# Dynamic Mechanical Properties of Cotton/Polypropylene Commingled Composite Systems

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**ABSTRACT:** The dynamic mechanical properties of cotton/polypropylene (PP) commingled composite system was studied with reference to the fiber content, chemical treatments with potassium permanganate and maleic anhydride modified PP, processing conditions and applied frequency. Side by side commingling of matrix and reinforcing fibers was adopted for the fabrication of composite laminates as they provide the shortest melt flow distance during the melting of matrix fibers. This method can also be used for the recycling of textile wastes. The storage modulus was found to increase with the fiber content across a range of temperatures. The loss factor was found to decrease with the increase in fiber content while the glass transition temperature increases. The chemical treatments increase the value of storage modulus. A master curve was constructed and also made a comparison between the experimental results and the theoretically predicted values. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 2624–2631, 2009

**Key words:** composites; poly(propylene)(PP); structure-property relations; dynamic mechanical analysis; commingling

## INTRODUCTION

Thermoplastic matrix composites (TPC) possess many advantages compared to thermoset matrix composites. Some of them are their higher fracture toughness, unlimited shelf life, good solvent resistance, recyclability and fast, clean and automated processability.[1] But the higher viscosity of the molten thermoplastics (500–5000 Pa s) compared to thermosets (100 Pa s) make some difficulties in the processing steps.[2] This affects the wetting and impregnation of the reinforcing fibers by the molten matrix and hence lowers the consolidation quality of a composite laminate. Some partially impregnated intermediate materials are required for the more efficient manufacturing of TPCs.[3] One way to obtain good impregnation is to use hybrid yarns, which give close contact between the reinforcement and matrix fibers.[4] This results in small flow paths for the molten TP matrix. Better impregnation can be attained by selecting TP fiber and reinforcement fiber with comparable diameters.[5] The consolidation consists of three important stages. They are coalescence of molten matrix, flow of matrix within and out of the reinforcing tows and void reduction by the application of pressure. The entrapped gases dissolve into the matrix in the void reduction phase.[6]

Natural fibers offer good opportunities as reinforcement materials for composites as they have good mechanical properties. These renewable raw materials have low density and possess high specific strength and modulus. They have ecological and environmental advantages over plastic reinforcements. Low cost, biodegradability, nonabrasiveness, generation of rural/agricultural economy etc. are the added advantages of natural fibers in composite manufacturing industry. Low processing temperatures, moisture absorption and poor wettability and adhesion with synthetic resins are their disadvantages. These factors may lower their strength, stiffness and environmental resistance. Various treatments and modifications are possible to increase the strength and environmental resistance of natural fiber reinforced plastic materials.[7–12]

In this study textile cotton yarn was used to develop hybrid yarns with polypropylene (PP) and hence to fabricate commingled composite laminates. Cotton plant (*Gossypium*) is a shrub native to tropical and subtropical regions around the world including the America, India, and Africa. The fiber is most often spun into thread and used to make soft textile clothes. When processed to remove seeds and traces

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of wax, proteins etc., the cotton consist of pure cellulose. The cellulose is arranged in a way that it gives a high degree of strength and durability to cotton fibers. Each fiber is made up of 20–30 layers of cellulose units coiled in a series. The kinking and interlocking makes them ideal for spinning.

The studies on the dynamic mechanical properties of the fiber reinforced plastics are of great importance as they undergo various types of dynamic stresses during the service. The physical and mechanical properties of a polymeric material are strongly dependent on its structure, morphology, and relaxation process.[13] Properties of matrix, reinforcement and their interface affect the voids and hence the consolidation quality.[14] Dynamic mechanical analysis (DMA) can be used to determine the viscoelastic properties of a composite. DMA has been widely employed for the determination of the interfacial characteristics of heterogeneous polymeric systems. Storage modulus gives an insight into the stiffness behavior and load bearing capability of a composite material.[15] It is a measure of the maximum energy stored in the material during one cycle of oscillation. Loss modulus is proportional to the amount of energy dissipated as heat by the sample. The mechanical damping coefficient is the ratio of the loss modulus to the storage modulus and is related to the degree of molecular mobility in the polymeric material. The glass transition temperature $T_g$ can be measured as the maximum of the transitions in the loss modulus or tanδ curve at low frequencies.[16]

The main goal of the present work is to analyze the effect of fiber content and chemical treatments (maleic anhydride modified PP and potassium permanganate) on the dynamic mechanical behavior of cotton/PP composites fabricated by their side by side commingling.

## EXPERIMENTAL

### Materials

Sanghi Polyesters Limited, Andhra Pradesh, India, kindly supplied the PP fibers used for this study. PP yarns used for the study have their denier value in the range of 790–800, fractional elongation of 0.266 and tenacity of 3.33 g per denier. The number average molecular weight of PP was $5.2 \times 10^4$ g/mol and weight average molecular weight was $3.1 \times 10^5$ g/mol. Commercially available "Vardhman" cotton threads (ART A-501) of Mahavir Spinning Mills, Ludhiana, India were used as reinforcement fibers. They have a specific density of 1.520, a breaking strength of 3.0–4.9 g per denier and breaking elongation of 8–10%. Other reagents used were of analytical grade.

**Figure 1** Winding machine developed to mingle and to wind the matrix and the reinforcing fibers on metal plates with a good alignment. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

### Fabrication of composite laminates

#### Winding and processing

To meet the difficulty of mingling the natural fibers and PP with proper fiber alignment, we designed and developed a winding machine to commingle and to wind them on a metal plate (Fig. 1). Initially the spools of the two different fibers were placed on holders. They were then allowed to mingle at a common point and by rotating the handle of the machine it was wound on the metal plate. When the winding reaches at one end of the plate, the lever is used to change the direction of the winding. The square shaped plate can be put in 90° opposite direction for the winding in a perpendicular path to the initial winding. For DMA analysis $[0_{12}/90_{12}]$ winding pattern was adopted. The plate with the windings of mingled cotton and PP was then compression molded under the specified conditions. It was then cooled under normal room conditions and cut into laminates.

#### Fabrication of samples to study the effect of fiber content

In order to study the effect of fiber content on the dynamic properties of $[0_{12}/90_{12}]$ laminates of PP/cotton composites, both fibers were mingled in various ratios as given in Table I. The corresponding

**TABLE I**
**Fiber Mingling Ratio During the Winding and the Corresponding Weight Ratio**

| Ratio in which PP and cotton fibers mingled | Weight percentages | |
|---|---|---|
| | PP | Cotton |
| 3 : 1 | 86.3 | 13.7 |
| 2 : 1 | 80.8 | 19.2 |
| 1 : 1 | 67.8 | 32.2 |
| 1 : 2 | 51.2 | 48.8 |

mass fraction is also given. These laminate were then compression molded for a holding time of 6 min, under a pressure of 0.6 MPa at 210°C.

### Chemical treatments and modifications

*$KMnO_4$ treatment.* A $[0_{12}/90_{12}]$ layer pattern was adopted to fabricate samples to study the effect of various treatments. During the winding of each layer acetone was applied to remove the sizing from the fiber surface 0.1% solution of $KMnO_4$ in acetone was applied on each layer. The sample was put in a hot air oven at 40°C for half an hour to remove acetone from the surface of the fibers. It was then processed at 210°C under 0.6 MPa pressure for 6 minutes.

*Treatment with maleic anhydride modified polypropylene (MAPP).* The number average molecular mass of Maleic Anhydride grafted PP used for coupling was 7000 g/mol. Initiator–dicumyl peroxide (0.1 g) was dissolved in 100 mL of acetone and 2 g of MAPP was added and applied on each layer during the winding on metal plates.

### DMA studies

DMA was done using a single cantilever bending system DMA. 2980 (TA Instruments) at a frequency of 1 Hz in nitrogen atmosphere. The dynamic storage modulus ($E^1$), loss modulus ($E^{11}$) and loss factor (tanδ) of the specimens were determined as a function of temperature from −70 to 160°C at a heating rate of 2°C/min.

## RESULT AND DISCUSSION

### Effect of fiber content on $E^1$ and tanδ

The dynamical mechanical properties of $[0_{12}/90_{12}]$ layered PP-cotton commingled composite were observed. The variation of storage modulus with fiber content as a function of temperature is depicted in Figure 2.

As the temperature increases the matrix softens and hence the storage modulus of neat PP and that of the composite decreases. As the temperature is increased, matrix molecules relax to the possible conformations. The thermal expansion occurs and it results in a decrease in intermolecular forces. In composites, the decrease is partially compensated by the rigidity of the fibers. At low fiber loadings, the matrix is not restrained by enough fibers and strain develops on matrix even at low stresses and it deteriorates the bonding with the fibers. The storage modulus is enhanced by the addition of further amount of fibers into the system. The influence of fiber content can be explained in terms of the relative (normalized) storage modulus ($Ec^1/Em^1$, the ratio of the storage moduli of the composite and matrix) with temperatures at different fiber loadings (Fig. 3). It can be observed that storage modulus of the composite increases with fiber loading. The restriction for the flow of the matrix increases with an increase in the fiber loading. Table II gives the variation of the modulus retention term of the composite with fiber volume fraction. It is clear from

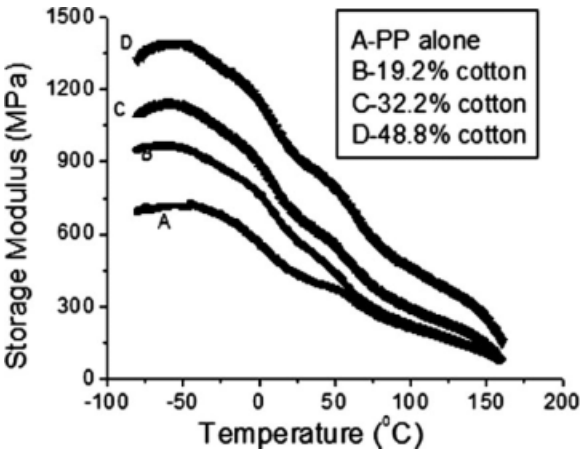



**Figure 2** Effect of fiber loading (wt %) on the storage modulus at various temperatures.

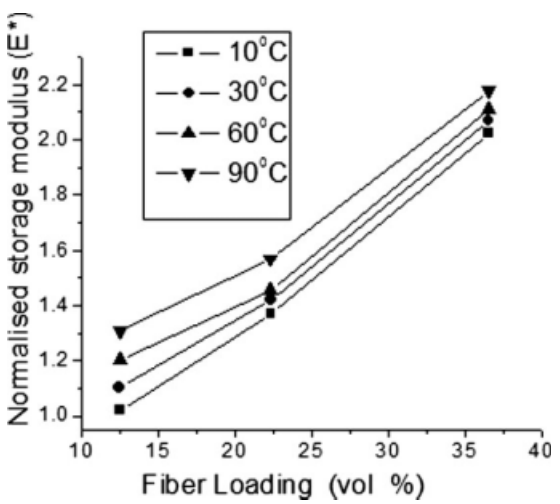



**Figure 3** Variation of normalized storage modulus ($E^*$) of cotton/PP composites at different fiber loadings.

**TABLE II**
**Variation of Modulus Retention With the Cotton Fiber Content**

| Fiber volume (%) | $(E_{30}^1/E_{10}^1) \times 100$ | $(E_{60}^1/E_{10}^1) \times 100$ | $(E_{90}^1/E_{10}^1) \times 100$ |
|---|---|---|---|
| 0 | 79.8 | 64.9 | 43.3 |
| 12.49 | 80.0 | 54.8 | 35.2 |
| 22.36 | 81.6 | 61.4 | 40.5 |
| 36.56 | 86.0 | 68.7 | 46.7 |

the table that the value of the modulus retention increases with the fiber content.

In the tanδ versus temperature graph (Fig. 4), the first maximum gives the glass transition temperature of the amorphous part in PP. On increasing the temperature, the value drops and then a second peak appears due to the rigid amorphous molecular segments present in the crystalline system. The tanδ value is found to be highest for the neat PP. This is due to the free movement of PP chains during the relaxation process. But in the composite the fiber restricts this movement and hence the intensity of the peak decreases. The position of the peak shifts to the higher temperatures with the increase in the fiber content. The restriction in the free movement of PP chains increases the value of the glass transition temperature.

### Effect of chemical treatments on $E^1$ and tanδ

The effect of chemical treatments with $KMnO_4$ and MAPP on the $E^1$ and tanδ at various temperatures are given in Figures 5 and 6. Both the treatments increase the storage modulus of the system compared to untreated ones. This is due to the increase in the interfacial adhesion between the fiber and matrix. From the figure it is evident that MAPP treatment is more effective in improving the storage

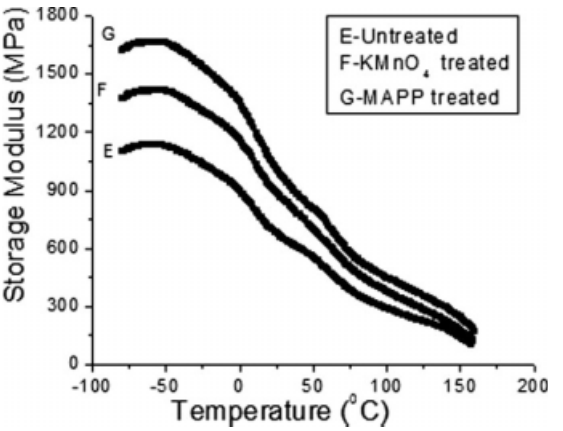



**Figure 5** Effect of chemical treatment on the storage modulus at various temperatures.

modulus of the system. The mechanism of the permanganate induced grafting of PP on cotton fiber is given in Scheme 1.

On treating with MAPP, the PP segment forms a compatible blend with the bulk PP through co-crystallization. The polar part, that is, the acidic anhydride group forms hydrogen bonds and chemical bonds with the hydroxyl group of the cellulose through esterification. Thus the coupling agent is strongly anchored on the fiber. The mechanism of the above is given in Schemes 2 and 3.

Treatment with MAPP is also helpful in reducing the fiber hygroscopicity as it decreases the quantity of highly hydrophilic hydroxyl groups of the cellulose. Dicumyl peroxide is a free radical generator and induces the formation of radicals on fiber and matrix and favors the coupling.

The tanδ peak is more intense for neat PP compared to the treated and untreated composites. It gives an idea about the damping behavior of the materials. In neat PP, the freedom for the movement

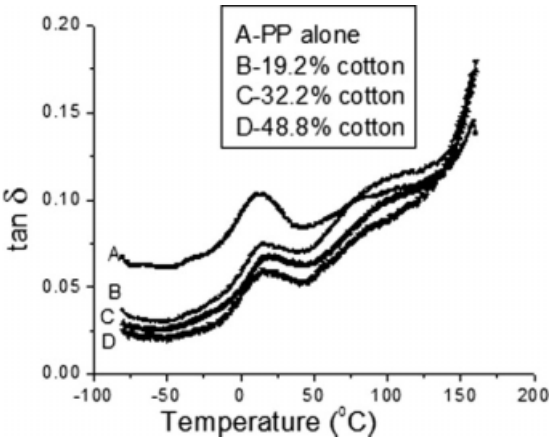



**Figure 4** Effect of fiber loading (wt %) on the damping factor (tanδ) at various temperatures.

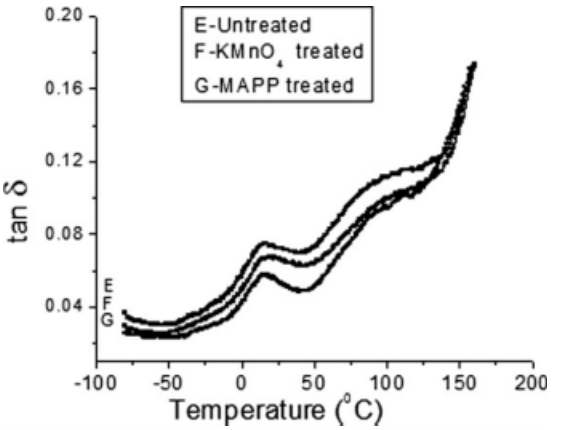



**Figure 6** Effect of chemical treatment on the damping factor (tanδ) at various temperatures of composite containing 32.2 wt % cotton.

$$\text{Cellulose–H} + \text{Mn(III)} \rightarrow \text{Cellulose–H–Mn(III)(Complex)}$$
$$\text{Cellulose–H–Mn(III)(Complex)} \rightarrow \text{Cellulose}^{\cdot} + \text{H}^{+} + \text{Mn(II)}$$
$$\text{Cellulose} + \text{PP} \rightarrow \text{Cellulose PP}$$
$$\text{Cellulose PP} + \text{nPP} \rightarrow \text{Cellulose PP}_{n+1}$$
$$\text{Cellulose PP}_{n+1} + \text{Mn(III)} \rightarrow \text{Cellulose PP}_{n+1} + \text{Mn(II)} + \text{H}^{+}$$

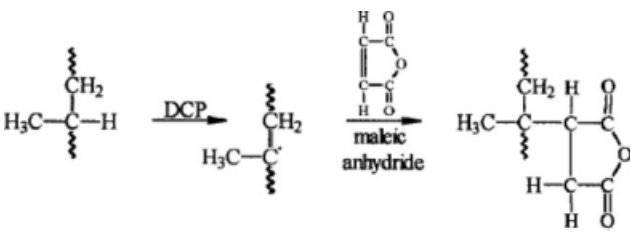
**Scheme 1** Mechanism of permanganate induced grafting of PP on cotton fiber.

of molecular chains dissipates some energy. As the reinforcing fibers hinder it, the intensity of the tanδ peak diminishes with the fiber content. As chemical treatments enhance the bonding between the matrix and the fiber, a reduction in the movement of PP molecules and hence a decrease in tanδ peak occurs. In MAPP, maleic anhydride groups are grafted on to the PP backbone. The increase in modulus and the decrease in loss factor are due to the esterification reaction between the cellulosic hydroxyl group of cotton fiber and the anhydride part of MAPP, which causes a reduction in the interfacial tension and an increase in the interfacial adhesion between the PP and cotton fiber. An increase in adhesion reduces the chance for both the fiber pull out and the debonding of fiber and matrix. The SEM photos given in Figure 7(a,b) shows reductions in fiber pull out by the chemical treatment with the MAPP compared to the untreated samples. The improved adhesion by fiber-matrix bonding transfers the stress efficiently from the matrix to fiber and leads to an improvement in the reinforcing effect.

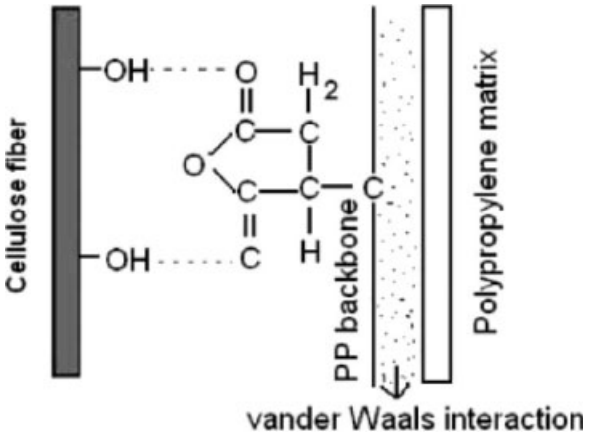
The glass transition temperature is increased by chemical treatments with $KMnO_4$ and MAPP. This is due to the increase in activation energy for the molecular relaxation of PP chains in a restricted environment caused by chemical bonding between the fiber and matrix. The covalent interaction between the MAPP and cellulosic surface raises the $T_g$ slightly.

### Effect of applied frequency on $E^1$ and tanδ

Figure 8 gives the variation of storage modulus with temperature at three different frequencies. It is found that the storage modulus increases with an




**Scheme 2** The mechanism for the formation of maleic anhydride modified PP.




**Scheme 3** Model for the formation of the interphase between MAPP and hydroxyl group of cellulose present in a natural fiber.

increase in applied frequency at all temperatures. Thus at higher frequencies the cotton fiber reinforced PP behaves like a stiff solid material with a high modulus.

In Figure 9 the temperature dependence of tanδ for cotton/PP composites with three frequencies 0.1, 1, and 10 Hz are given. The intensity of tanδ peak

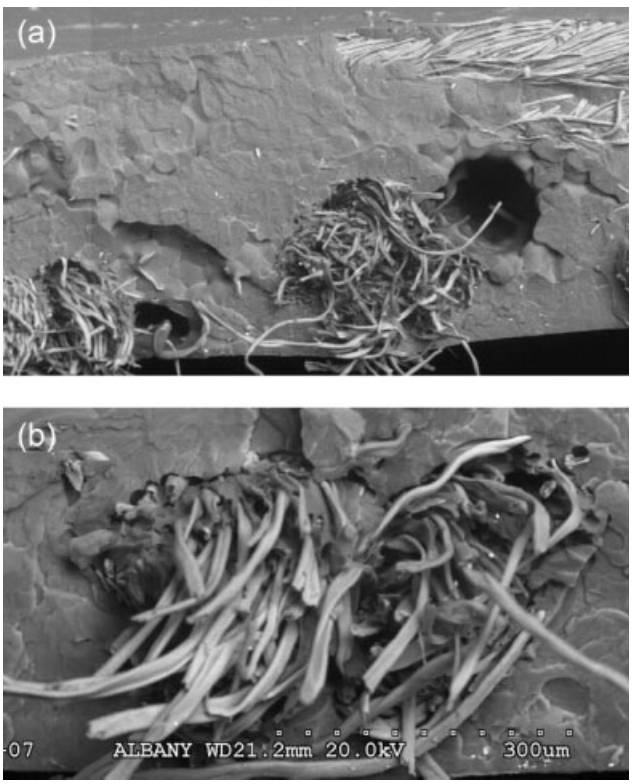



**Figure 7** (a) and (b) SEM photographs of the broken surface of untreated and MAPP treated cotton/PP commingled composite specimen. (a) Fiber pull out occurs for the untreated samples. (b) In treated sample breakage of fiber occurs at failure.

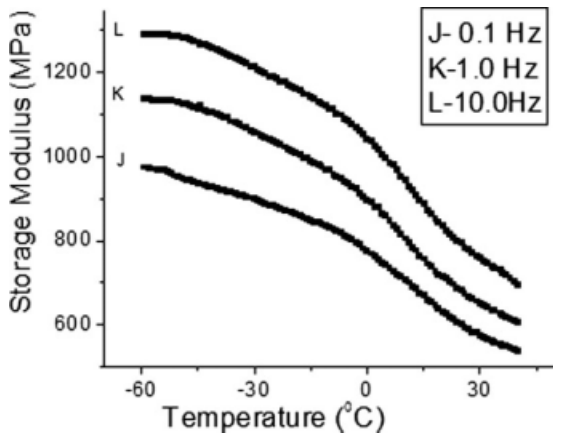



**Figure 8** Effect of frequency on the storage modulus at various temperatures.

decreases and the relaxation peak temperature increases with the increase in applied frequency. The damping peak is associated with the partial loosening of the polymer structure so that the movements of chain segments occur.

It is possible to interrelate the temperature at which a relaxation process is observed (T) with the frequency of the excitation (f) by the Arrhenius equation,

$$f = f_0 \exp \frac{-E_a}{\mathrm{RT}} \quad (1)$$

where $f_0$ is a constant, $f$ is the frequency of the test, $R$ the gas constant and $E_a$ the activation energy for the relaxation process. A plot of log f versus 1000/T gives a straight line with a slope that is proportional to the activation energy for the relaxation process of the composite system. The calculated values of the activation energies are given in Table III. It can be deduced from the table that activation energy of PP relaxations increases by the presence of cotton fibers.

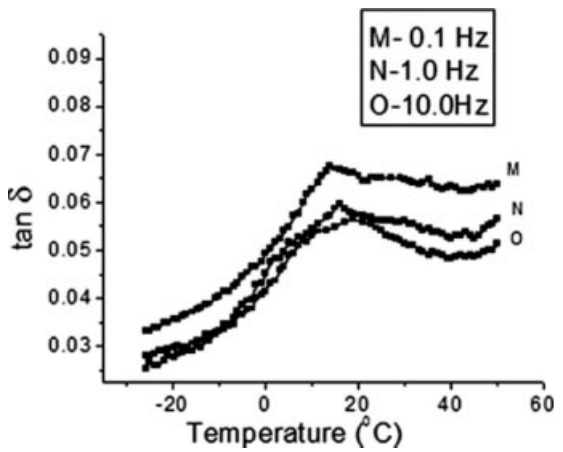



**Figure 9** Effect of frequency on the damping factor (tanδ) at various temperatures.

**TABLE III**
**Energy of Activation of Various Cotton-PP Composites**

| Sample | Activation energy (kJ/mol) |
|---|---|
| PP | 28.46 |
| 0.1249 $V_f$ (untreated) | 33.87 |
| 0.1249 $V_f$ (permanganate treated) | 37.84 |
| 0.1249 $V_f$ (MAPP treated) | 40.55 |

The chemical treatment further increases the value of the activation energy.

### Application of time-temperature superposition principle to the composite

W.L.F. equation can be used to describe the time-temperature behavior of a polymeric material around the glass transition region. It is assumed that the free volume increases linearly and the viscosity drops with the increase in temperature. According to time-temperature superposition principle viscoelastic property data collected at a given temperature can be superimposed with that collected at different temperatures by shifting the curves using shift factors. $E^1$ versus log time graph is plotted (Fig. 10) and the modulus curve at a particular temperature was shifted along the time axis until it overlaps with the reference curve. Values of shift factor log $a_T$ are obtained from the distance between the curves. It gives the rate of relaxation at some temperature in comparison to that at a higher temperature. Shift values at various temperatures were determined by taking 90°C as the reference temperature (Fig. 11). This principle can be used to predict the viscoelastic behavior of a material.

### Cole–Cole plots

The homogeneity of a material is indicated by the behavior of the Cole–Cole plots. A homogeneous

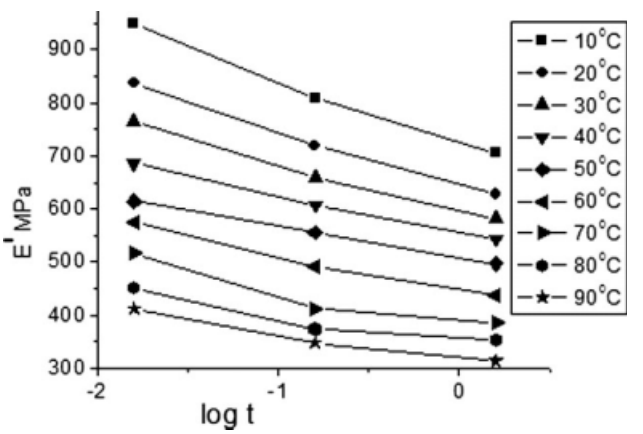



**Figure 10** $E^1$ versus log time graph for temperatures from 10 to 90°C.

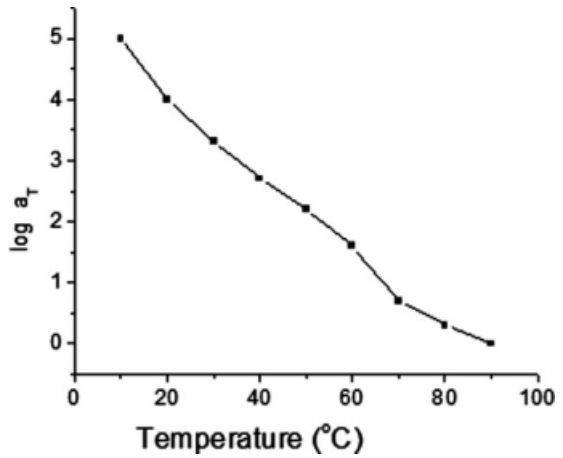



**Figure 11** log $a_T$ versus temperature graph.

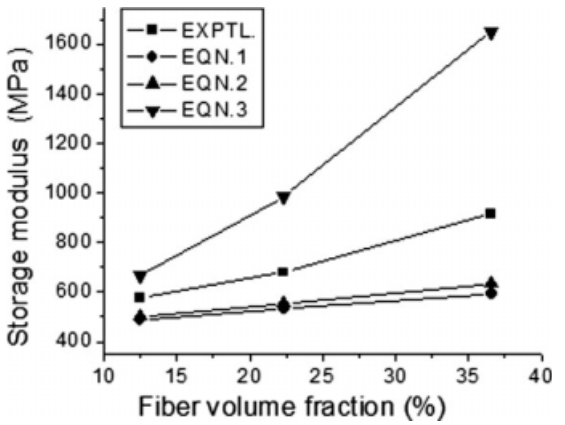



**Figure 13** Plots of experimental and theoretical storage modulus values against fiber loading at 1 Hz frequency.

polymeric system gives a semicircular diagram. Figure 12 gives the Cole–Cole plots obtained by plotting log $E^{1I}$ against log $E^{1}$ of untreated, $KMnO_4$ treated and MAPP treated composite samples. The imperfection of a semicircle indicates the heterogeneity of the system.

### Theoretical modeling of viscoelastic properties

Theoretical prediction of storage modulus

Several equations can be used to predict storage modulus of fiber reinforced composite systems. According to Einstein's equations

$$E_c = E_m(1 + V_f) \tag{2}$$

where $E$ is the storage modulus, subscripts $c$ and $m$ denotes the composite and the matrix and $V_f$ is the fiber volume fraction.

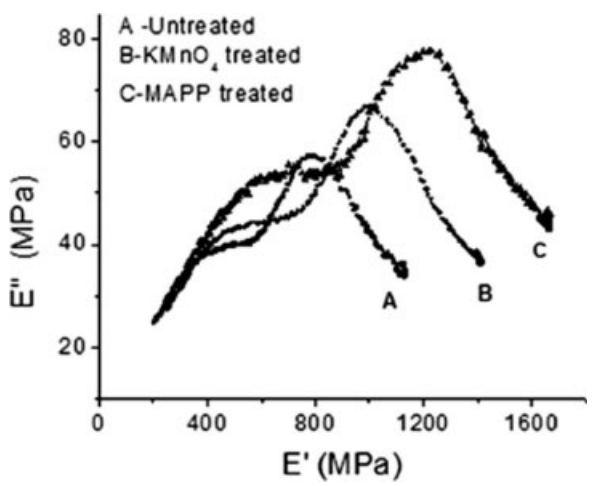



**Figure 12** Cole–Cole plots of untreated, permanganate treated and MAPP treated cotton/PP commingled composites.

As per the modified Einstein's rule,

$$E_c = E_m(1 + 1.25\ V_f) \tag{3}$$

Guth modified the Einstein's rule to

$$E_c = E_m(1 + 2.5\ V_f + 14.1\ V_f{}^2) \tag{4}$$

Figure 13 compares the theoretical and experimental values of the storage moduli at various fiber loadings. All the three theoretical models give storage moduli values comparable with the experimental data. But the value obtained by eq. (4) deviates much at high fiber contents. This may be due to the predominance of the square term in eq. (4).

Theoretical prediction of tanδ values

Predictive methods of damping behavior find much application in fiber reinforced plastic industry. Fibers and fillers usually decrease the damping factor (tanδ) as per the equation

$$\tan\delta_c = V_f \tan\delta_f + V_m \tan\delta_m \tag{5}$$

But for rigid inclusions, the first term due to the contribution by fibers can be neglected.[15,16]

Therefore eq. (5) changes to

$$\tan\delta_c = V_m \tan\delta_m \tag{6}$$

A stiffness term can be incorporated into the above equation by assuming that the matrix in the presence of fibers offers a stiffness equivalent to the minimum elastic modulus of the composite. This modification gives,

$$\tan\delta_c = V_m \left(\frac{E_m}{E_c}\right) \tan\delta_m \tag{7}$$

$E_m$ and $E_c$ are the storage moduli of the matrix and composite respectively. The plots of experimental

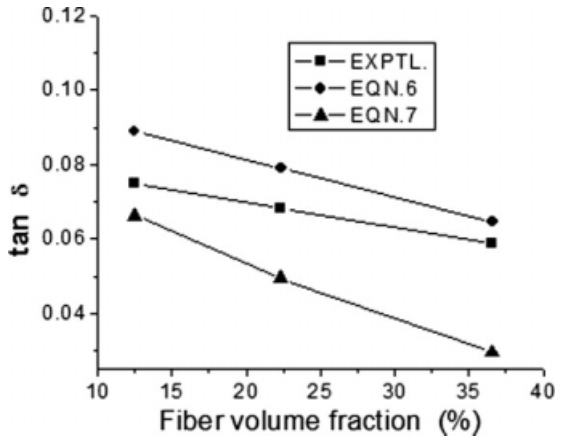



**Figure 14** Plots of experimental and theoretical tanδ values against fiber loading at 1 Hz frequency.

and theoretical tanδ values of untreated cotton/PP commingled composite against fiber loading at 1 Hz frequency is given in Figure 14. It can be seen from the figure that eq. (6) agrees better than eq. (7) with the experimental values at higher fiber loadings. The deviations may happen due to the omission of factors like the localized constraints imposed by the fibers on the matrix deformation, the transcrystalline growth, the presence of surface modifiers and finishers etc.

## CONCLUSIONS

DMA analyzes of cotton/PP commingled composites were studied with reference to the fiber content, chemical treatments, processing conditions, and applied frequency. The storage modulus and the glass transition temperature increased while the intensity of the damping peak decreased with the increase in fiber content. The chemical treatments with $KMnO_4$ and MAPP raised the value of storage modulus at all temperatures. This is due to an increase in interfacial adhesion between the fibers and matrix. An increase in frequency results in an increase in storage modulus but a decrease in the intensity of the tanδ peak. The nature of the Cole–Cole plot gives an idea about the heterogeneity and the extent of fiber-matrix adhesion. It is possible to construct a master curve to predict the mechanical behavior at another set of conditions. Theoretical models were used to predict the viscoelastic properties and compared the values with the experimental data.

## References

1. Svensson, N.; Shisoo, R.; Gilchrist, M. D. J Textl Inst 1998, 89, 635.
2. Mcdonnell, P.; Mcgarvey, K. P.; Ruchford, L.; Bradaigh, C. M. O. Compos A 2001, 32, 925.
3. Svensson, N.; Shisoo, R. J Thermoplas Compos Mater 1998, 11, 22.
4. Handermann, A. C. 20th Inl. SAMPE Technical Conference; SAMPE: Covina, CA, 1988; 681.
5. Golzer, M.; Brunig, H.; Mader, E. J Thermoplas Compos Mater 2007, 20, 17.
6. Leterrier, Y.; G'sell, C. Polym Compos 1994, 15, 101.
7. Pickering, K. L.; Beckerman, G. W.; Alam, S. N.; Aoreman, N. J. Compos A 2007, 38, 461.
8. Doan, T. L.; Gao, S. L.; Mader, E. Compos Sci Tech 2006, 66, 952.
9. Yuan, X.; Jayaraman, K.; Bhattacharyya, D. Compos A 2004, 35, 1363.
10. Cantero, G.; Arbelaiz, A.; Llano-Ponte, R.; Mondragon, I. Compos Sci Tech 2003, 63, 1247.
11. Zafeiropoulos, N. E.; Baillie, C. A.; Hodgkinson, J. M. Compos A 2002, 33, 1185.
12. Zafeiropoulos, N. E.; Williams, D. R.; Baillie, C. A.; Matthews, F. L. Compos A 2002, 33, 1083.
13. Qiu, W.; Endo, T.; Hirotsu, T. Europ Polym J 2006, 5, 1059.
14. Boucher, D. T.; Fisa, B.; Denault, J.; Gagnon, P. Compos Sci Tech 2006, 66, 555.
15. Joseph, P. V.; Mathew, G.; Joseph, K.; Groenincks, G.; Thomas, S. Compos A 2003, 34, 275.
16. Idikula, M.; Malhotra, S.; Joseph, K.; Thomas, S. J Appl Polym Sci 2005, 97, 2168.