

## INFLUENCE OF NANOPARTICLES ON THE FATIGUE CRACK GROWTH BEHAVIOR OF EPOXY RESINS

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### Abstract

The high stiffness of nanoparticles combined with a tremendous surface to volume ratio, due to their nano-scaled dimensions, make them potential candidates for mechanical reinforcement in polymeric matrices. In particular, toughening is achieved at very low filler concentrations. However, the dominating toughening mechanisms strongly depend on the particle sizes and their aspect ratios. In this study, the effect of non-carbon based nanofillers, namely spherical nanosilica and layered fluorohectorites, on the fatigue crack growth behavior is investigated. The results reveal that the type of nanoparticles strongly affects the degree of toughening and the mechanisms involved. Crack deflection, provoked by the large lateral extension of the fluorohectorites causes a toughness improvement of 70 % at 2.2 vol%.

### 1. Introduction

The long-term mechanical performance under dynamic loading conditions of polymer matrix composites is of prime concern in their adoption for industrial devices. The failure of these composites originates in the formation and subsequent propagation of microcracks. A profound knowledge of the crack propagation behavior of the polymer matrix material is of fundamental interest. The enhancement of crack resistance by toughening is improving the fatigue performance. The investigation of the fatigue crack propagation (FCP) rate under varying stress intensity ranges ( $\Delta K$ ) allows for a quantification of the three stages of fatigue crack growth the threshold value for crack initiation, the region of stable crack growth, described by the Paris law, eq. (1) [1], and the critical crack growth.

$$da/dN = C\Delta K^m \quad (1)$$

In the Paris law, eq. (1),  $a$  represents the crack length,  $C$  a material constant and  $m$  the slope of the curve on double logarithmic scale. The plastic zone size, ahead of the crack tip, is strongly dependent on the dynamic stress state applied, eq. (2) [2]. With increasing stress intensity factor, the size of the plastic zone is enlarged. Consequently, the plastic zone is equivalent to a sensor, changing its size, being highly sensitive to all changes in mechanical properties, attributed to the addition of differently shaped nanoparticles and the crack/particle interactions ahead of the crack tip in the nanocomposites.

$$d_p = \frac{1}{3\pi} \left( \frac{K_{\max}}{\sigma_y} \right)^2 \quad (2)$$

According to the crack tip plasticity theory of Irwin [2], in eq. (2),  $d_p$  represents the diameter of the plastic zone ahead of the crack tip,  $K_{\max}$  the maximum stress intensity factor and  $\sigma_y$  the yield strength of the matrix.

In this work the effect of nanoparticle geometry of non-carbon based filler materials on the FCP behavior is focused. Commercial spherical nanosilica (average diameter 23 nm) and surface modified synthetically prepared K-fluorohectorites characterized by large lateral extensions (5-7  $\mu\text{m}$ ) and high aspect ratios (up to 600) were used to examine the effect of particle size and geometry. The good compatibility of the epoxy resin and silica nanoparticles, due to proper surface treatment, is well known [3]. The fluorohectorites were rendered hydrophobically by cation exchange reaction allowing homogeneous particle dispersion. In addition, the synthetic fluorohectorites provide outstanding advantages compared to natural montmorillonite, including larger particle sizes, superb layer charge homogeneity and high phase purity leading to uniform interlamellar reactivity and surface chemistry [4].

The main toughening mechanisms appearing in epoxy based silica nanocomposites are particle pull-out in combination with plastic void growth on the nano-level involving slight crack deflection on the micro-level [3]. The lack of crack pinning in epoxy/silica nanocomposites is regarded to be due to the small particle sizes in comparison to the crack tip opening displacement [3], respectively plastic zone size. The morphology of the layered silicates is strongly determined by its degree of exfoliation. On the one hand, the exfoliation of smectite clays is accompanied with a high increase in nanocomposites modulus and tensile strength [5]. Whereas, an increase in fracture toughness is mainly reported for intercalated or phase separated morphologies, especially in the case of mica [6] and modified fluorohectorite [7] filled epoxy systems. As stated by Kinloch and Taylor [6], a certain particle size is necessary to achieve an effective interaction between the dispersed particles and the propagating crack, by provoking crack deflection and crack pinning. The large fluorohectorites, investigated in this study provide the opportunity to adjust the particle size and render the state of shear stiffness to improve the load bearing ability in layer stacking direction and the flexural rigidity of the tactoids [4].

Whereas a lot of effort was spent investigating the mechanical properties of epoxy based nanocomposites, the fatigue crack growth behavior was less discussed. Blackman et al. [8] revealed an improvement in the stress intensity range required for crack initiation by using nano-silica. Hedicke-Höchstötter et al. [9] observed a significantly improved fatigue crack propagation behavior of polyamide by adding up to 5 wt% exfoliated layered silicates (Nanofil 919). Although several attempts are presented in literature analyzing the effect of specific polymer/nanoparticle combinations in terms of fracture toughness and fatigue crack growth propagation, a comprehensive study discussing the effect of particle geometry of differently shaped nanoparticles in the same resin system is missing. This fact clearly shows the high importance of the presented study to analyze fatigue crack growth behavior by focusing on particle size and shape and discussing the involved toughening mechanisms.

## 2. Experimental

### 2.1. Materials

The epoxy matrix used in this study consists of a diglycidylether of bisphenol A (DGEBA) epoxy resin, epoxy equivalent weight 172 g/eq. (Epikote 0162, Momentive Specialty Chemicals, Germany), cured with methylhexahydrophthalic anhydride (Epikure 868, Momentive Specialty Chemicals, Germany) and additional 1 wt% *N,N'*-dimethylbenzylamine (Sigma-Aldrich, Germany) referred to the liquid matrix to accelerate curing.

Silica nanocomposites were prepared by using nanosilica, kindly provided as colloidal sol in DGEBA, Nanopox E470 (Evonik-Hanse, Germany, 40 wt% SiO<sub>2</sub>). The silica nanoparticles (mean diameter 20 nm) are synthesized and surface-modified, with an organosilane, in aqueous solution. The density of the amorphous nanosilica is approx. 2.2 gcm<sup>-3</sup>.

A synthetic Na-fluorohectorite was prepared by melt synthesis with an optimal chemical formula Na<sub>0.5</sub>[Mg<sub>2.5</sub>Li<sub>0.5</sub>]Si<sub>4</sub>O<sub>10</sub>F<sub>2</sub> [10], having a cation exchange capacity (CEC) of 110 meq./100 g as determined by the copper complex method [11]. The aspect ratio of the Na-fluorohectorite was adjusted to maximum 600 and the tactoids were rendered shear stiff by exchanging the intergallery cations with potassium [4]. Afterwards, the K-fluorohectorites were surface modified with Dodecylamine (97%, Sigma-Aldrich) using a standard procedure [12]. The density of the organophilized K-fluorohectrite (O/K-hect) is 2.7 gcm<sup>-3</sup>.

### 2.2. Preparation of Nanocomposites

Epoxy/silica nanocomposites were prepared by simple dilution of the masterbatch with neat DGEBA at 60 °C. Subsequently, the anhydride hardener and the required amount of *N,N'*-Dimethylbenzylamine was added to the mixture.

Following surface modification in aqueous media, the modified fluorohectorites were phase transferred into THF without former drying by repeated dispersing and centrifuging for two times with THF. As a general procedure, the organo-nanofiller suspension in THF was mixed with the epoxy resin in a round flask (2 L) for one hour using mechanical mixing. This was followed by removal of solvent in a rotary evaporator under vacuum at 80 °C. Subsequently, the anhydride hardener was added to the epoxy-organo-nanofiller mixture according to its stoichiometric ratio. The mixture was processed in a three-roll-mill Exakt E80 (Exakt Vertriebs GmbH, Germany) for achieving an optimal dispersion prior to curing (3 cycles, 300 rpm, ultimate gap distance 10 μm). Subsequently the required amount of *N,N'*-dimethylbenzylamine was added.

The final mixtures were degassed under vacuum at 60 °C for 15 minutes and cured at 140 °C for 11 hours in a release agent coated aluminum mold.

### 2.3. Characterization Methods

Powder X-ray Diffraction (PXRD) patterns of the final epoxy/clay nanocomposites were recorded to investigate interlamellar spacing of the organo-nanofillers. Samples were fine grinded using cryo-grinding (Pulversiette 14, Fritsch, Germany, 2 mm sieve) and the PXRD patterns were obtained in transmission geometry on a STOE Stadi P powder diffractometer

(STOE & Cie GmbH, Germany) equipped with a MYTHEN1K detector using  $\text{CuK}\alpha_1$  radiation ( $\lambda = 1.54056\text{\AA}$ ).

Thermogravimetric analysis (TGA) was applied to determine the amount of the organic modifier of the organo-nanofillers and as well the nanofiller content in the nanocomposites by using a TGA/STDA851e (Mettler Toledo, Germany) under oxygen flow (50 ml/min) at a heating rate of 10 K/min.

The dispersion of the epoxy silica nanocomposites was characterized using a LEO 922 A EFTEM transmission electron microscope (Carl Zeiss AG, Germany, 200 kV). Thin sections of 50 nm were cut on a Leica Ultracut microtome (Leica Biosystems GmbH, Germany, 1,5 kV) equipped with a glass knife. Fracture surfaces of selected samples were analyzed using a Zeiss 1530 (Carl Zeiss AG, Germany) scanning electron microscope equipped with a field emission cathode.

Fatigue crack propagation (FCP) experiments were performed at 23 °C and 50 % relative humidity employing a servo-hydraulic test machine (Hydropuls MHF, Schenck, Germany) using compact tension (CT) specimens (width 33 mm, thickness 4 mm). The rate of cyclic-fatigue crack growth per cycle,  $da/dN$ , was measured as a function of the applied stress intensity factor ratio,  $\Delta K$ . The loading follows a sinusoidal waveform with a frequency of 10 Hz and an R-ratio ( $K_{\min}/K_{\max}$ ) of 0.1. The calculation of the crack length was done considering the specimen's compliance as described in ISO15850, using an extensometer (632.13F-20, MTS, Germany) fixed to the front face of the CT-specimen.

### 3. Results and Discussion

#### 3.1. Organophilization of Nanoparticles

The amount of surface modifier was determined for the organophilized mica-like fluorohectorite (O/K-hect) using thermo-gravimetric analysis. The resulting values as well as the mean particle sizes and aspect ratios are given in table 1. Silica particles were used as received in the DGEBA matrix.

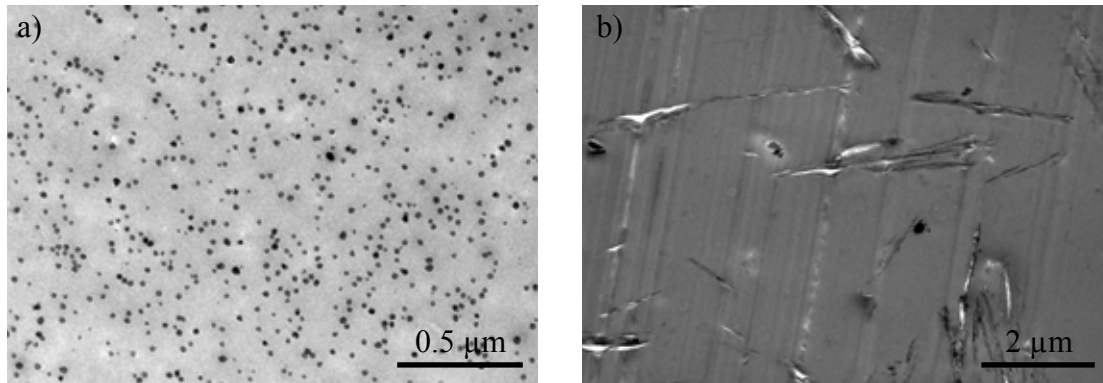
Particle	Amount of surface modifier / wt%	Mean length / nm	Intergallery distance / nm	Mean aspect ratio / $\mu\text{m}$
O/K-hect	4.4	4000	0.99	400
Silica	not determined	20 [3]	- (amorphous)	1

**Table 1.** Nomenclature and properties of the different nanofillers, employed.

#### 3.2. Morphology

TEM micrographs presented in Figure 1 clearly reveal the homogeneous dispersion of the nanosilica particles. Furthermore, the morphology of the O/K-hect nanocomposites is characterized by the very large fluorohectorite tactoids, well dispersed in the epoxy matrix. Additionally, the high aspect ratio and equal tactoid thickness of the O/K-hect particles are observable. Furthermore, the intergallery distance of the clay tactoids is analyzed by using powder x-ray diffraction measurements, revealing no intercalation during dispersion and curing process (Table 1). It is noteworthy that O/K-hect particles are modified solely on the external surfaces, since the internal planes are not accessible due to the collapsed structure of

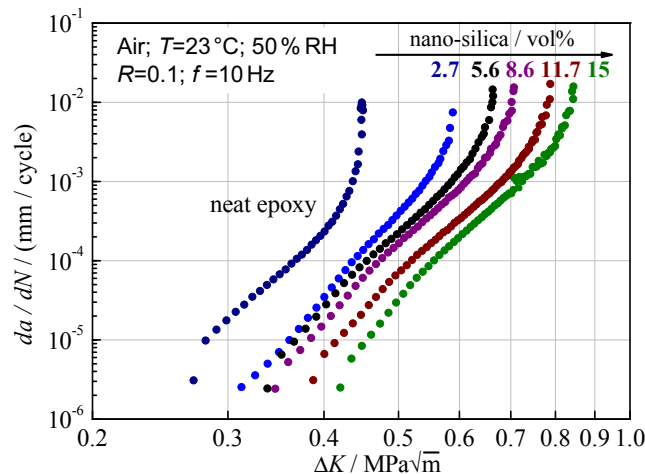
the galleries. Consequently, due to the smaller intergallery distance the shear stiffness of O/K-  
hect is much higher compared to conventional expanded or intercalated organoclays [13].



**Figure 1.** Transmission electron micrographs of the nanocomposites filled with a) 2.7 vol% SiO<sub>2</sub>, and b) 2.2 vol% O/K-hect.

### 3.3 Fatigue Crack Propagation

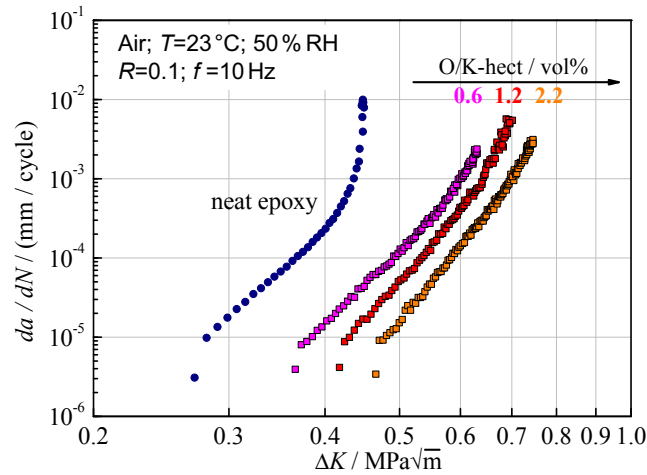
The effect of silica nanoparticles on fatigue crack propagation (FCP) behavior of the epoxy nanocomposites is shown in Figure 2. An improved crack resistance with increasing nanosilica loading is observed.



**Figure 2.** Fatigue crack propagation behavior of epoxy/silica nanocomposites (2.7 to 15 vol%).

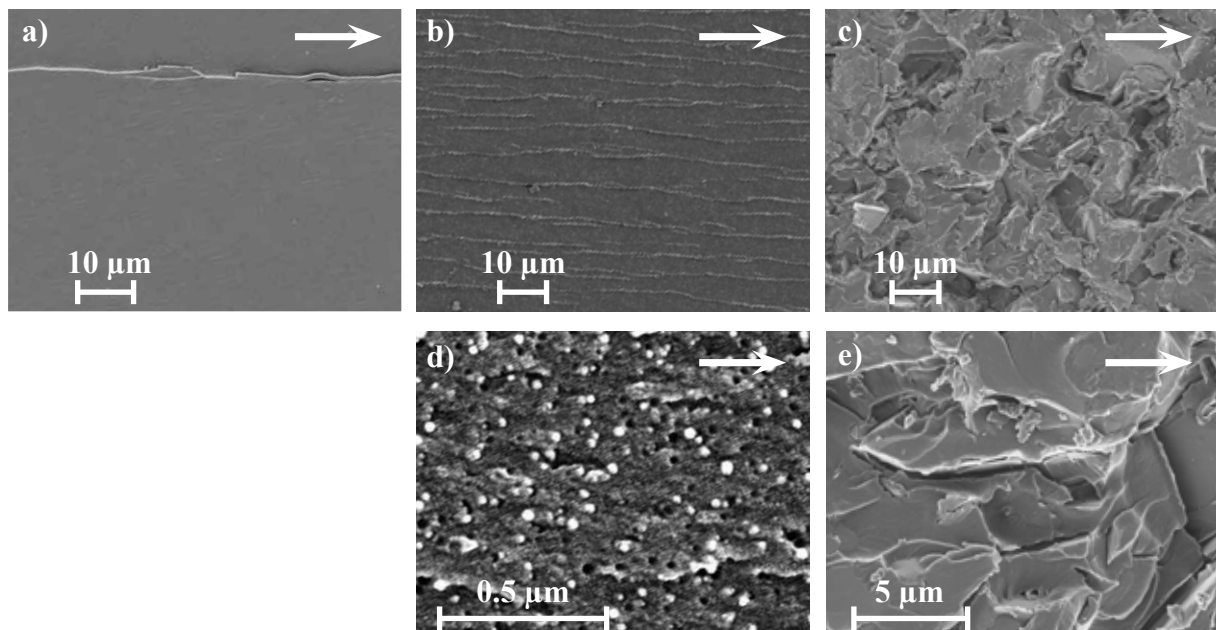
The threshold value of crack propagation ( $\Delta K_{th}$ ) and the material behavior under critical failure ( $\Delta K_{cf}$ ) are improved. At 15 vol% an improvement of 66 % in  $\Delta K_{th}$  and 88 % in  $\Delta K_{cf}$ , is obtained. The fracture surfaces of the nanocomposite containing 5.6 vol% nano-silica (Figure 4b and d) reveal particle debonding and plastic void growth as the main toughening mechanisms, combined with an enhanced shear yielding of the matrix. According to the model of Irwin [2], describing the increasing diameter of the plastic zone ( $d_p$ ) with respect of  $\Delta K$  ( $d_p \sim \Delta K^2$ , eq. (2)), the number of silica nanoparticles ( $n$ ) contributing to toughening increases, following a power law with the exponent of 6 ( $n \sim \Delta K^6$ ), being reflected in the more pronounced FCP improvement at higher crack propagation rates. This is also reflected in the reduction of the slope ( $m$ ) in the Paris regime (eq. (1)).

The role of O/K-heckt on FCP behavior of the epoxy nanocomposites is shown in Figure 3. An improved crack resistance with increasing O/K-heckt loading is already pronounced at very low amounts (0.6 vol%).



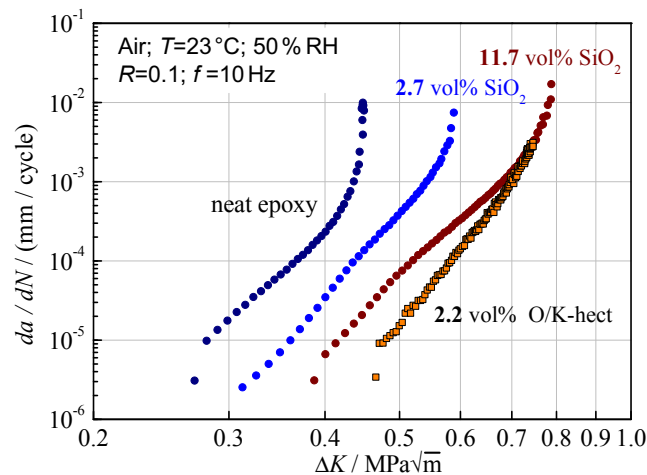
**Figure 3.** Fatigue crack propagation behavior of O/K-heckt nanocomposites (0.6 to 2.2 vol%).

The characteristic values  $\Delta K_{th}$  and  $\Delta K_{cf}$  are improved by 73 % and 67 % by adding 2.2 vol% O/K-heckt. The fracture surfaces (Figure 4c and e) of the nanocomposite (2.2 vol% O/K-heckt) reveal a very tortuous fracture surface, attributed to strong crack deflection and crack pinning, provoked by the large lateral particle size. Obviously, on a microscopic scale the crack is forced to propagate along the interface between the epoxy resin and the clay tactoids (particle debonding). As a consequence of the specific orientation and the high aspect ratio of the clay tactoids, the crack is deflected locally, increasing the crack path length and leading to an enlargement in the newly formed fracture surface (Figure 4e). Particle cleavage was not observed since the filler/matrix adhesion is regarded being moderate. The aliphatic dodecyl-tails of the surface modifier show neither entanglements, nor form any covalent crosslinking with the thermosetting matrix.



**Figure 4.** Fracture surfaces (SEM) of the different nanocomposites in the region of stable crack growth, a) neat epoxy, b) and d) nano-SiO<sub>2</sub> nanocomposites, c) and e) O/K-heckt nanocomposites.

In order to evaluate the influence of the differently shaped nanoparticles, a comparison of nanocomposites containing 2.7 vol% respectively 11.7 vol% nanosilica and 2.2 vol% O/K-hect is shown in Figure 5.



**Figure 5.** Comparison of the fatigue crack propagation behavior of nano-silica and O/K-hect filled epoxy.

Comparing the nanocomposites containing comparable nanofiller contents (2.7 vol% nanosilica respectively 2.2 vol% O/K-hect) the dependency of the FCP behavior on the stress intensity of the nanosilica and the O/K-hect nanocomposites, as expressed by the shape of the FCP curves, is similar. Although the toughening potential of the larger O/K-hect is more prominent, since  $\Delta K_{th}$  and  $\Delta K_{cf}$  are improved more significantly. Estimating and comparing the number of particles and their corresponding particle surface area in a reference volume, using the geometrical parameters of the fillers (table 1) reveals a much higher number (30'000 x) and surface area (1.5 x) in the case of nanosilica as compared to O/K-hect. Despite the lower number of particles and surface area, the toughening effect is more pronounced in the case of O/K-hect. Leading to the conclusion, toughening dominated by crack deflection in the case of O/K-hect is more effective compared to particle debonding, in the case of nanosilica.

In the region of unstable crack growth ( $\Delta K_{cf}$ ), the addition of 11.7 vol% nanosilica exhibits a crack resistance improvement, being comparable to the addition of 2.2 vol% of O/K-hect. Whereas the toughening efficiency of the nanosilica is less pronounced in the region of crack initiation ( $\Delta K_{th}$ ) and stable crack propagation (Paris regime). This phenomenon, accessible by fatigue crack growth experiments cannot be observed by quasi-static fracture toughness experiments investigating solely critical crack growth. In the region of crack initiation, the diameters of the plastic zones, determined according to the theory of Irwin (eq. (2),  $\sigma_y = 82$  MPa), are approx. 2  $\mu\text{m}$  and 4  $\mu\text{m}$  in the case of nanosilica (11.7 vol%) and O/K-hect (2.2 vol%) respectively. Due to the large average lateral extension of the O/K-hect (4  $\mu\text{m}$ ), the plastic zone can be completely spanned by a single tactoid, decelerating the propagation of damage zone at the crack tip. Additionally, for complete debonding of an O/K-hect, multiple fatigue cycles are necessary, since the crack propagation per cycle ( $da/dN$ ) is in the sub-micron range. At higher  $\Delta K$ , i.e. with increasing plastic zone size, several O/K-hect particles are required for effective crack deflection. Whereas in the case of nanosilica, the effectivity of debonding is multiplied due to the tremendously increased number of particles in the enlarged plastic zone, contributing to toughness enhancement by debonding. These mechanisms clearly explain the distinctive dependencies on  $\Delta K$  (stages of fatigue crack growth) applied towards the enhancement of crack resistance of the nanofillers, possessing variations in the geometry.

#### 4. Conclusion

In this study, surface modified spherical nanosilica and K-fluorohectorites (O/K-lect), characterized by large lateral extensions and aspect ratios, were employed to analyze the effect of geometrical appearance on the fatigue crack growth (FCG) behavior of an epoxy resin. The addition of nanosilica improved the FCG behavior by nanoparticle debonding and subsequent plastic void growth. The number of particles contributing to toughening increases remarkably with rising  $\Delta K$  due to plastic zone enlargement. The improvement in crack propagation resistance by the use of the large O/K-lect, even at very low amounts (0.6 vol%) has to be highlighted. The main toughening mechanism is crack deflection due to the large lateral extension being in the range of the plastic zone size. Especially in the region of crack initiation and stable crack propagation, the clay tactoids reduce the propagation of the damage zone in front of the crack tip remarkably, resulting in a hugely enhanced crack resistance of the nanocomposites.

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