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Morphology and Mechanical Properties of Poly(vinyl alcohol)/Poly(lactic acid) Blend Films Prepared from Aqueous Dispersions

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In this study, the preparation of poly(vinyl alcohol) (PVA)/poly(lactic acid) (PLA) blends of different compositions, 100/0, 75/25, 50/50, 25/75, and 0/100, by mixing water solutions of the former and water dispersions of the latter polymer, is reported. Two distinct dispersions of PLA are prepared using a commercial-grade polyester and two different surfactants, an anionic one and a neutral one. Films of PLA and of the corresponding blends are obtained by simply drying at 60 °C the water dispersions without or with the PVA. The films are characterized by infrared spectroscopy, differential scanning calorimetry (DSC), and scanning electron microscope (SEM) analysis. This evidences an island-like morphology, with the continuous phase consisting of a PVA rich phase at all compositions except 25/75, for which an inverted phase composition, with a continuous phase made mostly of PLA, is instead found. Voids caused by air bubbles trapped in the initial mixture are observed in particular in the formulations with the anionic surfactant. The trapped bubbles result in premature thermal degradation by thermogravimetric analysis (TGA) and mechanical failure during clamping. Films with the neutral stabilizer are tougher than the bare commercial PLA, with Young modulus and elongation at break depending on the combination of the composition and arrangement of blend phases.

1. Introduction

Poly(vinyl alcohol) (PVA) is a biodegradable,[1] biocompatible, and nontoxic polymer that finds applications in numerous industrial fields, such as in fabric and paper sizing, fiber coatings, adhesives, and barrier layer in packaging.[2,3] PVA is often used for food packaging applications due to its excellent oxygen barrier property.[4] It is produced by deacetylation of poly(vinyl acetate) (PVAc) and it is commercialized either as a fully hydrolyzed or partly hydrolyzed polymer.[5] Overall, 87–89% hydrolyzed products have a high degree of solubility in water, even if cold, but for complete dissolution heating to 85 °C is required. Higher hydrolysis grade products require progressively more energy to dissolve, because of their greater degree of crystallinity. For complete dissolution, these grades require heating to ≈95 °C.[6] The mechanical properties of the polymer depend on the deacetylation degree as well. Furthermore, they depend on the molecular weight and on the retained moisture.[7] Unless it is completely dry, fully hydrolyzed PVA has a ductile behavior with elongation at break of 25% and 200% at 1.8 wt.% of moisture content and fully wet, respectively [7] However, PVA has low strength and low mechanical resistance, particularly when wet. On the contrary, for many applications, such as high-performance films, fibers, and artificial ligaments and muscles, mechanically robust materials are needed.[8] Dissolution in water also limits its application in packaging films, where it can be used only as an internal layer in multilayer structures. A convenient strategy to overcome these limitations without loss of the advantages of PVA, such as biodegradability, is to blend PVA with stiff and water-insoluble biodegradable polymers.[9]

Water-soluble biopolymers, such as polysaccharides and proteins, have often been blended with PVA.[10] The resulting blends exhibit improved mechanical resistance with respect to the pristine polymers.[11] Often, an improvement in water resistance is also observed, thanks to the formation of strong hydrogen bonds between the hydroxyl groups of PVA and complementary groups in the biopolymers, such as for instance NH_2 groups of chitosan.[6,11] Blends of PVA with hydrophobic bio-related polymers such as poly(lactic acid) have been also reported. [9]

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Poly(lactic acid) (PLA) is a stiff, biodegradable, compostable, safe, and relatively cheap polymer already produced at an industrial scale from renewable resources.[9,12–15] When added to PVA it has been reported to strongly improve tensile strength and Young's modulus of the wet material.[16] Moreover, being hydrophobic, PLA also improves the water resistance of PVA.[16] On the other hand, the addition of PVA to PLA improves the thermal stability and the biodegradation rate of the former polymer.[17]

The main strategy reported so far for the preparation of PVA/PLA blends is melt processing. However, because of strong intra- and inter-molecular hydrogen bonding, semi-crystalline PVA is very difficult to process in the melt: its melting point (226 °C) is very close to its decomposition temperature (200–250 °C),[18] resulting in a narrow temperature window for processing. An alternative method to blend PVA and PLA is solvent mixing. Hexafluoroisopropanol is the most frequently used solvent, being able to solubilize both components.[16,19] However, this solvent poses severe risks for both operators and the environment.

An alternative method to obtain blends between water-soluble and water-insoluble polymers is emulsion blending.[20,21] This method is a variation of the more frequently used latex blending.[22] Latexes are dispersions or emulsions of a hydrophobic polymer in water. Latex blending consists of physically mixing two or more types of latexes to obtain a final formulation with improved or combined properties.[22] The main advantages of this methodology are the simplicity of procedure and the low environmental impact of the process due to the use of water as solvent. Besides, the presence of surfactants in the latex formulations may decrease the interfacial tension between polymers, thus lowering the coarsening rate of the domain structures.[23] Blends obtained by mixing latexes are made between hydrophobic components. On the contrary, emulsion blending enables the mixing of hydrophobic and hydrophilic components. An oil-in-water emulsion is prepared by mixing an organic solution of the hydrophobic polymer with a water phase containing the water-soluble polymer. After evaporation of the organic solvent, a latex composed of both polymers is obtained. This approach allows the blending of thermally sensible polymers that cannot be solubilized in a common solvent. For instance, emulsion blending was exploited for the preparation of gelatin/poly(butylene succinate-*co*-adipate) bio-based and biodegradable blends.[21] Regarding PLA, mixtures with hydrophobic polymers such as chitosan,[20,24] lignin,[25] and nanocellulose[26,27] were efficiently prepared through emulsion blending. In an interesting work aimed at the production of ternary chitosan/PVA/PLA blends, the preparation of a binary PVA/PLA blend through emulsion blending was reported.[20] However, the PVA/PLA blend prepared (50/50) was impossible to handle or mechanically characterize due to its extreme fragility.

Blends of hydrophobic and hydrophilic polymers can also be prepared by a mixed approach between latex mixing and emulsion blending. In these cases, a water solution of the hydrophilic polymer is mixed with the hydrophobic polymer latex to produce composites with combined properties. For instance, gelatinized starch plasticized with glycerol,[28,29] chitin,[30] or hydrophobically modified cellulose[31] water solutions were added to natural rubber latex (NRL) achieving composites with improved properties. Nevertheless, to the best of our knowledge, this mixed approach has not yet been reported for the preparation of biodegradable blends such as PVA/PLA ones.

In this work, PVA/PLA blends of different compositions, 100/0, 75/25, 50/50, 25/75, and 0/100, are prepared by simply mixing in the right proportion a preformed water dispersion of PLA with a water solution of PVA. The main goal is to assess the possibility to produce water-based blends of two biodegradable polymers, of which one is soluble and the other is not soluble in water. The stability and the rheological behavior of the mixtures are studied as a function of the blend composition and then the mixtures are used to produce films by solution casting. The obtained films are characterized by morphological, thermal and mechanical analysis. These blends may in the future be used for the preparation of barrier layers on paper to obtain biodegradable multilayer materials for packaging applications. Indeed, water-based formulations are particularly attractive for application as coating directly on paper after pulping.

2. Experimental Section

2.1. Materials

Poly(lactic acid) Ingeo PLA 4060D (PLA) was supplied by NatureWorks LLC (Plymouth, MN). PLA 4060D is an amorphous polymer with a L-lactide content of around 88 wt.%,[32] and a weight-average molecular weight (M_w) of 1.2×10^5 g mol^{-1}.[33] Poly(vinyl alcohol) POVAL 6–88 (PVA 6–88) and POVAL 4–88 S2 (PVA 4–88) grades were supplied by Kuraray Chemical. To obtain water solutions, 30 g of PVA 4–88 or 75 g of PVA 6–88 was slowly added into 125 mL of cold water under moderated speed stirring. For complete solubilization, another 125 mL of water was added, the temperature was increased up to 95 °C and the mixture stirred slowly for 2 h. Poly(vinyl alcohol) Gohsenol GH-17 R (PVA GH 17R) was supplied by Mitsubishi Chemicals Performance Polymers in water solution at 12 wt.%. Starch C*Icoat 07525 (starch) was provided by Cargill Deutschland GmbH. A solution of starch at 3 wt.% in ultrapure water was prepared by heating under reflux 6 g in 200 mL for nearly 1 h. Synperonic PE/F68 (SYN) was generously supplied by Croda Chemicals. Sodium dodecyl sulfate (SDS), ethyl acetate (purity ≥99.5%), and all other solvents were purchased from Sigma–Aldrich and used as received.

2.2. Preparation of PLA Dispersions

The procedure was adapted from a method previously described (first step in **Figure 1**).[34] 30 g of PLA was solubilized in 270 mL of ethyl acetate under vigorous stirring for 4 h (oil phase). Meanwhile, to obtain PLA_1, 1.68 g of SDS, and 210 g of starch solution (3 wt.%) were mixed; to obtain PLA_2, 5.04 g of SYN was solubilized in 210 g of pure water (water phase). After parting both the oil and the water phases each in six equal fractions, six equal mixtures were prepared by mixing in each case one oil phase with one water phase. Homogenization was then carried out with ultrasound treatment (Vibra-Cell Ultrasonic Liquid Processor VCX750, maximum power output: 750 W, equipped with a 13 mm diameter probe) in four continuous steps of 30 s each. The power amplitude was 50% in the first step and then 90%. Steps

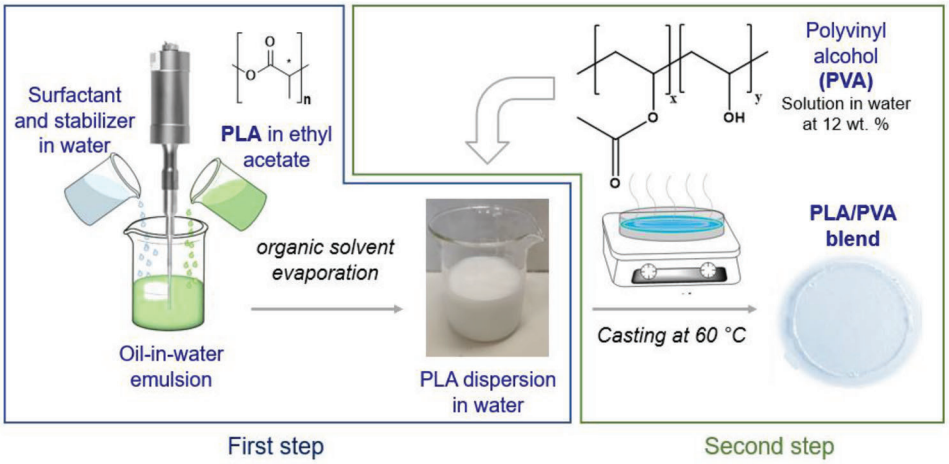

Figure 1. Cartoon of the procedure for the preparation of films of PVA/PLA blends. The panel on the left shows the first step of the procedure, that is the preparation of the PLA dispersions in water. The panel in the right shows the second step, that is the addition of the PVA solution in water to obtain the PLA/PVA blend.

were spaced out by 2 min during which the mixture was kept under mechanical stirring with an overhead stirrer at 200 rpm. All the resulting emulsions were collected together in a 2 L reactor and the organic solvent, ethyl acetate, was distilled off at 30–40 °C and 0.85 bar for 4 h while keeping the emulsion under stirring at 120 rpm. The final dry matter content at 200 °C was 12 wt.%.

2.3. Preparation of PVA/PLA Blends

Proper amounts of PVA solution were added to PLA dispersions to obtain PVA/PLA blends of the desired composition (Figure 1). As an example, to prepare PVA/PLA 50/50 blends, 2.8 mL of a PLA dispersion with dry content 12 wt.% and 2.8 mL of PVA solution at 12 wt.% concentration were mixed by stirring for 4 h at room temperature in a flask.

2.4. Preparation of Film

To prepare films of blends, 5.6 g of PVA/PLA latexes was cast onto polystyrene (PS) capsules (10 cm of diameter) and left to dry at 60 °C in the oven. In the case of PVA/PLA 100/0 films, drying was performed at room temperature.

Reference PLA films were obtained in a parallel plate hot press at 180 °C. 6 g of PLA 4060 D granules were pre-heated at 0 ton for 2 min, then pressed at 280 ton for 1 min, and finally cooled at room temperature. The procedure was repeated twice. The same procedure was used to obtain PLA_2 (PVA/PLA_2 0/100) films from the sample as a powder, obtained by drying the dispersion at room temperature.

2.5. Instruments and Methods

The diameter of the polymer particles was determined by dynamic light scattering (DLS) analysis at 25 °C using a NanoBrook Omni Particle Size Analyser (Brookhaven Instruments Corporation, USA) equipped with a 35 mW red diode laser (nominal 640 nm wavelength) and BI-SCP cell in backscattering (173°). To give reliable results, dilute suspensions (0.15% v/v) were analyzed. For data elaboration, NNLS inversion method was used by assuming the particles to be spheres. The reflective index of the dispersion medium and of the dispersed phase were set as 1.330 and 1.596, respectively. Average by volume values were reported. Each measurement was repeated five times on the same sample and the reported data were the average over the five measurements. The standard deviation of the data was assumed as data error.

The dispersions' stability was assessed through visual criteria and DLS analysis both after the preparation and after 1 week. Dispersions were assumed stable if no phase separation was observed and if the particle size variation was lower than the standard deviation on the particle size value.

A rotary Anton Paar MCR 102 rheometer, equipped with a cone-plate geometry CP50-1 (49 975 mm of diameter, 1° angle) probe, Peltier system for temperature control, and Anton Paar software for data acquisition and analysis was used for rheology analysis. A solvent reservoir was attached to prevent the sample from drying. Flow curves were registered at 25 °C in the range of shear rates from 0.1 to 1000 s^{-1}. Pre-shear at 100 s^{-1} for 60 s followed by a 120 s rest was applied to erase the effect of loading. Each measurement was repeated three times and the arithmetic mean was calculated on the collected data. The error was calculated as standard deviation of the data.

Scanning electron microscopy analysis (SEM) was accomplished with a Zeiss EVO 40 microscopy equipped with a LaB_6 source. Samples in the form of powder or film were gold sputtered before observation. Film sections were obtained by fracture in liquid nitrogen.

Differential scanning calorimetric analysis was conducted on a DSC 8000, PerkinElmer Inc. USA instrument equipped with IntraCooler II cooling device and Pyris software for instrument control, data acquisition, and analysis. The instrument was calibrated in temperature and energy with high-purity indium and lead as standards. Three to 10 mg of sample was analyzed in aluminum pans under a dry nitrogen atmosphere (30 mL min^{-1}).

Table 1. Features of the water dispersions of PLA and of the PVAs used to prepare the blends.

PLA	Surfactant, stabilizer	Dry matter content [wt.%]	Dispersed particle size [nm]	Polydispersity
PLA_1	SDS, starch	15.2	289.1 ± 5.5	0.194 ± 0.021
PLA_2	SYN	16.1	415.4 ± 7.1	0.290 ± 0.009
PVA	**Viscosity[a] [Pa s]**	**Hydrolysis degree[b] (HD)**	**T_m[c] [°C]**	**ΔH_m[c] [J g^{-1}]**
4-88	0.01	73.1	194.3	50.3
6-88	0.09	73.6	194.4	36.1
GH R17	2.4	75.2	191.6	39.6

[a] Determined for water solutions 12 wt. % at a shear rate of 0.1 s^{-1}; [b] by ^{1}H NMR analysis; [c] by DSC analysis.

For analysis samples were first heated up from 0 to 170 °C to erase the thermal history and to remove any trapped volatile substances. After 1 min at 170 °C, samples were cooled down to −50 °C (cooling step), maintained at −50 °C for 2 min, and finally heated up again to 170 °C (second heating step). Heating and cooling steps were all performed at 10 °C min^{-1}.

Thermogravimetric analysis (TGA) was carried out on a TGA 4000 (PerkinElmer Inc.) instrument with Pyris software for data acquisition and analysis. Samples (5–10 mg) were analyzed in an alumina pan at a heating rate of 10 °C min^{-1} from 30 to 900 °C under a nitrogen atmosphere (30 mL min^{-1}).

FT-IR spectra were recorded on Agilent Cary 630 FTIR spectrophotometer with ZnSe ATR element. Background and sample spectra were collected by accumulating 32 scans.

^{1}H-NMR spectra were recorded on Varian Mercury Plus 300 in D_2O at room temperature.

2.6. Mechanical Analysis

Films were sprayed with a water-based white paint (Marcotech ULTRA AU10 −322, San Marco Group Spa, Marcon (VE), Italy) to allow the acquisition of the deformation by Digital Imaging Correlation (DIC), (Dantec Dynamics, Skovlunde, Denmark). For a correct DIC reading of the pure PVA sample, before the spraying phase with the white water-based paint, the film was opacified by spraying with water and talc powder. The non-influence of the paint on the film thickness was verified with the stereomicroscope Leica MZ6, equipped with a Leica EC3 camera (Leica Microsystem, Wetzlar, Germany). After these steps, each disk was press-dried to prevent wrinkling. Subsequently, test specimens were cut into 10 mm × 100 mm rectangles, with a scalpel, according to ASTM D882 standard. The thickness of each sample was measured using a digital micrometer (Mitutoyo 293, 2 µm resolution). Afterward, the samples were conditioned at 25 °C in the presence of a saturated solution of $Mg(NO_3)_2$ to keep the relative humidity in the 50% ± 5% range, as indicated in ASTM D882 standard.

Mechanical tests in simple tension were performed using a universal testing machine (INSTRON 4467, USA), equipped with a 500 N load cell. Trials were carried out on five specimens for each formulation at room temperature with a 5 mm min^{-1} crosshead speed and with a gauge length of 50 mm. Preload was 2.5 N for PVA/PLA_x (x = 1 or 2) films 100/0 and 75/25, 1 N for PVA/PLA_x 0/100 and 50/50, and 0.5 N for the sample PVA/PLA_2 25/75. DIC was used to evaluate the strain until 0.2% for the determination of Young's modulus.

3. Results and Discussion

3.1. Preparation of PVA/PLA Blends in Water

PVA/PLA blends were prepared by mixing preformed dispersions of PLA with PVA solutions (Figure 1). In the first step, an aqueous dispersion of PLA was obtained by exploiting a procedure previously reported by our group[34] (Figure 1, left). The procedure consists in the preparation of an oil-in-water emulsion of PLA in ethyl acetate followed by the evaporation of the organic solvent. Two different PLA formulations were produced: one (named PLA_1) containing SDS as a surfactant and starch as a stabilizer and the other one (PLA_2) containing SYN as a surfactant (**Table 1**). SDS is a common low molecular weight anionic surfactant, while SYN is a polyethylene oxide-polypropylene oxide (PEG-PPG) block copolymer.[35] The two dispersions have comparable dry matter content (Table 1) and they are made of sub-micrometric particles that are larger for PLA_2 than PLA_1 (Table 1; Figure S1, Supporting Information). Dispersions are stable over several months, at least at 4 °C. In fact, no creaming or sedimentation was observed during 6 months of storing in fridge.

In the second step, the PLA dispersions were simply mixed with PVA solutions in water. Three different PVAs (4–88, 6–88, GH R17) having comparable HD (73–75%) but different molecular weight and thus viscosity in solution (Table 1), were tested. Solutions in water of the three PVA grades at the highest possible concentration that could be prepared at atmosphere pressure (12 wt. % for PVA GH 17R and 4–88, 30 wt.% for PVA 6–88) were added to PLA_1 and PLA_2 dispersions in the right proportion to obtain PVA/PLA 50/50 blends. No creaming or sedimentation were observed during either blending or standing at room temperature after preparation, thus indicating that PVA does not affect the stability of the pristine PLA dispersions.

The blends were cast onto dishes and left to dry at 60 °C in oven to obtain films. The dry temperature was selected as having been previously identified as the minimum film formation temperature (MFFT) for the PLA aqueous dispersions.[34] At drying temperatures above the MFFT, the particles of the bare water dispersion undergo deformation and cohesion, therefore producing a homogeneous and continuous polymeric film. When particles are dispersed in the presence of PVA, heating above the MFFT

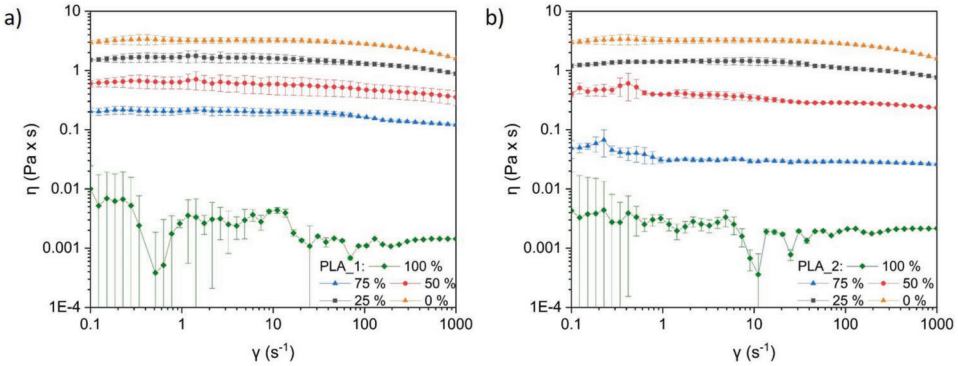

Figure 2. Viscosity as a function of the shear rate for PVA/PLA blends with different content (0, 25, 50, 75, and 100 wt.%) of PLA_1 a) and PLA_2 b) dispersions.

may promote some mixing (see below). On the other hand, PVA solutions in water can form homogeneous and continuous films even at room temperature.

The films obtained with PLA_2 dispersion looked less transparent than the ones with PLA_1 most likely because of the larger phase size domain obtained with the former than the latter dispersion. Indeed, as mentioned above, the particle size of PLA_2 is almost double that of PLA_1 (Table 1). Whatever the PLA used, films with PVA 4–88 were very fragile and fragmented (Figure S2e,f, Supporting Information). Similar results, albeit to a lesser extent, were observed with PVA 6–88 (Figure S2c,d, Supporting Information). On the contrary, films prepared with PVA GH 17R (Figure S2a,b, Supporting Information) resulted to be homogeneous and soft. As mentioned above, the three tested PVAs differ among them for the viscosity in solution (Table 1), whose value has the following order: PVA 4–88 < PVA 6–88 < PVA GH 17R. Since the three polymers have comparable degrees of hydrolysis, the difference in viscosity can be correlated to a difference in the average molecular weight ($\bar{M}_n^{4-88} < \bar{M}_n^{6-88} < \bar{M}_n^{\mathrm{GH\ 17R}}$), and the films behavior indicates that the molecular weight of 4–88 and 6–88 is too much low to provide adequate mechanical strength to the films. Consequently, PVA 4–88 and PVA 6–88 were discarded and PVA GH 17R was selected for the preparation of PVA/PLA blends of different composition.

3.2. Rheological Properties of Aqueous PVA/PLA Dispersions

PVA/PLA 75/25, 50/50, and 25/75 blends in water obtained with PVA GH 17R and PLA_1 or PLA_2 were characterized by rheological analysis under steady shear conditions (**Figure** 2). The PVA solution shows a viscosity almost constant with the shear rate; some shear thinning behavior was observed only after 100 s^{-1}. Blends with PLAs have a lower viscosity, the value decreasing with increasing PLA content. Both PLA_1 and PLA_2 dispersions showed low and shear rate-independent viscosity values (close to the detection limit) that are similar to water (Figure 2, green lines), as typically observed for low concentrations of hard-sphere colloids.[36] Therefore, the addition of PLA dispersions to the PVA solution has the effect of an increasing dilution of the latter. Accordingly, the plateau viscosity value of blends, taken at 0.1 s^{-1}, plotted as a function of the PLA content shows the typical power-law decay of polymer solutions of decreasing concentration (**Figure 3**). To evaluate if any other effect was present, pure water was added to PVA. The resulting viscosity was compared to those of the blends, and it was lower at any investigated composition (Figure 3), thus indicating that PLA particles contribute to the viscosity of the system, even if the viscosity of pure PLA dispersions is negligible. This effect is comparable to the one previously observed for the PLA_1 dispersion in the presence of xanthan gum which was interpreted as a contribution of both polymer and colloidal particles to the crowdedness of the system.[33]

The difference between the viscosity of the blends and of the diluted PVA was larger in the case of PLA_2 than PLA_1. For diluted, non-interacting hard colloids, the viscosity depends on the volume fraction occupied by the colloid.[37] If the PLA/PVA ratio and the density of the two phases for the blends were the same, the particle volume fraction would also be the same, and therefore, comparable viscosity would have been expected. In fact, the blend with the larger particles, namely PLA_2, has a

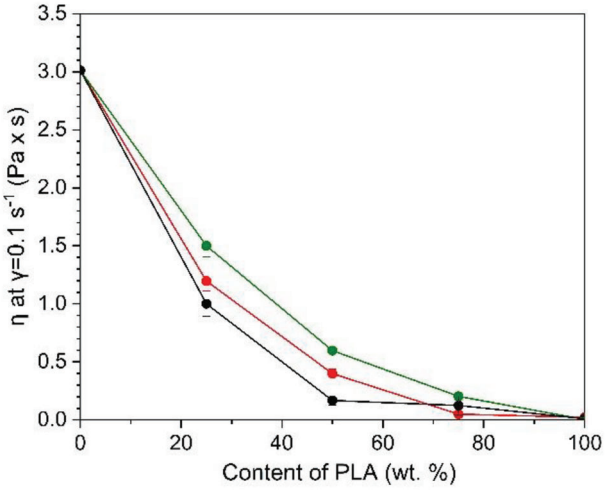

Figure 3. Viscosity values at a shear rate of 0.1 s^{-1} of PVA/PLA mixtures with PLA_1 (in red) and PLA_2 (in green) dispersions as a function of PLA content together with the viscosity values of PVA solutions in water at the same dilutions used in the preparation of the PVA/PLA mixtures (in black).

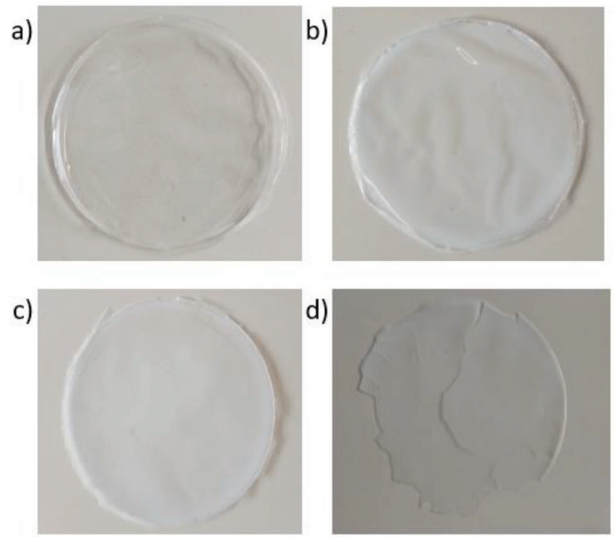

Figure 4. Pictures of PVA/PLA blend films prepared with PLA_1 dispersion with composition 100/0 a), 75/25 b), 50/50 c) and 25/75 d) wt. %.

lower number of particles as dispersed phase per unit of volume. Therefore, the observed difference between the viscosities' values for compatible concentration may be attributable to a difference in dispersed phase density, which would result in a different volume fraction, or to the presence of particle–particle or particle–PVA interactions. Whatever the physical mechanism responsible for the different viscosity, the origin of the difference must be identified in the surfactant, which is the only compositional parameter that differentiates the two systems and may affect particle-particle interactions as well as particle phase density depending on solubility in the polymeric phase.

3.3. Film and Phase Morphologies of the PVA/PLA Blends

PVA/PLA 75/25, 50/50, 25/75 blends obtained with either PLA_1 or PLA_2 dispersions were used to prepare films by solvent casting at 60 °C. The obtained films were poorly transparent but homogeneous and continuous (**Figure 4**), except for the blend PVA/PLA 25/75 with PLA_1 dispersion. This sample did not film and gave just fragile fragments (Figure 4d). Overall, films prepared with PLA_2 dispersion resulted to be softer and less fragile to handling then the ones containing PLA_1 dispersion.

ATR-FTIR analysis of the upper and lower surfaces of the films (Figure S3, Supporting Information) showed comparable relative band intensity, thus indicating a similar composition at the two surfaces. This data indicates that no macroscopic phase separation occurred during the drying stage. Indeed, in case of dispersion instability, sedimentation or creaming may occur, leading to a different PLA content at the lower or upper surface of the film, respectively.

The intensity of the large band at 3700–3000 cm^{-1} and of the peaks in between 3000 and 2840 cm^{-1} relative to the O-H and C-H stretching of PVA, respectively, increases with the increment of the PVA content, as expected. At 1750–1735 cm^{-1} it is possible to observe the C = O stretching that becomes broader as the content of PVA in blends increases. In previous studies, a shift of the carbonyl band of PLA to lower frequencies was ascribed to the presence of hydrogen bonds between PLA and PVA.[38] However, in our case, the absorption band of the residua acetyl groups of PVA (25–30%) partially overlaps with the PLA's C═O band, thus preventing any speculation (Figure S4, Supporting Information).

The signals ascribed to the CH_2 stretching of the emulsifiers (SDS and SYN) can be noticed, when they are not superimposed with the peak of the C—H stretching of PVA, between 2750 and 3000 cm^{-1}. In the blends containing the PLA_1 dispersion, the presence of starch as a stabilizer can be highlighted by the broad band around 3500–3000 cm^{-1} relative to the O—H group (often superimposed by the O—H stretching of PVA) and the typical stretching band of sugar rings at 1000 cm^{-1} (Figure S4, Supporting Information). It is possible to observe, as previously reported, that the neat PLA_1 and PLA_2 films prepared from dispersions at 60 °C show an enrichment of the stabilizer and the surfactant on the bottom surface.[34] Due to the overlap between the surfactant signals with those of the PVA, it is not possible to estimate whether this blooming effect occurs in the PVA/PLA blends. Nevertheless, strong polymer segregation in the mixtures can be excluded since no spectroscopic evidence was detected.

The SEM analysis of the sections of PVA/PLA blends showed the presence of sub-micrometric dispersed particles into a continuous matrix (sea-island morphology) (**Figure 5**) at all compositions, thus indicating a biphasic morphology. Although the preparation method may affect the morphology, the presence of two phases agrees with the previous literature, in which the PVA/PLA blends have been reported to be immiscible or partially miscible, depending on the blend composition and degree of hydrolysis of the PVA.[16,38–42] Homogeneous mixtures were reported only between PLA and non-deacylated or slightly deacetylated (<5%) PVAc.[43,44]

The composition of the blend phases can be deduced from their behavior in water since PVA is soluble in water while PLA is not. Blends with PVA as the continuous phase should break apart in water, while blends with PLA as the continuous phase should remain more intact. Based on the preparation method, in which a water phase containing dispersed solid submicrometric particles of PLA was added to PVA solutions, the continuous phase was expected to be made by mostly PVA. This was indeed the case for all samples, except PVA/PLA_2 25/75 which was still a continuous film after several hours in water. The SEM analysis of its surface after being withdrawn from water and dried was indeed comparable to the one of PLA_2 film treated under comparable conditions (Figure S7, Supporting Information) thus indicating that PLA is the main component of the continuous phase in this sample. This indicates that phase inversion occurred during film formation for this composition alone. The dimension of the dispersed phase did not always correspond to the size of the particles in the pristine PLA dispersions. The dispersed phase size ranged between 200 nm and 1 µm depending on the blend composition and on the used PLA (Figure 5). When compared to the pristine dispersions, the dispersed phase was larger for the 75/25 blends and comparable in size in 50/50 blends. In 25/75 blends, it was comparable in the case of PLA_1. In the case of PLA_2 it was smaller but, due to phase inversion, the dispersed phase was PVA and thus is not expected to have a connection to the PLA particle size (**Figure 6**a).

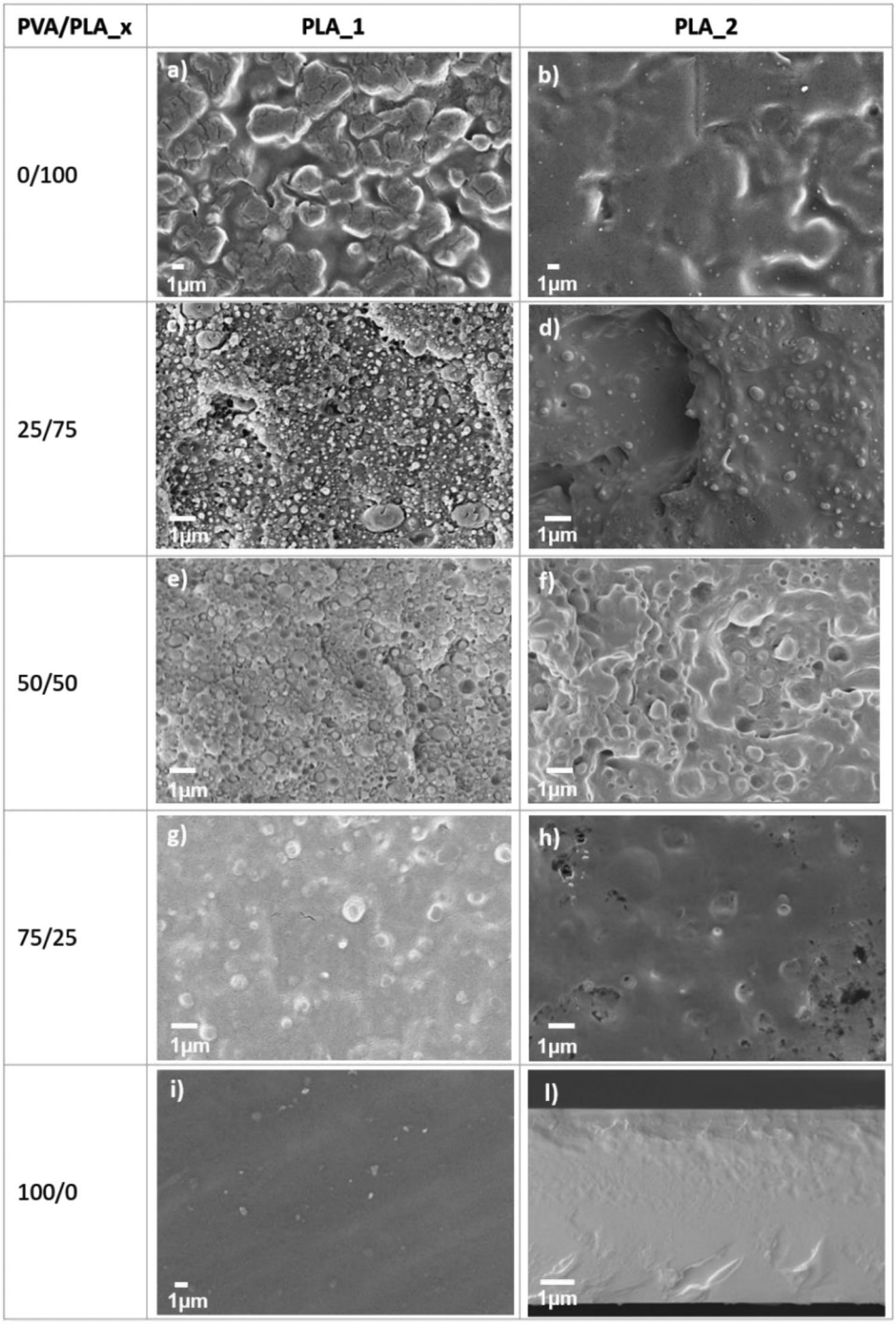

Figure 5. SEM pictures of surfaces a,b,i) and sections c–h,l) of PVA/PLA blend films prepared from PLA_1 (a,c,e,g) and PLA_2 dispersions (b,d,f,h) with composition of 0/100 (a,b), 25/75 (c,d), 50/50 (e,f), 75/25 (g,h), and 100/0 (i,l) wt.%.

Generally, it is possible to notice that the adhesion at the interface is better in the mixtures with PLA_2 (Figure 5b,d,f) than with PLA_1 (Figure 5a,c,d) thus indicating that the PEG-PPG copolymer (SYN) is a better compatibilizer for these blends then the SDS/Starch couple.

In blends PVA/PLA_1 25/75 and 50/50 (Figure 5c,e; Figure S5c–f, Supporting Information) a porous morphology is observed. The form of the voids excludes that they build up during sample fracture before SEM observation. Instead, they can be due to air bubbles trapped inside the film during its prepara-

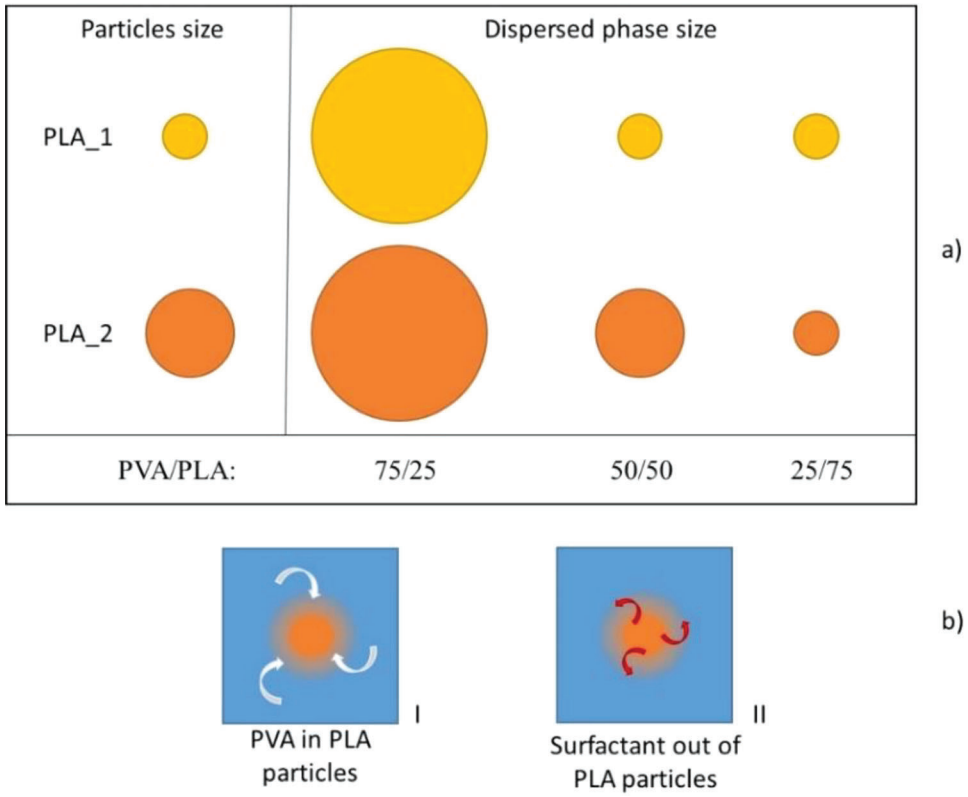

Figure 6. Cartoon illustrating a) the correlation between the particle size of PLA dispersions and the size of the dispersed phase in PVA/PLA blends of different composition, and b) the proposed mechanism of particle growing/contraction and the phase's distribution in the blends.

tion. The stabilization of air bubbles inside the viscous dispersion may depend on the structure and concentration of the surfactants and stabilizers present in the formulations. Bubbles are present more in PLA_1 than in PLA_2 samples (Figure 5e; Figure S5, Supporting Information). Additionally, it is possible to observe that the surface and section of pure PVA films are smooth and continuous (Figure 5i,l). On the contrary pure PLA films present some voids (Figure 5a,b; Figures S5a and S6a, Supporting Information) in larger amount in PLA_1 than in PLA_2. Therefore, SDS/starch is indicated as more effective than SYN to stabilize air bubbles.

3.4. Thermal Analysis of the PVA/PLA Blend Films

DSC analysis in the glass transition temperature (T_g) range (from −50 to 170 °C) of PVA/PLA blends, showed two distinct T_gs (**Figure 7**), hence revealing the presence of two distinct polymer phases in agreement with SEM observation (Figure 5) and previous literature.[16,38–42]

The T_g values of the PVA phase (T_g^2 in **Table 2**) are comparable to the one of the pure polymer in all blends except for a small shift in 25/75 PVA/PLA_2 that is still comparable to the uncertainty of the measurement (Figure 7b). Notice that this is the only blend

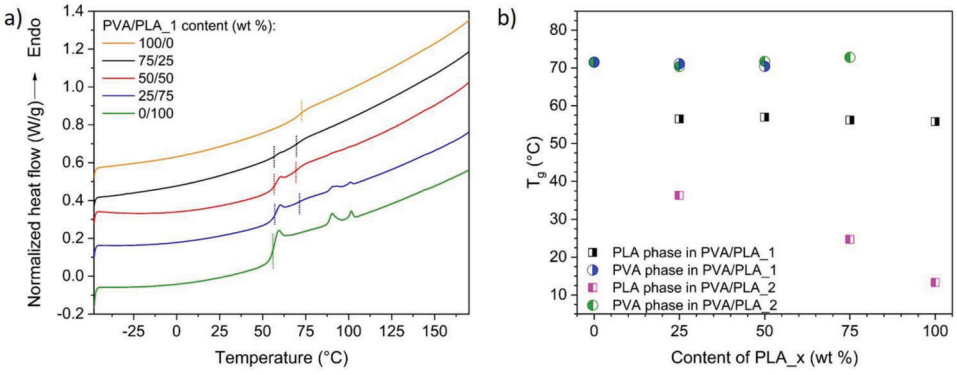

Figure 7. a) DSC thermograms of PVA/PLA blends prepared with PLA_1 dispersion. Second heating scan at 10 °C min^{-1}. Thermograms were arbitrarily vertically shifted for clarity. b) Glass transition temperature values detected in blends plotted as a function of the PLA_x content (wt.%) with x = 1 or 2.

Table 2. Glass transition temperatures of PLA (T_g^1) and PVA (T_g^2) phases, and endothermic peak maximum (T_m) by the second heating step from DSC analyses of the PVA/PLA blends.

PVA/PLA	PLA	T_g^1 [°C][a)]	T_g^2 [°C][a)]	T_m [°C][b)]
0/100 (rt)[c]	PLA_1	56.8	-	89.9
0/100	PLA_1	55.7	-	90.1[d)]
25/75	PLA_1	56.2	71.0	90.3
50/50	PLA_1	56.7	70.3	-
75/25	PLA_1	57.3	71.4	-
0/100 (rt)	PLA_2	12.9	-	41.1
0/100	PLA_2	13.3	-	53.3
25/75	PLA_2	24.7	72.8	-
50/50	PLA_2	n.d.[c)]	71.7	52.3
75/25	PLA_2	36.3	70.1	53.3
100/0	-	-	71.5	-

[a)] Values at the midpoint; [b)] Values at the peak maximum; [c)] rt = sample obtained by drying at room temperature; [d)] not properly detectable.

for which the continuous phase is indicated as made mostly of PLA. Therefore, no or negligible mixing of PLA in the PVA phase is indicated for all compositions. As for the T_g values of the PLA phase (T_g^1 in Table 2), in the case of blends with PLA_1, a similar result was detected with a modest shift within measurement uncertainty only in 75/25 PVA/PLA_1. Once again no or negligible mixing is thus indicated also for PVA in the PLA_1 phase.

In the blends containing PLA_2 formulation, the shift of the PLA's T_g toward the PVA one is much more relevant (Figure 7b). However, the T_g value of the pristine dispersion (12.9 °C) is much lower than the one of pure PLA (58.2 °C) due to the plasticization of PLA by the PEO and PEG blocks of SYN.[34,45,46] Therefore, the shift can be due to either loss of the surfactant or to mixing with PVA (Figure 6b).

If we assume that only the second-mentioned phenomenon occurs, the entity of the T_g shift in the blends can be exploited to calculate the amount of PVA in the PLA/SYN phase (PLA_2) through the Fox equation (Equation 1).

$$\frac{1}{T_g} = \frac{w_1}{T_{g,1}} + \frac{w_2}{T_{g,2}} \quad (1)$$

where T_g is the detected glass transition temperature of a mixture of two miscible components having glass transition temperature $T_{g,1}$, and $T_{g,2}$. w_1 and w_2 are the fractions by weight of the two components in the mixture.[47] By rearranging the equation, the percentage of PVA (w_1) mixed with PLA_2 responsible for the observed glass transition values can be calculated trough Equation (2).

$$w_1 = \frac{T_{g,1}\left(T_{g,2} - T_g\right)}{T_g\left(T_{g,2} - T_{g,1}\right)} \times 100 \quad (2)$$

The amount was found to be 78% and 57% for 75/25 and 25/75 PVA/PLA_2 composition, respectively. That means that, in the case of the blend 75/25, the amount of PVA would correspond more or less to all the PVA in the blend (75%) and then the material would consist in a single phase. On the contrary, the blend is made of two phases and the T_g of the pure PVA is still present in the DSC thermogram. The discrepancy is even more evident in the case of the 25/75 blend, where the phase responsible for the lowest T_g would consist in a homogenous mixture made of 57/43 PVA/PLA_2 and the amount of PVA in this phase would be much more than the total amount of PVA in the whole blend. Furthermore, if the T_g variation of the PLA phase were due just to a partial miscibility with PVA, the volume of the dispersed phase would have increased for all compositions. On the contrary, this occurred only in the case of PVA/PLA 75/25 blends. On the other hand, the simple migration of SYN out from the PLA phase would not explain the variation of volume. The dispersed phase in the blends differs by size from the pristine PLA_2 particles (Figure 6), with the dispersed phase smaller and larger in the 75/25 and 25/75 PVA/PLA_2 blends, respectively. A simple diffusion of the surfactant out of the PLA phase is suggested for the former composition, while the combination of diffusion in (of PVA) and out (of surfactant) with phase inversion is indicated for the latter (Figure 6b). The weight of each elemental process, namely diffusion in, diffusion out and phase inversion depends on the blend composition. For 50/50 blend composition, phase inversion does not occur and the two diffusion processes seems to have comparable, even opposite, effect and thus the dispersed phase in the blend has the same size of the pristine PLA_2 particles (Figure 6). Melting was observed at 41–53 °C for PLA_2 and PVA/PLA_2 /50/50 and 25/75 blends (Table 2). The peak is easily assigned for comparison to segregated surfactant (Table S1, Supporting Information) thus supporting the diffusion of SYN out of the PLA phase. The effect occurs in both blends, namely with PLA_2 and PLA_1. The only difference is that in the case of the blend with PLA_1 the surfactant did not act as plasticiser of the PLA phase before blending.

Overall, by combining the data from morphology analysis and DSC it can be concluded that PVA/PLA blends prepared from PLA aqueous dispersions are characterized by a phase-separated domain morphology with the continuous phase made up mostly of PVA (with eventually some diffused surfactant) at PVA/PLA 50/50 and 75/25 composition as well as PVA/PLA_1 25/75. The dispersed phase made of almost pure PLA, in the case of the blends with PLA_1, and of a mixture of PLA, PVA and SYN in the case of PLA_2. For PVA/PLA_2 25/75 blends an inverse phase composition is suggested with PLA as the main component of the continuous and PVA of the dispersed phases.

3.5. Thermal Stability of PVA/PLA Blend Films

The thermal stability of the blends was studied under a nitrogen atmosphere by TGA. All prepared blends (**Figure 8**) show a weight loss peak in the 30–180 °C range, which corresponds to the loss of absorbed water and increases with PVA content, as the more hydrophilic component of the blend. In the blends, this peak is also shifted toward higher temperatures (**Table 3**) with respect to pure PVA, suggesting that water is better retained, most likely because of the higher barrier for escaping opposed by the PLA component.

After water release, blend degradation is observed to occur in two or three steps depending on the blend composition (Figure 8). Similarly, the composition affects the peak temperature in the first derivative plots (Table 3).

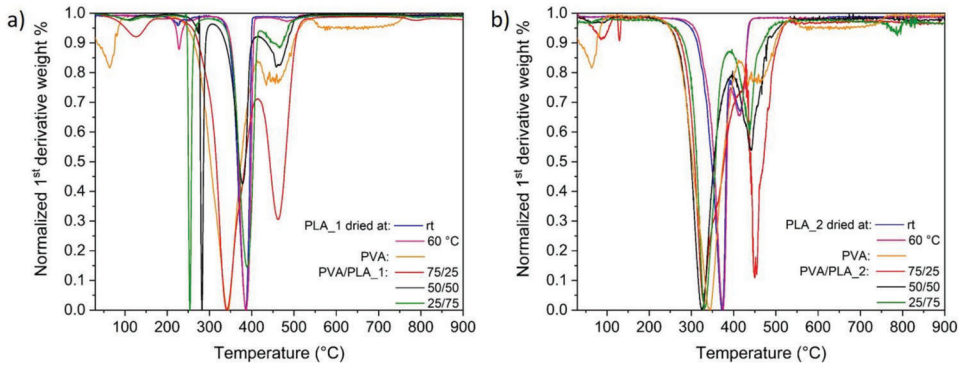

Figure 8. Comparison among the 1st derivative of the TGA curves of PVA/PLA blends prepared with the PLA_1 a) and PLA_2 b) dispersions. In the case of PLAs, the analysis was carried out on samples obtained by drying at room temperature (rt) or at 60 °C.

PLA resin degrades in a single step that starts at 375 °C (Figure S7, Supporting Information) and corresponds to the breaking of the ester bonds with consequent depolymerization.[48] The PLA_1 dispersion displays an additional small degradation peak in the DTGA plot (Figure 8) at lower temperature than the main one (T_d at ≈215 °C, Table 3) that can be ascribed to the presence of SDS as surfactant (Figure S8, Supporting Information). The intensity of this peak is higher when the dispersion is dried at 60 °C than at room temperature (Figure 8a). The result can indicate that some surfactant is segregated at the film surface as proved by IR spectra (Section 3.3). In fact, the components at the surface are usually observed to decompose before the ones in the bulk due to kinetic reasons, as the products of decomposition may escape faster when on the surface since they do not have to diffuse from the inside. The PLA_2 dispersion also presents an additional degradation step with respect to neat PLA (Figure 8b). This step is at higher temperatures than the main one (T_d in the 403–405 °C range). It is in the temperature range where SYN degrades (Figure S7, Supporting Information), and was thus assigned to the surfactant. No difference was noticed between the formulation dried at room temperature and the one dried at 60 °C, thus suggesting no segregation of this emulsifier (Figure 8b). SYN is expected to be more compatible than SDS with the blend components, thus reducing or avoiding segregation.

In PVA/PLA_1, the onset of the first degradation step lowers almost linearly with the blend composition (Table 3), moving from 286°C for pure PVA to ≈215 °C in the pure PLA_1. The opposite was observed with PLA_2 blends: the onset of degradation raising almost linearly to 328 °C in pure PLA_2 (Table 3). The two opposite shifts can be attributed to the lower and higher thermal stability of the surfactants with respect to the polymers. Their amount in the blends is proportional to PLA content and thus their effect depends linearly on composition.

By comparing the thermograms at different compositions with those of the pure components (Figure 8; Figure S7, Supporting Information), it is evident that in PVA/PLA 75/25 blends the thermograms are similar to the one of pure PVA: the first degradation process is almost superimposed to the one of the neat polymer while the second degradation step is extended over a larger temperature range and the third step has a larger relative mass loss than pure PVA. Furthermore, no well detectable step is observed in the temperature range where pure PLA degrades (Figure 8). Based on the observed phase morphology and on the DSC data

Table 3. Water content (%), first, second and third temperature of onset (T_{on}^1, T_{on}^2 and T_{on}^3), first, second and third temperature of maximum degradation rate (T_d^1, T_d^2 and T_d^3) and residuum after degradation (Res.) from TGA of PVA/PLA blends.

PVA/PLA	PLA	Water content[a] [%]	T_{on}^1 [°C][b]	T_d^1 [°C]	T_{on}^2 [°C][b]	T_d^2 [°C]	T_{on}^3 [°C][b]	T_d^3 [°C]	Res. [%][c]
0/100 (rt)	PLA_1	–	200.7	212.0	350.9	373.9	–	–	2.4
0/100	PLA_1	–	205.8	216.5	352.8	375.7	–	–	4.0
25/75	PLA_1	1.9	237.5	243.2	353.6	378.9	439.0	457.4	5.2
50/50	PLA_1	2.5	267.5	273.0	346.5	369.1	493.2	459.6	4.6
75/25	PLA_1	2.9	297.6	335.3	–	–	–	–	6.6
0/100 (rt)	PLA_2	–	328.0	361.3	393.5	403.8	–	–	2.4
0/100	PLA_2	–	335.1	363.4	399.0	404.3	–	–	1.5
25/75	PLA_2	–	292.4	322.4	404.9	429.3	–	–	1.3
50/50	PLA_2	1.4	280.5	315.0	411.8	433.3	–	–	4.1
75/25	PLA_2	2.5	288.3	318.2	433.3	444.3	–	–	6.4
100/0	–	6.0	286.1	335.5	422.0	447.3	–	–	2.0

[a] Weight loss % between 30 and 180 °C; [b] Temperature of the peak minimum in the first derivative TGA plots; [c] Residuum at 850 °C.

Table 4. Tensile properties of the PVA and PLA blends. Number in parentheses are the standard deviations.

Samples	Stress at break [MPa]	Elongation at break [%]	Young's modulus [GPa]
PLA4060D	31.2 (2.3)	3.8 (1.6)	3.04 (0.36)
PVA/PLA_1 75/25	21.1 (3.1)	141 (52)	0.56 (0.35)
PVA/PLA_2 100/0	21.5 (4.7)	178 (36)	0.41 (0.15)
PVA/PLA_2 75/25	23.2 (6.7)	132 (75)	1.16 (0.68)
PVA/PLA_2 50/50	14.8 (1.8)	75 (23)	0.69 (0.19)
PVA/PLA_2 25/75	5.2 (1.1)	0.49 (0.11)	1.62 (0.51)
PVA/PLA_2 0/100	7.2 (1.2)	190 (67)	0.36 (0.11)

of the PLA_2 blends (Section 3.4) the observation can be correlated to the partial miscibility of PVA in the dispersed PLA phase that induces the latter to degrade similarly to PVA. Accordingly, the peak in the DTGA plot decreases in intensity and shifts to lower temperature proportionally to the decrease of PVA content. It is thus likely that the composition of the mixed phase depends on the blend composition and the amount of PVA in the PLA rich phase decreases with the decrease of the PVA in the blend, irrespective of the phase morphology. A similar result was also observed in the case of the PVA/PLA_1 75/25 blend, thus also suggesting partial mixing of PVA in the PLA dispersed phase, even though no appreciable T_g shift was observed by DSC. This apparent discrepancy may be due to the small difference between the T_g of PLA_1 and PVA and thus to the fact that the moderate shift expected in the case of a partial mix may be comparable to measurement uncertainty. The increase of dispersed phase volume observed for this sample also supports the occurring of some mixing.

In the case of PVA/PLA_1 50/50 and 25/75 the degradation pathway is different, occurring in three-steps instead of two (Figure 8a). The first one has a very thin derivative peak and it is at a lower temperature than that of the pure components. These blends showed, by SEM analysis, the presence of a porous structure (Figure 5c,e; Figure S5c–f, Supporting Information). The presence of the first degradation process may be due to some components enriched at the air interface of pores in the PVA/PLA mixtures that can more easily vaporize than the molecules in the bulk. The second peak is completely superimposed to the one of pure PLA and it is therefore attributed to PLA domains that are not mixed with PVA, most likely domains at the blend surface. The last peak is finally attributed to the degradation of PVA.

3.6. Mechanical Properties of PVA/PLA Blend Films

All results obtained from tensile tests of the pure polymers and PVA/PLA blends suitable for testing are reported in **Table 4**. The presence of a single result with PLA_1 blend is due to the impossibility of testing the other blends, as the samples appeared to be either shattered (PVA/PLA_1 25/75) or too brittle (PVA/PLA_1 0/100 and 50/50) for clamping during tensile tests.

Comparing the strength data for all materials, the values are of the same order of magnitude, while Young's moduli are quite low, but in a range that is characteristic of polymeric films.[49] Except for the pristine PLA4060D and PVA/PLA2_ 25/75, the values of elongation at break are very high, especially for pure materials.

The effect of the surfactant is very evident by comparing PLA4060D with PVA/PLA_2 0/100. As the elongation at break increases from ≈ 4% up to 190% and the stiffness decreases by an order of magnitude, one can conclude that the SYN surfactant has a strong plasticizing effect, in agreement with DSC indication. In fact, as shown in **Figure 9**, the stress versus strain curves of the PLA4060D and the PVA/PLA2_ 0/100 at low values of strain (<10%) clearly show that PLA4060D is a rather brittle material, possessing a very small strain at break after yielding, while the PVA/PLA_2 0/100 deforms at constant stress for very high values of applied strain, thus displaying a cold draw behavior. The stress at break of PLA 4060D is in line with literature values measured for thin films.[50]

The effect of the SYN surfactant on the PVA/PLA blends can be better seen by comparing the mechanical properties when PLA_2 is gradually added to the PVA matrix (Table 4). The pure PVA matrix (PVA/PLA_2 100/0) has a ductile and very tough behavior, but as the content of PLA_2 is increased, strength and elongation at break of the blends start to decrease. This decrease is significant for each blend, but in almost all cases, the behavior remains ductile, except for the PVA/PLA_2 25/75 blend that becomes dramatically brittle. This can be easily observed in Figure 9, where all the blends and the pure PVA (PVA/PLA_2 100/0) are shown in a stress versus strain plot. This effect can be explained through the phase inversion that occurs when PLA_2 exceeds 75%. When this happens, the PVA becomes the dispersed phase, while the PLA is the continuous phase. However, the PLA in form of the continuous phase is not the ductile material corresponding to the PVA/PLA_2 0/100, but rather similar to PLA4060D, and further embrittled by the presence of PVA enclosures that do not exhibit a strong interfacial bond with the surrounding matrix.

An interesting feature can be appreciated by comparing the two blends having the same composition, but obtained with the two different surfactants (i.e., PVA/PLA_1 75/25 and PVA/PLA_2 75/25): the stress versus strain curves of these blends are very similar (Figure 9), with an adequate strength and an elongation at break >100%. This behavior seems to show that at this particular blend formulation, the precise nature of the surfactant does not have an effect on the mechanical properties. In any case, it is worth remarking that the presence of PVA in the blend seems to lead to surfactant expulsion from the PLA phase.

4. Conclusion

In this work, a new approach to tough weak hydrophilic polymers, such as PVA, with hydrophobic polymers by mixing in water with another biodegradable polymer, such as PLA, has been proposed. To this aim, PVA/PLA blends were prepared by exploiting an innovative approach based on a method that is a combination of latex mixing and emulsion blending. The procedure involves simply mixing water solutions of PVA and aqueous dispersions containing PLA submicrometric particles previously prepared. After simply drying at 60 °C the so prepared mixtures, PVA/PLA blend films can be obtained.

Among three different PVA grades with 73–75% hydrolysis degree, only the one with the highest molecular weight gave handleable PVA/PLA 50/50 blend films and it was thus used to

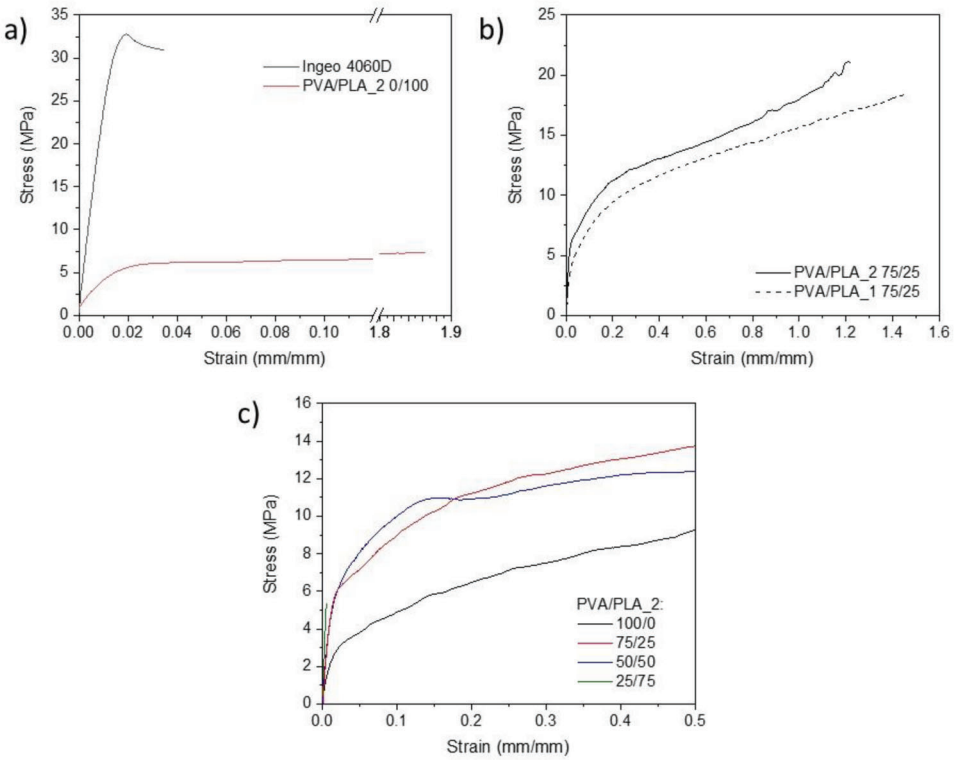

Figure 9. Stress versus strain for a) PLA4060D and PVA/PLA_2 0/100 b) PVA/PLA_1 75/25 and PVA/PLA_2 75/25 and c) PVA/PLA_2 100/0, PVA/PLA_2 75/25, PVA/PLA_2 50/50 and PVA/PLA_2 25/75. In Figure a) and c) the strain axis has been cut at lower strain values for ease of visualization.

prepare 25/75, 50/50, 25/75 PVA/PLA blends. PLA dispersions containing SDS or SYN as surfactant (PLA_1 and PLA_2, respectively) were used. All formulations with SYN gave handleable films, while with SDS non-continuous films were obtained with PVA/PLA_1 25/75 composition. All blends showed, by SEM analysis, island-like morphologies with the adhesion at the interface being better when the non-ionic (SYN) than SDS surfactant was used. Two distinct T_gs, with the one of PLA shifted toward the one of the PVA in the case of blends with PLA_2, were observed by DSC analysis. The shift was ascribed to a concomitant migration of the non-ionic surfactant, which is a plasticizer of PLA, out and of the PVA in the PLA phase. The system can be described as a dispersed phase of PVA-enriched PLA immersed in a continuous PVA matrix for all studied compositions except 25/75 PVA/PLA_2. In the latter case, an inversed phase composition is indicated by a combination of the SEM analysis and the behavior in water of the sample.

Blends containing intermediate or high amount of negatively charged PLA dispersion (from 50 to 75 wt.%) showed a porous morphology rich in voids, which causes the presence of an additional peak of thermal degradation at a lower temperature than the one of the pure components, thus decreasing the thermal stability of the blends. Furthermore, the materials resulted very brittle.

In general, the mechanical analyses highlighted that the dispersed PLA phase confers to the final PVA/PLA blends a higher rigidity and a reduced deformability with respect to pure PVA, as typically observed for polymer blends with a matrix-dispersed particle (sea–island) morphology. Indeed, the analysed PVA/PLA mixtures display a higher Young's modulus and a lower elongation at break in comparison with the pure PVA and PLA components in the blends.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

G.B. and L.M. prepared the samples and performed the thermal analysis; G.R. performed the mechanical tests; G.B. and G.S. performed the SEM analysis; G.B., G.R., and V.M. analyzed the mechanical data; G.B. and M.B. designed the experiments and analyzed the thermal data; M.C. performed the swelling test in water and reviewed the manuscript; V.M., F.M., E.B., and M.B. wrote the manuscript.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

blends, poly(vinyl alcohol), poly(lactic acid), water dispersions

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