

Influence of MMT Nanoclay on Impedance Spectroscopy Analysis of Naturally Woven Coconut Sheath/Polyester Hybrid Composite

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ABSTRACT: In this work, the impedance spectroscopy study has been carried out for the naturally woven coconut sheath fiber reinforced composite with the effect of adding different weight percentages of montmorillonite nanoclay and chemical activation of fiber. The dispersion mechanism of nanoclay with polyester, and the modification of the fiber surface have been studied by using X-ray diffractogram, transmission electron microscope and scanning electron microscope respectively. Infra-red spectra have also been taken to study the reactive compounds of treated fibers. The impedance spectrum shows significant improvement in A.C. conductivity, dielectric constant and loss tangent values by the fiber modification, using alkali and silane treatments, due to the structural topography changes at the fiber surface. The highest dielectric strength was found in alkali-treated coconut sheath/polyester composite due to increase in orientation polarization by the absorption of moisture content at fiber surface. The addition of different weight percentages of nanoclay with coconut sheath in all the treated conditions shows significant changes in the dielectric properties. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 3746–3756, 2013

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INTRODUCTION

The use of polymer nanocomposites offer incredible opportunities to develop revolutionary materials in the field of military, aerospace, electronics, automotive, and commercial applications.^{1–3} The incorporation of plant fibrous reinforcements in thermoset matrix with nanofillers leads to high performance composite materials having good mechanical properties as well as suitable for electrical applications. Nowadays natural fiber-reinforced composites have been found to be more popular dielectrics to meet applications, such as suspension insulators, bushings, studs, sleeves, and switch boards.⁴ Cellulose-based fibers as reinforcement in matrices have been used to develop more innovative products in automobile, construction, chemical, and paper industries.^{5–7} Owing to their light weight, less cost, easy availability, and eco-friendly nature, plant fibers can be a suitable replacement for synthetic fibers in such applications, where they are subjected to low load bearing capacity.^{8–10} Natural plant fibers have a moisture absorbing nature as they are received from lignocellulose, which is occupied by strongly

polarized hydroxyl groups.^{11,12} The major drawback of using natural fibers as reinforcement in hydrophobic resins is that they provide poor interfacial adhesion, due to poor wettability between the fibers and matrix. Suitable surface modification of natural fibers can improve their interfacial adhesion and hydrophilic character, which in turn, make them more compatible with thermosetting matrix. The interfacial properties also strongly affect the characteristics and performance of these composites.^{13–15}

The dielectric properties of natural fiber composites are influenced by many factors, such as the weight percentage of the fiber, fiber orientation, dispersion of fillers and chemical modification of fibers.^{16,17} The effect of fiber loading on the dielectric behavior of sisal-low density polyethylene has been studied in ambient temperature conditions. The authors found that dielectric constant values improved with fiber loading.¹⁸ Navin et al.¹⁹ have reported that the dielectric properties are affected by the orientation of sisal fiber (0 and 90° to the electric field) with increasing frequency. The interfacial bonding and

resistance to moisture absorption of natural fiber composites can be changed by a suitable chemical treatment of the fiber. Augustine et al.²⁰ have suggested that different types of chemical treatments can influence the dielectric properties, by creating efficient interfacial adhesion between sisal and low density polyethylene. The dielectric properties of Roystonea regia fiber reinforced epoxy matrix have been reported by Govardhan et al.²¹ It was found that the conductivity of alkali-treated composites is lower than that of untreated composites, and gets increased with frequency. The enhancement in dielectric properties associated with the interfacial adhesion of non-woven alfa fiber mixed with wool fibers, over a temperature range of room temperature to higher temperature has been studied by Triki et al.²²

Only limited research has been carried out on dielectric properties through chemical modifications of natural fiber reinforced composite, having short fiber as reinforcement. Therefore, the need of fiber reinforced composites as dielectrics with better mechanical strength is essential for suitable industrial applications. There are no articles reported by the combine effect of nanoclay and chemical treatment on dielectric behavior of the coconut sheath fiber reinforced polymer composites. Hence, in this investigation, the attempt has been tried to study the impedance spectroscopy analysis by the influence of Montmorillonite (MMT) nanoclay as secondary reinforcement in naturally woven coconut sheath. Impedance spectroscopy is an effective and versatile technique, to analyze the electrical property of a composite material, as it distinguishes between the fiber–matrix interface, dispersion of filler, and chemical treatment of fiber. In the impedance technique, the real and imaginary parts of impedance of the sample were measured simultaneously, as a function of frequency. The study of dielectric properties, such as A.C. conductivity (σ_{ac}), dielectric constant, loss tangent ($\tan \delta$) in this hybrid nanocomposite, will lead to assessing its conductivity and insulating character for suitable applications.

EXPERIMENTAL

Material

Naturally woven coconut fiber mat is used as a reinforcement, which is directly extracted from the outer bask of the coconut tree. Figure 1 shows the sized naturally woven coconut sheath. It contains thick and thin fibers arranged in a random architecture. Thick fibers are oriented in a fish bone shape, with the main fiber at the center. The thin fibers are arranged between thick fibers, which are made into a randomly oriented woven mat. Unsaturated isophthalic polyester resin was used as a matrix, which was procured from M/s Vasivibala resins (P) Ltd, Chennai, India. The organically modified MMT clay was selected as reinforcing filler for strengthening the matrix, and obtained from M/s Sigma Aldrich (P), Bangalore, India. For 100 g of resin, 1.5 mL of Methyl Ethyl Ketone Peroxide (MEKP) and Cobalt Naphthenate were taken for curing at room temperature.

Fiber Modification

Coconut sheaths were cut into the form of mats of 300 mm x 130 mm in size, and were immersed in a 4% NaOH solution at room temperature. The fiber mats were placed in the alkali (NaOH) solution for 1 h, and then washed several times with



Figure 1. Architecture of fibers in sized naturally woven coconut sheath. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

fresh water until all the NaOH deposition over the fiber surface was removed. The coconut sheaths were then dried at room temperature for 24 h followed by hot air oven drying at 80°C for 1 h. In the case of silane treatment, the pretreated NaOH coconut sheaths were immersed in 0.5% trichlorovinyl silane with an alcohol water mixture solution for 30 min. The pH value of the solution was maintained as 3.5.

Composite Preparation

Different weight percentage inclusions of clay, i.e. x wt % ($x = 1, 2, 3,$ and 5) have been added as secondary reinforcement to coconut sheath reinforced polyester composites. The fabrication of coconut sheath/MMT clay fiber reinforced hybrid composites was carried out in two steps. In the first step, the varying weight percentages of nanoclay were taken with unsaturated isophthalic polyester resin, and the above mixture was uniformly dispersed with the help of a high speed mechanical shear mixer at 500 rpm for about two hours with a radial turbine blade; they have been identified as optimum parameters from the preliminary investigation study.²³ The final product collected from the high shear mixer was allowed for the degassing process. In the second step, the nanoclay mixture was mixed with a curing agent and spread over the fiber mat with a steel brush in each layer, which were placed inside the closed mould of size 300 x 125 x 3 mm³ by keeping one over another, up to six layers (48 ± 2 wt %). The mold was first coated with white wax so that the cured specimen can be taken out of the mold with ease. The mold was closed by applying 100 kgf/cm² pressure using a compression molding machine, and allowed curing at room temperature for another 24 h. The post curing was also done for all the composites in hot air oven at 60°C for about 2 h.

Test Sample Preparation

After the composite plates were fabricated, the specimens were cut according to the dimensions specified in²⁴ for dielectric studies, in a CNC wood carving machine. The test samples were cut into pieces of 5 mm diameter. Uniformity of surface was obtained by rubbing the surface against 600-grade SiC emery.

Table I. Chemical Analysis of Naturally Woven Coconut Sheath

Fiber treatment	Cellulose content (wt %)	Lignin content (wt %)	Wax content (wt %)	Moisture content (wt %)
Untreated (UTC)	68.36	20.63	0.4062	8.79
Alkali-treated (ATC)	52.89	33.29	0.1224	12.66
Silane-treated (STC)	59.99	26.96	0.2653	11.50

The circular surfaces of the test samples were coated with conductive silver paste.^{25,26}

Characterization Analysis

An x-ray diffraction (XRD) pattern has been taken with a SHIMADZU, XD-DI unit with Cu K α radiation. Transmission electron microscope (TEM) measurements were taken by Technai Spirit, FEI, Netherlands instrument. Scanning electron microscopy (SEM) images are taken with a Hitachi S-3000 model. A Fourier transformer infra-red (FTIR) spectrum was taken to characterize the chemical modifications of fiber with an infra-red spectrophotometer (Shimadzu, Japan). Electrical measurements have been taken by means of a computer controlled HIOKI model 3532 LCZ Meter (frequency range 42 Hz to 1 MHz) at room temperature with silver as an blocking electrode.^{26,21} The maximum of $\pm 5\%$ error was detected in the dielectric measurements.

RESULTS AND DISCUSSIONS

Chemical Analysis

The chemical analysis of the untreated, alkali- and silane-treated coconut sheath fiber is presented in Table I. The determination of the lignin content in the treated coconut sheath was carried out according to the Klason method.²⁷ According to Kurshner and Hoffer's method, the percentage of cellulose content in the chemically treated coconut sheath was measured.²⁸ The wax content in the treated coconut sheath was determined following the method developed by Conrad.²⁹ Based on the procedure reported by Sreenivasan et al.,³⁰ the moisture content in the chemically treated coconut sheath was determined. From the

ble it is evident that after NaOH treatment percentage of cellulose considerably decreased. The percentage of moisture and lignin content is higher in the case of alkali-treated fiber, compared with the silane and untreated coconut sheath due to the destruction of cellulose structure. NaOH treatment removes the impurities and wax content in the coconut sheath; further silane treatment increases the wax concentration, and this may be due to the presence of trichlorovinyl silane.

IR Spectrum

The IR spectra of the untreated and treated (NaOH, Silane) coconut sheath are given in Figure 2. The broad spectrum at 3316 cm^{-1} is the characteristic band for O—H stretching and the peak at 2900 cm^{-1} is the characteristic band for C—H stretching. The breadth of the peak at 3316 cm^{-1} is related to OH stretching for hydroxyl group present in polysaccharide.³¹ However, this peak gets broader and less intense in the case of alkali-treated fiber. This may be due to the formation of more OH groups as a result of the breaking of crosslinks of hemicellulose with cellulose after alkali treatment.²⁰ It could have had more moisture content and ultimately higher polarity on fiber surface. The peak at 3316 cm^{-1} owing to O—H stretching in the IR spectrum of the silane-treated coconut sheath is less broad, than that for the NaOH-treated fiber, and broader than that of the untreated coconut sheath. As a result of silane treatment, the hydrophilic nature of the coconut sheath is partially reduced, and the water content therefore decreases.

Structure and Morphology

Figure 3 displays the XRD pattern of untreated and chemically treated coconut sheath. From Figure 3 it is observed that the two peaks situated at $2\theta = 15.4^\circ$ and $2\theta = 22.5^\circ$ can be

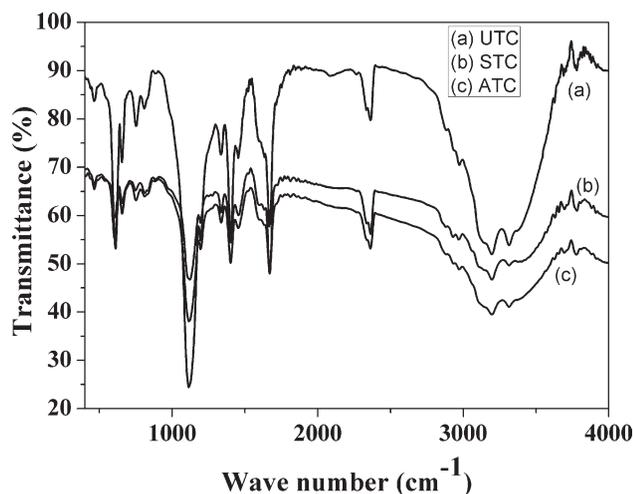


Figure 2. IR spectra of untreated, alkali- and silane-treated coconut sheath.

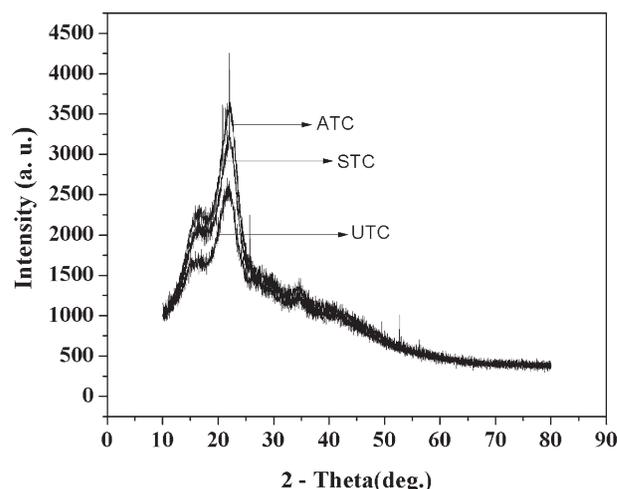


Figure 3. X-ray diffraction patterns for chemically treated coconut sheath.

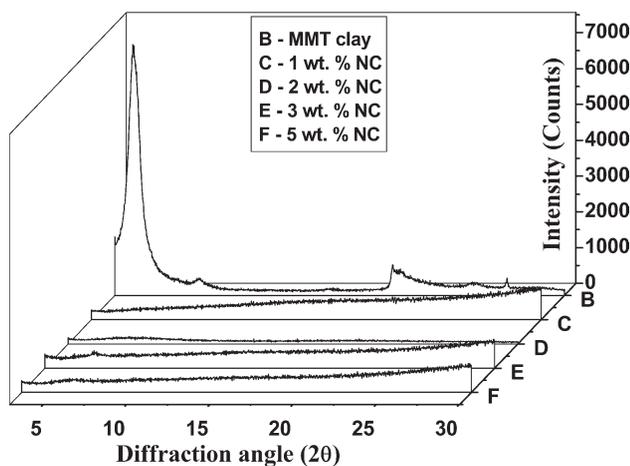


Figure 4. X-ray diffraction patterns for polyester and clay-filled polyester composite.

attributed to cellulose I and IV, both of which exhibit a monoclinic structure, which was already reported by many authors.^{32,33} These two peaks are attributed to the (2 0 0) and (1 1 0) crystallographic planes.³⁰ The crystallinity index (CI) was estimated by eq. (1) using the following expression³⁴:

$$CI = (I_{22.5} - I_{18.5}) / (I_{22.5}) \quad (1)$$

where $I_{22.5}$ is the height of the peak at $2\theta = 22.5^\circ$. This is due to the contribution of both the amorphous and the crystalline fractions. $I_{18.5}$ is the diffracted intensity at $2\theta = 18.5^\circ$ and is attributed to the amorphous fraction. The CI of the alkali-treated coconut sheath (42%) exhibits the highest percentage of CI compared with silane (38%) and untreated coconut sheath (34%). It is evident that NaOH treatment removes the noncellulosic amorphous components (hemicelluloses, wax, and impurities) leads to better packaging of cellulose chain and thus increases the degree of crystallinity in the alkali-treated coconut sheath. The density of the alkali-treated coconut sheath gets reduced from 1.3753 g/cm^3 (UTC) to 0.9796 g/cm^3 . This may be attributed to the increase in the absorption capacity of the alkali-treated fiber.

Figure 4 shows the X-ray diffractograms of virgin MMT nanoclay and clay-filled polyester nanocomposite, with varying weight percentages of nanoclay. From the XRD pattern for pure nanoclay, a definite sharp peak at 4.5° (2θ) has been observed and it is attributed to the (0 0 1) crystallographic plane.³ However, on adding different weight percentages of MMT nanoclay with the polyester nanocomposite, it shows a completely amorphous nature, due to the uniform distribution of nanoclay. This shows that the interlayer distance of organically modified clay layers are expanded, and randomly dispersed in the matrix. So that it forms intercalated/exfoliated structure of the nanocomposite.

Figure 5 shows the TEM images of different weight percentages of MMT nanoclay with the polyester matrix. [Figure 5(a–d)] show the separation of the clay platelet (1, 2, and 3 wt %) of MMT nanoclay in polyester by means of beach mark patterns, which attributed to the formation of intercalated/exfoliated

structure. The distance between the clay platelets gets increased by the delamination at lower clay content from the clay tactoid sheet. When the wt % of MMT nanoclay (5 wt %) increases the presence of clay aggregates have been noticed from the appearance of a dark black band river pattern [Figure 5(d)]. This could happen due to the immobility of clay in a highly viscous clay mixture, and it was constrained by the presence of the surrounding clay platelets.

Figure 6 shows the SEM images of an untreated (UTC), alkali-treated (ATC) and silane-treated (STC) coconut sheath. The presence of a waxy layer over the coconut sheath leads to a lack in bonding between the fiber and the resin. The SEM image with higher magnification [Figure 6(a)] reveals the presence of curling white colored ribbon like layers which are termed as waxy layers. The presence of waxy layers over the fiber prevents the formation of a strong interface between the fiber and resin. NaOH treatment has been done before silane activation to remove the waxy layer, and to create a rough surface over the fiber. This roughness could be observed in Figure 6(b). It can provide better mechanical interlocking between the fiber and matrix due to the exposure of a large contact surface. On the other hand, a coating of thin film deposition over the surface of silane-treated coconut sheath could be seen in Figure 6(c). Once the surface of the coconut sheath was covered by a thin film of trichlorovinyl silane, it promotes a good adhesion between the fiber and the polyester matrix. It leads to a strong covalent bond, which could happen by the good physical adhesion. Consequently, it can improve the adhesion force and surface energy at the fiber-matrix interface.^{5,7}

To study the morphology of the individual fiber in the coconut sheath, the SEM photographs were taken with higher magnification. Figure 7 shows the SEM micrograph of the individual (a) UTC, (b) ATC and (c) STC thick fiber. The deposition of impurities and white dot circular protrusions were seen in the surface topology of the untreated thick fiber [Figure 7(a)]. After the NaOH treatment, the impurities are removed and it is attributed to the formation of a rougher surface on the fiber [Figure 7(b)]. From Figure 7(b), it was also seen that a large number of circular pores is present on the surface, which is obtained from the removal of protrusions after the treatment. These pores can enhance the hydrophilic nature of the alkali-treated fibers by means of the water absorbing molecules. The separation of loosely bonded polished fiber structure with a thin film deposition was observed in silane-treated condition as shown in Figure 7(c). The removal of cementing material like waxy and artificial impurities exposes the segregation of fibers in fiber bundle called as fibrillation.²² It induces an increase in surface area available for contact with silane. Thus better fiber/matrix interface adhesion has occurred. This silane coating could shield the voids over the pretreated NaOH fiber surface. Hence, the water sorption in silane-treated fiber gets lesser than in the NaOH-treated fiber and higher than in the untreated coconut sheath, and this was already confirmed from the percentage of the moisture content in chemical analysis (Table I). The density values for untreated (1.013 g/cm^3), alkali-treated (1.1305 g/cm^3) and silane-treated (1.099 g/cm^3) composites were identified for without clay condition.

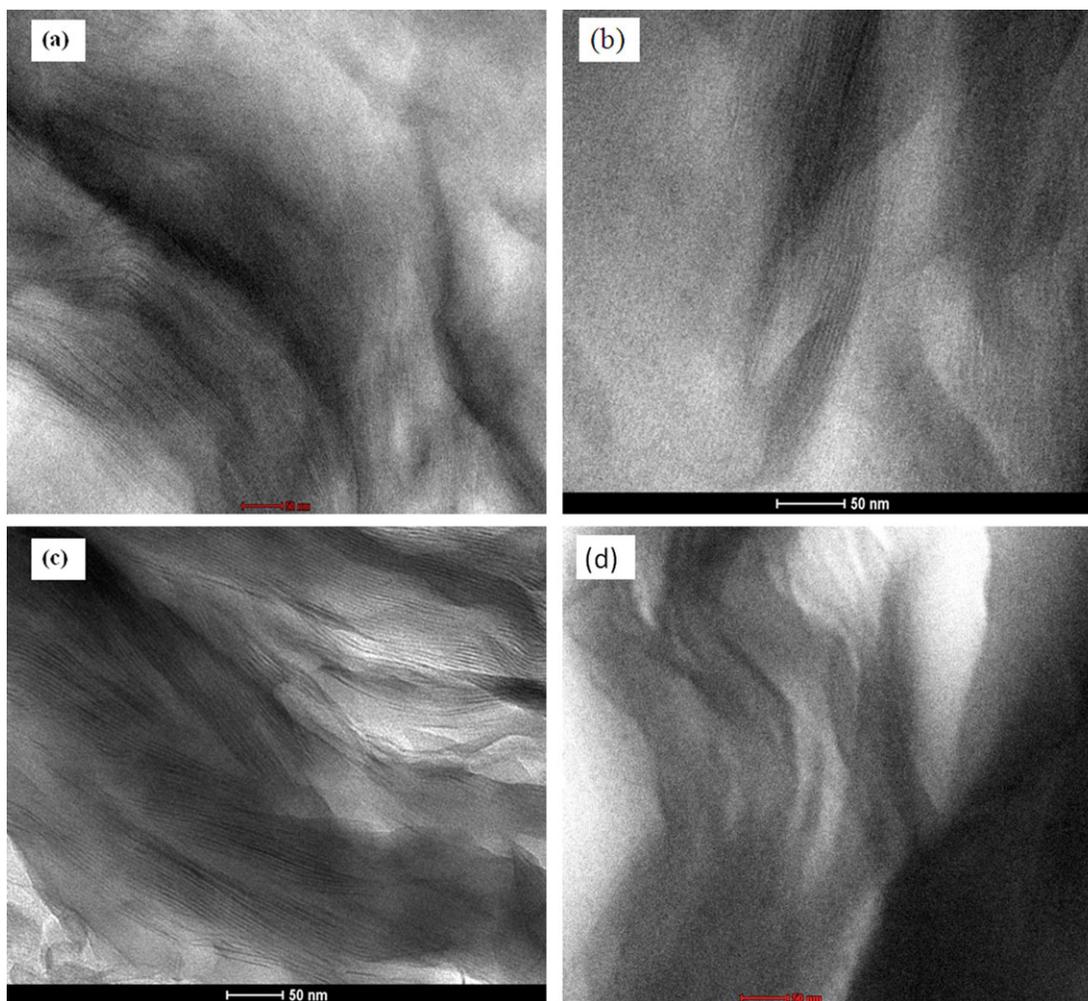


Figure 5. Transmission electron microscopy images of nanoclay-filled polyester composite (a) 1 wt % (b) 2 wt % (c) 3 wt % (d) 5 wt %. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Impedance Spectra Analysis

Figure 8 shows the Cole-Cole plot of all three specimens (UTC, ATC, and STC) with and without the addition of nanoclay. According to the Figure 8(a), a single semicircle in the high frequency region followed by low frequency spike was found for ATC and STC samples in without clay condition. In the case of UTC samples only a semicircle was obtained in high frequency region. It may happen due to the reduction in the carrier mobility. The same kind of observations was also reported by Annapurna et al.²⁶ on sisal fiber reinforced polyester composites. For all spectra the semicircle with their centre lying below the real axis indicates the non-debye type relaxation in the material before and after treatment due to distribution of relaxation times.^{35,36}

Conductivity Spectra Analysis

Figure 9(a) depicts the variation of A.C. conductivity of UTC, ATC, and STC coconut sheath at room temperatures. The spectra of two specimens (ATC, STC) exhibit “two well- defined regions”. From Figure 9(a) it is clear that the A.C. conductivity depends strongly on the treatment of the coconut sheath. Because of the restricted motion of the hydroxyl ions and other

cuticle waxy layers in the untreated fiber surface represents the A.C. conductivity region. NaOH-treated and silane-treated coconut sheaths show higher conductivity when compared with the untreated sample. Owing to chemical modification the waxy layers are removed, and this ensures better structure formation at the fiber surface. Hence, it results the variations in dielectric behavior due to the network formation by the packing of materials with different density. The different type of treatment increases the transition from the D.C. plateau to an A.C. conductivity dispersion region, shifting towards the higher frequency range when compared with the untreated one. This could be owing to the increase in carrier mobility at the interface between the high polarity-treated coconut sheath fiber and polyester matrix.³⁷ The dispersion region is characterized by the random hopping of mobile ions. Figure 9(b–d) shows the variation of the ac conductivity of the addition of different weight percentages of nanoclay with UTC+ x wt %, ATC+ x wt % and STC+ x wt % coconut sheaths at room temperatures. The addition of MMT nanoclay can influence the A.C. conductivity in ATC and STC reinforced composites than that of UTC composites. Whereas, in the case of UTC only the small variation was

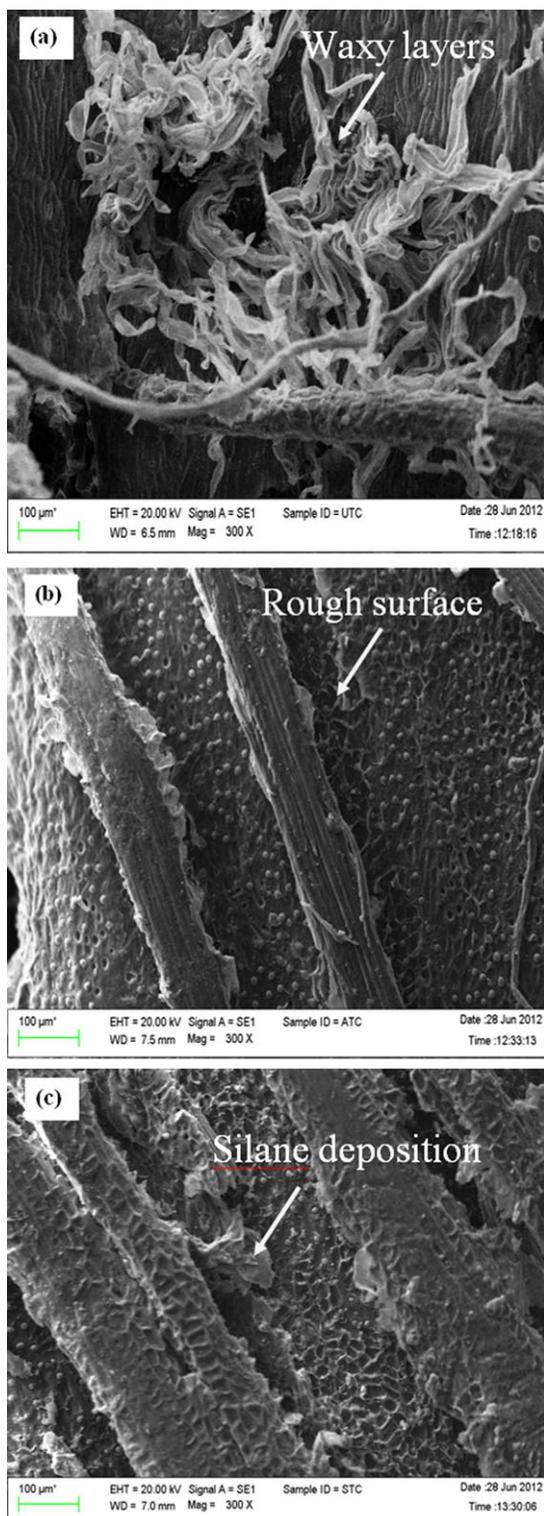


Figure 6. The SEM image of (a) UTC, (b) ATC and (c) STC coconut sheath. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

noticed with the addition of clay. It could be due to the hindering effect of waxy layers over the conductive interfacial regions. It is reported that the electrical conductivity³⁸ is mostly affected by the presence of the two interfacial layers in the polymer

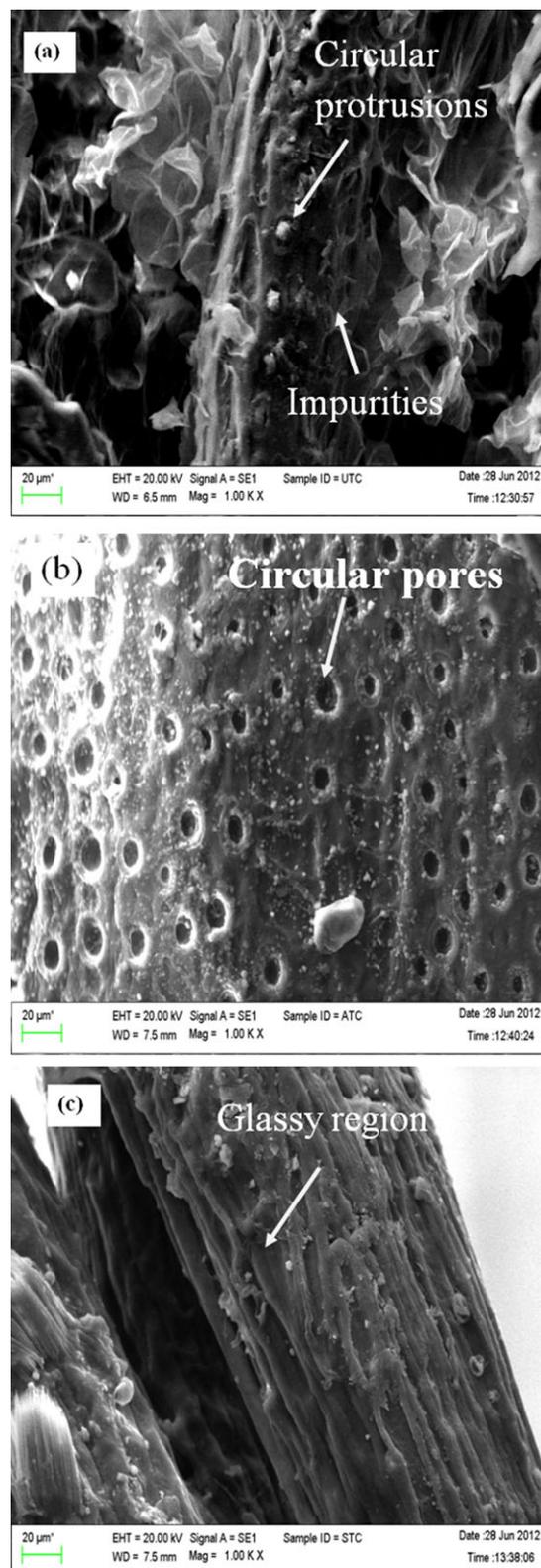


Figure 7. The SEM images of individual (a) UTC, (b) ATC, and (c) STC thick fiber. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

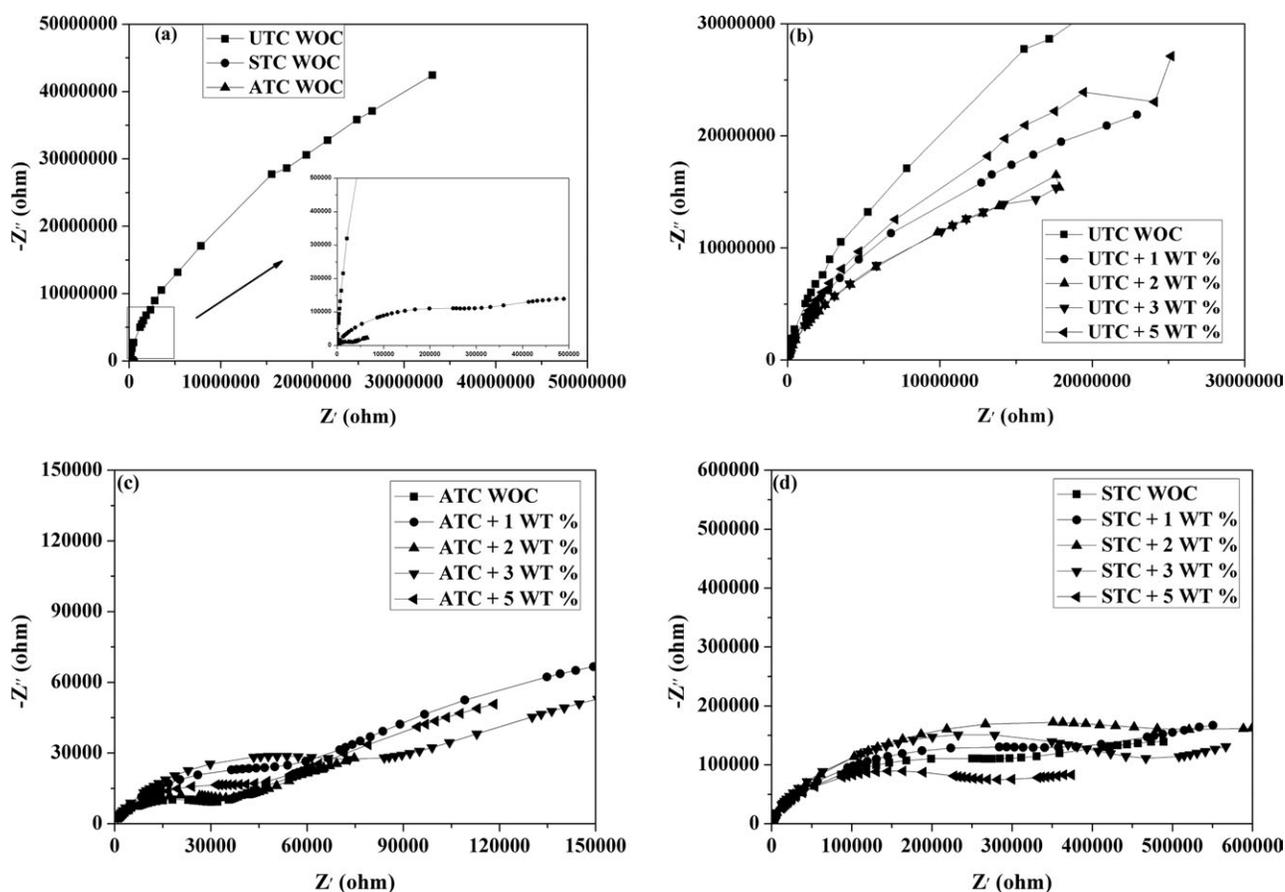


Figure 8. Cole-Cole plots for the composite in different conditions (a) UTC, ATC, and STC coconut sheath. The addition of different weight percentages of nanoclay with (b) UTC+ x wt %, (c) ATC+ x wt% and (d) STC+ x wt% coconut sheath at room temperatures.

nanocomposites. Due to the formation of an electrically conductive interface, these free charge carriers will be moving in the bulk of the material rather than accumulate at the interface region. For the untreated coconut sheath, the addition of nanoclay will enhance the conductivity due to the randomly oriented delamination of the nanoplatelet with the waxy layer. The highest conductivity is achieved by the addition of a lower weight percentage of clay content (< 3 wt %) and further addition can decrease the conductivity, but not lesser than the unfilled clay composite. This could happen due to the agglomeration of clay platelets [Figure 5(a,d)] and it can act as a barrier of the charge mobility by creating a torturous path that could decrease the conductivity. The amount of liquid absorbed by the coconut sheath varies with the nature of the chemical treatment. It is also realized that the moisture uptake of NaOH-treated coconut sheath is higher than that of silane and untreated samples. The presence of pores in the SEM image as shown in Figure 7 of NaOH-treated coconut sheath fiber could be the probable reason for absorbing more moisture content compared to UTC. In most of the cases the conductivity values are decreased for different weight percentages of nanoclay added to the NaOH-treated coconut sheath. This is possibly due to the decreased hydrophilicity of the NaOH-treated coconut sheath. This may have happened owing to the nanoclay platelets in the polyester resin diffusing into the voids of the fiber surface, and hence the

possibility of further liquid penetration is reduced. Geethamma et al.³⁹ have reported that the sorption of alkali-treated coir fiber is higher in distilled water than in artificial seawater. They also suggested that salt particles in artificial seawater diffuse into the voids of the compound, and in turn, the chances of additional water absorption are reduced.

The Experimental data of Figure 8(a–d) is found to obey Jonscher's power law.⁴⁰ The Jonscher's power law equation may be written as

$$\sigma(\omega) = \sigma_{dc} + A\omega^n \quad (2)$$

where n is the frequency exponent in the range $0 < n < 1$. Both σ_{dc} and A are constants. The frequency-independent conductivity is observed in the low frequency region, which indicates the dc conductivity of the material. In the high frequency region, the power law feature $\sigma(\omega) \propto A\omega^n$ is observed.

Dielectric Analysis

The frequency dependent electric parameters such as the complex dielectric constant (ϵ_r) and the tangent loss factor ($\tan \delta$) can be related to the dielectric constant (ϵ_r) expressed in the complex formalism

$$\epsilon^* = \epsilon' - j\epsilon'' = 1/(j\omega CoZ^*) \quad (3)$$

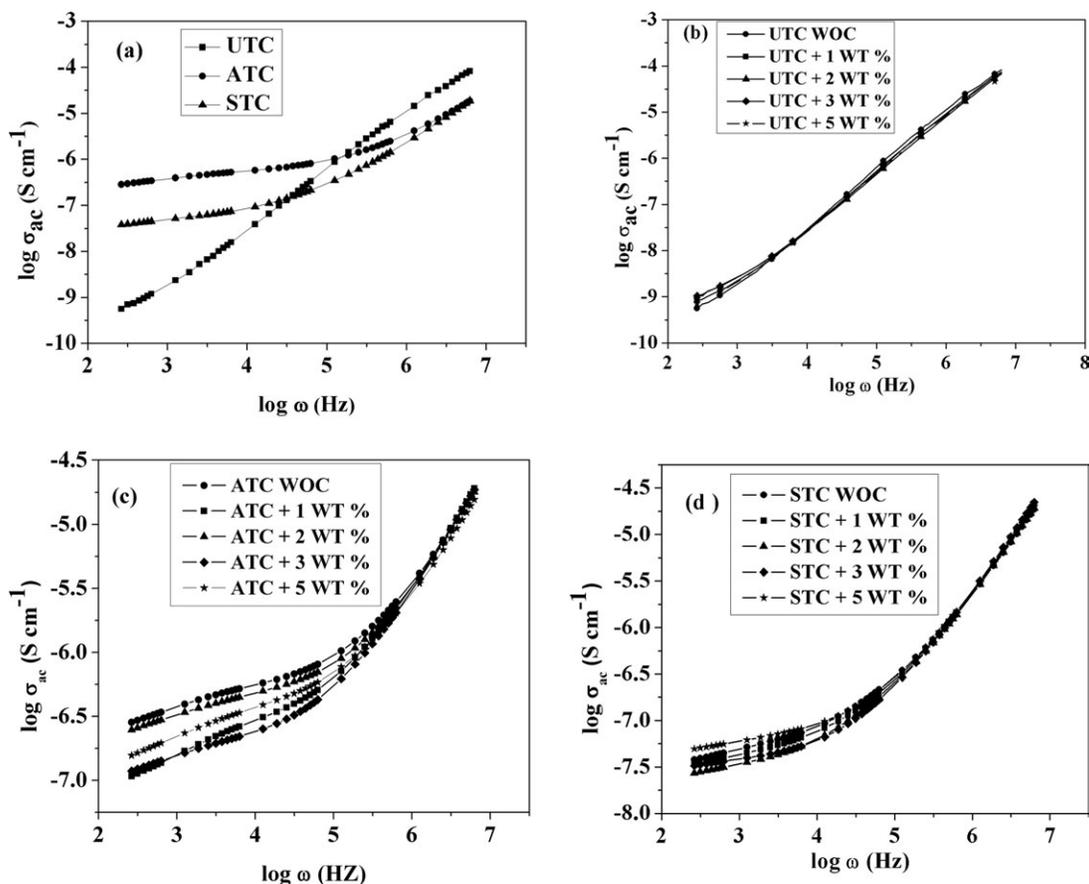


Figure 9. The variation of AC conductivity with angular frequency for (a) UTC, ATC, and STC coconut sheath. The addition of different weight percentages of nanoclay with (b) UTC+ x wt %, (c) ATC+ x wt %, and (d) STC+ x wt % coconut sheath at room temperatures.

$$\tan \delta = \varepsilon''/\varepsilon' \quad (4)$$

where ε' is the real part of complex permittivity or dielectric constant and ε'' is the imaginary part of the dielectric permittivity or dielectric loss, Z is the complex impedance, C_0 is the vacuum capacitance of the empty measuring cell, ω ($\omega = 2\pi f$ where f is the frequency) is the angular frequency and $j = (-1)^{1/2}$.

Figure 10(a–d) shows the variation of the dielectric constant for UTC, ATC, and STC coconut sheaths and the addition of different weight percentages of nanoclay with UTC+ x wt%, ATC+ x wt% and STC+ x wt% coconut sheaths at room temperatures. Generally, the dielectric constants of the natural fiber reinforced polymer composites depends on the atomic, electronic, interfacial, and orientation polarization.⁴¹ The effect of atomic and electronic polarizations are seen only at high frequencies. The influence of interfacial polarization arises in low frequency region due to the heterogeneity of composites. Hence, the dielectric constant value can be explained in terms of interfacial polarization. The observed variation in dielectric constant with frequency could be attributed to the formation of a space charge accumulation at the fiber/matrix interfaces.⁴² The dielectric constant was found to decrease sharply at low frequencies, followed by an intermediate plateau, and a leveling off at higher frequencies. At high frequencies, due to high periodic reversal of the

field at the interface, the contribution of charge carriers towards the dielectric constant decreases with increasing frequency. The effect of orientation polarization and interfacial polarization will depend upon the chemical treatment of fibers. Hence, the chemical treatment of coconut sheath increases the dielectric constant in low frequencies. It is clear from Figure 10(a), that the NaOH-treated coconut sheath shows higher dielectric constant at low frequency, when compared with the silane-treated and untreated coconut sheath. The possible reason for the high dielectric constant is due to NaOH treatment and it can remove the waxy layer and impurities, to create a rough surface over the fiber. In the NaOH-treated composite, the decrease in the dielectric value is observed to be higher for low frequencies and lower for high frequencies, compared to the other two cases. In NaOH treatment, the fiber / matrix interfacial adhesion was improved through proper bonding between the effective surface area of the coconut sheath and resin. The exposure of the increased surface roughness leads to fiber fibrillation in the coconut sheath after the NaOH treatment. In NaOH-treated composites, the number of interfaces is greater due to the separation of fibers from the fiber bundle. Hence, the contribution of interfacial polarization is increased, and, therefore, the dielectric constant values are maximum. The alkali solution influences not only the noncellulosic components but also the cellulosic

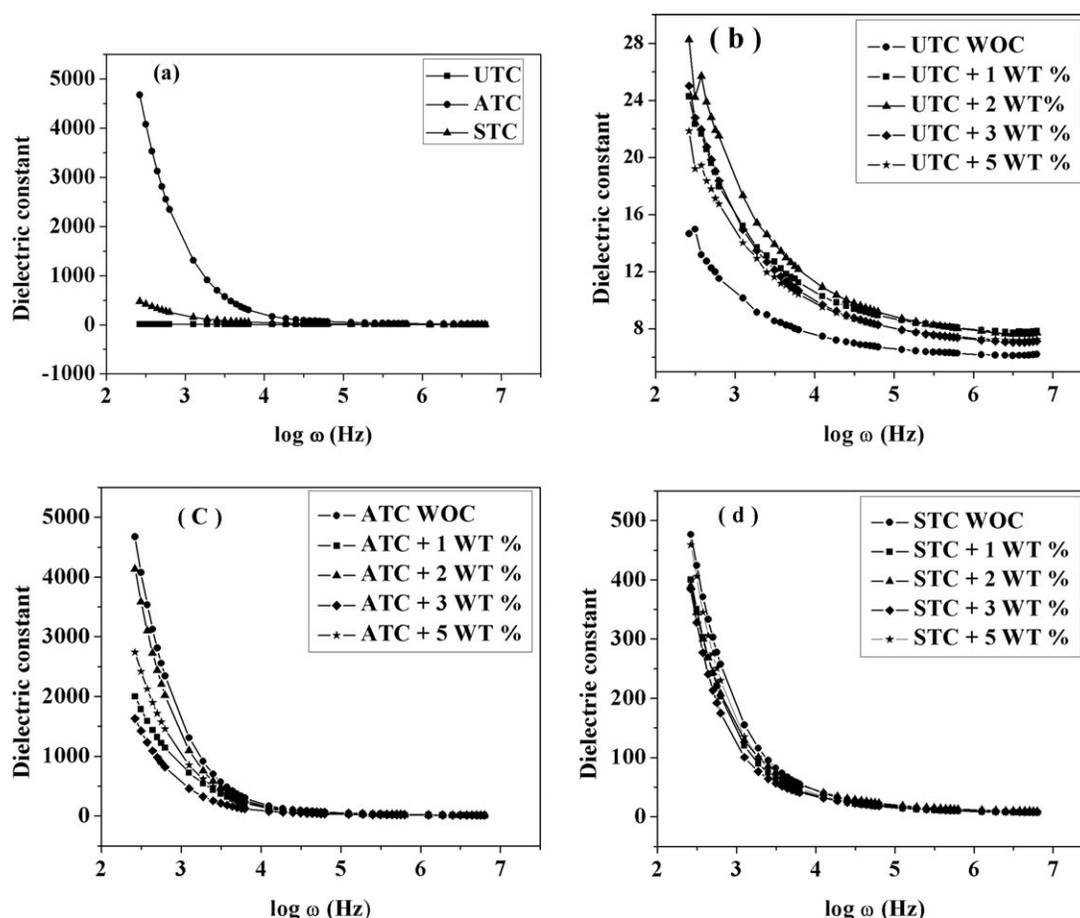


Figure 10. The variation of the dielectric constant for (a) UTC, ATC, and STC coconut sheath. The addition of different weight percentages of nanoclay with (b) UTC+ x wt %, (c) ATC+ x wt % and (d) STC+ x wt % coconut sheath at room temperatures.

components inside the plant fibers.⁴³ In alkali treatment much of the swollen cellulose frequently does not recrystallizes resulting in a large fraction of disordered amorphous cellulose at the expense of crystalline cellulose.^{43,44} However, the relative wt % of amorphous cellulose should be less than that of the crystalline cellulose.⁴⁴ This amorphization of cellulose might be also responsible for more hydroxyl group in fiber surface. Fraga et al.⁴⁵ have reported that dielectric constant of natural fiber reinforced polymer composites increased with the liquid uptake. In the alkali-treated condition, the dielectric strength values are decreased with the addition of different weight percentages of nanoclay. This is due to the decreased possibility of liquid uptake in the NaOH-treated coconut sheath/clay nanocomposite. However, lower dielectric constant values are obtained for alkalinized silane-treated composites, as compared to the NaOH-treated composites, as shown in Figure 10(d). The reason for the lower dielectric constant for the silane-treated coconut sheath was the formation of silanol groups, obtained by the reaction between the hydroxyl groups and trichlorovinyl silane at the fiber surface. The silane coupling agent diffuses into the cell wall through voids, and is coated in the interfibrillar region as shown in Figure 6(c). Hence, silane can act as a bridge between the fiber and matrix and create good fiber/matrix adhe-

sion. This strong interfacial bond changes its hydrophilic nature and decreases the dielectric constant, compared to the NaOH-treated condition. The same trend was also observed in the dielectric property with the addition of nanoclay in all types of composites. The lower dielectric strength was noticed for 2 wt % of nanoclay addition in alkali-treated coconut sheath reinforced composite, and hence, it possesses enhanced mechanical properties.⁴⁶

Dielectric Loss Factor (δ)

Tan (δ), termed as the loss tangent, is the measure of power lost by a material. Like dielectric strength the loss tangent also decreases with an increase in frequency in all types of composites. The variation of the loss tangent tan (δ) with angular frequency at room temperature is given in Figure 11. The pattern of variation is characterized by the occurrence of well defined peaks, which shift to higher frequencies with NaOH treatment, when compared with silane-treated and untreated coconut sheath. These loss peaks and their shifts with treatment, suggest a dielectric relaxation phenomenon in the material. Also, the shifting of peaks toward the higher frequency sides with treatment can be attributed to a gradual decrease in resistance with increasing frequency. Figure 11(a) presents the variation of the

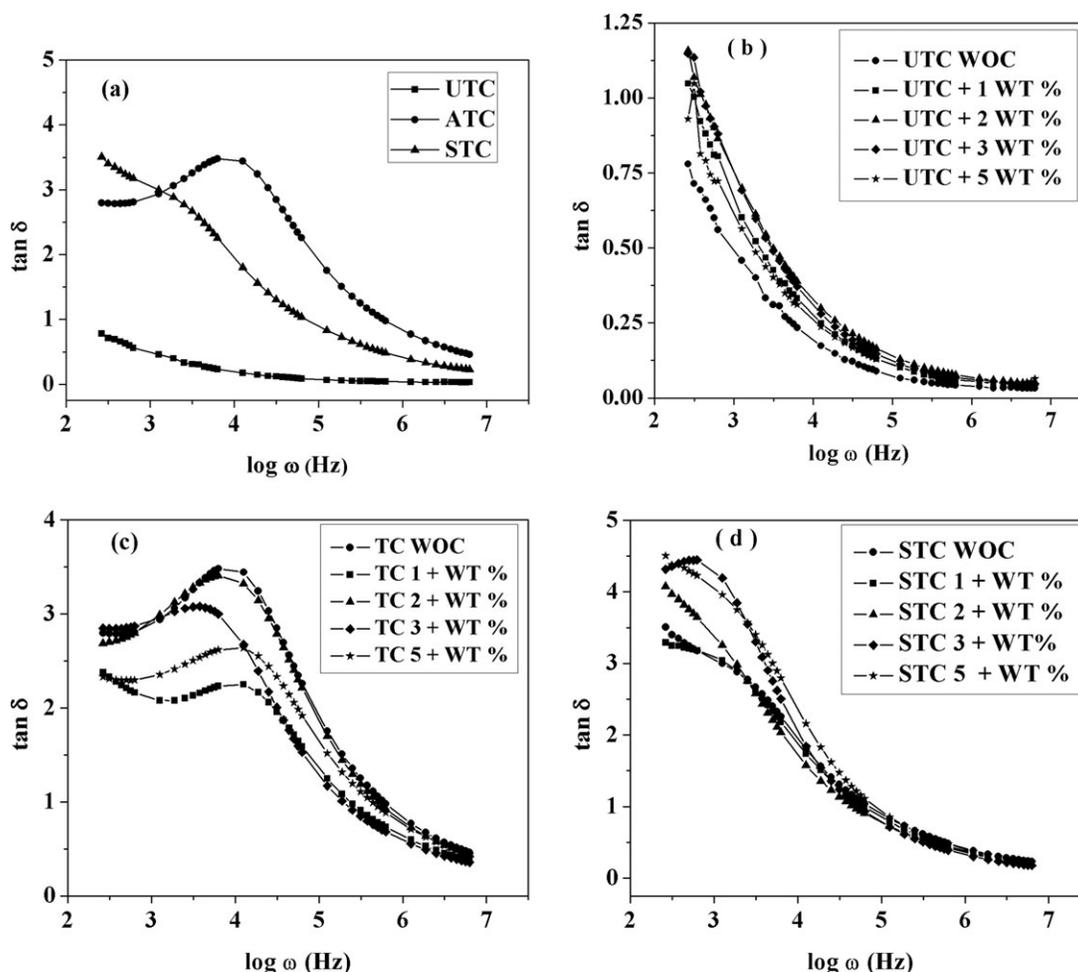


Figure 11. The variation of loss tangent $\tan(\delta)$ for (a) UTC, ATC, and STC coconut sheath. The addition of different weight percentages of nanoclay with (b) UTC+ x wt %, (c) ATC+ x wt %, and (d) STC+ x wt % coconut sheath at room temperatures.

dissipation factor in chemical modifications. A large increase in the loss tangent was noticed in NaOH-treated composites, which is probably due to the increased orientation polarization by the formation of moisture clusters at the voids of the fiber surface. In general, crystallinity results in a decreased dissipation factor, due to less amount of heat release.⁴⁷ However, we found an increase in the loss tangent value for NaOH-treated composites where it possesses a high crystallinity index compared to the other two cases. It is realized that the dissipation factor not only depends upon crystallinity, but is also affected by the presence of the hydroxyl groups. The increase in percentage of the polar groups was identified in alkali-treated fiber due to voids and amorphous cellulose. The variation of the dissipation factor with frequency as an addition of different wt % of nanoclay is presented in Figure 11(b–d) for untreated, NaOH- and silane-treated composites. In the case of NaOH-treated composites, the addition of clay can reduce the dissipation factor due to decrease in hydroxyl groups by the prevention of micro-cavities. But only the anomalous trend was noticed with the varying wt % of clay addition. It could be due to the change in state of combined morphology of intercalated and exfoliated structure with varying wt % of clay addition. In the case of silane

treatment, the coating and interlocking of silane over the fiber surface can increase the dissipation factor with the addition of nanoclay. It may be due to the decreasing percentage of pores over the fiber surface by the silane coating. Similar to ATC composites, the nonlinear trend was also been observed in silane-treated condition with respect to the wt % of nanoclay.

CONCLUSIONS

The coconut sheath/clay reinforced hybrid nanocomposites was successfully fabricated by the compression molding technique. X-ray diffractogram (XRD), Transmission electron microscope (TEM), and Scanning electron microscope (SEM) have been used and the results show the exfoliated/intercalated clay structure of the polyester nanocomposites. In all the composites, the dielectric constant decreased with frequency upon chemical modifications. The maximum increase in dielectric properties such as, A.C. conductivity, dielectric constant, and loss tangent was observed in NaOH-treated composites at lower frequency region than that of silane and untreated composites. This implies that the increase in polar groups and conductive network at interfaces can arise the orientation and interfacial

polarization after the NaOH treatment. The addition of nano-clay increases the dielectric behavior in untreated coconut sheath reinforced composites, whereas it decreases in the alkali- and silane-treated coconut sheath reinforced hybrid composites. The nonlinear trend was observed in varying weight percentages of clay in all treated composites. From this research, it is revealed that coconut sheath reinforced polyester composites not only act as insulators in as-received condition, but also exhibit charge holding conduction in composites fabricated with alkali-treated coconut sheath, filled with 2 wt % of clay.

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