Effect of reactive vinyl-based modifier on thermal and failure resistance of reinforced epoxy used in pipelines

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Abstract: In recent years, epoxy is used as the matrix for manufacturing composites that are used in medical and mechanical applications. For examples reinforced epoxy is applied in manufacturing human prostheses, scaffolds, fiberglass pipelines and other applications. In this work, we have applied a vinyl butadiene reactive modifier to systematically improve the failure resistance of an epoxy resin and its reinforcing composite. Vinyl-based modifier is known as a powerful toughening agent for epoxy-based thermoset polymers. Several mechanical tests including Impact resistance test and compression test has been performed. In order to evaluate the effect of rubber toughening on thermal resistance of reinforced epoxy, the dynamical scanning calorimeter has been utilized. In addition, damaged surfaces of fractured samples were investigated using scanning electron microscopy techniques. It is found that vinyl modifier improve the failure resistance of the reinforced epoxy resin. This can be attributed to the high cavitations of oligomer particles. However this improvement is accompanied with decreasing the thermal resistance of the material. This is the result of solving vinyl-based oligomer in the matrix during the mixing.

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1. Introduction

During the past century, polymer materials were utilized in production of coatings, composites, medical applications and other advanced structures (Tavakoli, 2002; Golestaneh *et al.*, 2010; Makinejad *et al.*, 2012; Atef *et al.*, 2010; Abdel- Hakim *et al.*, 2012; Valipour *et al.*, 2012; Vaziri *et al.*, 2011a; 2011b) . Among the polymers, epoxy thermoset polymer is one of the interesting polymeric materials used in medicines and fluid conveying applications. This resin is chemically constructed from the epoxide group that is a three-membered carbon, carbon, oxygen ring structure (Tavakoli, 2002);. Epoxies are one of the most widely used adhesives for structural applications as well as non-structural ones (Tavakoli, 2002). Epoxies have been used in a number of medical devices for bonding and sealing applications (Tavakoli, 2002). A clear, medical-grade low-viscosity epoxy adhesive has found application in fabrication of access ports that are implanted beneath the skin of patients requiring multiple injections. The epoxy adhesive passed biological and toxicity tests i.e. acute systemic and intracutaneous toxicity, implantation tests and cytotoxicity tests (Tavakoli, 2002). Use of epoxy resins in ultrasound catheters and pacemakers are the typical examples of its use in medical electronic packages (Tavakoli, 2002). Epoxies are also being used for joining filter components. Another application of epoxy in medicine is the use of a two- part epoxy for bonding end-caps to the main tube of a blood filter (Tavakoli, 2002). Other applications of epoxy include the fabrication of fiberglass composite structures. Reinforced composites are used in manufacturing large diameter pipelines that are increasingly used in conveying fluids i.e. oil, water etc. The high chemical and moisture resistance of fiberglass pipes make them one of the most appropriate candidates for fluid conveying especially in the corrosive ambient. Epoxy pipelines are resistance to acidic, basic, alkaline, sore water and other corrosive fluids. Several types of reinforcement such as glass fiber, carbon fiber, polymeric fiber etc. are used for reinforcing the epoxy matrix. Among them, glass fiber are increasingly used due to its low price and high strength, flexibility, impact resistance, chemical resistance and other appropriate characteristics.

While reinforced epoxies present good performance, they shows a brittle behavior compared to the conventional metallic materials such as steel, aluminum, alloys etc. Note that thermoset material exhibits very low impact strength and fracture resistance that make them sensitive to external damages when they are used in structures. Therefore several methods are used by engineers and manufacturers for enhancing the strength of fiberglass composite to prevent failure and critical damages during the operational life. Previous researches reveal that the oligomer modification, that is the addition of oligomer particulate phase to a brittle polymer matrix, is one of the most successful approaches for improving toughness of reinforced epoxy. Reactive oligomers can be used as rubber modifiers for toughening of epoxy. Rubber modification of epoxy has been studied by previous researchers. Ophir *et al.* (1995) investigated a modified epoxy composition for filament winding of pressure vessels. Their product showed an improved toughness with minimal sacrifice of its thermal and mechanical properties. Zhang *et al.* (1991) used carboxyl-terminated butadiene acrylonitrile (CTBN) to modify the toughness of reinforced epoxy tubes. They found that the ultimate strain was higher for the toughened pipes (Zhang *et al.*, 1991). Sanjana *et al.* (1985) reported that the toughness improvement of epoxy composites is affected by physical conditions as well as modifier type. Abadyan et. al. (Abadyan *et al.*, 2009a) observed that addition of amine-terminated butadiene acrylonitrile (ATBN) to epoxy matrix increases impact strength of modified hoop wound composite but reduces its compressive and interlaminar shear strength. Moreover incorporation of ATBN led to more favorable mechanical properties, from the viewpoint of both toughness and strength, relative to CTBN (Abadyan *et al.*, 2009b). Other researchers reported that the incomplete precipitation of oligomer molecules might enhance the toughness characteristics and decrease the other mechanical characteristics of a modified resin (DeCarli *et al.*, 2005). Moreover, in Ref. (Abadyan, *et al.*, 2010) it has been shown that the increasing in the loading rate of epoxy samples might lead to reduce the damage zone in the vicinity of the crack tips. This reference shows that cavitation has a great influence on the fracture toughness of epoxy matrix. In other works, the incorporation of two types of rubber modifier on fracture toughness of epoxy has been examined (Abadyan *et al.*, 2011; 2012a; 2012b).The researchers reported a synergistic toughening in fracture toughness of epoxy modified by a combination of reactive oligomer and waste tire particles (Abadyan *et al.*, 2011; 2012a; 2012b).

According to the best knowledge of authors there is lack of knowledge on the effect of modifiers on mechanical characteristics of reinforced epoxy. Therefore, in this work we utilize a vinyl-based oligomer to modify the glass reinforced epoxy in this work. Various kinds of physical and mechanical tests and microscopic techniques are conducted in this study. The obtained results are useful for design high toughness fiberglass composites for fluid conveying pipelines.

2. Experimental

2.1 Materials

The model system used in this study is based on a diglycidyle ether of bisphenol A epoxy. The trade name of the material is Araldite LY5052 from Hauntsman Co. The hardener part is a cycloaliphatic polyamine hardener with the trade name of HY5052 from Vantico. The liquid modifier is vinyl butadiene (VTB) copolymer with the trade name of Hycar from Novion Co. This type of modifier has 0 wt% of acrylonitrile content. The glass reinforcement used in this study was a glass rowing with 2400 tex from Vetrotex.

2.2 Sample preparation

The stoichiometric ratio of the resin and hardener were mixed and degassed at room temperature for 20 min. Then it was casted in a mould and was cured for 8h at 80 ºC in an oven. Same curing procedure was employed for all toughened epoxies. The modifier content was varied up to 20 phr. The obtained mixtures were mixed under vacuum for 20 min. Table 1 presents the epoxy formulations used.

All formulations made were then reinforced with glass fiber. For this purpose a filament winding machine has been used to wind the cylindrical composite fiberglass composite tubes. The glass roving reinforcement is first passed from a resin bath to wet the glass fiber with epoxy resin and then, the reinforced epoxy wind around a steel made mandrel. A hoop angle was employed to provide the tube samples. The samples then were cured at the same curing temperature that was used for the resin samples.

Table 1: Formulations made in this study

Sample code	Resin (phr)	Hardener (phr)	Modifier Content (phr)
E	100	38	0
E5	100	38	5
E10	100	38	10
E15	100	38	15
E20	100	38	20

2.3 Characterization techniques

2.3.1. Compressive test

Transverse compressive properties of hoop wound composite (compressive properties in the direction perpendicular to the fibers direction) were determined according to ASTM D5449 using tubular specimens. The tubes had dimensions of 100 mm inner diameter × 2 mm thick × 140 mm long.

2.3.2. Flexural test

Flexural strength of material is an indicative of the strength of samples in bending loadings. Therefore the flexural tests were performed according to ASTM D790 standard protocol.

2.3.3. Impact test

In order to evaluate the effect of modification on impact strength of material, special test has been conducted. The impact test of the composite has been conducted according to the test method described in reference (Abadyan, *et al.*, 2010; 2011).

2.3.4 DSC test

The glass transition temperatures of the samples were determined by a differential scanning calorimeter (DSC). The samples were heated from 60 to 130 °C at the heating rate of 10 °C/min.

2.3.5. Microscopy evaluation

The surfaces of the fractured specimens were examined using scanning electron microscope (SEM). In order to produce a conductive surface the fractured surface of samples were first coated with a thin layer of gold. SEM samples were coated with a thin layer of gold before examination to protect the fracture surfaces from beam damage and also to prevent charge build up.

3. Results and Discussion

3.1. Compressive properties

The compressive characteristic plays an important role in mechanical performance of reinforced epeoxy materials. Table 2 demonstrates the compressive strength of reinforced epoxy as a function of oligomer content. The compressive strength gradually slightly decreases with increasing vinyl-based modifier content (Table 2). This is the result of the lower strength of oligomer in comparison with the epoxy. Oligomers affect mechanical properties of reinforced epoxy depending on their chemical structure and geometrical parameters of precipitated particles (Abadyan *et al.*, 2009a). Note that rubbery and elastomer materials usually have a lower strength and modulus than those of thermoset resins.

Table 2: Compressive strength of samples

Sample	Compressive Strength (MPa)
E	423
E5	412
E10	388
E15	392
E20	380

3.2 Flexural test

Table 6 presents the flexural strength of composite tubes. The compressive property of final composite is affected by rubber modification. As seen, flexural strength of specimens decreases with increasing rubber content similar to that of compressive strength. These can be attributed to weakening effect of rubber modifiers in the matrix. However flexural strength is less affected by rubber modification in comparison with compressive properties.

Table 3: Flexural strength of samples

Sample	Flexural Strength (MPa)
E	78
E5	75
E10	73
E15	69
E20	71

3.3 Impact strength evaluation

Impact strength is known as a rough criterion for evaluating the toughness of a material. While it might be not accepted as a scientific data in scientific researches, however this produces a good physical interpretation of the toughness for engineers and designers. The impact strength (I_{imp}) of VTB-modified composite samples are measured and listed in Table 4. Increase in impact strength is reported in samples containing VTB oligomer. Increasing modifier content leads to an increasing in impact strength. As seen by addition of 15 phr VTB one can increase more than % in impact resistance of the material. This is the result of inducing cavitation and massive shear yielding in the epoxy matrix due to the stress concentration of VTB particles. An interesting point is that previous researches reveals less cavitation and void grows in the case of the impact test specimen compared to fracture toughness test samples. Decrease in cavitation and void growth corresponds to decrease in plastic deformation and energy absorption. It is the result of higher loading rate of impact test in comparison with fracture toughness test. Previous research showed that at high loading rate, toughening mechanisms such as cavitation and void growth are suppressed.

Table 4 Impact resistance of resin

Sample	I_{imp} (kJ/m^2)
E	5.91
E5	7.11
E10	7.84
E15	8.01
E20	7.19

3.4 Thermal behavior

An indicative of the thermal strength of a material is glass transition temperature. This parameter shows the temperature, in which the movement of the polymer branches increases dramatically due to the heat energy increases. The variations of glass transition temperature of the samples are listed in Table 5. Decrease in glass transition temperature of samples is observed due to vinyl-based rubber modifiers. As seen from Table 5, increase in modifier content leads to a slight decrease in glass transition temperature. The reduction in glass transition temperature of epoxy by addition of liquid rubber can be attributed to lack of complete precipitation of the rubber molecules from the matrix. Please note that rubber molecules can reduce the glass transition temperature.

Table 5 Glass transition temperature of resin

Sample	T_g (C)
E	110
E5	109
E10	109
E15	109
E20	108

3.4 SEM

Figure 1 shows the SEM micrographs of the fracture surface of impact test samples. Hackling type morphology is observed for unmodified matrix remaining between the fibers and in the case of modified resin, cavitated rubber particles are observed between fibers with no hackling in resin surface.

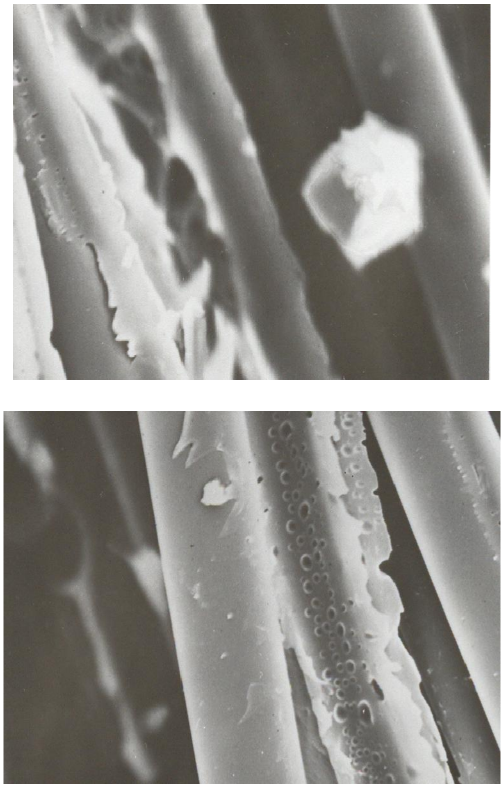

Figure 1. SEM micrographs of surface of composite impact samples: (a) E, (b) E10.

4. Conclusions

Herein, a liquid vinyl-based oligomer was employed as toughening agents in composite materials. The mechanical tests including compressive test, flexural test and impact strength test has been performed. Moreover, in order to interpret the mechanical test data, damaged surfaces of fractured samples were investigated using scanning electron microscopy (SEM) techniques. It is found that the compressive and flexural strength of resin decreased by oligomer modification. Results showed Moreover the impact strength of composite has been substantially improved. This is attributed to the high cavitations of modifier particles. However, these improvements are accompanied with a slight reduction in glass transition temperature. SEM fractography reveals that oligomers precipitate from the epoxy matrix which effectively increases epoxy toughness.

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