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Tensile properties of epoxy/1 wt% graphene nanocomposites prepared with ethanol

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Abstract. In this research, solution casting technique was applied to produce four types of nanocomposites. Different ethanol dosages; 0g, 1g, 3g, and 5g were used to disperse graphene in the epoxy matrix. It was observed that 1g dosage of ethanol was the most effective concentration to disperse 1wt% graphene in the epoxy matrix. At 1 g dosage of ethanol used, the Young's modulus, tensile strength, and toughness were increased by 130% ,76%, and 187% respectively. SEM images illustrated that the graphene was able to inhibit the advancing cracks and detoured cracks propagation. It is observed that the ethanol needs to be removed completely during processing to ensure its effectiveness, otherwise, the remaining ethanol can cause porosity which is undesirable to the tensile properties of the nanocomposites.

1. Introduction

Composites are materials which are comprising at least two or more phases that are chemically and physically bonded. Composite materials have a number of advantages, such as good resistance to corrosion, high fatigue strength and very low weight. In industry, composite materials have been widely used in aerospace, automotive, military, biomedical and sports leisure goods [1].

Because of their excellent thermal, chemical stability and mechanical properties when combined with fillers. Epoxy resin are used in numerous industrial applications particularly in aerospace, automotive and construction industries [2][3][4]. In recent years, epoxy resins have gained research interest in engineering applications due to their unique balance of chemical and mechanical and advantages of ease of processing [4][5]. However, due to the crosslinking structures which make the epoxy prone to crack and brittleness, the applications of epoxy resins remain limited.

Various studies have been carried out to increase the epoxy toughness. One of the popular methods is by adding Nano-filler such as graphene in the epoxy. Graphene-based polymer composite has attained great attention since the explosion of graphene research in 2004 due to its excellent performance in terms of thermal, mechanical and gas barrier [6]. Graphene-based materials have been extensively used in various fields such as composites, coatings, electronic devices, energy storage, sensors and biomedical [6]. Asif et al in their previous research have established that the Young's modulus and micro hardness of multi-layer graphene/epoxy have improved by 26% and 18% respectively [7]. In addition, the glass transition temperature (T_g) and storage modulus also improved in comparison to unreinforced epoxy.

Addition of Nano-filler such as graphene in epoxy can significantly enhance the physical and chemical properties of the composite at extremely low loadings provided that the filler is homogenously dispersed in the matrix [8][9]. The graphene; when dispersed homogenously acts as a barrier to hinder crack propagation and share the external stress in order to evade stress concentration which in turn improves the mechanical properties of the composite. In contrast, poorly dispersed graphene can act as a stress raiser and increase stress concentration, resulting the reduction of the mechanical properties [10][11]. Graphene also tends to re-aggregate in the matrix due to the strong van der Waal forces between discretely graphene particles, thus manual mixing is impractical to disperse graphene in epoxy [3][12][13].

Solvents are usually used to ensure uniform dispersion in matrices [12] by manipulating the presence of function group attached on the graphene surface. This method allows direct dispersion of graphene in organic solvents. This method is widely used for processing epoxy/graphene nanocomposites. By using mild sonication method for instance, physical and chemical interaction between the functionalised graphene and polymeric matrices can be enhanced [14]. Likewise, graphene can be easily dispersed in a suitable solvent using bath sonication technique, mixed with epoxy resin and the solvent is removed in a high temperature [15].

Solvents such as ethanol showed good dispensability and steadiness to disperse graphene. Besides that, several other solvents such as tetrahydrofuran, acetone, dichloromethane, isopropyl alcohol and water also used to produce epoxy/graphene composites. Nonetheless, not all are efficient dispersant agents for graphene [10]. Using less toxic and volatile dispersing solvents such as alcohols and water, dispersion stability and scalable routes to dispersion still remain as challenges [16]. In addition, accurate characterisation, safe handling and post-processing poses greater challenges from the manufacturing point of view. Another vital challenge to overcome is achieving uniform dispersion at an attractive cost.

Ethanol has been widely used to homogenously spread graphene in epoxy matrix. The usage of ethanol at low content (1 wt%) to disperse graphene has not been reported elsewhere. Several types of epoxy/1 wt%-graphene nanocomposites were fabricated and their tensile properties were studied. In our previous work, flexural strength and flexural modulus increased by 62% and 61% for samples toughened with 1wt% graphene [13]. Likewise, the highest impact strength was recorded for 1 wt% graphene dispersed with 1g ethanol, where an improvement of 9.5% was observed [13]. To the best of author's knowledge, very few studies have been reported on the tensile properties of epoxy/1 wt% graphene nanocomposites prepared with small percentage of ethanol. None of the previous studies, nevertheless, have given due attention to the influence of adding different concentration of ethanol to a fixed concentration of graphene.

2. Materials and Methods

Graphene Nano platelets with particle size of 2 μm and surface area of 300 m^2/g was acquired from Sigma Aldrich, UK. Ethanol concentrations of 0 g, 1 g, 3 g and 5 g was used to disperse 1wt% of graphene in epoxy. Epoxy (Miracast 1517A, density 1.13 g/cm3) and hardener (Miracast 1517B, density 1.1 g/cm3) was purchased from Miracon Sdn. Bhd, Seri Kembangan Malaysia. It has been demonstrated that low viscosity of hardener inhibit an underpinning of agglomeration by refining the dispersion as well as responsible for fast curing [17]. The time taken for the resin to reach gelation was 40 minutes, and it was cured at room temperature.

Bath sonicate was used to disperse graphene in ethanol and this procedure was carried out for 5 minutes. Then the graphene was thoroughly mixed with epoxy. The temperature of the ethanol and epoxy mixture then was set to 60°C for about 10 minutes to fully remove ethanol through evaporation. Then, hardener was added in the epoxy-graphene mixture. The mixture was hand mixing and stirred manually for another 10 minutes before it was poured into silicone mould for 12 hours curing process at room temperature. Finally, all samples were cured for 6 hours at 150^0C to achieve complete crosslink [18].

The procedures of making the silicone mould were rather simple and the gelation time was only about 25 minutes. The silicone mould materials which consists silicone rubber and curing agent were purchased from a local company namely Portal Trading Sdn. Bhd, Penang, Malaysia. The mixture of ratio 98:2 (silicone rubber: hardener) was poured into mould made from acrylic and left for curing around 24 hours. The schematic illustration of the samples fabrication is shown in Figure 1. The tensile samples were produced as per ASTM D638 standard and the schematic drawing is shown in Figure 2. Minimum five tensile samples were tested for each nanocomposite system.

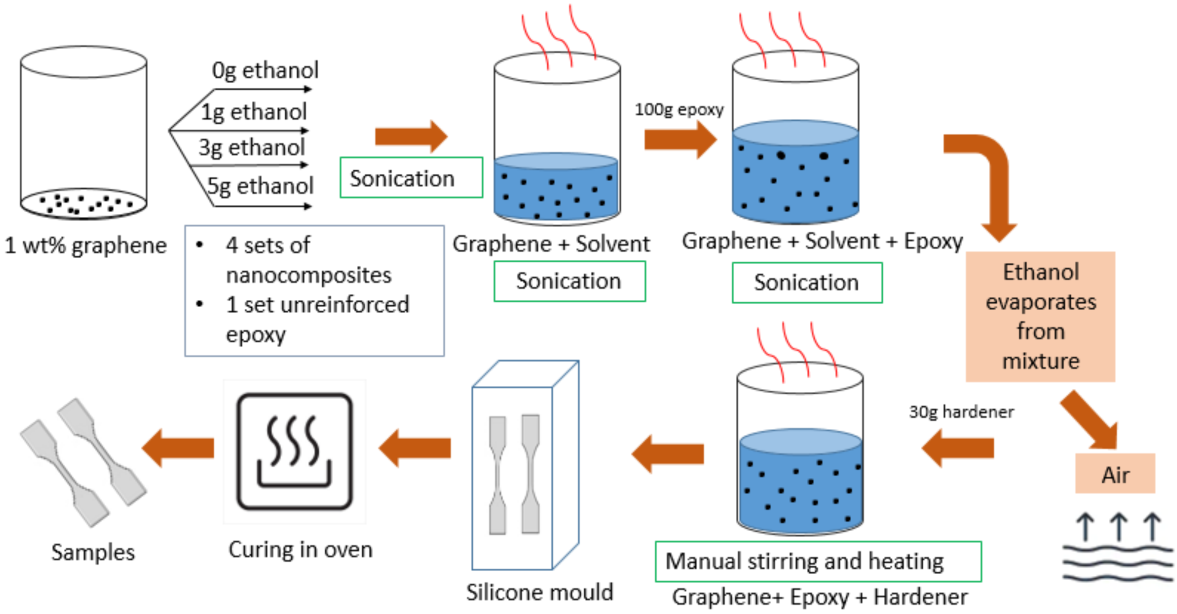

Figure 1. Preparation of nanocomposite samples.

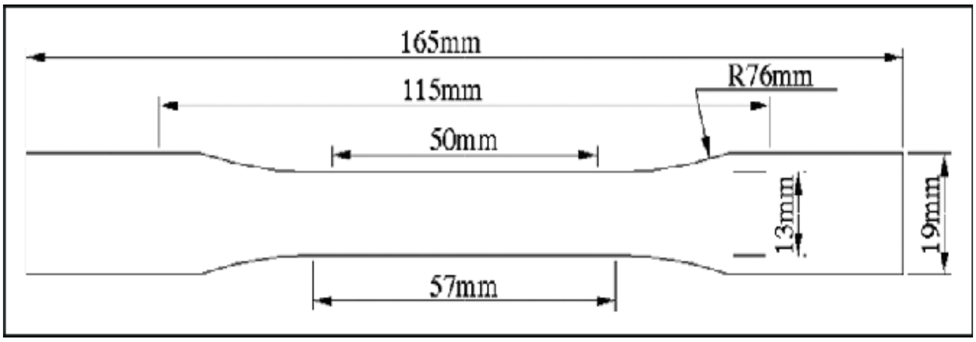

Figure 2. Schematic illustration of ASTM D638.

Five samples from each composition were prepared and tested by using Victor Universal Testing Machine (Victor VE 2302). The tensile crosshead speed was maintained 2 mm/min for all samples. Young's modulus (E) was obtained by the slope of elastic of a stress and strain graph, the value was calculated by the ratio of stress to its corresponding strain value.

$$E = \frac{Stress}{Strain} \qquad (1)[19]$$

$$\text{Where stress } (\sigma) = \frac{F}{A} \text{ and strain } (\epsilon) = \frac{\Delta l}{l_0} \qquad (2)[19]$$

Tensile strength (MPa) taken in this research was the maximum stress that a composite material can withstand while being stretched or pulled before breaking. As for the tensile strain, it was taken from the maximum point before failure. Finally, for toughness, (J.mm^{-3}) the value was obtained from the area under the stress-strain curve within the elastic limit as shown in Figure 3.

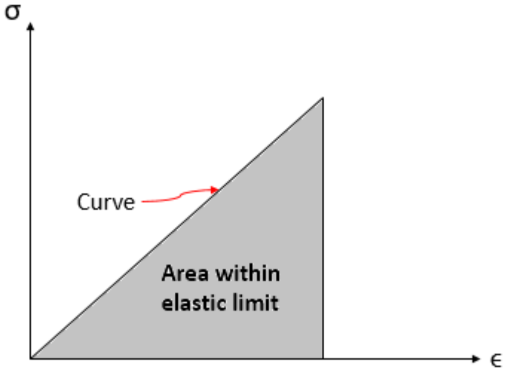

Figure 3. Schematic of area below stress-strain curve.

3. Results and Discussion

Figure 4 shows the stress versus strain curve for all nanocomposite samples prepared with different content of ethanol. It is observed that there is a variation in the stress-strain curve for samples prepared with low ethanol content. In general, all nanocomposite samples prepared with ethanol show good improvement compared with unfilled epoxy (ME). However, it is interesting to point out, without ethanol presence, the tensile stress value is somehow significantly high, however it is slightly lower than epoxy-1wt% graphene prepared with 1g ethanol. It is clearly seen that this sample showed the highest maximum value of stress compared to unfilled epoxy (ME). This can be related to the high aspect ratio of graphene and good bond between graphene and epoxy [20][1].

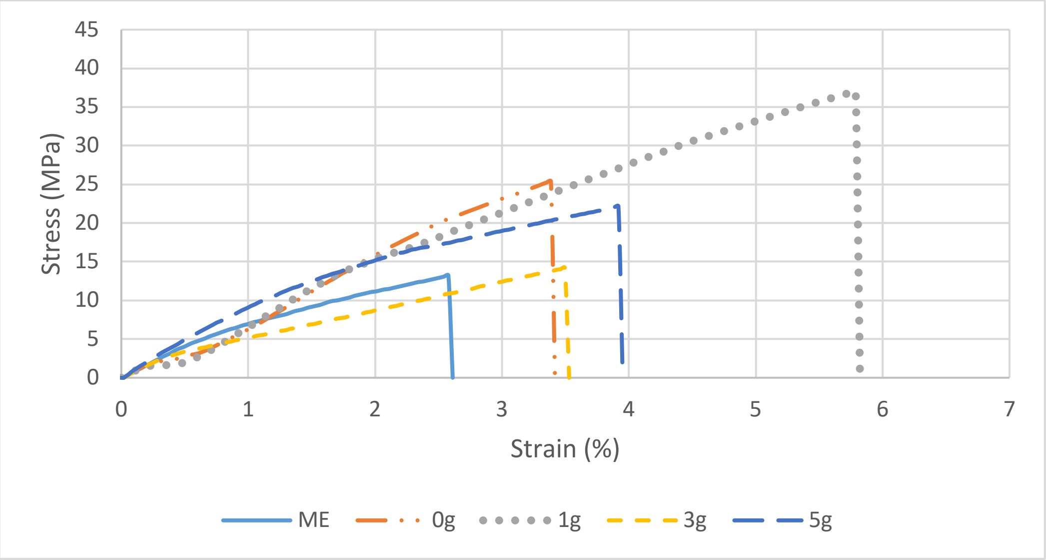

Figure 4. Stress-strain curve.

Figure 5 shows Young's modulus for unfilled epoxy and epoxy/1 wt% graphene samples. Unfilled epoxy recorded the lowest Young's modulus value of 4.1 GPa. The maximum improve in Young's modulus was observed in the sample of epoxy/1 wt% graphene prepared with 1g of ethanol, as 119% of enhancement was achieved. At higher ethanol content, the Young's modulus was improved 36% and 73% for samples prepared with 3g and 5g ethanol content. It is worth to mention, in the case of 3g ethanol content, the Young's modulus was slightly lower than expected value. This can be associated with several factors such as the porosity of samples caused by retained ethanol that acted as stress raiser and could be due to the presence of aggregates in epoxy matrix.

The variation of tensile strength for unfilled epoxy and its nanocomposite systems is shown in Figure 6. The lowest tensile strength recorded was 15.9 MPa in the case of unfilled epoxy. The highest tensile strength was in the case of epoxy/1 wt% graphene prepared with 1g ethanol, where an improvement of 76% was recorded. The lowest increase of 14% was obtained for epoxy/1 wt% graphene dispersed in 3g ethanol.

Figure 7 shows the graph of tensile strain for unfilled epoxy (ME) and its nanocomposites. In general, samples reinforced with graphene showed lower tensile strain compared to unreinforced epoxy. Unfilled epoxy recorded the highest flexural strain, this can be associated to lower strength value. In contrast, the minimum flexural strain was observed in the case of epoxy/1 wt% graphene prepared with 1g ethanol. Minimum flexural strain can be attributed to high stiffness.

The variation of toughness for all samples is presented in Figure 8. This toughness was obtained from area under stress-strain curve which represents energy required before the composites failure. Samples prepared with and without ethanol show good toughness. Epoxy/1 wt% graphene prepared without ethanol showed an increase of 152% compared with unreinforced epoxy. The maximum increase in toughness was observed in the case of epoxy/1 wt% graphene prepared with 1g ethanol, where a maximum increase of 187% was obtained. For 1 wt% graphene samples prepared with 3g and 5g of ethanol, the toughness improved 62% and 115 respectively.

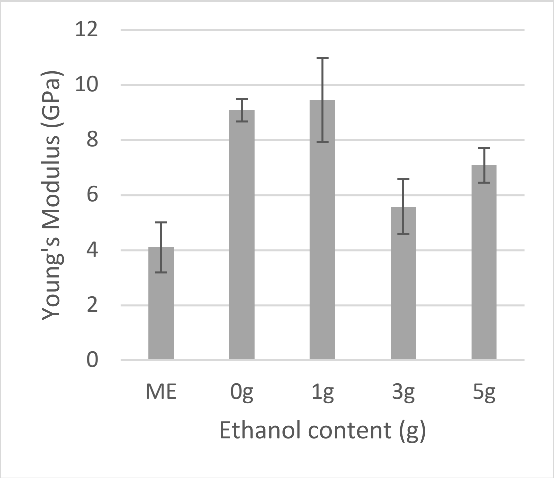

Figure 5. Young's modulus.

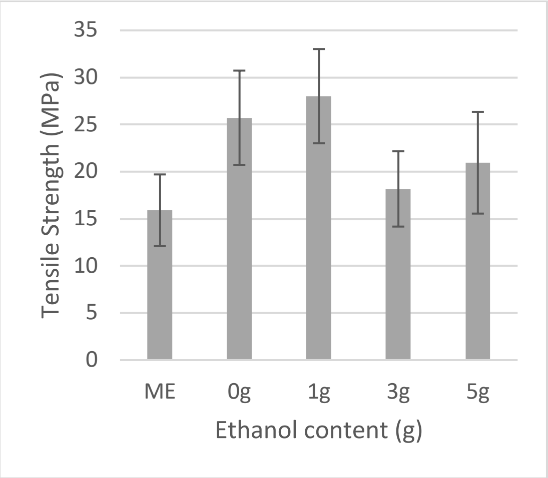

Figure 6. Tensile strength.

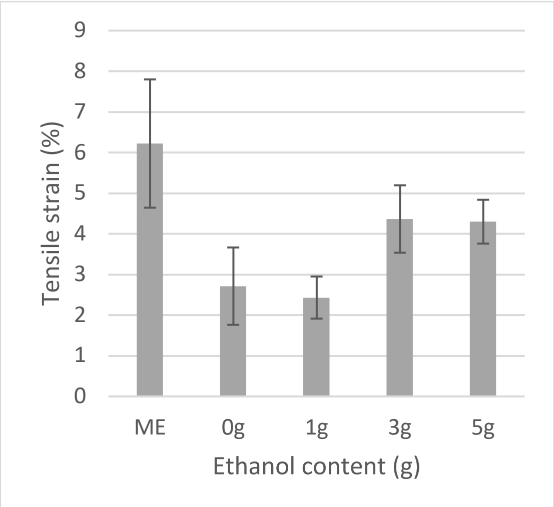

Figure 7. Tensile strain.

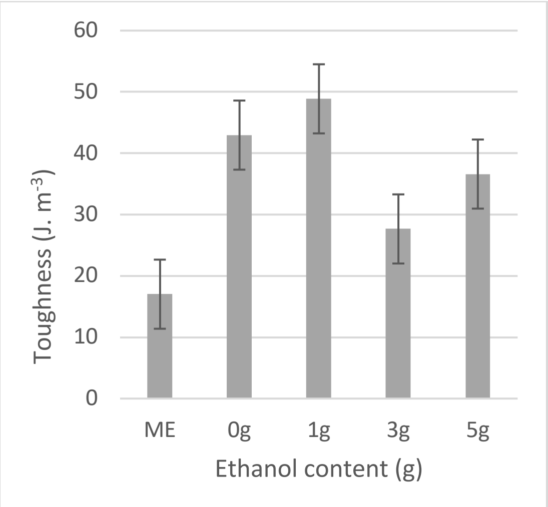

Figure 8. Tensile toughness.

4. SEM Images

Figure 9(a) shows a fractured surface of unfilled epoxy. The image shows a that a brittle fracture has taken place. In unfilled epoxy sample, there was no crack bridging pattern which can be observed. When the crack started, it travels without resistance resulting in straight fracture path. When graphene was introduced, the fracture mechanisms changed due to resistance by reinforcement as shown in Figure 9(b). The result indicates that the dispersal of graphene in the polymer matrix has lower efficiency compared with samples prepared with 1g ethanol [17]. Since this sample was prepared with mild sonication and without graphene being dispersed in ethanol agglomerates of 5 μm can be observed. When the resin cures, the epoxy chain slowly becomes fixed and impedes graphene from homogenously dispersed. Therefore, dispersion of graphene is not easy because of high viscosity and sticky nature of epoxy matrix. Graphene tends to form a cluster because of their weak intermolecular Van der Waals forces [6]. In Figure 9(c) the sample was prepared with 1g of ethanol, the size of agglomerates was significantly reduced to smaller size, hence produce better tensile properties. Figure 9(d) shows sample prepared with 3g ethanol where there is no specific crack pattern can be seen. However, during the processing, the ethanol was not completely removed and porosity was likely to occur. The porosity caused by retained ethanol can be observed for the samples prepared with 3g and 5g of ethanol. The porosity arises from the remained ethanol created stress raiser effect [6]. Pronounced effect in a brittle material is very likely compared to ductile material. When yield stress is surpassed at the point of maximum stress, plastic deformation take place particularly for ductile material. If the crack propagates and face the agglomerate, it will either diminished by agglomerate or diverted if loads are higher. Nevertheless, most part of the epoxy matrix is not completely toughened since graphene is only present in the form of clusters. This can be attributed to sample prepared with 3g of ethanol where the crack escalate via the brittle epoxy and fracture occurs due to poorly dispersed graphene. Hence the graphene reinforcement was not able to improve the tensile properties of epoxy.

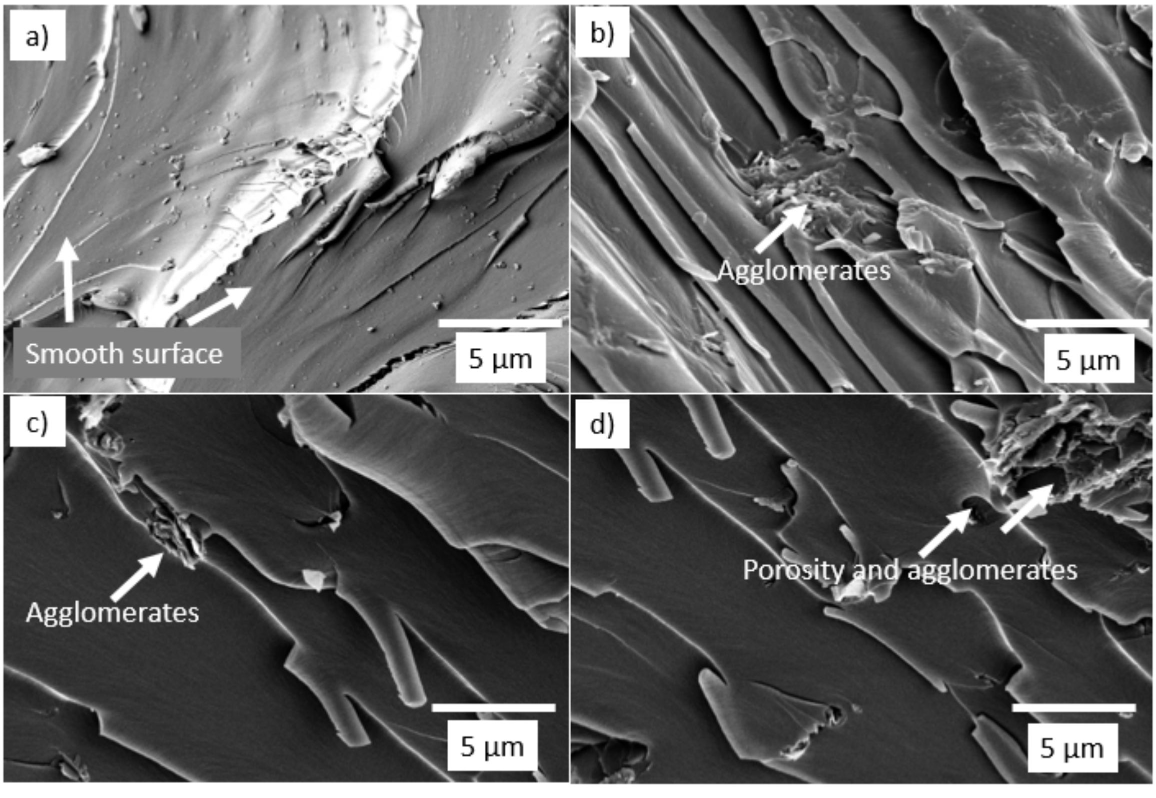

Figure 9. SEM Images of unfilled epoxy (a), Epoxy/1 wt% graphene prepared without ethanol (b), Epoxy/1 wt% graphene prepared with 1g ethanol (c), and Epoxy/1 wt% graphene prepared with 3g ethanol (d).

5. Conclusion

In this research unfilled epoxy (ME) and four different type of epoxy/1 wt% graphene composites dispersed with several ethanol concentrations were successfully produced. All composite samples were fabricated using solution casting technique. Overall, the results indicate that ethanol is an excellent processing solvent for 1 wt% graphene dispersed in the epoxy matrix. The highest increase in Young's modulus and tensile strength were recorded for sample 1 wt% graphene dispersed in 1g ethanol, with an improvement of 130% and 76% respectively. About 187% improvement in toughness was recorded, also dispersed with 1g of ethanol. SEM images revealed that graphene was able to inhibit the propagation of cracks and significantly increased the tensile properties by detouring the advancement of cracks. Inefficient evaporation of ethanol during processing led to the presence of tiny holes or also known as porosity, which of course very undesirable to the mechanical properties of the nanocomposites. For future research, it is recommended that the temperature of manual stirring to be increased from 60ºC to 80ºC to completely remove the remaining solvent.

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