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Effect of gamma radiation on the physicao-mechanical properties of gelatin-based films and jute-reinforced polymer composites

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International Conference on Applications of Radiation Science and Technology (ICARST 2017), 24 to 28 April 2017, Vienna, Austria

Background

The gelatin, a natural protein, biocompatible, biodegradable, edible, and soluble at the body temperature, which undergoes gelation at temperatures just above ambient. It is obtained by selective hydrolysis of collagen, which is a fibrous material that occurs in skin, bones and connective tissues of animals [1]. This biomaterial can be used as scaffolds in tissue engineering, and nanotechnology and micro-fabrication techniques applied to biomaterials are reviewed [2,3]. It can also be used for nerve regeneration. This polymer has putative bio-adhesive properties which could culture with neuron or Schwann cells to advance nerve axon regeneration [4]. It has been found that gelatin gels can be cross-linked by gamma-ray or electron beam that can control the enzymatic degradability over a wide range of degradation. Through the past few decades, HEMA is drawing the interest their biocompatibility makes them excellent candidate for the preparation of biomedical and pharmaceutical components [5]. HEMA, a vinyl monomer, is used as a coupling agent for natural fibres like jute, cotton, silk etc. [6–9]. So, in this study we have used HEMA for grafting [10,11].

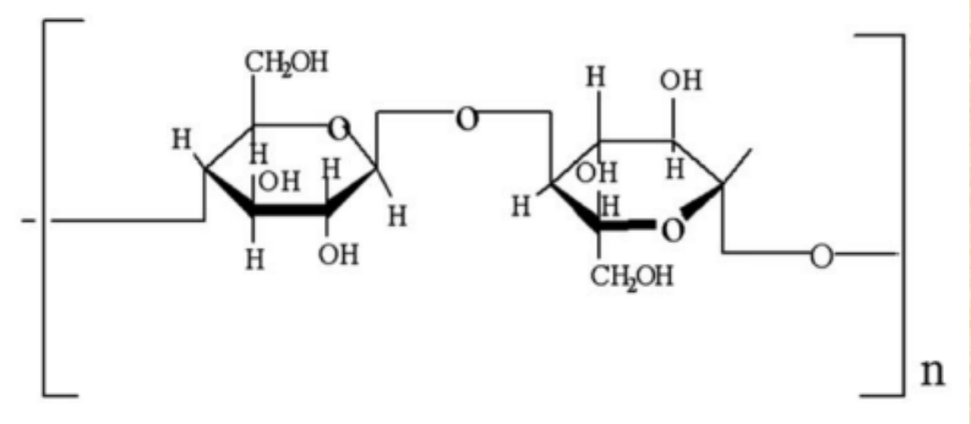
Furthermore, composite materials are widely used in civil, industrial and military applications mainly because of their excellent tensile and bending properties. Though synthetic fiber-reinforced thermoplastic composites attracted much attention due to its better durability and moisture resistance properties, the manufacture, use, and removal of traditional composite structure made of glass, carbon and aramid fibers are considered negative due to growing environmental consciousness. Due to the fact, alternative reinforcement with natural fiber in composites has gained much attention having low cost, low density, CO_2 neutrality, biodegradability and recyclable nature [12]. Among all the natural fibers, jute appears to be one of the most useful, inexpensive and commercially available lignocelluloses fiber. High-energy gamma radiation has been employed successfully for significant physical and chemical changes as well as changes in surface structure and surface energy of the fibers.

Purpose

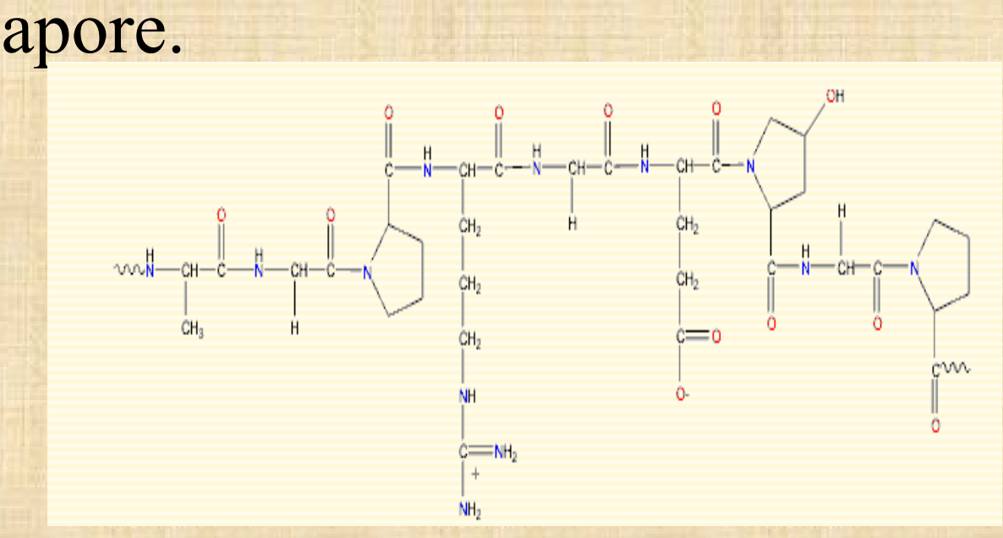
- The study deals with the development of a new method to enhance and improve the flexibility and mechanical properties of gelatin films. Another, aim is to develop and characterize cross-linked gelatin films with water soluble monomer 2-hydroxyethyl methacrylate (HEMA) using Co 60 gamma radiation.
- In addition, the advancement of a new method enhancing and improving the mechanical properties of jute reinforced polymeric composite materials.

Materials

- Gelatin (Bloom strength-185, Pharmaceutical grade), methanol, monomer (2-hydroxyethyl-methacrylate), photo-initiator (Darocur-1664) were purchased from E. Merck, Germany.
- Jute fabrics (bleached commercial grade made of tossa jute) were obtained from Bangladesh Jute Research Institute (BJRI), Dhaka, Bangladesh. Polypropylene was collected from Polyolefin Company Ltd., Singapore.



Scheme 1. Monomeric units of b-D-glucopyranose of jute.



Scheme 2. Structural unit of Gelatin.

Methods

Different formulations were prepared on weight basis and the films were made by casting. Films soaked in formulations and then irradiated by a Cobalt-60 gamma irradiator. Mechanical properties of both treated and untreated samples were analyzed by suitable techniques.

TABLE 1
Composition of different monomer formulations (%w/w)

Formulations	HEMA	MeOH	Photo-initiator
S1	10	88	2
S2	20	78	2
S3	30	68	2
S4	40	58	2
S5	50	48	2

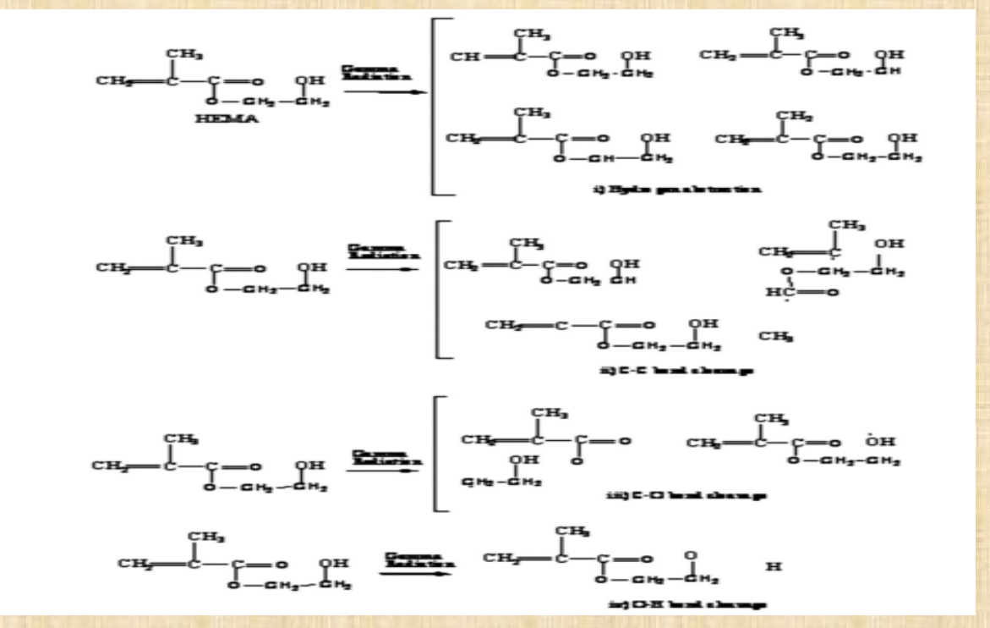
Composition of different monomer formulations (%w=w)

TABLE 2
Composition of HEMA blended gelatin formulations (%w/w) for film preparation

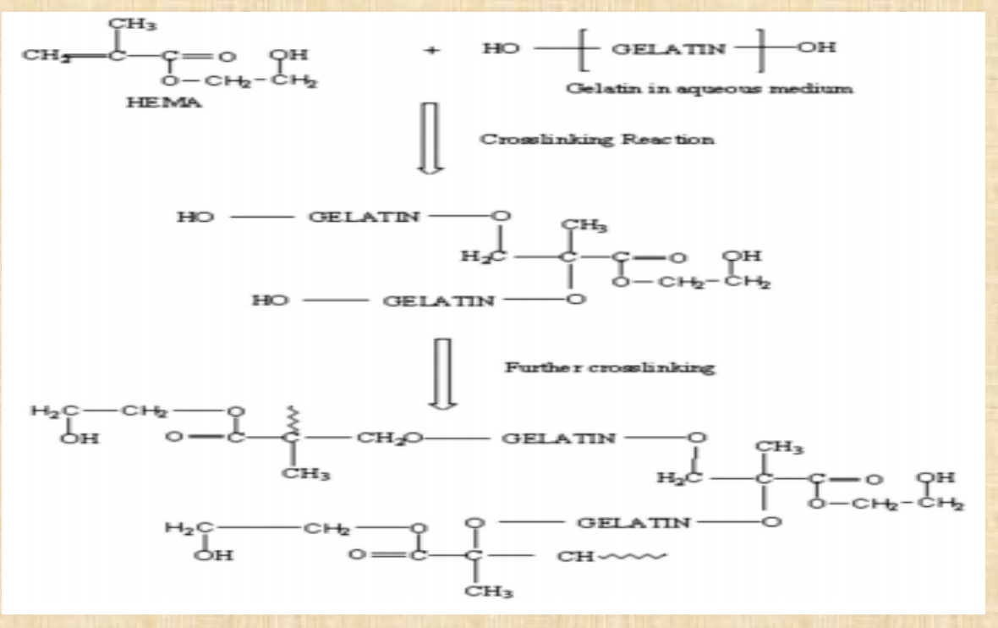
Formulations	HEMA	Gelatin	Water
B1	10	15	75
B2	20	15	65
B3	30	15	55
B4	40	15	45
B5	50	15	35

Composition of HEMA blended gelatin formulations (%w=w) for film preparation

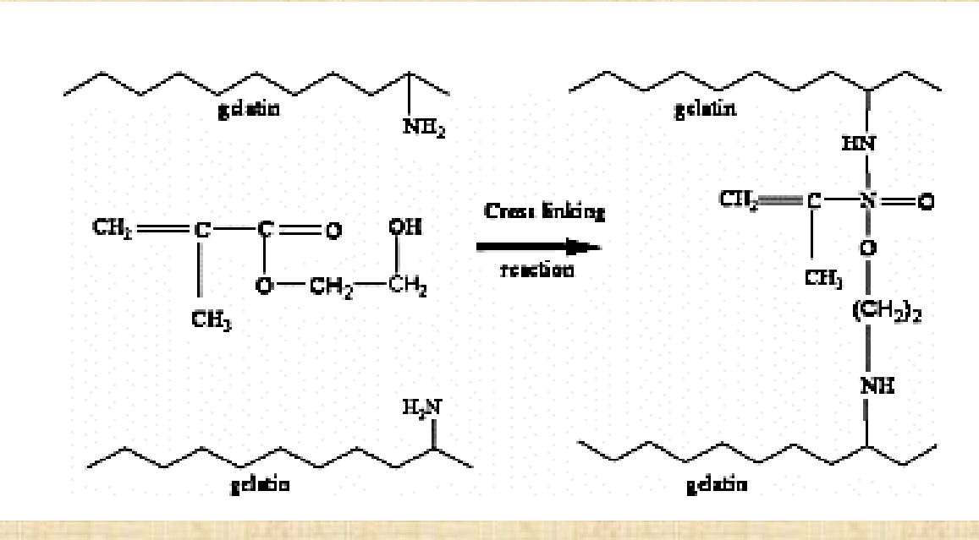
Results and Discussion



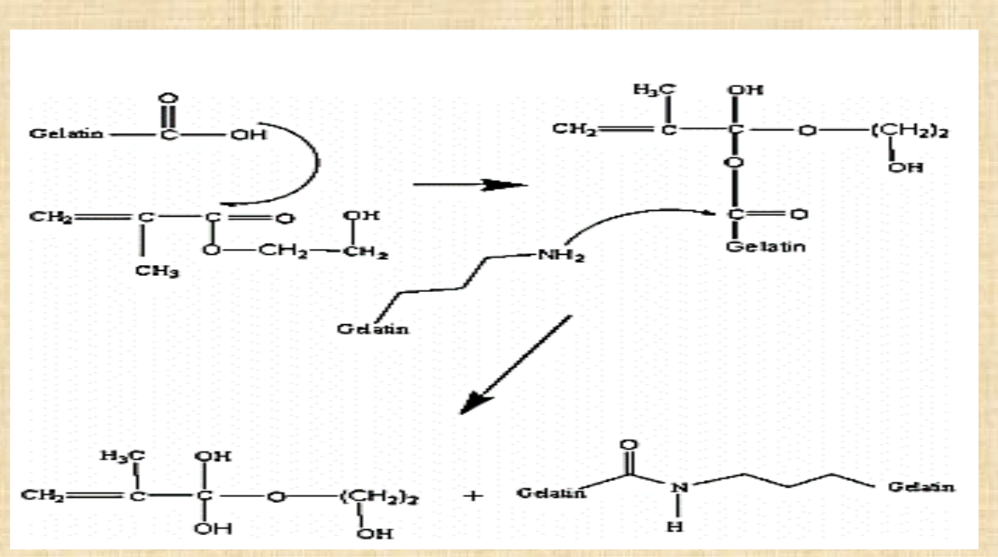
Scheme3: Probable free radicals generated from HEMA with the exposure of gamma radiation.



Scheme4: Proposed mechanism for the reaction of HEMA with the amine groups on gelatin to form cross-links.



Scheme5: Cross-linking of gelatin in aqueous medium with HEMA with the exposure of gamma radiation.



Scheme6: The sequence of reactions for the cross-linking of HEMA with gelatin at different sites with the exposure of gamma radiation.

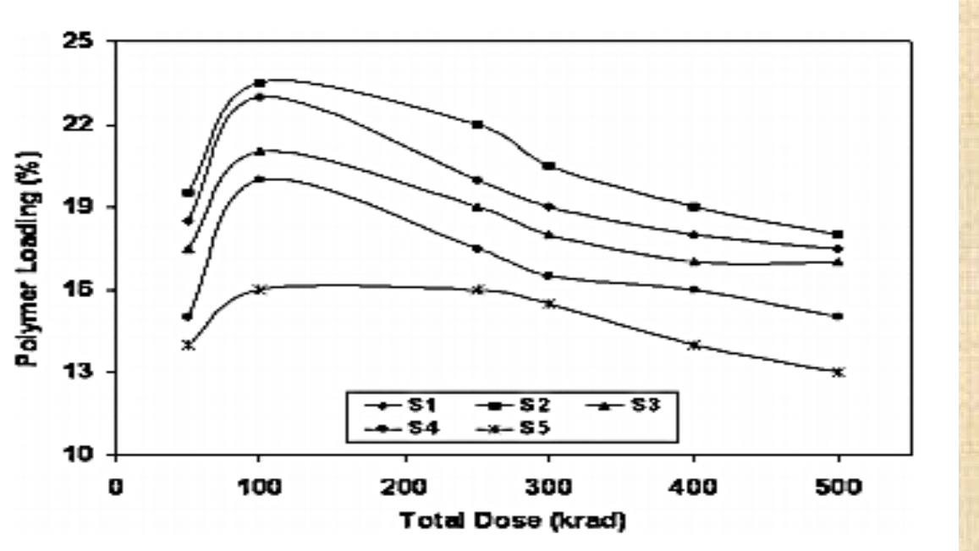


FIG. 1. Polymer loading (mass gain%) of gelatin films with respect to monomer (HEMA) formulation at 10 min soaking time against total dose (krad) of gamma radiation.

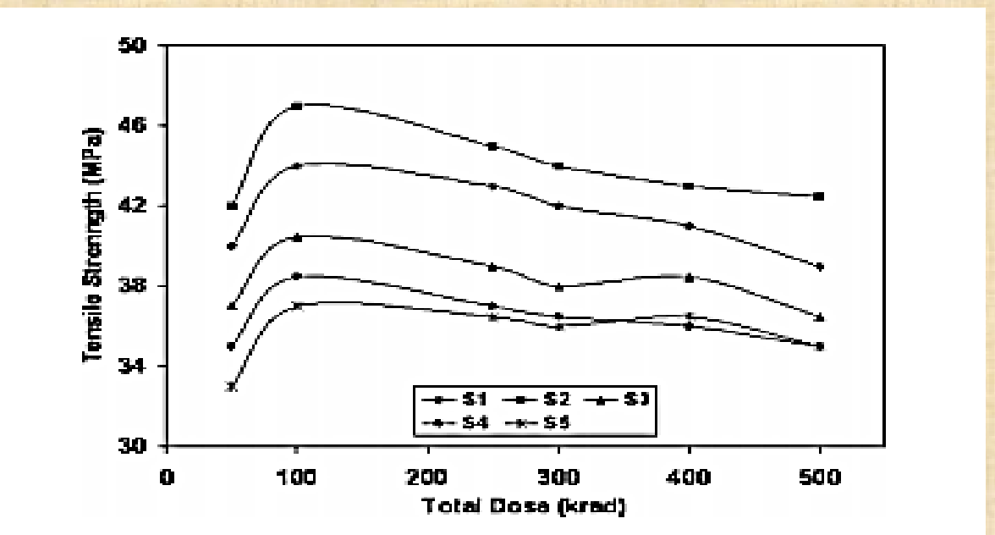


FIG. 2. Tensile strength (MPa) of the gelatin films against total dose (krad) of gamma radiation with respect to monomer formulation at 10 min soaking time.

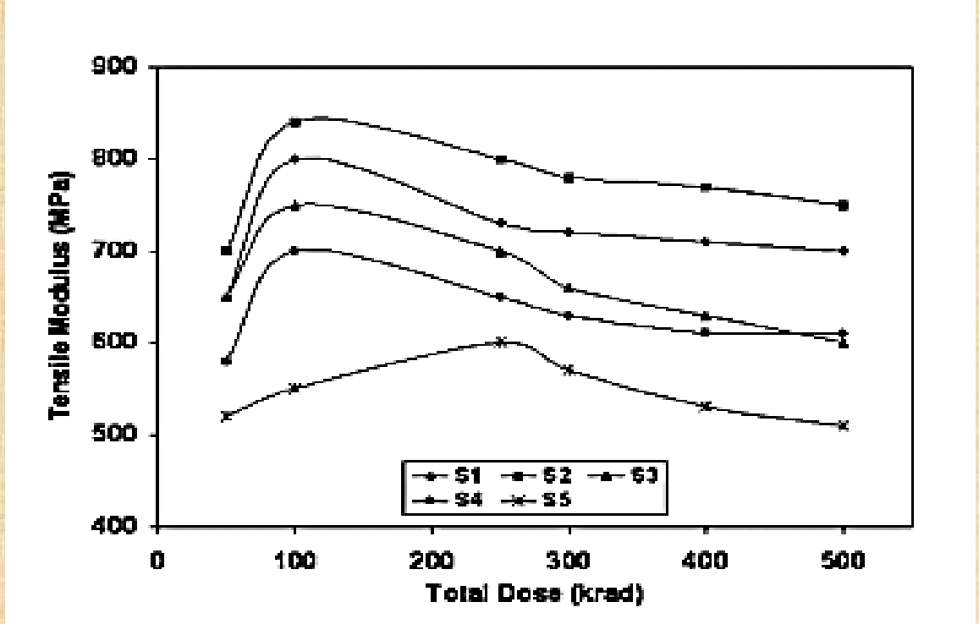


FIG. 3. Tensile modulus (MPa) of the gelatin films against total dose (krad) of gamma radiation with respect to monomer formulation at 10 min soaking time.

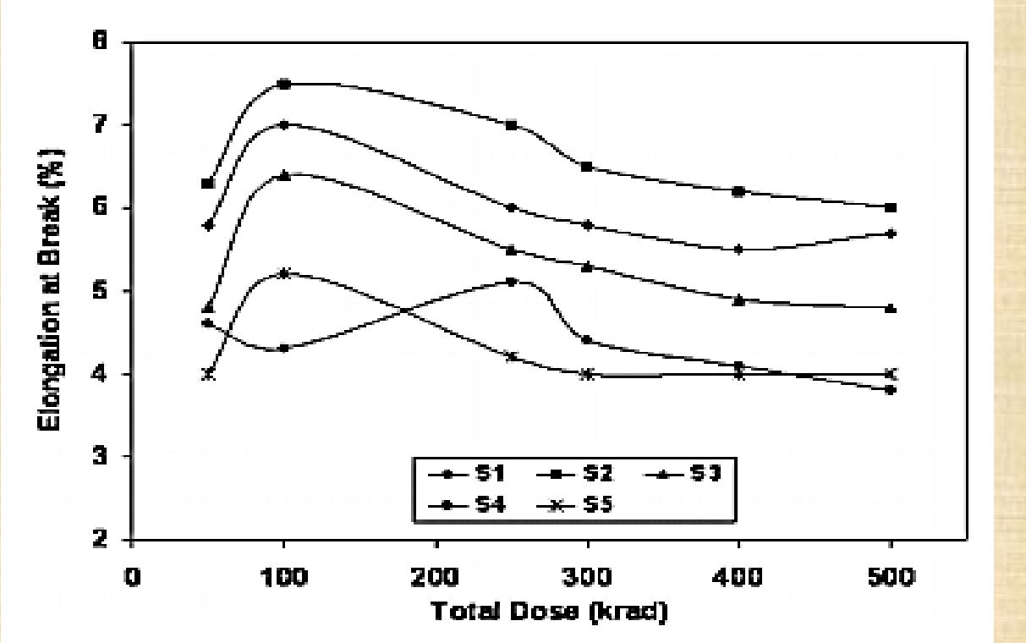


FIG. 4. Elongation at break (%) of the gelatin films against total dose (krad) of gamma radiation with respect to monomer formulation at 10 min soaking time.

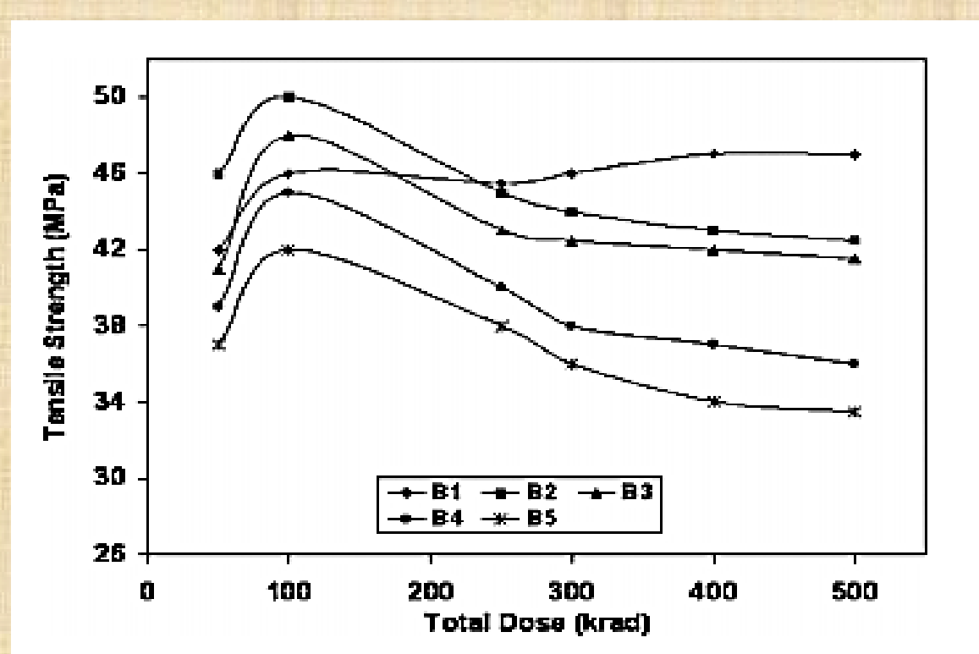


FIG. 5. Tensile strength (MPa) of the HEMA blended gelatin films against total dose (krad) of gamma radiation with respect to different blending formulations.

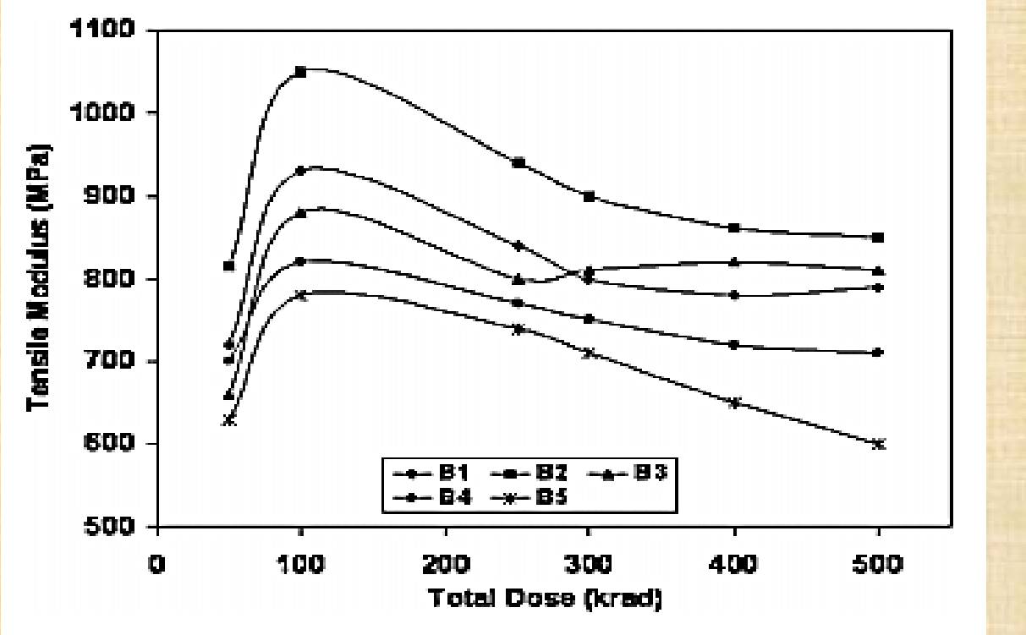


FIG. 6. Tensile modulus (MPa) of the HEMA blended gelatin films against total dose (krad) of gamma radiation with respect to different blending formulation.

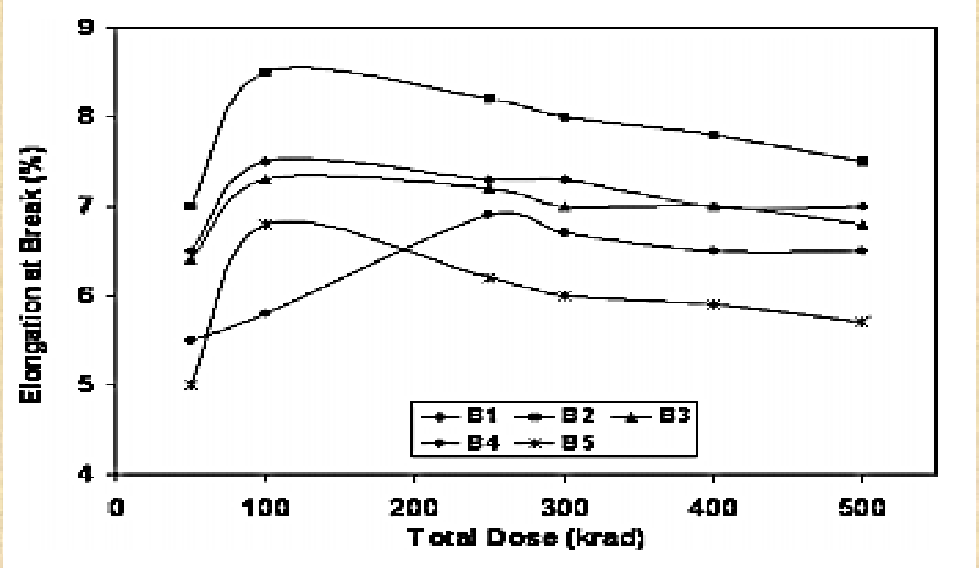


FIG. 7. Elongation at break (%) of the HEMA blended gelatin films against total dose (krad) of gamma radiation with respect to different blending formulation.

TABLE 3
Tensile properties of the pure gelatin film and the gelatin films irradiated under gamma radiation at different doses

Total dose (krad)	Tensile strength (MPa)	Tensile modulus (MPa)	Elongation at break (%)
0	27 ± 2	100 ± 12	4 ± 2
50	37 ± 2	200 ± 12	6 ± 2
100	42 ± 2	350 ± 12	7 ± 2
250	38 ± 2	300 ± 12	6.5 ± 2
300	36 ± 2	280 ± 12	6.5 ± 2
400	35 ± 2	260 ± 12	6.5 ± 2
500	35 ± 2	250 ± 12	6.5 ± 2

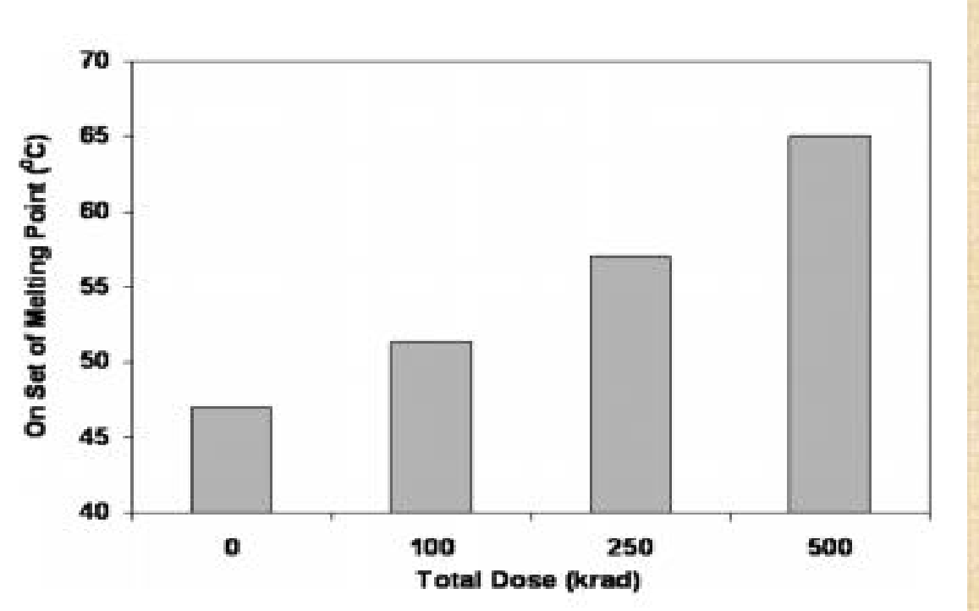


FIG. 8. Onset of melting point (°C) of pure gelatin films and gamma irradiated gelatin films at different doses.

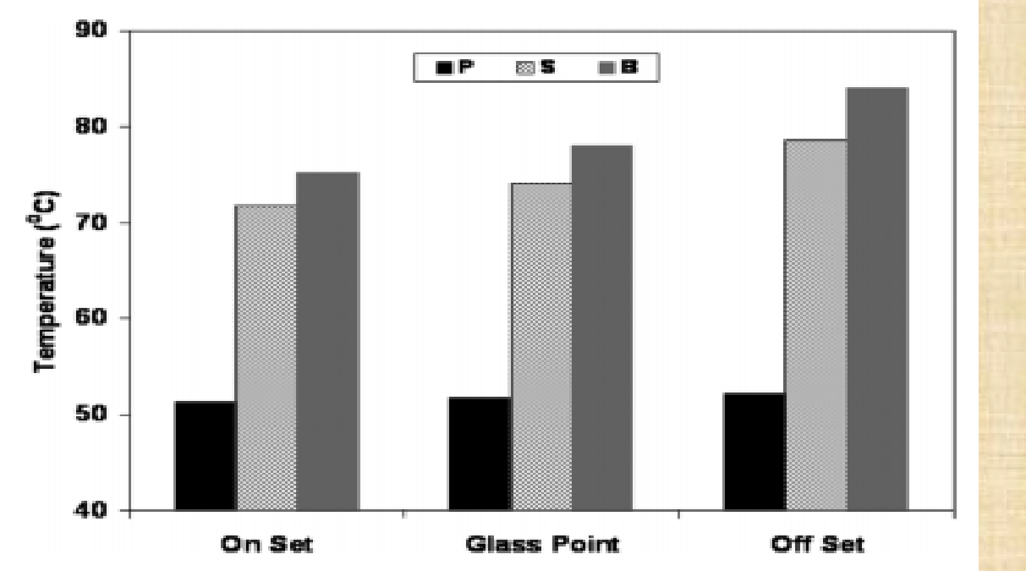


FIG. 9. Thermal properties of the pure and grafted gelatin films; P refers to pure gelatin film, S refers to gelatin films soaked in 20% HEMA irradiated at 100 krad, B refers to 20% HEMA blended gelatin films irradiated at 100 krad.

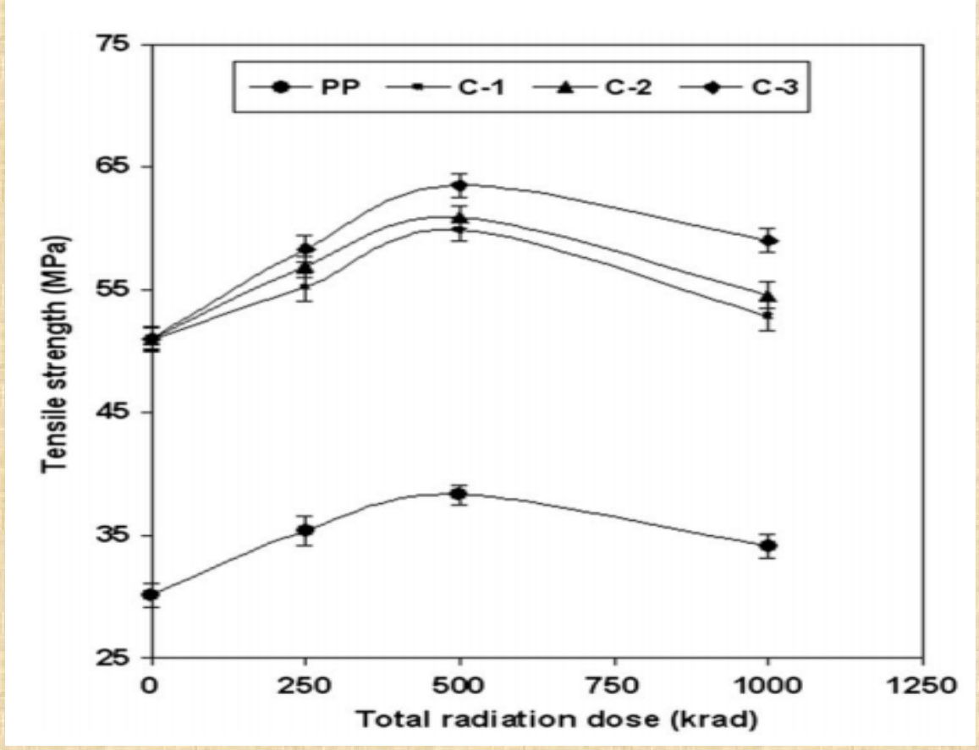


FIG 10.Tensile strength (TS) of irradiated composite against radiation dose.

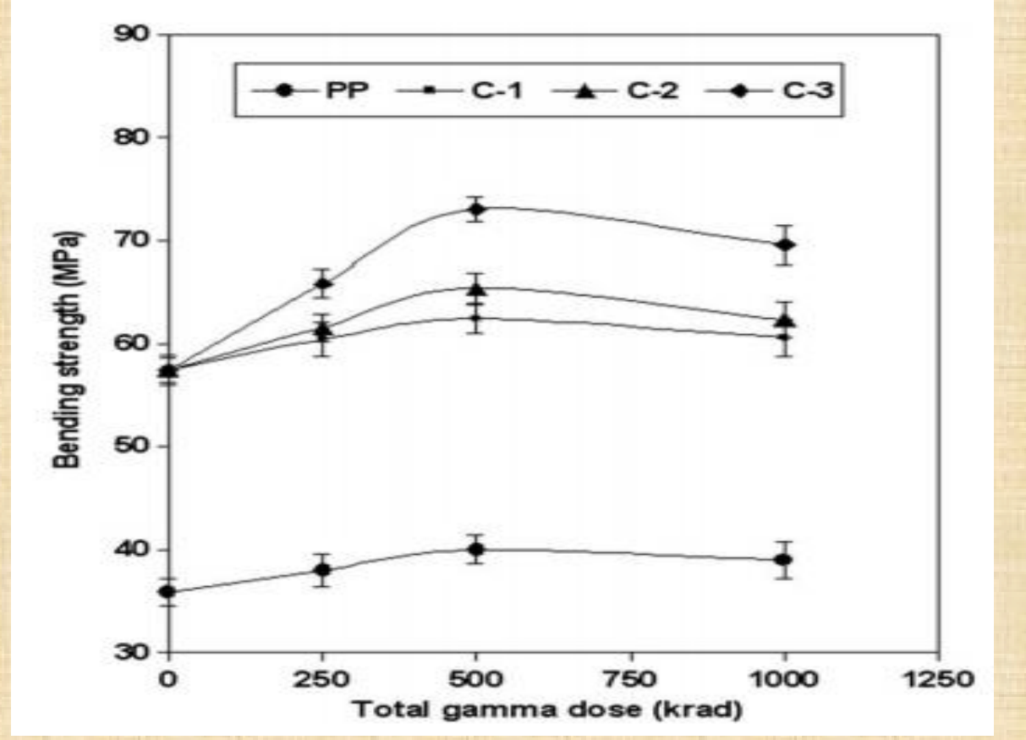
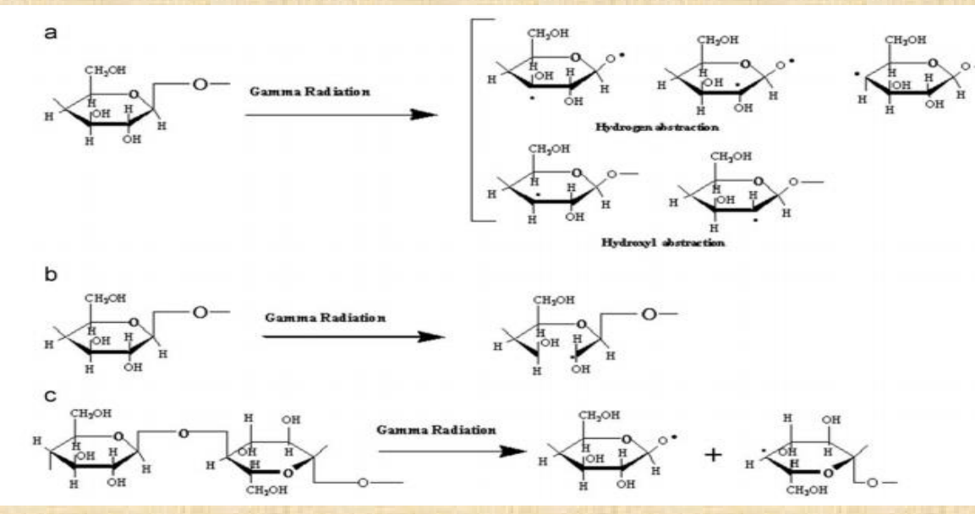
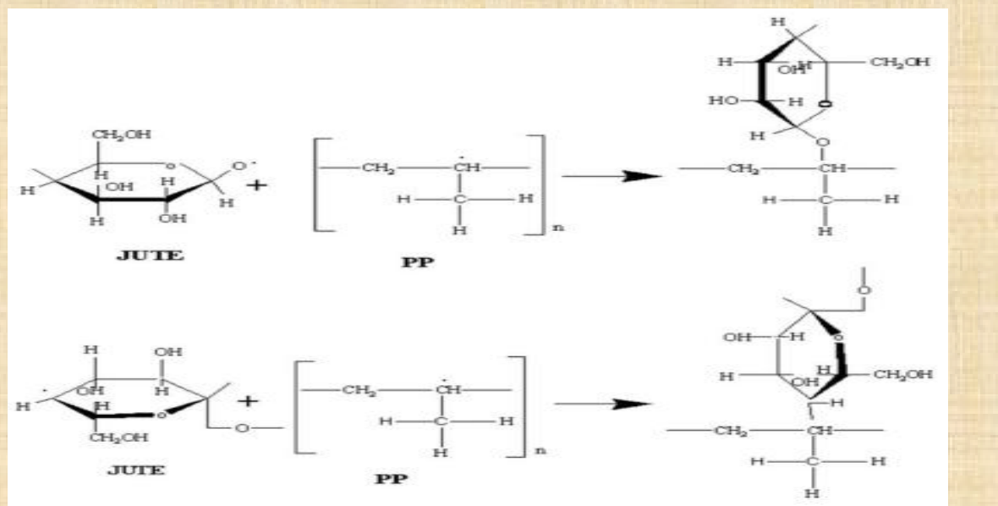


FIG 11.Bending strength (BS) of irradiated composite against radiation dose.



Scheme 7.Modes of free radical generation on irradiated jute fiber. Radicals are formed after C–H, C–O or C–C bond cleavages: (A) hydrogen and hydroxyl abstraction, (B) cycle opening and (C) chain scission.



Scheme8: A possible reaction mechanism between jute and PP due to gamma radiation.

Results and Discussion– con't

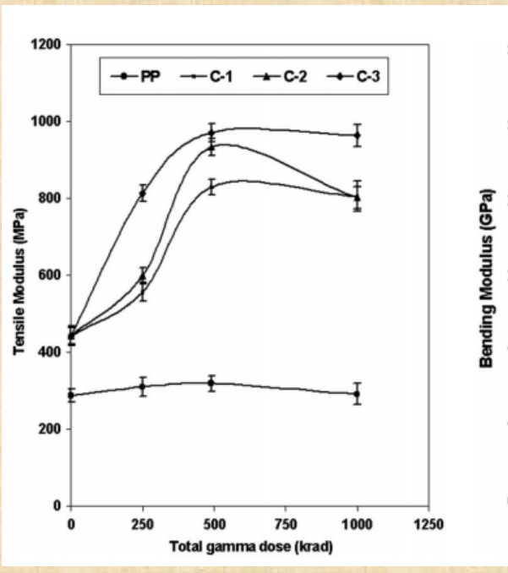


FIG11: Tensile modulus (TM) of irradiated composite against radiation dose.

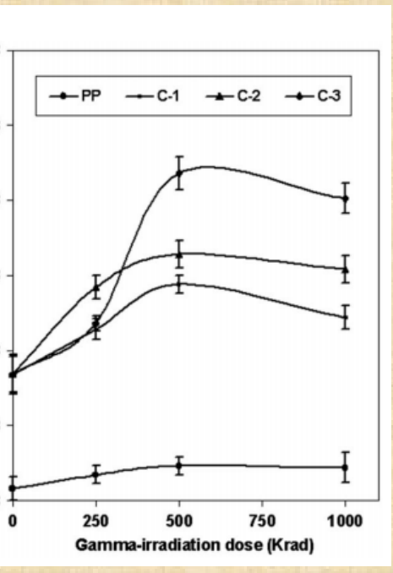


FIG 12: Bending modulus (BM) of irradiated composite against radiation dose

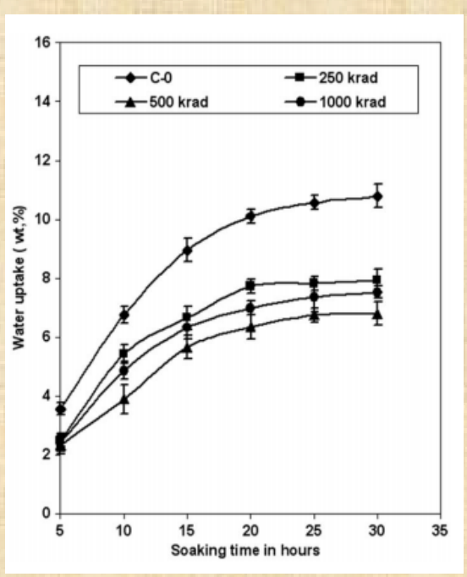


FIG13: Water uptakes of composites (both untreated and treated) against soaking time.

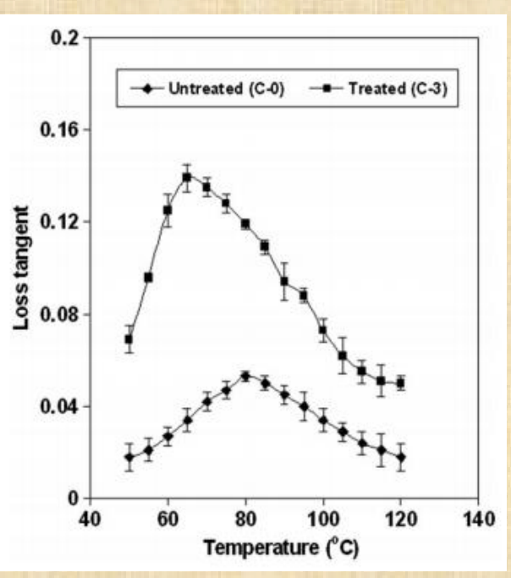


FIG14: Loss tangent vs. temperature curve of untreated (C-0) and treated (C-3) composites at 500krad of total dose at frequency 10kHz

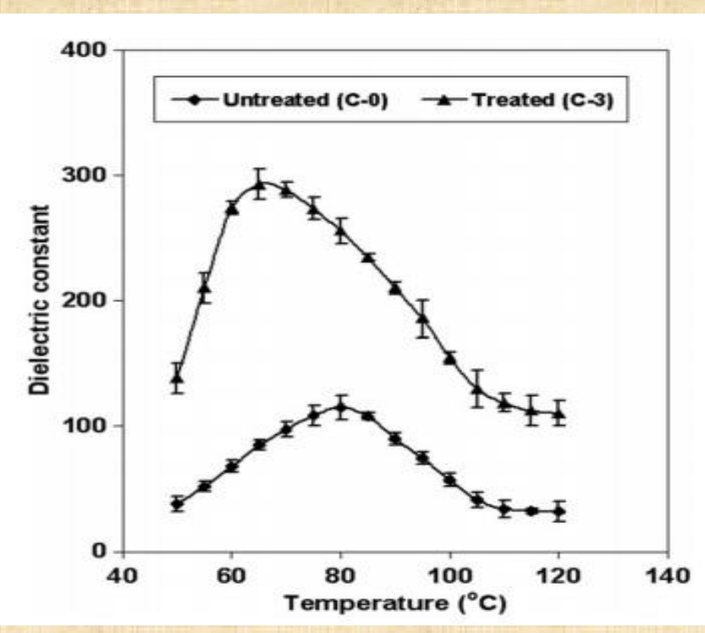


FIG 15: Dielectric constant vs. temperature curve of untreated (C-0) and treated (C-3) composites at 500krad of total dose at frequency 10kHz.

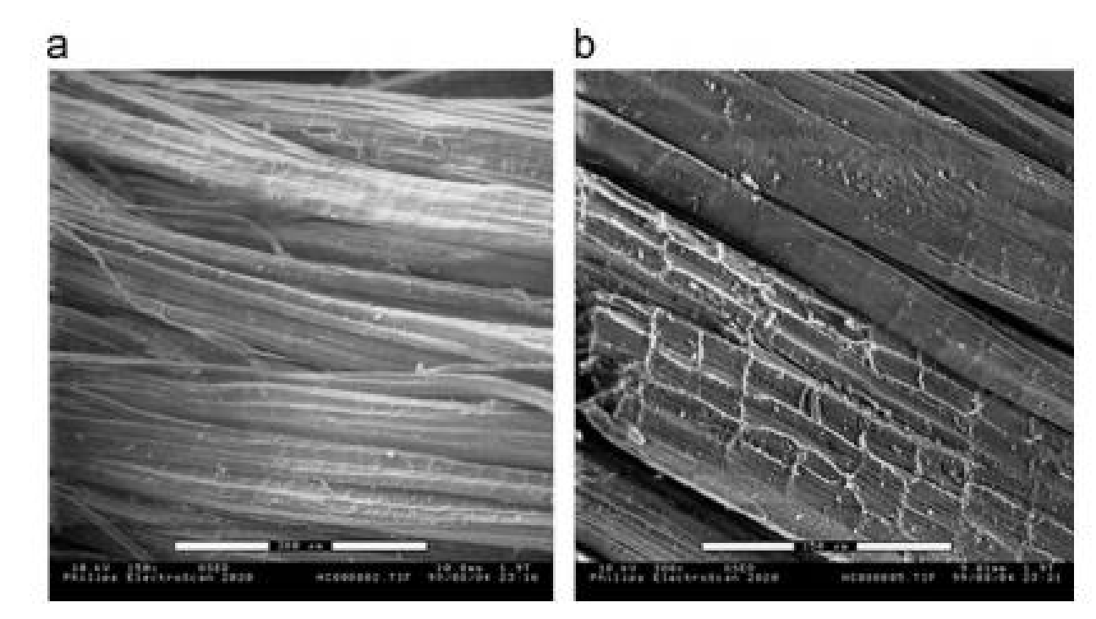


FIG16: SEM images of untreated (a) and 1000krad gamma treated (b) jute fabrics.

Summary and Conclusions

- TS, TM and elongation at break (%) of gelatin films were found to be 27MPa, 100MPa and 4%.
- After irradiation the mechanical properties increased significantly.
- Gelatin films soaked in formulations; 2-hydroxyethyl methacrylate (HEMA) (10– 50%, by wt), methanol and photo-initiator, then, treated by gamma ray which revealed the TS and TM of the films reached a peak of 47MPa and 840MPa, respectively, at 100 krad for 20% HEMA solution.
- With a series of gelatin blended solutions (10–50% by wt) of HEMA; again soaked and stood the TS and TM of the gelatin films to be 50MPa and 1050MPa which indicates changing properties.
- Also, the thermo-mechanical properties; the on set and off set of melting point and the glass point were increased for the treated films compared to untreated films.
- The maximum on set of melting point of the soaked and blended gelatin films were 71.8 ^{0}C and 75.2 ^{0}C, whereas for the pure film it was 51.3 ^{0}C.

☐ In case of composite materials, investigation showed that irradiated jute fabrics/irradiated PP-based composite produced the highest mechanical properties at 500krad of total dose compared to the non-irradiated jute fabrics/irradiated PP and irradiated jute fabrics/non-irradiated PP-based composites.
☐ Mechanical properties such as TS, TM, BS, BM and IS of the treated composites were found higher than that of untreated composites.
☐ The dielectric constant and loss tangent of the composites is found to depend on temperature.
☐ Phase transition, likely ferro-to paraelectric transitions takes place in the composites (both treated and untreated) in the temperature range 80–651^{0}C.
☐ The dielectric constant and loss tangent of the composites increased as a result of irradiation.
☐ Therefore, gamma irradiation is one of the powerful sources to improve the mechanical and dielectric properties of the hessian cloth reinforced PP composites.

References

[1]. Gul-E-Noor, F.; Khan, M.A.; Ghoshal, S.; Mazid, R.A.; Sarwaruddin Chowdhury, A.M.; Khan, R.A. Grafting of 2-ethylhexyl acrylate with urea on to gelatin film by gamma radiation. Macromol. Sci., Pt. A, 2009, 46, 615–624.

[2]. Langer, R.; Peppas, N.A. Advances in biomaterials, drug delivery, and bionanotechnology. J. Bioeng. Food Nat. Prod.2003, 49(12), 2990–3006.

[3]. Cohen, S.; Bano, M.C.; Cima, L.G. et al. Design of synthetic polymeric structures for cell transplantation and tissue engineering. Clin. Mater.1993, 13, 3.

[4]. Pei-Ru Chen, P.-R.; Pei-Leun Kang, P.-L.; Su, W.-Y.; Lin, F.-H.; Chena, M.-H. The evaluation of thermal properties vitro test of carbodiimide glutaraldehyde cross linked gelatin cells culture. J. Biomed. Eng. Appl. Basis Commun. 2005, 17, 44–49.

[5]. Dhananjay, S.; Bodas, S.; Desai, M.; Gangal, S.A. Deposition of plasma-polymerized hydroxyethyl methacrylate (HEMA) on silicon in presence of argon plasma. J. Appl. Surface Sci. 2005, 245, 186–190.

[6]. Khan, M.A.; Khan, R.A.; Aliya, B.S.; Nasreen, Z. Effect of the pretreatment with UV and gamma radiations on the modification of plywood surface by photo-cuing with epoxy acrylate. J. Polym. Environ.2006, 14, 100–111.

[7]. Honda, I.; Arai, K.; Mitomo, H.Characterization of Cross-links Introduced in Gelatin, John Wiley & Sons, Inc., Vol. 64, p. 1879–1891, 1997.

[8]. Khan, M.A.; Hassan, M.M.; Drazel, L.T. Effect of (HEMA) on the mechanical and thermal properties of jute-polycarbonate composite. Compos. Pt. A 2005,36, 71–81.

[9]. Ali, K.M.I.; Khan, M.A.; Ali, M.A.; Akhunzada, K.S. In-situ jute yarn composite with 2-hydroxyethyl methacrylate (HEMA) via UV radiation. J. Appl. Polym. Sci.1999, 71, 841–846.

[10]. Terao, K.; Karino, T.; Nagasawa, N.; Yoshii, F.; Kubo, M.; Dobashi, T. Gelatin microspheres crosslinked with gamma-ray: Preparation, sorption of proteins, and biodegradability. J. Appl Polym Sci.2004, 91, 3083–3087.

11. Xia, W.; Liu, W.; Cui, L.; Liu, Y.; Zhong, W.; Liu, D.; Wu, J.; Chua, K.; Cao, Y. Tissue engineering of cartilage with the use of chitosan-gelatin complex scaffolds. J. Biomed. Mater. Pt. B, 2004, 71, 373–380.

12. Mohanty, A.K., Khan, M.A., Hinrichsen, G., 2000b. Surface modification of jute and it's influence on performance of biodegradable jute fabrics/biopol composites. Compos. Sci. Technol. 60, 1115–1124