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Studies of physico-mechanical properties of photo-cured sodium alginate with silane monomer

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Abstract

Natural and biodegradable polymer SA was extracted from *Sargassum*. Sodium alginate films were prepared by casting and their mechanical properties like Tensile strength (TS), Elongation at break (Eb) were monitored. TS and Eb of the sodium alginate films were obtained as 24.0 MPa and 11.5%, respectively. The resulting films of SA were photo-cured with 3-(trimethoxysilyl)propylmethacrylate (silane) in order to improve the physico-mechanical properties. Several acrylic monomers of various functionalities were incorporated with silane monomer as additives (2%) like 2-Ethylhexylacrylate (EHA), 1,4-Butanediol diacrylate (BDDA), Trimethylolpropane triacrylate (TMPTA) with the aid of UV radiation. A series of formulations was prepared with the monomer silane, and the additives EHA, BDDA, TMPTA, and a 2% photoinitiator (Darocure-1664). Monomer concentration, soaking time, and radiation dose were optimized in terms of polymer loading and mechanical properties. Ten percent of silane treated films produced the highest TS at 5 min soaking time using 15th pass of UV radiation and the recorded value was 49.68 MPa. The highest value of Eb 21.5% was recorded in using additives 2% EHA in 10% silane monomer at 5 min soaking time. Further analyses of the prepared films were characterized by FTIR.
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Keywords: Seaweeds; Photo-grafting; Sodium alginate; UV radiation and silane

1. Introduction

Algae are one kind of sea seaweed. Algae, like any other plant, require three magical ingredients: (i) light, (ii) water, and (iii) nutrients. Algae have an exceptional faculty of containing the abundance of minerals and trace elements in the sea and sometimes, alginate may be prepared with a wide range of average molecular weights (50–100000 residues) to suit the application. Present them in a very strong concentration in mineral elements (iodine, calcium, phosphorus, potassium, magnesium, copper, zinc, cobalt, iron, fluorine, etc.) algae also contain almost all vitamins and amino acids. *Sargassum* species are the tropical equivalents of Ascophyllum and Fucus in terms of uses and applications. They are used as raw materials for alginate production and are also used as a component of animal feed and a source of liquid plant foods or plant biostimulants. There may also be nutraceutical or pharmaceutical applications for fucoidan and other bioactive extracts of the genus. Alginates are linear polyuronic acid hydrocolloids. They are produced by some brown seaweeds and certain species of bacteria. Polymer from seaweeds is used extensively as thickening, stabilizing, and emulsifying agent in both the chemical and food industries. Alginic acid (algin, alginate) is a heteropolysaccharide composed of linear sequences of D-mannuronic acid and its C-3 epimer, L-guluronic acid. The monomeric units are linked

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1, 4. Alginic acid polymers from interchain associations in the presence of di- and trivalent cations (particularly interchain calcium) produce hydrated gels. This ability of a gel to act in the presence of cations has led to a wide range of uses for this industrial polymer. Alginic acid is a structural component of the brown seaweed (*phaeophyceae*).

Silicones have very low glass transition and crystallization temperatures, and low surface energy and solubility parameter. Compared to the major organic polymers they are thermally stable, transparent to UV radiation, and highly permeable to small molecules. This unusual combination of properties is operative over a wide temperature range and less temperature dependent than most common organics. The origin of many of these properties lies in the strength and flexibility of the siloxane bond, its partial ionic character and the low interactive forces between the non-polar methyl group (Owen, 1981). Photo-curing technique proves to be an important method for photo-cross-linking polymers with at their functional group undergoes light induced reactions to form a cross-linked polymer. The term cross-linking is a well-known name in the radiation curing system, which is a three-dimensional network structure, formed by the interaction of electromagnetic radiation with polymeric materials. This network structure is performed under a wide variety of radiation conditions such as ionizing or non-ionizing radiation, photochemical or thermal chemical cure system. Sodium alginate (SA) was graft-copolymerized with methyl methacrylate in an alkali aqueous solution with potassium ditelluratoargentate(III) (DTA) as the initiator (Yinghai, Lanying, Junbo, & Zengqian, 2005). They studied that the grafting parameters, including total conversion, grafting efficiency, and percentage grafting, were evaluated comparatively. The dependence of these parameters on temperature and time, monomer concentration, initiator concentration, and SA backbone concentration was also investigated as well as proof of grafting also monitored. Polymer films of sodium alginate were produced and cured using ultraviolet (UV) radiation and different physico-mechanical properties were examined to improve the properties, prepared films were grafted by silane using UV radiation with photoinitiator and physico-mechanical properties of the treated film.

2. Materials and methods

2.1. Materials

Sargassum was collected from St. Martin's Island, in the north eastern coast of the Bay of Bengal, Bangladesh. The monomers 3-(trimethoxysilyl)-propylmethacrylate (silane), 2-Ethylhexyl acrylate (EHA), 1,4-Butanediol diacrylate (BDDA), and Trimethylolpropane triacrylate (TMPTA) and photoinitiator Darocure-1116 were obtained from Merck, Germany.

Table 1
Composition of formulation M_1 to M_4

Formulation	Silane (%)	MeOH (%)	Photoinitiator (%)
M_1	3	95	2
M_2	5	93	2
M_3	10	88	2
M_4	20	78	2

Table 2
Composition of formulation M_5 to M_7 (W/W)

Formulation	Silane (%)	EHA (%)	BDDA (%)	TMPTA (%)	MeOH (%)	Photoinitiator (%)
M_5	10	2	–	–	86	2
M_6	10	–	2	–	86	2
M_7	10	–	–	2	86	2

2.2. Method

Sodium alginate was extracted from *Sargassum.* Thin films (thickness 0.05 ± 0.03 mm) of sodium alginate were prepared by casting. After 24–30 h various properties like Tensile strength (TS), Elongation at break (Eb) were characterized. These were measured by a universal testing machine (INSTRON, model 1011, UK). The load capacity was 500 N, efficiency was within ±1%. The cross-head speed was 2 mm/min and the gauze length was 20 mm. All the test samples were conditioned at 20 °C and 50% relative humidity. All tests were carried out under the same conditions.

For grafting onto the sodium alginate film, various formulations, named M_1 to M_7, were prepared using several monomers such as silane, EHA, BDDA, and TMPTA in the presence of a photoinitiator, Darocure-1664, in methanol. The compositions of the formulations are presented in Tables 1 and 2. Prepared films were soaked in these formulations of monomer for various soaking times and then UV irradiated, using a UV minicure Machine (IST Technik, Germany) with intensity of the lamp 2 kW at 9.5 A current and the wavelength 254–313 nm a conveyer speed of 4 m/min. Films were kept on the conveyer belt to pass under the UV lamp, for each pass films moved 0.50 m under the UV lamp at conveyer belt speed. After 24 h, physical properties of the cured films were studied. The Polymer loadings (PL) of the films, after grafting using the monomer formulations, were determined as weight gain by the film following the treatment process; $\%PL = \{(W_2 - W_1) \times 100\}/W_1$, where W_2 and W_1 are the polymer weights after treatment and before treatment.

3. Results and discussion

3.1. Characterization of physical properties of sodium alginate film

Thin film of sodium alginate was prepared by casting from 5% sodium alginate solution, which was prepared in

water. Tensile strength (TS) and Elongation at break (Eb) were determined. TS of the sodium alginate film was 24.0 MPa and Eb was 11.5%.

3.2. Grafting onto sodium alginate film with 3-(trimethoxysilyl)propylmethacrylate (silane) monomer

3.2.1. Optimization of monomer formulation

The sodium alginate film was soaked in different formulations (M_1 to M_4) at soaking time 3 min to optimize monomer concentration. After soaking, the films were cured under UV radiation intensities (254–313 nm wave length of optimum UV passes). After 24–30 h of radiation the samples were subjected to different characterization tests to find an optimum formulation.

3.2.2. Polymer loading (PL)

Monomer concentration plays an important role because it affects the polymerization rate and the overall conversion as the properties of cross-linked polymerization (Rahman, Khan, Ali, & Mustafa, 2001; Saha, Khan, & Ali, 1994). The results of PL value of the cured films are presented in Fig. 1 against UV radiation passes as a function of monomer formulation for 3 min soaking time. It was observed from Fig. 1 that, the highest PL was found to be 5.30% with the treatment of monomer formulation M_3, containing 10% 3-(trimethoxysilyl)propylmethacrylate (silane), at 15th UV passes for 3 min soaking time. PL value increased with UV radiation doses, attained a maximum value and then decreased. In all cases the maximum PL values were obtained at 15th passes. Beyond 15th passes, the PL values decreases. At higher radiation, intensity, many primary radicals are produced which initiate radical–radical combination rather than monomer blend polymerization. At the higher UV intensity, degradation of the blend also takes place which also leads to lower PL values; this may be due to the radiation degradation of the film at higher UV passes (Khan & Ali, 1997; Khan, Ali, & Islam, 1996). Percentage of PL increase with silane, up to 10% but more than 10% silane, reduced the curing of sodium alginate film. At lower concentration, silane monomer promoted the reaction with the help of photoinitiator leading to network polymer structure by curing through the hydrolysis and condensation product of silane monomer. With the increase of silane concentration, the hydrolysis and condensation product also increase with the consequence of a faster rate of formation of three-dimensional networks causing restricted mobility (Viengkhon, Ng, & Garnett, 1997). The decrease in PL values at a higher silane concentration may be caused by the fact that, radical–radical recombination process may be dominating, thus creating homo-polymer rather than monomer, sodium alginate backbone reaction, where the hydroxyl group of sodium alginate may be reacting with Si free radicals in silane monomer.

3.2.3. Tensile strength

Tensile strength is a very important parameter in selecting diverse applications of polymer. The results of TS value are shown in Fig. 2, where TS values are plotted against number of UV passes as a function of monomer formulation with the silane monomer treatment, the TS value of the treated sodium alginate film increased, which may be due to the cross-linking of the hydroxyl and silane (C–O–Si bond) forming the three-dimensional network structure causing restricted mobility. From Fig. 2 the highest TS value was 31.22 MPa, achieved with the monomer formulation M_3 containing 10% silane, at 15th UV passes for 3 min soaking time. The presence of hydroxyl group of sodium alginate film may allow for photo-curing reaction with silane, a more link would have occurred. The hardness of the UV cured polymer films depends on the functionality of the acrylic monomer, but the polymer becomes brittle and twisted. Silane contains a monoacrylate group, which leads to a softer polymer and imparts some flexibility

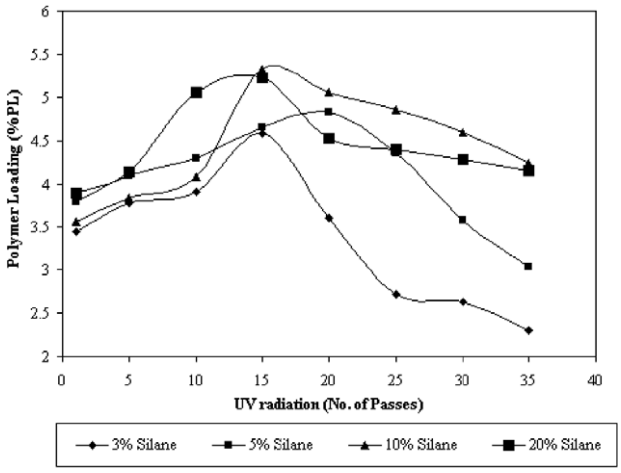

Fig. 1. The Polymer loading (PL%) of the treated sodium alginate film against number of UV passes (UV doses) with respect to monomer (silane) concentration for 3 min soaking time.

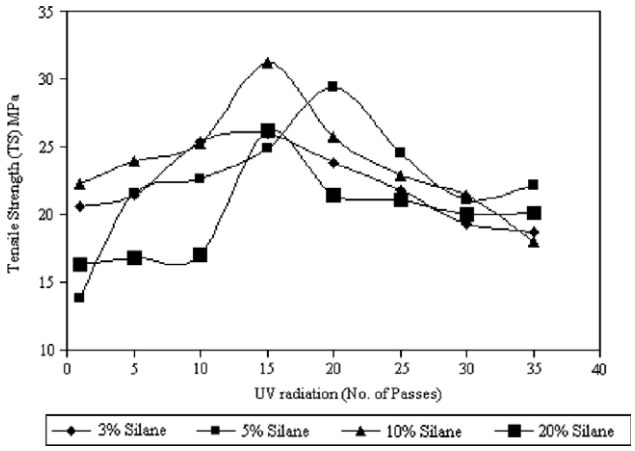

Fig. 2. Tensile strength (TS) of the treated sodium alginate film against number of UV passes (UV doses) with respect to monomer (silane) concentration for 3 min soaking time.

(Aspinall & Dasgupta, 1958). In this case, the sodium alginate films become brittle, twisted, and shrink after 10% silane concentration and the TS decreases. This may be due to the fact that, the homo-polymerization reaction between silane–silane radical is dominant and the reaction of sodium alginate film with silane is less prominent. It was observed that the TS value of the sodium alginate film increased with increase in radiation and on attaining a maximum level 15th UV pass, the TS value decreased. At higher radiation dose the polymer chain scission reduced the TS of the blend. This may be due to the degradation of polymer at higher radiation doses and the film becomes hard twisted and brittle.

3.2.4. Elongation at break (Eb)

The elongation property at break is related to the elastic and brittle character of the film. Silane gives brittleness and exhibits the lowest Eb, while MeOH gives a higher Eb with UV radiation doses. This is due to its inherent character for higher elastic property of rigid flexible or optimum character can be obtained by using the combination of silane and MeOH in different proportions. The results of Eb are plotted in Fig. 3 against the number of passes as a function of monomer composition for 3 min soaking time. From Fig. 3 maximum Eb 13.75% of the sodium alginate film is observed with the formulation M_4 containing 20% silane followed by M_3 containing 10% silane. There was a rise in elongation at the initial step of UV radiation like the TS value. The Eb value increases with the number of UV passes (15th UV passes) and after this the Eb value decreases because of higher UV dose degraded polymer, thus causing the Eb to fall after reaching the maximum. At M_3 the treated film gives higher TS but does not give higher Eb. TS is achieved in the overall cross-linking network within the cured film. Silane gives the highest TS up to a certain limit and after this it produces a brittle film that cracks easily during stretching (Haque, Mustafa, & Khan, 2007). It is concluded that TS and Eb are very much dependent on the monomer concentration are the functionalities of monomers. The combination of silane and MeOH at the ratio of 10 and 88 (M_3) yields the suitable condition for better cross-linking phenomenon at the equilibrium condition that creates the sodium alginate film with the highest TS and moderate Eb.

3.3. Optimization of soaking time

In M_3 formulation, physical properties are found to be of the highest value. So, to optimize the soaking time, sodium alginate films were soaked in formulation M_3 for different soaking times (1, 3, 5, and 7 min) and then irradiated under UV radiation. After 24 h of UV radiation, physical properties were investigated.

3.3.1. Polymer loading

Polymer loading at different soaking times is shown in Fig. 4. It was observed that the PL value increased with soaking time until it reaches to 5 min and give maximum value of 7.59% at 15th UV pass and beyond 5 min soaking time the PL value decreases with increase in soaking time. Soaking increased the surface area of the film. As a result the monomer can easily diffuse into the sodium alginate film and may be reacting with equatorial hydroxyl of sodium alginate in low swelling time. In a higher soaking time the film becomes of twisted shrinkage and pale to look at Norman (1937). The PL value increased with initial UV radiation doses, attained the maximum value at 15th passes of UV radiation and then decreased as the radiation dose increased. This may be the cause of radiation degradation at higher UV doses.

3.3.2. Tensile strength (TS)

Tensile strength at different soaking times is shown in Fig. 5 against number of UV passes in M_3 formulation. The highest TS value of 49.67 MPa was recorded with 5 min soaking time at 15th pass of UV radiation doses.

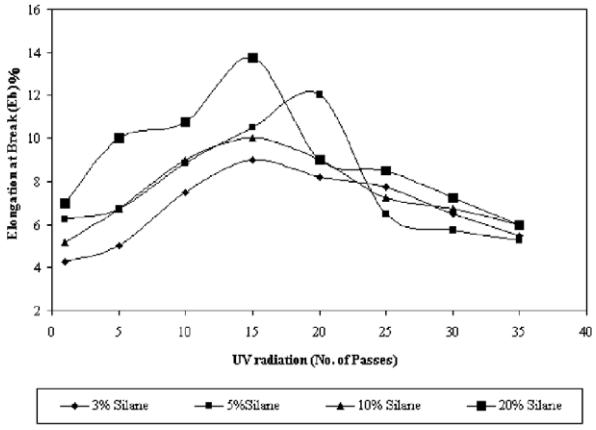

Fig. 3. Elongation at break (Eb) of the treated sodium alginate film against number of UV passes with respect to monomer (silane) concentration for 3 min soaking time.

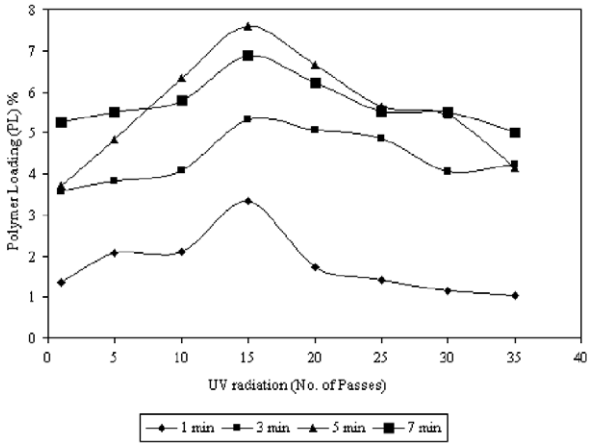

Fig. 4. The Polymer loading (PL%) of the treated sodium alginate film against number of UV passes with respect to soaking time for optimized (10% silane).

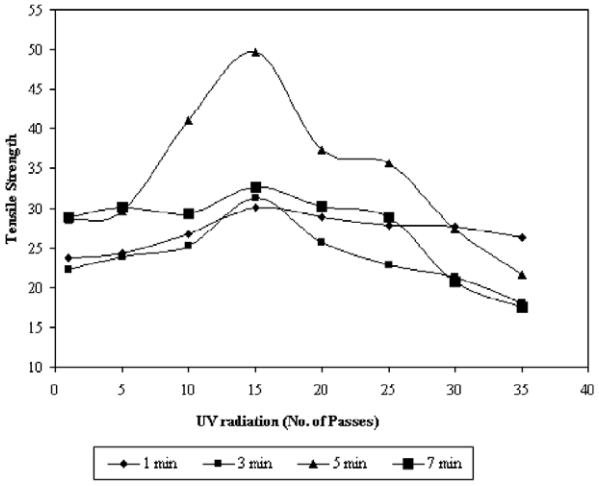

Fig. 5. Tensile strength (TS) of the treated sodium alginate film against number of UV passes with respect to soaking time for optimized (M_3) formulation.

TS value increased with the increase in soaking time. This may be due to the increase in soaking, leading to an increase in diffusion of the monomer into the side of reaction and the amount of curing increases. Hence the TS value increases after attaining the maximum value at 15th passes of UV radiation. It began to decrease with the increase of radiation dose. At higher UV radiation doses, scission of polymer cross-link network took place.

3.3.3. Elongation at break (Eb)

The results of Eb values are presented in Fig. 6 where the Eb values are plotted against the number of UV passes as a function of soaking time for M_3 formulation. The highest Eb value 22.5% was recorded at 5 min soaking time at 15th pass of UV radiation doses. For M_3 formulation, Eb increase with increase in soaking time and it reached the maximum value of 22.5 at 5 min soaking time, and then it began to decrease. It indicates that, in 5 min soaking time, the inherent character of film appears to be superior as compared to other soaking times. So optimization is established for 5 min soaking time and monomer formulation M_3 containing 10% silane.

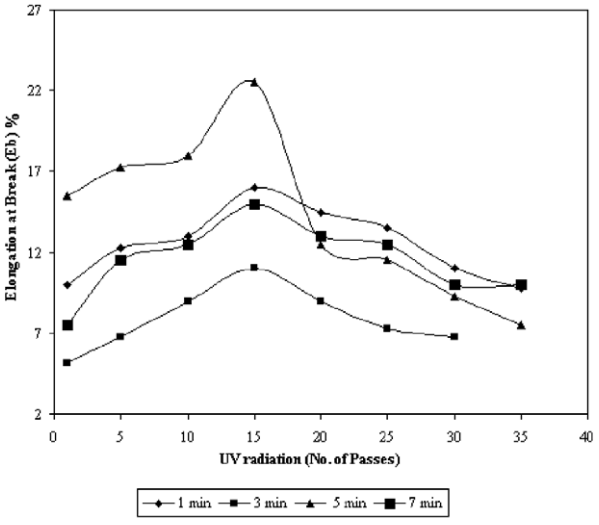

Fig. 6. Elongation at break of treated sodium alginate film against number of UV passes with respect to soaking time for optimized M_3 formulation.

3.4. Additives treatment with silane monomer

To further improve the properties of sodium alginate film, a number of additives (2%) such as 1,4-Butanediol diacrylate (BDDA), 2-Ethylhexyl acrylate (EHA), and Trimethylolpropane triacrylate (TMPTA) were used in the silane (10%) solution and subjected to grafting at optimized condition under UV-radiation.

3.4.1. Effect of additives on silane grafting

To study the effect of additives on the Polymer loading (PL), and mechanical properties like tensile strength and elongation at break value of the sodium alginate films were soaked for 5 min in a small amount of additive (2%) were incorporated in the randomized formulation M_3 for 5 min. The polymer loading is graphically represented in Fig. 7 and the increase of PL in the presence of additives is shown as TMPTA > BDDA > EHA > silane. TMPTA imparts the highest PL (18.9%) values among these additives. This is because triacrylate monomer possesses more curing speed than a monoacrylate monomer (Decker & Moussa, 1989) and TMPTA has tri-functional acrylate groups with branching effect to reach the alginate backbone in three different directions (Khan, Ali, & Idriss, 1993). Similarly the 2nd highest PL values (15.12%) have been achieved by BDDA due to the presence of two effective sites at two acrylate group for combination with the alginate backbone. The third highest PL value (9.8%) has been achieved by EHA due to the presence of one effective site at one acrylate group for combination with the alginate backbone and the lowest PL value (7.6%) has been achieved by silane. The tensile strength is graphically represented in Fig. 8 and the increase of TS in the presence of

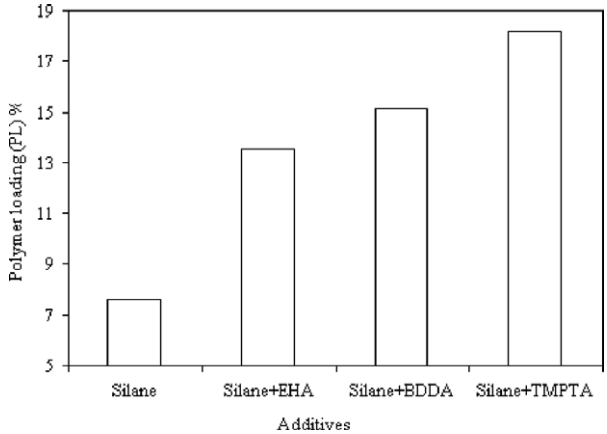

Fig. 7. Effect of additives on polymer loading of silane treated sample.

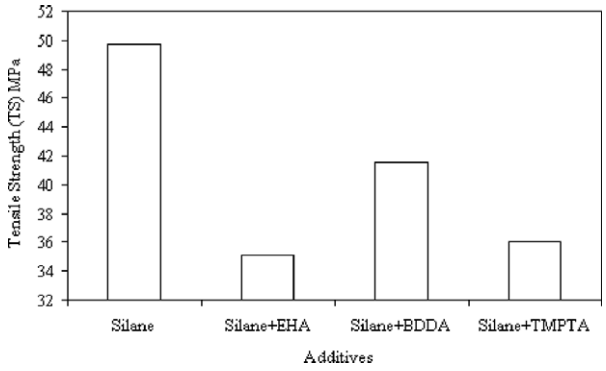

Fig. 8. Effect of additives on tensile strength of silane treated sample.

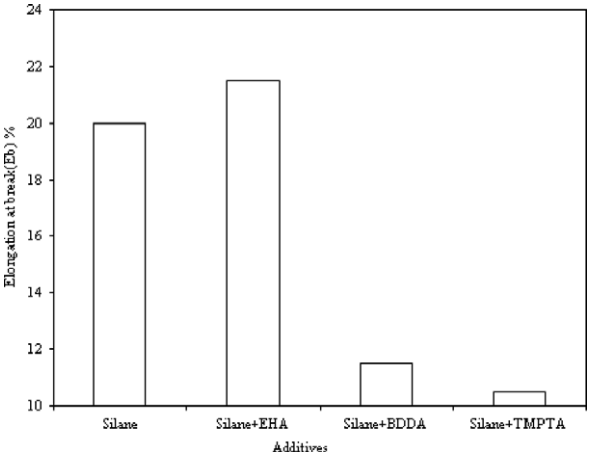

Fig. 9. Effect of additives on elongation at break of silane treated sample.

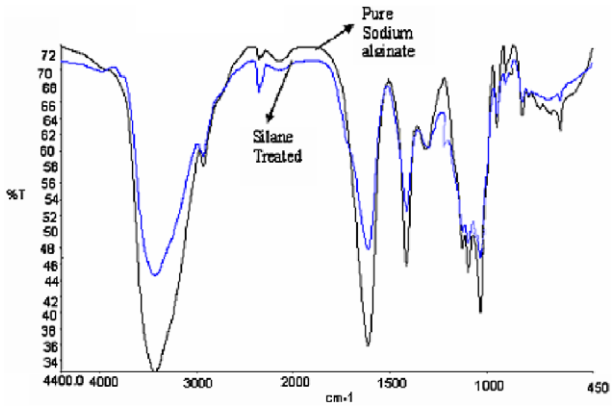

Fig. 10. FTIR spectra of treated and untreated film (450–4400 cm^{-1}).

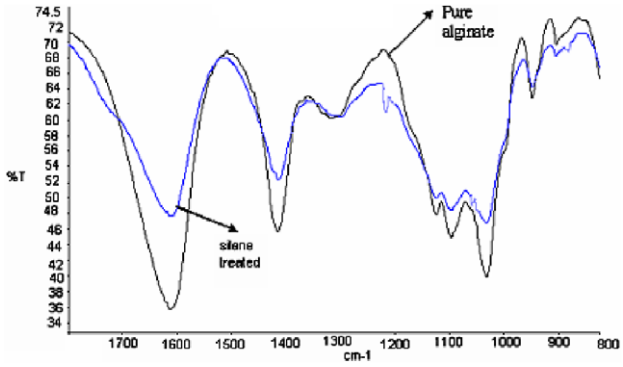

Fig. 11. FTIR spectra of treated and untreated film (700–1700 cm^{-1}).

additives is shown as silane > BDDA > TMPTA > EHA. Silane imparts the highest TS (49.7 MPa) values among these additives and TS values of the experiment have slightly increased very close to each other. This is because silane already consists of one acrylate group. That means there is no or a small effect by the acrylic functional group. More crowding and steric hindrance occur due to increase in the functional group as a result of which less cross-linking occurs. And monomer, monomer homo-polymerization occurs. The elongation at break graphically represented in Fig. 9 and the increase of Eb in the presence of additives is shown as EHA > silane > TMPTA > BDDA. EHA imparts the highest EB (21.5%) values among these additives.

4. Characterization by FTIR

Both untreated and silanized sodium alginate films were characterized by FTIR using KBr to confirm the chemical reaction between the silane and sodium alginate. The spectra of treated with silane and untreated sodium alginate film are shown in Fig. 10 for spectra 4000–700 cm^{-1} and Fig. 11 for spectra 1500–700 cm^{-1}. It is observed that some new absorption bands appear in the silanized curve. The absorption band at around 766 cm^{-1} can be attributed to the –Si–C stretching bond. A very weak peak is observed at around 847 cm^{-1} which also corresponds to Si–C bonds. The broad peak from 925 to 1105 cm^{-1} could be attributed to the presence of asymmetric stretching of –Si–O–Si or Si–O–C (1014–1090 cm^{-1}) bonds. The absorption bands for –Si–O are indicative of the existence of polysiloxane deposit on the sodium alginate and of Si–O–C, confirming the occurrence of a cross-linking between sodium alginate and coupling agent silane. A prominent absorption is also observed at around 1200 cm^{-1} which corresponds to Si–O–C bonds.

5. Conclusion

Sodium alginate films have remarkable physical properties, which could be used as shopping bags. However, further treatment with monomer and additives produces improved physical properties. Varying the concentration of monomer, a series of formulations could be prepared. In an optimized formulation, additives were added which also changed the property to a great extent. As a result, the treated film had a higher tensile strength and a lower brittleness. It was found that the tensile strength of the silane treated film could be increased up to 107% compared to the non-treated one and elongation at break of silane and additive EHA treated film increased up to 87%

compared to a non-treated film. These results are obtained by curing the films with UV radiation and stated monomers. It is anticipated that different monomers could be used to improve the physical properties, preserving their biodegradability at the same time. Several parameters of monomer treated films were optimized, the maximum value of tensile strength of the treated film was found to be 49.7 MPa for Formulation M_3 (10% silane, 88% MeOH, and 2% photoinitiator) at 5 min soaking time on 15th passes of UV radiation.

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