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Effect of crosslinking monomers on the physico-mechanical and degradation properties of photografted chitosan film

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Abstract

Chitosan was extracted from the dried prawn shell waste through the intermediate product chitin. Thin films of chitosan were prepared by casting and its mechanical properties like tensile strength, elongation at break were studied. The chitosan films were photocured with two types of monomers such as 5% ethylene glycol (EG) and 5% ethylene glycol dimethacrylate (EGDMA) to increase the physico-mechanical properties. Five percent of monomer solution were prepared in MeOH along with 2% photoinitiator; Irgacure-651. Soaking time and UV-radiation intensities were optimized with extent of polymer loading (PL) and mechanical properties such as tensile strength (TS) and elongation at break (Eb) of the cured films. Comparing the properties of EG and EGDMA treated chitosan film, EG showed the best performance. The EG-cured chitosan film with 20 min soaking time showed the highest tensile strength 49.6 MPa and elongation at break 37.2%. The treated films were investigated by FT-IR. The water uptake was determined for raw film 1781%, EG grafted chitosan film 64.4% and EGDMA grafted film 167%. The degradation properties in water, soil and simulated weathering condition were determined for the raw and cured chitosan films. It was observed that the raw film degrades more than that of the treated films.

Keywords: Prawn shell; Chitosan film; Ethylene glycol; Ethylene glycol dimethacrylate; Photocuring; UV-radiation; Degradation

1. Introduction

Chitin and its deacetylated form, chitosan have attained much attention in different type of applications. Chitosan is water soluble as the salt with various acids on the amino group of D-glucosamine unit (Sugimoto, Morimoto, Sashiwa, Saimoto, & Shigemasa, 1998). Partially acetylated chitosan that has about 50% D-glucosamine unit is only able to dissolve in water (Aiba, 1989). These biopolymers are biorenewable, biodegradable and biofunctional (Hirano, 1996; Shigemasa & Minami, 1995). Chitin was prepared from the fresh water prawn shell. About 230 mentionable rivers are criss-crossed over Bangladesh, which gives a lot of fresh water prawn along with a lot of salty water prawn from its 724 km long coastal border.

Ethylene glycol is a colorless, viscous and hydrophilic liquid capable of forming polymer. Some approaches for the graft copolymerization of hydrophilic polymer onto chitin and chitosan were reported as a technique to improve the affinity to water or organic solvents (Aoi et al., 1994; Blair et al., 1987; Hoffman et al., 1997; Kurita et al., 1994; Sugimoto et al., 1998; Yalpani et al., 1991). Grafting polyethylene glycol onto chitosan is a convenient approach to water-soluble chitosan derivatives (Dal Pozzo et al., 2000).

Use of multifunctional monomers in radiation crosslinking is very common. A multifunctional vinyl monomer promotes rapid free-radical propagation reaction leading to network (crosslinking) polymer structures through grafting via their double bonds. Multifunctional unsaturated acrylic monomer is used in the treatment of the polymer film to reduce the UV-radiation intensities to obtain optimum

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properties or to achieve an increased cure state at the same UV-radiation intensities (McGininse, 1986).

Hydrophilic monomer (EG) was selected to improve the mechanical properties of the hydrophilic chitosan films by keeping its inherent biodegradable behavior to some extent. The acrylic monomer, EGDMA with bulkier functional group than EG and with double bond was also used to observe the difference in performance of the two monomers. Photocuring provides some advantages like low energy consumption, ambient temperature operations, no emission of solvents, reduce reaction time, enhanced product quality, etc (Fouassier, 1995). The extent of grafting and homopolymer formation was found to depend on chitosan, amount of initiator, monomer concentration, reaction temperature and reaction time (Lagos & Reyes, 1988). In the present work, 5% EG is chosen as monomer formulation that was optimized in the work of Haque, Mustafa, and Khan (2005). The present study describes the physico-mechanical properties of EG and EGDMA cured chiosan films with dissimilar soaking time and UV-radiation intensities. The grafted and raw chitosan films were then subjected to water uptake and different degradation tests.

2. Experimental

2.1. Materials

Chitosan was extracted from the shell of fresh water Prawn; *Macrobrachium malcolmsoni* of Bangladesh. Ethylene glycol, sodium hydroxide, hydrochloric acid, acetone and acetic acid; purity 99.9% was supplied by Merck, Germany and were used without further purification. Photoinitiator (Irgacure-651) was supplied from Ciba-Geigy, Switzerland.

2.2. Preparation of modified chitosan films

Chitosan was extracted from prawn shell waste (Ferdous, Mustafa, & Khan, 2003). One percent chitosan solution was prepared in a 2% acetic acid aqueous solution. The films were prepared by a casting on glass plate at room temperature. Two types of formulations; 5% EG (F1) and 5% EGDMA (F2) along with 2% photoinitiator in methanol was prepared. The films were soaked into these formulations for dissimilar soaking times (5, 10, 20, 30, 40 min) and irradiated under UV-radiation of different intensities expressed in number of passes (5, 10, 15, 20 passes) using UV machine (IST Technik, Germany). The intensity of the lamp was 2 kW at 9.5 amp current and the wavelength was 254–313 nm with a conveyor speed of 4 m min^{-1}. The relative humidity of the room was around 60–65%.

2.3. Characterization

2.3.1. IR Studies

EG grafted and EGDMA grafted chitosan film (after benzene extraction) was investigated by FT-IR making KBr pellet. The FT-IR machine was of RX1, Perkin-Elmer, USA.

2.3.2. Polymer loading (PL)

The polymer loading of different soaking formulations with the film was determined on the basis of weight gained by the film after the entire treatment process.

2.3.3. Mechanical properties

The mechanical properties of both types of films were investigated after 20–24 h of UV-irradiation to ensure the completion of free-radical reaction. Tensile strength, elongation at break were measured by Universal Testing Machine (INSTRON, model 1011, UK) with load range – 500N, cross head speed – 2 mm min^{-1}, gauze length – 20 mm and efficiency within ±1%.

2.3.4. Water uptake

The water uptake of the EG cured and untreated films was periodically (1, 5, 10, 15, 20, 25, 30, 60 min) monitored up to 60 min to find the profile of water uptake.

2.3.5. Degradation study in water

After getting the water uptake value the water soaked films was wiped and dried. Then the weight loss percentage was determined. The loss of TS (%) and loss of Eb (%) are also measured.

2.3.6. Degradation study in soil burial test

The degradation tendency of the chitosan films in the soil was studied. For this purpose the treated films and untreated films were weighed individually and buried in the garden soil for 1, 2, 3, 4 and 5 days. After these periods, samples were withdrawn carefully, washed with distilled water, dried and reweighed. Finally, the weight loss of various degraded samples and reduction in tensile strength and elongation at break of the samples due to soil degradation were determined.

2.3.7. Simulated weathering effect

The effect of weathering treatment on the different physical and mechanical properties of cured and untreated films was determined using an accelerated weathering tester machine (model: Q-U-V, Q-Panel Co., USA). The temperature during the treatment was varied between 65 ± 2 °C (condensation) through alternating cycles of 4 h sunlight and 2 h condensation for a period of about 5, 15, 25, 35 and 45 h.

3. Results and discussion

3.1. Characterization of the treated films

Polymer loading (PL) and mechanical properties like tensile strength (TS), elongation at break (Eb) are investigated. The tensile strength of raw chitosan film is 28.8 MPa and Eb is 15.5%.

3.1.1. Optimization of soaking time

The results of PL, TS and Eb are cited in the Table 1; where, the values are tabulated against a number of UV-radiation pass as a function of soaking time for the soaking formulation F1 and F2. The PL, TS and Eb values for F1 and F2 formulations increase with increasing soaking time up to 20 and 30 min, respectively. Above these soaking times the PL value and tensile properties for both the formulations decrease with increasing soaking time.

From the table it is observed that the maximum PL value of 8.3% at the 15th UV passes is attained for 20 min soaking time for F1 formulation and the maximum PL value of 6.9% at 10th UV pass is attained for 30 min soaking time for F2 formulation. Soaking increases the cross-section area of the film by swelling. As a result more monomer can diffuse into the chitosan film. But in higher soaking time, the film becomes twisted, shrinkage (Khan, Ferdous, & Mustafa, 2005).

For F1 formulation the highest TS 49.6 MPa is observed at 20 min soaking time and at 15th UV passes. In the table for F2 formulation the highest TS value is 40.7 MPa at 10th pass for 30 min soaking time. The initial increase in TS may be due to the increased swelling, and leads to an increased diffusion of the monomer into the reaction sites and the amount of curing increase. The reason behind the decrease in TS at higher soaking time may be the homopolymerization of monomer at higher concentration.

For the soaking formulation F1, Eb reaches the maximum of 37.2% at 20 min soaking time and 15th UV pass. In the table for F2 formulation the maximum Eb 32.5% of the chitosan film is observed with 20 min soaking time at 10th UV pass. The second highest Eb 29% is obtained for 30 min soaking time at the 10th UV pass for F2 formulation. The inherent character of the film appears to be superior with 20 min soaking time as compared to other soaking times.

The PL value and tensile properties increase with initial UV-radiation doses, attains the maximum value at the 15th passes for F1 formulation and at the 10th passes for F2 formulation for the most cases of soaking time variations and then decreases as the radiation dose increases. This may be caused by the radiation degradation at higher UV doses (Khan, Rahman, Ghosh, & Chowdhury, 2003). Possibly more reaction sites get opened at higher dose of UV-radiation and make film with lower ductility.

3.1.2. Comparison of mechanical properties between the EG and EGDMA grafted chitosan films

The results of mechanical properties enhancement for the case of EG and EGDMA grafted chitosan films are plotted in Fig. 1. From the figure it is observed that EG grafted chitosan film shows 19.6% higher PL value, 22%

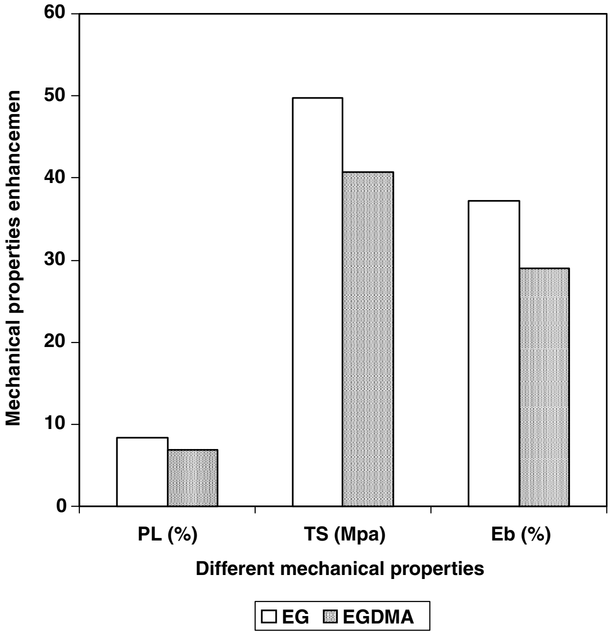

Fig. 1. Comparison of the different mechanical properties of EG and EGDMA grafted chitosan films.

Table 1
Polymer loadings (PL) and Tensile properties (TS, Eb) at different soaking times against number of UV pass

No. of passes		EG treated film (Soaking time in min)					EGDMA treated film (Soaking time in min)				
		5	10	20	30	40	5	10	20	30	40
5	PL	2.0	3.1	3.3	2.6	2.3	4.2	5.0	2.8	4.2	3.2
	TS	26.8	30.4	38.1	34.2	33.0	25.0	27.5	25.5	31.2	22.5
	Eb	15.2	19.2	25.5	23.8	22.5	14.5	20.5	20.0	24.2	11.0
10	PL	2.9	3.8	7.3	3.3	3.0	5.9	6.2	6.4	6.9	4.3
	TS	28.7	30.9	44.0	38.3	35.6	31.9	29.7	30.6	40.7	28.3
	Eb	18.1	22.7	29.5	25.5	24.0	18.7	26.5	32.5	29.0	16.2
15	PL	3.0	4.7	8.3	4.5	3.8	4.7	4.3	3.5	4.8	2.1
	TS	29.1	34.6	49.6	39.7	34.7	28.9	26.3	27.3	33.3	25.5
	Eb	19.2	28.0	37.2	32.0	25.7	15.0	21.0	27.5	26.0	15.0
20	PL	2.3	3.2	7.0	3.1	2.7	1.7	2.5	2.6	3.0	0.8
	TS	27.9	32.0	43.3	30.2	32.1	26.6	25.5	21.0	27.9	20.7
	Eb	16.1	17.7	29.2	22.1	21.2	12.2	19.2	23.4	17.5	13.3

higher TS value and 28.4% higher Eb value than EGDMA treated film. EG is a low molecular weight compound than EGDMA. So, it is possible for EG to make a denser crosslinking with chitosan than EGDMA. Another important reason behind the higher mechanical properties of EG is that the radical formation pattern of EG. In EGDMA only acrylic group goes into radical formation whereas in EG both the methylene and hydroxyl group have the chance to go into radical formation in photocuring procedure. This also helps to form more crosslinking between chitosan and EG than that of with EGDMA. The ending hydroxyl groups of EG in case of pendent linking also form a hydrogen bond with each other or with chitosan molecule. The both case is operated with same concentration (5%) of soaking material with a variation in soaking time. EG of same concentration gives better mechanical properties at 20 min soaking. On the other hand same concentration of EGDMA gives the highest properties at higher soaking time of 30 min. So, it can be concluded that EG grafted film gives better mechanical properties than EGDMA grafted chitosan film.

3.2. Reaction mechanism

The free radical produced in UV-radiation from the photoinitiator; Irgacure-651 is $^{\bullet}CH_3(P)$ (Fouassier, 1995) and the free radicals produced from chitosan (CS–OH) and monomers (M); EG (Patai, 1980) and EGDMA by photolysis may be the followings:

$$CS–OH + P^{\bullet} \rightarrow CS–O^{\bullet} + PH$$

$$CH_2OH–CH_2OH + P^{\bullet} \rightarrow {}^{\bullet}OCH_2–CH_2OH\ (75\%) + PH$$
$$\phantom{CH_2OH–CH_2OH + P^{\bullet}} \rightarrow {}^{\bullet}CHOH–CH_2OH\ (13\%) + PH$$

$$H_2C{=}CH_3CCOOCH_2–CH_2OOCCH_3C{=}CH_2 + P^{\bullet}$$
$$\rightarrow H_2C^{\bullet}–PCH_3CCOOCH_2–CH_2OOCH_3CC{=}CH_2$$

The grafted complex may be the following type:

$$CS–OM_x^{\bullet} + CS–OM_y^{\bullet} \rightarrow CS–OM_x–M_yO–CS$$
$$\text{(Grafted complex)}$$

3.3. Characterization of EG grafted and EGDMA grafted Chitosan film by FT-IR

The IR spectrum of EG grafted chitosan film is shown in Fig. 2. The IR range is taken from (4000–800) cm^{-1}. In the following spectrum of EG grafted chitosan, C—O stretching band of chitosan at 1073 cm^{-1} overlapped with C—O stretching band (1150 cm^{-1}) of PEG Sugimoto et al. (1998). The IR spectrum of EGDMA grafted chitosan is shown in Fig. 3. EGDMA, an acrylate monomer after grafting it produce peak at absorption 1723 cm^{-1} for the C=O stretching. But this peak gets submerged with the peaks at 1649 cm^{-1}and 1524 cm^{-1} those are obtained due to tautomeric effect of the amide group present in the acetylated chitosan. Rest of the peaks in these spectrums is similar to the peaks in the IR spectrum of raw chitosan.

3.4. Water uptake behavior

Percentage of water uptake of the F1, F2 treated and raw chitosan film is plotted against different immersing times in Fig. 4. It is observed for the sample during first few times, water uptake is faster and it then slows down and either attains an almost plateau or continue to decrease. The water uptake percentage is highest for the raw chitosan film and least for the EG treated

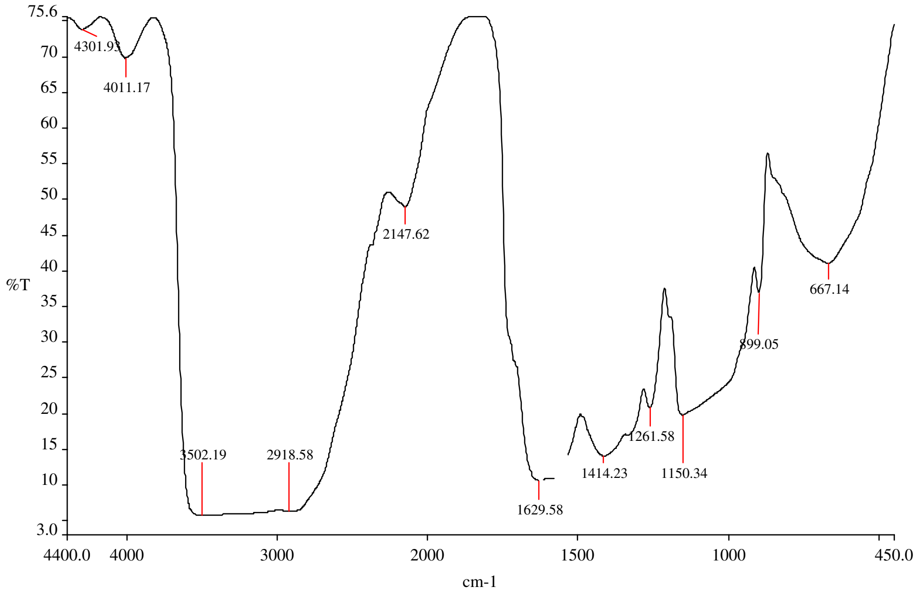

Fig. 2. IR spectrum of EG grafted chitosan film.

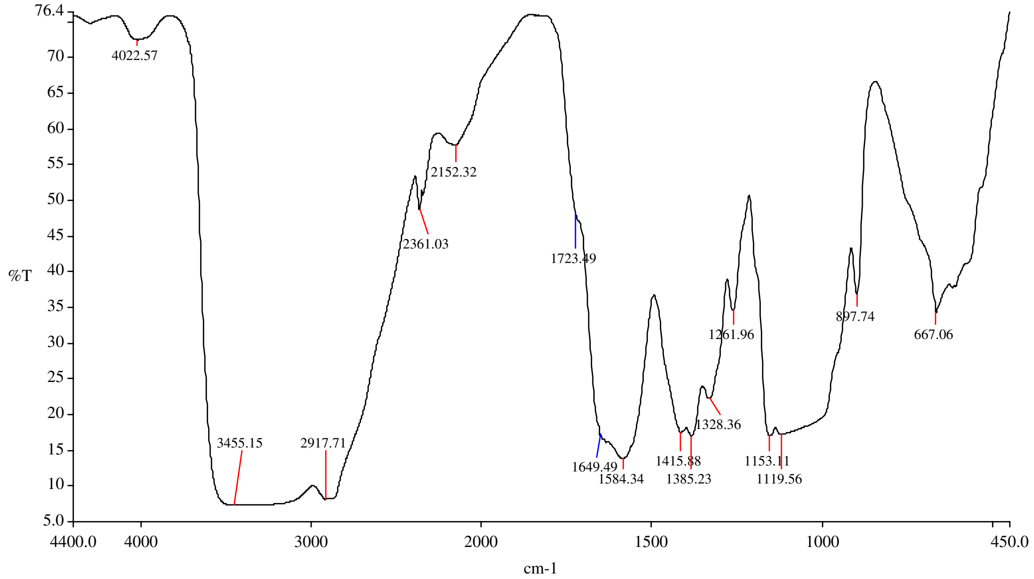

Fig. 3. IR spectrum of EGDMA grafted chitosan.

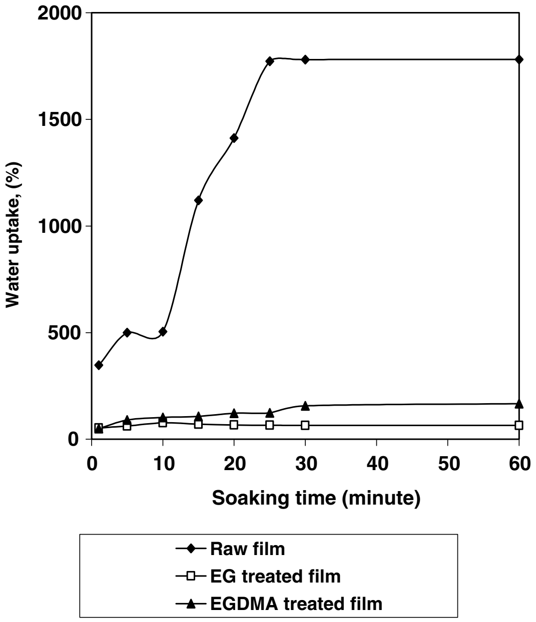

Fig. 4. Water uptake of raw, EG and EGDMA treated chitosan films.

film. The water uptake percent after 60 min is 1781% for raw film, 64.4% for EG treated film and 167% for EGDMA treated film. The lower water absorption of cured chitosan is due to the crosslinking of monomers with chitosan. More crosslinking lowers the void space within the polymer structure to get into the water in it. EGDMA treated film showed greater water uptake than that of EG. EGDMA is a comparatively larger molecule than EG, it may provides more intra and intermolecular space in the grafted polymer structure for water absorption.

3.5. Degradation studies

Weight loss (Wt) and tensile properties (TS and Eb) of the treated and untreated samples in water, soil and simulated weathering condition are periodically measured and the results are shown in Table 2.

The raw chitosan film after soaking in water is no more in condition to test its loss in weight (Wt), TS and Eb. The raw film swells very much with water soaking even with 1 min. The raw chitosan film is not soluble in water but it is damaged in structure to further test. The percentage of loss of weight, TS and Eb is shown in Table 2. for the treated films against the immersing time. From the table it is observed that highest weight loss occur in the EG treated film 22.1% and for the EGDMA treated film 3.8%. The EG treated film giving highest PL, TS and reduce water uptake shows the more weight loss behavior. On the other hand, EGDMA treated film loss a very low weight. The reason may be that in a cross-linked network, one hydrolysis event does not cause two new chains to form. So, cross-link density, strength, and weight will decrease, but the strength loss profile will more closely match the weight loss profile, since all chains bear the same proportion of the load in contrast to the semi crystalline polymers. Thus with random scission of a network structure, there is a more gradual strength loss without catastrophic failure Huang and Edelman (1995). So, it can be said that among the hydrolysable polymer, more cross-linked polymer would loss its weight and strength more than the lower cross-linked polymer. Here, EG and EGDMA both produce hydrolysable polymer but EG proved more crosslinking with chitosan by its high tensile strength and polymer loading than EGDMA. Probably that is why EGDMA

Table 2
Loss of properties of the raw and treated films in water, soil and simulated weathering condition

Aging time	Loss of properties (%)								
	Raw film			EG treated film			EGDMA treated film		
	Wt	TS	Eb	Wt	TS	Eb	Wt	TS	Eb
Degradation properties in water									
1 min	Could not measure			11.2	15.5	65.1	0.26	9.2	12.0
5 min				18.5	18.5	73.1	0.9	11.4	18.9
10 min				18.7	21.9	74.4	1.1	27.6	20.6
15 min				20.1	28.1	81.2	2.0	38.5	34.0
20 min				20.2	50.4	82.5	2.1	38.5	41.3
25 min				20.4	64.2	83.8	2.3	38.9	48.2
30 min				20.8	70.6	86.5	3.1	44.2	50.0
60 min				22.1	76.3	87.4	3.8	58.3	62.0
Soil burial test									
1 day	5.2	5.1	20.2	2.3	20.7	65.1	7.7	24.0	13.7
2 days	12.3	27.3	35.2	23.1	29.6	70.4	15.4	55.3	17.2
3 days	25.4	48.9	58.7	34.8	45.5	71.8	30.0	57.4	27.5
4 days	40.5	62.0	76.3	74.3	75.6	79.8	41.1	77.9	53.4
5 days	60.2	79.1	89.9	95.5	100	100	64.5	92.9	56.8
Simulated weathering test									
5 h	5.2	19.7	18.0	7.4	29.8	34.4	6.6	20.2	36.2
15 h	7.7	19.4	21.1	9.6	34.7	46.3	14.8	23.5	43.1
25 h	10.0	20.4	33.2	11.2	57.1	47.2	16.4	53.5	55.1
35 h	11.8	36.2	39.6	14.9	64.7	48.9	18.1	62.1	62.0
45 h	13.5	42.1	49.3	16.8	68.9	53.0	20.5	70.1	68.9

treated film loses less weight and strength than EG treated film. According to the weight loss reason EG treated film showed highest 76.3% and 87.4% loss of TS and Eb, respectively, EGDMA treated film showed 58.3% and 62% loss of TS and Eb, respectively.

From the table it is observed that in soil burial test the loss of weight is lowest for untreated film and maximum is for the EG treated film. It almost goes into vanish within 5 days. The maximum weight loss for EG is 95.5%. The weight loss for EGDMA in soil is 64.5% and for raw film is 60.2%. The loss of TS is highest for EG treated film around 100% within 5 days. The TS loss for raw chitosan film is 79.1% and for EGDMA treated film is 92.9%. The loss of Eb is highest for EG treated film around 100% within 5 days and the lowest 56.8% is for EGDMA treated film. The TS loss for raw chitosan film is 89.9%. The pattern of loss of weight, TS and Eb of the treated and untreated film depends on the microbial degradation process of the polymer. The moisture in the soil, microbes' content, temperature etc. affects the degradation procedure.

From Table 2 it is also observed that the highest weight loss is for the EGDMA treated film and lowest for the raw film. The weight loss is found 13.5% for raw chitosan film, 16.8% for EG treated film and 20.5% for EGDMA treated film. The highest TS loss is for the EGDMA treated film and lowest for the untreated film. The highest Eb loss is for EGDMA treated film and lowest for the raw film. The loss TS and Eb are found 42.1% and 49.3% for raw chitosan film; 68.9% and 53% for EG treated film; 70.1% and 68.9% for EGDMA treated film after 45 h of simulated weathering.

4. Conclusion

The TS and Eb of the raw chitosan film are satisfactory but the enhancement of the TS and Eb of the treated chitosan film is significant. The best formulation for grafting is identified for ethylene glycol monomer. The present investigation deals with the measurement of impact of water, soil (containing approximately 25% water) and simulating weathering to find out the conditions in which the developed chitosan film is completely degradable so that the treated chitosan film may be more suitable to use in all possible and desirable purposes. At the same time these products can be easily decomposed after use without posing any threat to the environment.

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