

## Nanosilica reinforced epoxy floor coating composites: preparation and thermophysical characterization

Mir Mohammad Alavi Nikje<sup>a\*</sup>, Mohammad Reza Khanmohammadi<sup>a</sup>, Amir Bagheri Garmarudi<sup>a</sup> and Moslem Haghshenas<sup>b</sup>

<sup>a</sup>Chemistry Department, Faculty of Science, IKIU, Qazvin, Iran

<sup>b</sup>Department of Chemistry & Polymer Laboratories, Engineering Research Institute, Tehran, Iran

### ARTICLE INFO

#### Article history:

Received December 5, 2011

Received in Revised form

December 17, 2011

Accepted 20 December 2011

Available online

22 December 2011

#### Keywords:

Reinforcement

Nanocomposite

Nanoparticle

Nano SiO<sub>2</sub>

Epoxy Flooring

### ABSTRACT

In this study, flooring grade epoxy/nanoSiO<sub>2</sub> nanocomposites were prepared by *in-situ* polymerization method. Nano silica was treated by coupling agent in order to surface treating and introducing of reactive functional groups to achieving adequate bonding between polar inorganic nano particles and epoxy organic polymer.  $\gamma$ -Aminopropyltriethoxysilane (Amino A-100) was used as an effective and commercially available coupling agent and nano silica treated in acetone media. SEM observations of cured samples revealed that the nano silica was completely dispersed into polymer matrix into nanoscale particles. Thermal and physical properties of prepared samples were investigated and data showed improvements in physical and mechanical properties of the flooring samples in comparison with unfilled resin.

© 2012 Growing Science Ltd. All rights reserved.

## 1. Introduction

Introducing of one and two dimensional nano particles into epoxy resins improve their properties and expand applications in various areas especially in laboratory research as well as industry. For approaching such improvements, there are various methods, which all of them have their own merits and drawbacks. Literature survey reveals using a lot of nano scaled particles in order to improving of epoxy polymers in various chemical structures and resin grades namely coating, powder coating, flooring and etc<sup>1-12</sup>. Johnsen and his co-workers reported the enhancing of modulus and toughness at least 8% and decreasing in Tg as 7 °C by using nano silica in epoxy polymers<sup>13</sup>.

Colloidal nano-silica particles were used to improve the scratch and mar resistance of waterborne epoxy coatings by directly blending by Songwei and et al. In this study and in order to enhancing the compatibility of nano-silica particles within polymer matrix, nano-silica particles were first modified

\* Corresponding author. Tel.: + 982813780040  
E-mail addresses: Drmm.alavi@gmail.com (Dr. Alavi Nikje)

with 3-glycidoxypropyl-trimethoxysilane (GPTMS). The synthesized nanocomposites showed superior scratch and mar resistance in comparison with unmodified samples and reduce the transparency and gloss of waterborne epoxy coatings less seriously<sup>14</sup>. Isothermal cure characterization of fumed silica/epoxy nanocomposites has been reported by Guang and co-workers<sup>15</sup>. In another research, mechanical properties of epoxy nanocomposites by sol-gel method has been investigated and data shown the enhancing of properties by incorporation of nano silica<sup>16</sup>. The effect of nanoparticles on structural morphology, thermal and flammability properties of two epoxy resins with different functionalities has been reported by Charalampos and his co-workers. In this study, they investigated the effect of layered silicate nanoclays, nano-silica and double-walled carbon nanotubes (DWNTs) on the thermal stability and fire reaction properties of two aerospace grade epoxy resins<sup>17</sup>.

The effects of silica and silicate nano fillers on the properties of epoxy coatings have been reported by Pascal and et.al<sup>18</sup>. In addition, studies have been reported during the past few years for the development of the high-performance nanocomposites, which consists the incorporation of a nanometer-size inorganic component into the organic resin matrix<sup>19, 20</sup>. The use of an additional inorganic phase to improve the properties of epoxy resins has been a common practice<sup>21-26</sup>. Nanoparticles can fill up the weak micro-regions of resins to boost the interaction forces at the polymer–filler interfaces. A dramatic increase in the interfacial area between fillers and polymer can significantly improve the properties of the polymer<sup>27</sup>. The reinforcement efficiency is reported to show strong dependence on dispersion of nanoparticles. Well-dispersed nanoparticles can effectively enhance the comprehensive properties of nanocomposites, which are unique and different from any other current composites<sup>28, 29</sup>. Today, a variety of coatings are manufactured and used for decoration as well as protection applications. The need for industrial heavy duty floorings are increasing. Epoxy based coatings have been developed as per requirements of end applications, mainly as flooring compound. Especially for surface protection against mechanical damages, epoxy based floorings are very useful. Of course efforts are being programmed to achieve higher qualities and protection.

In the present work, it has been tried to apply SiO<sub>2</sub> nano particles in epoxy flooring formulation as a reinforcing agent which would result in better performance in the industry. According to high active surface and surface- diameter ratio in nanoparticles, they would act as stress concentrators and a binding bridge at the inter-phase<sup>30-32</sup>.

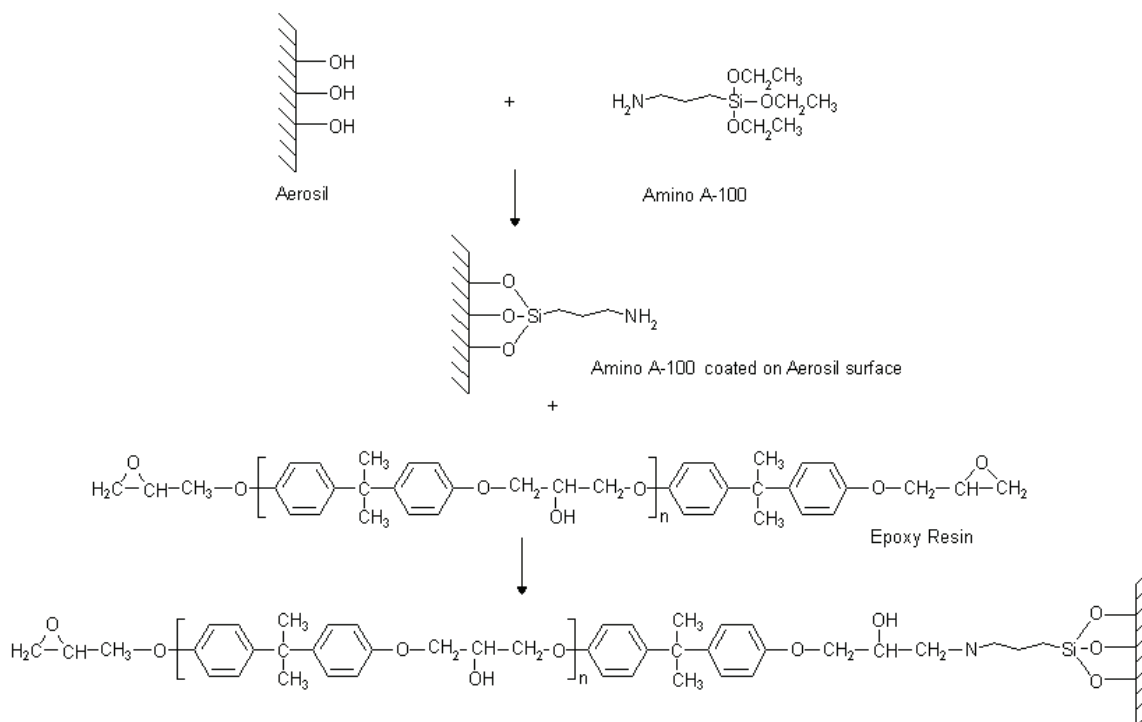
## 2. Results and discussions

### 2.1 Nanocomposite preparation

One of the main issues in preparation of nanocomposites is to disperse the nanoparticles in resin media which has been reported to increase the resin's viscosity. SiO<sub>2</sub> nanoparticles were pretreated by coupling agent in acetone. In order to prepare homogenous mixture of coupling agent and nanoparticles, mechanical homogenizer with 2000 rpm speed was used. In the next step, epoxy resin was added to the mixture. Acetone would decrease the viscosity of the preparing mixture providing well dispersed sample. Using a “high shear” laboratory-mixing device for mechanical mixing (2 h) and an ultrasonic homogenizer (30 min), it was tried to reach as complete as possible dispersion. Acetone content of the sample was removed by vacuum at 40 °C (12 h). The mixture was again homogenized by ultrasonic apparatus (30 min). The hardener was added to the formulation, being mixed by mechanical (30 min) and ultrasonic (15 min) equipments. The prepared composite sample was degassed (2 h), being cured in a chamber with room temperature. Table 1 shows the SiO<sub>2</sub> content of samples. The schematic mechanism of resin-nanoparticle preparation is shown in Fig. 1.

**Table 1.** Prepared nano SiO<sub>2</sub> – epoxy flooring samples.

| Flooring Sample | Nano SiO <sub>2</sub> (%) |
|-----------------|---------------------------|
| EP <sub>0</sub> | 0.0                       |
| EP <sub>1</sub> | 0.5                       |
| EP <sub>2</sub> | 1.0                       |
| EP <sub>3</sub> | 1.5                       |
| EP <sub>4</sub> | 2.0                       |
| EP <sub>5</sub> | 2.5                       |
| EP <sub>6</sub> | 3.0                       |

**Fig. 1.** Schematic steps for preparation of epoxy resin – nano silica.

## 2.2 Mechanical and physical properties

Reinforcement of epoxy flooring by SiO<sub>2</sub> nanoparticles would dramatically improve the tensile properties as denoted in **Table 2**.

**Table 2.** Effect of nano SiO<sub>2</sub> on tensile strength (MPa) and elongation at break (%) of epoxy flooring

| Sample          | Tensile Strength (MPa) | Elongation (%) |
|-----------------|------------------------|----------------|
| EP <sub>0</sub> | 3.2                    | 6.0            |
| EP <sub>1</sub> | 3.4                    | 7.2            |
| EP <sub>2</sub> | 5.0                    | 7.0            |
| EP <sub>3</sub> | 5.2                    | 8.5            |
| EP <sub>4</sub> | 8.7                    | 14.3           |
| EP <sub>5</sub> | 12.6                   | 31.6           |
| EP <sub>6</sub> | 11.2                   | 33.0           |

As a result, nanoparticles inherently possess high module and would strengthen the polymeric matrix when dispersed in the nano scale level. However improvement from 3.22 MPa (EP<sub>0</sub>) to 12.59 MPa (EP<sub>5</sub>) is really excellent as much more interfacial surfaces can be generated between polymer and

nanoparticles, which assists in absorbing the physical stress. The maximum tensile strength and elongation was in EP<sub>5</sub> which would drop in EP<sub>6</sub> sample with higher amount of SiO<sub>2</sub> nanoparticles.

There are several possible reasons for this decrement in tensile strength. One would be the weak boundaries between nanoparticles and probable micronized trapped bubbles. The other responsible reason may be the effect of high amounts of nanoparticles on homogeneity in crosslinking of the epoxy network. As the interfacial area of the particles is high, their interaction with epoxy chain would cause the lower homogeneity in crosslink density. Finally the heterogeneous dispersion of nanoparticles according to increment of resin's viscosity could be also mentioned as an important factor in mechanical failure. One of the main problems in floor coating by epoxy based materials is the existence of expansion joints on concrete surface, which their dimensional variations would cause the flooring to crack. The improvement in elongation at break of flooring would result in higher resistance against concrete dimensional variations. Interestingly the hardness and abrasion resistance of epoxy flooring would be increased by addition of SiO<sub>2</sub> nanoparticles (**Table 3**).

**Table 3.** Higher hardness and improvement of abrasion via reinforcement by nano SiO<sub>2</sub>

| Sample          | Hardness (Shore D) | Abrasion (mm <sup>3</sup> ) |
|-----------------|--------------------|-----------------------------|
| EP <sub>0</sub> | 58                 | 490                         |
| EP <sub>1</sub> | 61                 | 426                         |
| EP <sub>2</sub> | 61                 | 416                         |
| EP <sub>3</sub> | 62                 | 397                         |
| EP <sub>4</sub> | 62                 | 368                         |
| EP <sub>5</sub> | 63                 | 318                         |
| EP <sub>6</sub> | 67                 | 256                         |

### 2.3. Dynamic mechanical analysis

In all of the samples, T<sub>g</sub> would increase in accordance with amount of SiO<sub>2</sub> (Table 4).

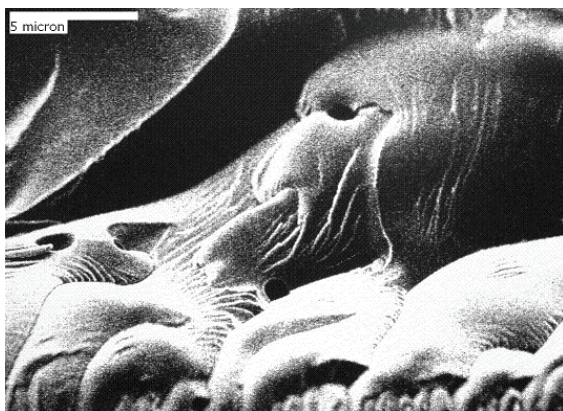
**Table 4.** Effect of nano SiO<sub>2</sub> on glass transition temperature and  $\delta_{\tan}$  of epoxy flooring

| Sample          | T <sub>g</sub> (°C) | Tan-Delta |
|-----------------|---------------------|-----------|
| EP <sub>0</sub> | 43.2                | 0.70      |
| EP <sub>1</sub> | 45.8                | 0.68      |
| EP <sub>2</sub> | 46.0                | 0.63      |
| EP <sub>3</sub> | 47.7                | 0.59      |
| EP <sub>4</sub> | 50.3                | 0.57      |
| EP <sub>5</sub> | 50.8                | 0.44      |
| EP <sub>6</sub> | 55.2                | 0.30      |

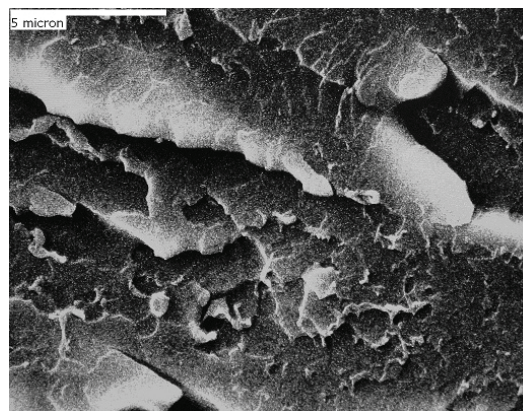
The Chemical bonding at the interface of the nanoparticles and polymer matrix could lead to hindered relaxational mobility in the polymer segments near the interface, which leads to increase of T<sub>g</sub>. The  $\delta_{\tan}$  would decrease with addition of nanoparticles (Table 4). The loss in the mobility of epoxy chain segments according to nanoparticle: matrix interaction would result in restricted chain mobility by improving the homogenized dispersion. Better dispersion would reduce the distance between nanoparticles providing better interaction with each other and also with epoxy matrix. In the other hand, dynamic modulus would be benefited by relative hindering of epoxy structure motion.

## 2.4. SEM results

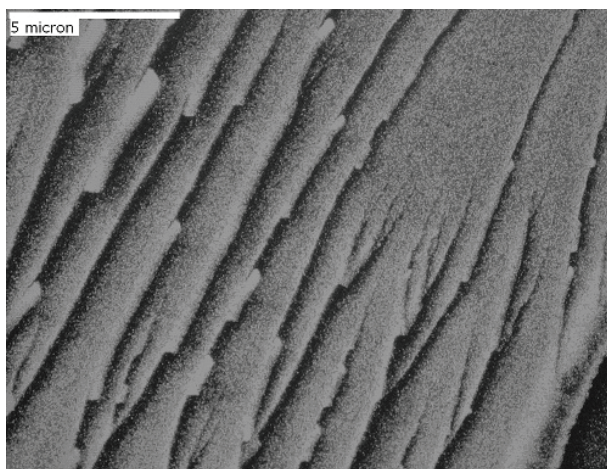
The dispersion of nanoparticles in the polymer matrix has been reported to have a significant impact on the mechanical properties of nanocomposites<sup>33</sup>. Achieving a homogenous dispersion is considered as a difficult goal according to their strong tendency in agglomeration. According to the SEM images from the dispersion of SiO<sub>2</sub> nano particles in the epoxy flooring matrix, it is concluded that good dispersion may occur by surface modification of the nanoparticles under an appropriate processing condition. Of course the homogenizing steps (sonification and high speed mechanical mixing) would be so effective. Investigating the breaking surface of nano composites (Fig. 2-4); it was observed that nano SiO<sub>2</sub> would affect the surface and breaking direction. As seen in figure 4, the breaking surface is more homogenous and edge of separations are in a same direction in comparison with neat flooring (Fig. 2) or low nano SiO<sub>2</sub> content samples (Fig. 3). As mentioned before, the bond between epoxy structure and nano SiO<sub>2</sub> would affect the glass transition temperature of flooring samples. Microscopic images from the surface showed symmetric breaking of the samples to be more observable in accordance with nano SiO<sub>2</sub> content. Homogeneity would be a good reason for achieving symmetric separation in the surface, thus it was concluded that nanoparticles would fill molecular cavities, providing better shaped network.



**Fig. 2.** Breaking surface of EP<sub>0</sub> sample (neat epoxy flooring)



**Fig. 3.** Breaking surface of EP<sub>2</sub> sample (1.0 % nano SiO<sub>2</sub> containing epoxy flooring)



**Fig. 4.** Breaking surface of EP<sub>5</sub> sample (2.5 % nano SiO<sub>2</sub> containing epoxy flooring)

### 3. Conclusions

Homogenizing the SiO<sub>2</sub> nanoparticles with sonification-mixing process would prepare a high performance epoxy flooring which is applicable in different industries. Coupling agent would provide the interaction between epoxy chain and SiO<sub>2</sub> molecules. High surface area/particle size ratio of nano-SiO<sub>2</sub> would be the main reason which influences the excellent physical properties.

### 4. Experimental

#### 4.1 Materials

The Bisphenol-A epoxy resin (Araldite<sup>®</sup> GY 6010) was supplied by JANA Resin Manufacturing Co. Its epoxy value was 0.5208-0.5498 eq per 100 g; weight per epoxide was 182-192 g per eq and residual epichlorohydrin below 100 ppm. Curing agent was a cycloaliphatic polyamine (Aradur 43) from HUNTSMAN<sup>®</sup> Co. with amine value of 260-280 mg KOH per g. The resin: hardener stoichiometric ratio was 100:60 pbw. Coupling agent is  $\gamma$ -aminopropyltriethoxysilane (Amino A-100) manufactured by Silquest<sup>®</sup> Chemicals which was added 5 pbw to the epoxy resin. Nano-SiO<sub>2</sub> was AEROSIL<sup>®</sup> 200 with specific surface area of 200 m<sup>2</sup>g<sup>-1</sup> and average particle size of 12 nm, from Degussa. Water free acetone was from Merck<sup>®</sup>

#### 4.2. Characterization methods

##### 4.2.1 Mechanical and thermal analysis

The tensile strength of cured flooring samples was determined, using an Instron testing machine at a crosshead speed of 5 mm min<sup>-1</sup> at room temperature, according to ASTM D638. Three specimens of each sample were tested. The thermomechanical properties of samples were investigated by a DuPont Instrument operating in the three-point bending mode under nitrogen atmosphere. Data were collected in -20 to 200 °C temperature range at a scanning rate of 5 °C min<sup>-1</sup>, using 10 Hz frequency. The friction resistance test was performed by an abrasion machine. Path length was 350 mm and speed was 2 mm s<sup>-1</sup>. The test sample was a 10 mm diameter disk with 10 mm thickness. Hardness of flooring samples was determined in Shore D scale.

##### 4.2.2. Scanning electron microscopy

The microscopic morphology of epoxy floorings was examined by a Cambridge scanning electron microscope, model 5360 (United Kingdom). The fracture surfaces were sputter coated with gold prior to scanning. It was tried to investigate the distribution of nanoparticles in the flooring medium, while the effect of nanoparticles on break shape and direction in the samples was studied.

### References

1. Cheng K.C., Lai K.C., and Chiu W. J. J. (1999) Kinetic approach for epoxy resins cured with diaminodiphenyl sulfone under non-isothermal conditions. *J. Appl. Polym. Sci.*, 71, 721-728.
2. May C.A. (1998) Epoxy Resins: Chemistry and Technology. 2<sup>nd</sup> ed., Marcel Dekker, New York, USA.
3. Lee H., and Nevellie K. (1967) Handbook of Epoxy Resin. McGraw-Hill, New York, USA.
4. Sun Y., Zhang Z., Moon K. S., and Wong C. P. (2004) Glass transition and relaxation behavior of epoxy nanocomposites. *J. Polym. Sci. Pol. Phys.*, 42, 3848-3858.



5. Cheng K.C. (1998) Kinetic model of diepoxides with reactive diluents cured with amines. *J. Polym. Sci. Pol. Phys.*, 36, 2339-2348.
6. Startsev O.V., Krotov A. S., and Startseva L. T. (1998) Interlayer shear strength of polymer composite materials during long term climatic ageing. *Polym. Degrad. Stabil.*, 2, 183-186.
7. Lee J. R., Park S. J., Seo M. K., Baik Y. K., and Lee S. K. (2006) A study on physicochemical properties of epoxy coating system for nuclear power plants. *Nucl. Eng. Des.*, 236, 931-937.
8. Sarathi R., Sahu R. K., and Rajeshkumar P. (2007) Understanding the thermal, mechanical and electrical properties of epoxy nanocomposites. *Mat. Sci. Eng. A-Struct.*, 445-446, 567-578.
9. Theodore M., Hosur M., Thomas J., and Jeelani S. (2010) Influence of functionalization on properties of MWCNT-epoxy nanocomposites. *Mat. Sci. Eng. A-Struct.*, 528, 1192-1200.
10. Mahrholz T., Stängle J., and Sinapius M. (2009) Quantitation of the reinforcement effect of silica nanoparticles in epoxy resins used in liquid composite moulding processes. *Compos. Part A-Appl. S.*, 40, 235-243.
11. Verónica P. S., and José M. M. M. (2006) Influence of the curing temperature in the mechanical and thermal properties of nanosilica filled epoxy resin coating. *Macromol. Symp.*, 233, 137-146.
12. Ratna D., and Toughened F. R. P. (2008) Toughened FRP composites reinforced with glass and carbon fiber. *Compos. Part A-Appl. S.*, 39, 462-469.
13. Johnsen B. B., Kinloch A. J., Mohammed R. D., Taylor A. C., and Springer S. (2007) Toughening mechanisms of nanoparticle-modified epoxy polymers. *Polymer*, 48, 530-541.
14. Songwei C, Bo Y., Shuxue Z., and Limin W. (2009) Preparation and characterization of scratch and mar resistant waterborne epoxy/silica nanocomposite clearcoat. *J. Appl. Polym. Sci.*, 112 (6), 3634-3639.
15. Guang C. H, and Jong K. L. (2010) Isothermal cure characterization of fumed silica/epoxy nanocomposites: The glass transition temperature and conversion. *Compos. Part A-Appl. S.*, 41(4), 473-479.
16. Jia L. T., Hung H., and Yi L. C. (2010) Investigating mechanical behaviors of silica nanoparticle reinforced composites. *J. Compos. Mater.*, 44 (4), 505-524.
17. Charalampos K., Everson K., and Baljinder K. K. (2011) The effect of nanoparticles on structural morphology, thermal and flammability properties of two epoxy resins with different functionalities. *Polym. Degrad. Stabil.*, 96 (4), 529-540.
18. Pascual S. V., Barrientos, R. S., Martín, M., and José M. (2010) Comparative study of the effect of addition of silica and silicate nanofillers on the properties of epoxy coatings. *Compos. Interface*, 17 (5-7), 513-532.
19. Miyagawa H., Rich M. J., and Drzal L.T. (2004) Thermophysical properties of anhydride-cured epoxy/nano-clay composites. *Polym. Composite*, 26, 42-51.
20. Yaping Z., Aibo Z., Qinghua C., Jiaoxia Z., and Rongchang N. (2006) Functionalized effect on carbon nanotube/epoxy nano-composites. *Mat. Sci. Eng. A-Struct.*, 435, 145-149.
21. Kinloch A. J., and Taylor A. C. (2003) Mechanical and fracture properties of epoxy/inorganic micro-and nano-composites. *J. Mater. Sci. Lett.*, 22, 1439-1441.
22. Zhu Z., Peng H., Rodriguez-Macias F., Margrave J. L., Khabashesku V. N., Imam A. M., Lozano K., and Barrera E.V. (2004) Reinforcing epoxy polymer composites through covalent integration of functionalized nanotubes. *Adv. Funct. Mater.*, 14, 643-647.
23. Li X. (1999) Ultrasonic waves in preparing of nanometer SiO<sub>2</sub>/epoxy nanocomposites. *Thermoset Resin*, 2, 19-23.
24. Salahuddin N., Moet A., Hiltner A., Baer E. (2002) Nanoscale highly filled epoxy nanocomposite. *Eur. Polym. J.*, 38, 1477-1482.
25. Ng C.B., Schadler L. S., and Siegel R. W. (1999) Synthesis and mechanical properties of TiO<sub>2</sub>-epoxy nanocomposites. *Nanostruct.Mater.*, 12, 507-510.
26. Wetzel B., Hauptert F., and Zhang M. Q. (2003) Epoxy nanocomposites with high mechanical and tribological performance. *Compos. Sci. Technol.*, 63, 2055-2067.
27. Song J. G. (1996) Polymeric nano-metered composites. *Mater. Rev.*, 4, 57-59.

28. Chisholm N., Mahfuz H., Rangari V. K., Ashfaq A., and Jeelani S. (2005) Fabrication and mechanical characterization of carbon/SiC-epoxy nanocomposites. *Compos. Struct.*, 67, 115-124.
29. Zhou Y., Pervin F., Rangari V. K., and Jeelani S. (2006) Fabrication and evaluation of carbon nano fiber filled carbon/epoxy composite. *Mat. Sci. Eng. A-Struct.*, 426, 221-228.
30. Zheng Y. P., Zheng Y., and Ning R. C. (2003) Effects of nanoparticles SiO<sub>2</sub> on the performance of nanocomposites. *Mater. Lett.*, 57, 2940-2944.
31. Ding H. Z., and Varlow, B. R. (2004) Effect of nano-fillers on electrical treeing in epoxy resin subjected to AC voltage. *Electrical Insulation and Dielectric Phenomena*, IEEE/CEIDP '04. Annual Report Conference, Publication Date: 17-20 Oct., 332-335, Colorado, USA
32. Kinloch A. J., and Taylor A. C. (2006) The mechanical properties and fracture behaviour of epoxy-inorganic micro- and nano-composites. *J. Mater. Sci.*, 41, 6271-6297.
33. Kansy J., Consolati G., and Dauwem C. (2000) Positronium trapping in free volume of polymers. *Radiat. Phys. Chem.*, 58, 427-431.