

THE PROCESSING OF EPOXY/MULTI-LAYER GRAPHENE NANOCOMPOSITES: EFFECTS OF ACETONE ON PROPERTIES

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Abstract

Epoxy/multi-layer graphene nanocomposites prepared with different acetone dosages (0 ml, 25 ml and 50 ml) were successfully produced. This study investigates the effectiveness of short-term dispersion and small dosages of acetone on the properties of nanocomposites. The maximum increase in glass transition temperature (T_g), storage modulus, flexural strength, flexural modulus, fracture toughness and microhardness were observed in the case of epoxy/0.1 wt % MLG dispersed in an epoxy matrix. Scanning Electron Microscopy (SEM) analysis revealed that a good dispersion of MLG in the epoxy matrix has the ability to prevent and stop crack propagation. The cracks became parabolic or emanated radially in comparison to monolithic epoxy samples. For samples prepared with acetone, smooth surfaces can be seen on the fractured samples due to retained acetone that acts as stress raisers, which result in straight crack propagation and consequently reduced mechanical properties of the nanocomposites.

Keywords: Acetone, Dispersion, Epoxy, Graphene, Mechanical properties.

1. Introduction

Properties of graphene/polymer nanocomposites are strongly dependent upon the state of dispersion in matrix [1]. The mechanical properties of a material can be improved forming uniformly dispersed graphene that shares external loads and stop cracks from advancing. Various methods are employed to avoid the aggregation and achieve uniform dispersion such as improved dispersion methods, functionalization, volume fraction, and the dispersion medium. Graphene can significantly improve the physical and chemical properties of the matrix at very low loadings [2, 3]. However, these improvements are only possible if graphene is homogeneously dispersed in the matrix [4].

Like graphene, epoxy has been widely used in aerospace, automotive, marine, sports materials, construction, structures, electrical and electronic systems, biomedical devices, thermal management systems, adhesives, paints, coatings, industrial tooling, and other general consumer products [5, 6]. Its flexibility makes it a good candidate to replace many conventional materials. The study of property improvement of epoxy/graphene nanocomposites is quickly progressing. Nevertheless, in practical terms, graphene is not suitable to be dispersed in epoxy just by simple mixing; it tends to reaggregate in the matrix due to the strong Van der Waals forces even after homogenisation. Using solvents as dispersing media has been generally accepted and known as the simplest method to distribute isolated graphene homogeneously in the nanocomposite materials. From literature, graphene was dispersed in water, ethanol, tetrahydrofuran (THF), dichloromethane (DCM), and N, N-dimethylformamide (DMF) at 1 g/L, with outstanding enhancement in the mechanical properties [7, 8].

The usage of DMF and ethanol as dispersants have even been reported by other researchers at concentrations of 1 g/2 L, 1 g/3 L, or 1 g/10 L [7, 9, 10]. Solvents with unknown concentrations were used in some studies. Several researchers have been using DMF in the processing of epoxy/graphene nanocomposites and the final materials showed enhanced mechanical properties and resistance to fatigue crack growth. According to Wei et al. [11], the modified graphene showed good dispersibility in acetone, DMF, ethanol, pyridine, methanol, tetrahydrofuran (THF) and water. However, short-term stability studies are only available in iso-propyl alcohol (IPA), dichlorobenzene (DCB), chloroform, dichloromethane and chlorobenzene. There are no short-term stability studies available for acetone; therefore, this study examines the short-term dispersion of acetone in the processing of epoxy/graphene nanocomposites.

The use of acetone could lower the viscosity of the polymer matrix as dispersion becomes easy in a low viscosity medium. Obtaining a good distribution of the graphene-reinforcement is one of the greatest challenges in the preparation of epoxy/graphene nanocomposites. Table 1 shows the tensile strength enhancement of graphene/nanocomposites using acetone as a dispersant. The prepared nanocomposites showed improved properties and the graphene dispersed in acetone showed good distribution in the polymer matrix. However, a study by D'Aloia et al. [10] showed that the tensile properties dropped 15% compared to neat epoxy due to higher graphene concentration between 1-1.5 wt % and formation of GNP agglomerates induced mechanical defects in the composite [11].

Table 1. Properties enhancement of graphene/nanocomposites using acetone as dispersant.

Year	Filler/wt %	Dispersion method	% increase	Mechanical properties	Reference
2019	GO/0.5	Ultra sonication	5	Tensile strength	[12]
2018	GNP/1.0	Ultra sonication	-15	Tensile strength	[10]
2014	GO/0.5	Bath sonic + mechanical mix	18.8	Tensile strength	[13]
2014	GO/0.5	Bath sonic + mechanical mix + ball mill	63.2	Tensile strength	[14]
2013	GS/3.0	Bath sonic + mechanical mix	19	Tensile strength	[15]

2. Materials

Multi-layer graphene (MLG) of 12 nm average thickness and 4.5 μm average lateral size with a surface area of 80 m^2/g and purity of 99.2% was purchased from Graphene Supermarket, USA. The MLG of 0.1 wt % was dispersed in 3 different acetone concentrations of 0 ml, 25 ml and 50 ml. The MLG was then dispersed in acetone by using bath sonicator for 30 minutes and mixed with epoxy resin. The temperature of acetone and epoxy was increased to 60 $^{\circ}\text{C}$ for 15 min to remove acetone. Then, the hardener was added in the epoxy-graphene mixture. Following thorough hand mixing for 10 min, vacuum degassing was carried out for 15 min. The resin was poured into silicone moulds and then cured at room temperature for 6 h followed by post-curing at 120 $^{\circ}\text{C}$ for 6 h [16].

The epoxy and hardener used in this research were Miracast 1517A and Miracast 1517B supplied by Miracon Sdn. Bhd., Seri Kembangan, Malaysia. The epoxy has a density of 1.13 g/cm^3 while the hardener has 1.1 g/cm^3 density. This epoxy system is a standard resin for composite industry and has low viscosity. The low viscosity of the hardener helps to improve the dispersion state and the fast curing to prevent the reinforcement agglomeration [8]. The gelation time of the resin was 40 min at Room Temperature (RT).

Characterization

Dynamic Mechanical Analyser (DMA 8000, Perkin-Elmer) was used to determine dynamic storage modulus (E') and loss modulus (E'') of the samples. The loss factor, $\tan \delta$, was calculated as a ratio (E''/E'). The glass transition temperature (T_g) was taken as the temperature value at the peak of $\tan \delta$ curves. Rectangular test specimens were of dimensions of 30 \times 6 \times 3mm. All tests were carried out by the temperature sweep method (temperature ramp from 70 $^{\circ}\text{C}$ to 140 $^{\circ}\text{C}$ at 5 $^{\circ}\text{C min}^{-1}$) at a constant frequency of 1 Hz.

A flexural test was performed using Victor Universal Testing Machine (Victor VE 2302). Five specimens were tested for each composition. The displacement rate for the tensile tests were kept to 1 mm/min. The test properties were carried out according to ISO 178 with a specimen thickness of 3 mm. The fracture toughness (K_{1C}) was obtained using a Single Edge Notch Three-Point Bending (SEN-TPB) specimen (ASTM D5045). The displacement rate used was 1 mm/min [17]. The

dimensions were 3×6×36 mm³ with a crack length of 3 mm at the centre of the sample. K_{1C} was calculated using linear fracture mechanics by following the relationship in Eq. (2). The calibration factor used is presented in Eq. (3).

$$K_{1C} = \frac{P_{max}(\frac{a}{w})}{BW^{3/2}} \quad (2)$$

where $f(a/w)$ is the calibration factor for the samples, which is given as:

$$f(\frac{a}{w}) = \frac{[(2 + \frac{a}{w})\{0.0866 + 4.64(\frac{a}{w})^2 + 14.72(\frac{a}{w})^3 - 5.6(\frac{a}{w})^4\}]}{(1 - \frac{a}{w})^{3/2}} \quad (3)$$

Vickers microhardness test was performed using the Buehler Micromet II for the monolithic polyester and its nanocomposites in air and after methanol exposure. The load applied was 200 g for 10 s and the readings were taken on samples according to standard ISO 178. Figure 1 shows the schematic illustrations of specimens used in the experimental works. Images of broken samples from flexural testing specimens were analysed using mini Scanning Electron Microscope (S3 Alliance, United States of America).

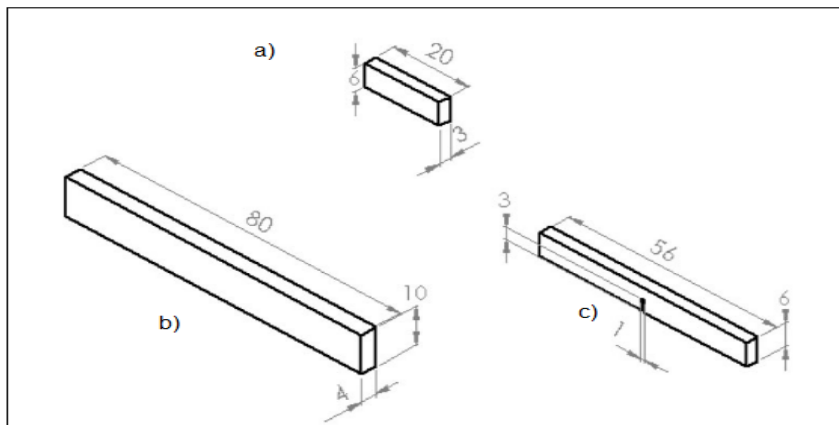


Fig. 1. Schematics of specimen: (a) Dynamic mechanical analysis, (b) Flexural test and (c) Fracture toughness K_{1C} .

3. Results and Discussion

Figure 2 shows the glass transition temperature of all nanocomposites. The glass transition temperature (T_g) was taken as the temperature value at the peak of $\tan \delta$ curves. All tests were carried out by the temperature sweep method (temperature ramp from 70 °C to 140 °C. T_g for monolithic epoxy was recorded at 114 °C. The T_g of 0.1 wt % epoxy/graphene without acetone increased to 120.1 °C. The T_g dropped to 107.4 °C in the case of epoxy/0.1 wt % graphene prepared with 25 ml acetone. The lowest T_g was observed at 96.74 °C in the case of epoxy/0.1 wt % MLG prepared with 50 ml acetone as a dispersant. It was observed that the retained acetone caused porosity that acted as a stress raiser and degraded the mechanical properties of produced nanocomposites [18].

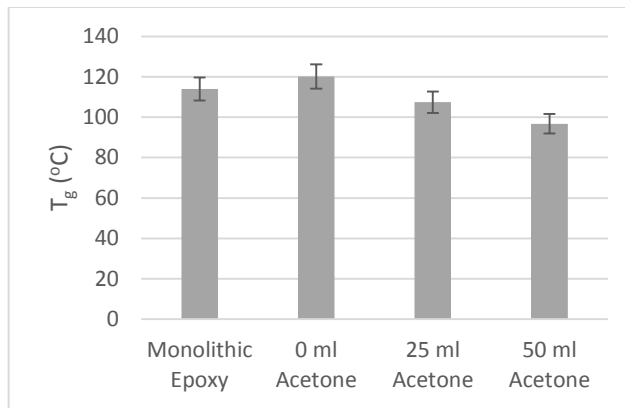


Fig. 2. T_g of monolithic epoxy and epoxy/0.1 wt % MLG processed with different dosage of acetone.

Figure 3 shows storage modulus for nanocomposites processed with and without acetone. Storage modulus is a measure of the elastic response of a material. It measures the stored energy. The highest storage modulus was recorded in the case of 0 ml acetone followed by monolithic epoxy. Both samples prepared with 25 ml and 50 ml acetone considerably recorded lower storage modulus. The presence of acetone not only reduced the storage modulus but also caused porosity in a variation of mechanical properties [18, 19].

Figure 4 shows a loss of modulus for all nanocomposite systems. The loss modulus is a measure of energy dissipation, though as a modulus it is hardness or stiffness of a material. Upon heating, loss modulus decreases because less force is required for deformation. Good dispersion of MLG has shifted the curve of epoxy/0.1 wt % graphene nanocomposite to the right whilst sample MLG dispersed with 50 ml acetone shifted the curve to the left indicating lower stiffness and stress regions that lead to low strength in the specimens.

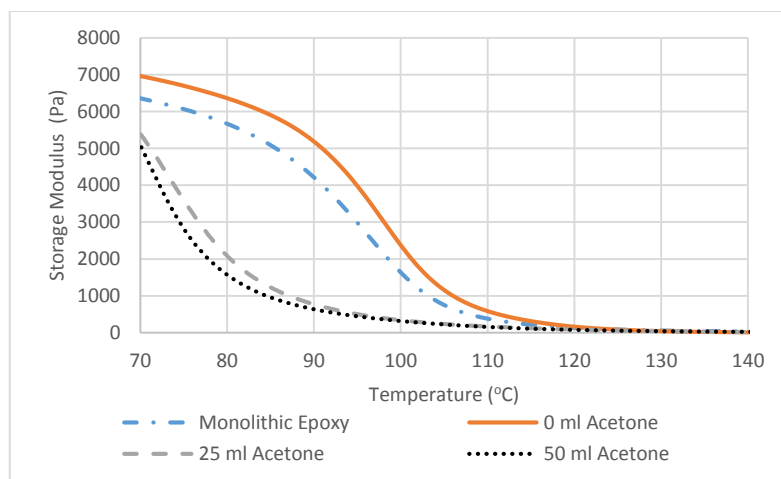


Fig. 3. Storage modulus of monolithic epoxy and epoxy/0.1 wt % MLG processed with different dosage of acetone.

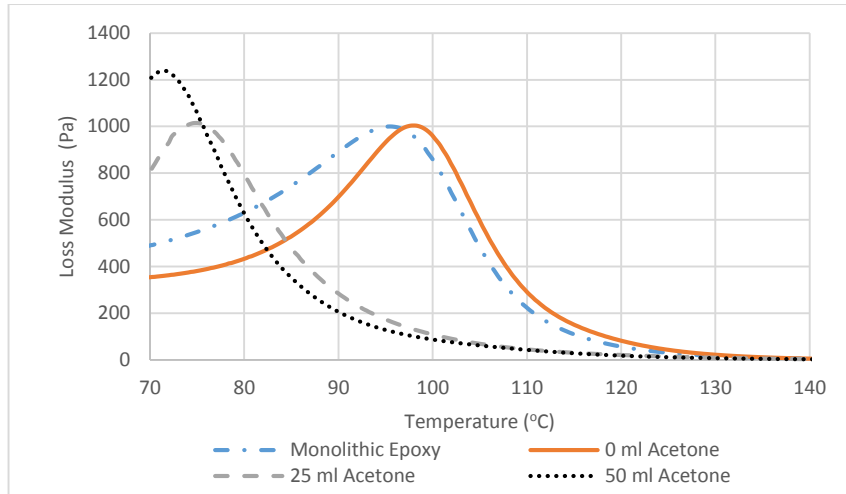


Fig. 4. Loss modulus of monolithic epoxy and epoxy/0.1 wt % MLG processed with different dosage of acetone.

Figure 5 shows the flexural strength of the nanocomposites with a monolithic epoxy recording of 113.5 MPa. The flexural strength improved by 5.3% in the case of epoxy/0.1 wt % MLG prepared without acetone. For the other two nanocomposites prepared with acetone, both samples recorded negative effects. The flexural strength decreased by 22% and 59% for nanocomposites prepared with 25 ml and 50 ml acetone.

Figure 6 shows the flexural modulus of the nanocomposites. It was observed that the flexural modulus increased 9% in the case of nanocomposites dispersed in epoxy resin compared to monolithic epoxy. The flexural modulus then dropped 13% in the case of epoxy/0.1 wt % MLG prepared with 25 ml acetone. The lowest modulus was recorded for nanocomposite prepared with 50 ml acetone with a 31% decrease.

The variation of flexural strain is shown in Fig. 7. The lowest flexural strain was observed for samples prepared without acetone with 1.23% whilst the highest was 1.7% for samples prepared with 50 ml acetone. The increase in stiffness and restriction in the movement of polymer chains by MLG caused a decrease in flexural strain. The decrease in stiffness, in contrast, is due to the plasticization effect caused by retained acetone in the matrix, which acts as stress raiser [18]. Consequently, the flexural modulus of the nanocomposites reduced.

Figure 8 shows the fracture toughness of monolithic polyester and the nanocomposites. The highest fracture toughness was obtained for samples prepared without acetone with K_{IC} value of 1.7 MPa m^{1/2}, or 21% increase compared with monolithic polyester. The lowest K_{IC} value was observed in the case of samples prepared with 50 ml acetone. The K_{IC} value was 28% lower than the monolithic epoxy.

The variation of Vickers hardness for all samples is shown in Fig. 9. The monolithic epoxy recorded a hardness value of 17.9 HV, in line to what has been reported by other researchers [20]. Compared with monolithic epoxy, an improvement of 22% was observed for nanocomposite systems prepared without

acetone. In the case of nanocomposites prepared with 25 ml acetone, the hardness increased by about 7.8%. This indicates that MLG is efficient at increasing hardness value of epoxy at concentrations of 25 ml.

However, the MLG showed a maximum decrease of 8.4% epoxy/0.1 wt % MLG prepared with 50 ml acetone. Atif et al. [18] also reported that porosity of the samples can be seen caused by retained acetone from the processing method. Besides that, the decrease in hardness and flexural properties can be associated with the reaggregation of the graphene, which occurred due to the large dosage of acetone used; similar to what has been reported in the case of N, N-Dimethylformamide (DMF) solvent [7].

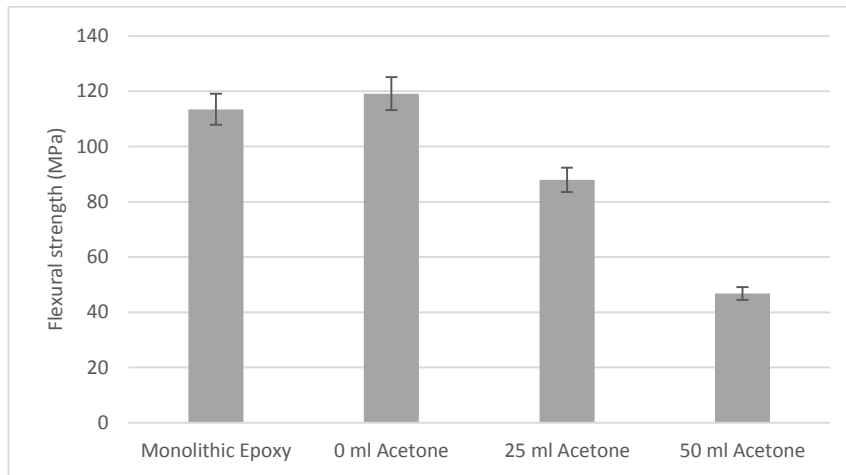


Fig. 5. Flexural strength of monolithic epoxy and its nanocomposites.

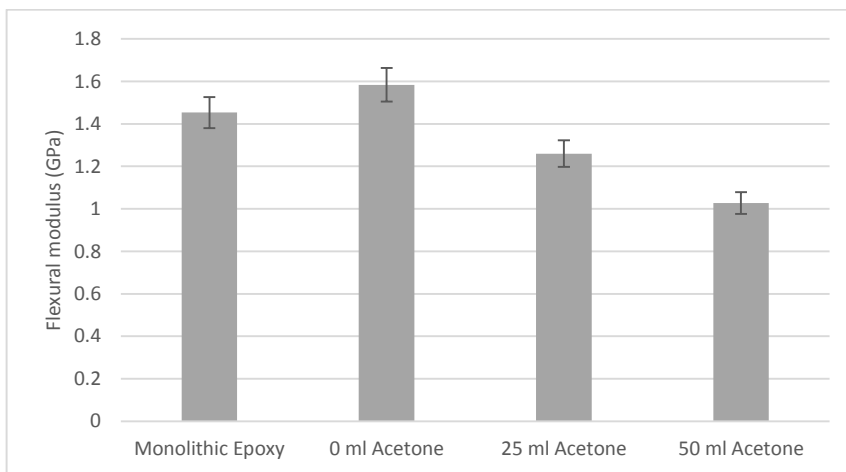


Fig. 6. Flexural modulus of monolithic epoxy and its nanocomposites.

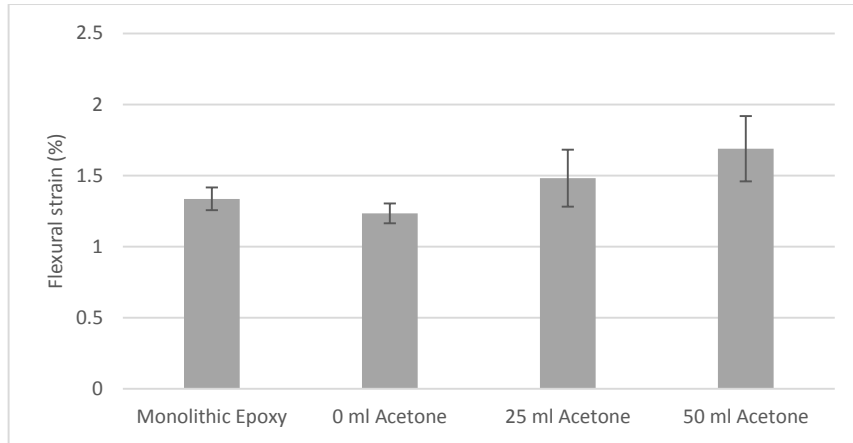


Fig.7. Flexural strain of monolithic epoxy and its nanocomposites.

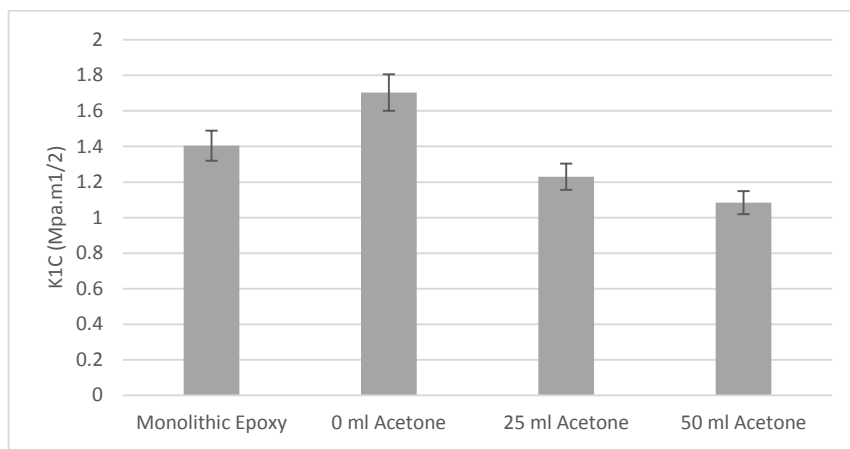


Fig. 8. Fracture toughness of monolithic epoxy and its nanocomposites.

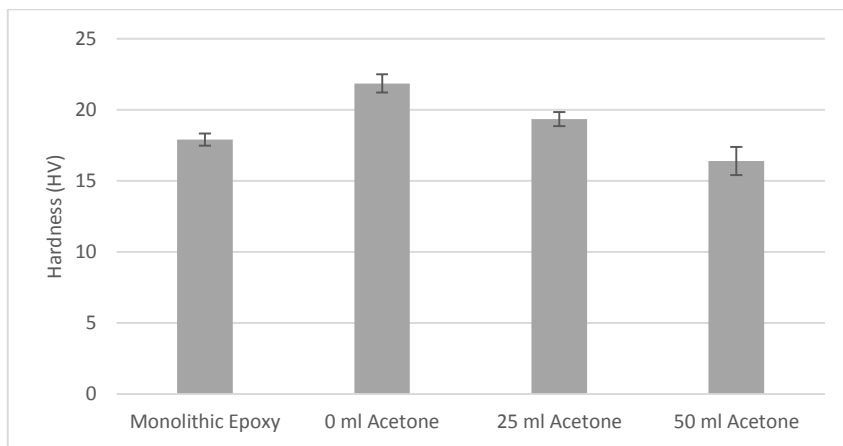


Fig. 9. Vickers hardness of monolithic epoxy and its nanocomposites.

SEM Analysis

Figure 10 shows the SEM micrograph of monolithic epoxy and its nanocomposites. From Fig. 10(a), the brittle failure has taken place since there is no crack bridge mechanism. However, for samples processed without acetone, fracture mode changes due to the obstruction caused by MLG, thus, the crack started to emanate radially as shown in Fig. 10(b). MLG has the ability to prevent and even stop crack propagation. The cracks became parabolic in comparison to monolithic epoxy sample. As for both samples prepared with acetone (Figs. 10(c) and (d)), smooth surfaces can be seen on the fractured samples due to the acetone that acts as a stress raiser and tends to produce porosity within the samples as a result of reduced mechanical properties of the produced nanocomposites.

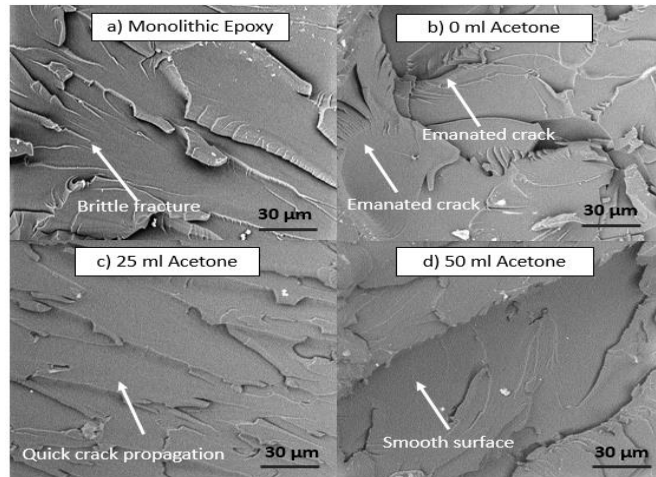


Fig. 10. SEM micrograph of: a) Monolithic epoxy, (b) Epoxy/0.1 wt % graphene dispersed in epoxy matrix, (c) Epoxy/0.1 wt % graphene dispersed with 25 ml acetone and (d) Epoxy/0.1 wt % graphene dispersed with 50 ml acetone.

4. Conclusions

Nanocomposites of three different types were successfully produced with different acetone concentrations. The MLG and dispersion medium significantly influenced the behaviour of the produced nanocomposites. The maximum increase in T_g , storage modulus, flexural strength, flexural modulus, fracture toughness and microhardness were observed in the case of epoxy/0.1 wt % MLG dispersed in the epoxy matrix. Nanocomposites prepared with acetone, on the other hand, decreased the properties of nanocomposites. Therefore, it is suggested that acetone of more than 25 ml shall not be used as a dispersant in epoxy processing. Acetone, if not completely removed causes porosity to the samples produced, which is undesirable to mechanical properties. This decrease can be associated with the large dosage of acetone used, which later acts as a stress raiser. In the future, smaller dosages of acetone could be used as a dispersant and the processing time could be increased to more than 20 minutes so that acetone can be completely removed from the nanocomposites. From this study, it can be concluded that acetone is not effective as a dispersant agent for multi-layer graphene in the epoxy system even though at 25 ml dosage.

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Nomenclatures

E'	Storage modulus
E''	Loss modulus
$f(a/w)$	Geometric shape function
K_{IC}	Fracture toughness
T_g	Glass transition temperature

Greek Symbols

$\tan \delta$	Ratio of loss to storage modulus
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Abbreviations

ASTM	American Society for Testing and Materials
DCB	Dichlorobenzene
DCM	Dichloromethane
DMA	Dynamic Mechanical Analysis
DMF	Dimethylformamide
GNP	Graphene Nano-Platelets
GO	Graphene Oxide
GS	Graphene Stack
IPA	Iso-Propyl Alcohol
ISO	International Organization for Standardization
ME	Monolithic Epoxy
MLG	Multi-Layer Graphene
RT	Room Temperature
SEN-TPB	Single Edge Notch Three-Point Bending
THF	Tetrahydrofuran

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