

EFFECTS OF CHEMICAL MODIFICATIONS AND MMT NANOCCLAY ADDITION ON TRANSPORT PHENOMENA OF NATURALLY WOVEN COCONUT SHEATH/POLYESTER NANOCOMPOSITES*

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Abstract Studies on the behavior of molecular transport properties such as thermal conductivity, gas permeability, volume and surface resistivity have been carried out for the naturally woven coconut sheath (CS) fiber reinforced composites with the addition of nanoclay and chemical treatment of fiber. The compression molding technique was used to fabricate the coconut sheath/clay reinforced hybrid composites. The morphological studies such as X-ray diffractogram (XRD), transmission electron microscopy (TEM) and scanning electron microscopy (SEM) have been carried out for polyester nanocomposites and coconut sheath fiber. The decreased gas permeability, thermal conductivity and volume and surface resistivity have been observed with increasing the weight percentage of nanoclay in polyester matrix. In chemical modifications, the alkali and silane treated coconut sheath reinforced composites have shown great influence on the transport properties due to the increasing hydrophilic nature by the topographical changes at the fiber surface. Dielectric strength has also been reported in this paper for all types of composites. Infra-red (IR) spectra have also been taken to study the physical and chemical structural changes of treated coconut sheath.

Keywords: Nanoclay; Coconut sheath; Gas permeability; TEM; SEM; FTIR.

INTRODUCTION

The polymer nanocomposite (PNC) is a new division of composites which was explicitly exposed to the research society by the Toyota research group due to the superior performance such as high specific strength, flame resistance, water barrier resistance and chemical resistance associated with PNC and finds its applications in defense sector, aerospace and automobile industries^[1, 2]. The encouraging barrier properties of nanocomposites motivate several researchers to focus the inclusion of nano-particle in polymer matrix^[3–5]. The property enhancement in nano filler addition is based on the various parameters such as type of filler, concentration of filler, chemical activation and method of dispersion^[6].

Polymer nanocomposites can be classified morphologically into unmixed, intercalated, and exfoliated state. Chemically modified montmorillonite (MMT) can have better dispersion with polymer matrix due to its organophilic nature. As a result of this, the intercalated/exfoliated form of dispersion is possible to achieve in polymer matrix. Vaia *et al.*^[7] found that the degree of exfoliation could be improved through the aid of conventional shear devices such as extruders, mixers, ultra sonic agitators and shear mixture. Hackman *et al.*^[8]

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reported that the epoxy/clay nanocomposite can be widely used in civil engineering application by sieving in moisture barrier and life time of the material can be enhanced by slow absorption of moisture. They concluded that the reinforcement of the nano fillers into the polymer matrix reduces the permeability. Among the various nano-particles, the MMT nanoclay has been used by many researchers due to the dispersion capability, swelling nature and curing mechanism with thermoset resin^[9, 10].

Natural fiber reinforced polymer composites are gaining widespread interest in recent years due to their biodegradability and cost effectiveness. All the fibers of natural origin are abundantly available and can be procured at affordable costs^[11]. Mainly the natural fibers find their application in the field of agricultural, marine and civil purposes for hoisting, upholstery and padding^[12]. Generally all the natural fibers are hydrophilic in nature and hence they are more prone to water absorption. Therefore the drawbacks of natural fibers reinforced composites can be rectified by appropriate chemical treatments and by the addition of nanoclay which can enhance the adhesion between the fiber and matrix^[13].

Li *et al.*^[14] have studied the thermal conductivity, thermal diffusivity and specific heat of flax fiber — high density polyethylene biocomposites at the processing temperature using line source technique. It was found that thermal conductivity, thermal diffusivity and specific heat decreased with increasing fiber content, but it was not affected significantly with increasing temperature. Debasmita *et al.*^[15] have determined the thermal conductivity of polymer composites filled with solid glass beads (SGB) and concluded that incorporation of SGB resulted in decrease of thermal conductivity of epoxy resin and thereby improved its thermal insulation capability. The thermal conductivity of carbon fiber reinforced polymer composites with the effect of volume fraction, fiber length and fiber orientation angle has been determined and concluded that the thermal conductivity of composites increases almost linearly with the increase of fiber content^[16]. Idicula *et al.*^[17] investigated the effect of chemical treatment of natural fiber and showed that the thermal contact resistance between the fiber and matrix got reduced due to the treatment of fiber. Lee *et al.*^[18] have studied the CO₂ gas transport in polymer system and reported that the permeability can be decreased with increasing clay content. Arunvisut *et al.*^[19] have studied the O₂ gas permeability test of LDPE/clay nanocomposites and concluded that the increase of reduction in gas permeability was observed with the increase in weight percentage of MMT.

Many works^[20–22] have been reported for polyester composites reinforced with natural fiber on mechanical and barrier properties. The hybridization effect of organoclay in natural fibers could provide constraint to molecule permeability and better interfacial bonding and it may lead to the superior performance in transport properties. However, no information is available on coconut sheath fiber/MMT reinforced polymer composites to study the molecular motion in applied thermal and electric fields. Hence in this work MMT nanoclay has been used as secondary reinforcement to fabricate the coconut sheath/nanoclay reinforced hybrid composite. The main intent of the present work is to investigate the influence of nanoclay addition and chemical modification of coconut sheath on the transport properties.

EXPERIMENTAL

Materials

Naturally woven coconut fiber mat is used as a reinforcement which is directly extracted from outer barks of the coconut tree. Unsaturated isophthalic polyester resin is used as matrix, procured from M/s Vasivibala Resins (P) Ltd, Chennai, India. The organically modified clay (a mined montmorillonite modified with 15 wt%–35 wt% octadecylamine and 0.5 wt%–5 wt% aminopropyltriethoxysilane), is used as reinforcement procured from M/s Sigma Aldrich (P) Ltd, Bangalore, India. One wt% of methyl ethyl ketone peroxide (MEKP) and 1 wt% Cobalt naphthenate have been used as catalyst and accelerator respectively for room temperature curing.

Chemical Modification

Alkali (NaOH) treatment

Coconut sheaths were cut in the form of mat of size 300 mm × 130 mm and were soaked in 4% NaOH solution in a water bath at room temperature for 60 min. The treated mats were washed several times with fresh water

until all the NaOH deposition over the fiber surface was removed. The mats were then left to dry at room temperature for 24 h followed by drying in an oven at 80 °C for next 1 h.

Silane treatment

The silane coupling agent used in this work was trichlorovinyl silane. A 0.5% of silane coupling agent was mixed with water uniformly using hand stirrer and the mixture was allowed to remain still for 1 h. The pH of the solution was maintained at 3.5 by adding acetic acid. Coconut sheath mats were dipped in the above solution and were allowed to remain there for 1 h. The solution was drained out and the coconut sheath fibers were dried in air for 24 h followed by drying in an oven at 80 °C until the fiber was fully dry.

Fabrication of Coconut Sheath/Clay Reinforced Hybrid Polyester Composites

The mixing of unsaturated isophthalic polyester resin and MMT is carried out at room temperature using high speed mechanical shear rotor which rotates at 500 r/min for about 2 h with radial turbine blade in polyester-clay solution. All these optimized mixing parameters have been chosen from preliminary works for getting intercalated/exfoliated state of nanoclay distribution^[23]. The mixing process consists of the addition of clay of 1 wt%, 2 wt%, 3 wt% and 5 wt% in the polyester resin followed by the addition of 1 wt% of catalyst and accelerator for room temperature curing. After the addition of curing agents in the polyester-clay mixture, it is poured over the fiber mat in such a way as to provide complete wetting on the surface of the coconut sheath of size (300 mm × 125 mm). Then it is placed inside the closed mould (300 mm × 125 mm × 3.2 mm) by keeping one by one successively up to six number of layers (48 wt%) which shows good mechanical properties^[24]. The mold was completely closed by applying 15 MPa pressure on compression molding machine in order to achieve 3 mm thickness of composite laminates. The laminates are cured at room temperature and left in the mold for another 24 h.

Characterization of Materials

To assess the state of clay dispersion in polyester resin and the effect of chemical treatment on the microscopic structures of coconut sheath, X-ray diffraction (XRD) spectra are collected using a SHIMADZU, XD-DI instrument by the step scanning rate of 2 (°)/min with Cu-K α radiation. The scanning angle (2θ) was taken from 3° to 30° for polyester nanocomposites and 5° to 80° for treated fibers. Chemical compositions of the raw, alkali and silane treated coconut sheath fibers are investigated by using an FTIR spectrometer (Shimadzu, Japan) in the mid IR range *i.e.*, from 400 cm⁻¹ to 4000 cm⁻¹. The chemically treated fiber surface of coconut sheaths is examined by SEM (M/s FEI, The Netherlands and model XL30 ESEM). For the higher magnification of coconut sheath fiber, the SEM micrograph was carried out using the instrument Carl zeiss Pvt.Ltd, UK, EVO MA15 model. All specimens were sputtered with 10 nm thick layer of gold coating prior to SEM observation. The polyester nanocomposite samples were sliced into 50 nm thickness with diamond knife by using an ultramicrotome. Thin sections were held by 200 mesh copper grids coated with carbon film. TEM images (Technai Spirit, FEI, and Netherlands) were taken on a 50 nm thin sections from samples containing 2 wt% and 3 wt% of nanoclay.

Thermal Conductivity

The thermal conductivity measurements were taken according to ASTM E 1530. The guarded heat flow meter method has been performed for thermal conductivity measurements. The readings were recorded by using the instrument named Unitherm model 2022 from ANTER Corp., Pittsburgh, PA (0.1 to 40 W/(m·K)). The 50 mm diameter circular specimens were used for taking measurements.

Gas Permeability Test

Lyssy Gas Permeability Tester (Elixir Technologies, Bangalore, India) is an extremely versatile instrument that can measure the permeability of any common gas or gas mixture through films and sheets. It is capable of measuring a broad range of low and high permeabilities (L100-5000). The carbon dioxide was selected as a gas source for this work. The gas permeability was measured by using monometric determination method. The tests were conducted according to ASTM D14382. The test results were recorded directly in mL/(m²·day).

Electrical Testing

Electrical resistance, such as volume and surface resistivity were measured in accordance with the ASTM D257 standard. The disk shaped samples having 100 mm diameter were used for the measurement using Keithley resistivity adaptor, model 6105. The resistance across the sample is measured in Knick model Teraohm meter. ASTM D149 was employed to find out breakdown voltage of the sample. The breakdown voltage of the composites was measured using an insulation break-down tester supplied by CEAST (Italy).

RESULTS AND DISCUSSION

Structure and Morphological Studies

The XRD patterns of pure nanoclay powder and nanocomposites containing 1 wt%, 2 wt%, 3 wt%, and 5 wt% clay are shown in Fig. 1. The XRD pattern of MMT shows diffraction peak at 4.5° , which corresponds to d -spacing of 1.963 nm. The sharp peak at around 4.5° is responsible for the crystalline nanoclay. It can be seen that there is no diffraction peak of clay inclusion in 1 wt%, 2 wt%, 3 wt% and 5 wt% clay nanocomposites. This indicates that either the d -spacing of the intercalated clay layers is larger than 1.963 nm ($2\theta < 3^\circ$) or they are exfoliated (*i.e.*, clay layers are separated/dispersed more than 7.5 nm) in the polyester resin. The increased d -spacing may be attributed to the intercalation of polyester chains into the clay layers during processing. Intercalated/exfoliated form of nano composites has been achieved by high speed shear mixing process when the addition of the nanoclay is less than 3 wt% which was ensured from the TEM microphotographs as shown in Fig. 2.

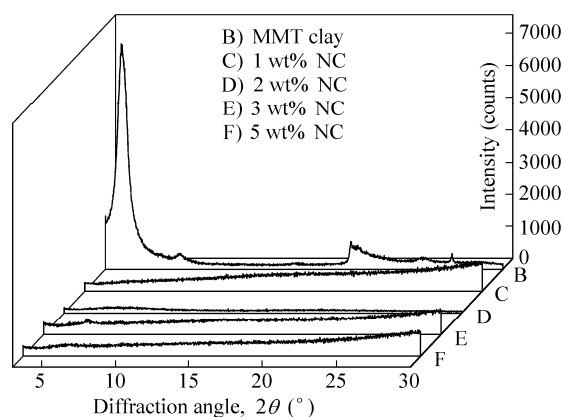


Fig. 1 XRD study of polyester and clay filled polyester nanocomposites

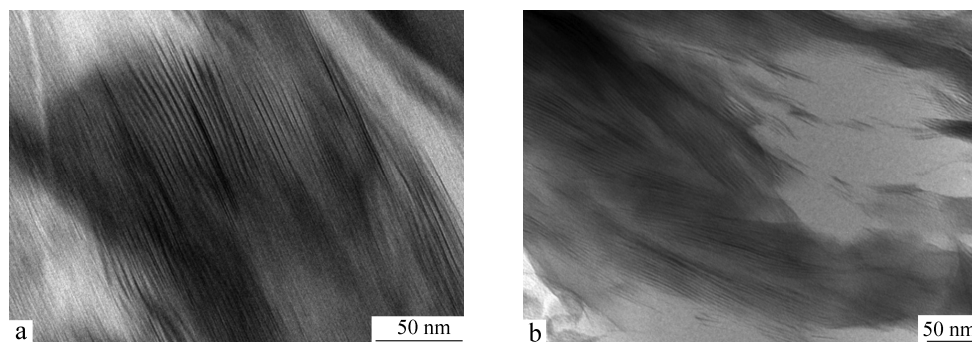


Fig. 2 TEM micrographs showing clay dispersion and exfoliation of nanocomposites containing (a) 2 wt% and (b) 3 wt% MMT

Figures 2(a), 2(b) demonstrates the intercalated/exfoliated state of nanoclay with 2 wt% and 3 wt%. The arrangement of thin grey dark lines like zebra pattern is noticed which indicates the segregation of individual

clay platelets due to the broken of van der Waal's bonds by high shear force.

Figure 3 shows the X-ray diffractograms for the untreated (UTC), NaOH (ATC) and silane treated (STC) coconut sheath fibers. Swelling of coconut sheath fiber in NaOH introduces considerable changes in crystallinity of fibers. Sodium hydroxide reacts with cellulose forming stable compounds like OH groups of cellulose with Na^+ ions. The deposition of Na^+ compound over the fiber surface is completely destroyed by subsequent washing with distilled water which leads to a lattice transformation from cellulose-I to cellulose-II^[25]. The relative degree of crystallinity of fiber structure can be expressed in terms of crystallinity index (CI). In Fig. 3, the intensity of peaks improves after NaOH treatment and the X-ray pattern shows the signs of the better crystalline structure because of the removal of amorphous constituents. But in the case of untreated coconut sheath the low resolution of peak is noticed and it indicates the low crystalline perfection and the deposition of noncellulosic matter^[26]. Figure 3 shows that in the case of coconut sheath the crystallinity index (CI) has been increased with alkali treatment, because of the removal of the cementing material such as hemicelluloses, waxes and impurities, which leads to a better mechanical interlocking with cellulose structure. In the X-ray diffractogram of silane treated case the less intensity of peak is identified and it indicates the less crystalline region due to the presence of amorphous nature of chemical compounds.

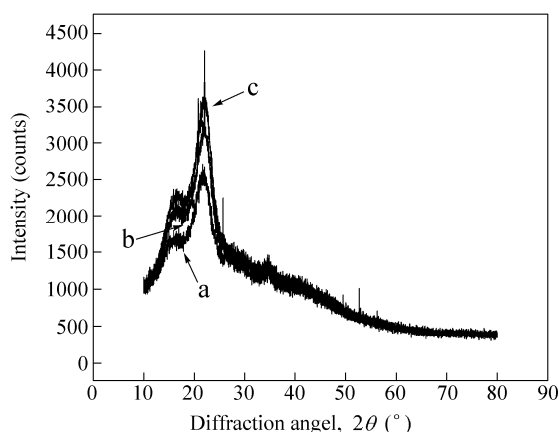


Fig. 3 XRD studies of chemically treated coconut sheaths: (a) UTC, (b) STC and (c) ATC

From Fig. 3, it is observed that all of the spectra contained two peaks that are particularly well defined for natural fibers. The two peaks situated at $2\theta = 15.4^\circ$ and $2\theta = 22.5^\circ$ can be attributed to cellulose I and IV which was already reported by many authors^[27, 28]. The CI was calculated according to Segal *et al.*^[29] in the following expression:

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

where $I_{22.5}$ is the peak intensity of the 002 lattice diffraction at $2\theta = 22.5^\circ$, and $I_{18.5}$ is the diffraction intensity at $2\theta = 18.5^\circ$. The peak intensity at $2\theta = 22.5^\circ$ ($I_{22.5}$) includes both the crystalline and amorphous fractions. The intensity at $2\theta = 18.5^\circ$ ($I_{18.5}$) is attributed to the amorphous fraction^[30]. The CI of the alkali treated coconut sheath (42%) exhibits the highest percentage of CI compared to silane (38%) and untreated coconut sheath (34%).

Figures 4(a)–4(c) shows the SEM images of UTC, ATC and STC. The appearance of waxy layer over the coconut sheath is identified from the white color cup-like structure and it leads to the incompatibility between fiber and matrix (Fig. 4a). The NaOH treatment removes the waxes and an impurity present on the fiber surface increases the roughness of fiber surface and causes the fibers to become stiffer as shown in Fig. 4(b). The rough surface of fibers tends to increase the interfacial adhesion between the fiber and the matrix by mechanical interlocking mechanism as shown in SEM micrograph of Fig. 4(b). NaOH treatment has been done before silane

activation to remove the noncellulosic compounds. On the other hand, a coating of thin film deposition over the surface of silane treated coconut sheath could be seen in Fig. 4(c). Once the surface of coconut sheath was covered by a thin film of trichlorovinyl silane, it promotes a good physical adhesion between fiber and the polyester matrix.

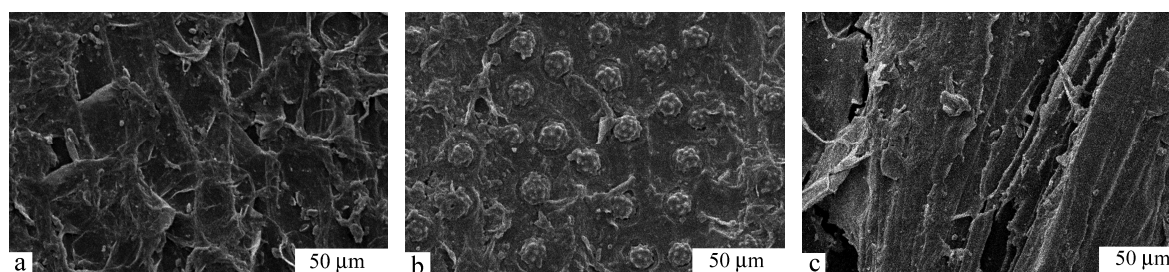


Fig. 4 SEM micrograph of the surface of (a) UTC, (b) ATC and (c) STC

The SEM micrographs of untreated, NaOH and silane treated coconut sheath fibers with higher magnification (1000 X) are shown in Figs. 5(a)–5(c). The surface topology of untreated coconut sheath fiber is shown in Fig. 5(a), which indicates an irregular surface due to globular protrusions. The modifications in surface topology of NaOH treated coconut sheath fiber is shown in Fig. 5(b). The disappearance of globular protrusions was noticed on the surface as a result of NaOH treatment, leading to the creation of a large number of voids^[31]. These voids support better mechanical port between the fiber and polyester matrix. Also the interaction of fiber surface with polyester matrix has improved due to the exposure of effective surface area of the fibers. The NaOH treated fiber has a rough surface topography as it is evident from the Fig. 5(b). These voids can enhance the hydrophilic nature of alkali treated fibers. Figure 5(c) shows the SEM micrograph of silane treated coconut sheath and it projects the silane coating as a roof covered over the fiber surface. The partial amount of voids is hidden by the coating of silane on fiber surface which reduces the amount of moisture intake through voids.

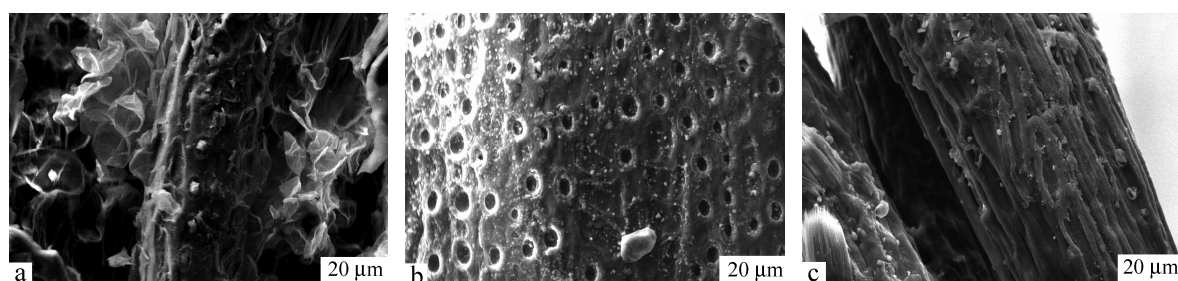


Fig. 5 SEM micrograph of individual coconut sheath fiber of (a) UTC, (b) ATC and (c) STC under high magnification

Infra-red (IR) Spectra

IR spectra of the untreated and treated (NaOH, silane) coconut sheath fibers are given in Fig. 6. The broad peak 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 broad peak at 3316 cm^{-1} has increased for the alkali-treated coconut sheath. This may be due to the presence of more hydroxyl groups as a result of the breaking of crosslinks of lignin and hemicellulose with cellulose after NaOH treatment.

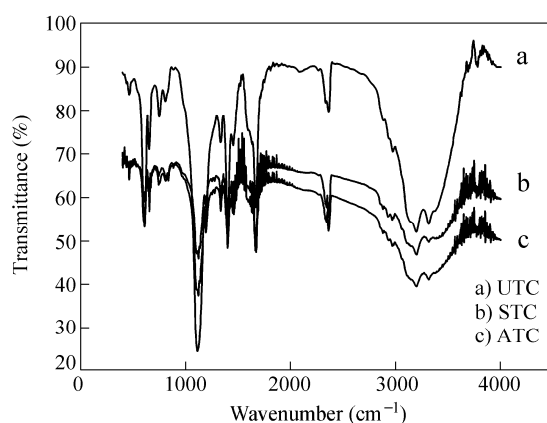


Fig. 6 IR spectra of untreated, silane and alkali treated coconut sheaths

Thermal Conductivity

Figure 7(a) shows the effect of chemical treatment on thermal conductivity. An increase of thermal conductivity was observed for coconut sheath/polyester composites compared to the pristine polyester (0.179 W/(m·K)). Generally the thermal conductivity increased with the addition of natural fiber as reinforcement due to the fact that the fibers can form conductive chains between them based on the architecture of the fibers^[32]. There is a significant decrease in thermal conductivity during NaOH treatment, whereas only a marginal decrease in silane treatment is noticed compared to the untreated coconut sheath/polyester composites. The cementing materials such as hemicelluloses, waxes and organic dusts are dissolved when NaOH reacts with hydroxyls groups.

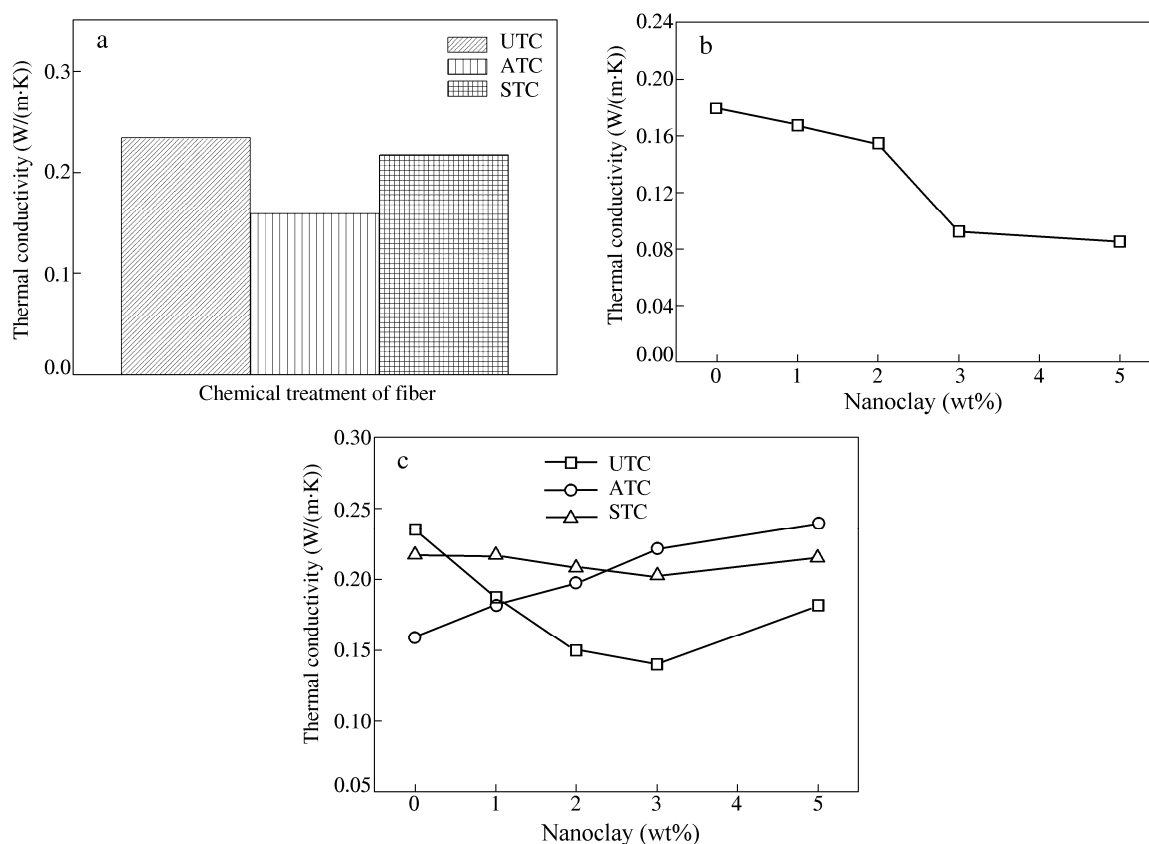


Fig. 7 Thermal conductivity of polyester composites with (a) chemically treated coconut sheath, (b) nanoclay and (c) nanoclay and chemically treated coconut sheath

The moisture content increases as a result of treatment by NaOH. Also the increase in amorphous cellulose at the expense of crystalline cellulose during NaOH treatment increases the sorption capacity of the fiber. Fiber fibrillation and amorphization of cellulose might be responsible for the decrease of thermal conductivity.

The thermal conductivity is improved by the woven architecture of fibers through the conductive chain in UTC/polyester composites. But in the case of NaOH treatment, the fiber fibrillation leads to split of fiber bundle into loosely segregated fibers and it causes conductive chain to break between fibers and it induces a decrease in the thermal conduction property. In the case of silane treatment, percentages of moisture traces get reduced due to the deposition of silane. The formation of silanol by the hydroxylation process forms strong covalent bonds^[33]. The polymerized silane can adhere to the polyester matrix by the van der Waal's forces. Silane coupling agents enter through the surface of voids and deposit in the interfibrillar region. As a result, silane-coupling agent forms a bridge between the fibers and matrix and it promotes better fiber/matrix adhesion. The formation of roof like structure covered by the silane coating on the coconut sheath fiber changes its hydrophilic characteristics. Thus the water absorption of composites gets reduced compared to NaOH treated composites. This could increase the thermal contact resistance at the interface which leads to the lowering of the thermal conductivity of these samples. Similar observation was reported for thermal conductivity of banana fibers/PP composites by Sherey *et al*^[34].

Figure 7(b) shows the variation of thermal conductivity of polyester matrix with the addition of nanoclay. The continuous decreasing trend was noticed with increasing the weight percentage of nanoclay in pristine polyester matrix. The linear decreasing rate was observed up to 2 wt% of nanoclay addition and after that a sudden decrease in thermal conductivity was noticed for 3 wt% of clay. The maximum of 53% of reduction in thermal conductivity was identified in the addition of 5 wt% of clay. The randomly dispersed nanoclay platelets in polyester matrix create the complicated path for heat flow which decreases the rate of flow through the specimens.

The dependence of thermal conductivity on the nanoclay addition and chemical treatments of coconut sheath is shown in Fig. 7(c). The thermal conductivity values show a decreasing trend for untreated coconut sheath/ polyester composites with the addition of 1 wt%, 2 wt% and 3 wt% of clay. The randomly disordered clay dispersion acts as a barrier for the heat flow to take place at the interface. Hence there is a slight drop in thermal conductivity. But a different scenario exists when there is an addition of 5 wt% of clay. A slight increase in thermal conductivity was observed and it could be due to the clay agglomeration but still it is lesser than that of the composites with no clays. In the case of alkali treatment, an increasing trend in thermal conductivity with the addition of 1 wt%, 2 wt% and 3 wt% of clay was observed. The presence of voids on the fiber surface is visible after the NaOH treatment and there may be the chance of penetration of clay into the voids and it tries to get interlocked within the voids. This leads to halt of uptake of water and thus increasing the thermal conductivity. A drop in thermal conductivity was identified in silane treated coconut sheath with the addition of (1 wt%, 2 wt%, 3 wt% and 5 wt%) nanoclay reinforced hybrid polyester composites. This may be attributed to the nature of clay which tries to decrease the thermal conductivity. The presence of clay over the surface creates an obstacle to the flow of heat at the fibre surface. Deposition of silane forms small patches over the fiber and reduces the effective surface area of the sheath surface. This reduction in surface area may result in the decrease in thermal conductivity, since the flow of heat is directly proportional to the available surface area. It was further confirmed from the following equation^[35]:

$$Q = KA\Delta T/L$$

where Q is the heat flow (W), K is thermal conductivity (W/(m·K)), A is the surface area (m²) and L is the thickness (m).

Gas Permeability

The test was performed using standard gas permeability equipment for all types of composite materials at room temperature. The cured coconut sheath/polyester composite laminates are machined by a diamond saw to obtain

a 110 mm × 110 mm × 3 mm size of specimen. The surface was polished with 600-grid SiC emery paper and cleaned with acetone. A micron level teflon coating was provided around the perimeter of the specimen to ensure the air-tight requirement of the experiment. The experimental results of CO₂ gas permeability of coconut sheath/MMT fiber reinforced hybrid polymer composites are shown in Fig. 8.

The maximum reduction of 88% in gas permeability was observed for alkali (NaOH) treated composites compared to UTC/polyester composites in Fig. 8. It is owing to the removal of waxy layer at the surface of untreated fiber. Thus it can provide better adhesion between the fiber and matrix and it reduces the chances of voids and micro-cavities at the fiber/matrix interface. The improved surface roughness of the fiber after the alkali treatment improves the effective surface area between the fiber and matrix and it also enhances the mechanical interlocking capability and provides the barrier to the gas flow along the interfacial region. But the reduction of gas permeability is decreased to 72% for silane treated condition; this could be due to the presence of physical adhesion between silane deposition with matrix. It may lead to the way for leakage of gas flow along fiber region. According to Fig. 8, it was observed that in untreated and treated (NaOH, silane) conditions the gas permeability is decreased with the increase in wt% of clay. It could be due to the formation of tortuous path achieved by the distribution of randomly disordered silicate clay platelets in polyester. In general, the rate of gas permeability in polymer nanocomposites is completely based on the degree of exfoliation or intercalation and the state of distribution of clay^[36].

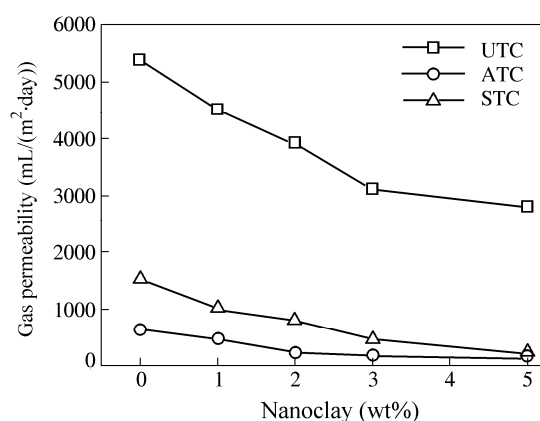


Fig. 8 Gas permeability results of coconut sheath/polyester composites with the effect of clay addition and chemical modifications

Volume and Surface Resistivity

The experiment used in this study is in accordance with the ASTM D 257 standard for the measurement of volume and surface resistivity. The top electrode is tightened using a screw arrangement and the bottom electrode is a rigid fixture. This setup ensures uniform pressure distribution over the measuring area. The dimensions of the electrodes used follow the ASTM standard.

Volume and surface resistance values were calculated by applying a DC voltage of 500 V across the specimens and the corresponding resistivities were calculated based on the standard relations.

$$\rho_V = AR_V/t \quad A = \pi (D_1 + g)^2/4$$

$$\rho_S = PR_S/g \quad P = \pi D_o$$

where, ρ_V is volume resistivity (ohm·m), ρ_S is surface resistivity (ohm·m), A is the effective area (m²) of the measuring electrode, R_V is the measured volume resistance (ohm), R_S is the measured surface resistance (ohm), [Dimensions of standard electrodes (gap length between electrodes $g = 5$ mm, outer diameter of electrode $D_o = 60$ mm, inner diameter of electrode $D_1 = 50$ mm)].

Figures 9 and 10 demonstrate the variation of volume resistivity and surface resistivity with varying weight

percentage of nanoclay. It was observed from the Fig. 9, that with the addition of MMT nanoclay, the resistivity values are decreased. However, the saturation was achieved at 2 wt% to 3 wt% of addition, and at 5 wt% of clay inclusions the resistivity values increased, but for the surface resistivity it is lesser than that of the pristine polyester. The trend clearly shows that the clay addition assists the flow of electrons in clay/polyester mixture due to the conductive nature of crystalline clay minerals. The X-ray studies have shown the crystallinity of MMT from the appearance of peak at the diffraction angle of 4.5° . In general in any polymeric material the flow of current mainly through the crystalline regions and the amorphous regions allow current to pass through mainly due to the moisture uptake^[37]. Effect of nanoclay and untreated, alkali and silane treated coconut sheath fiber reinforcement on volume and surface resistivity of polyester composites is given in Table 1. Unlike polyesters, the fall in resistivity was observed by the reinforcement of coconut sheath in polyester matrix as shown in Table 1. This increase in conductivity could be due to the presence of moisture and organic impurities, *e.g.* silica in coconut sheath fibres, and this was identified from the SEM image (Fig. 4b) by the appearance of white spots on the surface of the NaOH treated coconut sheath.

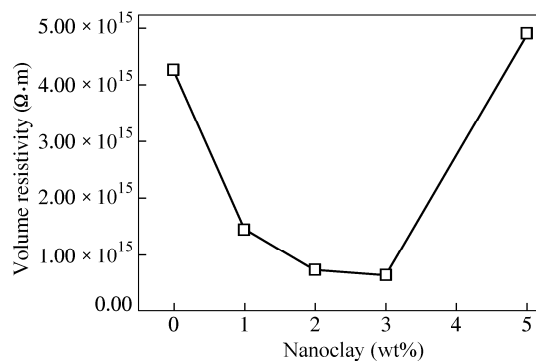


Fig. 9 Volume resistivity of polyester composites with varying wt% of nanoclay

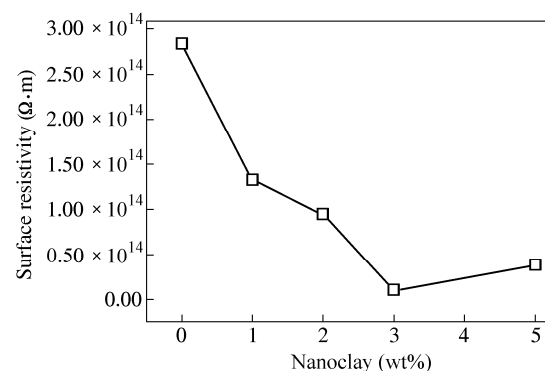


Fig. 10 Surface resistivity of polyester composites with varying wt% of nanoclay

Table 1. Volume and surface resistivity of nanoclay of chemically treated coconut sheath fiber-reinforced polyester composites

Weight % of nanoclay	Untreated		NaOH treated		Silane treated	
	Volume resistivity (Ω·m)	Surface resistivity (Ω·m)	Volume resistivity (Ω·m)	Surface resistivity (Ω·m)	Volume resistivity (Ω·m)	Surface resistivity (Ω·m)
0	0.308×10^{12}	5.0893×10^{10}	$< 10^6$	$< 10^6$	$< 10^6$	$< 10^6$
1	0.110×10^{12}	1.3194×10^{10}	$< 10^6$	$< 10^6$	$< 10^6$	$< 10^6$
2	0.454×10^{12}	9.4247×10^{10}	$< 10^6$	$< 10^6$	$< 10^6$	0.1696×10^9
3	0.450×10^{12}	8.4823×10^{10}	$< 10^6$	$< 10^6$	$< 10^6$	0.2167×10^9
5	0.162×10^{12}	1.4137×10^{10}	$< 10^6$	$< 10^6$	$< 10^6$	0.1319×10^9

Maximum values of volume resistivity and surface resistivity are obtained for untreated coconut sheath/polyester composites. Among the chemically treated coconut sheaths, the decrease in resistivity was observed for NaOH treated coconut sheath due to the increase in water uptake through voids by capillary action at the fiber surface. Volume resistivity values of all the NaOH treated composite samples remained lower than those of the untreated and silane treated composites. Untreated coconut sheath results in reduction of $-OH$ groups by the presence of waxy and globular protrusion on the fiber surface. But the chemical composition and cellulose structure of coconut sheath fiber are changed, and it increases the conductivity in alkali treated composites. This NaOH treatment could lead to the destruction of crystalline cellulose, which increases the amount of amorphous cellulose and leaves more hydroxyl groups in the fiber surface. The percentage of moisture content and other constituents of chemically treated (NaOH, silane) lignocellulose coconut sheath fibres is given in Table 2 and is showing a general decrease in resistivity with the increase in moisture content. In

fact, the difference in the amount of impurities may also be one of the main reasons for differences in resistivities between untreated and treated (NaOH) coconut sheath fibers.

Table 2. Percentage of chemical constituents in raw and chemically treated coconut sheath fibers

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

According to Table 1, an anomalous trend was observed for volume and surface resistivity values with the addition of different wt% of nanoclay in all condition of composites. In general, the incorporation of nanoclay on natural fiber reinforced composites can decrease the rates of water sorption ability^[12]. The volume and surface conductivity increases in a similar fashion for the addition of 1 wt% and 5 wt% nanoclay and decreases for 2 and 3 wt% of nanoclay addition for UTC/polyester composites. From the Table 1, it was observed that apart from the weight percentage of nanoclay, the volume and surface resistivity of natural fiber reinforced composites are influenced by the nature of fiber surface, diffusion of moisture content, formation of micro-cracks, fiber/matrix interface, exposed effective surface area and fiber architecture. The semi permeable membrane nature of nanoclay with coconut sheath fiber exhibits complex mechanism in the flow of water molecules along the fiber-matrix interface followed by diffusion from the interface into the matrix and the fiber. This may be the reason for the observed scatter in resistivity values obtained for coconut sheath/ polyester composites. Due to the limitation of measurement device the volume and surface resistivity values less than $10^6 \Omega\cdot\text{m}$ were not able to be recorded in the case of NaOH and silane treated coconut sheath/MMT reinforced hybrid composites.

Dielectric Strength

Breakdown voltage is a characteristic property of an insulator that defines the maximum voltage difference that can be applied across the material before the insulator collapses and starts conducting. ASTM D149 was employed to find out dielectric strength of the sample. The dielectric strength is calculated using the following standard relation:

$$D_s = B_v/t$$

where, D_s is dielectric strength (kV/mm), B_v is breakdown voltage (kV) and t is thickness (mm). Factors like thickness, impurity content, and amount of moisture, chemical composition and time of voltage applications may affect the dielectric strength of polymer materials^[38].

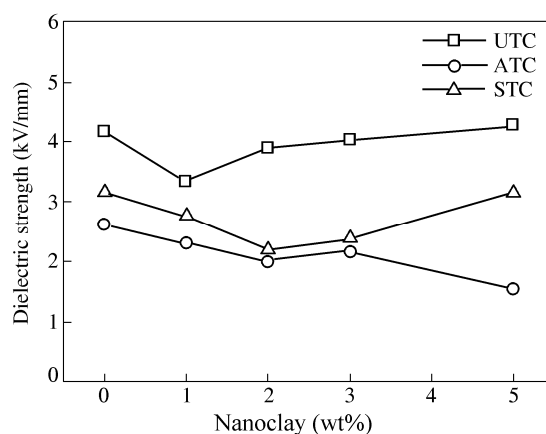


Fig. 11 Effect of nanoclay addition and chemical treatment of coconut sheath on dielectric strength of the composites

Figure 11 shows the variations of dielectric strength as a function of wt% of nanoclay and chemical treatment of coconut sheath samples. In all cases, it was observed that the dielectric strength reduced significantly due to the chemical treatment of coconut sheath used in the composites. Based on the SEM, XRD and FTIR results it can be explained that the chemical treatment of coconut sheath increases the water content of the amorphous cellulose structure and hence the composite with NaOH treated coconut sheath shows low dielectric strength compared with the silane and untreated samples. As mentioned before, the conductive medium of clay mineral decreases the dielectric strength of the composite with increasing the clay content up to 5 wt%. Exfoliated and intercalated clay platelets distribute the electric stress and decrease the path length for the break down.

CONCLUSIONS

The naturally woven coconut sheath (CS) fiber reinforced composites with the addition of nanoclay and chemical treatment of fiber was developed by using compression molding technique.

The lowest thermal conductivity was observed in ATC/polyester composites due to the increase in liquid uptake and it slightly increased for STC/polyester composites because of the formation of silane coating on fiber surface.

XRD, TEM and SEM have been carried out to assist the morphological state of polyester nanocomposites and chemically treated coconut sheath.

The addition of nanoclay increases the thermal conductivity for alkali treated composites whereas it gets reduced for untreated and silane treated coconut sheath reinforced composites.

A sudden decrease in gas permeability was observed in ATC/polyester composites compared to the UTC fiber reinforced composites due to the enhanced mechanical interlocking by the large exposure of effective surface area. In the case of STC/polyester, the coating of silane acts as a bridge between fiber and matrix forms strong interfacial adhesion at interface which can cause complicated flow of gas along the fiber/matrix interface. The formation of tortuous path by the addition of nanoclay significantly affects the rate of gas permeability in all types of composites.

Volume and surface resistivity are found to be decreased by the addition of nanoclay in polyester matrix, whereas in the case of coconut sheath reinforced hybrid composites the anomalous trend was noticed by the complex mechanism of diffusion of water. The dielectric strength in all the cases of composites gets reduced by the addition of nanoclay.

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REFERENCES

- 1 Lan, T. and Pinnavaia, T., *J. Chem. Mater.*, 1994, 6: 2216
- 2 Alexander, M. and Dubois, P., *Mater. Sci. Eng.*, 2000, 28: 1
- 3 Messersmith, P.B. and Giannelis, E.P., *J. Polym. Sci. Part A: Polym. Chem.*, 1995, 33: 1047
- 4 Chan, M.L., Lau, K.T., Wong, T.T., Ho, M.P. and David, H., *Composites Part B*, 2011, 6: 1708
- 5 Kim, J.K., Hu, C., Woo, R.S.C. and Sham, M.L., *Compos. Sci. Technol.*, 2005, 65: 805
- 6 Rashmi Renukappa, N.M., Ranganathaiah, C. and Shivakumar Kunigal, N., *Polym. Eng. Sci.*, 2011, 51: 1827
- 7 Vaia, R.A., Jandt, K.D., Kramer, J. and Pgiannaeles, E., *Chem. Mater.*, 1996, 8: 2628
- 8 Hackman, I. and Hollaway, L., *Composites Part A*, 2006, 37: 1161
- 9 Yasmin, A., Abot, J.L. and Daniel, L.M., *Scr. Mater.*, 2003, 49: 81

- 10 Chandradass, J., Ramesh Kumar, M. and Velmurugan, R., *J. Reinf. Plas. Compos.*, 2008, 27: 1585
- 11 Wang, W. and Huang, G., *Mater. Des.*, 2009, 30: 2741
- 12 Hepworth, D.G., Hobson, R.N. and Bruce, D.M., *Composites Part A.*, 2000, 31: 1279
- 13 Augustine, P., Kuruvilla, J. and Sabu, T., *Compos. Sci. Technol.*, 1997, 57: 67
- 14 Xue, L., Lope, G.T., Ikechukwuka, N.O. and Satyanarayan, P., *Compos. Sci. Technol.*, 2008, 68: 1753
- 15 Debasmita, M., Satapathy, A. and Patnaik, A., *Int. J. Plast. Technol.*, 2012, 1
- 16 Fu, S.Y. and Mai, Y.W., *J. Appl. Polym. Sci.*, 2003, 88: 1497
- 17 Idicula, M., Boudenne, A., Umadevi, L., Ibos, L., Candau, Y. and Thomas, S., *Compos. Sci. Technol.*, 2006, 66: 2719
- 18 Lee, J.H., Jung, D., Hong, C.E., Rheeand, K.Y. and Advani, S.G., *Compos. Sci. Technol.*, 2005, 65: 1996
- 19 Supong, A., Autthiphat, P., Anongnat, S., *J. Appl. Polym. Sci.*, 2007, 106: 2210
- 20 Vera Alvarez, A., Roxana Ruscekaite, A. and Analia, V., *J. Compos. Mater.*, 2003, 37: 1575
- 21 Velmurugan, R. and Manikandan, V., *Composites Part A*, 2007, 38: 2216
- 22 Cao, Y., Shibata, S. and Fukumoto, I., *Composites Part A*, 2006, 37: 423
- 23 Rajini, N., Winowlin Jappes, J.T., Rajakarunakaran, S. and Jeyaraj, P., *J. Reinf. Plast. Compos.*, 2012, 30: 1364
- 24 Winowlin Jappes, J.T. and Siva, I., *Polym-Plas. Technol. Eng.*, 2011, 50: 1600
- 25 Maya Jacob, J. and Sabu, T., *Carbohydr. Polym.*, 2008, 71: 343
- 26 Mahuya, D. and Debabrata, C., *J. Appl. Polym. Sci.*, 2006, 102: 5050
- 27 D'Almedia, J.R.M., Aquino, R.C.M.P. and Montriro., S.N., *Composites Part A*, 2006, 37: 1473
- 28 Helbert, W., Sugiyama, J., Ishihara, M. and Yamanaka, S., *J. Biotechnol.*, 1995, 57: 29
- 29 Segal, L., Creely, J.J., Martin, A.E. and Conrad, C., *Text Res. J.*, 1959, 29: 786
- 30 Sreenivasan, V.S., Ravindran, D., Manikandan, V. and Narayanasamy, R., *Mater Design.*, 2012, 37: 111
- 31 Calado, V., Barreto, D.W. and D'Almeida, J.R.M., *J. Mater. Sci. Lett.*, 2000, 19: 2151
- 32 Sreekumar, P.A., Agoudjil, B., Boudenne, A., Unnikrishnan, L., Ibos, L., Fois, M. and Thomas, S., *J. Reinf. Plas. Compos.*, 2012, 31: 117
- 33 Kumar, V. and Kumar, R., *J. Compos. Mater.*, 2012, 46: 3089
- 34 Sherely, A.P., Boudenne, A., Ibos, L., Candau, Y., Joseph, K. and Thomas, S., *Composites Part A*, 2008, 39: 1582
- 35 Kreith, F. and Bohn, M.S., "Principle of heat transfer", 6th ed., Cengage Learning Publishers, New Delhi, 2001, p. 6
- 36 Lu, C.S. and Mai, Y.W., *Compos. Sci. Technol.*, 2007, 67: 2895
- 37 Paul, A. and Thomas, S., *J. Appl. Polym. Sci.*, 1997, 63: 247
- 38 Kulkarni, A.G., Sathynarayana, K.G. and Rohatgi, P.K., *J. Mater. Sci.*, 1981, 16: 1720