

# Effect of Different Treatments on the Thermal Behavior of Reinforced Phenol–Formaldehyde Polymer Composites

RAJNI AGARWAL,<sup>1</sup> N. S. SAXENA,<sup>1</sup> KANAN BALA SHARMA,<sup>1</sup> S. THOMAS,<sup>2</sup> M. S. SREEKALA<sup>3</sup>

<sup>1</sup> Condensed Matter Physics Lab., Department of Physics, University of Rajasthan, Jaipur-302 004, India

<sup>2</sup> School of Chemical Sciences, M.G. University, Kottayam-686560, Kerala, India

<sup>3</sup> Rubber Research Institute of India, Kottayam-686009, Kerala, India

Received 23 July 1999; accepted 3 February 2000

**ABSTRACT:** Thermal behavior of oil palm fiber-reinforced phenol–formaldehyde (PF) resins with different chemical treatments were analyzed using Differential Scanning Calorimeter (DSC). A well-defined peak of crystallization was observed in all the samples. However, in one of them a second exothermic peak also emerged, which indicates some structural changes at high temperature. Crystallization kinetics has been studied in terms of activation energy of crystallization, dimensionality of growth and stability using various recent theories developed for nonisothermal crystallization. The results indicate the surface nucleation and crystallization through one-dimensional growth. Thermal stability of PF composites increases after chemical treatment, and is maximum for resin treated with peroxide PF composite in comparison to fiber-treated PF composites. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 603–608, 2000

**Key words:** oil palm empty fruit bunch fiber; activation energy; crystallization kinetics; glass transition temperature; thermal stability; dimensionality

## INTRODUCTION

A significant effort has been made recently to apply natural fiber reinforcement in synthetic polymer-bounded composite materials. These synthetic natural composites offer a better utilization of fibrous biomass.

Natural fibers having high content of cellulose have found use as a potential resource for making low-cost composites. These fibers are in abundance in developing tropical countries. Use of these fibers in composites is less attractive due to lack of good interfacial adhesion and poor resistance to moisture absorption.<sup>1</sup> This problem can be overcome by treating these fibers with suitable

chemicals. Good interfacial strength between fiber and plastic is the essential factor to achieve good fiber reinforcement.<sup>2</sup>

Chemical treatments usually change the physical and chemical structure of the fiber surface. Chemical analysis shows the high content of cellulose in oil palm fiber, which plays an important role in the fiber's performance.<sup>3</sup>

Oil palm empty fruit bunch (OPEFB) fiber can act as a better reinforcement in brittle plastics such as phenol–formaldehyde (PF), because it can improve the toughness of brittle plastics. Before reinforcement, surface modifications of the fibers by alkali treatment, potassium permanganate treatment, and peroxide treatment have been carried out.

Reinforcement using OPEFB fiber makes the composite light weight and inexpensive, with desirable thermal and mechanical properties and

---

Correspondence to: N. S. Saxena.

*Journal of Applied Polymer Science*, Vol. 78, 603–608 (2000)  
© 2000 John Wiley & Sons, Inc.

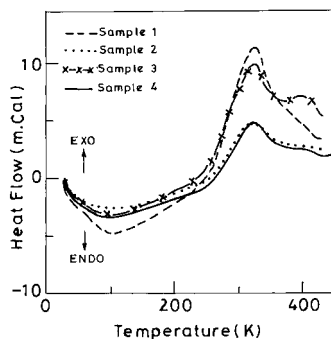
performance characteristics.<sup>4</sup> OPEFB fiber-reinforced phenol-formaldehyde composites are a cost-effective substitute for the conventional building materials. Reliable data of the thermal behavior such as crystallization kinetics of these materials is necessary for understanding them as building materials, and hence, using them for commercial applications. So far, no such study has been conducted in this field.

This article is an attempt to report the thermal characteristics of the OPEFB fiber-reinforced composites with PF resin. The effect of fiber treatment and resin treatment on the crystallization kinetics have been analyzed.

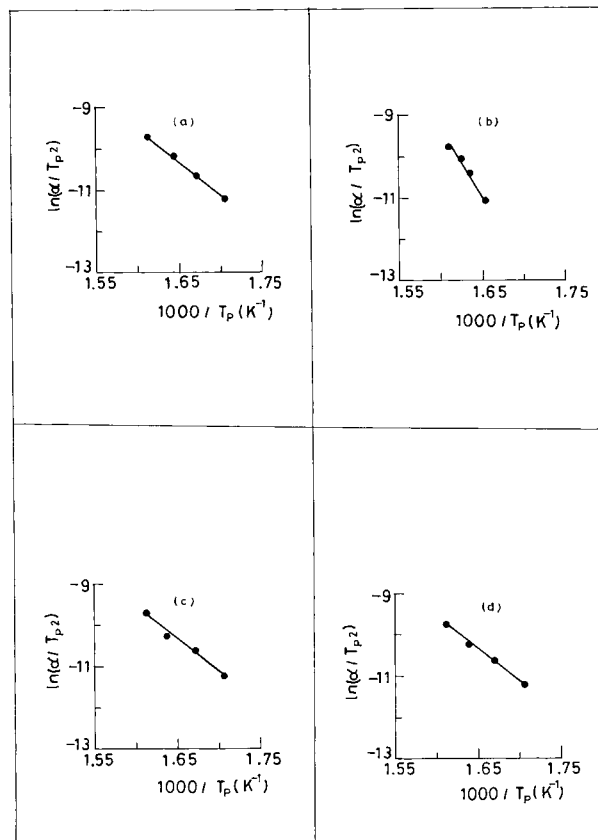
## MATERIALS

OPEFB fiber-reinforced phenol-formaldehyde composites were procured from the Rubber Research Institute of India, Kottayam. The solid content of the resin is  $50 \pm 1\%$ . Caustic soda was used as catalyst during the manufacturing. The hand layup technique followed by compression molding at  $100^\circ\text{C}$  for about 30 min was adopted for the composite preparation.<sup>4</sup>

The total processed fiber loading of the composite was kept constant, i.e., 40 wt %, with a 40-mm fiber length and average diameter of  $0.02 \times 10^{-4} \mu\text{m}$ . Chemicals used for fiber surface modification were potassium permanganate ( $\text{KMnO}_4$ ) and benzoyl peroxide. These chemicals were of reagent grades. The natural rubber latex used for oil palm fiber coating was of 10% dry rubber content. The coupling agents used for fiber surface modifications were triethoxy vinyl silane [ $\text{CH}_2\text{CHSi}(\text{OC}_2\text{H}_5)_3$ ] and toluene 2,4-di-isocyanate [ $\text{CH}_3\text{C}_6\text{H}_3(\text{NCO}_2)_2$ ]. These were procured from Union Carbide Co., Mon-



**Figure 1** DSC thermograms of treated and untreated composites.



**Figure 2** (a)  $\ln \alpha/T_p^2$  vs.  $1000/T_p$  plots for sample No. 1. (b)  $\ln \alpha/T_p^2$  vs.  $1000/T_p$  plots for sample No. 2. (c)  $\ln \alpha/T_p^2$  vs.  $1000/T_p$  plots for sample No. 3. (d)  $\ln \alpha/T_p^2$  vs.  $1000/T_p$  plots for sample No. 4.

treal, Canada, and Poly Sciences, USA, respectively.

## FIBER SURFACE MODIFICATIONS

### Permanganate Treatment (Sample Code 01)

Fibers were pretreated with alkali and then dipped in permanganate solution in acetone for about 2–3 min. The permanganate solutions of concentrations 0.01, 0.05, and 0.1% were used. Fibers were washed in distilled water and finally dried.

### Fiber Peroxide Treatment (Sample Code 02)

Fibers were coated with benzoyl peroxide from acetone solution after alkali pretreatment. Saturated solution of the peroxide in acetone was used. The fibers were then dried.

**Table I** Data for  $m$ ,  $n$ , and  $E_c$  of PF Composites

Sample Code	Heating Rate (K/min)	$\ln[-\ln(1-x)]$ vs $\ln\alpha$		$\ln[-\ln(1-x)]$ vs $1000/T$		Average $E_c$	$\ln(\alpha/T_p^2)$ vs. $1000/T_p$	
		$n$	$m$	$mE_c$	$E_c$ (kJ/mol)		$(m/n)E_c$	$E_c$ (kJ/mol)
1	5	1.026	1	125.447	125.447	124.713	122.324	119.224
	10			124.415	124.415			
	15			124.730	124.730			
	20			124.260	124.260			
2	5	0.933	1	129.104	129.104	128.810	126.684	135.780
	10			126.799	126.799			
	15			128.860	128.860			
	20			130.480	130.480			
3	5	0.960	1	153.290	153.290	152.680	148.214	154.390
	10			152.700	152.700			
	15			152.159	152.159			
	20			152.590	152.590			
4	5	1.224	1	123.980	123.980	124.600	119.674	97.770
	10			124.660	124.660			
	15			122.030	122.030			
	20			127.730	127.730			

**Resin Peroxide Treatment (Sample Code 03)**

PF resin was treated with benzoyl peroxide. Different quantities (0.1, 0.5, and 1.0% of the resin) of the peroxide was added into the resin and stirred for 1 h for intimate mixing. The peroxide can act as a free radical initiator and can take part in the crosslinking reactions.

**MEASUREMENTS**

A convenient way of studying crystallization kinetics is by means of Differential Scanning Calorimeter (DSC), in which the sample is heated at a constant rate and the change in heat with respect to an empty reference pan is measured. The small pieces of different samples of weight approximately 8.0 to 12.0 mg were kept in standard aluminium pans, and were scanned over a temperature range from 25 to 450°C at various heating rates.

A DSC scan of all the  $\text{KMnO}_4$  and peroxide treated samples at four different heating rates (5, 10, 15, and 20 K/min) were carried out using a DSC model 8230 B from Rigaku, Japan. All calorific measurements were done on a thermal analysis station TAS-100. The temperature precession of this equipment was 0.1 K, with an average standard error of about 1 K in the measured values.

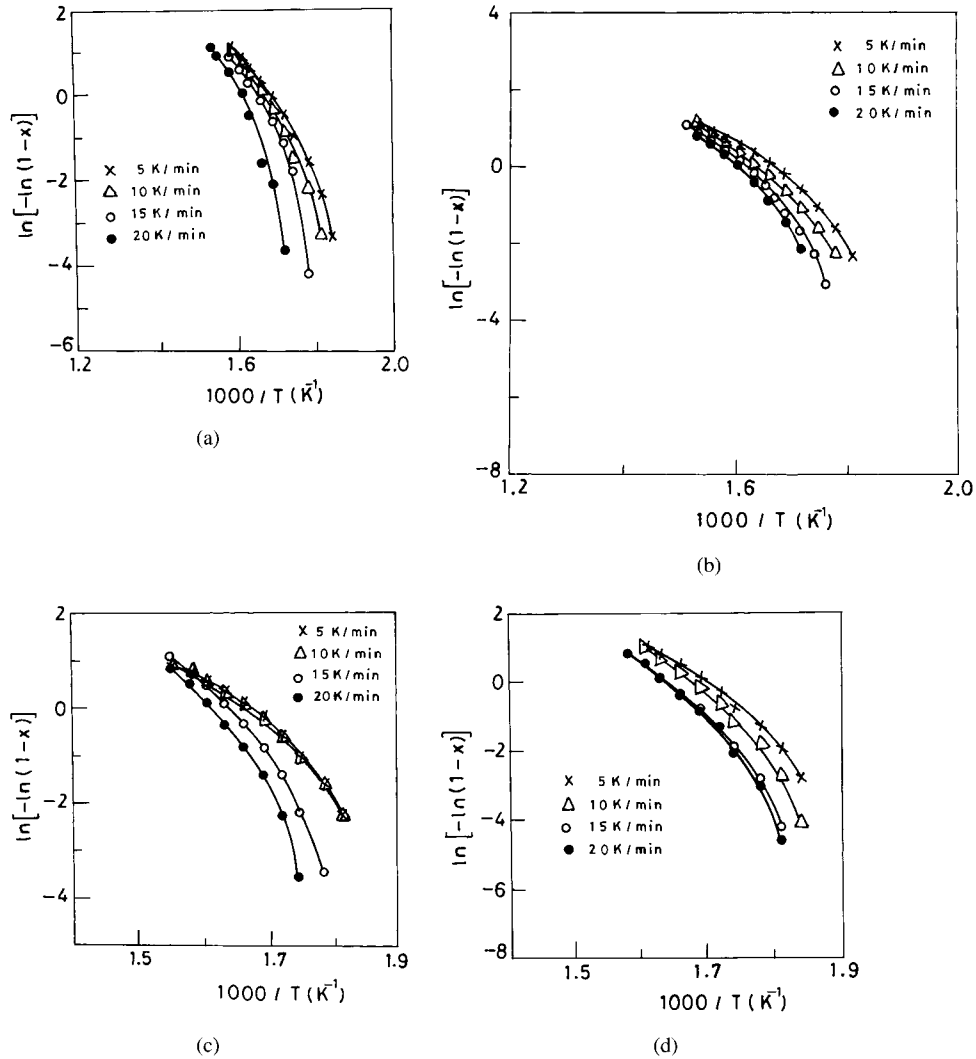
**DATA ANALYSIS AND RESULTS**

Typical DSC thermograms of untreated (sample code 04), treated with  $\text{KMnO}_4$ , and peroxide oil palm fiber-reinforced PF composites at a heating rate 10 K/min are shown in Figure 1. Modified Kissinger's equation and Matusita's equation for nonisothermal crystallization was used to analyze the experimental data. Activation energy for crystallization was evaluated using a modified Kissinger's equation for all the treated and untreated samples. Kissinger's equation<sup>5-7</sup>

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

where,  $k$  is a constant whose value depends on the thermal history of the sample.  $n$  and  $m$  are constants having values between 1 and 4, depending on the morphology of the growth.<sup>8</sup>  $\alpha$  is the heating rate, and  $T_p$  is the peak crystallization temperature.

The values of activation energies  $(m/n)E_c$  are evaluated from the slope of the curve between  $\ln \alpha/T_p^2$  and  $1000/T_p$  in kJ/mol (Fig. 2). The values of  $(m/n)E_c$  obtained from this curve are listed in Table I, column 8, for all the samples. To evaluate  $E_c$ , a knowledge of  $m$  and  $n$ , that is, some details of the crystallization process, is necessary. Therefore, to evaluate  $E_c$ ,  $m$ , and  $n$ , and arrive at the crystallization mechanism, the results were ana-



**Figure 3** (a)  $\ln[-\ln(1-x)]$  vs.  $1000/T$  for untreated composites at different heating rates (K/min). (b)  $\ln[-\ln(1-x)]$  vs.  $1000/T$  for  $KMnO_4$ -treated composites at different heating rates (K/min). (c)  $\ln[-\ln(1-x)]$  vs.  $1000/T$  for fiber peroxide-treated composites at different heating rates (K/min). (d)  $\ln[-\ln(1-x)]$  vs.  $1000/T$  for resin treated with peroxide composites at different heating rates (K/min).

lyzed using the method suggested specifically for nonisothermal crystallization by Matusita et al.<sup>9</sup>

For nonisothermal crystallization the volume fraction precipitated in a PF composite at a uniform rate  $\alpha$  is related to  $E_c$  through the expression:

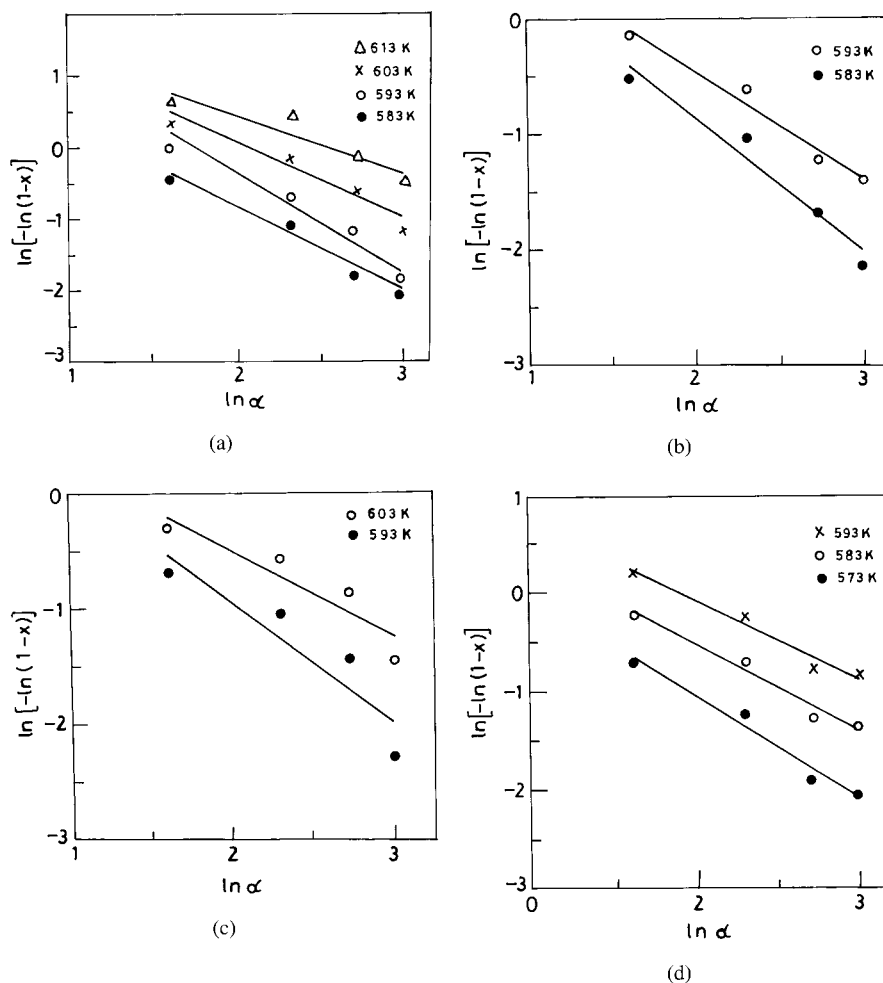
$$\ln[-\ln(1-x)] = -n \ln \alpha - 1.052mE_c/RT + \text{constant} \quad (2)$$

where  $n$  and  $m$  are numerical factors already mentioned above. When nuclei formed during the heating at constant rate  $\alpha$  are dominant,  $n$  is

equal to  $m + 1$ , and when nuclei formed during any previous heat treatment prior to thermal analysis are dominant,  $n$  is equal to  $m$ .<sup>8</sup>

The plot of  $\ln[-\ln(1-x)]$  against  $1000/T$ , where  $T$  is the temperature at which crystal volume fraction reaches a specific value, gives a straight line and slope of the line is  $1.052(mE_c/RT)$ .

The plot [Fig. 3(a)–(d)] is found to be linear over most of the temperature range. At high temperature or in the region of large crystallized fractions, a break in the linearity or a lowering of the initial slope is seen for all the heating rates. Gen-



**Figure 4** (a)  $\ln[-\ln(1-x)]$  vs.  $\ln \alpha$  for untreated composites at different heating rates. Temperature indicated in parentheses. (b)  $\ln[-\ln(1-x)]$  vs.  $\ln \alpha$  for  $\text{KMnO}_4$ -treated composites at different heating rates. Temperature indicated in parentheses. (c)  $\ln[-\ln(1-x)]$  vs.  $\ln \alpha$  for fiber peroxide-treated composites at different heating rates. Temperature indicated in parentheses. (d)  $\ln[-\ln(1-x)]$  vs.  $\ln \alpha$  for resins treated with peroxide at different heating rates. Temperature indicated in parentheses.

erally, this break in slope is attributed to the saturation of nucleation sites in the final stages of crystallization or to restriction of crystal growth by the small size of the particles. In all these cases where there is a change in slope, the analysis is confined to the linear region.

From the slope of the  $\ln[-\ln(1-x)]$  vs.  $1000/T$  data [Fig. 3(a)–(d)],  $mE_c$  was calculated for all the heating rates.  $mE_c$  was seen to be somewhat independent of the heating rate, and therefore, an average value of  $mE_c$  was calculated by considering all the heating rates. Values of  $mE_c$  obtained similarly for all the compositions are listed in Table I, column 5.

From the experimental data, it is possible to evaluate  $\ln[-\ln(1-x)]$  as a function of  $\ln \alpha$  at any

fixed temperature [Fig. 4(a)–(d)]. As shown in expression (2),  $n$  is obtained as the slope of the resulting line. The value of  $n$  evaluated for all other composites are listed in Table I, column 3. The value of  $n$  is found to be about one for all the composites. The value of  $m$  should be equal to  $n$ .

Values of  $E_c$  obtained by using these  $m$  values and the  $mE_c$  values obtained from the slope of  $\ln[-\ln(1-x)]$  vs.  $1000/T$  are listed in Table I, column 6. The value of  $E_c$  can also be evaluated by using these  $m$  and  $n$  values along with the  $(m/n)E_c$  values (Table I, column 9) obtained from the  $\ln \alpha/T_p^2$  vs.  $1000/T$  data. These values of  $E_c$  obtained by the two methods are in fair agreement.

Another peak is visible in thermogram of sample code 3 (resin peroxide treated, Fig. 1) in the

**Table II** Data for  $T_c - T_g$  of PF Composites

Sample No.	Heating Rate (K/min)	$T_g$ (°C)	$T_c$ (°C)	$T_c - T_g$ (°C)
1	10	104	326.1	222.1
2	10	105	329.0	224.0
3	10	103	338.4	235.4
4	10	99	326.0	227.0

exothermic region. This may be due to the introduction of some metamorphic state at higher temperatures or due to some structural changes. Exact reason is not predictable presently. However, further research is ongoing.

Thermal stability of a system is defined by the difference between crystallization temperature  $T_c$  and glass transition temperature  $T_g$ . The values of  $T_c - T_g$  for sample code 3 are higher than for all the other treated and untreated composites.  $T_c - T_g$  values for all the samples are given in Table II. Higher  $T_c - T_g$  values are the indication of thermal stability. The crystallization peak temperatures vary from 312 to 347°C, depending on the treatments and heating rates.

## CONCLUSIONS

Analysis shows that fiber treatment increases the thermal stability. The reason may be treatment of lignocellulosic fibers leads to the formation of a lignin-cellulose complex, which gives more stability to the fiber. In the case of resin treated with a peroxide composite, the distance between the two interlocks in the polymer network becomes more, and causes an increase in the porosity. Peroxide can also act as a free radical initiator, which may take part in crosslinking reactions. This may

be the reason for higher thermal stability in the case of resin treated with a peroxide composite.

Recent analysis developed for the nonisothermal crystallization process has been used to analyze the crystallization exotherms. Activation energies calculated from Kissinger and Matusita et al.<sup>9-11</sup> equations are approximately equal for all the samples. It has been possible to arrive at the mechanism of nucleation, which is surface nucleation with one-dimensional growth in these composites.

## REFERENCES

1. Kuruvilla, J.; Sabu, T.; Pavithran, C. *Compos Sci Technol* 1995, 53, 99.
2. Owolabi, O.; Czvikovszky, T.; Kovacs, I. *J Appl Polym Sci* 1985, 30, 1827.
3. Sreekala, M. S.; Kumaran, M. G.; Sabu, T. *J Appl Polym Sci* 1997, 66, 21.
4. Sreekala, M. S.; Sabu, T.; Neelkantan, N. R. *J Polym Eng* 1996/97, 16, 4.
5. Matusita, K.; Sakka, S. *Phy Chem Glasses* 1979, 20, 81.
6. Matusita, K.; Sakka, S. *J Noncrystall Solids* 1980, 38-39, 741.
7. Matusita, K.; Sakka, S. *Bull Inst Chem Res Kyoto Univ* 1981, 59.
8. Mahadevan, S.; Giridhar, A.; Singh, A. K. *J Noncrystall Solids* 1986, 88, 11.
9. Matusita, K.; Konatsu, T.; Yokota, R. *J Mater Sci* 1984, 19, 291.
10. Varma, D. S.; Varma, M.; Varma, I. K. *Thermochim Acta* 1986, 108, 199.
11. Kuzak, S. G.; Hietz, J. A.; Waitkns, P. A. *J Appl Polym Sci* 1998, 67, 349.
12. Geethamma, V. G.; Reethamma, J.; Sabu, T. *J Appl Polym Sci* 1995, 55, 583.
13. Prasad, S. V.; Pavithran, C.; Rohatgi, P. K. *J Mater Sci* 1983, 18, 1443.
14. Sapiuha, S.; Caron, M.; Schreiber, H. P. *J Appl Polym Sci* 1986, 32, 566.