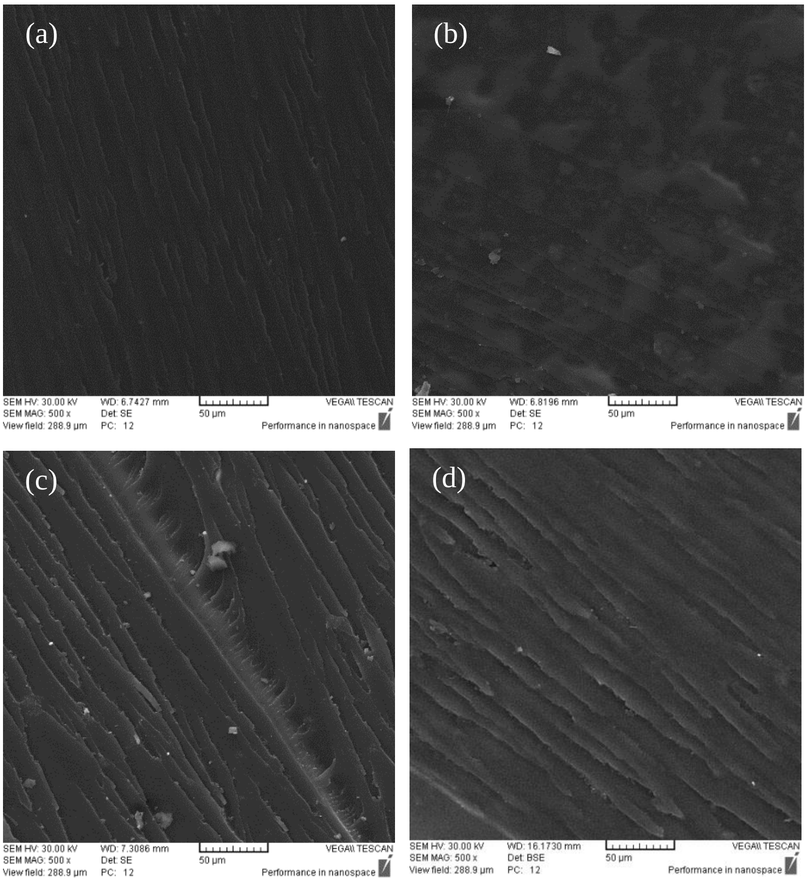


Fig. 6 SEM images of fracture surfaces (a) neat epoxy (b) 1 wt% CNF (c) 1wt% CNT (d) 0.5wt% CNT-0.5wt%CNF

nanofillers could be the reasons for such reduction in the impact energy of hybrid contents of nanocomposites.

Fig. 6 shows the fracture surfaces of epoxy and different types of nanocomposites. As it is clear, the fracture surface of neat epoxy is much smoother than nanocomposites. On the other hand, more cleavage patterns in the fracture surfaces of MWCNT and mixed content nanocomposites are a good indicator of tougher surfaces in these samples. In fact, the roughness of fracture surface can be suggested to be proportionally related to the fracture energy, such that higher fracture energy gives rise to rougher fracture surface (Zhou *et al.* 2008, Hedia *et al.* 2006). As mentioned earlier, the hybrid contents of nanocomposites resulted in higher impact energy which is in good agreement with the roughness of fracture surface shown in Fig. 6(d) In contrast, Fig. 6(b) demonstrated smoother surface in comparison with Fig. 6(c) that can be the sign of lower impact energy for CNF nanocomposites rather than samples reinforced with MWCNT.

5. Conclusions

The influence of nanoreinforcements such as CNT, CNF and hybrid contents of these nanoparticles on the impact behavior of epoxy-based nanocomposites was studied. The experimental results showed that the equally mixed content (0.5-0.5 wt.%) of MWCNT and CNF nanocomposites led to the best enhancement of the impact energy in comparison with the neat epoxy. However, 1 wt% of other mixture ratios of these nanofillers (0.3-0.7 and 0.7-0.3 wt.%) did not show any improvement relative to the nanocomposites with 1 wt.% of each nanoparticle individually. In conclusion, the application of functionalized MWCNT has resulted in higher impact resistance due to the fact that the reinforcement efficiency of MWCNT seems to be more than CNF nanoenhancers. Using SEM photography, different fracture micromechanisms were investigated for explaining the trends of experimental results.

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