

Characterization and Mechanical Properties of Water-Soluble Poly(vinyl alcohol) Grafted with Lactic Acid and Glycolic Acid

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ABSTRACT: Poly(vinyl alcohol) (PVA), fully or partially hydrolyzed, was reacted with D,L-lactic acid and glycolic acid in different conditions to synthesize polymers with pendant lactate and glycolate groups. Various degrees of grafting were obtained. ^1H - and ^{13}C -NMR analysis as well as thermal and mechanical methods were used to characterize the polymers. Such grafts lead to polymers with lower glass transition temperature, therefor enhancing the polymers solubility in cold water (10°C) and improving flexibility and elasticity as well as tear resistance. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 142–147, 2001

Key words: poly(vinyl alcohol); esterification; lactic and glycolic acids; water soluble; mechanical properties

INTRODUCTION

The chemical modification of poly(vinyl alcohol) (PVA) is an important technique to prepare materials with new properties. The presence of its hydroxyl groups makes it possible for it to react with different reagents.

Reactions between alcohols and lactic acid have been reported for many years. The esterification can take place with or without acid catalysts at various temperatures.^{1,2} The same esterification reaction occurs with lactide as well. The use of a catalyst like stannous octoate under vacuum at 130°C allows the polymerization of the monomer lactide to be linked to an alcohol.^{3,4} Recently, block copolymers of poly(ethylene glycol)–poly(lactic acid) have been prepared by the reaction of the —OH end groups of the PEG with

lactide in the presence of a catalyst and in the absence of water.⁵

The modification of secondary hydroxyl groups of PVA has been reported in the literature. More specifically, esterification of PVA is strictly correlated to the nature of the solvent used. Water, the most used solvent for PVA, is one in which the esterification of PVA can take place. Industrial companies like Du Pont de Nemours⁶ or Novartis⁷ have worked on the grafting of PVA with lactic acid and acrylic or methacrylic acid, respectively. Tsuda⁸ and other authors⁹ have shown that the reaction could occur with acid chlorides in a basic medium. Other solvents like DMSO^{10,11} or DMF^{12,13} are of interest as well. A mixture of DMF/toluene has been used by Onyari and Huang¹⁴ to synthesize copolymers of PVA-grafted PLA.

The aim of this article was to synthesize PVA derivatives soluble in cold water by reacting their hydroxyl groups with lactic and glycolic acids as well as lactide and to prepare materials with

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Table I Specifications of the PVA Samples Used

Polymer	\overline{M}_w (g/mole)	Hydrolysis Degree (%)
Mowiol 10/98	60,000	98
Mowiol 18/88	134,000	88
PVA (lab)	25,000	>99

lower T_g and, therefore, with different mechanical properties.

EXPERIMENTAL

Materials

Different types of poly(vinyl alcohol) were used: Mowiol 10/98, Mowiol 18/88, and PVA (lab). The Mowiol 10/98 and Mowiol 18/88 were obtained from Hoechst. The digits prior to the slash designate the viscosity (in Mpa.s) of the polymer and those after the slash indicate the degree of hydrolysis in mole percent. The PVA (lab) was prepared by hydrolysis of poly(vinyl acetate) (Rhône Poulenc) in methanol with potassium hydroxide. The molecular weights and the degree of hydrolysis of these polymers are gathered in Table I. D,L-lactic acid, D,L-lactide, glycolic acid, and stannous octoate were purchased from Aldrich. Only the D,L-lactide was purified by recrystallization from dry toluene and dried for 48 h in vacuum before use. Water and distilled DMF were used in this study as well.

Esterification of PVA with D,L-Lactic Acid or Glycolic Acid

PVA was dissolved in deionized water (20% wt solution) by heating to 60–80°C. Different ratios of D,L-lactic acid or glycolic acid were added. In a specific example, PVA (PVA (lab), 10 g, 0.227 mol, based on $-\text{CH}_2-\text{CHOH}-$ as the repeat unit) was dissolved in 50 mL of water. Then, D,L-lactic acid (20.47 g, 0.227 mol) was slowly added to the PVA solution. The esterification process was carried out by stirring and heating the reaction mixture at 100°C for 2 h, followed by complete removal of the solvent and the water produced by distillation. The product was redissolved in water at 25°C and reprecipitated twice in acetone (10 times in volume) so as to ensure the complete removal of unreacted lactic acid (or glycolic acid

when this acid is used). The final reaction product was dried under vacuum at 30°C for 24 h. Varied conversion percentages to ester, called also grafting percentages of the polymer, were obtained according to the nature of the PVA and the different PVA/acid ratios used.

Esterification of PVA with D,L-Lactide

PVA was also modified by D,L-lactide in absence of water leading to a PVA grafted with lactic acid oligomers. PVA (Mowiol 10/98, 1 g, 22.7 mmol) was dissolved in distilled dimethylformamide (10 mL, 10% wt solution) under nitrogen in an oil bath at 150°C. After decreasing the temperature to 120°C, D,L-lactide (0.819 g, 5.68 mmol), corresponding to a ratio D,L-lactide/Mowiol 10/98 equal to 0.25, and stannous octoate catalyst (10 mg, 1% wt to PVA) were injected under nitrogen. The mixture was then stirred for 24 h. After cooling to room temperature, the solution was directly precipitated in acetone (10 times in volume). The product obtained was reprecipitated twice from water. Then, the final polymer was dried under vacuum at 30°C for 24 h. Several ratios of lactide/PVA were used to prepare materials with different grafting percentages and different length of the grafts.

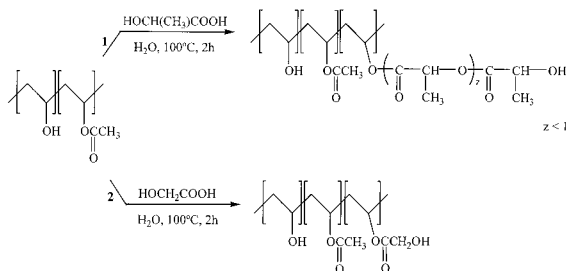
Characterization

Calorimetric studies were carried out on a differential scanning calorimeter (Mettler DSC 30, low-temperature probe) in sealed aluminum pans. Glass transition temperatures, T_g , were determined by a heating rate of 10°C/min⁻¹ after storage of the samples at 50% relative humidity and 20°C for 48 h. Two runs were carried out. The first T_g obtained corresponds to a material containing water and the second one to a material without water.

400 MHz ¹H and 100.6 MHz ¹³C-NMR spectra were obtained at 25°C with a Bruker DRX400 spectrometer using polymer solutions in D₂O and TMS as internal standards.

Solubility tests in water were carried out by putting a piece of film (polymer, 35–40 μm thickness) in a flask filled with water at 10°C. The solution was stirred in that flask. The solubility or nonsolubility of the film in water was observed as well. A time of disintegration and a time of dissolution were noticed for some cases.

Mechanical measurements were determined on films (35–40 μm thickness) stored at 50% rel-



Scheme 1 Esterification reaction of PVA with D,L-lactic acid (1) and glycolic acid (2).

ative humidity and 20°C. The tensile measurements were made on an Instron Model 1011 and the tear resistance properties on an Elmendorf Tearing Tester (Thwing-Albert Instrument).

RESULTS AND DISCUSSION

PVA Modified with D,L-lactic Acid and Glycolic Acid

Poly(vinyl alcohol) with or without acetate groups was esterified with acids in water (Scheme 1). No

catalyst was used for the reaction. The esters were synthesized after removing the solvent and the water produced during the reaction. Specific peaks in ¹H- or ¹³C-NMR spectra allowed the identification of these esters. Indeed, methylene and methine groups of an unmodified PVA are clearly visible at about 1.70 and 4.05 ppm, respectively, in ¹H-NMR (Fig. 1) and at 44.8 and 66.0 ppm in ¹³C-NMR (Fig. 2). When lactic acid is grafted to PVA, the proton spectrum shows methylene resonance at 1.80 ppm and methine resonance at 3.80 ppm. The ¹³C-NMR shows these resonances at 41.9 and 70.5 ppm, respectively. Previous works on esters of PVA have shown such shifts in NMR.^{9,15} In addition, the peaks at 1.45 and 1.60 ppm (Fig. 1) correspond to the methyl protons of the grafted lactate. These methyl groups are also visible at 16.5 and 20.0 ppm on the carbon spectrum (Fig. 2). This observation, showing different signals for the methyl group allowed us to conclude that the graft is sometimes an oligomer. In fact, commercial lactic acid in aqueous solution exists in the monomeric form but also as dimers and/or others. Those acids can react with the hydroxyl groups of the PVA as well, and remain even in water at ambient tempera-

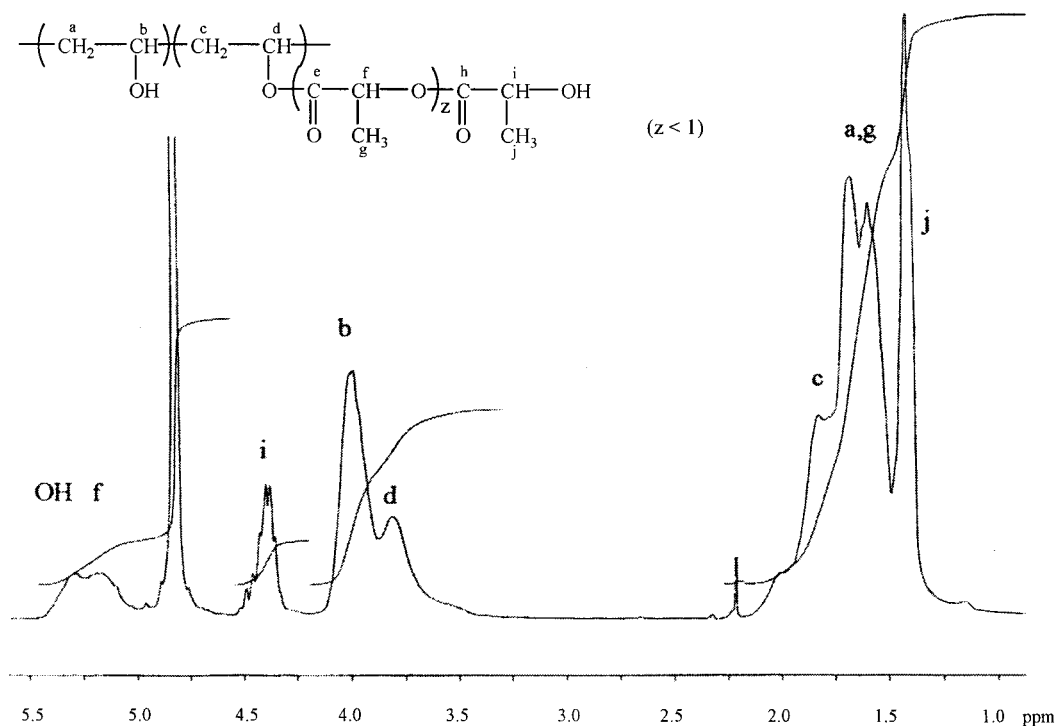


Figure 1 ¹H-NMR (400 MHz, 20°C, D₂O) spectrum of a PVA (lab)-grafted-lactic acid (sample PVA-LA-3).

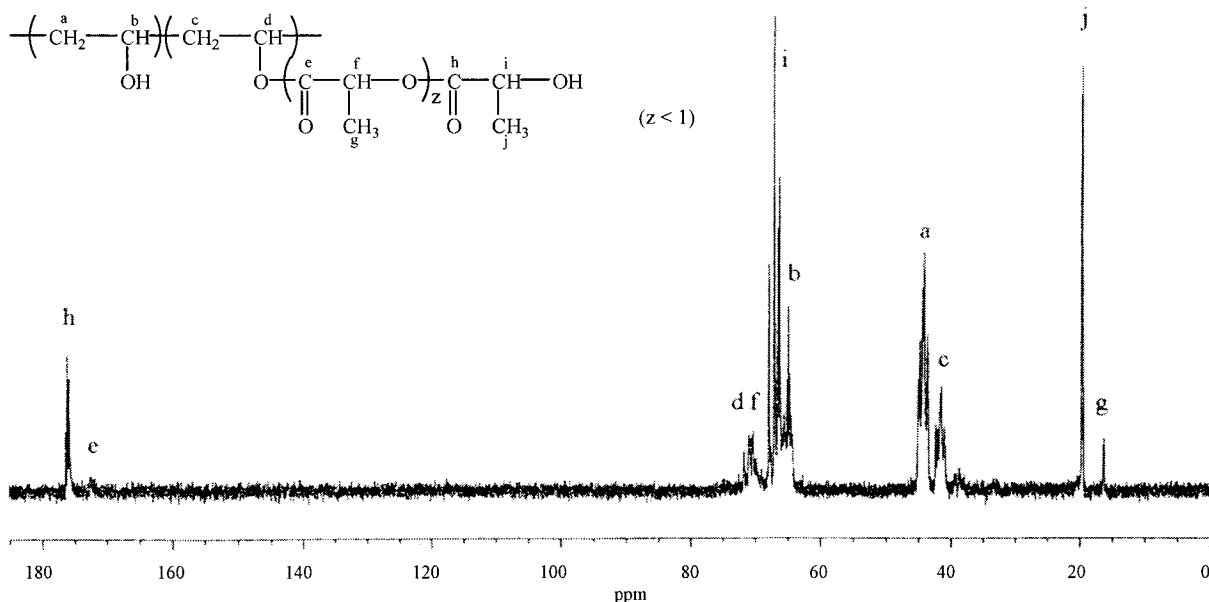


Figure 2 ^{13}C -NMR (100.6 MHz, 20°C, D_2O) spectrum of a PVA (lab)-grafted-lactic acid (sample PVA-LA-3).

ture. All the assignments correlated to lactic acid are in agreement with those of Vert et al. in their studies on monomers, oligomers, and polymers of lactic acid.^{16,17} The shifts of the peak, between monomer and oligomer, is also visible for the —CH group in proton (4.40 ppm, 5.20 ppm) or in carbon (67.0 ppm, 70.0 ppm) NMR and for the carbonyl group in ^{13}C -NMR (172.5 ppm, 176.1

ppm). Due to the overlap of proton peaks, the z -value (Scheme 1), corresponding to the length of grafted lactic acid, was impossible to determine exactly. Nevertheless, the value is very low, as seen from the integrations and from the comparison of the methyl peaks in carbon NMR for example. Less than two lactic acids are covalently bonded to one oxygen of the PVA.

Table II Esterification of PVA with D,L-Lactic Acid and Glycolic Acid

Polymer	Sample	$\frac{[\text{LA}]}{[\text{PVA}]}$	$\frac{[\text{GA}]}{[\text{PVA}]}$	G% (num.)	T_g (°C)		Solubility in Water at 10°C ^c
					1st Run ^a	2nd Run ^b	
PVA (lab)	Non-modified	—	—	—	39	82	no (20°C)
PVA (lab)	PVA-LA-1	1	—	33	10	43	yes
PVA (lab)	PVA-GA-1	—	1	32	−15	42	yes
PVA (lab)	PVA-GA-2	—	0.75	23	11	37	yes
Mowiol 10/98	Non-modified	—	—	—	35	78	no (23°C)
Mowiol 10/98	PVA-LA-2	1	—	28	−5	51	yes
Mowiol 10/98	PVA-GA-3	—	1	34	9	34	yes
Mowiol 10/98	PVA-GA-4	—	0.75	20	11	33	yes
Mowiol 18/88	Non-modified	—	—	—	35	71	yes
Mowiol 18/88	PVA-LA-3	1	—	14	−16	18	yes
Mowiol 18/88	PVA-GA-5	—	1	18	−2	39	yes
Mowiol 18/88	PVA-GA-6	—	0.75	8	25	46	yes

Characterization by NMR, DSC and solubility analysis.

^a Some water present in the polymer.

^b No water present in the polymer.

^c Solubility measurements carried out with a film of polymer (35–40 μm thickness).

Table III Mechanical and Solubility Properties of PVA Grafted with D,L-Lactic Acid and Glycolic Acid

	PVA-LA-2 Mowiol 10/98	PVA-LA-3 Mowiol 18/88	PVA-GA-2 PVA (lab)	PVA-GA-4 Mowiol 10/98	PVA-GA-5 Mowiol 18/88
Tensile strength at break (kg/cm ²)	287	334	183	260	208
Young's modulus (kg/cm ²)	216	264	92	201	114
Elongation at break (%)	179	173	200	164	164
Elmendorf tear resistance (kg/mm)	4.8	26	18.9	10.1	not determined
Solubility in water at 10°C ^a					
Disintegration time (s)	9	10	6	10	4
Dissolution time (s)	19	32	22	29	28

^a Solubility measurements carried out with a film of polymer (35–40 μm thickness).

PVA-grafted glycolic acid samples were characterized by NMR as well. Similar spectra were obtained. The methylene group of glycolic acid has a resonance at 4.27 ppm in ¹H-NMR and 60.0 ppm in ¹³C-NMR. The carbonyl group is visible at 174.3 ppm in accordance with values quoted in the literature.^{18,19}

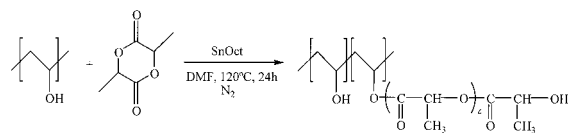
The integration ratios (¹H-NMR) between PVA and either lactic acid or glycolic acid allowed calculation of the percentage of the graft present in the polymer. These percentages, from 8 to 33%, are reported in Table II. All the materials presented in that table have also been characterized by a solubility test in water at 10°C and by DSC (*T_g* determination). A decrease of the glass transition temperature was observed in all modified PVA. The first run corresponds to a material with some humidity traces. Both water and graft act like a plasticizer in the macromolecular chains. As a result, the *T_g* can be very low, for example –16°C for a Mowiol 18/88 grafted with only 14% of lactic acid. The same compound has a *T_g* of 18°C after the second run, when no water is present in the polymer. The difference of 53°C between PVA-LA-3 and the unmodified Mowiol 18/88 (*T_g* = 71°C) is only due to the lactic acid graft. The same behavior was observed with glycolic acid grafts. All the new materials were soluble in water at 10°C. Better solubility in cold water was observed, especially for the grafted Mowiol 10/98 and PVA (lab). These initial polymers were soluble in water above 20°C when the PVA correspond to a piece of film (35–40 μm thickness) or around 60–80°C for the precipitated polymer.

Some samples were mechanically analyzed because of the modification of the glass transition

temperature of the polymers grafted with lactic acid and glycolic acid (Table III). The tensile strength at break, Young's modulus, elongation at break and the Elmendorf tear resistance were determined at room temperature to ascertain the quality of the materials in a packaging use for instance. Generally, those values are close to 0 for an unmodified PVA without acetate groups, and are slightly higher for a PVA with 12% acetates. However, the tension, elasticity, elongation, and resistance of the new materials were much improved. The most significant increases were obtained for PVA-LA-3, synthesized from Mowiol 18/88, with a tensile strength at break of 334 kg/cm² or an Elmendorf tear resistance equal to 26 kg/mm. These results were in total agreement with the very low *T_g* of this sample (–16°C first run, 18°C second run). Disintegration time in water at 10°C did not exceed 10 s, and no more than 32 s were necessary for complete dissolution.

PVA modified with D,L-Lactide

The esterification of poly(vinyl alcohol) with D,L-lactide in the presence of stannous octoate as a catalyst in DMF and under nitrogen at 120°C leads to a PVA backbone grafted with poly(lactic acid)



Scheme 2 Esterification reaction of PVA with D,L-lactide.

Table IV Esterification of PVA (Mowiol 10/98) with D,L-Lactide

Sample	[D,L-Lactide]; [Mowiol 10/98]	Substitution (%)	X_n of the Graft	T_g (°C)		T of Solubility in Water (°C)
				1st Run	2nd Run	
PVA-LA-A	0.10	10	2.0	6	45	10
PVA-LA-B	0.25	20	2.3	19	48	10
PVA-LA-C	0.50	38	3.5	0	17	insoluble

Characterization by NMR, DSC and solubility analysis.

(PLA) (Scheme 2). The properties of such materials vary according to the length and amount of PLA grafted.^{14,20} In our case, the solubility in cold water is a determining factor for any interest in the material. Table IV contains data corresponding to three PVA samples, synthesized from Mowiol 10/98, grafted with oligomers of lactic acid. The substitution percentage and the number average degree of polymerization (\bar{X}_n) were calculated by NMR. For an $\bar{X}_n = 3.5$ and a substitution of the hydroxyl groups equal to 38%, the material was insoluble in water. Nevertheless, T_g for the first run (0°C) and the second run (17°C) were very low, much lower than the second run T_g of PVA-LA-2 ($T_g = 58^\circ\text{C}$, Table II) corresponding to the same initial PVA. Thus, tension, elasticity, elongation, and resistance properties can certainly be improved despite the lack of solubility in water.

CONCLUSIONS

Esterifications of several PVA polymers, differing in their molecular weight and percentage of acetate groups, have been carried out, first with D,L-lactic acid or glycolic acid, and second with D,L-lactide. Water and no catalyst were used for the first reactions. The polymers obtained had the particular properties of being soluble in water at 10°C and exhibiting very low glass transition temperatures. The tension, elasticity, elongation, and resistance properties were consequently improved. Even better mechanical properties can be obtained with oligomers of lactic acid grafted on a PVA backbone by reaction with stannous octoate in DMF under nitrogen. However, limited solubility in water was observed. Thus, it is very important to synthesize polymers with nonpolymerized-grafted lactic acid to achieve solubility in cold water.

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