International Journal of Research in Advent Technology, Vol.6, No.8, August 2018
E-ISSN: 2321-9637
Available online at www.ijrat.org

Effect of PMMA on Microstructure and Mechanical Properties of Epoxy Polymer Blends

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Abstract- Polymer blends were prepared from the diglycidylether of bisphenol-A (DGEBA) epoxy modified with different weight percentage of poly-methyl-metacrylate (PMMA). The synergistic effects of PMMA on the mechanical properties of the epoxy were examined by tensile test, 3-point bending test, and fracture toughness test. The flexural strength of the epoxy monomer is reduced by the inclusion of the PMMA. Further investigations confirmed that epoxy/PMMA polymer blends also exhibited significant enhancement in the value of fracture toughness and tensile modulus. The synergetic mechanism was studied by means of SEM observation of fractured surfaces. The improvement in fracture toughness (K_{IC}) was verified and established by the morphology obtained by photomicrographs of SEM, which shows a uniform distribution of PMMA and moderately rough surface with sheared deformation and zig-zag cracks in the PMMA-modified epoxy resin system, which acts as a crack arrester and thereby preventing deformation as well as crack propagation.

Index terms: Polymer blends; fracture toughness; PMMA; Epoxy**.**

1. INTRODUCTION

Epoxy based polymer composites are extensively used in aerospace, automobiles and structural applications due to their admirable mechanical properties, physical properties, chemical resistance and better dimensional stability [1-3]. Epoxy monomers typically possess very high crosslink density after curing. However, owing to their high crosslink density, results in low fracture toughness and poor ductility, which restricts their industrial applications in many cases. To increase the fracture toughness, epoxy resins are toughened by adding different types of rubber and thermoplastics, such as ABS, polyetherimide, polysulfone, polyethersulfone [4-7].

Hu jin et al. [8] analysed the fracture toughness of composite made from epoxy blends modified with polysulfone. It was observed that, by adding polysulfone to neat epoxy, the flexural strength was decreased. However, fracture toughness increased significantly by 53 % with addition of polysulfone as compared to neat epoxy. B.B. Johnsen [9] investigated the effects of microstructure and toughening method of epoxy monomer with the addition of syndiotactic polystyrene (sPS). They formed epoxy blends modified with sPS, as toughening stage. They investigated Phase-separation of epoxy resin modified with sPS by this alternate methods i.e.., phase-separation by induced reaction and crystallisation-induced phase-separation. They observed that by adding one weight% of sPS gives an instant increase in toughness but the maximum toughness reached for reaction induced blends and they found no improvement for crystallisation induced blends.

Poly-Methyl-Metacrylate (PMMA*)* is a classical amorphous polymer which has the highest optical transmittance among any thermoplastics. PMMA is low cost thermoplastic and have high Young's modulus whose usage standing between commodity and engineering applications. In spite of its light weight and shatter-resistant, PMMA is more susceptible to scratching than the glass [10] .On the other hand, if PMMA is modified with other polymers, it is able to achieve high scratch resistance and superior mechanical properties [11]. With regards to PMMA as the toughening agent for epoxy, one important fact is that an initial homogeneous solution with diglycidylether of bisphenol-A (DGEBA*)* can be obtained over the complete composition range [12]. Many authors [13] also studied and revealed the possible feasible interactions between PMMA thermo plastic and Epoxy.

The aim of this work is to study the effect on fracture toughness and mechanical properties of epoxy resin with the addition of thermoplastic PMMA in different weight percent. The relationships between the toughness and their micro structural characteristics were revealed, and it is clearly established that the

fracture toughness values varies for different microstructure.

2. EXPERIMENTAL

2.1 Materials

The DGEBA epoxy monomer resin of commercial grade was supplied by Atul Ltd. Gujarat, India and has an epoxy equivalent weight of 180-190 gm/equivalent, with K-6 hardnerdiamino-diphenyl-methane (DDM) as curing agent. Poly-methyle-metacrylate (PMMA) of commercial grade was purchased from chemical house, Bangalore, India. Acetone $(CH_3)_2CO$, used as PMMA solvent, was purchased from Nice Chemicals (P) Ltd. Kerala, India.

2.2 Specimen Preparation

The epoxy is toughened with 2 to10 wt% PMMA using procedure mentioned [14] elsewhere. PMMA of measured quantity was dissolved in acetone and then mixed with the epoxy. The blend was stirred vigorously by using mechanical stirrer with 500 rpm for 30 minutes. The PMMA/epoxy blend was kept in magnetic stirrer with heater at 85 ^oC for 30 minutes in order to evaporate the solvent and cooled to room temperature. After cooling to room temperature, an equivalent amount [15] of DDM as hardener was poured to epoxy PMMA blend. This composition was thoroughly mixed for thirty minutes using stirrer and it is then placed in special vacuum chamber to remove bubbles entrapped with air. Clear Mixture was then poured in to test sample molds which has five specimen slots and previously coated with a mold releasing agent. It was cured at room temperature for 12 hours and post curing at 140 ^0C for 2 hours in an autoclave to relieve internal stresses. The autoclave was then turned off and the mould was retained in the autoclave for cooling entire overnight, after post curing specimens were removed from the mould.

2.3 Characterization

Neat epoxy and PMMA modified epoxy resins with five proportions of PMMA (2, 4, 6, 8 and 10 wieght%) were fabricated. UTM (AUTOGRAPH, Model AG-IS) was used for three-point bending test, tensile test and flexural test. ASTM E-399 standard test procedure for three point bending is used and critical stress intensity factor (K_{IC}) is calculated by measuring load and deflection. Batch of five Single edge notched samples of size 5x10x48 mm^3 were tested for 3 point bending and the average value was recorded. The flexural tests were carried out on AUTOGRAPH (Model AG-IS) as per ASTM D790 standards, using three-point bend arrangement for un-notched specimen size of 4x12x100 mm^3. Tensile test is carried out with same UTM by changing the fixture following ASTM D638 standard procedure. Each mechanical property was established by considering mean of five trial values after testing. SEM (VEGA3 TESCAN) was employed to elucidate the microstructure and morphology of the fractured surfaces of the three-point bending samples to check the distribution of PMMA particles and thin layer of gold sputter were coated to all fractured surfaces of specimens before morphology analysis.

3 RESULTS AND DISCUSSION

3.1 Fracture Toughness

The fracture toughness of the pure epoxy and PMMA-modified epoxy monomer was examined by calculating the critical value of stress intensity factor (K_{IC}). For the 3-point bending notched specimen, the K_{IC} values were obtained from the below equation [16]

$$K_{IC} = \frac{2.29PS}{BW^{3/2}} \qquad \text{Eq. (1)}$$

Where, P denotes breaking force in Newton, B represents thickness of specimen in mm, W denotes specimen width in mm, S denotes distance between the supports during testing and 2.29 is the correction factor. The fracture toughness (K_{IC}) values of the pure and PMMA-reinforced epoxy composites are tabulated in table 1. By adding PMMA into the pure epoxy monomer, enhance in fracture toughness was observed and reached the maximum value when 6 weight% of PMMA is added and then start to degrade. The pure epoxy resin was highly brittle and has a K_{IC} value of 0.73 MPa$\sqrt{m}$. In addition, there is remarkable increment in the value of K_{IC} with the addition of PMMA. It was found that K_{IC} increased by 1.12 MPa$\sqrt{m}$ for the addition of 6 wt% of PMMA as compared to pure epoxy monomer. The PMMA formed a second phase within the system and acted as stress absorber, further reducing chances of crack propagation and increasing the stress needed to fracture the samples. At the initial stage of crack propagation, the length of crack front increases, but presence of PMMA particles changes the direction of crack growth, hence more energy required to fracture the sample. The improvement of fracture toughness of brittle epoxy results from the interaction between

the dispersed PMMA as second phase and moving crack tip. This may be due to the restriction of mobility of polymer chains because of scattering of PMMA particles in the epoxy resin matrix and reduced cross-linking density in the epoxy matrix system obtained from the linear network and low density PMMA. It is important to note that the addition of PMMA above 6 wt% the fracture toughness reduced due to phase separation, less interfacial adhesion and linear chain linking of PMMA. Force versus deflection graph was used to calculate the crack length of specimens, and the results are tabulated in Table 1. The length of crack is increased with increasing PMMA composition up-to 8wt% PMMA.

3.2 Tensile Modulus data

The modulus of the neat epoxy, and entire PMMA mixed epoxy composites, was shown in Table 1. The Young's modulus was decreased to 2 Gpa after 6 wt % due to the macro phase separation at 8 and 10 weight% blends. The PMMA has moderately high Young's modulus with value of 2.62 GPa. This information reveals that the Young's modulus (E) of the epoxy resin is more often than not reduced by adding PMMA, apart from some cases where macro phase separation of the PMMA takes place.

3.3 Flexural Strength

The flexural strength test was carried out with a 3-point bending test and the values were calculated using the equation given below.

$$\sigma_f = \frac{3PL}{2bd^2} \qquad \text{Eq. (2)}$$

Where P denotes maximum load in Newton, L denotes span length in mm, b denotes specimen width in mm, d denotes specimen thickness in mm.

Table 1. Modulus, Fracture toughness, flexural strength and crack length of neat and PMMA-modified epoxy resins.

PMMA (Weight %)	**Modulus, E (GPa)**	**K_{IC} (MPa√m)**	**Flexural Strength in MPa**	**Crack length in mm**
0	2.07	0.73± 0.03	96.1± 3.1	0.48± 0.02
2	2.15	1.12 ±0.03	93.2 ±3.0	0.61± 0.05
4	2.23	1.15 ±0.03	90.2 ±3.0	0.82± 0.05
6	2.22	1.17 ±0.04	87.8 ±2.8	0.98± 0.05
8	2.13	1.10± 0.03	88.1 ±2.8	1.27± 0.04
10	2.00	0.84 ±0.03	73.1 ±2.5	1.24± 0.04

The calculated values of flexural strength (σ_f) of the pure epoxy resin and the PMMA added epoxy resin are tabulated in Table 1. When the PMMA percentage increased from 0 to 10 weight% in the epoxy matrix there is significance decrease in σ_f value from 96.1 MPa to 73.1 MPa. The reduction in the flexural strength can be accredited to the reduced cross-linking density in the epoxy blend due to the addition of PMMA [17].

4 MORPHOLOGICAL ANALYSIS

The fractured surfaces of the pure and the PMMA-added epoxy monomers were analysed with scanning electron microscopy (SEM) after the fracture toughness test. Figure 1(a) shows SEM photomicrograph of the pure epoxy resin which shows flat and glassy surface with smooth running cracks, representing a characteristic brittle fracture surface which is accredited of its poor toughness. However, in case of PMMA-epoxy blends, the phase separation of PMMA results in comparatively jagged surface with sheared deformation, which occur in the time of curing of the prepared PMMA modified epoxy specimens, thus prevents deformation and propagation of crack in the PMMA-added epoxy resin, as exposed in Figure 1(b), 2(a & b). This result evidently demonstrates that the fracture toughness of PMMA-added epoxy resin is notably higher compared to that of the pure epoxy monomer.

However, the photomicrograph of epoxy containing 6% PMMA shows a different morphology with a rough surface, an elongated stratified structure and well dispersed PMMA particles. The observed morphology confirms the presence of matrix plastic deformation, which in turns might explain the enhancement of mechanical properties of epoxy resin.

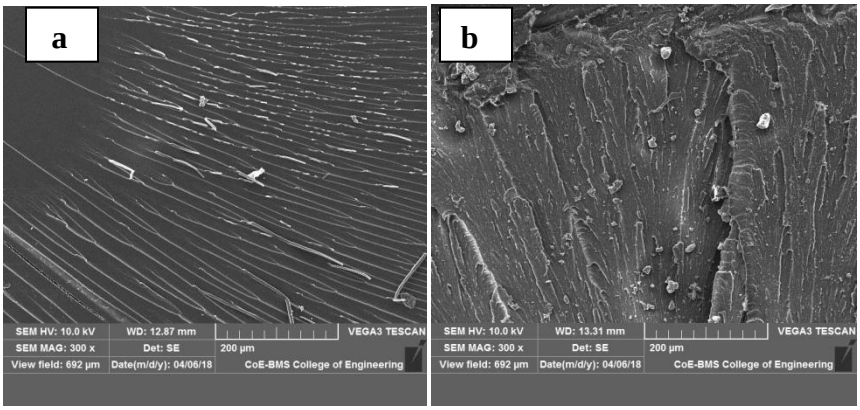

Fig1. Scanning electron micrographs showing fractured surface of (a) pure epoxy, (b) for samples containing 2 weight% PMMA.

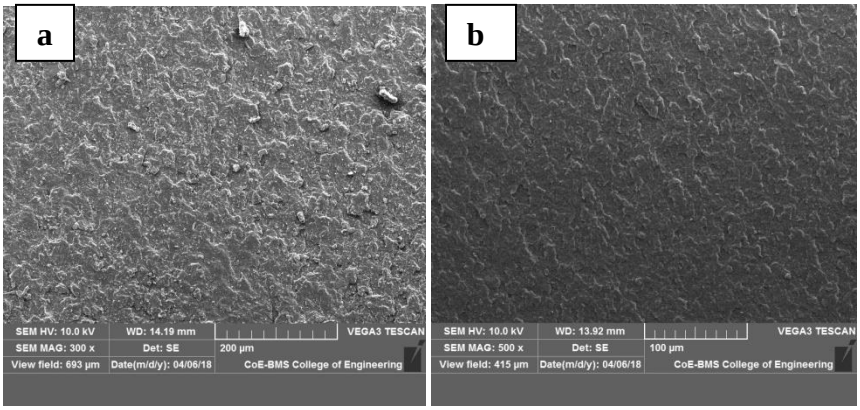

Fig 2. Scanning electron micrographs showing fractured surface of (a) 4 weight% PMMA; and (b) 6 weight% PMMA.

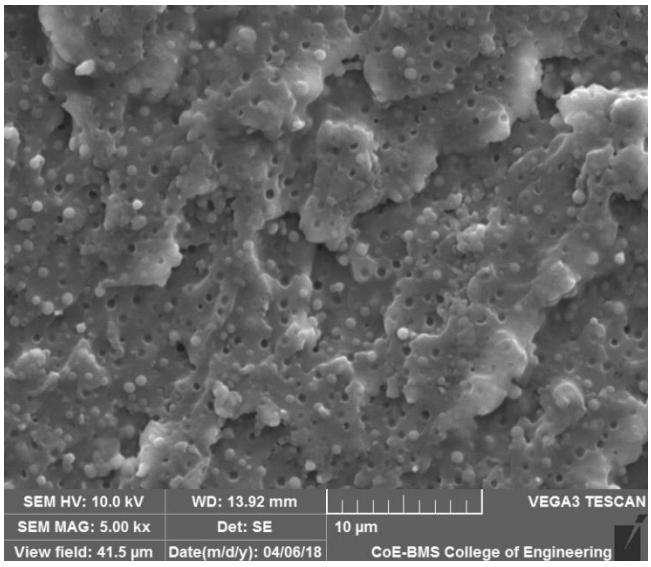

Fig 3. Magnified view of 6 wt % PMMA

Figure 3 shows the scanning electron photomicrographs of the fractured surfaces, showing ball-shaped PMMA particles in the epoxy resin matrix for test samples having 6 weight% PMMA and magnified view shows cavities in the surface near by the particles for the test samples having 6 weight% PMMA.

It is clearly observed that, in many locations of the fractured surfaces, the ball-shaped particles are missing, during fabrication or testing. During testing either they are trapped inside an opening on the opposite fractured surface, or because they have completely detached from the epoxy matrix and ultimately fallen from the fractured surface. These photomicrographs reveal that the PMMA particles look like loosely bonded to the epoxy. Surfaces of PMMA particle are clean, without any remaining epoxy pasted to them. PMMA is not easily wetted by epoxy nor attach well to the monomer because it has poor surface free energy [18]. Poor sticking together is anticipated between the epoxy matrix and thermoplastic phase, and therefore the PMMA can easily detach from the epoxy matrix during rupture.

5 CONCLUSIONS

The flexural strength, fracture toughness, modulus, crack length and fractured surfaces of the PMMA-added epoxy monomer were investigated and compared to those of the pure epoxy monomer. By the inclusion of the dissolved PMMA in the epoxy matrix, there is decrease in the flexural strength of the epoxy monomer but modulus is increased up to 6 wt% PMMA and significant improvement of the fracture toughness was observed. The improvement of fracture toughness was established by the photomicrographs of SEM, which showed a fairly jagged surface with sheared deformation and criss-cross cracks in the PMMA-added epoxy system, which restricts deformation and propagation of crack. SEM photomicrographs also confirmed that the presence of homogeneous and regular structure of PMMA embedded in polymer matrix.

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