

Thermal conduction and diffusion through polyester composites

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Received 4 October 2005; revised 20 March 2006; accepted 13 April 2006

Using Transient Plane Source technique, thermal properties like thermal conductivity, thermal diffusivity and specific heat of polyester composites of banana fibers (treated and untreated) are measured simultaneously at room temperature and normal pressure. The increase in thermal conductivity is observed in some treatments. The performance of the composite depends to a large extent on the adhesion between polymer matrix and the reinforcement. This is often achieved by surface modification of the matrix or the filler. Banana fiber was modified chemically to achieve improved interfacial interaction between the fiber and the polyester matrix. Various silanes and alkali were used to modify the fiber surface. Chemical modification was found to have a profound effect on the fiber/matrix interaction which is evident from the enhanced thermal conductivity values. Of the various chemical treatments, simple alkali treatment with 1% NaOH was found to be the most effective.

Keywords: Banana fibers, Polyester composites, Thermal conductivity, Thermal diffusivity

IPC Code: G01N25/18

1 Introduction

Natural fibers are abundantly available all over the world. The efforts to utilize all available natural resources including plants have led to the production of polymer composites from cellulosic fibers. Cellulosic fiber obtained from the pseudostem of the banana plant (*Musa sapientum*) is a best fiber with relatively good mechanical properties¹. The composites developed by using these fibers provide toughness and wood texture². Synthetic fibers like glass and carbon are used as reinforcement but due to their high cost and high energy requirement in their production, they are less suited for common applications. On the other hand, the abundant and renewable natural fibers can be used in such applications provided their properties are improved. The products produced using these fibers may be used in structural and other applications. Compared to inorganic fibers, the main advantage of these fibers are their low cost, low density, high specific strength and modulus, renewable nature and comparatively easy processability³. The properties of fiber reinforced composites depend on many factors, fiber aspect ratio, and fiber orientation as well as stress transfer efficiency of interfaces^{4,6}. These properties can be achieved by chemical modification of the matrix or the fiber which brought about higher interaction

between the fiber and the matrix. The modification of the fiber by several chemical methods is carried out. The treatment with alkali and also by other coupling agents like silanes, acetic acid, etc. has all been proved to be the best way to improve fiber/matrix adhesion.

The effect of chemical modifications of the fibers on the thermal properties of the polyester composites of banana fiber has been reported in this paper. The effect of various chemical modifications on the interfacial adhesion has been concluded and reported on the basis of thermal properties of the materials.

In our studies, we are using polyester composites of banana fiber having total volume fraction 0.4 of the fiber in all the composites.

2 Experimental Details

Banana fiber obtained from Sheeba fiber and handicrafts, Poovancode, Tamilnadu, India, was used as filler. Unsaturated polyester HSR 8131(Sp Gravity 1.12, viscosity 65 cps, gel time 25 min) obtained from M/s Bakelite Hylam, Hyderabad, India was used as matrix. Methyl ethyl ketone peroxide and cobalt naphthenate were of commercial grade supplied by Sharon Enterprise, Cochin. The various silanes, A174 (V-methacryloxypropyl-trimethoxysilane), A15 (vinyl-triethoxysilane) and A1100 (γ -aminopropyltriethoxy-

silane) were obtained from Sigma-Aldrich, India. NaOH and all other chemicals were of commercial grade.

Banana fibers were neatly separated by hand adhering pith, if any were removed and fibers were cut to uniform size of 30mm length. The fibers were then subjected to various chemical treatments. Modified fibers were then evenly arranged in a mould measuring 150×150 mm and pressed into a material. The composite sheets were prepared by impregnating the fiber with the polyester resin to which 0.9 volume percent cobalt naphthenate and 1% methyl ethyl ketone peroxide were added. The resin was degassed before pouring and the air bubbles were removed carefully with a roller. The closed mould was kept under pressure for 12 hrs, samples were post cured for 48 hrs at room temperature and test specimens of the required size were cut out from sheets. The total volume fraction of the fiber has been kept as 0.4.

A 0.6% of the respective silane was mixed with ethanol/water mixture in the ratio 6:4, mixed well and was allowed to stand for an hour. The pH of the solution was carefully controlled and maintained at 4 to bring out the complete hydrolysis of the silane by the addition of acetic acid/NaOH depending on the respective silane used. Neatly separated and cut cellulose fiber was dipped in the solution and was allowed to remain there for 1½ hr. The ethanol/water mixture was drained out and the fiber was dried in air for half-an-hour followed by drying in the oven at 70°C till the fiber was fully dry.

Cleaned and well-separated cellulose fiber were dipped in 0.5% and 1.0% solution of NaOH for half-an-hour and then washed in very dilute acid to remove any particles of alkali. Washing was continued till the fibers were alkali free. The washed fibers were then dried in the oven at 70°C for three hours.

Acetylation of the fibers was carried out as follows – The fibers were dipped in glacial acetic acid for 30 min, the acid was drained and the fibers were dipped in acetic anhydride containing a few drops of concentrated sulphuric acid for 5 min, washed in distilled water and then dried.

Thermal conductivity and thermal diffusivity of fiber reinforced polyester composites have been measured simultaneously at room temperature and normal pressure, using Transient Plane Source (TPS) technique. The 0.3 cm thick samples of 1.2×1.2 cm² were used. The TPS method consists of an electrically conducting pattern, which serves both as source of heat given to the material and as a sensor of

temperature increase in the samples. Assuming the conducting pattern to be in Y-Z plane of a co-ordinate system, the rise in the temperature at a point Y-Z at time t due to an output power²¹ per unit area Q is given by:

$$\Delta T(y, z, \tau) = \frac{1}{4\pi^{3/2}a\lambda} \int_0^\tau \frac{d\sigma}{\sigma^2} \int_A dy' dz' Q \left[y', z', t - \frac{\sigma^2 a^2}{\chi} \right] \times \exp \left[\frac{-(y-y')^2 - (z-z')^2}{4\sigma^2 a^2} \right] \quad \dots(1)$$

where

$$\chi(t-t') = \sigma^2 a^2, \theta = a^2/\chi \text{ and } \tau = [t/\theta]^{1/2} \quad \dots(2)$$

a is the radius of the hot disc (source and the sensor) which gives the measurement of the overall size of resistive pattern and θ is known as the characteristic time. σ is a constant variable, λ is the thermal conductivity in units of W/mK and χ is the thermal diffusivity in unit of mm²/s of the sample.

TPS element is made of a 10 µm thick nickel foil with an insulating layer made of 50 µm thick kapton, on each side of the metal pattern. The evaluation of these measurements was performed in a way mentioned by Gustafsson⁷. In experiments with insulating layers of such thickness, it is necessary to ignore the voltage recorded during the first few seconds because of the influence of the insulating layers. However, due to the size of the heated area of the TPS elements, the characteristic time of the experiment is so long that, it is possible to ignore a few seconds of recorded potential difference values and still obtain very good result. The change in the voltage was recorded with a digital voltmeter, which was on line to the personal computer. The power output to sample was adjusted according to the nature of the sample material and was in the range 6×10⁻⁶ - 16×10⁻⁶ W/m².

To record the potential difference variations, which normally are of the order of a few millivolts during the transient recording, a simple bridge arrangement has been used. If we assume 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:

$$\begin{aligned} \Delta E(t) &= \frac{R_s}{R_s + R_0} I_0 \Delta R(t) \\ &= \frac{R_s}{(R_s + R_0)} \frac{I_0 \alpha R_0 P_0}{(R_s + R_0) \pi^{3/2} a \lambda} D_s(\tau) \quad \dots(3) \end{aligned}$$

$$D_s(\tau) = [m(m+1)]^{-2} \int_0^\tau \frac{d\sigma}{\sigma^2} \left[\sum_{l=1}^m \left\{ \sum_{k=0}^m k \exp \frac{-(l^2 + k^2)}{4\sigma^2 m^2} \times L_0 \left(\frac{lk}{2\sigma^2 m^2} \right) \right\} \right] \dots (4)$$

Calculating $D_s(\tau)$ using a computer programme and recording the change in potential difference $\Delta U(t)$ one can determine λ . Similarly, thermal diffusivity χ can be determined by finding the values of characteristic time, θ , from Eq. (2).

The surfaces of these samples are smooth so as to ensure perfect thermal contact between the samples and the heating element, as the TPS sensor is placed in between the two samples material in the sample holder.

An important aspect of the design of any TPS element is that the pattern should be such that as large a part of hot area as possible should be covered by the electrically conducting pattern, as long as there is insulation between the different parts of the pattern. This is particularly important when insulating layers are covering the conduction pattern and the surface (s) of the sample. The temperature difference across the insulating layer could be considered constant after a short initial transient. The effective thermal conductivity and effective thermal diffusivity values of treated composites are presented in Table 1.

Experimental results show that the effective thermal conductivity of all the composites increases after the treatment of fibers with different chemicals to different extents compared to the effective thermal conductivity of the untreated composite. The increase in thermal conductivity indicates that the chemical treatment must have changed the nature of the fibers. The effective thermal conductivity of the composite depends upon the thermal conductivity of its individual components⁸.

Prediction of thermal conductivity of polymer composites has been made from time to time using

Table 1 — Thermal conductivity and thermal diffusivity of fiber treated polyester composites

Composite	λ_e (W/mK)	χ (mm ² /sec)
Matrix	0.18 ± 0.005	0.15 ± 0.008
Untreated	0.20 ± 0.006	0.21 ± 0.010
A151	0.23 ± 0.007	0.19 ± 0.009
A174	0.22 ± 0.006	0.26 ± 0.013
A1100	0.21 ± 0.006	0.20 ± 0.01
0.5% NaOH treated	0.21 ± 0.006	0.16 ± 0.008
1.0% NaOH treated	0.23 ± 0.007	0.17 ± 0.009
Acetylated	0.225 ± 0.007	0.18 ± 0.009

theoretical models⁹⁻¹¹. Out of these the one proposed by Y Agari *et al.*¹⁰ shows the closest approximation to the experimental data over that of a wide range of filler content for the composites in this study. Thermal conductivities of composites in parallel and series conduction can be estimated respectively using the following equations.

Parallel conduction:

$$\lambda_e = V \lambda_f + (1-V) \lambda_m$$

Series conduction:

$$\frac{1}{\lambda_e} = \frac{V}{\lambda_f} + \frac{1-V}{\lambda_m}$$

where λ_e is the effective thermal conductivity of the composite, and λ_m and λ_f are the thermal conductivities of the matrix and dispersed phase, respectively. V is the volume fraction of filler in the composite.

Another model used to calculate thermal conductivity of filler is Bruggeman's model^{12,13} which is a variable dispersion equation for the concentration of the dispersed phase V , larger than 10 or 15% volume fraction, which is good in predicting the effective thermal conductivity of a dispersed composite containing a wide range of filler sizes.

$$\frac{\lambda_e - \lambda_f}{\lambda_m - \lambda_f} \left(\frac{\lambda_m}{\lambda_e} \right)^{1/3} = (1 - V)$$

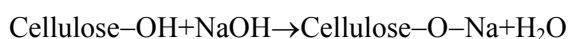
The calculated values of the thermal conductivity of the treated and untreated fibers from Bruggeman and Y. Agari models are given in Table 2. The results of both the models are in good agreement. The model results also show that the thermal conductivity of the composites increases after different chemical treatments to different extents.

Table 2 — Thermal conductivity of the treated and untreated fibers

Fibers	λ_f (W/mK)	
	Bruggeman model	Y. Agari model
Untreated	0.233	0.235
A151	0.307	0.326
A174	0.292	0.305
A1100	0.262	0.267
0.5% NaOH treated	0.262	0.267
1.0% NaOH treated	0.323	0.349
Acetylated	0.307	0.326

3 Results and Discussion

Banana fiber surface was treated with alkali of different concentrations and the treated fiber was used for the preparation of composites. The treated fibers enhance adhesion between fiber and matrix and it is demonstrated by change in thermal properties of the composite. The effectiveness of NaOH in modifying the surface of natural fibers is already present in literature¹³. It also increases polarity of the banana fiber surface¹. The NaOH treatment removes practically all non-cellulose components. Probable reaction involved in alkali treatment is



The thermal studies show that thermal conductivity is the maximum for composite prepared from 1% NaOH treated fiber. This can be attributed to the following reasons:

- (1) Due to alkali treatment the cementing materials get dissolved. The inter-fibrillar region becomes less dense and less rigid. The crystallinity of alkali treated fibers increases because of the removal of the cementing materials which leads to a better packing of cellulose chains¹⁴.
- (2) Surface area of the fiber increases due to the dissolution of lignin, hemi-cellulose and alien substances associated with the fiber. This results in a large area of contact between the fiber and the matrix leading to increase in thermal conductivity.
- (3) The dissolution of many substances on the fiber surface leads to increased polarity and decreased acidity of the fiber surface. This ultimately leads to increased polar-polar interaction with the matrix leading to higher thermal conductivity values.

Dissolution of the lignin affected by alkali treatment gives rise to free pores which improves the contact between fiber and the matrix. The effect of alkali treatment on the improvement in the properties of natural fiber composites¹⁵ is also reported by other researchers. Table 1 shows the values of effective thermal conductivity and thermal diffusivity of composites of banana fiber treated with alkali of different concentrations.

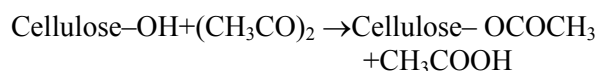
Silane coupling agents are successfully used with fillers and reinforcements, which have reactive -OH group on the surface. The adhesion is determined by the composition of the organo functional group of the

silane which is dependent on its ability to react with the polymer matrix. Various silanes have been tried to modify the surface of fibers. Silanes undergo hydrolysis to form silanols which further react with OH groups of the cellulose. The organo functional groups of the silanes in turn form interpenetrating polymer networks with the polyester.

Of the various silanes used, thermal conductivity is found to be the highest in case of silane A 151 (vinyl triethoxysilane) treated fiber composites. The reason can be attributed to the improved interaction between the organo functional group and the polyester matrix. Also, the increased acidity values¹⁵ lead to increased polarity and thereby improved interactions in case of silane A151 treated fiber composites. The effective thermal conductivity values of silane treated composites are slightly higher in comparison to untreated composite. The maximum increase in thermal conductivity is found to be for the silane with vinyl functional group.

It has been observed by other researchers that maximum wetting tension between an adhesive and a substrate is obtained when the surface energy of the substrate is as high as possible¹⁶. The surface free energy can be expressed in terms of the acid-base interactions. The extent of acid-base interaction becomes lower in case of A174 treated fiber composite compared to A151 treated and this leads to the decrease in interaction and thereby the decrease in thermal conduction. It is possible that silanols, formed by the hydrolysis of the alkoxy groups of the silanes, can selfcondense to form a thick layer of oligomeric silanol deposition in the fiber/matrix interface which can greatly reduce the efficiency of bonding¹⁷. This further reduces the thermal conductivity value in A1100 treated fiber composites.

Acetylation has been proved to be an effective method for the modification of cellulose fiber surface. The probable reaction between the fiber and acetic anhydride can be represented as:



Acetylation has rendered the fiber surface rougher. This enhances adhesion between fiber and matrix and hence increases the effective thermal conductivity of the composite.

Silanes with different organo functional groups (vinyl, methacryloxy and amine) have been used to precoat the fiber in order to examine the influence of silane treatment on thermal properties of the

composites. The adhesion of the poly siloxane layer depends on the chemical composition of the organo functional group of the coupling agent. Various silanes have been proved to be reasonably good in improving adhesion in cellulose/polyester systems. The reason for the improved interaction can be attributed to the changed polarity values leading to more polar-polar interactions and hence a strong interface. It is clear from Table 1 that various silane treatments of fibers increase thermal conductivity of the composites. Maximum increase in thermal conductivity is found to be for the silane with vinyl functional group. Acetylation of the fiber also increases the thermal conductivity of the composite to a good extent. However, alkali treatment has been proved to be the best as far as thermal properties and cost of the composite are considered as compared to other chemical treatments. Thermal properties of polyester composites of chemically treated fibers are consistent with mechanical properties as reported by Pothan¹⁵.

4 Conclusion

Natural fibers like cellulose have a surface chemistry that is incompatible for perfect bonding. Surface modifications by various chemical treatments lead to good interfacial strength and thereby improvement in their thermal and mechanical properties. Chemical modifications have improved the properties of banana fiber reinforced polyester composites.

The results show that the highest improvement in thermal conductivity is for the alkali treated fiber composite. The improvement in properties due to alkali treatment is mainly due to the better packing of

the cellulose chains, after the dissolution of lignin, which is the cementing material. Acetylation also improves thermal properties to a good extent. However, among the various silanes, only A151 (vinyl triethoxysilane) treatment of the fiber has improved thermal properties to some extent and the rest of the silane treatments are not much effective.

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