

Processing of polyester-halloysite nanotubes: effects of mild sonication technique on tensile properties

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ABSTRACT – This study offers new insights into the effects of sonication on tensile properties of halloysite nanotubes reinforced in unsaturated polyester. Mild sonication technique was used to study the light transmittance of halloysite nanotubes-polyester nanocomposites using UV-Visible spectroscopy. Mild sonication process up to 25 minutes was found to achieve stable dispersion, maximum values of T_g , storage modulus, loss modulus, Young's modulus and tensile strength in the case of 0.7 wt% halloysite nanotubes reinforcement. Halloysite particles at higher contents produced more agglomerates or particle clusters which lead to the detrimental effect as evidently shown by scanning electron microscopy images.

1. INTRODUCTION

Polyester resins are one of the most commonly used thermosetting polymers in composite structures because of their low cost and versatility [1], [2]. Polyesters are commonly used in coatings, construction, transportation, storage tanks and piping [3]. Since the discovery of polymer nanocomposites by Toyota, there has been an increasing interest on mechanical properties of clay-reinforced polymers [1], [4]. Extensive amount of literature has been published on the enhancement in mechanical properties of polymer nanocomposites, mostly reinforced with montmorillonite and bentonite fillers [5]. However very little attention has been paid to study the effect of mild sonication on halloysite nanotubes in unsaturated polyester.

The preparation of a nanocomposite requires good dispersion of the halloysite in polymer matrix at the nanometre scale. There are three types of morphologies for nanocomposites based on the degree of the clay dispersion: aggregated, intercalated and exfoliated [6]. In aggregated structure, clay tactoids are well distributed in polymer matrix but in intercalated structure, clay tactoids are delaminated. Thus, polymer chains can diffuse into the galleries between them. In the exfoliated structure, the clay tactoids are completely broken apart and homogeneously dispersed in the matrix [7]. Among these three morphologies, exfoliated structure is the most desirable state as it can provide excellent thermal and mechanical properties at very low clay contents [8]. However, the common problem when adding halloysite nanotubes to polymers is the dispersion of the particles. Exfoliated structure is highly desirable in achieving good mechanical properties, however the particles tend to

agglomerate and difficult to overcome. In polymer composites, lower clay concentration is one of the options that can be implemented as reported in previous studies [9]. Ideal clay reinforcement is below 2 wt% as dispersing higher weight fraction is difficult and deteriorates the mechanical properties, as the agglomerates act as stress concentration sites [10]. Dhakal et al. in their study reported an increase of 29% in the hardness of nanocomposites with 1 wt% of clay compared to pristine resin [11]. Esfahani et al. reported that 1.5 wt% nanoclay showed the highest impact strength [12]. Alamri et al. in their study revealed that a flexural strength of epoxy can be improved up to 46% with 1 wt% halloysite nanotubes reinforcement [13]. Sonication is useful to improve the dispersion of halloysite nanotubes in the polyester resin and reduce air bubbles at the interface between clay platelets and resin molecules. Sonication method can be categorised in two forms, mild sonication in a bath and high-power sonication using a tip [14]. Mild sonication in a bath uses ultrasonic devices to apply high impact of energy that introduces small shear forces. This method is very suitable for low viscosity resins and for a small volume [15]. High-power sonication on the other hand is mainly used for bigger volume. The aim of this work is to study the effect of halloysite dispersion in polyester resin and to examine the tensile properties of halloysite nanotubes-polyester nanocomposites.

2. RESEARCH METHODOLOGY

2.1 Materials and methods

Halloysite nanotubes as shown in figure 2.1, were used as a reinforcement filler and acquired from Sigma Aldrich (Irvine, UK). The diameter of halloysite nanotubes were between 30-70 nm and length 1–4 μm . Halloysite nanotubes have a structure with a density of 2.53 g/cm³ and a surface area 64 m²/g. The tubular morphology, high aspect ratio, and low percolation make halloysite nanotubes a good reinforcement for polyester. The polyester resin NORSODYNE O 12335 AL purchased from East Coast Fibreglass, UK, has a density of 1.2 g/cm³. The catalyst (hardener) was methyl ethyl ketone peroxide solution in dimethyl phthalate, also acquired from East Coast Fibreglass, UK. In order to produce monolithic polyester samples, the resin was mixed with Butanox M-50 catalyst with a polyester: catalyst ratio of 98:2.

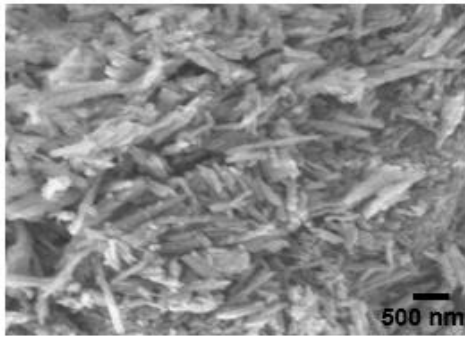


Figure 2.1 SEM image of halloysite nanotubes

Bath sonicator (Grant MXB6) was used to disperse halloysite nanotubes in polyester resin. The bath sonicator was rated for an average working power output of 89 Watt. The influence of sonication time and halloysite nanotubes concentration on dispersibility was studied on uncured samples (using dispersion bottles). UV-visible spectroscopy (Shimadzu 2600) was used to quantify the dispersion state of nano-fillers and optical clarity of samples at a fixed wavelength of 400 nm. To study the influence of concentration on the dispersibility of the halloysite nanotubes-polyester samples, different concentrations ranging from 0.1 to 1.5 wt% of samples have been prepared in dispersion bottles and sonicated for minimum 5 minutes and maximum of 25 minutes at 23 °C.

Dynamic Mechanical Analyzer (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 the ratio (E''/E'). The glass transition temperature (T_g) was taken as the temperature value at the peak of $\tan\delta$ curves. Rectangular samples with dimensions 15 x 5 x 3 mm were used and placed on a single cantilever clamp. The temperature applied was between 50-90 °C. A tensile test tests were performed using an Instron Universal Testing Machine (Model 3382). Five specimens were tested for each composition. The displacement rate for tensile tests were kept to 1 mm/min. Tensile test properties were carried out according to ISO 527 with a specimen thickness of 3 mm. Scanning electron microscopy (SEM) analysis using a FEI Quanta 200 (FEI, Cambridge, UK), was carried out on the fractured surfaces of tensile specimens to evaluate the fracture modes in the samples. The fractured portions were cut from the specimens and a layer of gold was applied using an Emscope sputter coater, model SC500A (Quorum Technologies, East Sussex, UK).

3. RESULTS AND DISCUSSION

Figure 3.1 shows light transmittance percentage against sonication time for halloysite nanotubes in polyester resin. Halloysite nanotubes were sonicated at different concentrations ranging from 0.1 wt% to 1.5 wt% into polyester resin. The readings were taken at different sonication time between 5 to 25 minutes. For samples without sonication, maximum light transmittance was observed for the reinforcement of 0.1 wt% halloysite nanotubes at 86.7%. The light transmittance decreases as halloysite nanotubes increases which caused by increase in the viscosity. Viscosity

increase with sonication time could be associated with the highly anisotropic shape of the halloysite particles [16]. Besides that, nanotubes breakage into smaller fragments during sonication was also responsible for the lower light transmittance values.

However, the breakage of halloysite nanotubes is totally depends on the sonication time. More breakage of halloysite nanotubes can be observed with increasing sonication time. Minimum light transmittance was observed for the case of 1.5 wt% halloysite nanotubes addition at 78%. After 10 minutes sonication, it was observed that the light transmittance values for all halloysite nanotubes in polyester dropped. For instance, at 0.1 wt% reinforcement the light transmittance dropped from 86.7% to 83% after 10 minutes sonication. At 1.5 wt% reinforcement, the light transmittance was 78.2% and dropped to 68.13% after 10 minutes sonication. The decrease in light transmittance after sonication suggests a tendency of halloysite nanotubes to disperse in polyester resin. Similarly, after 25 minutes of sonication, the light transmittance of all samples decreased. The shielding effect of halloysite nanotubes aggregates dispersed into small particles causes an increase in light absorption or reduced light transmittance. The results also suggest that the duration of sonication influences optical clarity of samples. Apart from that, halloysite nanotubes achieved stable dispersion in polyester resin after 25 minutes of sonication.

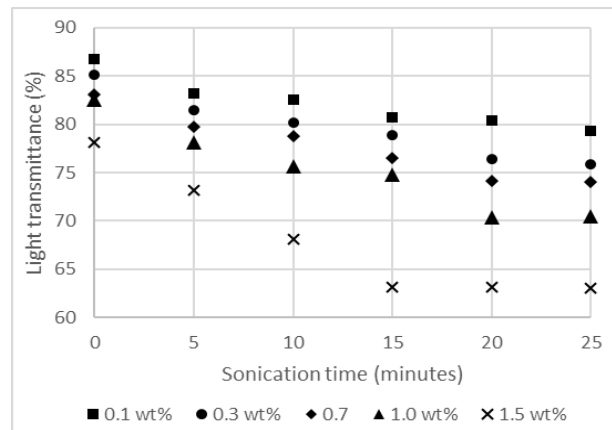


Table 3.1 Light transmittance of halloysite nanotubes dispersion in polyester resin against sonication time at $\lambda=400$ nm

Figure 3.2 shows the glass transition temperature (T_g) of the nanocomposites. Glass transition texture and high surface area of composites indicate restrictions in polymer chains. Both factors had influence the maximum exothermic heat flow temperature via reducing mobility of the polymer chains, as a result the T_g increased [17]. Minimum increase of T_g was observed in the case of 0.1 wt% halloysite nanotubes-polyester nanocomposites (increase by 2%), while maximum increase was observed in the case of 0.7 wt% (increase by 9%). Figure 3.3 (a) shows storage modulus of the nanocomposites.

The incorporation of halloysite nanotubes improved storage modulus. This can be attributed to the increased entanglements and interactions among polymer chains and halloysite nanotubes thereby reducing the movement

of polymer chains. Minimum improvement was observed in the case of 0.1 wt% halloysite nanotubes-polyester. At 50°C, the storage modulus improved by 64% compared to monolithic polyester. Maximum improvement of storage modulus was recorded in the case of 0.7 wt% halloysite nanotubes-polyester, where the storage modulus increased up to 210%.

However, in the case of 1.5 wt% halloysite nanotubes reinforcement, the storage modulus decreased 76%. This is due to the agglomerates particles that lead to an increase of stress concentration [18], [19]. Poorly dispersed halloysite nanotubes act as stress raiser and causes stress concentration which can degrade the tensile properties [20]. Figure 3.3 (b) shows loss modulus of the nanocomposites. Compared to monolithic polyester, the loss modulus of 0.1 wt%-1.0 wt% halloysite nanotubes-polyester showed significant enhancement. The loss modulus peaks were shifted to higher values as shown in Figure 3.3 (b).

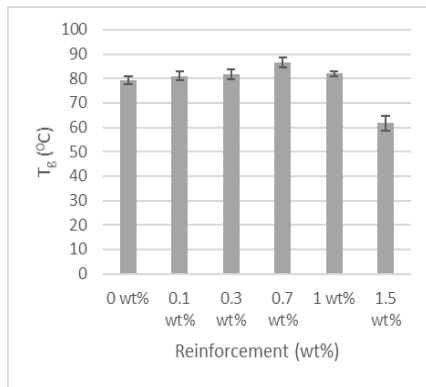


Figure 3.2 Glass transition temperature (T_g) of nanocomposites

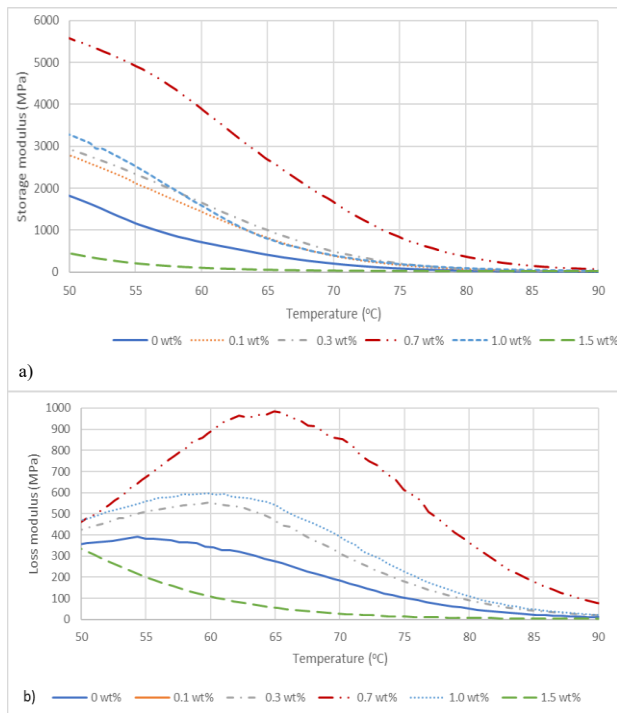


Figure 3.3 Storage modulus and loss modulus of nanocomposites

Figure 3.4 shows the Young's modulus of the nanocomposites. Monolithic polyester recorded the

lowest average value of Young's modulus with 0.75 MPa. The Young's modulus slightly increased at 0.1 wt% halloysite nanotubes reinforcement, where 15% of improvement was recorded. At 0.7 wt% reinforcement, the Young's modulus increased up to 27%. Figure 3.5 shows the tensile strength of all nanocomposite systems. Monolithic polyester was observed to have the lowest tensile strength. At 0.1 wt% reinforcement, an improvement of 7% was observed. The average tensile strength value reached its highest value of 55% at 0.7 wt% reinforcement. Interestingly, at 1 wt% reinforcement, the tensile strength improved 37%, about 18% lower than what has been achieved by 0.7 wt% halloysite nanotubes-polyester system. A 13% improvement in tensile strength was also recorded in the case of 1.5 wt% halloysite nanotubes reinforcement. The tensile strain graph is shown in Figure 3.6.

Monolithic polyester recorded the highest value of tensile strain with 12%. Nanocomposite systems show lower tensile strain value as the stiffness of the samples were improved. Minimum tensile strain value can be seen at 0.7 wt% reinforcement, where only 7% of strain was observed. The tensile properties increased due to the high surface area of the halloysite nanotubes; the higher the surface area, the more opportunity for filler-matrix interactions [21]. In the case of 1.5 wt% halloysite content, tensile properties were decreased. This phenomenon can be explained by the fact that higher halloysite has reduced the cross-linking of the matrix thus lowering the polymer chains bond between each other [22].

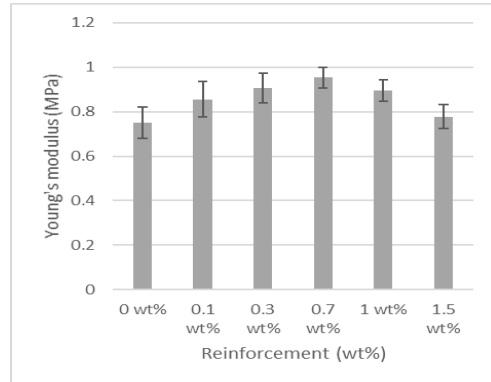


Figure 3.4 Young's modulus of the nanocomposites

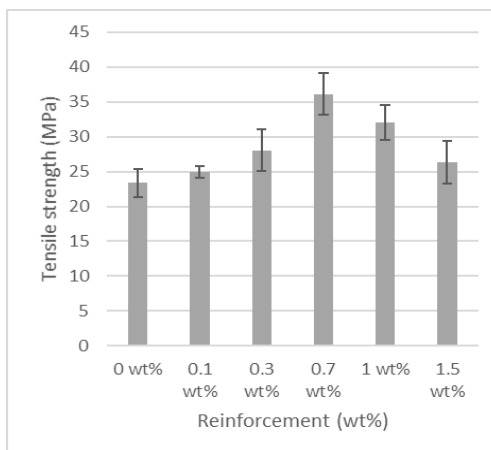


Figure 3.5. Tensile strength of the nanocomposites

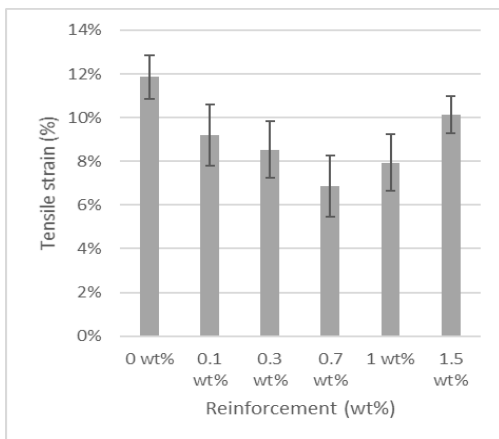


Figure 3.6 Tensile strain of nanocomposites

SEM Images

The fractured tensile samples were examined using scanning electron microscope (SEM). The image of monolithic polyester in Figure 3.7 (a) shows a straight crack propagation and also smooth surface. However, at 0.1 wt% halloysite nanotubes reinforcement, the fractured surface is having coarser profile compared to monolithic polyester. Short and round ended shape started to emanate radially and the crack lines were tortuous. At higher halloysite nanotubes reinforcement particularly in the cases of 0.7 wt% and 1 wt%. The surface roughness significantly increased. There are some of particle agglomerates of micron sizes in the case of 1.5 wt% as shown in Figure 3.7 (d). The agglomerates as shown in Figure 3.7 (e) consist numerous halloysite nanotubes in the polyester matrix. Besides that, the halloysite nanotubes agglomerates tend to sink to the bottom during curing, leading to cross-thickness inhomogeneity which may cause a deterioration in tensile properties [23]. Even though at 1.5 wt% halloysite nanotubes reinforcement stable dispersion was achieved after 25 minutes of sonication, the presence of agglomerates still clearly seen as shown in Figure 3.7 (f).

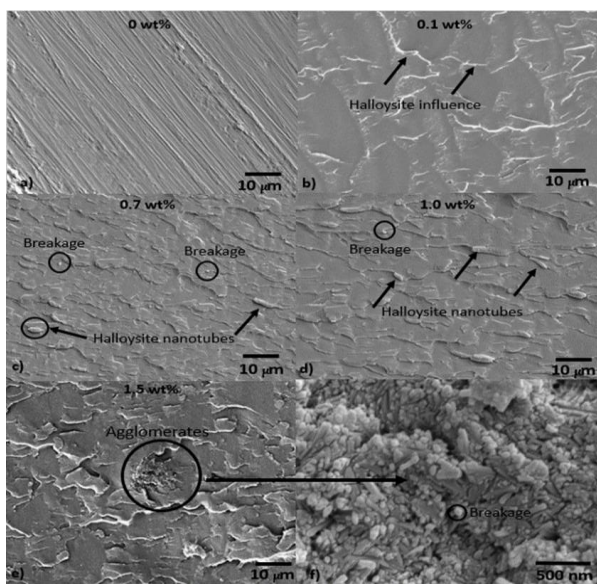


Figure 3.7 SEM images of the cured nano-composites

4. CONCLUSION

This study has identified that light transmittance decreases as halloysite nanotubes increases, which was caused by increase in the viscosity. Viscosity increase with sonication time could be associated with the highly anisotropic shape of the halloysite particles. Besides that, nanotubes breakage into smaller fragments during sonication was also responsible for the lower light transmittance values. The current results also suggest that the amount of halloysite nanotubes achieved their maximum T_g , storage modulus, loss modulus, Young's modulus and tensile strength at 0.7 wt% reinforcement. T_g , Young's modulus and tensile strength increased up to 9%, 27% and 55% respectively. Nanocomposite systems show lower tensile strain value compared to monolithic polyester as the stiffness of the samples were significantly improved. Minimum tensile strain value can be seen in the case of 0.7 wt% reinforcement, where only 7% of strain was recorded. In the case of 1.5 wt% reinforcement, the presence of agglomerates or particle clusters were responsible for the detrimental effect of the T_g , storage modulus, loss modulus and tensile properties of the nanocomposite system. This can be associated with the fact that higher halloysite content has reduced the cross-linking of the matrix thus lowering the polymer chains bond between each other.

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