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Secondary Crack Formation as Fracture Mechanism in Nanocomposites of Epoxy and Fullerene-Like WS_2

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Fullerene-like WS_2 (IF-WS_2) nanoparticles (NPs) were used as a toughening agent in epoxy nanocomposites. Already 0.5 % IF-WS_2 by mass increased the critical energy release rate G_{Ic} by 45 % to 62 %. Conic-section-shaped crack lines were observed on the fracture surfaces in some distance to the NPs. Nanomechanical AFM modulus measurements showed, however, no measurable differences between the modulus distribution in the vicinity of the NPs and the bulk epoxy. Possible secondary crack formation at the NPs explains the crack lines nicely. The crack line geometry allows determining the relative velocity of the secondary crack. Topographic AFM showed vertical steps several hundred nanometers high at the crack lines, indicating shear fracture and suggesting the presence of numerous subsurface cracks, which might explain the toughness increase.

Keywords: polymer, fullerene-like WS_2, nanoparticles, nanocomposite, epoxy, fracture mechanics, atomic-force microscopy (AFM).

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1. INTRODUCTION

Epoxy is a thermosetting polymer known for its high strength and modulus as well as for its easy processibality, but also for its inherent brittleness. This is why it is usually toughened by introducing another component, for example rigid nanoparticles (NPs). The critical stress-intensity factor K_{Ic} can usually be increased by 5 % to 30 % and the critical energy release rate G_{Ic} by 15 % to 75 %, respectively, for each percent of zero-dimensional NPs added by volume [1–4].

Recently, Shneider et al. showed that fullerene-like WS_2 (IF-WS_2) NPs can toughen epoxy considerably more (by up to 830 % per percent IF-WS_2 added by volume); based on SEM micrographs of fracture surfaces they explained this improvement with a possible region of enhanced modulus in the vicinity of the NPs [5]. Indeed, several researchers have suggested that nanocomposite matrices might exhibit inhomogeneous properties close to the NP filler [6,7].

This work aims at providing more information the fracture mechanisms responsible for the toughening effect of IF-WS_2 in epoxy nanocomposites.

2. EXPERIMENTAL PROCEDURE

IF-WS_2 NPs (density 6600 kg/m³ [5]) were purchased from *Nanomaterials Ltd.* (Israel) and were used either unfunctionalized or after functionalization with various silane surface modifiers, including epoxide or diamine functional groups or an alkyl chain [8]. They were dispersed within 100 parts by mass (pbm) epoxy resin (diglycidylether of bisphenol A, *Epikote 828 LVEL* from *Momentive*) with a three-roll mill; the product was then mixed with 40 pbm polyetheramine curing agent (*Jeffamine T-403* from *Huntsman*) and this mixture was cured in steel molds at 80 °C for 4 h, machined and then post-cured at 100 °C for 3 h. The NP loading was 0.5 % by mass, corresponding to 0.09 % by volume.

Single-edge-notched bending (SENB) specimens of $60 \times 15 \times 4$ mm³ were machined and tested at 5 mm/s according to ISO 13586. The fracture surfaces were investigated with a scanning electron micrsocope (SEM) at 5 kV after sputtering 2 nm of Pt on them. Atomic-force microscope (AFM) was done with a *MultiMode 8 AFM* from *Bruker* with a 10-µm piezo scanner in the Peak-Force Tapping mode with a soft probe (0.4 N/m, 2 nm nominal tip radius) for topographic imaging and a hard probe (40 N/m, 8 nm) for nanomechanical modulus mapping.

3. RESULTS AND DISCUSSION

3.1 Fracture toughness

The measured K_{Ic} was between 0.79 MPa m$^{1/2}$ and 0.86 MPa m$^{1/2}$ (15 % to 25 % increase over the neat epoxy) and the independently determined G_{Ic} was between 206 J/m² and 230 J/m² (45 % to 62 % increase). There was no correlation with the specific surface functionalization. The relative increase of 500 % in G_{Ic} (200 % in K_{Ic}) for each percent of NP added by volume agrees with that reported earlier [5].

3.2 Electron microscopy of fracture surfaces

SEM images of fracture surfaces show a satisfactory dispersion quality and uniform NP distribution (see Fig. 1); this agrees with the dynamic light scattering measurements which showed average agglomerate sizes of approx. 170 nm. Crack lines are visible around most NPs; they are often several hundred nanometers distant from the NPs and when this is the case, they frequently exhibit a conic-section shape.

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3.3 Modulus distribution

It has been proposed that both the crack lines and the enhanced toughness are due to matrix inhomogeneity close to the nanoparticles [5]. To test that, nanomechanical AFM modulus mapping was done on smooth ultramicrotome cuts on regions close to NPs. The matrix modulus was measured to be constant at (3250 ± 150) MPa up to a few nanometers away from the NP (agglomerate) edges (Fig. 2). If modulus inhomogeneities are present, they are too small in their lateral size and/or their magnitude to be resolved this way. It is thus unlikely that the observed crack lines are due to significant modulus inhomogeneities.

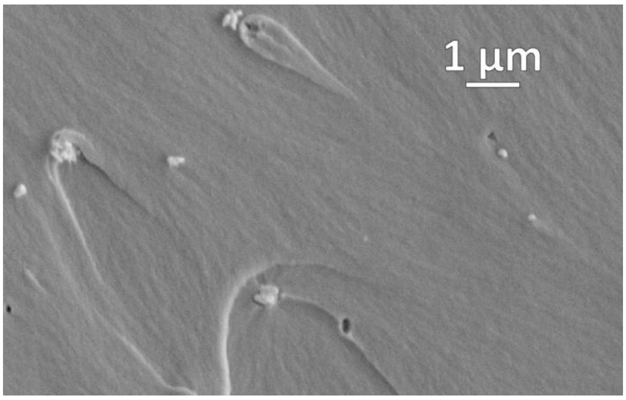


Fig. 1 – Representative SEM image of a nanocomposite fracture graphics

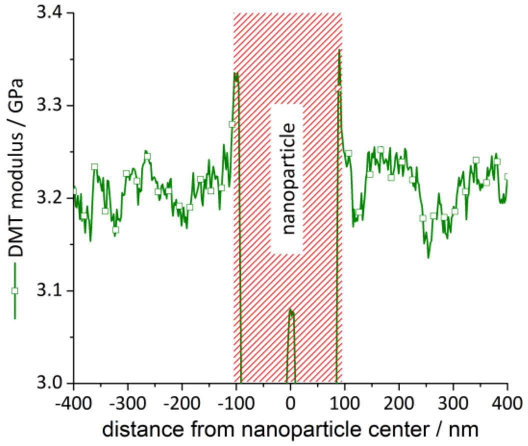


Fig. 2 – Modulus distribution over distance to a nanoparticle (agglomerate) as measured with nanomechanical AFM; outside the nanoparticle, the modulus is roughly constant

3.4 Secondary cracks

An alternative fracture mechanism might explain the observed phenomena better: The initiation of secondary cracks was long since recognized as the source of conic-section-shaped crack lines in unfilled polymers [9]. Likewise, the crack lines observed in the present study could be explained by secondary cracks, which initiate at the NP surfaces when the primary crack is a certain distance away from these NPs, and propagate radially from there: When the secondary cracks overlap with the primary crack, vertical shear fracture can take place, resulting in a vertical step that is visible as a crack line.

Assuming that both the velocity of the secondary crack v_s and that of the primary crack v_p are constant, such effect would result in a hyperbola, a parabola or an ellipse for geometric reasons (see Fig. 3). As v_s will, however, usually not be constant, differently shaped crack lines are more frequently observed.

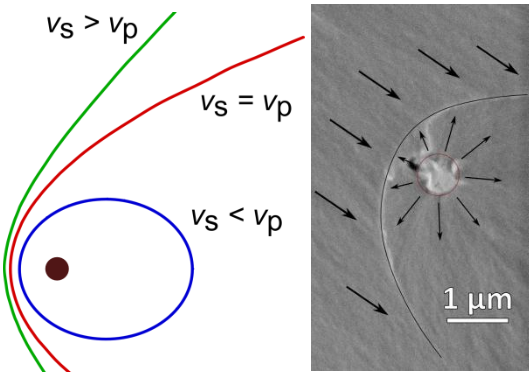


Fig. 3 – Left: shapes of an ideal secondary crack around a NP depending on the ratio of v_s to v_p. Right: electron fractograph showing a parabolic crack line; arrows indicate the presumed propagation direction of the primary and the secondary crack, respectively.

3.5 Step height

Topographic AFM measurements of the fracture surfaces like that in Fig. 4 showed vertical steps up to 300 nm at crack lines. Thus, not only was additional fracture surface created at crack lines, but fracture happened parallel to the main stress direction. Moreover, it is possible that numerous additional secondary cracks have been created that did not connect to the primary crack and thus remained subsurface. Nevertheless, the additional fracture surface created by them might be another factor explaining the toughness increase.

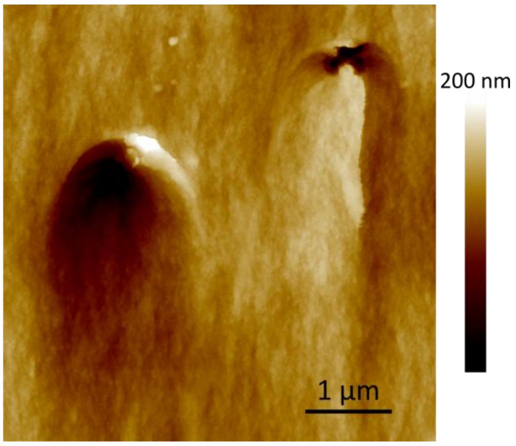
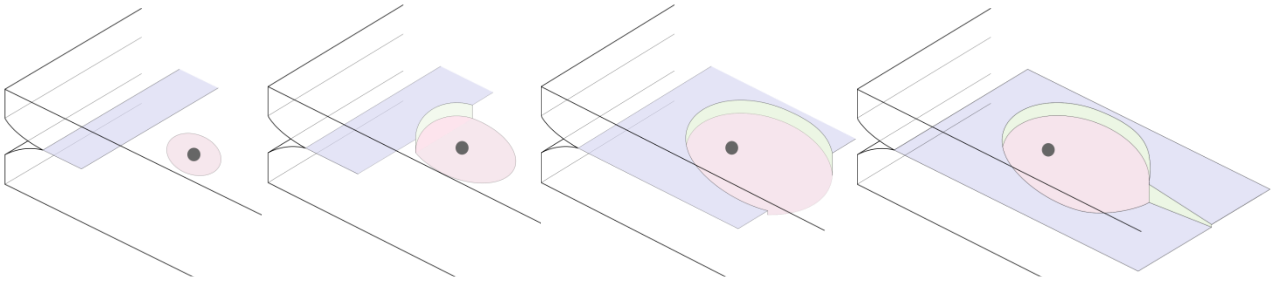


Fig. 4 – Topographic AFM image of the crack lines around two NPs

3.6 Secondary cracks or crack pinning

The authors believe that these secondary cracks do not form exclusively in epoxy–IF-WS_2 nanocomposites, but in many different kinds of brittle nanocomposites, but they might only be observable for particular NP (agglomerate) sizes.



(a) Secondary crack propagating radially (b) Cracks overlapping, shear fracture (c) Formation of elliptic shape (d) Formation of a crack-pinning tail

Fig. 5 – Schematic drawing of a secondary crack resulting in height steps, shear fracture and a crack-pinning tail.

It is worth mentioning that these secondary cracks result in crack lines that are very similar to what is usually called the *crack pinning* effect. It is indeed possible that reported crack pinning *tails* are in many cases just crack lines from secondary cracks. A mechanism how secondary cracks could result in crack-pinning tails is depicted in Fig. 5.

4. CONCLUSIONS

Introducing small loadings of IF-WS_2 into an epoxy matrix improves its fracture toughness considerably. Nanomechanical AFM modulus measurement was used to measure the modulus distribution in the vicinity of NPs, but no measurable modulus inhomogeneity was present. It is thus unlikely that modulus inhomogeneities cause the visible crack lines.

Instead, they are most likely due to secondary cracks that initiate at the NP surfaces and propagate radially from there. This results in shear fracture and height steps of up to 300 nm and quite likely causes numerous subsurface cracks. These effects combined might explain the considerable toughness increase. The proposed mechanism happens likely also in other kinds of nanocomposites, but might often be confused with crack pinning.

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REFERENCES

1. B. Wetzel, P. Rosso, F. Haupert, K. Friedrich, *Eng. Frac. Mech.* **73** No16, 2375 (2006).
2. B.B. Johnsen, A.J. Kinloch, R.D. Mohammed, A.C. Taylor, S. Sprenger, *Polymer* **48** No2, 530 (2007).
3. H.Y. Liu, G.T. Wang, Y.W Mai, Y. Zeng, *Composites B* **42** No8, 2170 (2011).
4. D.J. Bray, P. Dittanet, F.J. Guild, A.J. Kinloch, K. Masania, R.A. Pearson, A.C. Taylor *Polymer* **54** No26, 7022 (2013).
5. M. Shneider, H. Dodiuk, R. Tenne, S. Kenig, *Polym Eng. Sci.* **53** No12, 2624 (2013).
6. G. Liu, H. Zhang, D. Zhang, H. Zhang, Z. Zhang, X. An, X. Yi, *J. Mater. Sci.* **47** No79, 6891 (2012).
7. T.V. Prevenslik, *Proc. NAP* **3** No2, 02NNSA05 (2014).
8. D. Haba, Th. Griesser, U. Müller, A.J. Brunner, *J. Mat. Sci.* **50**, 5125 (2015).
9. *Fractography and failure mechanisms of polymers and composites* (Ed. A.C. Roulin-Moloney) (Essex: Elsevier Applied Science: 1989).