A study on role of nanosized SiO₂ on deformation mechanism of vinyl ester

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Abstract. Vinyl ester (VE) resins have good resistance against corrosive and hostile environments, and formation of micro cracks. They also have good thermal resistivity as well as mechanical properties which result in their usage in many applications such as sewer pipes, solvent storage tanks, and mining and other industrial equipments. In the present work, nanosized silica was employed as reinforcement to improve VE mechanical properties. Hence, to study the influence of nanosilica particles on the tensile strength, Young's modulus and toughness of mentioned nanocomposites, nanosilica-vinyl ester nanocomposites with different silica weight percentages (0.3, 0.75, 1) were fabricated. Moreover, the effects of nanosilica particles on the tensile fracture surfaces and VE deformation mechanisms were studied by scanning electron microscopy (SEM). It was observed that increasing the nanosilica fillers results in tensile strength deterioration as well as Young's Modulus increasing. Adding nanosilica reinforcements up to 0.3 (% wt) improves the fracture toughness while decreasing the fracture energy.

Keywords. Nanosized SiO₂; vinyl ester; deformation mechanism.

1. Introduction

Vinyl ester (VE) resins are one of the most well known thermosetting polymers (Peters 1998). They can be obtained from the reaction of an unsaturated carboxylic acid such as acrylic or methacrylic acid and an epoxy resin. Methyl ethyl ketone peroxide, benzoyl peroxide and trigonox are among most commonly used catalysts for vinyl esters. Often 0.2 to 0.4% by weight of cobalt naphthalene adds to vinyl ester resin as a promoter (Astrom 1997). These resins have good resistance against acids and alkalis (Suresha *et al* 2010). The unsaturated ends of vinyl ester resins make them very reactive. So, they can be solved in styrene and can be processed like unsaturated polyester. As a result, they will provide us the raw strength during the moulding process. Their good thermal resistivity, mechanical properties (especially high tensile and elongation), resistance against formation of micro cracks and high heat deflection temperature are remarkable. These resins impregnate glass fibres and other reinforcements well (Astrom 1997; Suresha *et al* 2010). Their resistance to corrosive and hostile environments degradation leads to their usage in many applications. Swimming pools, sewer pipes, solvent storage tanks, mining equipments, fiberglass reinforcement plastics tanks, coatings on other plastics and common materials such as steel and concrete are some examples of VE applications (Peters 1998; Wayne *et al* 1998; Ziaee and Palmese 1998). This is why the vinyl ester resins are of considerable commercial interest.

Vinyl esters such as bisphenol A and chlorendic polyesters are produced from expensive materials and often require time consuming processes (Peters 1998). It is better to reinforce vinyl ester resins by adding different organic and inorganic fillers such as multi-wall carbon nanotubes (MWCNT), single-wall carbon nanotubes (SWCNT), carbon nanofibres and nanoparticles like CuO, TiO₂, Al₂O₃, Fe₂O₃ to improve their mechanical properties such as Young's modulus, flexural modulus and even toughness.

Gryshchuk *et al* (2006) used MWCNT to modify vinyl ester and vinyl ester-based hybrid resins and examined the electrical conductivity, thermomechanical, fracture mechanical and failure properties of the fabricated nanocomposites. They found that MWCNT's effect on the electrical conductivity is more significant than mechanical behaviour.

Aviles (2011) studied oxidation and silanization of MWCNT in vinyl ester nanocomposites. He investigated mechanical properties of these composites and concluded that oxidizing MWCNT by HNO₃/H₂O₂ before silanization, resulted in significantly better attachment of the silane molecules to the carbon nanotube surface and lead to the better mechanical performance of the considered nanocomposite.

Guo *et al* (2007) focussed their attention on the study of CuO nanoparticle filled vinyl ester resin composites. They employed unmodified as well as silane modified CuO to fabricate vinyl ester resin polymeric nanocomposites. It was found that functionalization of nanoparticles had significant effect on the nanocomposite properties and the enhancement of tensile strength was the result of more uniform particle

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dispersion and chemical bond between nanoparticles and VE resin.

To the best of our knowledge and based on the previous researches, scientists studied roles of silica nanoparticles on the mechanical properties of epoxy (Rong *et al* 2001), polypropylene (Lee and Yee 2000) and polyimide (Ou *et al* 1998) and, upto now, there is no study related to investigation of the effect of nanoSiO₂ particles on the mechanical properties and deformation mechanisms of vinyl ester resin. Hence, in the present research, the hydrophobic silica nanoparticles have been utilized as reinforcement to evaluate their effects on the tensile properties and deformation mechanisms of vinyl ester resin.

2. Experimental

2.1 Materials

In this study, the bisphenol A based vinyl-ester resin (Swancor 901) was used as a polymeric matrix. It was composed of 50 %wt vinyl ester (Mw=970 g/mole) and 50 %wt styrene monomers. Purchased methyl ethyl ketone peroxide (MEKP) from Akzo Noble was utilized as catalyst. Cobalt has been employed to decompose and promote the catalyst at room temperature. Dimethylamine (DMA) and BYK-C8000 were used as accelerator and coupling agent respectively. Hydrophobic nanospherical silica (SiO₂) particles with 98.3% purity were purchased from Fadak Advanced Material Group. Hydrophobic silica particles were synthesized from sprayed droplets of a colloid containing SiO₂ nanoparticles with particle size of about 20–30 nm. The specific surface area of utilized silica nanoparticle was about 200–400 m²/gr and its density was about 50–300 gr/litr. The mentioned nanoparticles were treated with silane coupling agent during synthesis.

2.2 Nanocomposite fabrication

Based on weight percent of nanocomposite reinforcements, certain amount of nanoparticles was weighed and poured into 240 g vinyl ester resin. First of all, dispersing the nanoparticles in the resin was accomplished by a high shear mixer for 20 minutes. This method was used to utilize the high shear force for breaking down the silica aggregations. Then 1 (%wt) BYK-C8000 was added to system during mixing process. After that, the mixed samples were sonicated with probe ultrasonic device (AROAN ultrasonic processor) for 10 minutes. In order to prevent increasing the vinyl ester resin temperature during sonication process, a room temperature water bath was used. The trapped bubbles from the prepared mixture were extracted by vacuum chamber during degassing process. In the next stage, 2.2 (%wt) Cobalt, 0.5 (%wt) DMA and 1.1 (%wt) MEKP, were added to the prepared blend and mixed. After that, the second evacuation was performed on the mixture for degassing the new bubbles produced from the additive reactions with the resin and then

the mixture was poured into tensile standard silicon moulds according to D638 ASTM standard. To perform the post cure process, the samples were brought out from the moulds after 24 hours, heated in the 80 °C oven for 2 hours and then 105 °C for 1 hour.

2.3 Evaluation

2.3a Tensile test behaviour evaluation: The tensile strength, Young's modulus and toughness of the neat vinyl ester as well as fabricated nanocomposites containing 0.3, 0.75 and 1 (%wt) of nanosized silica particles were evaluated by SANTAM-150 tensile device. By utilizing tensile tests based on D638 ASTM standard, tensile properties such as tensile strength, elastic modulus, toughness and elongation percentage of neat vinyl ester resin and fabricated nanocomposites were measured.

The cross head speed of all tests was kept constant and it was 2 mm/min and the tests were done at room temperature. To ensure the reliability of test results, each test was repeated 5 times and finally the averages were reported.

2.3b Microscopic evaluation: Fracture surfaces of tensile samples were investigated by scanning electron microscopy to study the role of nanosilica particles on deformation mechanisms of VE resin as well as evaluate the fracture energy and it will be tried to compare with observed mechanisms.

3. Results and discussion

Figure 1 shows the effect of increasing the nanosized silica particle content on the stress-strain behaviours of fabricated nanocomposites.

It can be seen that the behaviour of stress-strain curves of different samples that differ in their silica content are approximately similar at low stresses. But, as the stress increases, they behave differently. For evaluating the effect of nanosilica weight percent on the toughness of the samples, the areas

Figure 1. Stress-strain curves of vinyl ester and its nanocomposites.

Table 1. Summarized mechanical properties of fabricated nanocomposites.

Nanosilica content (%wt)	0	0.3	0.75	1
Elongation (%)	5.69	5.39	2.19	1.75
Toughness (J/m ³)	350.46×10^{-3}	498.93×10^{-3}	88.985×10^{-3}	57.818×10^{-3}
Tensile strength (MPa)	84.2	80.4	60.8	52.2
Young's modulus (GPa)	3.215	3.223	3.446	3.984

under the stress-strain curves of each material were measured and reported in table 1.

Some other nanocomposite mechanical properties i.e., tensile strength, elastic modulus and elongation percentage as well as fracture energy or toughness are also given in table 1.

From table 1, it is obvious that increasing the silica content improves the elastic modulus of nanocomposites. The recent effect can be explained by the superior Young's modulus of these rigid reinforcements particles respect to the neat vinyl ester resin. Increasing the nanosilica weight percent results in decreasing the tensile strength. The tensile strength's dependence on nanocomposites to the stress transfer between the rigid fillers and matrix may be responsible for later effect (Hsueh 1987). If the interface between nano SiO₂ particles and vinyl ester was sufficiently strong, the stress would be transferred to the reinforcements successfully and, in this case, the strength of composite is high. But addition of more SiO₂ particles results in reduction of strength, because of very weak interfacial bonding (Fu *et al* 2008).

Giannellis (1996) investigated the effect of particle size on the tensile strength, and found that the higher surface area of small particles lead to easier stress transfer and strength enhancement. Based on Giannellis (1996) studies, it can be stated that increasing the nano SiO₂ content of nanocomposite results in increasing the reinforcement agglomerations and nano SiO₂ particle mean size and, therefore, decreasing the stress transfer and also tensile strength. Indeed by two distinct mechanisms, rigid and hard nano SiO₂ fillers influence the tensile strength. The first is the weakening role because of the produced stress concentration effect and second is the reinforcing effect due to their resistance to the crack growth. Thus, if the weakening effect is dominant, by increasing the filler content, the strength will be decreased (Fu *et al* 2008).

Since processing defects such as voids act as stress concentration points, they may severely deteriorate the tensile strength and cause premature failure of the prepared samples during loading (Zhang *et al* 2011).

The result obtained in the present work is similar to what was observed by other investigators. For example, Ou *et al* (1998) used SiO₂ as reinforcement for nylon 6 polymeric matrix. They investigated the influence of silica fillers on Young's modulus of fabricated nanocomposites. Figure 2 presents the results of various researches which have been carried out using silica filler in different polymer matrices as well as obtained results in this study. From this figure, we come to the conclusion that our nanocomposite elastic modulus behaves in way similar to Young's modulus of

Figure 2. Dependence of Young's modulus of vinyl ester matrix on nanosilica content. **Figure 3.** Variation of tensile strength of vinyl ester matrixes vs silica content.

other polymeric based nanocomposites reinforced with silica particles (Yang *et al* 1998).

Dekkers and Heikens (1983) studied the effect of glass bead content on tensile strength of fabricated polystyrene-glass bead nanocomposites. Figure 3 presents their reported results compared to other polymeric based composites reinforced with silica. It shows that, increasing reinforcement content leads to decrease in tensile strength of nanocomposites and confirms the similarity between Dekkers and Heikens (1983) and our research results.

Some V-shaped marks are seen in brittle polymer fracture surfaces that seem to depart from crack origin. They are named Chevron marks. Crack propagation direction can be recognized from Chevron marks (Guerrero *et al* 2002). Some curved lines and V-shaped marks can be seen clearly from figure 4 which is an SEM macrograph taken from the fracture surface of 0.3 (%wt) silica-vinyl ester nanocomposite.

The change in morphology at the end of Chevron marks proves catastrophic fracture.

Some step-like features can be recognized from figure 5. It means crack propagation cannot occur only across one plane; therefore, a crack will change its plane and propagate across different planes, resulting in creation of more free surfaces and, thus, enhancement of fracture energy (Guerrero *et al* 2002). Also, cracks bifurcate to dissipate the fracture energy in this way.

There are two important reasons for crack bifurcation. The first one is the crack velocity in homogeneous plates and second is the existence of several types of interfaces which are a suitable explanation for non-homogeneous materials i.e. the existence of inclusions and also particulate or fibre-reinforced composites. Moreover, variation of elastic modulus due to crack dynamic propagation leads to crack bifurcation (Papadopoulos 1988).

Figure 4. Chevron marks in 0.3 (%wt) silica-vinyl ester nanocomposite (Schematic of Chevron marks is at right-bottom).

Figure 5. Step-like crack propagation in fracture surface of 0.3 (%wt) silica-vinyl ester nanocomposite.

This sequence was reported in other amorphous polymers like PS and brittle materials such as organic and inorganic glasses (Ronald and Parrington 2002). In other words, using the micrograph taken from the fracture surface of neat epoxy specimen, the presence of three distinct regions can be seen considering brittle characteristic of the systems. The first zone is an initial region of fracture characterized by a smooth and flat surface. The second is a transition region, where the surface roughness steadily increases, and the third region of fracture appears with conical marks.

Despite the existence of Chevron marks in fracture surfaces, the sequence of crack propagation surrounding crack initiation was quite evident and included three stages. The first one is a smooth region called mirror-zone, the second comprising a slightly rougher region is called mist-zone or transition zone and the third is a microscopically rough region named hackle-zone.

Figure 6. Mirror zone in fracture surface of neat vinyl ester resin relating to slow crack growth.

Figure 7. Schematic of mirror zone in brittle fracture surfaces.

Mirror zone is associated with the slow crack growth. This zone can be recognized by its flat, smooth and featureless appearance and it is close to the crack initiation front.

The mirror zone in neat vinyl ester resin is clear in SEM photographs of fracture surface (figures 6 and 7).

Polymer brittleness affect the size of mirror zone. The size of mirror zone depends strongly on the shear yielding behaviour. If the polymer or fabricated nanocomposite is more brittle, the amount of plastic deformation will reduce, and, therefore, the extent of mirror zone will decrease. In other words, if the initial crack has long dispread time, it increases the extent of mirror zone (Zebarjad *et al* 2008).

By comparing the SEM photographs of fabricated nanocomposite and neat resin fracture surfaces, it is clear that the extent of mirror zone increases by adding nanosilica particles to the resin, and in 0.3 (%wt) silica-vinyl ester nanocomposite, the extent of mirror zone is the maximum. But after that, by adding more nanosilica particles to the resin, this surface area decreases (figure 8).

As it was discussed earlier, by calculating the surface area under each nanocomposite's stress-strain curve, it was

Figure 8. Influence of nanosized silica content on fraction of mirror zone surface area.

Figure 9. Mist zone in fracture surface of neat vinyl ester resin.

concluded that the toughness increases by adding reinforcements to the neat resin. Further, the maximum toughness would be achieved in 0.3 (%wt) silica-vinyl ester nanocomposite. But, after that, by adding more silica nanoparticles to fabricate nanocomposites, the toughness would decrease. This is consistent with the extent of each nanocomposite and neat resin mirror region.

Creation of micro-cracks surrounding the crack front leads to decrease of stress concentration at crack tip. This effect results in crack tip shielding. Any parameter that causes creation of tiny cracks such as matrix brittleness, aggregation of nanoparticles or reinforcements and also existence of voids in material structure, leads to formation of mist zones. The transition or mist region is located between mirror zone and hackle region. Its appearance is so misty and there is a slight change in the surface texture. In this region, crack growth changes from slow to fast. The mist zone in neat vinyl ester resin fracture surface is recognizable in its SEM photograph (figure 9).

In transition zone, the velocity of secondary fine crack formation is similar to initial crack velocity and it bangs into each other. This collision results in transition of mirror pattern to regular inequalities or, in other words, roughness on the fracture surface, and continues in the initial crack direction. Hackle zone feature is similar to river patterns which are observed on the cleavage facets of transgranular brittle metal fractures. It includes divergent lines which radiate outward from the crack origin point. The enhancement of roughness in this region is evident and clear (Kailash and Hareesh 2012). Also, in figure 10, mist zone and hackle zone can be seen clearly in neat resin.

Mist zone in reinforced as well as un-reinforced vinyl ester is seen in fracture surfaces of tensile samples. The related SEM micrographs are given in figure 11.

SEM micrographs show the hackle zones in the fracture surface of the samples. The zones include some divergent lines that point outward from crack or defect origin. As

Figure 10. SEM micrograph taken from fracture surface of pure resin.

Figure 11. SEM micrographs showing mist and hackle zones after tensile test: (a) un-reinforced resin, (b) vinyl ester/ 0.3 (%wt) silica nanocomposite and (c) 1 (%wt) silica-vinyl ester nanocomposite.

seen, they have river-like patterns which are created on small cleavage facets in brittle metals.

A large amount of fracture energy in final fracture stage dissipates through plastic deformation and also creation of additional fracture surfaces.

Figure 12. Fracture surface of broken tensile samples: (a) neat resin, (b) 0.3 (%wt) silica-vinyl ester nanocomposite and (c) 1 (%wt) silica-vinyl ester nanocomposite.

We compared the final fracture surface of nanocomposites and un-reinforced vinyl ester tensile test samples. It was found that, as the weight percent of nanosilica particles used in nanocomposites increased, the final fracture surface structure pattern became finer and rougher upto adding 0.3 (%wt) nanosized silica, but, after that, by adding more reinforcement, the fast fracture pattern got smoother and finer.

Figure 12 shows the sequence of vinyl ester structure changes caused by addition of nanosilica reinforcement.

4. Conclusions

In this work, vinyl ester based nanocomposites reinforced with SiO₂ particles were prepared and its properties were evaluated. In particular, mechanical properties and deformation mechanisms were investigated. It was concluded that, by adding nano SiO₂ particles, Young's modulus of vinyl ester resin would increase while tensile strength would decrease. Toughness of specimens in tensile test were calculated. It was noticed that, increasing the silica content up to 0.3 (%wt) in vinyl ester resin lead to an increase in the fracture energy. But, after that, it showed a decreasing behaviour. Moreover, by utilizing SEM macrographs of fracture surfaces, three main regions viz. mirror zone, mist zone and hackle region similar to Chevron marks and step-like crack propagation were diagnosed.

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References

- Astrom B T 1997 *Manufacturing of Polymer Composites* Department of Aeronautics, Royal Institute of Technology, Chapman & Hall, p 1
- Aviles F 2011 *J. Expr. Polym. Let.* **5** 766
- Dekkers M E J and Heikens D 1983 *J. Appl. Poly. Sci.* **28** 3809
- Fu S Y, Feng X Q, Lauke B and Mai Y W 2008 *J. Comp. (B)* **39** 933
- Giannelis E P 1996 *J. Adv. Mater.* **8** 29
- Gryshchuk O, Karger-Kocsis J, Thomann R, Konya Z and Kiricsi I 2006 *J. Comp. (A)* **37** 1252
- Guerrero C, Reyes E and Gonzalez V 2002 *J. Polymer* **43** 6683
- Guo Zh, Liang X, Pereira T, Scaffaro R and Hahn H T 2007 *J. Comp. Sci. Tech.* **67** 2036
- Hsueh C H 1987 *J. Amer. Cer. Soc.* **72** 344
- Kailash C and Hareesh V 2012 *J. Comp. (B)* **43** 3467
- Lee J and Yee A F 2000 *J. Polymer* **41** 8363
- Ou Y, Yang F and Yu Z Z 1998 *J. Polym. Sci. (B)* **36** 789
- Papadopoulos G A 1988 *J. Eng.Frac. Mech.* **31** 887
- Peters S T 1998 *Handbook of composites* 2nd edn, Chapman and Hall, London, Weinheim, New York, Tokyo. Melbourne, Madras
- Ronald J and Parrington P E 2002 *J. Pract. Failu. Analy.* **2** 16
- Rong M, Zhang M, Zheng Y, Zeng H and Friedrich K 2001 *J. Polymer* **42** 3301
- Suresha B, Seetharamu S and Sampath Kumaran P 2010 *Trib. Inter.* **43** 602
- Wayne D C, George P S, Peter J B, Michelle L and Travis J F 1998 *J. Appl. Poly. Sci.* **64** 769
- Yang F, Ou Y C and Yu Z Z 1998 *J. Appl. Poly. Sci.* **69** 355
- Zebarjad S M, Sajjadi S A and Hooshir Sadeghian M 2008 *J. Sci. Poly. Techn.* **5** 101
- Zhang A Z, Li D H, Zhang D X, Lu H B, Xiao H Y and Jia J 2011 *J. Expr. Poly. Let.* **5** 708
- Ziaee S and Palmese G R 1998 *J. Poly. Sci. (part B)* **37** 725