

# THE EFFECT OF METHANOL EXPOSURE ON THE FLEXURAL AND TENSILE PROPERTIES OF HALLOYSITE NANOCLAY/POLYESTER

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**Abstract**—In this study, halloysitenanoclay reinforced polyester composites were prepared by adding different weight percentage in unsaturated polyester resin and subsequently cross linked using mixture of methyl ethyl ketone peroxide. The effect of methanol immersion on the flexural strength and tensile strength of polyester halloysite nanoclay was experimentally investigated. After 30 minutes of immersion in methanol, samples were tested and analysed. From the experimental results, flexural and tensile properties of halloy sitenanoclay/polyester decreased as a result of methanol reaction on the polymer composites.

**Keywords**—Polyester composites, Halloysitenanoclay, Effect of Methanol, Mechanical Properties.

## I. INTRODUCTION

Recently, many researchers have focused on nanotechnology and nanomaterials since they exhibit some remarkable properties, as compared to other conventional micro or macro-sized analogues. To get improved properties in nanocomposites, layered materials of natural origin like clay type of compounds have been widely used for decades.

Clay/polymer nanocomposites offer excellent improvement in a wide range of physical and engineering properties for polymers with low filler content [1]–[6]. Unsaturated polyester resins are the most commonly used thermosetting system due to their low cost factor and versatility to be altered into enormous composite fabrications. Albeit polyester resins are extensively used as a matrix in polymer composites, curing of these resins results in brittleness due to their high cross linking level [7]. According to literatures, the additions of a halloysitenanoclay can improve flexural strength and tensile strength of the cured polyester resin [8]. At low loading content, typically less than 5wt%, polymers such as nylon-6 showed an increase in Young's modulus of 103%, in tensile strength of 49% and in heat distortion temperature of 146% [1], [9].

### 1.1 Liquid exposure to polymer

Premature failure of polymeric materials during their service under small loads is known as Environmental stress cracking or (ESC). This phenomenon typically occurs when a solid polymer is in contact to a vapor or liquid. As a result, the polymers can crack or fail spontaneously [10], [11]. It has been reported that unsaturated polyester can be affected by chemical medium therefore, filler reinforcement was applied to act as a liquid barrier [12].

The aim of this study is to investigate the tensile strength and flexural strength of the halloysitenanoclay/polyester composites after

methanol exposure. There were several publications available which acknowledged the mechanical properties improvement of nanoclay [4], [13], [14] but there is only limited literature discussed the influence of aggressive liquid like methanol on the mechanical properties of the unsaturated polyester composites. Methanol is one of the environmental stress cracking (ESC) agent for thermoplastics materials. It has high rates of diffusion and can cause bulk plasticization within short period of time [15]. In this study, the resistance of polyester composites towards methanol was evaluated through flexural and tensile tests.

## II. DETAILS EXPERIMENTAL

### 2.1 Matrix

The unsaturated polyester resin of the NORSODYNE O 12335 AL was purchased from East Coast Fibreglass, United Kingdom. The resin has 1200kg/m<sup>3</sup> density and methyl ethyl ketone peroxide, solution in dimethyl phthalate was used as catalyst.

### 2.2 Halloysitenanoclay

Halloysitenanoclay was used as reinforcement agent in this study, supplied by Sigma Aldrich. The diameter is between 30-70nm and length between 1-3µm. It has low electrical, thermal conductivity and strong hydrogen interactions, on account of which the inner hydroxyl groups show greater stability than the surface hydroxyl groups in halloysite. The filler has high aspect ratio and low percolation show interesting applications as reinforcements in various nanocomposites.

### 2.3 Composite preparation

For the neat polyester fabrication, the resin (Norsodyne O 12335 Al) was mixed with the ratio 98% and 2% catalyst (Butanox M-50). It was then homogenized in bath sonicator for five minutes. The mixture was poured into silicone mould and demould after 24

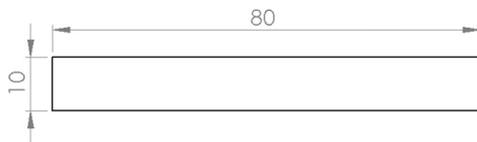
hours. Then, the composites were post cured at 60°C for two hours. Halloysitenanoclay with different weight percentage 0.1%, 0.5% and 1% were used to reinforce the polyester. The preparation of the composites according to ISO 178 and ISO 527-2 flexural and tensile properties were carried out subsequently.

**Table 1. Formulation of Norsodyne O 12335 Al, Butanox M-50 and Halloysitenanoclay**

NorsodyneO 12335 Al Resin	Butanox M-50 Catalyst	Halloysitenanoclay Filler
98.0	2	0.0
97.9	2	0.1
97.5	2	0.5
97	2	1.0

**2.4 Flexural test**

Flexural strength test was measured under a flexural testing method by using Universal Testing machine based on the ISO 178. The dimensions of the samples were 80 mm x10 mm x 4mm. The test speed used in this experiment was 2 mm/min with 56mm span length. All tests were performed at room temperature. Under environmental condition, samples were immersed for 30 minutes at room temperature followed by flexural testing. The flexural tests took place at room temperature with the dimensions of 80mm x 10mm x 4mm. At least five samples of each composite were prepared. Flexural strength ( $\sigma$ ) and flexural modulus (G) were determined by using equations 1 and 2.



**Fig.1. Specimen configuration for flexural test**

$$\sigma_f = \frac{3PL}{2bd^2} \dots\dots (1)$$

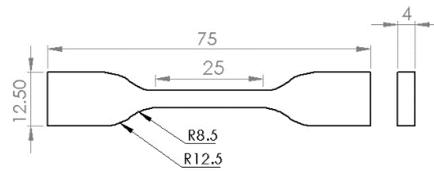
- P (Load at fracture point (N))
- L (Length of the support span)
- b (Width)
- d (Thickness)

$$G = \frac{\sigma_f}{\epsilon_f} \dots\dots (2)$$

**2.5 Tensile test**

Tensile tests were performed by using INSTRON 3382 at room temperature. Samples for tensile were prepared and tested according to ISO 527 with sand paper tabs attached to both ends of specimens by adhesives. The samples were also immersed in methanol for 30 minutes prior to the tensile tests. The specimen gage length was 25mm and the testing speed was set to 0.5mm/min. The tests were carried out with minimum five specimens and the mean value was

defined. The dimension is shown in Fig. 2. The ultimate tensile strength was calculated



**Fig.2. Tensile test configuration**

Ultimate tensile strength was determined by using equation 3

$$\text{Ultimate tensile strength} = \frac{\text{Maximum load in N}}{\text{Cross sectional area in mm}^2} \dots\dots(3)$$

Young’s modulus was determined by using equation 4

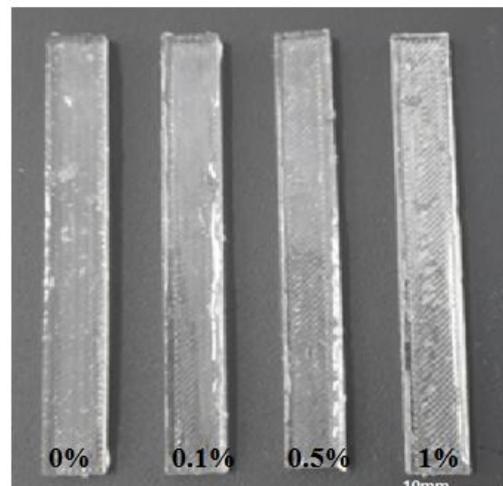
$$\text{Young’s modulus (E)} = \frac{\text{Stress } (\sigma)\text{N}}{\text{Strain } (\epsilon)\text{mm}^2} \dots\dots\dots (4)$$

**III. RESULTS AND DISCUSSION**

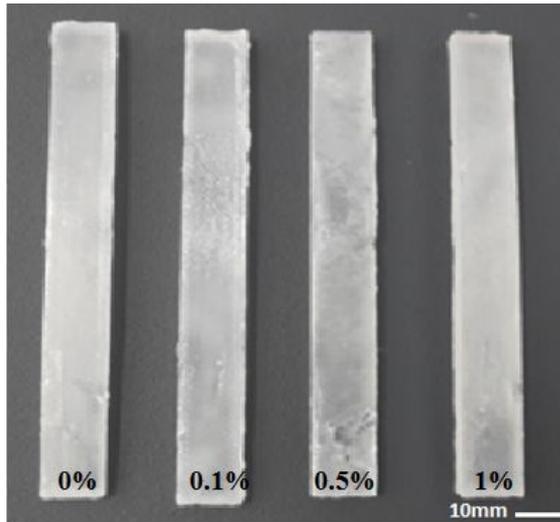
It was observed that after samples were immersed in methanol, the surface of the composites became ‘slick’ probably due to the reaction between methanol and polymer matrix. The methanol absorption on the matrix interface could also be responsible for this physical change. It is likely that methanol diffuse into the microvoids formed by cavities and cracks as identified by other researchers[16], [17]. Poor clay dispersion is also linked to the methanol absorption [18]. Apart from that, halloysitenanoclay is possibly act to plasticize the polyester network and decrease the crosslink density [13].

**3.1 Flexural test results**

The samples were compared before and after methanol immersion. From physical inspection, it can be clearly seen that the polyester and its composites are sensitive to methanol where considerable swelling occurs, with a noticeable softening of the polymer composites. This phenomenon was also observed by Arnold in amorphous polymers[15], [19].

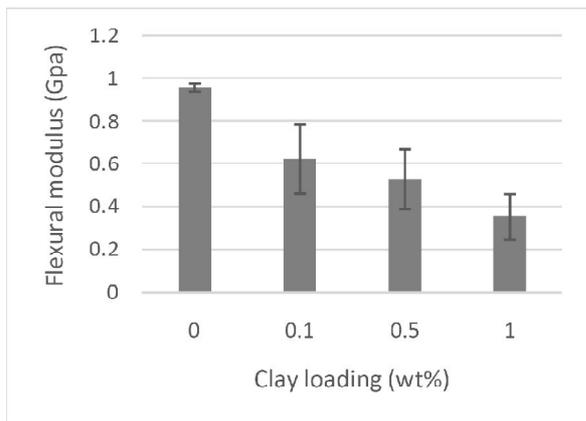


**Fig.3. Flexural samples before methanol immersion**



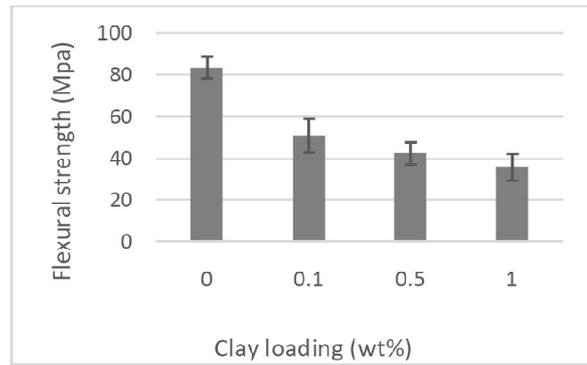
**Fig.4. Flexural samples after methanol immersion**

Several researchers have suggested that liquid absorption of clay/polymeric matrix nanocomposites is significantly influenced by two factors; clay is water rich hence easily absorb more liquid[20] and another factor is related to the clay dispersion which decrease the mean free path of methanol molecules to get through the nanocomposites network compared to the neat polymer[18]. Agglomeration of clay particles also have been disclosed in [21]. Fig. 5 illustrates the flexural modulus of the composites. It is noticeable that neat polyester obtained the highest flexural modulus followed by 0.1wt%, 0.5wt% and 1wt%. The flexural modulus reduction is 35%, 44.79% and 63.54% compared to unreinforced polyester resin. This trend indicates that the incorporation of nanoclay contributed to the reduction of flexural modulus.



**Fig.5. Flexural modulus of halloysitenanoclay/polyester composites after methanol immersion**

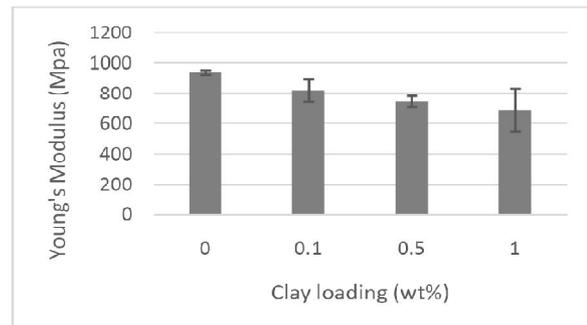
The same tendency is manifested in the flexural strength where the increase of halloysitenanoclay reinforcement decreased the flexural strength values. In case of 0.1wt% reinforcement the flexural strength decreased about 38.84%. In case of 0.5wt%, 49.14% of reduction was observed and in case of 1wt%, 56.95% of flexural strength reduction was obtained compared to neat polyester.



**Fig.6. Flexural strength of halloysitenanoclay/polyester after methanol immersion.**

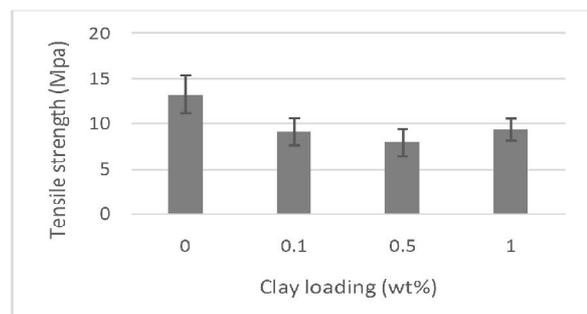
**3.2 Tensile test results**

Fig. 7 represents the results of tensile modulus for methanol immersed specimens at room temperature. It is apparent that the methanol causes change in the modulus. The Young's modulus decreases for all halloysitenanoclay reinforced samples. The reduction in Young's modulus for 0.1wt%, 0.5wt% and 1wt% compared to neat polyester specimens is 14.5%, 20.51% and 26.47%.



**Fig.7. Young's modulus of halloysitenanoclay/polyester composites exposed to methanol**

Fig. 8 shows the tensile strength results for the composites. The tensile strength for 0.1wt%, 0.5wt% and 1wt% of halloysitenanoclay incorporations compared to the neat counterpart reduced about 31.148%, 40.12% and 29.67% respectively. Neat polyester obtained the highest tensile strength with 13.298MPa while the lowest at value observed at 0.5wt% of halloysitenanoclay reinforcement with 7.96MPa.



**Fig.8. Tensile strength of the halloysitenanoclay/polyester composites**

In general, the more deformation the composites accept before failure the tougher the material will be. Fig. 9 demonstrates that the composites were having low strain values than the neat polyester. The strain values for neat polyester, 0.1wt%, 0.5wt% and 1.0wt% is 9.37%, 7.01%, 6.67% and 6.77% respectively. Therefore, it can be concluded that the deformation of the composites due to stress is lowered with the increment of halloysitenanoclay content.

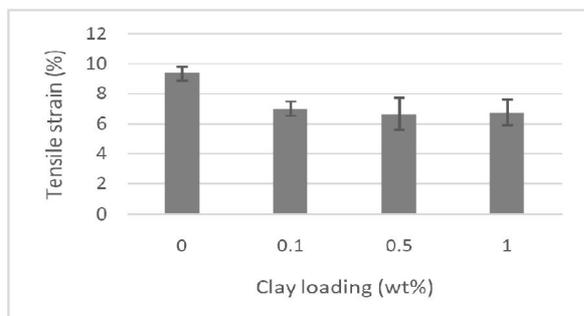


Fig.9. Tensile strain of halloysitenanoclay/polyester composites exposed to methanol

### 3.3 SEM Images

The scanning electron microscopy (SEM) images of fractured samples are shown in Fig. 10, Fig. 11 and Fig. 12. Fig. 10 reveals the smooth surface of neat polyester. In Fig. 11, halloysitenanoclay with 0.5wt% reinforcement can be clearly seen. The halloysitenanoclay dispersion is good compared to higher percentage of reinforcement. Agglomeration of halloysitenanoclay at 1wt% reinforcement can be observed in Fig. 12. It can be concluded that agglomeration is likely to occur at higher halloysitenanoclay content which can be associated with methanol absorption and decreased in flexural and tensile properties of the composites.

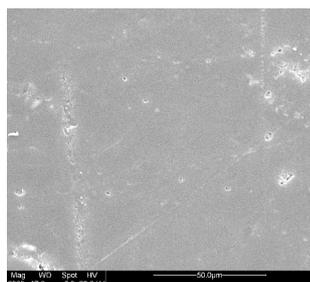


Fig. 10. SEM image of neat polyester

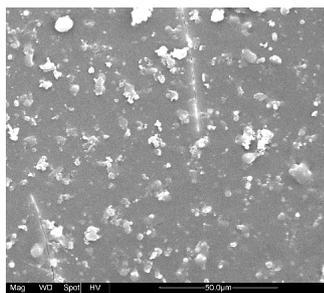


Fig. 11. The dispersion of halloysitenanoclay 0.5wt% reinforcement

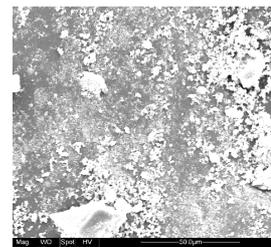


Fig. 12. Agglomeration of halloysitenanoclay with 1wt% reinforcement

## CONCLUSIONS

Obviously, methanol is a severe liquid medium for halloysitenanoclay/polyester composites. The addition of halloysitenanoclay has no positive influence on the flexural and tensile properties of the composites after methanol exposure. The flexural and tensile strength of the composites was considerably decreased after 30 minutes of methanol exposure. Based on SEM images, the poor dispersion of clay particles at higher content was seen to cause agglomeration. The addition of halloysitenanoclay possibly has decreased the crosslink density, as a result, the mechanical properties were also decreased. Nevertheless, further studies need to be carried out in the future, especially with the crosslink density, which can be achieved via equilibrium swelling data and liquid absorption rate at a longer period of time.

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