Effect of Nanoclay on the Dielectric, Transport, Thermal and Fire Properties of Coconut Sheath/MMT Clay Polyester Hybrid Composites

N. Rajini, J.T. Winowlin Jappes, S. Karthikeyan and A. Varada Rajulu

Abstract The emission of the inorganic pollutant and the non-biodegradable compounds to the atmosphere has been a threatening aspect for the increase of the environmental deterioration and posing a human health hazard. Therefore, the developing of the research in the field of science and engineering is mainly focused to create the eco-friendly environment. It is the fact that this research investigated the use of the natural fiber as reinforcement for the possibility of producing composite laminates as an alternative to the synthetic fibers in the industrial application ranging from building construction, existing house holding components like the roofs and the door panels, automotive, and the food packaging, where a good fire performance and the mechanical properties are essential. Therefore, it is necessary to design an eco-friendly material with all beneficial at the same time without compromising the basic mechanical properties. Hence in this chapter, the conductivity and the barrier properties of CS/PE composites were experimented with the effect of chemically treated CS and oMMT nanoclay addition. Thermo-gravimetric analysis has also been performed to study the effect of varying the weight of the nanoclay on the thermal stability of the CS/PE composites.

Keywords Clay · Conductivity properties · Barrier properties · Thermal properties

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N. Rajini (✉) · J.T. Winowlin Jappes · S. Karthikeyan
Department of Mechanical Engineering, Kalasalingam University,
Anand Nagar, Krishnankoil 626126, Tamil Nadu, India
e-mail: rajiniklu@gmail.com

A. Varada Rajulu
International Research Center, Center for Composite Materials,
Kalasalingam University, Anand Nagar, Krishnankoil 626126,
Tamil Nadu, India

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1 Introduction

Recently, the importance of blended nanoclay in polymer matrix composites explored significantly by many commercial applications such as fire retardant, food packaging, electronic circuit boards and automotive industries (El-Khodary et al. 2008; Sengwa and Sankhla 2008; Zheng and Wong 2003). The addition of nanoclay in polymer matrix can enhance the functional properties of nanocomposites due to the uniform distribution of particle with increasing surface area. Indeed, to achieve the higher mechanical properties, the nanocomposite requires the addition of reinforcing element. Based on the demand of application, the reinforcement can be in the form of particulate, fiber or woven fabric. Nowadays due to the advancement of biocomposites, there are lots of plants fibers have been used as primary reinforcement element in dielectric applications. Moreover, the conductive behavior of natural fibers due to the presence of water molecules can influence the dielectric characteristics of composites. Similarly, the addition of clay in polymer as particulate reinforcement can act as either insulator or conductor depending upon the type (from the source where it has been extracted) of clay. Accordingly, some of the researchers have studied the performance of dielectric properties of natural fibers in the applications such as stabilizer cover, bushings, sleeves and electronic circuit boards (Mukherjee et al. 1978).

By considering the effect of natural fibers and nanoclay particulate as primary and secondary reinforcement in polymer matrix on dielectric and other transport properties were found to be studied only limited. Apart from all other advantages of eco friendly circumstances, the natural fibers also have some demerits. Normally, the natural fibers are hydrophilic in nature and it’s have a major drawback of moisture absorption capability due to the presence of chemical constituents such as hemicelluloses, lignin and pectin. These components were found to be the responsible factors for providing strong polarized hydroxyl groups in plant fibers (Hepworth et al. 2000; John and Thomas 2008). So, the presence of moisture content on the fiber surface does not exhibit the better compatibility with hydrophobic polymer matrix. It will create a poor interfacial adhesion between fiber and matrix, which in turn, reduce the performance of the composite in all the aspects. Hence, it requires some topography changes on fiber surface by the chemical treatment so that the enhancement of fiber and matrix adhesion will get improved. Moreover, the morphological changes on fiber surface can create a strong fiber/matrix adhesion which can enhance the characteristics and performance of these composites (John and Anandjiwala 2008; Edeerozey et al. 2007; Alvarez et al. 2003).

Having all said, the factors like fiber length, fiber content, addition of particulate, manufacturing method, treatment of fibers were found to be influenced the dielectric properties composites(Lai et al. 2005; Kumar et al. 2011). Some of the published work related to impedance spectroscopic using natural fiber as reinforcement in thermoset and thermoplastic polymer matrix has been described as below.

The dielectric behavior of Low density polyethylene/sisal fiber composite has been studied and reported as the enhanced dielectric constant was observed with the increasing amount of fiber content in matrix (Paul et al. 1997).

The parameters such as fiber orientation and varying frequency were found to be influence the dielectric strength of the composites (Navin et al. 2005). In addition, the effect of chemical treatment of natural fiber composites on dielectric properties has also been studied with regards to change in magnitude of interfacial adhesion. Paul et al. (1997) studied the dielectric properties with the improved interfacial bonding between sisal and low density polyethylene with imposing different kind of chemical modifications. The dielectric properties of alkali treated Roystonea/epoxy matrix exhibits lower conductivity value than that of unmodified one, and found to be increased with frequency (Gould and Rao 2011). Similarly, the effect of hybridization associated with the dielectric properties has also been studied using the combination of two different natural fibers such as short alfa fiber and wool fibers for varying temperature (Triki et al. 2011). However, the dielectric property of composites with the influence of nanoclay as secondary reinforcement in untreated and chemically treated natural fiber composites was found to be scanty. Therefore, there are lot scope is available for studying the importance of fiber reinforced composites with the addition of nanoclay particulate on dielectric properties. So that the better suitable dielectric composite can be identified for different industrial application without sacrificing the strength of composites.

Moreover, the enhanced barrier behavior of nanocomposite motivates material researchers to spotlight the influence of nano-particle in polymer matrix (Messersmith and Giannelis 1995; Linchan et al. 2011; Kim et al. 2005). Lee et al. 2005 have carried out CO_2 gas permeability studies in polymer system and found that the permeability can be significantly reduced due to the uniformly distributed clay content. Permeability test was carried out for LDPE/clay nanocomposites in O_2 gas environment and determined that the increasing amount of clay content can decrease the rate of permeability, however it was applicable only for certain wt% beyond that the permeability was found to be getting increased (Arunvisut et al. 2007).

Among the different types of properties of composites it is essential to study the characteristics of molecular barrier properties, such as, gas permeability, thermal conductivity, and surface and volume resistivity of a composite. Generally, these transport properties of composites are significantly affected by the fiber size, fiber content, fiber orientation, and chemical modification of fiber surface and the addition of the filler. The dielectric parameters, such as the AC conductivity (σ_{ac}), dielectric constant (ε_r) and dielectric loss tangent (tan δ), were measured for CS/MMT hybrid composites in the frequency range of 42 Hz to 1 MHz at room temperature. Besides the behavior of the molecular transport properties such as thermal conductivity, gas permeability, volume and surface resistivity has been studied. Scanning Electron Microscopic investigation (SEM) has been carried out to find the silica rich area on the coconut sheath fiber.

2 Materials and Methods

2.1 Fabrication of Hybrid Polyester Nanocomposites

The fabrication process of the composite is one of the vital criteria, which decides the strength of the composite. Among all the fabrication processes, the compression molding method provides better cohesion in the prepared composite structure. In this work the fabrication of the coconut sheath fiber/MMT nanoclay reinforced hybrid polymer composites was carried out in two steps. In the first step, the proportionate wt% of nanoclay was taken according to the wt% of the unsaturated isophthalic polyester resin, and the above mixture is stirred by the high speed mechanical shear mixer at 500 rpm for about 2 h, with a radial turbine blade. In the second step, the CS/MMT clay/PE hybrid composites were fabricated using the compression molding machine by the following procedure.

The final product collected from the high shear mixer was allowed for the degassing process. The mats were impregnated with the clay-polyester mixture to which 1.5 vol% of cobalt naphthenate and MEKP were added. The middle plate is placed over the bottom plate with the help of circular pins to maintain the position fixed, as shown in Fig. 1a. Then the clay-resin mixture with the curing agent was spread over the CS fiber mat with a steel brush in each layer, which was placed

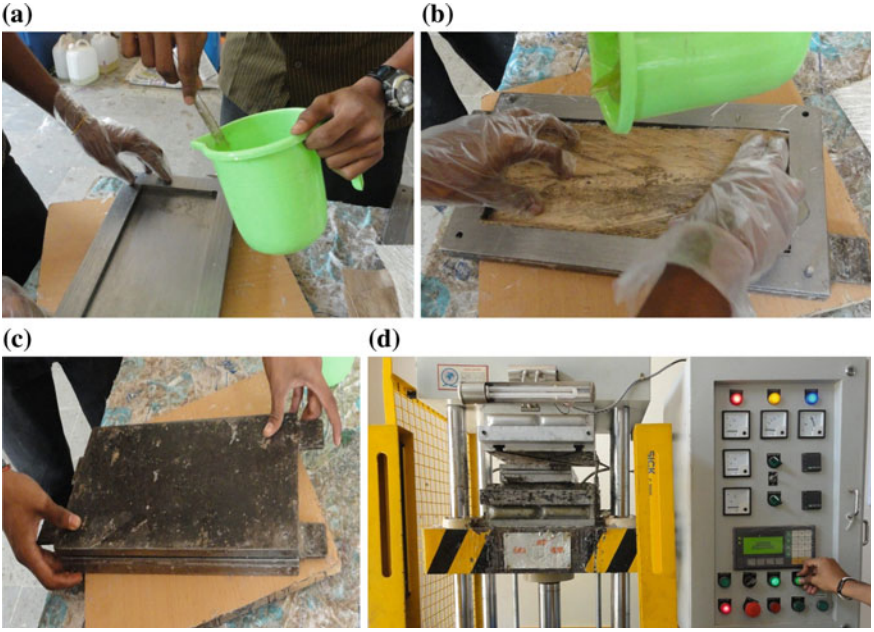


Fig. 1 Steps involved in fabrication process. **a** Positioning of mold. **b** Fiber arrangement. **c** Closed mold. **d** Mold placed in the compression machine

inside the mold cavity of size 300 × 125 × 10 mm^3 (see Fig. 1b) by keeping one over another up to six layers (48 ± 2 wt%). The stacked CS fiber mats were rolled with the help of a roller in such a way as to remove the air bubbles. The top plate was placed over the middle plate in such a way as to cover the CS fiber mats and positioned by the circular pins at the corners, as shown in Fig. 1c. The mold was closed completely by applying 150 kgf/cm^2 pressure in order to obtain the 3 mm thickness plate using the compression molding machine, as shown in Fig. 1d. The compressed mold was allowed for room temperature curing, for another 24 h. Finally, the split mold was separated by removing the pins at the corners. The rectangular composite plate of size 300 × 125 mm^2 and thickness of 3 mm was carefully removed through the cavity of the middle plate. Then, the test specimens of the required size were cut from the fabricated composite sheet.

2.2 Impedance Measurement

For the dielectric analysis, the samples were placed between two parallel plate electrodes. A sinusoidal voltage creating an alternating electric field was applied to these electrodes thus producing polarization in the samples, which stimulates oscillations at the same frequency as the electric field, but has a shift in phase angle. This phase angle shift was measured with respect to the applied voltage and the measured current, which in turn was separated into capacitive and conductive components. Measurements of capacitance and conductance were used to calculate the dielectric parameters. Figure 2a shows the computer controlled LCR meter for the measurement of conductivity (frequency range 42 Hz–1 MHz), at room temperature condition. The calibration was done for the range of ±5 % error before the experimentation of dielectric measurements. Figure 2b shows the connections to the sample with the holder.

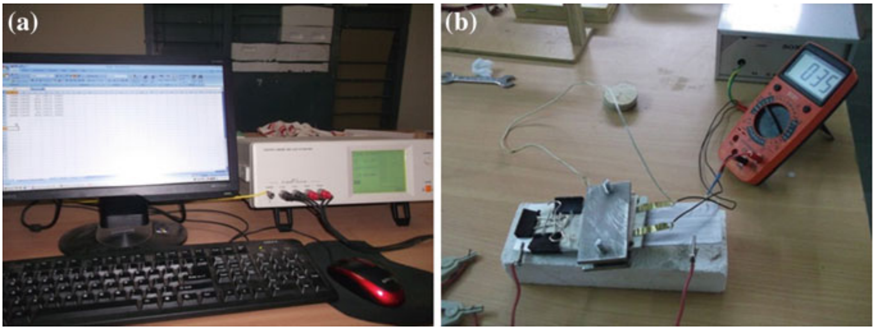


Fig. 2 **a** LCZ meter. **b** Connections to the samples with the holder

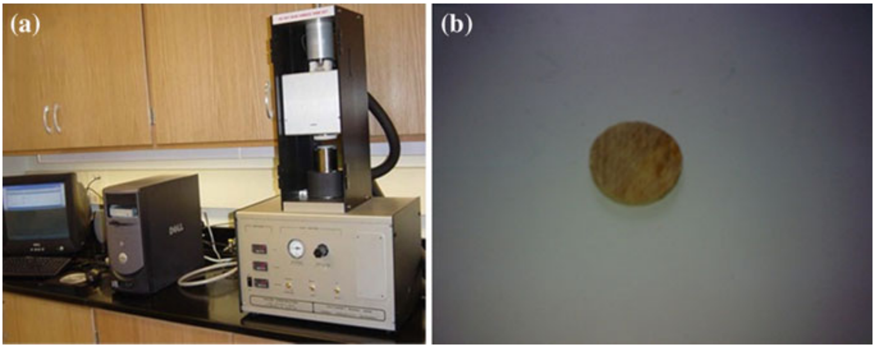


Fig. 3 Thermal conductivity. **a** Measuring apparatus. **b** Sample

2.3 Thermal Conductivity

As per the ASTM E-1530 standard the thermal conductivity property of CS/MMT hybrid composite was recorded. The measurements were taken using the conductivity meter, Unitherm model 2022 from ANTER Corp., Pittsburgh, PA, as shown in Fig. 3a. The 50 mm diameter sample was used for the testing (Fig. 3b). In this work, the thermal conductivity was directly measured by the guarded heat flow meter method, which is a computerized thermal conductivity measuring system.

2.4 Gas Permeability

The Lyssy Gas Permeability equipment is used to measure the permeability of any common gas oragas mixture through thin films and laminates. The permeability measuring equipment is shown in Fig. 4 (Elixir Technologies, Bangalore, India). In this work, it was used to measure the permeability of CO_2 gas through the composites. ASTM D14382 was followed for the measurement. The samples of coconut sheath/polyester composite laminate were prepared for the size of 110 × 110 × 3 mm^3. Figure 5a, b presents the photographs of uncoated and Teflon coated composite samples. Before the Teflon coating the surface was smoothened using 600-grid SiC emery sheet and cleaned with acetone.

2.5 Volume and Surface Resistivity

Volume resistivity can be used as an important parameter while designing an insulator for specific applications. Surface resistivity is the resistance to leakage current along the surface of an insulating material. Surface conductivity helps in assessing the surface contamination of the material.

Fig. 4 Gas permeability measuring unit

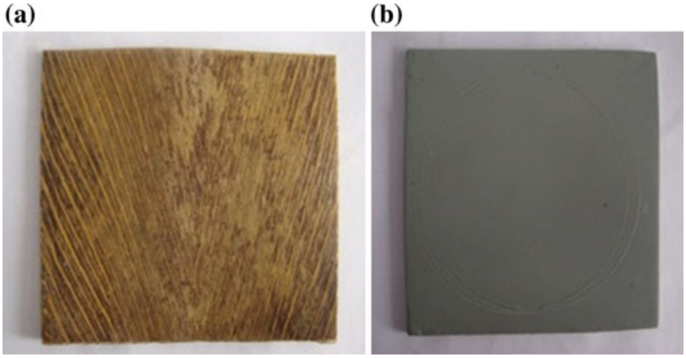


Fig. 5 Gas permeability samples, **a** as—fabricated. **b** Teflon coated

ASTM standard of D257 was used for the measurement of volume and surface resistivity. The Keithley resistivity adaptor, model 6105 was used to record the volume and surface resistivity (see Fig. 6a). The resistance across the sample was measured with a Knick model Teraohmmeter (see Fig. 6b). Disk shaped samples having a 100 mm diameter (see Fig. 6c) was used for the measurement.

The volume and surface resistance values were calculated based on the standard relations.

$$\left.\begin{aligned} \rho_V = A_e R_V \big/ t \quad A_e = \pi (D_1 + g)^2 \big/ 4 \\ \rho_S = P\,Rs/g\,(\text{here}\; P = \pi\, D_o) \end{aligned}\right\} \tag{1}$$

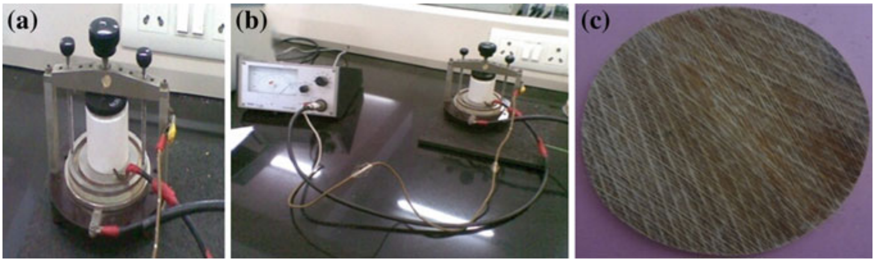


Fig. 6 **a** Connections between the power supply and the ohmeter. **b** Resistivity adapter. **c** Disk shaped sample

2.6 Breakdown Voltage

Breakdown voltage is the ability of an insulator to withstand the maximum voltage difference that can be applied across the material, before the insulator collapses and starts conducting. The ASTM D149 method was employed to find out the dielectric strength of the sample using the breakdown voltage. Figure 7a shows the high voltage electrical connections to the hydraulic oil tank. In order to withstand the

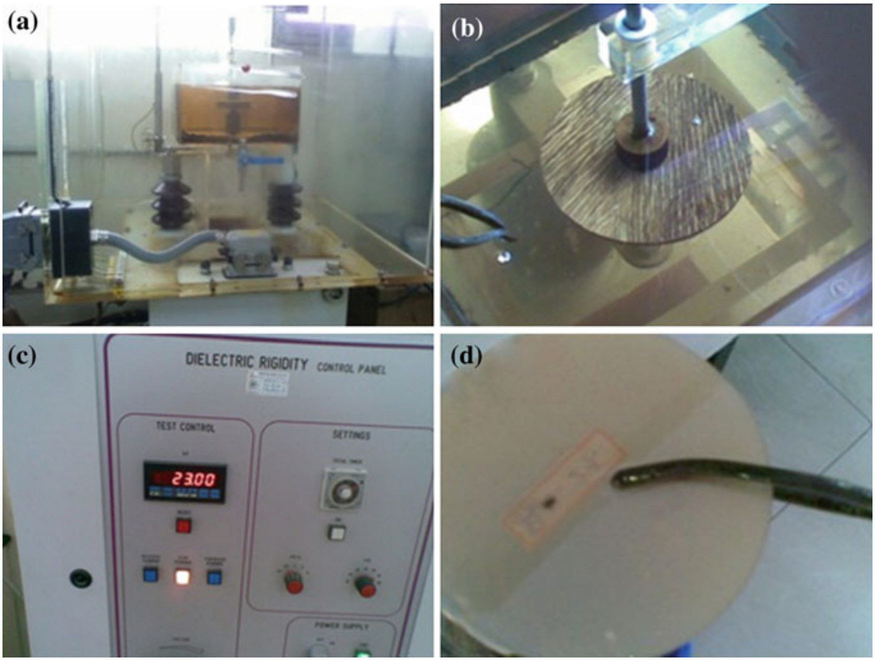


Fig. 7 **a** Hydraulic oil tank. **b** Sample inside the oil tank. **c** Breakdown voltage measuring setup. **d** Break down sample

applied high voltage, the sample of the size 100 mm in diameter was placed inside the hydraulic oil, as shown in Fig. 7b.

The dielectric strength was calculated using the following standard relation given in Eq. 2.

$$D_S = B_y/h \tag{2}$$

where, D_S is the dielectric strength (kV/mm), B_V is the breakdown voltage (kV) and h is the thickness (mm) of the specimen.

In this work, the breakdown voltage of the composites was measured, using an insulation breakdown tester supplied by CEAST (Italy) as shown in Fig. 7c. The B_V is directly measured from the setup given in Fig. 7c. The black mark in the sample, as shown in Fig. 7d, indicates the failure of the materials due to the applied electric field.

2.7 *Thermo-Gravimetric Analysis*

The thermal stability of the polyester nanocomposites is assessed using SII EXSTAR TG 6000 module. About 3–6 mg powder of sample is subjected to dynamic TGA scans at an increased heating rate of 5 °C/min in the range of ambient temperature to 800 °C in N_2 atmosphere. The TG curves are analyzed as the percentage of weight loss as a function of temperature. The average of three powder samples are reported in each cases and that are obtained from the three different locations of same specimen using diamond cutter.

2.8 *Cone Calorimetric Analysis*

Fire resistant properties of coconut sheath reinforced polyester composites have been carried out on a cone calorimeter in accordance with ISO 5006-1. The test specimen of size 100 × 100 × 10 mm^3 has been taken for the measurements. All the data collected from the cone calorimeter test are available in engineering units.

Conditions of the test:

- Specimen position: horizontal
- Heat flux: 50 kW/m^2
- Spark igniter was used
- Scan: 1800 s.

3 Results and Discussions

3.1 Characterization Studies

The XRD spectrum of pure organically modified oMMT clay and the polyester reinforced with particulate nanoclay composites with 1, 2, 3, and 5 wt% are given in Rajini et al. (2012). The Pure oMMT clay exhibits a diffraction peak at 4.5° and it indicate the d-spacing of 1.963 nm. This high intensity peak at around 4.5° indicates the crystallinity behavior of nanoclay. In the other cases composites there was no peak was identified at the same two theta angle. It represents that the distance between the nanoclay particles exceeds the value of 1.963 nm ($2\theta < 3°$) or it could be well dispersed in the matrix. At the same time, the inclusion of higher weight percentage of nanoclay(5 wt%) found to be shifting diffraction peaks towards lower angle side, which could be the reason for the decreasing distance between the clay platelets. The uneven curing process due to the addition of clay particle creates the possibility of intercalated nanocomposites. From this observation, it was found that the separation of clayplatelets has also depends on the wt% of clay content. Since, higher the wt% of clay content will not allow the particles to segregate easily due to the constraint of surrounding fillers. The similar kind of observation has also been reported by Yasmin et al. (2003).

Based on our previous work, it was found that the distribution of the nano particle in polyester matrix can be seen clearly like zebra pattern, which indicates that the platelets were separated from the stack due to the shearing force by mechanical stirring (Rajini et al. 2013). Moreover, the aggregate was found to be inevitable in the case of higher amount of clay content. Accordingly, anything less than 5 wt% of clay content was observed to produce better performance. In addition, the FTIR and chemical analysis were performed on untreated and chemically treated coconut sheath fiber in regards to understand the variation in chemical proportions after the removal of weak and unwanted contaminants. The FTIR spectrum as well as the varying proportion of chemical constituents obtained from the conventional chemical analysis was already reported in our previous work (Rajini et al. 2013).

3.2 Conductivity Spectra Analysis at Room Temperature

The frequency dependence of the AC conductivity (σ_{ac}) of CS/MMT clay reinforced hybrid composites at room temperature, in a wide range of frequencies was measured. It is clearly found that the σ_{ac} of the hybrid composite is higher in the alkali treated condition, and that may be due to the incorporation of more polar molecules (hydroxyl groups) present in the fiber.

Rajini et al. (2013) studied the variation of the A.C. conductivity of the composites with UTC, ATC and STC coconut sheaths at room temperatures. The spectra of the two specimens (ATC, STC) exhibit "two well—defined regions". From their observation it is clear, that the A.C. conductivity depends strongly on the treatment of the coconut sheath. Moreover, they also showed 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 the MMT nanoclay can influence the A.C. conductivity in the ATC and STC reinforced composites more than in the UTC composites (Rajini et al. 2013).

All the data obtained from the experimentation is found to obey Jonscher's power law (Joseph and Thomas 2008). Jonscher's power law equation may be written as

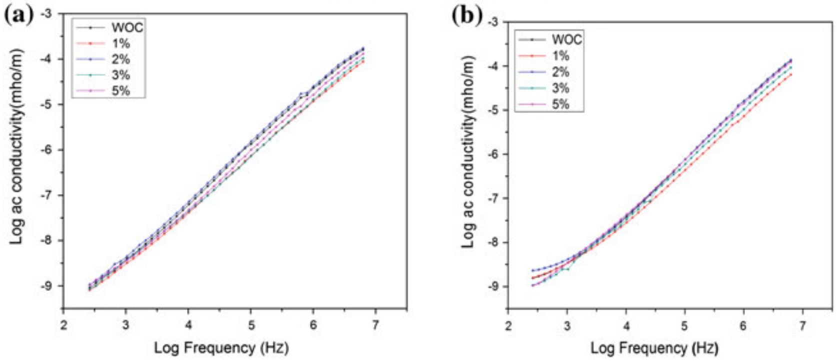
$$\sigma(\omega) = \sigma_{dc} + A\omega^{n} \tag{3}$$

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 $\sigma(\omega) \alpha A\omega^{n}$ is observed.

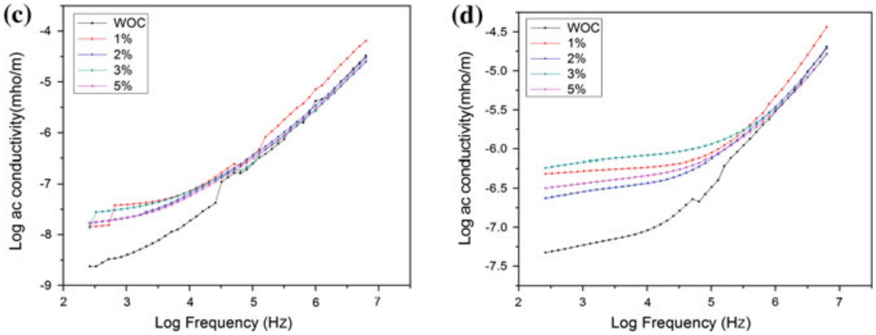
3.3 Effect of Temperature on Dielectric Properties of CS/MMT Hybrid Composites

The AC Conductivity versus frequency is drawn and shown in Fig. 8a–f for the untreated and chemically treated CS reinforced nanocomposite with lower and higher temperatures. The two selected temperatures are 50 and 90 °C. This is because of molecular mobility due to the increasing frequency. From the Fig. 8a, it was found the conductivity was increased linearly with the increase of frequency. At the same time there is no variation was found for the addition of varying % of nanoclay addition. The similar trend was also observed at the high temperature condition also (see Fig. 8b). But, the entirely different type of ac conductivity curve was observed in the case of for the alkali and silane treated composites in Fig. 8c–f. A two stage curve was observed throughout the entire frequency region for the alkali and silane treated composites. A significant change in ac conductivity value was observed for all the wt% of clay addition. In low frequency region, the difference was found to be large and then it merged into single line at high frequency domain. The conductivity increases as the temperature increases for a frequency at a particular composition. This effect is created because of the ionic motion of composite atoms. As the temperature increases the atoms gets their energy and gets ionize. The plots were also drawn for all the combination to identify the behavior of

Untreated CS/MMT composite



Alkali treated CS/MMT composite



Silane treated CS/MMT composite

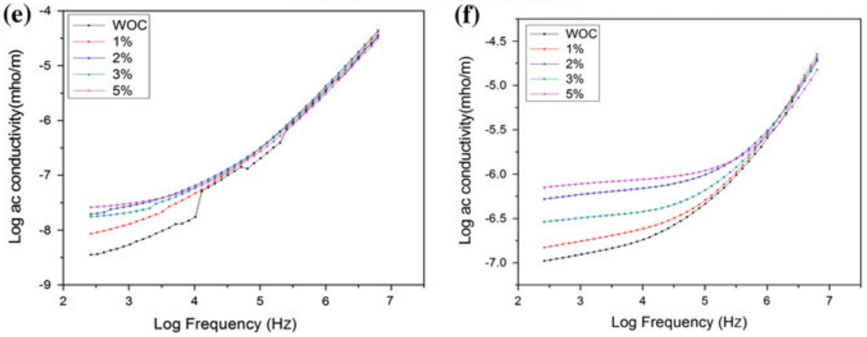
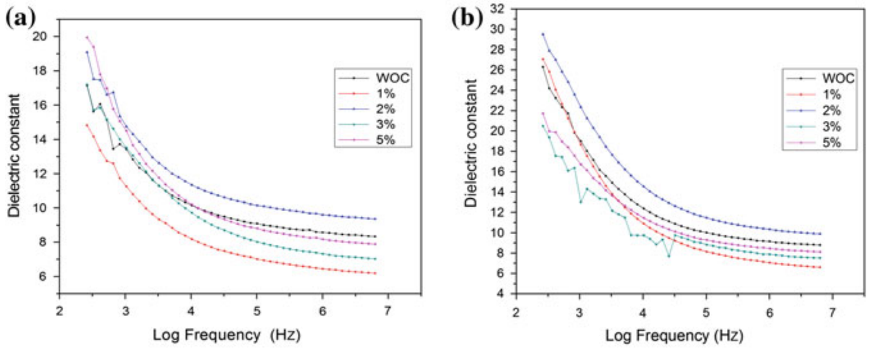


Fig. 8 Effect of temperatures on the variation of the AC conductivity for clay filled UTC, ATC and STC coconut sheath composite

dielectric constant and dielectric loss factor for same two temperatures (Figs. 9 and 10). Figure 9 clearly shows that the dielectric constant decreases with the increase in frequency. The decreasing rate is high at lower frequencies and very low or nearly same at higher frequencies. This is because of the absence of water dipole.

Untreated CS/MMT composite



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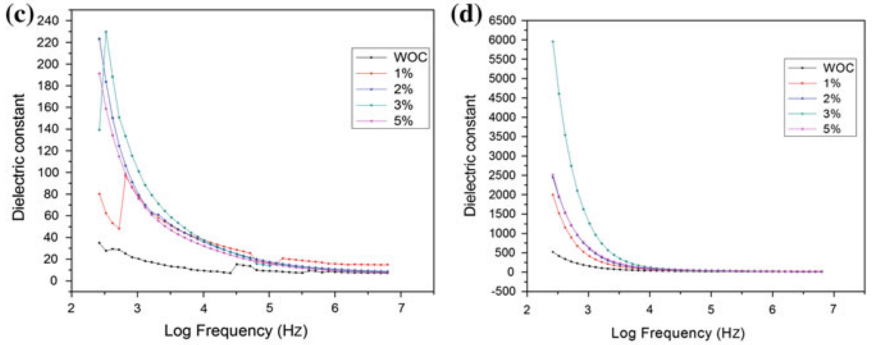

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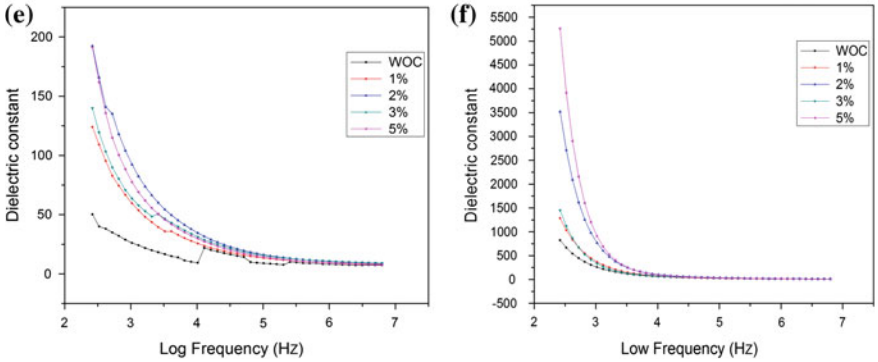
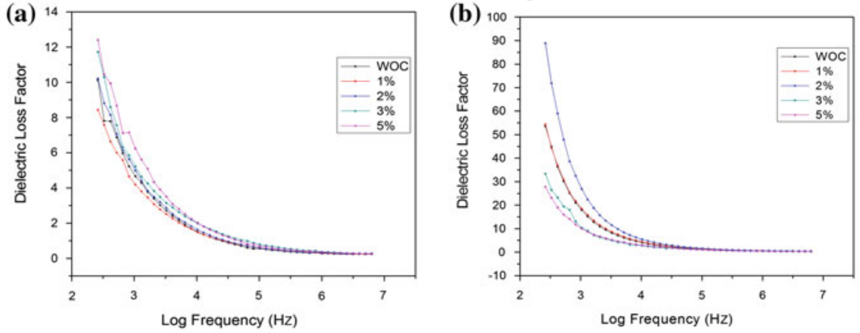
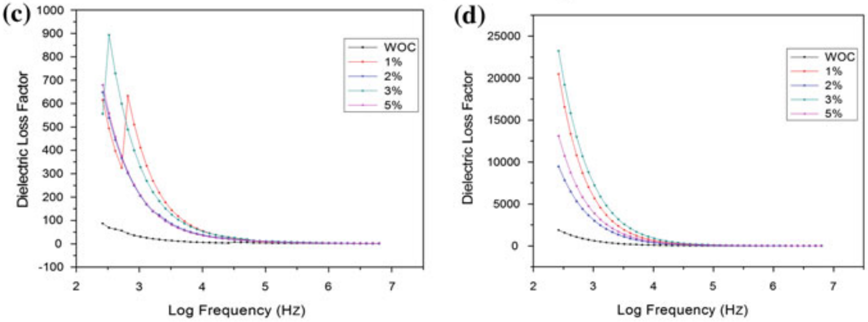


Fig. 9 Effect of temperatures on the variation of the dielectric constant for clay filled UTC, ATC and STC coconut sheath composite

Untreated CS/MMT composite



Alkali treated CS/MMT composite



Silane treated CS/MMT composite

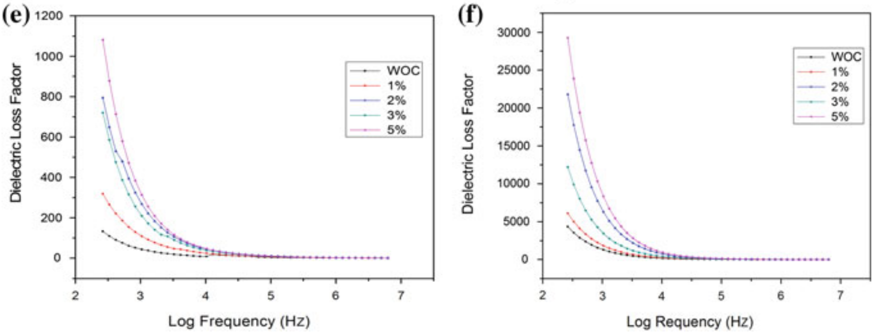


Fig. 10 Effect of temperatures on the variation of the dissipation factor for clay filled UTC, ATC and STC coconut sheath composite

As temperature increases, the dielectric constant increases due to the enhanced conductivity of the composite at higher temperatures, because when temperature increases the mobility of molecular dipoles increases. Similarly, the presence of cellulose content in the natural fibers is highly related to the resistivity of the fiber, more the cellulose content can lower the resistivity.

From the Fig. 10a–f, one can be interfered that for untreated samples dissipation factor decreases as the frequency increases and the values coincide as the frequency is further increased whatever the temperature. But in case of silane treated and alkali treated samples the values first increases, reaches a peak and then decrease at higher frequency irrespective of the temperature. Thus the values tend to become similar. This may be accounted due to ionic migration conduction at low frequencies. The peak is associated with molecular dipole rotation and occurs when molecular rotation can just keep with the alteration of electric field, a type of molecular resonance condition. Irrespective of the chemical treatment, the addition of clay content with the varying wt% found to be influence the dielectric strength and dielectric loss factor. However, there is no specific trend was observed with the increasing percentage of nanoclay.

3.4 Thermal Conductivity Behavior of CS/MMT Hybrid Composite

The behavior of thermal conductivity by the effect of nanoclay addition and chemical treatment of the CS/MMT hybrid composite is shown in Fig. 11. Form Fig. 11, it can be clearly seen that the thermal conductivity decrease with the addition of nanoclay with the varying wt%. The presence of nanoclay is distributed randomly throughout the polymer matrix and acts as a block for the heat source motion. Hence, there is a decrease in the thermal conductivity was noticed. But it was not the case for the addition of higher wt% of clay. A slight increase in thermal conductivity is observed, perhaps it could be due to the clay agglomeration, but still it is was found to be lower than pure polymer. The increasing trend of thermal conductivity was observed in the alkali treated CS composites with the effect of varying wt% of clay. A decrease in the thermal conductivity was noticed for the

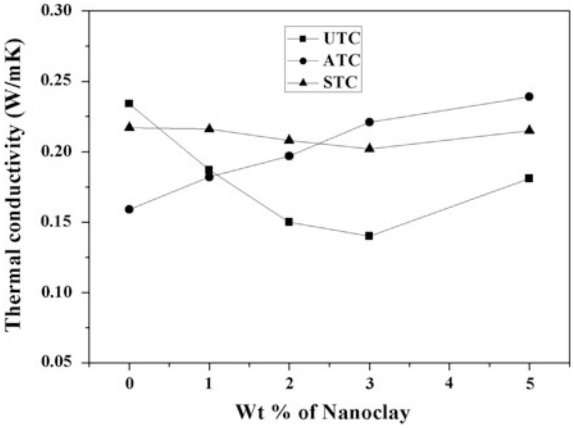


Fig. 11 Effect of nanoclay addition and chemical treatment of coconut sheath on thermal conductivity

silane treated CS due to the presence of nanoclay. In can happen due to the heat insulated behavior of clay which tries to decrease the thermal conductivity, except in the NaOH treated condition. The silane coating over the fiber surface can reduce the direct exposure of coconut sheath fiber surface. The reduction of surface area decreases the thermal conductivity, since the flow of heat is directly proportional to the available surface area. It is further confirmed by the following equation (Kreith and Bohn 2001):

$$Q = KA\,\Delta T/h \tag{5}$$

where Q is the heat flow (W), k is the thermal conductivity (W/mK), A is the surface area (m^2), ΔT is the temperature difference between two ends of composite and h is the thickness (m).

3.5 Gas Permeability Properties of CS/MMT Clay Hybrid Composites

In this section, the effect of parameters such as clay addition and chemically treatment CS fiber is studied on the CO_2 gas permeability in polyester matrix. Figure 12 shows the experimentation results of CS/polyester composites with the combination of clay and chemical treatment of CS fibers. From Fig. 12, the maximum drop in gas permeability was clearly observed in the alkali (NaOH) treated composites compared to the UTC/polyester composites. It can happen due to removal of unwanted contaminants at the surface after the alkali treatment of CS fiber. The flow of gas was restricted since the reduction of crack and voids due to the formation of strong interfacial adhesion. Moreover, the removal of contaminants leads to the way for better compatibility between the fiber and matrix which in turn increases the surface to area contact between fiber and matrix. Hence, the closely

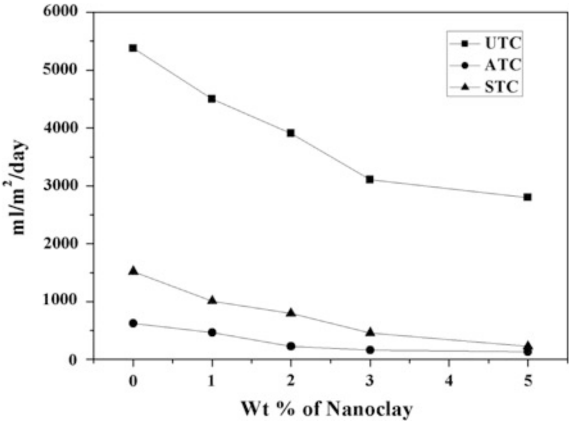


Fig. 12 Gas permeability results of the CS/PE composites with the effect of clay addition and chemical modifications

packed materials will arrest the options of gas travel in random direction. Besides, the interlocking of nano fillers inside the pores of fibers and dispersion with the polymer matrix can create the complicated path for the flow of gas. But the reduction of gas permeability is decreased by 72 % in the STC composites; this can be due to the presence of chemical coupling between the silane and the matrix. It may lead the way to a leakage of gas flow along the fiber region.

3.6 Thermo-Gravimetric Analysis (TGA)

The thermal behavior of the CS/polyester composite samples were investigated at the heating rate of 5 °C/min from ambient temperature to 800 °C under nitrogen atmosphere at a flow rate of 60 ml/min. The TGA curves of the untreated, alkali and silane treated coconut sheath without nanoclay and varying wt% percentage of nanoclay loaded polyester hybrid composite are represented in Fig. 13a–d. It is evident from the Fig. 13a that the initial degradation (10 wt%) was started at

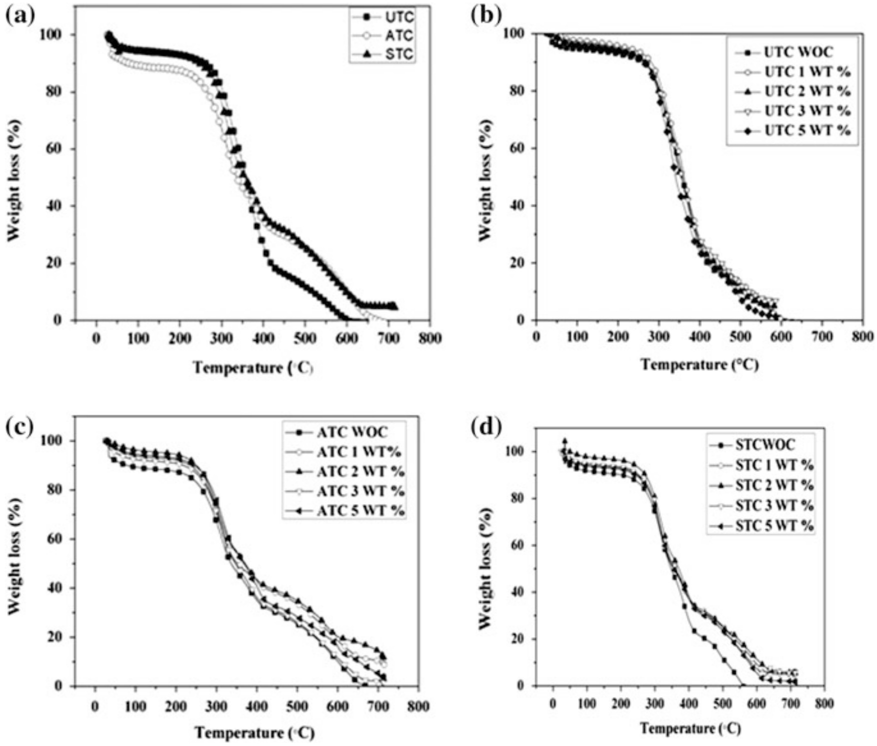


Fig. 13 The TGA curves for untreated, alkali and silane treated coconut sheath, **a** without nanoclay and **b–d** with varying wt% percentage of nanoclay

254.4 °C and 100 % degradation was noticed at 490 °C for untreated composites. At the same time, the initial degradation temperature of the alkali treated composite was decreased to 120 °C, whereas silane treated composites raises it to 238.7 °C. This may be due to the changes in the rate of dehydration of the fibers after the chemical treatment. However, as for as the major weight loss (100 %) is concerned, there was a substantial enhancement in the thermal stability noticed for both alkali and silane treated composites. The alkali treated composites raise the final degradation temperature to 608.2 °C giving a charred residue of 4.8 %, whereas the silane treated raises it to 713.4 °C giving a charred residue of 3.2 %. This could happen due to the better interfacial bonding and the breakage of decomposition products (cellulose, hemicelluloses, lignin and waxes) at the second stage lead to the formation of charred residue.

Figure 13a also reveals that the untreated coconut sheath covered by the waxes, greasy layer and the surface impurities restricts the rate of heat flow along the fiber orientation and causes the slow decomposition process which is observed from the lesser slope in TGA curve. From the curve, the first range of weight loss which begins from 30–110 °C is due to the loss of water content by the fiber. At about 200–350 °C, the degradation occurred which is associated with the thermal decomposition of the lignin and the hemicelluloses. The final stage of weight loss occurs at temperature of about 350–400 °C, which indicates the degradation of α-cellulose and other non-cellulosic compounds (Pracella et al. 2006). During alkalization, it was observed that the coconut sheath fiber started degrading at 200 °C and displayed a lower thermal stability and it might be due to the less dehydration by the appearance of the amorphous cellulose and the lignin content (Rajini et al. 2013).

The thermal degradation behavior of the clay unfilled CS/polyester composites (untreated, alkali and silane) and the CS/polyester nanocomposites with various percentage of clay loading is shown in Fig. 13b–d. The TGA of all the composites follow a two-stage decomposition behavior. Figure 13b shows the TGA for the clay filled UTC/polyester hybrid nanocomposites. Initial thermal decomposition (10 wt %) of the UTC/polyester composites without the addition of clay starts at 254.4 °C. On the addition of the clay in the UTC/polyester composites, the decomposition starts at higher temperature. For UTC with 1 wt% clay, the decomposition starts at 269 °C, for 2 wt% clay, the decomposition starts at 261 °C and for 3 wt% clay it starts at 276 °C. This suggests that the addition of clay increases the thermal degradation temperature of the UTC/polyester composites and it reaches a maximum value for 3 wt% clay. The addition of 5 wt% clay in the UTC composites does not show any improvement in decomposition and in fact, it decreases the initial degradation temperature to 236 °C. The formation of the agglomeration with 5 wt% of clay content could not penetrate into the surface of UTC due to the coverage of the inorganic contaminates (waxes and dusts). It could make a weak interface in the UTC composite and lead to the increase in weight loss. However, for the ATC and the STC samples, the enhanced thermal stability was observed even for the addition of 5 wt% clay (Fig.13c, d). A significant shift in the degradation temperature for the initial and the final decomposition was noticed for the alkali and silane treated composites with the varying wt% of nanoclay. The increase in the thermal properties of the hybrid nanocomposites is predominant at higher temperature (>400 °C) with the increase in the clay content but in an anomalous manner This encouraging thermal behavior of clay blended polyester composite can happen because of varying interaction between the distributed clay and polyester matrix to large surface area and attributed to the strong rigid interface. Among all the composites, the final residue in the CS/polyester clay filled nanocomposites is comparatively higher than the unfilled clay composites.

3.7 Fire Properties

The fire properties of untreated and treated CS fiber reinforced composites have been studied with the aid of cone calorimeter experiment. Figure 14 shows the HRR curves for the polyester (PE), untreated coconut sheath (UTC), silane treated coconut sheath (STC) and the alkali treated coconut sheath (ATC) reinforced composites in without clay (WOC) condition that were obtained from cone calorimeter, as a function of time. Only one peak in HRR curve of polyester matrix was observed in Fig. 14 and it can be due to the greater rate of combustion of matrix by quicker thermal decomposition. In all CS reinforced composites, the UTC is one which shows a higher HRR value compared to the other two composites. It should be due to the poor interfacial adhesion between the fiber and the matrix by the presence of the waxy layer and the inorganic contaminates over the fiber surface. This weak interface can separate the two phases (reinforcement and polymer) apart in case of fire.

However, as for as HRR is concerned, the mean (average) heat release rate value for ATC sample is 122.512 kW/m^2 whereas it rises into 152.59 kW/m^2 for UTC. The minimum value of mean HRR is found to be 85.67 kW/m^2 in the case of silane

Fig. 14 HRR curves for CS fiber reinforced composite with unfilled clay

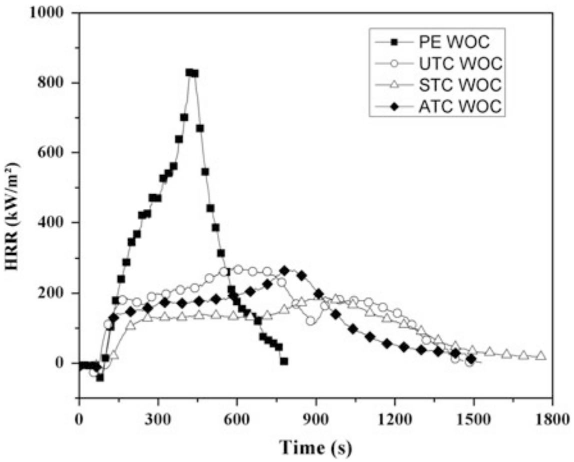
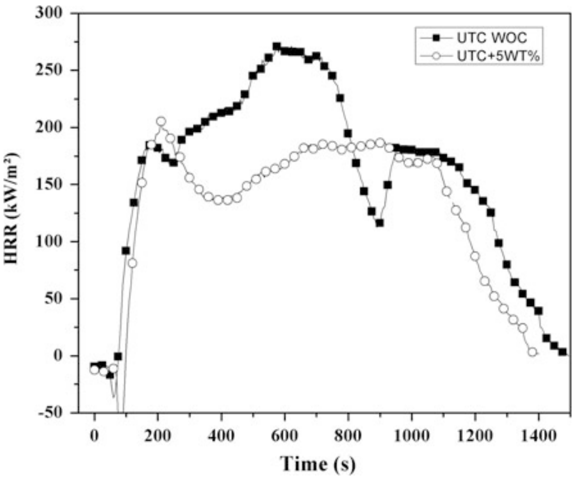


Fig. 15 HRR curve for UTC with the addition of 5 wt% of nanoclay



treated composite. In alkali treated condition, the removal of organic impurities can form the openings between the thin fibers which form spider-web like porous structure. The deposition of silane forms a chemical bond between the fiber surface and the matrix through a siloxane bridge. Thus, during the fire, the polymer layer present at the surface tends to burn first and the siloxane layer which act as a barrier improves the flame-out time of the composite. After the siloxane layer is burnt it results in the formation of char which acts as an insulating barrier at the interface of the composite thus resulting in the decreasing of HRR. Figure 15 shows the variation of HRR without and with the addition of 5 wt% of nanoclay to UTC reinforced composites. Nanoclay addition was found to have much influence on the conventional composite in all the conditions of the coconut sheath up to the time period of 600 s beyond that it was not valid for silane treated composite. It promotes the formation of the charred residue like a porous structure, which covers on the fiber surface and acts as a protection barrier against the heat conduction and the mass transport, leading to enhanced flame retardancy. It can also change the melt flow index of the polymer and the increase in the viscosity resulting in a reduced flame spread. Even the clay agglomeration in higher wt% of nanoclay in the matrix could create the torturous path of fire advance and it can increase the flame out time of composites.

3.8 CO and CO_2 Yield

The Fig. 16 shows the average values of (a) CO yield, and (b) CO_2 yield where PE (C1), PE + 5 wt% (C2), UTC WOC (C3), UTC + 5 wt% (C4),STC WOC (C5), STC + 5 wt% (C6), ATC WOC (C7) and ATC + 5 wt% (C8). From the above Fig. 16a, it is inferred that the pristine polyester emits more CO than the other fiber

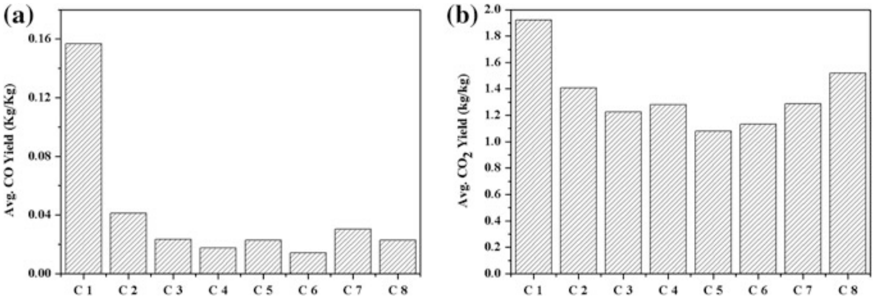


Fig. 16 Comparison of average value of **a** CO yield, **b** CO_2 yield for PE, UTC, STC and ATC reinforced composites with the addition of 5 wt% of nanoclay

reinforced composites. An increase in the heat release rate is attributed to increase in the yield of CO gas. When the clay is incorporated into the pristine polyester, the CO yield is reduced significantly. This shows clearly that the addition of clay to the polymer reduces the toxic CO emission. This is because the clay is naturally a fire retardant and thus the clay particles present in the polymer improves the flame out time of the polyester composite and thus results in the reduction of CO emission. However, with the addition of combustible CS fiber, the amount of CO gets reduced when compared to PE. The lowest value of CO yield was observed in silane treated CS composites which indicated that the complete combustion had taken place. The higher amount of CO_2 was evolved in the polyester matrix as shown in Fig. 16b and it may be due to the breakdown of the ester bonds within the resin. In the case of the clay unfilled CS fiber reinforced composites, the lower value of CO_2 was observed for UTC composites. However, unlike CO yield the controlling mechanism of CO_2 yield is complex and is dependent on factors other than just the heat release rate. With the addition of clay, the CO_2 yield follows the same trend of CO yield for the ATC and the STC fiber reinforced composites except the UTC.

4 Conclusions

This chapter is mainly focused on the fabrication of polyester/clay nanocomposites and coconut sheath fiber reinforced hybrid composites. The effects of chemical treatment (NaOH, silane) on the coconut sheath fiber are studied, with the changes in the physical and chemical properties. The addition of organoclay as a secondary reinforcement in the CS/PE composites can further enhance the properties of the hybrid composites to a certain absolute level. This chapter focuses on the research findings on the dielectric, transport, and the thermo-gravimetric analysis, properties of CS/MMT clay reinforced hybrid polyester composites. A detailed report, on the summary of the findings in the chapter is given below:

- The dielectric behavior was found to be influencing the CS polyester composites with the effect of chemical treatment and addition of nanoclay. The alkali and silane treated composites have shown significant variation dielectric behavior due to the changes in surface morphology and chemical composition. However, the increasing percentage of clay content does not show any specific trend in dielectric spectra.
- The temperature is found to be one of the most influencing parameter affects the dielectric behavior of natural fiber reinforced composites. The increasing temperature can increase the behavior of dielectric characteristics due to the hindering effect of ionization on fiber surface.
- The thermal conductivity of CS/polyester is as follow as per the ascending order below: UTC > STC > ATC. It implies that the increase in the moisture content due to the alkali treatment of CS fiber could be the reason for this lower thermal conductivity value.
- A significant reduction of gas permeability was noticed in the CS/MMT composites with the addition of nanoclay content. The randomly distributed clay in polymer matrix can reduce the micro voids and which can create the torturous path. So that the complication was found in the flow thus decreases a rate of flow considerably. Moreover, the improved adhesion between the fiber and matrix after the removal of contaminates should also be the reason for the decrease in gas permeability.
- According to the TGA results, the thermal stability of the alkali and silane treated condition gets reduced, because the presence of more water content after the removal of globular protrusion seeks to absorb more OH groups.
- But with the addition of nanoclay, the degradation shifted to a higher temperature for the fiber reinforced composites in all conditions, because of the resistance to the heat flow along the tortuous path produced by the dispersed nanoclay.
- The effect of chemical treatments on CS fiber exhibits good fire resistance properties. Similarly, encouraging results were also found in the UTC with the addition of 5 wt% clay content.

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