
Tailoring the Mechanical Performance of Epoxy Resin by Various Nanoparticles

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SUMMARY

Flexible organic elastomeric nanoparticles (ENP) and two kinds of rigid inorganic silica nanoparticles were dispersed respectively into a bisphenol-A epoxy resin in order to tailor and compare the performance of mechanical properties. It was found that the well-dispersed flexible ENP greatly enhanced the toughness of the epoxy with the cost of modulus and strength. Comparatively, the rigid silica nanoparticles improved Young's modulus, tensile strength and fracture toughness simultaneously. Both fumed and sol-gel-formed nanosilica particles conducted similar results in reinforcing the epoxy resin, although the latter exhibited almost perfect nanoparticle dispersion in matrix. The toughening mechanisms of nanocomposites were further discussed based on fractographic analysis.

1. INTRODUCTION

Polymer nanocomposites are expected to be able to bridge the gap between polymers and ceramics. This is presumably due to the predominant interfacial interaction between nanoparticles and polymer segments, especially when the interparticle distance is reduced and the interphase may activate filler-filler interactions. Compared to polymers with micro- or macro- sized fillers, polymer nanocomposites were found to be able to provide dramatic improvements in various properties. It has been reported that stiffness, strength and toughness can be enhanced simultaneously by well-dispersed nanoparticles in epoxy matrix¹⁻³. However, large surface area induced by nanoparticles usually leads to particle agglomeration in polymer matrix, which may act as defects and result in negative effects on the performance of nanocomposites. Consequently, the properties of

nanocomposites often depend on the size of the effective particles and the degree of distribution rather than the properties of the particles applied.

Processing technique becomes a key challenge in nanocomposite researches and applications. In the past two decades, many excellent works have been done in this aspect. Several techniques have been developed, such as using chemical treatments to modify surface characters of nanoparticles^{4,5}, mixing nanoparticles and polymer into solvent and dispersing them by ultrasonication⁶, or preparing nanocomposites by *in-situ* approaches⁷.

In the present work we have chosen flexible organic elastomeric nanoparticles (ENP) and two kinds of rigid inorganic nanosilica particles to tailor the various mechanical properties of the bisphenol-A epoxy resin. These nanoparticles used were

introduced into the epoxy resin by different processing methods, such as mechanically mixing method or *in-situ* sol-gel technique. Mechanical properties of the nanocomposites were compared as a function of the characteristics of nanoparticles, the dispersion state of nanoparticles as well as the nanoparticle volume contents. In addition the related fracture mechanisms were discussed.

2. EXPERIMENTAL

2.1 Materials and Sample Preparations

The epoxy resin used in this study was standard diglycidyl ether of bisphenol-A resin (DGEBA) with an epoxide value of 0.51, supplied by Wuxi Resin Factory of China. The methyl hexahydrophthalic anhydride (MHHPA) was selected as the hardener produced by Puyang Huicheng Chemical Co. Ltd. The elastomeric nanoparticles (ENP) with a mean diameter of about 90 nm were supplied by SINOPEC Beijing Research Institute of Chemical Industry. The preformed fumed nanosilica particles

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(Aerosil 200, 12 nm in diameter) were provided by Degussa AG. The master batch of nanosilica/epoxy (Nanopox E470) was supplied by nanoresins AG, Germany, which was produced by a special sol-gel technique. The master batch contains 40 wt.% of spherical silica nanoparticles with a mean diameter of about 20 nm in an epoxy matrix that is very similar to DGEBA resin.

For preparing the samples, master batch of each system was firstly composed. The fumed nanosilica/epoxy master batch was obtained by using a high-speed dissolver (VMA Getzmann, Germany), while the ENP/epoxy master batch was prepared by using a three-roll mill (EXAKT, Germany). Thereafter, certain amount neat resin was further added into the master batches in order to reach the desired particles volume content of each system, i.e. 1, 3, 6, 9, 14 vol.%, respectively. Consequently the stoichiometric amount of curing agent was added at 60 °C and then degassed in a vacuum oven for 30 minutes. Once a homogeneously dispersed solution was obtained, the mixtures were then cast into a preheated mold for curing procedure. The curing condition was same for all material systems: 30 min at 90 °C, followed by 60 min at 120 °C, 30 min at 140 °C and then 120 min at 160 °C.

2.2 Characterizations

2.2.1 Morphology

Thin section specimens of the nanocomposites, approximately 60–90 nm thick, were cut from a mesa of about 1 × 1 mm² and collected on 200 mesh copper grids in a trough filled with water. The morphology of SiO₂ and ENP nanoparticle dispersion in the epoxy matrix was examined by transmission electron microscopy (TEM; FEI Tecnai20).

High resolution SEM was performed on the fracture surfaces of the tensile samples with a HITACHI S-4300 microscope equipped with field

emission. Typically, the acceleration voltage was set at 10 kV. All specimens were coated with an approximate 10 nm thick gold layer before observation.

2.2.2 Mechanical Properties

The tensile tests were conducted using an Instron 5848 micro-Tester according to the standard ASTM D-638. The test velocities were kept constant at 1 mm/min and the strain in the gauge length was measured using a clip-on extensometer.

2.2.3 Fracture Toughness

Compact tension approach was used to evaluate fracture behavior of the modified epoxies, with a specimen dimension of 12 × 36 × 36 mm³ (thickness × length × width). A pre-crack was made by lightly tapping a fresh razor blade into the bottom of the saw slot in the specimen. By this technique, the crack can pop into the material over several millimeters, thus yielding a very sharp natural crack. At least five specimens were tested for each formula. All tests were performed on the Instron 5548 testing machine. The crosshead rate was 1 mm/min. The actual initial crack length was measured after the fracture test by an optical microscope equipped with a micrometer scale. The fracture toughness, K_{IC} , was calculated. The value of G_{IC} could be calculated from the values of K_{IC} and E , referring to the reference⁸. The value of the fracture energy, G_{IC} , was calculated by equation 1:

$$G_{IC} = \frac{K_{IC}^2}{E} (1 - \nu^2) \quad (1)$$

Where E is the modulus of elasticity obtained from the tensile tests, and ν is the Poisson's ratio of the polymer, taken as 0.35 suggested in the literature⁹.

3. RESULTS AND DISCUSSION

3.1 TEM

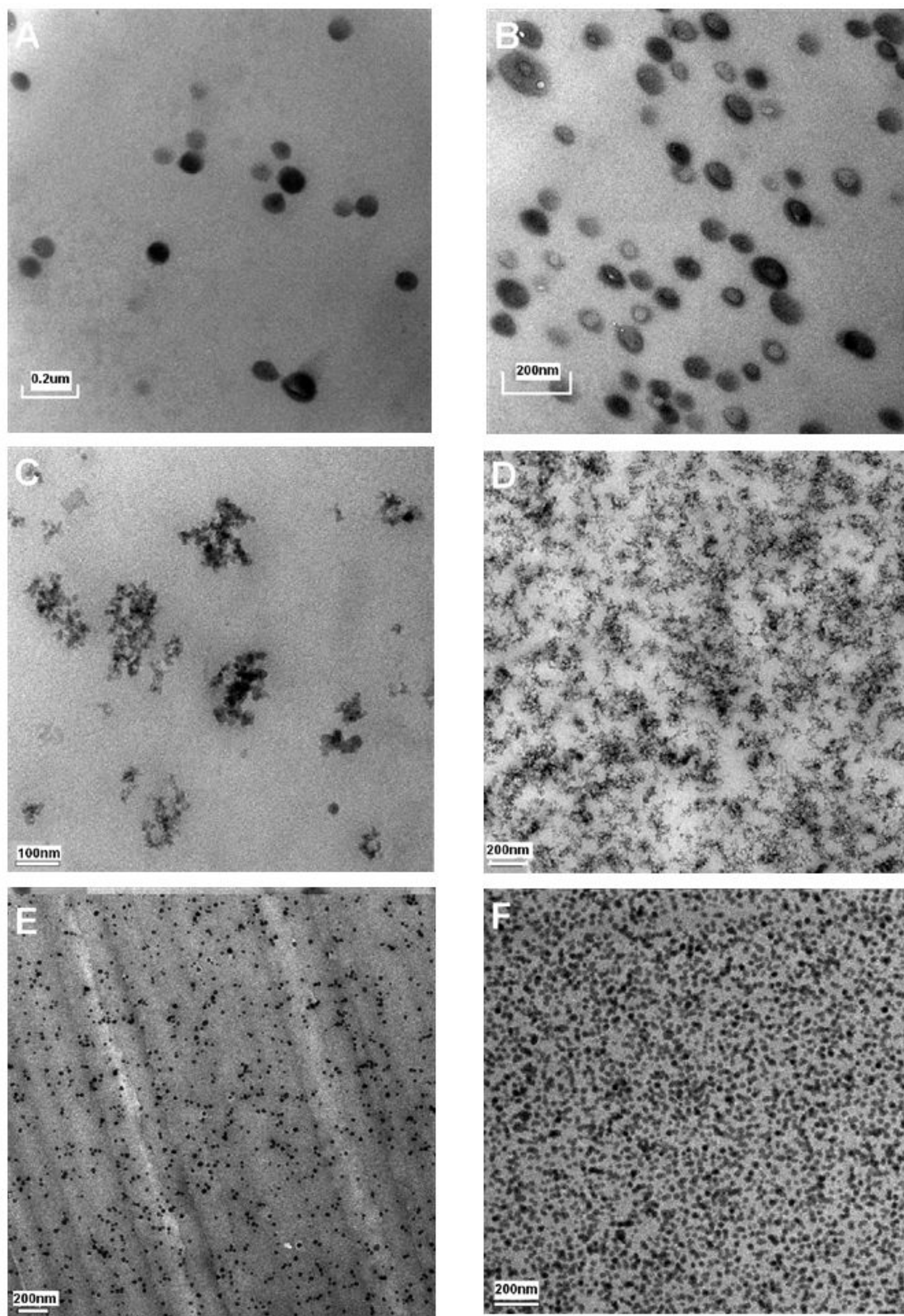
The dispersion states of nanoparticles in polymer matrix have a significant influence on the mechanical performance of composites^{10,11}. **Figure 1** shows the typical TEM images of nanoparticles filled polymer matrix at varied volume contents. As given in **Figures 1a** and **1b**, the ENP nanoparticles with an average diameter around 100 nm were almost homogeneously dispersed in epoxy matrix from 1 vol.% up to 6 vol.%. Mechanically dispersed fumed nanosilica particles with an average diameter of 12 nm are not performed as single particles but clusters. The diameter of the clusters is around 100 up to 200 nm shown in **Figures 1c** and **1d**. The special sol-gel technique sounds the best solution of particle dispersion in the current cases, performed almost perfectly single nanosilica particles (with a diameter of 20 nm) in epoxy matrix as given in **Figures 1e** and **1f**.

3.2 Mechanical Properties

3.2.1 Tensile Properties

Figure 2a shows typical stress-strain curves of nanocomposites at 6 vol.% of filler content. As compared to neat epoxy, the improved Young's modulus and tensile strength were observed for nanosilica particles without trading off the failure strain. Unlike the nanosilica/epoxy systems, decreased modulus and tensile strength were found for ENP nanocomposites. It is clear that the stiffness of nanoparticles is one of the key factors which influence the mechanical performance of nanocomposites. Moreover, the obtained modulus and strength are straightly dependent on the volume fraction of nanoparticles as shown in **Figures 2b** and **2c**. The improvement in Young's modulus of nanosilica/epoxy nanocomposites by the high-speed mixing could reach up to 17% for 6 vol.% of nanosilica, while about

Figure 1. TEM images of epoxy nanocomposites. A: 1 vol. % ENP; B: 6 vol. % ENP; C: 1 vol. % fumed nanosilica; D: 6 vol. % fumed nanosilica; E: 1 vol. % nanosilica prepared by sol-gel technique; F: 6 vol. % nanosilica prepared by sol-gel technique



10% increase of tensile strength at the same volume fraction shown in **Figure 2c**. **Table 1** summarizes the tensile test results of ENP and silica based nanocomposites.

Many theoretical models have been developed in order to predict the Young's modulus of particle-modified polymers. One of the most commonly

used models is Halpin-Tsai model¹². This model gives the modulus of the composites as a function of the modulus of the matrix polymer, E_m , and of the particles, E_f , as well as a function of the aspect ratio by the shape factor of fillers based on several assumptions, such as perfect bonding between nanoparticles and matrix and no agglomeration in nanocomposites.

The predicted composite modulus E_c can be written as:

$$E_c = \frac{1 + \eta \zeta V_f}{1 - \eta V_f} E_m \quad (2)$$

where ζ is the shape factor, V_f is the volume fraction of fillers, and

$$\eta = \left(\frac{E_f}{E_m} - 1 \right) / \left(\frac{E_f}{E_m} + \zeta \right) \quad (3)$$

Halpin and Tsai pointed out that the value of ζ must lie between zero and infinity. They suggested that the value of ζ should correlate with the geometry of the reinforcing phase, especially with the aspect ratio (w/t) of the fillers, where w is the length of the filler and t is its thickness. They recommended using $\zeta = 2$ for the modulus perpendicular to the loading direction. For the spherical particles used in the present work the aspect ratio is unity, and hence $\zeta = 2$ was used. **Figure 2b** presents the predictive results of both SiO_2 /epoxy systems using the Halpin-Tsai model. The very good agreement between the predictions and experimental data indicated that the uniform dispersion and the good bonding between nanosilica and matrix were achieved.

In contrast with the increased ENP content, a different tendency was shown in **Figure 2b** on the stiffness of nanocomposites. As expected, Young's modulus of ENP/epoxy decreased with the addition of ENP, which was ascribed to the soft nature of the filler. The Young's modulus decreases straightly from 3.11 GPa of neat epoxy down to 2.4 GPa when 9 vol.% of ENP was added. Correspondingly, the tensile strength dropped by about 25% from 82.6 MPa of the neat matrix to 62.4 MPa of 9 vol.% ENP/epoxy. This is consistent with the results in the literature¹³. As rubber possessed lower tensile strength comparing with epoxy, the increased resin ductility induces an increased shear deformation, which resulted in a linear decline of tensile strength of ENP/epoxy nanocomposites.

Figure 2. Typical stress-strain curves (with 6 vol.% nano-fillers) and normalized properties of nanocomposites filled with different nanoparticles. In Figure 2B the solid line is predicted by using the Halpin-Tsai model, and the dash line is predicted by using the rule of mixtures

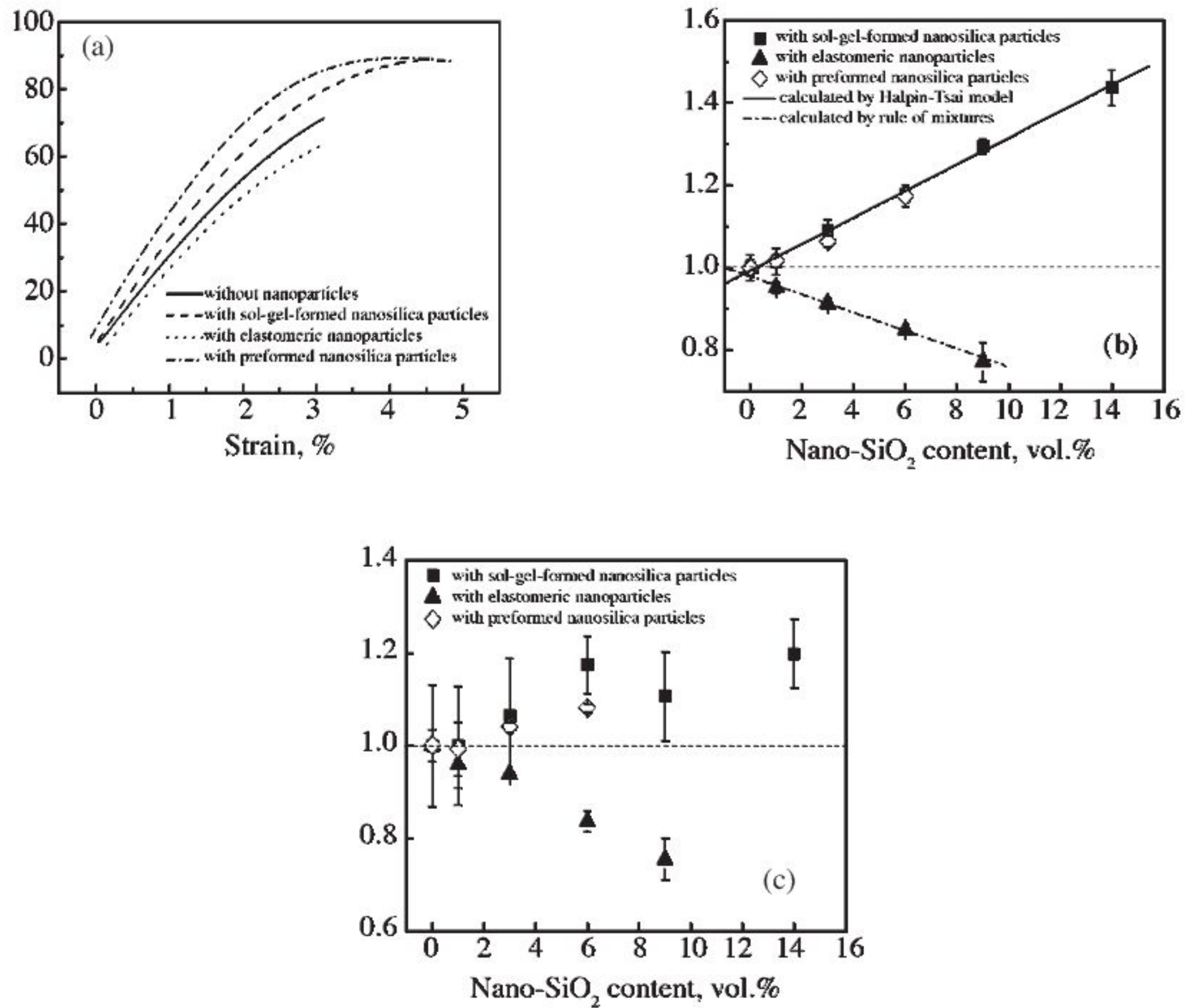
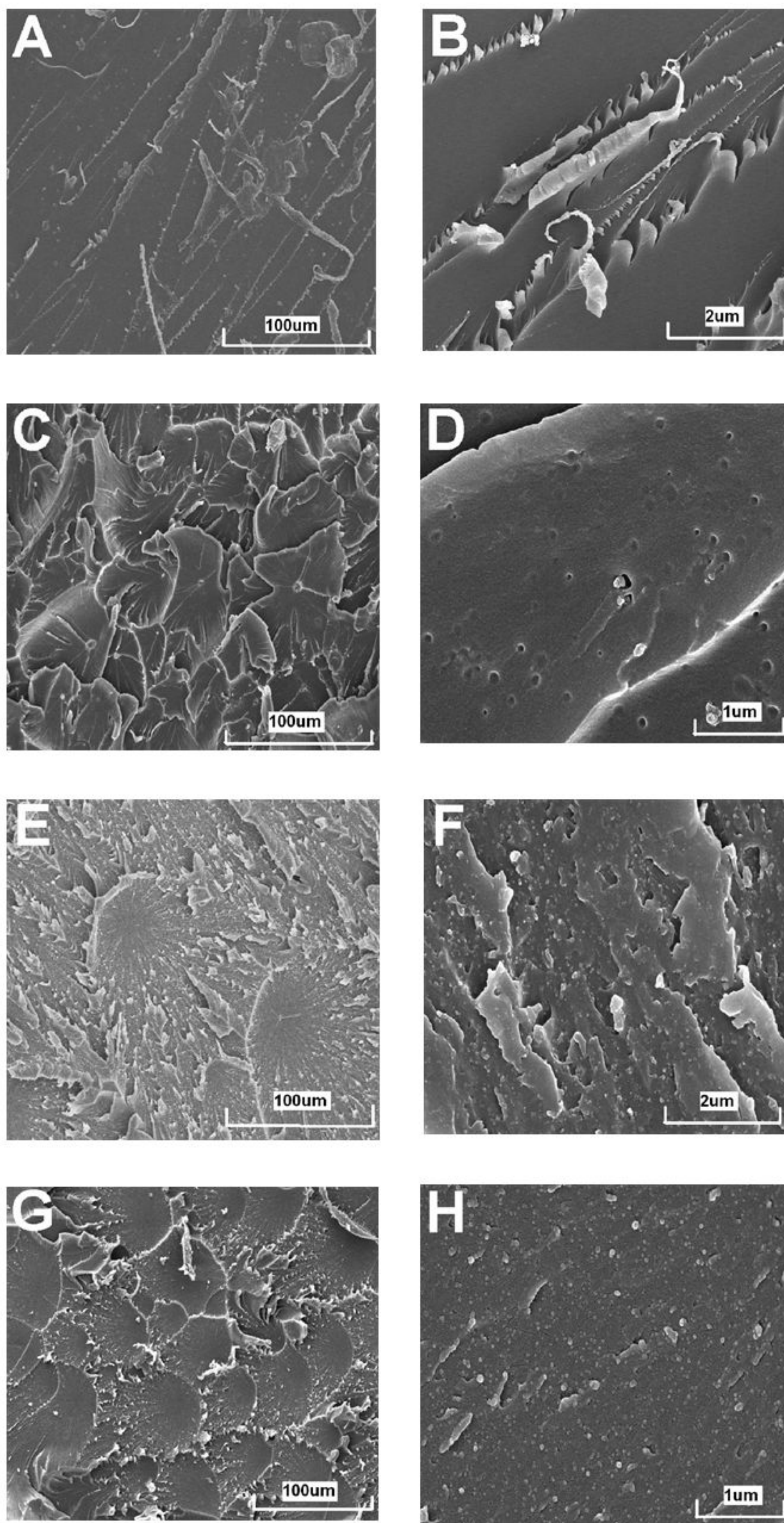


Table 1. Mechanical properties of nanocomposites

Samples	Content [vol.%]	Modulus [GPa]	Strength [MPa]	Strain [%]	K_{IC} [MPa·m ^{1/2}]	G_{IC} [J/m ²]
ENP	0	3.11±0.10	82.6±2.8	3.9±0.5	0.66±0.06	124.8
	1	2.96±0.04	79.3±4.3	4.6±1.1	0.82±0.05	189.7
	3	2.84±0.04	77.5±0.3	5.7±1.0	1.12±0.07	371.9
	6	2.64±0.03	69.1±1.9	4.1±0.6	1.26±0.07	492.9
	9	2.4±0.15	62.4±3.8	6.1±1.6	1.45±0.05	695.9
Fumed nanosilica	0	3.11±0.10	82.6±2.8	3.9±0.5	0.66±0.06	124.8
	1	3.16±0.04	81.9±4.8	4.4±1.4	0.76±0.07	161.7
	3	3.31±0.04	85.9±0.9	5.3±0.6	0.85±0.04	192.0
	6	3.65±0.08	89.2±0.7	4.5±0.8	0.98±0.07	231.3
Nanosilica prepared by sol-gel technique	0	2.75±0.05	73.5±9.6	3.5±1.1	0.55±0.12	95.1
	1	2.79±0.09	73.5±9.4	3.2±0.9	0.57±0.11	102.8
	3	3.00±0.07	78.2±9.1	3.8±1.4	0.68±0.05	135.9
	6	3.24±0.04	86.3±4.6	4.0±0.7	0.71±0.05	138.0
	9	3.56±0.05	81.4±7.0	3.0±0.6	0.75±0.05	137.2
	14	3.95±0.12	88.1±5.4	3.2±0.6	0.83±0.05	154.1

Figure 3. SEM images of tensile fracture surfaces of epoxy nanocomposites. A and B: neat epoxy resin; C and D: 6 vol.% ENP; E and F: 6 vol.% fumed nanosilica; G and H: 6 vol.% nanosilica prepared by sol-gel technique



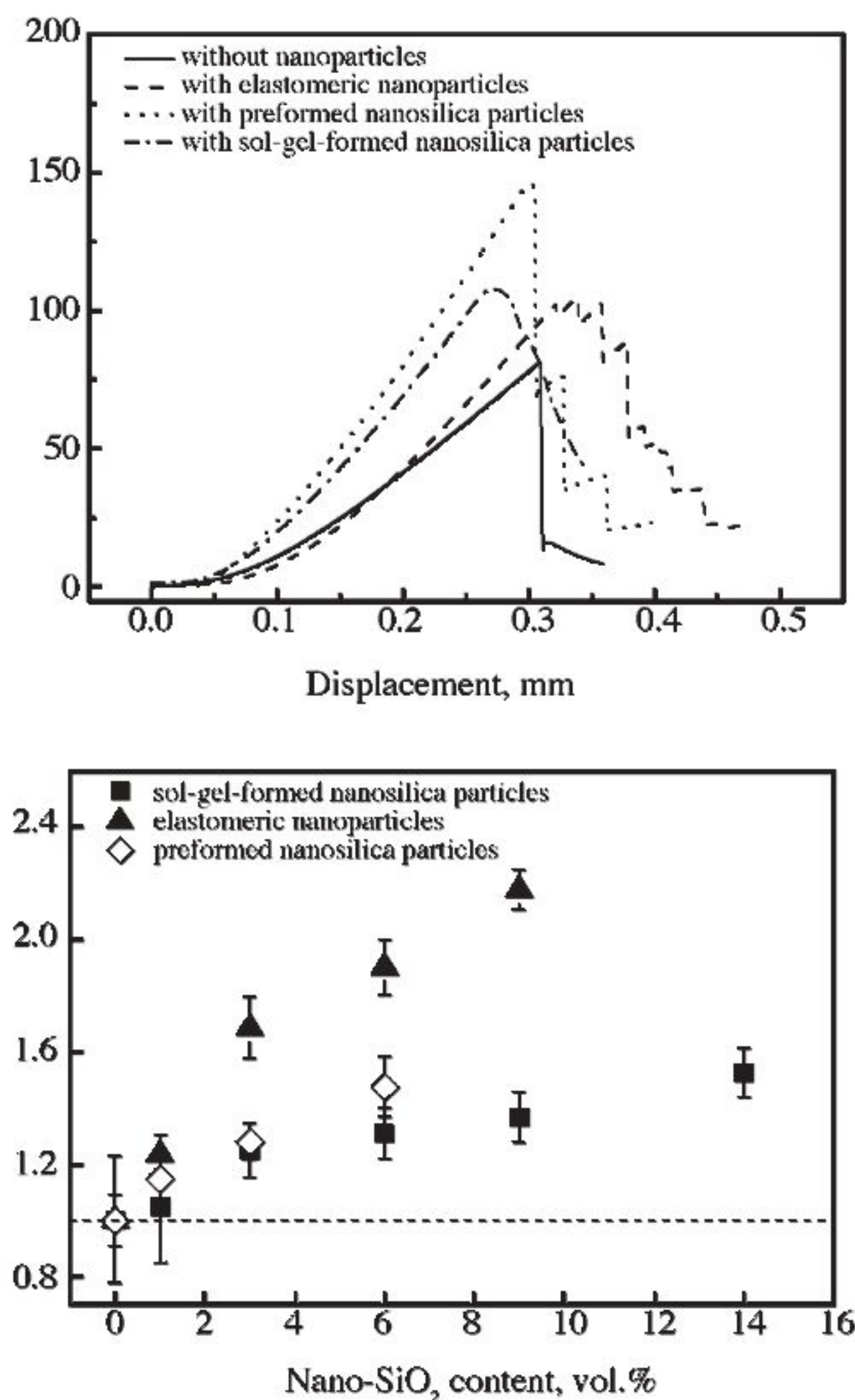
3.2.2 Morphology of Fracture Surface

SEM fracture photographs of tensile test specimens partly reflect some fracture mechanisms of these nanocomposites. **Figure 3a** shows the typical brittle fracture surface of the neat epoxy with ribbons and fracture steps and rather smooth areas in between. However, the addition of ENP yields a much rougher fracture surface and a lot of lotus-leaf shape dimples can be observed. It can also be seen that there were a large number of voids and debonding phenomenon in epoxy matrix as shown in highly magnified image (**Figure 3d**). By contrast, the fracture surface of nanosilica/epoxy composites was rougher and a lot of dimples increases as a function of increasing content of nanosilica, seen **Figure 4e**. The typical size of single granule on fracture surface is about 40 nm (**Figure 3f**). Compared to the average diameter of the nanosilica (12 nm by the high-speed mixing, 20 nm by the sol-gel technique), these granules had a bigger mean size, which indicated that nanoparticles would have a polymer shell. Thus relatively good particle-matrix adhesion is expected and this shell should finally affect the properties of nanocomposites.

3.2.3 Fracture Toughness

Figure 4a shows the typical load-displacement curves of pre-notched compact tension (CT) specimens for 6 vol.% nanosilica-filled composites and neat matrix, respectively. Compared to the neat resin, both ENP and nanosilica modified epoxies dispersed by high-speed mixing underwent unstable crack propagation when the maximum load was reached. However for the nanosilica/epoxy system prepared by the sol-gel method, in spite of the very sharp natural pre-cracks in the specimens, nearly no stick-slip behavior was observed during the whole measurement period of each specimen. It is clear, in the present study, that epoxy can be toughened more or less by all

Figure 4. The fracture toughness of nanocomposites filled with different nanoparticles. A: typical load-displacement curves of CT samples of the nanocomposites (with 6 vol. % nano-fillers); B: normalized K_{IC} values of the nanocomposites



these three types of nanoparticles. **Figure 4b** shows the normalized fracture toughness as a function of nanoparticle volume fraction. The toughening efficiency was realized for both types of nanocomposites. Furthermore the improved fracture toughness, K_{IC} , depended strongly on the volume fraction of nanoparticles in the matrix. 9 vol.% ENP contributes about 120% improvement in toughness, while the same amount of SiO₂ yields only about 30% improvement. Such variation further indicated that different toughness mechanisms between rigid and soft fillers.

In general, for ENP nanocomposites, nano-rubber particles dispersed in the epoxy matrix can act as cores for dissipation of mechanical energy by cavitations and shear yielding. ENP particle/resin debonding could be considered as the most important mechanisms for the high fracture toughness of the modified epoxy resins. For rigid inorganic fillers, numerous studies have shown that the toughening effect has rather complicated aspects. The crack front bowing, enhanced matrix shear yielding and micro-cracking pinning effect of rigid particles

has been considered as the major toughening mechanisms^{14,15}. But those mechanisms might not be suitable for the epoxy/nanoparticles systems because these toughening mechanisms do not take into account the contributions of particle-matrix interphase and the size effect of nanoparticles. Our previous work¹⁶ investigated the correlations between interparticle distance and mechanical properties. We have pointed out that, in case of perfect nanoparticle dispersion, when the nanoparticle volume content reaches up to 7%, the distance between nanoparticles should be smaller than the diameter of nanoparticles. The interphase region may dominate the performance of the nanocomposites. This might due to the fact that nanofillers can influence the epoxy network structure, especially the zone near the surface. Rosso *et al.*¹⁷ also confirmed such core-shell structure with the rigid particle inside and a soft polymer shell.

4. CONCLUSIONS

In this paper flexible organic elastomeric nanoparticles and rigid inorganic silica nanoparticles were dispersed respectively into an epoxy resin in order to study the performance of mechanical properties. The results showed that well-dispersed ENP can greatly toughen the epoxy resins, but with the cost of reduced modulus and strength. Fumed nanosilica/epoxy composites prepared by the high-speed mixing can simultaneously improve the stiffness, strength and fracture toughness of epoxy, which could reach to a similar effect of nanocomposites prepared by the sol-gel technique, although the latter exhibited much better nanoparticle dispersion. The stiffness of nanoparticles is one of the key aspects in this study for improving the mechanical properties of nanocomposites. Different toughening mechanisms of rigid and soft nano-fillers were compared, confirmed by SEM images of fracture surfaces.

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