

A Toughened Epoxy Resin by Silica Nanoparticle Reinforcement

P. Rosso,¹ L. Ye,² K. Friedrich,¹ S. Sprenger³

¹Institut für Verbundwerkstoffe GmbH, Erwin-Schrödinger-Str. 58, 67663 Kaiserslautern, Germany

²Centre for Advanced Materials Technology, School of Aerospace, Mechanical and Mechatronic Engineering, The University of Sydney, Sydney, NSW 2006, Australia

³hanse chemie AG, Charlottenburger Str. 9, 21502 Geesthacht, Germany

Received 13 April 2005; accepted 13 April 2005

DOI 10.1002/app.22805

Published online 30 January 2006 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Within this study the influence of adding 5 vol % of silica nanoparticles, obtained via a sol-gel process, on an Araldite-F epoxy was investigated. To characterize toughening effects, compact tension specimens were used to obtain K_{IC} and G_{IC} . Additionally, tensile strength and E-Modulus were measured as well as differential scanning calorimetry and dynamic mechanical thermal analysis were carried out to evaluate the influence on the thermal properties of the epoxy because of addition of the particles. Elec-

tronic microscopy was used to check dispersion quality and fracture surfaces, in transmission mode and scanning mode, respectively. The addition of 5 vol % silica-nanoparticles could improve the stiffness and the toughness of an epoxy resin at the same time. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 1849–1855, 2006

Key words: nanocomposites; toughness; thermosets; fracture

INTRODUCTION

In the recent years a lot of research is going on in the field of reinforcing thermoplastic and thermosetting polymers with organic and inorganic nano-sized particles. Focusing on epoxy as a popular thermosetting material, it is well known that the reinforcement due to different types of particles can markedly change the mechanical, thermal, and tribological properties. On the microscale, rubber particles^{1,2} or even microvoids^{3,4} are used to toughen epoxy resin whereas silica particles can be used to improve mechanical properties such as Young's modulus and yield stress.⁵ It is also interesting, that fracture toughness increases with increasing particle size when it ranged in the microscale 2–42 μm .⁶ Further, it is also known, that the bonding of the particles to the matrix, e.g., the interface, can play an important role in the performance of the material, especially at elevated temperatures. The material's behavior is mostly limited when it comes to the phase separation of the particles from the matrix. Therefore, a chemical compatibility is required between the single components, mostly improved by any previous grafting processes. This problems, however, can be overcome since the nanotechnology was introduced to epoxy resins. Nano-sized fillers acting as a part of the microstructure now and interfacial

interactions mainly control the new properties of the materials. This opens a new path to tailor high performance polymeric materials. Zhang et al.⁷ reported a successful application with regard to improving wear resistance by using SiO_2 nanoparticles.

When nanoparticles are used as a reinforcement in polymers, a homogeneous dispersion is required to achieve the above-mentioned effects. As the particles tend to agglomerate, special techniques had to be developed and used to achieve a homogeneous dispersion. One solution is the mechanical mixing using high shear forces for deagglomeration whereas another technique is applying ultrasonic vibration. Chemical methods could be used likewise, such as a sol-gel process, to obtain nanosilica particles filled epoxy.⁸

In this study a silica nanoparticle reinforced epoxy resin (Nanopox F 400, diglycidyl ether of bisphenol A (DGEBA)) provided by hanse chemie AG, Germany, was used. Nanopox® F products are colloidal silica sols in a resin matrix with surface-modified, spherically shaped silica nanoparticles having diameters below 50 nm and an extremely narrow particle size distribution. These nanospheres are agglomerate-free dispersed in the resin matrix. The nanoparticles are chemically synthesized from aqueous sodium silicate solution. In this unique process the binding agent is not damaged, in contrast to processes in which powdered fillers are dispersed with solvents or other equipment using high shear energy.⁹ The OH-groups on the surface of the silica particles are reacted with organosilanes, which are selected regarding the epoxy

Correspondence to: P. Rosso (rosso@ivw.uni-kl.de).

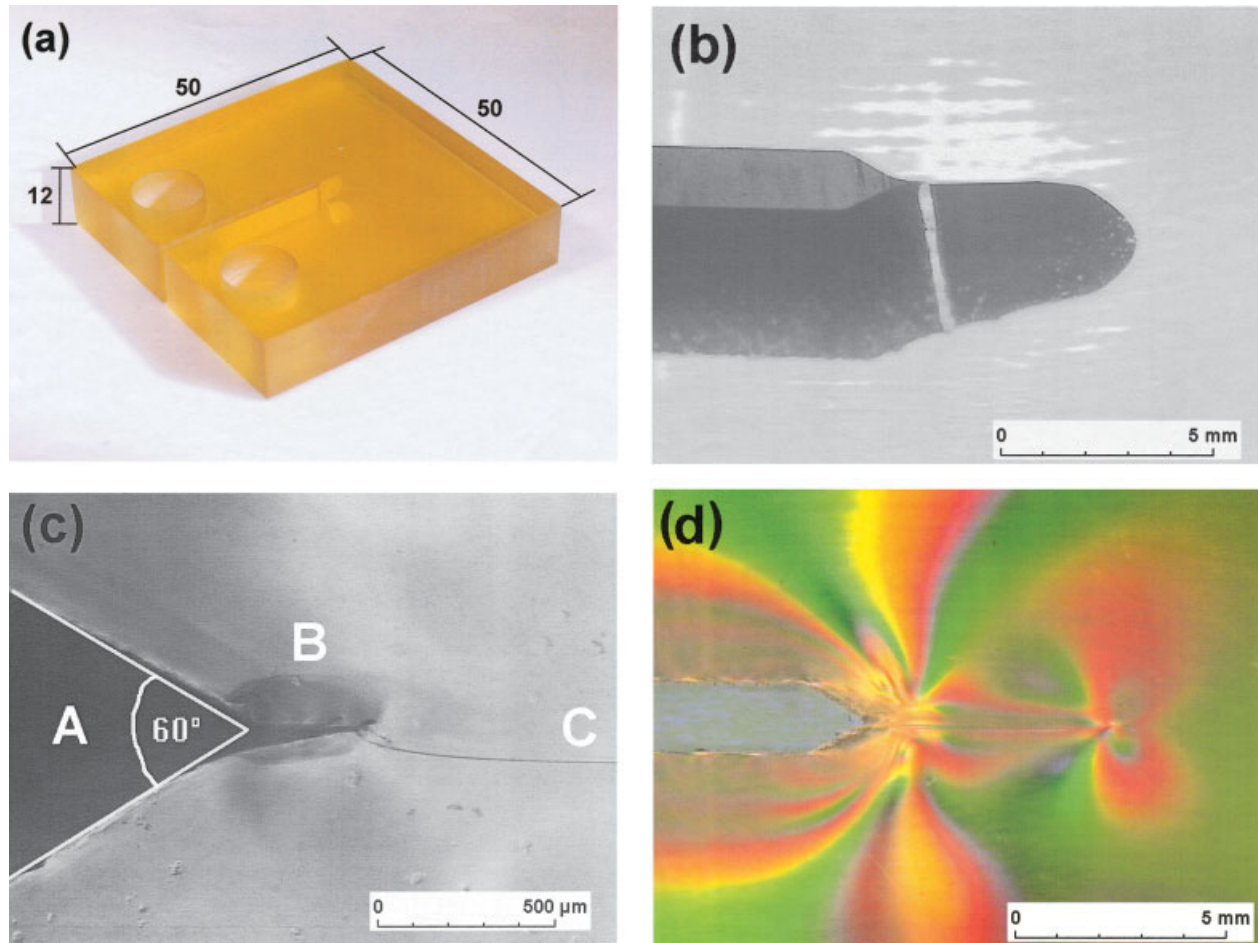


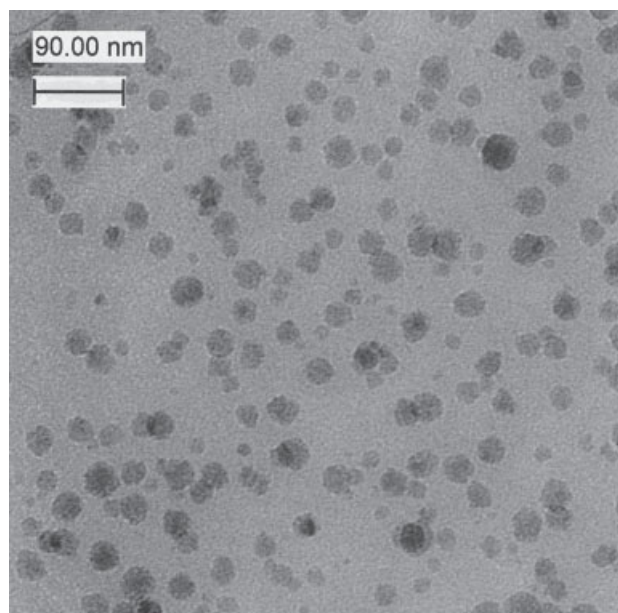
Figure 1 CT-specimen and crack-tip formation due to razor blade tapping. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

in which the particles are incorporated. Thus a hydrophobic organic surface coating is formed.

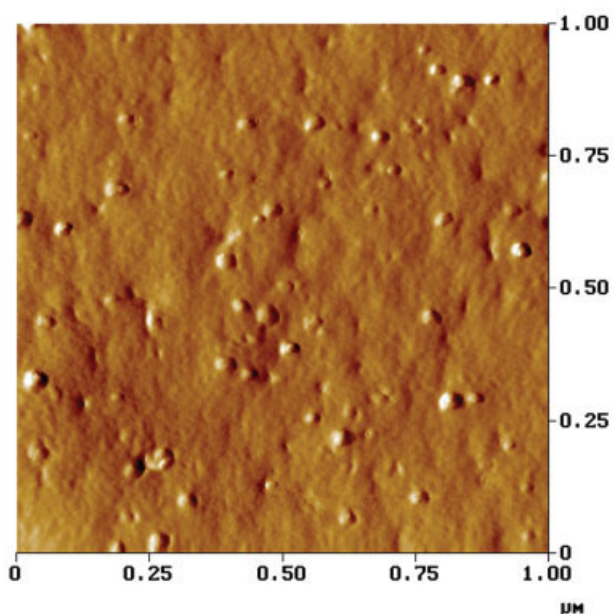
EXPERIMENTS

The raw epoxy resin was Araldite-F, a diglycidyl ether of bisphenol A (DGEBA) resin, produced by Ciba-Geigy, Australia. For the preparation of unreinforced and filled plates, the following procedures were applied: The epoxy liquid was degassed in a vacuum oven (about -100 kPa) at 100°C for about 2 h; then the vacuum was removed and Piperidine (Sigma-Aldrich) hardener was added at a ratio of 100 : 5 by weight while stirring slowly; the resin was then cast into preheated aluminum and silicon molds and cured at 120°C for 16 h. The mold was left in the oven and allowed to cool gradually to room temperature. The stoichiometry between the used hardener and the backing material (DGEBA) in the high concentrated silica nanoparticle reinforced epoxy resin (40 wt %) was considered and balanced. The pure and reinforced-epoxy were mixed using a simple laboratory stirrer for 20 min at room temperature before the degassing step.

Compact tension (CT) specimens were machined from these blades according to ASTM Standard D 5045-02, with a specimen width $W = 50$ mm and thickness $B = 12$ mm. The thickness, which is twice that normally adopted to CT-specimens of polymers in literature, was chosen so as to meet the plain strain criterion. The precrack was introduced to the sample by razor blade tapping, using a specially designed clip holding a fresh razor blade, followed by slightly tapping using a hammer. It was shown in previous work¹⁰ that razor blade tapping is an appropriate method to produce the precrack in pure and rubber-toughened epoxy specimens; it produces the smallest precrack tip radius, hardly causes residual stress around the precrack tip and gives reasonable values of fracture toughness. As the same pure epoxy material was used in this study, similar observations could be detected and verified as explained in Ref. 10. Figure 1(a) shows a global view on the sample with the most important measures. The crack tip zone is enlarged in Figure 2(b), where the natural formation of the crack tip radius can be seen. Figure 1(c) illustrates three sig-



(a)



(b)

Figure 2 (a) TEM and (b) AFM—records of 5 wt % nano-silica-reinforced epoxy. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

nificant zones in the crack tip region: Zone A describes the notch produced by the saw blade (60°), followed from zone B, which shows a bit of plastic deformation caused by the tapping, and finally zone C is shown, the natural precrack tip. Figure 1(d) demonstrates also the state of residual stresses determined by polarised light microscopy. The stress distribution, illustrating through the patterns, shows a high concentration in the plastically de-

formed region, whereas at the crack tip a reasonable residual stress through matrix cooling or shrinkage behavior is given. The approach of the linear elastic fracture mechanics assumes the plastically deformed zone in front of the crack tip to be small compared with that of the crack length. This requirement is fulfilled when razor blade tapping is used to introduce a natural precrack.

Microtensile bars were removed from the silicon molds where no additional trimming was needed except polishing the surfaces. DMA specimens ($60 \times 10 \times 3 \text{ mm}^3$) were also cut from the bigger blades.

The static mechanical and fracture toughness tests were carried out on a universal test machine, Zwick 1474, equipped with a 1 kN/10 kN load cell. The testing speed was kept constant at 1 mm/min for tensile tests and fracture toughness tests.

TA Instruments DMA 2980 (ramp, $2^\circ\text{C}/\text{min}$; frequency, 1Hz; load-amplitude, 10 N) was used in dual cantilever mode and TA Instruments DSC 2920 (ramp, $10^\circ\text{C}/\text{min}$) for recording the heat flow and calculating the glass transition temperature T_g .

RESULTS AND DISCUSSION

As mentioned in the introduction, one of the main criteria to obtain “nano-effects” is the need of a good dispersion of the particles. Figure 2 shows a TEM- and a AFM-micrograph, where a nearly perfect distribution of the particles is obtained. An agglomerate-free state is reached and the observation of five ultra-thin layers showed a good dispersion on each sample. The particle size is exactly in the range of the supplier’s information, namely below 50 nm. If the dots in the TEM-picture are bigger and more black, it means that two or more particles are overlapping in depth direction. It can also be seen that sometimes a white marginalized layer is visible around the particle, which indicates the surface treatment of the particles. The AFM-record additionally approved the particle size and distribution.

Table I shows the results from the tensile and fracture toughness tests. The nanoparticles could not improve the absolute tensile strength of the material

TABLE I
Results of Mechanical and Fracture Toughness Tests

Properties	Araldite-F	Araldite-F + 5% Nano SiO ₂
Tensile strength (MPa)	66.5 ± 0.8	66.6 ± 0.4
Yield strain (%)	7.21 ± 0.5	6.5 ± 0.7
Strength at break (MPa)	65.4 ± 1.4	58.1 ± 4.5
Strain at break (%)	8.09 ± 0.6	8.4 ± 1.2
E-Modulus (GPa)	3.2 ± 0.4	3.9 ± 0.2
K_{IC} (MPa m ^{1/2})	0.967 ± 0.071	1.660 ± 0.110
G_{IC} (kJ m ⁻²)	0.247 ± 0.036	0.596 ± 0.079

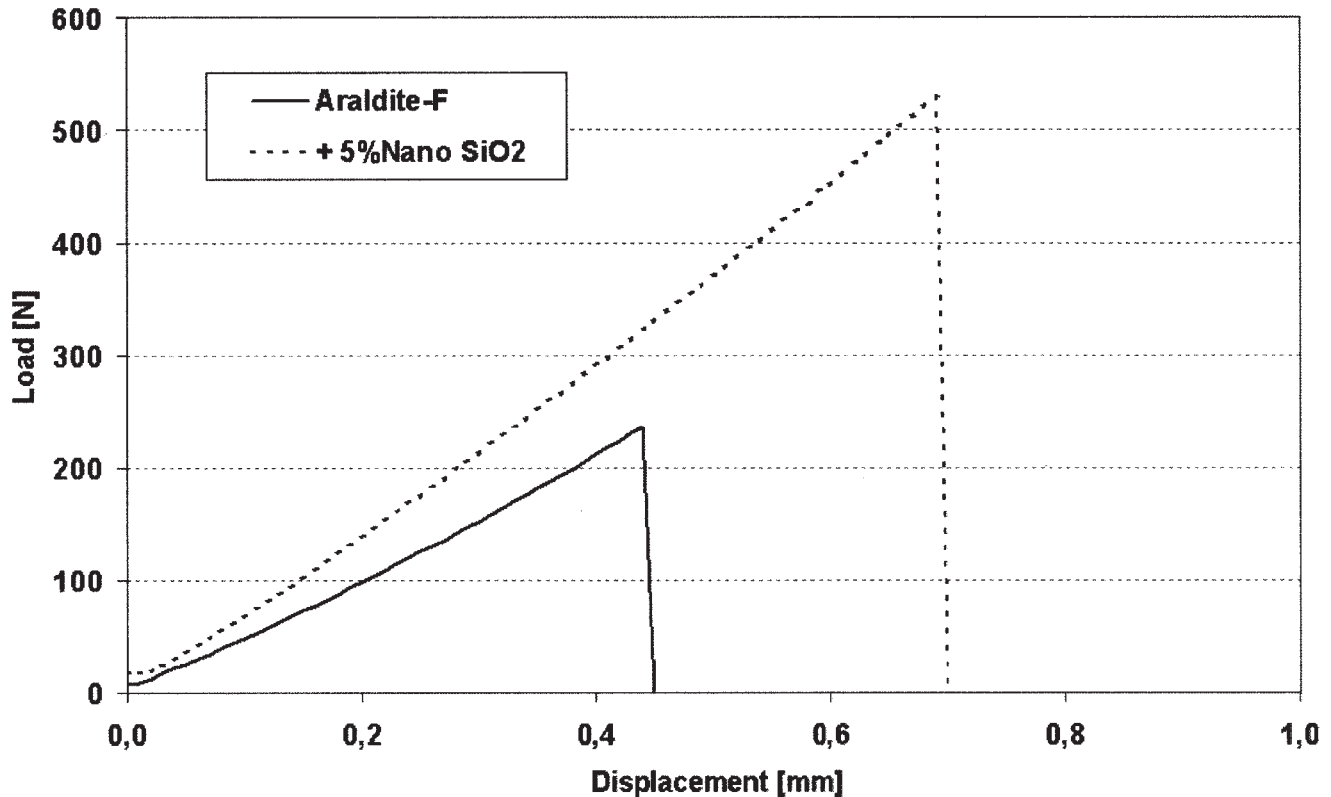


Figure 3 Load-displacement plots during testing of CT-samples.

but affect the yielding behavior. By the addition of 5 vol % SiO_2 the material behaves more ductile and shows a more distinctive yielding zone. At the same time the stiffness could be improved more than 20% as it can be seen from the E-Modulus values. Considering K_{IC} and G_{IC} , the toughness improvement is clearly recognizable. Figure 3 shows exemplarily one load-displacement plot for each material. No stick-slip behavior was observed, rather a fracture in a brittle manner. The reason for the significant increase in toughness can be explained by having a look at the fracture surfaces in Figure 4 (arrow shows the crack tip). In case of the pure epoxy a mirror-like fracture surface is determined. The formation of river line patterns¹¹ is observed to a greater and lesser extent in both cases, the pure and modified epoxy. Local stress concentrations in the resin can be dissipated because of slipping and gliding processes at low testing speeds (1 mm/min). The nanoparticles cause a high deflection of the crack growth and thus increasing the fracture surface. The height and the amount of the pattern steps is markedly increased as the higher magnification at the crack tip region in Figure 4 shows. A further energy absorption mechanism is based on the increase of the matrix plasticity. Shear yielding of the matrix leads to the formation of shear bands. In Figures 5(a) and 5(b) one flow line of the same size is shown for the pure and nano-reinforced epoxy,

respectively. Mostly, they are oriented 45° to the direction of the principal stress. It can be seen that the nano-reinforced epoxy shows a textured surface when it is compared with the very smooth surface of the pure epoxy. Moreover, the neat epoxy shows a step-line fracture whereas at the filled epoxy both stages are connected somehow. The arrows in Figures 5(c) and 5(d) illustrate the sliding of chain segments on a nano-scale provoked through the nanoparticles. A further possible reason for the toughness increase could be particle matrix debonding, in other words, energy consumption at the interface. As the coefficient of thermal expansion is more than five times higher for the epoxy compared with that for the SiO_2 , this mismatch could lead to shrink coating. The resolution of the scanning electron microscope (SEM) is admittedly not high enough to see the single nanoparticles. Nevertheless, it can be concluded that the nanoparticles enhanced the shear deformation of the matrix and thus influence the crack propagation due to the formation of nano- and microscale shear bands.

The differential scanning calorimetry (DSC) measurements provide T_g values of 95 and 89°C for the Araldite-F and the reinforced-Araldite-F, respectively. Additionally, the DMA spectra show that because of the addition of the particles a slight difference in the thermal behavior is recognizable. The graph in Figure 6 shows the increased stiffness

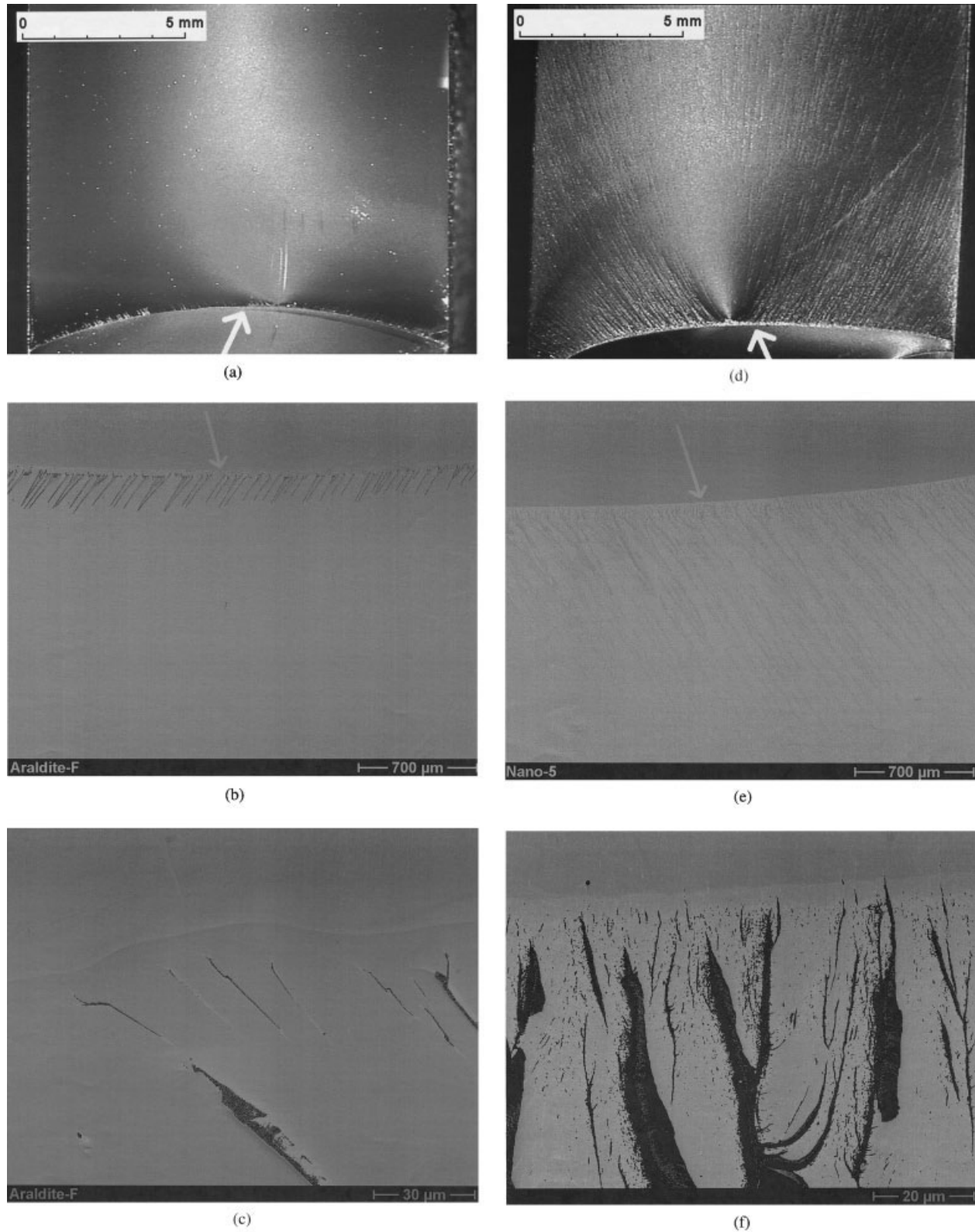


Figure 4 Fracture surfaces after crack opening of CT-samples; left: Araldite-F, right: nano SiO₂-reinforced.

one more time. The β -relaxation peak at -75°C of the nano-reinforced Araldite-F points to some chemical effects caused by the addition of the particles. One

possible explanation could be that the material used for surface modification of the nanoparticles provokes this kind of plasticizer effect in that temper-

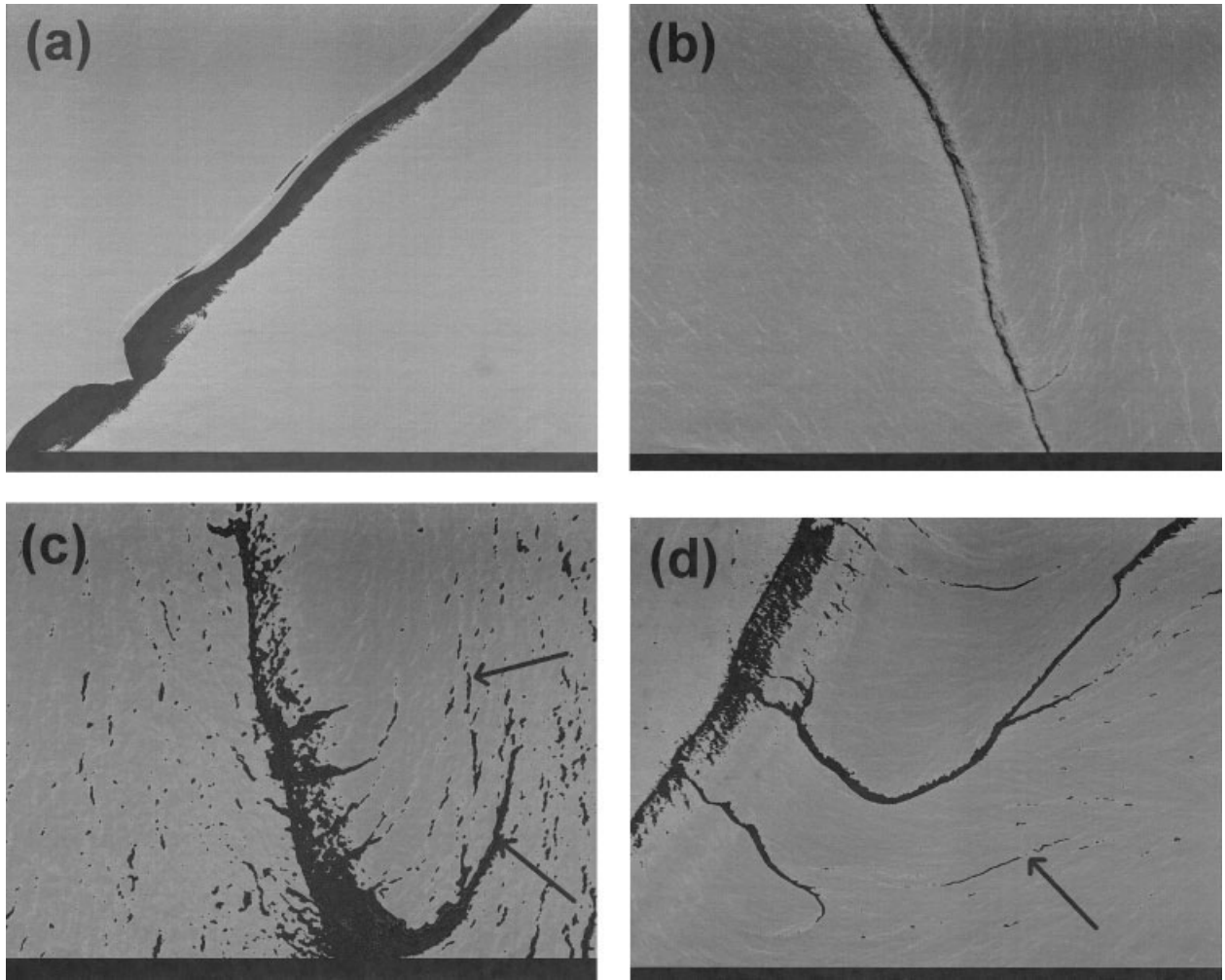


Figure 5 High magnification SEM at the crack tip zone.

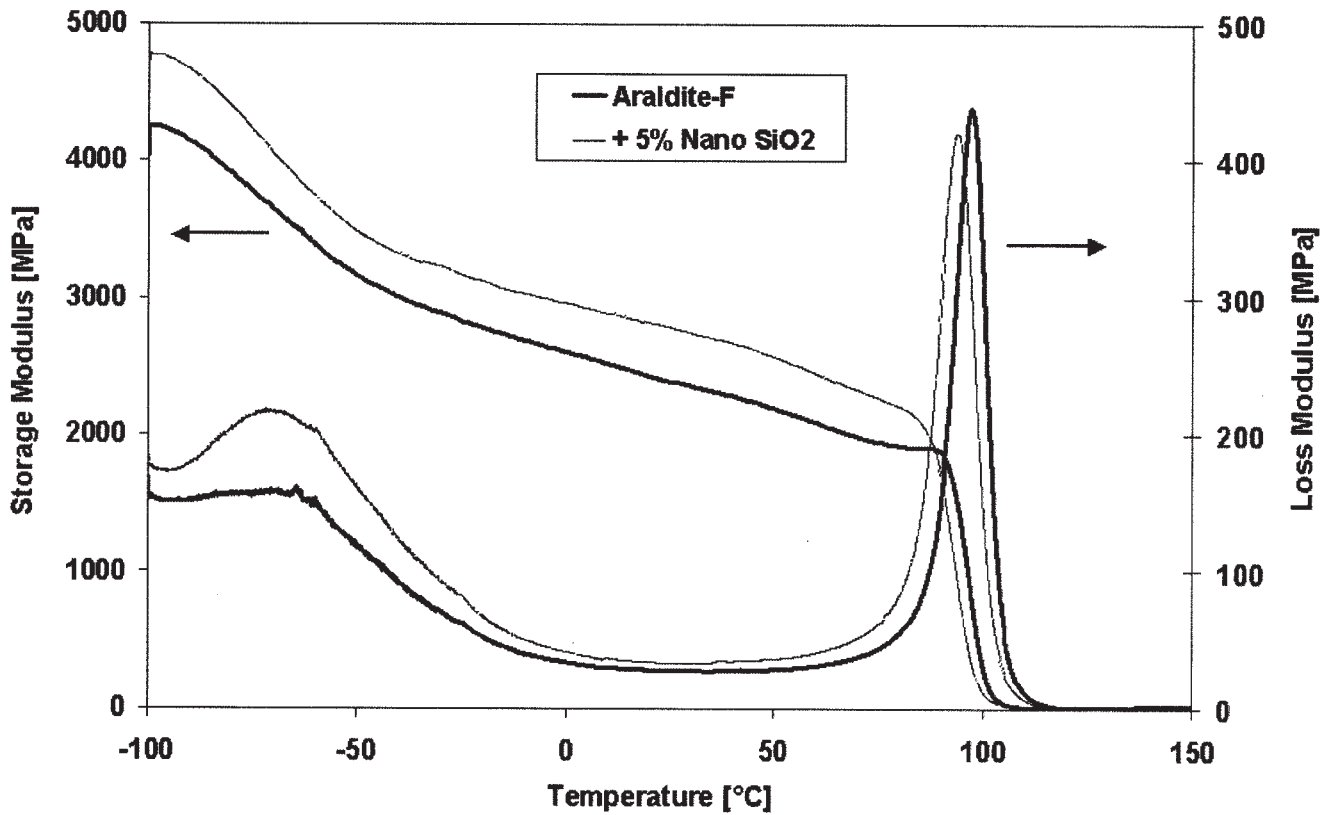


Figure 6 DMA-Spectra of pure and modified epoxy.

ature range. Also, the epoxy-hardener-ratio could be no longer correct as the added epoxy with nanoparticles may affect the crosslinking of the epoxy. However, the damping behavior $\tan \delta$ (not illustrated) shows no effect in that region.

CONCLUSIONS

It was shown in this study that the addition of 5 vol % silica-nanoparticles could improve the stiffness and the toughness of an epoxy resin at the same time. The E-Modulus from the tensile test was increased by more than 20% whereas fracture toughness values K_c were improved by 70% and G_c by more than 140%. Moreover, the nano-reinforced material behaved more ductile and showed a bigger yielding than the pure epoxy. The glass transition temperature was decreased from 95 to 89°C (DSC) when the particles were added. The nano-silica also improved the stiffness under dynamical loading from cryogenic temperatures up to T_g .

The authors gratefully acknowledge the support of hanse chemie AG for providing them with material samples. P. Rosso is also grateful for the financial support during his stay at CAMT, Australia.

References

1. Xiao, K.; Ye, L. *Polym Eng Sci* 2000, 40, 2289.
2. Xiao Keqin Ye, L. *Polym Eng Sci* 2000, 40, 70.
3. Huang, Y.; Kinloch, A. J. *Polymer* 1992, 33, 1330.
4. Bagheri, R.; Raymond, A. P. *Polymer* 1995, 36, 4883.
5. Wang, H.; Bai, Y.; Liu, S.; Wu, J.; Wong, C.P. *Acta Materialia* 2002, 50, 4369.
6. Nakamura, Y.; Yamaguchi, M.; Okubo, M.; Matsumoto, T. *Polymer* 1992, 33, 3415.
7. Zhang, M. Q.; Rong, M. Z.; Yu, S. L.; Wetzels, B.; Friedrich, K. *Wear* 2003, 253, 1086.
8. Kang, S.; Hong, S. I.; Choe, C. R.; Park, M.; Rim, S.; Kim, J. *Polymer* 2001, 42, 879.
9. www.hanse-chemie.com
10. Xiao, K.; Ye, L.; Kwok, Y. S. *J Mater Sci* 1998, 33, 2831.
11. Hull, D. *Fractography*; Cambridge University Press: Cambridge, UK, 1999; p 91ff.