Thermo-Physical Analysis Of Natural Fiber Reinforced Phenol Formaldehyde Biodegradable Composites

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Abstract

Natural fiber reinforced composites are composite materials which contain reinforced fibers from natural sources. Natural fiber composites can provide an effective and renewable solution for environment-friendly construction materials. For example, building insulation materials which are made of natural fibers can improve energy efficiency and reduce material waste generation. The fibers used in these composites are extracted mainly from plant sources such as bamboo, jute, sisal, and flax. Natural fibers have excellent mechanical and energy-dampening properties, making them ideal for manufacturers looking to replace traditional synthetic fiber reinforcements. They are also gaining popularity as replacements for plastic and metal components in many consumer goods. In this paper desert plant prosopis juliflora fibers were used as reinforcement in phenol formaldehyde resin to make composites. TGA, DSC and DMA were performed to analyze the change in thermal stability and mechanical properties of the prosopis juliflora fiber reinforced phenol formaldehyde composites. The alkali-treated fibers were prepared by immersing the PJ fibers in a 1% sodium hydroxide solution for 24 hours. The fibers were washed and dried before being mixed with the phenol formaldehyde resin. The composites were prepared with untreated and alkali-treated reinforced fibers. All specimens were left to cure at room temperature overnight.

Keywords: Alkali treatment, phenol formaldehyde composites, biodegradable.

Abbreviations: PJ; prosopis juliflora, PFC; phenol formaldehyde composites, TGA; Thermo-Gravimetric Analysis, DSC; Differential scanning calorimetry DMA; Dynamical Mechanical Analysis, FRPFC; fiber reinforced phenol formaldehyde composite.

Introduction

Natural fiber reinforced phenol formaldehyde composite materials are becoming increasingly important in today's manufacturing world due to their biodegradable, light-weight and eco-friendly properties. They have been extensively used in automotive, aerospace, construction, electrical and other industries due to their superior mechanical and thermal properties. In order to better understand and optimize the properties of these composites, a thermo-physical analysis is usually conducted. This analysis studies the thermal and physical properties of the composites such as thermal stability, Glass transition temperature, crystallization temperature, modulus of elasticity, damping factor. This analysis helps in understanding how the natural fibers affect the properties of the composites and how the composite material can be engineered to possess better performance [1-2]. Natural fibers can also be used as a substitute for artificial materials in applications such as automotive seat seating and furnishings, roof insulation panels, thermal resistant curtains and apparel, and acoustic insulation. The use of natural fibers also has the potential to reduce the burden of industrial waste, as they are naturally biodegradable and recyclable unlike artificial fibers [3]. Natural fibers can be used for production of furniture, packaging, flooring, and other items that require strength, texture, and thermal resistance. Their heat resistance and insulation properties also make them suitable for use in thermal stability applications. Examples of these applications include Fire-resistant door and wall panels, Fire-resistant insulation panels, Thermal energy storage systems, Heat shielding for aircraft, Fire and heat protective clothing, Heat-resistant pipes and housing for electronics [4].

Materials

First of all, stems were collected from plant prosopis

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juliflora in the different desert region of district Bikaner situated in Rajasthan state in India. After that stem were dipped into Normal water filled in bucket for 25 days. After 25 days stems were taken out from bucket and washed with distilled water to remove excessive Surface impurities. Soaking process loosens the fibers of stem so that fibers can easily extract from each stem. Some of the extracted Fibers were dipped into Sodium Hydroxide (NaOH) 6% wt Concentration to improve the bonding between prosopis juliflora fiber and polymer matrix. Then fibers were dried in an oven at 40˚C temperature for 24 h and chopped in desired length for further using to fabricate composite materials. NaOH treatment gives high mechanical strength to the fiber and creates roughness on surface of fiber to increase the bonding between fiber and matrix [5].

The procedure to make the composite material is as follows:

Phenol crystals and formaldehyde was taken in a beaker in a ratio of 2:1 in the presence of alkali medium catalyst such as NaOH. After that this mixture was heated for 2 hours at a constant temperature of 60°C under standard atmospheric conditions. After the reaction was completed, the crystal-like solid formed in the beaker can be extracted. This solid will be an insoluble product because phenol and formaldehyde react to form a condensation polymer, which is insoluble in water. After the crystal-like solid is separated from the beaker, it will need to be dried and cut in desired shaped for further testing [6].

Figure 1.1 Phenol-Formaldehyde composites

Experimental Studies

(a) Thermo gravimetric analysis (TGA)

Thermo gravimetric analysis (TGA) technique used to measure the weight loss of a material as a function of temperature or time. It is based on the fact that the energy absorbed or released when breaking or forming chemical bonds during a chemical reaction is proportional to the change in weight of the material, as measured by an analytical balance. TGA is often used to measure the degree of thermal transformation of a material, or to determine the presence of volatile materials in a sample. It can also be used to measure the degree of conversion of a polymer, the oxidation rate of an organic material, or the degradation of

a material [7]. Thermo gravimetric analysis was conducted in LNMIIT Jaipur district situated in Rajasthan, India. The fibers with a weight of 15mg were placed in an alumina crucible and underwent the pyrolysis process with nitrogen (30mL/min). The temperature was set between 30 °C and 500 °C with a constant heating rate.

(b) Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) is a type of calorimetric technique used to measure the heat of a material in response to a controlled temperature program. In DSC, two identical samples are placed into pans and monitored for heat while a temperature program takes the material through a range of temperatures. The heat absorbed or released can be monitored, allowing for the determination of a material's thermal properties [8].

(c) Dynamical Mechanical Analysis (DMA)

DMA is a sensitive technique to measure the mechanical properties of materials, including their elastic modulus, glass transition temperature, and damping. This data is then used to investigate the microstructure and interaction between polymers and fillers to improve the material's structure and properties [9,10].

experimental conditions for DMA
Heating rate – 5˚C/min
Temperature range – 30˚C to 150˚C
Frequencies - 1 Hz
Maximum load range – 5N to 10 N
Deformation mode – Stress/strain scan
Sample dimensions - Length -9.50 mm, Width -8.90 mm, Thickness -1.08 mm.

Results and Discussion

(a) Thermo-gravimetric analysis of prosopis juliflora fiber reinforced phenol formaldehyde composites

Thermo-gravimetric analysis (TGA) is an important technique that can be used for measuring changes in the mass of a material due to thermal degradation. TGA can be used to measure the glass transition temperature for the polymers used in the composite structure. TGA analysis was done for pure PFC and 5% wt. PJ fiber reinforced phenol formaldehyde composites up to 500˚C at different heating rates from 5˚C/min. to 20˚C/min.

From the presented TGA curves of PF composites reinforced with *prosopis juliflora* fiber, it can be seen that the first mass loss occurs between temperature 40˚C to 100˚C for every composites, this temperature range is corresponding to the moisture evaporated. As temperature increases more monomer molecules evaporate which lead to the massive decrease in weight of the sample. The secondary weight loss can be seen between 100˚C to 200˚C,

which is corresponding to the decomposition of organic matter such as hemicelluloses, lignin, and fats present in the *Prosopis juliflora* fiber. This weight loss is accompanied by a rapid increase in the thermal degradation of the phenol-formaldehyde resin matrix [10].
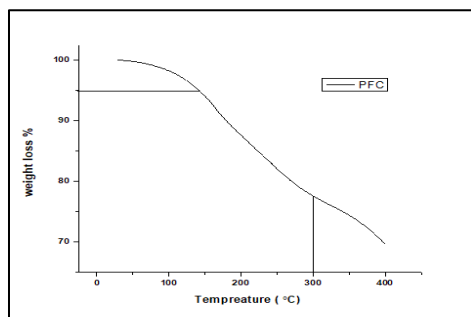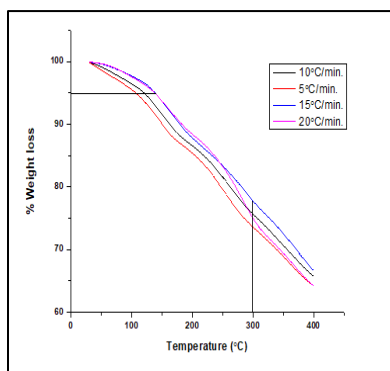

Figure 1.2 TGA curve of Pure PF resin

Figure 1.3 TGA curve untreated PJ fiber reinforced composite at heat rates from 5˚C/min to 20˚C/min.
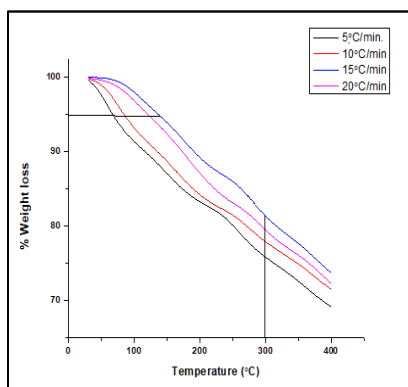

Figure 1.4 TGA curve treated PJ fiber reinforced composite at heat rates from 5˚C/min to 20˚C/min.

From the figure 1.3 and 1.4, it is evident that phenol formaldehyde composites showed an increasing temperature at 5% mass loss with heat rate. This suggests that the phenolic resin starts reacting at higher temperatures and decomposes; leading to mass loss, when there is an increase in the heat rate. Thus, higher heat rate can cause a higher rate of decomposition and hence higher temperature at 5% mass loss for phenol formaldehyde composites. This suggests that phenol formaldehyde composites have an endothermic character where the reaction proceeds with the absorption of heat energy. Higher heat rate means more energy is supplied to the reaction leading to a higher

temperature at 5% mass loss. It appears that the alkali treated fiber sample has a lower time-to-failure temperature than the untreated fiber sample for all tested ramp-rates. This suggests that the alkali treated phenol formaldehyde sample may have higher thermal stability and could be a better candidate for products that require higher thermal stability. This is because the mass residue of the treated composite was higher than the untreated composite when subjected to increasing heating rates of 5˚C/min, 10˚C/min, 15˚C/min, and 20˚C/min [10].

(b)   Differential Scanning Calorimetry DSC analysis of prosopis juliflora fiber reinforced phenol formaldehyde composites

Differential scanning calorimetry (DSC) is a technique used to analyze the thermal properties of materials. It typically involves measuring the heat of fusion, which is the energy released during the transition of a material from solid to liquid, and the heat of crystallization, which is the energy released during the crystallization of a material. In the case of *Prosopis juliflora* fiber reinforced phenol formaldehyde (PF) composites, a DSC analysis can help characterize the effects of the reinforcement on the thermal properties of the PF composite, including the glass transition temperature and the thermal decomposition temperature.

(i) Glass transition temperature

The glass transition temperature (T_g) is the temperature at which a polymer transitions from a hard, brittle glassy state to a soft, rubbery state. The glass transition temperature (T_g) is the temperature at which an amorphous material, such as glass or a polymer, goes from a brittle solid to a rubbery or viscous liquid. It is the point at which a solid becomes a liquid without undergoing any crystallization. The T_g is the point at which the material's viscosity undergoes an abrupt change; at temperatures below the T_g, the material is rigid and brittle, while above the T_g, the material is viscous and pliable. The glass transitions appear as a first step in the baseline of the recorded DSC signal. Then a big peak when the polymer reached its crystallization temperature [11].
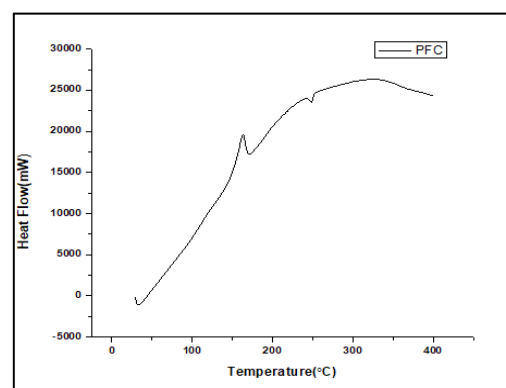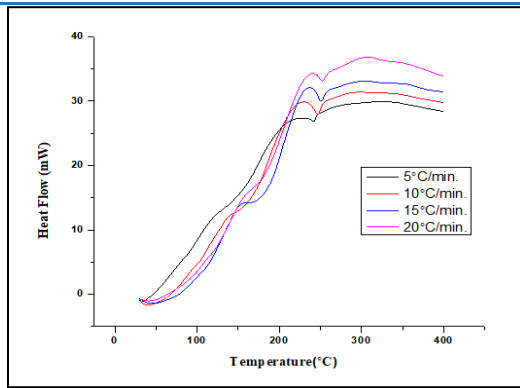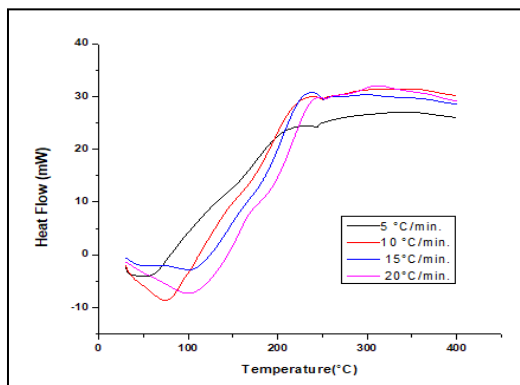

Figure 1.5 DSC thermo-gram of PF composite

Figure 1.6: DSC thermo-gram untreated PJ fiber reinforced PF composite with different heat rates

Figure 1.7: DSC thermo-gram treated PJ fiber reinforced PF composite with different heat rates

Then finally a big dip when the polymer reached its melting temperature. DSC thermo gram of pure phenol formaldehyde composites PF and 5% wt. untreated and treated Prosopis juliflora PJ fiber reinforced Phenol formaldehyde composites at constant heating rates 5˚C/min. to 20˚C/min. are shown in figure 1.2, 1.3 and 1.4 respectively.

Table 1.1: Glass transition temperature for Untreated and treated 5% wt. PJ Fiber reinforced PF composites

Heat Rates (°C/min.)	Glass transition temp T_g (°C) of untreated composites	Glass transition temp T_g (°C) of treated composites
5	46.10	50.5
10	48.74	58.0
15	49.20	62.2
20	52.60	69.5

It is clear from figure 1.5 that Phenol formaldehyde composite without any reinforced fiber has glass transition temperature at 45˚C where as it is clear from figure 1.6 and 1.7 that prosopis juliflora fiber reinforced composites found higher glass transition temperature than pure phenol formaldehyde composite. it can be concluded that from table 1.1 that the presence of the reinforced fiber increases the glass transition temperature of the composite material. It is clear that untreated fiber reinforced composite has glass transition temperature 46.1˚C to 52.6˚C with increasing heat rate 5˚C/min. to 20˚C/min. and treated composite found Tg values ranging from 50.5˚C to 69.5˚C with increasing heat rate 5˚C/min. to 20˚C/min.

This shows that reinforced fiber can significantly increase the glass transition temperature of composite material comparing with the untreated materials. This increase can be attributed to better dispersion, higher degree of interface interactions and increased filler to matrix interactions as a result of the reinforced fiber treatments. From the results of this study, it appears that fiber reinforcement is an effective way to increase the glass transition temperature of the composite material. This higher glass transition temperature indicates improved toughness and better resistance to temperature fluctuations, enabling the composite material to be used under more extreme conditions [11].

(c) **Dynamic mechanical analysis (DMA) of PFC and prosopis juliflora fiber reinforce PFC**

Materials properties such as storage modulus (E'), loss modulus (E'') and damping (tan δ) can be measured over a range of temperatures and frequencies by using DMA tecnique. Storage modulus (E') is a measure of the elasticity and stiffness of the material, which is defined as the ratio of the applied force to the resulting strain of the material. The storage modulus typically decreases with increasing temperature, frequency and strain. Sample were taken in bar form with dimension length 9.50 mm, width 8.90 mm and thickness 1.08 mm. Dynamic mechanical analysis (DMA) is a technique used to measure the mechanical properties of materials, such as stiffness and damping, by measuring the response of the material to an externally applied force [12].

(i) **Effect of temperature on dynamic storage modulus (E')**

Dynamic storage modulus (E') represents the ability of a material to store energy when subjected to a periodic external force. As a material is deformed, it stores energy in the form of elastic deformation. This energy can be released when the material returns to its original shape. The dynamic storage modulus quantifies the amount of energy that can be stored per unit volume of the material. The variation of storage modulus as a function of temperature of PFC phenol formaldehyde composite and FRPFC Fiber reinforced phenol formaldehyde composite are shown in fig.1.8 The modulus of the FRPFC increases from 0.68 GPa for composites containing no PJ fiber around 1.26 GPa for composites containing PJ fiber[12].
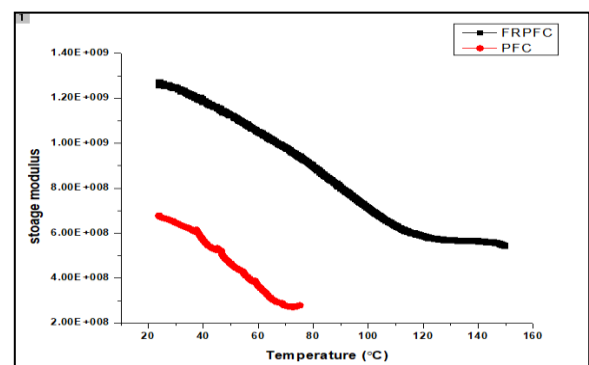
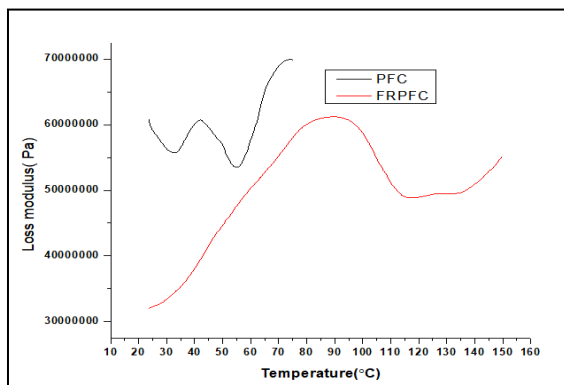**Figure 1.8:** storage modulus variations with temperature obtained by DMA for PFC and FRPFC

This increase in the modulus of the matrix suggests that the addition of fibers provides additional strength, stiffness, and

rigidity to the composite structure. The increase in reinforcement from the fibers is likely responsible for the significant increase in the stiffness of the matrix. Reinforcement effect refers to the ability of fibers to improve the strength and durability of the interface between two materials. The fibers provide an additional layer of protection that is able to transfer the stresses placed on the interface to a greater degree than would otherwise be possible. This is because the fibers act as a bridge between the two materials, increasing their contact area and strengthening the bond between them. This leads to a stronger interface that can better withstand the stresses that might otherwise cause damage or weaken the interface.

As the temperature increases, E' decreases and then there is a sharp decrease is found in the E' value at the glass transition region as shown in fig. This behavior can be attributed to the increase in the molecular mobility of the polymer chains above Tg. This decrease is due to the moisture absorption and associated plasticization effect in natural fiber composites. The increase of temperature leads to increase of moisture absorption because of the energy barrier reduction; this process causes the decomposition of the hydrogen bonds between the reinforcing elements which reduces the modulus of elasticity of the composite.

(ii) Effect of temperature on dynamic Loss modulus (E'')

When the material is subjected to a loading cycle and is given by the equation $E''=E'/\omega$ (Where E'' is the Loss modulus, E′ is the Elastic modulus and ω is the angular frequency). The Loss modulus indicates how much energy is lost in the form of heat and how the material will behave when subjected to cyclic loading [12].


Figure 1.9: Loss modulus variations with temperature obtained by DMA for PFC and FRPFC

It is clear from the figure 1.9 that insertion of fiber into matrix increase broadening in peak of loss modulus. The loss modulus peak of FRPFC fiber reinforced composites is broad and sharp compared to the pure PFC phenol formaldehyde composite which causes a decrease in the relaxation time of the FRPFC as compared to the PFC. This behaviour is attributed to the higher thermal conductivity of the FRPFC as compared to the PFC. The heat is thus conducted quickly, resulting in faster relaxation of the material. Furthermore, the incorporation of fiber also imparts increased stiffness and strength to the composite, making it more resistant to bending and impacts. This

increases its structural integrity and thereby increases its overall performance [12].

(iii) Effect of temperature on damping factor (Tanδ)

The mechanical loss factor or Damping factor (tan δ) is the ratio of loss modulus (E') to the storage modulus (E''). It gives the balance between elastic and viscous phase in polymer materials.
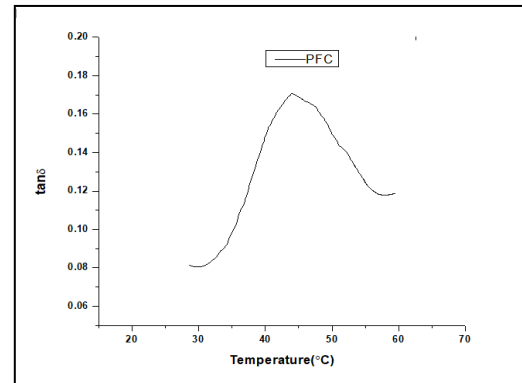
Figure 1.10: tanδ variations with temperature obtained by DMA for PFC
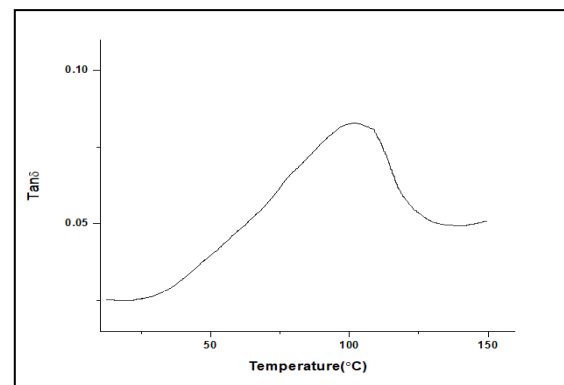
Figure 1.11: tanδ variations with temperature obtained by DMA for FRPFC

It is clear from above figure 1.10 and 1.11 in transition region damping increases with increasing temperature and rubbery region it decreases with further increase in temperature. The peak of this curve gives the information about value of glass transition temperature. As the temperature below T_g, the polymer chains become more rigid and less able to move freely, which further reduces the damping properties. On the other hand, when temperature is greater than T_g, the segments tend to move freely, and chain segments interact with each other which increases energy loss through dissipation. Therefore, damping goes a maximum at a certain transition region, and then it goes decreasing to a lower level [12].

It is also clear from graph that height of tanδ peak of FRPFC is less than height of PFC. this may be due to the restricted movement of molecules of polymer composites. Polymer molecules are prevented from sliding past each other as the rigid fibers restrict the amount of movement that can occur. tan δ values are commonly used as an indication of the quality of the interface between two materials. A decrease in the peak height indicates good adhesion and that there has less energy lost at the interface. This lower energy loss is

indicative of a good bond between the two materials. From figure 1.10 it is clear that pure phenol formaldehyde composite has T_g at 45°C this result also supports the result found from DSC of PFC (figure 1.5) where as in figure 1.11 Tg value of FRPFC shifts at higher temperature same results was obtained from DSC curve [12].

Conclusion

TGA thermo-gravimetric results suggests that the phenol formaldehyde PF composite made from alkali treated 5% wt. of prosopis juliflora PJ natural fiber has more thermally stable than PF composite reinforced with untreated PJ fiber This suggests that the alkali treated phenol formaldehyde sample may have higher thermal stability and could be a better candidate for products that require higher thermal stability. This is because the mass residue of the treated composite was higher than the untreated composite when subjected to increasing heating rates of 5°C/min, 10°C/min, 15°C/min, and 20°C/min. from the DSC results It is clear that untreated 5% wt. PJ fiber reinforced PF composite has glass transition temperature 46.1°C to 52.6°C with increasing heat rate 5°C/min. to 20°C/min. and PJ treated PF composite found Tg values ranging from 50.5°C to 69.5°C with increasing heat rate 5°C/min. to 20°C/min. This shows that reinforced fiber can significantly increase the glass transition temperature of composite material comparing with the untreated materials. Overall, it can be concluded that the glass transition temperature of the composite material can be greatly enhanced by adding reinforced PJ fibers. The heat rate affects the Tg value, with an increase in it leading to higher Tg. The reinforcement materials provide higher stiffness, strength, hardness and wear resistance to the composite material. This increased performance is due to better bonding between the resin matrix and the fibers which prevent any cracks or splits in the material. All these advantages of reinforced PJ fibers make them the preferred choice for a variety of composite materials. DMA analysis it has been clear that the storage modulus increases from 0.68 GPa for composites containing no PJ fiber around 1.26 GPa for composites containing PJ fiber. A decrease in the tanδ peak height indicates good adhesion and that there has less energy lost at the interface. This lower energy loss is indicative of a good bond between the two materials.

Conflicts of Interest

The authors declare no conflict of interest.

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