Use of oligomer modifier to enhance the fracture characteristics of glass reinforced composites for civil and medicine

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Abstract: Glass reinforced composite materials are used in civil engineering and medical applications. This material is one of the conventional constitutive materials which present good mechanical properties with low price. Herein we enhance the impact resistance of the glass-reinforced composite using oligomer modification agent. Mechanical fracture toughness tests have been conducted using standard test samples. The obtained test results show that the fracture toughness of Oligomer modified glass-reinforced composite is enhanced by addition of the Oligomer to the glass reinforced composite. Moreover the damaged surfaces of fractured samples were investigated using scanning electron microscopy (SEM) techniques.
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1. Introduction

In recent years glass reinforced polymeric (GRP) composite materials becomes one of the most-applied materials in engineering, medicines and many branches of applied sciences. With recent developments in medicine, GRP materials are used in making prostheses, making human artificial parts, dental applications, and other medical applications. The GRP composites are commonly used in reinforcing old structures, bridges and other applications.

Despite the excellent tensile properties of GRP material, this material suffers from a low fracture roughness. This is due to the brittleness of polymeric matrix materials such as epoxy, etc. This restricts its application in structural applications since they exhibit a low fracture resistance (Vaziri *et al.*, 2011a, 2011b; Valipour *et al.*, 2012). For example, for GRP made leg prostheses or for bridge structures several static and dynamic loading might be happened during the operational life of the structure. These loadings induce micro-cracks, defects and void nucleation that act as failure points in the matrix. Considering these issues one can conclude that the enhancing the fracture toughness of composite materials for high performance applications is very crucial.

Addition of secondary polymeric phase such as Oligomer oligomer to the epoxy polymer matrix is an appropriate method for improving impact resistance of these composites (Riew and Kinloch, 1996; Gabr *et al.*, 2010a; 2010b; Kim and Mai, 1991). Other methods of improvement might not be as effective as addition of Oligomer to the composites. Oligomer material might be utilized as a safe modifier with less glass transition temperature for GRP toughening (Kim and Mai, 1991). The modification of composites has been studied in previous publications. For example, Ophir *et al.* (1995) investigated modified GRP composite for producing high pressure storage vessels. In another work, Zhang *et al.* (1995) used CTBN to modify the toughness of composite pipes. Previous research showed negligible increase in impact strength of composites which was the result of low toughenability of the resin used (Sanjana *et al.*, 1985). 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). Sobrinho et al. (2011, 2012) applied a CTBN-modified epoxy system for development of composite pipes for riser application in deep water. The influence of matrix toughening and the number of composite layers on the mechanical behavior of the tubes were investigated by hydrostatic and split-disk tests (Sobrinho *et al.*, 2011; 2012). Moreover, exploring the energy absorption of hybrid modified epoxies containing soft particles has been accomplished in (Abadyan *et al.*, 2011). They observed that addition of 3rd polymeric phase (coarse waste tire particles) to a modified epoxy (bi-modal epoxy) might reduce the energy absorption of the composite. Moreover it has been demonstrated that the enhancing the loading rate of modified epoxy samples might lead to reduce the energy absorption of samples (Abadyan *et al.*, 2010). This reference shows that cavitation has a great influence on the fracture toughness of epoxy matrix. Moreover, the incorporation of two types of rubber modifier on toughness and energy absorption of bi-modal composite epoxy has been examined (Abadyan *et al.*, 2012a;2012b). There are several other works that can produce useful data for increasing the fracture toughness of the GRP composites.

There is still lack of knowledge on the role of modifier particles in the overall performance of wound composites. Only few works has been focused systematically on investigation of the impact resistance of composite materials. Therefore, the goal of the current investigation is to study the role of rubber modification in fracture toughness of GRP tubes in a more systematic fashion. Fracture toughness tests have been conducted in combination with scanning electron microscopy (SEM). A Hycar1300×16 oligomer is used to modify the epoxy matrix and the corresponding wound composites.

2. Experimental

2.1 Materials

The typical resin system used in this work for fabrication of composite samples is diglycidyle ether of bisphenol A epoxy resin (trade name of Araldite LY5052) and a polyamine hardener (trade name of HY5052). In order to fabricate glass-reinforced samples, glass fiber roving has been used for filament winding the test samples. Reinforcement used was a glass rowing with 2400 tex from Vetrotex. The reactive oligomer modifier is used was the Hycar1300×16 with 16 wt% of acrylonitrile, from Novion company.

2.2 Sample preparation

In order to make the samples, the stoichiometric ratio of the curing agent and resin were cured for 8h at 80 ºC. The modifier content (Oligomer content) was varied from 0 up to 20 phr. We added the Oligomer modifier before adding the hardener agent. After preparing the resin samples, we fabricated the filament wound composite samples. All formulations were reinforced with glass fiber. First resin has been modified with Oligomer material and then the compound has been glass reinforced in the machine resin bath before applying on the mandrel. For this purpose we used a 3-degree of freedom (3-DOF) filament wound automatic machine. After that, we cured the samples according to the datasheet instruction above. The composite formulation used is listed in Table 1.

2.3 Characterization techniques

In order to evaluate the behavior of Oligomer modified samples, we have used two techniques including measuring the impact resistance and glass transition temperature of the wound samples.

Table 1. Resin formulations made in this study

Sample code	Resin (phr)	Hardener (phr)	Modifier Content (phr)
NC	100	38	0
CV5	100	38	5
CV10	100	38	10
CV15	100	38	15
CV20	100	38	20

2.4 Interlaminar shear strength

Interlaminar shear strength (ILSS) of GRP samples are measured using cubic test samples loaded in Three-point bending state. ASTM D2344 guideline was followed to measure the ILSS of composite. The direction of glass fibers in the test sample are shown in figure 1.

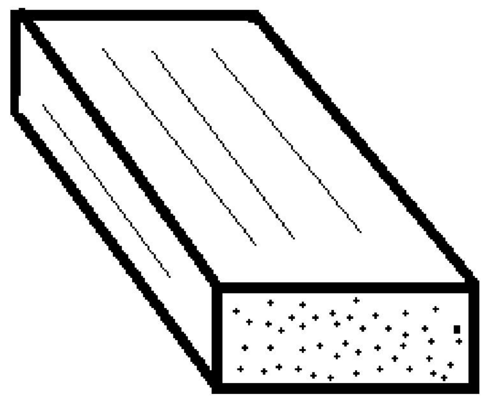


Figure 1. Direction of fibers in the ILSS test samples

2.5 *Fracture toughness evaluation*

The GRP composite laminates are tested at room temperature using the double-cantilever beam (DCB) specimen according to ASTM D5528 standard protocol. The DCB specimens are machined from the cured GRP laminates along the longitudinal direction of the fiber using a saw. Afterwards cut samples are polished with fine sand papers to reduce the roughness of samples. The DCB specimen is shown schematically in Figure 2. The loading hinges were mounted at the end of DCB specimen arms.

2.6 SEM Microscopy evaluation

The surfaces of the 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. After that, the surface has been investigated under a high electrical voltage differences.

2.7 Optical Microscopy evaluation

Reflected light optical microscopy (OM) was applied to investigate the fracture surface of fracture toughness samples. An Olimpus microscope with ×70 magnification is utilized for observation

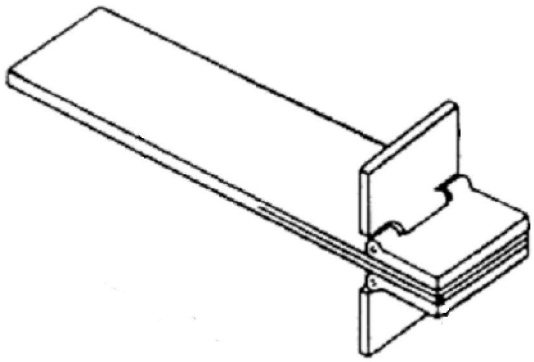


Figure 2. DCB samples for mode I fracture toughness test

3. Results and discussion

1.1 Fracture toughness test

In this work, mode I inter-laminar fracture toughness was determined from double cantilever beam (DCB) test using ASTM D5528 standard. According to this standard a non-adhesive aluminum film was inserted in the mid-plane of the GRP laminate during hand layup. This thin film forms an initiation site for the onset of delamination at the test. The free ends of the specimen was opened by controlling the crosshead speed with the recommended speed of 2 mm/min. Then, the changes of the load, load point displacement and crack growth were measured during the test.

The results of the fracture toughness evaluation test of the samples are listed in table 2. As seen, addition of the Oligomer modifier to the epoxy polymeric matrix of the GRP composite can increase the fracture toughness of the final GRP composite samples. As seen neat epoxy has the fracture toughness of 600J/m^2. However this tale reveals that by addition of 15 percent Oligomer, more than 40 % increase in the fracture toughness of the GRP material is observed. This is the results of cavitation and shear yielding of modified resin in the vicinity of the crack tip of the GRP samples. However by increasing in the Oligomer content beyond 15 %, a reduction in the fracture toughness of the modified GRP is observed. This observation shows that there are an optimum value of Oligomer modifier content for fracture toughness modification. This is an important issue for engineers in designing and manufacturing high-fracture toughness GRP structures.

Table 2. Impact strength of composite tubes

Sample	Interlaminar Fracture toughness
CN	600
CV5	740
CV10	820
CV15	850
CV20	830

1.2 ILSS test

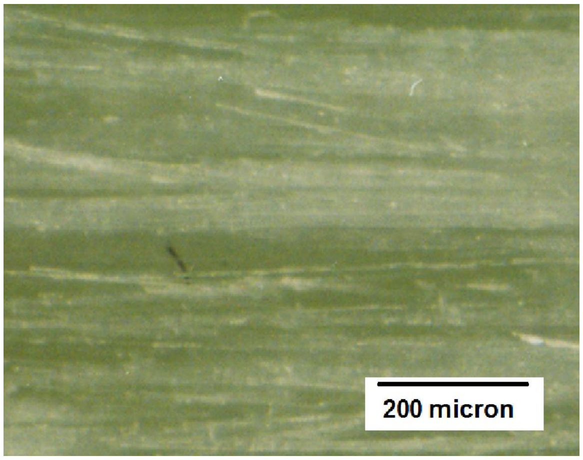
Interlaminar shear strength (ILSS) is an important parameter in predicting the low velocity impact damage initiation of laminated or wound composites. Table 3 presents interlaminar shear data obtained from cubic test samples which show some reduction in the interlaminar shear strength (ILSS) with increasing in Oligomer content. Modification of GRP influences ILSS of modified composite as reported by other researchers and results shows that ILSS decreases slightly with Oligomer content.

Table 3. ILSS of GRP composite

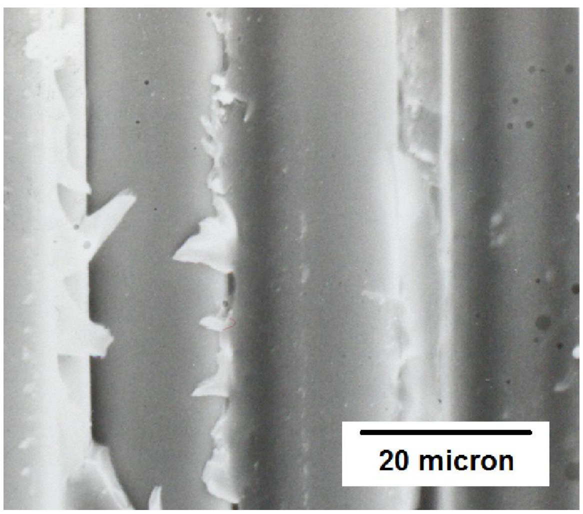
Sample	ILSS (MPa)
CN	39
CV5	35
CV10	34
CV15	35
CV20	30

1.3 Fractography

In this paper both OM and SEM are applied for investigate the fracture surface of modified samples. Figure 3 (a) shows the OM fractograph of the fractured samples. The white regions present the glass fibers that are detached from the matrix due to the stress at the crack tip of the samples. Note that the OM are not able to shows the fracture mechanisms. For investigating the fracture mechanisms SEM are required. Figure 3 (b) shows the SEM photo. As mentioned before, in order to produce a conductive surface the fractured surface of samples was first coated with a thin layer of gold. After that, the surface has been investigated under a high electrical voltage differences. In figure 23we present the SEM images of the fracture surface of samples. In the case of modified resin, cavitated rubber particles are observed in the resin surface. On the fracture surface of the samples small dark spots are observed. These spots are the cavitated Oligomer particles that are cavitated during the stress concentration around the crack tip. This mechanism can be schematically explain as in the figure 4.



(a)



(b)

Fig. 3: SEM micrographs of surface of composite fracture toughness samples: (a) TOM, (b) SEM.

The mechanisms of enhancing fracture toughness resistance of composite materials by Oligomer can be illustrated in figure 4. First, the solution of Oligomer in the epoxy matrix (0) precipitates into two distinct phase of epoxy and Oligomer spheres (1) during the curing process. By applying an impact loading on the specimen, the external stress induces during growth of the crack (2) which causes the matrix to cavitate (3) and voids nucleate. The size of these cavities increases by increasing the stress during crack propagation (4) and produce a plastic deformation in the matrix. These plastic deformation and holes can pin and arrest the microcracks that occur during the fracture loading (5).

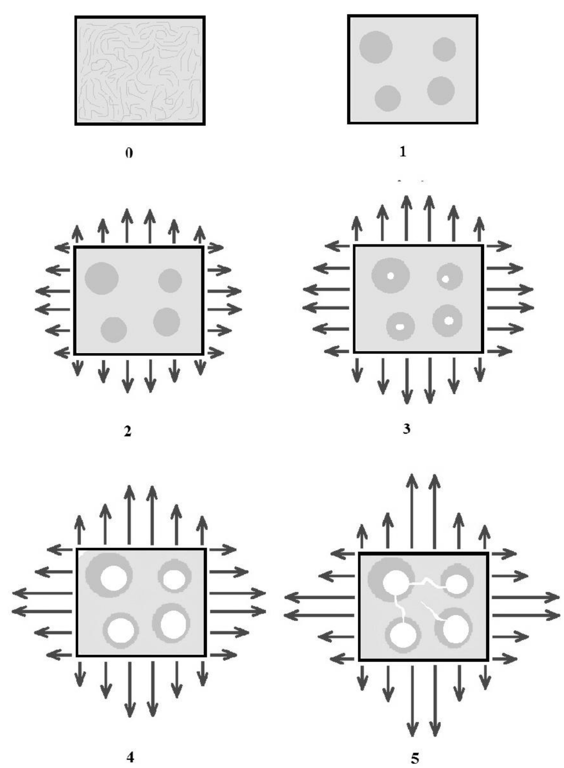


Fig. 4: Mechanisms of Oligomer in increasing the impact resistance of composite samples: The solution of liquid oligomers in the epoxy matrix (0) precipitates into two distinct phase of epoxy and Oligomer spheres (1). Applying the external stress during impact (2) causes the matrix to cavitate (3). The cavities increase by increasing the stress during crack growth (4) and they pin the microcracks that occur during the crack growth (5).

4. Conclusions

In this work fracture toughness of the Oligomer modified GRP are evaluated. Epoxy-based glass reinforced composite is one of the most common composite that is used for its good mechanical properties and low price. The optical and scanning electron microscopy has been conducted to better understand the composite behavior during the fracture toughness test. Fracture toughness of composites has been influenced by Oligomer modification. The obtained test results show that the fracture toughness of Oligomer modified GRP composite is enhanced by addition of the Oligomer. However there is an optimum Oligomer content that beyond it no modification can be observed by increasing in modifier content. As a drawback, Oligomer materials reduce the ILSS of the modified GRP.

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