

Synthesis and Properties of Novel Polyvinyl Alcohol–Lactic Acid Gels

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Received 5 June 2007; accepted 18 December 2008

DOI 10.1002/app.29909

Published online 20 April 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: This article describes a process for esterifying polyvinyl alcohol (PVA) with L-lactide (LLA) and D,L-lactic acid (LA), using ethyl acetate and *N,N'*-dimethylformamide at temperatures varying from 120 to 150°C. The grafting process was carried out under nitrogen to avoid possible oxidation or other degradation of the process ingredients and product. Lower T_g values were obtained for the PVA/LLA graft copolymers of higher LLA content suggesting some compatibility in the amorphous phase. Higher T_g values were observed for PVA/LA graft copolymers that yielded tough polymer films. The structure of the copolymers was studied by solid-state ¹³C-NMR, infrared spectroscopy, and differential scanning calorimetry (DSC). The PVA/LA films exhibited melt processability and good mechanical properties such as yield strength, tensile energy at break, modulus, and elongation at break. The polymer films produced through com-

pression molding at 100°C showed good swelling properties. The transport coefficient (n) values determined from the plot of $\log(M_t/M_\infty)$ vs. $\log t$ indicate Fickian behavior, and they are consistent with the reported literature values for other PVA systems. The nature of water in gels [bound water (W_b), freezing (W_f), and freezing bound (W_{fb}), and water content (W_t)] was evaluated from DSC data. The results demonstrate that PVA/LA hydrogels with good combination of thermal, physicochemical, and swelling properties can be prepared via the lactic acid esterification of PVA polymer process described. Besides being melt processable, the PVA/LA gels exhibit a melting point, which indicates possibly use of higher temperatures. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 2053–2061, 2009

Key words: polyvinyl alcohol; lactic acid; graft copolymers; gel; swelling; biosensor

INTRODUCTION

Hydrogels may be considered as three-dimensional polymeric networks capable of absorbing large amounts of water or organic solvents without dissolving. The increasing interest of hydrogels for various biomedical applications such as scaffolds for tissue engineering is largely attributable to their good biocompatibility, very low interfacial tension with biological fluids, high permeability to small molecules, biodegradability, consistency similar to soft tissue, and viscoelastic behavior. They may be described as a continuous network of chains cross-linked by physical or chemical junctions. Polyvinyl alcohol (PVA) hydrogels are used in medical applications including ophthalmic contact lenses, drug delivery, and tendon repair. Aqueous solutions of PVA form a gel by undergoing freezing–thawing cycles.^{1–4} Although physically crosslinked PVA hydrogels show improved mechanical properties,^{5–7} often they lack optical clarity.⁸ Highly elastic PVA gels can be prepared by first heating the PVA to

achieve dissolution, followed by freezing–drying cycles.¹ Transparent and highly elastic PVA gels can be prepared using aqueous dimethylsulfoxide (DMSO) solutions.^{9–11} PVA and other hydrogels with improved properties have been reported in the literature with a wide range of applications.^{12–26} PVA blends studied include PVA–collagen, PVA–hyaluronic acid–ethylene vinyl alcohol copolymers, PVA–hyaluronic, PVA–hydroxypropyl methylcellulose, starch–poly(ethylene-VA), poly(ethylene-co-VA)/nylon 6,12, PVA/polypyrrole, PVA/chitosan, PVA–alginate, poly(*p*-dioxanone)/PVA,¹² sericin/PVA blend membranes,¹³ and PVA/propylene oxide and epichlorohydrin.¹⁵ Polylactide²⁴ and PCL grafts²⁵ incorporated onto vinyl alcohol and poly(vinyl alcohol-co-vinyl acetate).

PVA is also widely used in fibers, adhesives, textile, and paper-sizing applications. Among the shortcomings of PVA is that it is not melt processable. Although PVA can be modified to enhance its melt processability, it is often not soluble in cold water and not crystalline, which are desirable properties for certain applications. Although PVA is a biodegradable and biocompatible polymer with good mechanical properties in the dry state, its highly hydrophilic properties limits its scope of

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applications, particularly in the wet state. In this study, the hydrophobicity of PVA was improved by the chemical modification using L-lactide (LLA) and D,L-lactic acid (LA). Polylactic acid (PLA) is a biodegradable and biocompatible polymer that has previously been studied in our group extensively.^{1,27} As early as in 1996, we reported some preliminary findings on graft copolymers of PVA and PLA.²⁸ The objective of this study was to develop melt-processable PVA/LA graft copolymers and investigate the properties as well as the effect of influential factors such as composition, catalyst, temperature, and reaction time.

EXPERIMENTAL

Materials

PVA was purchased from Aldrich (MW 86,000) and Polysciences (MW of 133,000 and a degree of hydrolysis of 99 mol %). LLA, LA, 85% solution in water was obtained from Aldrich; stannous 2-ethyl hexanoate, antimony (111) oxide, and tetrabutyl orthotitanate were obtained from Sigma; and dibutyl tin dilaurate was obtained from Polysciences. *N,N'*-Dimethyl formamide (DMF), toluene, chloroform, methylene chloride, tetrahydrofuran (THF), and anhydrous ethyl alcohol (90%) used were all of analytical grade.

Preparation of graft copolymers of PVA and L-lactide

PVA (20 g; 86,000) and stannous 2-ethyl hexanoate (4.5 wt % based on PVA) were weighed into the reaction vessel, and then 50 mL ethyl acetate was added. The mixture was heated using a silicone oil bath at 120°C under nitrogen purge and continuous stirring using a magnetic stir bar. After about 30 min, varying amounts of LLA were added to obtain PVA/LLA graft copolymers of 10–100% lactide content. The reaction was done at 120°C for 24 h. The copolymers were purified by dissolving in acetone, and then they were precipitated into hexanes. The samples were filtered, rinsed with hexanes, and dried in vacuum oven at 50°C for 24 h. The copolymers of LLA content greater than 50 wt % were obtained in quantitative yields exceeding 95% as white powders. NMR and IR were used to verify the incorporation of lactide onto PVA.

Preparation of PVA hydrogels

An aqueous solution of 10 wt % PVA was prepared by dissolving 20 g PVA in 200 mL distilled water in a 500-mL beaker. The mixture was heated at about 90°C, under stirring with magnetic bar for at least 2 h to achieve dissolution and homogenization. The

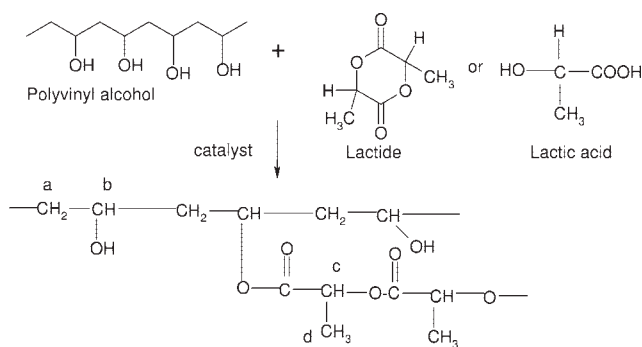
polymer solution was rapidly cooled in a dry ice bath and transferred into a freezer and maintained below –20°C. After being frozen for 24 h, the PVA gel was allowed to thaw at room temperature for 3 h and returned back to the freezer. The PVA gels were subjected to at least four freezing–thawing cycles to yield polymer gel. The PVA gels were dried at 50°C in vacuum oven to constant weight.

Preparation of PVA/LA hydrogels

PVA, D,L-lactic, and stannous 2-ethyl hexanoate were weighed into the reaction vessel equipped with nitrogen inlet, magnetic stir bar, Dean-Stark trap, and condenser fitted with a calcium sulfate drying tube. About 20 g PVA, stannous 2-ethyl hexanoate (0.1–4.5 wt % based on PVA), and corresponding amount of lactic acid were used to obtain graft copolymers of 25–75 wt % lactic acid content. About 200 mL DMF and 50 mL toluene were added to the mixture. The reaction was carried out at 150°C (Note: At lower temperatures from 120 to 135°C, no swollen hydrogels were obtained) in a silicone oil bath placed on heating mantle under continuous stirring for 24 h. The reaction was done with azeotropic removal of water via the Dean-Stark trap. The clear polymer mixture obtained was cooled to room temperature, and then 300 mL of methylene chloride was added to yield highly swollen, tough PVA/LA hydrogel network. The PVA/LA gels were left immersed in methylene chloride for 24 h and transferred into another large beaker containing 200 mL THF. This step was repeated at least three times to ensure the removal of leachable materials and impurities. Subsequently, the gel was immersed in 200 mL ethyl alcohol (fresh ethyl alcohol used daily) for at least 3 days. The purification steps involving methylene chloride, THF, and ethyl alcohol were used to ensure the removal of residual DMF. Lastly, the gels were dried at 50°C in vacuum oven to constant weight (48–72 h). The preparation of PVA homopolymer was also done without the addition of lactic acid; however, no swollen hydrogel was obtained. The reaction scheme is shown in Scheme 1.

Fabrication of gel films

PVA/LA films were prepared by compression-molding using a Carver laboratory press using appropriate rectangular steel plates of 3.44-mm thickness, sandwiched between two Teflon-coated polyimide films. Compression molding was done at 100°C. The thick polymer gel was initially softened for about 15 min, and then the load gradually applied to 8 metric tons over 15 min and lastly 10 metric tons applied for a further 15 min. The hot steel plates were finally



Scheme 1 Schematic route for preparing PVA/LA graft copolymers.

cooled to room temperature at 10 metric tons. The rectangular tough polymer sheets were placed in polyethylene bags and annealed at room temperature for at least 7 days prior to analysis. Thin PVA/LA films were obtained by directly placing (without rectangular mold) the polymer sheet sample between two polyimide films and processed as described earlier, but for a total of 20 min.

Characterization of PVA-LA gel films

Differential scanning calorimetry (DSC) data were obtained using a DSC 2920 TA instrument using 10–15 mg sample sealed in aluminum pans and thermal data recorded from -90 to 250°C (I and II scans) at $20^{\circ}\text{C}/\text{min}$. For the swollen hydrogels, the different states of water were investigated by taking about 20 mg sample, sealed in aluminum pan. DSC curves were recorded from -70 to 40°C (I and II scans) at $5^{\circ}\text{C}/\text{min}$. High-resolution solid-state crosspolarization/magic angle spinning (CP/MAS) ^{13}C -NMR spectra were obtained using a Bruker NMR at 75.4 MHz. Fourier transform IR were measured using a Nicolet 60X spectrophotometer equipped with an infrared microscope accessory (IR-Plan Spectra Tech). Tensile properties were determined using Instron testing machine 1011 as per ASTM D-63884 method, using a load cell of 100 lbs. Testing was done using 5 to 10 dump-shaped specimens using a gauge length of 15.62 mm (0.62") and crosshead speed of 50.8 mm/min (2.00"/min) and the tensile strength at yield and break (MPa), modulus (MPa), and elongation at break evaluated.

Swelling experiments

The dynamic swelling measurements were done by first weighing the test specimens (17 mm \times 10 mm \times 2.9 mm), and then immersed in excess distilled water in scintillation vials at 23°C . They were removed at different time intervals, blotted free of surface moisture with filter paper and the weight recorded using a Mettler analytical balance (accuracy

± 0.0001 g). The procedure was repeated until constant weight was achieved (equilibrium water uptake). To verify the reproducibility of results, five replicate tests were done for each sample. The swelling ratio, degree of swelling, transport mechanism, and diffusion coefficients were evaluated from the swelling measurements.

RESULTS AND DISCUSSION

Chemical structure analysis using NMR and FTIR

Table I summarizes the FTIR data obtained for PVA and PVA/LA graft copolymers. Characteristic peaks include 3313 (OH stretch), 2920 (CH stretch), and a broad crystallization sensitive PVA band at 1140 shoulder, overlapping the 1095 (C—O stretch). The small peak at 1656 cm^{-1} is attributable to some double bonds present. The FTIR spectra for PVA/LA graft copolymers showed the characteristic carbonyl ester peak at 1730 cm^{-1} in addition to other assigned peaks for PVA. More importantly, a broad band was observed in the region $3150\text{--}3550\text{ cm}^{-1}$ suggesting the presence of broad range of associated hydroxyl groups.

Figure 1 gives the typical ^{13}C -NMR spectra obtained for PVA/LA graft copolymers of various compositions. The ^{13}C -NMR for PVA CH (b) appears as three splitting peaks 1, 2, and 3 at chemical shifts of 76.1, 70.4, and 64.8 ppm, respectively. The methylene CH_2 (a) signals are observed at 44.8 ppm. The methyl CH_3 (d) signal at 17.4 ppm is attributable to PLA. The PLA methine CH (c) signals occur at 70 ppm, thus overlapping with PVA CH (b) signals. The chemical shifts for PVA/LA copolymers were observed at 75.2, 69.3, and 63.6 ppm attributable to PVA methine (carbon b), and the methylene (carbon a) signals are observed at 43.9 ppm. Besides the PVA signals, additional peaks at 19.9 ppm is attributable to methyl (carbon d) and methine (carbon c) signals occurring downfield at 69–70 ppm. Intramolecular hydrogen bonding interactions commonly occurs in PVA polymers. As shown, the PVA

TABLE I
IR Data for PVA and PVA/LA Copolymers

Characteristic peak wave numbers (cm^{-1})	Inference
PVA	
3313	OH stretch
2920	CH aliphatic stretch
1140–1095	C—O stretch
PVA/LA	
3150–3550 (broad)	OH stretch (hydrogen bonding)
2950–2980	CH aliphatic stretch
1730	Carbonyl ester stretch

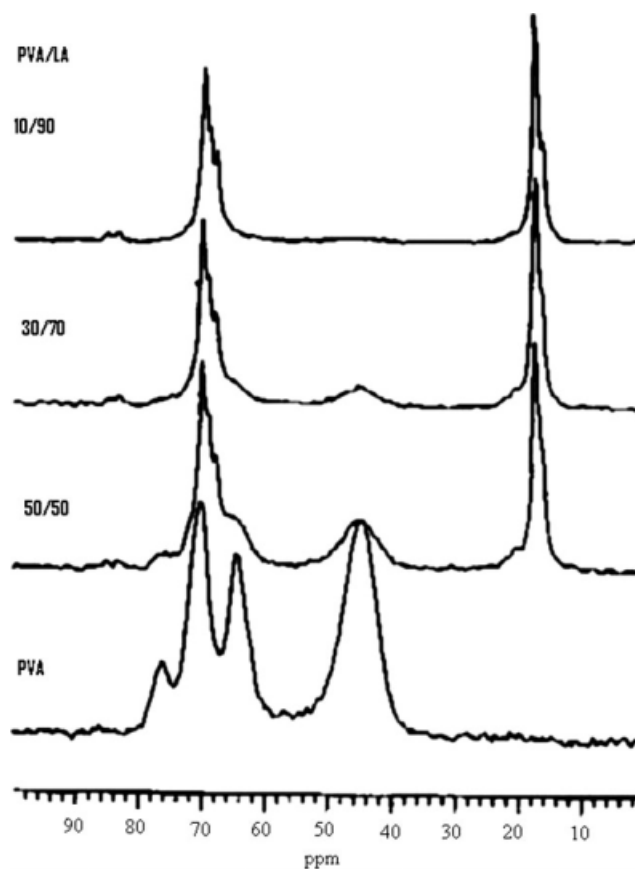


Figure 1 Solid-state ^{13}C -NMR of PVA/LLA graft copolymers.

methine carbon splits into a triplet of greater width as indicated (peaks 1, 2, and 3). The degree of grafting could not be determined because the polymer films were insoluble in common NMR solvents. Moreover, solid-state NMR gives broad peaks that overlap, thus making it difficult to evaluate the degree of grafting.

As shown in Table II, the PVA/LLA copolymers (Method 1) containing greater than 50 wt % LLA

were obtained in very high yields (95–97%). Lower T_g values were obtained for the graft copolymers of high LLA content suggesting some compatibility in the amorphous phase. DSC showed T_g values of 22.3 to 58.7° C. Carlotti et al.²⁹ observed that PLA grafted with lactic and glycolic acids showed lower glass transition temperature, and improved flexibility and elasticity as well as tear resistance.

The DSC spectra (I scan) of PVA powder (MW 133,000) showed the characteristic PVA melting temperature at 230°C. The second scan revealed T_g , T_m , and enthalpy of fusion values of 74.0°C, 226°C, and 53.9 J/g, respectively. The PVA/LLA lactide copolymers were fine powdery material. However, for the LA grafting reaction on PVA, more interesting results were observed. We tried the grafting reaction at 135°C for 24 h, but no gelation occurred (powdery material was obtained). Nevertheless, when the reaction was done at the slightly higher temperature of 150°C for 12–24 h, gelation occurred to yield tough, tear-resistant graft copolymer gels, which immediately swelled upon solvent addition into the reaction medium. Therefore, the preferred embodiment for grafting process if tough copolymer films are desired is to conduct the reaction at 150°C for about 12 h in DMF solvent. The kinetics of grafting reaction was not investigated in our study to understand the reasons for the difference observed.

The glass transition temperature obtained compares well with the reported values of 70–80°C.³⁰ Assuming an enthalpy of fusion of crystalline PVA³⁰ to be 156 J/g, the estimated crystallinity of PVA powder used is 34.6% and PVA gel formed showed decreased crystallinity of 28.8%. This is attributable to the differences in extent of physical crosslinks and annealing conditions. The PVA/LLA polymer gels prepared at 150°C exhibited semicrystalline behavior and a very broad melting point over the range 154–186°C. Typical T_g values (Table III) obtained for PVA/LLA gels varied from 84.1 to

TABLE II
DSC Data for PVA and PVA/LLA Graft Copolymers

PVA/LLA (wt %)	Yield %	T_g	II scan					
			T_{m1}	ΔH_{m1}	T_{c1}	ΔH_{c1}	T_{m2}	ΔH_{m2}
100/0	–	78.5	–	–	–	–	228.1	65.8
90/10	89.9	77.8	–	–	–	–	226.3	57.2
80/20	76.6	77.7	–	–	–	–	228.1	59.7
70/30	69.9	78.2	–	–	–	–	225.4	54.7
60/40	59.5	78.4	–	–	–	–	227.8	59.0
50/50	95.8	38.0	–	–	–	–	218.2	37.1
40/60	94.5	35.1	–	–	–	–	218.3	26.2
30/70	95.7	22.3	–	–	–	–	217.7	18.2
20/80	96.7	2.3	131.2	17.2	107.4	–16.2	220.1	12.7
10/90	97.0	58.7	177.1	54.3	109.8	–45.0	–	–

Temperature in °C and ΔH in J/g; graft copolymers were synthesized at 120°C in ethyl acetate solvent.

TABLE III
DSC Data for PVA and PVA/LA Graft Copolymers

PVA/LA content (wt %)	T_g	II scan		ΔH_m
		Onset T_m	T_m	
PVA/LLA				
PVA (133,000)	74.0	214.6	225.5	53.9
33/67 ^a	73.5	–	216.9	80.6
33/67 ^b	84.1	124.6	161.6	15.5
40/60	84.1	–	154.4	11.3
50/50	85.7	–	186.1	19.7
75/25	85.8	163.1	185.5	19.7
100/0 ^c	74.0	215.3	226.2	53.9
100/0 ^d	77.6	220.2	230.9	45.0

Temperature in °C and ΔH in J/g.

^a Polymerization conditions (135°C/24 h) (no gelation).

^b Polymerization conditions (150°C/12 h) (gel formed).

^c PVA 133,000 powder.

^d PVA gel (freezing-thawing).

85.7°C, ~ 10°C higher than the starting PVA polymer (74.0°C), as well as PVA gel (77.6°C). This suggests appreciable crosslinking attributable to a combination of physical (hydrogen bonding) interactions and increased intramolecular interactions arising from the lactic acid grafting reaction (Scheme 1). The carbonyl groups of the PLA provide additional junctions for hydrogen bonding. The T_m values obtained for PVA/LA gels also indicate a decrease of 40 to 72°C, reflecting the decreasing PLA crystallites length segments as a result of the grafting reaction.

As shown in Table III and Figure 2, the T_g values for PVA/LA graft copolymers that exhibited tough polymer films are much higher than the powdery materials (Table II) obtained from the grafting reaction of LLA and PVA. The higher T_g values reflect the crosslinking reaction in the former materials. The degree of crystallinity for PVA/LA gels was not evaluated because the actual content of the lactic acid in the graft copolymers could not be determined using the ¹³C-NMR data.

Table IV shows the tensile strength at yield and at break, modulus, and elongation at break, respectively, obtained for the PVA/LA gels as a function of the LA. In retrospect, the tensile strength (MPa) values obtained in our study are higher than the results obtained for PVA polymer gels prepared from aqueous DMSO/water solutions^{8,31} and irradiation using the freezing-thawing method.²

The values compare well with PVA gels prepared using glutaraldehyde,³² formaldehyde acetalization,³³ thiol (SH) end groups,³⁴ and paraformaldehyde.³⁵ The modulus values for PVA/LA gels generally showed an increase with increasing LA content as shown in Table IV. The 1% secant modulus (MPa) were 52.1 ± 10.5 , 524 ± 57 , and 632 ± 27 MPa for copolymers containing 50, 60, and 66% LA

content, respectively. The corresponding elongations at break (%) for PVA/LA graft (greater than 50% LA) copolymers varied from 191 to 462%. Modulus values of 451 to 569 MPa and elongation at break (158–200%) have been reported in the literature for PVA with thiol end groups of varied compositions.³⁴

Swelling properties of PVA/LA gels

The equilibrium degree of swelling of polymers is directly related to the solvent sorption rate, which indicates the solvent uptake per unit time. The swelling ratio was evaluated as the weight ratio of the swollen polymer (W_s) divided by the dried polymer (W_d).

$$S_r = \frac{W_s}{W_d} \quad (1)$$

As shown in Table V, the highest swelling ratio was achieved for the PVA/LA (75/25%) gel. The PVA gel obtained using the freezing-thawing method yielded the lowest degree of swelling. The swelling of hydrogel membranes is mainly due to

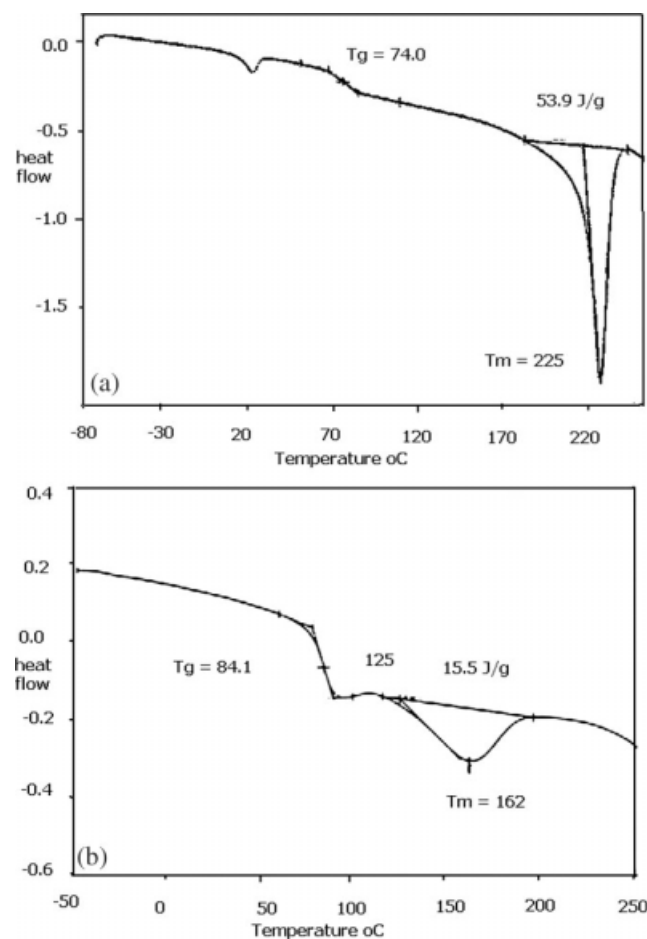


Figure 2 a) DSC spectra (II scan) of PVA graft copolymer; (b) DSC spectra (II scan) of PVA/LA (33/66 wt %) graft copolymer.

TABLE IV
Mechanical Properties of PVA/LA Graft Copolymers

%LA	Tensile strength (MPa)	Tensile energy at break (MPa)	Modulus (MPa)	Elongation at break (%)
25	24.0 ± 1.4	23.8 ± 1.3	–	21.5 ± 9.8
50	31.3 ± 0.8	31.2 ± 0.8	58.0 ± 13.5	462.3 ± 5.0
60	28.9 ± 0.6	28.6 ± 0.7	692.2 ± 120.1	207.1 ± 25.3
66	30.3 ± 1.1	29.6 ± 1.3	892.9 ± 57.2	191.4 ± 8.0

the amorphous region.³⁶ For semicrystalline polymers, a network of amorphous chains is formed with the crystallites acting as the junction points. It may therefore be deduced that an increase in crystallinity is usually accompanied by the decrease in the degree of swelling. This is consistent with the DSC thermal data in Table III. The PVA/LA gel prepared in our study involved the use of racemic LA to yield the graft copolymers shown in Scheme 1. Presumably, this causes an increase of amorphous region reducing the crystallinity of the PVA/LA gels.

The velocity of the swollen front that separates the inner unswollen glassy region from the outer swollen, rubbery region is important in drug delivery applications and evaluation of transport mechanisms. The solvent uptake is defined as follows:

$$\frac{M_t}{M_\infty} = \frac{(W_t - W_0)}{(W_\infty - W_0)} \quad (2)$$

where M_t is the mass of penetrant sorbed at time t ; M_∞ is the mass of penetrant sorbed at equilibrium; W_t is the weight of polymer specimen at time t ; and W_0 is the initial weight of polymer specimen.

The relative importance of diffusion and relaxation transport mechanisms was evaluated by fitting solvent uptake data for short times ($M_t/M_\infty \leq 0.6$) using the equation.^{37–40} The thickness dependence is a valuable means of identifying the transport mechanism, since case II transport will scale with t/L and anomalous transport may have a complex dimensional dependence.⁴¹

$$\frac{M_t}{M_\infty} = Kt^n \quad (3)$$

where k is the constant characteristic of polymer–solvent system.

The transport coefficient (n) was determined from the plot of $\log(M_t/M_\infty)$ vs. $\log t$. The n values of 0.499–0.504 shown in Table V indicate Fickian behavior and are consistent with the reported literature values of 0.45 to 0.50 for various PVA systems.^{42,43} Characteristic value of $n = 0.5$ indicates Fickian diffusion; $n = 1$ implies case II (relaxation controlled); values between $n = 0.5$ – 1.0 indicates anomalous transport and $n > 1$ suggest super case II transport mechanism.

The rate of approach to equilibrium in the swelling experiments was assessed by evaluating the diffusion coefficient (D) using Crank's diffusion equation for short time-limiting cases.⁴⁴

$$\frac{M_t}{M_\infty} = \left(\frac{4}{\pi^{0.5}}\right) \left(\frac{Dt}{L^2}\right)^{0.5} \quad (4)$$

where t is the time (s); $M_t/M_\infty < 0.6$; L is the initial thickness of polymer slab (assumed constant for short time approximation); and M_∞ is the weight of polymer at equilibrium.

The diffusion plot was obtained by a plot of M_t/M_∞ versus $t^{1/2}/L$. Figure 3 shows typical water sorption rates profile obtained for PVA/LA (33/66 wt %) gel. Overall results show that the PVA/LA water diffusion coefficient (D_w) values are slightly higher than PVA gel. Typical D_c (cooperative diffusion coefficient) values reported using quasi-elastic light-scattering measurements for PVA (MW 110,000) chemically crosslinked with glutaraldehyde varied from 2.94 to 4.86×10^{-7} cm²/s.⁴⁰

TABLE V
Swelling Ratio, Transport Exponents, and Water Diffusion Coefficients of PVA/LA Gels

Sample PVA/LA	Transport exponent n	K	Correlation coefficient	Swelling ratio	$10^7 D_w$ (cm ² /s)
100/0	0.504 ± 0.01	0.225	0.996	1.57 ± 0.02	2.51 ± 0.18
75/25	0.499 ± 0.01	0.164	0.999	3.78 ± 0.04	nd
33/66	0.502 ± 0.00	0.230	0.999	2.55 ± 0.03	2.10 ± 0.08

nd, not determined.

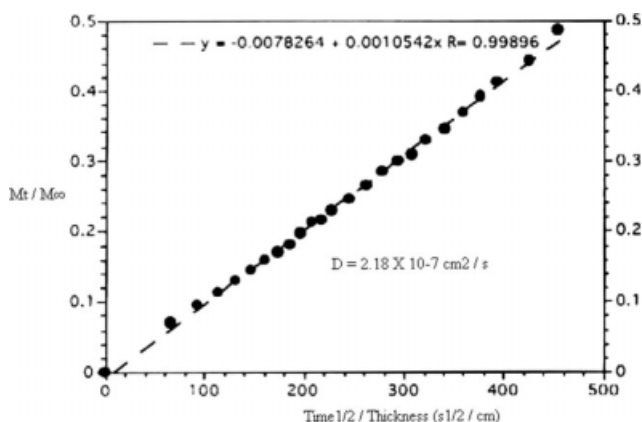


Figure 3 Water sorption rates of PVA/LA (33/66 wt %).

Furthermore, we also investigated whether the difference in D_w values was due to the states of water in the swollen gels.

Nature of water in gels

Water molecules in polymer membranes may exist in two or more different states. DSC can be used to estimate the relative amounts of free, freezing bound, and nonfreezing water in swollen hydrogels.⁴⁵ Bound water (W_b) refers to the water molecules bound to the polymer through hydrogen bonding. The rest of the water "free water" does not participate in direct hydrogen bonding and consequently has a greater degree of mobility. Studies on the nature of water in gels are important because they influence the permeability behavior of solutes. In this study, the amount of bound water (W_b) was estimated by subtracting the amounts of freezing (W_f) and freezing bound (W_{fb}) from the total water content (W_t) of the gels using the following equations.⁴⁶

$$W_b = W_t - (W_f + W_{fb}) \quad (5)$$

$$W_b = W_t - \frac{(\Delta H_{\text{endotherm}})}{H_f} \quad (6)$$

where $\Delta H_{\text{endotherm}}$ is the observed endothermic heat (J/g) and ΔH_f (heat of fusion of ice) = 333.69 J/g (79.7 cal/g).

The DSC spectra of the PVA and PVA/LA gels are presented in Figure 4. The melting endotherm for the former occurs at -3.77°C when compared with 0.98°C for the latter. The endothermic peak for PVA (II scan) can be resolved into two peaks, i.e., at

about 0°C (free water = bulk water) and at -4°C (freezing bound water).

The freezing bound water occurs at a slightly lower melting temperature because of the weak interaction of the water and polymer chain. However, in case of PVA/LA (33/66 wt %) gel, no phase transition was observed for bound water (W_b). Table VI gives the estimated amounts of water (W_b , W_{fb} , and W_f).

As shown in Table VI, PVA gel contains lower amount of bound water and higher amount of "free water." PVA/LA gel exhibited higher amount of bound water. Other studies have shown that, the permeability of polymer hydrogels dramatically increase with the increase in free water content.⁴⁷ More recently it has also been demonstrated²⁹ that poly(vinyl alcohol) (PVA), fully or partially hydrolyzed, react with LA and glycolic acid under different conditions to synthesize polymers with pendant lactate and glycolate groups. Such graft polymers showed lower glass transition temperature, enhancing the polymers solubility in cold water (10°C) and improving flexibility and elasticity as well as tear resistance. The graft copolymers obtained in our study exhibited melt processability and appreciable swelling properties in both aqueous

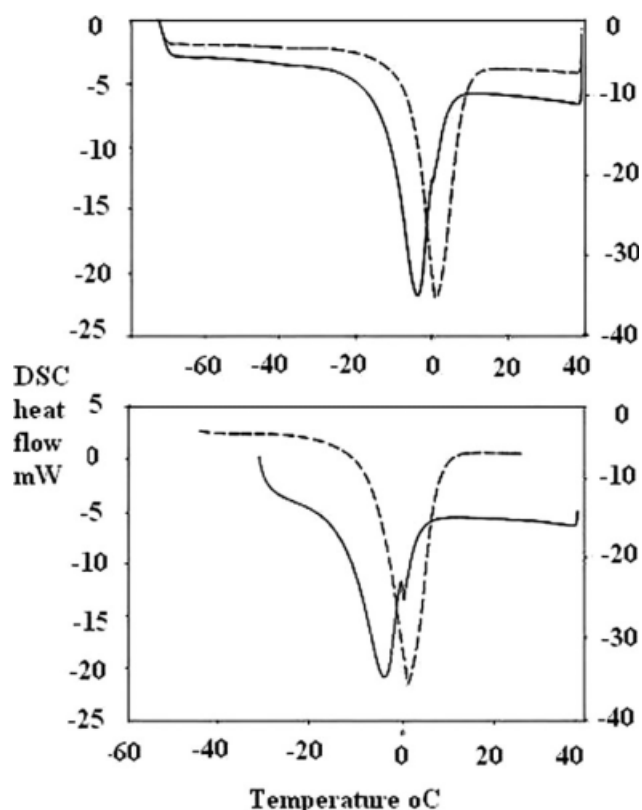


Figure 4 DSC spectra of water-swollen PVA (T) and PVA/LA (B) (33/66 wt %) hydrogels (I and II scan).

TABLE VI
Results of Bound Water, Freezing Bound Water and Free Water in
PVA/LA (33/66 wt %)

Sample content PVA/LA	DSC scan	Total H ₂ O (W _t)	Bound H ₂ O (W _b)	Free H ₂ O (W _f + W _{fb})	% Free H ₂ O (W _f + W _{fb})
100/0	I	0.32	0.047	0.27	85
	II	0.32	0.063	0.26	80
33/66	I	0.69	0.22	0.47	68
	II	0.69	0.23	0.47	67

and organic solvents. However it is not possible to elucidate the mechanism of the crosslinking reaction of the LA grafting reaction onto PVA from our study, and therefore further work is in progress. The effect of various influential factors such as composition, temperature, solvent, time, and catalysts are being studied further to better understand the gelation process and kinetics. Hydrogel-based technologies for the controlled release of proteins and pharmaceutical drugs have generated a lot of interest. The high aqueous content in PVA/LA hydrogels offer a "drug-friendly" environment useful in controlled release applications.

CONCLUSION

PVA/LA graft copolymers were prepared using two methods. The graft copolymers obtained by the esterification reaction of LA and PVA using DMF solvent yielded polymer gels that exhibited tough and tear resistance film properties. The tensile strength, modulus, and elongation for the graft copolymers studies showed good mechanical properties when compared with other PVA gels reported in the literature. The graft copolymers prepared are melt processable and characterized by semicrystalline properties, which indicates the potential in applications requiring use of higher temperatures. Further study of the polymer films produced through compression molding at 100°C showed good swelling properties. The transport mechanism of the hydrogels obtained exhibited Fickian behavior. The DSC study of the nature of water in the PVA/LA gels showed that the PVA gel contains lower amount of bound water and higher amount of free or bulk water. On the contrary, the PVA/LA gels exhibited higher content of bound water, consistent with the degree of swelling obtained. The results indicate that DSC can be used to estimate the relative amounts of free, freezing bound, and nonfreezing water in water-swollen membranes. The presence of such states of water is important because it may influence permeability

behavior of solutes. Elastic hydrogels are used in medical applications because they may enhance the transmission of mechanical stimuli such as in bioimplants and biosensor applications. Further characterization of the kinetics of PVA/LA gels formation is in progress. The potential applications of the graft copolymers as controlled release vehicles for pharmaceuticals and agrochemicals, as well as use in biosensor technology and biomedical applications are also being investigated.

The authors thank Fulbright Program and the Institute of Materials Science, University of Connecticut, Storrs, and the University of Nairobi for various supports.

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