

Influence of Acetic Acid Treatment on Crystallization Kinetics and Thermal Stability of Oil Palm Fiber Reinforced Phenol-Formaldehyde Composites

Richa Agrawal

Department of Physics, G. N. Khalsa College, Matunga, Mumbai, India.

richa.agarwal@gnkhalsa.edu.in

Abstract: Lignocellulosic Oil-palm fibers, an industrial waste of oil mills have been utilized for the fabrication of the composites. Oil palm fibers, obtained from oil palm empty fruit bunches have been treated with acetic acid and reinforced in a thermosetting phenol formaldehyde matrix. Untreated as well as acetic acid treated composites were having 40% fiber reinforcement by weight. Composites were heated at a rate of 10 K/min in a Rigaku 8230 B model, differential scanning calorimeter (DSC) attached to a thermal analysis station (TAS 100) to understand the crystallization kinetics of the fabricated composites. Activation energies of the composites have been evaluated, employing Kissinger's equation and Matusita peak shift method. Crystallization process has also been explained in terms of important kinetic parameters like the activation energy of crystallization, nucleation process and dimensionality of growth.

Keywords: Lignocellulosic fiber, phenol formaldehyde resin, DSC, Chemical treatment, Activation energy, thermal stability

I. INTRODUCTION

Increasing environmental concerns and the growing demand for lightweight materials have accelerated research into lignocellulosic fiber-based composites [1]. Natural fiber reinforced polymer composites have emerged as promising alternatives to conventional synthetic fiber reinforced composites due to their sustainability, low density, biodegradability, and cost-effectiveness. Lignocellulosic oil palm fiber [2], a by-products of the palm oil industry, is among the most abundant natural fibers available in tropical regions. Large quantities of oil palm biomass are generated annually, creating both environmental challenges and opportunities for value-added utilization. The incorporation of oil palm fibers into polymer matrices has been widely investigated as an effective strategy for converting agricultural waste into high-performance composite materials. Among various thermosetting polymers, phenol-formaldehyde (PF) [3], a thermosetting resin has attracted significant interest as a matrix material because of its excellent thermal stability, flame retardancy, dimensional stability and chemical resistance. PF resin matrices are particularly suitable for applications requiring high temperature resistance and structural integrity under harsh [4,5] conditions. Natural fiber reinforced in PF matrices find applications in automotive interior components [6–8], construction and building materials [9,10], and electrical insulation [11].

The lignocellulosic composition of oil palm fibers [12], consisting primarily of cellulose, hemicellulose, and lignin, enables them to act as reinforcing agents in thermosetting matrices. However, the inherent hydrophilic nature of natural fibers and the relatively hydrophobic polymer matrices often result in weak interfacial adhesion [13], which can adversely affect the mechanical and thermal performance of the resulting composites.

To overcome these limitations, various chemical treatments have been developed to modify the surface properties of natural fibers and improve fiber-matrix interactions. Surface modification techniques [14] such as alkalization, silane



treatment, and acetylation alter the chemical structure of the fiber surface by reacting with hydroxyl groups present in cellulose. These treatments remove surface impurities, reduce moisture absorption, and increase surface roughness, thereby enhancing interfacial bonding with the polymer matrix. Acetylation process introduces acetyl groups into the fiber structure, which reduces hydrophilicity and improves compatibility with polymer matrices and enhances thermal performance [15].

Understanding the crystallization kinetics of polymer composites is crucial for optimizing processing conditions and tailoring their final properties. DSC is widely employed to study crystallization processes under non-isothermal conditions, allowing the determination of important parameters such as glass transition temperature (T_g), crystallization temperature, crystallization enthalpy and activation energy of crystallization. The glass transition temperature reflects the mobility of polymer chains and defines the temperature range over which the material transitions from a rigid glassy state to a more flexible rubbery state. Similarly, the enthalpy released during crystallization provides information about the degree of crystallinity and structural ordering within the composite. These parameters are critical in determining the performance and reliability of polymer composites. Several kinetic models, including the Kissinger [16] and Matusita [15] approaches, have been developed to evaluate the activation energy and describe the mechanisms governing crystal nucleation and growth [15] in polymer systems. These kinetic analyses provide valuable insight into the energy barriers associated with crystallization and the role of reinforcement in modifying the crystallization behavior of polymer matrices.

Previous studies have investigated the influence of fiber treatment on the mechanical [17] and thermal properties [18] of oil palm fiber reinforced phenol-formaldehyde composites. The effect of acetylation [19] on wood fiber shows an increase in the interfacial shear strength, when reinforced in polystyrene matrix. Acetylation [20] of coir and oil palm empty fruit bunch fibers shows an improvement in the mechanical properties. These studies have shown that surface modification of fibers can significantly improve interfacial bonding and enhance composite performance. However, although several investigations have reported improvements in mechanical properties and thermal stability, systematic studies focusing on the crystallization kinetics and associated activation energy of treated oil palm fiber reinforced PF composites remain limited.

Present work aims to investigate the crystallization kinetics and thermal behavior of acetic acid treated oil palm fiber reinforced phenol-formaldehyde composite in comparison with untreated fiber reinforced composite. Differential scanning calorimetry is employed to analyze the crystallization process and evaluate the activation energy of crystallization using established kinetic models of Kissinger [16] and Matusita [15]. Additionally, the enthalpy released during crystallization, glass transition temperature, and thermal stability of the composites are examined to understand the influence of acetic acid treatment on the thermal performance of the composite system. The results of this study are expected to provide deeper insight into the structure-property relationships governing the crystallization and thermal behavior of oil palm fiber reinforced PF composites.

II. EXPERIMENTAL

2.1 Materials

Oil-palm empty fruit bunches were procured from Oil Palm India Ltd., Kottayam, India. Phenol-formaldehyde resole type resin was procured from West Coast Polymers Pvt. Ltd, Kannur, Kerala, India. All the chemicals used for fiber surface modifications were reagent grade.

2.2 Acetic acid treatment on the surface of the fiber

Fibers were treated with glacial acetic acid for one hour and further treated with acetic anhydride containing concentrated H_2SO_4 , as catalyst for five minutes. Fibers were then washed with water and dried. The extent of acetylation was estimated by titrimetric method. The number of O-acetyl groups in the certain amount of acetylated fiber is estimated by hydrolyzing with excess of caustic soda. The untreated alkali is then determined by titrating against normal oxalic acid. Fibers were then washed with water and dried.



2.3 Composite Fabrication

Fibers from oil-palm empty fruit bunches were processed by retting process. The pithy material was removed and the fibers were washed after which they were dried at 60 °C. The dried fibers were treated with acetic acid as described in the previous sections to obtain treated fibers. Fibers were then chopped into 40 mm length segments. Randomly oriented mats were prepared by hand lay-up method and this was followed by compression molding at 100 °C for about 30 min.

III. RESULTS AND DISCUSSION

Oil-palm fiber is rich in cellulose content and contains cellulose about 65% (ASTM D 1106) and 19% (ASTM D 1104) respectively. Density and diameter of oil-palm fiber vary from 0.7-1.55g/cm³ and from 50-500 μm respectively. Scanning electron micrograph (SEM) of the oil-palm fiber surface reveals the presence of micro-pores and a waxy cuticle on the surface on the surface as shown in figure 1. Waxy layer weakens the interaction of the fiber with the PF resin. SEM of the cross-section of the oil palm fiber is represented in figure 2, which shows a lacuna like opening in the middle.

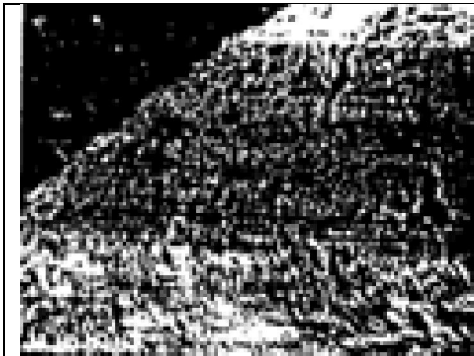


Figure 1: Oil palm fiber surface (magnification x 400).

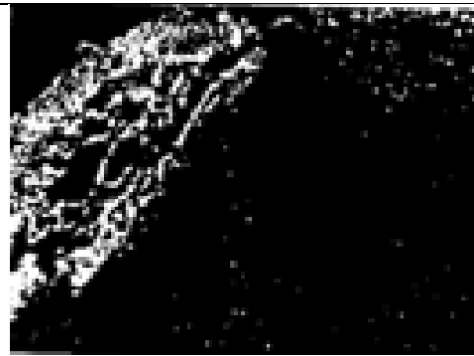
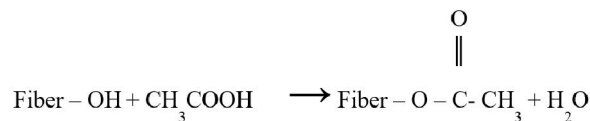


Figure 2: Oil palm fiber cross-section (magnification x 400).

The –OH group of the fiber reacts with acetic acid (CH₃COOH) as shown in the reaction below.



The SEM of the acetic acid treated fiber is shown in figure 3. Acetic acid treatment removes the cuticle layer from the fiber surface making it rough and thin. The change in topology of the fiber surface after acetylation facilitates better reinforcement and fiber matrix interaction. A Differential scanning calorimetry (DSC) study was performed on a Rigaku 8230 B model attached to a thermal analysis station (TAS 100) at different heating rates. The temperature precision of the instrument is ± 0.1 K with an average standard error of about ±0.01K in the measured values. Samples of approximately 15 mg have been weighed by a high performance Sartorius balance, with an accuracy of 0.1 μ gram. The DSC equipment was calibrated prior to the measurements, using high purity lead (Pb), tin (Sn) and indium (In) standards of well-known melting points. Samples were taken in standard aluminum pans and heated in the furnace attached to DSC from room temperature to 450 °C at the heating rates of 5, 10, 15 and 20 K/min.



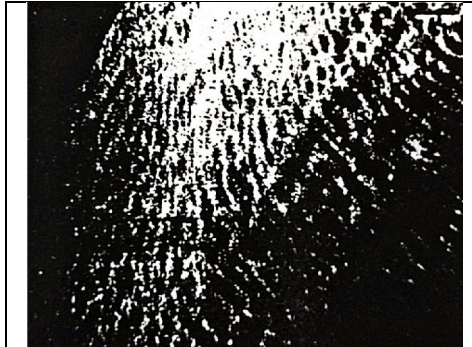


Figure 3: Acetic acid treated Oil palm fiber surface (magnification x 400).

DSC thermogram of acetylated composite at the heating rate of 10 K/min is shown in figures 4. The figure comprises all the features of a non-isothermal crystallization curve, Starting from a glass transition region to a well-defined crystallization peak. The composite shows a conventional peak of crystallization along with a second peak of crystallization as was also observed in our previous work [18]. The activation energy of the second crystallization peak comes out to be less than that of the first peak. The activation energy for non-isothermal crystallization process has been determined using Kissinger's equation given as

$$\ln(\alpha^n / T_p^2) + \ln K = -mE_c / RT_p \quad (1)$$

where K is a constant, containing factors depending on the thermal history of the samples, n and m are constants may vary between 1 and 4 depending upon the morphology and growth. of a composites, α represents the heating rate and T_p is the peak crystallization temperature. The values of the activation energy $(m/n)E_c$ can be determined from the slope of a $\ln \alpha$ versus $1/T_p$ curve as shown in figure 5. Values of the activation energy obtained from such curves are listed in Table 1, for untreated as well as acetic acid treated fiber reinforced composite.

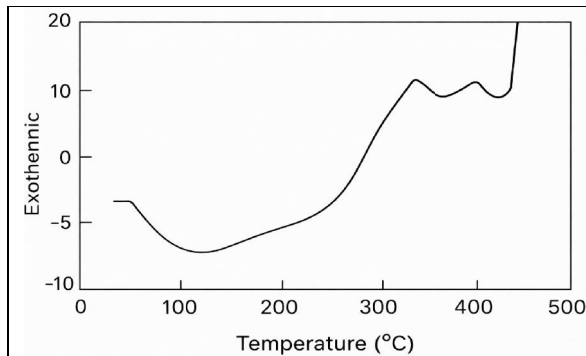


Figure 4: DSC thermogram of acetic acid treated fiber reinforced composite.

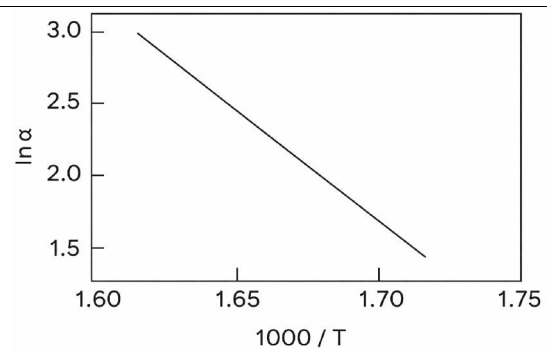


Figure 5: $\ln \alpha$ versus $1000/T$ graph of acetic acid treated fiber reinforced composite.

Matusita's equation for a non-isothermal crystallization process can be written as

$$\ln[-\ln(1-x)] = -n \ln \alpha - 1.052 mE_c / RT + \text{constant} \quad (2)$$

where x is the crystallized fraction at a uniform heating rate, n and m are numerical factors depending upon the nucleation process. The Activation energy for crystallization has been evaluated from the slope of a $\ln[-\ln(1-x)]$ versus $1/T$ curve at different heating rates for all the composites as shown in figures 6, for acetic acid fiber reinforced composite. The values of mE_c so obtained for different heating rates for a particular composite show a weak



dependence on the heating rate, so an average value of mE_c has been taken for calculations. The value of the Avrami exponent (n) can be evaluated by the slope of a $\ln[-\ln(1-x)]$ versus $\ln \alpha$ curve as shown in figure 7 at different temperatures. The value of Avrami's exponent (n) is evaluated for untreated [18] fiber reinforced composite and acetic acid treated fiber reinforced composite comes out to be 1.29 and 1.12 respectively. Both values are near to one, revealing that surface nucleation with one-dimensional growth is present in the untreated and acetic acid treated fiber reinforces composite.

Activation energies evaluated by Matusita's equation is also listed in Table 1. The difference in activation energy as calculated with Kissinger and Matusita's equations may be attributed to different approximations used in the formation of the models. The Kissinger's equation basically gives the variation of peak crystallization temperature with heating rate. According to Kissinger's equation [16], transformation under non-isothermal condition is represented by a first order ($n = 1$) reaction.

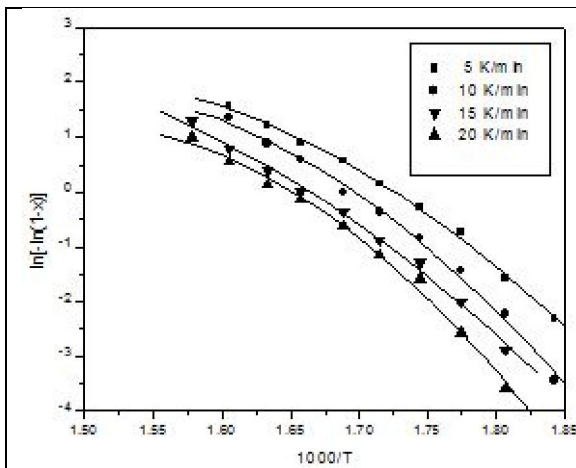


Figure 6: $\ln[-\ln(1-x)]$ versus $1000/T$ curve of acetic acid treated fiber reinforced composite.

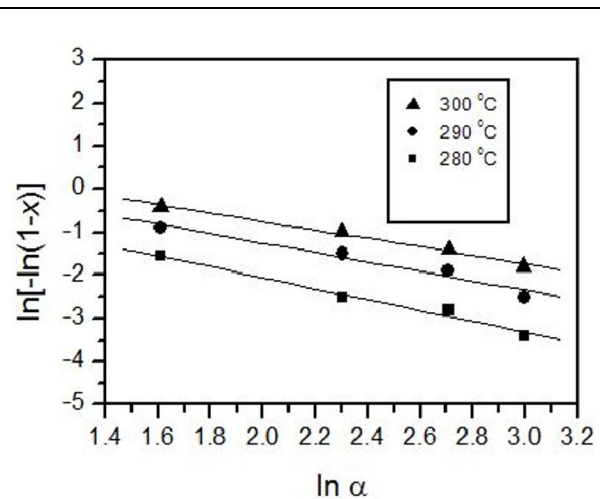


Figure 7: $\ln[-\ln(1-x)]$ versus $\ln \alpha$ curve of acetic acid treated fiber reinforced composite.

The concept of nucleation and growth has not been included in Kissinger's equation. Matusita [15] and collaborators have developed the equation on the basis that crystallization does not advance by n^{th} order reaction but by nucleation and growth process. They emphasized that different crystallization mechanisms such as bulk crystallization followed by two- or three-dimensional growth or surface crystallization followed by linear growth should be taken into account for evaluating E_c . Matusita's equation is independent of the heating rate. In addition to activation energy, Matusita's equation provides information about the Avrami's exponent and the dimensionality of growth.

Table 1. Activation energy, kinetic parameters, ($T_c - T_g$) data and enthalpy released during crystallization for untreated and treated composites.						
Composite	Activation energy (E_c) (kJ/mol)				$T_c - T_g$ (K)	ΔH_c (mcal/mg K)
	Kissinger's Equation (E_c)	Matusita's equation				
		n	m	E_c		
Untreated	130.40	1.29	1	144.86	228.0	594.23
Acetylated	139.58	1.12	1	142.51	233.3	587.45



The difference between the crystallization temperature and the glass transition temperature gives the information about the thermal stability of the composites. The higher the difference of ($T_c - T_g$), greater is the thermal stability [21]. Higher value of the difference between the crystallization and glass transition temperature suggests a delay in the crystallization process of the acetylated composite. The difference shows that the thermal stability of the acetic acid treated composite has increased after the chemical. Enthalpy released during crystallization ΔH_c for the acetic acid treated fiber reinforced composite is found to decrease when compared to the untreated fiber reinforced composite.

IV. CONCLUSIONS

The crystallization parameters as well as crystallization temperature depends weakly on the heating rate for untreated as well as treated composites. The analysis of crystallization exotherms using Kissinger's and Matusita's equations reveals that activation energies evaluated by both the equations are in good agreement. The crystallization energies of the untreated and acetic acid treated fiber reinforced composite are not very different, indicating that chemical treatment does not change the nucleation mechanism of the composites. Surface nucleation with one-dimensional growth is present in the untreated as well as treated composites. Acetic acid treated fiber reinforced composite a second peak of crystallization is also visible. Thermal stability of the acetic acid treated composite has increased after acetic acid treatment.

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