Hybrid effects in the fracture energy of nanocomposites

Stern, Nadya

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Hybrid Effects in the Fracture Energy of Nanocomposites

Thesis Submitted for the Degree of
“Doctor of Philosophy”

By
Nadya Stern (Lerman)

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Of Jerusalem

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*This work was carried out under the supervision of Professor
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Letter of contribution

Following is a list detailing each contributor's part to the completion of this work.

Chapter	Name of contributor	Institute	Nature of contribution
1 – Micromechanics of Nanocomposites	Dr. Liying Zhang	Nanyang Technological University	Co-Author
2 - Hybrid effects in the fracture toughness of polyvinyl butyral-based nanocomposites	Dr. Itay Dyamant	Oran Safety Glass	Assistance in performing impact tests.
	Mr. Eldad Shemer		

Abstract

This work aims to investigate the micromechanics of nanocomposites, with an emphasis on fracture energy. A broad analysis, with various matrices and nanofiller revealed that generally nanocomposite systems fail to meet their theoretical tensile strength and the elastic modulus, which were predicted by the micromechanics. Yet, the addition of nanofillers may significantly increase the fracture toughness. In this context, we investigated the fracture toughness of nanocomposites systems, and in these the specific cases of positive hybrid effect, the influence of nanofiller geometry and chemical structure and the mechanical behavior of nanocomposite system with a unique application. Hybrid nanocomposite materials comprise more than one type of nano-metric filler and may express a property which is higher than either the property of each one on the nanocomposites alone or of the arithmetic sum of their contributions – a positive hybrid effect. With the purpose of investigating the fracture toughness of nanocomposites, we examined three main systems, with various polymeric matrices (thermoplastic, semi-crystalline, thermoset) for diverse applications, and numerous nanofillers with different geometries and chemical structures, prepared by several methods. Therefore, this research deals with the fracture energy of hybrid nanocomposites, while taking a critical approach toward the currently prevailing engineering practice of applying classical composites micromechanics to nanocomposites.

The **first** part seeks to investigate the possibility of a hybrid effect in the fracture toughness of hybrid nanocomposite systems. For this purpose, we have chosen to examine a system of polyvinyl butyral (PVB) matrix with carbon nanotubes treated with carboxylic groups (CNTs-COOH) and nanoclays (NCs) as nanofillers. PVB is an amorphous thermoplastic polymer, which is commonly used in armored glass applications. CNTs-COOH and NCs are known for their good mechanical properties, and along with the fact that nanofillers cause lower degree of opacity due to their small dimensions and that NCs allow high level of transparency, this system is a good candidate for such applications. A system of PVB/0.2%-CNT-COOH/2%-NC has introduced a significant positive hybrid effect in the fracture toughness. This effect was related to level of roughness of the fracture surface rather than to the quality of dispersion. Therefore, we have concluded that this effect stems from nanofiller-crack front interactions mechanisms, such as pull-out and crack front bowing, independently of the stress transfer mechanism.

Following the conclusions of the first part, the **second** part was targeted to investigate the influence of nanofillers geometry and chemical structure on the fracture toughness and the possibility of hybrid effect. For this purpose, we have used isotactic polypropylene (iPP) along with different types of nanoparticles. iPP is a thermoplastic semi-crystalline matrix with oriented CH₃ groups, used in many different applications. We divided the nanofillers into two groups: (a) nanofillers with different geometries (fibrous and platelets) and similar chemical structures - vapor grown carbon nanofibers (VGCFs) and graphene nanoplatelets (GNPs); nanoclays and SiO₂ nanofibers, (b) nanofillers with similar geometries and different chemical structures (organic and inorganic) – VGCFs and ZrO₂ nanofibers; GNPs and NCs. Composite and hybrid systems were prepared, while referring to the division by their properties. All composite systems exhibited superior properties over the neat matrix of iPP. The system of iPP/0.5%-GNP/0.5%-VGCF presented a positive hybrid effect in the total fracture toughness and in the dynamic damping capacity of the system. Among the parent composites iPP/0.5%-GNP sample exhibited the highest fracture toughness, probably due to the good interaction of the GNPs with the polymer. The main conclusion of this chapter was that the fracture energy depended on a set of parameters with an emphasis on the matrix–filler interactions, which affected the crack front propagation. Therefore, we should examine each system separately to identify its typical structure and composition-dependent crack front interaction mechanisms, instead of concluding about general rules for nanocomposite and hybrids.

Based on the conclusion of the second part, according to which, each system and its behavior should be analyzed individually, we have chosen an interesting system of thermochromic ionogel for the **third** part. The ionogel comprises thermoset polyurethane (PU), which is also well utilized in the armored glass industry, swollen inside an ionic liquid (IL). The resulted structure of PU/IL may modify its optical appearance from transparent to opaque as a function of temperature. We examined the influence of different ionic liquid uptakes and the addition of different nanofillers (GNP and SiO₂ nanofibers) on the mechanical properties and on the damping capacity of such system. The influence of nanoparticles on the mechanical properties (and hybrid effects) of the systems is inseparable from the influence of IL on these properties. The results displayed that overall, the addition of IL to the PU reduced the damping capacity, the mechanical properties and the fracture resistance for non-composite, composite and hybrid systems, so that the insertion of nanofillers could not compensate for the inferior properties of the swollen PU. Whereas the overall effect of the IL was to reduce damping it was suggested that it reflected the net result of two

opposing effects on the properties of the system – plasticization that increased the damping capacity, overridden by swelling and filling of the free volume that weakened the structural integrity of the system. The conclusions of this chapter are compatible with the main observation of the thesis (and of Chapter 3), that each system should be considered by its own specific properties. In the case of the PU/IL system, the effect of IL presence on the mechanical system constitutes another point of complexity.

The main conclusion of this thesis is that classical micromechanics is not applicable to nanocomposites – including fracture toughness – in general so that each nanocomposite system should be analyzed individually according to its constituent properties, the quality of the dispersion and the type of interaction between the particles and the matrix. It is proposed that well dispersed nanocomposites ought to be considered as solid solutions.

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Preface

The evolution in recent years of the science of composite materials to the nanodimension - corresponding to the inventions of nanoparticles of extremely high mechanical properties - has generated a host of questions with regard to the behavior of nanocomposites. One of the main questions asked by composites scientists, is whether nanocomposites can in fact utilize the high properties of the nanoreinforcement so that they be fully expressed in those of the subsequent nanocomposites. Looking deeply in the field of nanocomposites we have found out that there has been a real need to understand the actual role of micromechanics in nanocomposite systems. Whereas many studies have been done to investigate and develop the models of micromechanics established for microcomposite systems, no comprehensive study has been done to verify its validity to nanocomposite systems. The lack of such understanding prompted this pioneering work, aiming to clarify this important issue.

Accordingly, the first research question of this study pertained to the applicability of classical micromechanics to nanocomposites. For this purpose, we have performed a preliminary comprehensive literature analysis, by broad scanning of different types of nanomaterials and different nanoparticles, and by referring separately to two property groups, namely quasi-static stiffness and strength and fracture toughness. Correspondingly, we have researched the actual strength and elastic modulus of several polymer nanocomposite systems to conclude whether and how they are compatible with the main micromechanics mechanisms. A similar research has been performed on fracture mechanisms. Regarding the strength and the elastic modulus of nanocomposites, it was found that micromechanics models did not work for nanocomposites and that the reinforcing potential of nanoparticles was not fully realized so that the experimental properties were lower than the theoretical values. Regarding fracture, it was shown that an enhancement of fracture toughness of polymers could be obtained by introducing various nanoparticles and that optimized toughness could be achieved by incorporation of proper size, type and amount of nanoparticles, which in turn determine the energy dissipating interaction of the crack front with the nanoparticles.

The preliminary study has provided the background for this thesis and has culminated in a number of research questions. It sets the general background and defines the key issues for the thesis and is utilized as its Introduction chapter. It is followed by three chapters, devoted to three specific

case studies which pertain to fracture toughness of nanocomposites. They are: hybrid effects in the fracture toughness of polyvinyl butyral-based nanocomposites; the effects of geometry and chemical composition of nanoparticles on the fracture toughness of iPP nanocomposites; and the mechanical behavior of nanocomposites and hybrids of a polyurethane-ionic liquid matrix based systems for advanced optical activity.

CHAPTER ONE – Introduction

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6.1 Micromechanics of Nanocomposites

Nadya Stern and Gad Marom, The Hebrew University of Jerusalem, Jerusalem, Israel
Liyang Zhang and Xiao Hu, Nanyang Technological University, Singapore

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6.1.1 Introduction

The title of this chapter refers to two dimension scales that are three orders of magnitude apart: the nano and micro dimensions. Nano refers to the size range of the reinforcement, which has become highly relevant to composite materials in the last two decades mostly due to the introduction of carbon nanotubes (CNTs). Micro is the scale used most appropriately for mechanical models and in analyses of mechanical properties of structural materials. Therefore, the question that this chapter attempts to solve is how the threefold scale reduction of the reinforcement is manifested in both the mechanical models and mechanisms of the composite materials. Obviously, the best way to do this is to evaluate each mechanical model and mechanism with respect to their scale sensitivity. For example, assuming that the strength of composite materials depends on an effective stress transfer mechanism from the matrix to the fiber, the question that is paused is how the stress transfer model should be modified – if at all – to allow for nanosize reinforcement.

In the following sections, we focus on three property categories, namely the strength (ultimate stress), stiffness (Young's modulus), and toughness (fracture energy). For each category, the existing models of particulate and discontinuous composites are presented and discussed in terms of either their direct applicability to nanosize reinforcement or of the need for modified and alternative models. A number of additional factors – that are typical of nanoparticles – will be considered as well, including their 3-D geometry, high surface to volume ratio, orientation, quality of dispersion, hybridization and interparticle confinement.

6.1.2 Nanocomposites

The development of nanoparticles of unique mechanical and physical properties enabled generation of a new family of composite materials classified as nanocomposites, where nanoparticles perform as reinforcement. Even a small amount of nano-dimensional reinforcements may show high improvements across the range of mechanical, optical, electrical, and thermal properties.¹ These properties depend on the type of nanoparticles, their shape and area-to-volume ratio, and on the interfacial interactions with the matrix. The reinforcements can be classified according to their shape: nanoparticle, nanoplatelet, and nanofiber, as shown schematically in Fig. 1.²

Of the various properties that determine the contribution of the nanoparticles to the properties of the nanocomposite, their nanometric size is of utmost significance. As illustrated in Fig. 2, small changes in particle size display a significant difference in surface area/volume ratio. Therefore, nanosized dimensions increase significantly the surface area to volume ratio of the reinforcement, which is critical since the chemical and physical interactions occur at the interfacial region between the polymer matrix and the filler. In order to provide sufficient surface area for an interaction to obtain the desired improvement of the matrix properties, only minor quantities of nanoreinforcement are needed to generate massive surface interactions, as opposed to the addition of micro- or macro-reinforcement. Such interactions can totally modify the properties of the matrix and the micromechanics of reinforcement, hence nanocomposites are nicknamed "interface materials" and they depend tightly on the type and the nanometric size of the reinforcement.

6.1.3 Micromechanics of Strength

The strength (as well as some other properties) of composites are commonly given by rule of mixtures (ROM) that express it as a weighted average of the properties of the parent constituents (many textbooks present those rules and models, e.g., Ref. [3]). For example, the strength (σ_c) of a unidirectional fiber reinforced composite (shown schematically in Fig. 3) is given by:

$$\sigma_c = \sigma_m \phi_m + \sigma_f \phi_f \quad (1)$$

where ϕ is the volume fraction of the matrix (m) and fibers (f), respectively. This seemingly trivial expression, however, is based on the assumption that under an externally applied stress the constituents, namely the matrix and the fibers, react identically so that they undergo exactly the same strain ($\epsilon_m = \epsilon_f$), which is equal to that of the composite structure (ϵ_c). This assumption holds only when the interfacial fiber-matrix bond strength is sufficiently high so that no slippage can occur between the constituents, implying that an effective matrix-fiber stress transfer mechanism is operational. Such mechanism is classically expressed by the fiber critical length (l_c), defined as the shortest length required for the fiber to break under external stress, and given by:

$$l_c = r \sigma_f / \tau_{if} \quad (2)$$

where r is the radius of the fiber and σ_f and τ_{if} are the strength of the fiber and the interface, respectively.

Fig. 1 Classification of nanoparticles based on the number of their nano-dimensions and aspect ratio.

Fig. 2 Dependence of surface area to volume ratio on the particle size.

Fig. 3 A schematic presentation of a unidirectional continuous fiber reinforced composite showing the longitudinal and transverse directions.

Fig. 4 A schematic presentation of a unidirectional discontinuous fiber reinforced composite showing the longitudinal and transverse directions (a) and of an in-plane randomly dispersed similar system (b).

For an efficient stress transfer mechanism, which fulfils the condition $\varepsilon_{rm} = \varepsilon_f = \varepsilon_{cr}$, the actual fiber length ought to be significantly higher than the critical length ($l \gg l_c$), so that the average stress in the fiber – which includes the stress building regions along $l_c/2$ at its two ends – is close to the maximum stress in the fiber ($(\sigma_f)_{\max}$), which in turn is equal to the applied stress. This is by and large the case for a continuous composite as depicted in Fig. 3.

However, for a unidirectional discontinuous system (shown schematically in Fig. 4(a)) and for nanocomposites (as discussed below), this condition is not always met and the ROM of Eq. (1) is modified to include the average fiber stress in Eq. (3):

$$\sigma_c = \sigma_m \phi_m + \langle \sigma_f \rangle \phi_f \quad (3)$$

where $\langle \sigma_f \rangle$ is the average fiber stress given by Eq. (4):

$$\langle \sigma_f \rangle = \frac{1}{l} \int_0^l \sigma_f dz \quad (4)$$

and dz is an infinitesimal fiber length. As a result, the strength of the composite includes a reinforcement efficiency factor (η) which depends on the length of the fiber (l) relative to the load transfer length (l_t), as presented by Eqs. (5) and (6):

$$\sigma_c = \sigma_m \phi_m + 1/2 (\sigma_f)_{\max} \phi_f \quad \text{for } l < l_t \quad (5)$$

$$\sigma_c = \sigma_m \phi_m + (1 - l_t/2l) (\sigma_f)_{\max} \phi_f \quad \text{for } l > l_t \quad (6)$$

Considering a nonaligned discontinuous composite, a number of models and approximations for the strength of in-plane isotropic composites (shown schematically in Fig. 4(b)) have been presented over the years in the scientific literature; many of

them are discussed in Ref. [4]. In one of the first models, the Kelly–Tyson Model, the strength is given by a linear combination of the longitudinal and transverse strength components of the randomly aligned reinforcement, where the contribution of the fibers is moderated by two efficiency factors, namely, for the fiber length (η_{LS}) as in Eqs. (5) and (6), and fiber orientation η_0 . It is usually accepted that for random-in-plane fiber composites η_0 takes the value of 3/8 and considering the strength of the matrix as an upper bound for the transverse strength, the strength of random discontinuous composite is given approximately by:

$$\sigma_{c(\text{random})} = \sigma_m \phi_m + \eta_0 \eta_{LS} \sigma_f \phi_f \quad (7)$$

where $\eta_0 = 3/8$. More detailed explanations can be found in Ref. [5].

Now, the basic analyses of the stress transfer mechanism and the critical length which culminates in Eq. (3) and of the efficiency factors for random discontinuous systems in Eq. (7) do not pose any restrictions on the actual dimensions (length and diameter or thickness) of the reinforcement. Hence, disregarding potential effects that are typical of the nanoparticles, such as enhanced interfacial effects, we can assume that Eq. (3) is valid as an expression of the strength of unidirectional nanocomposites.

A condition which is inherent in Eq. (3) is that an effective stress transfer mechanism from the matrix to the reinforcement exists, which in turn is based on the stress transfer model expressed by Eq. (2) for fiber reinforcement. More generally, for nanoparticles with at least one dimension significantly longer than the others, the aspect ratio is defined in Fig. 1 as l/d both for rod-like and platelet nanoparticles (it is noted that for $l=d$, e.g., spheres, the aspect ratio is 1). Commonly, rod/tube-like and platelet-like nanoreinforcements exhibit potentially very high aspect ratios – so an effective stress transfer mechanism should be expected. For example, the following calculation for a single walled carbon nanotube (SWCNT), based on generic literature nominal data, shows that the condition of $l \gg l_c$ is undoubtedly met:

For SWCNT

$$d = 1 \text{ nm}; \sigma = 50 \text{ GPa}; \tau = 29 \text{ MPa} (0.1\% \text{ in epoxy}); l = 10 - 100 \mu\text{m}$$

$$l_c = \frac{1 \cdot 10^{-9} \cdot 50 \cdot 10^9}{2 \cdot 29 \cdot 10^6} = 860 \text{ nm}$$

Why is it then that despite the potential giant contributions of nanoparticles (e.g., the strength of multi-walled carbon nanotube (MWCNT) is at least three orders of magnitude higher than that of a graphite fiber) – the strength of nanocomposites is way below the predicted values. The answer is that an effective stress transfer mechanism, namely, $l \gg l_c$ can be achieved only if – on the one hand – the nanoparticles are not damaged in the mixing process and the nominal value of l is retained, and if – on the other hand – a high level of exfoliation is accomplished so that the effective diameter d is as close as possible to the nominal one. An additional essential prerequisite for an efficient stress transfer mechanism is that a strong interface between the nanoparticles and the matrix is formed.

However, since the surface area of CNT is large, the attraction forces between the nanotubes and the agglomerates are strong (van der Waals (VDW) attraction energy of 500 eV/ μm for tube–tube contact⁶), making the exfoliation process very difficult and challenging. In order to achieve the full potential of the improved properties provided by nanoparticles, and particularly by CNT, good exfoliation through the matrix is essential. As reported in many studies,⁷ highly entangled CNTs (comprising high effective diameters), which are difficult to disperse in polymer solutions and polymer melts, resulting in composites with performance far below the theoretical predictions. Among additional causes for deviations of performance from theoretical predictions is inter-particle confinement, where the limited space in the matrix due to a huge number of particles even for small particle contents generate may produce different morphologies.

A literature survey of recent experimental studies of mechanical properties of different nanocomposites shows that essentially the strength results fail to fulfill the expectations based on the properties of the nanoparticles. Whereas hundreds of articles in the field of composite materials are written every year, this literature survey aims to come to an overall conclusion, based on a variety of articles from different areas and years. Only part of the articles compared their experimental results to the ROM predictions. In such cases, the theoretical values were calculated here, based on Eq. (1), taking into account the literature values of the constituents. The mechanical properties mentioned in the articles will be examined based on the ROM and the hypothesis that the strength increases with the concentration of the nanofiller.

6.1.3.1 The Strength of Nanocomposites of Carbonaceous Nanoparticles

6.1.3.1.1 Properties of carbonaceous nanoparticles

Our survey covers the literature in the last 15 years, and presented here as articles, which investigated the mechanical properties of nanocomposite materials. Many researchers investigated the family of organic carbon fillers, which include mostly CNT, vapor grown carbon nanofibers (VGCF) and graphite nanoplatelets (GNPs). Different articles proposed different values, depending on the production methods, the number of layers, and the specific type of the reinforcement. Coleman *et al.*⁸ wrote an extensive review on the properties of CNT polymeric composites. They included the steps of finding the mechanical properties of the CNTs themselves, starting from theoretical calculations and up to actual measurements. The expectations predicted a modulus similar to that of the graphite in-plane, which is known as 1.06 TPa. Different measurements showed modulus values of 0.012–1.3 TPa and strength values of 11–63 GPa for MWCNT, and modulus values of 0.32–1.5 TPa and strength values of 10–52 GPa for SWCNT. Yu *et al.*⁹ managed to measure the mechanical properties of an individual MWCNT, by a stress–strain test through a method they developed, using atomic force microscopy (AFM) and scanning electron microscopy (SEM). The group measured the properties of

the outermost layer, which is the main layer that contributes to the load transfer mechanism during a tensile test. They measured among 19 MWCNTs, prepared by the arc discharge method. The experimental results showed that the tensile strength values ranged from 11 to 63 GPa, while Young's modulus values ranged between 270 and 950 GPa. The actual experimental results are lower than the theoretical values for flawless SWCNTs. A possible explanation for that downward bias is the presence of defects and shear loads or twist loads during the test. Measurements for SWCNTs were harder to perform and their properties were expected to be higher than the properties of MWCNTs. Yu *et al.*¹⁰ used the same method to measure the properties of 15 types of SWCNTs and found strength values of 13–52 GPa and Young's modulus values of 320–1470 GPa. They did not find an obvious dependency between the tubes diameter and their properties. High quality SWCNT and arc discharged MWCNT were measured to have values of 1 TPa modulus and tens of GPa for strength, while chemical vapor deposition (CVD)-MWCNTs are expected to show lower values.⁸ Lau *et al.*¹¹ reviewed composite materials with polymer matrices and CNT or CNT/NC as reinforcements. They presented references that corroborated the claim that nanotubes have lower modulus than the expected value from a graphene sheet, and reviewed modulus values of 0.27–5.5 TPa.

Xie *et al.*⁷ summarized the theoretical and experimental properties of the CNTs to be 1 TPa for the elastic modulus and 50–500 GPa for the strength of SWCNT, and 0.3–1 TPa for the elastic modulus and 10–60 GPa for the strength of MWCNT. However, Miyagawa *et al.*¹² summarized different values for nanotube properties. Their summary included more types of CNTs: SWCNTs, double-walled CNTs (DWCNTs) and MWCNTs. The summarized moduli and strengths were of different types such as tensile, flexural and compressive. The range of values for SWCNTs modulus was 0.01–3.58 TPa, for the modulus of MWCNTs it was 0.027–2.44 TPa and the modulus of DWCNTs was 0.0161 TPa. The range of values for SWCNTs strength was 0.5–45 GPa, for MWCNTs strength it was 0.1–135 GPa and for DWCNTs strength it was 1.21 GPa. Tibbetts and Beetz¹³ tested VGCF with average diameter of 7.5 μm , which presented a tensile strength of 2.92 GPa and a modulus of 237 GPa. They concluded that smaller diameters lead to higher property values. Van Hattum *et al.*¹⁴ also studied the mechanical properties of VGCF, and reported modulus of 165 GPa for fibers with diameter below 10 μm , and also reported that larger fiber diameters lead to lower modulus. They reported tensile strength values of 0.7–2.8 GPa. Another commonly used organic filler is graphene. Gómez-Navarro *et al.*¹⁵ reported a Young's modulus of 0.25 TPa for a single graphene sheet. Lee *et al.*¹⁶ reported a modulus of 1 TPa and strength of 130 GPa for bulk graphite, measured by AFM. Dikin *et al.*¹⁷ and Compton *et al.*¹⁸ mentioned the mechanical properties of graphene oxide (GO)-paper to be 32–40 GPa for the stiffness and 125 MPa for the strength.

This short introduction of the mechanical properties of CNTs shows a large variance between the values, for the predicted values as well as for the experimental values. Many times the measured values of the properties did not reach the high theoretical expected values. It is imported to notice that the placing of different values into the ROM, may lead to different conclusions.

6.1.3.1.2 Polypropylene matrices

Polypropylene (PP) is a commonly used matrix for polymeric nanocomposites. This part surveys composite materials with PP matrix and carbon nanofillers. Lozano and Barrera¹⁹ dispersed VGCFs in PP matrix, by mixing followed by hot press. The addition of nanofibers did not show significant improvement of the ultimate tensile strength (UTS), and they concluded that the nanofibers were insignificant in the improvement of the strength. They mentioned that the lack of strengthening of the composites was a consequence of polymer matrix increased brittleness, due to its inability to further crystallize on deformation, due to the molecular mobility restrictions caused by the fiber dispersion. This inability caused by the molecular restrictions, which in turn caused by fiber dispersion. Kumar *et al.*²⁰ used single substance of 5 wt% VGCF, which showed good dispersion by SEM and laser scanning confocal microscopy (LSCM) analysis. A significant improvement was observed in the compressive strength, but there was almost no change in the tensile strength. Kearns and Shambaugh²¹ prepared PP fibers that contained SWCNTs. The tensile strength increased with the CNT loading at 0.5 and 1% of CNTs. However, fibers with 1.5 and 2% of CNTs showed lower strength than PP alone. They ascribed this phenomenon to the fact that a high percentage of CNT make the spinning hard and also may have higher sensitivity to impurities, compared to low percentages. Impurities can create a local occlusion in the fiber and reduce the strength and the ability to spin. The authors compared their results to the theoretical expectations by the ROM, and used the theoretical value of 200 GPa as the strength of CNT. The experimental results were lower than the estimated ones, as seen in Fig. 5, where a similar comparison is presented based on their values. Beside the comparison of their results to the predicted values by ROM, they applied this comparison on other articles, which also showed lower values than the predicted for poly(methyl methacrylate) (PMMA)/CNT and petroleum pitch/CNT. The PP and the pitch utilized the CNT better than the PMMA (Fig. 5). Xie *et al.*⁷ reviewed their article, in which they prepared PP/CNTs composite, and also PP/composite compatibilized with maleic anhydride (MA) grafted styrene-(ethylene-co-butylene)-styrene copolymer (MA-SEBS) up to 10 wt% of CNT. They formed the composite by melt stirring and ball milling. Because of the high aspect ratio and stiffness of the CNTs, the tubes reinforced the PP matrix effectively. The addition of MA-SEBS improved the interaction between the CNT and the matrix and enhanced their interfacial adhesion, and by that increased the tensile strength, which was particularly emphasized at high filler contents. This improvement however was nonlinear, as reconstructed in Fig. 6. Wakabayashi *et al.*²² studied the mechanical properties of PP/graphite nanocomposite. They used the method of solid-state shear pulverization (SSSP), performed by modified twin-screw extrusion. The materials were mixed together and then pulverized into powder, to produce a composite with 3 wt%. Thermogravimetric analysis showed that the actual content of the composites was 2.5 ± 0.2 wt%. Photographic, transmission electron microscopy (TEM) and field-emission scanning electron microscopy (FESEM) images showed uniform dispersion of the graphite, and X-ray powder diffraction (XRD) test indicated that graphite was well exfoliated by the SSSP. The composite material showed an improvement of about 60% in the yield

Fig. 5 A comparison of observed results to theoretical predictions predicted by the rule of mixtures (ROM). The observed results do not reach the theoretical expectations. After Kearns, J.C., Shambaugh, R.L., 2002. Polypropylene fibers reinforced with carbon nanotubes. *Journal of Applied Polymer Science* 86, 2079–2084.

Fig. 6 The tensile strength increases with the content of carbon nanotube (CNT) at low contents and tends to plateau at higher contents. An addition of maleic anhydride grafted styrene-(ethylene-co-butylene)-styrene copolymer (MA-SEBS) increases the adhesion between the CNT and the matrix, and therefore improves the tensile strength. After Xie, X.-L., Mai, Y.-W., Zhou, X.-P., 2005. Dispersion and alignment of carbon nanotubes in polymer matrix: A review. *Materials Science and Engineering: R: Reports* 49 (4), 89–112.

strength. They were expecting enhanced mechanical properties because after the SSSP process, the graphite was well dispersed and had high aspect ratio. Deng *et al.*²³ dispersed MWCNTs in PP matrices with different melt flow index (MFI), where part of the MWCNTs were coated with high density polyethylene (HDPE). For drawn PP composite tapes of the medium MFI the tensile strength increased with the draw ratio up to a ratio of 20, after which the strength started to decrease. The authors suggested that CNT bundles acted as crack initiators during the deformation of highly oriented tapes due to more organized crystals in the tape, and that the interface between the polymer and the CNTs was destroyed at high draw ratios. They used the ROM of Eq. (7) to calculate the strength of isotropic ($\eta_0=0.2$, $\eta_L=1$) and oriented ($\eta_0=1$, $\eta_L=1$) composites, showing that the effective strength generally decreased with increasing filler contents of coated MWCNTs. They noted that the coated MWCNTs in oriented PP tapes achieved the highest effective tensile stress and the back calculated CNT strength agreed with the experimental value measured by AFM.

In summary, this survey of PP nanocomposites provides very little support – if at all – to the theory that the strength increases with the filler content, except for very low filler contents. Only in a few cases, where the properties of the nanoparticles represent the lower scale of their wide property spectrum, do the experimental results exceed the calculated predictions.^{20,21}

6.1.3.1.3 Epoxy matrices

Gojny *et al.*²⁴ compared the mechanical properties of epoxy matrix with different kinds of CNTs. They produced SWCNTs, DWCNTs and MWCNTs by CVD-grown method, while DWCNTs and MWCNTs appeared both as purified and as amino functionalized groups (NH₂). They compared the performance of epoxy/CNT composites to the performance of neat epoxy and epoxy/carbon black (CB). MWCNTs and MWCNTs-NH₂ showed the best dispersion with only few agglomerates, DWCNTs and DWCNTs-NH₂ showed single tubes along with broken-up agglomerates, SWCNTs showed single tubes with primarily small agglomerates, and CB showed homogeneously dispersed aggregates. They measured the UTS and found that SWCNTs and DWCNTs moderately increased the UTS, while MWCNTs slightly decreased it. CB did not show a significant effect on the UTS at low contents of filler. SWCNTs had the highest properties, the highest aspect ratio and the highest specific surface area (SAA) and they did not have inactive internal layers. Higher SSA increases the tendency to agglomerate. DWCNT has lower SSA and lower aspect ratio than SWCNT, but they are less prone to agglomerate. The MWCNT can carry the load only at the outmost layer and not in the internal ones, a fact that reduces the part of the total weight with which the surface area actually participates in the reinforcement mechanism. The reduction of the UTS of films with MWCNTs may be caused by the fact that at higher filler contents such as 0.3 and 0.5 wt%, there are more poorly impregnated agglomerates, which act like imperfections and cause early failure. DWCNTs-NH₂ presented the highest values (10% higher than neat epoxy), while MWCNTs-NH₂ showed similar properties to neat epoxy. The functionalization of the CNT improved the dispersion and the UTS by polarization of the CNT and by incorporation of the nanotube into the epoxy network by covalent bonding. Rafiee *et al.*²⁵ studied the mechanical properties of epoxy with graphene platelets (GPLs), SWCNTs and MWCNTs. The GPLs were prepared by thermal reduction of graphite oxide and the fillers were dispersed using sonication and mixing. They used the low filler content of 0.100 ± 0.002 wt% for all the samples to obtain a relatively uniform dispersion of the GPL. They found that the improvement of the tensile strength was much more significant for the GPL (40%) compared to each one of the nanotubes (14% for MWCNT and 11% for SWCNT). They suggested that the reason for this difference is the high SSA of the graphene, wrinkled surfaces that form better adhesion with the epoxy, and the two-dimensional planar geometry of the graphene. Ramana *et al.*²⁶ studied epoxy with MWCNTs. MWCNTs were treated with H₂SO₄ and HNO₃ for surface modification, and then compared to neat (untreated) MWCNTs. The composite was prepared using sonication, up to the content of 1%. The flexural strength of the neat MWCNT increased with increasing weight percent of the filler. The functionalized 1 wt% MWCNTs led to a further increment in the strength. The functionalized groups may lead to multiple bonding that increases the network formation. They attached covalently to the epoxy matrix during the curing process, and dispersed in more uniform way, allowing for a better load transfer mechanism, while the pristine MWCNT showed some agglomerates. While the crack of neat MWCNT propagated quickly along the crack direction, leading to the failure of the entire composite, the crack of the treated MWCNT was formed mainly in the interface between CNTs and led to a pull out mechanism.

In summary, similarly to the PP matrix nanocomposites, the epoxy nanocomposites do not reach the predicted ROM values. Only in a few cases, where the properties of the nanoparticles represent the lower scale of their wide property spectrum, do the experimental results exceed the calculated predictions.

6.1.3.1.4 Other matrices

Wang *et al.*²⁷ studied biopolymer chitosan with MWCNTs (treated with H₂SO₄ and HNO₃), using a sonicator and homogenizer with filler contents between 0.2 wt% and 2%. SEM, TEM and optical microscopy (OM) analysis showed good dispersion of the MWCNTs at 0.8 wt%, with marginal aggregation, while SEM and OM showed aggregates at 2 wt%. SEM morphology analysis also indicated that most of the tubes fractured and did not only pull out during the failure. A raise in the tensile strength was observed with an increasing amount of MWCNT up to 0.8 wt%, in which an improvement of 99% was achieved. With further increase of CNT content, the strength remained unchanged due to the aggregation that occurs at higher loadings. This improvement compared to neat epoxy was attributed to the reinforcement of finely dispersed CNTs and to the hydrogen-bond interactions between the chitosan matrix and the functionalized MWCNTs. Abbasi *et al.*²⁸ studied the flow-induced orientation of polycarbonate/MWCNTs, prepared by melt mixing masterbatch, using a twin-screw extruder. They used different types of molding in order to prepare composites with various content of MWCNTs (different shear or deformation rate). SEM, TEM and AFM analyses indicated that the tubes were well dispersed and oriented in the appropriate shear flow direction. They tested the mechanical properties of the samples that were prepared by microinjection molding, with filler content of 0–10%. They noticed a small reduction in the tensile strength with the increasing content of MWCNTs up to 1 wt%, and above this content, an increase in the strength. They attributed this to the formation of a filler network at higher contents of MWCNTs. They summarized the results that the content of the filler (nanotube loading) have only a small influence on the tensile strength, with only a small increase with the filler content, likely due to weak interactions between the MWCNTs and the chains of polycarbonate, causing an inability of the CNTs to reach their theoretical high strength. Park *et al.*²⁹ dispersed MWCNTs in HDPE by ball milling and then melting, mixing, and hot pressing. Different ball milling times indicated that longer times led to smaller surface area, smaller aspect ratio and more defects of the MWCNTs. MWCNT/HDPE samples contained filler contents between 24 and 47 vol%. Measuring of the tensile strength showed that the value increased with the volume fraction of the reinforcement. They also noticed that the strength improved with milling time up to 60 min, due to better dispersion, and decreased at longer times. Longer times damaged the original properties of the CNTs and caused nonuniform stress distributions and lower strength.

Liang *et al.*³⁰ prepared composites of poly(vinyl alcohol) (PVA)/GO using the sonication method. The GO was prepared from graphite by the modified Hummers method (oxidation by acid solutions, stirring, sonication, and centrifugation). SEM images and XRD analyses showed that the GO was well dispersed and fully exfoliated in the PVA matrix. They predicted that the

mechanical properties would increase after the addition of the GO, due to the high aspect ratio of the platelets, the good dispersion and the good interaction between the GO and the PVA, which arises from the H-bonds. They found an increase of the tensile test with the increase of the GO content, and the highest improvement, 76%, was observed for the highest reported content of 0.7 wt%. They related this enhancement mainly to the strong interactions between the GO and the PVA, because the quality of dispersion and the aspect ratio of GO were not changed. Zhao *et al.*³¹ studied the mechanical properties of a composite material that contains PVA/GO. The graphite was treated with KMnO_4 and concentrated H_2SO_4 to obtain graphite oxide. The graphite oxide was sonicated in a water solution to exfoliate the GO. XRD, TEM, SEM, and AFM tests indicated that generally the graphene was fully exfoliated and well dispersed (for 1.8 vol%). The tensile strength increased with the increasing volume fraction of graphene, especially for samples with low filler content. Their possible explanation was attributed to a large aspect ratio and the interaction between graphene and the matrix, which inhibits the movement of the polymer chains. After 1.8 vol%, at which an improvement of 150% was observed, there was only a marginal increase of the tensile strength (from 42 to 43 MPa). They suggested that at high concentrations, the sheets are restacking due to the VDW forces, and the slippage of piled graphene nanosheets (GNS) during the tensile testing, leading to a less effective enhancement of the properties. They used the term mechanical percolation to describe the critical point of the mechanical properties upon the nanosheet content (1.8 vol% in this case). Below this point, the sheets are well dispersed and allow enhanced mechanical properties, which are significantly improved with the increasing amount of GO. Above this point, the sheets are very close and VDW interactions may lead to their restacking, and therefore cause a depression with regards to the mechanical improvement. Gan *et al.*³² studied a silicone rubber (SR) with graphene nanoribbons (GNRs). To obtain the GNRs, MWCNTs were unzipped using strong oxidants such as potassium permanganate and sulfuric acid. The nanofillers were dispersed by the sonication method, and all the samples were vulcanized. The GNRs were oxidized to have carboxylic acid groups and hydroxyl groups along their edges, and the oxidation degree was lower than the degree of GO. The resulting GNRs had different widths due to the different diameters of the inner and outer tubes. The GNRs were dispersed randomly without obvious aggregations, probably due to possible interactions between GNRs and SR. XRD revealed first that the GNRs were distributed in the SR but without damaging the main structure, secondly that the crystallinity of the composite was decreased and thirdly that there were interactions between the SR and the GNRs. The addition of GNRs into the SR, showed an enhancement of the mechanical properties, which increased with the increasing amount of filler. The highest value was observed for the highest filler content of 2 wt%, which led to improvement of 67% in the tensile stress. They explained the good results by the uniform dispersion and by the good interactions between SR and GNRs. Kanagaraj *et al.*³³ dispersed CNTs in HDPE. The CNTs were chemically treated with sulfuric and nitric acid and the composites were prepared using sonication and injection molding. They prepared samples with volume fractions of 0.11–0.44%. They tested the ultimate stress, which showed an enhancement with the increasing amount of filler, explained by the strong interfacial interactions between the filler and the matrix, leading to a better load transfer mechanism. Wang *et al.*³⁴ prepared PVA/SWCNTs oriented nanocomposite tapes by solvent casting followed by solid state drawing. The tensile strength was tripled by the addition of 1 wt% of SWCNTs compared to neat PVA tapes. They used Eq. (7) to calculate a strength of 88 GPa for SWCNTs – close to the reported tensile strength of the tubes. The authors concluded that this high value reflected the achievement of three conditions: high level of dispersion, good interfacial interactions, and high level of filler alignment.

To summarize, it is noted that although graphene fillers enhance the composite values more than the tubes, in most cases the experimental strength results still fall short of the predictions.

6.1.3.2 The Strength of Nanocomposites of Inorganic Nanoparticles

6.1.3.2.1 Clay nanoparticles

Another reinforcement commonly used in the field of composite materials is nanoclays (NCs). NCs are nanoplatelet particles that consist of alumina-silicate layers and are considered a smectite-type of layered silicate.³⁵ They have an aspect ratio of 100–1000, low price, large surface area, high availability, and high cation exchange ability.³⁶ It is very difficult to find the mechanical properties of NC, which exhibit different values for different layers and different layer thickness. A successful measurement of a single layer of clay has yet to be reported. Values of Young's modulus for different clays are reported in the literature between 0.15 and 400 GPa.^{37,38} Shelley *et al.*³⁹ choose the value of 178 GPa as a reasonable clay modulus value for calculating ROM.

Vu *et al.*⁴⁰ studied the tensile strength of sodium montmorillonite (MMT) clay nanolayers within *cis*-1,4-polyisoprene (synthetic) natural rubber (NR) and epoxidized natural rubber (ENR), using a bender mixer. Two sets of ENR were used which differ in mol% of epoxy (ENR25 and ENR50). The clay was dispersed as a pristine layered silicate (Na-Mt), and as organically modified layered silicate (C1, C2, and C3) using ion exchange with ammonium cations, to receive different modifications. They used relatively high filler contents of 10–30%. Intercalation and possible exfoliation of the clays in NR and ENR were observed by XRD. Different modifications caused different qualities of exfoliation in different types of matrices. In addition, an intercalation of both the NR and the ENR was observed between the interlayers of the clay. Pristine clay showed an improvement in the tensile strength compared to unfilled ENR, due to the intercalation and increased active surface area of the clays, having values similar to those of ENR with precipitated silica (Hi-Sil), and higher than the strength of the matrix with modified clays. The NR matrix draws out a different picture, where the modified clays show higher values than the NR with Hi-Sil, due to better polymer–filler interactions, poorer filler–filler interactions, and improved filler dispersion. Among the modified clays, the modification that showed the better exfoliation also exhibited higher strength. Manias *et al.*⁴¹ reviewed the material properties of nanocomposites that contained PP and MMT. In this work, they mixed PP with fluoro-organic MMT (F-MMT), which showed high intercalation using XRD.

The addition of f-MMT showed almost no change at the yield stress relative to neat PP. They also compared between nanocomposites PP/f-MMT properties and conventionally filled PP/f-MMT macrocomposites, which remained in tactoids and did not intercalate or exfoliate. The macrocomposite presented values that were a little lower than the values of the nanocomposite. Shelley *et al.*³⁹ tested the transverse and longitudinal tensile properties of nylon-6/NCs composites prepared by extrusion. They examined two filler concentrations: 2 and 5 wt%. Nylon-6/5 wt% clay presented higher yield strength than nylon-6/2 wt%, which had higher yield strength than pristine nylon, for both loading directions. The nylon-6/5 wt% sample in the longitudinal direction showed the greatest improvement of 175% for the strength compared to pristine nylon-6. In addition, whereas the pristine nylon-6 and the nylon-6/2 wt% nanocomposite exhibited isotropic behavior, the nylon-6/5 wt% nanocomposite was 13% anisotropic. The authors concluded that the clay lamellae oriented in the flow direction and induced the nylon-6 chains to be favorably oriented in the same direction during the extrusion process. They related the enhancement in the mechanical properties to the movement limitation of more polymer chains that interacted with clay lamellae.

Lee *et al.*⁴² studied the tensile properties of biodegradable aliphatic polyester (APES) with two types of organoclays (organically modified MMT): Cloisite 10A and Cloisite, differ in ammonium cations content between the silicate layers (dimethyl benzyl hydrogenated-tallow for 10A and methyl tallow bis-2 hydroxyethyl for 30B). The samples were prepared by the melt intercalation method and contained filler content between 1 and 30% for both of the clay types. The XRD analysis indicated a higher intercalation level for Cloisite 30B than 10A caused by strong hydrogen bonding interactions between the hydroxyl group of Cloisite 30B and the carboxyl group of APES. The Cloisite 10A have weaker interactions due to the lower polarity of the ammonium cation in its gallery. TEM images showed that Cloisite 30B were well dispersed in APES, while Cloisite 10A showed some aggregates, especially at higher contents. According to their explanation, Cloisite 30B also demonstrated higher tensile strength than 10A, due to the same interactions, particularly at higher filler contents. They also saw that the strength of APES/Cloisite 10A-30 wt% showed the lowest value among the composites, and they explained it by low dispersion quality and aggregated clays at this content. Haraguchi *et al.*⁴³ prepared nanocomposite hydrogels with 1–8 wt% of poly(*N,N*-dimethylacrylamide) (PDMAA) and 2.5–7 wt% of inorganic clay or 1–5 wt% of methylenebis(acrylamide) cross-linker (OR), by in-situ free radical polymerization, where part of the gels were dried afterwards. They compared the results of DMAA/NC to poly(*N*-isopropylacrylamide) (PNIPA) with clay, from their other study. XRD and TEM analyses showed an exfoliation and a uniform dispersion of the clay. DMAA/NC showed high strength compared to DMAA/OR and similar to NIPA/NC. The tensile strength of DMAA/NC and NIPA/NC improved as the concentration of the clay grew. They saw that the number of cross-linked chains of DMAA/NC also increases with increasing amount of clay, with a sharper increase at higher contents. They proposed an explanation by which an addition of clay sheets between neighboring clay platelets may increase the cross-linking. Wang *et al.*⁴⁴ studied epoxy nanocomposites with highly exfoliated pristine NCs that was prepared by "slurry-compounding," which included a sonication process, in an amount between 1 and 5 wt%. The quality of dispersion was defined by OM and TEM for epoxy/S-clay 2.5 wt% samples. The optical microscope indicated good dispersion with aggregates smaller than 3 μm , like the TEM indicated exfoliated and uniformly dispersed tactoids consist of few layers of clay. The tensile strength decreased with increasing filler loading. The authors proposed the following explanations: trapped bubbles, weak boundaries between particles increasing with filler content, and heterogeneous network density due to the high viscosity, caused by large interfacial area and interaction of the well-dispersed and exfoliated clays.

6.1.3.2.2 Other nanoparticles

Other inorganic reinforcements were studied as well. Chan *et al.*⁴⁵ studied composites of PP with CaCO_3 of 4.8–13.2 vol% nanoparticles using melt mixing. TEM images showed that nanoparticles up to 9.2 vol% were well dispersed, while higher content showed more aggregates. They explained this result by the fact that at higher contents, the particles are closer to each other and therefore may flocculate after the mixing ended. They tried different mixing times, but saw no influence of the mixing on the mechanical properties. They measured only small changes in tensile strength and yield stress. They explained these results by the nucleation of CaCO_3 , which decreased the size of the spherulites and therefore decreased the mechanical properties. They also noticed that higher improvement was observed at lower vol%, after which the dispersion was worse. Yang *et al.*⁴⁶ studied the mechanical properties of PP/ CaCO_3 . They used three types of PP: polypropylene homopolymer (PP1), polypropylene-ethylene copolymer (PP2) and a mixture of these two types (PP3; PP1:PP2 = 1:1). The composite materials were prepared by a twin-screw extruder, and contained CaCO_3 of 2–40 wt%. For PP1, the tensile strength of the composite with low filler content (up to 10 wt%) was higher than that of the pure polymer, but exhibits a decrease with an increasing filler content. High filler content (above 20 wt%) showed a rapid drop and tensile strength was lower than that of the pure polymer. For PP2 the tensile strength demonstrated almost no change at lower filler content and an immediate decrease at high contents, much lower than that of pure PP2. The tensile strength of PP3 presented a slow decrease with increasing content at lower filler contents and a fast decrement at high contents. They noticed that the yield strength at low filler contents increased only for PP1, and decreased or did not change for PP2 and PP3. The dispersion was good at all the types of the composites, and they figured that the difference was because the stronger bonding between the particles and the matrix at the case of PP1, so the filler could participate at the load transfer mechanism. At levels of high filler content, all the materials showed a serious reduction in strength, compared to the pristine matrix, due to the difficulty of dispersion at such high contents. As the particles agglomerate, the interparticle bonds in the agglomerates are much weaker relative to the matrix, so they cannot bear the load effectively. They examined also the flexural strength, and saw that all the PP composites showed a moderate increase with increasing filler content at low content, and a drastic increase with increasing filler content at high contents. The flexural strength and the flexural modulus increased with the filler content. For PP/ CaCO_3 30 wt%,

only few agglomerates were observed by SEM analysis, which indicated relatively good dispersion and strong interfacial interactions. Youssef *et al.*⁴⁷ studied the mechanical properties of chitosan with ZnO and Ag nanoparticles. The chitosan was prepared by solution casting, with formic or acetic acid. Polyethylene glycol (PEG) at known amounts was added to chitosan, and hydroxyl ethyl cellulose (HEC) was blended with chitosan. Ag was added as silver nitrate that was reduced afterward, and the ZnO was added as particles, after it was synthesized. They tested the mechanical properties of chitosan that contained Ag-NPS and ZnO-NPS, all of them were prepared with 1% PEG and 20% HEC. The mechanical properties for the chitosan with formic acid were higher than those of the chitosan contained acetic acid. The addition of Ag particles did not have an effect with the increasing amount of the filler at the load at maximum, in both types of acid. The addition of ZnO showed only slight improvement in the mechanical properties.

Kuo *et al.*⁴⁸ studied the properties of polyether-ether-ketone (PEEK) with SiO₂ and Al₂O₃ nanoparticles. The composites were prepared by ultrasonication and then vacuum assisted compression molding, and resulted in filler contents up to 10 wt% with different particle sizes. SEM-EDS analysis showed a reasonably uniform dispersion up to 5 wt%, while the amount of agglomerates increased with increasing content. Al₂O₃ showed better dispersion than SiO₂ of 30 nm size, possibly due to their spherical shape, while SiO₂ of 15 nm size showed the best dispersion. They measured the UTS and saw a maximum value at filler contents of 5 wt% (Al₂O₃) and 7.5 wt% (SiO₂), suitable with the SEM results. SiO₂ particles of 15 nm size presented the highest values, but slightly decreased at 10 wt%, probably due to poorer dispersion and more clustering at higher filler contents. They compared these results to the predicted ones by a modified ROM, reducing the contribution of the filler by an order of magnitude, considering the strength to be 1500 MPa for SiO₂ and 2000 MPa for Al₂O₃. The predicted values were up to 21% higher than the experimental ones.

6.1.3.3 The Strength of Hybrid Nanocomposites

Hybrid composite materials comprise more than one type of reinforcement. A combination of two reinforcements may lead to hybrid effects and synergistic interactions. A positive hybrid effect is an improved outcome compared to the optimum of the individual dispersants alone. The field of hybrid effects continues to draw increased attention particularly for nanocomposites, where intimate mixing of the nanoparticles is expected to produce positive hybrid effects. Common combinations may include two different types of organic fillers such as CNTs and graphene, or a combination of organic filler and inorganic fillers such as CNTs and NCs. Praveen *et al.*⁴⁹ used styrene butadiene rubber (SBR) that contained CB and NC fillers, prepared by roll milling. XRD and TEM images indicated that NC were intercalated and exfoliated in a considerable level. The addition of CB had a significant influence on the dispersion and the levels of intercalation and exfoliation of NC. CB increased the interlayer distance but did not allow an exfoliation. However, at high filler contents of both fillers, mainly intercalation and some aggregation were presented, due to the high overall filler contents and due to the reinforcing effect of CB on the intercalated structure. The hybrid composite that contained 20 phr of CB and 10 phr of NC showed a hybrid effect in the mechanical properties of tensile strength and stress at 100% elongation. The tensile strength of SBR/NC/CB is 21.8 MPa, compared to 8.6 MPa and 2.6 MPa of SBR/CB and SBR/NC, respectively; and the stress at 100% elongation of SBR/NC/CB is 6.11 MPa, compared to 2.5 MPa and 2.4 MPa of SBR/CB and SBR/NC, respectively. Due to the layered arrangement of the NC, the chains may slip and therefore preclude the breaking of the molecules at high strain. The structure of rubber that is bound to CB contributes to the strength. The relatively low viscosity of the SBR simplifies the partial exfoliation of NCs.

Li *et al.*⁵⁰ presented a study of PVA film reinforced by CNT and GO, prepared by ultrasonication. AFM characterization indicated that the GO was fully exfoliated. FESEM showed that whereas films that contained CNTs alone exhibited aggregation and poor dispersion, GO sheets were able to disperse CNTs in aqueous solution through non-covalent interactions, using hydrophilicity, and therefore improve the dispersion. The yield strength of the hybrid composite was improved by 48% compared to pure PVA, which was a much higher improvement than that of CNT/PVA and GO/PVA summed together. The authors had also tested the tensile properties at different filler contents with fixed GO:CNT ratio of 2:1. The highest value of the yield strength was received for 2 wt% of CNT, showing an improvement of 76.5% compared to pure PVA; and the highest value of the tensile strength was received by 3 wt% of CNT, showing an improvement of 80.3% compared to pure PVA. Further increase of the filler content showed lower tensile and yield strength. The authors explained these results by the facilitated dispersion at low filler contents compared to aggregates at higher filler contents, therefore decreasing the efficiency of the reinforcement.

6.1.3.4 Summary

With a few exceptions, it is seen that the strengths of nanocomposite materials fail to fulfill their expected values. Moreover, the experimental strength values, except for low nanoparticle concentrations, do not necessarily exhibit a steady increase with the nanoparticle concentration.

6.1.4 Models of Elastic Modulus of Particulate Composites

As in the previous section on strength, we begin our analysis of the elastic modulus of nanocomposites by referring to the common ROM based models which express it as a weighted average of the properties of the parent constituents. Because of the recently

growing interest in nanoparticle reinforced composites, many new studies have been performed recently to revisit the models for the elastic constants of particulate composites as exemplified by references.^{51,52} Still, the starting point is often the Halpin-Tsai classical model, which is generalized to account for the longitudinal and transverse moduli of aligned discontinuous-fiber composites as in Fig. 4(a), written respectively as:

$$\frac{E_L}{E_m} = \frac{1 + (2l/d)\eta_L\phi_f}{1 - \eta_L\phi_f} \quad (8)$$

$$\frac{E_T}{E_m} = \frac{1 + 2\eta_T\phi_f}{1 - \eta_T\phi_f} \quad (9)$$

where

$$\eta_L = \frac{(E_f/E_m) - 1}{(E_f/E_m) + 2(l/d)} \quad (10)$$

and

$$\eta_T = \frac{(E_f/E_m) - 1}{(E_f/E_m) + 2} \quad (11)$$

For in-plan isotropy (Fig. 4(b)), the following empirical equation is often used, where the contribution of the longitudinal modulus of the orientated discontinuous fiber composite is weighted at 3/8 (compare with Eq. (7)):

$$E_{c(\text{random})} = 3/8E_L + 5/8E_T \quad (12)$$

The above equations are relevant in principle to particulate reinforcement such as discontinuous fibers or platelets of aspect ratios bigger than 1. For particulate composites with particles of aspect ratio of 1, such as spheres, different models for the modulus exist, which consider the geometry of the particles, the particle/matrix modulus ratio and the volume (weight) fraction of the particles. Although the models consider by and large polymer matrices, they refer also to composites of non-polymeric matrices such as metallic and ceramic.⁵¹

One of the earlier models for the modulus of particulate composites was proposed by Paul,⁵³ who suggested an approximate solution based on a two-phase model of cubic inclusion within a cubic matrix, at whose boundary a uniform stress is applied (Fig. 7).

The result can be formulated as follows:

$$\frac{E_c}{E_m} = \frac{1 + (\chi - 1)\phi_f^{2/3}}{1 + (\chi - 1)(\phi_f^{2/3} - \phi_f)} \quad (13)$$

where χ is the modulus ratio of filler to matrix. Using the same model and solving it for a uniform normal displacement at the boundary, Ishai and Cohen⁵⁴ formulated the following solution:

$$\frac{E_c}{E_m} = 1 + \frac{\phi_f}{\chi/(\chi - 1)/\phi_f^{1/3}} \quad (14)$$

and it was suggested by the authors that Eqs. (13) and (14) express upper and lower bounds respectively (e.g., a comparison with Eqs. (13) and (14) of experimental results for glass bead-epoxy composites⁵⁵). Based on different particle geometries and fundamental assumptions, other models exist in the literature. A review of many of the models including comparisons with experimental results can be seen in Whitney and McCullough.⁵⁶

It is clear that although the predictions are far apart, they commonly present a steady increase in the modulus of a particulate composite as a function of the content of the particles, though by different functions.

Fig. 7 A model for the calculation of the elastic modulus of particulate composites based on a cubic particle in a cubic matrix. Ishai, O., Cohen, L., 1967. Elastic properties of filled and porous epoxy composites. *International Journal of Mechanical Sciences* 9, 539–546.

As stated above for the strength, the different models for the modulus of nanocomposites according to the geometry of the nanoparticles (e.g., Eqs. (8), (9), (12)) do not pose any restrictions on the actual dimensions (length and diameter or thickness) of the reinforcement. Hence, disregarding potential effects that are typical of the nanoparticles, such as enhanced interfacial effects, we can assume that those models account for nanoparticles too.

6.1.4.1 The Modulus of Different Nanocomposite Systems

A literature survey of recent experimental studies of Young's modulus of different nanocomposites shows that basically the stiffness increases as a function of the nanoparticle content and that the behavior can be accounted for by a selection of ROM and other models based on the particle type (shape and properties). Unlike the models, however, the experimental studies show that the stiffness increase is bounded by particle content, at which interparticle interactions interfere with the stiffening mechanism.

This section reviews studies of the modulus of different nanocomposite materials and the experimental results thereof are compared to the theoretical values as predicted by the ROM and by the Halpin-Tsai model discussed above. Further, we will compare the predicted values to the experimental ones. Also, similar comparisons are made for hybrid nanocomposites, which contain more than one type of filler, relating to ROM for hybrids. This section will also discuss nanocomposites that contain carbon fillers, clay fillers and others.

6.1.4.1.1 PP matrices

This section is devoted to nanocomposites of PP matrices. As was described in Section 6.1.3.1, Kumar *et al.*²⁰ studies PP/VGCFs composites. By an addition of 5 wt% filler they received a significant improvement of 54% (compared to pristine PP) in the tensile modulus. They also calculated the predicted modulus by the ROM using 450 GPa as the modulus of VGCF and 5 GPa as the modulus of the oriented PP fiber. The calculated modulus was 17 GPa, while the observed modulus was lower – 7.1 GPa. ISCM, SEM images and XRD indicated a good dispersion and high degree of orientation of VGCFs inside the PP fiber. Kearns and Shambaugh²¹ tested also the modulus of PP/SWCNT and found out that it increased with the increasing loading percent, at 0.5 and 1%. Xie *et al.*⁷ prepared PP/CNT composites, and PP/composites compatibilized with MA-SEBS, with filler contents up to 10 wt% of CNT; the addition of CNTs and MA-SEBS improved the modulus but the addition of CNTs alone presented higher results. In another work, Wakabayashi *et al.*²² studied the mechanical properties of PP/graphite nanocomposite. The composites were prepared by single-screw melt extrusion (2.8 wt%) and SSSP (2.5 wt%) methods, and their performances were compared. SSSP presented uniform and better dispersion and exfoliation than single extruder, which showed only poor dispersion. Both types showed an improvement of the modulus, but the improvement of the composite prepared by SSSP was higher (100%) than for the composite prepared by single-screw extrusion (40–45%). The authors explained this by the good dispersion and the high aspect ratio of the graphite after SSSP, compared to merely graphite incorporation for the single-screw extruder. Assuming 2.5 wt% of 3D perfectly bonded, randomly oriented, flat platelets, with aspect ratio of 300–500 and a modulus of 500 GPa, calculations by Mori-Tanaka micromechanics analysis defined an upper limit of 4500–6300 MPa for Young's modulus, threefold higher than the experimental modulus of the SSSP processed nanocomposite.

6.1.4.1.2 Epoxy matrices

Epoxy is another commonly used matrix for nanocomposite materials. As reported above, Gojny *et al.*²⁴ studied composites with different CNTs types inside an epoxy matrix: SWCNTs, DWCNTs, MWCNTs, DWCNTs-NH₂, and MWCNTs-NH₂ and compared them to CB. All kinds of CNTs showed an increased modulus compared to the pristine epoxy, under the condition of sufficiently high adhesion and the impregnation. SWCNT showed that the modulus increased with the content of filler. DWCNT-NH₂ also increased with filler content, but it was slighter at high concentrations. The moduli of MWCNTs and DWCNTs increased with filler content up to 0.1% and 0.3%, respectively. The authors' explanation to these results was re-agglomeration that happened at high contents. DWCNT-NH₂ showed the best result at 0.5%, and exhibited an improvement of 15% compared to neat epoxy. MWCNT-NH₂ demonstrated large improvements compared to neat epoxy, but did not increase with increasing amount of filler. The functionalized CNTs showed higher improvement in modulus than the non-functionalized ones, due to the ability to form covalent bonds with the matrix. Rafiee *et al.*²⁵ studied the mechanical properties of epoxy with 0.1 wt% of GNPs, SWCNTs, and MWCNTs. The graphene showed the highest Young's modulus and they explained this fact by its high SSA, wrinkled surface, and the two dimensional planar geometry. They calculated the predicted values of modulus by the Halpin-Tsai model. For that purpose, they assumed that SWNT and MWNT are randomly oriented discontinuous fibers. To calculate the modulus of epoxy/NP by the HT model, they assumed that GPLs acted as an effective rectangular solid fiber, and manipulated the equations of the model. They used the following modulus values for the fillers: SWCNT – 1 TPa, MWCNT – 450 GPa, and GNP – 1.01 TPa. The experimental results were lower than the predicted for both types of CNTs. In contrast, the experimental results for GNP were higher than predicted by the modified model. They suggested that the latter observation resulted from the discrepancy between the model assumption of a rectangular shape and the actual wrinkled structure. Ramana *et al.*²⁶ prepared epoxy composites with H₂SO₄ and HNO₃ treated and untreated MWCNTs at different contents of up to 1 wt%. The flexural modulus increased with the increasing weight percent of the CNTs. The functionalization of 1 wt% of CNT led to further increase compared to untreated CNT. Functionalized groups covalently attached to the epoxy matrix, presented better dispersion, improved the load transfer mechanism and showed the highest modulus. Li *et al.*²⁷ prepared an epoxy resin with few layer graphene (FLG) and GNP by in situ

Fig. 8 A comparison of measured and predicted modulus of polyacrylonitrile (PAN)/single walled carbon nanotube (SWCNT) composites. The experimental results were higher than the predicted values. After Ko, F., Gogotsi, Y., Ali, A., *et al.*, 2003. Electrospinning of continuous carbon nanotube-filled nanofiber yarns. *Advanced Materials* 15, 1161–1165.

polymerization. By controlling shear and temperature conditions, they managed to well exfoliate particles with aspect ratios higher than 300 and an average thickness of 5 nm, showing that 4 wt% of optimized FLG flakes increased the modulus by 160%.

6.1.4.1.3 Carbonaceous nanoparticles

Ko *et al.*⁵⁸ studied fibers, composed of polyacrylonitrile (PAN) and purified high-pressure CO disproportion (HiPCO) SWCNT and prepared by electro-spinning. They tested Young's modulus using AFM. The measured modulus increased with increasing amount of SWCNT, and showed higher values than those predicted by the ROM, assuming 1 TPa modulus for SWCNT (some of their results are reconstructed in Fig. 8). Suggested reasons for the higher values, according to the authors, were underestimation of SWCNT modulus, increased matrix stiffness due to matrix-SWCNT interaction, higher weight percent of SWCNT in average or sectional. Mack *et al.*⁵⁹ studied electrospun PAN nanofiber with GNP up to 5 wt%. TEM analysis confirmed the incorporation of the GNP in the matrix, and SEM images showed a quite uniform particle size distribution. Young's modulus, which was measured by AFM, increased with the increasing amount of GNP. The authors explained this by the high stiffness and high aspect ratio of GNP, which increased the efficiency of the stress transfer mechanism. Wang *et al.*²⁷ investigated chitosan/MWCNTs composite, with filler contents up to 2 wt%. The modulus increased with the increasing content of CNTs up to 0.8 wt%, after which it presented smaller increase. They explained the improvement by the reinforcement of fine dispersed MWCNTs and the hydrogen-bond interactions between chitosan matrix and functionalized MWCNTs, and the moderate improvement at higher contents by MWCNTs aggregation.

Kanagaraj *et al.*³³ studied chemically treated CNT dispersed in HDPE, containing volume fractions in the range 0.11–0.44%. Young's modulus increased with increasing amount of filler, up to 22.2% improvement at the highest amount. They explained this result by increased surface area per unit volume, which would lead to a more effective load transfer mechanism. They compared their results with the modified ROM and to the Halpin–Tsai model, assuming that the CNTs are randomly oriented and using 910 GPa as the modulus of CNT. The authors used the equation for randomly oriented short fibers (Eq. (15)), which is analogous to Eq. (7):

$$E_c = (\eta_0 \eta_l E_f - E_m) \phi_f + E_m \quad (15)$$

where E_c is the modulus of the composite, η_0 is the orientation efficiency factor, η_l is the fiber length efficiency factor, E_f is the modulus of the filler, E_m is the modulus of the matrix, ϕ_f is the volume fraction of the filler and $\phi_m = 1 - \phi_f$ is the volume fraction of the matrix.

The experimental modulus was in good agreement with the values predicted by the Halpin–Tsai model, and lower but still in reasonable agreement with the modified ROM. The agreement of the experimental with the predicted values and the linear dependence on the filler concentration were taken to indicate an efficient load transfer mechanism. Liang *et al.*³⁰ prepared composites of GO that were well dispersed and fully exfoliated in PVA matrix. They found an increase in Young's modulus with increasing GO content. They compared their experimental Young's modulus to the calculated values by Halpin–Tsai model, both for randomly oriented and for unidirectional (parallelly aligned to the sample film) fillers. Young's modulus value of GO was assumed to be 0.25 TPa. The comparison showed better agreement with the unidirectional model. This agreement indicated effective load transfer mechanism through the interface, probably due to the strong hydrogen-bonding interactions. Abbasi *et al.*²⁸ investigated flow-induced orientation of polycarbonate/MWCNTs, using different types of molding and different rates of injection, with filler contents up to 10%. A morphological analysis showed well dispersed and shear-flow oriented tubes. Young's modulus

increased monotonically with the filler content, and presented a plateau at high filler levels. The effect on the modulus was marginal, probably due to the weak interactions between the filler and the matrix. Higher injection speed showed higher Young's modulus, but not in a markedly significant manner. The improvement was explained by the higher degree of alignment and chain orientation, as the microinjection molding produced very fast cooling conditions, thus inhibiting polymer chains relaxation.

As described above, Zhao *et al.*³¹ studied the properties of PVA with GO, up to 3 vol%. The sample of 1.8 vol% GO presented fully exfoliated and well dispersed fillers. Young's modulus increased with the increasing volume fraction of GO, and presented the highest value at 1.8 vol%, which was more than 10 times higher than the pristine PVA. Above 1.8 vol%, there was only a slight increase of the modulus. They explained the improvement by the large aspect ratio of the GO sheets and by the strong PVA-GO interaction. They compared the experimental results to the predicted values by Halpin-Tsai model for both unidirectional and randomly oriented fillers, taking the modulus of monolayer graphene to be 1.0 TP. Basically, the experimental results agreed with the theoretical prediction for the randomly dispersed GO. Gan *et al.*³² studied a SR with GNRs, which were oxidized and randomly dispersed without apparent aggregations. The addition of GNRs into the SR showed an enhancement of the mechanical properties, which was increased with increasing the filler content. The highest value was observed for the highest filler content of 2 wt%, which led to an improvement of 93% in Young's modulus. The authors explained the good results by the uniform dispersion and by the good interactions between SR and GNRs. Sellam *et al.*⁶⁰ created transparent films of PVA/5.4 wt% GO, where the GO were highly organized in a multilayered arrangement by a spray assisted layer-by-layer (LbL) procedure, and compared it with PVA/5.4 wt% GO composite prepared by solution cast. Young's modulus of the sprayed composite was almost doubled, while the modulus of solution casted composite was improved only by 60%. The authors used the Halpin-Tsai model to back calculate the stiffness of GO and found it to be 120 GPa for the sprayed composite and 51 GPa for solution casted composite. They explained the good results for the sprayed composites by the nanoscale organization combined with hydrogen bonding interfacial interactions, which together allow an effective stress transfer mechanism.

6.1.4.1.4 NC particles

As previously reviewed, Vu *et al.*⁴⁰ studied the tensile properties of sodium MMT' clay nanolayers within *cis*-1,4-polyisoprene (synthetic) NR and two sets of ENR with different epoxy mol%. The clay was used in two forms: pristine (Na-Mt) and organically modified (C1, C2, and C3), at filler contents of 10–30%, and compared them to a reference filler (Hi-Sil). The clays were intercalated and possibly exfoliated in NR and ENR, while different modifications showed different qualities of exfoliation in different types of matrices. ENR with pristine clay showed a high modulus at small strains, which was explained by the high effective volume fraction. At high strains, pristine clay showed higher values than the C1 and C2 modification, attributed to a stronger polymer network in the first. The NC modified composites with NR, showed much higher values than composites with precipitated silica (Hi-Sil), and for 10% of filler C2 showed better results than C1. In another study, Manias *et al.*⁴¹ mixed PP with highly intercalated f-MMT. They also compared micro (conventionally) filled PP/2C18-MMT' composites, which remained in tactoids and did not intercalate or exfoliate, to nanocomposites PP/f-MMT. Young's modulus showed a steep increase up to 3 wt%, a smaller increase above 4 wt% MMT', and no significant improvement for "micro" composites. MMT' functionalized with MA samples were also prepared, and showed an enhancement in the modulus compared to non-functionalized MMT', due to better load transfer caused by better adhesion to the matrix.

As described above, Shelley *et al.*³⁹ studied the longitudinal and transverse tensile properties of nylon-6/NC composites, using 2 and 5 wt% filler concentrations. There were no significant differences between the longitudinal and transversal directions in the initial modulus and the modulus increased with increasing filler content. They retrieved the value of the modulus of the clays from the ROM to be 58 GPa, which was significantly lower than the literature value of 178 GPa, associating the lower experimental value with the contribution of the clay modified matrix to the ROM value. Lee *et al.*⁴² studied the tensile properties of biodegradable APES with two types of organically modified MMT: Cloisite 10A and Cloisite 30B, with filler contents of 0–30%, as was reviewed in Section 6.1.3.1 above. Cloisite 30B showed better dispersion and intercalation than Cloisite 10A. Cloisite 30B also demonstrated higher modulus than Cloisite 10A, particularly at higher filler contents. For both, the modulus increased with the filler content. The same arguments used to explain the strength behavior were used for the modulus, pointing at the hydrogen bonds that Cloisite 30B might form with the matrix. Haraguchi *et al.*⁴³ compared nanocomposites hydrogels of PDMAA/NC, PDMAA/OR, and NIPA/NC (from their previous study). The moduli of DMAA/NC and NIPA/NC improved with increasing clay loading. DMAA/NC showed higher tensile modulus than DMAA/OR and slightly lower than NIPA/NC. They proposed an explanation for the difference between DMAA/NC and NIPA/NC by their different networks: NIPA/NC had larger amount of cross-linking chains, but shorter typical change length. Similarly, Wang *et al.*⁴⁴ studied epoxy/NC nanocomposites, with filler contents of 1–5 wt%, of good dispersion and exfoliation. They found that Young's modulus of the composites increased gradually with the filler content, presenting significant improvement compared to the neat epoxy. Bilotti *et al.*⁶¹ prepared a composite system of polyamide 6 (PA6) with sepiolite clay (fiber like geometry – 1D) by melt compounding, and compared their results to selected publications on PA6/smectite MMT' clay (platelet like geometry – 2D). Young's modulus of PA6/sepiolite increased with the filler content up to 5 wt% (the highest filler content used), due to good dispersion and hydrogen bonding interactions between the filler and the matrix. The authors analyzed the results of the different systems by the Halpin-Tsai model for unidirectional and randomly oriented fillers, using the values of 3 and 200 GPa as Young's moduli of PA6 and NCs, respectively. 1D fillers showed better reinforcement in oriented systems, and 2D fillers presented better performance in isotropic composites, but only for high aspect ratios (>100). Composites with MMT showed higher Young's modulus, which was explained by the higher degree of particle orientation. Composites with sepiolite showed higher effective aspect ratio (extracted from the Halpin-Tsai model) and better reinforcing efficiency.

Fig. 9 A comparison of experimental (for different mixing times) and predicted moduli of polypropylene (PP)/CaCO₃ composites. The moduli were predicted by the upper and the lower rule of mixtures (ROM), respectively. The measured moduli are lying between the theoretical values, for all mixing times. After Chan, C.-M., Wu, J., Li, J.-X., Cheung, Y.-K., 2002. Polypropylene/calcium carbonate nanocomposites. *Polymer* 43, 2981–2992.

6.1.4.1.5 Other nanoparticles

Another already reviewed article written by Chan *et al.*⁴⁵ on composites of PP with CaCO₃ of 4.8–13.2 vol%, while nanoparticles up to 9.2 vol% were well dispersed, but showed more aggregates at higher contents. They measured a significant improvement of the modulus with increasing content of CaCO₃. They also paid attention to the fact that higher improvement was observed at lower concentrations up to 9.2 vol%, after which the dispersion was poorer. They compared the results to upper and lower bounds (based on the classical longitudinal and transverse ROM of continuous fiber reinforced composites, respectively). They showed that the experimental results were located between those bounds, depending on the residual particle aspect ratio, wherein for high aspect ratio the results coincided with the upper bound, and vice versa. A similar comparison presented in Fig. 9, based on their results. TEM and SEM images showed low aspect ratio particles and destroyed spherulites due to CaCO₃ nucleation effects, respectively. The authors explained that decrease in crystallinity and in spherulite size may decrease the modulus by decreasing the load-bearing capacity. They concluded that the modulus improved mainly by the strong interactions between the particles and the matrix.

As previously described, Yang *et al.*⁴⁶ studied the mechanical properties of PP/CaCO₃ with filler contents of 2–40 wt%, using three types of PP: polypropylene homopolymer (PP1), polypropylene-ethylene copolymer (PP2) and a mixture of these two types (PP3, PP1:PP2=1:1). All the types exhibited good dispersions. The flexural moduli of all the compositions presented either moderate or steep increases with increasing filler content at low and high contents, respectively. The study of Youssef *et al.*⁴⁷ which was reviewed in Section 6.1.3.1, examined the mechanical properties of chitosan, prepared using formic or acetic acid, with ZnO or Ag nanoparticles. The addition of Ag showed an improved Young's modulus for both types of acids, and the values increased with the increasing loading of Ag nanoparticles. The mechanical properties of the formic acid treated chitosan were higher than those of the acetic acid treated chitosan. The addition of ZnO exhibited only slight increases of the mechanical properties.

Kinloch and Taylor⁶² mixed an epoxy resin with different micro and nano inorganic fillers, and studied their mechanical properties. They used the following types of fillers in their research: Mica R120 (micro, without surface treatment), Cloisite Na⁺ (nano, without surface treatment), Cloisite 25A (nano, treated with 2MHTL8), Cloisite 30B (nano, treated with MY2EtOT), and Nanomer I30E (nano, treated with octadecylamine). XRD analysis showed that only Nanomer I30E was exfoliated, Cloisite 25A and Cloisite 30B were intercalated, while Cloisite 30B showed higher interlayer space, and Mica R120 and Cloisite Na⁺ were particulate. SEM images indicated that all the filler types were randomly orientated. The authors found that the modulus increased with the increasing amount of modifier for all the samples. The highest values were obtained for the samples that contained Mica R120 and Nanomer I30E, while the others showed only a small improvement. Mica R120 showed higher values than Nanomer I30E, especially in higher filler contents. They compared the experimental values to the theoretical values to the ROM and the Halpin-Tsai model. Eventually, they chose to use the Halpin-Tsai model, claiming the ROM to be an upper bound only rarely reached. They used both the regular form of the Halpin-Tsai and the Van Es models, using the value of 10 for the filler aspect ratio. These models generated theoretical values that were very close to the experimental ones, while Mica the R120 results exceeded the theoretical values. However, the experimental results were significantly lower than the ROM and the regular Halpin-Tsai predictions, as seen in the reconstructed Fig. 10.

As presented in Section 6.1.3.1, Kuo *et al.*⁴⁸ studied the properties of PEEK with SiO₂ and Al₂O₃ nanoparticles, with filler contents up to 10 wt%, using two particle sizes. The modulus showed an increase with increasing nanofiller concentration up to

Fig. 10 Comparison of experimental and theoretical moduli of epoxy composites with different filler types. The experimental results are lower than the rule of mixtures (ROM) and the regular Halpin-Tsai predictions, but in agreement with the Halpin-Tsai Van Es model. After Kinloch, A., Taylor, A., 2003. Mechanical and fracture properties of epoxy/inorganic micro-and nano-composites. *Journal of Materials Science Letters* 22, 1439–1441.

10 wt%. SiO_2 particles of 30 nm size showed the highest values, while the Al_2O_3 of the same size showed slightly lower values, attributed to the spherical shape of the Al_2O_3 nanoparticles. SiO_2 particles of 15 nm size showed lower values. The authors suggested that extra fine particles might not be able to utilize their full load transfer capability to stiffness enhancement and that they might increase the free volume, allowing higher mobility of polymer chains, thus decreasing Young's modulus. The authors also compared their results to those predicted by the modified ROM, reducing the contribution of the filler by factor of 10, considering the moduli to be 73 GPa for SiO_2 and 393 GPa for Al_2O_3 . Still, the calculated results were higher than the experimental ones for both fillers. Moreover, the predicted values the Al_2O_3 were higher than those of the SiO_2 composites, which contradicted the experimental data.

6.1.4.1.6 Hybrid nanocomposites

A number of references in the literature are devoted to the study of Young's modulus of hybrid nanomaterials. Li *et al.*⁵⁰ prepared PVA films with CNT and GO. Young's modulus of the hybrid composite was improved by 31% compared to pure PVA, which was much higher than the improvement of CNT/PVA and GO/PVA together. To compare their results to the ROM prediction the authors used the equation for nonaligned short fibers (Eq. (15)), where E_c is the modulus of GO-CNT/PVA, $\eta_0=1/5$ is the orientation efficiency factor for randomly oriented fiber, η_l is the fiber length efficiency factor ($\eta_l=1$ for fillers of aspect ratios above 10), E_c is the modulus of CNT/PVA, E_m is the modulus of GO/PVA, ϕ_f is the volume fraction of CNT and $\phi_m=1-\phi_f$ is the volume fraction of the matrix. They considered Young's modulus of CNT to be 1 TPa. The calculated E_c was 4.11 GPa, and the experimental value was very similar – 4.10 GPa. From the high correlation between the values, the authors concluded that the CNTs were well dispersed and that there was an efficient load transfer mechanism from the matrix to CNT-GO fillers. An examination of Young's modulus of composites with fixed GO:CNT ratio of 2:1, and increasing GO-CNT contents up to 5 wt% of CNT, confirmed a linear increase of the modulus with the filler content. The sample that contained 5 wt% of CNT, showed an improvement of 106% compared to pure PVA. The authors attributed this enhancement mainly to the high moduli of GO and CNT compared with that of PVA. In another study, Chatterjee *et al.*⁶³ prepared epoxy composites of GNP and acid oxidized CNTs. A uniform distribution of self-aligned CNTs on the surfaces of the GNPs was observed, creating a more effective co-reinforcing network in the matrix. A good dispersion of GNP was achieved up to 0.5 wt%. The authors reported that the residual tube length after the dispersion process was shorter than the original. They tested the flexural modulus of composites that contained only GNP of 5 μm and of 25 μm size, up to 1 wt%. All the samples that contained GNP showed an improvement of the modulus compared to neat epoxy, which depended on the GNP concentration. GNP of 25 μm size presented better performance than GNP of 5 μm , which the authors attributed to the higher aspect ratio of the first. Hybrid nanocomposites were examined too, where improvements of 17% relative to pure epoxy, and of 9% and 5% compared to epoxy/CNT and epoxy/GNP, respectively, were measured. The authors explained the improved hybrid properties by the cited argument that the CNT decreased the π - π interaction between the graphene sheets thereby improving their dispersion.

6.1.4.2 Summary

To summarize the literature survey of the modulus of nanocomposite materials, it is concluded that this property complies better with micromechanical models than the strength. This observation is supported by various studies that investigated both properties

simultaneously and compared them with the respective theoretical predictions of the corresponding micromechanics models. The modulus therefore appears to be less sensitive to the efficiency of the stress transfer mechanism than the strength. Yet, with few exceptions, the modulus values of nanocomposites fall well below the expected values based on the properties and potential contributions of nanoreinforcements such as CNT and graphene. It is thought that in some of the cases, where a good fit with theoretical predictions was observed, the inherent properties of the nanoparticles were undervalued, while in others, modified ROM were applied, which reduced significantly the contribution of the nanofillers.

Many of the reasons why composites micromechanics models do not work for nanocomposites are given by Andrews and Weisenberger,⁶⁴ who reviewed nanocomposite materials with CNTs. They showed that the reinforcing potential of CNT was not fully realized so that the experimental properties were lower than the theoretical values particularly for filler contents of 10% and above. Weak interfacial interactions, poor dispersion, degradation of the tubes during the preparation processes, the curviness of the tubes that reduces their properties by a factor of 50–200 compared to straight tubes, were among the listed reasons. Another claim, concerning specifically MWCNT, was that since only the outermost layer carries the load, the modulus contribution of MWCNT should be normalized with respect to their entire cross sectional area.

An additional consideration is that of the effect of the nanoparticles on the matrix. The interaction between the nanoparticles and the matrix on the molecular level may affect the morphology of the matrix, for example, by nucleation, which must also result in a deviation from the ROM.

6.1.5 Fracture Mechanics and Toughness of Polymer Nanocomposites

Unlike the static properties strength and stiffness, fracture mechanics and toughness of nanocomposites are independent of an effective stress transfer mechanism, although they do depend on the geometry of the nanoparticles. The main factor that determines the mechanics of toughness is the type of interactions between the crack front and the nanoparticles, which delay or arrest the crack propagation. In general, we identify two essentially different interactions, depending on the geometry of the nanoparticles as expressed by their aspect ratio.

For tube or rod-like geometries, fracture energy is dissipated initially in shear failure of the particle/matrix interface followed by work of friction while the nanoparticles are being pulled out from the matrix. With no restrictions on the actual dimensions of the reinforcement, the classical model (Eq. (16)) that describes the pull-out energy dissipated in fracture of discontinuous fiber reinforced composites should apply for nanoreinforcements as well.⁶⁵ Moreover, a number of reports exist, which show that strongly bonded, surface treated CNT can bridge the crack front and then break eventually upon crack propagation, while dissipating high fracture energy by both breaking and pull-out. This is exemplified in Fig. 11, where fracture surfaces of a CNT reinforced interleaf of carbon fabric-epoxy laminate are shown.⁶⁶

$$\gamma_{po} = \frac{\phi_f \tau_{if} l^2}{24r} \quad (16)$$

where γ_{po} is the pull-out component of the fracture surface energy, τ_{if} is the fiber-matrix interfacial shear strength, and l and r are the fiber length and radius, respectively.

For low aspect ratio particles, for example, spheres, other particle-crack front interactions may occur wherein, for example, the particles act as pinning positions to the crack front, turning the crack propagation process to a series of catastrophic crack arrest-jump steps. A classical model of this mechanism known as the crack-front bowing mechanism was proposed by Lange and Radford⁶⁷ and Lange⁶⁸ and presented schematically in Fig. 12.

According to this model, the fracture energy should increase as the crack front – which is momentarily pinned at the inhomogeneities – bows out, thus increasing its total length. The analytical model expresses the fracture energy increase quantitatively as a function of the length increase of the bowed crack front, given by the distance between the particles and their size and volume fraction. The extensive energy absorption is manifested by excessive fracture surface roughness that can be assessed by quantitative AFM as demonstrated in Ref. [69].

Fracture toughness is regarded as a significant property in determining whether the material is suitable for certain specific applications without fracturing.^{70,71} To study the effects of nanofillers on the fracture toughness of polymer nanocomposites, it is natural to make a distinction based on the nanofiller typology, i.e., CNTs, layered nanofillers, either graphene or clay and nanoparticle.

A literature survey of recent studies of fracture toughness of nanocomposites shows that this property is enhanced significantly for even minor additions of different nanoparticles, demonstrating that either or both mechanisms are active in the energy absorption process.

6.1.5.1 CNT Filled Polymer Nanocomposites

CNTs were used as a reinforcing agent in polymer matrix composites owing to their high aspect ratio and unique properties such as high mechanical, electrical and thermal properties. The results acquired from the relevant works which studied the fracture toughness of nanocomposites containing CNTs are presented in Fig. 13.^{24,72–84} The addition of CNTs into polymer resin leads to

Fig. 11 Top view of a Mode II fracture surface of a carbon nanotube (CNT) reinforced interleaf of carbon fabric-epoxy laminate, showing pulled-out CNT attached to carbon fibers (a); broken CNT that bridge a crack (b); pulled-out CNT protruding from an epoxy rich zone (c). It is noted that the CNTs seem to be fully exfoliated and uniformly dispersed throughout the entire interleaf. Reproduced from Lyashenko-Miller, T., Fitoussi, J., Marom, G., 2016. The loading rate effect on Mode II fracture toughness of composites interleaved with CNT. *Nanocomposites* 2, 1–7.

Fig. 12 A moving crack front is momentarily pinned at positions of inhomogeneities in the matrix, followed by its bowing out, before breaking away catastrophically. After Lange, F., 1970. The interaction of a crack front with a second-phase dispersion. *Philosophical Magazine* 22, 0983–0992.

the improvement of fracture toughness depending on the dispersion method and surface functionalization employed on the CNTs.

Chandrasekaran *et al.*⁷⁴ dispersed multi-wall CNTs (MWCNTs) in the epoxy resin by applying very high shear rate ($250,000 \text{ s}^{-1}$) on the mixture using three roll mill. The increase in the fracture toughness for MWCNTs/epoxy nanocomposites was only 8%

Fig. 13 Percentage of enhancement in fracture toughness in polymer nanocomposites with addition of carbon nanotubes (CNTs).

at 0.5 wt% of MWCNTs content. Thostenson and Chou⁸⁴ optimized the processing conditions for the dispersion of MWCNTs in the epoxy resin using three roll mill. The fracture toughness increased by 123% at 0.5 wt% of MWCNTs content. Yu *et al.*⁷³ dispersed a high loading of 3 wt% MWCNTs in the epoxy resin by sonication. The fracture toughness of the nanocomposites was 1.6 times higher than that of the pure epoxy. Gkikas *et al.*⁷⁸ studied the effect of sonication conditions on the fracture toughness of MWCNTs/epoxy nanocomposites. The amplitude and duration of the sonication process played a key role in the dispersion of the MWCNTs in the epoxy resin. The toughness increased by 95% at 0.5 wt% MWCNTs at full amplitude (100%) sonication power for 1 h. Further sonication resulted in a reduction in fracture toughness of the nanocomposites. High-intensity ultrasonic liquid processing was also employed to homogeneously disperse MWCNTs in epoxy resin.⁷⁵ It was found that the enhancement in the fracture toughness reached a maximum of 40% increase at 0.3 wt% MWCNT. At higher contents, the fracture toughness decreased with filler loading.

In addition to dispersion methods, surface functionalization of CNTs through either physical or chemical methods is another effective approach to uniformly disperse CNTs and create an interaction between CNTs and matrix resins simultaneously. Gojny *et al.*^{24,79} studied the effect of surface functionalization of CNTs on the fracture toughness of nanocomposites. Amino-functionalization facilitated the dispersion as well as created interfacial bonding between the CNTs and the matrix resins. For example, the fracture toughness increased significantly by 43% with 0.5 wt% amino-functionalized DWCNTs, whereas the toughness increased by 31% with 0.5 wt% non-functionalized DWCNTs as compared to the neat epoxy resin. Ganguli *et al.*⁷⁷ compared the effect of dispersion technique and surface functionalization of MWCNTs on the fracture toughness of nanocomposites. At 0.1 wt% loading, both ball-milled and acid-treated MWCNT nanocomposites performed better than the neat resin. An increase of 39% in the fracture toughness was achieved at 0.15 wt% loading with ball-milled MWCNTs. In contrast, 80% of enhancement in the fracture toughness was achieved at 0.15 wt% acid-treated MWCNTs. Sun *et al.*⁸² reported that surface functionalization can effectively improve the dispersion and adhesion of SWCNTs in the epoxy resin, which led to the enhancement in the fracture toughness of the nanocomposites. An increase of 18% at 1 wt% of functionalized SWCNTs was achieved. In contrast, only a 3.6% increase in toughness was observed at 1 wt% for pristine SWCNTs. The authors also pointed out that the improvement was not as significant as expected due to the fact that surface functionalization agent caused curling of the SWCNTs. Keeping CNTs straight in the matrix resin is needed to fully realize the potential of SWCNTs in polymer resins. Lachman and Wagner⁸¹ studied the effect of the molecular nature of the interface between an epoxy matrix and MWCNTs on the fracture toughness of the resultant nanocomposites. Various functionalized MWCNTs, namely, pristine, carboxylated and aminated MWCNTs, were examined. The nanocomposites containing 0.34 wt% the pristine, carboxylated and aminated MWCNTs showed improvement in the fracture toughness by 19%, 43% and 51%, respectively. Among them, the aminated MWCNTs performed the best since highly functionalized NH_2 -CNTs were likely to promote better nanotube-matrix interfacial adhesion. Tang *et al.*⁸³ studied the fracture toughness of ozone functionalized MWCNTs/epoxy nanocomposites. It was reported that the toughness increased by 30% and 52% with the pristine MWCNTs and ozone functionalized MWCNTs, respectively, as compared to the neat epoxy resin. Yi *et al.*⁷² found that at 0.5 wt% of oxidized MWCNTs, the fracture toughness demonstrated a significant improvement of 24%.

Based on the results reported by various researchers, a large proportion of the enhancement in the fracture toughness was between 10 and 60% at low CNTs loading (0.1–0.5 wt%). Fig. 14 shows the ideal failure mechanisms of CNTs proposed by Gojny *et al.*²⁴ In the initial stage, a CNT is embedded in the matrix (Fig. 14(a)). When a crack front reaches the interface between the CNT and the matrix, debonding of the CNT occurs in the case of a weak interface (Fig. 14(b)). In contrast, strong interfacial bonding will lead to the rupture of the CNT (Fig. 14(c)) or the rupture of the outer wall and partial bridging by the inner wall of the CNT (Fig. 14(d)), and a partial debonding of CNT (Fig. 14(e)) allows a crack bridging. In-situ TEM was used to observe the crack nucleation and propagation in MWCNTs/polystyrene nanocomposites.⁸⁵ It can be seen that the pull-out of CNTs aligned parallel to the crack tend

Fig. 14 Schematic illustration of proposed failure mechanisms of carbon nanotubes (CNTs). (a) Initial state of the CNT; (b) debonding of the CNT; (c) rupture of the CNT; (d) fracture of the outer layer and pull-out of the inner layer of the CNT; and (e) bridging and partial debonding of the CNT. Gojny, F.H., Wichmann, M.H., Fiedler, B., Schulte, K., 2005. Influence of different carbon nanotubes on the mechanical properties of epoxy matrix composites – A comparative study. *Composites Science and Technology* 65, 2300–2313.

Fig. 15 Schematic illustration of proposed mechanisms of polymorphic transformation. Chen, X., Liang, Y.N., Yin, M., *et al.*, 2016. Exceptional enhancement of ductility and toughness in poly(vinylidene fluoride)/carbon nanotubes composites. *Journal of Applied Polymer Science* 133, 10.1002/app.43610.

to bridge the crack. Hsieh *et al.*⁸⁰ studied the contribution of different toughening mechanisms to the fracture toughness of MWCNTs/epoxy nanocomposites. The results indicated that the toughening effect was mainly contributed from the debonding and pull-out of the CNTs. Wagner *et al.*⁸⁶ discussed the pull-out mechanism and concluded that the length of CNTs plays a key role with respect to the toughening strategy from the theoretical aspect. CNTs with length below the critical length will pull-out from the matrix rather than rupture, whereas CNTs will rupture rather than pull-out if the length is above the critical length.

Recently, a facile methodology combining solution mixing and melt blending was employed by Chen *et al.*⁷⁶ to fabricate MWCNTs/poly(vinylidene fluoride) (PVDF) nanocomposites. Pristine CNTs were directly dispersed in the matrix without any surface modification. The toughness improved by 386% with only 0.2 wt% MWCNTs loading. The polymorphic transformation was found to be the main contributing factor to the toughness. Under stress, γ phase in MWCNT/PVDF nanocomposites around CNTs transformed into β phase (Fig. 15), creating plasticization and resulting in the enhanced toughness. Both the CNTs pull-out and polymorphic transformation contributed to the high fracture toughness. Wichmann *et al.*⁸⁷ studied the realization of the potential of the fracture toughness of nanoparticles, which is expected to show higher results compared to micro-size fibers, based on the conventional energy dissipation mechanism. They used the pull-out mechanism to discuss this assumption. Some experimental results indicated that composite materials with small amounts of finely dispersed nanoparticles of a high aspect ratio produced fracture toughness that was higher than the simple ROM prediction. Based on the classical equation of the pull-out contribution, they compared the pull-out energy dissipation by a single microfiber to that of a large number of parallel CNTs of an

equivalent volume fraction. Based on their model, the pull-out energy of the nanocomposite was 4–100 times higher than that of micro-carbon-fiber composites.

6.1.5.2 Layered Nanofiller Filled Polymer Nanocomposites

6.1.5.2.1 Graphene/polymer nanocomposites

Graphene as the thinnest material in the carbon family has an extremely high surface area, excellent mechanical properties and extraordinary electron mobility. Compared with CNTs, graphene performed better in the toughening effect owing to its intrinsic properties. The results acquired from the relevant works, which studied the fracture toughness of nanocomposites containing graphene, are presented in Fig. 16.^{25,63,74,88–98}

Rafiee *et al.*²⁵ compared GNPs with CNTs in terms of fracture toughness enhancement. The fracture toughness of the nanocomposite with 0.1 wt% GNPs showed 53% increase over epoxy resin compared to 20% improvement for 0.1 wt% MWCNTs. 65% increase of the toughness with only 0.125 wt% of functionalized graphene sheets (FGSs) was observed as well by the same group.⁹⁶ The superiority of GNPs was ascribed to the improved mechanical interlocking at the interface between GNPs and matrix as a result of the enhanced specific area of GNPs. Zaman *et al.*⁸⁹ prepared two types of GNP/epoxy nanocomposites using the combination of sonication and chemical modification to investigate the effect of interface on the structure and properties of the nanocomposites. The fracture toughness increased by 93% and 43% with functionalized GNPs (m-GNPs) and non-functionalized GNPs, respectively, at 4.0 wt%. A facile approach was also developed by Zaman *et al.*⁸⁸ for the mass production of chemically modified graphene. An increase of 124% in the fracture toughness with the addition of 0.49 vol% of m-GPs was achieved. The modification of GNPs resulted in the exfoliation of the graphene sheets and the bridging of GNPs with matrix molecules for high interface strength. Bortz *et al.*⁹⁵ studied the toughness enhancement of epoxy using GO. Improvement of 63% in the fracture toughness through the incorporation of 0.5 wt% of GO was achieved. The presence of the GO sheets induced the deflection of the cracks, increasing the required strain energy for the continuation of fracture. The size of the GNS had a pronounced effect on the fracture toughness of the nanocomposites. Chatterjee *et al.*⁶³ used two different dimensions of GNPs with flake sizes of 5 μm and 25 μm to investigate the influence of nanofiller size on the toughness. At 2 wt% GNPs loading, the fracture toughness increased up to 82% over the neat epoxy with 25 μm GNPs, whereas 60% of improvement was obtained with 5 μm GPs. The superiority of bigger size GNPs can be explained by their higher aspect ratio, which is beneficial to actively control the failure mechanisms in the nanocomposites. Chatterjee *et al.*⁹¹ also studied the influence of expanded GNPs (EGNPs) filled with epoxy. An increase of 66% in toughness was obtained at a loading with 0.1 wt% of amine functionalized EGNPs compared to the neat epoxy. Similar study was conducted by Chandrasekaran *et al.*⁹⁰ with GNPs dispersed in epoxy matrix. The fracture toughness slightly decreased by 1.7% at 0.1 wt% GNPs. Upon further increasing GNP content, an increase in toughness of 43% was obtained for 1.0 wt% GNPs. Chandrasekaran *et al.*⁷⁴ compared the toughening effect of thermally reduced graphene oxide (TRGO) with GNPs. For GNP/epoxy nanocomposites, the percentage of enhancement was 24% and reached 40% for the TRGO/epoxy nanocomposites. The partial functionalization and fewer numbers of layers stacked in TRGO resulted in better toughening effects than GNPs. Jiang *et al.*⁹³ studied the toughening effects of 3-aminopropyltriethoxysilane functionalized silica nanoparticles attached GO (ATGO) in epoxy. By adding small amounts of ATGO (0.1 wt%), 57% improvement in the fracture toughness was obtained. Li *et al.*⁹⁴ synthesized two kinds of modified GO with amino (APIS-GO) and epoxy groups (GPIS-GO). The enhancement in the fracture toughness was 20% and 43% for the nanocomposites containing APIS-GO and GPIS-GO, respectively. The better effectiveness in enhancing the toughness for GPIS-GO was ascribed to the better distribution of the filler and the formation of a larger amount of soft interphase. Tang *et al.*⁹⁸ investigated the effect of TRGO dispersion on the fracture toughness of the epoxy resin. The highly and poorly

Fig. 16 Percentage of enhancement in fracture toughness in polymer nanocomposites with addition of graphene.

dispersed TRGO at 2 wt% loading resulted in 52% and 24% enhancement in the toughness of the epoxy resin, respectively. Ahmadi-Moghadam and Taheri⁹² examined the fracture toughness of an epoxy resin reinforced with different concentrations of GNPs. GNPs effectively and efficiently enhanced the fracture toughness of the epoxy resin. The improvement reached to 90% at 3 wt% of GNP loading. Shokrieh *et al.*⁹⁷ studied the effects of GNPs and GNSs on the fracture toughness of epoxy resin. It was found that the fracture toughness increased by 39% and 16% using 0.5 wt% GNPs and GNSs, respectively. The greater impact of GNPs on the fracture toughness was owing to their higher SSA.

Fig. 17 shows the proposed failure mechanisms in graphene filled nanocomposites. In Fig. 17(a), the crack front can either get deflected or bifurcates and goes around the particle when it meets the surface of the graphene sheets. When the crack gets deflected, a height difference between the original crack and the deflected crack (Fig. 17(b)), as a result, the crack takes a tortuous path accounting for the rough fracture surfaces. In the case where the graphene sheets is perpendicular to the direction of crack propagation, the crack propagates in between the graphene sheets and finally passes through by separating the graphene layers when the crack meets the edges of the graphene sheets (Fig. 17(c)). The two dimensional (2D) layered structure of the graphene sheets promotes the ease of shearing between the graphene layers. A combination of crack propagation at different height level and separation between the graphene layers can also occur. A deflected crack goes around the graphene sheets where it meets the edges of the sheets. At this juncture, it is possible for the crack to pass through the sheets causing the formation of a "dimple type" fracture surface (Fig. 17(d)).

6.1.5.2.2 NC/polymer nanocomposites

Similar to graphene, NCs are 2D nanoparticles but of layered mineral silicates. They have been used for the enhancement in fracture toughness of polymers owing to their exfoliated arrangement in the polymers. The results acquired from the relevant works, which studied the fracture toughness of nanocomposites containing NCs, are presented in Fig. 18.^{44,99–104}

Early studies in the fracture toughness of the NC filled polymer nanocomposites were conducted by Zerda and Lesser.¹⁰⁵ The improvement in the fracture toughness of the nanocomposites indicated an effective toughening effect of NCs. Similar findings

Fig. 17 Schematic illustration of proposed failure mechanisms of graphene nanocomposites. (a) Crack bifurcation/pinning; (b) crack propagation at different heights; (c) crack propagation by separating the graphene layers; and (d) a combination of crack deflection and separation between the graphene layers. Chandrasekaran, S., Sato, N., Tölle, F., *et al.*, 2014. Fracture toughness and failure mechanism of graphene based epoxy composites. *Composites Science and Technology* 97, 90–99.

Fig. 18 Percentage of enhancement in fracture toughness in polymer nanocomposites with addition of nanoclays (NCs).

Fig. 19 Percentage of enhancement in fracture toughness in polymer nanocomposites with addition of nanosilica.

were present by Liu *et al.*¹⁰² An increase of 70% with 4 wt% NCs was observed. Qi *et al.*¹⁰³ investigated the effects of different NCs on the fracture toughness of the epoxy resin. Four types of NCs including pristine MMT- Na^+ , Cloisite 30B, Nanomer I.30E and MMT-cetylpyridinium chloride (CPC) were studied. For the nanocomposites with 5.0 wt% fillers, an increase of 52% for MMT- Na^+ /epoxy, 20% for Cloisite 30B/epoxy, 53% for Nanomer I.30E/epoxy and 65% for MMT-CPC/epoxy were observed, respectively. Wang *et al.*⁴⁴ studied the fracture toughness of the epoxy with highly exfoliated NCs. An increase of 80% in the fracture toughness with 2.5 wt% NCs was observed. They also studied the fracture toughness of epoxy with silane-modified clay (SMC) Wang *et al.*¹⁰⁴ The toughness increased by 56% and 77% for the nanocomposites containing 1 wt% and 2 wt% SMC, respectively, but decreased after further increasing the content of SMC. The fracture toughness of NC/epoxy nanocomposites was also reported by Zappalorto *et al.*¹⁰⁰ The maximum increase was 49% for the nanocomposites containing 1 wt% NCs. Guevara-Morales and Taylor¹⁰¹ investigated the fracture toughness of the nanocomposites containing two types of surface-treated NCs (Cloisite 30B and Nanomer I28E). An increase of 40% and 22% was observed for the nanocomposites containing 5 wt% Cloisite 30B and Nanomer I28E, respectively.

The toughening mechanisms acting in the NCs filled nanocomposites were identified as crack deflection and plastic deformation of the matrix around the NCs following the debonding of the NCs.¹⁰¹ Wouterson *et al.*⁹⁹ studied the hybrid reinforcement comprising of NCs and hollow microspheres in the fracture toughness of epoxy resin. It was found that the toughness increased by 64.3% for 30 vol% BJO microspheres only; whereas an increase of 93.6% was observed when 2 wt% of NCs was added. It is clear that hybrid reinforcement is more effective in increasing the fracture toughness of polymers.

6.1.5.3 Nanosilica Filled Polymer Nanocomposites

Compared with rubber toughened polymers, the use of inorganic rigid fillers provides toughening effects of polymer matrix without sacrificing the modulus. Among the different types of inorganic fillers, nanosilica has been a popular option. The results acquired from the relevant works, which studied the fracture toughness of nanocomposites containing nanosilica, are presented in Fig. 19.

Brunner *et al.*¹⁰⁶ studied the fracture toughness of the epoxy with nanosilica. The addition of 7.2 wt% nanosilica contributed to 53% of the improvement in the toughness. Similar study was also conducted by the other group from Imperial College London.^{107–110} The introduction of the nanosilica particles into the epoxy resin increased the toughness and the maximum enhancement reached to 72% for the nanocomposites containing 20.2 wt% nanosilica. Liu *et al.*¹¹¹ conducted a systematic study on the effect of nanosilica on the fracture toughness of the epoxy resin. It was found that the toughness increased gradually with increasing nanosilica loading. The toughness increased by 122% for the composites containing 20 wt% nanosilica compared with the neat epoxy resin. Dittanet and Pearson¹¹² studied the effect of nanosilica content and particle size on the fracture toughness of the nanocomposites. The fracture toughness showed significant improvements with the addition of nanosilica and increased with increasing the filler content. However, the effect of the particle size on the fracture toughness was negligible. The toughening mechanisms of nanocomposites containing nanosilica were studied by Liang and Pearson.¹¹³ Two types of nanosilica particles with different average particle sizes (20 and 80 nm in diameter) were evaluated as toughening agents for epoxy resin. Results demonstrated that the particles size in the range of 20–80 nm had a negligible effect on improving the fracture toughness. Interestingly, the nanosilica performing better than the micron size glass spheres in toughening effect was observed. Zamanian *et al.*¹¹⁴ carried out a similar study on the fracture toughness of nanosilica filled nanocomposites by changing the particle size. They found a 52% improvement for epoxy with 4 wt% 12 nm silica, whereas at the same content, the toughness increased by only 20% for an epoxy with 40 nm particles.

For all the polymers containing nanosilica, the toughening mechanisms include (1) localized shear bands initiated by the stress concentrations around the periphery of the nanosilica particles, and (2) debonding of the nanosilica particles followed by subsequent plastic void growth of the polymers.¹⁰⁷

Similar to NCs, the incorporation of the second filler to the nanosilica filled nanocomposites can optimize the fracture toughness. Hsieh *et al.*¹¹⁵ investigated the hybrid systems containing nanosilica and MWCNTs. Both the presence of nanosilica particles and MWCNTs led to a significant improvement in the fracture toughness of the composites. For example, the fracture toughness increased by 49% for the hybrid nanocomposite containing both 0.18 wt% MWCNTs and 6.0 wt% nanosilica particles. In contrast, only a 9% improvement was achieved for the MWCNTs-free system containing 6 wt% nanosilica particles. Chen *et al.*¹¹⁶ studied the fracture toughness of the nanocomposites with GO coated nanosilica. The incorporation of 10 wt% pristine nanosilica resulted in 15% decrease in the fracture toughness compared with the neat epoxy resin. In contrast, 89% of the enhancement was obtained for the nanocomposites loaded with 10 wt% GO coated nanosilica. The presence of the GO served as an unconventional coupling agent of the silica filler, which effectively enhanced the interfacial interaction between the nanosilica and the matrix, and thus greatly improved the toughness of the epoxy resin.

6.1.5.4 Summary

The enhancement in fracture toughness of polymers can be obtained by introducing of CNTs, graphene, NCs and nanosilica. The optimized toughness can be achieved by incorporation of proper size, type and amount of nanofillers, which in turn determine the energy dissipating interaction of the crack front with the nanoparticles. The homogenous dispersion of nanofillers in the polymer resin is essential to achieve the optimal mechanical performance of the nanocomposites. Two distinct methods, i.e., mechanical dispersion and surface functionalization are usually used for the dispersion of nanofillers. CNTs showed good toughening effects at low loading (0.1–1.0 wt%). Above 1 wt%, high viscosity of the systems hindered the dispersion of CNTs, causing the formation of the agglomerates. Compared with CNTs, the studies on graphene demonstrated a better toughening effect at very low loading (under 1 wt%). In the case of NCs and nanosilica, the toughening effect was inferior compared with CNTs and graphene and an enhancement in fracture toughness was only observed at much higher loading (1.0–20 wt%).

6.1.6 Concluding Remarks

Iijima's 1991 paper on carbon nanostructures¹¹⁷ generated unprecedented interest in the prospects of harnessing CNTs for ultra-high mechanical property composite materials. Obviously, micromechanical models had been implicit a priori in the expectation for such extremely high mechanical properties with even small concentrations of nanoreinforcement. However, as shown in this chapter, micromechanical models and mechanisms fail by and large to predict the mechanical properties of nanocomposites, with the exception of fracture toughness; the latter property is controlled by the specific type of energy dissipating interaction of the crack front with the nanoparticles. Indeed, a number of examples are presented above, wherein the fillers are supposedly well dispersed and not agglomerated and where for low filler contents an apparent linear behavior of the strength and modulus is observed. However, this cannot be accepted as a conclusive proof that the stress transfer mechanism in those nanocomposites is sufficiently effective. Moreover, in most of the examples the empirical values fall significantly below the predicted ones.

Of course, the problem in nanocomposites might be that there are too many unknowns: what are the inherent mechanical properties (the modulus and the strength) of the nanoparticles; are they aligned, 2D, 3D or random; are they fully dispersed; what is their actual aspect ratio? Regarding the matrix, how are the properties of the matrix – thermoplastic (semicrystalline or amorphous) or thermoset – altered by the addition of nanofillers? And, what is the nature of the particle-matrix interface? The real question that we face with already such a large number of studies in the literature is what if we did know and use the relevant input data for the micromechanics models – would it then be possible to make reliable micromechanics-based predictions of the properties of nanocomposites? Can the threefold scale difference between the nano and micro dimensions be reconciled.

We suggest that the question whether ROM and stress transfer models apply to nanocomposites relates to the structural difference between composites and nanocomposite materials. Whereas the first is characterized by a distinct interface between the matrix and the reinforcement, rendering it a heterogeneous material, the latter is a quasi-homogeneous molecular blend, similar to a solid solution. Thus, as stated already by Calvert,¹¹⁸ “we do not expect a molecular mixture with nanoparticles to act like a true composite.” Hence, for nanocomposites, different nanomechanisms ought to be considered, which relate to interactions between the reinforcement and the polymer matrix on a molecular scale. It is proposed that nanocomposites should be regarded as, and treated like, molecular composites or self-reinforced polymers. Then, for a uniformly dispersed, quasi-homogeneous molecular blend (such as a solid solution) ROM should apply in principle. However, the contribution of the matrix ought to be based on its modified property as induced by the nanoparticles (e.g., by nucleation or confinement). As for the classical stress transfer mechanism, its applicability will depend – in addition to the prerequisites listed above – on the residual aspect ratio of the nanoparticles.

See also: 6.2 Computational Multiscale Modeling – Nanoscale to Macroscale. 6.3 The Elusive Interphase/Interface in Polymer Nanocomposites

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

Nadya Stern^a, Itay Dyamant^b, Eldad Shemer^b, Xiao Hu^c and Gad Marom^a

^aThe Casali Center of Applied Chemistry and the Center for Nanoscience and Nanotechnology, The Institute of Chemistry, The Hebrew University of Jerusalem, Jerusalem, Israel; ^bOSG Armor R&D, Oran Safety Glass Ltd, Kibbutz Tzuba, Israel; ^cSchool of Materials Science and Engineering, Nanyang Technological University, Singapore, Singapore

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.

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Carbon nanotubes (CNT); fracture toughness; hybrid effect; mechanical properties; nanoclay (NC); nanocomposites; polymer-matrix composites (PMCs)

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

CONTACT Nadya Stern nadya.berman@mail.huji.ac.il

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potentially required to match and surpass properties of classical composites of high concentrations.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.^{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.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 mixtures behavior).^{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. In 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.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.^{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,^{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™ with density of 1.065 g/cm³ 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 nanocomposite⁹) 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 by²³

$$\gamma = \lambda \frac{f}{t} - \frac{W_\lambda A_0}{2t} \quad (1)$$

where γ is the fracture surface energy, λ is the extension ratio, f is the tearing force, t is the thickness of the specimen, W_λ 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 λ , 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 $\frac{W_\lambda A_0}{2t}$ is negligible compared to $\lambda \frac{f}{t}$. Hence, it is commonly assumed that – since $\lambda \approx 1$, the equation is reduced to^{23,24}:

$$\gamma = \frac{f}{t} \quad (2)$$

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

Figure 2. Typical sample of trouser-leg tear test divided into areas: 1 – unstrained area, 2 and 2' – areas with uniform strain, 3 – area without homogenous strain. After.²¹

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 $\tan \delta$, 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

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.

compared to the reference of neat PVB is for the PVB/NC-2% sample. Of the CNT-COOH parent composites and of the hybrids, PVB/CNT-COOH-0.2%/NC-2% showed the highest results compared to PVB alone (confirmed by one-tailed *t*-tests). These compositions were then selected and samples were prepared by 700 W sonication power.

The fracture energy results are presented in Figure 4, showing that the 700 W is significantly advantageous

Figure 4. A comparison of the fracture surface energy of selected PVB samples: neat PVB (gray), nanocomposites prepared by 100 W sonication (pink diagonal line), nanocomposites prepared by 700 W sonication (cyan squares). Samples prepared by 700 W exhibit higher values. Each column presents the average of at least 7 measurements.

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

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		1/3	2/3		
PVB/NC-1%	2/5	2/5			1/5
PVB/CNT-COOH-0.1%/NC-1%		1/4			3/4
PVB/CNT-COOH-0.1%		1/5	1/5	2/5	1/5

demonstration in Figure 5. Also indicated in the table is the number of results per damage class. Despite the qualitative nature of the results, it can be concluded that the hybrids exhibited notably higher impact resistance with the highest proportion of *full arrest*.

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.

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.

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

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.

Figure 6. STEM images of samples prepared by sonication power of 100 W: (a) PVB/NC-2%; (b) PVB/CNT-COOH-0.2%/NC-2%. Seen are both aggregates and single particles. (c) CNT-COOH aggregate in a PVB/CNT-COOH-0.2%/NC-2% film. The white spheres are holes formed in the microtomic process and should be regarded as artifacts.

Figure 7. STEM images of samples prepared by sonication power of 700 W: (a) PVB/CNT-COOH-0.2%; (b) PVB/CNT-COOH-0.2%/NC-2% (part of the CNT broke during the sonication process and lost their original length); (c) PVB/NC-2% (a relatively uniform particle distribution).

Figure 8. XRD results of: PVB/NC-1%, PVB/CNT-COOH-0.1%/NC-1% (sonication power of 700 W) and PVB/NC-2% and PVB/CNT-COOH-0.2%/NC-2% (sonication power of 100 W), compared to NC powder. A right shift of the peak is observed with no apparent intercalation.

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.

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 $\tan\delta$ 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.

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. **Figure 10.** $\tan\delta$ (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.

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

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

Figure 11. SEM images of fracture surfaces of PVB samples (700 W): (a) PVB/CNT-COOH-0.2%; (b) PVB/NC-2%; (c) PVB/CNT-COOH-0.2%/NC-2%. The hybrid film seems to present the highest roughness.

Table 3 RMS Roughness values of the tear surfaces of the 700 W parent and hybrid composites with reference to the neat PVB. Each value is an average of three measurements.

Film composition	R_q (nm)
PVB-reference	263.1 ± 50.7
PVB/CNT-COOH-0.2%	462.3 ± 105.5
PVB/CNT-COOH-0.1%/NC-1%	918.5 ± 30.0
PVB/ NC-2%	619.7 ± 67.2

Figure 12. The linear correlation between fracture surface energy and roughness of the reference and nanocomposite samples.

fracture energy is the energy dissipated in creating new surfaces; hence, the larger the new surface the higher the dissipated energy.

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.

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Article

The Effects of Geometry and Chemical Composition of Nanoparticles on The Fracture Toughness of iPP Nanocomposites

Nadya Stern ^{1,2,*}, Xiao Hu ² and Gad Marom ¹

¹ The Institute of Chemistry, The Casali Center of Applied Chemistry and the Center for Nanoscience and Nanotechnology, The Hebrew University of Jerusalem, Jerusalem 9190401, Israel; gad.marom@mail.huji.ac.il

² School of Materials Science & Engineering, Nanyang Technological University, Singapore 639798, Singapore; ASXHU@ntu.edu.sg

* Correspondence: nadya.berman@mail.huji.ac.il

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Abstract: This research deals with possible hybrid effects in the fracture energy of hybrid nanocomposites while taking a critical approach toward the currently-prevailing engineering practice of applying classical composite micromechanics to nanocomposites. For this purpose, different nanoparticles were embedded in an isotactic polypropylene matrix. The particles had different geometries (fibrous and platelets) and different chemical structures (organic vapor grown carbon nanofibers (VGCF); graphene nanoplatelets (GNP); and inorganic nanoclays, SiO₂ nanofibers, and ZrO₂ nanofibers). Almost all the composite systems presented improvements in the fracture energy, whereas the iPP/VGCF/GNP presented a positive hybrid effect. The main conclusion was that each nanocomposite system should be analyzed individually according to the constituent properties; the quality of the dispersion; and, primarily, by the type of interaction between the particles and the matrix.

Keywords: nanocomposites; hybrid; toughness; polymers

1. Introduction

It is well-known that nanofillers may increase the properties of the matrix in composite materials. The combination of two different fillers in one matrix generates a hybrid composite material that may present enhanced properties due to the combination of the fillers. Wtaife et al. produced a fiber-reinforced concrete (FRC) hybrid with polyvinylalcohol (PVA) and polyolefin fibers and showed that the hybrid composite improved the tensile strength of the concrete and changed it from a brittle to a ductile material while reducing its compressive properties [1]. Chen et al. prepared a flame-retardant polypropylene (PP) films with graphene nanoplatelets (GNP) alone and with magnesium hydroxide (MH). This combination resulted in enhanced thermal stability, reduced burning rate, improved tensile performance, and improved Young's modulus [2].

Shajariet et al. studied a system of polypropylene with carbon nanotubes (CNT) and stainless-steel fibers (SSF) at different filler loads. For a specific total load (1.75 vol% of each filler), the hybrid system that contained both types of fillers had the highest yield strain and highest electromagnetic interference (EMI) [3]. Li et al. investigated a system of poly(vinyl alcohol) enclosed in multiwalled CNT and fully exfoliated graphene oxide (GO) sheets and tested different filler compositions. They found that the system that contained 1 wt% of GO and 0.5 wt% of CNT could receive a hybrid and even a synergistic effect on the yield strength and Young's modulus (increased by 48% and 31%,

respectively). Such increases are higher than the sum of the improvement of each of the parent composites alone [4]. Zakuwan et al. examined a system of k-carrageenan with hybridization of cellulose nanocrystals (CNCs) and organically modified montmorillonite (OMMT). The total filler composition was 4%, with a ratio of 1:1 among the fillers. This led to the highest tensile strength and Young's modulus [5].

Another property that can present a hybrid effect is toughness, as was demonstrated in our previous work; here, the PVB (polyvinyl butyral) that contained both surface-treated CNT and nanoclay introduced an improvement of 181% versus neat PVB [6]. El Miri et al. produced a system of PVA with cellulose nanocrystals (CNC) and graphene oxide nanosheets (GON). The sample that contained 5% filler in the ratio of 1:2 CNC:GON presented an improvement of 159% in toughness, 124% in tensile test, and 320% in Young's modulus [7]. Valentini et al. studied ethylene-propylene-diene terpolymer rubber (EPDM) with carbon black (CB) and graphite nanoplatelets (GNPs). The presence of both fillers enhanced the Young's modulus, maximum strength, damping, and thermal conductivity [8]. Saharudin et al. analyzed a composition of halloysite nanotubes (HNTs) and CNT embedded in epoxy. The hybrid set demonstrated the highest percentage of improvement: 45% for tensile strength, 49% for Young's modulus, 46% for flexural strength, 17% for flexural modulus, and 125% for fracture toughness [9].

Despite these significant improvements achieved by nanofillers, we found that the nanocomposite systems failed to reach their theoretical values of mechanical properties as predicted by the models of micromechanics. This finding reflects mainly the tensile strength and Young's modulus, where nanosystems suffer from aggregation, which impairs load transfer. This state may be different for the fracture toughness, which increases through mechanisms other than load transfer, e.g., crack front bowing and pull out [10,11]. Based on these findings, we examined the effect of geometry and chemical structure of the nanofillers on the fracture energy, and possible hybrid effects of hybrid systems comprised of isotactic polypropylene with different nanofillers. We divided the fillers into two groups: The first group comprised particles of similar chemical structures and different geometries, i.e., vapor-grown carbon nanofibers (VGCF) and graphene nanoplatelets (GNP), or nanoclays (NC) and silicone dioxide nanofibers (SiO_2). The second group comprised particles of similar geometry and different chemical structure, i.e., NC and GNP, or VGCF and zirconium dioxide nanofibers (ZrO_2). The fracture energy was calculated by a unique method while taking a critical approach regarding the ability of the micromechanics to predict the properties of nanocomposite systems.

2. Materials and Methods

2.1. Materials

The iPP ($M_w = 5135\,000\text{ mol g}^{-1}$, Capilen U77A) was supplied by Carmel Olefins, Haifa, Israel) and used as the matrix. The VGCF samples (graphitized up to $2800\text{ }^\circ\text{C}$, average diameter 150 nm , length $10\text{--}20\text{ mm}$, density 2.0 g/cm^3) were provided by Showa Denko KK, Tokyo, Japan. The GNP (size of less than $2\text{ }\mu\text{m}$, few nm thickness, surface area of $750\text{ m}^2/\text{g}$, bulk density of $0.2\text{--}0.4\text{ g/cm}^3$) were supplied by Sigma Aldrich. The NC (Nanomer-1.30E, montmorillonite clay surface modified with 25–30% octa-decylamine, bulk density of 0.41 g/cc , thickness of 8 nm , particle size below $20\text{ }\mu\text{m}$) were produced from Nanocor Inc. (Arlington Heights, IL, USA) and provided by Sigma Aldrich (St. Louis, MO, USA). The SiO_2 nanofibers (amorphous, diameter of $414 \pm 96\text{ nm}$, surface area of $710 \pm 50\text{ m}^2/\text{g}$) and ZrO_2 nanofibers (diameter of $173 \pm 47\text{ nm}$, surface area of $10 \pm 3\text{ m}^2/\text{g}$) were supplied by Kertack Nanotechnology (Vodickova, Czech Republic). An antioxidant Irganox B-225 was provided by Ciba (Basel, Switzerland).

2.2. Sample Preparation

All nanocomposite samples were prepared by the same method. First, two films of weighed iPP were prepared by hot pressing and then a weighed quantity of filler was sandwiched between them, hot pressed again, and cut to flakes by scissors. The flakes were then extruded by twin screw

microcompounder (DSM Xplore, 15 cc Micro Extruder; Geleen, The Netherlands), along with an addition of 0.1 wt% Irganox B-225 antioxidant to receive composite fibers of iPP with dispersed fillers. The melt blending process was carried out at 195 °C (under N₂ gas, for 15 min, at 100 rpm). The resulting fibers were cut to flakes by scissors and then hot pressed at 200 °C (for 10 min, under the pressure of 0.87 MPa) to receive the final composite film, with a thickness of 0.2 mm.

2.3. Characterization

2.3.1. Mechanical Properties

The fracture surface energies were tested by Mode I tensile test using Instron 3345 universal testing machine with a load cell of 500 N. The specimens were 50 mm long and 30 mm, wide with an initial cut of different lengths. Loading the specimens is demonstrated in Figure 1. The specimens were pulled apart at a constant speed of 0.5 mm/min at room temperature.

Figure 1. The geometry of the Mode I test specimen [12].

2.3.2. Electron Microscopy

The quality of dispersion was analyzed by XHRSEM (extra high-resolution scanning microscopy) MagellanTM 400L. The operating voltage and current were 2–5 kV and 50 pA, respectively. The samples were tested after the tensile test using a designated cross-section stub. The samples were coated with a mixture of Au-Pd for 60 s using a SC7640 Sputter.

2.3.3. Dynamic Mechanical Properties

The dynamic mechanical properties were characterized with a dynamic mechanical analyzer (DMA) Q800 V21.3 Build 96 instrument. The test was performed under tensile mode at 1 Hz and −40 °C to 60 °C with heating rate of 5 °C/min.

3. Results

3.1. Mechanical Properties

3.1.1. Fracture Surface Energy of Initiation (γ_I)

The value of γ_I may be calculated by different methods [13]. After some trial and error, the energy of initiation, γ_I , was calculated from the following equation:

$$\gamma_I = \frac{U_I}{2 \cdot b \cdot c}$$

where U_I is the area under the graph up to the point where the tear starts to propagate (Figure 2a), b is the thickness of the sample, and c is the length of the cut. A graph of γ_I versus the cut length shows an exponential trend—this asymptotically converges at higher cut lengths (Figure 2b). The

final value is defined as the average value of the energies for cut lengths of 15 mm, 20 mm, and 25 mm (cut length that experiences minimum plastic deformation).

Figure 2. (a) Typical load displacement curve denoting the area of U_I and (b) a plot of the fracture surface energy of initiation vs. the cut length, marking the regime where the average value was calculated.

Figure 3 indicates that there are no significant differences between the fracture energies of initiation (γ_I) among the different samples. The iPP/0.5%-SiO₂ has the highest value, while its hybrid composition presents the lowest along with NC. The initial energy is the summed energy up to the point where propagation starts.

Figure 3. Fracture surface energies of initiation (γ_I) for all the nanocomposites. Each value is an average of at least seven measurements, showing the average standard deviations.

3.1.2. Total Energy Dissipated in The Fracture Process (γ_F)

The value of γ_F was calculated using the following equation:

$$\gamma_F = \frac{U_F}{2 \cdot b \cdot (d - c)}$$

where U_F is the area under the graph up to the point of total tear (Figure 4a) and d is the width of the sample. A curve with a linear fit was generated from the graph of γ_F versus the cut length (Figure 4b). The fracture energy at 25 mm (where the fracture is mainly controlled with fewer catastrophic fractures) was calculated from the linear fitting equation and defined to be the final γ_F value. Here, the term “fracture energy” is equivalent to the term “total fracture energy (γ_F)”.

Figure 4. (a) Typical load displacement denoting the area of U_F for the complete fracture and (b) a plot of the total fracture surface energy vs. the cut length, presenting the linear regression fit from which γ_F was calculated (for iPP-reference).

Unlike the fracture energy of initiation, the fracture energy (γ_F) has significant differences between the various samples (Figure 5). Here, all composites are improved versus the neat iPP. The hybrid sample of iPP/0.5%-GNP/0.5%-VGCG demonstrates the highest value among all the different samples and therefore expresses a positive hybrid effect. We assume that the variation in the total energy among the different samples results mainly from the required energy for crack propagation, because most of the samples have very similar initial fracture energy. This is an unambiguous indication that the fracture propagation of the hybrid nanocomposite is significantly slowed down. This property is highly important for the fracture resistance of composites, where structures that already contain an initial damage will exhibit controlled crack propagation.

Figure 5. Total fracture surface energies (γ_F) for all the nanocomposites. Each value is an average of at least seven measurements, showing the standard deviations.

3.2. Morphological Analysis

Cross-section SEM images (Figure 6) of the surface fracture show a surface suitable for fracture mechanism. All surfaces are rough and similar. The qualitative roughness of the composite samples is higher than the roughness of the neat iPP sample. This also has a lower fracture energy. Although only two samples are presented, all samples give similar observations. However, no quantitative measurements were done because this hypothesis has already been discussed in a previous paper [6].

Figure 6. SEM images of cross sections of the fracture surfaces, demonstrating significant levels of roughness.

SEM images of cross section were captured after a Mode I tensile test of the samples. A closer look at the neat iPP indicates a stalactite-like shape representing plastic deformation in the tensile direction (Figure 7a). At higher magnifications, a formation of fibrous-like microstructure is seen. These microfibrils bridge matrix cracks by the crazing mechanism (Figure 7b), which can reduce the stress at the crack tip by a factor of seven [14].

Figure 7. SEM images of iPP cross-sections after Mode I tensile testing at different magnifications. (a) Plastic deformation of stretched polymer at 10,000× magnification and (b) crazing of the polymer at 50,000× magnification. The dashed red circles show areas of crack bridging by microfibrils.

Figure 8 introduces the cross section of selected nanocomposites with superior properties. The system of iPP/0.5%-GNP that achieved the highest fracture energy among the parent composites demonstrates poor dispersion and large aggregates. However, there is substantial interaction between the polymer and the GNP. In contrast to the GNP, the VGCF are uniformly dispersed in the matrix, and single fibers are observed throughout the sample. The hybrid system also presents well dispersed VGCF alongside poorly dispersed GNP. The SEM images indicate that the GNP are found near the VGCF in the matrix, but the two fillers do not interact directly with each other. The last nanocomposite is iPP/0.5%-SiO₂, which also has increased fracture energy. The SEM image of this

nanocomposite demonstrates good interactions between the fibers and the matrix—there are smaller aggregates here than are seen in GNP (bundles of a few fibers). The iPP/0.5%-SiO₂ material also has pulled out SiO₂ fibers. Hence, we see that the two main mechanisms that contribute to the increased fracture energy may exist simultaneously, regardless of the level of dispersion.

Figure 8. SEM images of nanocomposite cross-sections after mode I tensile. From left to right: iPP/0.5%-GNP, iPP/0.5%-GNP/0.5%-VGCF, iPP/0.5%-VGCF, and iPP/0.5%-SiO₂.

3.3. Dynamic Mechanical Properties

DMA results of $\tan\delta$ for the chosen set (Figure 9) indicates the different behavior of the hybrid sample. The presence of GNP had no real influence on the $\tan\delta$, while VGCF decrease its value versus the neat iPP. Such a reduction may result from the restriction of polymer chain mobility by attraction with the nanofiller as described [15]. Unlike the VGCF, the GNP form aggregates, and therefore, have less common surface with polymer chains, and they do not limit the motion to the same extent [16–18]. Nevertheless, the contrasting responses of the two fillers lead to the highest ability to absorb energy, expressed in increased damping.

Figure 9. Dynamic mechanical analysis energy dissipation results of one hybrid nanocomposite system.

4. Discussion

The nature of the fracture process (either controlled or catastrophic) depends on the length of the cut. Samples with lower cut length will experience more controlled fracture, while samples with higher cut length will experience more catastrophic structure. In controlled fracture propagation, all

of the invested elastic energy from the tensile is converted to create a new surface during the crack propagation via breaking of the structural bonds. In a catastrophic fracture, the elastic invested energy is much higher than the required energy for surface formation—this excess energy is dissipated as heat, kinetic energy, plastic deformation, etc. A good example of catastrophic failure is glass breakage, in which some of the energy is dissipated via the sound of the breaking glass and not in the creation of a new surface. During crack propagation, a strain energy (proportional to c^2 , when c is the crack length) from unloaded regions near the crack tip is released. At the same time, energy for bond breakage (proportional to c) is invested. The applied stress increases up to the onset of crack propagation; thereafter, the crack propagates at a constant strain energy release rate at controlled process [19]. The nature of the complete fracture process depends on the initial cut (crack) length changing from catastrophic to controlled for shallower cuts. Theoretically, a complete conversion to fracture surface energy of the strain energy dissipated in the fracture process will occur for a cut length equal to the width of the sample.

The results indicated that there were no significant differences for γ_I between the samples, and only one sample (iPP/0.5%-SiO₂) exhibited a significantly higher value. This may be attributed to the relatively high fracture surface area of the SiO₂ nanofibers, which allows the iPP to intercalate in between the nanofibers, leading to better interactions between the filler and the polymer. The fracture energy of initiation is a function of the stored energy up to fracture onset, which in turn depends on the quasistatic mechanical properties (modulus and strength) of the composites. Conversely, for γ_F , all the composite samples reached an enhanced fracture energy, in comparison to the neat iPP, wherein different energies were measured, reflecting their different compositions, geometries, and structures. Considering that all the samples were treated identically, the results and the quality of dispersions were a product of the type of nanoparticle and its interface with iPP. As pointed out in the previous section, SEM analysis (Figure 7) revealed that fibrous nanofillers (VGCF, SiO₂, and ZrO₂) dispersed better than platelet fillers (GNP, NC). Nevertheless, it seems that the major factor for high fracture energy is the nature of the interactions between the advancing crack-front and the nanoparticles. The iPP/0.5%-GNP nanocomposite, which presented the best nanoparticle (GNP)-iPP affinity, exhibited the highest value of fracture energy regardless of the poor GNP dispersion quality, showing mainly large aggregates. Moreover, the nanohybrid of iPP/0.5%-GNP/0.5%-VGCF reached the highest value relative to all the nanocomposites and thus exhibited a positive hybrid effect. These results stem from the behavior of the respective parent nanocomposites as follows. The iPP/0.5%-VGCF nanocomposite in itself exhibited higher values than the neat iPP, showing the best dispersion of fully exfoliated single nanofibers with no aggregates. These well dispersed individual nanofibers of high aspect ratio could increase the energy by the classical debonding/fiber breakage/pull-out mechanism of fiber reinforced composites [10,20]. Conversely, the iPP/0.5%-GNP nanocomposite contained GNP aggregates of micro dimension, which contributed to the improvement of the fracture energy by the classical mechanism of crack-front pinning at adjacent particles and bowing away from them to increase the crack front surface area [21].

It is noted that the overall content of nanoparticles in the hybrids was twice of those in the parent composites. Yet, we suggest that the significantly high fracture toughness of the nanohybrid in this system may reflect a hybrid effect, wherein the energy dissipation that derives from the simultaneous occurrence of both the crack-front bowing and pull-out mechanisms is higher than the arithmetic sum of the weighted average contributions of the GNP and VGCF alone. This was corroborated by the DMA results showing that the nanohybrid exhibited the highest energy damping capacity by far, which was in agreement with the γ_F value of this system.

Another system that presented a large fracture energy improvement was the iPP/0.5%-SiO₂ nanocomposite, which likewise exhibited a good affinity to the iPP matrix. Both the GNP and the SiO₂ nanofibers have high surface areas, which may increase the adhesion with the iPP matrix, and, as a result, activate the mechanism of fracture energy dissipation more effectively.

In summary, the addition of nanoparticles raised the fracture toughness of the iPP matrix in all of the composite systems, regardless of the type of nanoparticle; the quality of the dispersion seemed to play a lesser role in improving toughness. Accordingly, nanoparticles of fibrous geometry

presented more uniform dispersions of exfoliated particles than those of the platelet geometries, which generated higher fracture toughness values. Conversely, aggregated GNP nanoparticles produced higher fracture resistance than the individually dispersed VGCF. Apparently, the enhancement of fracture toughness by the nanoparticles is a product of the specific interactions that they generate with the advancing crack front. These interactions, such as fiber pull-out and crack-front pinning and bowing, which leave their marks on the fracture surfaces, depend for each particle on its chemical nature and affinity to the matrix, its physical properties and its geometry.

5. Conclusions

The hybrid effect in nanocomposite hybrid systems in an iPP matrix was studied for different types of fillers and divided by their geometries and chemical structures. A system that contained both GNP and VGCF had a positive hybrid effect both in the total energy of fracture and in the dynamic energy damping of the system. Of the parent composites, the GNP sample exhibited the highest fracture toughness, probably due to the good interaction of the GNP with the polymer. Overall, the fracture energy depends on a set of parameters with an emphasis on the matrix–filler interactions. These interfere with the crack front propagation. Hence, no general rules can be formulated for nanocomposites/hybrids; rather, each system should be examined individually to identify its typical structure and composition-dependent crack front interaction mechanisms.

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CHAPTER FOUR – *Thermochromic Ionogel Polyurethane Nanocomposites: Swelling by Ionic Liquid, Energy Damping and Mechanical Properties*

Nadya Stern ^{1,2}, Gad Marom ¹ and Xiao Hu ²

¹ The Institute of Chemistry, The Casali Center of Applied Chemistry and the Center for Nanoscience and Nanotechnology, The Hebrew University of Jerusalem, Jerusalem 9190401, Israel; gad.marom@mail.huji.ac.il

² School of Materials Science & Engineering, Nanyang Technological University, Singapore 639798, Singapore; ASXHU@ntu.edu.sg

Abstract

Nanocomposites of a thermochromic ionogel - already demonstrated in glass panels to lower indoor temperatures - was prepared and characterized for its mechanical properties, including the influence of the addition of SiO₂ nanofibers and graphene nanoplatelets. The preparation was based on swelling of a thermoset polyurethane by an ionic liquid (IL), wherein the polymer network absorbed a mass more than 7 times its original weight. The swelling showed an interesting effect on the damping of the system, presenting reduced damping after swelling, followed by an increase after more than 50 wt% IL. Other mechanical properties were reduced by the swelling. Nanofillers did not increase the mechanical properties of the system due to the reduction of its crosslinking level and presented a hybrid effect of the lowest damping as was tested by dynamical mechanical analysis (DMA). The glass transition temperature of the polyurethane was also reduced by the nanofillers while the hybrid system exhibited the lowest glass transition temperature.

1. Introduction

Ionic liquids (IL) are receiving scientific attention due to their unique material properties such as non-volatility, recyclability, and non-flammability. These properties are possible because IL are salts that are liquid below 100 °C. ILs are applicable to many different fields and have been reported previously with regard to polymer electrolytes, biological systems, lubrication, battery technology, and chemical reactions [1,2]. Polyurethanes (PU) are a class of polymers that contain urethane groups and frequently prepared by the reaction of a hydroxyl group from diols or polyols with an isocyanate. PU may be produced from a wide range of source materials with different precursor architecture, and hence may be thermosets or thermoplastics with the concomitant implications on the material properties [3,4]. Due to the wide versatility of the properties of PU, it is used in a wide range of applications. One familiar application is armored glass, where the PU functions as one of the glass layers and contributes to the ballistic resistance [5,6].

Recently, an interesting material was presented by Lee et al. [7], based on a combination of PU and IL. They synthesized and examined different systems of PU with various types of ionic liquids, to achieve the desired thermochromic property, whereby the ionogel is transparent below the lower critical solution temperature (LCST) and opaque above it. The variation of the ILs resulted in ionogels with a range of LCSTs. They demonstrated that this ionogel applied in glass window panels was able to lower indoor temperatures and place it as an attractive candidate for glass applications. Their final systems contained 30-70 wt% of IL, which was found to be the optimum practical range. Here, we focus on one type of IL, and present a neat-PU that swells in an IL and reaches a weight 7 times higher than the neat-PU. This tunability, along with the existing varieties of IL, allows us to first synthesize the PU alone, and then immerse it in the desired IL to reach the preferred optical and mechanical properties of the ionogel

The swelling by IL is especially interesting since it is a non-volatile liquid, and therefore its mass does not change during the measurement, as seen in a published report on swelling of wood [8]. When the liquid was non-volatile, it swelled in two different regions –the cell walls and the cell cavities, while only the liquid in the cell walls participates in the swelling. Number of studies were done to investigate the swelling properties of a binary mixture of water/IL [9,10] or IL alone [11]. Here, we describe a system of a high level of IL swelling which to the best of our knowledge has not been presented in the literature yet. This result does not impinge on the thermochromicity for such an ionogel, which is its main application.

Due to the potential of such ionogels in armored glass panels it is necessary to investigate its mechanical properties. In addition to the classical structural properties such as tensile stress and Young's modulus, we have also tested the fracture surface energy, which is known as an indicator for impact resistance [12]. Another critical property is damping, which is the ability of the material to dissipate energy and identified by finding $\tan\delta$. The damping is measured by dynamic mechanical analysis, and it quantifies the response of the material to a periodic stress, such as a sinusoidal input function, exploiting the fact that the strain and stress are out of phase [13]. The measurement of $\tan\delta$ as a function of frequency may be useful for mechanical applications that should function under a range of frequencies [14], such as impulse response, as may occur, for example in a car accident. Therefore, here we have tested the mechanical properties of our system by different techniques, followed by more standard characterization techniques, such as morphological and thermal analyses.

Another aspect evaluated was the influence of nanofillers on the PU system. For this purpose, we chose two types of fillers – SiO₂ nanofibers and graphene nanoplatelets (GNPs). Those fillers have

different geometries and different chemical structures. We have also tested the possibility of the existence of a hybrid effect in a sample that contained both types of fillers for different properties.

2. Experimental Section

2.1. Materials

The components for the PU synthesis were polypropylene oxide (PPO) with $M_n = 4000$ Da (Sigma-Aldrich) and hexamethylene diisocyanate trimer (Tolonate HDT-90), supplied by Vencorex Chemicals. The synthesis solvent was methyl ethyl ketone (MEK, HPLC grade), supplied by Tedia. The synthesis catalyst was dibutyltin dilaurate (95%), supplied by Sigma-Aldrich. The IL for swelling was 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[C_4mim][NTf_2]$), supplied by Sigma-Aldrich. The SiO_2 nanofibers (amorphous, 414 ± 96 nm diameter and 710 ± 50 m²/g surface area) were provided by Kertack Nanotechnology (Vodickova, Czech Republic) and the GNP (surface area of 750 m²/g, thickness of few nm, bulk density of 0.2–0.4 g/cm³ and less than 2 μ m size) were supplied by Sigma-Aldrich.

2.2. Sample Preparation

The PU was synthesized following the method presented by Lee et al [1]. All components were kept dry before the synthesis (PPO and IL were freeze dried) and MEK were kept in molecular sieves. 5.3 mg of nanofillers were added to 9.4 g of PPO (SiO_2 nanofibers were crushed by mortar and pestle) and then mixed in a vortex shaker. The mixture was sonicated for 10 minutes (80% amplitude, 5 seconds pulse, 5 seconds off) by an ultrasonic processor VCX 130, Sonics. 4 gr of MEK were added, followed by vortex shaker mixing and 15 minutes sonication. Another 4 gr of MEK were added, followed by vortex shaker mixing and 45 minutes sonication. 1.2 g of HDT and 0.33-0.34 g of dibutyltin dilaurate (10 wt% in MEK) were added to the solution, mixed for 5 minutes at 300 rpm using a stirrer and sonicated for 5 more minutes. The sonication was carried out in an ice bath. The final mixture was solvent cast in a Teflon mold, covered with glass and cured in the oven at 50 °C for 24 hours, followed by placement in a vacuum oven at 50 °C overnight. The neat PU was prepared by mixing all polymer components followed by mixing for 5 minutes at 300 rpm using a stirrer and sonicated in a bath sonicator for 30 minutes (Elma ultrasonic cleaner).

2.3. Swelling of PU

Neat-PU uniform sized samples (20×20 mm² area, 1 mm thickness) were immersed in an IL solution at three different temperatures. The mass of the neat-PU was measured by analytical scale before the uptake and during the swelling process. The swelling proceeded until the samples were not stable anymore and started to crumble. The uptake was calculated by the following equation:

$$(1) \quad uptake (\%) = \frac{(W_s - W_d)}{W_d} \times 100$$

Where W_s is the weight of the neat-PU sample in the swollen state and W_d is the weight in the dry state.

2.4. Sample characterizations

2.4.1. Dynamic Mechanical Analysis (DMA) for damping

The samples had cylindrical geometry with a 10 mm diameter and tested by a compression test in multi-frequency mode 10% strain, using a TA Instrument Discovery HR 30 rheometer. The frequency range was 0.1-100 Hz. Except for the temperature test, the measurements were performed at room temperature.

2.4.2. Damping (by rheometer)

The samples had cylindrical geometry with 25 mm diameter and tested in frequency sweep mode, using TA instrument DMA Q800. First, a run at the frequency range of 0.1-100 Hz was performed, and then the test was focused at 40-80 Hz with higher resolution. Except for the temperature test, the measurements were performed at room temperature.

2.4.3. Mechanical properties (by Instron)

The PU specimens were loaded in tensile test mode utilizing an Instron 4502 universal testing machine and a load cell of 10N. All samples had a thickness of about 1 mm. For the tensile test, a rectangular specimen with 30 mm length and 5 mm width was used. The tensile test was performed at a constant crosshead speed of 10 mm/min. For the trouser tear test, a trouser shape specimen with 50 mm length, 20 mm width and initial cut of 30 mm was used. The test was performed at a constant crosshead speed of 50 mm/min. All tests were completed at room temperature.

2.4.4. Morphological characterization (SEM and STEM)

The quality of dispersion was observed by scanning electron microscopy (SEM) and scanning transmission electron microscopy (STEM), utilizing an extra high-resolution scanning microscopy (XHRSEM), MagellanTM 400L. The operating voltage and current for SEM analysis were 18 kV and 50 pA. The samples were coated by a mixture of Au-Pd for 60 s, using a SC7640 Sputter. The operating voltage and current for STEM mode were 5-10 kV and 50 pA. The samples were inserted into epoxy resin and kept in the oven for few hours, then sliced using a diamond and placed on a dedicated grid.

2.4.5. Degree of crosslinking

The degree of crosslinking (by weight) was tested using chloroform. First, the mass of different samples without IL was measured by analytical scales, then immersed in chloroform for two days, re-dried by vacuum oven and then their weight was measured again by the same analytical scale.

2.4.6. Differential Scanning Calorimetry (DSC)

Thermal analysis was performed under nitrogen in a temperature range of -100-25 °C, by heating rate of 10 °C/min, by Mettler DSC 822e.

3. Results

3.1. Swelling of PU in IL

Figure 1a presents the uptake graphs of the neat-PU swollen by IL. It is evident that the faster and stronger swelling occurs at room temperature. An extra graph of swelling vs. the square-root of time (Figure 1b) was added to reveal the type of diffusion. The graph shows that there is no linear behavior as a function of the square-root of time, and the behavior appears to be consistent with that described in the literature as non-Fickian (anomalous) diffusion, and specifically sigmoidal diffusion, characterized by non-linear behavior at the beginning of the curve, follow by an inflection point, and a decrease in the absorption rate at long times, as can be seen here, in Figure 1b. From these results, which describe the course of swelling, the appropriate diffusion time for a specific application can be worked out.

Figure 1: The uptake of the IL in neat-PU for different temperatures as a function of time, expressed by (a) min and (b) sec^{1/2}. At room temperature the PU exhibited the most significant swelling. Each measurement is an average of 3 samples.

3.2. Damping by DMA and rheometer

Energy dissipation or damping is an important property for applications such as safety glasses. The damping value may be identified by DMA or rheometer systems. Here, the damping properties of the different samples were tested for variant uptakes of IL by a DMA measurement of $\tan\delta$ as a function of different frequencies. The damping property is described by the ratio between the loss modulus (the viscous modulus, indicating the ability of the material to dissipate its energy as heat) and storage modulus (the elastic modulus, indicating the ability of the material to store energy), and basically is the angle that indicate the time interval between the applied force and the reaction. In a simpler way, the damping is the ratio between the viscous and the elastic response of a viscoelastic material such as certain polymers, while a higher damping value characterizes a more dissipative material and lower damping indicates more elastic material that will store the energy and then release it during load removal. The DMA determined the damping by a compression test using E' and E'' as storage and loss modulus, respectively.

Fig. 2 presents the DMA damping results of $\tan\delta$ as a function of frequency. Four peaks are observed as marked. Whereas the processes marked by the respective peaks have not been identified, a comparison of the different systems is still meaningful for each peak as shown by the bar diagram. These four peaks are related to the properties of the PU itself, since it exists for samples that contained only PU, without an addition of IL or nanofillers. Different reasons may cause the multi-peak of $\tan\delta$ as a function of frequency, such as different interfaces or different segments of the PU chain. The exact identification of those peaks requires another profound study

and may be interesting as a topic for a new study. Here, where the total damping is considered, the specific processes represented by the peaks could have been disregarded. For the neat PU, the DMA results showed that the damping decreases with increasing uptake, meaning it reacts in a more elastic way (Figure 2). The graphs maintained their shape after the addition of the IL.

Figure 2: The damping by DMA of neat-PU film with different uptakes of IL. The left figure presents the complete curve while the right figure presents a comparison between the different samples.

A similar observation to the neat PU presented in Figure 3 was found for PU/0.5%-SiO₂. We see that higher uptake led to lower damping. The graph's shape with the four peaks is maintained after the addition of nanofillers to the polymeric matrix.

Figure 3: The damping by DMA of PU/0.5%-SiO₂ film with different uptakes of IL. The left curve presents the full curve while the right graph presents the comparison between the different samples.

Figure 4 demonstrated an interesting behavior of the PU/0.5%-GNP, where the damping decreased with the increasing uptake up to 54 wt% IL, similar to the previously presented results, but started to rise again in higher degree of uptake (71 wt% IL). This composite composition again presents the four-peak shape.

Figure 4: The damping by DMA of PU/0.5%-GNP film with different uptakes of IL. The left curve presents the full curve while the right graph presents the comparison between the different samples.

Figure 5 presents the behavior of the hybrid sample of PU/0.25%-SiO₂/0.25%-GNP. This system, which contains two types of fillers, also presents four peaks. A single degree of uptake (54 wt%) was tested and demonstrated IL decreased the damping (Figure 5). However, higher degrees of uptake were not tested.

Figure 5: The damping by DMA of PU/0.25%-GNP/0.25%-SiO₂ film with different uptakes of IL. The left figure presents the full curve while the right figure presents a comparison between the different samples.

To underline the effect of IL on damping, a comparison was made for all the samples without IL and with ~50 wt% IL, which is presented in Figure 6. The results showed that for all of the samples an uptake of ~50 wt% IL reduced the damping, while the ratios between the samples were preserved for the samples with and without IL; the neat-PU demonstrates the highest value, after that the PU/0.5-SiO₂, followed by PU/0.5%-GNP, and the last one was the hybrid PU/0.25%-SiO₂/0.5%-GNP that exhibited the lowest value, in what seems like a hybrid effect.

Figure 6: The damping by DMA of all samples without and with 50 wt% of IL. The left curve presents the full curve while the right graph presents the comparison between the different samples.

Another interesting assessment was to compare between the damping of PU/IL at different temperatures. As stated previously, the ionogel system of PU/IL revealed thermochromic behavior around its LCST (just below 70 °C). Therefore, here we tested the PU with 54 wt% IL samples at two temperatures – below (30 °C) and above (95 °C, the LCST). The peaks here are different from the peaks of the other DMA graphs due to a difference in the testing conditions (as reported in section 2.4.1.).

Figure 7: The damping by DMA of the neat-PU sample with 54 wt% below (30 °C) and above (95 °C) LCST. The left curve presents the full curve while the right diagram presents the comparison between the different samples.

The results of the DMA test showed that the addition of IL decreased the damping of the sample in comparison to a non-swelled polymer. This trend was noticed for all the samples. An additional observation was provided by the PU/0.5%-GNP composite, where the damping started to rise again after an uptake degree of 54 wt%. All the specimens presented the same graph shape with four peaks. The addition of nanofillers decreased the damping compared to the neat PU, both for the swelled and non-swelled samples. For comparison, an additional test for the damping properties was performed using the rheometer. Unlike the DMA, the rheometer utilized the shear oscillatory mode to determine the damping, using G' and G'' as storage and loss modulus, respectively. Figure 8 presents the damping of the different samples with different degrees of IL uptake. Here, all samples produced similar behavior, where the damping of the swollen samples reduced at relatively low degree of uptake and elevated again at uptakes higher than 50 wt% IL.

Figure 8: The damping by rheometer of all the samples with different percentages of IL.

Figure 9 (a) displays a more convenient way to compare between the different samples. Here, all the composite systems showed similar and higher damping than the neat PU before the matrices were immersed in the IL. After ~50 wt% IL the hybrid PU/0.25%-SiO₂/0.25%-GNP acted almost as PU-neat, PU/0.5%-SiO₂ exhibited only slight increase, and PU/0.25%-GNP demonstrated the highest value.

Figure 9: The damping by rheometer of (a) all samples with and with ~50 wt% of IL for comparison. (b) PU-neat sample with 50 wt% IL below (30 °C) and above (80 °C) LSCT.

The damping results pointed on some diversity between different modes of damping tests (DMA and rheometer). While both modes indicated that the addition of IL decreased the damping, the rheometer test indicated that above a certain degree of uptake, the damping starts to rise up again for all samples, while under the DMA analysis such a trend was evidenced only for the PU/0.5%-GNP specimen. Moreover, while DMA showed that the addition of nanofillers to the matrix decreased the damping, the rheometer presented the opposite result. Mechanical properties

3.3. Mechanical properties

The characterization of the mechanical properties of the system is critical for its application. Here, we tested the mechanical properties by tensile mode, using a dedicated machine. The tensile strength and Young's modulus were evaluated by tensile tests, while the fracture surface energy was tested by the trousers tear test. Mechanical properties are particularly important for application such as energy absorbing glass windows. A typical curve of tensile test is presented in Figure 10b. All the samples, both of swollen and non-swollen systems, expressed a linear stress-strain curve until their tearing, as demonstrated in Fig 10a.

We tested swollen specimens with a single degree of IL uptake of 30 wt%, since it showed thermochromic characteristics, along with being convenient enough to perform the tensile test. The addition of 30 wt% IL offered the lower mechanical properties compared to PU without IL.

Figure 10: Typical curves of (a) trouser tear test and (b) tensile test, as demonstrated by PU/0.5%-SiO₂ swollen in 30 wt% of IL.

It was seen clearly that the addition of IL decreased both the tensile strength and the Young's modulus for neat PU and composite samples, as showed in Figures 11a and 11b. In comparison between neat-PU and the nanocomposite systems, it seems that the nanofillers decreased or did not influence the Young's modulus, both for the swelled and the non-swelled PU (Figure 11a). The tensile stress (Figure 11b), on the other hand, was not reduced by the nanofillers, and even

increased, especially for PU/0.5%-SiO₂. However, this was observed only for the non-swollen PU, and it seems that the addition of the IL screened this influence.

Figure 11: The mechanical properties of all the samples without IL and with ~30 wt% of IL - tensile stress (left) and Young's modulus (right). All samples were tested by tensile test and each result is an average of at least 5 samples.

Figure 12 introduces the results for the fracture surface energy of the PU. All samples produced a typical trouser tear test curve (presented in Fig 10b) and the average energy for the plateau energy was used to calculate the fracture surface energy by the following equation:

$$(2) \quad \gamma = \frac{f}{t}$$

Where γ is the fracture surface energy, f is the tearing force and t is the thickness of the specimen. The results, which presented in Figure 12, indicated that the addition of nanofillers reduced the energy, both for the swelled and non-swelled samples. The addition of SiO₂ nanofibers reduced it more than the addition of GNP. The addition of the IL also decreased the fracture surface energy, for all the specimens.

Figure 12: The mechanical fracture surface energy of all the samples without IL and with ~30 wt% of IL. The samples were tested by trouser tear test and each result is an average of at least 5 samples

Quite similar observations were found for the tensile properties and the fracture surface energy, where the addition of IL always reduced the properties. As for the composite specimens compared to neat polymer, a reduction was observed for the Young's modulus and the fracture surface energy, while a slight increase was presented for the tensile strength.

3.4. Morphological analysis

The sample morphology is an important characteristic, which may assist in understanding the mechanical properties of the final product. The morphology of the samples was characterized by SEM for the non-swelled samples that contained SiO₂ nanofillers. The composition of the fibers were verified as SiO₂ by the EDX detector. Nevertheless, due to a technical difficulty to detect the GNP nanofillers inside the samples, we used STEM. SEM images, as presented in Figure 13 showed that SiO₂ nanoparticles were well dispersed in the PU matrix, both for PU/0.5%-SiO₂ and for PU/0.25%-SiO₂/0.25%-GNP samples. We have also noticed that the SiO₂ nanofibers were wrapped by the polymer matrix.

Figure 13: SEM images of SiO₂ nanofibers in different samples. The diameters of the fibers are labeled in the left-side images.

A similar observation was found for the GNP nanofillers by STEM, as shown in Figure 14. The GNP were well dispersed in the polymeric matrix.

Figure 14: STEM images of GNP in different samples. The GNP are the black particles.

Generally, the morphological analysis indicated good degree of dispersion for both fillers, in all tested specimens.

3.5. Degree of crosslinking

Another important characterization for the understanding of the composites properties is the degree of crosslinking, which indicate the level of crosslinking bonds. The degree of crosslinking (by weight) for the non-swollen samples presented uniform behavior, where the addition of nanofillers (for all of the systems) showed a similar decrease in comparison to the neat PU.

Sample	Wt% of Crosslinking
PU-neat	84%
PU/0.5%-GNP	62-64%
PU/0.25%-GNP/0.25%-SiO ₂	62-64%
PU/0.5%-SiO ₂	62-64%

Table 1: Degree of crosslinking for the different samples without IL.

3.6. Characterization by DSC

Another important property for the full characterization of the samples is the thermal characterization. Such characterization was performed for the non-swelled samples by the differential scanning calorimetry analysis. Figure 15 presented a reduction of the glass transition temperature (T_g) of the composite samples in comparison to the neat PU, where PU/0.5%-GNP demonstrated the lowest reduction, after that the PU/0.5%-SiO₂ and the hybrid PU/0.25%-SiO₂-/0.25%-GNP exhibited the largest reduction and therefore the lowest T_g, slightly lower than PU/0.5%-SiO₂.

Figure 15: DSC curve for all of the different samples without IL.

4. Discussion

The PU based nanocomposite system studied in this chapter is designated for a special optical behavior. Its optical properties are manifested in a unique feature to change from transparent to opaque at a chosen temperature. As shown above, the system is a thermochromic ionogel, whose optical behavior depends on its loading with an ionic liquid (IL). Because the internal molecular structure of the swollen matrix and the temperature of the optical transition depend on the IL content, it is essential to investigate the kinetics of the swelling process of the thermoset PU with the IL.

The driving force for swelling is the increased entropy of the polymer-solvent mixture, leading to an expanded polymer network [15]. With the aim of understanding the swelling ability and the diffusion mechanism of the PU polymer, two types of graphs were charted. The first graph (Figure a) provides as evidence the ability of the PU to swell IL. This synthesized PU is a chemically crosslinked polymer, which is able to swell IL up to more than 7 times of its weight in the dry state. Many times, with a certain degree of swelling, the polymeric network is forced to less preferable configurations, lowering the entropy and resisting the swelling [15]. Nonetheless, in our case the swelling proceeded and did not stop but up to a certain degree, it exerted too much pressure on the polymeric network and destroyed its structure.

Regarding the swelling in different temperatures, the elevation of temperature may lead to a destruction of the hydrogen bonding in the polymer and denouement of interpenetrated polymer chains [16]. This is similar to our case, where decreased swelling at 50 °C compared to RT on the other hand, may be explained due to the special nature and properties of the PU/IL ionogel. The thermochromic property of the ionogel is based on strong hydrogen interactions between the PU and the IL in temperatures below the LCST that allows the homogeneous and transparent appearance, which alternate to a repulsive interactions and IL-rich domains that lead to phase separation and an opaque appearance. More specifically, oxygen atoms on the PPO domain of the PU may interact with hydrogen species of the imidazolium cation of the IL. The oxygens atoms of the IL anion [NTf₂] interact with the PPO to balance the PPO-cation interactions. Above the LCST temperature (around 70 °C), these interactions change to repulsion and IL-rich domain [7]. Although 50 °C is below the LCST, it may be that the interactions start to change into repulsion about this temperature compared to room temperature, and therefore lead to reduction in the swelling. The increased swelling at RT compared to 4 °C may be explained by network expansion caused by enhanced chain mobility [17], and enhanced diffusion and penetration due to increased entropy and internal energy [18].

Diffusion into polymers is frequently described as Fickian, including related mechanisms such as pseudo-Fickian, sigmoidal, two-stage and Case II. As the kinetics of swelling is beyond the scope of this chapter, so is a detailed discussion of diffusion mechanisms, and the emphasis here is on the uptake of IL, being the parameter, which determines the optical transition temperature. An additional drawing of the existing data (Figure 1b) has led to the conclusion that swelling occurred by the non-Fickian diffusion, which does not follow Fick's law. It is well known that the diffusion into viscoelastic polymers does not entirely follow Fick's law, due to the polymer deformation caused by the diffused fluid that leads to a stress driven diffusion, which in turn functions as a barrier to the fluid infiltration [19,20]. There are a few types of non-Fickian diffusion, while in our case it seems to behave as the sigmoidal diffusion [19,21]. A sigmoidal diffusion characterized by slow diffusion at the beginning, accelerated by the first dose of diffused molecules, and finally starts to slow down again toward a plateau. As we already mentioned, non-Fickian diffusion experiences a deformation, which in our case may be related to the disruption of the hydrogen bonds of the polymer.

For a better understanding of the properties and the applications of our system, we have verified its damping properties. The damping defined as the maximum of the tan δ peak, where the polymeric chains can move and cause friction. The damping of polymers tends to decrease at elevated frequencies and therefore behave in a more elastic way [22,23], while at lower frequencies the

damping is higher due to higher flow of the material [24]. Generally, the viscoelastic properties depend on the chain's mobility and the interaction between the components of the molecule [8]. Since we tested the damping by different equipment (DMA and rheometer), working in different modes, we did not always receive the same trends. Yet, we did notice some interesting results. The most consistent trend was that the damping decreases with the increasing swelling of the IL by PU up to a certain degree of uptake. This result was consistent for both DMA and rheometer, for all the samples. An interesting phenomenon was that for PU/0.5%-GNP by the DMA test and for all the systems by the rheometer, the damping started to increase again after certain degree of uptake. Different reports found a connection between the crosslink density and the damping properties. Lower crosslink density describes a more flexible material that allows better energy dissipation than the more brittle material, produced by higher crosslink density [15]. IL may act as a physical crosslinker at lower degrees of swelling, however, as the degree of swelling keep rising, the excess of IL may use as a plasticizer. The IL is composed of large molecules in size, which at small degrees of uptake, may limit the segments motion by steric obstruction, and therefore increase the polymer rigidity and decrease it's damping [8]. At high percentages of swelling, the IL may penetrate the PU network, screen the hydrogen interaction in the polymer, allow more chain motion and by that increase the energy dissipation and the damping.

A difference was found between the DMA and the rheometer on the influence of nanofillers on the damping. Whereas DMA tests showed that nanofillers decrease the damping, the rheometer suggested that nanofillers increase or do not change the damping. This difference is considered insignificant as both tests (DMA and rheometer) indicated that for 50 wt% of IL swelled in the PU, the swollen systems exhibited significantly lower damping values. Smaller damping values due to the addition of nanofillers may be due to polymer chain mobility restriction, resulting from the interactions between the chains and the fillers and a possible confinement of the chains by the nanofillers [25, 26]. The DMA results suggests a hybrid effect since the hybrid PU/0.25%-SiO₂-/0.25%-GNP exhibits the lowest value for the swollen (and partially for the non-swollen) state. Such effect may be resulted by a combined contribution of fillers with different geometries and structure to the production of more interaction and maybe more intense confinement. An indication for the good filler-matrix interaction may be seen in the SEM images (Figure 13) of the nanocomposite systems that contain SiO₂ nanofibers. The well-dispersed fibers are protruding out of the matrix, while they are wrapped by the polymer. Such interactions are made possible also due to the -OH groups of the silica, which may provide hydrogen bonding with the matrix. GNP were also well dispersed, as it may be noted from the STEM images (Figure 14). The platelet geometry of the GNP grants it a very high surface area to volume ratio, and along with good and singular

dispersion, allows it to maximize the available space for interaction. The combination of the different geometries may lead to higher restrictions of the chains. The opposite trend, of higher damping with the addition of nanofillers, may be due to the reduced degree of polymer crosslinking (as presented in Table 1 and discussed further), which is induced by the fillers, and allows higher mobility of the chains, which is manifested in higher energy dissipation and eventually higher damping.

Another agreement between DMA and rheometer was that damping values of PU-neat swelled by ~50 wt% of IL demonstrated a decrease in the damping at the transition from temperatures above the LCST to temperatures below LCST. The degree of uptake of these samples (~50 wt%) is around the area where the damping starts to increase again. It means that at lower swelling the IL interacts with the polymer chains and limits its motion in a way similar to crosslinking, and around this amount of swelling, the excess of the IL expands the distance between the polymer chains and acts as a plasticizer. At temperatures above LCST, the hydrogen bonding between the polymer and the IL are replaced by repulsion, resulting in phase separation, a property that enables the thermochromic application. Hence, at such elevated temperatures it may be similar to the case of lower swelling, where the amount of IL that interacts with the polymer chains acts as a crosslinker and decreases the motion of the chains.

Other important properties are the static mechanical properties (tensile stress, Young's modulus) and the fracture surface energy. For all the samples, the addition of the IL diminished all the properties. The reduction of the mechanical properties by the increasing degree of swelling is known since the solvent operates as a plasticizer and weakens the mechanical strength [27]. This may be explained by the fact that the chains in the non-swollen polymer exhibit more entanglements and therefore are more resistant to deformation than chains of swollen polymer [28].

Regarding the nanoparticles, frequently, the reason for reduced mechanical properties may be a poor dispersion. However, the morphological characterization presents good and uniform dispersion. The SiO₂ nanofillers were dispersed uniformly and singularly, as it may be evidenced by Figure 13. No aggregation was observed. These observations were relevant for both PU-/0.5%-SiO₂ and PU/0.25%-SiO₂/0.25%-GNP, meaning that the addition of SiO₂ does not improve or reduce the quality of dispersion, and therefore does not have any influence. STEM images (Figure 14) presented similar results for the samples that contained GNP nanofillers – good dispersion, no aggregation, and no influence if the hybrid sample compared to the GNP parent sample. Nanofillers can contribute to the mechanical properties, especially for the fracture toughness, where fillers of fibrous (SiO₂) or platelets (GNP) geometry may contribute by either pull-out or bowing the fracture front. A necessary condition to improve the mechanical properties is good interactions between the

nanofillers and the matrix. Although it is difficult to indicate the existence or non-existence by STEM images, the wrapping of the SiO₂ by the PU matrix may suggest good interactions between them. These interactions may be for example hydrogen bonding between the PPO of the PU and the -OH groups of the SiO₂ nanofibers.

Observations from morphological characterization do not explain the reduced mechanical properties. That led us to perform another test to determine the degree of crosslinking (by weight). The result of this test (Table 1) stated that samples with nanofillers have lower degree of crosslinking than PU-neat. It seems that nanofillers interrupt the formation of the crosslinked network. All samples with nanofillers showed the same reduction in the degree of crosslinking. The nanofillers are inserted into the matrix *in-situ* during the PU synthesis, they may disturb the formation of part of the crosslinking sites, maybe by steric repulsion. Too high degree of crosslinking is also not good for the mechanical properties since it reduces the amount elasticity of the polymer and forces it to break at lower elongation and lower stress. Yet, the existence of the crosslinking junctions allows the high elongation of the polymer while maintaining its shape. Thus, it is important that the network will exhaust all its possible bindings to receive the best performance for this system.

From the theoretical point of view, the addition of well dispersed nanofillers should increase the fracture toughness, especially when the fillers have good interaction with the matrix. This is particularly relevant for fibers and platelets, which may contribute to the fracture energy by the pull-out mechanism, in addition to the crack front bowing, due to their high aspect ratio geometry. Yet, it seems that the insertion of the fillers prevents the extraction of all potential bonding of the polymer network, forming “defects” in the polymer. Those “defects” decrease the mechanical properties, screen every potential increase of the nanocomposite.

We did notice that not all the particles had the exact same influence on the PU properties. First, the addition of SiO₂ nanofibers to the non-swelled PU increased its tensile stress. This may be due to the uniform dispersion and the good interactions between the SiO₂ nanofibers and the PU matrix, which may allow the load transfer mechanism. The GNP on the other hand, did not show any significant influence for any of the properties. Nevertheless, the SiO₂ nanofibers reduced the fracture surface energy more than GNP only. This may be due to different geometry or size, in a way that the SiO₂ defects the network by the reduction of crosslinking and produces defects in the polymer network from one hand but may not compensate this reduction by enough reinforcement. It is well known, that as for many other properties, when it comes to nanofillers, different effects of the nanofillers on T_g may be seen. The measurements of the optical transition temperature of the neat PU (without IL) presented lower values for the composite samples. Such reduction may be

due to the plasticizing effect of the particles (usually for small and well-dispersed particles) or due to interference of the nanoparticles with the crosslinking system, both resulting in elevated free volume, which allows more motion of the polymeric chains and therefore reduces T_g [29]. All the nanofillers lowered the T_g compared to the neat PU. The GNP revealed more moderate reduction than SiO₂ nanofibers, while the hybrid system PU/0.25%-SiO₂/0.25%-GNP displayed a hybrid effect for the T_g and demonstrated the lowest T_g value. Such effect may exist due to the combination of both fillers.

In a general look on the nanofillers, the GNP and the SiO₂ nanofibers differ by their geometries and by their chemical structures. Nevertheless, it seems that both fillers interact with the polymer, possibly by hydrogen bonds of -OH groups on their surfaces. It seems that the SiO₂ nanofibers were well dispersed and had good filler-matrix interaction. Alongside, it may be that GNPs interact even better with the matrix owing to their plate geometry, which provides more surface area to interact with, even though their dispersion may be poorer. As a result, the GNPs appear to interact more significantly and confine the chains more than SiO₂ nanofibers, which in turn showed better dispersion. As a result, despite the reduction of the crosslinking level, the PU/0.5%-SiO₂ presented higher tensile strength than the neat PU at the non-swollen state and lower T_g due to its effective dispersion. On the other hand, the PU/0.5%-GNP demonstrated a moderate decline of the fracture energy due to their good interaction with the matrix, and steeper decline of the damping (by the DMA) due to same interactions that allow more confinement and better limitation of chain mobility. The hybrid system PU/0.5%-SiO₂/0.5%-GNP presented hybrid effects for part of the properties, probably by the combination of the properties of both samples.

The results of this work are in a good agreement with our previously published works, that in the case of nanocomposites we should treat each sample differently and we cannot always predict its final mechanical properties. In this case, since we used the nanofillers during the *in-situ* polymerization, they changed the level of crosslinking and by that made the prediction of the final properties even more difficult. Indeed, despite the good dispersion of the nanofillers inside the PU matrix we did not receive any improvement.

5. Conclusions

Thermochromic ionogel systems, based on polyurethane swollen by ionic liquid and designated for optical glass panel applications, were investigated with reference to their swelling behavior and the effect of the addition of nanoparticles. The systems were characterized for different temperatures and uptakes of ionic liquid by their mechanical properties and energy damping capacities for IL

uptakes which facilitated the clear-opaque optical transition. The main observations regarding the effects of the essential presence of IL on the mechanical properties were of a significant lowering of the damping capacity and of a reduction in the mechanical properties as well as of the fracture resistance. The effect of the IL was dominant even in systems of nanocomposites and hybrids. It is suggested that the ionic liquid has two simultaneous effects: The first is plasticization that induces easier polymer segmental movement and in turn might increase the damping capacity. The second - which overrides the plasticization effect - is a volumetric effect typical of swelling, wherein the penetrating molecules of the diffusing agent (the ionic liquid) act to enlarge the free volume, thereby generating significant internal stresses that may undermine the structural integrity of the system.

In conclusion, it appears that the mechanical properties and the structural integrity and the energy damping capacity, which suffer from the essential presence of the ionic liquid in the polyurethane, are not enhanced by the addition of nanoreinforcement. Yet, it is important to note - based on our previous experience [12] - that this PU-IL system is potentially suitable for safety glass panel applications, which offer a temperature triggered clear-opaque transition. However, new strategy may be needed to further enhance its mechanical properties.

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CHAPTER FIVE – Discussion and Conclusions

For some 50 years now, the most suitable models to describe the mechanical properties of composite materials were given by micromechanics. A typical attribute of micromechanics of classical composite materials is that they disregard the actual composition of the composite structure and as such they have been considered universal rules. The inventions of nanoparticles in recent years e.g., carbon nanotubes and graphene raised question on the validity of that convention of universal models. In 1992, a *News and Views* article by Calvert published in *Nature* suggested that nanocomposites in fact form a new class of fine-scale composites and raised the question of how they would perform mechanically in comparison with classical micrometer-scale composites. In our attempt to spell out the premise of this thesis we have asked the question of how the two-dimensional scales that are three orders of magnitude apart are reflected in their respective mechanical models. In other words, the question that this research was trying to answer first was how the 3-fold scale reduction of the reinforcement (namely, the nano scale, which refers to the size range of the reinforcement, and the micro scale, which is the scale used most appropriately for mechanical models) is manifested in the mechanical models that predict the behavior of composite materials.

Accordingly, our preliminary study investigated the applicability classical micromechanics to nanocomposites, with an emphasis on fracture energy. Consequently, the first question was whether nanocomposites follow the same rules as microcomposites and whether the mechanics of nanocomposites can be described by micromechanics. Our preliminary study comprised a broad analysis of different nanocomposite systems and their experimental properties, relating to the relevant micromechanics models for each property (strength, Young's modulus, and fracture toughness). We also considered the nanofiller properties (geometry and chemical structure) and the possibility of nanofiller hybridization, covering a relatively wide range of nanoparticles and polymer matrices.

The main observations and conclusions of our preliminary study indicated that the classical micromechanics models of strength and elastic modulus fail to predict the experimental properties of the systems. The experimental values are way lower than the predicted ones, indicating that the outstanding properties of the nanoparticles do not contribute to those of the nanocomposites. Contrarily, the fracture toughness and fracture energy dissipation mechanisms can be enhanced

significantly by the addition of nanoparticles to the matrix, depending on the particle properties and on its interactions with the crack front. Examples for such mechanisms are presented below, in Figure 1.

Figure 1: SEM images of a) iPP/0.5%-GNP/0.5%-VGCF - demonstrating bridging mechanism, b) iPP/0.5%-SiO₂/0.5%-NC - demonstrating fiber pull-out mechanism

These primary conclusions shifted the aim of our study toward the direction of fracture toughness and led to the examination of fracture mechanisms for different polymeric nanocomposite systems, with an emphasis on the potential for a positive hybrid effect considering a range of nanoparticle properties (geometry and chemical structure).

With regard to the multifaceted character of fracture toughness of nanocomposites, three themes had been identified and chosen by our study to represent the versatile behavior of nanocomposites in fracture processes. These were hybridization by mixing of different types of nanoparticles, testing of different geometries such as nanofibers versus nanoplatelets, and of different chemical compositions and of different polymer matrices, including plasticized thermoses.

The first system that we have tested was PVB with CNT-COOH (0.2 wt%) and NC (2 wt%). The PVB is commonly used in the field of armored glass, as one of the main glass layers. Therefore, its fracture toughness may increase the protection provided by the whole window. CNT and NC are a classical nanofillers with very impressing mechanical properties, while both contain -OH groups, which may interact with the -OH groups of the PVB. As always, it is a big challenge to

insert the nanofillers in such manner that they will be effectively dispersed and express their properties. Different wt% of the nanoparticles were tested to find the one with the higher fracture toughness, which was measured by the trouser tear test. Further, a modification of the preparation method (higher sonication power) was performed, and STEM analysis indicated that the dispersion was indeed better. For this set of films an additional increase of the fracture toughness was demonstrated. Also, the results showed that the addition of nanofillers may indeed significantly improve the fracture toughness of the polymeric matrix, where the parent composites PVB/CNT-COOH-0.2% and PVB/NC-2% demonstrated 105 and 118% enhancements, respectively, compared to the properties of the neat matrix. Moreover, a combination of two different nanofillers (composites PVB/CNT-COOH-0.2%/NC-2%) may lead to a positive hybrid effect in the fracture toughness, which was expressed by the improvement of 181%, only 42% lower than the combined improvements of PVB/CNT-COOH-0.2% and PVB/NC-2%. Furthermore, quantitatively impact test introduced higher impact resistance for hybrid films. SEM images of the fracture surface implicated that there was a correlation between the roughness of the sample and its fracture toughness, but only qualitatively. This assumption was confirmed by the optical profilometer, which presented a substantial linear correlation of the fracture surface with the fracture surface roughness. This correlation indicated the dependence of the fracture toughness and specifically the hybrid effect on the interaction of the nanofillers with the crack front, which may be expressed by the toughness extension. Those results encouraged us to dive deeply for better understanding of the influence of parameters such as filler geometry and chemical structure on the fracture toughness and the ability to generate a hybrid effect, which were studied at the following part.

To study the influence of nanofillers geometry and chemical structure, a system of semi-crystalline thermoplastic iPP with nanofiller of different geometries and chemical structures was examined. The nanofillers in this part were divided into two separate groups, depending on their properties – (a) nanofillers with similar geometries and different chemical structures (fibrous geometry - VGCFs and ZrO₂ nanofibers; platelets geometry - GNPs and NCs), and (b) nanofillers with similar chemical structures and different geometries (organic - VGCFs and GNPs; inorganic - NCs and SiO₂ nanofibers). Each filler was added at the weight percent of 0.5%. Additionally, we examined hybrid systems of iPP/0.5%-GNP/0.5%-VGCF, iPP/0.5%-GNP/0.5%-NCs, iPP/0.5%-ZrO₂/0.5%-VGCF and iPP/0.5%-NC/0.5%-SiO₂. An initial cut with different cut length was done in rectangular samples, and further the samples were tested by a tensile test of mode I type. An

analysis of the raw data generated the fracture energy (initial and total). Samples with shorter cut length presented more controlled mode of fracture (where all the released energy was invited in the fracture), while samples with longer cut length presented more catastrophic mode of fracture (where the released energy was much higher than the required energy for the fracture).

There was almost no difference of the initial energies between the samples, but all composite samples demonstrated enhanced fracture toughness (total energy) compared to neat iPP. The composition of iPP/0.5%-GNP presented the most superior fracture toughness among the parent composites. Morphology analysis performed by SEM, implicated a poor level of GNP dispersion in iPP. On the other hand, the same analysis indicated good GNP-iPP interactions, which are probably the reason for the superior properties. On the other hand, VGCF was well dispersed in the polymer, but iPP /0.5%-VGCF demonstrated lower energy than iPP/0.5%-GNP. These finding led to the conclusion that the fracture toughness depends on a set of parameters of the matrix and particles (geometry, matrix-filler interactions etc.) and not necessary the level of dispersion. In addition, the sample of iPP/0.5%-GNP/0.5%-VGCF expressed a positive hybrid effect in the fracture toughness. iPP/0.5%-GNP may contribute the crack front bowing mechanism, while iPP/0.5%-VGCF may provide the pull-out mechanism.

We concluded that among all the contributive parameters, the matrix-filler interactions play the main role, by interfering with the crack front propagation by interactions such as crack front bowing and pull-out. These interactions depend on the geometry of the particle, its chemical nature, its affinity to the matrix etc. Consequently, each system should be examined by itself to define its specifical properties and interaction, and no general rule can be formulated for all nanocomposite systems.

Equipped with insights from the previous chapters, a study on the mechanical behavior of nanocomposites systems in PU-IL thermochromic ionogel, designed for advanced optical application. This application allows the PU-IL to change its appearance from transparent to opaque and backwards, as a function of temperature. The uptake of the polymer was tested in different temperatures (4 °C, RT and 50 °C), and found that the RT presented the highest rate and the highest degree of uptake. The synthesized PU in this part was thermoset and was able to swell IL in an amount of 7 times more than its original weight, following a non-Fickian diffusion. To study the

influence of nanofillers, two types of nanofillers were added to the ionogel to receive the nanocomposites PU/0.5%-GNP, PU/0.5%-SiO₂ and the hybrid PU/0.25%-GNP/0.25%-SiO₂.

The damping capacity of systems was verified by the maximum of the $\tan\delta$ peak of the graph. The damping capacity was measured using both DMA and rheometer. We tested different samples, with different degrees of swelling, with and without nanofillers. The results showed that PU-IL composition expressed lower damping capacity than PU without IL. This trend was repeated for all systems, including the composites and the hybrid. For part of the samples the damping capacity began to rise again after higher degrees of uptake. The addition of IL to the PU decreased the tensile strength, the elastic modulus, and the fracture toughness of all samples. The IL may function as a plasticizer and thus increase the damping capacity. In addition, it may increase the free volume which may induce an internal strength and interfere with the structure of the system. Nanofillers as well decreased or did not change the damping in comparison to the neat PU or PU-IL. A good level of both nanofillers dispersion was observed by SEM. Nevertheless, the addition of nanofillers did not improve the mechanical properties in comparison to the neat PU or PU-IL. Therefore, another test was performed, and it was noticed that the degree of crosslinking of the polymer decreased after the addition of nanofiller, which may explain the poor results. This part again led us to the conclusion that each system should be specified and optimized for its own unique properties.

- To sum the main conclusions of this work, we may say that the micromechanics fails to predict the real performance of nanocomposites, even for fracture energy. Therefore, different nanomechanisms should be considered for nanocomposites, which relate to interactions between the reinforcement and the polymer matrix on a molecular scale. Nanocomposite properties are composition specific (properties of the components: nanoparticle and matrix), and depend on levels of exfoliation and dispersion, and interaction at the interface. They cannot be expressed by classical micromechanics models, rather – fresh models should be considered, which are applicable to the molecular level. Therefore, it is proposed that well dispersed nanocomposites ought to be considered as molecular composites or solid solutions.

תקציר

עבודה זו מכוונת לחקור את המיקרומכניקה של הננו-מרוכבים, עם דגש על אנרגיית השבירה. בחינה נרחבת עם מגוון מטריצות וננו-מלאנים גילתה שככלל, מערכות ננו-מרוכבות לא משיגות את החוזק והמודולוס האלסטי התאורטיים אשר צפויים להם על-פי המיקרומכניקה. עם זאת, הוספה של ננו-מלאן עשויה להגדיל את אנרגיית השבירה באופן משמעותי. בהקשר זה, בחנו את אנרגיית השבירה של מערכות ננו-מרוכבות, ובתוך כך מקרים מיוחדים של אפקטים היברידיים חיוביים, ההשפעה של הגיאומטריה ושל ההרכב הכימי של הננו-מלאן, וההתנהגות המכנית של מערכת ננו-מרוכבת בעלת יישום ייחודי. חומרים ננו-מרוכבים היברידיים מכילים יותר מסוג אחד של מלאן ננומטרי ועשויים לבטא תכונה שגבוהה יותר מכל אחת מתכונות הננו-מרוכבים בנפרד או מאשר הסכום האריתמטי של תרומתן – אפקט היברידי חיובי. במטרה לבחון את אנרגיית השבירה של ננו-מרוכבים בחנו שלוש מערכות עם מטריצות פולימריות שונות (תרמופלסטיות, סמי-גבישיות ותרמוסטיות) המיועדות ליישומים שונים, ומספר ננו-מלאנים בעלי גיאומטריות ומבנים כימיים שונים, שהוכנו על ידי מספר שיטות הכנה. לפיכך, מחקר זה עוסק באנרגיית השבירה של היברידיים ננו-מרוכבים תוך כדי נקיטת גישה ביקורתית על הפרקטיקה ההנדסית הרווחת כיום של השמת המיקרומכניקה הקלאסית של מרוכבים על ננו-מרוכבים.

החלק הראשון מחפש לחקור את האפשרות של אפקט חיובי באנרגיית השבירה של מערכות היברידיות ננו-מרוכבות. לשם מטרה זו, בחרנו לבחון מערכת של מטריצת פוליויניל-בוטירל (PVB) עם ננו-צינוריות פחמן אשר מטופלות בחומצה קרבוקסילית (COOH-CNT) וננו-חרסיות (NC) בתור ננו-מלאנים. PVB הוא פולימר אמורפי ותרמופלסטי, המשמש בתעשיית הזכוכיות המשוריינות באופן תדיר. COOH-CNT ו-NC ידועים בשל תכונותיהם המכניות הטובות, ויחד עם העובדה שננו-מלאנים יוצרים דרגת עכירות נמוכה יותר בשל מימדיהם הקטנים ו-NC מאפשרים דרגת שקיפות גבוהה, מערכת זו היא מועמדת טובה ליישום מסוג זה. מערכת של PVB/0.2%-CNT-COOH/2%-NC הציגה אפקט היברידי חיובי משמעותי באנרגיית השבירה. אפקט זה היה קשור לדרגת החספוס יותר מאשר לטיב הפיזור. לכן, הסקנו כי אפקט זה נובע ממנגנונים של אינטרקציות ננו-מלאן – חזית השבר, כגון שלילת סיבים והקשתת חזית השבר, ולא במנגנון העברת מאמץ.

בעקבות מסקנות החלק הראשון, הפרק השני התמקד בחקירת השפעת הגאומטריה וההרכב הכימי של הננו-מלאנים על אנרגיית השבירה ועל הסבירות לקיום אפקט היברידי. לשם מטרה זו השתמשנו בפוליפרופילן איזוטקטי (iPP) יחד עם סוגים שונים של ננו-מלאנים. iPP היא מטריצה תרמופלסטית סמי-גבישית עם קבוצות CH_3 מוכוונות, המשמש ביישומים רבים. את הננו-מלאנים חילקנו לשתי קבוצות: (א) – ננו-מלאנים בעלי גיאומטריה שונה (סיבית וחרסיתית) והרכב כימי דומה – סיבי פחמן (VGCF) וננו-חרסיות גרפן (GNP); ננו-חרסיות ו-ננו-סיבים של סיליקה (SiO_2), (ב) ננו-מלאנים בעלי גיאומטריה דומה והרכב כימי שונה (אורגני ואי אורגני) – ננו-סיבים של VGCF וזירקוניה (ZrO_2) ; GNP ו-NC. מערכות מרוכבות והיברידיות הוכנו בהתייחס לחלוקה לפי תכונות. המערכות המרוכבות הניבו תכונות נעלות ביחס למטריצת ה-iPP לבדה. המערכת של iPP/0.5%-GNP/0.5%-VGCF הראתה אפקט היברידי חיובי עבור

אנרגיית השבירה ועבור קיבולת הארנגיה הדינמית. בין יחידות האם של החומרים המרוכבים, iPP/0.5%-GNP הפגין את האנרגיה הגבוהה ביותר, ככל הנראה בעקבות האינטרקציה הטובה של GNP עם הפולימר. המסקנה העיקרית של פרק זה הייתה שאנרגיית השבירה תלויה בסט של פרמטרים בדגש על האינטרקציות של המטריצה והמלאנים, אשר משפיעה על התקדמות חזית השבר. עקב כך, יש צורך לבחון כל מערכת בנפרד על-מנת לאפיין את המבנה הייחודי שלה ואת מנגנון אינטרקציות חזית השבר שלה, במקום להסיק חוקים כלליים עבור ננו-מרוכבים והיברידיים.

בהתבסס על מסקנות החלק השני, לפיהן כל מערכת והתנהגותה צריכה להיבחן באופן אינדובידיאלי, בחרנו מערכת מעניינת עבור הפרק השלישי. מערכת זו הינה יונג'ל תרמוכרומי עם התנהגות אופטית ייחודית, שנוצרה על ידי יישום פיזיקלי. היונג'ל עשוי מפוליאוריתאן תרמוסטי (PU), שגם הוא מושמש על ידי תעשיית החלונות הממוגנים, אשר מותפח על-ידי נוזל יוני (IL) ויכול לשנות את הופעתו האופטית משקוף לאטום כפונקציה של טמפרטורה. בחנו את ההשפעה של אחוזי התפחה שונים ושל הוספת ננו-מלאנים שונים (GNP וננו-צינוריות SiO_2) על התכונות המכניות ועל קיבולת אנרגיית הדעיכה (damping) של מערכת כזו. הצירוף של הנוזל היוני ל-PU הוריד את קיבולת ה-damping, את התכונות המכניות ואת אנרגיית השבירה עבור חומרים לא-מרוכבים, מרוכבים והיברידיים, כך שהכנסת הננו-מלאנים לא הצליחה לפצות על התכונות הירודות של ה-PU המותפח. לנוזל היוני הייתה השפעה כפולה על תכונות המערכת – פלסטיזציה אשר העלתה את קיבולת ה-damping ונפח חופשי שעשוי להחליש את מבנה המערכת.

המסקנה הכוללת של מחקר זה היא שבאופן כללי מיקרומכניקה קלאסית אינה ישימה עבור ננו-מרוכבים – כולל אנרגיית השבירה – ועל מערכת להיות מנותחת בנפרד בהתאם לתכונות המרכיבים שלה, איכות הפיזור ובעיקר סוג האינטרקציות בין הננו-מלאנים למטריצה, המשפיעות על התקדמות חזית השבר. אנו מציעים להתייחס לננו-מרוכבים בעלי פיזור טוב כאל תמיסות מוצקות.

עבודה זו נעשתה בהדרכתם והנחייתם של פרופסור גד מרום ופרופסור הו קסיו

**NANYANG
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OF JERUSALEM

אפקטים היברידיים באנרגיית השבירה של חומרים ננו-מרוכבים

חיבור לשם קבלת תואר "דוקטור לפילוסופיה"

מאת

נדיה שטרן (לרמן)

הוגש לסנאט האוניברסיטה העברית בירושלים

חשוון תשפ"א, אוקטובר 2020

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I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarised materials, and has not been submitted for a higher degree to any other University or Institution.

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Chapter 1 is published as

Stern, N., Marom, G., Zhang, L., & Hu, X. (2018). 6.1 Micromechanics of Nanocomposites.

The contributions of the co-authors are as follows:

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The contributions of the co-authors are as follows:

- Prof. Marom and Prof. HU have supervised this work.
- Dr . Dyaman and Mr. Shemer helped us to perform the ballistic test.

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[Nadya Stern Lerman]