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Gamma Radiation Induced Biodegradable Shellac Films Treated by Acrylic Monomer and Ethylene Glycol

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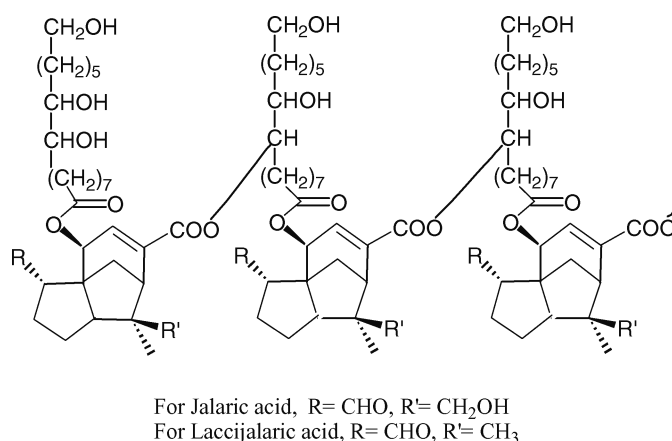
In this study the mechanical properties of shellac films, prepared by solution casting, were evaluated with varying amounts of Ethylene Glycol (EG) and 2-Ethyl-2-(hydroxymethyl)-1,3-propanediol-trimethacrylate (EHMPTMA). Mechanical properties such as tensile strength (TS) and elongation at break (Eb) of the raw shellac film were found to be 1.86 MPa and 4%, respectively. A series of formulations was prepared using shellac and varying percentages of EG and EHMPTMA in methanol. The films were prepared and irradiated under gamma (Co-60) radiation at different doses (50–500 krad). Grafting of EHMPTMA showed better results compared to raw shellac and EG treated films. Thermal properties, degradation tests in water and soil of the films were also evaluated.

Keywords: Thin film, polymer, shellac, acrylic monomers, gamma radiation

1 Introduction

Shellac is a polymeric resin, secreted by the insect *Kerria lacca Kerr* which is a parasitic insect commonly found on certain trees and bushes of India, Bangladesh, Burma and Thailand (1, 2). Even though this natural resin from renewable resources shows a distinct batch-to-batch variation (3), shellac is mainly a complex mixture (Scheme 1) of polyesters of straight-chain hydroxy fatty acids and sesquiterpenic acids such as aleuritic acid, shellolic acid and jalaric acid (Scheme 2), lac wax (a mixture of higher alcohols, acids and their esters), lac dye (a mixture of anthroquinoid derivatives) which were reported in many investigations (4–6).

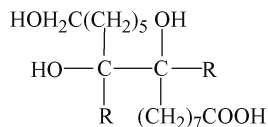
Shellac is soluble in solvents containing alcoholic hydroxyl groups, aqueous alkaline solution or acetone in the presence of a polar solvent, but insoluble in water, esters, ether, hydrocarbons and chlorinated solvents (7–9). From early times, shellac was used for various purposes, for example, as a dyeing material and for medicinal purposes. Nowadays, it is used in pharmaceutical industries for its excellent film forming and acid resistance properties. It is used to coat, to increase shine and as enteric coating of



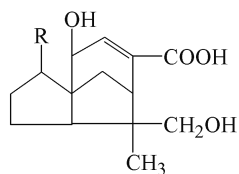
Sch. 1. Structure of shellac.

the products. In food and paint industries, shellac is widely used. In food, it is used as a moisture barrier, nutritional supplements, health supplements and nutraceuticals. Shellac is used to coat citrus and apples to preserve for long time, since it is one of the few materials allowed for this purpose (3, 10–12). Electrolysis of shellac leads to the formation of adherent films onto different metal anodes (13). Partial hydrolysis of shellac has been done to modify the physicochemical and mechanical properties (14). Use of acrylic resin makes the shellac more eco-friendly and opens the new path for its utilization (15). As shellac film is brittle in nature (16), scientists worked to improve its mechanical

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Aleuritic acid



R= COOH, shellolic acid
 R= CHO, jalaric acid A

Sch. 2. Structure of complex acid constituents in shellac.

properties significantly using plasticizers such as triethyl citrate (TEC) (17). Scientists studied NO₂ initiated graft copolymerization of shellac with methyl methacrylate (18). Vinyl monomers were also used for graft copolymerization with shellac initiated by alkaline potassium permanganate (19). The objective of this work was to improve the properties of shellac film using Ethylene glycol (EG) and a tri-functional acrylic monomer named 2-Ethyl-2-(hydroxymethyl)-1,3-propanediol-trimethacrylate (EHMPTMA). EG is a hydrophilic liquid and capable of forming a polymer. Grafting of EG on to a polymer is an effective technique to improve the affinity to water and organic solvents. EG is colorless, viscous, and a hydrophilic liquid which is capable of enhancing good mechanical properties of the natural polymer as reported earlier using UV radiation (20). Previous work also established that multifunctional unsaturated acrylic monomer can be used for the treatment of the polymeric film to reduce the UV-radiation intensities to obtain optimum properties (21).

The present study deals with the development of a new method to enhance the mechanical properties of the shellac film in many respects. For this purpose, varying percentages of these two monomers were applied and finally the films were irradiated under gamma radiation at dissimilar radiation doses.

2 Experimental

2.1 Materials

Shellac was collected from the Lac Research Station, Bangladesh Agricultural Research Institute, Chapai Nawabgonj, Bangladesh. Ethylene Glycol (EG), 2-Ethyl-2-(hydroxymethyl)-1, 3-propanediol-trimethacrylate (EHMPTMA), Methanol (extra pure) and acetone were purchased from E. Merck, Germany.

Table 1. Composition (% w/w, based on shellac) of different formulations

Components	Formulation						
	F1	F2	F3	F4	F5	F6	F7
Shellac	100	97	95	93	97	95	93
EG	0	3	5	7	0	0	0
EHMPTMA	0	0	0	0	3	5	7

2.2 Methods

2.2.1. Extraction of pure shellac

Raw shellac (seed lac) contained various impurities. It was dissolved in methanol and filtered to remove the impurities. The filtrate was dried at room temperature to collect the pure shellac.

2.2.2. Preparation of formulations

Pure shellac was dissolved in methanol along with varying percentages of monomers such as EG and EHMPTMA to prepare various formulations. Table 1 showed seven types of such formulations (F1-F7).

2.2.3. Preparation of shellac films

The formulated solutions were cast on silicon paper (release film) mounted on level glass plate. The solutions were kept at room temperature for about 48 h. After formation of the films, they were peeled off and cut into a dimension of 50 × 10 mm². Average thickness of the films was 0.1 to 0.3 mm.

2.2.4. Irradiation of the films

The films were then irradiated (prepared from the formulations F1 to F7) under gamma radiation (Co-60) at different doses, such as 50, 100, 250 and 500 krad at a dose rate of 350 krad/hour.

2.2.5. Property measurement

Irradiated films were kept in desiccators at room temperature and 65% relative humidity for few days before various testing and all the tests were carried out under similar conditions.

2.2.5.1. *Tensile properties.* Tensile properties; tensile strength (TS) and elongation at break (Eb) of the cured films were measured with Universal Testing Machine (Hounsfield Series S, UK). The load capacity of the machine was maintained 500 N with crosshead speed 10 mm/min and gauze length of 20 mm.

2.2.5.2. *Thermal properties of the films.* The melting temperature (MT) and the co-efficient of thermal expansion (CTE) of the polymeric films were measured using Thermo-mechanical Analyser (LINSEIS TMA, L-77, USA). The experiment was carried out in an inert atmosphere at a

heating rate of 5°C/min. The dimension of the sample was: $5 \times 5 \times 2 \text{ mm}^3$.

2.2.6. Degradation studies

2.2.6.1. *Degradation study in water.* The weight loss of the raw and irradiated films was periodically measured (6 to 600 h) upon exposure to water at room temperature. After predetermined time intervals, the films were removed from water and carefully blotted with tissue paper to remove water on the film surface and dried at room temperature for 24 h. Then, the weight loss percentage was determined.

2.2.6.2. *Soil burial test.* Shellac films were buried into the soil to study the degradation tendency. Raw shellac film and monomers grafted films were weighed individually and buried in garden soil for 1 to 30 days. Moisture content of the soil was maintained at around 15–18%. After these periods, the films were withdrawn cautiously from the soil, washed, dried and reweighed. At the end, the weight loss of the samples was calculated.

3 Results and Discussion

Most of the data presented in this paper are average values of at least five samples and the results obtained are within the accuracy of $\pm 1\%$.

3.1 Effect of Gamma Radiation on Pure Shellac Film

Pure shellac films were prepared by casting. The TS and Eb of the pure shellac film was 1.86 MPa and 4%, respectively. Pure shellac films were irradiated under gamma radiation at different doses (50, 100, 250, 500 krad) at a dose rate of 350 krad/hr to determine the effect of gamma radiation on the shellac films. The results are shown in Figure 1. From the figure, it is observed that at 50 krad radiation dose, TS of the pure shellac film is 1.3 MPa which is lower than that of the untreated film (1.86 MPa). The highest TS of the irradiated pure shellac film is 3.7 MPa which is obtained at 100 krad radiation dose. At higher radiation dose TS value decreased and the lowest TS value is 0.57 MPa which is observed at 500 krad radiation dose. In the case of Eb, the highest value 4.8% is obtained at 50 krad radiation dose which is better than the untreated shellac film (4%). Eb values of the irradiated films are then gradually decreased as the radiation dose increased. At 100, 250 and 500 krad radiation doses the Eb values are almost 3.2, 2.7 and 1.8%, respectively. The higher radiation dose (500 krad) shows the lowest Eb value which is about 1.8%.

A desired amount of crosslinking or chain scission occurs when the polymers are irradiated. Crosslinking leads to the enhancement of mechanical properties such as TS, Eb, modulus of elasticity, hardness and softening temperature (22). When high energy ionizing radiation (gamma radiation) imposed to shellac films, crosslinking and chain

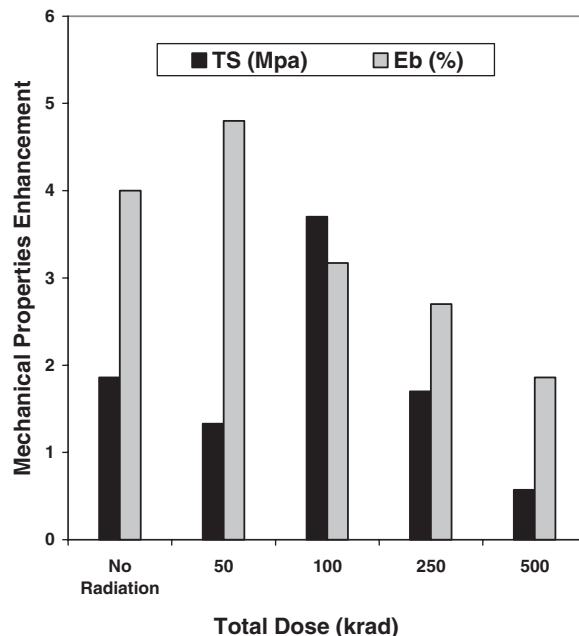


Fig. 1. Effect of gamma radiation on the mechanical properties of pure shellac film.

scission occurs simultaneously. Shellac films showed poor mechanical properties at low radiation dose because of the weak intra molecular bonds. But, a higher radiation dose produces a denser network structure because of crosslinking. A further increase of radiation dose causes a decrease of TS because of radiation degradation of the polymeric film. So, a slight increase in mechanical properties of pure shellac film at higher radiation dose was predicted. Use of gamma radiation, which is high energy ionizing radiation, is one of the efficient methods for the modification of natural polymer (22, 23).

3.2 Modification of Shellac Film using Different Monomers

In order to modify the mechanical properties of shellac film, monomers (EG and EHPTMA) were used during the preparation of film. Monomers were mixed with shellac solutions in different percentages (%) such as 3, 5, and 7. More than 7% of monomers in shellac make the films soft and it is difficult to study the mechanical properties of these films. On the other hand, lower monomer content (less than 3%) makes the films brittle and cracked during drying. So, the above-mentioned compositions were selected for investigation. The films were prepared by casting the solutions. It was found that shellac film without grafting shows the lower mechanical properties like TS and Eb.

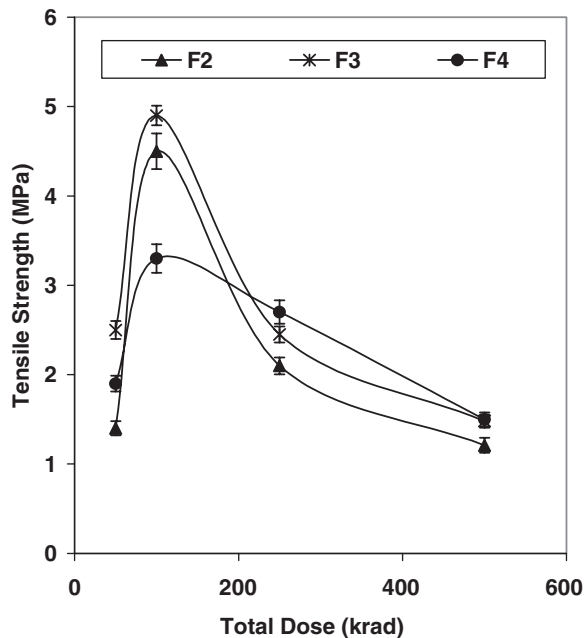


Fig. 2. Tensile strength of the irradiated shellac/EG film against various radiation doses.

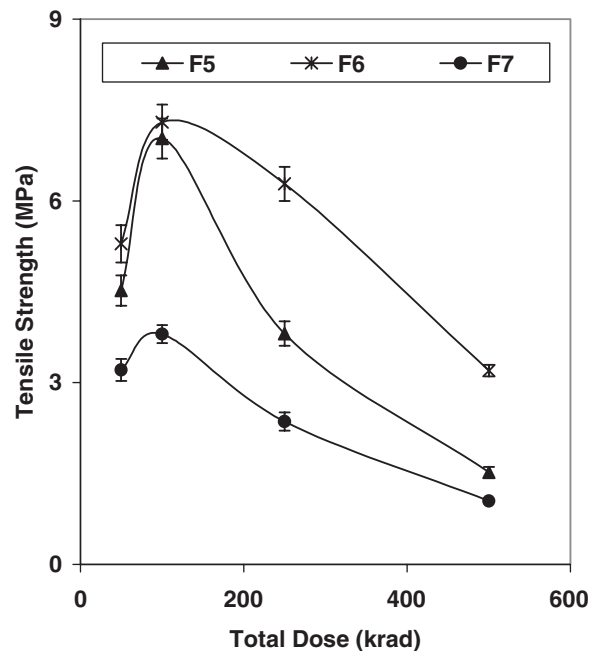


Fig. 3. Tensile strength of the irradiated shellac/EHMPTMA film against various radiation doses.

3.3 Tensile Strength (TS) Measurement

Tensile property plays very important role in selecting diverse applications of polymer and polymer-grafted substrates. The TS values of the EG and EHMPTMA treated shellac films are presented in Figures 2–3 against total radiation dose. Figure 2 represents the TS of the EG treated (F2–F4) films. From the figure it is observed that TS value increases with the increase of radiation dose and also with the increase of % of monomer. At 50, 100, 250 and 500 krad radiation dose the TS values of F3 formulation are about 2.5, 4.9, 2.4 and 1.4 MPa, respectively. Initially, the TS value increases gradually with the increase of radiation dose and then decreases with the increase of radiation doses. Monomer formulation containing 5% EG performs better TS than the others. The TS values of the 3, 5 and 7% (F2–F4) EG treated films at 100 krad radiation dose are 4.5, 4.9 and 3.3 MPa, respectively. Among the three types of formulation, F3 (5% EG) films shows the best TS which is 4.9 MPa at 100 krad radiation dose. After that, the TS values decreases as the radiation dose and the EG percentages increases.

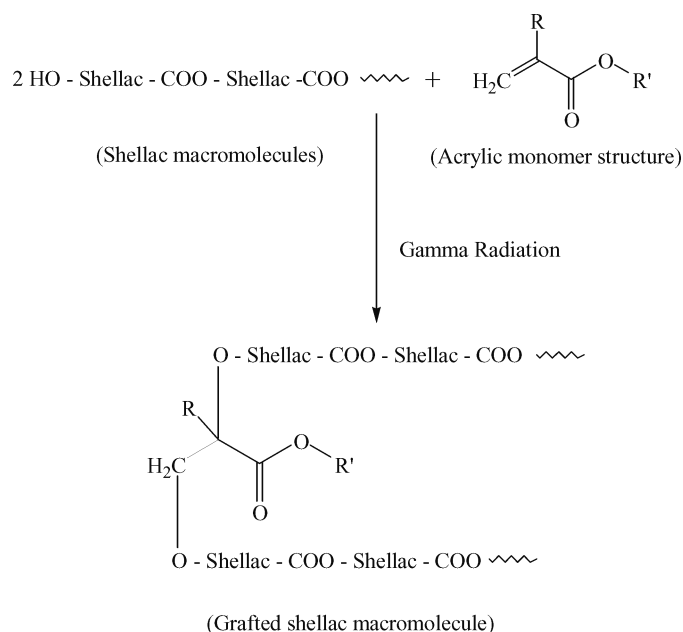
The TS values of the EHMPTMA (F5–F7) treated films are cited in Figure 3. From the figure, it is clear that the TS values increase following the similar trend like the EG formulations. It can be seen that F6 (5% EHMPTMA) formulation gives the best result than the others (F5 and F7). At 50, 100, 250 and 500 krad radiation dose, the TS values for the F6 are approximately 5.3, 7.3, 6.3 and 3.2 MPa, respectively. All the values are higher than the values of F5 (3% EHMPTMA) and F7 (7% EHMPTMA) formulations.

The highest TS value for EHMPTMA treated film is 7.3 MPa for F6 formulation at 100 krad radiation dose. So, it is clear that in both cases 5% monomer showed the best result. Among the EG and EHMPTMA treated films the EHMPTMA treated films shows the best TS at 100 krad radiation dose which is 7.3 MPa. It is expected that the acrylic group (from EHMPTMA) reacted with the shellac macromolecules in the presence of gamma radiation and formed a complex. This might be for the enhancement of the TS of the grafted shellac films. This mechanism is demonstrated in Scheme 3.

TS value increases may be due to the cross-linking of the hydroxyl group in shellac with the acrylic group of monomers. In each case, TS value increases with the increase of monomer concentration up to 5% and then decreases. At higher monomer concentration, monomer-monomer recombination leads homo-polymer formation which decreases the TS value (20). From the figures, it is clear that TS of grafted film is higher than that of irradiated pure shellac film. In each figure, it is observed that TS increases with the increase of radiation doses and the highest TS is obtained at 100 krad dose. After that, TS reduces. This may be caused by radiation degradation at higher radiations (24).

3.4 Elongation at Break (Eb) Measurement

Flexibility of a polymer is an essential parameter that is very actively considered during the application of the polymer. Flexibility and elasticity are two related phenomena



Sch. 3. Probable reaction mechanism between shellac and acrylic monomer with the exposure of gamma radiation.

that are associated with the stability of the application of polymer in a certain area. The polymeric films are prepared in mixing of different monomer concentrations (F2 to F7) with shellac and treated under gamma radiation. These films were elongated to such an extent that the films break. The extent of elongation of these gamma irradiated films at the breaking point are plotted against total dose from Figures 4 to 5. It can be seen that in all cases the Eb values increases at the initial radiation dose (50 krad), after that, the value decreases as the radiation dose increases due to the radiation degradation of the film (25). On the other hand, the Eb value increases with the increase of monomer percentages and further increase of monomer decreases the Eb values significantly.

In every case, (EG and EHMPTMA treated film) 5% monomer at 50 krad radiation dose showed the best result. The Eb values for EG and EHMPTMA treated films are 3.4 and 8.5%, respectively at 50 krad radiation dose. The highest elongation 8.5% is attained by the formulation F6 (at 50 krad) that contains 5% EHMPTMA which is shown in Figure 5.

When monomer is used, it may be graft copolymerized with the shellac. When the films are irradiated, hydroxyl group of shellac initiated to form a cross-linked network with the acrylic group of the monomers. Monomer formulation is very important because the polymerization rate and overall conversion, as well as the crosslinked polymerization properties depend on it (20). The functionality of the acrylic monomer affects the hardness of the radiation-cured polymer films (26). So, optimization is established for 5% monomer formulation.

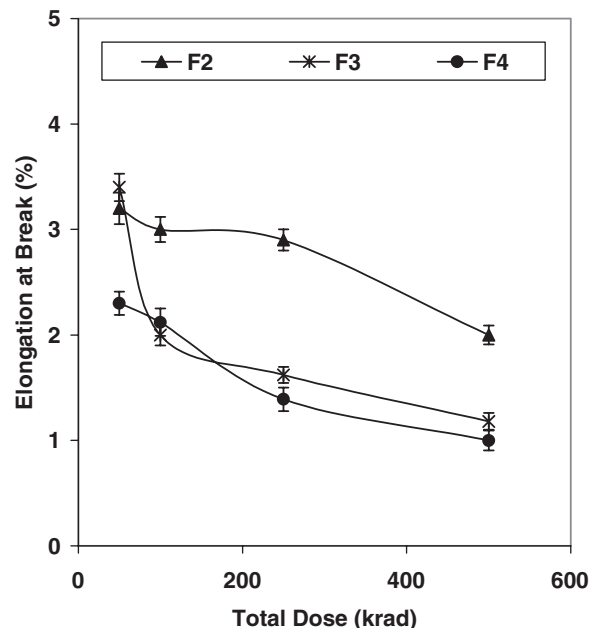


Fig. 4. Elongation at break of the irradiated shellac/EG film against various radiation doses.

3.5 Comparison

The highest Tensile strength (TS), Elongation at break (Eb) of F1, F3 and F6, formulation containing shellac films (at 5% monomer concentration) are compared in Figure 6. From the figure, it is observed that the highest TS obtained in the case of 5% EHMPTMA containing shellac film at 100

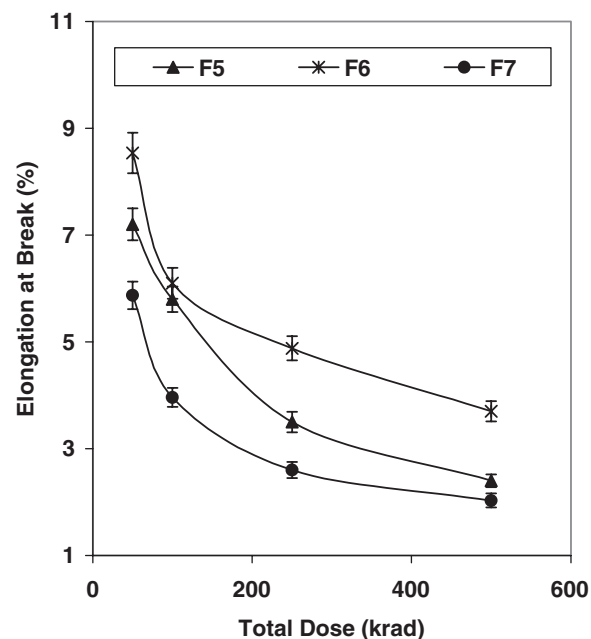


Fig. 5. Elongation at break of the irradiated shellac/EHMPTMA film against various radiation doses.

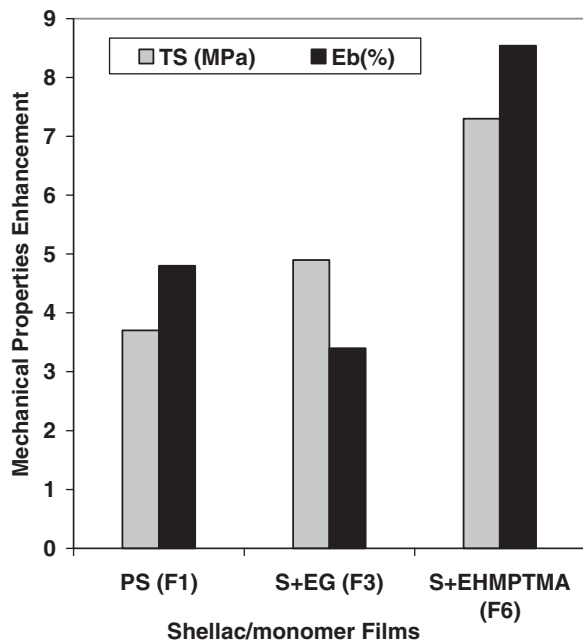


Fig. 6. Comparison of the tensile strength and elongation at break of EG and EHMPTMA grafted shellac films containing 5% monomer.

krad radiation dose. But highest elongation is found in the case of 5% EHMPTMA containing shellac film at 50 krad radiation. EHMPTMA (containing three acrylic groups) showed better grafting than EG (containing one functional group). Grafting of acrylic monomers on to bulk polymers depends on their functionalities, structure, concentration of the monomer, as well as radiation intensity and curing time (27).

3.6 Thermal Properties of the Films

The thermal properties such as melting point (MP) and the co-efficient of thermal expansion (CTE) of the pure shellac film and various monomers containing (formulations F3 and F6) shellac films are shown in Figures 7 and 8. From Figure 7, it is found that the melting temperature of the pure shellac film is 47.9°C. On the other hand, the thermal properties of the monomer containing (5%) films decreased compared to that of pure shellac. For example, shellac + EG and shellac + EHMPTMA films showed the melting temperature of 44.8 and 42.1°C, respectively. All the monomers have very low melting temperatures, as a result, the melting properties decreased when shellac films contain monomers. When monomer treated shellac films irradiated, two types of polymerization reactions may occur, first is heterogeneous reaction (monomer + shellac) and the other is homogeneous reaction (monomer + monomer); as a result, the tensile properties improved as mentioned earlier but melting properties decreased.

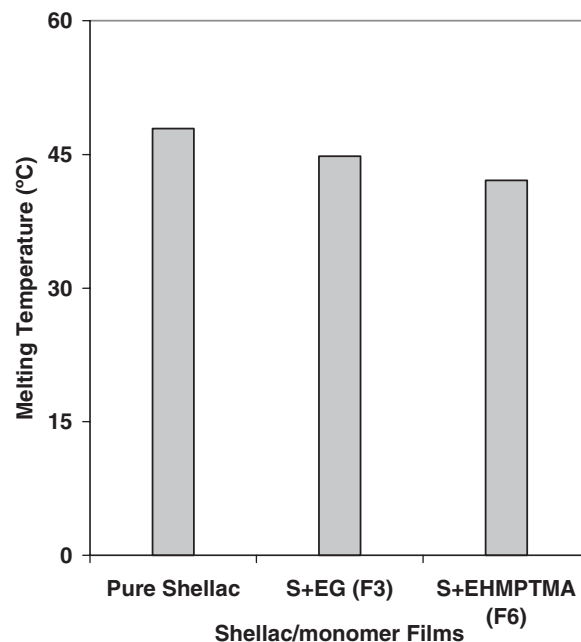


Fig. 7. Effect of different monomers on the melting point of the films.

Coefficient of thermal expansion (CTE) of the polymer is very important and the values are always negative. The CTE of pure shellac film and various monomers containing (formulations F3 and F6) shellac films are shown in Figure 8 where the CTE values are presented at three different temperatures, i.e., 25, 50 and 100°C, which are at room temperature, at near melting point and above the melting point, respectively. Here, the CTE values of the pure shellac films decreased from 25°C (room temperatures) to 100°C. The cause for the decrease of CTE values is, above the melting point of pure shellac (47.9°C), the shellac films become molten, as a result the CTE values decreased significantly. But monomers containing shellac films showed a different trend where the CTE values decreased up to 50°C and then increased. All the monomers used here have very low melting points. It may be that homo-polymer or unreacted monomer inside shellac may be responsible for the increase of CTE values.

3.7 Degradation Studies

Degradation study of the treated (F3 and F6) and untreated films are periodically measured in water and garden soil. The percentages of weight loss are cited in Tables 2–3.

The films were soaked in water for different immersing times (shown in Table 2) and dried at room temperature for 24 h, and their degradation property was measured in extent of weight loss. The percentage of weight loss is shown in Table 2 for the EG and EHMPTMA containing shellac films, along with raw films against the immersing time. From the table, it is observed that the highest weight loss 3.8% occurs

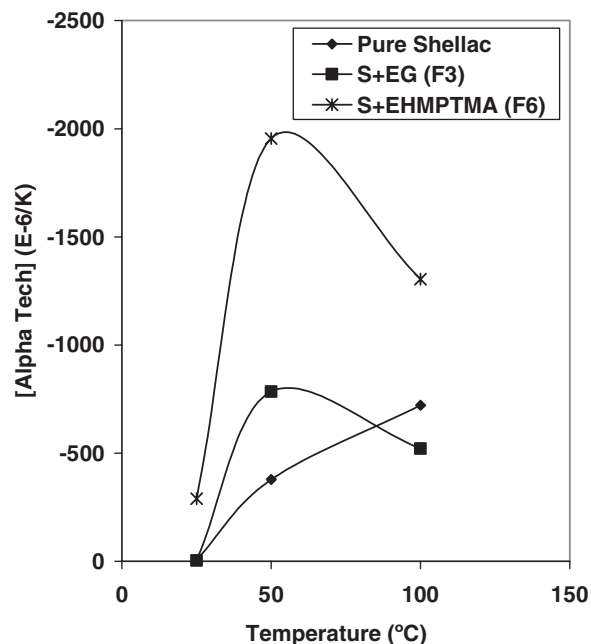


Fig. 8. Effect of different monomers on the CTE of the films.

for the EHMPTMA treated film. EG treated film shows the least weight loss behavior. It is known that more crosslinked polymer loses its weight more than the least crosslinkable polymer (20). The highest TS of EHMPTMA treated film proved that it becomes more crosslinkable with shellac than EG. So, this may be the reason behind the least weight loss of EG treated films, which is 3.1%.

Shellac films both treated and untreated were buried in garden soil for 1 to 30 days to study the effect of such environment conditions on the degradability of the sample (Table 3). After certain periods, samples were withdrawn carefully, washed with distilled water and dried at room temperature and the weight was taken. From the table, it is observed that untreated film shows the least weight loss in a soil burial test. Untreated film loses its weight by about 11.3%. The highest weight loss is achieved for EHMPTMA

Table 2. Loss of weight (%) of the raw and treated shellac films in water

Aging time	Loss of weight (%)		
	Raw shellac film	EG treated film	EHMPTMA treated film
6 h	0.03	0.31	0.17
24 h	0.12	0.61	0.43
72 h	0.25	0.87	0.92
120 h	0.86	1.21	1.32
240 h	1.01	1.65	1.93
360 h	1.68	2.06	3.06
480 h	1.92	2.65	3.68
600 h	1.98	3.1	3.89

Table 3. Loss of weight (%) of the raw and treated shellac films in soil

Aging time	Loss of weight (%)		
	Raw shellac film	EG treated film	EHMPTMA treated film
1 day	0	0	0
5 days	1.49	1.5	1.88
10 days	2.06	2.82	2.59
15 days	3.78	5.03	8.93
20 days	5.96	8.95	16.52
25 days	8.75	15.16	20.81
30 days	11.32	22.5	29.8

treated film, which is about 29.8%. Weight loss of the EG treated films is the lowest among the EHMPTMA treated films, but higher than the raw ones. In the soil burial test, the weight loss pattern depends on the moisture in the soil, microbes' content, temperature and overall microbial degradation process of the polymer (20).

4 Conclusions

We have successfully modified the shellac films by grafting acrylic monomer named EHMPTMA and EG. It was found that, with respect to monomer concentrations and radiation doses, the films showed the highest performance at 5% monomer concentration in shellac (wt/wt) and 100 krad radiation dose. Optimum grafting conditions increased the TS at 100 krad (total dose) and Eb at 50 krad (total dose) than that of raw shellac film. The result illustrates that the monomer EHMPTMA performed the best grafting and showed the highest TS (7.3 MPa) and Eb (8.5%). The present study also figured out the degradation study (in water and soil) and revealed in which conditions the shellac films degrade easily and become more advantageous.

References

- Martin, J. (1982) *Shellac*. Kirk-Othmer Encyclopedia of Chem. Techno., 20, 737-747.
- Chauhan, V.S., Sri Ram, N., Subramanian, G.B.V. and Singh, H. (1973) *J. Chromat.*, 84(1), 51-58.
- Krause, K.P. and Müller, R.H. (2001) *Int. J. Pharma.*, 223(1-2), 89-92.
- Bose, P.K., Sankaranarayanan, Y. and Sen Gupta, C. (1963) *Chemistry of Lac*, Indian Lac Research Institute, Chapt. IV.
- Yates, P. and Field, G.F. (1960) *J. Amer. Chem. Soc.*, 82(21), 5764-65.
- Christie, W.W., Gunstone, F.D. and Prentice, H.G. (1964) *J. Chem. Soc. Suppl.*, 1, 5833-5837.
- Gardner, W.H. and Whitmore, W.F. (1929) *Ind. Eng. Chem.*, 21(3), 226-229.
- Schaeffer, B.B., Weinberger, H. and Gardner, W.H. (1938) *Ind. Eng. Chem.*, 30(4), 451-454.

9. Chang, R., Iturrioz, G. and Luo, C. (1990) *Inter. J. Pharma.*, 60, 171–173.
10. Li, X. and Vasavada R.C. (1999) "Shellac." *Handbook of Pharmaceutical Excipients*, 3rd Edition, p. 462.
11. McGuire, R. and Hagenmaier, R.D. (1996) *Biological Control.*, 7, 100–106.
12. Sheorey, D.S., Shastri, A.S. and Dorle, A.K. (1991) *Part 1, Int. J. Pharma.*, 68, 19–23.
13. Bhadani, S.N., Kumari, M., Sumanta, K. and Gupta, S. (1993) *J. Appl. Polym. Sci.*, 49(8), 1471–1474.
14. Limmatvapirat, S., Limmatvapirat, C., Luangtana-anan, M., Nunthanida, J., Oguchi, T., Tozuka, Y., Yamamoto, K. and Puttipatkhachorn, S. (2004) *Int. J. Pharma.*, 278, 41–49.
15. Ansari, M.F. and Goswami, D.N. (2006) *Pigment and Resin Technology*, 35, 183–187.
16. Pearnchob, N., Dashevsky, A. and Bodmeier, R. (2004) *J. Control Release*, 94(2–3), 313–321.
17. Specht, F., Saugestad, M., Waaler, T. and Müller, B.W. (1998) *Pharm. Technol. Europe*, 10, 20–28.
18. Mishra, M.K. and Bhadani, S.N. (1983) *Die Makromolekulare Chemie*, Rapid Communications, 4, 199–201.
19. Mukherjea, R.N. and Sanyal, S. (1972) *J. Polym. Sci. Part A-1: Polymer Chemistry*, 10, 1553–1555.
20. Haque, P., Mustafa, A.I. and Khan, M.A. (2007) *Carbohydrate Polymers*, 68(1), 109–115.
21. McGinise, V.D. (1986) *Encyclopedia of Polymer Science and Technology*, Wiley InterScience, 418.
22. Peppas, N.A. (1987) *Hydrogels in Medicine and Pharmacy*, CRC Press: Boca Raton, Vol. 1, pp. 1–25.
23. Song, C.L., Yoshii, F. and Kume, T. (2001) *J. Macromol. Sci., Part A-Pure and Applied Chemistry*, 38(9), 961–971.
24. Khan, M.A., Ali, K.M.I., Al Imam, M.R. and Mannan, R. (1997) *J. Polym. Plast. Technol. Eng.*, 36, 89–104.
25. Ferdous, S., Mustafa, A.I. and Khan, M.A. (2003) *J. Macromol. Sci., Part A-Pure and Applied Chemistry*, 40, 817–832.
26. Viengkhou, V., Ng, L.T. and Garnett, L. (1997) *J. Radiat. Phys. Chem.*, 49, 595–603.
27. Ali, K. M.I., Khan, M.A. and Ali, M.A. (1996) *J. Appl. Polym. Sci.*, 60, 879–885.