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Dynamic mechanical analysis and thermal degradation of jute fiber reinforced BSFT ($Ba_{0.6}Sr_{0.4}Fe_xTi_{(1-x)}$ $O_{3-\delta}$), (x=0.1)- polypropylene composite

Reenu Jacob* & Jayakumari Isac
Department of Physics, C M S College, Kottayam 686 001, India

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Recent research shows that the natural fibers from renewable natural resources have greater potential than other man-made fibers. Attempts have been carried out to study the effect of fiber loading and temperature on jute fiber reinforced BSFT ($Ba_{0.6}Sr_{0.4}Fe_xTi_{(1-x)}$ $O_{3-\delta}$), (x=0.1)-polypropylene composites using DMA and thermal techniques. The intrinsic design and morphology of the components of the system define the dynamic mechanical properties of the composite. For lower temperatures, the storage modulus (E') values are maximum for the neat PP whereas at temperatures above T_g, the E' values have been found to be maximum for composites with higher fiber loading, proving that the incorporation of jute fiber in BSFT-polypropylene matrix induces reinforcing effects at elevated temperatures. The loss modulus and damping peaks have been found to be lowered by the incorporation of fiber. Cole–Cole analysis throws light on the phase behavior of the composite samples. Thermo gravimetric analysis result on the enhanced thermal stability by the incorporation of fibers. The whole study reveals the enhancement in the dynamic, mechanical and thermal properties of the BSFT-PP composite on incorporation of jute fiber.

Keywords: Fiber-reinforced composites, BSFT, Dynamic modulus, Thermal properties, Cole-Cole plots

1 Introduction

Manufacturing high performance quality materials from renewable resources is one of the major achievements by researchers across the world. Polymer composites open a quality impact on material scientists because of their potentially novel characteristics. Introducing natural fibers to the ceramic polymer composite has gathered interest because of their specific properties, low cost, market appeal, renewable and nonabrasive nature. Research on new composites with reinforced jute fiber has gained well attention due to their immense applications[1,2]. The quality and performance of such reinforced composites depend on the material design.

Dynamic mechanical analysis (DMA) is considered as the most powerful tool to analyze the material behavior. DMA tests are used for investigating the structures and visco elastic behavior of polymeric materials for determining the relevant stiffness and damping characteristics for various applications. The polymeric materials with good dynamic properties have profound importance when determined over a range of temperature and frequencies.

DMA always gives reliable report on the mobility of polymers and the effect of fillers on the chain mobility[3]. DMA tests are mainly done to study the modifications in the composite with the incorporation of fiber and the performance as a function of properties. The literature is rich with different findings from this area. The enhancement in the damping in polymer composites with different fiber matrix combinations has been studied earlier[4,5]. Saha *et al.*[6] has given comparative results on the damping of unmodified and chemically modified jute-polyester composite samples. The visco elastic behavior of various polymer composites and blends are reported by Joseph *et al.*[7]. Valea *et al.*[8] have worked on the influence of cure conditions and the exposure to various chemicals on the dynamic mechanical properties of several vinyl esters[9]. The improvement in the thermal stability of ceramic composites, when jute fibers are reinforced, is also reported[1].

In the present work, the influence of jute fiber with temperature change on the visco elastic properties of BSFT ($Ba_{0.6}Sr_{0.4}Fe_xTi_{(1-x)}$ $O_{3-\delta}$),(x=0.1)-PP composite has been reported. The height of transition temperature (T_g) is taken as a measure of the interfacial interaction and the effect of fiber content on the T_g values is reported as well. The T_g values of the composite samples and the slight positive shift in T_g are determined from the loss modulus and the tanδ curves to understand the fiber/matrix adhesion. Thermo grams

*Corresponding author (E-mail: reenujacob12@gmail.com)

give a quality check on the thermal stability of the jute fiber reinforced composites.

2 Experimental Details

2.1 Materials

The jute fibers bought from the farmlands of Calcutta, well cleaned and chopped to small pieces (~2 cm length) are treated in NaOH (5%) solution at ambient temperature. The alkali treated fibers are washed thoroughly to remove the excess alkali content. Fibers are then air dried for 24 h followed by oven drying at 55 °C for another 24 h. The alkali treatment enables to prevent themicrobial degradation, hemi cellulose and lignin are removed and the inter fibrillar regions get more aligned along the direction of tensile load[10]. Isotactic PP (Koylene 3060) having a density of 0.90 g/cm^3 is supplied by Indian Petro Chemicals Limited, Baroda.

For the jute reinforced composite preparation, ceramic sample BSFT selected is synthesized, ball milled and calcined at 950 °C. Ceramics with the chemical formula ($Ba_{0.6}Sr_{0.4}Fe_xTi_{(1-x)}$ $O_{3-\delta}$), (x=0.1) (BSFT) is prepared by the solid-state reaction technique through mechanically assisted synthesis via high-energy ball milling process. The reagent grade raw materials selected are of high purity barium carbonate, strontiumcarbonate, ferric oxide and titanium dioxide powders and weighed according to their molecular formula. The synthesis of BSFT is already reported[11]. Along with BSFT, polypropylene (PP) and alkali treated jute fibers are also weighed and mixed according to the rule of mixtures.

2.2 Composite preparation

Two different percentage proportions of the jute reinforced BSFT-polypropylene composites are prepared-20% jute-BSFT-PP and 30% jute-BSFT-PP. Brabender mixer is used to obtain a higher degree of blending and homogenous mixing of materials to form composites. Maintaining the temperature at 160 °C, PP along with jute fibers and ceramic sample (BSFT) are added to achieve optimum properties. After proper mixing the components are subjected under pressure in a hydraulic press at 180 °C to form composite laminates and the finished laminates are finally allowed to cure for characterization studies. A dynamic mechanical thermal analyzer Perkin Elmer DMA 8000 is employed for dynamic mechanical property evaluation of the jute reinforced BSFT-polypropylene composites. The experiment is conducted under tensile mode at a frequency of 1 Hz. Two samples of dimensions 10.01×0.956×0.23 mm^3 and 10.04×0.967×0.2 mm^3 are measured. The testing temperature ranges from -37 °C to 100 °C with the heating rate at 2 °C/min. Composites with different percentages of fiber loading are examined using scanning electron microscope (SE) model JEOL JSM-35 C and Cambridge 250 MK3 stereo scan.

3 Results and Discussion

3.1 Effect of fiber loading on storage modulus (E') with temperature

Figure 1 shows the variation in the modulus which occurs due to the material design. Storage modulus (E') actually measures the stiffness of the sample. Storage modulus versus temperature curves for neat PP and for reinforced jute composite with different fiber content are analyzed. The dynamic modulus is higher in the glassy region for the fiber filled system. In the case of the neat PP sample, the rate of decrease of E' is clear on passing through the glass transition temperature (T_g). It is due to the increased segmental mobility of the polymer chains above T_g. The drop in the modulus on passing through the glass transition temperature is considerably reduced for jute reinforced BSFT-PP composites which prove the reinforcing effect of jute fiber on the modulus above T_g than below it[1].

The effectiveness of fillers on the moduli of the composites can be defined by coefficient C as:

$$C = [E'_g / E'_r(\text{comp})]/[E'_g / E'_r(resin)] \quad \ldots (1)$$

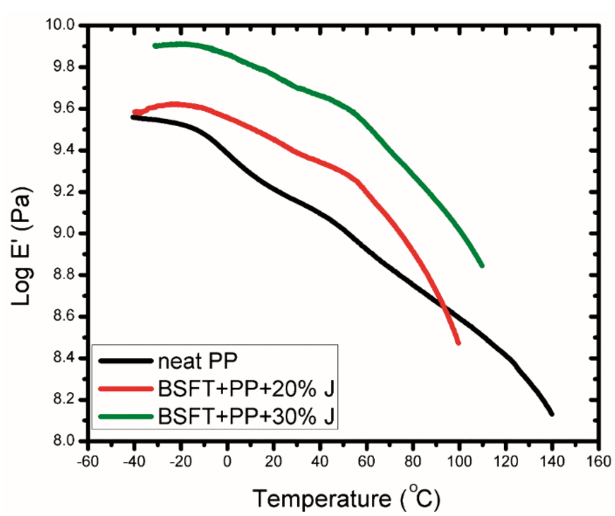

Fig. 1 — The effect of temperature on the storage modulus (E') of the neat PP and the jute reinforced BSFT-PP composites

where E'_g and E'_r represent the storage modulus values in the glassy and rubbery region, respectively. The C value obtained is 0.53 for 20% jute fiber loading while 0.512 for 30% fiber loading. The higher the value of the constant C, the lower will be the effectiveness of the filler. However, the dynamic modulus curve shows an increase in the E' value above the T_g region in the rubbery plateau for the jute reinforced composites than pure PP. This enhancement in the modulus is due to the greater restriction imposed by the jute fibers on the matrix, which in turn increase the stress transfer at the fiber interface. Also, the interference effect of neighboring chains increases the E' value and greater molecular cooperation is required allowing the relaxation process to take place.

There is a large decrease in modulus with increasing temperature. But the drop is less as the fiber loading percentage increases. Also, it is clear that the difference between the modulus of the glassy state and rubbery state is lesser in the jute reinforced BSFT-PP composites than in the neat PP. This difference can be explained as the combination of the hydrodynamic effects and mechanical restraint of the fibers embedded in the visco elastic medium which reduce the mobility and deformability of the matrix[9,12]. At low temperature, jute fibers' contribution to stiffness of the material is less and hence E' values of neat PP and jute reinforced BSFT-PP composite are close to each other. At higher temperatures water molecules adhering on to the fiber will escape imparting stiffness[9,13] and thus contributing to the enhanced modulus of the composite at high temperatures.

3.2 Effect of fiber loading on loss modulus (E'') with temperature

Figure 2 shows the variation of loss modulus with temperature of composites of neat PP and the jute reinforced BSFT-PP composites. The loss modulus E'' is defined as the viscous response of the material. It measures the energy dissipated as heat per cycle under sinusoidal deformation, when different systems are compared at the same strain amplitude. The loss modulus curves decrease with increase of fiber content at temperatures below the glass transition. The effect of the filler contribution is prominent above the glass transition temperature.

Also, it is observed that the loss modulus curve broadens when the fiber content is increased to 30%. The observed broadening may be explained as due to the inhibition of relaxation process within the composites[1]. The maximum dissipation occurs at T_g where E'' value also reaches maximum. The broadening of the loss modulus curve also represents the presence of an increased range of order.

3.3 Morphology results

The surface morphology of the composites is observed under the scanning electron microscopy. Figure 3(a, b) shows SEM images of the fracture surface of jute reinforced BSFT-PP composites. Agglomeration is evident in both composites. SEM of the jute reinforced BSFT-PP composite with 20% fiber loading shows fiber/matrix de bonding and fiber pull out while SEM of the jute reinforced BSFT-PP composite with 30% fiber loading shows good fiber/matrix adhesion.

3.4 Effect of fiber loading on damping factor (tanδ) with temperature

Figure 4 shows the effect of fiber loading on damping factor (tanδ) with temperature. The tanδ denotes the damping term relating to the impact resistance of a material. Figure 4 depicts the effect of temperature on tanδ for neat PP and also for the jute reinforced BSFT-PP composite. This damping occurs

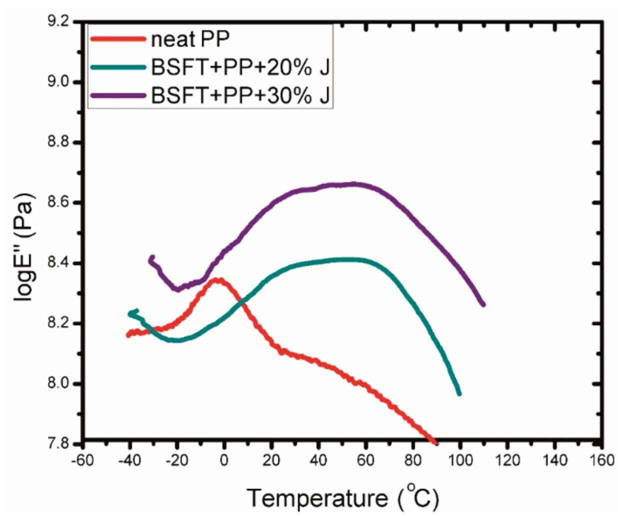

Fig. 2 — The variation of loss modulus with temperature of composites of neat PP and the jute reinforced BSFT-PP composites

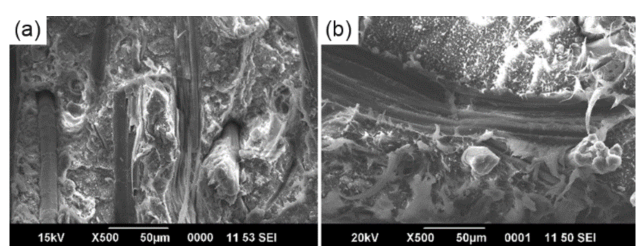

Fig. 3 — SEM images of the fracture surface of jute reinforced BSFT-PP composites

at the glass transition region where the material changes its rigidity. For PP there are three different relaxation processes due to molecular motions:

(i) γ-relaxation process with very short motions at low temperatures below -50 °C.

(ii) β-relaxation at 0 °C will be dominant mainly due to the transition from the glassy to rubbery state. The molecular motions of the amorphous phases are usually constrained by the crystallites.

(iii) At temperatures close to melting point, α- relaxation takes place in the inter phase of crystallites. This depends on molecular weight and occurs at temperatures above 100 °C.

For the jute reinforced BSFT-PP composite damping is affected through the introduction of fibers. Incorporation of fibers decreases the tanδ peak height by reducing the molecular movement. Magnitude of the tanδ peak is definitely a quality check of the nature of the polymer system. In an unfilled system, the chain segments are free from restraints. However, the addition of fiber reduces the magnitude of the tanδ peak more than shifting the temperature. Due to the decreased mobility of the chains by the addition of fibers T_g value also gets shifted. The stress surrounding the particles also induces T_g shift[9,14]. Fibers with good interface bonding dissipate less energy. When the fiber content is increased the composite is strained to less degree. Hence the tanδ curves get lowered for 30% fiber loading due to the increased interfacing. Further the molecular relaxations which are present in the composite make the peaks broaden. The width of the tanδ peak hence indicates the increased volume of the interface.

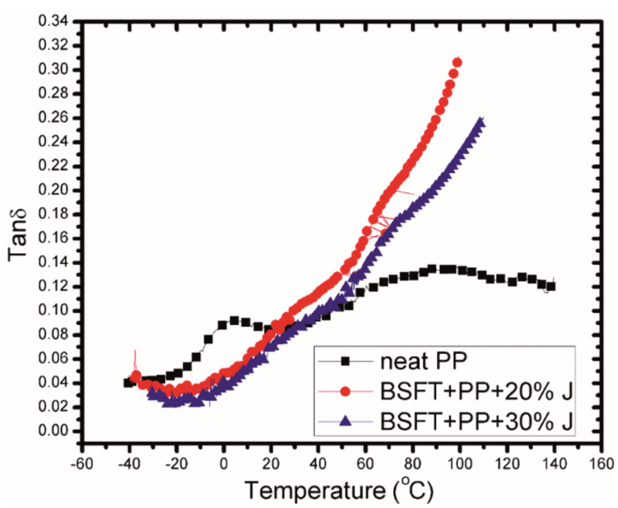

Fig. 4 — The effect of fiber loading on damping factor (tanδ) with temperature

The quantitative measurement of constraint chains helps to study the crystallinity of semi crystalline polymers. The decrease of mechanical loss factor (tanδ) as the fiber content is increased denotes fatigue improvement and an enhancement in the elasticity of the composites[15].

Table 1 represents the T_g values of neat PP and jute fiber reinforced BSFT-PP composites from tanδ (max) and E'' max. The T_g values obtained from the loss modulus peaks for the jute reinforced composites are found to be less than that obtained from the damping peaks of neat PP. The loss modulus peak shows double humped nature when fibers are added. With increase in temperature, the loss modulus peak, which corresponds to the glass transition temperature, shows a slight shift to higher value.

3.5 Cole-Cole plots

Linear visco elastic mechanical properties of the polymer composites are well explained by Cole-Cole plots. It is drawn by plotting the storage modulus (E') against loss modulus (E'') for a particular frequency. It measures the structural modifications happened by the incorporation of fibers to PP and hence gives the dielectric relaxation data. Cole-Cole plots shape points to the homogeneity of the system if perfect semicircular curves are obtained. Figure 5 depicts the heterogeneity of the composite prepared. The surface

Table 1 — T_g values of neat PP and jute fiber reinforced BSFT-PP composites from E'' (max)

Composite	T_g from E'' (max) (°C)
Neat PP	-3.05
20J:10C:70PP	59.8
30J:10C:60PP	62

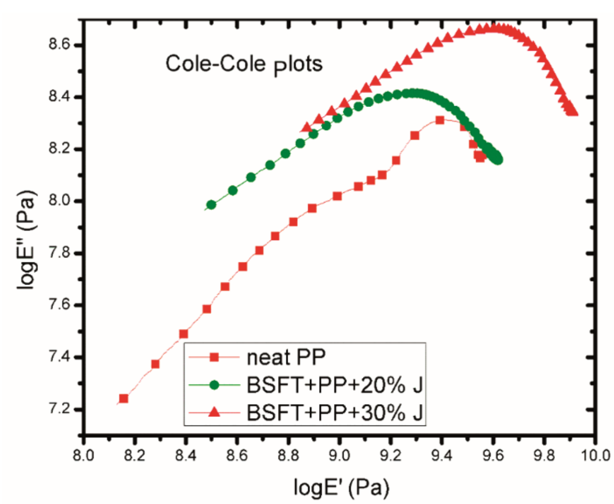

Fig. 5 — Cole-Cole plots of jute fiber reinforced BSFT-PP composites

characteristics and the methods affect the shape of Cole-Cole plots and contributing to the dynamic mechanical properties of the composite prepared. The imperfect semicircular shapes also report to the relatively good interfacial adhesion at fiber loading[9].

3.6 Thermal studies

3.6.1 Thermo gravimetric analysis

The thermo gravimetric analysis (TGA) technique throws light on the degradation temperatures and absorbs moisture content of materials. The jute reinforced BSFT-PP composites prepared are heated from 40 °C – 600 °C at heating rate of 20 °C/min. The thermal degradation behavior of composite with 20 wt% and 30 wt% jute fiber loading has been studied by TGA techniques. TGA peak temperature describes the beginning point (T_i) of the major weight loss, and the final temperature (T_f), the end of the degradation. A major drop in the mass of the sample shows the thermal degradation of the materials, but degradation temperature increases on adding the jute fiber. The thermal stability improvement is found to have due to the additional intermolecular bonding between fiber and matrix, allowing more thermal energy distributed over these bonds within interface[16].

TGA curves of BSFT-PP composite before jute fiber loading show a gradual decrease in mass as the temperature increases. But when the jute fiber composites (20% jute- BSFT-PP and 30% jute -BSFT-PP) are considered then degradations are more prominent with major weight loss. The peaks at low temperatures are due to removal of moisture, while the maximum degradation occurs at the transition temperature 457.57 °C with fall rate of 7.309 mg/min. It is well proved that the thermal stability of the composite is increased when the fiber content is increased stabilizing the transition temperature. The rate of degradation also has affected by the jute fiber content variation. The jute reinforcement in between the matrix resin molecules has offered resistance towards degradation with the increase in fiber content[17]. From the results obtained it is clear that components are partially miscible with a single T_g value[18-21]. Figure 6(a) depicts the TGA curves of the jute reinforced BSFT-PP composites with and without jute fiber addition.

3.6.2 Differential thermal analysis and differential scanning calorimetry

Differential thermal analysis (DTA) is a dynamic temperature technique while differential scanning

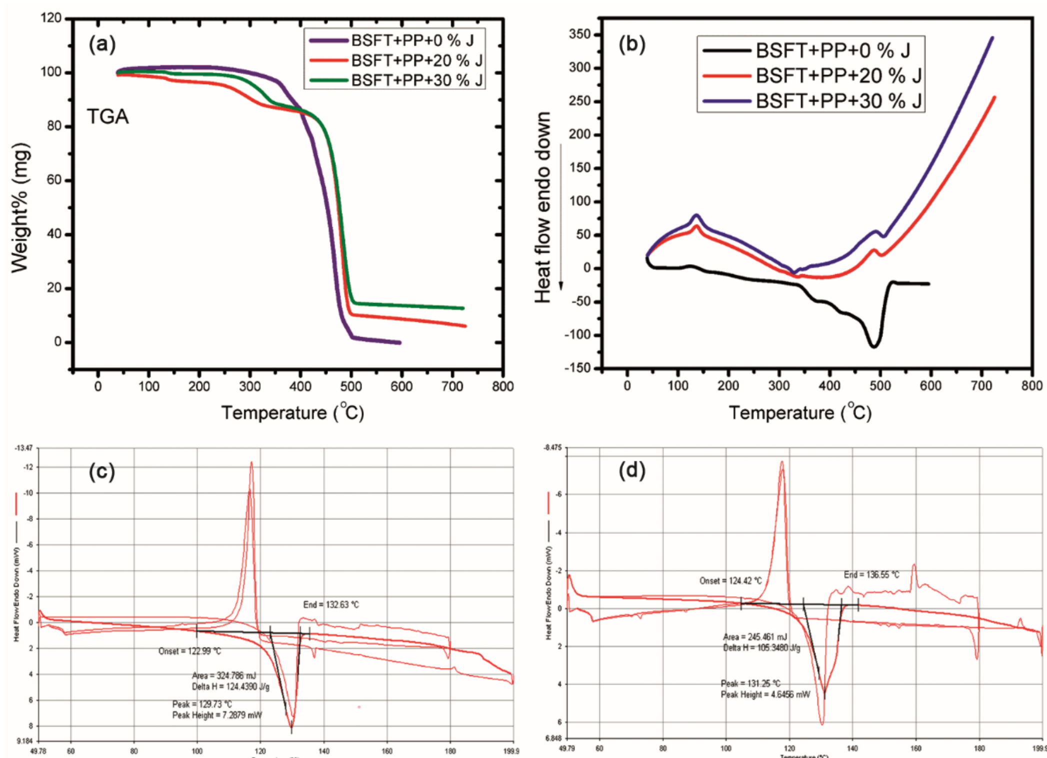

Fig. 6 — (a) TGA curves of the jute reinforced BSFT-PP composites before and after jute fiber loading, (b) DTA curves of jute reinforced BSFT-PP composite before and after jute fiber loading and (c, d) DSC curves of jute fiber reinforced BSFT-PP composites

calorimetry (DSC) measures the heat flow by measuring the temperature difference. Both give quality information about the thermal properties of the components. The mechanical behavior of polymer composites suddenly changes at their glass transition temperature which is the fingerprint of every polymer composite. The thermal degradation occurs after the materials absorb sufficient heat energy. As in Fig. 6(b) DTA curve shows the thermal stability attainment with jute fiber reinforcement. The degradation processes involve the breaking down of the fibers and matrix structures creating molecular chain ruptures. Both DTA and DSC curves are helpful for information like the degree of intermolecular interactions, degree of crystallization and degree of miscibility[16]. Figure 6(c, d) depicts the DSC curves showing the change in the melting point with the increase in fiber loading. The transition temperature has minimal change but the melting temperature has shifted to the higher value (up to 4 °C) because of the increase of fiber content. The nucleating effect of jute fibers increases the crystallinity also. The transition temperature indicates lesser mobility with good molecular interaction between the components**.**

4 Conclusions

Dynamic mechanical analysis of jute fiber reinforced BSFT-PP composites are investigated under fiber loading effect. The dynamic modulus shows a sudden decrease with incorporation of fiber below the glass transition temperature but has a positive effect on the temperatures above T_g. Improvement in properties is observed maximum for composites with 30% fiber loading with increase of frequency. The slight positive shift of T_g to higher temperatures supports the good fiber/matrix adhesion, which is well clear from the SEM. At the 30% fiber loading the loss modulus peak gets broadened proving the improved fiber/matrix adhesion again.

Cole–Cole plots show imperfect semicircular curves pointing to the heterogeneity of the system as well as the good interfacial adhesion at high fiber loading. The thermal study done gives information regarding the thermal stability of the composite. It is clearly proved that the thermal stability enhances with the incorporation of jute fiber to the BSFT-PP composite. Reinforcement of thermally stable jute fibers acts as barriers to prevent degradation. The optimum utilization of the jute reinforced BSFT-PP composite opens new world of advanced materials processing good stiffness, damping behavior and thermal stability.

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