

# Effect of Montmorillonite Modification on Ultra Violet Radiation Cured Nanocomposite Filled with Glycidyl Methacrylate Modified Kenaf

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**Abstract.** In this study nanocomposite cured by ultra violet radiation, were produced using modified montmorillonite (MMT) as reinforcing agent, chemically modified kenaf bast fiber as filler and unsaturated polyester as the matrix. Kenaf bast fiber was chemically modified with glycidyl methacrylate (GMA) whilst MMT were modified with cetyl trimethyl ammonium bromide (CTAB) and glycidyl methacrylate (GMA). Fixed 12 percent of GMA modified kenaf bast fiber with different percentage (i.e., 1, 3 and 5) of unmodified and modified MMT loading was used to produce the composite. The performed of GMA reaction with hydroxyl group of cellulose in kenaf bast fiber was evaluated using Fourier Transform infrared (FTIR) spectroscopy. GMA-MMT filled composite showed higher mechanical properties than MMT and CTAB-MMT filled composite. However, the increase of MMT, CTAB-MMT and GMA-MMT loading resulted in the reduction of mechanical properties. Scanning electron microscopy (SEM) analysis showed the evidence of compatibility enhancement between MMT and kenaf bast fiber with unsaturated polyester matrix.

## 1. Introduction

High demand and interest of lignocellulosic reinforced polymer composites is due to the cost rising, inadequate and non-renewability of synthetic materials. The use of lignocellulosic fibers as reinforcement material in polymer composites is based on several advantages such as renewable source, environmentally friendly, economical and mechanical performance that are comparable to those of synthetic fibers. In addition, using lignocellulosic fibers in polymer composites is known to be an alternative to solve the problem of decreasing petroleum resources [1].

Natural fiber particularly bast derived from flax, hemp, jute and kenaf have been applied by many researchers as reinforcement in polymer composite [2-4]. Besides providing good mechanical properties of the produced composite, the composition of the polymer matrix can be reduced through the inserting of natural fiber thus reducing the manufacturing costs and the use of non-renewable resources materials. However, high content of polysaccharides (cellulose and hemicellulose) and lignin in natural fiber has restricted its use in the production of composite [5]. Hydrophilic properties exhibited by natural fiber cause incompatibility with the hydrophobic polymer matrix which in turn weaken the mechanical properties of the composite. Therefore, natural fiber treatment or modification has been studied by many parties and it was proven to improve the compatibility between the polymer matrix and natural fibers [6, 7]. Based on a report, maleic anhydride treated kenaf dust composites have shown better tensile properties in comparison to those untreated one as a result of esterification where the hydroxyl group of kenaf reacted with the anhydride group of maleic anhydride to form an ester linkage [8, 9].

Based on a number of previous studies, the utilization of nano filler especially montmorillonite (MMT) in polymer matrix has managed to increase the strength and modulus of the composite [10,



11]. Small sized MMT provide high surface area and aspect ratio that mend the adversarial effect of irregularities of natural fiber in polymer composite. However, the performance of the nano filler filled polymer composite is depends on the interfacial interaction between the polymer matrix and filler because it determine the stress transfer efficiency of the components. Moreover, nano filler dispersion also played an important role in ensuring a uniform distribution of stress during load imposed. Appropriate modification of MMT is expected to increase the nano filler interaction with the polymer matrix and also to improve the dispersion of nano filler in the polymer matrix. Thus, this study focuses on the effect of MMT modification on mechanical and physical performance of the ultra violet (UV) radiation cured unsaturated polyester nanocomposite reinforced with glycidyl methacrylate (GMA) modified kenaf bast fiber.

## 2. Materials and Methods

Kenaf bast fibers were supplied by Forest Research Institute Malaysia (FRIM). Unsaturated polyester (UPE) resin (Reversol P-9728 P) was obtained from Syntomer, plc. Photoinitiator IRGACURE 1800 was purchased from Ciba Specialty (Singapore) Pte. Ltd. Montmorillonite (MMT) was obtained from Nanocor, USA. Hexadecyl trimethyl ammonium bromide also known as cetyl trimethyl ammonium bromide (CTAB) was supplied by Sigma-Aldrich. Glycidyl methacrylate (GMA) was acquired from Fluka Chemika.

### 2.1 Chemical modification of kenaf bast fibers

GMA was diluted in *N,N*-dimethylformamide (DMF) at a weight ratio of 3:7. To prevent the occurrence of copolymerization of GMA during reflux, 5 wt% (based on GMA) of hydroquinone was added as an inhibitor. Oven-dried kenaf bast fibers were fed into the reaction flask containing the GMA solution. The reaction was carried out for 2 hours at a temperature of 90°C. The modified kenaf bast fibers were then filtered and rinsed with acetone. The fibers were further washed by refluxing with excess fresh acetone for 3 hours to ensure the solvent, unreacted reagent, and any non-bonded polymer formed during the reaction were eliminated.

### 2.2 Ion substitution of MMT

CTAB solution of 0.225 mol based on the MMT cation-exchange capacity (CEC) (145 meq/100g) was prepared by dissolving CTAB into a mixture of ethanol and distilled water. Ethanol to distilled water ratio was 1:1. MMT was incorporated into distilled water and stirred using a high speed motor stirrer. CTAB solution was then added to the MMT and stirred at the speed of 500 rpm in a water bath at 80°C for 12 hours. Modified MMT was filtered and washed repeatedly with ethanol and distilled water to remove excessive CTAB. It was then oven dried for 48 hours.

### 2.3 Chemical modification of MMT

GMA was diluted in DMF at a volume ratio of 5:3. Hydroquinone of 5wt% based on GMA was added as an inhibitor. Oven dried MMT was then added into the GMA solution and the reaction was carried out for 3 hours at a temperature of 90°C. Reacted MMT was then filtered and refluxed with acetone for 2 hours before being dried in an oven for 24 hours.

### 2.4 Composite preparation

Kenaf bast fibers were cut into 5 mm long segment. The fiber mat was prepared by soaking the weighted fibers in distilled water for 10 minutes and arranged randomly in a deckle box with nylon mesh covered at the bottom to drain out water. The mat was oven dried at 105°C for 24 hours. The fiber mat was then hot-pressed for 1 hour at 100°C to give the thickness approximately of 1 mm. MMT, CTAB-MMT and GMA-MMT nano filler was poured into the UPE at 1, 3 and 5% separately. The mixtures were blended using a high-powered mixer at 600rpm and further mixed using three-roll mill for 1 hour. Photoinitiator IRGACURE 1800 of 3 wt% was then added into the mixture and stirred. Mix UPE/nano filler/IRGACURE 1800 was applied to the fiber mat using hand lay-up process in a

steel mold. Curing process took place in a UV 1<sup>st</sup> ultraviolet machine at a conveyor speed of 10 m/min for 20 cycles for both sides of the composite.

## 2.5 Testing and characterization

*2.5.1 Fourier transforms infrared (FTIR) analysis.* Infrared spectra were obtained using Nicolet Avatar 360. The purpose of using FTIR was to determine the functional groups formed from the modification of kenaf bast fiber with GMA.

*2.5.2 Tensile test.* A number of specimens were cut out from the composite sheets. A tensile test was performed on an Instron Merlin Series in accordance to ASTM D 638.

*2.5.3 Scanning electron microscope (SEM) analysis.* Surface morphologies of composite fractured tensile specimens were examined using Jeol JSM-7000F scanning electron microscope (SEM).

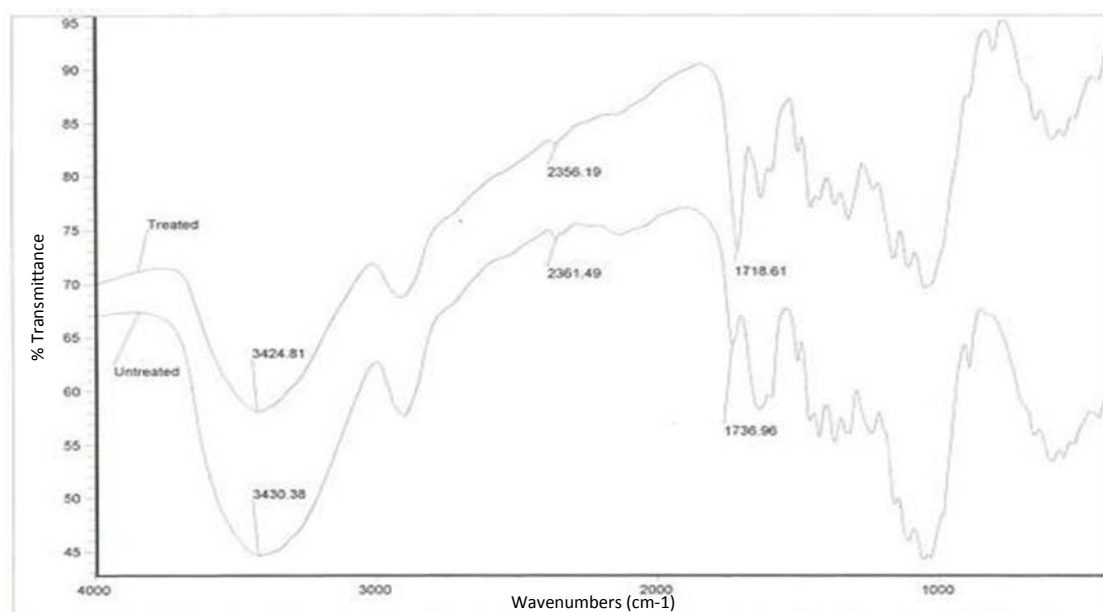
*2.5.4 Water absorption and thickness swelling.* The test was conducted in accordance to ASTM D 579. Rectangular specimens were cut out and oven dried at 80°C for 24 hours before it were cooled at room temperature in a desiccator and weighted. The specimens were immersed in distilled water at room temperature for 24 days. Weight and thickness were measured every 24 hours.

## 3. Results and Discussions

### 3.1 FTIR Analysis

Figure 1 shows the FTIR spectra of untreated and GMA treated kenaf bast fiber. It can be seen that peaks at 3430 cm<sup>-1</sup> and 3424 cm<sup>-1</sup> had appeared for unmodified and modified kenaf bast fiber, respectively. It indicates the presence of hydroxyl (OH) group in the fiber. However, the decreased intensity of OH peak of GMA modified kenaf bast fiber compared to the unmodified kenaf bast fiber is clearly be seen, which designated to the reduction of OH group in the fiber [12].

The peaks located at 1736 cm<sup>-1</sup> for unmodified kenaf bast fiber and 1718 cm<sup>-1</sup> for modified kenaf bast fiber were attributed to the carbonyl (C=O) group. Modified kenaf bast fiber shows higher absorption as compared to unmodified kenaf bast fiber which indicates the merged between the fiber and GMA had occurred. High frequency of carbonyl group at 1700 cm<sup>-1</sup> region for unmodified kenaf bast fiber is attributed to the presence of ester wax [13].



**Figure 1:** FTIR spectra of untreated and GMA treated kenaf bast fiber.

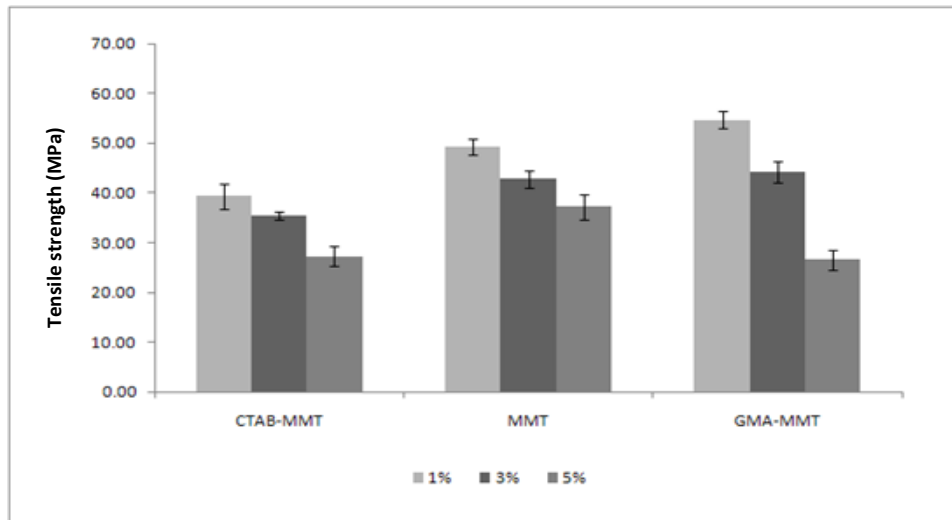
### 3.2 Tensile strength and modulus

Figure 2 shows the effect of MMT modification and loading on tensile strength of 12% of GMA modified kenaf bast fiber reinforced composite. It can be seen that composite with 1% loading of GMA-MMT shows the highest tensile strength. However, at 5% loading of GMA-MMT, the composite shows the lowest tensile strength value. CTAB-MMT shows lower tensile strength compared to that MMT and GMA-MMT at 1% loading. Figure 3 shows the results of the tensile modulus of the same samples. The similar pattern of outcomes as tensile strength was observed.

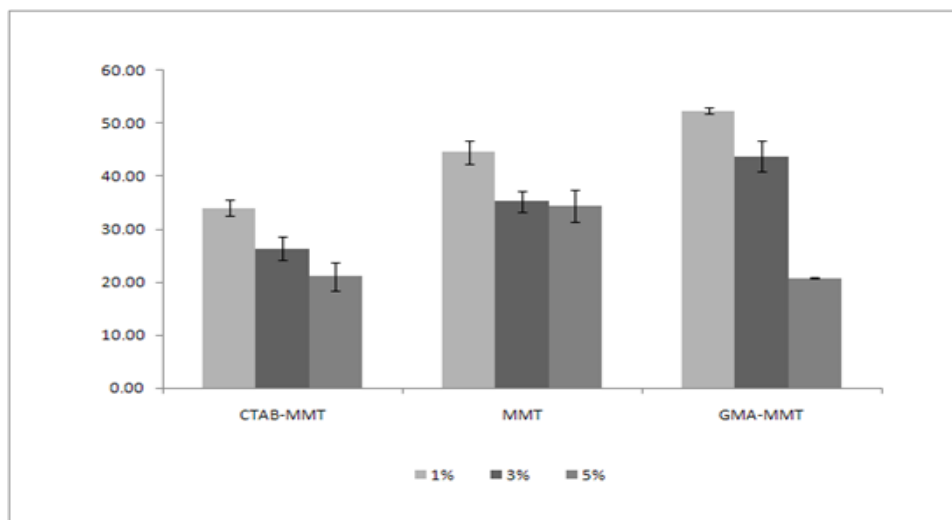
The existence of reactive sites resulted from chemical modification on the surface of MMT with GMA allows the occurrence of crosslinking between the matrix and MMT. It has improved the interfacial adhesion thus enhance the compatibility between the polyester matrix and the MMT. Besides, micron sized GMA-MMT yielded large surface area that subsequently assists good interaction with polymer matrix. The strong interaction has enabled the modified filler to be a reinforcing agent in the composite that can resist well when tensile force is applied [14]. Moreover, the presence of modified kenaf bast fiber that has good interfacial interaction with polymer matrix has augmented the tensile strength and modulus of the composite.

The decline in tensile strength and modulus with the addition of GMA-MMT at 3 and 5% is caused by the poor penetration of UV radiation in the composite. This is due to the dark colour given by MMT and kenaf bast fiber after being modified with GMA. With the increasing of GMA-MMT percentage, the composite dark colour is raised and limits the penetration of UV radiation only to the surface of the composite. Furthermore, the decrease of tensile strength and modulus also contributed to the dispersion of the filler in the polymer matrix. The separation of platelets is important in providing good dispersion and to avoid agglomeration of MMT in the polymer matrix [15]. However, at higher filler loading, shear forces exerted by high power mixer and two-roll mill was not able to well separate the MMT platelets. The same situation applies to the MMT and CTAB-MMT which reflected by the decreased of tensile strength and modulus with the increasing of filler loading.

Lower tensile strength and modulus of CTAB-MMT compared to MMT and GMA-MMT at 1% loading was due to the nano size of the filler. Although CTAB-MMT has good interaction with the polymer matrix, the addition of this nano filler in the composite is less effective because of their smaller size [16]. This causes the tensile strength and modulus of the composite is much depends on the reinforcing effect given by the GMA modified kenaf bast fiber.



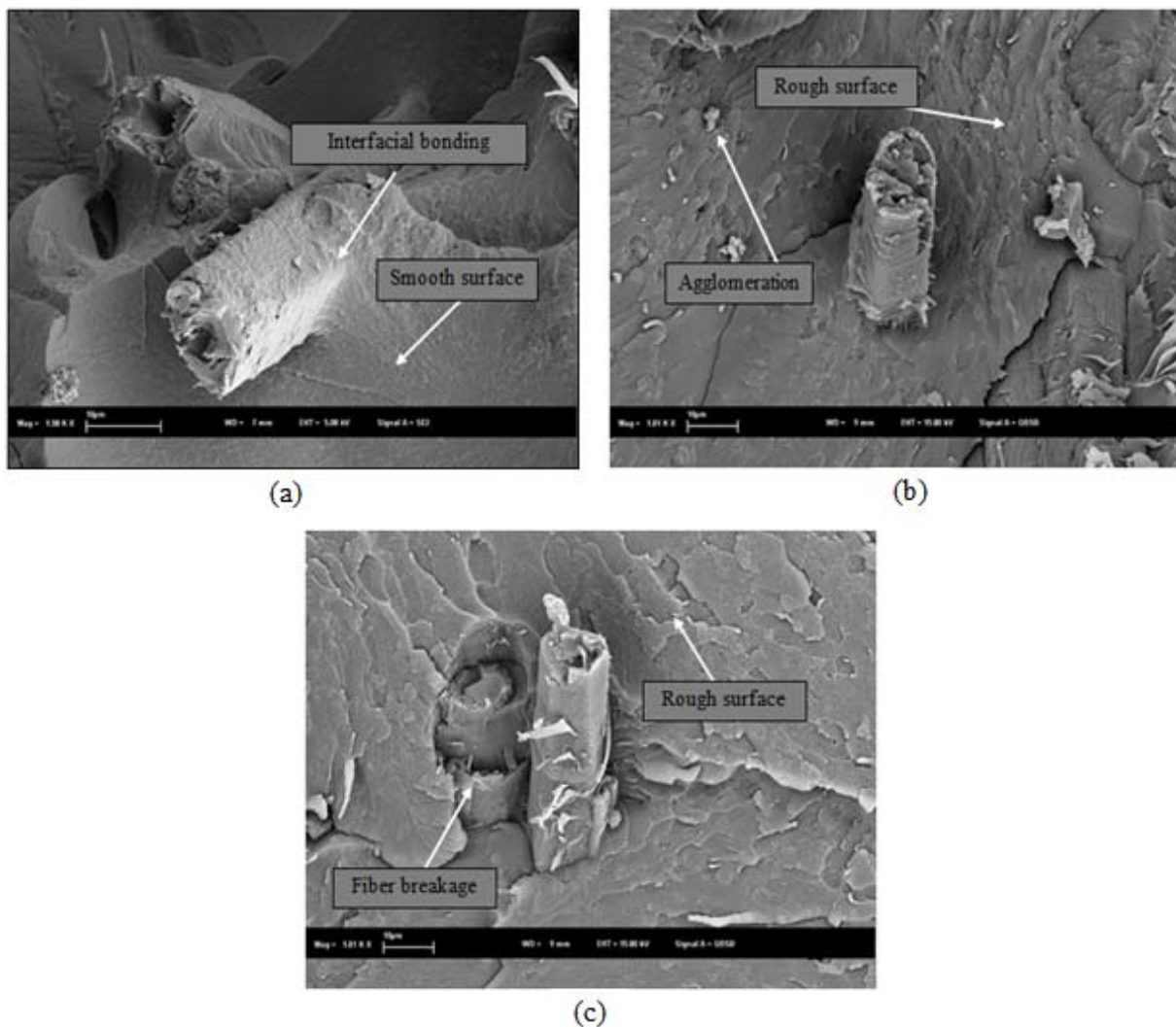
**Figure 2:** Tensile strength of 12% of GMA modified kenaf bast fiber reinforced composite with different loading of MMT, CTAB-MMT and GMA-MMT



**Figure 3:** Tensile modulus of 12% of GMA modified kenaf bast fiber reinforced composite with different loading of MMT, CTAB-MMT and GMA-MMT

### 3.3 SEM micrographs

Figures 4(a), (b) and (c) show the SEM micrograph of unmodified MMT, CTAB-MMT and GMA-MMT contained in 12% of GMA modified kenaf bast fiber reinforced composite, respectively. It can be seen that the composite contain unmodified MMT has smooth surface of polymer matrix with non-agglomeration observed which implies that MMT is well dispersed. The figure also shows the occurrence of good interfacial bonding between GMA modified kenaf bast fiber and polymer matrix. In contrast, CTAB-MMT and GMA-MMT contained composite shows rough surface of the polymer matrix. Agglomeration can be observed on CTAB-MMT composite indicates that the poor dispersion of nano filler in polymer matrix. Fiber breakage spotted on GMA-MMT composite signified good matrix-fiber adhesion strength.



**Figure 4:** SEM micrographs of (a) unmodified MMT (b) CTAB-MMT and (c) GMA-MMT filled 12% of GMA modified kenaf bast fiber reinforced composite

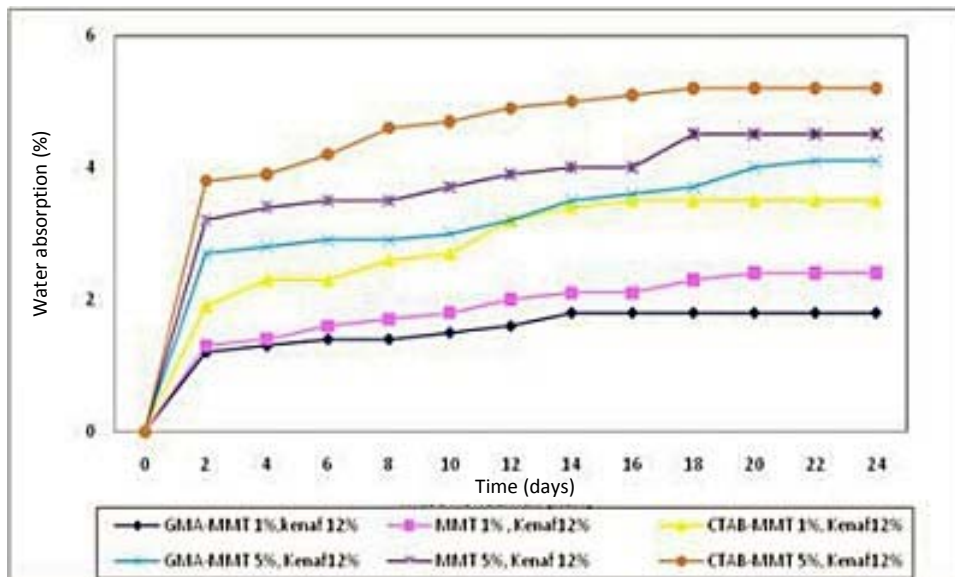
### 3.4 Water absorption and thickness swelling properties

Figures 5 and 6 show the effect of MMT modification and loading on the percentage of water absorption and thickness swelling of 12% of GMA modified kenaf bast fiber reinforced composite, respectively. Both figures show a similar pattern where composite contain 5% CTAB-MMT exhibit the highest percentage of water absorption and thickness swelling. It was then followed by composite contain 5% MMT, 5% GMA-MMT, 1% CTAB-MMT and 1% MMT. The lowest percentage of water absorption and thickness swelling is indicated by 1% GMA-MMT.

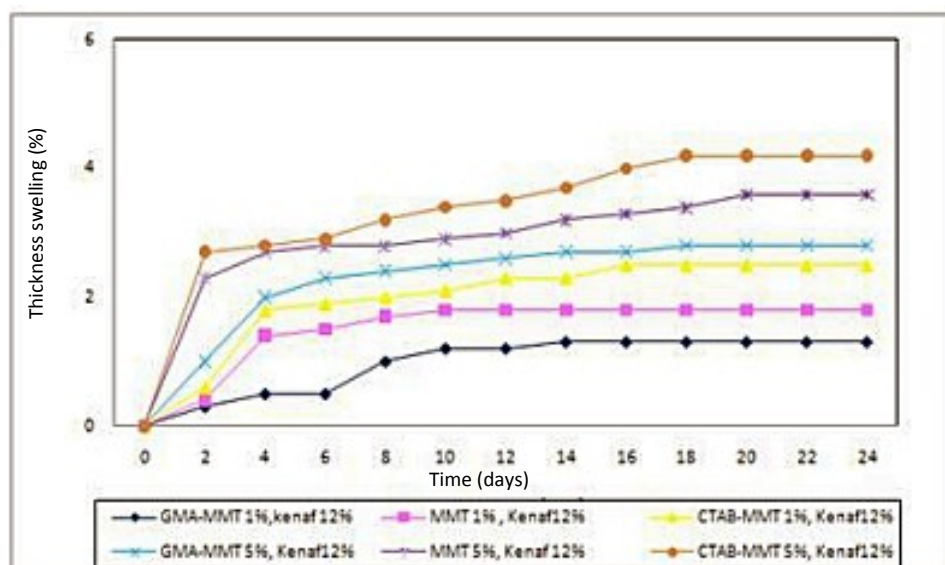
Naturally, MMT contains hydroxyl group (OH) on the surface and in the gallery that attract to moisture. Modification of MMT with CTAB expanded the gallery space thus revealed more OH group to allow the interaction with water molecules. This phenomenon occurs when the layer of MMT silicate intercalated or exfoliated. With higher loading (5%) of CTAB-MMT, more hydrophilic material contained in the composite hence increases the tendency of the composite to absorb water. This directly destabilized the dimensional of the composite by increasing the thickness of the composite.



In contrast, modification of MMT with GMA has managed to make the MMT particles more hydrophobic. This is the result of OH group on MMT particle has been replaced with methacrylate groups. This causes the percentage of water absorption demonstrated by GMA-MMT contained composite is the lowest, consequently lowering the percentage of thickness swelling of the composite. However, the increase of water absorption and thickness swelling percentage at high unmodified and modified MMT loading might be caused by the agglomeration of MMT on the surface of the composite which cause concentration of water uptake at certain points along the composite [17].



**Figure 5:** Water absorption of 12% of GMA modified kenaf bast fiber reinforced composite with different loading of MMT, CTAB-MMT and GMA-MMT



**Figure 6:** Thickness swelling of 12% of GMA of kenaf bast fiber reinforced composite with different loading of MMT, CTAB-MMT and GMA-MMT

#### 4. Conclusions

From this study, it can be concluded that the modification of kenaf bast fiber with GMA has reduced the OH content which promotes good fiber-matrix interfacial bonding. Modification of MMT with GMA has improved the tensile properties of the composite at 1% loading. An observation attributed to the improvement of interfacial adhesion between the polyester matrix and GMA-MMT. CTAB modified MMT demonstrate the lowest tensile properties at 1% loading due to the small size of the filler that less effective to the composite. Further loading of nano filler decreases the tensile properties of the composite cause by the poor dispersion of the filler in the polymer matrix. SEM micrographs show the interaction of the fiber to matrix and the filler to matrix. GMA-MMT at 1% loading composite shows the lowest percentage of water absorption and thickness swelling due to the OH group on MMT has been replaced with methacrylate groups.

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