

Measurement of effective thermal conductivity and thermal diffusivity for assessing the integrity of fiber to matrix bond in natural fiber composite

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Thermal conductivity and thermal diffusivity of pineapple leaf reinforced phenol formaldehyde composite have been studied with special reference to chemically treated fibers using the transient plane source (TPS) technique, at room temperature and normal pressure. All the composites were made of 40% fiber by weight. The fibers were treated with alkali, silane and toluene diisocyanate. It was found that, thermal conductivity and thermal diffusivity of the composites increase after chemical treatment. The thermal conductivity of alkali treated fiber was found to be maximum in the present study. The thermal conductivity of treated and untreated fibers was calculated theoretically by Bruggman's model. The results of model calculation showed an increase of thermal conductivity of treated fiber over the thermal conductivity of untreated fiber.

[Keywords: Thermal conductivity, Thermal diffusivity, Phenol formaldehyde composite, Composite, Phenol formaldehyde]

1 Introduction

Fiber reinforced plastics are widely used for structural and non-structural applications¹ due to the high specific strength and modulus of the 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 over the synthetic fiber like, glass, carbon and boron. The main advantages of natural fibers are low cost, low density, high specific strength, easy processibility, non-toxic, abundance in nature and easy biological degradation²⁻⁴. All these advantages have diverted the attention of scientists and engineers towards the reinforcement of polymer with natural fibers.

Among various available natural fibers pineapple leaf fiber (PALF) exhibits excellent physical and mechanical properties due to high cellulose content and comparatively low microfibrillar angle⁵⁻⁹. To improve some of the physical and chemical properties (high polar nature of

cellulose fiber) of this fiber, chemical treatment is done. Among the matrix resins, phenol formaldehyde has been commonly used for making thermosetting composites due to its stable thermosetting properties.

Thermo-physical properties, like thermal conductivity and thermal diffusivity¹⁰⁻¹¹ of a composite, are important parameters for scientists and engineers to decide its end use. The present study is aimed at observing variation in these thermal properties by chemically treating¹²⁻¹³ fibers with alkali, toluene diisocyanate and silane in the phenol formaldehyde matrix, as compared to untreated resin reinforced with fibers, as it has been found that, physical and chemical structure of fiber change due to reaction of OH group of cellulose with above said chemicals.

2 Materials Preparation

For preparing these composites pineapple leaf fiber, phenol formaldehyde and coupling agents are the basic components. The resole type phenol formaldehyde resin is obtained from Coast Polymers

Pvt. Ltd., Kannur, Kerala, India while pineapple leaf fiber are supplied by South India Textile Research Association, Coimbatore. The coupling agents used for fibre surface modifications are, triethoxy vinyl silane, toluene diisocyanate and sodium hydroxide that were procured from Carbide Company, Montreal, Canada and Poly Science, USA, respectively.



Fig. 1 — Schematic diagram of the TPS sensor

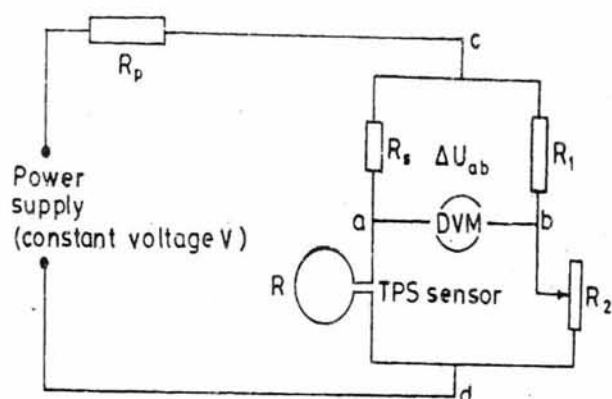


Fig. 2 — Bridge circuit diagram for the TPS technique, where R_1 and R_2 are the resistance, R_p is the effective resistance of the wires outside the arms of bridge, R_s is the resistance of the TPS element and DVM is the digital voltmeter. ΔU_{ab} is the potential difference between the points a and b in the bridge circuit

2.1 Alkali treatment

Fibers were immersed in 5 % solution of sodium hydroxide for 48 h, at room temperature. Fibers were then washed many times in distilled water and finally washed with water containing a little acid and dried.

2.2 Isocyanate treatment (TDI)

The alkali treated fibers were taken in a round-bottomed flask and soaked in chloroform containing dibutyl tin dilaurate as catalyst. Toluene

diisocyanate was added dropwise into the flask, using a pressure-equalizing funnel. The reaction was allowed to take place for two hours with continuous stirring. After refluxing with acetone, the purified fibers were washed with distilled water and dried in oven.

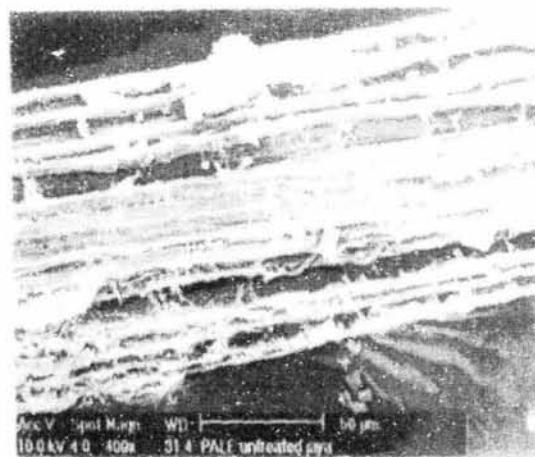


Fig. 3 — SEM photomicrograph of surface of untreated PALF

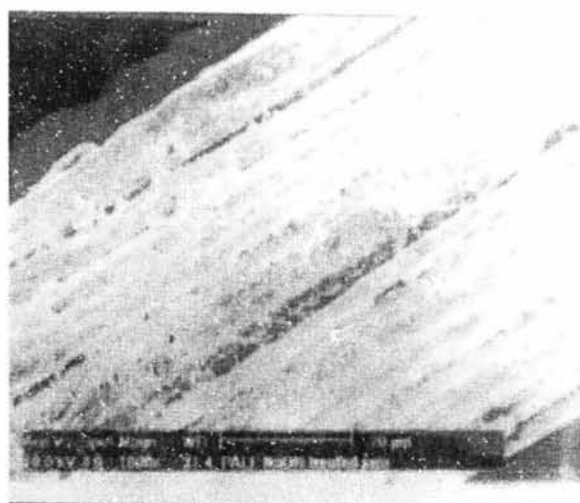


Fig. 4 — SEM photomicrograph of surface of NaOH-treated PALF

2.3 Silane treatment

The pre-treated fibers were dipped in alcohol-water mixture (60:40) containing triethoxy vinyl silane as coupling agent. The pH of the solution is maintained in between 3.5 and 4. Fibers were washed in distilled water and dried.

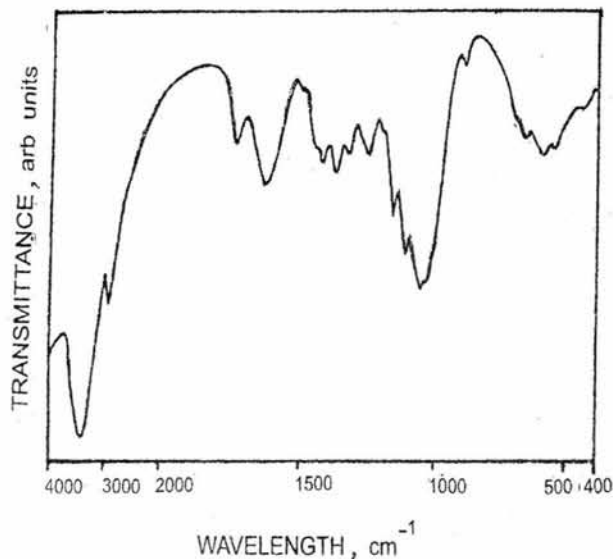


Fig. 5 — IR spectrum of untreated PALF

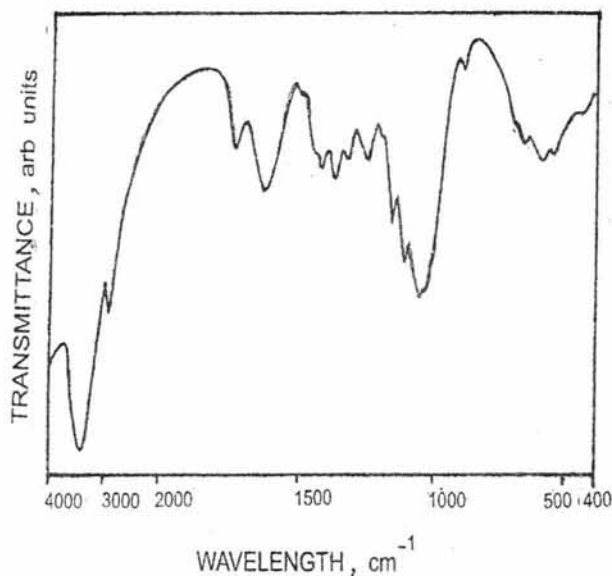


Fig. 6 — IR spectrum of NaOH-treated PALF

3 Experimental Technique and Theory of Transient Plane Source Technique (TPS)

Simultaneous measurements of thermal conductivity and thermal diffusivity of all the composites have been made, at room temperature and normal pressure, using TPS method. The sample size used for the study is 1.9×1.9 cm². Thickness of the samples is approximately 0.3 cm.

The TPS technique has proved to be a precise and convenient method for measuring the thermal transport properties of electrically insulating

materials. The TPS method consists of an electrically conducting pattern (Fig. 1) in the form of a bifilar spiral, which also serves as a sensor of the temperature increase in the sample. In Fig. 1, K-4521 is the design number of the sensor and K stands for kapton. The sensor is sandwiched between the thin insulating layers of kapton. Assuming the conductive pattern to be in the Y-Z plane of a coordinate system, the rise in the temperature at a point y-z at time *t* due to an output power per unit area *Q* is given by¹⁴:

$$\Delta T(y, z, t) = \frac{1}{8\pi^{3/2}c\rho} \int_0^t \frac{dt'}{\kappa^{3/2}(t-t')^{3/2}} \int_A dy' dz' Q(y', z', t') \exp\left[\frac{-(y-y')^2 - (z-z')^2}{4\kappa(t-t')}\right] \quad \dots(1)$$

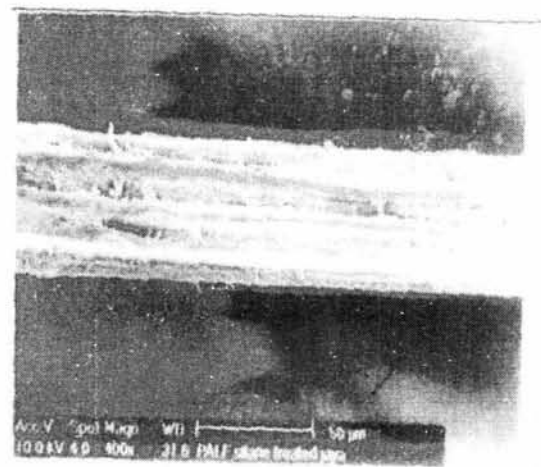


Fig. 7 — SEM photomicrograph of surface of silane-treated PALF

where ρ is the density, *C* the specific heat and κ the thermal diffusivity. If one of the integral variable is changed as:

$$\kappa(t-t') = \sigma^2 a^2 \quad \dots(2)$$

Then Eq. (2.3) changes as:

$$\Delta T(y, z, t) = \frac{1}{4\pi^{3/2}a\lambda} \int_0^t \frac{d\sigma}{\sigma^2}$$

$$\int_A dy' dz' Q(y', z', t - \sigma^2 a^2 / \kappa) \exp\left[\frac{-(y - y')^2 - (z - z')^2}{4\sigma^2 a^2}\right] \quad \dots(3)$$

where

$$\kappa = \frac{\lambda}{\rho c} \quad \dots(3.1)$$

Here, a is the diameter of the hot disk, which gives a measurement of the overall size of resistive pattern and σ is a constant variable and λ is the thermal conductivity in units of W/m K. If $\Delta T(\tau)$ is the mean value of the time-dependent temperature increase of the TPS element, then $\Delta T(\tau)$ is calculated by averaging the increase in temperature of TPS element over the sampling time; because the concentric ring sources in TPS element have different radii and placed at different temperatures during the transient recording¹⁵ which is given by:

$$\Delta T(\tau) = \frac{P_o}{\pi^{3/2} a \lambda} D_s(\tau) \quad \dots(4)$$

where

$$D_s(\tau) = \{m(m+1)\}^{-2} \int_0^\tau \frac{d\sigma}{\sigma^2} \left[\sum_{l=1}^m \sum_{k=1}^m l k \exp\left(-\frac{(l^2 + k^2)}{4\sigma^2 m^2}\right) I_0\left(\frac{l k}{2\sigma^2 m^2}\right) \right] \quad \dots(5)$$

Here, l and k are integers, P_o the total output power and I_o the modified Bessel function. For experimental purposes the authors have considered m concentric rings, which is the case of sensor (Fig. 1). The temperature increase $\Delta T(\tau)$, because of flow of current through the sensor, gives rise to a change in the electrical resistance $\Delta R(t)$, which is given as¹⁵:

$$\Delta R(t) = \alpha R_o \Delta T(\tau) \quad \dots(6)$$

Here, R_o is resistance of TPS element before the transient recording has been started and α is the temperature coefficient of resistance of the material of plane source, which gives rise to potential drop. A simple bridge arrangement as shown in Fig. 2, has been used to record the potential difference variations, which normally are of the order of a few milli-volts during the transient recording. If one assumes that, the resistance increase will cause a

potential difference variation $\Delta U(t)$ measured by the voltmeter in the bridge, the analysis of the bridge indicates that:

$$\Delta E(t) = \frac{R_s}{R_s + R_o} I_o \Delta R(t) = \frac{R_s}{R_s + R_o} \frac{I_o \alpha R_o P_o}{\pi^{3/2} a \lambda} D_s(\tau) \quad \dots(7)$$

Here:

$$\Delta E(t) = \Delta U(t) [1 - C \Delta U(t)]^{-1} \quad \dots(8)$$

and

$$C = \frac{1}{R_s I_o \left[1 + \frac{\gamma R_p}{\gamma(R_s + R_o) + R_p} \right]} \quad \dots(9)$$

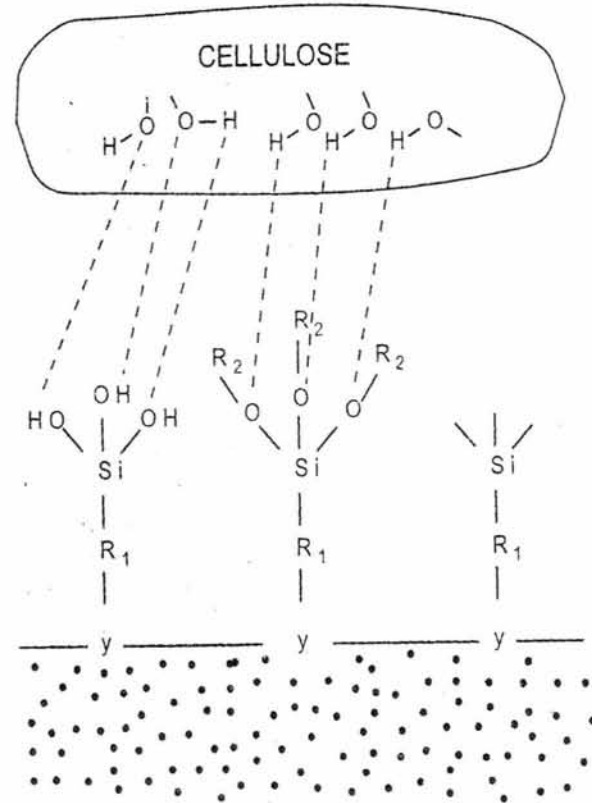


Fig. 8 — Hypothetical structure of silane-treated composite at the interfacial area of PALF and PF

The definition of various resistances is found in Fig. 2. R_s is a standard resistance with a current rating that is much higher than I_o , which is the initial heating current through the arm of the bridge containing the TPS-element. γ is a constant, which

is chosen to be 100 in the present measurement. Calculating $D_s(t)$ using a computer program and recording the change in potential difference $\Delta U(t)$, one can determine λ . Thermal conductivity and thermal diffusivity of all the samples have been measured using the TPS (Gustaffson)¹⁴ method, which are reproducible within 2 %.

4 Model Used

The thermal conductivity of untreated and treated fibers was calculated by employing Bruggman's model¹⁶. This model is valid for the concentration of dispersed phase larger than 10 volume percentages. The equation is as follows:

$$\frac{(\lambda_c - \lambda_f)(\lambda_m)^{1/3}}{(\lambda_m - \lambda_f)(\lambda_c)^{1/3}} = (1 - V) \quad \dots(10)$$

Here, λ_f , λ_m , λ_c are the thermal conductivity of the filler (PALF), matrix (PF) and the composite, respectively, and V is the volume fraction of the dispersed (filler) phase.

Table 1 — Experimentally obtained value of effective thermal conductivity (λ_c) and thermal diffusivity (κ_c) of the composites and theoretically calculated value of thermal conductivity of the fibers (λ_f)

Composites	λ_f (W/mK)	λ_c (W/mK)	κ_c (mm ² /s)
Untreated	0.21	0.26	0.12
Alkali-treated	0.44	0.35	0.22
Silane-treated	0.35	0.32	0.18
Isocyanate-treated	0.32	0.31	0.16

5 Results and Discussion

In Table 1, the experimental values of effective thermal conductivity and thermal diffusivity of untreated and different, chemically treated (alkali, silane and isocyanate) pineapple leaf fibers (40 % by weight for all composites), reinforced in phenol formaldehyde have been given. Thermal conductivity of the said composites has also been calculated by Bruggman's model, which is given in the same Table 1. From the study of experimentally determined values of thermal conductivity, it is observed that thermal conductivity of composites increases after treating the fiber with various chemicals. However, the increase depends upon the nature of chemical treatment. In the present study, the increase is found to be maximum for alkali treated fiber. The rise is minimum for isocyanate treated fiber.

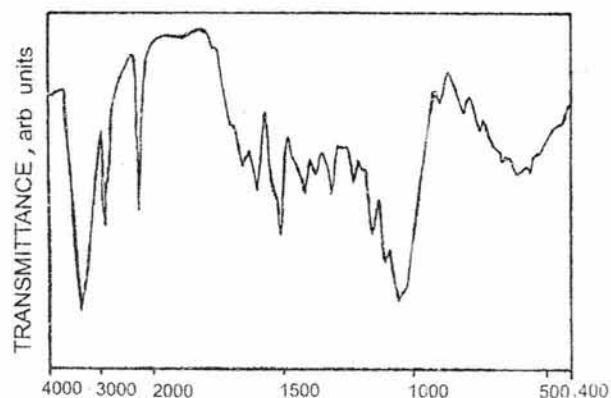


Fig. 9 — IR spectrum of isocyanate-treated PALF



Fig. 10 — SEM photomicrograph of surface of isocyanate-treated PALF

Alkali treatment reacts with fiber in two different ways as follows: The reaction of a bunch of the fiber with NaOH leads to irreversible mercerization effect, which in turn increases the amount of amorphous cellulose, at the expense of the crystalline cellulose, and increases the fiber surface adhesion by removing natural and artificial impurity, thereby producing rough surface topography. Thus, fiber becomes thinner, porous and rough, which is clear from the SEM micrographs (Figs 3 and 4). The fibrillar structure as well as porosity of the individual fiber is revealed, which becomes clear and compact in alkali treated fiber, due to dissolution of waxy materials (Fig. 4). Also, decrease in fiber diameter is being observed in

the same microgram (Fig. 4) by 10-20% depending upon the fiber¹⁷.

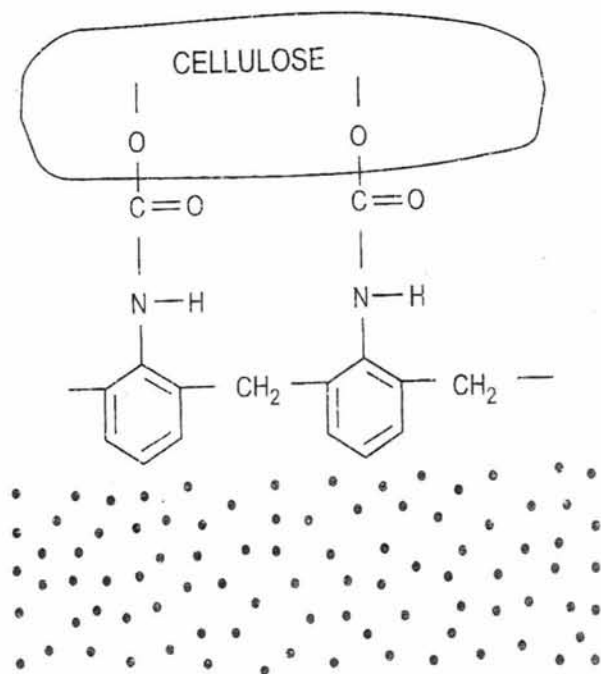


Fig. 11 — Hypothetical structure of isocyanate-treated composite at the interfacial area of PALF and PF

Figs 5 and 6 show the IR spectrum of untreated and NaOH-treated PALF, respectively. From the IR spectrum (Fig. 5), the following peaks have been observed. The strong broad peak in 3300-3400 cm^{-1} range in the spectrum is the characteristic hydrogen bonded OH stretching vibrations. In the spectra, emergence of new bands at 2900 cm^{-1} , 1730 cm^{-1} is the characteristic bands for CH stretching vibrations and carbonyl (C=O) stretching, respectively. With the alkali treatment (Fig. 6), this carbonyl (C=O) disappears. It has been reported¹⁷ that, in alkali treatment, a substantial portion of uranic acid – a constituent of hemicellulose xylan – is removed, resulting in the disappearance of this peak. The band at 1370, 1330 and 1310 cm^{-1} are due to CH deformation, OH in-plane bending and CH_2 wagging, respectively. Also, rough surface topography improves the fiber-matrix adhesion. All these effects contribute towards thermal conductivity in a positive way.

The influence of silane treatment on the thermal properties of composite is shown in Table 1. It is clear that, both effective thermal conductivity and thermal diffusivity of silane-treated composite is higher, as compared to those of untreated

composite. Silane treatment on fiber¹⁷, makes the fiber less hydrophilic, reduces its diameter and creates a rough surface topography, which is clear from SEM photograph (Fig. 7). This in turn is a possible cause of increase in the thermal conductivity of silane-treated fiber. This is also verified from the theoretically calculated value of thermal conductivity of silane-treated fiber, using Bruggman's model. In the composite, the hydrolyzed silanol forms a hydrogen bond with OH group of cellulose and forms a hydrogen bond (Fig. 8), while polymerized silane adheres to matrix (PF), mainly because of a van der Waal's type force. Thus, a silane-coupling agent forms a bridge between fiber and matrix, as is clear from the hypothetical structure of the composite (Fig. 8). As a result of this, the effective thermal conductivity of the composite also increases, as the linkage between fiber and matrix improves.

The effect of isocyanate treatment on fiber is that NCO of isocyanate links with cellulose of fiber through strong covalent bond, which is confirmed by IR spectra of isocyanate treated fiber (Fig. 9). In the spectra, emergence of new bands at 3310 cm^{-1} , 2260 cm^{-1} , 1700 cm^{-1} , 1538 cm^{-1} and 1280 cm^{-1} are due to stretching of various N-H, $\text{N}=\text{C}=\text{O}$, C=O, C-N-H and $\text{C}-\text{N}-\text{H}$ groups, respectively. Thus, an isocyanate-coupling agent forms a bridge between fiber and matrix that improves linkage between fiber and matrix. SEM micrograph (Fig. 10) shows the surface of isocyanate treated fiber. A clear coating of isocyanate is evident from Fig. 10. This treatment produces a better interaction between fiber and matrix in isocyanate treated fiber composites and hence a possible rise in effective thermal conductivity can be explained.

As the linkage between isocyanate compound and fiber is a covalent bond (Fig. 11), while that between silanol and fiber is a hydrogen bond. Therefore, phonons, which are responsible for conduction, have lower velocities in isocyanate treated composite as compared to silane-treated composite. This results in a small rise in thermal conductivity in case of isocyanate treated composite.

6 Conclusion

The above study is suggestive of the fact that, chemical treatment of fiber is important and will be responsible for increasing the fiber matrix adhesion

and hence, the effective thermal conductivity and thermal diffusivity of the composites.

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