Fracture behaviours of in situ silica nanoparticle-filled epoxy at different temperatures

Hui Zhang [a], Long-Cheng Tang [a,b], Zhong Zhang [a,*], Klaus Friedrich [c], Stephan Sprenger [d]

[a] National Center for Nanoscience and Technology, 100190 Beijing, China
[b] Department of Modern Mechanics, University of Science and Technology of China, 230027 Hefei, China
[c] Institute for Composite Materials, University of Kaiserslautern, 67663 Kaiserslautern, Germany
[d] nanoresins AG, 21502 Geesthacht, Germany

ARTICLE INFO

ABSTRACT

Fracture behaviours of nanosilica filled bisphenol-F epoxy resin were systematically investigated at ambient and higher temperatures (23 °C and 80 °C). Formed by a special sol–gel technique, the silica nanoparticles dispersed almost homogenously in the epoxy resin up to 15 vol.%. Stiffness, strength and toughness of epoxy are improved simultaneously. Moreover, enhancement on fracture toughness was much remarkable than that of stiffness. The fracture surfaces taken from different test conditions were observed for exploring the fracture mechanisms. A strong particle–matrix adhesion was found by fractography analysis. The radius of the local plastic deformation zone calculated by Irwin model was relative to the increment in fracture energy at both test temperatures. This result suggested that the local plastic deformation likely played a key role in toughening of epoxy.

1. Introduction

Homogeneous and non-agglomerate dispersion of nanofillers in polymers is a major challenge for fabricating polymeric nanocomposites, especially when an attempt of scale-up the dispersing processes from laboratory to industrial level is favored [1]. Due to lower expense and compatibility to the subsistent industrial equipments, the mechanical mixing, i.e. directly introducing nanofiller powder to polymers, becomes one of the most commonly used processing approaches nowadays. Unfortunately, numerous works have found that the traditional mechanical mixing has a great difficulty in the preparation of agglomerate-free nanocomposites. Addition of high loading nanofillers dramatically increases the viscosity of polymer mixture, which hinders its subsequent compounding with fibers using impregnation processes, e.g. resin transfer moulding. Moreover, the micrometer and submicrometer agglomerates in nanocomposites often exert adverse effects on the mechanical properties of pristine polymers, counteract the positive effects of nanofillers. Accordingly, the results obtained from this kind of composites do not represent the properties of real nanocomposites and even lead to some misunderstanding in nanocomposite researches.

In comparison with the mechanical mixing methods, the sol–gel technique introducing nanofillers into pre-polymers by chemical reaction has been proved to be effective in fabricating agglomerate-free nanocomposites [2,3]. With the development of this technique, colloidal nanosilica sols in epoxy resins or acrylate monomers can be commercially produced in large quantities [4]. Owing to the uniform dispersion, narrow size distribution and quasi-spherical shape of nanosilica, the composites prepared may serve as an ideal model material for investigating the structure–property relationship of nanocomposites. In recent years several works have been focused on this kind of sol–gel-formed nanosilica/polymer systems [5–10]. As reinforcements, silica nanoparticles simultaneously improved the elastic modulus, fracture toughness and scratch resistance of polymers without significantly thickening the matrices [3,11]. The enhanced mechanical properties appeared did not attenuate when nanosilica loading was up to 50 wt.% [2]. The silica nanoparticles also caused a much smaller viscosity increase of polymer systems, as compared to the preformed fumed silica [3]. A small amount of silica nanoparticles can modify the adhesion property of rubber-modified epoxy adhesive [5]; in particular, they exhibited a synergistic effect with reactive liquid rubber in toughening epoxy resin [6]. More recently, it was found based on TEM images together with other thermomechanical analyses that the silica nanoparticles shifted the resin/hardener ratio, forming a core–shell structure, which influenced the matrix physicochemical properties to some degree [8]. This finding, from a certain angle, supported our previous hypothesis that with reduction of

* Corresponding author. National Center for Nanoscience and Technology, No. 11 Beiyitiao Zhongguancun, Beijing 100190, China. Tel./fax: +86 10 82545586.
E-mail address: zhong.zhang@nanoctr.cn (Z. Zhang).

Table 1
Mechanical properties of bisphenol-F epoxy nanocomposites

Nanosilica content [vol.%]	Temperature [°C]	Tension property				Microhardness [MPa]	Impact energy [kJ/m²]	K_{IC} [MPa m$^{1/2}$]	G_{IC} [J/m²]
		E [GPa]	σ_y [MPa]	σ_B [MPa]	ε_B [%]				
0	23	3.02 ± 0.20	82.39 ± 1.25	78.98 ± 3.55	4.85 ± 0.75	176.58 ± 1.18	33.70 ± 3.70	0.64 ± 0.07	118.50
	80	2.78 ± 0.01	57.60 ± 0.81	44.09 ± 3.41	5.14 ± 0.65	–	–	0.56 ± 0.04	100.20
1	23	3.22 ± 0.02	82.94 ± 0.50	78.55 ± 3.74	4.98 ± 0.26	180.50 ± 2.45	48.33 ± 1.52	0.65 ± 0.04	115.42
	80	2.90 ± 0.06	59.37 ± 0.14	48.39 ± 5.73	4.36 ± 0.70	–	–	0.64 ± 0.04	122.06
3	23	3.29 ± 0.08	82.43 ± 1.31	78.10 ± 3.68	4.11 ± 0.59	186.39 ± 2.75	49.09 ± 7.67	0.78 ± 0.04	160.57
	80	2.91 ± 0.09	59.72 ± 0.75	45.78 ± 2.21	4.10 ± 0.54	–	–	0.75 ± 0.08	168.63
6	23	3.49 ± 0.03	83.88 ± 1.13	76.15 ± 4.36	3.89 ± 0.39	194.24 ± 6.28	45.27 ± 1.99	0.85 ± 0.02	182.94
	80	3.25 ± 0.03	59.71 ± 0.04	44.61 ± 2.62	4.70 ± 1.21	–	–	0.90 ± 0.07	217.05
7	23	3.67 ± 0.08	83.92 ± 0.83	75.53 ± 3.87	3.83 ± 0.06	194.24 ± 2.55	52.57 ± 4.49	0.89 ± 0.03	189.33
	80	3.19 ± 0.03	60.27 ± 0.23	45.33 ± 3.07	3.91 ± 0.34	–	–	0.99 ± 0.04	267.88
8	23	3.60 ± 0.06	83.80 ± 2.41	78.87 ± 3.32	2.97 ± 0.37	199.14 ± 3.53	42.97 ± 8.24	0.92 ± 0.03	204.97
	80	3.36 ± 0.07	60.68 ± 0.56	48.15 ± 2.79	4.57 ± 1.22	–	–	1.04 ± 0.07	281.75
10	23	3.92 ± 0.11	85.90 ± 0.64	74.65 ± 3.11	3.98 ± 0.06	202.09 ± 4.32	54.78 ± 2.36	0.99 ± 0.03	217.34
	80	3.43 ± 0.07	59.12 ± 0.11	43.81 ± 1.38	4.57 ± 1.34	–	–	1.10 ± 0.08	307.78
13	23	4.13 ± 0.01	83.37 ± 3.99	80.33 ± 2.84	2.99 ± 0.76	214.84 ± 2.35	35.79 ± 8.65	1.03 ± 0.04	225.27
	80	3.73 ± 0.08	59.79 ± 1.04	53.23 ± 6.09	3.00 ± 0.79	–	–	1.12 ± 0.09	295.89
15	23	4.47 ± 0.05	88.94 ± 0.68	82.76 ± 4.21	3.03 ± 0.41	217.78 ± 2.16	43.66 ± 2.76	1.13 ± 0.03	252.95
	80	3.98 ± 0.19	59.18 ± 0.99	45.02 ± 1.26	8.04 ± 3.74	–	–	1.26 ± 0.03	348.15

interparticle distance, the interphase around nanoparticles may construct a three-dimensional physical network dominating the performance of nanocomposites [11].

On the other hand, although sol–gel-formed silica nanoparticles have been reported to toughen different epoxy systems effectively, their toughening mechanisms (i.e. failure modes) have not yet been clear. Various mechanisms have been proposed in literatures, e.g. crack deflection [7], particle debonding and subsequent void growth [9], yielded zone and nano-voids development [10]. These failure modes may occur simultaneously, interplaying with each other and contributing the fracture toughness more or less. Furthermore, the dependency of the type of matrix used and test conditions applied should be considered. It is believed that further elaborate experiments are still needed to deeply understand the toughening phenomena.

In the present work we have chosen a 40 wt.% nanosilica/epoxy masterbatch for preparing a series of epoxy-based nanocomposites with various nanosilica loadings. The major objective is to understand the dependence of fracture behaviours on the nanoparticle loading and test temperatures. Moreover, the toughening mechanisms were discussed, supported by fractography analysis and modeling attempts.

2. Experimental

2.1. Materials and preparation

We chose a bisphenol-F epoxy resin as a matrix (specific equivalent weight of 172 g/equiv). Its K_{IC} value was about 0.64 MPa m$^{1/2}$ (Table 1). A bisphenol-F epoxy masterbatch containing about 40 wt.% of silica nanoparticles (Nanopox F520, specific equivalent weight of 275 g/equiv), and an acid anhydride curing agent (Albidur HE600, specific equivalent weight of 170 g/equiv) were supplied by nanoresins AG, Germany. Silica nanoparticles were formed in situ by a special sol–gel technique. Fig. 1 shows that the nanosilica (8 vol.%) dispersed in the epoxy resin in the form of separated individual spheres. Actually, the agglomerate-free composites can be obtained even at nanosilica loading up to 15 vol.%. The average diameter of silica nanoparticles was about 25 nm measured with TEM. The samples were designated as 'Fx', where 'F' means bisphenol-F epoxy matrix, and 'x' represents the volume fraction of nanosilica in this sample (Table 1). For example, 'F8' means a bisphenol-F epoxy sample containing about 8 vol.% nanosilica particles.
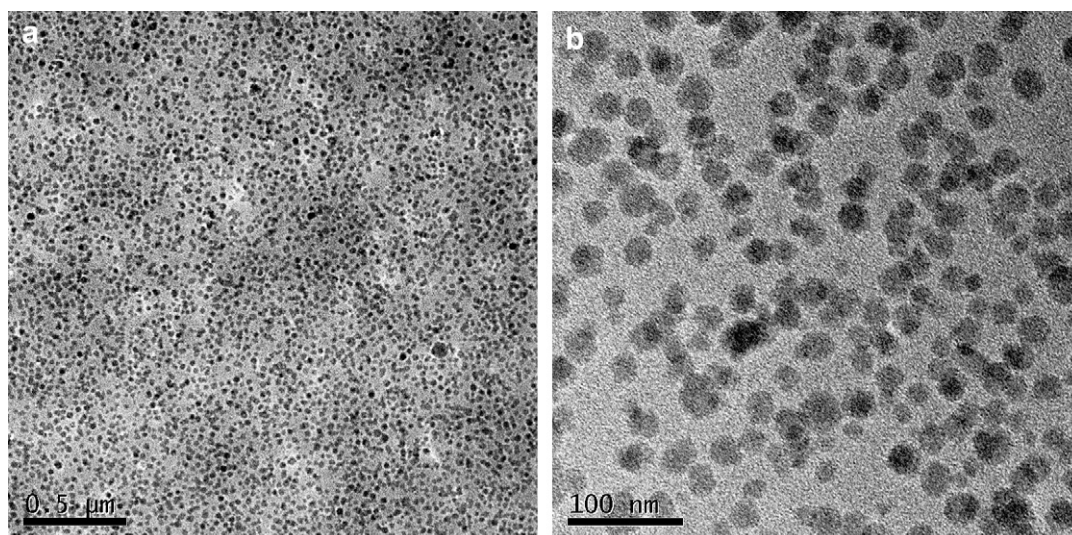

Fig. 1. Transmission electron microscopy (TEM) micrographs taken from epoxy-based nanocomposites with 8 vol.% silica nanoparticles: (a) lower magnification and (b) higher magnification.