Hybrid effects in the fracture toughness of polyvinyl butyral-based nanocomposites

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ABSTRACT
Hybrid polyvinyl butyral (PVB) nanocomposite films comprising surface-treated carbon nanotubes (CNT-COOH) and nanoclays (NC) were tested for their “trouser-leg” fracture toughness in comparison to the values of the respective CNT and NC parent composites and to that of the pristine PVB film. Relative to the fracture toughness of the pristine PVB, the parent composites PVB/CNT-COOH-0.2% and PVB/NC-2% and the PVB/CNT-COOH-0.2%/NC-2% hybrid exhibited 105, 118, and 181% improvements, respectively. These were both impressive fracture toughness improvements and a significant hybrid effect – the latter being only slightly lower than the nominal maximum effect of 223% based on the combined improvements of the parent composites. Part of the samples was tested qualitatively by ball impact test of ballistic glass samples with relevant films. Among these samples, the hybrid film presented the best result. A significant linear correlation between fracture surface energy and roughness values was taken to reflect a fracture resistance mechanism of crack front slowdown by its interactions with nanoparticles.

1. Introduction
Hybridization with more than one type of reinforcement has been shown classically in fiber-reinforced composites to generate synergism, which can potentially produce positive hybrid effects in the mechanical properties. Positive hybrid effects (for two types of reinforcement, e.g. carbon and aramid fibers) are generally defined either as a positive deviation from the rule of mixtures behavior (considering the weighted contributions of the reinforcements and the matrix) or, more generally, as a hybrid property that is higher from those of any of the constituents alone. A large number of examples exist in the literature, entailing different constituents and different mechanical properties, with emphasis on modulus strength and fracture toughness, as presented in a variety of papers.1–6

The re-discovery of carbon nanostructures in the 1990s7 – and eventually of a host of other nanoparticles – generated immediate interest in the prospects of harnessing nanoparticles to ultra-high mechanical property composite materials, termed nanocomposites. It was their nominal mechanical properties, being orders of magnitude higher than those of classical reinforcement fibers, which made nanoparticles attractive as reinforcement constituents, wherein low concentrations would be...
potentially required to match and surpass properties of classical composites of high concentrations.\cite{8} It is important to note, however, that a number of requirements ought to be fulfilled for nanoreinforcement to perform up to its theoretical potential, which include a uniform dispersion of individual (exfoliated) nanoparticles, good interfacial bonding to the polymer matrix and a high aspect ratio.\cite{9, 10} The requirement of high aspect ratio is elaborated as follows. The general definition of nanoreinforcement refers to particles with at least one nanometric dimension, thus dividing the family of nanoparticles to three subfamilies as shown in Figure 1. Of them, only two subfamilies, the 1-D and 2-D nanoparticles are suitable for reinforcement, as they may present a high geometrical aspect ratio, which can be above the theoretical critical aspect ratio.\cite{11}

As shown recently in an extensive review of the mechanical behavior, based on a survey of a large number of scientific articles on a wide range of nanocomposite materials, the strength and modulus fail to fulfill their expected values and the experimental values, except for low nanoparticle concentrations, do not necessarily exhibit a linear increase with the nanoparticle concentration (a rule of mixture behavior).\cite{12-15} A number of reasons have been listed to explain the observation that the reinforcing potential of nanoparticles is not fully realized, including weak interfacial interactions, poor dispersion, and degradation of the nanoparticles during the preparation processes, undermining an effective stress transfer mechanism, which is essential for the reinforcing process. If fact, it was claimed that nanocomposites should not be expected to act like a true composite and that they rather be regarded as a molecular mixture with nanoparticles, for which the micromechanical models of strength and modulus do not apply.\cite{16}

In contrast, it has been shown that the fracture toughness of polymers can be enhanced significantly by the introduction of nanoparticles to form nanocomposites. This is because fracture toughness of nanocomposites – unlike the static properties – depends on the mechanisms of energy dissipation by crack front interactions with the nanoparticles, such as pinning of the crack front and particle pull-out, and not on a stress transfer mechanism. Thus, the enhancement of fracture toughness can be obtained by introducing nanoparticles such as CNT, graphene, nanoclays, and nanosilica, where optimized toughness can be achieved by incorporation of a proper size, type and amount of nanoparticles, which in turn determine the energy dissipating mechanisms.\cite{17-19}

The fact that fracture toughness depends on the specific interactions between the crack front and the nanoparticles, as determined by their particular properties,\cite{20-22} calls for the use of two or more types of nanoparticles to form hybrid nanocomposites. And so, the motivation for the present study was to explore the conditions that may produce positive hybrid effects in the fracture toughness of nanocomposites based on nanoclay (NC) and treated carbon nanotubes (CNT-COOH), which represent an arbitrary case, where the two types of nanoparticles differ in both their chemical nature and geometry.

2. Experimental section

2.1. Materials

Poly vinyl butyral (PVB) films of Willing®Architex\textsuperscript{TM} with density of 1.065 g/cm\textsuperscript{3} and thickness of 0.76 mm were supplied by OSG, Israel. Multi-walled CNTs functionalized with COOH groups, small concentrations of OH groups, length of 1–2 μm, tube diameter of 10–30 nm, and purity above 95% were provided by Cheap tubes, USA. Nanoclay, Nanomer-1.30E, montmorillonite clay surface modified with 25–30% octadecylamine, bulk density of 0.41 g/cc, thickness of 8 nm, and particle size below 20 μm were produced from Nanocor, and supplied by Sigma Aldrich, Israel. Chloroform with purity rank of CP was provided by Bio-Lab Ltd, Israel.

2.2. Sample preparation

Polyvinyl butyral was dissolved in chloroform and stirred at room temperature for 48 h. The solutions were divided in two and each half underwent the following process: 30 ml of the solution were sonicated either at 100 or 700 W (which are commonly acceptable sonication energies for nanocomposite\textsuperscript{7}) with half of the nanofiller for 20 min, 70 more ml were added for an additional sonication period of 20 min, and then the remaining 150 ml were added for a concluding sonication of 20 min. Finally, the two solutions were combined and mixed together, cast into a Teflon template and allowed to dry slowly over 5 days to obtain ~500 μm thick nanocomposite films with different weight percentages (wt.%) of fillers (CNT-COOH and NC). An ultrasonic cell crusher (economy) JY88-11N of Ningbo Sklon Lab Instrument was used for 100 W sonication and Syclon Ningbo Haishu Sklon Electronic Instrument was used for 700 W sonication.

Figure 1. Classification of the particles according to their geometries into three groups: nanoparticles, nanofibers, and nanoplatelets. The aspect ratio is the ratio between the long and the short dimensions, as noted.
2.3. Mechanical characterization

Fracture surface energy was tested by the Mode III trouser-leg tear test using Instron 3345 universal testing machine with load cell of 500 N. The specimens were 5-cm long and 2-cm wide with an initial cut length of 3 cm. Loading of a trouser-leg specimen is demonstrated in Figure 2 the specimens were pulled apart at a constant speed of 50 mm/min. Testing was performed in the 25–28 °C temperature range.

The fracture surface energy is equal to half of the tear energy and expressed by

$$\gamma = \lambda \frac{f}{t} - \frac{W_A A_0}{2t}$$

where $\gamma$ is the fracture surface energy, $\lambda$ is the extension ratio, $f$ is the tearing force, $t$ is the thickness of the specimen, $W_A$ is the stored energy function, and $A_0$ is the cross-sectional area of uncut specimen. The trouser-leg tear specimen can be divided into 3 regions: 1 – unstrained, 2 and 2’ – regions of uniform strain that fits the extension ratio $\lambda$, and 3 – region of non-homogenous strain (Figure 2). For non-perfectly elastic polymers, with small strains in regions 2 and 2’ (as in this study), the term $\frac{W_A A_0}{2t}$ is negligible compared to $\lambda \frac{f}{t}$. Hence, it is commonly assumed that – since $\lambda \approx 1$, the equation is reduced to:\n
$$\gamma = \frac{f}{t}$$

Impact test was performed by a falling ball instrument. The weight of the ball was 260 g and the falling height was 10.9 m. Test specimens of simulated ballistic glass were prepared by the standard commercial manufacturing process (temperature and pressure) by inserting a PVB film between two glass layers of 0.38 mm thickness and 300 × 300 mm area.

2.4. Morphological characterization

The quality of dispersion was analyzed by STEM, a mode of extra high-resolution scanning microscopy (XHRSEM), MagellanTM 400L. The operating voltage and current were 18–20 kV and 50 pA – 0.2 nA, respectively. The samples were inserted into epoxy resin and kept in the oven for few hours, then sliced using a diamond knife to a thickness of ~170 nm, and placed on copper or carbon grid.

The level of clay intercalation/exfoliation was tested by X-ray diffraction D8 Advance, in the range of 0°–60° for 2-Theta.

The fracture surface of PVB/NC samples was examined by a high-resolution scanning electron microscope (HRSEM), Sirion. The operating voltage was 5 kV. The samples were coated by a mixture of Au-Pd for 60 s, using a SC7640 Sputter.

2.5. Thermal characterization

Thermal analysis was performed by dynamic mechanical analysis (DMA), TA Instruments, Q800, V20.24 Build 43. The samples were cut into rectangular shape of 6 × 0.5 cm and scanned from −100 °C to 100 °C at a heating rate of 3 °C/min, in a tensile mode at a constant test frequency of 1 Hz. Glass transition temperature was calculated from the peak of tanδ, given by the ratio of storage to loss modulus.

2.6. Surface roughness measurements

Quantitative roughness measurements of fracture surfaces (after tear test and re-coating like the SEM specimens) were performed by an optical profilometer ContourGT Optical Profile, Bruker to measure the RMS roughness ($R_q$) defined as the root mean square average of the roughness profile ordinate. Each sample was measured in three different zones and an arithmetical average $R_q$ value was calculated.

3. Results

3.1. Mechanical properties

The fracture surface energy values of the parent nanoparticle-reinforced composites and of the hybrids, prepared by 100 W sonication, are presented in Figure 3. Part of the specimens prepared by 100w (PVB/NC-1%, PVB/CNT-COOH-0.025%/NC-0.25% and PVB/CNT-COOH-0.05%/NC-0.5%) showed some reduction in the fracture energy. In addition to a lower quality of the dispersion, other significant factors might also be active, particularly a relatively small number of large aggregates. The only apparent significant improvement
over the 100 W sonication, wherein all the samples exhibit significant improvements compared to the neat polymer (confirmed by one tailed t-test). The most meaningful observation is the apparent hybrid effect as the fracture energy of the PVB/CNT-COOH-0.2%/NC-2% hybrid is significantly higher than either of those of the PVB/CNT-COOH-0.2% and PVB/NC-2% parent composites (confirmed by one tailed t-test). Relative to the fracture toughness of the neat PVA the parent composites PVB/CNT-COOH-0.2% and PVB/NC-2% and the PVB/CNT-COOH-0.2%/NC-2% hybrid exhibited 105, 118, and 181% improvements, respectively. This is an impressive hybrid effect – only slightly lower than the nominal maximum effect of 223% based on the combined improvements of the parent composites.

Next, the results of the falling ball impact tests are presented for 100 W sonicated samples. It is noted that these tests were qualitative – aimed at assessing the feasibility of nano-hybrid films for safety glass – and were evaluated by visual examination, classifying the results by the extent of damage exhibited by the polymer layer as shown in Table 1, measured by the length of the observed tear with respect to the size of the overall damage zone. In this test, the damage classes are penetration (it is noted that no cases of full penetration occurred here), extensive, medium, small and minor, which express relative tear length ranging from 0.50 to a local minimal tear and to a full arrest of the impactor (with no visible tear damage). Two types of damage are displayed for

Figure 3. Fracture surface energy results of parent and hybrid (NC/CNT/PVB) nanocomposite compositions prepared by 100 W sonication. Each column presents the average of at least 7 measurements.

Figure 4. A comparison of the fracture surface energy of selected PVB samples: neat PVB (gray), nanocomposites prepared by 100W sonication (pink diagonal line), nanocomposites prepared by 700W sonication (cyan squares). Samples prepared by 700W exhibit higher values. Each column presents the average of at least 7 measurements.
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categories: phase separation, intercalation, and exfoliation. Phase separation describes stacked layers of clays dispersed in the polymer; intercalation occurs when polymeric chains infiltrate into the galleries between the clay layers, increasing the interlayer space while retaining the periodic arrays; exfoliation is manifested in a complete separation and dispersion of individual layers. Fully exfoliated nanoclays are expected to be efficient reinforcing nanoparticles due to their potentially high aspect ratio. A common method to evaluate the quality of dispersion is the small angle X-ray diffraction (SAXS) analysis, which produces the inter-layer distance $d$. Figure 8 present SAXS traces of the different composite samples and of an NC powder reference. The main observation is an approximately 0.7 degree shift to higher 2-theta values of the composites relative to the NC reference, whereas the differences between the different composites seem to be minor. The calculated values of the inter-layer distance $d$ in the clay lattice are summarized in Table 2.

Despite the fact that single platelets of nanoclays were seen in the STEM and SEM images, the SAXS results, which reflect average values, indicate no significant intercalation and exfoliation. In fact, the average values of the composites are even smaller than the reference. Two complimentary observations are that the higher sonication power seems to be more effective and that the presence of the CNT in the CNT/NC hybrids has no effect on the inter-layer distance.

3.2. Morphology analysis

Morphology analyses of the films were carried out by STEM, XRD, and SEM to determine the quality of the dispersions with reference to their uniformity and particle exfoliation. STEM analyses were selectively applied to samples that presented enhanced fracture surface energy values. Images of such 100 and 700 W samples – both composites and hybrids – are presented in Figures 6 and 7, respectively. Comparative viewing of the images reveals that sonication with a 700 W power of the PVB/NC composites is more effective in producing uniformly dispersed individual NC particles with smaller aggregates than samples prepared by 100 W sonication. Regarding the PVB/CNT-COOH-0.2% composites prepared by 700 W, exhibit non-uniform dispersions which contain small aggregates and single nanotubes. Some of the tubes, however, seem to have been broken and their lengths are shorter than the original one (1–2 μm). Regarding the PVB/CNT-COOH-0.2%/NC-2% hybrids, samples prepared by 700 W, show a more uniform dispersion of individual particles and aggregates. No interaction was observed between the two types of particles.

It is a standard practice to classify the dispersion quality of nanoclays in polymeric matrices into three categories: phase separation, intercalation, and exfoliation. Phase separation describes stacked layers of clays dispersed in the polymer; intercalation occurs when polymeric chains infiltrate into the galleries between the clay layers, increasing the interlayer space while retaining the periodic arrays; exfoliation is manifested in a complete separation and dispersion of individual layers. Fully exfoliated nanoclays are expected to be efficient reinforcing nanoparticles due to their potentially high aspect ratio. A common method to evaluate the quality of dispersion is the small angle X-ray diffraction (SAXS) analysis, which produces the inter-layer distance $d$. Figure 8 present SAXS traces of the different composite samples and of an NC powder reference. The main observation is an approximately 0.7 degree shift to higher 2-theta values of the composites relative to the NC reference, whereas the differences between the different composites seem to be minor. The calculated values of the inter-layer distance $d$ in the clay lattice are summarized in Table 2.

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Supplementary information on the nature of the NC composites was obtained by taking SEM images of

Table 1. Falling Ball Impact Test Results, classified by the tear damage size, of the 100 W parent, and hybrid composites with reference to the neat PVB.

| Film composition       | Extensive | Medium | Small | Minor | Full Arrest |
|------------------------|-----------|--------|-------|-------|-------------|
| PVB-reference          | 2/5       | 1/3    | 2/3   | 1/5   | 1/5         |
| PVB/NC-1%              | 2/5       | 1/4    | 1/5   | 2/5   | 1/5         |
| PVB/CNT-COOH-0.1%/NC-1%| 1/4       | 3/4    | 3/4   | 3/4   | 3/4         |
| PVB/CNT-COOH-0.1%      | 1/5       | 1/5    | 2/5   | 1/5   | 1/5         |

Figure 5. After impact (falling ball) samples: (a) PVB/NC-1%, the arrow pointing at a wide tear damage in the polymer film within the impact point of the glass specimen; (b) PVB/CNT-COOH-0.1% with no apparent damage to the polymer film within the impact point of the glass specimen.
particles. The extents of intercalation/exfoliation in both cannot be decided.

As polymer morphology is also manifested in the glass transition temperature, dynamic mechanical analysis (DMA) was performed and its results are presented in Figure 10. As can be seen, the composition of the samples does not have a significant effect on the glass transition temperature, manifested by the tanδ peak temperature in the range 30–34 °C.

Finally, the tear surface morphology of the trouser leg specimens was examined by SEM analysis. Surface images of the parent and hybrid composites are shown in Figure 11 at two magnifications. Looking at the higher magnification images it appears that the hybrid tear surface exhibits the highest roughness, which may account for its highest fracture toughness. Validation of this qualitative impression was achieved by carrying out roughness measurements with an optical profilometer to measure the RMS roughness ($R_q$) defined as the root mean square average of the roughness profile ordinate. The results are presented in Table 3. It is seen that the roughness of the tear surfaces of the composites is way higher than that of the PVB reference and that of the hybrid is by far the highest.

post-impact samples (Section 3.1) of PVB/NC-2% prepared by 700 W sonication. The images presented in Figure 9 show typical NC aggregates and individual NC particles. The extents of intercalation/exfoliation in both cannot be decided.

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composite and hybrid samples exhibited even slightly smaller average interlayer distances compared to the NC powder (indicating lack of intercalation or exfoliation). Similar observation were already reported in the literature for high temperature dispersion processes.25,26

The observation that high fracture energies were exhibited by the nanocomposites regardless of the quality of exfoliation is a strong indication that mechanisms other than stress transfer, which do not depend on the particle aspect ratio, control the fracture process. The fracture toughness in general and the hybrid effect specifically depend on the amount of energy that is dissipated in the interaction between the advancing crack front and the nanoparticles, which is expressed in turn by the extent of fracture surface roughness. In addition to particle dependent specific mechanisms, the main quantitative parameter that controls the crack front interaction is the number of particles. The 700 W mixing generates smaller aggregates – hence a higher number of particles. Also, for the same reason, exfoliation of the NC would have a similar effect. Different interaction mechanisms, e.g. debonding and pull-out of nanoparticles and crack front pinning may exist, which must be identified and studied to understand how parameters of nanoparticle geometry, concentration, dispersion, and bonding play their parts. Then, micromechanics models can be developed and hybrid effects be understood.

Regardless of the type of interactions of the crack front with the nanoparticles, their intensity determines the level of fracture toughness and their ultimate impression on the fracture process is expected to generate plastic deformation of the matrix – manifested by the fracture surface roughness. Accordingly, a plot of the fracture surface energy against the roughness RMS, $R_{q}$, is expected to exhibit a linear correlation, which indeed is the case as presented in Figure 12. Obviously, the

### Table 2. SAXS tests results of NC compositions.

| Film composition          | Sonication Power (W) | d (Å) |
|---------------------------|----------------------|-------|
| NC powder                 |                      | 20.31 |
| PVB/NC-1%                 | 100                  | 17.58 |
| PVB/CNT-COOH-0.1%/NC-1%   | 100                  | 17.62 |
| PVB/NC-2%                 | 700                  | 18.36 |
| PVB/CNT-COOH-0.1%/NC-1%   | 700                  | 18.34 |

![Figure 9. SEM images of cross-sections of a PVB/NC-2% nanocomposite, sonication power of 700 W: (a) Aggregates of clay in the matrix, the clay did not preserve its layered arrangement, showing no apparent polymer intercalation; (b) Single clay particles. The particles seem to have lost their original dimensions.](image)

![Figure 10. tanδ (DMA results) of samples prepared by: (a) 100 W; and (b) 700 W. In the inset, the peak range is enlarged for precise $T_g$ measurements.](image)

### 4. Discussion

The results of the fracture toughness of the nanocomposite films exhibited a significant hybrid effect for the hybrid sample with respect to the parent composites. The qualitative ball impact results of the simulated ballistic glass with the hybrid films were the best among the tested samples. The hybrid effect was achieved despite the fact that there was no significant improvement in the quality of the NC dispersion in the hybrid samples compared to the parent composites. In fact, all the NC
5. Conclusions

A significant positive hybrid effect in the fracture surface energy was achieved for NC/CNT-based PVB hybrids. The fact that the hybrid effect was unrelated to the quality of the dispersion and that it correlated with the level of roughness of the fracture surface was taken as a strong indication that mechanisms other than stress transfer, which do not depend on the particle aspect ratio, control the fracture process. Different interaction mechanisms with the advancing crack front may exist, which respectively enhance plastic deformation of the matrix manifested eventually in fracture surface roughness. Such mechanisms must be identified and studied to understand how parameters of nanoparticle geometry, concentration, dispersion, and bonding play their parts in generating a hybrid effect.

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Disclosure statement

No potential conflict of interest was reported by the authors.
References

1. S. Chatterjee, F. Nafezarefi, N. Tai, L. Schlagenhauf, F. Nüesch and B. Chu: 'Size and synergy effects of nanofiller hybrids including graphene nanoplatelets and carbon nanotubes in mechanical properties of epoxy composites'. Carbon, 2012, 50, (15), 5380–5386.

2. S. Kumar, L. Sun, S. Caceres, B. Li, W. Wood, A. Perugini, R. Maguire and W. Zhong: 'Dynamic synergy of graphitic nanoplatelets and multi-walled carbon nanotubes in polyetherimide nanocomposites'. Nanotechnology, 2010, 21, (10), 105702.

3. Y. Li, T. Yang, T. Yu, L. Zheng and K. Liao: 'Synergistic effect of hybrid carbon nanotube–graphene oxide as a nanofiller in enhancing the mechanical properties of PVA composites'. J. Mater. Chem., 2011, 21, (29), 10844–10851.

4. L. Liu and J. C. Grunlan: 'Clay assisted dispersion of carbon nanotubes in conductive epoxy nanocomposites'. Adv. Funct. Mater., 2007, 17, (14), 2343–2348.

5. G. Marom, S. Fischer, F. Tuler and H. Wagner: 'Hybrid effects in composites: conditions for positive or negative effects versus rule-of-mixtures behaviour'. J. Mater. Sci., 1987, 13, (7), 1419–1426.

6. S. Praveen, P. Chattopadhyay, P. Albert, V. Dalvi, B. Chakraborty and S. Chattopadhyay: 'Synergistic effect of carbon black and nanoclay fillers in styrene butadiene rubber matrix: development of dual structure'. Composites Part A., 2009, 40, (3), 309–316.

7. S. Iijima: 'Helical microtubules of graphitic carbon'. Nature, 1991, 354, (6348), 56–58.

8. G. Schmidt and M. M. Malwitz: 'Properties of polymer–nanoparticle composites'. Curr. Opin. Colloid Interface Sci., 2003, 8, (1), 103–108.

9. P. C. Ma, N. A. Siddiqui, G. Marom and J. K. Kim: 'Dispersion and functionalization of carbon nanotubes for polymer-based nanocomposites: a review'. Composites Part A., 2010, 41, (10), 1345–1367.

10. E. T. Thostenson, C. Li and T. W. Chou: 'Nanocomposites in context'. Compos. Sci. Technol., 2005, 65, (3–4), 491–516.

11. L. Vaisman, H. D. Wagner and G. Marom: 'The role of surfactants in dispersion of carbon nanotubes'. Adv. Colloid Interface Sci., 2006, 128–130, 37–46.

12. C. M. Chan, J. Wu, J. X. Li and Y. K. Cheung: 'Polypropylene/calcium carbonate nanocomposites'. Polymer, 2002, 43, (10), 2981–2992.

13. J. C. Kearns and R. L. Shambaugh: 'Shambaugh, Polypropylene fibers reinforced with carbon nanotubes'. J. Appl. Polym. Sci., 2002, 86, (8), 2079–2084.

14. M. A. Rafiee, J. Rafiee, Z. Wang, H. Song, Z. Z. Yu and N. Koratkar: 'Enhanced mechanical properties of nanocomposites at low graphene content'. ACS Nano, 2009, 3, (12), 3884–3890.

15. J. Shelley, P. Mather and K. DeVries: 'Reinforcement and environmental degradation of nylon-6/clay nanocomposites'. Polymer, 2001, 42, (13), 5849–5858.

16. G. Marom and H. D. Wagner: 'Should polymer nanocomposites be regarded as molecular composites?'. J. Mater. Sci., 2017, 52, (14), 8357–8361.

17. N. Stern, G. Marom, L. Zhang and X. Hu: 'Micromechanics of Nanocomposites', Chap. 6, 'Comprehensive Composite Materials II', (eds. C. H. Zweben, P. Beaumont, T. Peijs and E. T. Thostenson), 1–27; 2017, Amsterdam: Elsevier.

18. M. H. Wichmann, K. Schulte and H. D. Wagner: 'On nanocomposite toughness'. Composites Sci. Technol., 2008, 68, (1), 329–331.

19. I. Greenfeld and H. D. Wagner: 'Nanocomposite toughness, strength and stiffness: role of filler geometry'. Nanocomposites, 2015, 1, (1), 3–17.

20. F. Lange: 'The interaction of a crack front with a second-phase dispersion'. Philos. Mag., 1970, 22, (179), 0983–0992.

21. F. Lange and K. Radford: 'Fracture energy of an epoxy composite system'. J. Mater. Sci., 1971, 6, (9), 1197–1203.

22. P. K. Mallick: 'iber-reinforced composites: materials, manufacturing, and design. Vol. xvii, Boca Raton, FL, CRC Press.

23. G. Anderton and L. Treloar: 'Fracture and tearing in oriented polyethylene'. J. Mater. Sci., 1971, 6, (6), 562–571.

24. G. Marom, H. Harel and J. Rosner: 'Fracture energies of composite propellants'. J. Appl. Polym. Sci., 1977, 21, (6), 1629–1634.

25. S. S. Ray and M. Okamoto: 'Polymer/layered silicate nanocomposites: a review from preparation to processing'. Prog. Polym. Sci., 2003, 28, (11), 1539–1641.

26. F. Perrin-Sarazin, M. T. Ton-That, M. Bureau and J. Denault: 'Micro-and nano-structure in polypropylene/clay nanocomposites'. Polymer, 2005, 46, (25), 11624–11634.