Chapter 4

Structural, Optical and Dielectric properties
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4. STRUCTURAL, OPTICAL AND DIELECTRIC PROPERTIES

4.1. INTRODUCTION

Dielectric behavior exists in all forms of matter. Dielectric polarization arises when an electric field was applied to the material then charges in a molecule or atom will displace with respect to each other. Based on the displacement of charges with respect to the applied field these Dielectrics were classified into two types

a) Non-polar dielectrics

b) Polar dielectrics.

In a materials which the Molecules have centre of positive charge coincide with centre of negative charge or in a material which consists zero dipole moment are known as Non-polar dielectrics and

In a materials which the Molecules have centre of positive charge not coincide with centre of negative charge or in a material which consists permanent dipole moment are known as Polar dielectrics.

When a non-polar atom exposed with applied electric field then the centre of positive charge and negative charge should be displace with each other, causing electronic polarization ($P_e$). When a material containing non-polar molecules is subjected to an electric field, the displacement of atomic nuclei relative to one other induces dipole moments in the molecules called atomic polarization ($P_a$). These two polarizations together constitute a distortion polarization ($P_d$).
In the absence of electric field on polar molecules which consists permanent dipole moment and they oriented randomly. When an electric field subjected to the material consists polar molecules then the permanent dipole moment of these molecules get oriented along the direction of the electric filed, called Orientational polarization ($P_o$). The alignment of the permanent dipole [174] along the field increases as the electric field strength increases.

Thus the total polarization of a dielectric material is

$$P_T = P_e + P_a + P_o = P_d + P_o$$

When a polar dielectric is subjected to the external electric field then dipoles are tend to oriented along the direction of applied filed due to the torque exerted on polar molecules. This torque aligns all the dipoles along the direction of applied filed. If the applied filed is very strong, then all the dipoles get aligned completely and the polarization may reach the saturation value. The polarizability is a measure of resistance offered by the atom or molecule to the displacement of the center of charges, or orientation of its dipole moment in the electric field. When a temperature increases on polar dielectric, then the orientation of dipoles will decreases even though electric field is applied, due to the thermal vibrations of the molecules, which produces random dipole orientations.

In general, the total polarizability of dielectric material is

$$\alpha_T = \alpha_e + \alpha_a + \alpha_o$$
The permittivity of polar molecules has very high compare with permittivity of non-polar molecules because of an additional amount of polarization due to orientation. But the temperature effect on this permittivity of polar materials falls rapidly with raising temperature than non-polar materials. This causes decrease in orientational polarization.

The most important properties for dielectric resonator applications are dielectric constant ($\varepsilon_r$), factor ($Q_0$) and temperature coefficient of resonant frequency.

The dielectric constant ($\varepsilon_r$) of the material determines the resonator’s dimensions at some specified frequency. Wavelengths within the dielectric resonator are shorter by a factor of $1/(\varepsilon_r)$. This gives rise to a first order working equation

$$D = \frac{C}{f_0(\varepsilon_r)^{1/2}}$$

Where ‘C’ is a constant related to the velocity of light.

The unloaded Q factor ($Q_0$) depends on both dielectric and environmental losses. Q is defined by the ratio between the stored energy [175] to the dissipated energy per cycle. In terms of frequency and the impedance method, this ratio can be expressed as

$$Q_0 = \frac{f_0}{f_1 - f_2} = \frac{f_0}{\Delta f}$$

The temperature coefficient of resonant frequency ($T_f$) combines three independent factors: the temperature coefficient of the dielectric constant ($\varepsilon_r$); the thermal expansion of the material ($\alpha_L$ and the
thermal expansion of the dielectric resonator’s environment ($r_d$)
Resonant frequency shifts due to intrinsic material parameters and
the environment are related by the following equation:

$$\tau_f = - \left( \frac{1}{2} r_d + a_L + A \right)$$

Here ‘A’ is independent on the position of the dielectric
resonator relative to the top and bottom of the cavity walls. The typical
range of values of A is between 0.05 and 1.0.

The dielectric constant ($\varepsilon_r$) of the material is required to
calculate the dimensions of the dielectric resonator for a given
frequency. This parameter is typically measured by methods described
and observed in infrared, visible and Ultraviolet. In
the process of orientational polarization conduction and dipolar losses
occurred. With the help of the polarization mechanism the interfacial
losses may be observed. This mechanism was analyzed in the
Maxwell-Wagner capacitor model and in Volger’s [178] and Krotzsch’s
[179] development of it. Due to jump motion of charge carriers, the
relaxation observed in the equality of conductance activation energy
and that of the temperature dependence of frequency corresponding to
maximum $\tan \delta$ [180].
In an alternating electric field, the dielectric relaxation occurs during the polarization. With this subjecting electric field (step field) is not followed by an instantaneous response of polarization. The time dependent polarization and a distortion polarization $P_i(t)$, which tends to an equilibrium value. This delayed component is generally given by dipolar and interfacial polarization. The tendency towards equilibrium of the system following the application or removal of the external field is called dielectric relaxation.

The dielectric relaxation process of polarization becomes apparent when the frequency of the applied field $E$ is not far from being of the same order of magnitude as its resonance frequency, $\omega_r$. The resonance frequencies of electronic and ionic polarization are known to be about $10^{14}$ and $10^{12}$ Hz's respectively [181-185]. On the other hand, the relaxation time of the polarization of ionic space charge typically varies from a few seconds to minutes.

The dielectric properties in the low frequency region have been explained to be based on the contributions of the space charge polarization and the dipolar polarization associated with either dipoles produced by lattice defects and impurities or permanent dipoles.

In recent years, composites reinforced with fillers and cellulose fibers have greatest importance in this current arena due to the threats of uncertain petroleum supply and concerns about environmental pollution. Natural fiber reinforced polymer composites have superior properties like high strength, toughness, low cost, and
biodegradable. By comparing with synthetic fibers these natural fibers exhibit low properties. The main drawback in the natural fibers is their hydrophilic nature which causes the poor interfacial adhesion between matrix and fiber. But the synthetic fibers are moisture repellence due this composite reinforced with synthetic fiber show better properties [186-188].

On the other hand some other reported the hydrophilic nature of natural fibers reduced by chemical treatment of fibers by different methods. Many researchers used different methods in the processing composite. silane, titanate and zirconate coupling agents used as chemical reagents used for treatment of natural fibers, this results increasing in mechanical properties of sisal/ polyester composites. It was observed that this treated fibers shown improved acid–base characteristics and resistance to moisture. Composites produced from these treated fibers showed slightly better mechanical properties [189-191].

Many of them reported possible to usage of these composites in various types of applications, but from the last two decades researches had focused on dielectric applications of the natural fibers reinforced composites. The natural fiber reinforced composite materials have been used as dielectric materials in microchips, parts of transformers, terminal, connectors, switches, circuit boards, etc. Therefore, studies of dielectric properties of natural fibers reinforced composites materials are very important. The dielectric strength and
volume resistivity of the natural fibers reinforced composites have been observed by various observers [192-193]. Pothan et al. [194] have observed that the electrical and mechanical properties of banana fiber reinforced polyester composites. In this study it was identified the dielectric constant values decreases by making the chemical treatment of natural fibers. Dielectric constant values of resulted composites decrease. Some other observed increase in conductivity with reinforced sisal and natural rubber [195]. It was observed the dielectric properties of banana fiber reinforced with phenol formaldehyde composites have been also studied with respect to fiber loading, fiber treatment and hybridization with glass fibers [196]. With the surface modifications of fibers observed decrease in dielectric properties of the composite.

In this present work, the effect of fiber loading and chemical treatment was identified on Dielectric properties of treated and untreated composite has been investigated. Unsaturated polyester resins were chosen for making fiber reinforced plastics (FRPs) because of their easy handling and fabrication, good strength and low cost in comparison to epoxy or phenolic resins. The chemical treatment observed on cow dung fibers by using XRD and FTIR.
4.2 RESULTS AND DISCUSSIONS

4.2.1 XRD Analysis of Treated and Untreated Fibers

The X-ray diffraction profiles of treated and untreated cow dung fiber used in this study is shown in Fig.4.1 and Fig 4.2. From the figures it was observed the important variation in treated and untreated cow dung fibers, the intensity change at diffraction peaks. By comparing the intensity of untreated sample with treated sample for treated sample have lower intensity peak and untreated sample have higher intensity peak. From the Fig 4.3 It was also observed in both samples obtain two intensity peaks and these two intensity peaks smeared and appears as one broad peak. This could be related to high amounts of amorphous materials such as hemicelluloses. It was analyzed from diffractograms, the range of diffraction peaks for 2θ diffraction angle in untreated fiber was 18.82° to 21.26° and in treated fiber 18.44° to 20.79°. The d-spacing observed for untreated fiber at major peak was 4.17 Å and for treated fiber it was 4.26 Å, from these d-spacing values it was observed there is an increment in treated fiber compare with untreated fiber It is sown from Fig 4.1 and Fig 4.2. This increment in d-spacing could obtain due to removal of hemicellulose and lignin from fibers in chemical treatment.

H.N Dhakal et al., observed the influence of chemical treatment hemp fibers on the spectrum corresponding to the un-treated hemp fiber shows diffraction peaks at 2θ angles: 15.08° and 22.34°. For NaOH treated hemp fiber, the diffraction peaks at 2θ angles were
14.52° and 21.76°. The d-spacing value for un-treated hemp was 5.88 Angstrom (Å) whereas the d-spacing value for treated sample was 6.11 Angstrom (Å), nearly an increase of 4% in d-spacing value (interplaner distance) [205].

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**Fig. 4.1 XRD results for untreated fiber**

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<tr>
<td>18.82</td>
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<td>21.26</td>
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Fig. 4.2 XRD results for treated fiber

Diffractogram : Treated

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<th>Counts</th>
<th>InT/100</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>18.44</td>
<td>4.8073</td>
<td>260</td>
</tr>
<tr>
<td>2</td>
<td>20.79</td>
<td>4.2696</td>
<td>538</td>
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Fig. 4.3 XRD results for Untreated and treated fiber
4.2.2. Fibers Characterization with FT-IR

FT-IR spectra of raw and surface modified Cow dung fibers were taken with KBr pellets on PERKIN ELMER RXI Fourier Transform Infrared Spectrophotometer. FT-IR spectrum (Fig.4.4&4.5) of raw cow dung fibers showed a broad peak at 696.16 cm\(^{-1}\) (due to out of plane -OH bending), 873.31 cm\(^{-1}\) (due to b-glyco-sidic linkage), 1255.46 cm\(^{-1}\) (due to –C-O-C- and –C=O stretching in xylan side substituent and lignin aromatic C=O stretching), milder peaks at 1376.2–1491.73 cm\(^{-1}\) (due to –CH, -CH2 and -CH3 bending), 1718.50 cm\(_{-1}\) (due to H-O-H bending of absorbed water and for lignin C-H deformation), 2001.54 cm\(_{-1}\) (due to O-H stretching of absorbed moisture), 2494.96 cm\(_{-1}\) (due to C-H stretching in polysaccharide chains), 2914.78 cm\(_{-1}\) (for C-H stretching vibration of aliphatic methylene group) and an intense broad peak ranging from 3094.20 to 3629.56 cm\(_{-1}\) (due to the hydrogen bonded -OH vibration of the cellulose structure fiber). However on treatment of Lignocellulosic fibers with dilute NaOH solution strong bands at 1629.68 and 1259.54 cm\(_{-1}\) have been found to disappear due to removal of substational portion of uranic acid, lignin, adhesive pectins and hemicelluloses. The peak at 1629.68 is assigned to carbonyl group of pectins it is shown from Fig 4.5. From FT-IR spectra it has been observed that the intensity of adsorption band at 3395.9 cm\(_{-1}\) (due to -OH group) decreases after the fibers surface modification, which supports the development of hydrophobic character onto natural fibers.
Fig. 4.4 FT-IR Results for Untreated fiber

Fig. 4.5 FT-IR Results for treated fiber
4.2.3. **EDAX Analysis On Untreated and Treated Fiber Hybrid Composites**

By using EDAX, the composites specimens of its composition were analyzed. The analysis of the composites prepared under different conditions is presented in the following paragraphs.

**4.2.3.1. Untreated Cow Dung Fiber**

EDAX analysis of specimen is shown Fig. 4.6. From this figure it is observed that the presence of compositional elements in specimen was C, O, Si, Cl, which it gives the information there exist the unwanted elements other than C, O, Si. It was identified it consist high peaks of other elements. This results get affect the composites properties due poor interracial bonding in between the fiber and matrix. It is shown in below figure.

![Fig. 4.6 Compositional analysis in Untreated Cow dung fiber composite](image-url)
4.2.3.2. Treated Cow Dung Fiber

EDAX analysis of specimen is shown Fig. 4.7 from this figure it is observed that the presence of compositional elements in specimen was C, O, Si. It was identified it consist high peaks for the elements of C, O, Si, for remaining the presence of cow dung fiber it shows saturation with low peaks. This attempt gives a full information fiber material makes a strong interracial bonding with matrix. It is showed in below figure.

![EDAX analysis of specimen](image)

Fig. 4.7 Compositional analysis in treated Cow dung fiber composite

4.2.4. Dielectric Properties

4.2.4.1. Dielectric Constant, Loss and Dissipation Factor

Dielectric constant is defined as ratio of capacitance of a capacitor in consisting as dielectric to the capacitance of a capacitor
in vacuum i.e. without any dielectric. It is also called relative permittivity and is denoted by symbol ($\varepsilon_r$). This Dielectric constant provides the information about its dielectric strength of an insulation material. This parameter helps to select suitable value of capacitor which is used for improve electric power in electrical system installation and it also reduces power loss in transmission lines by designing and fabricating suitable value of capacitor. If a substance has high dielectric constant when it is placed in between two conducting plates it reduces their electric field. Due to this reason various researchers to design capacitance of suitable value. The dielectric constant $\varepsilon_r$ of specimens can be calculated from capacitance by using the following equation.

$$\varepsilon_r = \frac{Ct}{\varepsilon_0 A}$$

Where ‘$\varepsilon_r$’ is relative permittivity, ‘C’ is capacitance of insulation material, ‘t’ is the thickness of specimen, ‘$\varepsilon_0$’ is permittivity of free space and ‘A’ is area of test specimen under electrode. For specific samples, dielectric constant varies in direct proportion with capacitance. Further dissipation factor $\tan\delta$, which is a measure of power dissipated, has been calculated from the following equation.

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

Where ‘$\varepsilon_r'$’ is loss factor and ‘$\varepsilon_r$’ is dielectric constant.

The equipped samples were cut as per the ASTM in dimensions (10mm×10mm×3mm by using diamond cutter for the purpose of
determining dielectric properties of materials. These samples were coated with silver paste on either side and allow drying in air. After drying copper wires were fixed on both sides of the samples, which acted as formal electrodes. The dielectric properties i.e. dielectric constant, dielectric loss and dissipation factor for all samples were measured at room temperature in the frequency range (1kHz-5MHz) by using an LCR impedance analyzer (Hioki 3532 -50 lcr hitester).

The dielectric constant, loss factor and dissipation factor of optimized samples of glass fiber, Untreated and treated cow dung/glass fiber reinforced UPE composites have been depicted in Figs. 4.9 – 4.17.

It has been observed from Fig. 4.9 and 4.10 which represents the variation of the dielectric constant of cow dung/glass fiber reinforced polyester as a function of frequency. The dielectric constant increases with increase volume fraction of fiber content [204]. It was observed dielectric constant ($\varepsilon_r$), values mainly depend upon the contributions of interfacial, orientation, atomic and electronic polarizations in the material. The variation in conductivities or polarizations of the resin and filler, the interfacial polarization occurs. These are also depends upon the volume fraction of fillers too. It was identified natural fibers are absorb water molecule from the atmosphere because natural fibers have hydrophilic nature [200]. Generally, these water molecules are highly polar in nature, due to this cause for given fiber loading the dielectric constant increases at
low frequencies and decreases at high frequencies due to decrease in orientation polarization. It was found at low frequencies the complete orientation of molecules takes place and with comparing to the electronic and atomic polarizations for orientation polarization requires more time to reach the equilibrium static field. On the other hand with increasing volume fraction of fiber content, dielectric constant also increases at low frequencies due to increasing more polar molecules with increasing fiber content. As frequency increases the \( \varepsilon_r \) reduces due to the lag in orientation of polarization [203].

In contrast of the above effect, alkali treatment of Cow dung fiber has decreases their dielectric constant compare with raw fiber composite. Because it decreases orientation polarization of treated fiber in composites, due to elimination of hemicelluloses and lignin from cellulose fiber. This result lowers the value of dielectric constant when compare with raw fibers. The effect of chemical treatment on cow dung fibers was it reduces moisture behavior of fibers because of –OH groups in fiber were blocked [197-199]. Thus resultant decrease in hydrophilicity of the polymer composites leads to lowering of orientation polarization and subsequently dielectric constant value [200-201].

From Figs.4.12 to 4.17 it has been observed that dielectric loss and dissipation factor is also affected by chemical treatments fiber. As same as the above discussed dielectric constant, further similar to the result obtained in the study of dielectric loss and dissipation factor. It
has been found dielectric loss and dissipation factor should be higher in untreated composites compare with treated composites. It may be due to the incorporation of functional groups of different nature onto lignocellulosic fibers after their surface modification. On the other hand it is difficult to explain dielectric loss or dissipation factor depends upon fiber orientation [202].

4.2.4.2. Dielectric Strength Test

The composite specimens were made as per the ASTM D149 to measure the dielectric strength. The specimens having dimensions of 120mm x 120mm x 3mm are reinforced with fibers in a single direction along 120mm length. The dielectric break down voltage is determined at six points for each specimen, and average value was considered for analysis. The points selected are distant enough so that there is no flashover. The test is carried out at 50Hz frequency and room temperature. Digital micrometer of 0.001mm least count is used to find the thickness of the specimen at break down point and the test was repeated for all specimens fabricated from different kinds of fibers.

The magnificent effect found that the dielectric strength of hybrid fiber composites (Figure 4.8) increases with increase in percentage weight of cow dung in present study. It very often phenomenon which is not observed in various natural fiber composites. Dielectric strength of hybrid fiber composites observed in the present research work of the hybrid composite can certainly be
considered for electrical insulation applications.

![Graph showing dielectric strength with increasing cow dung wt%]

Fig. 4.8 Dielectric strength with increasing cow dung wt%
Fig. 4.9 A, B, C, D, E, and F represents (A=0%, B=2%, C=3%, D=5%, E=7% and F=10% of cow dung fiber) Dielectric Constant VS frequency of Untreated Cow dung fiber Composite
Fig. 4.10 G, H, I, J, and K, represents (G=2%, H=3%, I=5%, J=7% and K=10% of cow dung fiber) Dielectric Constant VS frequency of treated Cow dung fiber Composite.
Fig. 4.11 Comparative diagram of Dielectric Constant VS frequency of Untreated and Treated Cow dung fiber Composite.
Fig. 4.12 A, B, C, D, E, and F represents (A=0%, B=2%, C=3%, D=5%, E=7% and F=10% of cow dung fiber) Dielectric Loss VS frequency of Untreated Cow dung fiber Composite
Fig 4.13 G, H, I, J, and K, represents (G=2%, H=3%, I=5%, J=7% and K=10% of cow dung fiber) Dielectric Loss VS frequency of treated Cow dung fiber Composite.
Fig. 4.14 Comparative diagram of Dielectric loss VS frequency of Untreated and Treated Cow dung fiber Composite.
Fig. 4.15 A, B, C, D, E, and F represents (A=0%, B=2%, C=3%, D=5%, E=7% and F=10% of cow dung fiber) Dissipation factor VS frequency of Untreated Cow dung fiber Composite
Fig. 4.16 G, H, I, J, and K, represents (G=2%, H=3%, I=5%, J=7% and K=10% of cow dung fiber) Dissipation factor VS frequency of treated Cow dung fiber Composite.
Fig. 4.17 Comparative diagram of Dissipation factor VS frequency of Untreated and Treated Cow dung fiber Composite.