

## Crystallization kinetics of pineapple leaf fiber reinforced phenol formaldehyde composites

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Kinetics of crystallization in pineapple leaf fiber reinforced phenol formaldehyde (PF) composites has been studied employing Differential Scanning Calorimetry (DSC). Kinetic parameters such as activation energy in crystallization as well as in glass transition region have been investigated at different percentage of fiber (typically at 15, 20, 30, 40 and 50% by weight) and at different heating rate (typically at 5, 10, 15, 20 K/min). The obtained data has been analyzed in terms of modified Kissinger equation and also using Matusita's equation to determine the activation energy. The results from one model are compared with the value obtained from the other equation. It is found that, activation energy depends upon the fiber percentage whereas it shows a weak dependence on heating rate.

[**Keywords:** Crystallization kinetics, Phenol formaldehyde composites, Composites, Fibre reinforced composites, Activation energy]

### 1 Introduction

Thermosetting materials like phenolic resins are good industrial material due to good heat resistance, electrical insulation, dimensional stability and chemical resistance character. Because of inherent brittle character of these resins their use is limited. Therefore, inclusion of fiber reinforcement like glass followed by carbon and boron took place during last few decades for structural and non-structural applications<sup>1</sup> due to their high specific strength and modulus of reinforcing fiber. The uses of such composites are limited to aerospace and other specific sophisticated industries only due to their high cost.

The natural fibers like pineapple leaf, jute, sisal, etc. are useful and viable substitutes for synthetic fibers. The main advantages of natural fibers are low cost, low density, high specific strength, easy processibility, non-toxic, abundance in nature and easy biological degradation<sup>2-4</sup>. All these advantages have diverted the attention of scientists and engineers towards the reinforcement of these natural fibers in the polymer matrix.

Among various available natural fibers, pineapple leaf fiber (PALF) which has high cellulose content

(81.5%), exhibits excellent physical and mechanical properties, for example, high tensile strength (170 MPa), high Young's modulus (6260 MPa) and high density (1.526 g/cc)<sup>5</sup>. These properties of PALF have diverted the attention in producing composites containing this fiber in a polymer matrix. Therefore, these fibers have been selected in the present studies. For deciding proper composition of polymer matrix and fiber percentage, large spectrum of these composites has been taken (fiber's fraction 15, 20, 30, 40 and 50% by weight in the composite). Among the matrix resins, phenol formaldehyde (PF) has been selected to its important thermosetting properties.

Non-isothermal crystallization behaviour of polymers and composites are of vital importance for scientists and engineers to decide appropriate use of a composite, because most of the processing techniques occur under non-isothermal conditions<sup>6-7</sup>. So, the aim of the present studies is to throw light on the composite's various transition regions like, glass and crystallization region with special attention to activation energy, both in glass transition and crystallization regions at different heating rates (typically 5, 10, 15 and 20 K/min). Among the popular theoretical models, Matusita<sup>8-10</sup> and

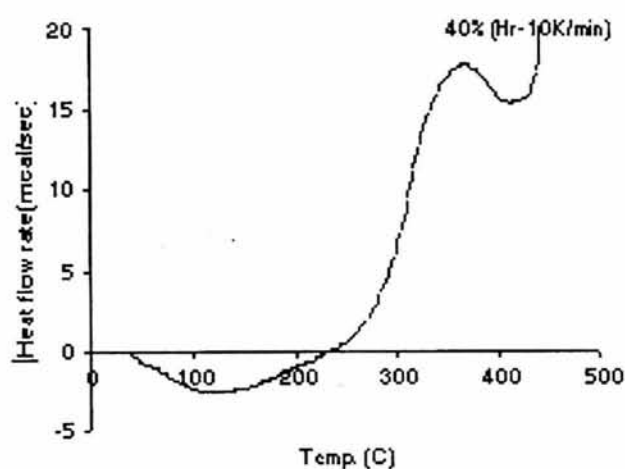


Fig. 1 — Variation of temperature versus heat flow rate

Kissinger<sup>11</sup> equations have been employed for the study of kinetics of these regions.

## 2 Material Preparation and Method

For preparing these composites, pineapple leaf fiber and phenol formaldehyde is required. The resole type phenol formaldehyde resin is obtained from Coast Polymers Pvt. Ltd., Kannur, Kerala, India, while pineapple leaf fibers are supplied by South India Textile Research Association, Coimbatore, Kerala. The pithy material of pineapple leaf is removed by retting process. The fibers were cut into 40 mm length and randomly oriented mats are prepared. Composites have been prepared by hand lay-up method followed by compression at 100 °C for about 30 min. Composites having weight percentages of 15, 20, 30, 40 and 50% have been prepared. The volume percentage can be found out from the knowledge of density of particular composite, density of pineapple leaf fiber and the matrix (PF).

Differential Scanning Calorimeter (DSC) thermograms of all the composites have been taken using Rigaku-8230 model coupled to a Thermal Analysis Station (TAS). The temperature precision of the

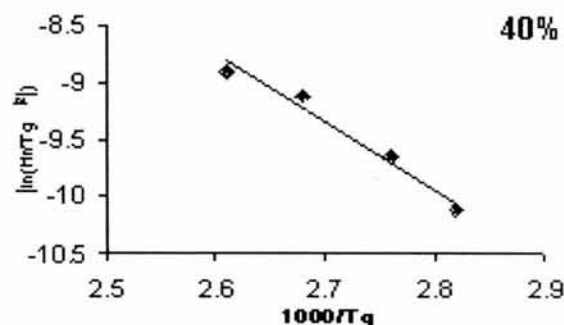
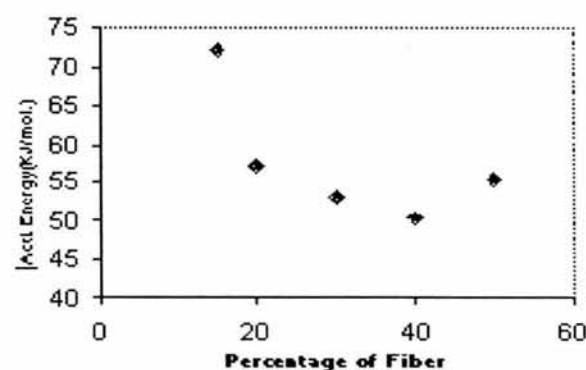
Fig. 2 —  $1000/T_g$  versus  $\ln(Hr/T^2)$ 

Fig. 3 — Percentage of fiber versus activation energy

instrument is 0.1 K, with an average standard error of about 1.0 K in the measured values. The samples having masses between 8 and 10 mg were taken and scanned at the said heating rates.

## 3 Results and Discussion

The typical DSC thermograms of PALF reinforced PF composites (fiber fraction 15, 20, 30, 40 and 50% by weight) at different heating rates (5, 10, 15, 20 K/min.) have been taken and symbolic thermogram for 40% fiber fraction is shown in Fig. 1. A dip is obtained in all the thermograms at all the heating rates. This dip is interpreted as the glass transition region.

The activation energy is a very important parameter that gives information about the nucleation and growth processes in the solids. The experimentally obtained data are analyzed on the basis of Kissinger equation in order to determine activation energy. The equation can be written as:

$$\ln(Hr/T^2) = -E/(RT) + \text{const} \quad \dots(1)$$

here  $Hr$  being heating rate.

Table1 — Glass transition activation energy ( $E$ ) of PALF reinforced PF composites

Sample code	15%	20%	30%	40%	50%
Activation energy $E$ (KJ/mol)	72.2	57.1	53.05	50.4	55.3

Fig. 2 shows the plot of  $\ln(Hr/T_g^2)$  as a function of  $1000/T_g$  for composite having fiber fraction 40% in the glass transition region. The slope of the straight line gives information about the activation energy in this region. The value of the activation energy for various said composites is given in Table 1.

Activation energy is that amount of energy, which is absorbed by a group of atoms so that, a jump from one meta-stable state to another state of higher stability is possible. So, this should be involved in the molecular motions and rearrangements of atoms around the crystallization temperature.

When the sample is reheated in DSC furnace, the atoms undergo infrequent transitions between the local potential minima, separated by different energy barriers in the configuration space, where each local minimum represents a different structure. The most stable local minimum in the glassy region has lowest internal energy. Accordingly, the atoms in a composite having minimum activation energy have higher probability to jump to the meta-stable (or local minimum) state of lower internal energy and hence are the most stable. The variation of the activation energy ( $E_g$ ) with the fiber percentage is shown in Fig. 3.

The decrease in the activation energy is observed with the rise in fiber percentage. For higher fiber fraction, the change is small. This suggests that, after a certain fiber fraction, the energy needed to raise the atom to higher state does not change appreciably, probably due to cross-linking of the fibers themselves.

The crystallization process under non-isothermal conditions has also been analyzed in terms of onset crystallization temperature  $T_c$  and activation energy for crystallization  $E_c$  using Kissinger equation and Matusita's equation.

Johnson-Mehl-Avrami<sup>12-13</sup> equations have been developed basically to study the kinetics of phase transformations involving nucleation and growth process under isothermal conditions. However, extending the use of the JMA equation, Matusita have suggested an equation, which is applicable for non-isothermal crystallization and is given by<sup>9</sup>:

$$\ln[-\ln(1-X)] = -n \ln(Hr) - 1.052 E_c / RT_c + \text{const} \quad \dots (2)$$

where  $X$  is the volume of the fraction crystallized at any temperature and,  $m$  and  $n$  the constants related to the crystallization mechanism. For the evaluation of  $E_c$ , by

Table 2 — The activation energy  $E_c$  of PALF reinforced composites using different models (crystallization region)

Fiber % (by weight)	Activation energy ( $E_c$ ) kJ/mol	
	Kissinger model	Matusita model
15%	128 ± 2.3	128.1
20%	88.8 ± 1.73	86.25
30%	110.08 ± 1.69	106.7
40%	97.7 ± 0.68	88.6
50%	98.6 ± 1.27	92

knowing the slopes of the plot of  $\ln[-\ln(1-X)]$  against  $1000/T_c$  at different rates are computed. The activation energies as calculated from the slope of these plots are listed in Table 2.

It is also found that, there is a weak dependence of activation energy on the heating rate, so an average value has been taken for a particular composite. Values of  $E_c$  obtained by the two equations are in good agreement with each other.

#### 4 Conclusions

The systematic investigation of crystallization kinetics of pineapple leaf fiber reinforced phenol formaldehyde leads to the following conclusions:

1. It has been found that, the activation energy in glass transition region ( $E_g$ ) of the composite decreases with the increase in the fiber fraction in the crystallization region and this decreases the rate of crystallization. Since the rate of crystallization is inversely proportional to the thermal stability, it is found to be higher in fiber reinforced composite as compared to the pure PF.

2. Activation energy of composites in crystallization region shows weak dependence on the heating rate while depends fully upon fiber fraction in the composite.

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