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Comparative study of XRD patterns of chemically treated, 6 MeV electron beam irradiated, 6 MV photon beam irradiated, and plasma exposed fibers of *luffa cylindrical*

C PARIDA*[1] and B MALLICK[2]

[1]Department of Physics, OUAT, Bhubaneswar-751003, Odisha, India
[2]Institute of Physics, Bhubaneswar-751004,Odisha,India
**sivaji_1976@yahoo.co.in*

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Abstract. This paper compares the effect of chemical treatment, 6 MV photon beam , 6 MeV electron beam and plasma exposure on the structural properties of fibers of *luffa cylindrica (LC),* a common tropical fruit , rich in cellulose using X-ray diffraction pattern (XRD). There are no XRD peaks found in the spectra of photon beam irradiated LC fiber indicating complete destruction of cellulose crystallinity..Both crystalline and amorphos cellulose are detected in the XRD patterns of electron beam irradiated, plasma irradiated and chemically treated LC fibers. Crystallite size, percent of crystallinity are evaluated in the treated LC fiber.

Keywords- Cellulose; electron beam; photon beam; medical LINAC

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1. Introduction

Research in recent years has been focused on biodegradable composite materials to tackle the issues of global warming,. In order to achieve the goal of recyclable and biodegradable composites, natural plant fibers are preferred to be used as reinforcements in composite materials. Cellulose is the major component of all natural fibers along with hemicellulose and lignin. Cellulose is the most abundant natural long chain polymer which is used as a renewable source in a wide range of applications like veterinary foods, production of wood , electronic paper, diaphragm, organic light emitting diodes, scaffolds for tissue engineering etc.. It is a linear polysaccharide having thousands of glucose units connected by β-(1, 4)-D-glycosidic linkage [1]. The Young's modulus of cellulose is 137 GPa and this high modulus of the cellulose is due to molecular alignment and dense

packing in the unit cell. Due to this high youngs modulus, natural fibers are now capable of replacing synthetic fibers as reinforcements in polymer matrix producing green composites. These green composites are completely biodegradable in nature having advantages such as recyclability, low cost, low density, high modulus and strength. However the use of natural fiber is limited due to poor thermal stability, poor bond strength , moisture absorption having high affinity to water leading to poor interfacial bonding due to presence of hydroxyl(-OH)group in its back bone [2]. Therefore continuous research is going on to minimize the disadvantages of natural fibers. Thus to make the fibers more hydrophobic and for enhancing the bonding between the fiber and the polymer matrix, those are exposed to various treatments such as chemical treatment and physical treatments before reinforcement in composite materials.

Chemical treatment is a very common method and it breaks down the composite fiber bundle into smaller fibers leading to reduction in fiber diameter. The reduction in fiber diameter increases the aspect ratio (width/height) which leads to the development of a rough surface topography that results in better fiber-matrix interface adhesion . Further chemical treatment increases the number of possible reactive sites and allow better fiber wetting. It also has an effect on the chemical composition of the fibers, degree of polymerization, and molecular orientation of the cellulose crystallites. Physical treatments such as ion beam irradiation, photon beam irradiation, electron beam irradiation, plasma exposure etc are favoured to chemical treatments because of less toxicity, economically viable, environment friendly [3]. Presently radiation is considered as a very important tool to improve material properties by surface modification. The gamma ray or photon beam is the flow of energy with sped of light where as the electron beam is flow of electrons with energy [4]. The radiation is classified into two parts one is electromagnetic rays like x-rays, gamma rays etc and the other is corpuscular rays like alpha rays, electron beam etc. . However Photon and electron beam irradiation requires more energy (>3MeV) for modifying the surface of the fiber. Such high energy irradiation may cause dissipation of excess heat due to breakage of C-C, C-H bonds during breakdown of cellulose. In that context plasma treatment on natural fiber is also preferred as a convenient physical method. It's a well- kept process , without use of chemicals and water ,requires less energy , reduces the use of hazardous substances and avoid generation of waste , low operating cost and finally time saving . In plasma treatment gaseous plasma like nitrogen, oxygen, helium, methane, ethylene, air,

ammonia etc can be used. N_2 gas plasma is preferred for its low ionization level and low penetrating power.

The current research uses the fruit of *Luffa cylindrica* (LC), which is a common tropical fruit of Odisha . The LC fiber is commonly called sponge gourd, bath sponge or dish cloth gourd. It is a member of cucurbitaceous family. The fibers are composed of 60% cellulose, 30% hemicellulose and 10% lignin[5] . The absence of a detailed study of its characteristics and properties in the scientific literature and high % of cellulose makes this fiber material our topic of research The novel aspect is in terms of modification of surface of LC fibers by chemical treatment, high energy 6MeV electron beam , 6 MV photon beam irradiation and plasma exposure, before using these fibers as reinforcement.. The purpose of the present work is to study and compare the effect of various treatments on the fibers of LC.

Many compatible and contradictory results were discussed by researchers before. Yasko Kodama et. al in 2016 reported that gamma irradiation had no effect on the cellulose peak intensities with no change in the crystalline index of cellulose [6]. However the effect of gamma irradiation (10 kGy/hr) on cotton cellulose was studied by E. Takacs et. al. in 2000 and they reported transformation of crystalline cotton cellulose to amorphous cellulose due to high penetrating power of gamma rays [7]. Han et. al. in 2006 reported that electron beam irradiation is effective in the formation of active functional groups and removal of impurity from the fiber surface leading to enhanced adhesion with polymer matrix [8]. Treatment of microcrystalline cellulose (MCC) with high energy (3MeV) electron beam resulting in decrease in molecular weight and crystillinity was discussed by M. Driscoll et. al. in 2009 [9].

2. Experimental

2.1 Chemical treatment

The dried LC fibers are subjected to chemical treatment such as treatment with alkali followed by bleaching and acid hydrolysis. Every step of chemical treatment to LC fiber is discussed as follows.

2.1.1 Alkali treatment

For alkali treatment, the LC fibers were soaked in a 5% NaOH solution at 80^0C for 1h. The hydrogen bonds are normally formed between the –OH groups of the cellulose molecules and –OH group of matrix. But in wet condition the hydrogen bonds are formed between the –OH groups of

the cellulose molecules and water rather than between –OH group of matrix. Hence, the composites reinforced with such fibers undergo swelling and shrinkage in moist environments affecting their dimensional stability. To improve interfacial bonding and to reduce moisture absorption the LC fibers are treated with alkali. During alkaline treatment given to the LC fibers, the hemicelluloses and lignin present in the LC fibers are eliminated. In this way the number of —OH groups present in the fiber is reduced leading to increase in hydrophobicity of fibers which strengthen the bonding between fiber and matrix. There is disruption of hydrogen bonds in the network structure of cellulose due to the alkali treatment and it increases the surface roughness and the adhesion between fiber and matrix. Addition of aqueous sodium hydroxide (NaOH) to natural fiber also promotes the ionization of the hydroxyl group to the alkoxide .

$$\text{Fiber} - \text{OH} + \text{NaOH} \rightarrow \text{Fiber} - \text{O} - \text{Na}^{+} + \text{H}_2\text{O}$$

2.1.2 Bleaching

The alkali treated LC fibers were bleached with 2% sodium hypochlorite solution. The mixture was continuously stirred for 2h at 80^{o}C. The colour of the bleached LC fibers appear yellowish from black. Bleaching is mainly used with the objective of increasing whiteness of the fibers. Lignin and extractives etc contribute to the darkness and are removed during bleaching. This treatment has the main objective to attack and remove lignin. Despite the fact that lignin increases the stiffness of the fiber, it is inflexible and prevents reorientation of fibers required for proper transfer of load .

2.1.3 Hydrolysis

The bleached LC fiber/water suspension was prepared and kept on an ice bath.H_2SO_4 was added slowly under continuous stirring to the suspension placed in an ice water bath, until the final concentration of 60% H_2SO_4 was reached. The obtained suspension was then heated at 45°C under continuous stirring for 2h. In order to remove excess acid the mixture was washed and centrifuged using an ultracentrifuge at 30^{o}C for 20 minutes with 7000 rpm. Acid hydrolysis leads to the isolation of micro and nano-fibers with a high degree of crystallinity by removing the amorphous regions of the raw cellulose material. Acid hydrolysis decreased the degree of polymerization (DP) and molecular weight of the bleached fibers.

2.2. Electron beam irradiation

Electron beam of energy 6 MeV was obtained from the medical LINAC (Millenium True Beam linear accelerator, Varian) installed in Health Care Global Panda Cancer Hospital, Cuttack, Odisha, India. The LC fiber was mounted below cotton gauge of 3 inch thickness and was irradiated with a rate of 600MU/min to attain a dose of 1Gy.

2.4 Photon beam irradiation

The LC fibers were subjected to treatment with photon beam. X-ray photon of energy 6MV was extracted from the medical LINAC of Hemalata Hospital and Research Centre (HHRC), Bhubaneswar, India for the *LC* fibre irradiation work. The fibers were irradiated at1Gy .

2.5 Plasma exposure

LC fiber was exposed to N_2 cold gas plasma vacuum reactor installed at IOP Bhubaneswar, Odisha, India. The LC fiber was irradiated with nitrogen cold plasma for 120 sec at 2kV.

2.6. X-ray diffraction pattern

The crystallinity index and crystallite sizes of the irradiated fibers were obtained using WXRD/SHIMADZU/JAPAN at a scanning speed of 10˚/minute from Bragg's angle 10˚ to 80˚ at room temperature of 26˚C .

3. RESULTS AND DISCUSSION

3.1 XRD of chemically treated LC fibers

The fig 1 depicts the XRD patterns of chemically treated LC fiber. It shows two intense peaks at 15.87^o and 22.86^o. The peak at 15.87^o corresponds to amorphous cellulose or cellulose II of [101] crystallographic plane and the peak at 22.86^o correspond to crystalline cellulose [cellulose I] of [002] crystallographic plane[4]. The presence of these peaks indicate that the chemically treated LC fibers are partly crystalline and partly amorphous in nature. Cellulose is a long chain polymer with large number of identical monomers known as glucopyranose units. The unit cell of glucopyranose is monoclinic with two principal planes of reflection such as [002] and [101]. The amount of crystalline cellulose or cellulose I in the total cellulose is expressed by X-ray crystallinity index as

defined by equation $I_C(\%) = \frac{I - I_{am}}{I} \times 100$. I and I_{am} denote the intensity of 002 crystalline plane and intensity of the 101 amorphous phase respectively. The

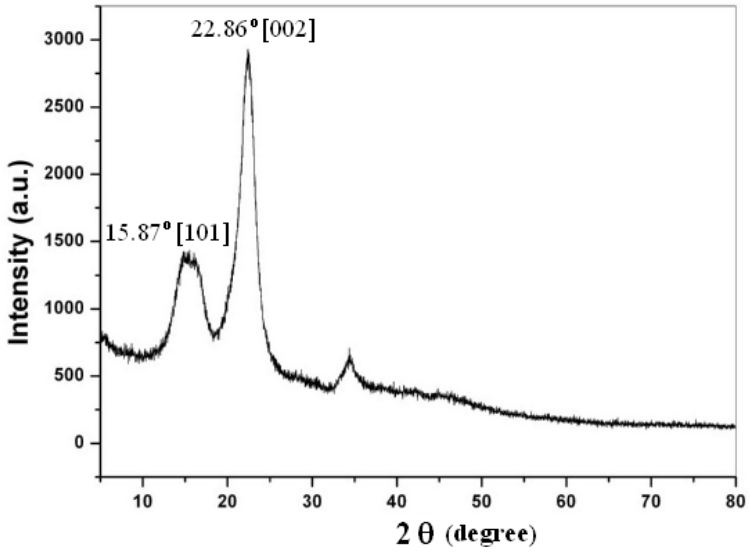

Fig.1.: XRD pattern of chemically treated LC fibers**.**

crystallinity index was found to be 60.3%. The high crystallinity index of cellulose in chemically treated LC fiber explores the possibility of increasing the crystallinity of poymer composites with reinforcement of these fibers**.** Further the crystallite size was obtained from Scherrer's formula,

$$D = \frac{k\lambda}{\beta \cos\theta}$$

and found to be 44nm.Here k is the shape factor which is 0.9, λ is the wavelength of incident X-rays which is 1.54 A^o.

3.2 XRD of electron beam irradiated LC fiber

The fig 2 depicts the XRD patterns of electron beam irradiated LC fiber. Cellulose is mainly crystalline and is characterized by a sharp XRD peak around 22^0. However when the LC fiber is treated with electron beam of 6MeV the sharp crystalline peak is replaced by a broad scattered peak at 22.7 ^{0}denoting crystalline phase of cellulose and 14.9 ^{0}denoting the amorphous phase. The presence of broad peak suggests that irradiation cleaves the crystalline region by breaking the glycosidic linkage and converts it into an amorphous phase.The Lc fiber treated

with electron beam is more amorphous compared to chemically treated LC fiber High amorphous nature implies increase of roughness of fiber surface motivating better fiber matrix adhesion. Crystallinity index of the fiber was obtained to be 38% only and the crystallite size at 22.7^{o} is found to be 36 nm for electron beam irradiated LC fiber.

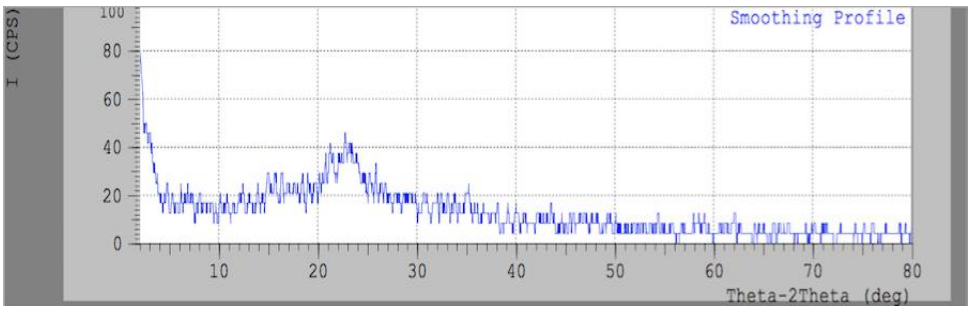

Fig 2. XRD spectra of electron beam irradiated LC fiber

3.3 XRD of photon beam irradiated LC fiber

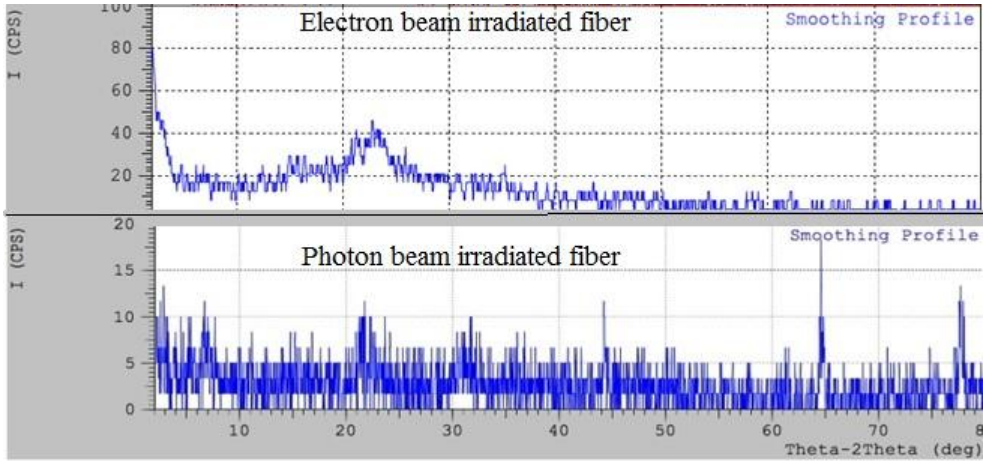

Fig.3. XRD patterns of electron beam irradiated and photon beam irradiated LC fibers

Fig 3 depicts the XRD spectra of both 6 MeV electron beam and 6 MV photon beam irradiated LC fiber. It is noticeable from fig.3 that there is much change in crystalline nature of cellulose present in both electron beam and photon beam

irradiated LC fiber compared to that of chemically treated LC fibers. Unlike electron beam irradiated LC fiber, there is no distinct peak for LC fiber irradiated with photon beam. That indicates the complete destruction of both crystalline and amorphous cellulose due to chemical reaction occurred between the fiber and high energy X-ray photons. But electron beam has comparatively less penetration ability. Due to which crystalline cellulose is converted to amorphous cellulose instead of complete destruction and therefore a broad amorphous peak around 22.7^{o} is detected in the LC fiber exposed to electron beam .Absence of any peaks in XRD patterns of gamma irradiated LC fiber indicates complete breakage of glycosidic linkage and loss of crystallinity [9]. As the photon beams are highly penetrative in nature, their influence is more prominent in destroying the crystallinity. This leads to increase in surface roughness and surface area motivating better bonding between gamma irradiated LC fiber and polymer matrix.

3.4 XRD of plasma irradiated LC fiber

XRD pattern of LC fiber exposed to plasma for 120 sec at 2kV is given in Fig.4. It is characterized by crystalline peak of cellulose at 22.46^{0} .The peak at 22.46^{0} for cellulose appears sharp compared to broad peak at 22.7^{0} in electron beam irradiated LC fiber as shown in fig.3. This indicates the LC fiber exposed for 120 sec at 2kV is more crystalline compared to electron beam irradiated LC fiber. Again the crystallinity index $\boldsymbol{I_C(\%)}$ of the fiber was evaluated is 66.35% .

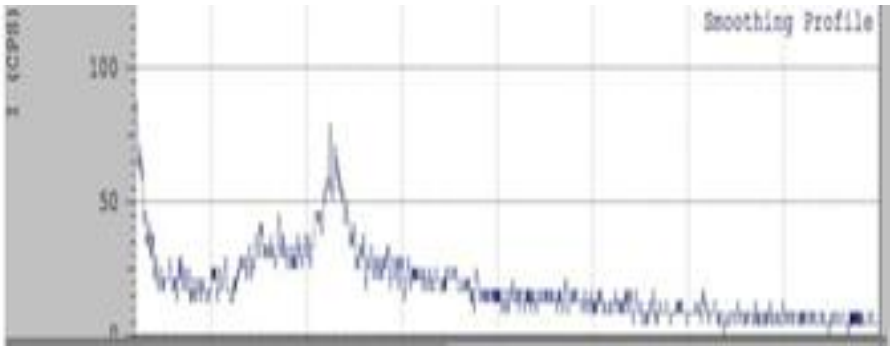

Fig 4. XRD pattern of plasma irradiated LC fiber

The crystallite size, percent of crystallinity and interplanar spacing for crystalline cellulose present in LC fiber with different treatments are given in tabular form in table 1.

Table 1. Crystallite size, percent of crystallinity and interplanar spacing in LCfiber exposed to various treatments

Nature of LC fiber	Crystallite size in nm	Percent of crystallinity in %	Interplanar spacing(d) in A^0
Chemically treated LC fiber	70	60.3	3.8855
Electron beam irradiated LC fiber	43.8	38	3.90010
Photon beam irradiated LC fiber	-----	-------	--------
Plasma irradiated LC fiber	27.18	66.35	3.95231

The crystalline structure of cellulose present in natural fiber has been studied since its discovery in the 19th century. Two different crystalline allomorphs have been identified by the X-ray diffraction (XRD) patterns of treated LC fiber *viz.* cellulose I and cellulose II . Cellulose I is the crystalline form and is most abundant form found in nature. Cellulose crystallites are thought to be imperfect, and thus a significant portion of the cellulose structure is less ordered. This portion is often referred to as amorphous or Cellulose II . Currently, cellulose I is receiving increased attention due to its potential use in bio energy production .Percent crystallinity has been used to describe the relative amount of crystalline material in cellulose. Table 1 betokens that LC fiber treated with photon beam of 6MV is completely amorphous and LC fiber treated with plasma is having maximum crystallinity of 66.35%. Both the crystallographic planes are distinctly visible and prominent in chemically treated LC fiber.

4. Conclusion

Four efficient methods such as chemical treatment, electron beam irradiation, gamma irradiation and plasma exposure to modify the properties of LC fibers are discussed. It is found that photon beam completely destroyed the crystalline structure of cellulose present in the fiber due to its highly penetrating nature. Whereas in case of electron beam irradiated fiber, only 38% crystallinity is reported. The percent of crystallinity in chemically treated LC fiber and plasma

exposed LC fiber are 60.3% and 66.35% respectively. Thus the crystallinity index or %of crystallinity of cellulose varies from 0%in gamma irradiated LC fiber to maximum of 66.35% in plasma exposed LC fiber.Amorphous and crystalline cellulose both have different applications in various fields can open the possibilities of using these irradiated fibers in biomedical industry. This variation in crystallinity of cellulose can be explored while fabricating composite materials using LC fibers as reinforcement in composite materials. . These low crystallinity nature of composites are features of good bone implant and bone bonding. They may provide the proper boney substrate when used with LC frame work.

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