Effect of gamma irradiation on mechanical properties of poly (lactic) acid–*luffa* fiber composites

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DOI: 10.5185/amp.2018/403
www.vbripress.com/amp

Abstract

Modification of surface of natural fiber by gamma irradiation is an effective and economical technique and of viable interests in the terrain of biocomposites. The response of doses (0.5 Gy,1Gy and 2 Gy) of gamma irradiation of 6MV energy on the structural, tensile and flexural properties of composites using poly lactic acid (PLA) and fibers of *luffa cylindrical* (LC) is studied. Preliminary results suggests promising mechanical properties. After reinforcement of irradiated LC fiber, the tensile strength and flexural strength of the virgin PLA matrix increases by 60% and 155% respectively. The E-modulus of the composites are also heightened with addition of irradiated fiber up to the limit of 1 Gy of irradiation dose and then decreases with higher dose of irradiation. Furthermore the tensile strength and flexural strength of the composites increases with incorporation of very low content of LC fiber up to 2wt% and decreases with higher loading of fibers (5wt% and 10wt%). Modulus of composites is enhanced with increase in wt of fiber content in the composites. Moreover beefore reinforcement the LC fibers are modified with Ca salts in order to explore the use of these composites in biomedical territory.

Keywords: LC fiber, PLA, tensile strength, flexural strength, gamma irradiation.

Introduction

To tackle the issues of global warming and disposal of final product, research in recent years has been zoomed in on biodegradable composites. In order to realize the goal of recyclable and biodegradable composites, natural fibers became apparent as the choice to be used as reinforcements in composite materials. The present research uses the fruit of Luffa cylindrica (LC), a common tropical fruit of Odisha as reinforcement in poly lactic acid (PLA) producing green composites. PLA is a completely biodegradable and bioactive polymer which is derived from renewable resources like starch **[1]**.The innovative aspect of this current work is modification of surface of LC fibers by Ca salts, before using these fibers as reinforcement. The modification of the surface of the fiber by Ca salts explores the possibility in using these composites in bio medical applications. PLA is hydrophobic and LC fibers are hydrophilic **[2]**. They are thermodynamically incompatible and it leads to poor mechanical properties of the composites. As the chemical nature of fiber and matrix are different, various treatments like chemical treatment, electron beam irradiation, gamma irradiation, plasma treatment, UV exposure etc are given to the fiber before reinforcement to improve compatibility between LC fiber and PLA matrix.

Ionizing radiation on natural fiber is an assuring technique for increasing fiber matrix adhesion. It has advantages like saving chemicals, environment friendly, reduction of time etc. Gamma rays are electromagnetic radiation of very short wavelength about 0.01 A^0. They are highly piercing in nature and induce ionization and excitation of molecules of irradiated sample. The greater part of chemical changes of irradiated materials results from electron-electron interactions. When a radiation is besieged on a material, it causes ionization with ejection of secondary electrons. These secondary electrons cause further ionization. However if the radiation energy is not sufficient for ionization, it produces an excited molecule. This excited energy is mainly localized in weak bonds of the molecules. It eventuates the scission of bonds and free radicals are produced aftermath. Hence chemical changes occurring in a material exposed to gamma irradiation results in genesis of positive ions, electrons, excited molecules and free radicals. LC fibers are composed of 60% cellulose, 30 % hemicelluloses and 10 % lignin**[3]**. Celluloses are long chain polymers composed of identical units known as gluco pyranose. unit is linked to its neighbor by glycosidic linkage**[4]**. Cellulose comprises of both amorphous and crystalline region. Radiation influences both crystalline and amorphous regions of cellulose while lignin is radiation resistant. The amorphous region posseses random configuration and when irradiated by gamma, indivisual molecules start slipping over one another. This movement cause scission of the linkage. However at the same time cross linking introduces conjuction between molecular chains mainly in the amorphous region and it prevents further scission.

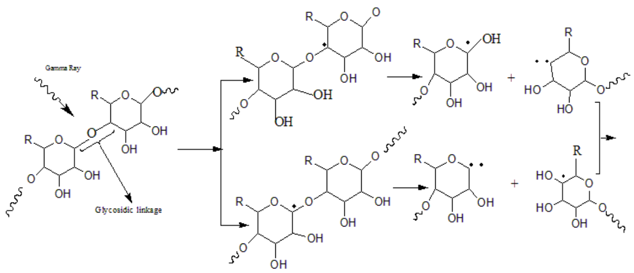

Fig. 1. Chemical changes in cellulose due to gamma irradiation.

Fig. 1 depicts the chemical changes occurring in cellulose when the natural fibers are gamma irradiated. Free radicals are formed on the gamma irradiated fibers i.e electrons are available on the surface of the molecules. As they are very much reactive in nature, the formation of free radicals supplements further chemical reactions. The aromatic rings of the gluco pyranose units are bulky, due to which electrons cannot come easily to the surface. Hence free radicals(R) are formed only on either sides of the glycosidic linkage. With increase in the irradiation dose the number of free radicals and number of individual chains from celluose is increased. Here after breaking the bond with carbon atom, oxygen atom is forming a bond with H-atom and the cellulose is getting oxidised, which causes splitting of the chain. The splitting of this glycosidic bond is the main reason for depolymerisation/degradation of cellulose and formation of reducing sugar e.g glucose.

Typically when a polymer is irradiated with gamma, there is struggle between scission and cross-linking. If chain scission reaction predominates crosslinking, then the material degrades. The degradation mechanism holds true for structures like cellulose which contains tetra substituted carbon atoms. Due to degradation of cellulose into fragments, surface area increases which enhances the bonding between fiber and matrix.

There has been a series of researches published in recent years on the effect of radiation on natural fibers and their composites. G. Rajesha Shetty et al in 2016**[5]** reported the consequence of gamma irradiation (100KGy, 200KGy) on methyl cellulose extracted from silk fibroin. The results revealed that the irradiation didn't affect the crystallographic structure of cellulose but changed the optical properties. Raghabendra Sipreet B.S et al in 2015**[6]** probed the influence of gamma irradiation (1KGy to 20 KGy) on the composites using bis phenol – A as matrix and jute with pineapple fiber as reinforcement. The composite irradiated with 5KGy dose delivered maximum tensile strength (23.91MPa) and maximum young's modulus (3279 MPa). The effect of gamma irradiation (10KGy to 100 KGy) on the morphology, thermal behavior and mechanical properties of wood-polypropylene composites has been investigated by Diène NDIAYE et al in 2014**[7].** The results indicated that gamma radiation improves the mechanical properties while the thermal stability is decreased. It was reported that up to a certain limit of gamma irradiation doses (50KGy), the mechanical properties of composites such as tensile strength and bending strength are increased. Beyound this the values remain constant. Maximum tensile strength was reported to be 13.75MPa at 50 KGy. Ke-qin Wang et al in 2010**[8]** studied the influence of gamma irradiation (0KGy to 200 KGy) on cellulose derived from phragmitis communistrim. They reported that irradiation caused fragmentation of cellulose fibers and their structures were damaged. Degree of crystallinity of cellulose fibers dropped from 78.4% to 40.7%. R.Sanchez-Orozo et al in 2009**[9]** expressed the influence of gamma irradiation (600 KGy, 1800KGy, 3500KGy) on degradation of orange peels. They revealed that chain scission, alteration of structures of irradiated samples and breakage of glycosidic linkages due to irradiation.

There is lack of scientific resources about the gamma irradiated LC fiber and its composites with PLA. The main objective of our research is to transform the low priced, readily available agricultural waste, *i.e.* fruit of LC in to a high value product. The specific purpose of this present work is to study the effect of very low dose of irradiation (0.5 Gy, 1Gy and 2 Gy) of 6MV energy on the performance of LC fiber and PLA composites.

Experimental

Materials

Poly lactic acid (PLA) of grade 4042D (molecular weight Mw ~ 600,000) was purchased from Nature Works, USA. The LC fiber was collected from local forest area. The chemicals such as calcium chloride ($CaCl_2 \cdot 2H_2O$, 97%), disodium hydrogen phosphate ($Na_2HPO_4 \cdot 2H_2O$, 99.5%), all of AR grade were procured from E. Merck, India.

Modification of surface of LC fiber by ca salt

The LC fibers were cut into small pieces of length around 2 cm, washed thoroughly to remove impurities like oil, dust etc. These were left for drying at 70˚C in vacuum oven for 20 minutes. The dried LC fiber was immersed in $CaCl_2$ solution for 12 h at room temperature of 30˚C to deposit Ca on its surface. The LC fiber modified with $CaCl_2$, were re-immersed in Na_2HPO_4 solution for 12 h at room temperature to deposit compounds of calcium phosphate over it**[10]**.

Physical treatment of LC fiber (photon beam irradiation)

The hydrophilic nature of the natural fibers leads to poor adhesion between fiber and matrix and this is the main drawback in fabrication of composites. In wet conditions, therefore, such composites show very poor mechanical properties. To improve interfacial bonding and to reduce moisture absorption, 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. These fibers were irradiated at three different doses 0.5Gy, 1Gy and 2 Gy. The irradiated fiber were then mixed with PLA in different wt proportion to form composites using injection molding technique.

Composite processing

Prior to use, the PLA pellets and LC fiber were dried under vacuum at 80˚C for 24 h. The polymer and fiber were mixed mechanically at 100 rpm with a micro-compounding molding equipment (DSM Micro 15 cc compounding system, DSM research, The Netherlands) 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. The PLA pellets and irradiated LC fibers with different doses are mixed in different wt proportion to produce 10 different composite samples for characterization. B0 is the virgin PLA. In B1, B2 and B3 samples, the PLA and 2% wt fibers are mixed with irradiation dose of 0.5Gy, 1Gy and 2Gy respectively. In B4,B5 and B6 samples , the fiber loading is at 5% and irradiation dose of 0.5Gy, 1Gy and 2Gy respectively .And finally in B7,B8 and B9 samples, the fiber loading is at 10% and irradiation dose of 0.5Gy, 1Gy and 2Gy respectively.

Wide angle x-ray diffraction

Ni filtered Cu Kα radiation having wavelength 0.1542 nm was generated at 40 KV and 35 mA using WXRD/SHIMADZU/JAPAN. The X-ray diffractograms were recorded from Bragg angle 10˚ to 80˚ at room temperature of 28˚C by goniometer equipped with scintillation counter at a scanning speed of 10˚/minute.

Measurement of mechanical properties

The tensile and flexural properties of the composite specimen were measured with Universal testing machine, (3382 Instron, UK) according to ASTM D638 and ASTM D790 respectively. System control and data analysis were performed using Datum software. All results given are the average values of five measurements.

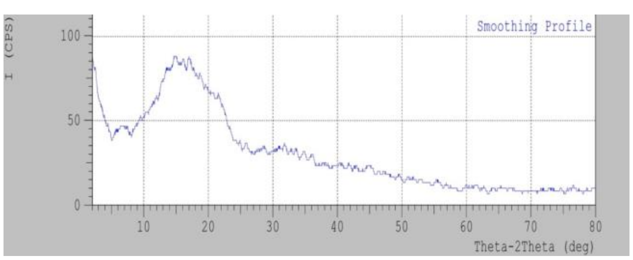

Fig. 2. XRD spectra of sample B5 (PLA with 5% fiber having irradiation dose 1 gray).

Results and discussion

Crystallinility index of cellulose in injection molded PLA-luffa fiber composite

XRD pattern of injection molded PLA reinforced with photon beam (1 Gy) irradiated LC fiber at 5 wt% (sample B5) is shown in **Fig. 2.** Cellulose is a high molecular weight linear polymer composed of D-glucopyranose units linked by β-1, 4-glycosidic bonds. Hydroxyl groups present in cellulose macromolecules are involved in a number of intra- and intermolecular hydrogen bonds, which result in various ordered crystalline arrangements. Cellulose normally posseses two different allomorphs, cellulose I and cellulose II. The peak around 15º corresponds to amorphous cellulose or cellulose II of [101] crystallographic plane and the peak around 22.86º correspond to crystalline cellulose [cellulose I] of [002] crystallographic plane[10].

XRD peak in fig b appears as a broad scattering peak indicating the amorphous region of composite. Absence of a sharp peak around 22˚, which portends crystalline cellulose-I, corroborates the fact that the crystallite cellulose degrades due to irradiation of gamma on the fiber. The crystallinity of the fiber is reduced after gamma irradiation. Gamma ray produces ions in the fiber which can initiate chemical reaction and cleavage of chemical bond such process degrades the cellulose. Hence gamma irradiation disturbs the crystalline structure and allows the penetration of chemicals into the crystalline regions to reform chemical bonds. In addition the PLA chains are poorly ordered due to the rapid cooling during injection molding method and it supplements the amorphous nature of the composites.

Effect of irradiation on tensile stress of LC fiber composites

It is acclaimed that the strength of reinforcement (LC fiber) is actually responsible for the mechanical properties of the composites. Therefore study of variation of the strength of the composite with different irradiation doses on fiber and wt of fiber in the matrix is crucial.

From **Table 1** it is ascertained that the tensile strength of all the composite samples (B1-B9) increase in comparison to virgin PLA(B0).

Table 1. Values of tensile stress, tensile modulus at maximum load of composites at different irradiation doses.

Sample	Tensile stress at maximum Load(MPa)	Tensile Modulus (MPa)
B_0	30.425	2242.61
B_1	48.340	2275.53024
B_2	49.025	2583.02746
B_3	48.859	2349.40529
B_4	45.949	2411.51390
B_5	45.393	2285.33897
B_6	46.133	2576.19762
B_7	41.920	2415.77892
B_8	39.475	2623.98510
B_9	43.268	2218.76354

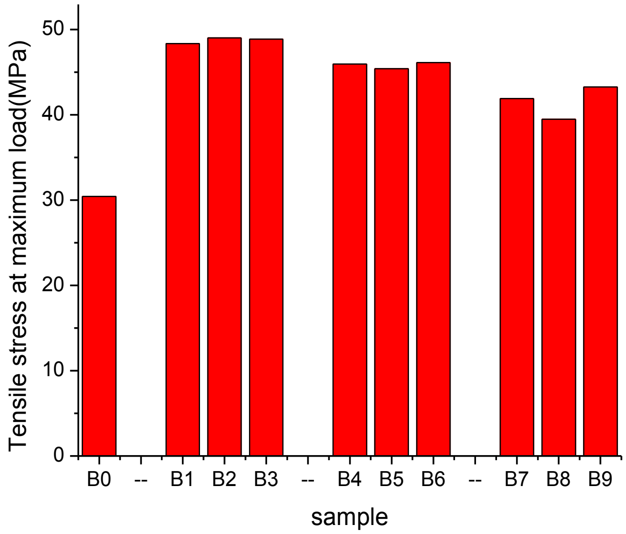

Fig. 3. Variation of tensile stress with irradiation dose.

The tensile stress at maximum load for virgin PLA is 30.425MPa. The maximum tensile stress is registered as 49.025 MPa for sample B_2 (PLA+2% Fiber with 1 Gy irradiation). After reinforcement of irradiated LC fiber, the tensile stress is increased upto 60%. This increase in strength may be attributed to fragmentation or degradation of cellulose and interaction of active hydroxyl group (-OH) present in the cellulose of LC fiber. This enhancement may also be due increase in oxygen containing functional group (-OH), which plays an important role in improving the degree of adhesion at interface between fiber and matrix. However there is no significant change in the tensile stress with variation in irradiation doses. Similar results are observed for flexural properties where the flexural stress is maximum at 93.036MPa for sample B_4 (PLA+5%Fiber with 0.5 Gy irradiation). Here the flexural stress increases by 155% compared to the virgin PLA.

Effect of irradiation on modulous of composites

Table 1 and **Table 2** portray that the value of modulus is minimum for virgin PLA (2242.61MPa for tensile and 3226.12MPa for flexural). It increases for all other composite samples. The maximum tensile modulus (2623.98MPa) is obtained when 10 wt% LC fiber composite is irradiated with 1 Gy dose with 17% increase compared to virgin PLA. There is no large variation in modulus of composites due to variation in irradiation doses. Similar trends are found for flexural properties as depicted in **Table 2**. When the gamma ray irradiated LC fiber is reinforced with the matrix PLA to form composite, the flexural modulus increases from 3226.12MPa in virgin PLA to 3718.904 MPa in B6(PLA+5% Fiber with 2 Gy irradiation) with 15% enhancement of modulus. Enhancement of modulus betokens better bonding between fiber and matrix due to gamma irradiation.

Table 2. Value of flexural stress at maximum load and flexural modulus of matrix and composites.

Sample	Flexural stress at maximum load(MPa)	Flexural modulus (MPa)
B_0	36.12	3226.12
B_1	91.17	3611.064
B_2	87.452	3433.678
B_3	93.036	3686.416
B_4	91.318	3682.318
B_5	88.702	3702.789
B_6	90.782	3718.904
B_7	87.109	3699.376
B_8	65.766	3354.63
B_9	71.875	3335.264

Effect of fiber loading on tensile stress

Fig. 4 betokens that tensile stress of all the composites are enhanced in comparison to virgin PLA. However when the wt of fiber in the matrix increases, tensile stress reduces. This may be due to inadequate dispersion of fiber in the matrix due to increased loading.

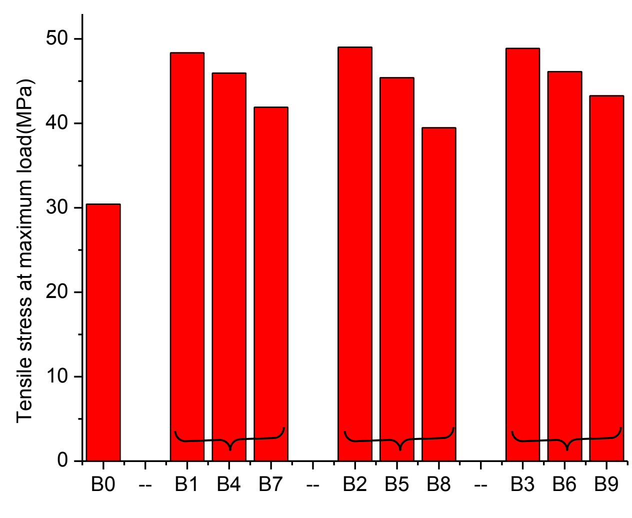

Fig. 4. Variation of tensile stress with fiber loading.

Effect of fiber loading on modulus of composites

As fibers are more rigid than the matrix, the enhancement in the modulus occurs after incorporation of fiber into the matrix. It increases the stiffness and reduces the ductile behavior of all the samples. But the modulus is decreasing with increasing in fiber loading. The proportion of fiber is more than that of PLA i.e there is more fiber surface and less polymer surface for stress transfer. Here the reinforcement fiber acts as a barrier to transfer the stress load from small portion of PLA matrix. Hence modulus reaches a plate value and starts decreasing with further reinforcement of fiber.

Conclusion

The maximum tensile modulus and flexural modulus of LC fiber - PLA composites are found to be 2.623 GPa (sample B_8, PLA+10%Fiber with 1Gy irradiation) and 3.718 GPa (sample B_6,PLA+5% Fiber with 2 Gy irradiation) respectively. Simlarly the tensile stress is increased by 60%, with maximum value of 49.025 MPa for sample B_2 (PLA+2%Fiber with 1 Gy irradiation). The flexural stress is increased by 155% compared to the virgin PLA with maximum value of 93.036MPa for sample B4 (PLA+5%Fiber with 0.5 Gy irradiation).

Incorporation of gamma irradiated LC fiber enhances the stiffness of the composites. There is improvement observed in strength and stiffness of the composites for very low dose of irradiation on LC fiber (0.5Gy, 1Gy, 2Gy). The increase in mechanical strength of composites with incorporation of irradiated LC fiber is an indication of enhanced chemical bonding between irradiated LC fiber and matrix. This fact is supported by results from XRD which shows degradation of cellulose enhancing fiber matrix adhesion. The composites using LC fibers having mechanical strength as mentioned above are suitable for use as low strength materials such as house panels, doors, windows, fiber board etc. .

Acknowledgements

The authors are grateful to Laboratory of Advanced Research in Polymeric Materials (LARPM) CIPET,Govt of India for synthesis and characterization of the samples.
This work is financially supported by UGC NEWDELHI(F PSO-021/15-16(ERO)), Govt of India.

Author's contributions

Conceived the plan: C Parida
Performed the expeirments: S Patra,C Parida,P chatterjee
Data analysis: C Parida, S Patra
Wrote the paper: C Parida, S Patra, K L Mohanta
Authors have no competing financial interests

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