Preparation and Characterization of Films Based on Crosslinked Blends of Gum Acacia, Polyvinylalcohol, and Polyvinylpyrrolidone-Iodine Complex

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ABSTRACT: In an attempt to develop iodine-release systems based on polymeric blend for biomedical applications, our research group prepared blends of gum acacia (GA), polyvinylalcohol (PVA), and polyvinylpyrrolidone-iodine (PVP-I) complex. The blends of GA/PVA and GA/PVA/PVP-I prepared from the aqueous solutions of the polymers were crosslinked with glutaraldehyde to increase the water resistance of the films and to improve their thermal and mechanical properties. The crosslinked GA/PVA and GA/PVA/PVP-I blend films were characterized by FTIR spectroscopy, DSC, and TGA. The swelling behavior of the prepared blends was investigated and crosslinked GA/PVA blend films were found to be pH sensitive. The properties of PVP-I containing blends differed from those prepared without it probably due to the formation of an intermolecular interaction between PVP-I and the hydroxy-polymers. The results indicated that after crosslinking the blends showed improvement in water resistance, thermal, and mechanical properties. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 775–781, 2008

Key words: crosslinking; blends; gum acacia; polymer-iodine complex

INTRODUCTION

The utilization of polymer blends in drug delivery systems has been done successfully because of the simple and efficient methods of preparation of polymer matrices from blends having desired combination of properties. Blends of polyvinylalcohol (PVA) with natural polymers e.g., hyaluronate,[1] pullulan,[2] chitosan,[3–6] collagen,[7] starch,[8] and cellulose[9] with improved biodegradability, mechanical and thermal properties have been reported. A group of researchers produced bioartificial materials based on the blends of poly (vinylalcohol-*co*-acrylic acid) and dextran.[10] However, PVA has not been blended with gum acacia (GA) and polyvinylpyrrolidone-iodine complex (PVP-I) for the purpose of producing an iodine-release system. GA is a water-soluble polysaccharide obtained from the gummy exudates of the acacia tree. Structurally its central core is D-galactose and D-glucuronic acid to which are attached sugars such as L-arabinose and L-rhamnose. GA is used in pharmaceuticals and more generally as food additives and thickening agents. However, GA has not been used widely as a natural polymer in biomedical applications probably because of its complex branched structure, low thermal stability, and poor mechanical strength of its films. Recently Aminabhavi and coworkers developed polymer matrix tablets based on the graft copolymers of acrylamide with GA.[11] We blended GA with PVA and PVP-I and crosslinked the blend films with glutaraldehyde to prepare water insoluble polymeric blend systems that can release iodine for a prolonged period of time. PVP-I complex is a water soluble disinfectant that has many applications in medicine as a broad spectrum antiseptic having bactericidal, fungicidal, sporicidal, protocidal, and virucidal properties.[12] PVP-I has also been incorporated into some polymeric systems to impart an antimicrobial property to the biomaterials.[13,14] Although several iodine-release systems based on iodine incorporated synthetic polymers have been used for water disinfection,[15,16] there has been no report on the incorporation of less toxic PVP-I in natural polysaccharide-based systems for similar applications.

Water swellable polymer matrices incorporated with elemental iodine have been found to release various forms of iodine in aqueous solution e.g., I_2, HOI, I^-, I_3^-, H_2OI^+, IO_3^-, and OI^-. Out of these, the most potent biocidal forms of iodine are molecular iodine (I_2), hypoiodous acid (HOI), and iodide ion (I^-). The difference between a molecular iodine incorporated polymer and an iodophor e.g., PVP-I containing polymer is that the latter carries practi-

cally all the iodine in a complexed form so that the concentration of free iodine in the polymer matrix is very low. The bactericidal activity of PVP-I complex in aqueous solution is the concentration of uncomplexed or free iodine at the wall of the bacterium. Our attempt to incorporate PVP-I into the polymer blend of GA/PVA will reduce the drawback associated with the presence of elemental iodine i.e., high toxicity, high level of irritation, and staining power.

In the present article we report the preparation, properties, and characterization of crosslinked GA/PVA and GA/PVA/PVP-I blends and the changes in their swelling, thermal and mechanical properties with respect to simple blends.

EXPERIMENTAL

Materials

The GA, hydrochloric acid, and glutaraldehyde (25% solution) were supplied by Merck (India) Limited. The PVA, with an average molecular weight of 14,000 (98–99% hydrolyzed) was obtained from S. D. fine-chem, India. The PVP-I complex was purchased from Sigma, USA.

Methods

Preparation of GA/PVA and GA/PVA/PVP-I blend films

GA/PVA blend films were prepared by using 12% (w/v) aqueous solutions of the two polymers. The ratios (w/w) of GA and PVA in the films were 35/65, 25/75, and 15/85. When PVP-I complex (6% w/v) was used as an ingredient, different ratios of GA and PVA were mixed with a fixed concentration of PVP-I solution. The solutions were cast onto polyethylene sheets at room temperature and dried.

Crosslinking of GA/PVA and GA/PVA/PVP-I blend films

Blend films of GA/PVA and GA/PVA/PVP-I prepared by the method described above were kept in a vacuum oven at 37°C for 24 h before crosslinking. The films were then dipped into 25% aqueous solution of glutaraldehyde containing a few drops of dilute hydrochloric acid (10% v/v) at room temperature for different periods of time (30, 60, and 120 min). The crosslinked films were thoroughly washed with distilled water to remove the unreacted glutaraldehyde molecules and were kept in the vacuum oven at 37°C for 24 h to allow the remaining crosslinker molecules to react completely.

CHARACTERIZATION

FTIR spectroscopy

The FTIR spectra of the samples were recorded on a Perkin–Elmer 1750 FTIR spectrophotometer (Perkin–Elmer Cetus Instruments, Norwalk, CT) using KBr pellets coated with thin films of the polymer samples. The compositions (w/w) of the crosslinked samples chosen were 35/65 (GA/PVA) and 35/65/7.5 (GA/PVA/PVP-I) crosslinked for 60 min and those of the simple blends were 35/65 (GA/PVA) and 35/65/7.5 (GA/PVA/PVP-I).

DSC analysis

The DSC studies of the samples were carried out on Perkin–Elmer Pyris-6, DSC, Germany, over a temperature range of 40°–300°C at a heating rate of 10°C/min in nitrogen atmosphere.

Thermogravimetric analysis

TG studies were carried out to determine the weight loss of the polymer samples as a function of temperature, initial decomposition temperatures for the first (IDT_1) and second stages (IDT_2) and integral procedural decomposition temperatures (IPDT). TGA analyses of the simple and crosslinked blends were carried out in TGA-51, 6TA Instruments, USA, at a heating rate of 10°C/min over a temperature range of 50°–550°C in nitrogen atmosphere.

Swelling studies

Water absorption capacity of the crosslinked GA/PVA and GA/PVA/PVP-I blend films was determined by immersing the dry and weighed strips of the films (20 × 20 × 3.43 mm^3) in distilled water at room temperature and at different pH (2.4, 4.0, 7.2, and 9.2) at room temperature. The samples were taken out from water at various time intervals and weighed after blotting out the excess water from the surface of the films with filter paper. They were put back in water immediately after weighing. The percent water absorption of the prepared blends was calculated using the following equation:

$$\text{Percentage swelling} = [(W_s - W_d)/W_d] \times 100$$

where W_s and W_d are the weights of the films in the swollen and dry states, respectively. The experiment was repeated thrice for each specimen to keep the experimental error minimum.
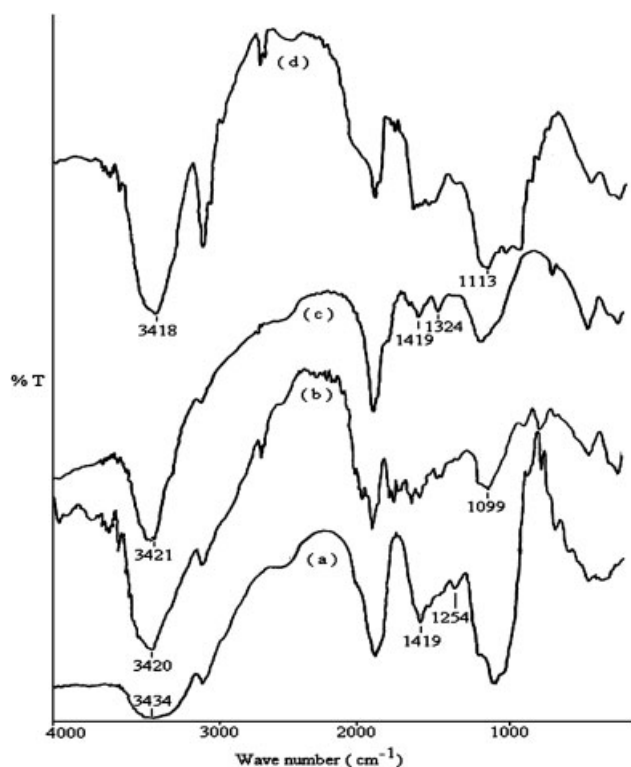
Figure 1 FTIR spectra of (a) GA, (b) PVA, (c) GA/PVA and (d) crosslinked GA/PVA blends.

Measurement of the mechanical properties

The tensile strength, E-modulus, and % elongation at break of simple and crosslinked blend films ($110 \times 17 \times 3.43 \text{ mm}^3$) were measured at room temperature on a tensile test machine Zwick/Z010, Germany. The rectangular specimens were mounted between the grips of the machine before applying the stress at a tensile speed of 50 mm/min.

RESULTS AND DISCUSSION

GA was blended with PVA to improve the mechanical strength of the natural polysaccharide that otherwise produces brittle and weak films. The compositions of the blend films prepared were 35/65, 25/75, and 15/85 (w/w) of GA and PVA. To impart antimicrobial property to the GA/PVA blend and to use it as an iodine-release system, water-soluble PVP-I complex was used as an ingredient. The blend films of GA/PVA and GA/PVA/PVP-I were crosslinked to produce water resistant but swellable, tough, and thermally stable polymer films.

FTIR spectroscopy was used to investigate the crosslinking reaction between the hydroxyl groups of GA/PVA blend and the aldehyde groups of the crosslinker. The spectra of GA/PVA and GA/PVA/PVP-I samples were compared to study the changes after incorporating PVP-I complex.

Figure 1 presents the FTIR spectra of GA, PVA, GA/PVA, and crosslinked GA/PVA blends. The FTIR spectrum of GA/PVA blend showed the presence of strong —OH absorption at 3421 cm^{-1} [Fig. 1(c)]. The band at 1419 cm^{-1} [Fig. 1(a)] characteristic of gum has been present though its intensity has been significantly reduced in its blend with PVA. The absorption band at 1254 cm^{-1} related to C—O—C of the polysaccharide's rings has shifted to higher frequency in the blend [1324 cm^{-1} Fig. 1(c)]. Also the band at 1099 cm^{-1} due to C—O stretching in the spectrum of PVA [Fig. 1(b)] is absent in the blend. The changes in the IR spectrum suggest a probable interaction between the two polymers in the blend. The reaction between the hydroxyl groups of GA/PVA blend and the aldehyde groups of glutaraldehyde has been confirmed by the presence of a strong peak at 1113 cm^{-1} due to C—O—C bonds of the acetal groups in the IR spectrum of the crosslinked sample [Fig. 1(d)]. Figure 2 shows the FTIR spectra of PVP-I complex, GA/PVA/PVP-I, and crosslinked GA/PVA/PVP-I blend. The strong absorption peak at 1285 cm^{-1} in PVP-I complex [Fig. 2(a)] due to vibration of —OH of —C—O···H···O—C— was absent in the spectrum of GA/PVA/PVP-I blend [Fig. 2(b)] showing some bonding changes in the region —O·····H$^+$(I$_3^-$)·····O—. Notable feature in the FTIR spectrum of crosslinked GA/PVA/PVP-I blend is the presence of a broad peak of
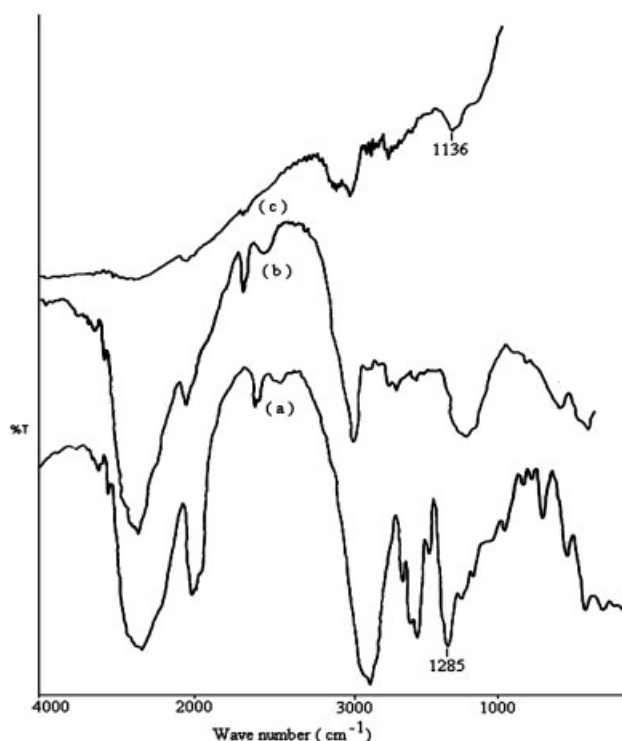
Figure 2 FTIR spectra of (a) PVP-I, (b) GA/PVA/PVP-I, and (c) crosslinked GA/PVA/PVP-I blends.
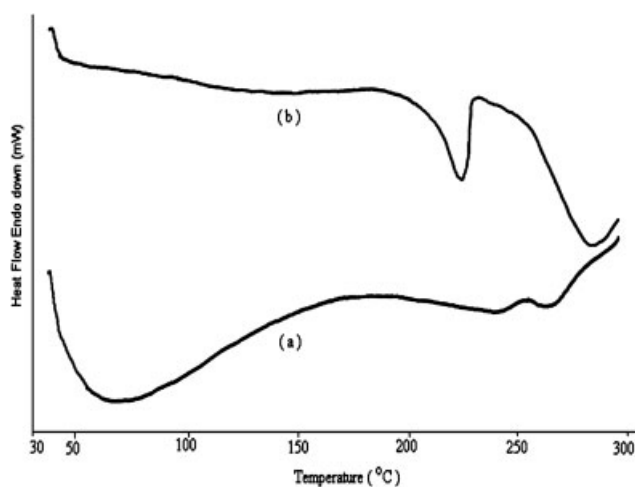
Figure 3 DSC curves of (a) pure GA, and (b) pure PVA.

medium intensity at 1136 cm^{-1} [Fig. 2(c)]; this can be assigned to the formation of acetal groups between the —OH and —CHO groups.

DSC analysis was used to estimate the changes in thermal properties of the GA/PVA blends after adding PVP-I complex in the mixture and after crosslinking of the simple blends with glutaraldehyde. Figures 3 and 4 show the DSC curves of pure GA, pure PVA, and the blends prepared from GA, PVA, and PVP-I complex.

The DSC scan of pure GA [Fig. 3(a)] shows a very broad endothermic peak around 70°C and another with a very small area at 243°C. The first endotherm can be related to the melting and partial thermal decomposition of the complex polysaccharide consisting of several sugar units present as branches and sub-branches. The thermal decomposition of GA below 100°C interferes with the glass transition of the polymer. The DSC curve of pure PVA [Fig. 3(b)] shows a sharp melting peak at 225°C and its ΔH value of 61.471 J/g suggests a high degree of crystallinity. It does not show a glass transition temperature that probably became suppressed due to the presence of moisture.[17] Figure 4(a) representing the DSC scan of the simple blend of GA/PVA shows the formation of a homogeneous blend of the two polymers. The absence of the broad endothermic peak of GA at 70°C and the lowering of melting peak of PVA are marked changes observed in the DSC curve of GA/PVA blend. The changes point to the suppression of an initial thermal decomposition of GA and an imperfect crystallization of PVA due to blending. The sample containing PVP-I complex shows a sharp melting endotherm at about 125°C [Fig. 4(b)] that appears at a much lower temperature compared with that of the blend containing no PVP-I. This seems to indicate the formation of an intermolecular interaction between PVP-I and the

hydroxyl polymers. The presence of such an interaction was indicated by FTIR spectroscopy.

The crosslinked blend of GA/PVA shows a T_g at about 69°C and twin melting peaks at 165 and 178°C, which could be related to the glass transition of the amorphous component and melting of the crystalline component, respectively [Fig. 4(c)]. The appearance of twin melting peaks for the crosslinked PVA membranes has been reported by Sridhar and coworkers.[18] Figure 4(d) shows a lower T_m for the crosslinked blend of GA/PVA/PVP-I compared with that of the simple blend and the presence of twin melting peaks. This suggests the occurrence of crosslinking reactions. DSC analysis of the samples has proved that the thermal stability of GA has indeed improved after blending and crosslinking.

The data obtained from thermogravimetric analysis of the samples are presented in Table I. The thermal stability of pure GA was found to be much lower than that of pure PVA. A significant weight loss of about 76% occurred during the first phase of decomposition between 42 and 85°C and was related to the thermal degradation of the natural gum. Compared to this, GA/PVA blend showed much higher thermal stability and only 23% weight loss occurred during the first phase of decomposition between 50 and 250°C. The initial decomposition temperature for the second stage (IDT$_2$) of the GA/PVA blend is
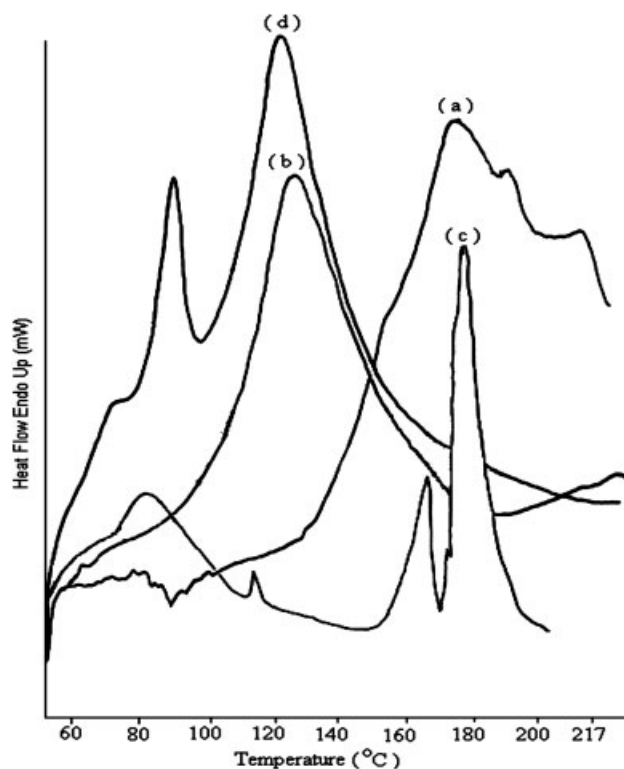
Figure 4 DSC curves of (a) GA/PVA (35/65), (b) GA/PVA/PVP-I (35/65/7.5), (c) crosslinked GA/PVA (35/65), and (d) crosslinked GA/PVA/PVP-I (35/65/7.5) blends.

TABLE 1
Themogravimetric Data

Samples	IDT$_1$ (°C)	IDT$_2$ (°C)	IPDT (°C)	Temperatures (°C) at various weight losses		
				20%	50%	80%
GA	70	95	112.14	78	82	102
PVA	80	250	303.32	275	300	345
GA/PVA	70	270	314.90	240	350	510
GA/PVA crosslinked	89	281	360.09	319	392	536
GA/PVA/PVP-iodine	85	275	310.50	315	385	530
GA/PVA/PVP-iodine crosslinked	90	280	332.69	282	388	>500

270°C compared with 95°C for pure gum. This shows that the thermal stability of GA has greatly increased after blending it with PVA. Pure PVA lost only 5% of its initial weight at ∼ 200°C and most of its weight loss occurred between 250 and 360°C. IDT$_2$ increased to 275°C for the crosslinked blend of GA/PVA and 50% weight loss of the sample occurred at 385°C compared with 350°C for the uncrosslinked blend. The increase in IPDT of the crosslinked sample over the simple blend indicates that the crosslinking reaction has taken place. Interestingly, the simple blend of GA/PVA/PVP-I showed thermal stability as high as that of crosslinked GA/PVA confirming the formation of intermolecular interaction between PVP-I and the other two polymers.

The relative thermal stability of the samples was evaluated by comparing the integral procedural decomposition temperatures (IPDT). It is clear from the values that the thermal stability of GA/PVA blend remains unchanged after incorporating PVP-I into the mixture and that the thermal stability of all the samples improved after crosslinking.

Figures 5 and 6 show the % swelling values of GA/PVA and GA/PVA/PVP-I blend films cross-linked for different periods of time. The water absorption capacity of the crosslinked blend films of GA/PVA decreased as the time of crosslinking reaction increased from 30 to 120 min. The results indicate a similar pattern for the crosslinked blend films of GA/PVA/PVP-I, though the maximum swelling percentage of iodinated films was much less than that of films without PVP-I. Figure 5 shows that the maximum degree of swelling for GA/PVA film crosslinked for 60 min is 170% while that attained by GA/PVA/PVP-I film crosslinked for the same amount of time is 92% as shown in Figure 6. This large difference in the degree of swelling between crosslinked GA/PVA and GA/PVA/PVP-I could be related to the increased degree of interaction between the GA/PVA and PVP-I complex. Evidence of such interaction has been found in the FTIR spectrum and the DSC curve of PVP-I incorporated blend film. Some of these samples showed maximum degree of swelling in 2–4 h followed by a fall due to the release of iodine from the matrices in the aqueous medium. We observed similar decrease in the % swelling values by some iodine containing
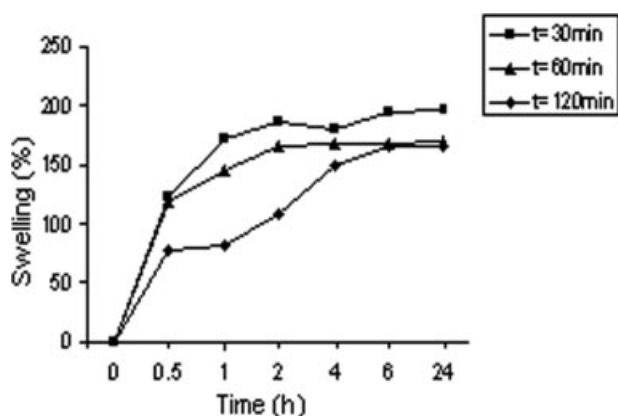

Figure 5 Swelling behavior of GA/PVA blends crosslinked for different periods of time.
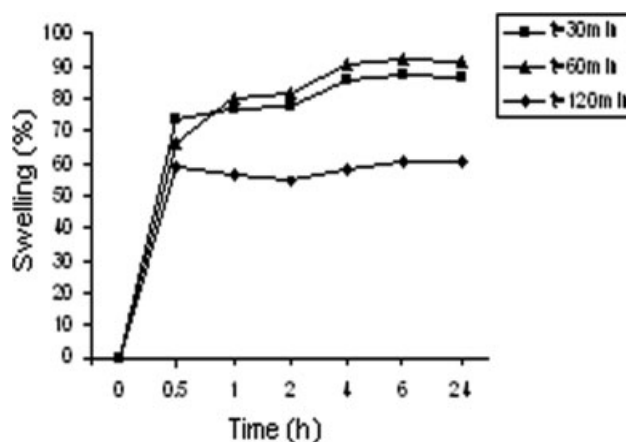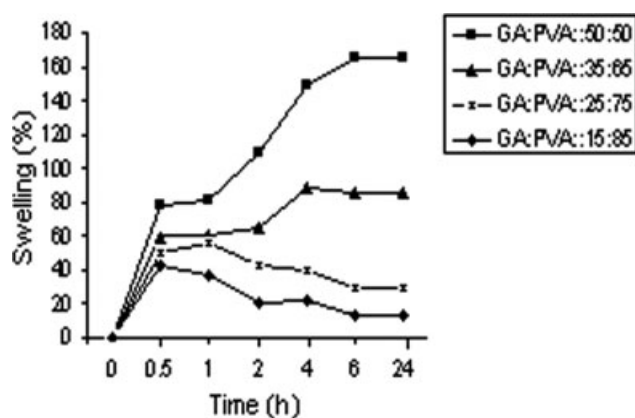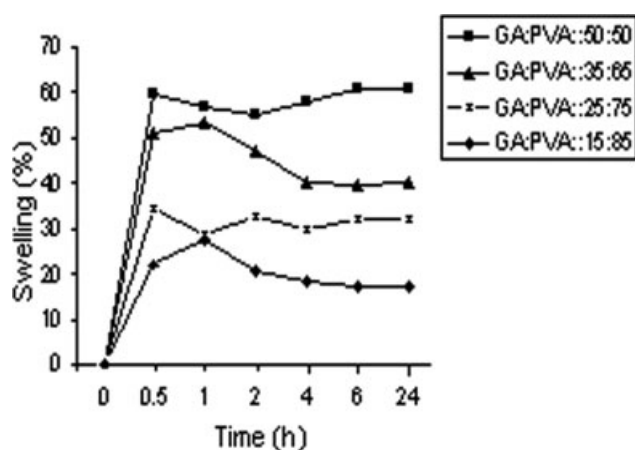

Figure 6 Swelling behavior of GA/PVA/PVP-I blends crosslinked for different periods of time.

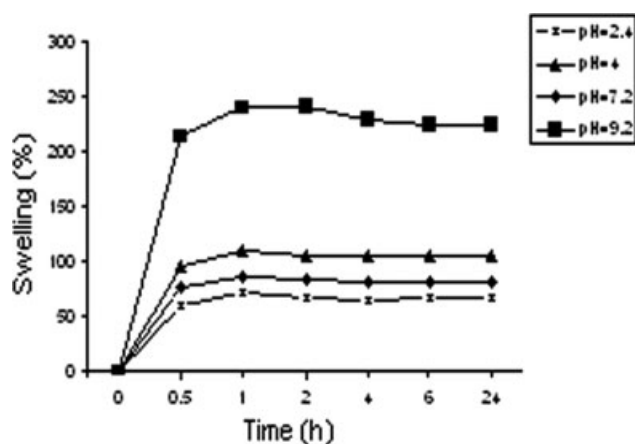**Figure 7** Swelling behavior of crosslinked GA/PVA blends for different compositions of GA and PVA.

Figure 9 Swelling behavior of crosslinked GA/PVA blends at different pH.

polymers due to the release of iodine in water through a mechanism of diffusion.[19,20]

The swelling behavior of the prepared blends of GA/PVA and GA/PVA/PVP-I using different ratios of the two polymers and crosslinked for 60 min are shown in Figures 7 and 8. The results show an interesting trend in the swelling behavior of the GA/PVA blend films. It was observed that as the ratio of PVA increased in the blend the % swelling values decreased. This indicates that as the percentage of PVA increased in the blend the extent of crosslinking increased and the % swelling values decreased. However, pure PVA crosslinked by the same method absorbed higher amount of water (51.92% in 24 h) than the sample of a blend with a composition of 15/85 GA/PVA (13.06% in 24 h). This shows that the crystallization of an increasing content of PVA, which acts as a crosslinker, is not the only factor contributing to the lower degree of swelling but the interaction between GA and PVA and the chemical crosslinking of the blend also contribute to the

higher crosslinking degree. The attempt to crosslink only GA by the same method was not successful.

The water absorption capacity of the blend film was found to be greatly dependent on the pH of the surrounding medium. According to the available literature[21] the increased water uptake capacity of modified GA at high pH values can be attributed to the increased ionization of —COOH groups of glucuronic acid leading to the expansion of polymer network. Figures 9 and 10 show the % swelling values of crosslinked GA/PVA and GA/PVA/PVP-I at different pH and it is obvious that the former is more pH sensitive than the later. This can be attributed to the increased interaction of various groups in the blend containing PVP-I and as a result there has been no such relaxation of the polymer at a higher pH.

The tensile properties of GA/PVA and GA/PVA/PVP-iodine blend films were determined to see the effects of incorporating PVP-I in the blend and crosslinking, on the mechanical properties of the films. The tensile strength, *E*-modulus, and % elongation at

Figure 8 Swelling behavior of crosslinked GA/PVA/PVP-I blends for different compositions of GA and PVA.

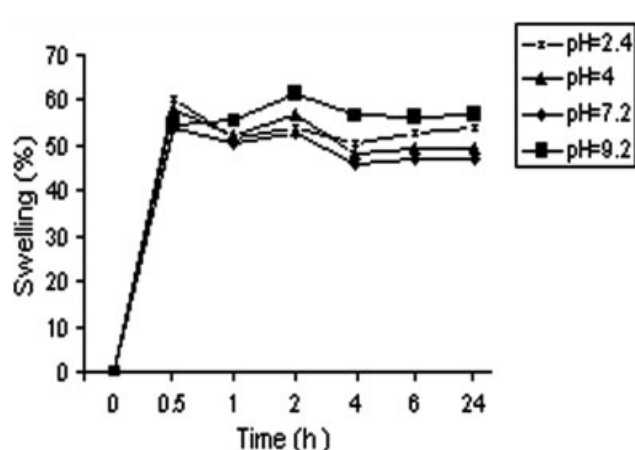**Figure 10** Swelling behavior of crosslinked GA/PVA/PVP-I blends at different pH.

break of the crosslinked GA/PVA films and after incorporating PVP-I into the blend are shown in Figure 11. As expected, the tensile strength and *E*-modulus of the films of GA/PVA increased after crosslinking. Interestingly the tensile strength of the blend films also increased after incorporating PVP-I in the mixture though the *E*-modulus of the iodinated blend decreased. This can be attributed to the slight brittleness that appeared in the blend films as PVP-I was introduced. Figure 12 presents the tensile properties of crosslinked GA/PVA blends with various contents of GA. The strength and modulus showed the highest values with the lowest content of GA.

CONCLUSIONS

The studies carried out to prepare and characterize polymeric blends based on a natural biodegradable polymer, GA and a synthetic biomaterial, PVA with an iodophor, PVP-I complex, led to some interesting results.

The blending of GA with PVA and PVP-I could improve its properties and thus the features necessary for the use of the blend as a matrix for release of iodine could be achieved. The crosslinking of GA/PVA blends with glutaraldehyde led to an improvement in water resistance, thermal and mechanical properties. Incorporation of PVP-I followed by crosslinking of the blend led to slight increase in the brittleness of the film but the effect was not detrimental to our interests. Blending of PVP-I with GA/PVA resulted in the formation of an intermolecular interaction between PVP-I and the hydroxypolymers and thus affected the swelling behavior, thermal, and tensile properties. Thus it can be concluded that polymeric blends based on crosslinked GA/PVA/PVP-I blend have the potential to be used
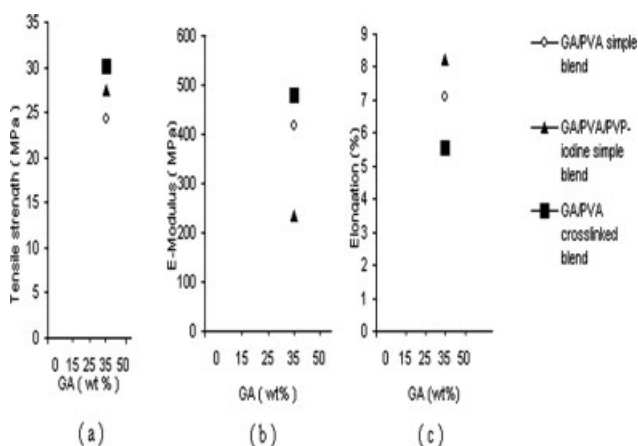
Figure 12 The tensile properties of crosslinked GA/PVA blends (a) The tensile strength, (b) *E*-modulus and (c) elongation at break with different compositions of GA and PVA.

as iodine-release systems for biomedical applications.

References

1. Kim, S. H.; Hyun, K.; Moon, T. S.; Mitsumata, T.; Hong, J. S.; Ahn, K. H.; Lee, S. J. Polymer 2005, 46, 7156.
2. Teramato, N.; Saitoh, M.; Kuroiwa, J.; Shibata, M.; Yosomiya, R. J Appl Polym Sci 2001, 82, 2273.
3. Kim, J. H.; Kim, J. Y.; Lee, Y. M.; Kim, K. Y. J Appl Polym Sci 1992, 45, 1711.
4. Mangala, E.; Suresh Kumar, T.; Baskar, S.; Panduranga Rao, K.; Trends Biomater Artif Organs 2003, 17, 34.
5. Abou-Aiad, T. H. M.; Abd-El-Nour, K. N.; Hakim, I. K.; Elsabee, M. Z. polymer 2005, 02, 122.
6. Scotchford, C. A.; Cascone, M. G.; Downes, S.; Giusti, P. Biomaterials 1998, 19, 1.
7. Chen, L.; Imam, S. H.; Gordon, S. H.; Greene, R. V. J Environ Polym Degrad 1997, 5, 111.
8. Otey, F. H.; Mark, A. M.; Mehltretter, C. L.; Russell, C. R. Ind Eng Chem Prod Res Dev 1974, 13, 90.
9. Nishio, Y.; Manley, R. St. Macromolecules 1988, 21, 1270.
10. Barbani, N.; Bertoni, F.; Ciardelli, G.; Cristallini, C.; Silvestri, D.; Coluccio, M. L.; Giusti, P. Eur Polym J 2005, 41, 3004.
11. Toti, U. S.; Soppimath, K. S.; Mallikarjuna, N. N.; Aminabhavi, T. M. J Appl Polym Sci 2004, 92, 2245.
12. Berkelman, R. L.; Holland, B. W.; Anderson, R. L. J Clin Microbiol 1982, 25, 635.
13. Kohlhass, L. M.; Sandrik, J. K. Clin Ortho Relat Res 1975, 113, 184.
14. Birnbaum, L. M.; Hopp, D. D.; Merteus, B. F. Plast Reconstr Surg 1982, 69, 956.
15. Punyani, S.; Narayanan, P.; Vasudevan, P.; Singh, H. J Appl Polym Sci 2007, 103, 3334.
16. Tyagi, M.; Singh, H. J Appl Polym Sci 2000, 76, 1109.
17. Hassan, C. M.; Peppas, N. A. Advances in Polymer Science, Vol. 153; Springer-Verlag: Berlin, 2000; p 37.
18. Smitha, B.; Sridhar, S.; Ravi kumar, Y. V. L.; Ramakrishna, M. J Polym Mater 2005, 22, 433.
19. Mazumdar, N.; Vardarajan, R.; Singh, H. J. M. S. Pure Appl Chem A 1996, 33, 353.
20. Mazumdar, N.; Vardarajan, R.; Singh, H. Oriental J Chem 2002, 18, 417.
21. Reis, A. V.; Guilherme, M. R.; Cavalcanti, O. A.; Rubira, A. F.; Muniz, E. C. Polymer 2006, 47, 2023.

Figure 11 The tensile properties of GA/PVA (35/65), crosslinked GA/PVA (35/65), and GA/PVA/PVP-I (35/65/7.5) blends (a) the tensile strength, (b) *E*-modulus and (c) elonga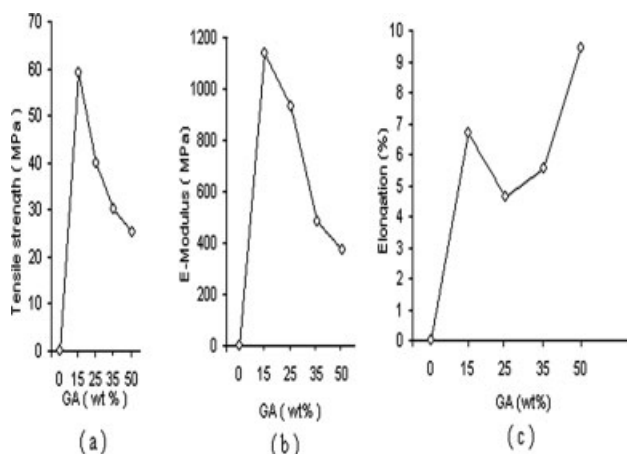tion at break with different compositions of GA and PVA.