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Frequency dependence of dielectric properties of beam irradiated *luffa* fiber composites

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Abstract. In this present inspection, the dielectric properties of biodegradable composites are studied using biodegradable polymer poly (lactic) acid (PLA) and natural fiber of *luffa cylindrica* (LC) fabricated using injection molding technique. Before reinforcement in PLA matrix, LC fibers were irradiated with 6 MV gamma rays generated from medical LINAC at room temperature 26°C in presence of air. The effects of irradiation dose and wt of fiber in composites on electrical properties such as dielectric constant and dielectric loss factor were investigated at room temperature 30^{o}C with variation in frequency from 100Hz to 1MHz. The incorporation of irradiated LC fiber in the PLA matrix increases the dielectric constant, dielectric loss of the composites compared to virgin PLA matrix. Dielectric constant and dielectric loss factor of all the composite samples decreased with increase in frequency.

Keywords. LINAC, gamma irradiation, dielectric constant, dielectric loss

PACS/topics: 41.75Fr, 77.22-d, 77.22Gm

1. Introduction

Now a days, traditional synthetic or manmade fibers are being replaced by natural fibers, because of their low cost, light weight, easy availability, non toxicity, biodegradability and environment friendly nature [1-4]. Natural fibers are mainly composed of cellulose, hemi-cellulose and lignin, which make them hydrophilic in nature with a tendency to absorb moisture. As a result, natural fibers have very low reactivity and poor compatibility with the polymers affecting the interfacial adhesion between them. Therefore fiber modification is necessary to overcome these limitations. Usually fibers are modified by chemical and physical treatments. The use of ionizing radiation for modification of natural fiber draws great attention because of its advantages like no use of chemicals, low processing time leading to energy saving. Also it follows a clean waste free procedure leaving no bad impact on environment. Usually electron beam and gamma rays are used in radiation processing, which bring significant structural changes in the fiber with very low irradiation dose [2-7]. The LC fibers are cost effective, readily available as agricultural waste with low CO_2 emission along with high electrical resistance, good thermal and acoustic insulating properties. Most importantly they are biodegradable and can be recycled. Composites made from these natural fibers and biodegradable polymer matrix are known as biodegradable composites having low weight per unit volume resulting in higher specific strength and stiffness[8-9].

Cellulose is the major component of LC fiber and it contains 60% of cellulose. Celluloses are long chain polymers composed of identical units known as gluco pyranose unit which are linked to its neighbour by glycosidic linkage[9]. Two important chemical changes such as cross linking and chain scission occur when the cellulose rich LC fiber is irradiated with gamma rays. The degradation mechanism holds true for structures like cellulose which contains tetra substituted carbon atoms. Upon irradiation on fibers, free radicals are formed which are responsible for the bonding between fiber and matrix[8]. Further the surface area increases due to defibrillation of cellulose fibers leading to enhanced compatibility between fiber and matrix.

The current research ventured to synthesize composites using PLA matrix reinforced with gamma irradiated LC fibers expecting better fiber matrix adhesion as they both have –OH groups. Complete absence of data of dielectric properties of composites using PLA and LC fiber in literature motivated our research. The biodegradable nature of PLA fascinates us to carry out the work and the dielectric properties like dielectric constant, dielectric loss factor of the prepared composite materials were studied with variation in irradiation dose given to the LC fiber in the frequency range from 100 Hz to 1 MHz. The fabricated biodegradable composite materials can be explored to be used as electrical panels, switches, studs, capacitors etc.

2. Experimental

2.1 Material

PLA of grade 4042D (molecular weight Mw ~ 6, 00, 000) was purchased from Nature Works, USA. The LC fibers were collected from local forest area.

2.2 Gamma irradiation of LC fiber

To improve interfacial bonding and to reduce moisture absorption, the LC fibers were subjected to treatment with X-ray photon of energy 6MV extracted from the medical LINAC of Hemalata Hospital and Research Centre (HHRC), Bhubaneswar, India. The fibers were irradiated at three different doses of 0.5Gy, 1Gy and 2Gy.

2.3 Composite processing and fabrication

Prior to use, the PLA pellets and the irradiated LC fibers were dried in vacuum at 80° C for 24 h. The PLA and LC fiber were mixed mechanically at 100 rpm with a micro compounding molding equipment at 170°C for 10 minutes. The molten composite samples were transferred after extrusion through a preheated cylinder to the mini injection molder in order to obtain the desired specimen samples for various measurements and analysis.

2.4 Types of samples for characterization

A total of 10 different composite samples were prepared with PLA matrix and different wt proportions of irradiated LC fibers. B0 is the virgin PLA matrix. In B1, B2 and B3 samples, the PLA is mixed with 2% wt of LC fiber at gamma irradiation dose of 0.5Gy, 1.0Gy and 2.0Gy respectively. In B4, B5 and B6 samples, the 5% wt of LC fiber is loaded with gamma irradiation dose of 0.5Gy, 1.0Gy and 2.0Gy respectively. Finally B7, B8 and B9 samples are loaded with 10% wt of fiber irradiated at irradiation dose of 0.5Gy, 1.0Gy and 2.0Gy respectively.

2.5 *X-Ray diffraction*

WXRD/SHIMADZU/JAPAN, goniometer facilitated with scintillation counter records the Bragg's angle from 10˚ to 80˚ of the X-ray diffractograms at 28˚C, to analyze the orientation distribution of the crystallites. Ni filtered Cu Kα is radiation at a wavelength of 0.1542 nm, generated at 40 kV, 35mA was used as X-rays. The LC fibers are rich in cellulose (60%).The celluloses are natural polymers having large inter-planner spacing up to the order of 5.9 A^o. Hence the peaks are expected between 10^0 and 50^0. However all the samples were scanned between 10^0 and 80^0 to detect the presence of any other components.

2.6. Dielectric properties measurements

Rectangular shaped specimens of 10mm × 10mm × 2mm were prepared for study of electrical properties. Samples were shaped by cutting from the composite specimens using a die. The rectangular surfaces of the test samples were coated with conductive silver paint. The test samples were fixed between two electrodes and kept inside the sample holder. Measurements were carried out at room temperature 26°C with varying frequency from 100 Hz to 1 MHz to examine various dielectric properties such as dielectric constant, dielectric loss of the matrix as well as of the composite samples.

3. Results and Discussion

XRD patterns of virgin PLA is shown in figure 1. It shows two broad peaks at 15.74˚ and 32.04˚suggesting amorphous nature of PLA.

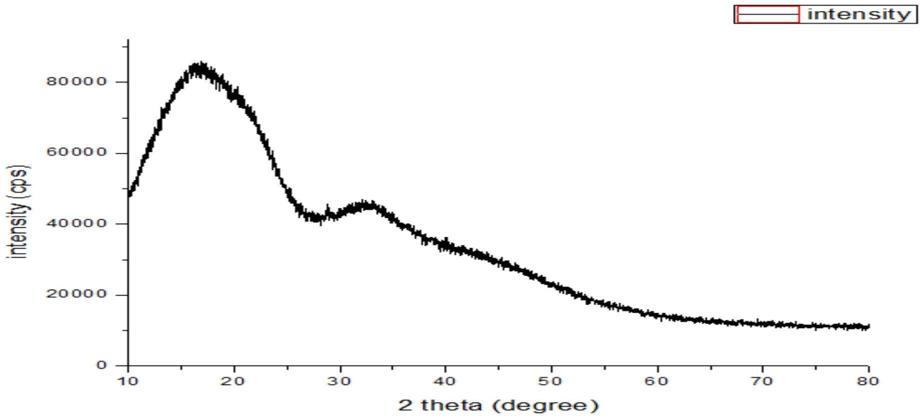

Fig.1. XRD pattern of virgin poly (lactic) acid

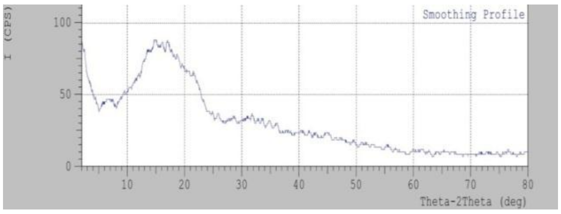

Fig.2. XRD spectra of sample B_5 (PLA with 5% fiber having irradiation dose 1 Gy)

XRD pattern of injection molded PLA reinforced with gamma irradiated LC fiber(1 Gy) at 5 wt% loading (sample B5) is shown in figure 2. The peak appears around 16^0,corresponds to amorphous cellulose or cellulose-II of (101) crystallographic plane [10]. It appears as a broad scattering peak having FWHM 0.76° indicating the amorphous nature of the composites.The crystallite size of composites were determined at this peak from XRD analysis using Debye-Scherrer expression,

$$D=K\lambda /\beta\cos\theta$$

where D= crystallite size, K= shape factor = 0.9, λ= Wavelength of Cu 1.5496 Å, β = FWHM (full width at half maximum) and θ= Bragg's diffraction angle.

The crystallite size is found to be 10.3nm.Further absence of sharp peak in fig.2 indicates destruction of crystallite cellulose when the LC fiber is irradiated with gamma . Exposure to gamma irradiation produces ions in the material which can initiate chemical reaction and cleavage of chemical bonds leading to degradation of the cellulose. Also the PLA polymer chains are poorly ordered due to the rapid cooling during injection molding while fabricating the composite materials leading to the amorphous nature of the composites .

3.1. Effect of frequency on dielectric constant of matrix and composites

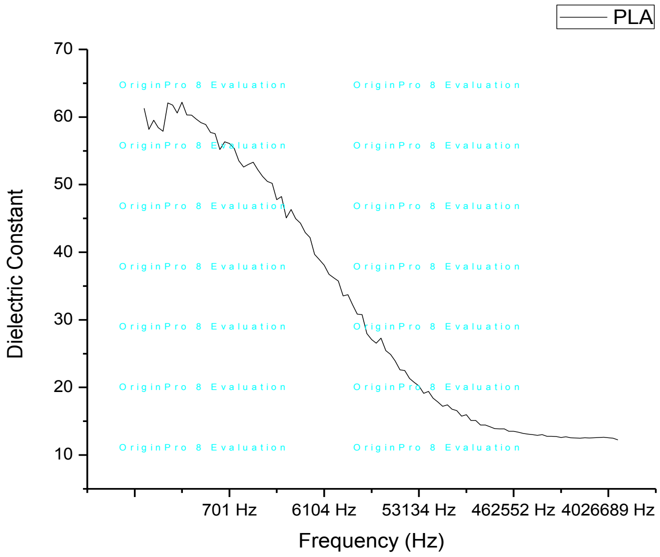

Fig.3. Dielectric constant of PLA matrix with variation in frequency

The dielectric constant of a material is a measure of polarization of the medium when the medium is subjected to an external electric field. A higher value of dielectric constant implies greater polarization of the medium. The different types of polarizations possible in a composite material may be electronic polarization, atomic polarization, orientation polarization and interfacial polarization. For heterogeneous materials like composites the interfacial polarization is due to differences in conductivities of the LC fiber and PLA matrix. The effect of interfacial polarization is noticeable at low frequency resulting in high dielectric constant. Low frequency leads to larger time interval ensuring complete orientation of polar molecules for which orientation polarization is high at low frequencies. Thus high dielectric constant at low frequency is due to interfacial and orientation polarization.

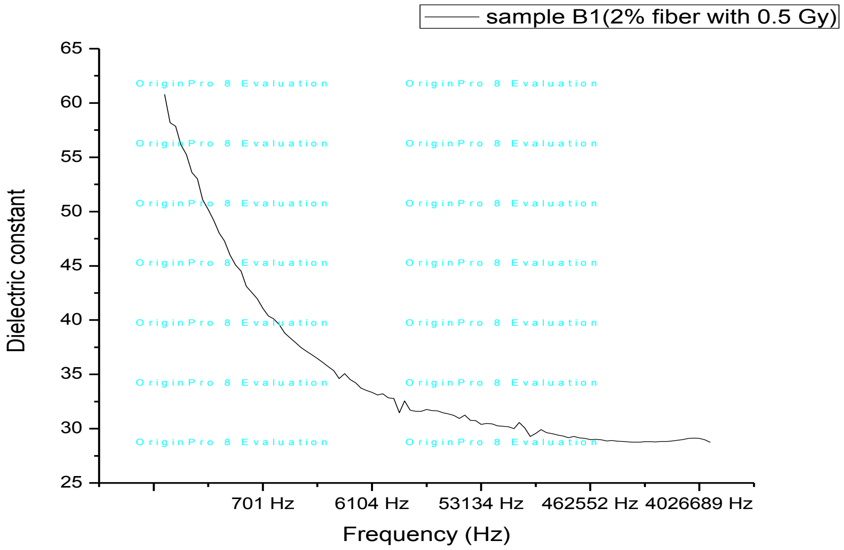

Fig.4. Dielectric constant of composite sample B1 (PLA with 2%fiber radiated at 0.5Gy) with variation in frequency

Figure 3 and Figure 4 depict the frequency dependence of virgin PLA matrix and composite sample B1 (PLA matrix reinforced with 2% LC fiber irradiated at 0.5Gy) respectively. PLA contains ester linkage on its polymer chain and the ester is a polar molecule. In addition, PLA contains polar hydroxyl groups.The presence of polar hydroxyl groups and ester contribute for high dielectric constant of PLA.In both PLA matrix and composite, the material's net polarization and hence its dielectric constant drops with increase of frequency. With increase in frequency, the time interval decreases and the polar molecules are not able to orient properly in accordance with external electric field. The dielectric constant of virgin PLA decreases from 61 at 100 Hz to 10 at 100 MHz.

Whereas the dielectric constant of the composite sample B1 decreases from 61 to 30 in the same frequency range.

3.2 Effect of gamma irradiation dose on dielectric constant

Table 1 betokens the values of dielectric constant of virgin PLA and three composite samples B1, B2 and B3 at frequencies 100 Hz and 1000 Hz.

Table 1. Values of dielectric constant of matrix and composite samples at different frequencies and irradiation dose

Sample	Dielectric Constant	
	At 100 Hz	At 1000 Hz
B0 (virgin PLA)	61	52
B1 (PLA with 2% fiber irradiated with gamma ray of 0.5Gy)	60.80	38.808
B2 (PLA with 2% fiber irradiated with gamma ray of 1.0Gy)	97.15	80.2875
B3 (PLA with 2% fiber irradiated with gamma ray of 2.0Gy)	92.437	78.825

Table 1 depicts that, the dielectric constant for PLA matrix (sample B0) at 100 Hz is 61, which does not change for the samples B1 with gamma irradiation dose of 0.5Gy. However, the dielectric constant increases from 61 in virgin PLA matrix to 97.15 in sample B2 where the irradiation dose on fiber is 1.0Gy and to 92.437 in sample B3 with irradiation dose on fiber is 2.0Gy. The dielectric constant increases by 59.26% when LC fiber irradiated with 1.0Gy gamma is reinforced. The table further detects decrease in dielectric constant of samples by increasing frequency. The 59.26% increase in dielectric constant at small irradiation dose of 1.0Gy is an important result achieved. When the LC fibers are exposed to gamma irradiation there is breakage of polymer chains of cellulose present in the fiber due to which more and more polar groups are revealed leading to increase of dielectric constant.

3.3 Effect of fiber loading on dielectric constant of matrix and composites

Table 2 shows the effect of wt of LC fiber in PLA matrix on dielectric constant

Table 2. Values of dielectric constant of matrix and composite samples at different fiber loading

Samples	Dielectric constant at 100 Hz
B0 (virgin PLA)	61
B2 (PLA with 2% fiber irradiated with gamma ray of 1.0Gy)	97.15
B5 (PLA with 5% fiber irradiated with gamma ray of 1.0Gy)	219.9
B8 (PLA with 10% fiber irradiated with gamma ray of 1.0Gy)	126.15

From table 3 the dielectric constant of virgin PLA is 61 at 100Hz which increases when LC fiber is reinforced to form composite materials. The presence of polar hydroxyl groups in the backbone of LC fiber further enhances the dielectric constant of composites. With increase in wt of fiber in PLA matrix, number of polar molecules increases leading to increase of the dielectric constant of the composite. The dielectric constant of 61 in virgin PLA increases to 219.9 in sample B5 when 5% LC fiber is loaded in the matrix.

3.4 Effect of frequency on dielectric loss of matrix and composites

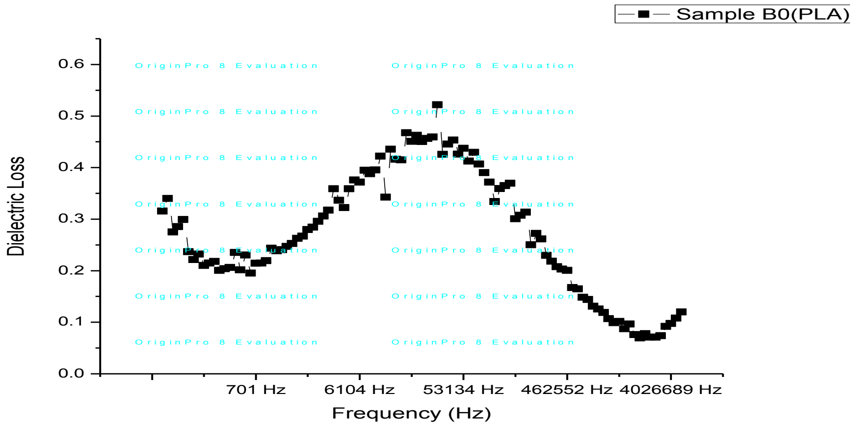

Fig.5. Variation of dielectric loss with frequency for PLA matrix

The variation of dielectric loss with frequency of the virgin PLA matrix is shown in fig. 5. The dielectric loss is minimum in lower frequency region because there is sufficient time left for the molecules to align according to external alternating electric field. But when the frequency of external electric field increases, the time decreases leading to difficulties in alignment of molecules and hence dielectric constant decreases followed by increase in the dielectric loss. The loss is maximum at a particular frequency known as resonance frequency. Beyond resonance frequency, the loss factor decreases with increase on frequency. Table 4 betokens the effect of irradiation dose on dielectric loss factor.

Table 4. Values of dielectric loss with variation with irradiation dose

Sample	Dielectric loss	
	At 100 Hz	At 1000 Hz
B0 (virgin PLA)	0.31559	0.23865
B1 (PLA with 2% fiber irradiated with gamma ray of 0.5Gy)	0.51106	0.20397
B2 (PLA with 2% fiber irradiated with gamma ray of 1.0Gy)	0.22299	0.09996
B3 (PLA with 2% fiber irradiated with gamma ray of 2.0Gy)	0.19626	0.08573

With increase in irradiation dose on the fiber more polar molecules present which increases the dielectric constant and conductivity of the sample. Increase in conductivity leads to decrease in dielectric loss with increase in irradiation dose. It is evident from table 4 that the dielectric loss is minimized with addition of both gamma irradiated irradiated LC fibers.

3.5. Effect of fiber loading on dielectric loss of PLA matrix and composite samples

Table 5

Samples	Dielectric loss at 100 Hz
B0 (virgin PLA)	0.31559
B1 (PLA with 2% fiber irradiated with gamma ray of 0.5Gy)	0.51106
B4 (PLA with 5% fiber irradiated with gamma ray of 0.5Gy)	1.36
B7 (PLA with 10% fiber irradiated with gamma ray of 0.5Gy)	1.21948

Table 5 predicts that the dielectric loss factor is minimum at 0.3 for virgin PLA matrix (sample B0) and its true for all frequencies. However when PLA matrix is reinforced with irradiated LC fibers, loss factor for sample B1(2% fiber) , sample B4(5%fiber) and sample B7 (10% fiber) increased to 0.57, 1.36 and 1.21 respectively at 100Hz. As wt of LC fiber increases in the matrix, the number of polar groups also increases. It accounts for higher interfacial and dipole orientation polarization and higher losses. The moisture present in the LC fiber contributes for dipole and interfacial polarization and it accounts for higher loss factor values of the composites at lower frequencies. Interfacial polarization is due to the movement of charge particles across the boundaries of the two phases. It generates a large effective dipole moment due to large charge displacements. The dielectric losses are therefore huge due to internal friction which cause higher losses with increase in wt of fiber in the matrix.

4. Conclusion

Values of dielectric constant, dielectric loss factor of virgin PLA matrix along with composites made from gamma irradiated LC fibers reinforced with PLA matrix were experimentally found out. Dielectric constant of all the samples decrease with increase in frequency, however increase with increase in fiber loading and irradiation dose. With increase in irradiation dose, there is more exposure of polar –OH groups present in the LC fiber leading to increase in dielectric constant. The dielectric constant of virgin PLA was increased by 260% i.e from 61 to 219.9 with reinforcement of gamma irradiated LC fiber.This can be considered as a very important finding.

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