

Mechanical Properties Development of Sodium Alginate Films with Additives by UV-radiation Processing

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ABSTRACT: To improve mechanical properties of polymer films; sodium alginate (SA) films were prepared with ethylene glycol (EG) and photocured. The formulation was prepared at various concentration with EG and photoinitiator (2%) in methanol. The mechanical properties were optimized in case of monomer (EG) concentration, soaking time, and radiation dose of intensities. The highest polymer loading (PL) was 7.1% and tensile strength (TS) of the film was 37.9 MPa were found for 3 min soaking in 5% EG containing formulation at 20th pass of UV radiation; the highest value (22%) of elongation at break (Eb) was obtained at 1 min soaking time at 15th passes of UV doses. The mechanical properties improvement of the films var-

ied acrylic monomers; such as 2-ethylhexylacrylate (EHA), 1,4-butanediol diacrylate (BDDA), and trimethylpropane triacrylate (TMPTA) were used as additives (2%) in the optimized formulation. The highest PL (12.7%) and TS (42.2 MPa) of the films are at 5% EG, 2% TMPTA, and 2% photoinitiator in methanol at 3 min soaking time at 20th pass of UV radiation. The highest Eb (25%) was obtained using additives 2% EHA additives in 5% EG and 2% photoinitiator in methanol at 3 min soaking time. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 275–281, 2012

Key words: sodium alginate; additives; ethylene glycol; UV radiation processing; photoinducing; polymeric film

INTRODUCTION

Alginic acid is a naturally curing hydrophilic colloidal polysaccharide obtained from the various species of brown seaweeds (*phaeophyceae*). Alginates are the salt of alginic acids. Alginate is a natural polysaccharide with a large available quantity in nature. The molecules are long chains that contain two different acidic components, abbreviated here for simplicity to mannuronic (M) and glucuronic (G). It is a linear copolymer consisting mainly of residues of 1, 4-linked β -D-mannuronic acid and α -1,4-linked L-glucuronic acid.¹ These monomers are often arranged in homopolymeric blocks separated by regions approximating an alternating sequence of the two acid monomers. Sodium alginate (SA) is an abundant polysaccharide, which can be obtained from marine algae. Alginate has many useful properties and is very user-friendly and consumer-friendly, because it is renewable, biodegradable, vegetal and not animal in origin, and completely safe by all known. It has been widely used in food, fabric, and medical fields because of its remarkable gelation properties, application in hemostatic materials. Moreover, blending of SA with other poly-

mers creates a new application field for SA. The uses of alginates are based on three main properties. The first is their ability, when dissolved in water, to thicken the resulting solution (more technically described as their ability to increase the viscosity of aqueous solutions). The second is their ability to form gels; gels form when a calcium salt is added to a solution of SA in water. The gel forms by chemical reaction, the calcium displaces the sodium from the alginate, holds the long alginate molecules together and a gel is the result. The third property of alginates is the ability to form films of sodium or calcium alginate and fibers of calcium alginates.

Alginate fibers can be made by extruding an aqueous solution of SA into an aqueous calcium chloride bath. During the production process, the preparation conditions can be altered to produce fibers with different amount of sodium and calcium contents. As a water-soluble polymer, alginate is an excellent gel forming material capable of holding a large amount of water. In recent years, alginate has been widely used in the wound management industry as a novel material for the manufacture of "moist healing" products such as gels, foams, and fibrous nonwoven dressings that are used to cover wounds. In these applications, alginate materials are used either in the dry form to absorb wound fluid, or to donate water to a dry wound when used in the hydrated gel form. In either case, the interaction of the alginate materials and wound surface creates a moist local

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environment. Alginate fibers are particularly useful as raw materials for the production of highly absorbent wound dressings. SA films, SA and carrageenan blend films were prepared and characterized, which was shown those films could be worthy of using as membrane.^{2–5} Radiation processing is being applied in many fields of the national economies of developed and developing countries. Sterilization, polymer crosslinking, tire belt vulcanization, art objects' observation, selected food items' irradiation are among the well-established technologies in this field. Both types of irradiators, gamma sources and electron accelerators are being applied in the process. In the last few years, considerable success has been achieved in modifying the natural polymers through radiation processing to meet specific applications. It has been demonstrated that processing of natural polymers through radiation is simple, effective and commercially attractive. During a short span, many of these research and development activities have successfully progressed demonstrating their commercial utility in the areas of health care, agriculture, and environment in some countries. Polymeric films of SA were cured and grafted by silane using ultraviolet (UV) radiation. The physicochemical properties were improved of the films by using UV radiation.^{6–9} Photocuring technique proves to be important methods for photocrosslinking of polymers at their functional group undergo light induced reactions to form a crosslinked polymer. The term crosslinking is a well-known name in the radiation curing system, which is a three-dimensional (3D) network structure, formed by the interaction of electromagnetic radiation with polymeric materials. Ethylene glycol (EG) molecule contains two primary-OH groups. Its chemical reactions are, therefore, those of primary alcohols twice over. Generally, one -OH group is attacked completely before the other reacts. In this work, polymer films of SA were prepared and physicochemical properties were studied for improving the properties. The films were entrapped by EG with additives as 2-ethylhexylacrylate (EHA), 1,4-butanediol diacrylate (BDDA), and trimethylpropane triacrylate (TMPTA) by inducing UV radiation. The analyses of raw and cured films were characterized by FTIR (Fourier transform infrared spectroscopy).

EXPERIMENTAL

Materials

SA [C₅H₇O₄COONa] was supplied by LOBA chemical (Merck). The monomers EG [OHCH₂CH₂OH], monofunctional 2-ethylhexyl acrylate (EHA) [CH₃(CH₂)₇O(CO)CH₃], difunctional 1,4-butanediol diacrylate (BDDA) [CH₂(OCO)₂CH₂], and TMPTA

[C₁₅H₂₀O₆] and photoinitiator Darocure-1116 (Hydroxy alkyl phenyl ketone derivatives) were obtained from Merck (Germany).

Method

For grafting on to the SA films different monomer formulations (W/W) of 3, 5, 10, and 20% EG concentration with 2% Photoinitiator (Darocure-1116) in methanol named M₁–M₄, respectively, are prepared. Three formulations of 2% different additives as EHA, BDDA, and TMPTA in 5% EG with 2% photoinitiator in 91% methanol are also prepared named M₅–M₇, respectively. SA powder was kept in water for swelling then stirring completely dissolved. Thin films (thickness 0.05 ± 0.03 mm) of 3% SA were prepared by casting on glass plate at room temperature. The SA films were soaked in these formulations for various soaking times and then cured under different UV radiation intensities (expressed in number of passes as 5, 10, 15, 20, 25, 30, and 35) using a UV manicure machine (IST Technik, Germany) with intensity of the lamp 2 kW at 9.5 A current and the wavelength 254–313 nm a conveyer belt speed of 4 m/min; for each pass films moved 50 cm under the UV lamp. The mechanicals properties like tensile strength (TS) and elongation at break (Eb) were characterized by universal testing machine (INSTRON, model 1011, UK). The load capacity was 500N, efficiency within ± 1%. The cross-head speed was 2 mm/min and gauze length 20 mm. All the test samples were studied at 25°C and 60% relative humidity. The polymer loadings (PL) of different soaking formulations with the films are determined on the basis of weight gain be each film after the entire treatment process; %PL = $\frac{W_2 - W_1}{W_1} \times 100$, where W₂ and W₁ are the polymer weight after treatment and before treatment. Fourier transforms infrared spectroscopy (FTIR) spectra are characterized by the pure potassium bromide pellet technique on RX1, Perkin-Elmer.

RESULTS AND DISCUSSION

Grafting onto SA films with EG

Optimization of monomer formulation

The SA films were first soaked in different formulations (M₁–M₄) for 3 min soaking time to optimize monomer concentration. After soaking, the films were cured under UV radiation at various intensities (254–313 nm wave length of optimum UV passes) after 20–24 h the samples were subjected to different characterization tests to find an optimum formulation. Monomer concentration plays an important role, because it affects the polymerization rate and

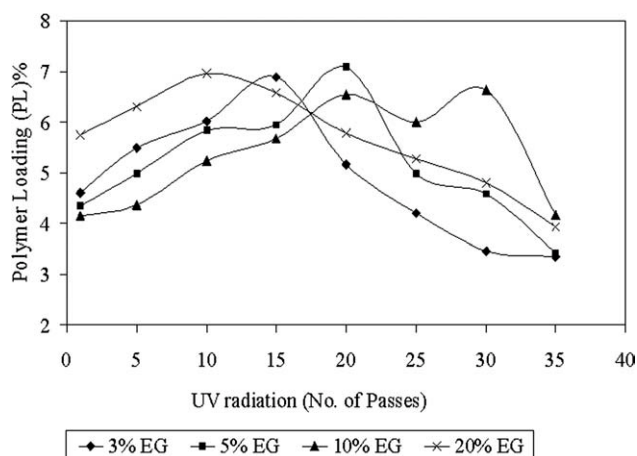


Figure 1 Polymer loading % (PL) of the treated SA film against UV intensities (No. of passes) with respect to EG concentration for 3 min soaking time.

the overall conversion as the properties of cross-linked polymerization.^{10,11}

Polymer loading

PL value increased with UV radiation doses attained a maximum and then began to decrease. In all cases, the maximum PL values are obtained at 20th pass. Beyond 20th pass, the PL values decrease due to the degradation of polymer chain of SA at higher UV passes.^{12,13} The results of PL value of the cured films are presented in Figure 1 against UV radiation intensities expressed in number passes as a function of monomer formulation for 3 min soaking time. It is observed from the Figure 1 that the highest PL is found 7% with formulation M₂ at 20th UV passes at 3 min soaking time. Percentage of PL increased with EG up to 5% then began to decrease with increase of EG with the addition of more than 5% EG in the formulation. At low concentration EG monomer promotes reaction with the help of photoinitiator leading to network polymer structure through hydroxyl group of EG with aid of UV radiation. With the increase of EG concentration, more free radical was produced with the consequence of faster rate of formation of 3D networks causing restricted mobility.¹⁴ The decrease in PL values at higher EG concentration may take place because of radical-radical recombination process may be dominating, thus creating homopolymer rather than EG/SA backbone reaction, where the carboxyl groups of SA may be reacted with free radicals of carbon in EG monomer.

Tensile strength

The results of TS value are shown in the Figure 2; Where, TS values are plotted against number of UV passes as a function of different EG formulations. TS

is very important in selecting diverse application of polymer. The TS value of the treated SA film increases due to the crosslinking of the hydroxyl of SA and hydroxyl of EG (C—O—C) forming the 3D network structure causing restricted mobility. From the Figure 2, the highest TS value was 34.5 MPa, achieved with the monomer formulation M₂ at 20th UV passes for 3 min soaking time. The presence of hydroxyl group of SA film may be allowed for photocuring reaction with EG and crosslink occurred. The TS of the UV cured polymer films depends on the functionality of the free radicals of EG. In this case, the SA films become brittle, twisted and shrinkage above 5% EG concentration and then TS decrease, this may be due to fact that, the homopolymerization reaction between C—C radicals (EG-EG) is dominant and the reaction of SA film with EG is less prominent. It is observed that the TS value of the SA film increases with increase in radiation and attaining a maximum level 20th UV passes, then TS value decreased. This may be due to the degradation of polymer at higher radiation doses and film becomes hard twisted and brittle. The TS of pure (3%) SA dog mode shape films (thickness 0.13 ± 0.01 mm, width 5.00 mm) were 40.77 MPa.

Elongation at break

The results of Eb are plotted in Figure 3 against number of UV passes as a function of monomer composition for 3 min soaking time. The Eb is related to the elastic and brittle character of the film; EG gives brittle and exhibited lowest Eb, MeOH gives higher Eb with UV radiation doses. The inherent character for higher elastic property of rigid, flexible, or optimum character can be obtained by using the combination of EG and MeOH in different

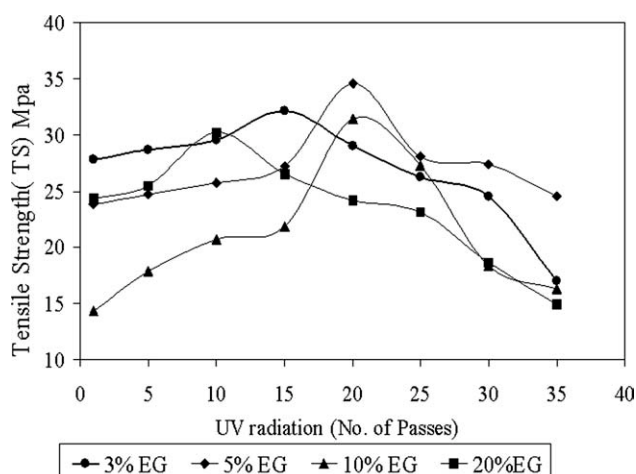


Figure 2 TS of the treated SA film against number of UV intensities passes with respect to EG concentration for 3 min soaking time.

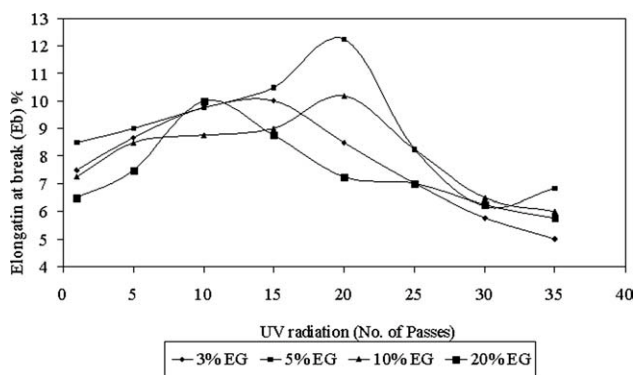


Figure 3 Eb of the treated SA film against number of UV intensities passes with respect to EG concentration for 3 min soaking time.

proportion because EG has brittle, twisted character. From the Figure 3, the maximum Eb 12.2% of the SA film is observed with the formulation M₂ at 20th passes of UV radiation. There is a rise in elongation at the initial step of UV radiation like TS value. The Eb value increases with the number of UV passes (20th UV passes) and after this Eb value decreases. At M₂ the treated film gives higher TS and Eb value. TS is achieved the overall crosslinking network within the cured film. EG gives the highest TS up to a certain limit and after this produces brittle film that cracks easily during stretching on the other hand MeOH increases high elasticity and improves some flexibility. The combination of EG and MeOH at the ratio of 5 : 93 yields the suitable condition for better crosslinking phenomenon that creates the SA film with highest TS and moderate Eb. The Eb of pure (3%) SA dog mode shape films (thickness 0.13 ± 0.01 mm, width 5.0 mm) was 22.50%.

Optimization of soaking time

To optimize the soaking time; SA films were immersed in different formulations during 1, 3, 5, and 7 min, then irradiated under UV radiation. PL and mechanical properties were investigated. SA film treated with M₂ formulation showed the higher mechanical properties.

Polymer loading

PL values are plotted (Fig. 4) against number of UV passes as a function of soaking time. The PL value increases with soaking time up to 3 min and gives a maximum value of 7% at 20th UV passes, but above 3 min of soaking the PL value decreases. Soaking time increases the cross-section area of the film at the same time the film surface becomes light. As a result, monomer can easily diffuse in the SA film and may react with equatorial hydroxyl of SA in low swelling time. In higher soaking time (above 3 min) the film

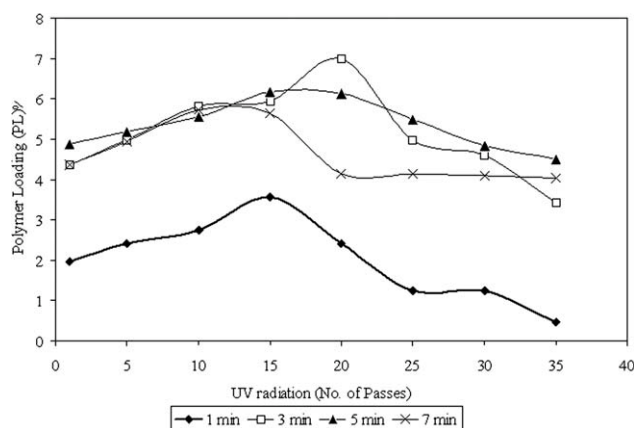


Figure 4 PL of the treated SA film against number of UV passes with respect to soaking time for optimized M₇ (5% EG, 2% TMPTA 91% MeOH, and 2% photoinitiator) formulation.

becomes twisted, shrinks, and pale to look at comparatively to the films of lowest soaking time.^{15–17} The PL value increases with initial UV radiation doses, attains the maximum value at 20th passes of UV radiation, and then decreases as the radiation dose increases.

Tensile strength

The TS values are plotted (Fig. 5) against number of UV passes as a function of soaking time. The highest TS value of 34.5 MPa is achieved with 3 min soaking time at 20th pass of UV radiation doses. TS value increases with the increase of soaking time. This may be due to the increase of soaking time, leading to increased diffusion of monomer into the side of reaction and the amount of curing increases. After attaining the maximum, an increase in the number of passes up to the 20th passes beyond which it decreases as

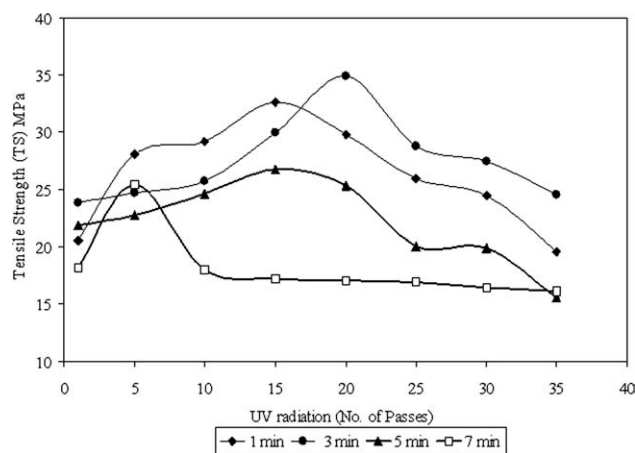


Figure 5 TS of the treated SA film against number of UV passes with respect to soaking time for optimized M₇ (5% EG, 2% TMPTA 91% MeOH, and 2% photoinitiator) formulation.

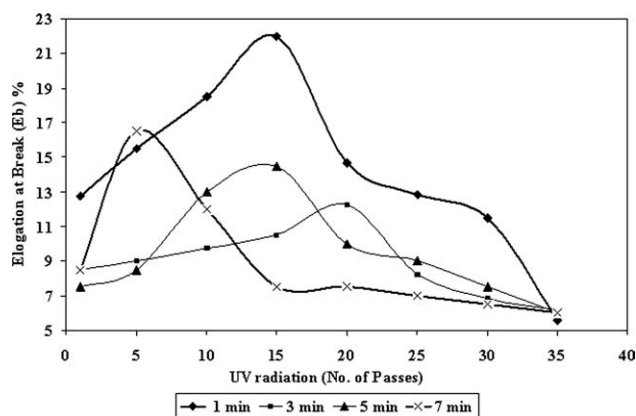


Figure 6 Eb of the treated SA film against number of UV passes with respect to soaking time for optimized M_7 (5% EG, 2% TMPTA 91% MeOH, and 2% photoinitiator) formulation.

the radiation pass are increase. Similar agreement are stated that in 10% silane (2% photoinitiator with 88% methanol) monomer concentration in 5 min soaking time at 15th passes of UV radiation; the TS values increase after attaining the maximum value 49.67 MPa, which was began to decrease with the increase of radiation dose. At higher UV radiation doses, scission of polymer crosslinked network took place.

Elongation at break

The results of Eb are plotted (Fig. 6) against number of UV passes as a function of soaking time. The maximum Eb 18.5% of the SA film is observed with 1 min soaking time the monomer formulation M_2 at 10th of UV radiation, following by 12.2% for 3 min soaking time at 20th UV passes. There is a rises in elongation at the initial step of UV radiation like TS value. The Eb value increase with the increase of soaking time and number of UV passes (20th UV passes) and after this Eb value decreases. The Eb increases with the increase in soaking time, and it reached the maximum indicating that the inherent character of film appears to be superior as compared to other soaking times. So, optimization is established for 3 min soaking time and monomer formulation M_2 containing 5% EG.

Additives treatment with EG

To improve the properties of SA film some additives (2%) as BDDA, 2-ethylhexyl acrylate (EHA), and trimethylolpropane triacrylate (TMPTA) were used in the EG (5%) solution and immersed for grafting at optimized condition (3 min soaking time and 20th UV passes).

Effect of additives on EG grafting

To study the effect of additives on the PL and mechanical properties like TS and Eb on the EG treated SA films with additives (2%) were incorporated in the optimized M_2 formulation at 3 min with different UV radiation. Showing the PL of the films in Figure 7, it was found that TMPTA produced highest PL followed by BDDA and EHA. The increase of PL in the presence of additives is found as $TMPTM > BDDA > EHA > EG$. The highest value of PL was recorded as 12.7% for TMPTA. Similarly second highest PL values (11.3%) has achieved by BDDA due to presence of two effective sites at two acrylate group for combination with alginate backbone. The third highest PL (7.1%) has achieved by EHA due to the presence of one effective site at one acrylate group. The lowest PL (7%) has achieved by EG. This is because triacrylate possesses more curing speed than a monoacrylate monomer and TMPTA has tri functional acrylate groups with branching effect to reach alginate backbone in three different directions.^{16–18} The significant change of TS in the presence of additives can be represented by the series of $TMPTA > BDDA > EG > EHA$. In Figure 7, TMPTA imparts the highest TS (42.2 MPa) values among these additives. The lowest TS (29.5 MPa) has achieved by EHA because it has low glass transition temperature for this reason the film become softer, brittle character. The significant change of the Eb in the presence of additives can be represented by the series of $EHA > BDDA > EG > TMPTA$ (Fig. 7). EHA imparts the highest Eb (25%) because it has low glass transition temperature.¹⁹ Similar phenomena are also stated by M.Z.I. Mollah et al. (2008) who observed that PL values increase by $TMPT > BDDA > EHA > silane$ and TS values increase by $silane > BDDA > TMPTA > EHA$ consequently. They also stated that there is no or small effect by

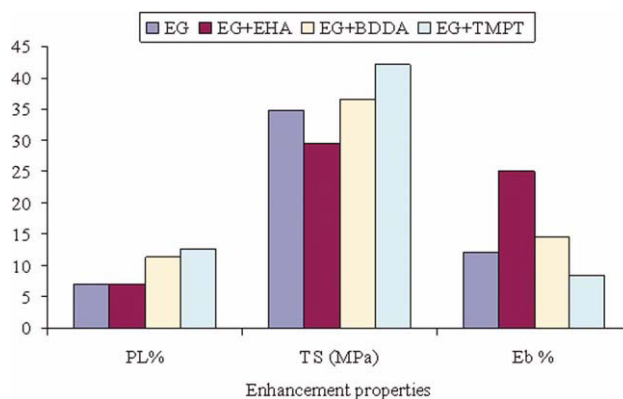


Figure 7 Effect of additives on Enhancement Properties (PL%, TS, and Eb%) of EG treated sample. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

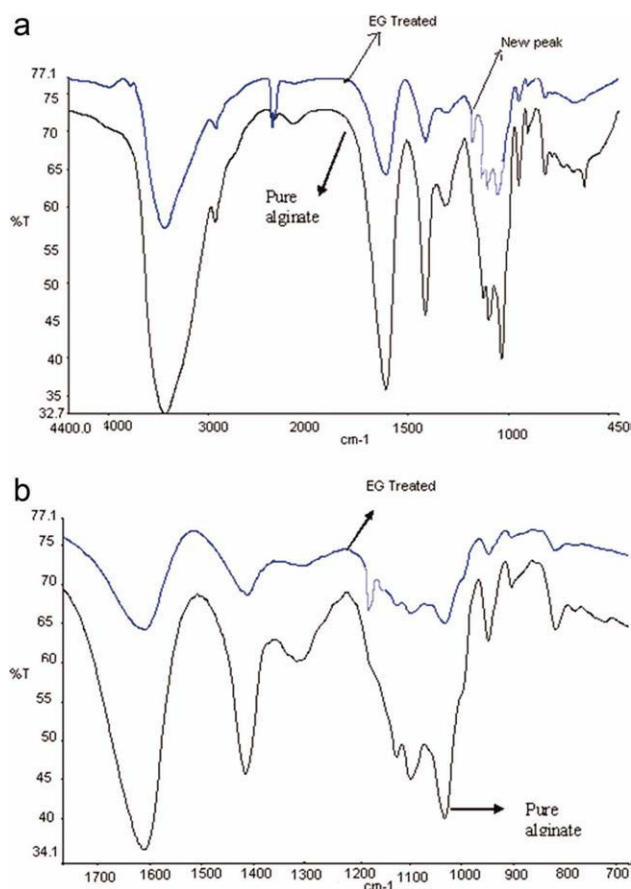


Figure 8 (a) The FTIR Spectra of treated (EG) and untreated film ($450 - 4400 \text{ cm}^{-1}$). (b) The FTIR Spectra of treated (EG) and untreated film ($700 - 1700 \text{ cm}^{-1}$). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the acrylic functional group; more crowding and steric hindrance occur due to increase in the functional group as a result of which less crosslinking and monomer-monomer homopolymerization occurs.

Characterization of pure and EG treated SA films by FTIR

The mechanical reaction backbone between EG and SA (treated with EG and untreated) alginate were characterized by FTIR using potassium bromide pellet (KBr) technique. The spectra of treated with EG and untreated alginate is shown in Figure 8(a) for the spectra $450 - 4400 \text{ cm}^{-1}$ and Figure 8(b) for the spectra $700 - 1700 \text{ cm}^{-1}$. In spectrum of SA characteristic peaks, namely stretching vibration bands of carboxylate at 1612 cm^{-1} and hydroxyl group at 3430 cm^{-1} have been observed. In the spectrum of the grafted SA the aforementioned bands of SA were retained. At the same time the bands of ester carbonyl groups appeared at $1600 - 1700 \text{ cm}^{-1}$ and the characteristic $-\text{C}-\text{O}-\text{C}-$ peaks of treated film between 1154 and 1280 cm^{-1} . It has been also observed that some new absorption bands appear in

EG treated curve. The new absorption bands appear between 1210 and 1230 cm^{-1} could be attributed to the presence of asymmetric stretching of $-\text{C}-\text{O}-\text{C}$ (1220 cm^{-1}). IR spectra analysis also used to prove the grafting sides by making use of the vibration in the intensity of the $-\text{OH}$ absorption band. The intensity of the $-\text{OH}$ band in the spectrum of EG treated was less than that in the spectrum of pure SA, which indicate that the grafted chain were through the hydroxyl groups of SA. Similar types of IR spectra were optimized treated with silane and untreated sample of alginate film.²⁰

Gel content

The gel content of the cured films was obtained by extracting a known weight of the film with hot benzene in a soxhlet for 48 h. A known amount of the film was wrapped with a net specially made stainless steel that was put into the soxhlet and extracted with the solvent. The final weight of the extracted dry film facilitates the determination of the gel content, which was calculated using the following formula:

$$\% \text{gel} = 100 - [100(W_o - W_e)/W_o]$$

where W_o is the weight of the cured film before the extraction, and W_e is the weight of the extracted film after drying it at 105°C until a constant weight is achieved.

The gel content is a representation of crosslinking density in the cured film as a whole. The gel content of the optimized monomer treated (3% alginate solution with 0.5% starch in M_4 formulation) alginate film was determined through hot benzene extraction process. The results of gel content of the films against UV radiation doses as a function of soaking time are shown in Figure 9. The gel content values increase with the increase of UV radiation doses and

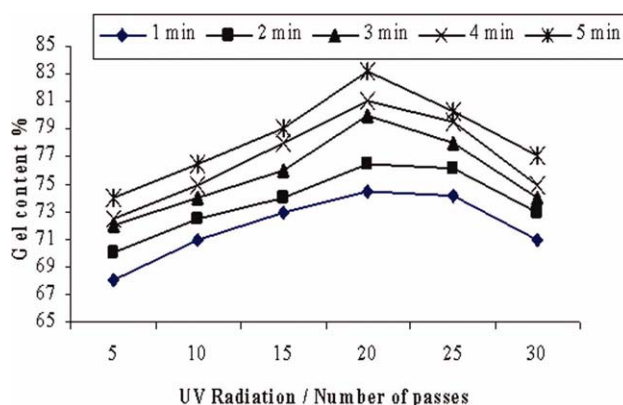


Figure 9 Gel content of optimized monomer soaked (M_4 with 0.5% starch) cured alginate film of EG soaking time against number of UV passes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

after a certain UV dose (20th pass) the gel content decreases. The maximum gel content is obtained at 20th UV pass for all soaking times but the highest gel content (83.10%) was found for 5 min soaking time at 20th UV pass. This result seems that at higher UV dose, the radiation degradation of the film is dominant.

CONCLUSIONS

The treatments with monomer and additives effectively improved mechanical properties of SA films and might have some biodegradation properties. It is extent that to be optimized formulation, additives were added which also changed the property of the SA film. Therefore, treated film had high TS and low brittleness. The TS of treated with EG and additive TMPTA film could be increased up to 75.7% compared to the untreated sample; the Eb treated with EG and additive EHA film increased up to 117.4%, compare with untreated sample. It is anticipated that different monomers could be used to improve the physical properties, preserving, and mechanical properties. Obviously, some parameters were optimized; the maximum (42.2 MPa) TS for M₇ formulation (5% EG, 2% TMPTA 91% MeOH and 2% photoinitiator) at 3 min soaking time on 20th passes of UV radiation of the monomer treated films.

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