Research Journal of Physical Sciences ISSN 2320–4796
Vol. **14(2),** 9-13, August **(2026)** *Res. J. Physical Sci.*

Insights into Crystallization Kinetics of Acrylonitrile Grafted Oil Palm Fiber Composites under Non-Isothermal Conditions

Richa Agrawal
Department of Physics, G. N. Khalsa College, Matunga, Mumbai, India
richa.agarwal@gnkhalsa.edu.in

Available online at: www.isca.in, www.isca.me
Received 21st March 2026, revised 28th April 2026, accepted 19th May 2026

Abstract

The development of thermally stable and sustainable polymer composites reinforced with natural fibers has gained considerable interest for advanced engineering applications. Oil palm fibers, an industrial waste of oil mills has been utilized as reinforcement in resole type phenol formaldehyde resin for composite fabrication. The crystallization kinetics and thermal behavior of untreated and acrylonitrile grafted oil palm fiber reinforced phenol-formaldehyde composites have been systematically investigated and compared. Differential Scanning Calorimetry (DSC) was employed to examine the non-isothermal crystallization behavior of the composites. Key thermal parameters, including, crystallization temperature, enthalpy of crystallization and glass transition temperature (Tg) were determined from the DSC thermograms. The activation energy of crystallization was evaluated using established kinetic models to gain insight into the nucleation and growth mechanisms during crystallization. The effect of fiber-matrix interaction resulting from surface modification is apparent on the thermal behavior of the composite. These findings provide important insight into the structure-property relationship of chemically modified oil palm fiber reinforced phenol-formaldehyde composites and demonstrate their potential for applications requiring thermally stable, environmentally sustainable composite materials.

Keywords: Lignocellulosic fiber, phenol formaldehyde resin, acrylonitrile grafting. differential scanning calorimetry, chemical treatment, activation energy, thermal stability.

Introduction

Natural resources are diminishing and the need of wood-based products for household chores is never lasting. In this scenario natural fiber reinforced composites may be the solution for simultaneously preserve the natural resources and development of sustainable new material[1]. In recent decades, natural fiber reinforced polymer composites have attracted considerable attention as sustainable alternatives to conventional wood-based products and synthetic fiber reinforced composites. Oil palm fibers, obtained from agricultural residues of the palm oil industry, represents an abundant and renewable lignocellulosic resource[2].

The utilization of oil palm fibers in polymer composites not only enhances thermal and mechanical performance of the matrix but also provides an environmentally sustainable solution for the management of agro-industrial waste[3,4]. Natural fiber reinforced composites are biodegradable, have low density and are cost effective, which makes them favorable for several engineering applications. Natural fibers such as jute, sisal, bamboo, coir, pineapple and oil palm fibers have been widely investigated as reinforcement materials in thermosetting and thermoplastic polymer matrices[5]. Among the various thermosetting polymers, phenol-formaldehyde (PF) resin is particularly useful due to its excellent thermal stability, flame resistance, dimensional stability and chemical resistance[6]. Natural fiber reinforced composites have found applications in building and construction materials, automotive and automobile industries, packaging and furniture industries[7,8]. In the 1940s Henry Ford introduced the use of natural fiber composite for automotive components. Later natural fiber composites have been used in the interior of vehicles such as BMW, Mercedes and Audi[9,10].

However, the hydrophilic nature of natural fibers and the hydrophobic nature of polymer matrices often lead to poor interfacial adhesion, which adversely affects the overall properties of the composites[11]. Therefore, chemical modification of natural fibers has been widely employed to improve fiber-matrix interaction and enhance the performance of the resulting composites[12,13]. Among the various surface modification techniques, grafting reactions are particularly effective in altering the surface characteristics of natural fibers. Acrylonitrile grafting introduces polar nitrile functional groups onto the fiber surface, which can significantly improve compatibility with the resin matrix and enhance the interfacial bonding[14]. This modification not only improves mechanical properties but also influences the thermal behavior and crystallization characteristics of the composite system. Improved interfacial adhesion can alter the nucleation behavior of the composite, thereby affecting crystallization kinetics and the overall thermal performance of the composite material.

Understanding the crystallization kinetics of polymer composites is essential for optimizing processing conditions and predicting the final material properties[3]. Differential scanning calorimetry (DSC) is widely used to investigate crystallization processes under non-isothermal conditions. From DSC analysis, parameters such as crystallization temperature, enthalpy of crystallization and crystallization rate can be determined. Kinetic models developed by Kissinger and Matusita are commonly applied to evaluate the activation energy of crystallization and to understand the nucleation and growth mechanisms of the composites[15,16]. Apart from crystallization kinetics, other thermal parameters such as the glass transition temperature (Tg), enthalpy released during crystallization and thermal stability are crucial in determining the performance of polymer composites[17]. The glass transition temperature reflects the mobility of polymer chains and indicates the transition from a rigid glassy state to a more flexible rubbery state. These parameters collectively determine the applicability of the composite materials in high-temperature or thermally demanding environments[18].

Several investigations have been reported on the thermal properties of natural fiber reinforced PF composites, studies focusing on the crystallization behavior, activation energy of crystallization, enthalpy release, glass transition temperature and thermal stability of chemically modified oil palm fiber reinforced PF systems remain relatively limited. The present study aims to investigate the crystallization kinetics and thermal behavior of acrylonitrile grafted oil palm fiber reinforced phenol-formaldehyde composites and to compare these properties with those of untreated oil palm fiber reinforced composites[15,16]. The results are expected to provide deeper insight into the structure-property relationships governing chemically modified oil palm fiber reinforced PF composites and contribute to the development of improved sustainable composite materials for advanced engineering applications.

Materials and Methods

Materials: Material for the composite fabrication were procured from the following sources.

Table-1: Material and Suppliers.

Material	Supplier
Oil-palm empty fruit bunches	Oil Palm India Ltd., Kottayam, Kerela, India
Phenol-formaldehyde resole type resin	West Coast Polymers Pvt. Ltd, Kannur, Kerala, India

Oil palm fiber Details: Oil-palm fiber is rich in cellulose content and contains holocellulose and lignin about 65% (ASTM D 1106) and 19% (ASTM D 1104) respectively. Density and diameter of oil-palm fiber vary from 0.7-1.55g/cm^3 and from 50-500µm respectively. Scanning electron microscope (SEM) studies reveals the presence of micro-pores and wax like layer on the surface of the oil-palm fiber as shown in Figure-1.

Acrylonitrile grafting of the fibers: Fibers were bleached with 2% alkali for 30 min and then oxidized with 0.02 ml^{-1} $KMnO_4$ (liquor ratio, 1:150) for 10 min. They were then washed with water after which they were placed into 1% H_2SO_4 containing acrylonitrile in the ratio 30:1. After this treatment, the fibers were then placed in a thermostatic water bath at 50^{0}C for 2 h. They were then washed and dried. These grafting fibers were isolated from any homo-polymer formed (PAN) by soxhlet extraction using dimethyl formamide.

Composite Fabrication: Fibers from oil-palm empty fruit bunches were obtained by retting process. In retting process fruit bunches were kept in water for a long time to remove the pithy material from the fibers. Fibers were then washed and dried at 60^{0}C. The dried fibers were acrylonitrile grafted as described in the previous sections to obtain treated fibers. Fibers were then chopped into 40 mm length segments. Randomly oriented mats of the oil palm fibers were prepared by the hand lay-up method and this was followed by compression molding at 100^{0}C for about 30 min. All these chemicals used for the fiber surface modifications were reagent grade. Acrylonitrile grafted oil palm fiber reinforced composite has 40% fiber loading by weight.

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

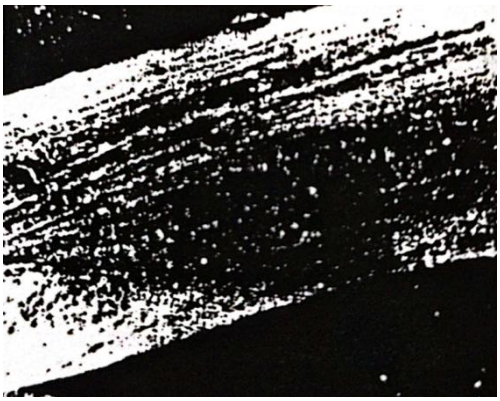

Figure-2: Surface topology of acrylonitrile grafted Oil palm fiber (x 400).

Results and Discussion

Oil-palm fiber has low lignin and high cellulose content. Presence of lignin content in the fiber retards the polymerization rate and due to high cellulose content grafting reaction is favored. Scanning electron micrograph of grafted oil-palm fiber shows the fibrillated porous structure as shown in Figure-2. Initiation of longitudinal cracks visible on the grafted surface may be due to the presence of grafting material. Matrix resin fills the pores and gaps between the fibrils leading to a better coupling, which enhances the thermal performance of the acrylonitrile grafter composite.

Differential scanning calorimetry (DSC) measurements were carried out using a Rigaku 8230 B model equipped with a thermal analysis station (TAS 100) to investigate the crystallization kinetics of untreated and acrylonitrile-grafted oil palm fiber-reinforced composites at various heating rates. The instrument offers a temperature precision of ±0.1K. Approximately 15mg of each sample was accurately weighed using a high-performance balance with a sensitivity of 0.1μg. Prior to analysis, the DSC was calibrated using high-purity standards of lead (Pb), tin (Sn), and indium (In), each possessing well-established melting points. The samples were placed in standard aluminum pans and subjected to heating from room temperature up to 450°C, at controlled heating rates of 5, 10, 15, and 20K/min.

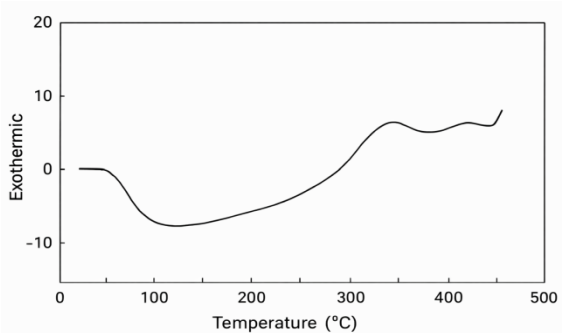

Figure-3: DSC thermogram of acrylonitrile grafted oil palm fiber reinforced composite.

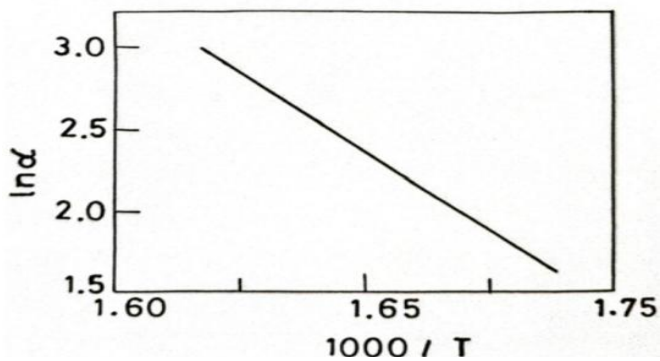

Figure-4: In α versus 1000/T graph of acrylonitrile grafted oil palm fiber reinforced composite.

The DSC thermogram of the acrylonitrile-grafted oil palm fiber-reinforced composite at a heating rate of 10K/min is presented in Figure-3. The treated composite exhibits a typical crystallization peak along with a subtle secondary crystallization peak, consistent with observations reported in our earlier study[3]. The activation energy associated with the non-isothermal crystallization process was evaluated using Kissinger's equation, as expressed in the corresponding equation.

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

In this relation, K is a constant that incorporates factors related to the thermal history of the samples, while n and m are constants (ranging from 1 to 4), dependent on the morphology and growth characteristics of the composite. The term α denotes the heating rate, and T_p represents the peak crystallization temperature. The activation energy, expressed as $(m/n)E_c$, was determined from the slope of the linear plot of ln α versus $1/T_p$, as illustrated in Figure-4. The calculated values of activation energy of untreated and acrylonitrile-grafted oil palm fiber-reinforced composite are summarized in Table-1.

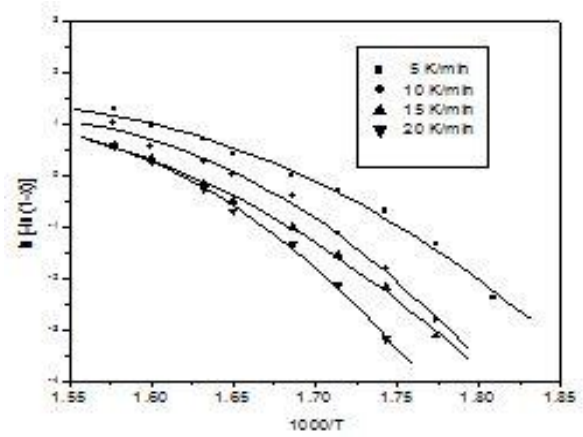

Figure-5: ln[-ln(1-x)] versus 1000/T curve of acrylonitrile grafted fiber reinforced composite.

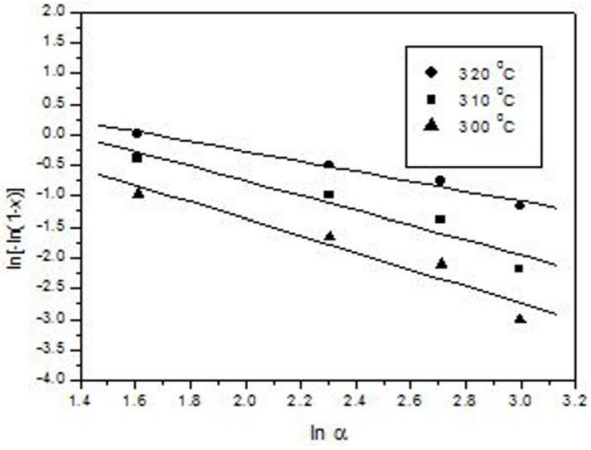

Figure-6: ln[-ln(1-x)] versus ln α curve of acrylonitrile grafted oil palm fiber reinforced composite.

Table-1: Activation energy, kinetic parameters, (T_c –T_g) data and enthalpy released during crystallization for untreated and acrylonitrile grafted 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
Acrylonitrile grafted	167.21	1.11	1	136.88	255.5	266.47

Matusita's equation for a non-isothermal crystallization process is given as

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

Where, *x* represents the crystallized fraction at a given constant heating rate, while *n* and *m* are numerical parameters associated with the nucleation mechanism.

The activation energy for crystallization was determined from the slope of the plot of ln[-ln(1-*x*)] versus 1/*T* at different heating rates for all composites, as illustrated in Figure-5 for the acrylonitrile-grafted composite. The values of mE_a obtained at various heating rates for the acrylonitrile fiber-reinforced composite exhibit only a weak dependence on the heating rate. Therefore, an average value of mE_c was considered for subsequent calculations.

The Avrami's exponent (*n*) was evaluated from the slope of the plot of a ln[-ln(1-*x*)] versus ln *α*. Figure-6 presents the corresponding data for the acrylonitrile-grafted oil palm fiber-reinforced composite at different temperatures. The calculated values of the Avrami's exponent are 1.29 for the untreated composite[3] and 1.11 for the treated composite, indicating that crystallization in these systems proceeds predominantly through surface nucleation accompanied by one-dimensional growth.

The activation energies calculated using both approaches are summarized in Table-1. The observed variation in activation energy values obtained from Kissinger's and Matusita's equations can be attributed to the differing assumptions and approximations inherent in these models. Kissinger's equation primarily describes the dependence of the peak crystallization temperature on the heating rate. It assumes that the transformation under non-isothermal conditions follows first-order reaction kinetics (n=1), without incorporating the concepts of nucleation and crystal growth. In contrast, Matusita and co-workers developed their model based on the premise that crystallization proceeds through nucleation and growth mechanisms rather than an nth-order reaction. This approach accounts for different crystallization modes, including bulk crystallization with two- or three-dimensional growth, as well as surface crystallization with one-dimensional (linear) growth, for a more accurate evaluation of the activation energy (E_c). Notably, Matusita's equation is independent of the heating rate, and the slight variations observed in E_c values at different heating rates fall within the experimental error range. Furthermore, beyond providing activation energy, Matusita's model also enables the determination of the Avrami exponent and offers insight into the dimensionality of crystal growth.

The thermal stability of the composites can be accessed through their glass transition temperature (T_g) and crystallization temperature (T_c)[19,20]. An increase in T_g for the treated composites indicates restricted molecular mobility due to improved interfacial bonding between the fiber and matrix. Similarly, a shift in T_c reflects changes in crystallization behavior, suggesting enhanced structural ordering. Overall, higher T_g and T_c values for the acrylonitrile-treated composites imply improved thermal stability compared to the untreated system.

The difference between the crystallization temperature and the glass transition temperature is a strong indication of thermal stability of the composites, i.e. higher the value of (T_c - T_g) greater is the thermal stability (6). Acrylonitrile grafted oil palm fiber reinforced composite has minimum value of ΔH_c and maximum thermal stability[17].

Conclusion

A weak dependence of crystallization temperature on the heating rate is observed for both untreated and treated composites, indicating a consistent crystallization behavior under non-isothermal conditions. The activation energies obtained from both models are in close agreement, confirming the reliability and validity of the applied kinetic approaches. The comparable crystallization energy values for untreated and chemically treated composites further suggest that the nucleation mechanism remains essentially unchanged after treatment.

The acrylonitrile-grafted oil palm fiber-reinforced composite exhibits surface nucleation with one-dimensional growth, along with a faint secondary crystallization peak, which may be attributed to heterogeneous structural regions or secondary crystallite formation. Notably, grafting significantly enhances the thermal stability of the composite, as evidenced by improved thermal parameters, while also delaying the crystallization process, possibly due to restricted chain mobility and improved

interfacial interactions. Overall, although acrylonitrile treatment modifies the thermal behavior and stability, it does not alter the fundamental mechanism of nucleation, highlighting its role in enhancing performance without disrupting the inherent crystallization pathway.

Acknowledgements

Author is thankful to Dr. N. S. Saxena, Condensed Matter Physics Lab, Department of Physics, University of Rajasthan, Jaipur, India for guiding and providing the lab facilities. Thanks are due to Dr. S. Thomas (School of Chemical Sciences, M. G. University, Kottayam, Kerala, India and Dr. M.S. Sreekala (Rubber Research Institute of India, Kottayam, Kerala, India) for the help in sample preparation.

References

1. A.K. Bledzki, J. Gassan. (1999). Composites reinforced with cellulose based Fibres. *Prog. Polym. Sci.*, 24, 221–274.

2. Rama Rao, P., & Ramakrishna, G. (2022). Oil palm empty fruit bunch fiber: Surface morphology, treatment, and suitability as reinforcement in cement composites- A state of the art review. *Cleaner Materials*, 6, 100144.

3. Richa Agrawal , N.S. Saxena, K.B. Sharma , S. Thomas , M.S. Sreekala. (2000). Activation energy and crystallization kinetics of untreated and treated oil palm fibre reinforced phenol formaldehyde composites. *Materials Science and Engineering A*, 277, 77–82.

4. Sreekala, M. S., Kumaran, M. G., & Thomas, S. (1997). Oil palm fibers: Morphology, chemical composition, surface modification, and mechanical properties. *Journal of Applied Polymer Science*, *66*(5), 821–835.

5. Lertwattanaruk, P., & Suntijitto, A. (2015). Properties of natural fiber cement materials containing coconut coir and oil palm fibers for residential building applications *Construction and Building Materials*, *94*, 664–669.

6. Ravindran, L., M. S., S., Kumar S., A., & Thomas, S. (2022). A comprehensive review on phenol-formaldehyde resin-based composites and foams. *Polymer Composites*, 43(12), 8602–8621.

7. Akar, M. A., Tosun, A. T., Yel, F., & Kumlu, U. (2022). The Usage of Natural Fibers for Automotive Applications. *Macromolecular Symposia*, 404(1), 2100414.

8. Rama Rao, P., & Ramakrishna, G. (2022). Oil palm empty fruit bunch fiber: Surface morphology, treatment, and suitability as reinforcement in cement composites- A state of the art review. *Cleaner Materials*, 6, 100144.

9. Alam, M. A., Sapuan, S. M., Ya, H. H., Hussain, P. B., Azeem, M., & Ilyas, R. A. (2021). Application of biocomposites in automotive components: A review. In *Biocomposite and Synthetic Composites for Automotive Applications* (pp. 1–17). Elsevier.

10. Adlie, T. A., Ali, N., Huzni, S., Ikramullah, I., & Rizal, S. (2023). Impact of Zinc Oxide Addition on Oil Palm Empty Fruit Bunches Foamed Polymer Composites for Automotive Interior Parts. *Polymers*, 15(2), 422.

11. Ali, A., Shaker, K., Nawab, Y., Jabbar, M., Hussain, T., Militky, J., & Baheti, V. (2018). Hydrophobic treatment of natural fibers and their composites—A review. *Journal of Industrial Textiles*, 47(8), 2153–2183.

12. Felpeng P. Liu, Michael P. Wolcott, Douglas J. Gardner, Tim, G . Rials. (1994). Characterization of the interface between cellulosic fibers and a thennoplastic matrix. *Composite Interfaces*, 2(6), 419–432.

13. Cruz, J., & Fangueiro, R. (2016). Surface Modification of Natural Fibers: A Review. *Procedia Engineering*, 155, 285–288.

14. Singha, A. S., & Rana, R. K. (2012). Chemically induced graft copolymerization of acrylonitrile onto lignocellulosic fibers. *Journal of Applied Polymer Science*, 124(3), 1891–1898.

15. Kissinger, H. E. (1957). Reaction Kinetics in Differential Thermal Analysis. *Analytical Chemistry*, 29(11), 1702–1706.

16. Matusita, K., & Sakka, S. (1980). Kinetic study of crystallization of glass by differential thermal analysis—Criterion on application of Kissinger plot. *Journal of Non-Crystalline Solids*, 38–39, 741–746.

17. Muthukumar, C., Krishnasamy, S., Thiagamani, S. M. K., Nagarajan, R., & Siengchin, S. (2022). Thermal Characterization of the Natural Fiber-Based Hybrid Composites: An Overview. In S. Krishnasamy, S. M. K. Thiagamani, C. Muthukumar, R. Nagarajan, & S. Siengchin (Eds.), *Natural Fiber-Reinforced Composites* (1st ed., pp. 1–15). Wiley.

18. Abdollahiparsa, H., Shahmirzaloo, A., Teuffel, P., & Blok, R. (2023). A review of recent developments in structural applications of natural fiber-Reinforced composites (NFRCs). *Composites and Advanced Materials*, 32, 26349833221147540.

19. Veerasimman, A., Shanmugam, V., Rajendran, S., Johnson, D. J., Subbiah, A., Koilpichai, J., & Marimuthu, U. (2022). Thermal Properties of Natural Fiber Sisal Based Hybrid Composites – A Brief Review. *Journal of Natural Fibers*, 19(12), 4696–4706.

20. Mohammad Asim, Mohd T. Paridah, M. Chandrasekar, Rao M. Shahroze, Mohammad Jawaid. (2020). Thermal stability of natural fibers and their polymer composites. *Iranian Polymer Journal*, 29, 625-648.