Available online at www.sciencedirect.com

SCIENCE DIRECT®

Carbohydrate Polymers 63 (2006) 500–506

Carbohydrate Polymers

www.elsevier.com/locate/carbpol

Preparation and characterization of ultra violet (UV) radiation cured bio-degradable films of sago starch/PVA blend

Mubarak A. Khan [a,*], S.K. Bhattacharia [a], M.A Kader [b], K. Bahari [c]

[a] *Radiation and Polymer Chemistry Laboratory, Institute of Nuclear Science and Technology, Bangladesh Atomic Energy Commission, P.O. Box 3787, Dhaka 1000, Bangladesh*

[b] *Department of Applied Chemistry and Chemical Technology, University of Dhaka, Dhaka, Bangladesh*

[c] *Malaysian Institute of Nuclear Technology Research, Bangi, 43000 Kajan, Malaysia*

Received 16 November 2004; received in revised form 2 June 2005; accepted 11 October 2005

Abstract

Polymer films of sago starch/polyvinyl alcohol (PVA) were prepared by casting and cured under ultra violet (UV) radiation. Different blends were made varying the concentration of sago starch and PVA. Tensile strength (TS) and elongation at break (Eb) of the prepared films were studied. Films made up of sago starch and PVA with a ratio of 1:2 showed the highest TS and Eb. The physico-mechanical properties of prepared films were improved by grafting with acrylic monomers with the aid of UV radiation. A series of formulations was prepared with two monomers 2-ethyl 2-hydroxymethyl 1,3 methacrylate (EHMPTMA) and 2-ethylhexylacrylate (EHA) and a photoinitiator. Monomer concentration, soaking time and radiation dose were optimized in terms of grafting and mechanical properties. The highest TS was at 50% EHMPTMA and 48% EHA and 2% photo initiator at 5 min soaking time and recorded value was 6.58 MPa. The prepared films were further characterized with NMR spectroscopy and scanning electron microscope (SEM).

Keywords: Bioblend; Sago starch; PVA; UV radiation; Monomer treatment; Photocuring

1. Introduction

Starch, an omnipresent bio-material, is one of the most abundant and inexpensive poly-saccharide sources which have the unique characteristic of 'bio-degradability' and easily dissolve in water (Cascone et al., 2001; Zhai, Yoshii, Kume, & Hashim, 2002). Blends of starches and synthetic polymers have been extensively studied since these blends can be prepared so they are biodegradable (Arvanitoyannis, 1999; Graaf & Janssen, 2000; Graaf & Janssen, 2001; Kaplan, 1998). Biodegradable polymers with controllable lifetime were considered as promising alternatives to non degradable ones (Albertson, 1980; Albertson, Barenstedt, & Karlsson, 1994). Biodegradable polymer films have been made from low density polyethylene (LDPE), rice starch and potato starch (Arvanitoyannis, Biliaderis, Ogawa, & Kawasaki, 1998; El-Rahim, Hegazy, Ali, & Robic, 2004). It was found that the presence of high starch content (>30%) had an adverse effect on the mechanical properties of LDPE/starch blends. Both gas permeability and water vapor transmission rate increased proportionally to the starch content in the blend. But addition of additives like starch to PE promotes the microbial consumption and PE chain oxidation reaction (Jana, Banerjee, & Maiti, 1998; Raj, Raj, & Kumar, 2002; Wool, Raghavan, Wagner, & Bilick, 2000). Polyethylene film with prooxidants UV degradation promoters and low level (<10%) of granular starch was successfully used for shopping and garbage bags and agricultural Mulches.

Chemical modification of starch via graft copolymerization of vinyl monomer has been studied in recent years (Athwalle & Vidyagauri, 1998; Kiatkamjormwong, Chomsaksakail, & Sonsuk, 2000). Nowadays, radiation processing technology is being used to improve the properties of polymer product because of its tendency to undergo the chemical reaction between the polymer molecules under irradiation (Gehring, 2000). PVA/starch blend hydrogel was prepared using gamma and electron beam irradiation (Zhai et al., 2002; Zhai, Yoshii, & Kume, 2003). It was shown that there was a grafting reaction between PVA starch molecules besides cross linking of PVA molecules under irradiation. Radiation modification of starch-based plastic sheets was studied (Zhai et al., 2003).

---

* Corresponding author. Tel.: +880 2 7217643; fax: +880 2 8613051.
E-mail address: makhan@bangla.net (M.A. Khan).

0144-8617/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2005.10.019

The investigation showed that the properties of starch based sheet were improved by radiation induced cross linking. Application of radiation for grafting (Tamada, Seko, & Yoshii; 2004) and crosslinking (Zhao, Mitomo, Nagasawa, Yoshii, & Kume; 2003) is used for synthesis of various polymeric materials. Photo-curing technique proved to be an important method for crosslinking polymers because their functional groups undergo light induced reactions (Foussier & Rabek, 1993). Excitation of photoinitiator produces reactive radicals that initiate subsequent reactions in the polymer bioblend thus facilitating crosslinking between the two polymer chains (Kaplan, 1998; Salamone, 1996).

In this work, polymer films of sago starch/polyvinyl alcohol (PVA) were produced, cured using ultraviolet (UV) radiation and different physico-mechanical properties were studied. The prepared films were grafted with acrylic monomer using UV radiation and the physico-mechanical properties of the treated film were studied. Prepared films were further characterized with NMR and SEM.

2. Experimental

2.1. Materials

Sago starch was collected from Malaysian Institute of Nuclear Technology, Malaysia. Polyvinyl alcohol, PVA (MW 15,000) was purchased from Fluka, Switzerland, and photo-initiator Darocure-1664 from Merck (Germany). The monomers 2-ethyl 2-hydroxymethyl 1,3 methacrylate (EHMPTMA) and 2-ethylhexylacrylate (EHA) and photoinitiator Darocur-1664 were obtained from Merck Germany.

2.2. Method

Since, the sago starch does not dissolved in water, starch and polyvinyl alcohol were blended in hot water at about 70 °C for about 15 min to form a homogeneous solution. Several formulations were prepared with this solution, varying the concentration of polyvinyl alcohol (PVA). Table 1 represents the different composition of the blend. Polymer films were prepared by casting on silicon cloth, using these formulations. The films were cured under UV radiation. The tensile properties (TS and Eb) of the sago starch/PVA films were measured with a universal testing machine (INSTRON, model 1011, UK). The load capacity was 500 N. The cross-head speed was 2 mm/min and length was 20 and 10 mm width. All the test samples were conditioned at 20 °C and 50% relative humidity. All tests were carried out under the same conditions.

Table 1
Composition (w/w) of sago starch/PVA blend

Sample no.	Sago starch (%)
Z1	33
Z2	38
Z3	43

Table 2
Composition of the monomer formulations (w/w)

Formulations	EHMPTMA (%)	EHA (%)	Photoinitiator (%)
F1	10	88	2
F2	20	78	2
F3	30	58	2
F4	50	48	2

For grafting on sago starch/PVA films, four formulations, named F1–F4, were prepared with two monomers; EHMPTMA and EHA in the presence of a photoinitiator, Darocure-1664. The compositions of the formulations are presented in Table 2. Prepared films were soaked in these formulations of monomer for various soaking times and then UV irradiated under UV radiation, using a UV minicure machine (IST Technik, Germany). The intensity of the lamp was 2 kW at 9.5 A current and the wavelength was 254–313 nm with a conveyer speed of 4 m/min. Films are kept on the conveyer belt to pass under the UV lamp. For each pass, films are gone by 50 cm under UV lamp with conveyer belt speed. After 24 h, the physical properties of 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; $\%PL=\{(W_2-W_1)100\}/W_1$ where $W_{2,}$ W_1 were the polymer weights after treatment and before treatment.

3. Result and discussion

3.1. Optimization of the composition of sago starch/PVA

3.1.1. Tensile strength of sago starch/PVA

A series of formulations were made using sago starch/PVA (Z1, Z2 and Z3) made. The effect UV radiation dose on sago starch/PVA was displayed Fig. 1. It was observed that tensile strength (TS) initially increased with the increase of radiation intensity and after reaching a maximum value, TS value began to decrease. The increase in TS is due to the increase of cross-linking density of polymer chain. At higher radiation doses, the polymer chain scission that reduced the TS of the blend. The highest TS value of the film sago starch/PVA was obtained from Z1 (at 20 passes) and amount to 4.5 MPa. Fig. 1 also showed that TS value decreased, with an increase in sago concentration.

3.1.2. Elongation at break (Eb)

Elasticity is considered as an important parameter of any polymer. It is related with elongation at break (Eb). The effect of UV radiation dose on Eb is shown in Fig. 2. It was observed that Eb increased with an increase of radiation, showing the same pattern of TS values, and reaching of a maximum value and then decreased with an increase of radiation dose. The highest Eb value of sago starch/PVA was obtained for Z1 composition at 20 passes. The cross-linking density increased with an increase in UV radiation dose, thus resulting in higher Eb. Higher UV dose degraded polymer, thus causing the Eb to fall after reaching the maximum.

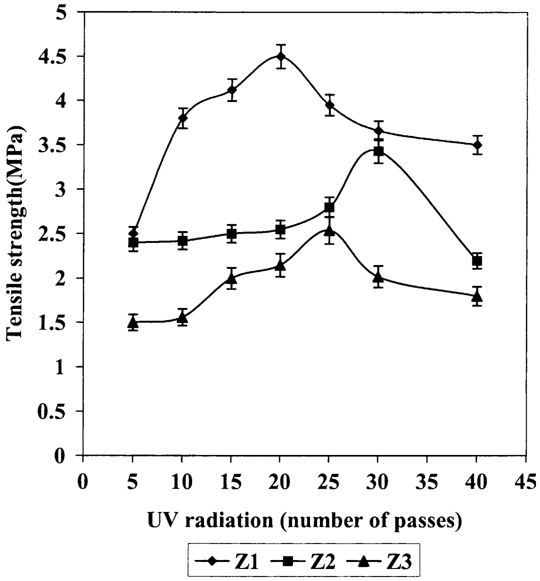

Fig. 1. Tensile strength of different sago starch/PVA film against UV radiation doses.

Since, Z1 composition at 20 UV passes exhibits the optimum performance, this composition is used for later investigation.

3.2. Grafting with acrylic monomer onto sago starch/PVA

Studies of sago starch/PVA film revealed its comparatively lower mechanical properties like TS and Eb. A suitable monomer could play an important role in improving the blend properties (Rahman, Khan, Ali, & Mustafa, 2001). The functionality of acrylic monomer, which controls the physical properties of the UV cured film (Ferdous, Mustafa, & Khan, 2003). The triacrylate monomer gives a higher curing speed than the monoacrylate monomer (Decker, 1998). Generally, multifunctional unsaturated vinyl monomers are used in radiation cross-linking. The reactivity of these monomers depends on various factors such as number of double bonds shape, and size (Khan, Ali, Yoshii, & Makuuchi, 2001). A multifunctional vinyl monomer promotes rapid free radical propagation reaction leading to network (crosslinking) polymer structures through grafting via their double bonds. Different formations (F1, F2, F3, F4) were made using two monomers, EHMPTMA, a denser tri-functional monomer, and EHA and a photoinitiator, Darocure1664. Films were soaked in monomer formulation for 3 min to optimized a definite formulation for curing bio-blend films of under UV radiation at different doses (2, 4, 6, 8 and 10 passes). After 24 h of UV irradiation, several physical properties of films were investigated.

3.2.1. Polymer loading (PL)

Polymer loading on the sago starch/ PVA blend (Z1 composition of the blend) using the formulations (F1–F4), under UV radiation was investigated and presented on Fig. 3. The figure revealed that polymer loading increases with the increase in radiation intensity and reaches a maximum value. From Fig. 3, it is observed that PL values increases with UV radiation intensity and after attaining a maximum value, it begins to decrease. The PL values decreased with further increase in radiation intensity. The maximum value of sago starch/PVA blend was found to be 8.2% using F4 formulation (50% EHMPTMA) at sixth UV pass. EHMPTMA promoted a rapid free radical induced propagation reaction with the help of photo initiator leading to a network polymer structure through curing using their double bonds. After highest value of PL, the residual in saturation increases, thus resulting in a faster rate of three dimensional network structures, causing restricted mobility. At higher radiation intensity, many primary radicals are produced which initiate radical–radical combination rather than monomer blend polymerization. At the higher UV

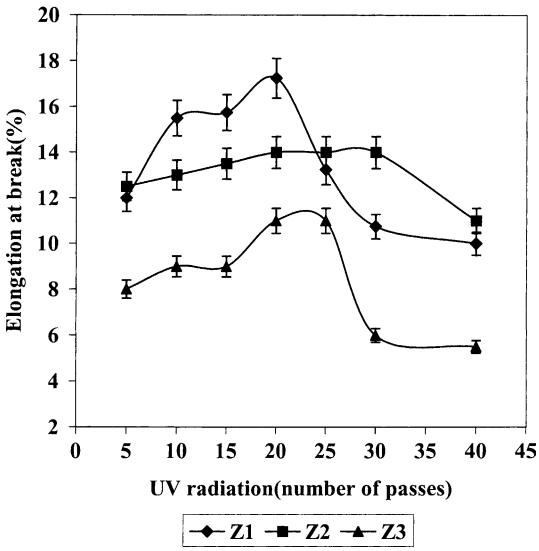

Fig. 2. Elongation at break of different sago starch/PVA film against UV radiation doses.

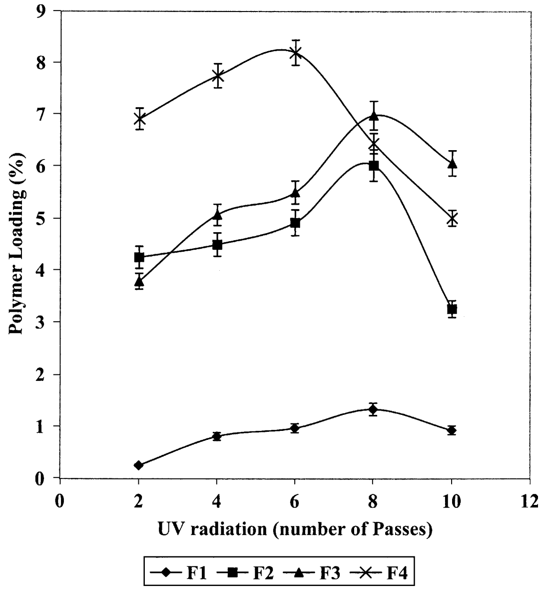

Fig. 3. Polymer loading of sago starch/PVA film in different monomer formulation against different UV radiation doses at 3 min soaking time.

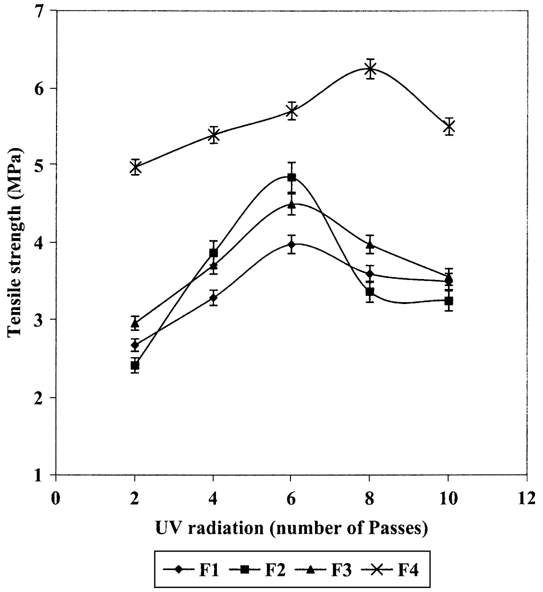

Fig. 4. Tensile strength of sago starch/PVA film in different monomer formulation against different UV radiation doses at 3 min soaking time.

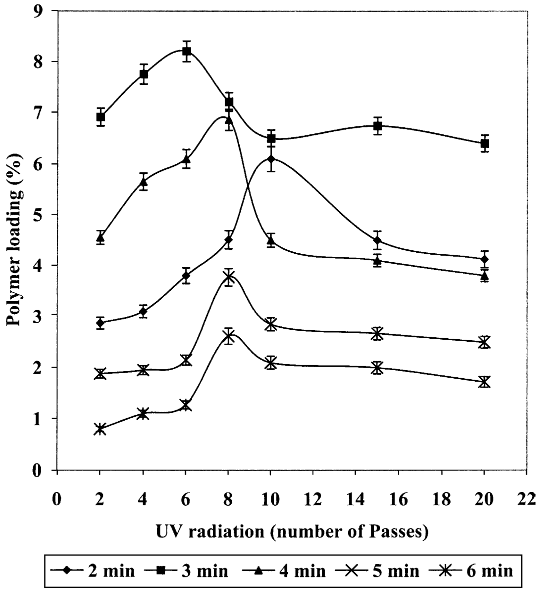

Fig. 6. Polymer loading of sago starch/PVA film at different soaking time against different UV radiation doses in formulation 4.

intensity, degradation of the blend also takes place, which also leads to lower PL values. Fig. 3 also depicts that concentration EHMPTMA in the monomer formulation has significant influence on polymer loading. PL values increased with higher concentration of EHMPTMPA.

3.2.2. Tensile strength (TS)

Variation of tensile strength of grafted blend (Z1 composition of the blend) with UV radiation doses, in the prepared formulation of monomer at 3 min soaking time is presented in Fig. 4. This figure revealed that TS values increased with UV radiation doses up to a certain limit and then decreased. It also shows that concentration of EHMPTMA had made an impact on the TS values. At higher concentration of EHMPTMA, TS values are greater, probably due to the occurring cross-linking between the monomer and blend. However, at higher UV radiation, cleavage of the chain takes place resulting in TS value. The maximum value of TS (6.25 MPa) is found at eight passes of radiation dose in formulation F4 (50% EHMPTMA). This value was 39% greater than that of the non-grafted blend.

3.2.3. Elongation at break (Eb)

Elongation at break of the grafted blend in the monomer formulations is presented in Fig. 5 and shows a similar pattern to the tensile strength. Initially Eb values increase and reach a maximum value and then began to fall. The highest value of Eb

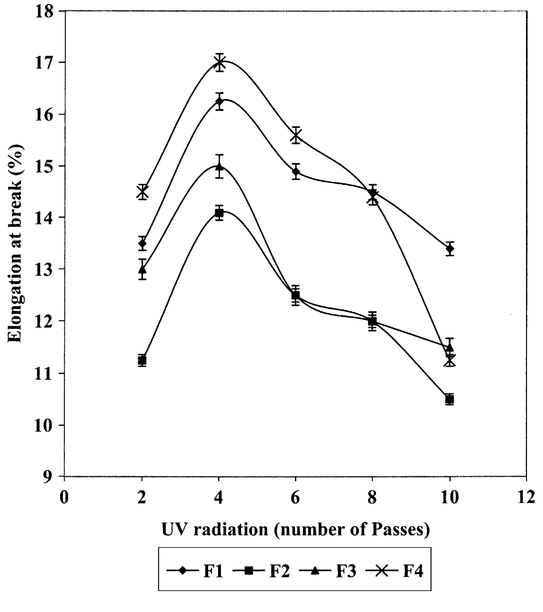

Fig. 5. Elongation at break of sago starch/PVA film in different monomer formulation against different UV radiation doses at 3 min soaking time.

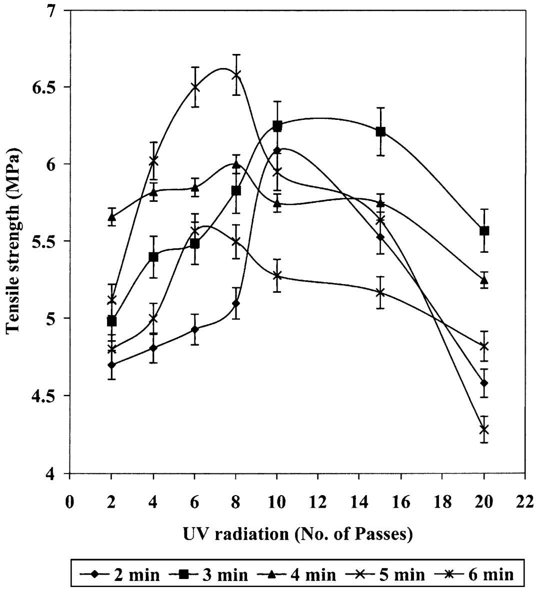

Fig. 7. Tensile strength of sago starch/PVA film at different soaking time against different UV radiation doses in formulation 4.

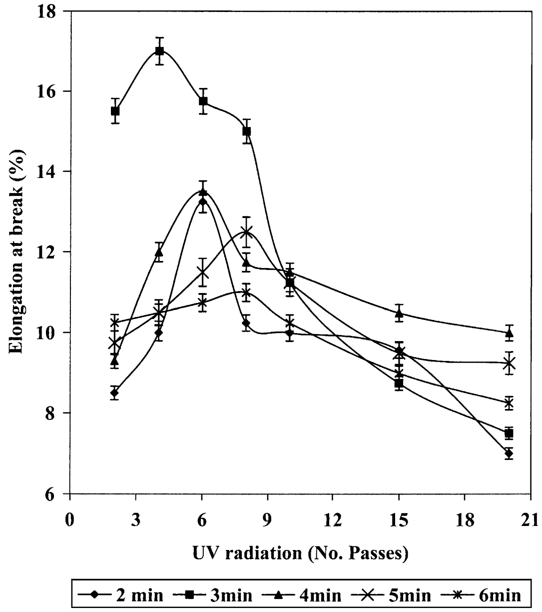

Fig. 8. Elongation at break of sago starch/PVA film at different soaking time against different UV radiation doses in formulation 4.

is found at four passes of UV radiation and 50% EHMPTMA. The mechanical and physical properties of the photocured films are directly related to the functionality and the glass transition temperature (T_g) of the monomer (Ali, Khan, & Ali, 1998). Generally multifunctional monomers increase the TS values and decrease the Eb value. Monofunctional monomer increases the Eb values and decrease TS values. However, some monofunctional monomers with low glass transition temperature enhance both TS and Eb values of the photocured film.

3.3. Effect of soaking time on polymer loading and mechanical properties of sago starch/PVA

Sago starch/PVA blend grafted with formulation 4 (F4) showed the best mechanical properties. Experiments were carried out at different soaking times under different UV radiation intensity using formulation 4 and several physical properties were measured.

3.3.1. Polymer loading studies

Polymer loading (PL) onto sago starch/PVA blend (Z_1 composition of the blend) was investigated at different soaking times (2–6 min) under UV radiation. The results are shown in Fig. 6 where PL values are plotted against number of UV radiation passes. It was observed that PL values increased up to 3 min of soaking time and then gradually decreased. Soaking increases the cross-sectional area of the film, at the same time the surface became lustrous. As a result monomers can easily diffuse into the bio-blend film and react with the functional groups (Ferdous et al., 2003). At higher soaking times, the film became twisted and shrinkage

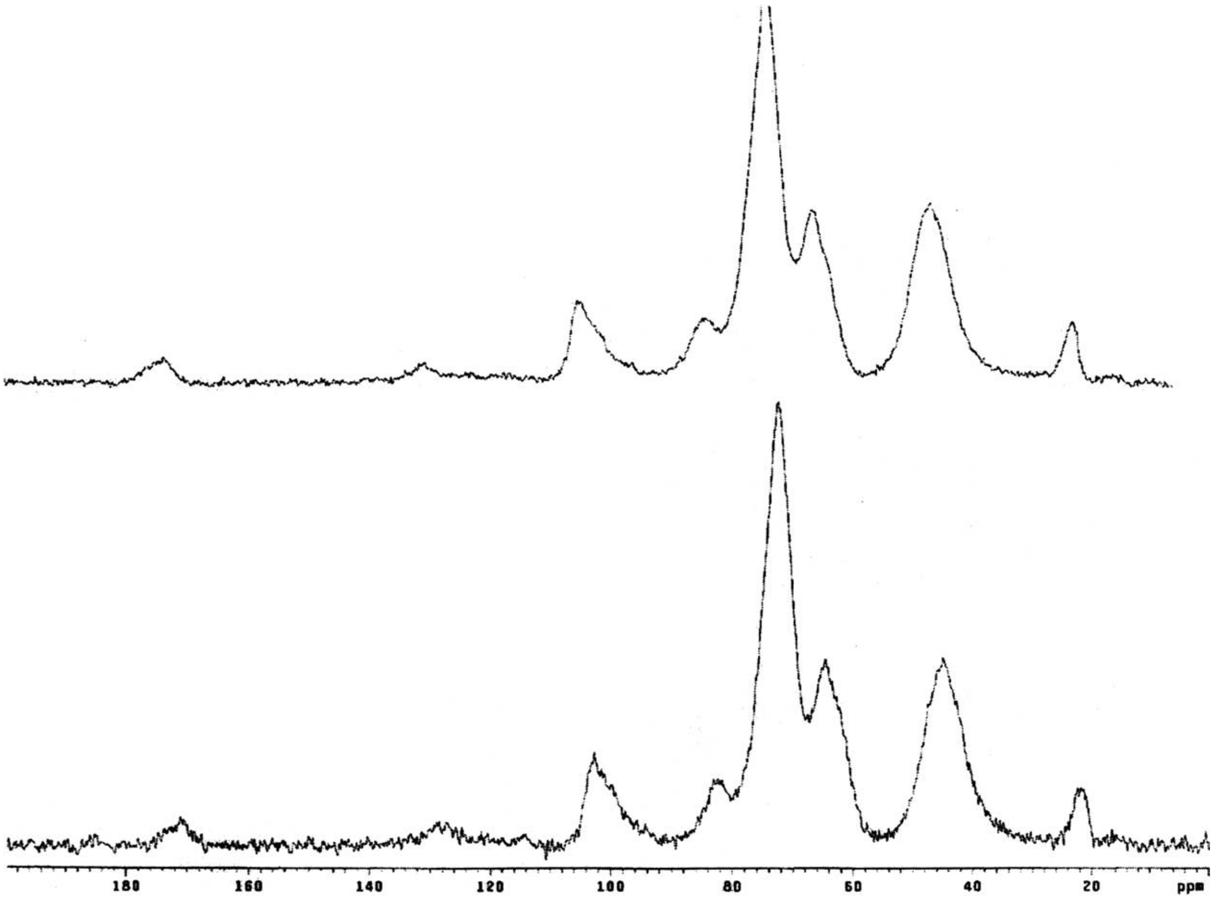

Fig. 9. NMR spectra of sago starch/PVA and PVA.

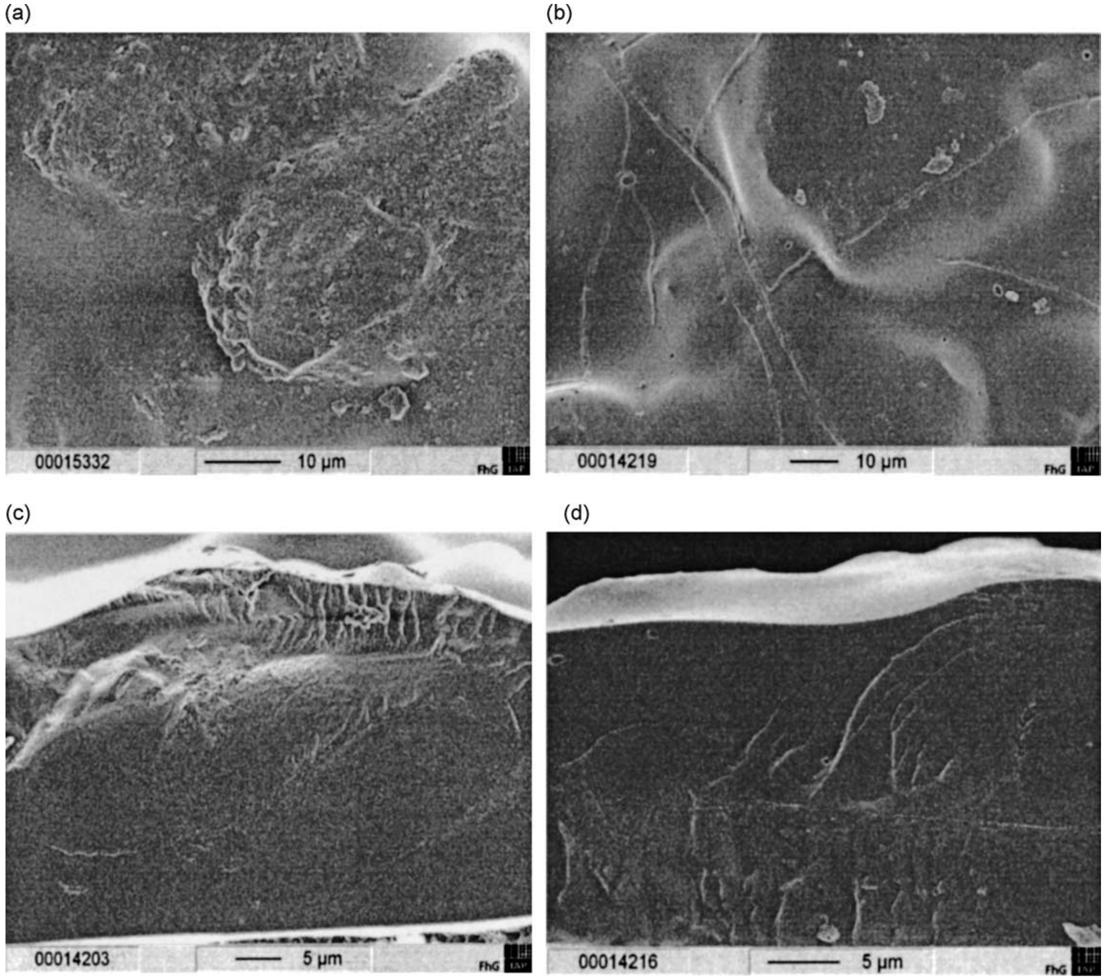

Fig. 10. (a) SEM micrographs of non-grafted (non-treated) sago starch/PVA film; (b) SEM micrographs of grafted (treated) sago starch/PVA film; (c) SEM micrographs of the cross section of non-grafted (non-treated) sago starch/PVA film; (d) SEM micrographs of the cross section of grafted (treated) sago starch/PVA film.

occurred (Ferdous et al., 2003). Initially, PL values increase with UV radiation intensity. After attaining a maximum value, it began to decrease because of radiation degradation of polymer at higher doses. Maximum value PL is found at 3 min soaking under six passes of UV radiation and the value is 8.2%.

3.3.2. Tensile strength

The results of TS values under UV radiation in different soaking time are presented in Fig. 7. The highest TS value (6.58 MPA) was recorded at the sixth pass of UV radiation at 5 min soaking time. TS values tend to increase with soaking time up to eight radiation passes. This may be due to an increased diffusion of the monomer into reaction sites, which facilitate cross-linking between monomer and the blend, and thus, TS values increase (Ferdous et al., 2003). TS values decreased after attaining a maximum value.

3.3.3. Elongation at break (Eb)

Eb values are plotted against the radiation doses at different soaking times and are shown in Fig. 8. The highest elongation at break was recorded for the films soaked for 3 min. However, for all soaking times, TS values first increased and then began to decrease. Therefore, overall optimized value is attained at 3 min soaking time for formulation 4 (50% EHMPTMA) in terms of physical properties.

3.4. NMR spectra

Both non-grafted and grafted films were characterized with NMR. Fig. 9 shows the NMR spectra for sago starch/PVA and PVA. The starch/PVA and PVA lines are superimposed. The NMR spectra of both blends (non-grafted and grafted) were shown identical.

3.5. Scanning electron microscope (SEM) study

The surface topography of the non-grafted and grafted surface films were studied with scanning electron microscope and are shown Fig. 10(a) and (b), respectively. Figure depicts that some holes and embedded particles are found in the films.

However, the grafted film is more homogenous than the non-grafted one. Cross-sections of films were also studied with SEM and are shown on Fig. 10(c) and (d), respectively. Cross sections of both the films are completely homogeneous. But some holes and cracks are found in the non-grafted film. The grafted film is more homogeneous.

4. Conclusion

Varying the concentration of starch and PVA, a series of polymer blend was prepared. High starch content promoted brittleness and lower tensile strength. However, high starch content also promoted biodegradability of the blend. Monomer treatment of the film, using UV radiation, improved the physical properties of the polymer film. As a result, treated film had high tensile strength and low brittleness. It was found that the tensile strength of the monomer treated film could be increased up to 46% compared to the nontreated one. This result is obtained using EHMPTMA and EHA monomer and curing the films UV radiation. It is anticipated that different monomers could be used to improve the physical properties, preserving its 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 6.58 MPa for formulation F4 (50% EHMPTMA, 48% EHA and 2% photoinitiator) at 5(five) min soaking time on eighth passes of UV radiation. SEM studies, also, revealed that monomer treatment endows the resulting polymer film with an improved and homogeneous surface.

References

Albertson, A. C. (1980). Microbial and oxidative effect in degradation of polyehene. *Journal of Polymer Science*, *25*, 1665–1671.

Albertson, A. C., Barenstedt, C., & Karlsson, S. (1994). Degradation of enhanced environmental degradable polyethylene in biological aqueous media mechanism during first stages. *Journal of Polymer Science* , 1097–1105.

Ali, M. A., Khan, M., & Ali, K. M. I. (1998). Relationship between physical–mechanical properties and glass transition temperature of UV cured polymer. *Polymer–Plastics Technology and Engineering*, *37*(2), 175–189.

Arvanitoyannis, I. S. (1999). Totally and partially biodegradable blend based on natural and synthetic macromolecules: Preparation, physical properties, and potential as food packaging material. *Journal of Macromolecular Science, Part C—Reviews in Macromolecular Chemistry and Physics*, *C39*(2), 205–271.

Arvanitoyannis, I., Biliadois, C. G., Ogawa, H., & Kawasaki, N. (1998). Biodegradable film made from low density polyethylene (LDPE), rice starch and potato starch for food packaging applications; Part 1. *Carbohydrate Polymers*, *36*, 89–104.

Athawale, V. D., & Vidyagauri, L. (1998). Graft co polymerization on to starch. Grating of acrylic acid and preparation of its hydrogels. *Carbohydrate Polymers*, *35*, 21–27.

Cascone, M. G., Barbani, N., Cristalini, C., Ginsfi, P., Ciardelli, G., & Lazzari, L. (2001). Bio artificial polymeric materials based on polysaccharides. *Journal of Biomaterials Science, Polymer Edition*, *12*(3), 267–281.

Decker, C. (1998). Special review: The use of use of UV irradiation in polymerization. *Polymer International*, *45*, 133–141.

EL-Rahim, H. A. A., Hegazy, E. S. A., Ali, A. M., & Robic, A. M. (2004). Synergistic effect of combining of VV–sunlight–soil burial treatment on the biodegradation rate LDPE/starch blends. *Journal of Photochemical and Photobiology A: Chemistry*, *163*(3), 547–556.

Ferdous, S., Mustafa, A. I., & Khan, M. A. (2003). Mechanical properties of photocured films of chitosan/PVA and PEO/PVA blend with acrylic monomers. *Journal of Macromolecular Science*, *A40*, 817–832.

Foussier, J. P., & Rabek, J. F. (Vol. Eds.) (1993). *Radiation curing in polymer science and technology: Vol. 1.5*. London: Elsevier.

Gehring, J. (2000). With radiation crosslinking of engineering plastics into the next millennium. *Radiation Physics and Chemistry*, *57*(3–6), 361–365.

Graaf, R. A., & Janssen, L. P. B. M. (2000). The production of a new partially biodegradable starches plastic by reactive extrusion. *Polymer Engineering and Science*, *34*, 2–10.

Graaf, R. A., & Janssen, L. B. P. M. (2001). Properties and manufacturing of new starch plastic. *Polymer Engineering and Science*, *41*, 3–12.

Jana, T., Banerjee, R., & Maiti, S. (1998). Degradation of polythene starch blends in soil. *Journal of Applied Polymer Science*, *42*, 2691–2701.

Kaplan, D. L. (1998). *Biopolymers from renewable resources*. Berlin: Springer, pp. 30–43.

Khan, M. A., Ali, K. M. I., Youshi, F., & Makuchi, K. (2001). Effect of crosslinking monomers on the performance of electron beam-induced biodegradable Bionolle–rubber blends. *Journal of Applied Polymer Science*, *82*, 799–807.

Kiatkamjormwong, S., Chomsaksakail, W., & Sonsuk, M. (2000). Radiation modification of water absorption of cassava starch by acrylic acid/acryl amide. *Radiation Physics and Chemistry*, *59*, 413–427.

Rahman, M. M., Khan, M. A., Ali, K. M. I., & Mustafa, A. I. (2001). Effect of calcium carbonate on the performance of UV curing of partex surface. *Journal of Applied Polymer Science*, *81*, 1854–1867.

Raj, B., Raj, A. E., & Kumar, K. R. (2002). Moisture sorption characteristics starch/low density polyethylene films. *Journal of Applied Polymer Science*, *84*, 1193–1202.

Salamone, J. C. (1996). *Polymeric materials encyclopedia* (Vol. 7) (pp. 5155–5169).

Tamada, M., Seko, N., & Yoshii, F. (2004). Application of radiation-graft material for metal absorbent and crosslinked natural polymer for healthcare product. *Radiation Physics and Chemistry*, *71*, 221–225.

Wool, R. P., Raghavan, D., Wagner, G. C., & Bilick, S. (2000). Biodegradation of dynamics of polymer starch composites. *Journal of App Polymer Science*, *77*, 1643–1657.

Zhai, M., Yoshii, F., & Kume, T. (2003). Radiation modification of starch-base plastic sheets. *Carbohydrate Polymers*, *52*, 311–317.

Zhai, M., Yoshii, F., Kume, T., & Hashim, K. (2002). Synthesis of PVA/starch grafted hydro gel by irradiation. *Carbohydrate Polymers*, *50*, 295–303.

Zhao, L., Mitomo, H., Nagasawa, N., Yoshii, F., & Kume, T. (2003). Radiation synthesis and characterization of the hydrogels based on carboxymethylated chitin derivatives. *Carbohydrate Polymers*, *51*, 169–175.