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Temperature Dependence of Thermo-Mechanical Properties of Banana Fiber-Reinforced Polyester Composites

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Abstract

Using a Dynamic Mechanical Analyzer (DMA), mechanical properties like modulus and phase transition temperature of polyester composites of banana fibers (treated and untreated) are measured simultaneously. The shifting of phase transition temperature 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 alkalies 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 values of phase transition temperatures. Of the various chemical treatments, simple alkali treatment with 1% NaOH was found to be the most effective.

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Keywords

Banana fibers, polyester composites, chemical treatment, modulus, phase transition temperature

1. Introduction

Polyesters of several diverse types are useful as polymers. Polyester resins are widely used in construction, transportation and marine applications. Network formation distinguishes polyester resins from linear (thermoplastics) polyesters such as PET (polyethylene terephthalate). Cross-linking is achieved either by use of polyols such as glycerol, as in the case of saturated polyesters (glyptal), or by the use of unsaturated di-carboxylic acids, such as maleic anhydride in the case of unsaturated polyester resins. Extensive research work has been carried out by

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scientists to improve mechanical and thermal properties of thermoplastics and thermosets. This is done by reinforcing these resins with synthetic or natural fibers. 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. Synthetic fibers like glass and carbon are good reinforcement materials but due to their high cost and high-energy requirement in their production, they are less suited for common applications. Cellulosic fiber obtained from the pseudostem of the banana plant (*Musa sapientum*) is a suitable fiber with relatively good mechanical properties [1]. The high cellulose contents (64%) and low microfibrillar angle (11°) of banana fiber indicates that it has a potential as a reinforcing material [2]. Besides the toughness and wood texture [3] of the composites using these fibers, the energy requirement in their production is low, which is a considerable engineering advantage.

As the use of polymer products in general, and of composites in particular, is increasing day by day, the dangers they pose to the environment are also increasing. Most of the polymer composites have glass fiber as reinforcement. As glass fibers/fabric are non-degradable, the disposal of the composites containing them as reinforcement is a difficult problem. Moreover, the fibers are non-renewable. At present, the trend is slowly changing towards using natural fibers as reinforcements. The composites made with natural fiber reinforcements are known as 'green composites' [4]. The products produced using these fibers may be used in structural and other applications. Compared to inorganic fibers, the main advantages of these fibers are their low cost, low density, high specific strength and modulus, renewable nature and comparatively easy processibility [5]. Properties of fiber-reinforced composites depend on many factors, such as fiber aspect ratio, and fiber orientations as well as stress transfer efficiency of interfaces [6–8]. The most advantageous properties can be achieved by chemical modification of the matrix or the fiber that brings about higher interaction between the fiber and the matrix. Modifications of the fiber by several chemical methods has been carried out: treatment with alkali-like NaOH silanes, acetic acid, etc. have all been proved to be satisfactory ways of improving fiber/matrix adhesion.

The aim of the present study has been to investigate the effect of chemical modification of fibers on the mechanical properties (modulus and mechanical loss factor) and the phase transformation temperature of the material — properties that indicate the structural and thermal stability of the material. It has also been aimed to correlate the earlier studied mechanical [9, 10] and thermal [11] properties of the composite with the same chemical modification of the fibers reinforcing the polyesters using the data obtained from the present study using a Dynamic Mechanical Analyzer. In our studies we are using polyester composites of banana fiber having total volume fraction 0.4 of the fiber in all composites.

2. Material Preparation

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-methacryloxypropyltrimethoxysilane), A151 (vinyltriethoxysilane) and A1100 (γ -aminopropyltriethoxysilane) were obtained from Sigma-Aldrich, India. NaOH and all other chemicals were of commercial grade.

2.1. Preparation of Composites

Banana fibers were neatly separated by hand, adhering pith, if any, was removed and fibers were cut to uniform size of 30 mm 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. Composite sheets were prepared by impregnating the fiber with the polyester resin to which 0.9 (vol%) 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 h, samples were post-cured for 48 h 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.

2.2. Fiber Surface Modifications

2.2.1. Silane Treatment for Cellulose Fibers

An amount representing 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 about the complete hydrolysis of the silane by the addition of acetic acid or NaOH depending on the respective silane used. Neatly separated and cut cellulose fiber was dipped in the above solution and was allowed to remain there for $1\frac{1}{2}$ h. 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. The chemical structures of the various silane are as shown in the Fig. 1.

Silane coupling agents are successfully used with fillers and reinforcements that have reactive $-\text{OH}$ groups on the surface. The adhesion is determined by the composition of the organo-functional group of the silane, which determines 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 (Fig. 2) that further react with $-\text{OH}$ groups of the cellulose.

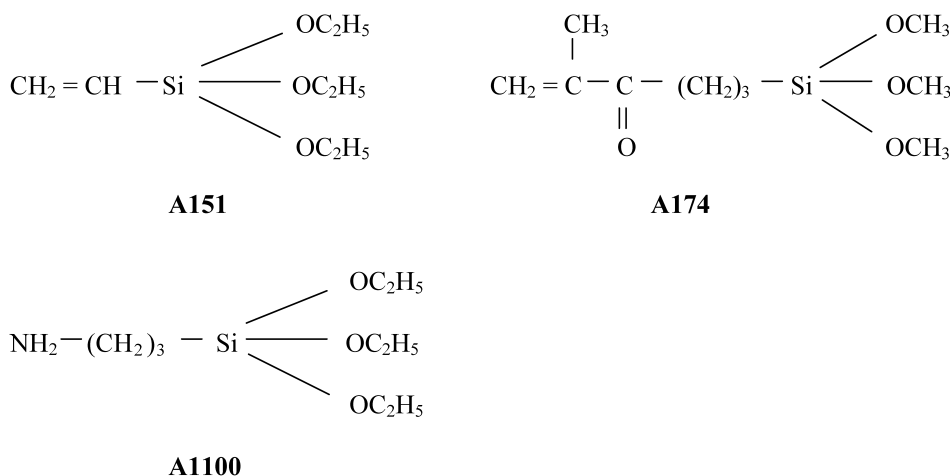


Figure 1. Chemical structures of the various silane.

The organo-functional groups of the silanes in turn form an interpenetrating polymer network with the polyester.

2.2.2. Treatment With NaOH

Cleaned and well separated cellulose fibers were dipped in 0.5% and 1.0% solutions of NaOH for half an hour and then washed in very dilute acid to remove any traces of alkali. Washing was continued till the fibers were alkali free. The washed fibers were then dried in the oven at 70°C for 3 h.

Banana fiber surface was treated with alkali of different concentrations to produce a treated fiber that enhances adhesion between fiber and matrix; this was used for the preparation of composites. The probable reaction involved in alkali treatment is



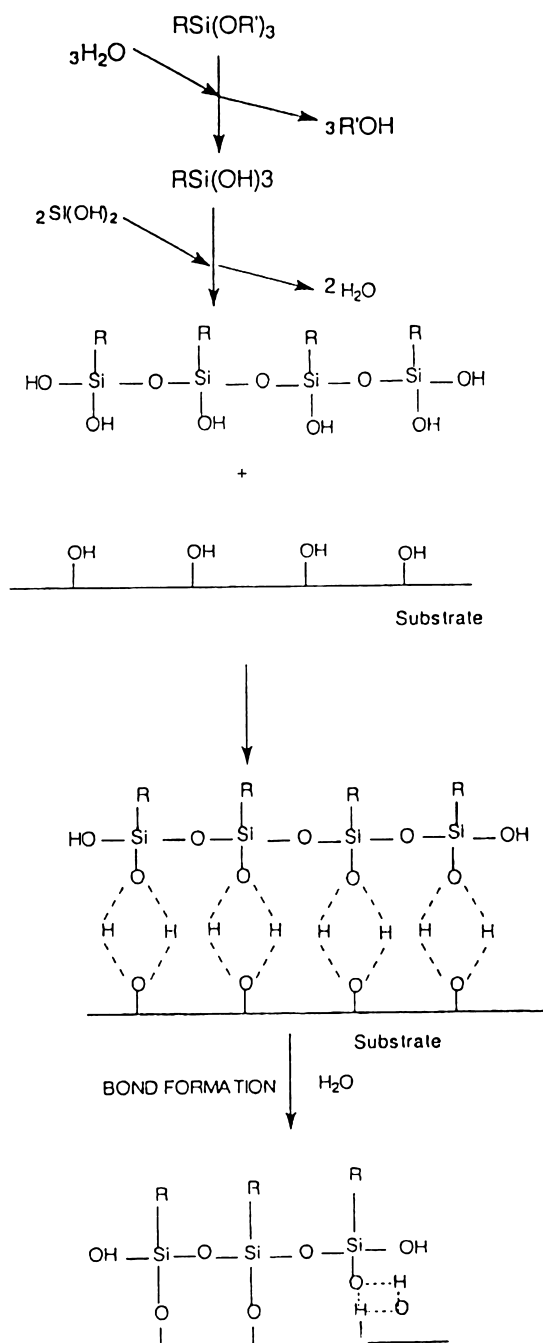
The NaOH treatment removes practically all non-cellulose components and increases the polarity [1] of the fiber. The effectiveness of NaOH in modifying the surface of natural fibers has already been discussed in literature [12].

2.2.3. Treatment With Acetic Anhydride

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 sulfuric acid for 5 min, washed in distilled water and then dried.

The probable reaction between the fiber and acetic anhydride can be represented as:



**Figure 2.** Interaction of silane with cellulose.

3. Experimental

DMA is a sensitive technique that characterizes the mechanical response of materials by monitoring property change with respect to the temperature and frequency of applied sinusoidal stress. In this instrument, a sinusoidal stress is applied to a sample and the amplitude and phase of the resultant displacement are measured [13]. By measuring both the amplitude of the deformation at the peak of the sine wave and the lag between the stress and strain sine waves, quantities like the modulus, viscosity and the damping can be calculated.

This technique separates the dynamic response of materials into two distinct parts: an elastic part (E') and a viscous component (E''):

$$E^* = E' + iE'',$$

where complex modulus E^* is defined as the instantaneous ratio of the in-phase or elastic response E' (which is proportional to the recoverable or, stored energy) and viscous response E'' (which is proportional to the irrecoverable or, dissipated energy).

Mechanical loss factor ($\tan \delta$) is another useful parameter, which can be very useful in order to compare viscoelastic responses of different materials. This factor is given by

$$\tan \delta = E''/E',$$

where $\tan \delta$ (damping factor) is the ratio of energy dissipated to energy stored. This property is indicative of how efficiently the material loses energy to the molecular rearrangement and internal friction.

Samples to be used in DMA were cut into the size between 4–6 mm in width and 20 mm in length to conform to the dimensional limits for single cantilever bending clamp fixtures. The average thickness for each sample was based on separate measurements, taken at the two ends. After mounting the sample in a single cantilever bending clamp, the furnace was sealed off, then scanned over a temperature range from room temperature to 180°C. The sample was held at that temperature for 5 min. The heating rate was 2°C/min for all temperature scan tests. Frequency of oscillations was fixed at 1 Hz and strain amplitude 0.01 mm within the linear viscoelastic region. The storage modulus E' , loss modulus E'' and mechanical loss factor ($\tan \delta$) have been determined during the test as a function of increasing temperature.

4. Results and Discussion

The variation of modulus and $\tan \delta$ vs. temperature of banana fiber-reinforced polyester composite for different fiber treatments are shown in Figs 3 and 4. Figure 3 shows the temperature dependence of modulus of various samples treated with different chemicals. The moduli reported herein are the loss and storage modulus of the material which depend upon various factors like chemical treatment, fiber length,

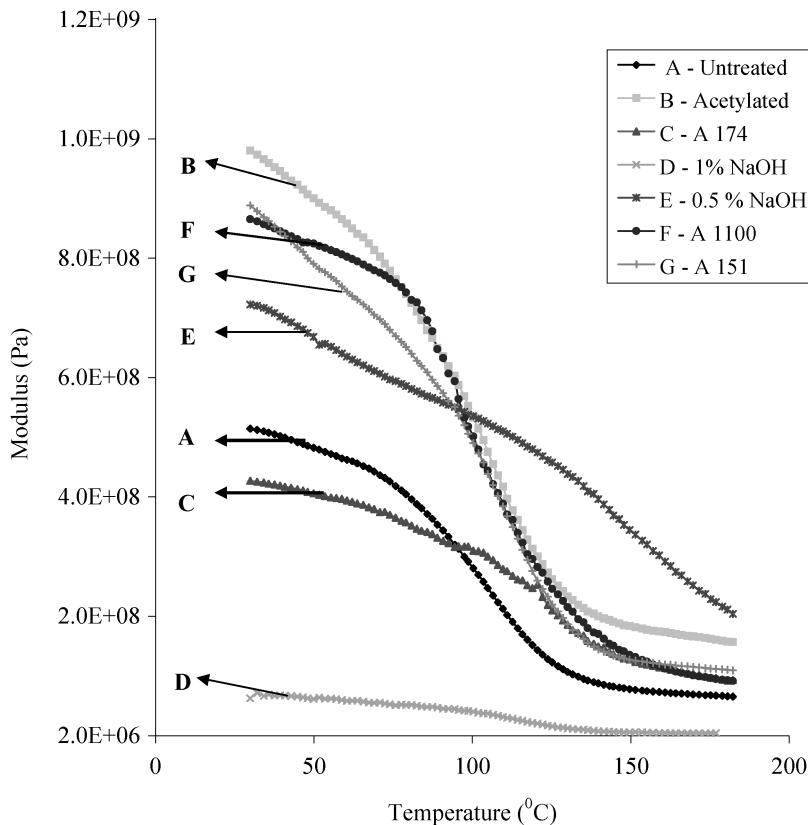


Figure 3. Plot of modulus vs. temperature of the treated and untreated banana fiber-reinforced polyester composites.

fiber orientation, etc. which is due to the effective transfer of internal stresses and strains developed in the fiber–matrix contact region. In view of this, all the factors except chemical treatment are identical for all the samples and have no effect on modulus. In case of NaOH-treated fiber, the lignin between the fibers gets dissolved and thereby induces a better packing of cellulose chains. So, mobility of molecular segments is restricted due to increased contact between the fiber and matrix, which results in the lower values of modulus.

On the other hand, increase in strength and modulus of composite containing fibers treated by acetylation and silane treatment is explained as follows.

The hydrophilic fiber –OH group increases the strength of the chemical interlocking at the hydrophilic centers of the polymer resin. Thus, effective stress transfer takes place at the interface between fiber and matrix that may enhance the modulus due alleviation of strain in the material. But in case of A174, some of these hydrophilic –OH groups are replaced by hydrophobic centers, which lead to easy debonding of the fibers [14, 15]. This results in decrease in values of modulus and strength.

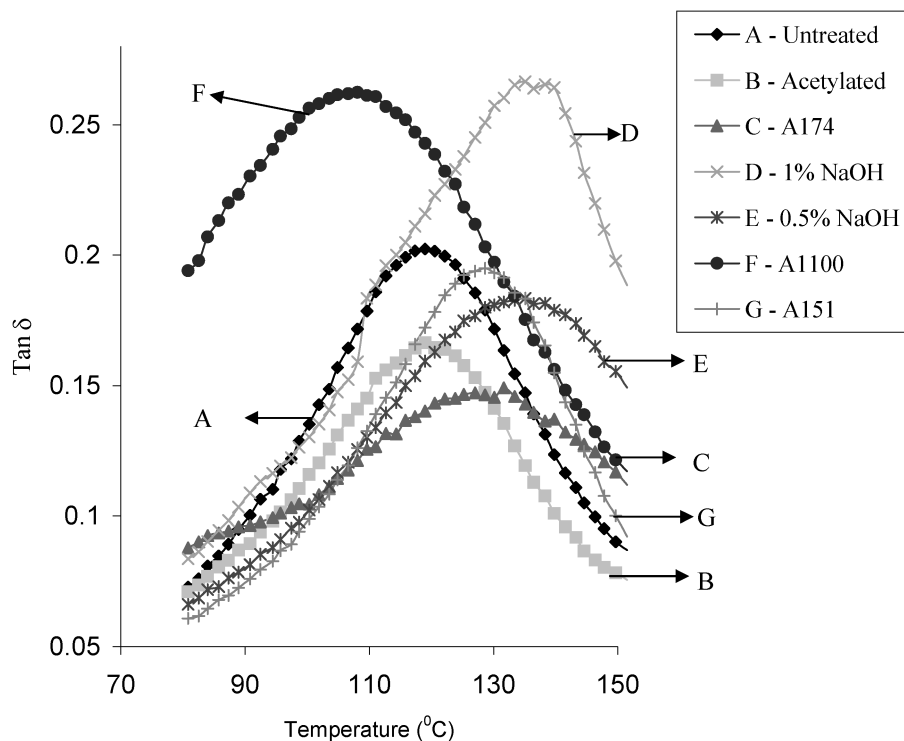


Figure 4. Plot of $\tan \delta$ vs. temperature of the treated and untreated banana fiber-reinforced polyester composites.

The observed variation shows a demarcation into three temperature regions, which can be explained as follows.

Region I: From Room Temperature to 60–70°C

As temperature increases, modulus shows a small decrement for all samples. This fact can be explained with the help of the Crankshaft model [13], which treats the molecule as a collection of molecular segments that have some degree of free movement. Therefore, in this region, the molecules are tightly compressed and have less possibility of free movement in all directions that is observed by the slow decrement in modulus.

Region II: From 60 to 130°C

The modulus shows a sharp decrease with increase in temperature. As the temperature is increased, the material starts expanding and an increase of free volume takes place. This increase in the free volume enhances the movements of side chains and localized bonds resulting in the bending and stretching of side chains over the polymer backbone. Therefore, the mobility of molecular chain segments increases, which in turn reduces the modulus of polymer composites.

Region III: Beyond 130°C

Beyond this temperature, the material attains the maximum mobility of the molecular chain segments producing a constant value of modulus. The constant value of modulus also ensures no further bending and stretching of the side chain over the polymer backbone.

The plot of $\tan \delta$ (mechanical loss factor) vs. temperature is shown in Fig. 4. The values of $\tan \delta$ increase up to a characteristic temperature (T_p) and then gradually decrease with further increase in temperature. As discussed above, an increase in free volume with temperature results in movement of large segments of the chain. Beyond this temperature (T_p), materials assume a rubbery state and therefore, movement of segments become slaky, which results in decrease in $\tan \delta$, and the value becomes constant at a slightly higher level than the minimum value observed in the temperature range from room to 60–70°C.

It has been found that the surface of the banana fiber exhibits the presence of the waxy layers, which may reduce the adhesion of the fibers with the matrix resin. There are reports [9] that the fiber–matrix adhesion plays an important role in overall performance of the composites which also influences the effect of different treatment. The phase transition temperature values of untreated and treated fiber polyester composites are presented in Table 1.

4.1. Silane-Treated Cellulose Fiber

The effect of treatment with three silanes on the variation of $\tan \delta$ with temperature has been studied. The transition temperature of silane A151 (vinyl triethoxysilane) was found to be the highest (129.1°C) as compared to A174 (127.03°C) and A1100 (108.6°C) as indicated in Table 1. This higher value is attributed to the improved acid–base interaction between the organo-functional group and the polyester matrix. It is noteworthy that the increased acidity values [16] lead to increase in the polarity and thereby improved interactions as compared to other silane-treated fiber composites. It is possible that silanes formed by the hydrolysis of the alkoxy groups

Table 1.

Phase transition temperature of the treated and untreated fibers-reinforced polyester composites

S. No.	Polyester composite	T_p (°C)
1	Untreated	120.5
2	A151	129.1
3	A174	127.03
4	A1100	108.6
5	0.5% NaOH	131.4
6	1% NaOH	136.4
7	Acetylated	122.6

of the silanes can self condense to form a thick layer of oligometric silanol deposition at the fiber–matrix interface which can greatly reduce the efficiency of bonding. This further shifts the transition temperature to a lower temperature, namely 108.6°C of A1100 treated composite.

4.2. Cellulose Fiber-Treated With Sodium Hydroxide

A variation of $\tan \delta$ with temperature shows that phase transition temperature (136.4°C) is maximum for the composite prepared from the fibers that had been treated with higher concentrations of alkali, i.e. 1% NaOH as compared to fibers treated with 0.5% NaOH (131.4°C). This is because, with alkali treatment of the fibers, the cementing materials, that is, the lignins between fibers get dissolved. The interfibrillar region becomes less dense (more porous) and less rigid. Crystallinity of alkali-treated fiber increases because of the removal of the cementing materials that leads to a better packing of cellulose chains [17]. The free pores improve the contact between fiber and the matrix. The dissolution of cementing material also leads to increased polarity, due to the increased polar–polar interaction with the matrix leading to a higher value of transition temperature.

On the other hand, the polyester particles sticking on the fiber surface and the broken fibers offer improved fiber–matrix adhesion. Tensile strength and tensile modulus are both maximum for alkali-treated fiber composites [16].

4.3. Acetylated Cellulose Fiber

Acetylation has been proved to be an effective method for the modification of cellulose fiber surface. Acetylation has rendered the fiber surface rougher. This enhances the adhesion between fiber and matrix and hence phase transition temperature has been found to be at 122.6°C as shown in Table 1.

4.4. Comparison of the Effectiveness of Different Treatments

Silanes with different organo-functional groups (vinyl, methacryloxy and amine) have improved acid–base interaction between the organo-functional group and polyester matrix as compared to acetylated cellulose fiber. It is clear from Table 1 that maximum phase transformation temperature (129.1°C) is found for the silane with a vinyl functional group whereas acetylation of fiber shifts the phase transition temperature to 122.6°C. Alkali treatment has been proved to be the best as a result of the improvement of packing of cellulose chains and increased polar–polar interaction with the matrix. Maximum phase transition temperatures were found for the alkali-treated polyester composites.

5. Conclusion

Surface modifications by various chemical treatments lead to good interfacial strength and thereby improvement in mechanical properties of natural fiber composites and also shift the phase transition to higher temperature. The improvement in

mechanical properties (maximum phase transition temperature) due to alkali treatment is mainly due to better packing of cellulose chains, after the dissolution of lignin, which acts as cementing material. These studies are consistent with mechanical and thermal transport properties such as thermal conductivity and thermal diffusivity of the composites as reported by other authors.

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