A New Proposed Model for Dielectric Behavior of PVC/Rice Husk Composites

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ABSTRACT: Ecofriendly materials are becoming a need of the day. We have severe setback when there is lot of use of agro wastes in plastics. To reduce pure plastic use in agriculture, this study has been made to find some remedial measure. In the process, we sought the effect of addition of rice husk (RH) in polyvinylchloride (PVC) on the dielectric properties at different frequency and temperature has been studied. Measurements have been performed in the frequency range from 1 to 10 kHz and temperature range of 32–80°C. The experimental results show that dielectric constant (ε′) increases with the addition of RH in PVC. Dielectric constant (ε′) decreases with increasing frequency, which indicates that the major contribution to the polarization comes from orientation polarization. Dielectric constant (ε′) increases with increasing temperature due to greater freedom of movement of dipoles within PVC at higher temperatures. A theoretical model for dielectric constant with temperature and frequency dependent is proposed. Experimental results are in good agreement with the proposed theoretical model. J Appl Polym Sci 000: 000–000, 2012

Key words: composites; dielectric properties; fibers; polyvinyl chloride (PVC); theory

INTRODUCTION

Through many years, the concepts of cost reduction in plastics by the use of natural fiber-based fillers have been in vogue. Use of agro fillers in the development of polymer composites fulfills the objective of ecofriendly materials. Other main advantages of these natural fiber fillers are their low density, low cost, recyclability, and of their renewable nature. In view of this, agro fibers are becoming more and more useful material for reinforcement day by day. Rice husk (RH) is a major agro waste product in the world. Typical composition of RH reported earlier has 16–22% α-cellulose, 20–27% lignin, 15–30% ash, and the length of husks varies from 2 to 5 mm.[1] The presence of cellulose content in RH directs absorption of moisture from the environment.[2] It is reported in literature that combination of different fibers or fillers with polymer matrices can result in polymer–matrix composites, which are important in industry for dielectric properties to use as capacitor and fulfills our concept of cost reduction.[3]

Polyvinylchloride (PVC) is a cheap versatile thermoplastic, which has good chemical and weathering resistance.[4] Because of this reason, it is finding increasing use in outdoor applications such as wood and aluminum.[5] PVC products are also used in automobile industry and electrical industry. The ability of PVC to use in various functions is due to the capability of PVC to mix with various fillers to suit different applications.[6–8] The interaction between the polymer and filler at the interface depends on the type of filler and its properties.

Ben Amor et al.[9] reported dielectric properties of short palm tree lignocelluloses fibers reinforced polyester resin in the frequencies ranging from 1 to 100 kHz. They found three relaxation occurred: (i) orientation polarization due to polar water molecules present in palm fiber, (ii) relaxation associated with the conductivity occurring due to diffusion of charge carriers above glass transition, and (iii) interfacial relaxation because of charge accumulation at the interface of palm fiber polyester.[9]

Dielectric loss of sisal/coir hybrid fiber-reinforced natural rubber composites as a function of fiber loading was earlier studied by Hassena et al.[10] They found that the dielectric constant was higher for the fiber-filled systems and attributed it to the polarization exerted by the fibers in matrix.[10] In another study on polymer filled with lignocellulosic material, low-electric permittivity composite was prepared and used as insulator to cut off the energy flow.[11] The most attractive features of these filled composites are that their dielectric properties can widely be tailored by choice of shape, size, and concentration of filler in the polymeric matrix.

Chand and Jain[12] have investigated the dielectric properties of sisal fiber-reinforced polyester

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composites.[12] They found that addition of sisal fiber increased the dielectric constant. It is necessary to know the influence of RH addition on dielectric behavior of PVC composites. Also there is no theoretical model to predict dielectric constant of RH-filled PVC composites at various temperatures and frequencies.

In this article, dielectric constant for RH-filled PVC composites is determined at various temperatures and frequencies. A general model for dielectric constant with frequency and temperature dependence for lignocellulosic fiber-reinforced polymer composites is developed. The model is based on constant modification in the Curies ($1/T$) temperature dependence law. The dielectric property of RH PVC composites is predicted by the proposed theoretical model. The values of dielectric constant calculated by the proposed model are validated with the experimental values.

EXPERIMENTAL PROGRAM

Materials

The PVC used in this study is a suspension resin with solution viscosity *K*-value 67, grade H 072. The homopolymer PVC is a medium molecular weight resin designed for general purpose and rigid applications. Rice straws used, in this study, were obtained from Betul M.P. (India) in the form of agriculture residues.[1]

Methods

PVC composites used, in this study, were the same which were reported earlier.[1] Ingredients were mixed at 170°C for a period of 10 min on a two-roll mill and placed in a steel mold. PVC composites prepared had 0, 20, 30, and 40 wt % RH.

Dielectric measurements

Capacitance (C) and tan δ values of RH-filled PVC samples were measured by using a Hewlett-Packard, LCR Meter, model 4274 A, in the temperature range 32–80°C and frequency range from 1 to 10 kHz. Heating rate was kept constant at 2°C/min. Dielectric constant k was calculated by using the relation

$$\varepsilon' = \frac{C}{C_0}$$

where C and C_0 are the capacitance values with and without sample, respectively;

$$C_0 = \left[\frac{(0.08854A)}{d}\right]\text{pF}$$

TABLE I
Density Values of the Compositions Used in the Study

Sample no.	PVC (%)	RH (%)	Density (g/cc) (RH PVC composites)
1	100	0	1.37
2	80	20	1.31
3	70	30	1.27
4	60	40	1.18

where A (cm^2) is the area of the electrodes, and d (cm) is the thickness of the sample.

tan δ being the dissipation factor and is defined as

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'}$$

where ε'' is the dielectric loss.

Density measurements

Density of all the samples of RH-filled PVC composites used in the study is listed in Table I.[1]

THEORY FORMULATION

Theoretical prediction of dielectric constant requires the calculations of polarizability of the inclusion. This concept is used here to predict the dielectric constant with modification in the existing polarizability equations.

Effect of temperature on dielectric constant ε′ of RH PVC composites

Several theoretical models for calculating the electrical and mechanical properties of composites have been proposed earlier.[13] Increase in moisture content increases the dielectric constant of insulating materials ε' of the RH PVC composites is determined in the temperature range ranging from 32 to 80°C. Increasing the temperature decreases the moisture content. The temperature dependence of dielectric constant of RH PVC composites predicted based on moisture content and density of composite. It is assumed that when electric field is applied on any polymer it induces dipole moment per unit volume. From the theory of molecular dipoles, if the electric field E induces an average dipole moment (p_0) per unit volume, then dielectric constant is given by eq. (1).[14]

$$\varepsilon' - 1 = \frac{\bar{P}}{\varepsilon_0 \bar{E}} \quad (1)$$

where $\bar{P}$ is the polarization vector, ε_0 is the permittivity of free space, $\bar{E}$ is the electric field, and ε' is the dielectric constant.

The other reason of increase in dielectric constant is polarization. Taking this concept into consideration and from Curies ($1/T$) dependence law, the polarization is proportional to the electric field $\overline{E}$. In addition, it can be proposed that the polarization depends inversely on the temperature.

$$\bar{P} = \frac{Np_0^2\bar{E}}{3kT} \tag{2}$$

By substituting the values of $\overline{P}$ from eq. (2) in eq. (1), eq. (1) can be written as follows:

$$\varepsilon' - 1 = \frac{\bar{P}}{\varepsilon_0\bar{E}} = \frac{Np_0^2}{3\varepsilon_0 kT} \tag{3}$$

On rearranging eq. (3), dielectric constant can be written as follows:

$$\varepsilon' = 1 + \frac{Np_0^2}{3\varepsilon_0 kT}$$

where ε' is the dielectric constant, p_0 is the dipole moment in PVC chain, $p_0 = 1.31D$,[15] k is the Boltzmann constant $= 1.38 \times 10^{-28}\left(\frac{J}{K}\right)$, T is the absolute temperature (K), N is the concentration of the carriers, and ε_0 is the permittivity of free space.

To study the contribution of RH addition in PVC on the dielectric constant a factor, ε'_f is introduced, which depends upon the weight fraction of RH and moisture content present in it. By using the above equation and the contributing factor dielectric constant of RH PVC composite can be written as,

$$\varepsilon' = 1 + \varepsilon'_m + \varepsilon'_f \tag{4}$$

where ε'_m is the contribution factor of PVC and ε'_f is the contribution of RH.

To calculate ε'_f, it is assumed ε'_f is a function of moisture,

$$\varepsilon'_f \propto f(m) \tag{5}$$

On removing the proportionality constant, eq. (5) becomes

$$\varepsilon'_f = wf(m)$$

where $f(m)$ is the function of moisture content in the composite, w is the of weight fraction of RH present in the composite,

$$w = (1 - x)$$

where x is weight fraction of PVC

Moisture content for Samples 1–4 was 0, 0.012, 0.031, and 0.136, respectively.

Another factor, $f(t)$ is also introduced, which is a temperature dependent quantity, whose value is assumed as follows:

$$f(t) \propto (T)$$

$$\varepsilon' = 1 + \frac{xp_0^2}{3\varepsilon_0 kT} + (1 - x)f(m) + f(T) \tag{6}$$

$f(T)$ can be defined as follows:

$$f(T) = aT$$

On substituting $f(T)$ value in eq. (6), we get

$$\varepsilon' = 1 + \frac{xp_0^2}{3\varepsilon_0 kT} + (1 - x)f(m) + Ta \tag{7}$$

a is fitting parameter, which is calculated from eq. (7). It is proposed that $f(m)$ is a function of density because the charge carriers depend on the amount of humidity present in the composite and can be defined as follows:

$$f(m) = d^{bT}$$

where b is the slope of moisture content with concentration, T is the temperature at which measurement is made, and d is the density of the composite.

On substituting the value of $f(m)$ in eq. (7), we get the following equation for dielectric constant of composite based on the temperature, eq. (7) becomes as below,

$$\varepsilon' = 1 + \frac{xp_0^2}{3\varepsilon_0 kT} + (1 - x)d^{bT} + aT \tag{8}$$

Thus, the temperature dependence of ε' can be calculated by eq. (8).

Effect of frequency on dielectric constant (ε') in the PVC RH composites

To propose the frequency dependent equation for PVC RH composite, eq. (1) is again considered, here polarization is defined as,

$$\bar{P} = Np_0$$

In the case of PVC RH composites, N is defined as concentration of particles, P, where p_0 is the dipole moment.

PVC chain and RH particles behave as dipoles. From the theory of molecular dipoles, it is known that dipole moment (p_0) is proportional to the electric field ($\overline{E}$),

$$p_0 = \alpha\varepsilon_0\bar{E} \tag{9}$$

where α is a constant.

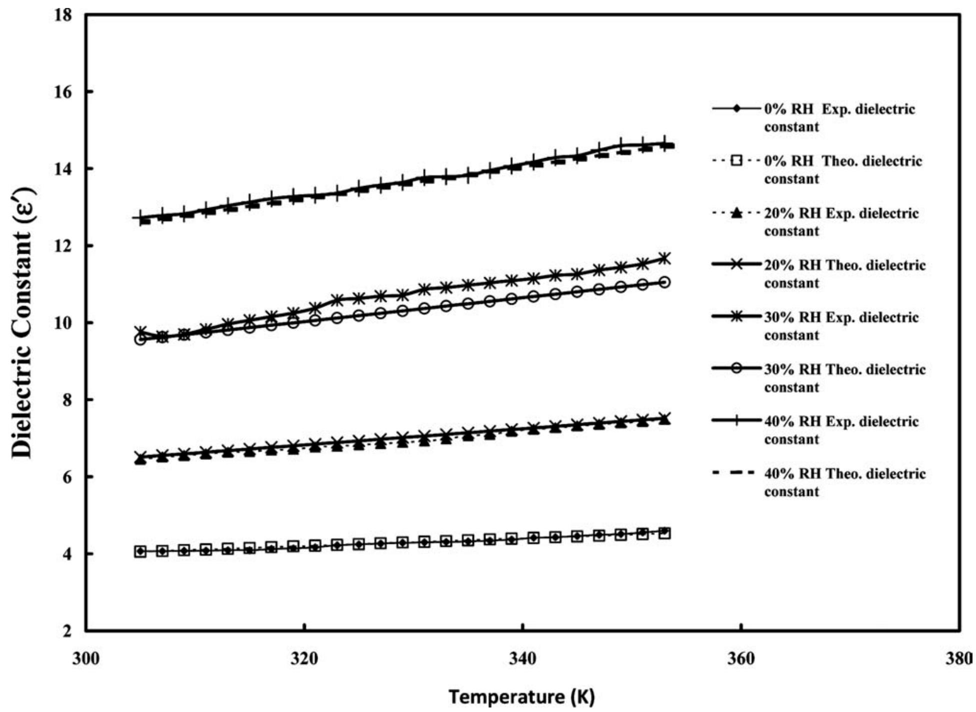

Figure 1 The dielectric constant for different compositions of PVC and RH at 1 kHz with theoretical results from 32 to 80°C.

Substituting in eq. (1), it becomes

$$\varepsilon' - 1 = \frac{N\alpha\varepsilon_0\bar{E}}{\varepsilon_0\bar{E}}$$

$$\varepsilon' - 1 = N\alpha$$

$$\varepsilon' = 1 + N\alpha \quad (10)$$

The constant α is the polarizability of the atom, which is the measure of how easy it is to induce a moment in an atom with an electric field. α is calculated by the following equation[16]

$$\alpha = \frac{4\pi e^2}{m\omega^2} \quad (11)$$

Using eqs. (10) and (11), following can be written as,

$$\varepsilon' = 1 + \frac{4\pi e^2 N}{m\omega^2} \quad (12)$$

Initially considering the case of pure PVC, where e is the charge of electron 1.6×10^{-19}C, N is the concentration of carriers, m is the weight of the sample (mass), and ω is the angular frequency.

For composite, contribution of both PVC and RH is considered two factors c' and c'' are added, respectively, in the above equation, which is the contribution of RH, i.e.,

$$\varepsilon' = 1 + \frac{4\pi e^2 N}{m\omega^2} + [c' + c''] \quad (13)$$

c'' can be calculated by the following equation,

$$c'' = s(1 - x)$$

where $(1 - x)$ the concentration of rice is husk in the composite and s is the moisture content in it. c' is the difference in the Experimental and above theoretically calculated dielectric constant without the constant.

On substituting the above equation in eq. (13), it becomes

$$\varepsilon' = 1 + \frac{4\pi e^2 N}{m\omega^2} + [c' + s(1 - x)] \quad (14)$$

Thus, the frequency dependent ε′ can be calculated by eq. (14).

RESULTS AND DISCUSSION

Density values listed in Table I are 1.37, 1.31, 1.27, and 1.18 g/cc for Samples 1–4, respectively. Sample 4 has maximum density, because it has maximum RH, and Sample 1 has no RH content. Maximum dielectric constant is found in case of Sample 4. This high-dielectric constant is due to the presence of maximum RH content in the composite, which has moisture in it. Earlier studies of electrical properties of natural fiber-filled polymers indicated their suitability as insulator resources for unique applications bushing and switch boards.[16]

Figure 1 shows the dielectric constant for different compositions of PVC and RH at 1 kHz with

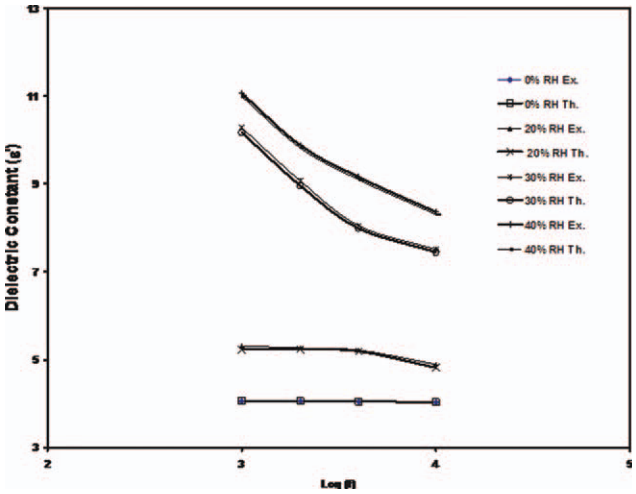

Figure 2 The dielectric constant for different compositions of PVC and RH at room temperature with theoretical results for different frequencies. [Color figure can be viewed in the online issue, which is available at

theoretical results from 32 to 80°C. Temperature dependence of the dielectric constant or the physical properties are usually due to the molecular mobility of its components and here the continuous increasing dielectric constant shows that the molecular mobility is high, i.e., molecules can move freely by increasing temperature. Plots of dielectric constant ε′ at 1 kHz for Pure PVC as a function of temperature is shown in Figure 1, experimental results shows that values of dielectric constant is in the range of 4–4.5 at 1 kHz. These values increases consistently, this increase in dielectric constant is due to polarization of PVC chain. This is clearly explained by proposed model. Experimental and theoretical results based on the proposed model for temperature and frequency dependence for RH PVC composites are shown in Figure 1. Experimental results show that dielectric constant increases with the RH concentration and same trend is observed in the theoretical results.

When 20% RH is added in 80% PVC the range increases from 4–4.5 to 5–7, thus it is to be clearly understood that the polarization is now contributed by percentage of RH along with PVC chain. Similarly, when 30% RH is mixed in 70% PVC, the dielectric constant increases from 5–7 to 9–13 and by mixing 40% RH it increases from 9–13 to 12–15. Hence, a continuous increasing trend is seen in dielectric constant by increasing the amount of RH.

Dielectric constant is found to be higher for the fiber-filled systems, which was attributed to the polarization exerted by the incorporation of fibers into matrix.[17] Uchino et al.[15] reported the development of polymer composites with lignocellulosic material and determined the dielectric properties of the composites.[15]

Figure 2 shows the variation of determined experimentally and calculated theoretically dielectric constant for different compositions of RH and PVC at room temperature. It can be seen in Figure 2 that increases in frequency decreases the dielectric constant. The phenomenon of polarization is responsible for decreasing dielectric constant on increasing frequency. Continuous decrease in dielectric constant at room temperature with increase in frequency clearly explains the accumulation of charges at RH/PVC interface. Dielectric constant decreased with increase in frequency due to the decreased interfacial and orientation polarization at higher frequencies. Dielectric constant increases with increase in RH loading, which is hydrophilic.[17]

The effect of mixing RH in PVC resulted in increase in dielectric constant over whole measurement frequency range. This effect is predominant at lower frequencies. These results are similar to the observation of Paul et al.[18] for sisal fiber LDPE composites. Dielectric constant of treated rice husk filled PVC composites is shown in Figure 3, it is clear from figure that treated samples shows same trend seen in untreated samples. Treatment of rice husk decreases the dielectric constant. Above investigation clearly reveals that dielectric constant is lower for treated composites over the untreated one. This is because of the free radials generation during composites fabrication at high temperature. Composites containing 20% and 30% rice husk (both treated and untreated) undergo a definite phase transition. The effect of PVC is dominated in the composites containing less than 30% of rice husk and hence there is no clear evidence of phase transition in those composites. The transition temperature is same for both the treated and untreated composites containing 20% rice husk. Whereas, the transition temperature in untreated composite is higher than that of the treated composites of 30% rice husk. During composites preparation, initiator produces free radicals in the treated composites and they contribute to reduce the electrical insulating properties.

Figure 3 shows the variation of tan δ with temperature with temperature range ranging from 32 to 80°C for Samples 1–4 at 1, 2, 4, and 10 kHz frequencies, respectively. These plots show that tan δ increased with increase in temperature but decreases with increasing frequency for all the samples. The increase in dissipation factor with increase in RH concentration is due to the interfacial polarization occurred in the composites. Table II gives the tan δ peaks of all the compositions. Tan δ peak in Sample 1 appeared at 74°C, at all the frequencies, which is near to T_g of compound PVC. In case of Sample 2, a peak appeared around 52°C corresponding to all frequencies, which is due to the unadsorbed moisture present on the surface of RH for all the frequencies.

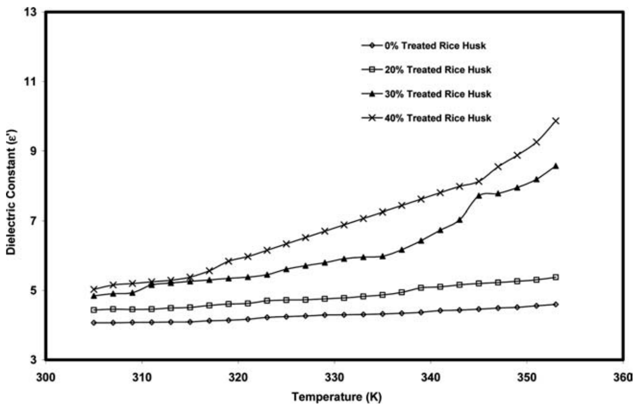

Figure 3 Dielectric Constant for different compositions of PVC and treated rice husk at 1 kHz for 32°C to 80°C.

In case of Sample 3, first tan δ peak appeared at 76°C for 1 kHz, which is due to moisture content absorbed in the composite, at 10 kHz a peak appeared at 58°C, due to unadsorbed moisture on the surface. In case of Sample 4, first tan δ peak appeared at 64°C for 1, 2, 4, and 10 kHz frequencies, another peak appeared at 74°C for 1, 2, and 4 kHz frequencies. The dissipation factor attained high values, which decreased when frequency increased, exhibiting the relaxation processes.

Continuous decrease in dielectric constant at room temperature with increase in frequency clearly explains the accumulation of charges at rice husk/PVC interface. Interface is clearly visible in a typical SEM photo Figure 5(a,b) of 80/20 composition for treated and untreated rice husk filled samples. Dielectric constant decreased with increase in frequency due to the decreased interfacial and orientation polarization at higher frequencies. Dielectric constant for untreated composite is found higher than those of the treated composites. All the curves obtained for the composites containing 20% rice husk shows the same pattern. The effect of mixing rice husk in PVC resulted in increase in dielectric constant over whole measurement frequency range. Figure 6(a,b) shows the ac conductivity variation with temperature for different amount of untreated

TABLE II
Tan δ Peaks for Different Compositions Used in the Study

Weight % of RH in the composite	Frequencies			
	1 kHz	2 kHz	4 kHz	10 kHz
0%	74°C	74°C	74°C	74°C
20%	52°C	52°C	52°C	52°C
30%	76°C	–	–	58°C
40%	74°C	74°C	74°C	–
	64°C	64°C	64°C	64°C

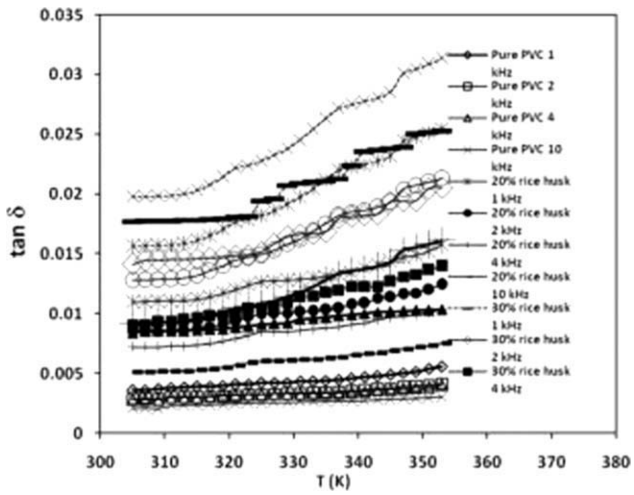

Figure 4 The dissipation factor (tan δ) for different compositions of PVC and RH at various temperature for different frequencies.

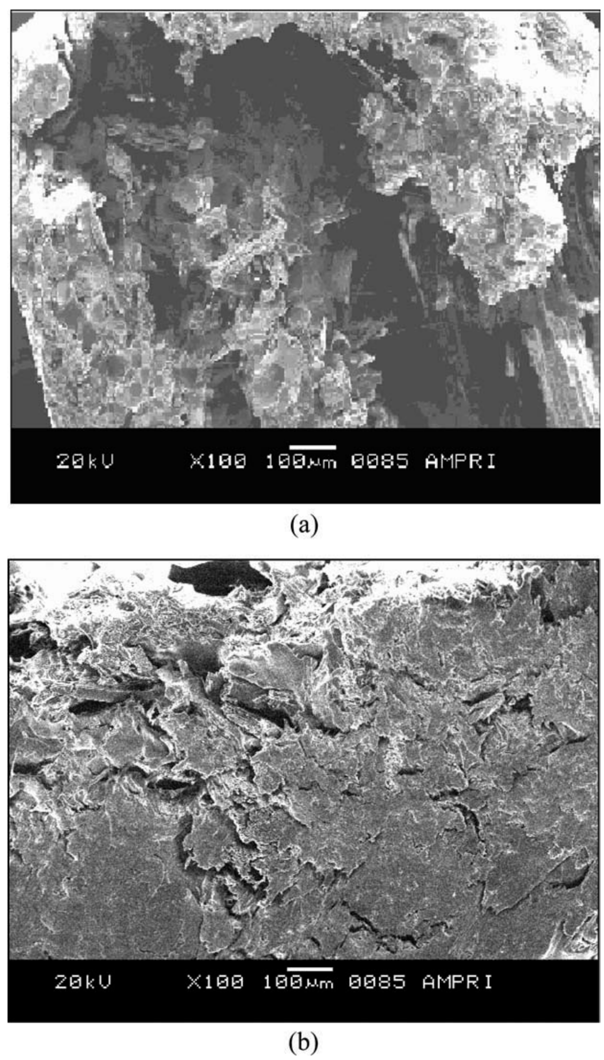

Figure 5 (a,b) shows the microstructure of (a) untreated rice husk/PVC composite (80/20), (b) Treated rice husk/PVC composite (80/20).

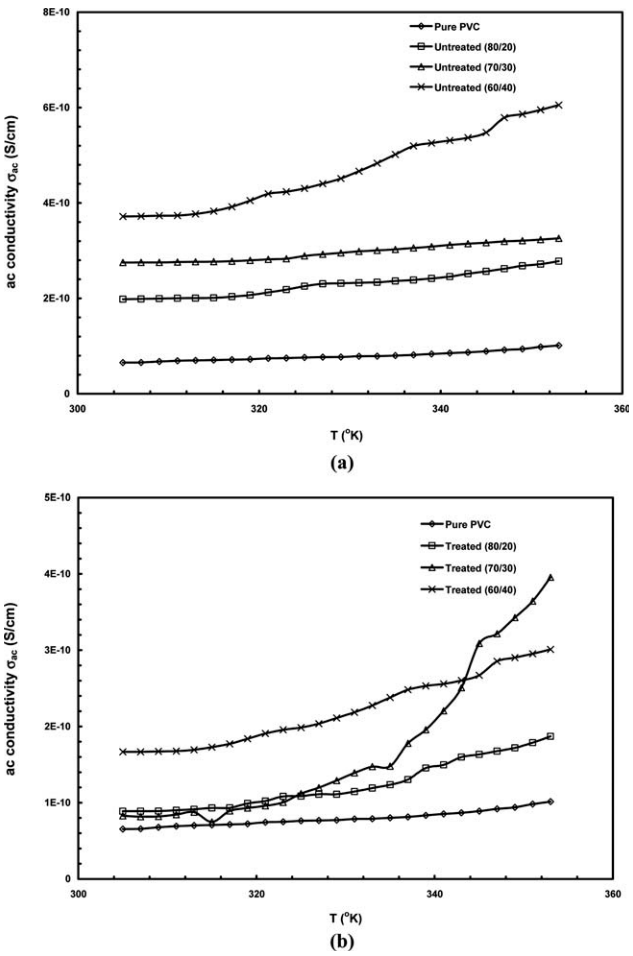

Figure 6 (a,b) shows ac conductivity of (a) untreated rice husk/PVC composite (b) Treated rice husk/PVC composite at 1 kHz from 32°C to 80°C.

and treated rice husk composites at 1 kHz respectively. Table III gives the ac conductivity values of untreated and treated composites. The ac conductivity of the composites increased with increasing temperature, maximum ac conductivity is seen in case of 40 wt% rice husk.

CONCLUSIONS

Dielectric properties can be effectively customized. New reasonable model based on existing equations is formulated and experimentally verified. Frequency and temperature dependent parameters were experimentally obtained and taken as contribution for the proposed model. Dielectric constant for composites with various fibers to matrix ratio is determined with this model. Dielectric constant of the composite was highly influenced by the fiber composition.

TABLE III
Peaks for ac Conductivity (σ_{ac}) at Room Temperature and 1 khz for Treated ands Untreated Samples

	σ_{ac} (at room temperature and 1 khz)		
Sample	20% rice husk	30% rice husk	40% rice husk
Treated	8.88E-11	8.29E-11	2.15E-10
Untreated	1.98E-10	2.75E-10	3.72E-10

- Dielectric constant of RH-filled PVC composite increased with the increase in RH content temperature.
- Proposed frequency and temperature dependent model to calculate the dielectric constant of the RH-filled PVC compound matches with the experimental results.
- Tan δ peaks at different frequencies are dominant in case of 30 and 40 wt % of RH composite.

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