Flexural Properties of Halloysite Nanotubes-Polyester Nanocomposites Exposed to Aggressive Environment

Mohd Shahneel Saharudin, Jiacheng Wei, Islam Shyha, Fawad Inam

Abstract—This study aimed to investigate the effect of aggressive environment on the flexural properties of halloysite nanotubes-polyester nanocomposites. Results showed that the addition of halloysite nanotubes into polyester matrix was found to improve flexural properties of the nanocomposites in dry condition and after water-methanol exposure. Significant increase in surface roughness was also observed and measured by Alicona Infinite Focus optical microscope.

Keywords—Halloysite nanotubes, polymer degradation, flexural properties, surface roughness.

I. INTRODUCTION

UNSATURATED polyester resins are one of the most commonly used thermosetting polymers because of their low cost and versatility [1]. Unsaturated polyesters are also used in coatings, construction, transportation, storage tanks, and piping. In many studies, the polymerization of polyester caused brittleness due to higher crosslinking level, and the incorporation of nanofillers is to enhance the mechanical properties of the cured polyester resin [2], [3].

Failure on polymeric materials is often caused by environmental effect such as liquid exposure and UV (ultraviolet) radiation [4], [5]. Extensive amount of literature has been published on the enhancement in mechanical properties of polymer nanocomposites, particularly reinforced with montmorillonite and bentonite fillers. In recent years, there has been an increasing interest on mechanical properties of halloysite nanotubes-reinforced polymers.

In applications of polymer nanocomposites, the contact with liquid environment is inevitable that can lead to failure [6], [7]. The failure is caused by the swelling and degradation of the polymer matrix as it interacts with the penetrating liquid environment [8]. However, the degree of swelling and degradation can be reduced by using nanofillers such as nanoclay [9] as evidently shown by several researchers [10], [11].

The knowledge of the limitations of the polymeric matrices and ageing mechanisms in the presence of various liquid media is significant to guarantee successful composites application [12], [13]. For example, water diffusion is well known to limit the use of fiber-reinforced polymer composites [14]. However, the present information is insufficient especially about the influence of nanofillers on the mechanical properties of polymers when exposed to severe liquid media. This research emphasizes on the application of polyester where contact with methanol and water is possible, such as in automotive applications (coating), which may lead to the degradation of the resin. The halloysite nanoclay–polyester nanocomposites were evaluated through flexural and surface roughness test.

II. EXPERIMENTAL SECTION

A. Materials

Halloysite nanoclay was used as reinforcement and acquired from Sigma Aldrich. The diameter is between 30 and 70 nm with length 1–4 mm and has a tube-like morphology. The filler has a density 2.53 g/cm^3 and surface area is 64 m^2/g. The tube-like morphology, high aspect ratio, and low percolation make halloysite nanoclay a potential reinforcement for polyester. Polyester resin (NORSODYNE O 12335) AL acquired from East Coast Fibreglass, UK. Thorough hand mixing and vacuum degassing was done for 10 min. The mixture was poured into moulds and cured at room temperature for 24h followed by post curing at 60 °C for 2h according to a process. Five different fractions of halloysite nanoclay (0, 0.1, 0.3, 0.7, and 1.0 wt.%) were used to reinforce the polyester. A mixture of water and methanol in ratio (2:1) was used as liquid media.

B. Characterisation

Five different specimens were immersed in water-methanol liquid with a ratio of 2:1 followed by light transmittance evaluation. Specimens then were tested under flexural test and the displacement rate used was 1 mm/min [1]. Flexural test was conducted according to ISO 178 with the dimensions of 80x10x4 mm. The energy absorbed was calculated by the area under the force-displacement curve. An Alicona optical microscope was used to study the topographical features of the produced samples. The Alicona Infinite Focus optical microscope (G4, Alicona, Graz, Austria) was used to produce visual micrographs and determine surface roughness.

C. Results

The variation of light transmittance test is presented in Fig.

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1. It can be seen that the incorporation of halloysite nanotubes reduced the light transmittance. As the halloysite nanotubes increased, the light transmittance decreased. Monolithic polyester recorded 74% of light transmittance while 1wt.% halloysite nanotubes recorded 65% of light transmittance. After water-methanol exposure, the light transmittance was slightly dropped (Fig. 2). In case of monolithic polyester, the light transmittance was 70% and 1 wt.% reinforcement recorded 52% of light transmittance. The water-methanol absorbed on the surface of specimens could be the reason of reduced in light transmittance. The variation of flexural modulus is shown in Fig. 3. It can be clearly seen that the incorporation of halloysite nanotubes improved the flexural modulus both in air and after water-methanol exposure. Monolithic polyester recorded only 0.74 GPa flexural modulus. The modulus then increased at 0.1 wt.% reinforcement. It increased to 0.76 GPa compared to monolithic polyester. The maximum flexural modulus was observed in case of 1 wt.% reinforcement. The flexural modulus increased 65%. After water-methanol absorption, the flexural modulus slightly reduced. For instance, 1wt.% halloysite nanotubes-polyester system dropped from 1.22 GPa to 1 GPa. The flexural modulus dropped 22% after water-methanol exposure. In addition, monolithic polyester dropped from 0.74 GPa to 0.6 GPa (dropped 19%).
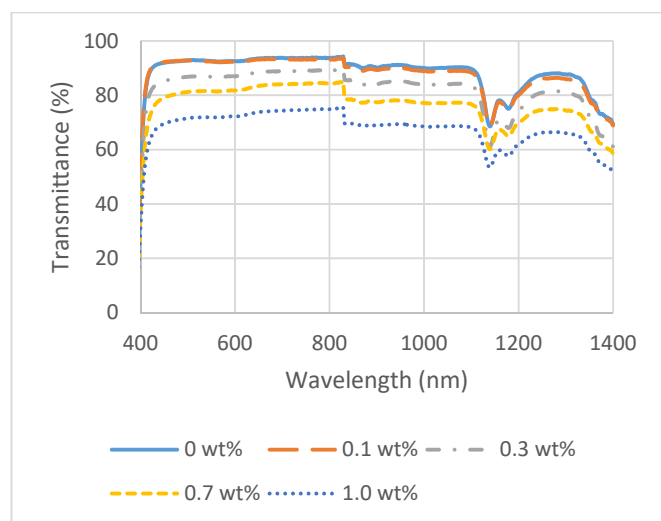

Fig. 1 The light transmittance of nanocomposites in air

The variation in flexural strength can be observed in Fig. 4. The lowest flexural strength was found with only 54 MPa. The value slightly increased at 0.1 wt.% halloysite nanotubes reinforcement, where an improvement of 4.6% was observed. The highest flexural strength was also observed in case of 1 wt.% halloysite nanotubes-polyester system. The flexural strength increased from 54.5 MPa to 81 MPa, where 49% of increase can be observed. The variation of flexural strain is presented in Fig. 5. After water-methanol exposure, the flexural strength decreased. It can be observed, for samples reinforced with 1 wt.% halloysite nanotubes, the flexural strength decreased from 81 MPa to 60 MPa. The flexural

strain (%) decreased with the increased of halloysite nanotubes. The lowest strain values for unexposed samples were observed for 1 wt.% halloysite nanotubes-polyester system. Only 5% flexural strain was recorded. This indicates the stiffness of the composites. After water-methanol exposure, the flexural strain increased. It can be seen that the flexural strain increased from 5% to 7% in case of 1 wt.% reinforcement. There are several possibilities of this phenomenon. Firstly, water-methanol liquid caused plasticization effect on the polymer [15]. Another possibility is the fibres and matrix debonding due to poor interface interaction between them [16]–[18]. The variation of energy absorbed is shown in Fig. 6. In general, the energy absorbed increased with the addition of halloysite nanotubes. However, the exposure towards water-methanol reduced the energy absorbed for all composites system. In case of 1 wt.% reinforcement, the energy absorbed dropped from 3.5 J to 2.6 J (25% decrease).
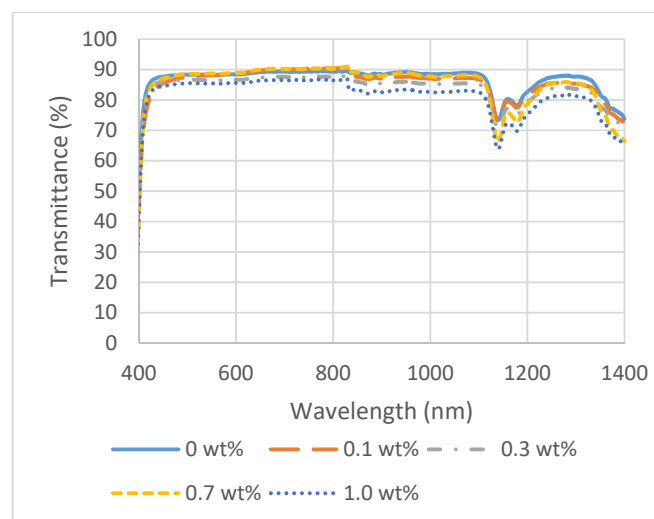

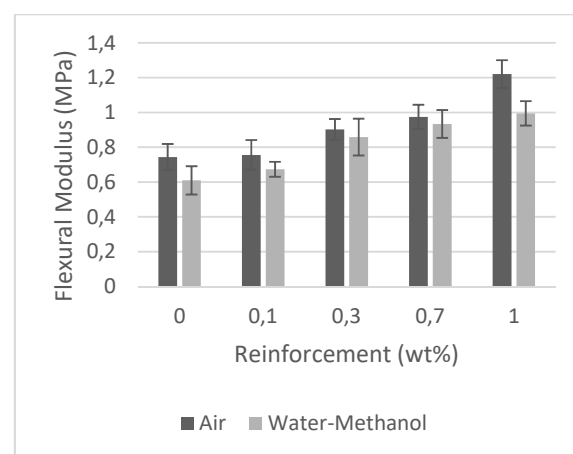Fig. 2 The light transmittance of nanocomposites after water-methanol exposure

Fig. 3 Flexural modulus of nanocomposite

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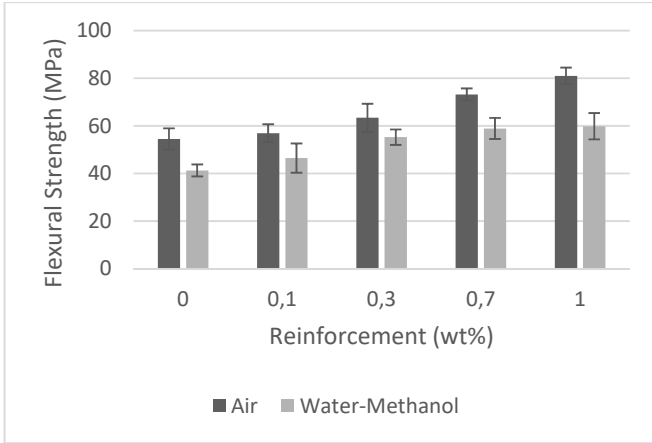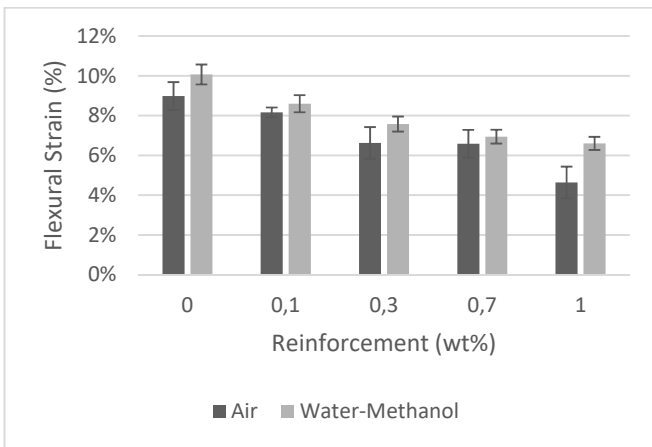Vol:11, No:4, 2017

Fig. 4 Flexural strength of nanocomposites

Fig. 5 Flexural strain of nanocomposites

The topographical study was carried out on fractured three-point bend samples. The surface roughness (R_a) of monolithic polyester of 0.1 wt.%, 0.3 wt.%, 0.7 wt.%, and 1 wt.% reinforcement is shown in Fig. 7. In dry condition, monolithic polyester recorded the lowest surface roughness with just 0.3 μm. At 0.1 wt.% reinforcement, the R_a increased to 0.37 μm. Further increase of R_a was observed in case of 0.3 wt.% and 0.7 wt.% with R_a values which were 0.46 μm and 0.0.49 μm, respectively. The maximum surface roughness was observed in the case of 1 wt.% reinforcement. The R_a increases from 0.3 μm to 0.51 μm (70% increase). For samples immersed in water-methanol, it can be observed that the R_a values were slightly increased compared to dry condition. The minimum surface roughness was observed for monolithic polyester with 0.38 μm R_a. The maximum R_a values were observed in the case of 1 wt.% reinforcement with 1.1 μm. In general, root-mean-square roughness of profile (R_q) also followed similar trend as shown in Fig. 8. In dry condition, the minimum R_q was observed for monolithic polyester (0.4 μm). The maximum R_q on the other hand was observed in case of 1 wt.% reinforcement (0.63 μm). After water-methanol immersion, monolithic polyester R_q mean value became 0.48 μm. As for the 1 wt.% reinforcement, the R_q increased to 1.6 μm. The mean peak to valley height of roughness profile R_z

also showed similar trend for all nanocomposites system in dry and after water-methanol exposure (Fig. 9). Water entering the nanocomposites results in degradation of flexural properties. Liquid exposure also caused swelling to the nanocomposites and weakening halloysite nanotubes-polyester bonding strength. Reduction in strength and increase of surface roughness indicate the degradation of the interface.
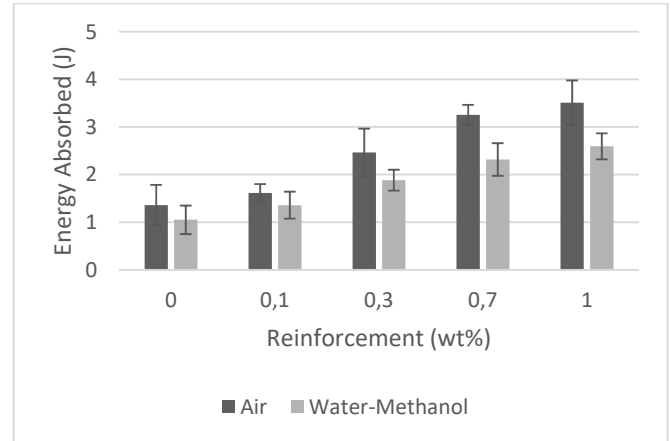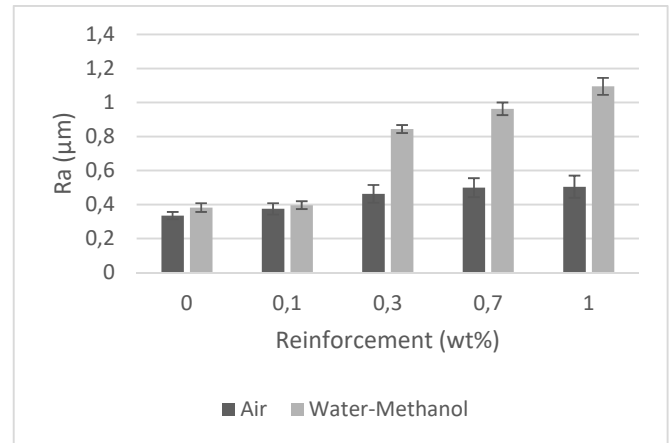

Fig. 6 Energy absorbed by nanocomposites

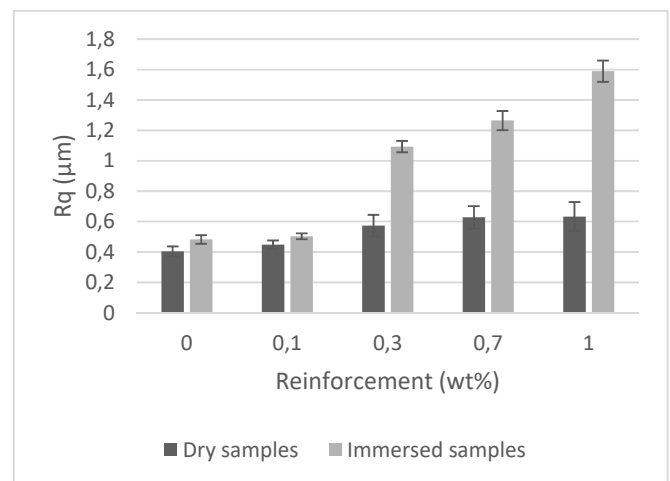Fig. 7 Average roughness of nanocomposites

Fig. 8 The nanocomposites root mean square of surface roughness
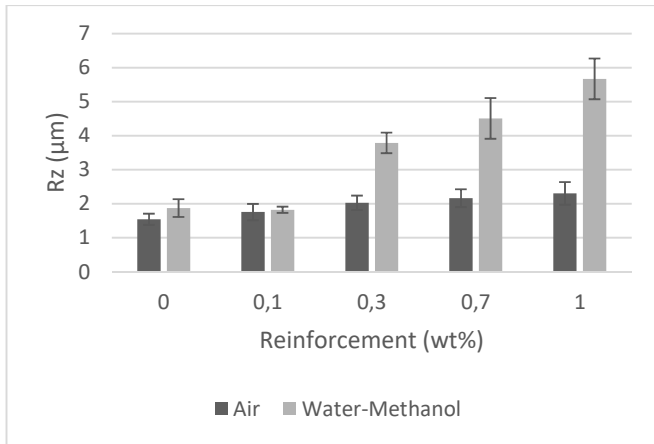
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Fig. 9 Difference between tallest peak and deepest valley of nanocomposites

D.SEM Images

The fractured surfaces of specimens were viewed to study the influence of halloysite nanotubes on the possible fracture modes in the nanocomposites. The SEM images halloysite nanotubes are presented in Fig. 10. As clearly seen, the nanofillers are in tubular form structure. Fig. 11 is monolithic polyester exposed to water-methanol. The straight crack propagation can be observed for the monolithic polyester SEM image. This can be associated with the very quick and straight crack movement. Monolithic polyester tends to have smooth surface than halloysite nanotubes reinforced polyester. Fig. 12 represents the 1 wt.% halloysite nanotubes reinforcement. The image clearly shows the formation of micro layers which cannot be seen in monolithic polyester SEM image. The increase in micro-layers can be linked with the crack deflection by halloysite nanotubes [12]. The halloysite nanotubes provide protection against water-methanol from entering nanocomposites through capillarity and further damaging the nanocomposites [19].
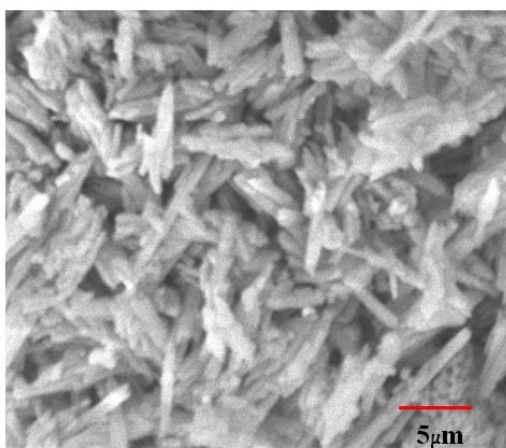

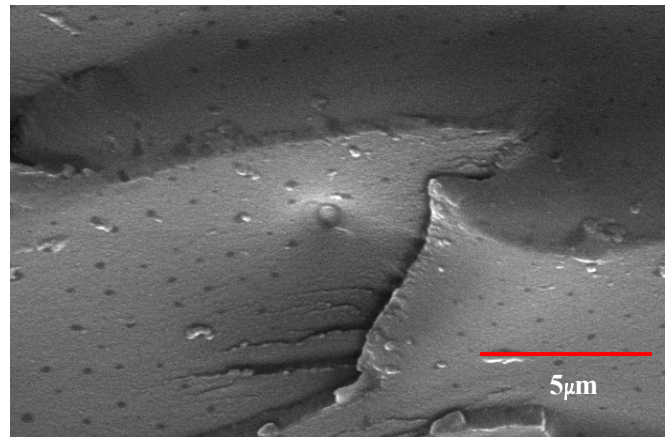Fig. 10 SEM image of halloysite nanotubes tubular structure

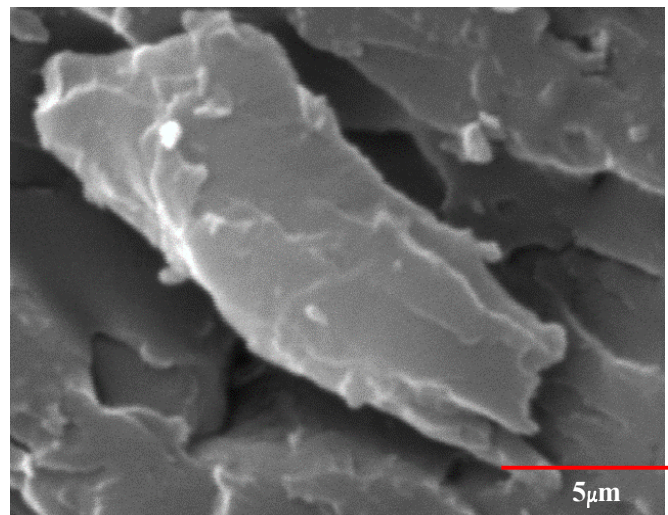Fig. 11 SEM image of monolithic polyester exposed in water-methanol

Fig. 12 SEM image of 1 wt.% halloysite nanotubes-polyester nanocomposite exposed in water-methanol

III. CONCLUSION

Nanocomposites of five different weight fractions of halloysite nanoclay reinforcement were successfully fabricated. The degradation of mechanical properties was studied after an exposure of 24h in water-methanol system. In this research, the addition of halloysite nanoclay strengthens the polyester matrix up to a concentration of 1 wt.%. The flexural modulus improved up to 65%. The flexural strength of the composites increased up to 49%. For both conditions in air and after water-methanol exposure, the stiffness of the composites considerably improved compared to monolithic polyester. After water-methanol exposure, the flexural modulus and flexural strength slightly decreased compared to unexposed samples. In the case of 1 wt.% reinforcement, the flexural modulus dropped from 1.22 GPa to 1 GPa. The flexural strength dropped from 81 MPa to 60 MPa. The flexural strain on the other hand increased with the water-methanol exposure. Monolithic polyester for instance, the flexural strain increased from 9% to 10%. For 0.1 wt.% halloysite nanotubes reinforcement, the flexural strain

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increased from 5% to 7%. For samples immersed in water-methanol, R_a values were increased compared to dry condition. The minimum surface roughness was observed for monolithic polyester with 0.38 μm surface roughness (R_a). The maximum R_a values were observed in the case of 1 wt.% reinforcement with 1.1 μm.

Undoubtedly, in normal condition, the incorporation of halloysite nanotubes improved flexural properties of the composites and contributed to the increased of surface roughness. However, after short term water-methanol exposure, the flexural properties of nanocomposites decreased and surface roughness increased. This phenomenon occurred as a result of water-methanol absorption. The liquid penetrating along the matrix and halloysite nanotubes interface and degrades the interfacial bond strength as a consequence contributed to the lower flexural properties.

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