

## Novel poly(vinyl alcohol)-g-poly(hydroxy acid) copolymers: Synthesis and characterization

Ainhoa Lejardi<sup>a</sup>, Agustín Etxeberria<sup>b</sup>, Emilio Meaurio<sup>a</sup>, Jose-Ramon Sarasua<sup>a,\*</sup>

<sup>a</sup>School of Engineering, University of the Basque Country (EHU-UPV), Alameda de Urquijo s/n, 48013 Bilbao, Spain

<sup>b</sup>Department of Polymer Science and Technology, Institute of Polymer Materials, University of the Basque Country (EHU-UPV), M. de Lardizabal 3, 20018 Donostia, Spain

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### ABSTRACT

Poly(vinyl alcohol) (PVA) was reacted with three hydroxy acids (HA), namely D,L-lactic acid (LA), glycolic acid (GA) and D,L-3-hydroxybutyric acid (HB). The graft copolymers obtained were thoroughly characterized by <sup>1</sup>H and <sup>13</sup>C NMR, FTIR, and DSC. Copolymer compositions were in the range 14–45 mol% HA with average lateral chain lengths in the range 1.1–1.3. The C=O stretching band, arising from the lateral polyester chains, presents significant differences from that of pure polyesters. In case of the VALA and VAGA copolymers, carbonyl groups are almost completely interassociated with hydroxyl groups and as a result the carbonyl band presents a single contribution; however, splitting appears in VAHB. The band at about 1735 cm<sup>-1</sup> already observed for Poly(3-hydroxybutyrate) P3HB was reexamined in the light of molecular models for VAHB and the splitting observed was attributed to C–H•••O=C and to O–H•••O=C hydrogen bonding. The thermal analysis of copolymers demonstrates that esterification suppresses crystallinity and increases free volume, both accounting for a T<sub>g</sub> reduction with regard to PVA. The stronger intermolecular hydrogen bonding interactions found in PVA with the chemically modified PVAs opens an interesting way towards miscibility with polyesters and other polymer systems containing carbonyl groups.

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### 1. Introduction

In recent years the number of research works devoted to the synthesis of macromolecular designs (such as block, comb, brush or star polymers) based on biocompatible and biodegradable polymer materials has shown a noticeable increase [1]. The control of the macromolecular structure can lead to versatile polymers with tuned chemical, physical and mechanical properties. The synthesis of Bio-related polymers can be accomplished using different methodologies such as gene technology, enzymatic polymerization and finally pure chemical synthesis reactions. Polymers containing reactive groups are one interesting starting point for the architectures based on chemical synthesis.

Poly(vinyl alcohol) (PVA) is a well known water-soluble polymer with widespread commercial applications [2]. The repeating unit of PVA contains reactive hydroxyl groups that can be converted to ester groups through esterification with acids or ring opening reactions. Due to its biodegradable nature PVA is a particular synthetic vinyl polymer, although biodegradability is somewhat

low. Furthermore, PVA has been cleared by the US Food and Drug Administration (FDA) as a safe component for coating and adhesives in contact with fatty foods [3]. It is also used as a component of cosmetics, bacteriostatic agents, externally applied medicines and biomedical materials [2–5].

As biomedical material, PVA has found applications for the production of soft contact lenses or artificial muscles [2]. In these cases, the base polymer is crosslinked to avoid dissolving in the aqueous medium. There are, however, alternative routes to increase the water resistance of PVA. One of them is blending PVA with biodegradable materials of hydrophobic nature to obtain polymer blends with tuned hydrophilicities. Biodegradable polyesters (such as polylactides) can be appropriate blending counterparts since they carry hydrogen bond acceptor groups, needed to promote the miscibility of the system through the establishment of specific interactions. However, these blends show phase separation and poor compatibility according to different investigations [6–8]. Chemical modification of PVA, particularly grafting with biodegradable hydroxy acids, might improve its miscibility with hydrogen bond acceptor counterparts for several reasons. First the introduction of bulkier lateral groups should decrease the high autoassociation density of PVA, which generally impairs its inter-association. Second, the modification reaction moves away the

\* Corresponding author.

E-mail address: [jr.sarasua@ehu.es](mailto:jr.sarasua@ehu.es) (J.-R. Sarasua).

hydroxyl groups bonded to the chain skeleton of PVA to the end of the lateral chains, where the formation of intermolecular hydrogen bonds should be favoured due to reduced steric hindrances [9].

Grafting of PVA with Lactic acid has been already reported [10–12], but some properties of the resulting products are apparently inconsistent. Carlotti et al. grafted PVA with LA after water removal (i.e., in the melt) without catalysts, obtaining water-soluble polymers in all cases [11]. They reported LA compositions ranging from 14 to 33 mol % and estimated grafted chain lengths below two repeat units (grafted chain lengths could not be determined exactly because of overlapping of the proton peaks in the  $^1\text{H}$  NMR spectra). On the other hand, Ding et al grafted PVA with Lactic acid by melt polycondensation using stannous chloride as catalyst, obtaining non-water-soluble polymers in all cases [12]. These authors reported LA compositions from 21 to 53 mol % and the degrees of polymerization were in the 1.7–2.2 range. Surprisingly, even though some of the copolymers obtained by both researchers show very similar compositions, water resistances are completely different.

The present paper deals with the synthesis and detailed characterization of PVA modified with lactic acid (LA), glycolic acid (GA) and hydroxybutyric acid (HB). Grafting PVA with HB was investigated for the first time in our lab as described here and in ref. 14. Grafting with GA has only been reported by Carlotti et al, but the copolymers were not characterized in detail (particularly the polymerization degree of the lateral chains was only roughly estimated) [11]. Uncatalyzed grafting conditions will be used for two reasons: on the one hand, we would like to understand the structural features explaining the improved water solubility of these materials. On the other hand, their blends should cover wider hydrophilicity ranges. Moreover, we are more interested in substituting the largest possible amount of vinyl alcohol groups rather than in lengthening the lateral chains. Actually, our best bet would be the synthesis of the corresponding poly(vinyl hydroxyester)s; i.e., the polymers resulting from the double bond addition polymerization of vinyl glycolate, vinyl lactate and vinyl hydroxybutyrate. However, neither the monomers nor the polymers are commercially available, and the synthesis of the poly(vinyl hydroxyester)s starting from the raw chemical compounds can be a formidable research work. Therefore, a simpler route is chosen in this paper: the esterification of PVA with the corresponding hydroxy acids.

The miscibility of these copolymers with selected counterparts has been already investigated in our research group. Blends with poly( $\epsilon$ -caprolactone) (PCL) show phase separation, but compatibility is strongly improved [13]. It is necessary to realize that, unfortunately, the vinyl alcohol repeat units still dominate the composition of the obtained graft copolymers, and their total substitution seems not actually possible. Blends with poly(vinyl pyrrolidone) PVP show stronger intermolecular interactions than those reported for other hydroxylated polymers; and particularly the formation of double hydrogen bonds is reported for the first time in polymer blends in the solid state [14].

## 2. Materials and methods

The biodegradable hydroxy acids selected to modify the PVA chain, D,L-lactic acid (LA), glycolic acid (GA) and hydroxybutyric acid (HB), were obtained from Sigma–Aldrich. Poly(vinyl alcohol), PVA ( $M_w$  20,000), was also obtained from Sigma–Aldrich and characterized by  $^{13}\text{C}$  NMR. The analysis of the methine Carbon at triad sequence level [15] gave the following relative intensities: (mm) = 0.207, (rm) = 0.515 and (rr) = 0.278. The isotacticity coefficient  $\sigma$ , where  $\sigma = (\text{m}) = (\text{mm}) + (\text{mr})/2$ , took a value of 0.465,

close to atactic. Also, 1% of residual acetylation grade was determined [16].

### 2.1. Esterification of PVA

PVA was esterified with varying feed ratios of LA, GA and HB (see scheme 1 and Table 1) to obtain modified polymers of different composition. In a specific example, PVA (10 g) was dissolved in hot distilled water (50 mL). LA (20 g) was then slowly added to the reactor. The esterification process was carried out in two stages, first the solution was maintained at 100 °C for 2 h, and then water was removed till dryness by evaporation at about 120 °C. The product was redissolved in water at 25 °C and reprecipitated twice in acetone (10 times in volume) to remove unreacted acid and the poly(lactid acid) chains formed as byproduct. The precipitate was additionally purified in a Soxhlet for 24 h with chloroform to assure complete removal of residual monomer and byproducts. Finally, the modified PVA was dried under vacuum at 30 °C for 24 h.

### 2.2. Differential scanning calorimetry (DSC)

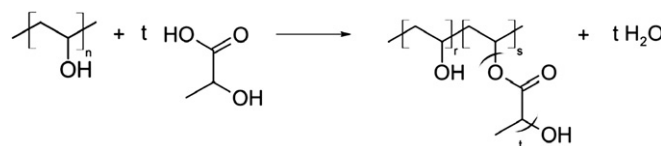
Calorimetric studies were carried out on a differential scanning calorimeter (Mettler DSC 2920) in sealed aluminium pans. The weight of sample used was in the 5–10 mg range. The scans were carried out from 20 to 220 °C at a heating rate of 20 °C  $\text{min}^{-1}$ . The instrument was calibrated using an Indium Standard (melting point 156.6 °C).

### 2.3. Infrared spectroscopy (FTIR)

Infrared spectra of modified PVA were recorded on a Nicolet AVATAR 370 Fourier transform infrared spectrophotometer (FTIR). Samples were prepared by casting 0.2 wt % hexafluoroisopropanol (HFIP) solutions on KBr pellets.

### 2.4. Nuclear Magnetic Resonance (NMR)

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded in a Bruker Avance DPX 300, which corresponds to 300.16 and 75.5 MHz frequencies for  $^1\text{H}$  and  $^{13}\text{C}$  respectively, in 5 mm o.d. sample tubes using 0.7 mL of deuterated dimethyl sulfoxide ( $\text{DMSO-d}_6$ ), at room temperature



Scheme 1. Esterification of PVA with D,L-lactic acid.

Table 1

Reaction feed ratios, naming conventions and glass transitions for the polymers synthesized in this study.

Hydroxy acid	Molar feed ratio [Acid]/[PVA]	Copolymer Name <sup>a</sup>	T <sub>g</sub> (°C)
–	–	PVA	74
LA	1/1	VALA28	57
LA	4/1	VALA45	68
GA	1/4	VAGA24	48
GA	4/1	VAGA44	38
HB	4/1	VAHB14	60

<sup>a</sup> The naming convention for the copolymers uses the letters VA to indicate vinyl alcohol, the following two letters refer to the hydroxy acid used in the modification reaction, and the last two numbers indicate the hydroxy acid molar % according to  $^1\text{H}$  NMR.

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