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CRYSTALLIZATION KINETICS AND THERMAL BEHAVIORS OF MULTI-WALLED CARBON NANOTUBE DISPERSED JUTE REINFORCED COMPOSITE

Muhammad Hasibul Hasan and Md. Sazib Mollik
Department of Manufacturing and Material Engineering, Faculty of Engineering, International Islamic University Malaysia, Jalan Gombak, Kuala Lumpur, Malaysia
E-Mail: hasibulhasan@iium.edu.my

ABSTRACT

Carbon nanotubes (CNTs) were dispersed within polyester resin to improve the thermal properties and to understand the degradation mechanism and reaction kinetics of jute reinforced composite. Viscoelastic behavior via dynamic mechanical analysis, strain rate effect and hygrothermal behavior of CNT filled jute composite were studied. The crystallization kinetics and microstructures were investigated with differential scanning calorimeter (DSC), X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively. Multiwalled CNT with 0, 1 and 3wt% was added within polyester resin matrix, whereas around 70% volume fraction of jute fiber is maintained in each sample. In dynamic mechanical analysis (DMA), 3% CNT filled composite showed better storage modulus and loss modulus values before the hygrothermal test. Due to the exposure to temperature (80 ^{o}C) and relative humidity (95% RH) for 15 days in environment chamber, both storage and loss modulus of this composite reduced by around 10%.

Keywords: carbon nanotubes, DMA, DSC, SEM, XRD, hygrothermal effect.

INTRODUCTION

Jute is one of the most important agro-fibers (lignocellulosic fiber) worldwide attracting attentions as a prospective reinforcement of polymer composites because of its inborn properties such as low density, high tensile modulus and low elongation at break. Furthermore, its specific stiffness and strength are comparable with artificial fibers. It has been found that natural fibre composites possess excellent electrical resistance, good thermal and acoustic insulating properties and high resistance to fracture [1]. Among all the natural fibre reinforcing materials jute is one of the most promising material that have being relatively inexpensive and commercially available in the required form [2]. In recent years, natural fibre reinforced composites have highly expanded because of potential structural materials. Composites reinforced with such natural fibres have thus been a subject of intense study for low strength, low cost application in contrast to the synthetic fibre reinforced composites [3].

Research on carbon nanotube (CNT)-based composites has focused over the past decade on polymer and ceramic matrices [4, 5]. Recently, the interest in developing CNT composites has grown significantly with potential applications for thermal management and mechanical reinforcement [6-8]. Key requirements to achieve both properties are uniform dispersion of the CNTs in the matrix, and good interfacial bonding between the reinforcement and the matrix.

As effective nanoscale reinforcement, carbon nanotubes (CNTs) have attracted great interests in the field of conducting polymer nanocomposites. These nanocomposites should possess good mechanical properties, excellent electrical and thermal conductivities, which are considered useful attributes for many applications in the electronics industry [9]. However, the high aspect ratio and the flexibilities of CNTs along with the van der Waals forces between them cause CNTs to be severely entangled in close packing upon synthesis. Furthermore, the chemically inert nature of CNTs leads to poor dispersibility and weak interfacial interactions with polymer matrix.

Jute composite materials consist of high strength and modulus embedded in or bonded to a matrix with distinct interfaces (boundary) between them. In this form, both fibers and matrix retain their physical and chemical characters. They produce a combination of properties that cannot be achieved with either of the constituents acting alone. Overall, jute is the main load carrying member at the same time as the nearby matrix keeps them in the ideal location and orientation acts as a load transfer medium between them and protects them from environmental damage resulting from elevated temperature and humidity. In this study, Bangla tossa special jute and different weight percentages of CNT were used. This fiber was chosen because it has some special characteristics due its extra strength, such as its fibre being silkier, stronger and softer than other grades of jute. Moreover, 5% NaOH fiber treatments are required to increase the adhesion between the hydrophilic natural fibers and the hydrophobic polyester matrix. To the best of the authors' knowledge, this is the first time Bangla tossa special jute and carbone nano-tube have been introduced into the composite system for the purpose of producing a material with better thermal stability.

MATERIAL AND METHODS

MATERIAL

Jute fiber and coupling agent

Tossa jute fibers (Corchorus olitorius) of Bangla tossa special grade were obtained from Bangladesh Jute Research Institute (BJRI), Dhaka, Bangladesh. The fibres were stored at room temperature. There were another three matrix materials with reinforced material that were used such as polyester resin, hardener (methyl ethyl ketone peroxide) and cnt. It is principally suitable for hand lay-up due to its low viscosity and non-thixotropic nature.

METHODS

Fiber treatment

Jute fibres were cut to 30 cm in length and were soaked in a 5% NaOH solution at 30 ^{o}C. The fibres were kept immersed in the NaOH solution for 2, 4, 6 and 8 h. The fibres were then washed several times with fresh water to remove any NaOH on the fibre surface and finally washed again with distilled water. The fibres were then dried at room temperature for 48 h and subsequently dried using oven-drying at 70 ^{o}C for 6 h. This fiber treatment can improve the fibres quality as well as reinforced composites.

Composite processing

A simple hand lay-up technique was used for preparation of specimens. Jute polyester composites containing raw jute with cnt and jute fibres were fabricated in the form of a square shape of size 32 mm as their length, 32mm as their width and 3mm as their thickness. This hand lay-up processed 32cm×32cm×3mm sheet were used to make samples for tensile testing (ASTM 412-IV) and flexural testing (ASTM D790) as per ASTM standards. The resin was mixed with hardener and cnt. The polyester resin to hardener ratio was 25% wt to 5% wt. There were several cnt ratios sued, i.e. 1% wt, 3%wt and 5% wt. The jute fibres were dried at room temperature 48 hours prior to use. The jute fibers ratio was 70% for every specimen. All specimens are fabricated individually to avoid voids and cutting effects during machining. Specimens are prepared to required dimensions according to ASTM standards.

Dynamic mechanical analysis test

Dynamic mechanical properties of jute composite samples with different filler loadings undergoing cyclic stress with certain frequency were measured as a function of temperature. Besides the information on the Tg value, three important values can also be obtained for the complete understanding of the viscoelastic behaviour of the jute composite samples which are dynamically stressed under the effect of temperature. These are storage modulus (E′), loss modulus (E″) and tangent delta (δ). The test was done from 30 ^{o}C to 150 ^{o}C at a constant heating rate of 5 ^{o}C /min and frequency of 1 Hz with sample specimen was 3mm thickness and 50 mm length by using bending mode.

Differential scanning calorimeter (DSC) test

Differential Scanning Calorimeter (DSC) is the most versatile thermal analysis, which can be used to measure the temperature and heat flow which can help the phase conversions in materials. In this method, sample and an inert reference are heated and cooled in a measured environment condition. Heating or cooling program need to expose for the reference pan. This heating and cooling rate can be affected to the result. In order to achieve better result, a lower rate is superior. When the sample temperature is higher than the heat flow rate will be adjusted automatically with reference temperature. In order to possess and maintain the temperature because it can be needed heating power for sample and reference. The difference between the sample and reference are heat, where the heat change is directly related to the heat flow. DSC measurements afford quantitative and qualitative information about the physical and chemical changes so that contain endothermic or exothermic processes. DSC is mainly used to analyze the glass transition temperature (Tg), crystallization temperature (Tc), melting temperature (Tm) and energy absorbed during the phase change. In this work, DSC was done by using Perkin Elmer Instrument (Japan) according to ASTM E1356. The temperature range was 0^{o}C to 380^{o}C with a heating rate of 10^{o}C/min.

Hygrothermal treatment

The specimens were hygrothermally conditioned in a humidity cabinet where the environments were retained at a temperature of 80 ^{o}C and 95% relative humidity (RH). The humidity cabinet was an inbuilt thermometer for measure the temperature and hygrometer for measure the relative humidity. The temperature difference was maintained between 0-0.5 ^{o}C, whereas the RH deviation was permitted in the range of 0-1%. The composite laminates were placed on holed trays. Hygrothermal test was done for 360 hours.

MORPHOLOGICAL ANALYSIS

Scanning electron microscopy and FESEM

Scanning electron microscopy was performed on small pieces taken from the injection molded samples using a low voltage scanning electron microscope (SEM) (JEOL JSM-6400). The fracture surfaces of impact samples were coated with a thin layer of gold before scanning electron microscopy. The SEM's images were taken at x100, x300 and x500 magnifications. The SEM is conceivably the most consistently utilized instruments for the characterization of nanomaterials. With an SEM it is possible to obtain secondary electron images of organic and inorganic materials with nanoscale resolution allowing topographical and morphological studies to be carried out

by scanning an electron probe across a surface and monitoring the secondary electrons emitted. From SEM test it can be observed the fracture surface of tensile fracture specimen. Fracture surface after tensile testing were experimental using a field emission SEM (JEOL, Model, JSM-6700F) under a voltage of 10KV. Before microscopy, each samples needed for coating with gold because to avoid electrostatic charging and poor image resolution.

X-diffraction (XRD) analysis

XRD involves monitoring the diffraction of X-rays after they interact with the sample. It is a crystallographic method used for identifying and measuring numerous crystalline phases present in solid materials and powders. XRD is one of the most utilized systems for defining the structure of inorganic and organic materials. In this research, XRD was used to determine crystallinity of the hybrid composite using XRD-6000 Shimadzu. During XRD, the target sample was jute composite, the axis range was 10-80^{o} and the rotation was 2^{o}/min. The voltage and current were 40 kV and 30 mA, respectively.

RESULT AND DISCUSSIONS

Dynamic mechanical analysis (DMA)

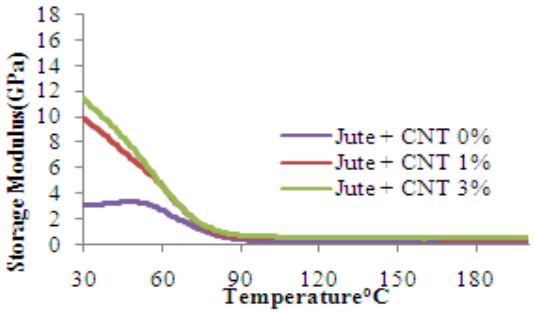


Figure-1. Storage modulus of jute composite before hygrothermal effect.

In the glassy region for both storage and loss moduli are independent of the degree of cross link bonding. Glass transition region and rubbery region clearly show the effect of light cross link. From the DMA test shown in Figure-1, it was observed that the storage modulus is highest at room temperature (11.35 GPa) for a 3% addition of cnt in the tossa jute composite and linearly decreases at around 100 ^{o}C. Tossa jute samples with 1% and 0% cnt showed a storage modulus of around 10.85GPa, and 3.13GPa at -30 ^{o}C, respectively. The 1% addition of cnt clearly showed no benefit to the storage modulus for jute composites, and this may be due to the light cross-link reaction. It is well known that thermoset resin shows different properties depending on the cross-link densities. For storage modulus glass transation temperature was 46.67 ^{o}C, 35.4 ^{o}C, 37.7 ^{o}C for 0%, 1% and 3% CNT.

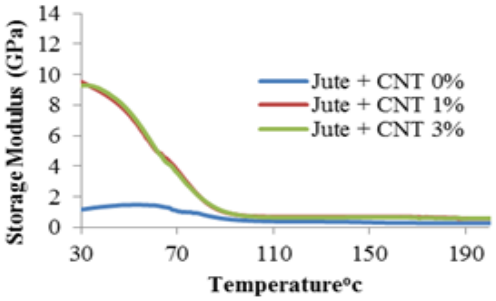


Figure-2. Storage modulus of jute composite after hygrothermal effect.

Figure-2 showed the effect of hygrothermal degration of the sample. The storage modulus was reduced by 11%, 16.91%, and 21.55%, for 0%, 1%, and 3% additions of cnt, respectively. The combined adverse effect of high temperature and humidity lowered the strength of the cross-link structure. Hydrophobic reinforcement jute also absorbed moisture, which further reduced the storage modulus. For storage modulus glass transation temperature was 59.7 ^{o}C, 30.1 ^{o}C, 32.78 ^{o}C for 0%, 1% and 3% CNT.

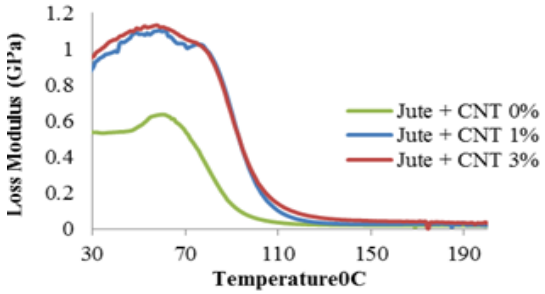


Figure-3. Loss modulus of jute composite before hygrothermal effect.

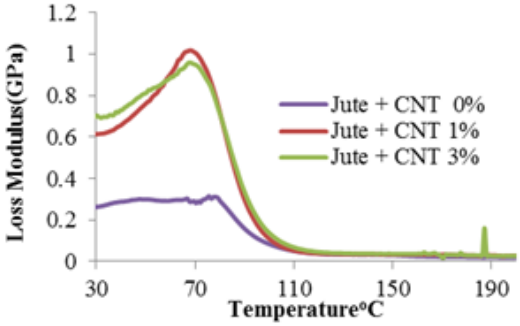


Figure-4. Loss modulus of jute composite after hygrothermal effect.

Figure 3 and 4 illustrates the loss modulus of the tested samples from the viscous response. It measures the energy dissipated as heat, representing the viscous portion of DMA. It is assumed that all the spikes are due to the cold crystallization temperature, where transfer occurs from the glass transition top to the rubbery region. Before hygrothermal test Tg was 59.7 ºC, 53.45 ºC, 55.67 ºC for 0%, 1% and 3% CNT. The loss modulus showed a high value (0.66GPa) for 3% cnt and was lowest (0.32GPa) for 0% addition of cnt in the composite. A lower loss modulus was observed for 0% and 3% cnt infused samples, and this may be due to cnt's imposed restriction to the expansion of the molecular chain in the amorphous region. As expected, due to hygrothermal degradation, all the samples showed a lower value for their loss modulus, except for 1% cnt. The effect of humidity and temperature on the loss modulus for 1% cnt jute composite is insignificant.

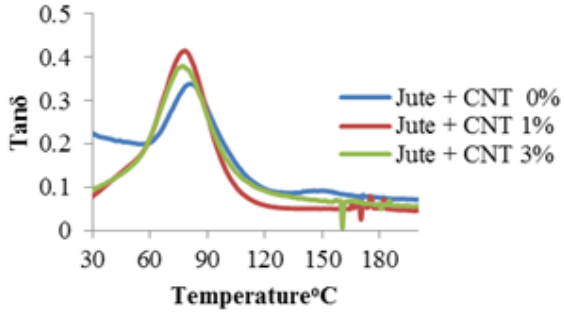


Figure-5. Tan delta of jute composite before hygrothermal effect.

Tangent delta (tanδ) as a function of temperature is shown in Figure-5. The ratio of loss to storage modulus is tanδ, and is known as damping. As the stiffness of the material increases, the tanδ value decreases, demonstrating a lower damping effect or a reduced energy loss. The value of tanδ increases with the increase of temperature up to 90ºC. 0% 1% and 3% cnt infusions in the composite decreased the value of tanδ, pointing towards the observation that higher and lower tanδ values.

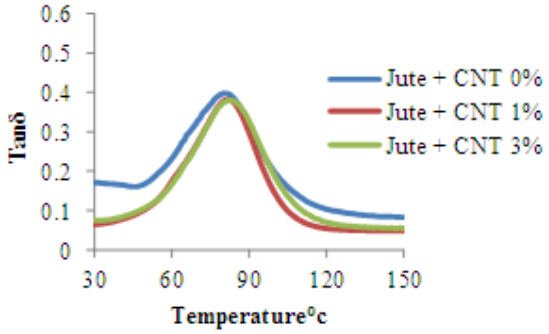


Figure-6. Tan delta of jute composite after hygrothermal effect.

XRD analysis

Crystallinity patterns for jute composites are shown in Figure-7, where almost all the peaks exhibited similar pattern. The XRD peak for cnt 1% is much sharper and narrower than cnt 3% filled composite, indicating better crystallinity. The percentage of crystallinity (% X) that was obtained from XRD curves where 3% cnt was added shows the maximum value of 21.64%. The percentage change of relative crystallinity of three different compositions of jute composite was clearly visible. Cnt 1% was less crystalline than cnt 3% filled composite, whereas cnt 3% showed a higher crystallinity as compared to the other materials tested.

Table-1. Percentage of crystallinity of jute composite.

Test specimen	Percentage of crystallinity obtained from XRD (%X)	d-spacing (Å)
Jute+cnt 0%	20.50	7.37
Jute+cnt 1%	20.80	8.75
Jute+cnt 3%	21.64	8.29

From Table-1, cnt 1% shows the maximum d-spacing value 8.75 Å whereas cnt 0% and cnt 3% shows d-spacing values of 7.35 Å and 8.29 Å, respectively. The percentage of higher crystallinity value depends on d-spacing values. Lin and co-researchers (2010) found that higher values of d-spacing were directly proportional to the dispersion of nanofillers. Moreover, Lin observed that the percentage of crystallinity increased when d-spacing increased.

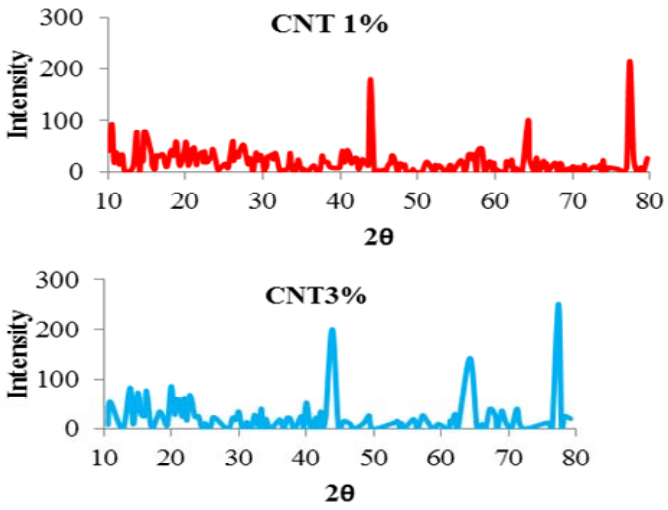


Figure-7. XRD curves for jute composites.

Differential scanning calorimeter (DSC) analysis

Thermal transitions of the cnt filled jute composite via Differential Scanning Calorimeter (DSC) are measured for glass transition temperature (Tg), crystallization temperature (Tc) and finally decomposition temperature. Heat flows versus temperature change are plotted for different percentage of cnt filled composites illustrated in Figure-8. Exothermal or endothermic reaction can be characterized from the spike of the DSC curves. As indicated in the Figure-4, all the samples experienced exothermic phase transformation. The first exothermic peak was exhibited at 35 to 67 ºC, and represents the crystallization temperature (Tc) and melting temperature (Tm) between 343 ºC to 372 ºC for cnt 1% filled composite, as opposed to the cnt 3% crystallization temperature being 37 ºC to 68 ºC. Furthermore, the melting temperature was between 365 ºC to 387 ºC.

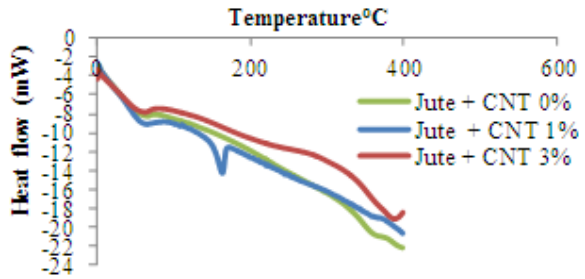


Figure-8. DSC curves for jute composite.

Hygrothermal test analysis

The amount of moisture absorption by jute composites in humid conditions is a function of time exposed. Moisture absorption occurs according to Fick's second law of diffusion. From Figure, it is observed that cnt 1% filled composite absorbed highest percentage of moisture (0.29%) between 13 days as opposed to the 3% cnt filled samples (0.28%). According to literature review, after a certain period the moisture uptake will reach a saturation level and the sample weight increase or decrease gradually thereafter. Since no steady region is reached for all the samples up to 15 days, it requires more exposure time to reach the saturation point for these samples.

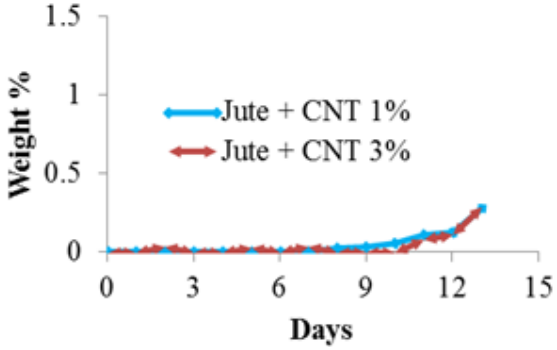
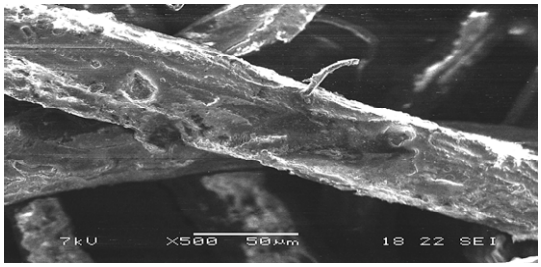


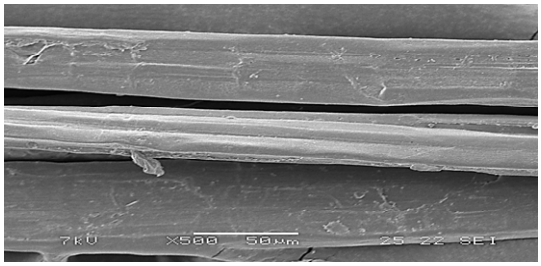
Figure-9. Percentage weight gain of jute composites.

SEM/FESEM

Untreated and 5% NaOH treated jute fibers are shown in Figure-10. A close look clearly shows that the surface roughness of the treated fibers is significantly higher than the untreated surface. Enhance surface roughness helps better bonding between the polyester resin and the reinforced jute fibers.



a)



b)

Figure-10. a) 5% NaOH treated jute fiber b) Untreated jute fiber.

CONCLUSIONS

Fiber surface treatment indicated the reduction of hemi-cellulose, lignin, some protein, fat and wax and higher percentage of cellulose (62 to 65%) in the final treated jute fiber. Apart from the three major components of cellulose, hemicellulose and lignin, the three-dimensional structure of jute fiber is the built up of different inter-molecular and intra-molecular forces, as chemical, physical and hydrogen bonds present between them. Raw jute is bio-degradable, thermal degradable, photodegradable, mechanically degradable, hydrophilic and high viscoelastic in nature. NaOH treatment reduced the contents of fungus- bacteria which causes the degradation of this reinforced material and enhanced permeability and capillarity.

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