

Dielectric Properties of Short Sisal Fibre Reinforced SBR Composites

R. Prasantha Kumar and Sabu Thomas*

*School of Chemical Sciences, Mahatma Gandhi University, Priyadarshini Hills P.O,
Kottayam - 686 560, Kerala, India, Email: sabut@md4.vsnl.net.in*

SUMMARY

Short sisal fibre reinforced SBR(styrene-butadiene rubber) composites were prepared by reinforcing SBR with short fibres in an open mixing mill. The dielectric constant, volume resistivity and dissipation factor ($\tan\delta$) of these composites have been monitored as a function of frequency, fibre length, fibre concentration and chemical treatment. Dielectric constant values were found to increase with fibre loading. Fibre treatments such as hydration, salt water, mercerization, acetylation and benzylation were carried out to improve the adhesion between the fibre and the matrix. A two component dry bonding system consisting of HMT (hexamethylene tetramine) and resorcinol was incorporated into the mixes in order to impart greater interfacial adhesion between fibre and matrix. The influence of chemical modifications of fibres on the electrical properties of the composites has been studied. The fibre filled system showed higher dielectric constant values than pure gum due the polarization exerted by the presence of short fibres. Volume resistivity is found to be greater for treated composites due to the increased hydrophobicity of fibres after chemical modification. A percolation threshold is obtained at 8% volume loading of fibres. The estimated value of filling factor and effective co-ordination number is 0.95 and 22.5, respectively. SEM studies were conducted to explain the morphology of the treated fibres and the composites.

Key Words: Sisal fibre, Styrene-Butadiene Rubber, Reinforcement, Interfacial Adhesion, Composites, Dielectric properties

1. INTRODUCTION

Composite materials based on natural polymers and their fibres demonstrate remarkable environmental and economical advantages and therefore have generated a lot of interest recently /1-10/. It is well known that the performance and the mechanical properties of the composites depend on the properties of the individual components and their interfacial compatibility. The cellulose fibres, one of the components of the investigated composites has a strong polarity due to hydroxyl groups and the ether links (C-O-C). This makes cellulose more compatible with polar acidic or basic rather than with non-polar polymers /11/. Because of this inherently poor compatibility between the hydrophilic cellulose fibres and typical hydrophobic high commodity thermoplastics such as polyolefines, a pre-treatment of the fibres or surface modification /3-5/ of the matrix polymer /6/ or the incorporation of surface modifiers/7-10/ is generally required.

Polymers are, in general, good electrical insulators, with volume resistivities up to 10^{22} ohm-cm /14/. Various polymers are commonly used in the electronics industry as housings or assemblies. Many applications require that the polymer be made conductive in order to

* Corresponding author

shield electronic components from electromagnetic interference. Conductive reinforcement may be added to the polymer in order to achieve conductivity as well as to improve mechanical properties.

Nowadays, many rubber and plastic compounds are used in antistatic applications such as wire and cable sheathing, shielding against electromagnetic interference, etc. In order to dissipate static charges, the polymers have to be made conductive in many of the above applications. This is accomplished by adding conductive materials like metals, various polar fibres, carbon black, graphite, various metals including aluminum, nickel, stainless steel, etc [12,13,15]. Incorporating conductive fillers into the polymer can significantly modify the conductivity of a composite.

Fillers in the form of fibres and flakes were found to be most effective due to the lower volume fractions needed to achieve a targeted conductivity. It was observed that the volume fraction needed to achieve certain conductivity decreased with increasing aspect ratio [15]. Addition of the conductive fillers into the polymer modifies not only the conductivity of the polymer but also the dielectric properties.

Although most polymers are poor electrical conductors, several polymer applications require moderate to high electrical conductivity. Rubbers containing conductive reinforcements provide electrical conductivities and EMI shielding comparable to that obtained from secondary metallization techniques, while affording higher mechanical strength and greater cost savings. Only a few studies have investigated the microstructure of composites to explain the changes in electrical conductivity. However, many of these explanations are qualitative or semi-quantitative.

Previously, we have reported the effect of untreated and treated short sisal fibres on the mechanical [16,17], processing [18], and melt rheological behaviour [19,20] of polystyrene (PS) and styrene-butadiene rubber (SBR) composites. Recently, Paul *et al.* [21] have reported the electrical properties of sisal and pineapple fibre reinforced polyethylene composites. But the electrical properties of natural fibre filled elastomer composites have not yet been reported.

The objective of this study is to characterise the dielectric properties of composites of SBR, incorporated

with short sisal fibres. The electrical properties of the composites have been analysed with special reference to the effect of fibre length, fibre concentration and fibre treatment. The electrical conductivity of the system was also examined and the percolation threshold of the system is analysed.

2. EXPERIMENTAL

Materials and Methods

2.1. Materials

Synaprene-S (SBR-1502) was obtained from Synthetics and Chemicals, Bareilly, U.P., India. The properties of the rubber bale used for the entire work are reported in Table 1. Sisal fibre (*Agave sisalana*) was supplied by a local processing unit at Marthandam situated in the state of Tamil Nadu. The chemical constituents of sisal fibres were already reported elsewhere [16]. These fibres have an average density [22] of 1.45 g/cm³ and 0.1212 mm diameter, respectively. A two component dry bonding system consisting of HMT and resorcinol were obtained from S.D. Fine Chemicals, Bombay. All other ingredients used were of commercial grade.

2.2. Methods

2.2.1. Chemical modification of fibres

i) Hydration:

Short sisal fibres were washed several times with water in order to remove the easily extractable impurities from the surface of the fibres. The fibres were air dried and designated and used as untreated fibres.

ii) Salt water treatment

The raw fibres were soaked in a 10% solution of NaCl for 1 hr, taken out and dried in air.

iii) Mercerisation

The short sisal fibres of lengths 6mm were immersed in an 18% solution of caustic soda for 1 hr. These fibres were washed and air dried for further treatment. The extent of benzylation on to the fibre is analysed by IR studies.

Table 1
Formulation of Recipe from A to S

INGREDIENTS	MIXES												
	A	B	C	D	E	F	G	H	L	N	Q	R	S
<i>Synaprene</i>	100	100	100	100	100	100	100	100	100	100	100	100	100
<i>Sulphur</i>	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2
<i>Stearic Acid</i>	2	2	2	2	2	2	2	2	2	2	2	2	2
<i>Zinc Oxide</i>	5	5	5	5	5	5	5	5	5	5	5	5	5
<i>Resorcinol</i>									5				
<i>HMT^a</i>									2.5				
<i>CBS^b</i>	1	1	1	1	1	1	1	1	1	1	1	1	1
<i>TDQ^c</i>	1	1	1	1	1	1	1	1	1	1	1	1	1
<i>Sisal Fibre</i>	-	2	6	10	6	6	6	6	6	6	6	6	6
<i>[length (mm)]</i>													
<i>Diff. Treatments</i>													
<i>(a) Water(untreated)</i>	-	35	35	35	5	10	15	20	35				
<i>(b) NaCl treated</i>										35			
<i>(c) Mercerization</i>											35		
<i>(d) Acetylation</i>												35	
<i>(e) Benzoylation</i>													35

a- Hexamethylene tetramine

b- N-cyclo hexyl benzothiazole sulphenamide

c- 2,2,4-Trimethy 1,2-di hydroxy quinoline polymerised.

iv) Benzoylation

The mercerised fibres were agitated with 50ml benzoyl chloride for 15 min., filtered, washed thoroughly with water and dried. These fibres were dried further in air oven at 70°C and kept in polyethene bags for mixing. The extent of benzoylation on to the fibre was evaluated by IR studies.

v) Acetylation

The short sisal fibres were first immersed in aqueous NaOH solution at 35°C for one hour, washed with water and then soaked in glacial acetic acid, followed by acetic anhydride. The fibres were washed, dried and kept in air tight polythene bags. The acetylated fibres are characterised by IR spectroscopy.

vi) Incorporation of dry bonding system

A two component dry bonding system consisting of hexamethylene tetramine and resorcinol are used as the bonding agent. This was added into the mix during the milling process as per the mixing sequence given in table 1.

2.2.2 Composite sample preparation

SBR mixes were vulcanized by using a conventional vulcanization (CV) system based on a test recipe as shown in Table 1. Short sisal fibres of length viz., 2, 6 and 10mm were incorporated into the styrene-butadiene rubber matrix at different concentrations, viz., 5, 10, 15, 20, and 35 parts per hundred rubber (phr) on a laboratory two roll open mixing mill (150 × 300 mm) having a mill roll speed ratio, 1:1.25. The details of mixing and processing features of these composites were already reported elsewhere [16-18]. The samples for electrical property measurements were prepared by compression moulding the samples into 2mm thick sheets in a hydraulic press at a temperature of 150°C.

2.2.3. Experimental evaluation

Dielectric constant of the material is evaluated as per the ASTM-D150-74. For this, disc samples of 2mm thickness and 10 mm diameter were used. The test samples were coated with conductive silver paint on either sides and copper wires were fixed on both sides

of the samples as electrodes. Then, the test specimen was placed between two electrodes and the capacitance is measured. Next the test specimen is replaced by air and once again, the capacitance value is measured. The dielectric constant is measured from the ratio of two measurements. The capacitance, resistance and dissipation factor were measured directly using a 4192 LF Impedance Analyzer (Hewlett-Packard, USA) by varying the frequency. The capacitance and $\tan\delta$ of composites were measured at frequencies ranging from 31.6 - 10MHz at room temperature.

2.2.4. Analysis of Electrical Properties

(i). Dielectric Constant

Dielectric constant of an insulating material is defined as the ratio of the charge stored in an insulating material placed between two metallic plates to the charge that can be stored when the insulating material is replaced by air (or vacuum). The dielectric constant, E' was measured from capacitance using the equation

$$E' = \frac{C t}{E_0 A} \quad (1)$$

where C is the capacitance, t , the thickness, E_0 , the permittivity of air ($8.85 \times 10^{-12} \text{ F m}^{-1}$) and A , the area of cross section of the sample.

(ii). Volume Resistivity

The most desirable characteristic of an insulator is its ability to resist the leakage of the electrical current. Insulation resistance depends upon the volume resistivity of the insulating material. Thus, the volume resistivity(ρ) is defined using the equation,

$$\rho = \frac{A}{t} (R_v) \quad (2)$$

where ρ , volume resistivity, R_v , volume resistance(Ω), A , Area of cross section of the sample and t , the thickness of the sample.

(iii). Conductivity

The conductivity (σ) is calculated according to the following equation,

$$\sigma = \frac{1}{\rho} \quad (3)$$

where ρ is the volume resistivity.

(iv). Dissipation Factor

It is a measure of the electrical loss or the amount of energy dissipated by the insulating material when the voltage is applied to the circuit. Most rubbers have a relatively lower dissipation factor at room temperature. Dielectric loss (loss factor) is the product of dielectric constant and the dissipation factor ($\tan \delta$) and is related by the equation,

$$\tan \delta \times E' = E'' \quad (4)$$

2.2.5. Morphology of fibres and composites

Tensile/tear failure surfaces of the composites and the treated fibre surfaces were examined by scanning electron microscope. The fracture surface of the samples was sputtered with gold for 24 hrs. using a fine coat ioniser JFC-1100. The photographs were taken in JEOL scanning electron microscope-model JSM 35 C.

3. RESULTS AND DISCUSSION

Dielectric properties of glass fibre/carbon black filled epoxy resin have been studied as a function of frequency and temperature by Sastry *et al.* /23/. Electrical and electromechanical measurements were done on rubber filled with carbon black by Burton and co-workers /24/. The modeling of dielectric properties of wood-polymer composite, by considering it as a multi-component layered system, was performed by Hoffmann and co-workers /25/. Miyauchi and Togashi /26/ explained the electrical properties and the conductive mechanism of polymer-filler particles using polymer grafted carbon black.

Usually, most of the elastomeric materials are considered as electrical insulators. The dielectric behaviour of an insulating material can be assessed from its dielectric constant, dissipation or power factor ($\tan \delta$) and the volume resistivity.

3.1. Dielectric constant as a function of frequency

Dielectric polarization is the polarized condition of a dielectric resulting from an applied AC or DC field. There are two types of charging currents and condenser charges, which may be described as rapidly forming or instantaneous polarizations, and slowly forming or absorptive polarizations. The total polarizability of the dielectric is the sum of contributions due to several types of displacement of charge produced in the material by the applied field. The relaxation time is the time required for polarization to form or disappear. The magnitude of the polarizability, k , of a dielectric is related to the dielectric constant, E' by the following equation,

$$k = \frac{3(E' - 1)}{4\pi(E' + 2)} \quad (5)$$

The k values obtained by utilizing DC and low-frequency measurements are a summation of electronic, E , atomic, A ; dipole, P_0 ; and interfacial, I , polarizations. The contributions to dielectric constant at low frequencies for a material having interfacial, dipole, atomic, and electronic polarization contributions are additive.

Generally, the dielectric constant of a composite material arises due to polarization of molecules and the dielectric constant increases with increase in polarizability. The different types of polarizations possible in a composite material are the polarization arising from (1) electronic polarization (2) atomic polarization and (3) orientation polarization due to the orientation of dipoles parallel to the applied field [27].

For heterogeneous materials like composites, there is also the possibility of interfacial polarization, which arises due to the differences in conductivities of the two phases [28]. The time required for each type of polarization to reach the equilibrium level varies with the nature of polarization. The orientation polarization requires more time compared to electronic and atomic polarization to reach static field value. Therefore, the orientation polarization decreases with increase in frequency. The interfacial polarization generally occurs at much lower frequencies.

The plots in Figures 1, 2 and 4 show the reduction of dielectric constant (E') in three stages i.e., at low, medium and high frequencies. The E' shows a high value at low frequencies, a levelling off for medium range and very low value for high frequencies. In the first stage, the high values of dielectric constant can be attributed to the interfacial polarization effects. In these composites, due to the presence of different conductivities of the matrix and the fibres, interfacial polarization occurs leading to an increase in E' . Since interfacial polarization decreases with increase in frequency, as the frequency increases to 100Hz, the dielectric constant decreased considerably.

In the region of $3.16 \times 10^2 - 10^5$ Hz frequencies, the E' has contributions from orientation, atomic and electronic polarizations. Here the dispersion region spreads over a wide range of frequencies. Above 3.16×10^5 Hz, the E' further reduces due to the drop in orientation polarization. At this frequency the drop in E' increases with increase in fibre content. This may be due to the increase in polar nature, which leads to a decrease in orientation polarization at higher rate compared to the composites with lesser number of dipoles.

3.2. Dielectric constant as a function of fibre length

The variation of dielectric constant values as a function of frequency with different fibre lengths at a constant loading of fibres (35phr) is plotted in Figure 1. It can be observed that E' values first increase with the incorporation of 2mm fibre length and then decreases at 6mm fibre length. Finally, the E' increases again at 10mm fibre length. This behaviour of the material can be explained in terms of interfacial polarization. At a constant loading of fibres at 35phr and at a length of 2mm, the number of interfaces per unit volume element is high and this results in high interfacial polarization. The number of interface decreases as the fibre length increases and therefore the value decreases at 6mm fibre length. Since the sisal fibre is a lignocellulosic one, it undergoes bending and curling at higher fibre length (10mm length) due to its intrinsic flexible nature. This leads to high extent of fibre entanglement. In

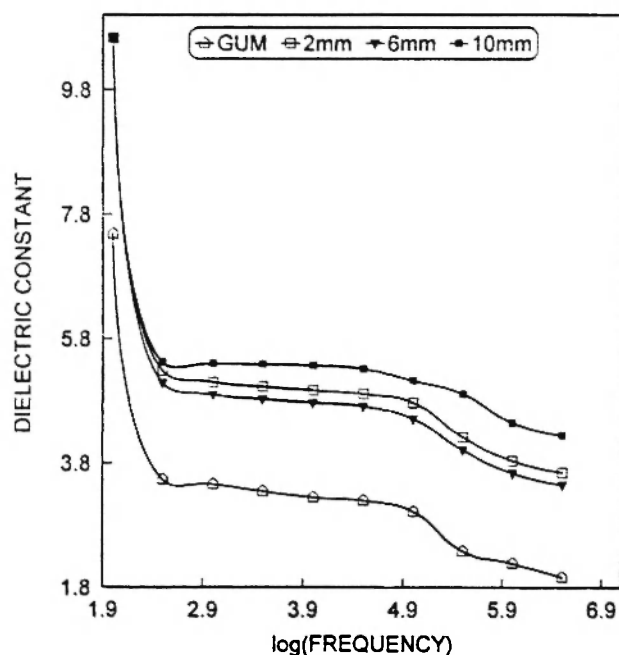


Fig. 1: Effect of fibre length on the dielectric constant of sisal-SBR composites as a function of frequency.

addition, at high fibre length fibre-fibre interaction is higher than the fibre-matrix adhesion. As a result, the values of dielectric constant showed marginal enhancement at 10mm fibre length.

3.3. Dielectric constant as a function of volume of fibres

The effect of volume of fibres (%) on the dielectric constant values of sisal-SBR composites as a function of logarithm of frequency is shown in Figure 2. It is obvious that dielectric constant increased with increase in volume of fibres (%) at all frequencies. At a given fibre loading, the dielectric constant values are almost the same over a wide range of frequencies in the plots but are different at very low frequencies and very high frequencies.

The temperature and frequency dependence of E' is controlled by the polarity of the polymer, i.e., whether it contains permanent dipoles or not. SBR is a hydrocarbon polymer, which contains only carbon, and hydrogen atoms and therefore has low dielectric constants, which change very little with temperature and

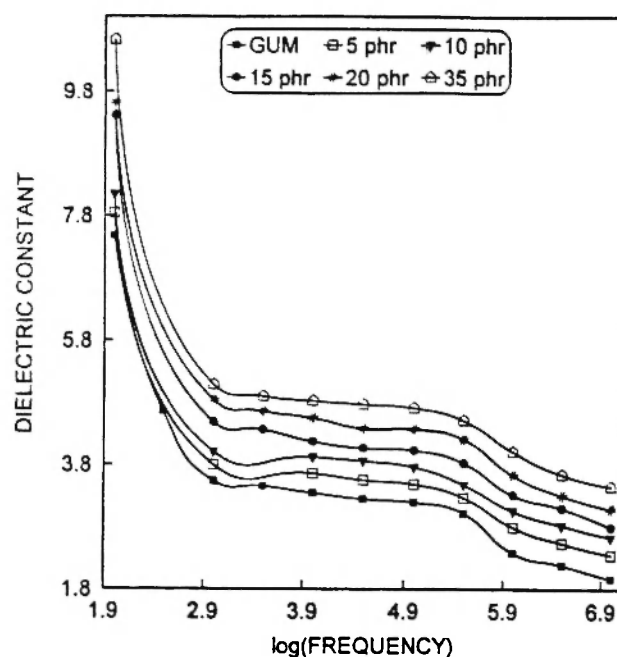


Fig. 2: Effect of volume of fibres on the dielectric constant of composites as a function of frequency.

frequency.

For a non-polar material, E' equals the square of the refractive index, n as given by the equation:

$$E'(\text{nonpolar insulator}) = n^2 \quad (6)$$

SBR is a non-polar molecule, which is having instantaneous atomic and electronic polarizations. The refractive index of SBR is 1.51 and hence $E' = 2.28$ as per the above equation, while the experimental value is 2.92. The higher experimental value may be due to the occurrence of interfacial polarization, which arises due to the presence of impurities.

The behaviour at low frequencies can be explained by assuming interfacial polarization. This type of polarization results from the heterogeneity present as impurity in the composite material. Interfacial polarization decreases with increasing frequency and it influences the low frequency dielectric properties. If there is a greater polarizability of the molecule, dielectric constant will be higher. Therefore the polarizability decreases with increase in volume of fibres, i.e., due to the increased number of polar groups.

The atomic and electronic polarizations are instantaneous and are observed at high frequencies. Thus, orientation polarization is produced in addition to the induced polarization, when polymers containing polar groups are placed in an electric field. The dipole or orientation polarization is due to the presence of polar groups present in the cellulose fibre composites. The effect of orientation polarization and interfacial polarization will depend upon the concentration of fillers. Hence the dielectric values increase with volume percent of fibres in all frequencies, especially at low frequencies, i.e., values increase as the fibre content increases from 0 - 17.7 volume percent of fibres.

The dielectric properties of polymers are affected adversely by the presence of moisture, and this effect is greater in hydrophilic than in hydrophobic polymers, as shown by the Clausius-Mossette equation [26],

$$P = \left(\frac{E' - 1}{E' + 2} \right) \frac{M}{\rho} \quad (7)$$

where P , is the polarization of a polymer in an electric field related to the dielectric constant E' , ' M ' is the molecular weight and ' ρ ' is the density,.

Since the composite is heterogeneous, the interfacial polarization also exists. The complete orientation of the molecules is possible at low frequencies, while at medium and high frequencies, the same is not possible. At low frequencies, the effect of orientation and interfacial polarization increases with the increase in volume of fibres. In agreement with the law of harmonic mixture, the plots of reciprocal of dielectric constant ($1/E'_c$) against the volume of fibres (%) are linear for short sisal fibre reinforced SBR composites (Figure 3). Extrapolation of the plot to V_f , volume of fibres (%) = 0, yields,

$$\lim_{c \rightarrow 0} 1/E'_c = 1/E'_2 \quad (8)$$

where E'_2 is the dielectric constant of SBR gum compound. The theoretically obtained E'_2 value is in close agreement with the experimentally obtained value (the theoretically obtained E'_2 values are 2.32, 2.11; experimentally observed E'_2 values are 2.2, 1.9 respectively for the 3.16 and 10 MHz frequencies.

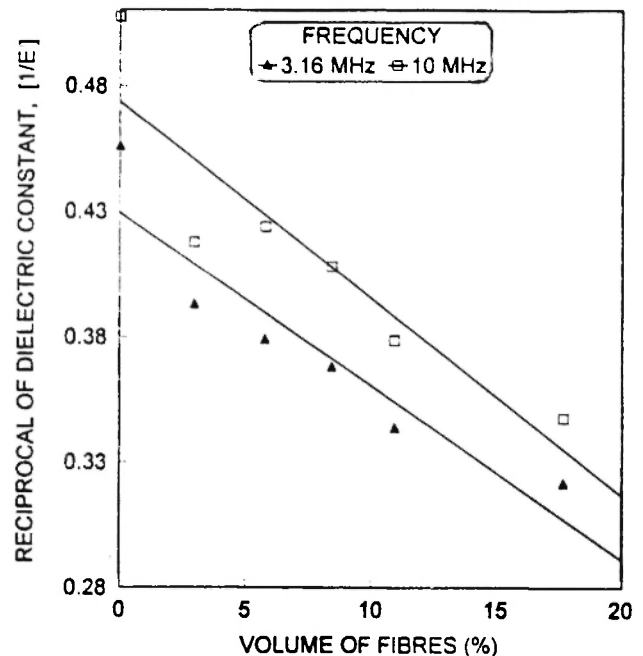


Fig. 3: Plot of reciprocal of dielectric constant as a function of volume of fibres.

3.4. Dielectric constant as a function of chemical modification of sisal fibres

Figure 4 shows the effect of chemical modification of fibres on the dielectric constant values of composites. In these composites also, the E' values decrease with frequency in three steps, due to the relaxation in interfacial and dipole polarizations. On analyzing the figure, it is seen that all treated fibre composites have low dielectric constant values than the untreated ones. This is due to the decrease in the orientation polarization of the molecule as a result of increased hydrophobicity of the treated fibre i.e., decrease in the percentage of moisture content in the fibre. The orientation polarization is reduced as a result of decrease of polar groups in the treated fibre composites. As a result, the dielectric constant of the fibre composites containing chemically modified fibres is lower than those of the untreated fibre composites. The decrease of dielectric constant in treated composites is also may be due to the increase of interfacial adhesion between the fibre and the rubber matrix and due to the chemical bonding between the fibre and the matrix. The dielectric constant varies in the order untreated >

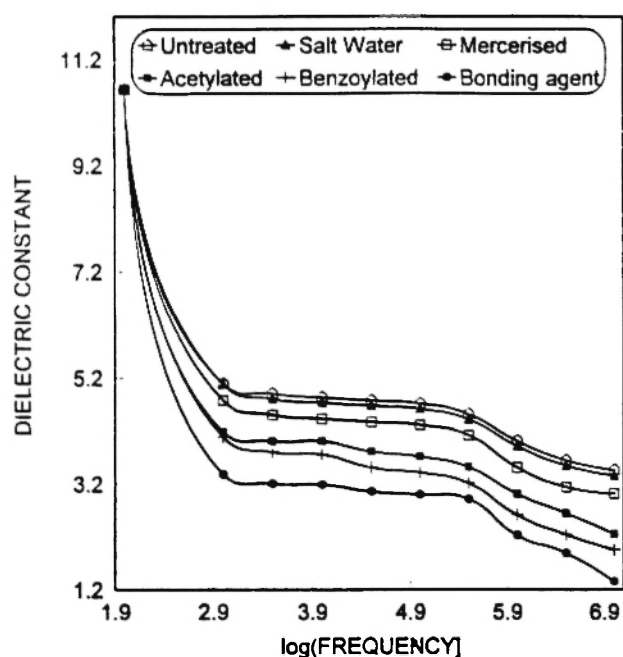


Fig. 4: Effect of various chemical treatments on the dielectric constant of composites as a function of frequency.

saltwater treated > mercerised > acetylated > benzoylated > bonding agent added composites.

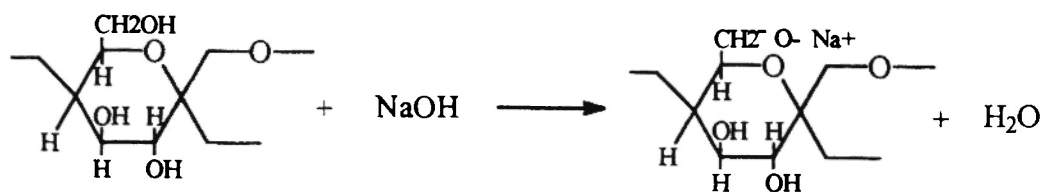
During salt water treatment, the fibres get a shiny appearance which does not have any appreciable effect on the interfacial adhesion with the rubber matrix. Hence, the dielectric constant value shows only a slight decreasing trend. However, other chemical treatments have a strong influence on the properties. The cellulosic hydroxyl groups in the fibre are relatively unreactive, since they form strong hydrogen bonds. Alkali treatment may destroy the hydrogen bonding in cellulose hydroxyl groups, thereby making them more reactive (Scheme 1). As a result of these chemical treatments (mercerisation, acetylation and benzoylation), the hydrophobicity of the fibre is increased. The improved interaction between the sisal fibre and the SBR matrix in the case of these chemical modifications reduces the hydrophilicity of the composite, which, in turn, reduces the orientation polarization. The orientation polarization decreases considerably because of the decrease in water content in the fibre and hence the dielectric constant values also decrease. A hypothetical mechanism has been stated and

a reaction pathway is shown in schemes 2 & 3 in order to illustrate the structural changes as a result of chemical modifications (acetylation and benzoylation).

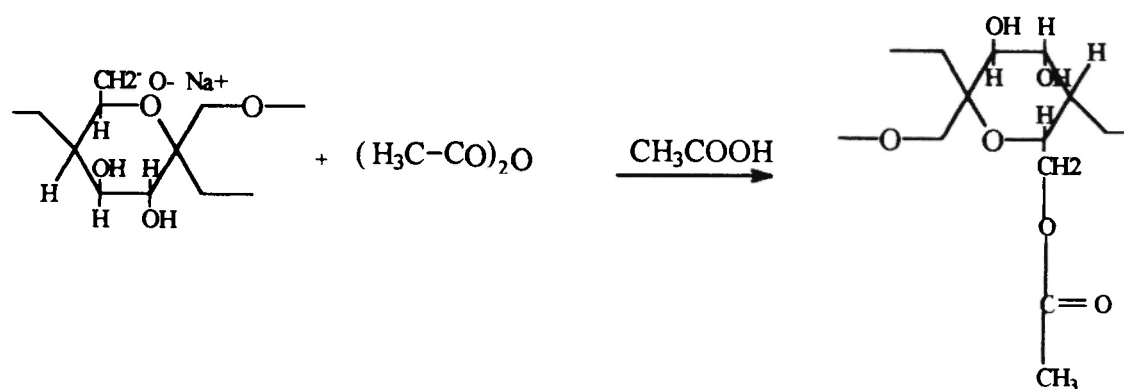
The two component dry bonding system incorporated into the mix during the composite preparation creates an in-situ resin by the condensation reaction, which acts as a binder in between the fibre and the matrix. This removes the voids between the fibre and the rubber matrix and thereby eliminates the pockets for the moisture. The reaction between the fibre and rubber matrix can be represented as a hypothetical mechanism (Scheme 4).

3.5. Volume resistivity as a function of fibre loading

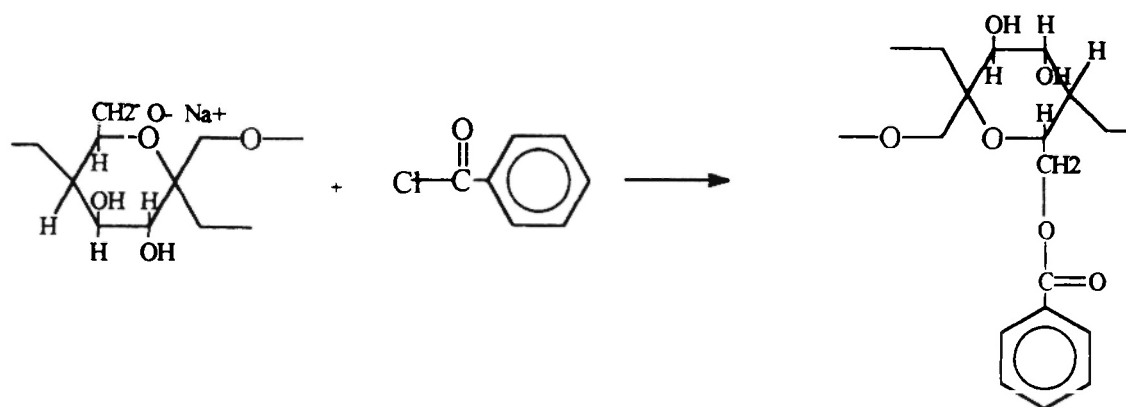
The most desirable characteristic of an insulator is its ability to resist the leakage of electric current. Hence it is very important to study the volume resistivity of insulating materials. Figure 5 shows the plot of volume resistivity as a function of frequency for sisal-SBR composites at different volume of fibres. The volume resistivity of the material decreases with increase of frequency and fibre concentration, i.e., electric conduction increases with increase of frequency and fibre content. The decrease in resistivity up on the incorporation of short fibres may arise from the presence of more polar groups, which facilitate the conducting process. The incorporation of short fibres into elastomers generally decreases the volume resistivity and there is a critical loading of fibre, i.e., percolation threshold, 8% volume loading of fibres, at which the composites change from insulating to conducting material. A study of the dielectric property is of importance as it provides a measure of the amorphous fraction of the materials and is sensitive to orientation effects, mobility and to the number and interactions of the dipoles participating. Dutta *et al.* /29/ have reported studies on the mechanical and electrical anisotropy of pineapple fibres and found a sharp increase of dielectric constant and a fall of loss factor along the fibre direction compared to the transverse direction. It was established that the crystallinity is greater along the fibre direction. With regard to physical processes involved in the conduction of electricity, various mechanisms have been proposed /30/. The



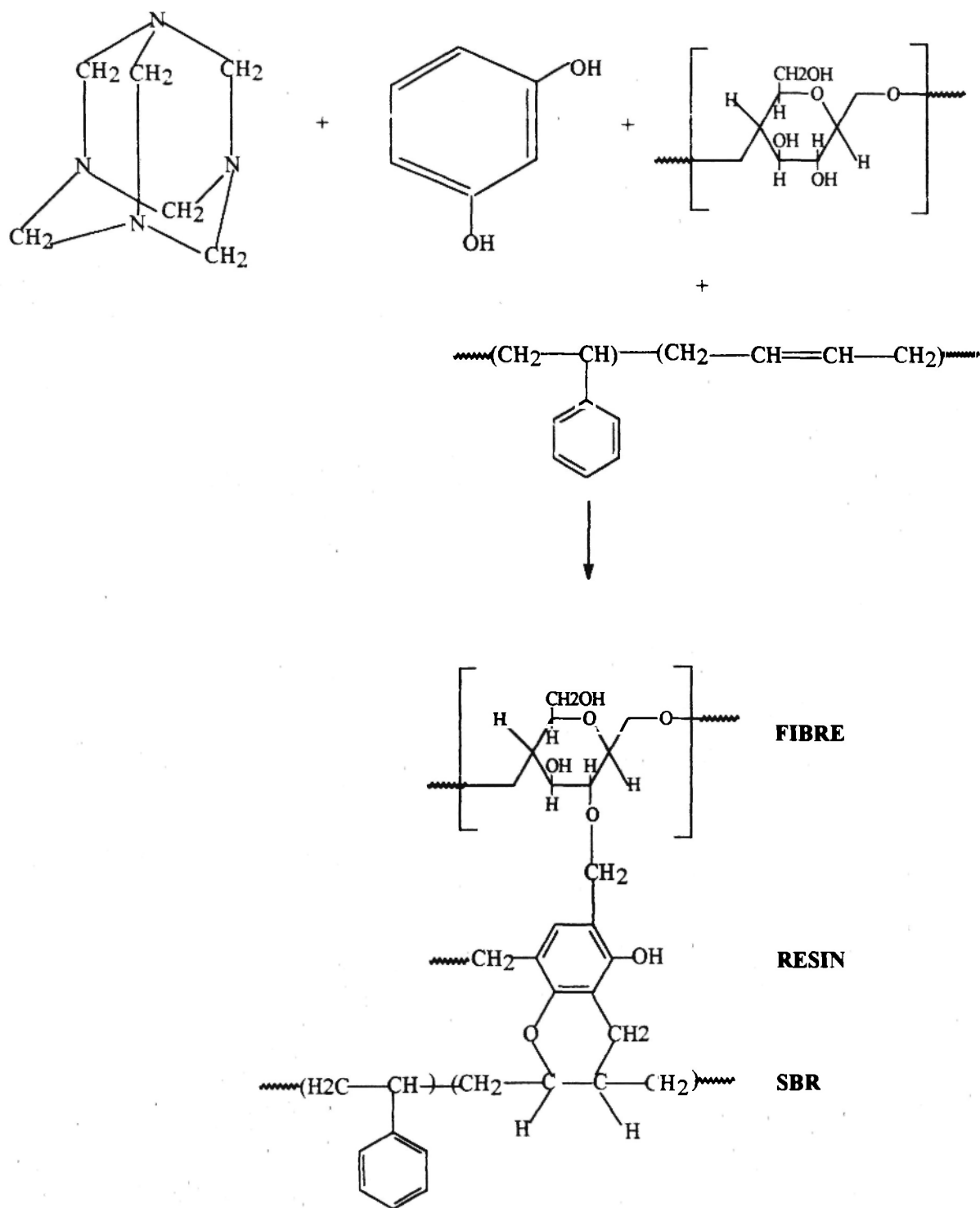
Scheme 1: Hypothetical mechanism showing the effect of mercerization on the chemical structure of sisal fibre.



Scheme 2: Hypothetical mechanism showing the effect of acetylation on chemical structure of sisal fibre.



Scheme 3: Hypothetical mechanism showing the effect of benzylation on chemical structure of sisal fibre.



Scheme 4: Hypothetical mechanism showing the effect of in situ resin on the interface of the rubber matrix and fibre.

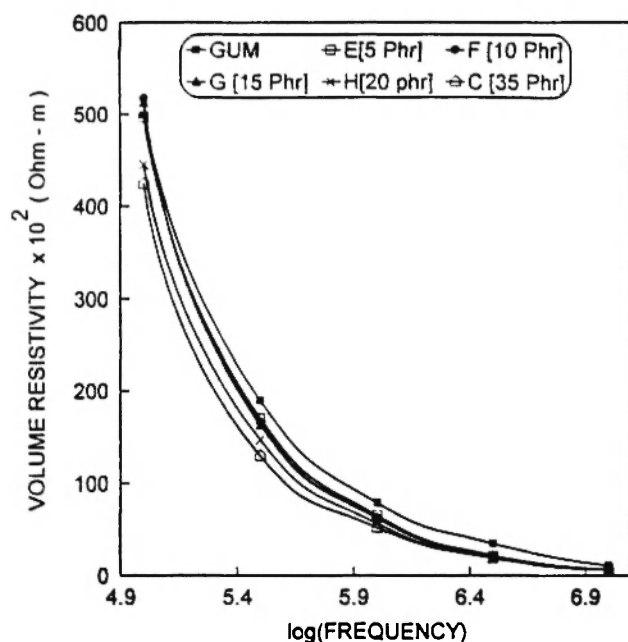


Fig. 5: Effect of volume of fibres on the volume resistivity of composites as a function of frequency.

dominant processes depend upon the composition of the composite, chemical structure, physical texture and morphology and conditions of measurement /31/. It is known that in any polymeric material, the current mainly flows through the crystalline regions and amorphous ones allow current to pass through mainly due to presence of moisture. Since sisal fibres are lignocellulosic in nature, they absorb moisture. The presence of moisture and fibre content increases the conduction.

3.6. Volume resistivity as function of chemical modification

The effect of volume resistivity of all chemically modified composites as a function of frequency is shown in Figure 6. As expected, the volume resistivity of the filled system is higher than the neat SBR. All the treated fibre composites have higher volume resistivity than untreated fibre composites.

The dielectric constant depends on the resistivity by the equation /32/,

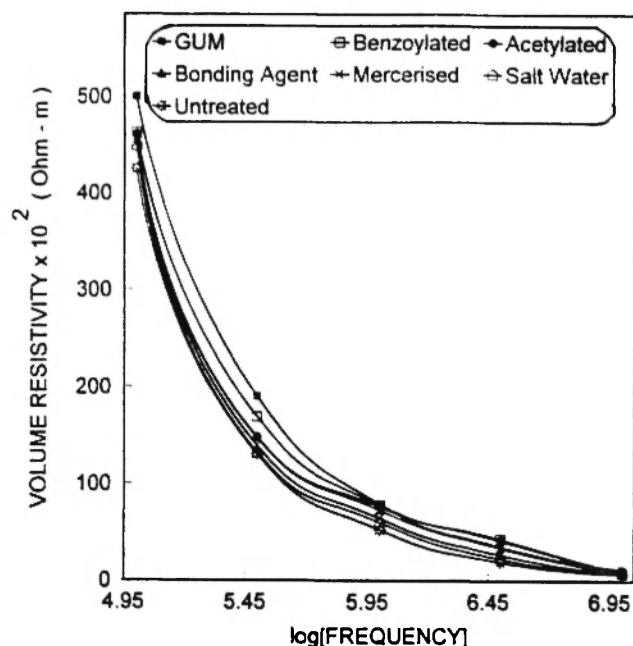


Fig. 6: Effect of various chemical modifications of fibres on the volume resistivity of composites as a function of frequency.

$$\log R_{10}(298^\circ\text{K}) = 23 - 2E'(298^\circ\text{K}) \quad (9)$$

where R is the universal gas constant and E' is the dielectric constant. The equation shows that the electrical resistance of composites decreases exponentially with increasing dielectric constant.

The electronic conduction increases with increasing frequency and the volume of fibres. In any polymeric composite material, most of the conduction occurs through the crystalline regions, and the amorphous (non-crystalline) region allows the flow when the moisture is present in the voids or interfaces between the medium and reinforcement /33/.

Sisal, being a lignocellulosic fibre, having 14% moisture content, appears to absorb moisture from its surroundings. The chemical modification of fibre surface results in conductivity changes of fibres and the degree of dispersion. The composite containing treated fibres showed lower conductivity than untreated ones. This is due to the good interfacial adhesion between the fibre and the rubber matrix. In addition to that the chemical modification reduces the hydrophilicity of the system which, in turn, reduces the conductivity.

3.7. Dependence of electrical conductivity on fibre content

The effect of electrical conductivity on the fibre loading at 10 MHz is shown in Figure 7. Up to 8.43 volume percent of fibres the response of electrical conductivity shows a gradual increase in nature. A change of slope occurs at 8.43 volume percent of fibres. As the fibre content increases, the aggregates are more tightly packed and pressed against each other, resulting in the reduction of internal contact resistance. The net resistance decreases with increasing fibre content. Thus inter aggregate conduction occurs at fibre content due to the overlap of wave functions. The conductivity of the material depends on the state of dispersion in the percolation region. When the volume fraction of conductive particles reaches a critical value (ϕ_c), the percolation concept predicts a change in conductance value. At the threshold, the conductive phase forms a conductive network in the insulating phase and the system is said to percolate.

An insulating material like a fibre composite contains many individually separated fibres. The pathways of low resistivity should be extended throughout the material in order to take place conduction. A schematic model shows the floppy and rigid regions, which correspond, to the distribution of the conductive phase in an insulating medium (Scheme 5).

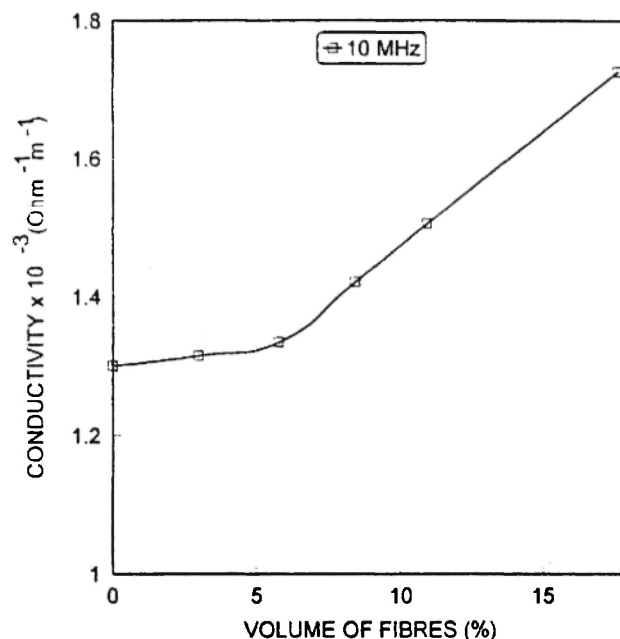
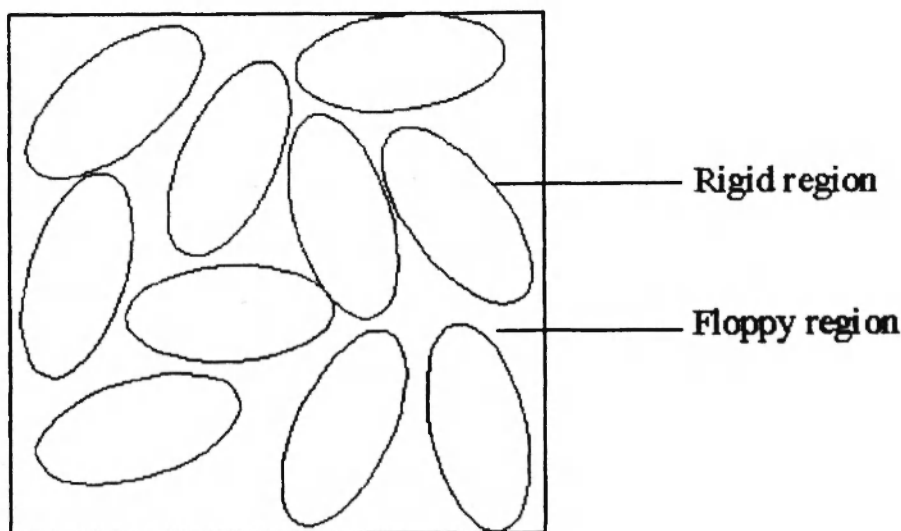


Fig. 7: Effect of volume of fibres on conductivity of composites for 10MHz.

The relation between critical percolation value, ϕ_c , and the percolation threshold, P_c , is given by Zallen [34],

$$\phi_c = fP_c \quad (10)$$



Scheme 5: Schematic model shows the floppy and rigid regions corresponds to the insulating medium.

where f is the filling factor and its value lies between zero and unity.

On analysing Figure 7, it is clear that a change in slope has occurred at 8.43 volume percent of fibres. This is the critical concentration value, P_c , 0.0843, at which the percolation threshold occurs in these composites. The estimated value of volume fraction (ϕ_c) corresponding to P_c is 0.08. Substituting values of ϕ_c and P_c in equation (10), the value of ' f ' is obtained as 0.95, which indicates that the conductive phase is arranged in the form of rods of uniaxially random close packing [34].

The effective co-ordination number, Z , is calculated as 22.54 from the following equation,

$$P_c = 2f / Z \quad (11)$$

Percolation theory [34] is explained by the scaling law model and is shown as,

$$\sigma = \sigma_o (P - P_c)^\beta \quad (12)$$

where σ , conductivity of the composite, σ_o , conductivity of the conducting phase, P , volume fraction of the conductive phase, P_c , critical volume fraction of the conductive phase and β , critical exponent for percolation. The value of β is obtained as 1.88 from the slope of plot $\log \sigma$ vs $\log (P - P_c)$ (Figure 8). As per the existing percolation concept β does not exceed a value of 3/4.

3.8. Dissipation factor as a function of fibre concentration

Dissipation factor or loss tangent is the ratio of the electrical power dissipated in a material to the total power circulating in the circuit. It is directly analogous to the $\tan \delta$ function relevant to dynamic mechanical testing. The visco-elastic nature of the polymer creates similarities in the material response to both mechanical and electrical stimuli. In DMA (dynamic mechanical analysis), the relationship between storage and loss moduli is shown as,

$$\tan \delta = E'' / E' \quad (13)$$

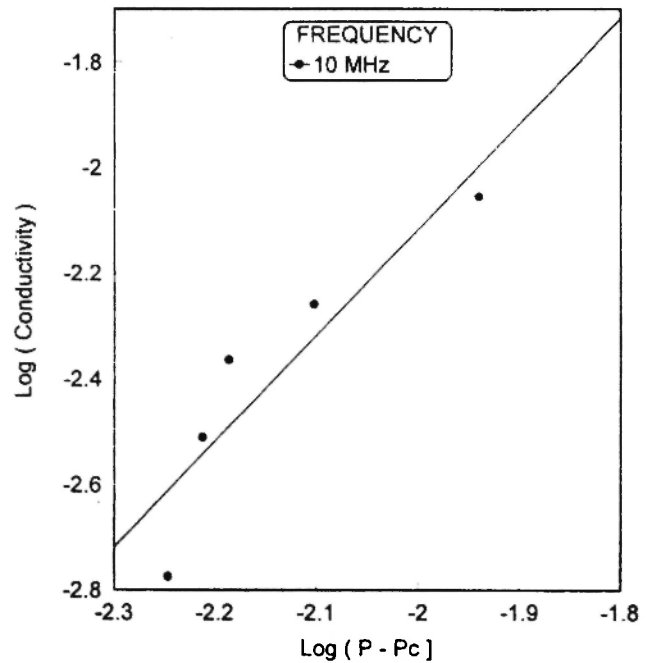


Fig. 8: Plot of $\log \sigma$ Vs $\log (P - P_c)$ showing percolation concept.

Under dynamic excitation, the independent and measured variables move out of phase like in stress-strain measurements in mechanical tests and voltage and current in the electrical tests. The measurement of dissipation factor ($\tan \delta$) and loss factor (E'') of insulating material is important since the loss tangent is a measure of the alternating current electrical energy which is converted to heat in an insulator. This heat raises the insulator temperature and accelerates its deterioration. The effect of dissipation factor ($\tan \delta$) as a function of the logarithm of frequency at different volume of fibres (%) is plotted in Figure 9. As the frequency and short fibre concentration increases in the mixes, the dissipation factor also increases for gum and composites. The two important factors contributing to the loss factor (E'') are the dipole polarization and ionic conductance. The numeric value of $\tan \delta$ is determined by both polarity and carrier mobility.

A strong relaxation is observed with a peak at a frequency of 10 Hz. This is due to the α -transition. The position of the peaks is identical for both filled and unfilled systems. The addition of short fibres does not

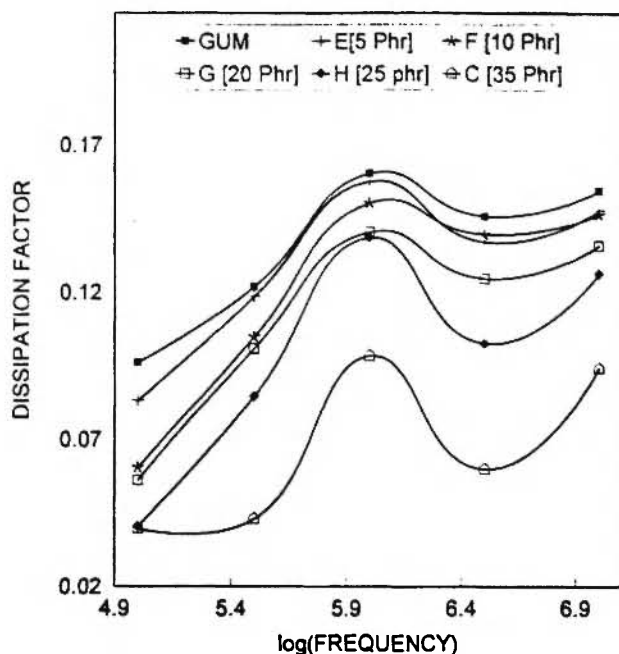


Fig. 9: Effect of volume of fibres on dissipation factor of composites as a function of frequency.

affect the relaxation mechanism but decreases the relaxation magnitude at each frequency. At all frequencies, the intensity of dielectric loss increases regularly and decreases as a function of increase in volume of fibres (%).

3.9. Dissipation factor as a function of fibre modification

Figure 10 shows the effect of chemical treatment of the fibre surface on the dissipation factor as a function of the logarithm of frequency. As the frequency increases the dissipation factor increase for the sisal/SBR composites. Also, it is seen from the figure that the dissipation factor and magnitude of relaxation vary with the nature of treatment. These chemical modifications do not affect the relaxation mechanism, but rather increase the relaxation magnitude at each frequency.

Scanning Electron Micrographs (SEM) of tensile and tear failure surfaces of composites at 35phr fibre loading were analyzed in detail. The decreased hydrophilicity of the treated fibres can be well explained based on the morphology of the system. The fracture

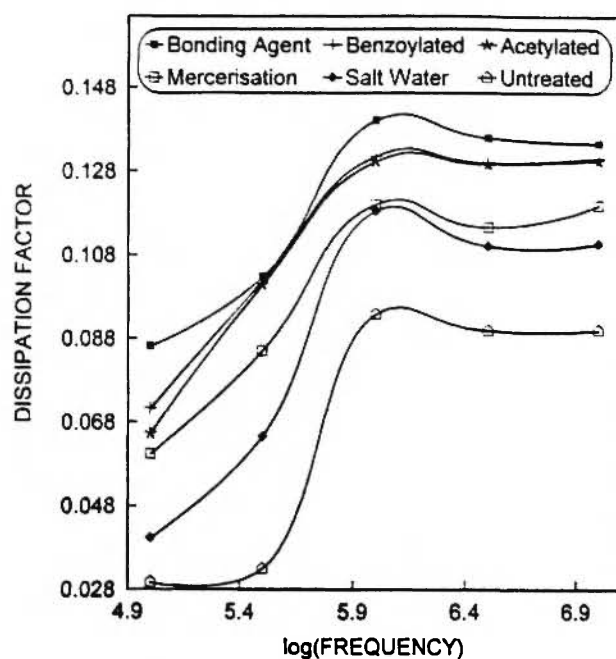


Fig. 10: Effect of various chemical treatments on dissipation factor of composites as a function of frequency

surface of the untreated fibre composites show fibre pull out and the fibre is very clean without any rubbery particles on them (Figure 11), whereas in treated fibre composites, rubber (matrix) particles are stuck on the fibre surface (Figure 12). The sticking of rubber segments indicates a strong interfacial adhesion occurred between the fibre and the rubber matrix (Figure 13) which is due to the chemical bond formation caused at the $-\text{CH}_2\text{OH}$ group [Scheme 4].

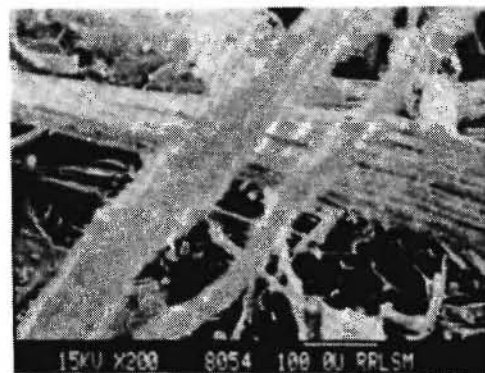


Fig. 11: SEM showing pull out of fibres from the fractured surface(mix C).

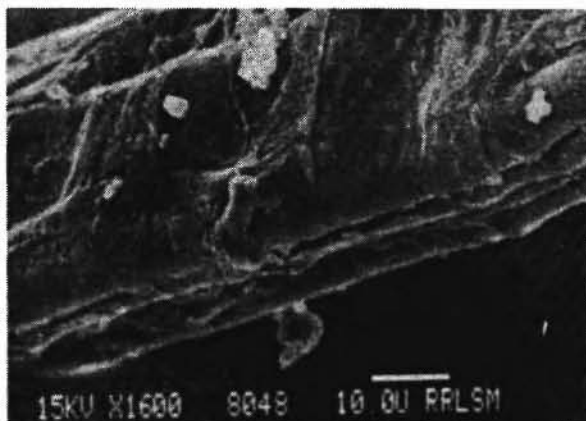


Fig. 12: SEM showing rubber fragments adhered on the fibre surface(mix L).

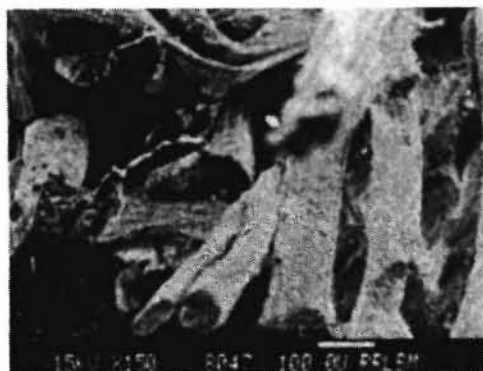


Fig. 13: SEM shows the interface in treated sisal/SBR composite(mix S).

High electrical discharge region in any material will decay the electric charge at a rate that is determined by the permittivity and volume resistivity. Polymers have a very high resistivity so that charges can be retained over a very long time due to the chain flexibility and segmental mobility. Sisal, being lignocellulosic, increases the conductance of the material, which reduces the accumulation of free charges on the surface of the reinforced composite. In packaging industry, the charge accumulation is alleviated by adding antistatic agents. One of the techniques used to increase the electrical conductivity of polymers is to incorporate conductive particles such as metallic powders, flakes, and fibres, into the matrix [35,36]. Thus sisal/SBR composites can be effectively used for antistatic applications.

4. CONCLUSION

The electrical properties such as dielectric constant, volume resistivity and dielectric loss factor of sisal fibre reinforced styrene butadiene rubber composites have been studied as a function of fibre length, fibre content, frequency, chemical modification of fibres and the incorporation of the bonding agent. The increased values of dielectric constant with fibre length are associated with interfacial polarization, the value of which depends upon the interfaces. At the optimum loading, the fibres tend to orient in the rubber matrix with better adhesion. The increased values of dielectric constants with fibre loading were due to increased orientation and interfacial polarizations. The dielectric constants of treated composites were found to be lower than those of untreated composite.

The volume resistivity of the composites was found to decrease with fibre loading but increased with chemical modification of fibres. The dielectric dissipation factor values of composites were found to be increased with increase in fibre loading. Finally, it is important to mention that these composites can be successfully used in antistatic applications in order to dissipate static charges.

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