Hygrothermal Aging on Heat Treated Kenaf Mat-Unsaturated Polyester Composite made by Resin Transfer Molding Process

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Abstract. Kenaf fiber mat reinforced unsaturated polyester composites were subjected to water immersion tests in order to study the effects of water absorption on the mechanical properties. The composites samples consist of untreated and heat treated kenaf mat composites which fabricated by resin transfer molding process. The heat treatment of fiber was undertaken by placing the kenaf mat into circulating oven at 140ºC for 10 h. Water absorption tests were conducted by immersing specimens in a distilled water bath at room temperature, 60ºC and 90ºC until saturation condition obtained.The water absorption patterns of composites at room temperature followedFickian behavior, while hygrothermal aging at 60ºC and 90ºC exhibited pseudo-Fickian behavior. The heat treatment on kenaf fiber reduced the water uptake and enhanced the flexural properties of its composites. Moisture absorption of samples during hygrothermal process reduced the flexural properties of composite samples, particularly at elevated temperatures. The re-drying process could not restore the flexural properties of samples. The failure modes of composites in all of temperature, observed by SEM fractographic studies discussed.

Keywords: Hygrothermal; kenaf; heat treatment; flexural properties

Introduction

Nowadays, kenaf become a popular reinforcing agent for in polymer–matrix composites. Kenaf fibers have several advantages, such as good mechanical performance, low density, and biodegradability [1]. Kenaf fibers are lignocellulosic fibers from hibiscus cannabinus plant sp. that composed of cellulose, hemicellulose, lignin, pectin and etc. Cellulose has both crystalline and amorphous strutures, while the lignin and hemicellulose have a completely amorphous structures.

Modifications on kenaf fiber are being intended to improve the properties of its composite. As a fiber modification method, the heat treatment method improves the mechanical properties of sisal fibers composites without changing the composistion of fiber [2,3].

However other research [4] proved that the heat treatment on wood degraded the chemical constituents and changes the crystallinity in fiber structures. Cao et al. research explained that the heat treatments on kenaf fibers affect the crystallinity and the single fiber tensile strength [5].

As a famous industrial method for fibers composites fabrication, resin transfer molding (RTM) method produce composites with low void content, good dimensional tolerances, good process control, minimal waste, and good surface finishing. The composites fabricated by RTM have higher mechanical properties as compared with the composites produced by hand lay-up method [6] or compression molding method [7]. Rassman et al. [8] signified that the RTM process can be applied for mixture of kenaf fibers and unsaturated polyester resin to produce composites panels. In other research, Rassman et al. [9] reported that kenaf fiber-polyester composites produced by RTM have higher impact energy than the kenaf fiber composite reinforced by vinyl ester and epoxy resin. However a few researchs presented for treated non-woven kenaf fiber mat produced by resin transfer molding, especially for heat treatment of non woven kenaf fiber mat.

In application, the changes of temperature and moisture condition have many important effects on durability and properties of natural fiber polymer composite properties. The combination of temperature and moisture absorption exposure reduces the interfacial interaction between hidrophilic fiber and hydrophobic polymer matrix. It creates the poor stress transfer efficiencies that reduces mechanical properties of composites [10]. However the modification on natural fiber could reduce the sensitivity of mechanical and thermal properties to moisture uptake [11].

The objective of research was to investigate the effects of hydrothermal aging on the water uptake behavior and mechanical properties of non-woven heat treated kenaf fiber-unsaturated polyester composites produced by RTM. Several experiments were conducted to verify the effect of hydrothermal on samples property, such as flexural strength test, water uptake test and SEM micrograph observation. The final data provided the failure mode of composites.

Experimental

Materials

Non-woven kenaf fiber mats were supplied by Kenaf Fiber Industries Sdn. Bhd with 1350 g/cm^{-2} of areal density. Kenaf fibers has 251.43 MPa in tensile strengh, 19.69 GPa in elasticity modulus and 1.292 gr/cm^3 in density. The matrix used was unsaturated polyester (Reversol P9565) that mixed with 1% wt. cobalt naphthalene and 1% wt. methyl ethyl ketone peroxide. The mechanical properties of unsaturated polyester resin are 59.07 MPa in tensile strength and 2.91 GPa in tensile modulus.

Heat treatment

Non-woven kenaf fibers mat were heated for 10 h at 140^{o}C in drying oven. This treatment is an optimum heat treatment treatment that refer to Cao et al. [5] research on kenaf fiber. After treatment, kenaf mats were cooled in room temperature and kept in sealed plastic bag.

Processing

RTM machine used in this research was Innovator Megaject 3250 (8000) with 2 reciprocating pumps. The hardener to unsaturated polyester ratio was 1:100. The pump and mold pressure were set at 1.3 bar and 0.6 bar, while the vacuum pump was set at -0.55 bar. The mold was made from aluminum with the cavity dimension of mold is 30 cm x 60 cm x 0.7 cm. Prior to RTM process, the kenaf mats were dried at 60^{o}C for 3 h. The fiber volume fractions are kept constant at 30%.

Water absorption studies

The flexural samples were used for measuring the weight change in water absorption test. Before hydrothermal process, all of samples were dried in an oven at 60 ^{o}C for 24 h and then were cooled at room temperature in a desiccator. During hydrothermal process, the conditioned specimens were fully dipped into waterbath at room temperature, 60^o and 90^{o}C and were removed at different period of time for weighing. The weight gain percentage of water uptake were measured at different time intervals until obtain saturation. The weight gain of water uptake were evaluated from equation (1) and the graph of moisture content versus square root of time was plotted [10].

$$M(\%) = \left[\frac{M_1 - M_0}{M_0}\right] \times 100 \qquad (1)$$

Where $M(\%)$ is weight gain of water uptake in percentage, M_1 is weight of the wet sample at given time, M_0 is initial weight of sample. After hydrothermal aging process, the specimens were re-dried in drying oven at 60^{o}C for 24 h and were cooled in room temperature until constant weight for flexural test.

Scanning Electron Microscope (SEM)

Micrographs of surface and fracture surface of samples were taken using a scanning electron microscope (SEM) Model **TM 3000 Hitachi.**

Before observation, the samples were coated with gold by means of a plasma sputtering apparatus for 1 min.

Flexural properties of composites

The three-point bending test was performed according to ASTM D790 method. The test was conducted at universal testing machine model Instron 5960 with a crosshead speed of 2 mm/min with 5 kN load cell and 130 mm in span length.

Results and Discussion

Water absorption

Fig. 1(a-c) show the percentage of water uptake as a function of $t^{1/2}$ for neat resin and composites at room temperature, 60^{o}C and 90^{o}C, respectively.

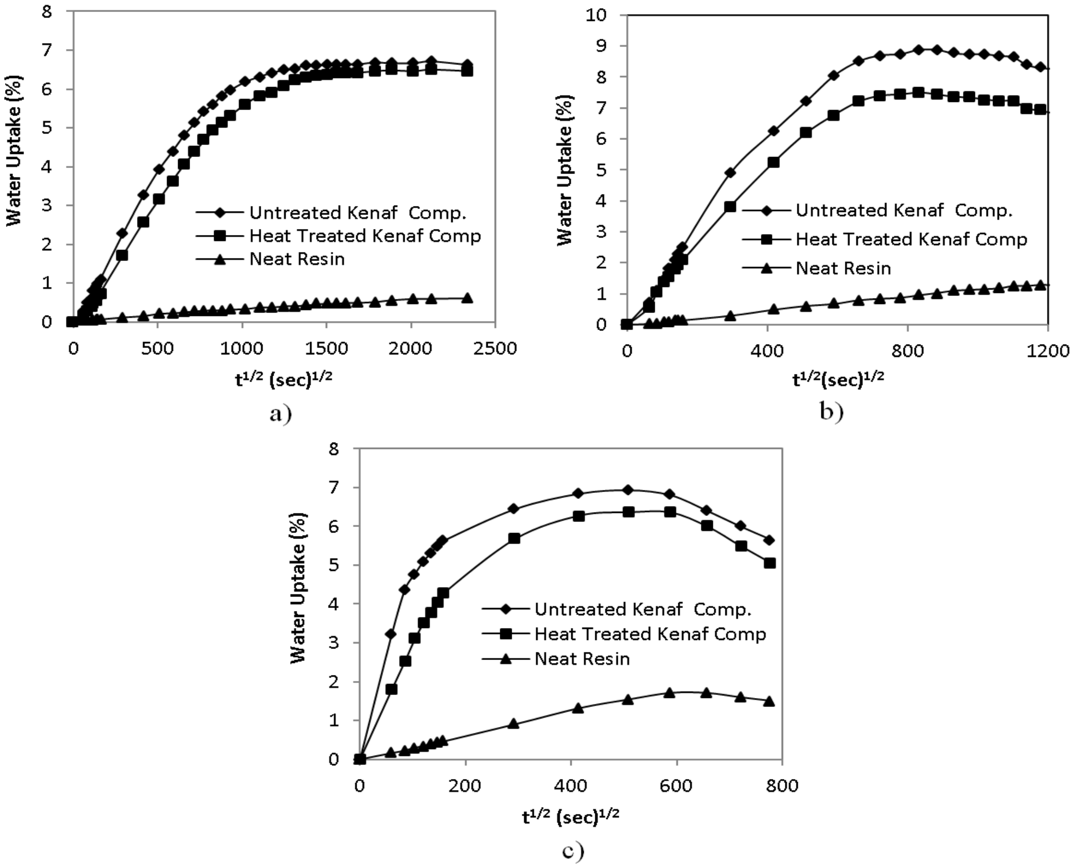


Figure 1. The water uptake percentage of water for neat resin and kenaf fiber reinforced unsaturated polyester composites at : (a) room temperature; (b) 60^{o}C; (c) 90^{o}C.

The neat resin samples absorb water much lesser than the composites. Untreated kenaf fiber composite is the fastest samples that absorb water at all of aging temperature. Water uptake at room temperatures can reaches saturation condition, while the water uptake at elevated temperature decrease after saturation obtained. It denotes that the water absorption behavior at room temperature followed Fick's law. While hygrothermal aging at 60^{o}C and 90^{o}C disagree to Fickian behavior, where the moisture weight gains neverreaches equilibrium after initial take off [12].

The deviation from Fickian water uptake behaviour at 60^{o}C and 90^{o}C is related to the high expansion of micro cracks in the composites (see Fig. 2), which leads to water transport to the fiber and decreased fiber–matrix adhesion [13]. It also promotes the fiber–matrix debondingin composites [14]. Furthermore, the leached out of composites constituent in elevated temperature aging also promote the deviation of Fickian mechanism [13].

From Fig. 1(a-c), the water uptake of heat treated kenaf fiber composites indicate lesser water absorption than untreated kenaf-reinforced unsaturated polyester composites. Lesser water absorption may be attributed to the decrease of hydroxyl groups number and the change of fiber structures or cell wall size (cells shrinking) of kenaf fibers after heat treatment [15-17]. It affects the microspores closure in kenaf fiber cell and limits the penetration of water molecules in kenaf fibers. Estevez et al. [18] explained that heat treatment in lignocellulose as wood, decrease swelling, decrease the wettability, produce dehydration and increase the hydrophobicity.

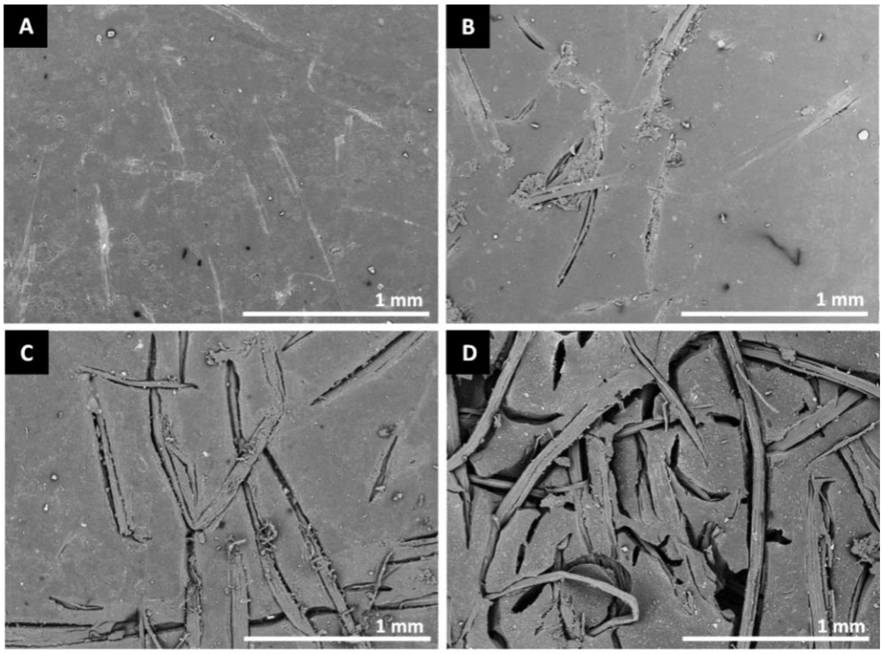


Figure 2. SEM micrographs of composite surface after aging at (a) control (b) room temperature (c) 60^{o}C (d) 90^{o}C.

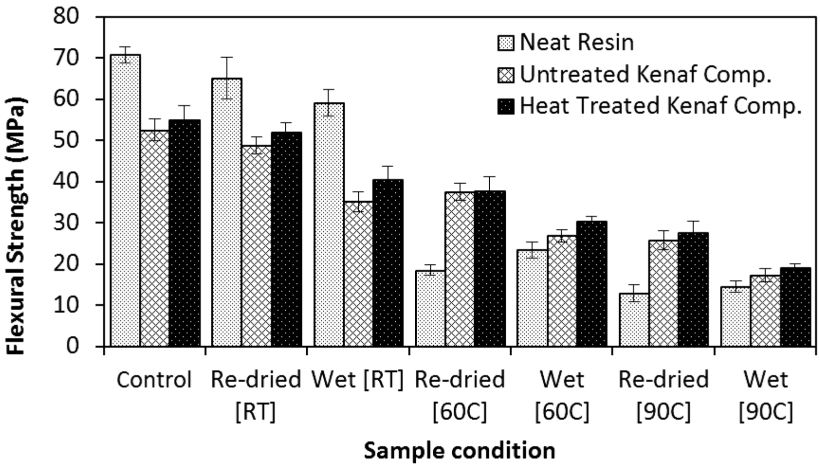
The expansions of micro crack decrease the fiber–matrix adhesion and lead the water transport in composites. Akil et al. [19] signified that the glass temperatures (T_g) of unsaturated polyester matrix are obtained at 90.3^{o}C – 102.1^{o}C. Furthermore, hydrothermal aging can significantly reduce T_g because of the plasticization mechanism of thermoset polymer [20-22]. The hydrothermal aging over T_g of matrix leads the degradation of polymer and induces the leached out of matrix content into the water [20]. The leached out of matrix during elevated temperature aging promotes the micro crack growth of composites (see Fig. 2 (a-d) and results the non-fickian behavior of kenaf fiber composites.

Mechanical Properties of Composites

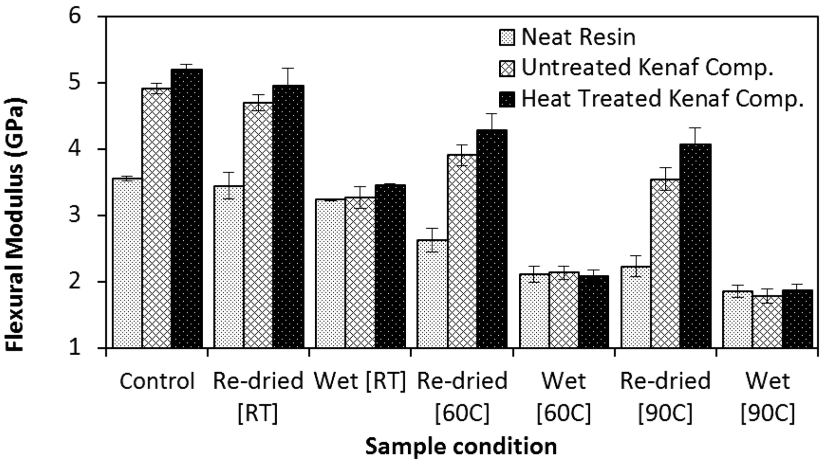
Flexural strength and flexural modulus for kenaf fiber reinforced unsaturated polyester composites after hydrothermal aging are summarised in Fig. 3 (a–b). From Fig. 3 (a-b), the heat treated kenaf fiber composites have higher flexural properties as compared to untreated ones before hydrothermal process. Sreekumar et al. [3] stated that the heat treatment does not affect the sisal fiber surface significantly, but the heat treatment enhances the mechanical properties of sisal fiber reinforced unsaturated polyester. Heat treatment increases the crystallinity of sisal fibers and reduces the intensity of hemicellulose bandwith in FT-IR spectra [2]. In this research, heat treatment of kenaf fiber at 140^o for 10 h removes the moisture of kenaf fiber thoroughly and may leads to good fiber/matrix interaction. The better adhesion between matrix and fibers enhances the mechanical properties of composites.

Fig. 3 (a-b) show that flexural strength and flexural modulus decline after aging both for re-dried or wet samples. It can be associated to moisture absorption of the kenaf fibers that promote the interfacial bonding damages between fiber and matrix [10]. The kenaf fibers of composite absorb higher amount of water than matrix due to the high amount of hemicellulose content and a large number of porous tubular structures that promote the liquid penetration. The penetration of water molecules create swelling stresses that induce composite failure [10,23]. Furthermore, the water molecules can act as a plasticizer and damage the rigidity of the cellulose structure [10].

The highest degradation rate for kenaf fiber reinforced unsaturated polyester composite is recorded for specimen after exposed to 90^{o}C, and followed by 60^{o}C, room temperature aging, respectively. The water molecules of moisture during hydrothermal process induce interfacial crack, microcrack and voids in composites system. Wherein the micro crack’s size can be penetrated by water and enhance swelling stresses of composites [10,23]. This mechanism aggravates to the weakening of fiber–matrix adhesion in elevated temperature aging [7,10].



a)



b)

Figure 3. (a) Flexural strength and (b) Flexural modulus of neat resin and kenaf fiber/unsaturated polyester composites after hydrothermal aging at room temperature, 60^oC and 90^oC.

The flexural strength and modulus for re-dried composite samples after hydrothermal aging have higher value than wet samples. The re-drying process of samples reduces the plastisization effect of kenaf fiber and provides effectively reinforcement in composite. However the strength and modulus of composites are still lower than composites standard values. This trend also occurs at room temperature, 60^oC and 90^oC aging although the strength and modulus for higher temperature aging are lower than room temperature.

The re-dried samples from elevated temperature aging have lower flexural strength and modulus than standard and room temperature immersion. It is caused by the removal of water bound attached to the polar groups of polymer after re-drying process.

Fig. 4 (a-d) present the micrographs of flexural fracture surfaces of the composites for heat treated kenaf fiber composites in control condition and after hygrothermal aging process

Figure 4**.** SEM micrographs of heat treated kenaf fiber/unsaturated polyester after hydrothermal aging at a) Control condition b) Room temperature (c) 60^{o}C (d) 90^{o}C.

Fig. 4 (a) shows that the controlled heat treated kenaf fiber reinforced unsaturated polyester composite are failed by a combination of both fiber pull-out and fiber fracture. After immersion in room temperature, the fracture composite surface (see Fig. 4 (b)) is dominated by long fiber pull out. The fracture surface of composite after 60^{o}C aging (see Fig. 4 (c)) shows shorter the length of fracture fiber as compared to those exposed to the room temperature immersion. The fracture surface of the composite after 90^{o}C aging (see Fig 4 (d)) has shorter fiber fracture than composites samples after 60^{o}C aging. After hydrothermal aging at 90^{o}C, a wider interfacial gap between fiber and matrix is observed. It signifies that the hydrothermal aging at 90^{o}C damages the matrix and fiber content of composites. This damages can be related to the non-fickian behavior of composite at elevated temperature aging.

Conclusions

Heat treatment of kenaf fibers at 140^{o}C for 10 h enhances the flexural strength and the flexural modulus of its composites. Heat treated kenaf reinforced composites absorb lesser water than untreated kenaf reinforced composite. It occurs at room temperature, and elevated temperature aging condition. The water absorption of composites at room temperature immersion is found to follow Fickian behavior, while the hydrothermal aging processes at 60^{o}C and 90^{o}C result in non-Fickian behaviour, while the hygrothermal aging processes at 60^{o}C and 90^{o}C result in pseudo-Fickian behavior both for neat resin and its composites. The water absorptions at elevated temperatures induce a significant material degradation. Hygrothermal aging at room temperature or elevated temperature reduce significantly the flexural properties due to the degradation of the fiber–matrix interface and the formation of microcrack in unsaturated polyester matrix.

Acknowledgements

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