Films made from polyethylene-*co*-acrylic acid and soluble biopolymers sourced from agricultural and municipal biowaste

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ABSTRACT: Blends were obtained from polyethylene-*co*-acrylic acid (PEAA) with 248 kDa molecular weight and two water soluble biopolymers isolated from the hydrolysate of postharvest tomato plant and urban biowaste compost. The two hydrolysates were constituted respectively from a polysaccharide (SP) with 27 kDa molecular weight and a lignin-like polymer (LP) with 75 kDa molecular weight containing aliphatic and aromatic C moieties substituted by carboxyl, hydroxyl, and amino groups. Evidence was obtained for reactions occurring between the biopolymers and the synthetic polymer leading to new polymers with 151 to 1243 kDa molecular weights. The thermal and mechanical properties of the blends were studied. Compared with neat PEAA, the PEAA-LP blends containing 5 to 10% LP exhibited 2 to 5× higher molecular weights, 10 to 50% lower crystallinity, 2 to 6× higher Young's modulus, over 3× higher stress at yield point and somewhat lower strain at break (55–280% vs. over 300%). On the contrary the PEAA-SP blends exhibited 6 to 13% lower crystallinity and the same mechanical properties as neat PEAA. The results offer scope for investigating biopolymers sourced from other biowastes to understand more the reasons of the observed effects and exploit their full potential to modify or to replace synthetic polymers. Perspectives of economic and environmental benefits are discussed. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41909.

INTRODUCTION

This work addresses two current important issues: (i) the valorization urban and agriculture wastes as source of chemicals and (ii) the manufacture of biocompatible polymer blends. Both wastes contain natural polymers, such as cellulose, hemicelluloses, and lignin. Aside cellulose finding widespread use in the manufacture of articles for everyday life use, hemicelluloses and lignin are not suitable at the same purpose because of low molecular weight and lack of adequate mechanical properties. Synthetic polymers from fossil sources have a range of mechanical properties which allow manufacturing most of the articles currently used. However, due to their low biodegradability, they are not compatible with the environment. For this reason, current research trend pursuits the manufacture of biopolymers and/or of their blends with synthetic polymers.

Several blends have been reported to be made from synthetic ethylene copolymers containing alcoholic[1–10] or acidic[11–13] functional groups, such as polyethylene-*co*-vinyl alcohol (EVOH) or polyethylene-*co*-acrylic acid (PEAA), and from natural polysaccharides such as starch or lignocellulosic materials including corn fiber and sugar cane bagasse. These products have been proposed for various applications such as the manufacturing of mulch films for use in agriculture, packaging and plastic bags. In these materials, the synthetic polymer provides the required mechanical properties and is compatible with the lignocellulosic fillers by virtue of its hydroxyl and carboxyl groups. A most recent article[14] has reported the manufacture and properties of films made from EVOH and soluble lignocellulosic biopolymers (LP) isolated from municipal biowastes. To the authors knowledge, aside from this case, biowastes as source of saccharide and/or lignocellulosic polymers to blend with synthetic

polymers have not been investigated. Yet, the manufacture of such blends would be a rather desirable integration of chemistry with agriculture and the environment. This applies particularly to LP which have also been reported[15] highly efficient as biostimulants to enhance tomato plant growth and productivity, and also as photosensitizers to promote solar environmental remediation.

This article reports the manufacture and characterization of films made from PEAA containing 20% acrylic acid repeating units and the above LP or soluble saccharide biopolymers (SP), respectively obtained from composted urban biowastes or postharvest tomato plants. The choice of these materials stemmed from several reasons. In the previous work,[14] evidence was obtained for a condensation reaction occurring between LP and EVOH containing 38 mol % ethylene repeating units. Following this reaction, the films containing 6 to 7% LP bonded to the synthetic polymers exhibited up to 3× higher yield strength than the neat synthetic polymer. On the contrary, at higher LP concentration the films mechanical properties were very poor. These results offered intriguing scope for investigating LP effects in blends with other synthetic polymers. On the other hand, previous work had demonstrated that both SP[16] and LP[15] contained hydrophilic functional OH and COOH groups. The synthetic PEAA polymer is film forming, and has good mechanical properties and hydrophylic functional groups.[13,17] Thus, PEAA, SP, and LP have in principle the required features to yield mechanically strong film forming blends containing chemically compatible ingredients. However, as SP were found mainly constituted by carbohydrate moieties[16] and LP mainly by lignin-like structures,[15] different behavior was to be expected from the blends made from PEAA and SP, and from PEAA and LP, hereinafter, respectively referred to by the acronyms PEAA-SP and PEAA-LP.

Demonstration of the performance of PEAA-SP and PEAA-LP blends was worthwhile to pursue for several reasons. Urban biowastes as source of LP are a negative cost[18] residual material. Thus, partial substitution of PEAA with LP implies a significant reduction of the cost impact of the starting components in the finished film product. Exploitation of agriculture and urban biowastes, in place of dedicated crops, for the manufacture of environmentally compatible materials is socially more acceptable. Valorization of agriculture and urban biowastes as source of added value marketable chemical products is expected to benefit the management of wastes and society with reduced cost and environmental impact. In such context, the use of SP sourced from exhausted tomato plants grown on soil treated with LP as plant biostimulant not only allows to compare the effects of saccharide versus lignin-like matter on the properties of the pristine synthetic polymer, but also prospects a fascinating virtuous recycling of natural organic C over agriculture, consumers and the chemical industry.

EXPERIMENTAL

Materials
The LP was available from previous work.[14,15] It was obtained from a compost (CVDF) sampled from the ACEA Pinerolese waste treatment plant in Pinerolo (Italy). This plant processes by anaerobic fermentation the organic humid fraction of municipal biowastes obtained from separate source collection to yield biogas and the digestate (D) recovered from the plant biogas production reactor. The CVDF was obtained from a 35/55/10 w/w/w D/home gardening and park trimming residues/sewage sludge mix aged for 110 h by composting under aerobic conditions. The compost was hydrolyzed at pH 13 and 60°C to yield the soluble hydrolysate which was separated from the insoluble residue (INR1). The former was filtered through 5 kD molar mass cut off ultrafiltration membrane and dried to yield the solid LP in 15 wt % yield, relatively to the starting compost. The SP was obtained from ciliegino Naomi F1 postharvest tomato plants (PHTP). The PHTP material was ground to less than 1 mm size using the SF75 mill made by Cimma Spa, Pavia, Italy. The fine powder was hydrolyzed as above. The liquid/solid mix was allowed to settle to separate the supernatant liquid phase containing the soluble hydrolysate (SH) from the insoluble residue (INR2). The latter, obtained in 50% yield, was further hydrolyzed by heating at 60°C in concentrated HCl for 2 h. The solid/liquid acid suspension was centrifuged to separate the insoluble residue (INR3) from the acid solution containing the SP from. The latter was dried under vacuum in a rotary evaporator and then stored over KOH and P_2O_5 to constant weight. The yield of SP was 45 wt % relative to the starting INR2. Polyethylene-co-acrylic acid, acrylic acid 20 mol % (PEAA), CAS Number 9010-77-9 and all other reagents and solvents were supplied by Sigma Aldrich and used as purchased.

Preparation of PEAA-SP and PEAA-LP Films
For the preparation of the PEAA-SP films, the PEAA and the SP were dissolved separately in N-methyl-2-pyrrolidone (NMP) in 1/10 w/V solid/liquid ratio by heating at 110°C. The appropriate amount of SP solution was then added to the PEAA solution to obtain the desired SP/PEAA ratio in the solution. The solution was then stirred at 110°C for 2 more hours, cast onto a ceramic plate, and heated at 100° for 12 h to yield a film coating the ceramic plate surface. The coated plate was finally immersed in a water bath to yield a free standing film. This was withdrawn from the water bath and dried in a stream of 60 to 80°C air. For the preparation of PEAA-LP films, the PEAA solution was prepared as above. The LP was dissolved in water at 50 to 80 g/L concentration. The LP solution was centrifuged before use to separate any insoluble residue. Then, the appropriate amount of LP solution was added drop wise to the hot PEAA solution to allow water distillation and to obtain a final homogenous solution containing the desired amounts of PEAA and LP. Heating of this solution was continued to complete removal of the residual water added with LP as measured by the collected volume of the distilled water. The solution was then heated under vacuum to evaporate some NMP. The solvent evaporation was continued to obtain a viscous flowing liquid which could be poured and spread on a hot casting ceramic plate. This was treated as above to obtain the final PEAA-LP free standing film. Either the PEAA-SP and the PEAA-LP films, during immersion in the water bath, released soluble colored material, presumably being unreacted SP or LP (see Results and Discussion). The recovered free standing film was washed again with water to remove the residual solvent and unreacted SP or

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LP. This operation was repeated until the final collected water washing was colourless. Films of 150 μm thickness were typically obtained. The films were obtained from the respective solutions containing SP/PEAA and LP/PEAA in the 0.1 to 0.4 weight ratio range. These films looked homogeneous and transparent. They could be bent at 180 degrees angle without breaking. Films prepared at higher SP or LP/PEAA w/w ratio were not homogeneous, due to the formation of particles deposited over the film surface. These films were fragile. Neat PEAA films were prepared by the same solvent casting procedure using the above PEAA solution in NMP, without addition of SP or LP.

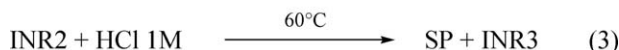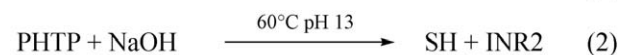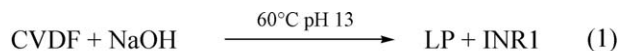### Determination of the Net Organic Matter Contributed by SP or LP in the PEAA Films

The organic fraction (X_{org}) contributed by SP or LP in the film was calculated based on elemental N and volatile solids (VS) analytical concentration values, according to eq. (1).

$$X_{org} = \frac{W + \frac{W \cdot E}{100 - E} - \frac{A}{100}}{D - W - \frac{W \cdot E}{100 - E}} \qquad (1)$$

In this equation X stands for SP or LP, X_{org} is the weight of X net organic matter per unit weight of PEAA net organic matter in the film, W is the N content per unit weight of film sample, E is the wt % ash content in the film sample, A is the N wt % in neat PEAA, D is the N/VS w/w ratio in neat LP or neat SP. The VS and N contents in the neat SP and LP samples and in the PEAA-SP and PEAA-LP films were determined, respectively by calcination at 650°C and by microanalysis, according to previously reported procedures.[14,15]

Molar Mass Characterization of PEAA-SP and PEAA-LP Films

The molecular characterization of neat PEAA, SP, and LP was performed by a multi-angle laser light scattering (MALS) on-line to a size exclusion chromatographic (SEC) system.[19,20] The molecular characterization of PEAA-LP and PEAA-SP films was performed by a conventional SEC system. Since blends are multicomponent systems with specific refractive index increment per unit concentration increment (dn/dc) the SEC-MALS characterization for the films it is not appropriate. The relative calibration of the conventional SEC system was performed by using Pullulan. This material is a linear homopolysaccharide of glucose described as an α-(1,6) linked polymer of maltotriose subunits.[21] It is available from Sigma Aldrich[22] as set of 10 different polysaccharides analytical standards for GPC with molecular weight (M_W) comprised between 0.320 and 800 kDa. The SEC chromatographic system consisted of an integrated GPCV 2000 system from Waters (Milford, MA, USA) equipped with two on-line detectors: a MALS Dawn DSP-F photometer from Wyatt (Santa Barbara, CA) and a 2414 differential refractometer (DRI) from Waters used as concentration detector. In conventional SEC only the online DRI concentration detector it is used. The SEC chromatographic experimental conditions were the following: 2 Polar Gel columns (M and L) from Polymer Laboratories, 90% dimethylsulfoxide (DMSO) + 10% H_2O as mobile phase, 80°C of temperature, 0.6 mL/min of flow rate, 200 μL of injection volume, about 1.5 mg/mL of sample concentration.

$$CVDF + NaOH \xrightarrow{60°C \; pH \; 13} LP + INR1 \qquad (1)$$

$$PHTP + NaOH \xrightarrow{60°C \; pH \; 13} SH + INR2 \qquad (2)$$

$$INR2 + HCl \; 1M \xrightarrow{60°C} SP + INR3 \qquad (3)$$

Scheme 1. Reactions (1) to (3) to obtain soluble (LP, SH, and SP) and insoluble (INR1, INR2, and INR3) hydrolysates from urban biowaste compost (CVDF) and postharvest tomato plants (PHTP).

Other Measurements

Gas chromatography–mass spectrometry (GC-MS) analyses were carried out after prior derivatization. In a typical derivatisation, 10 mg of the sample was solubilized in 1 mL of pyridine. Then, 300 μL of BSTFA (N,O-bis(trimethylsilyl) trifluoroacetamide) was added to a solution. The mixture was heated for 45 min at 60°C under magnetic stirring. GC-MS analyses were performed using a GC Agilent 6890 (Agilent Technologies) fitted with a mass detector Agilent Network 5973 and Agilent J&W HP-5 capillary column 30 m long, 0.25 mm internal diameter and 0.25 μm film thickness, operated from 80°C (3 min) to 300°C at 5°C/min. Fourier transform-infrared (FT-IR) spectra were recorded in ATR mode in a Perkin Elmer Spectrum BX spectrophotometer equipped with DTGS detector and working with 16 scans at 4 cm^{-1} resolution in the 4000 to 400 cm^{-1} range. The FT-IR analysis was carried out directly on the films or on KBr pellets for neat SP and LP. Thermogravimetric analysis (TGA) was performed using a Mettler-Toledo 851^e thermobalance. Differential scanning calorimetry (DSC) was carried out using a Mettler-Toledo DSC 821^e apparatus. Samples of about 5 mg were employed. The instrument was calibrated with high purity standards at 10°C/min. Dry nitrogen was used as purge gas. The mechanical tests were performed using a dynamical-mechanical analyzer DMTA V (Rheometric Scientific). All tests were carried out at a temperature of 25°C using the rectangular tension geometry on specimen machined into bars with size of 20 × 5 × 0.15 mm with a gauge length of 10 mm. The stress-strain mechanical analysis was performed at a strain rate of 0.01 s^{-1} with a preload force of 0.01 N. Five measurements were carried out on different specimens for each sample.[23]

RESULTS AND DISCUSSION

Chemical Nature of SP and LP

The SP and LP used in this work had very different chemical composition, reflecting their different origin and isolation experimental conditions (Scheme 1). Due to the biological nature of the sourcing materials, the SP and LP cannot be represented by a single well defined chemical formula as pure synthetic products. The former ones are more likely mixtures of different molecules. According to Table I, the sourcing CVDF and PHTP, and their alkaline hydrolysates obtained in reactions (1) and (2), contain a variety of C types and functional groups, that is, aliphatic (Af), aromatic (Ph), methoxy (OMe), amide (CON), ammine (NR), alkoxy (RO), phenoxy (PhOY), anomeric (OCO), carboxylic acid (COOH), phenol (PhOH), and ketone (C=O) C atoms. These C moieties are consistent with the presence of the main proximates of the vegetable world. In

Table I. Concentration Values as mol % of total C for Functional Groups and C Types[a] in Sourcing Materials and Products Obtained According to Scheme 1

Sample[b]	Al	NR and OMe	OR	OCO	Ph	PhOX	COY	C=O
CVDF	32.86	8.33	23.85	6.34	12.30	6.73	8.21	1.37
LP	36.90	7.24	13.22	4.18	13.39	6.84	13.53	4.69
INR1	31.70	8.43	24.58	6.14	11.49	7.23	7.74	2.68
PHTP	14.34	7.22	49.60	11.62	6.82	3.44	6.28	0.61
SH	47.37	9.39	10.39	2.19	11.50	3.81	14.37	0.97
INR2	5.00	7.97	58.98	13.19	7.00	3.66	2.97	1.22

[a] Aliphatic (Al), amine and methoxy (NR and OMe), alkoxy (OR), anomeric (OCO), aromatic (Ph), phenoxy and/or phenol (PhOX), carboxyl (COY), keto (C=O) C, R = alkyl C and/or H, X = alkyl and/or aryl C, and/or H, Y = amide N and/or OH.
[b] See Scheme 1.

essence, the alkoxy (OR) and anomeric (OCO) C are contributed by polysaccharides, the aromatic phenyl (Ph) and penoxy (PhOH) C are contributed by lignin matter and the carboxyl and amino groups are contributed by proteins. These proximates are not simply mixed physically. They are more likely bonded to each other in complex ways. This makes difficult a quantitative proximates' separation.

For the purpose of this work it was attempted to obtain a fraction mainly constituted by soluble poly or oligosaccharides, and a fraction mainly constituted by soluble lignin-like matter. Materials solubility was essential to obtain blend films by solvent casting. Soluble SP and LP were obtained through reactions (1) to (3). The data in Table I indicate that the two SP and LP sourcing materials, respectively named PHTP and CVDF, are very different for the relative content of saccharide and lignin-like matter. The relative contents of the OCO and OR, and of the Ph and PhOH, C moieties demonstrate that CVDF is much richer in lignin-like matter, while PHTP contains more saccharides. The large difference between the two materials is mainly due to the fact the PHTP is fresh vegetable matter, while CVDF is a compost, depleted of saccharide matter during prolonged aerobic fermentation. Table I also shows that for each sourcing material, the soluble alkaline hydrolysates (LP and SH) are richer in lignin-like matter, while the insoluble residues (INR1 and INR2) are richer in saccharides. As a consequence, the material with the highest content of lignin-like matter is LP, while INR2 has the highest content of saccharides. These materials were chosen to manufacture new composites with PEAA. However, since INR2 was insoluble, reaction (3) was carried out to obtain the soluble saccharide polymer (SP).

The chemical composition of SP was confirmed by ^{1}H NMR and GC-Mass spectroscopy. The ^{1}H spectrum contained major signals at 3 to 4 ppm, typical of CH—X, X=OR, NH_2 protons in saccharide and/or aminoacids moieties, at 5.3 ppm assigned to the anomeric proton in saccharides, and smaller signals at 1 to 2.0 ppm assigned to protons in aliphatic C chains, in acetyl and/or in NH_2 functional groups.[24] Aromatic proton signals were absent. Analysis by GC-Mass spectroscopy confirmed that SP organic matter contained mainly hexose and pentose saccharides. The GC signal areas of these saccharides relative to the total signals' area of the chromatogram amounted to about

86%. The remaining signals area was associated mostly to % carboxylated compounds such as glucofuranuronic acid, hexadecanoic acid, galactofuranuronic acid, galacturonic acid, glucopyranuronic acid, D-glycero-L-manno-heptonic acid-γ-lactone. Consistently with the GC Mass spectroscopy results the SP IR spectrum [Figure 1(C)] contained absorption bands due to C=O(OH) (1700), 1631 (O—H; N—H), and C—O (1000–1100) vibrations.

The SP and LP contained different amounts of elemental N and mineral elements, as shown in Table II. They had weight average
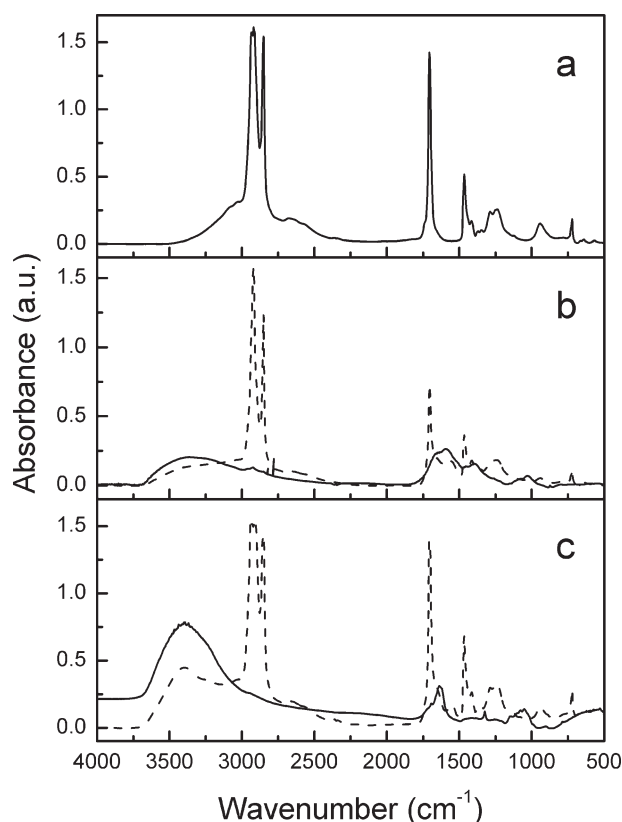

Figure 1. IR spectra of PEAA (a), LP (b, solid line), PEAA-LP 0.2 films (b, dashed line), SP (c, solid line), and PEAA-SP 0.2 films (c, dashed line).

Table II. Analytical Values and/or Chemical Composition Data for Neat PEAA, LP, and SP Blend Films

Sample and/or raw component w/w ratio in NMP solution	LP/PEAA or SP/PEAA net organic matter w/w ratio in NMP solution	N (wt %)	Ash (wt %)	LP/PEAA or SP/PEAA net organic matter w/w ratio in film	IR absorbance ratio[a]
PEAA	–	0.19	0.00	–	0.06
LP	–	0.54	54.2	–	–
SP	–	5.20	32.4	–	–
PEAA-LP 0.1	0.068	0.58	0.00	0.055	0.15
PEAA-LP 0.2	0.130	0.84	1.86	0.093	0.26
PEAA-LP 0.3	0.204	1.01	1.93	0.107	0.31
PEAA-LP 0.4	0.260	1.27	2.89	0.139	0.41
PEAA-SP 0.1	0.046	0.24	1.48	0.056	0.16
PEAA-SP 0.2	0.091	0.16	0.81	0.000	0.16
PEAA-SP 0.3	0.137	0.34	1.56	0.186	0.18

[a] Ratio of IR absorbance at 1550 cm^{-1} to absorbance at 2915 cm^{-1}.

molecular weight (M_w) of 27 and 75 kDa, respectively, as shown in Table III. According to the collected data they are by all means biopolymers, which differ one from the other for molecular weight and chemical nature. In essence, SP contains mainly saccharide repeating units and falls into the category of polysaccharides. The LP, by virtue of its aliphatic-aromatic character, is a lignin-like polymer, differing from natural lignin[24] for the solubility properties and relative composition of C-types and functional groups.

Chemical Nature of Blend Films

To understand the chemical nature of the blend films it was necessary first to determine their chemical composition, i.e. the relative contents of PEAA, LP, and SP. As the biopolymers are soluble in water, while PEAA is insoluble in water, during the

Table III. Macromolecular Features of Neat PEAA, LP, SP, and of Blend Films

Sample	M_p[a] (kDa)	M_w[b] (kDa)	M_w/M_n[c]	Mass recovery[d] (%)
PEAA	67.1	248.5	2.3	62
LP	61.5	75.1	1.5	89
SP	14.3	27.4	1.5	96
PEAA-LP 0.1[e]	725.2	1242.7	6.7	60
PEAA-LP 0.2[e]	496.6	715.5	3.2	76
PEAA-LP 0.3[e]	527.2	428.4	2.6	59
PEAA-LP 0.4[e]	493.4	520.4	2.6	62
PEAA-SP 0.1[e]	65.4	123.6	1.7	78
PEAA-SP 0.2[e]	66.4	181.8	2.4	77
PEAA-SP 0.3[e]	65.4	151.4	2.2	75

[a] Molecular weight peak value.
[b] Weight average molecular weight.
[c] Polydispersity index.
[d] Calculated from the chromatogram area.
[e] Raw materials weight ratio used in the films preparation.

water washing of the cast films from the NMP solution, release of LP and SP in water occurred. This was evidenced by the color of the collected washings. Thus, the LP/PEAA and SP/PEAA w/w ratio in the film recovered from the final water washing was expected different from the components weight ratio in the NMP solution before casting the film. For convenience, hereinafter the investigated blend films are identified by the components acronyms followed by the number indicating the biopolymer (SP or LP)/PEAA weight ratio in the NMP solution. For examples, PEAA-SP 0.1 stands for the PEAA-SP blend obtained from the NMP solution containing SP and PEAA at SP/PEAA raw matter w/w ratio.

The presence of the residual saccharide (SP) and lignocellulosic (LP) materials in the films recovered from the final washing was confirmed by IR spectroscopy. Figure 1 shows the *vis-a-vis* comparison of the IR spectra of the neat PEAA, LP, and SP materials and of the blend films. Bands assignments are given according to literature.[25,26] It may be observed that the commercial PEAA is characterized [Figure 1(A)] by strong bands at 2800 to 3000 cm^{-1} and at 1700 cm^{-1} arising from the stretching vibrations of C—H and C=O(OH) bonds. By comparison, LP [Figure 1(B)] and SP [Figure 1(C)] show relatively very weak bands at 2800 to 3000 cm^{-1}, while the main bands fall at 1630 to 1550 cm^{-1}. These bands arise from the vibrations of COO^-, CONH, and OH functional groups. For both SP and LP the absorption at 1700 cm^{-1} arising from COOH groups is small or covered by the broad bands at 1630 to 1550 cm^{-1}. The blend films showed the bands of LP and SP together with those of PEAA, as depicted in the typical spectra shown in Figure 1(B) for the PEAA-LP 0.2 and PEAA-SP 0.2 blends.

The presence of water insoluble SP and LP in the films indicated that a change of solubility properties occurred for the material present in the film compared with the pristine SP and LP soluble materials. This was a first indication that a reaction between PEAA and SP and LP occurred during the films preparation with formation of a new polymer containing SP and LP
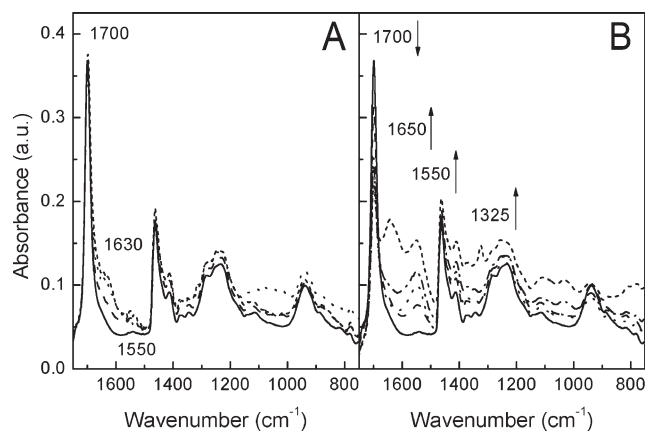
Figure 2. (A) IR spectra of PEAA (solid line), PEAA-SP 0.1 (dashed line), PEAA-SP 0.2 (dotted line), and PEAA-SP 0.3 (short dashed line). (B) (A) IR spectra of PEAA (solid line), PEAA-LP 0.1 (dashed line), PEAA-LP 0.2 (dotted line), PEAA-LP 0.3 (dash dotted line), and PEAA-LP 0.4 (short dashed line).

chemically bonded to PEAA. However, determining the relative chemical composition of the new polymers was rather difficult. A main problem was that the neat SP and LP materials are mixtures of molecules (see the Chemical Nature of SP and LP Subsection). These molecules might have different reactivity toward PEAA. Thus, the molecules bonded to PEAA in the film might have a different chemical composition from those leached into the film washing bath. The second problem is that SP and LP contained aliphatic C atoms and OH functional groups which were analytically hard to distinguish from those belonging to PEAA. Under these circumstances, a quantitative estimate of the SP and LP film content was attempted through the determination of elemental N and ash content in the neat PEAA, LP, and SP materials, and in the blend films. Table II reports the raw analytical data, the LP/PEAA and SP/PEAA net organic matter w/w ratios in the films calculated using eq. (1) against the raw matter and the net organic matter w/w ratios in the NMP solution before casting the film. The LP/PEAA net organic matter weight ratios in the film (y) and in the NMP solution (x) result linearly related according to eq. (2).

$$y = a + b \cdot x \qquad (2)$$

where $a = 0.0123 \pm 0.0104$, $b = 0.502 \pm 0.0644$, and R (correlation coefficient) = 0.976. The value of the b coefficient indicates that about 50% of the LP present in the NMP solution remains bonded to PEAA in the film. The SP data do not yield as good correlation; i.e. $a = -0.01514 \pm 0.06043$, $b = 1.10426 \pm 0.70765$, and R (correlation coefficient) = 0.741. The reason is probably the low N content of SP, not enough higher compared with N content found in the cast PEAA film content to appreciate the contribution by the small amount of added SP within the constraints of the analytical approach.
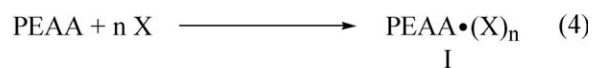
Validation of the analytical approach was sought by IR spectroscopy. Table II reports the ratio of the IR absorbance at 1550 cm^{-1} to the absorbance at 2915 cm^{-1} for PEAA and the composite blends. The plot of the IR absorbance ratio (y) against the LP/PEAA ratio (x) in the NMP solution (Table II) fits well eq. (3).

$$y = a + b \cdot x \qquad (3)$$

where $a = -0.0651 \pm 0.0153$, $b = 1.306 \pm 0.0949$, and $R^2 = 0.992$. The corresponding plot for the PEAA-SP blends yields $a = 0.08584 \pm 0.02841$, $b = 0.79061 \pm 0.33266$, and R (correlation coefficient) = 0.859. The plots of the above absorbance ratios against the components weight ratios in the films yield $a = 0.0387 \pm 0.0212$, $b = 2.529 \pm 0.230$, and R (correlation coefficient) = 0.988 for the LP blends, and $a = 0.11757 \pm 0.0339$, $b = 0.37071 \pm 0.34905$, and R (correlation coefficient) = 0.600 for the SP blends. It may be observed that the absorbance ratios correlate equally well with the LP/PEAA ratios in the NMP solution and in the film. On the contrary, for the SP bends, the absorbance ratios correlate much better with the SP/PEAA ratios in the NMP solution than in the film. This supports the previous statement about the analytical approach based on N and ash analysis not being sensitive enough in the case of the SP blends to appreciate reliably the small amounts of added SP in the film.

In addition to supporting the presence of LP and SP in the film and validate the analytical approach to assess the chemical composition of the blends, the IR spectra provide further important information related to the chemical reaction between the biopolymers and the synthetic polymer. Figure 2 reports the spectral patterns in the 1750 to 800 cm^{-1} range for all blend films fabricated in the investigated weight ratio ranges. In the spectra of PEAA-SP [Figure 2(A)] one can observe only the increase of the band at 1630 and at 1000 to 1100 cm^{-1} upon increasing the SP/PEAA raw matter w/w ratio. This fact does not yield any more information other than the one already given by Figure 1. However, in the spectra of PEAA-LP [Figure 2(B)] one may observe that the increase of the intensity of the band at 1550 cm^{-1} (used in the above absorbance-weight ratio correlations) corresponds to the decrease of the PEAA COOH band at 1700 cm^{-1}. Together with this fact, two new bands arise at 1642 and 1325 cm^{-1}, which are well evident in the spectrum of the film containing the highest LP/PEAA w/w ratio. These two bands arise from C=O and C—N stretching vibrations of amide functional group.[25] The band at 1642 cm^{-1} is specifically assigned[26] to the C=O stretching (amide I band) and/or N—H bending (amide II) vibrations of primary amides. The increasing intensity of these two new bands, coupled to the decreasing intensity of the PEAA COOH band at 1700 cm^{-1}, is consistent with a reaction occurring between the PEAA COOH groups and the LP amino groups shown in Table I which leads to formation of primary amide groups.

All data together appear consistent with the following reaction Scheme 2 occurring between PEAA and the waste sourced material (X = SP or LP). Reaction (4) yields the donor acceptor complex I. This product in reaction (5) partly converts to II

$$PEAA + n\,X \longrightarrow PEAA\bullet(X)_n \qquad (4)$$
$$\text{I}$$

$$PEAA\bullet(X)_n \longrightarrow PEAA\text{-}(X)_m \qquad (5)$$
$$\text{II}$$

Scheme 2. Reactions (4) and (5) between PEAA and SP and/or LP.

where X is covalently bonded to PEAA. Product I is soluble in NMP, but it decomposes to into the starting reagents by addition of water. On the contrary, product II is stable and insoluble in water. This property is well consistent with the formation of stable amide bonds as suggested by Figure 2(B) spectra for the reaction between PEAA and LP. Equation (3) and Figure 2 confirm that the available film samples containing product II cover a range of chemical compositions useful to investigate how the nature and concentration of the LP and SP biopolymers affects the thermal and mechanical properties of the PEAA blends.

Macromolecular Mass and Solubility of PEAA, LP, and SP, and of the Blend Films

For the molar mass characterization it was necessary to search the best solvent where the investigated products were completely soluble at molecular level. No solvent meeting this requirement was found. The best results were obtained with the mixed 90% dimethylsulfoxide (DMSO)−10% H_2O solvent. Table III reports the relevant data for the investigated samples obtained by the SEC molecular characterization performed in this solvent. These are the peak molecular weight (M_p), the weight average molecular weight (M_w), the polydispersity index M_w/M_n, where M_n denotes the numeric average molecular weight, and the sample mass recovery. This last parameter represents substantially the sample soluble fraction, calculated from the area of the chromatogram after an accurate calibration. The mass recovery data indicate that the solubility of neat SP and neat LP in the mixed solvent is nearly complete, i.e. 88 to 96%. Considering that these products contain 32 to 54% mineral matter, the entire amount of the products organic fraction is likely to be comprised in the SEC recovered mass. By comparison, the solubility of neat PEAA and of the composite films is shown to be only partial, ranging from 59 to 78%. Considering these amounts of recovered mass, it may be assessed that the molecular weight values given in Table III represent the large majority of the sample matter.

The figures in Table III indicate relevant differences between the neat PEAA, SP, and LP materials, and the PEAA-SP and PEAA-LP blends. The molecular weight and sample solubility of the PEAA-SP blends have values comprised between those of neat PEAA and SP. In essence the molecular weight of the blends is somewhat lower than that for neat PEAA, but much higher than that for neat SP. The blends solubility is higher than that for neat PEAA and lower than that for neat SP. By comparison, the PEAA-LP blends have molecular weight 2 to 5× that for neat PEAA, and on the average the same solubility of neat PEAA. The observed changes of solubility properties and/or molecular weight features of the PEAA, SP, and LP organic matter in the composites, compared with the neat PEAA, SP, and LP, is the likely results of reaction (5). The effects of this reaction are particularly strong in the case of PEAA and LP. Figure 3, reporting the differential molecular weight distribution patterns of the neat PEAA and biopolymers, and of the PEAA-LP blends, depicts this situation. It may be clearly observed that the neat PEAA pattern consists of three broad bands indicating three molecular pools with peaks at 70, 100, and 400 to 700 kDa in the order of decreasing intensity. The PEAA-LP show also three peaks at nearly the same molecular weight values as
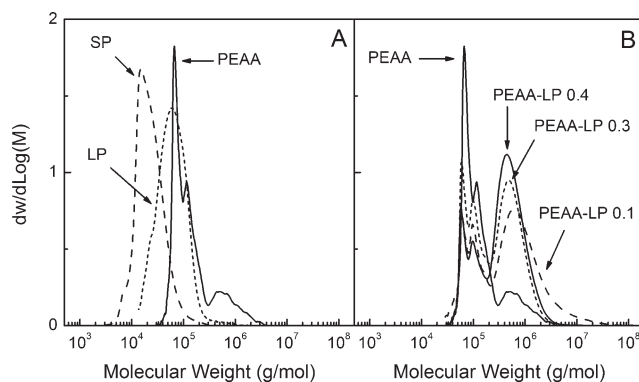

Figure 3. Comparison of differential molecular weight distribution $dw/d\mathrm{Log}(M)$ of neat PEAA and biopolymers (A) and of PEAA-LP blends (B).

in neat PEAA. However, the peak at 400 to 700 kDa is the most intense. The results are particularly striking if one considers that the 5× increase of the PEAA-LP 0.1 M_W compared with the M_W of neat PEAA occurs upon reacting PEAA with relatively small amounts of LP (i.e. 0.1 g of LP per g of PEAA). Indeed the data in Table II indicates that the amount of LP organic matter in the sample is only about 5%. For all PEAA-LP blends, the molecular weights are rather higher than one could reasonably expect on the basis of the added amount of LP in the reaction mix and on a simple physical mixture of two separate components remaining distinct within the blend structure. It is more reasonable to expect such molecular weight features by imagining that the small amount of biopolymer molecules reacted to bridge several PEAA molecules, thus leading to the formation of a new high molecular weight polymer. In this respect the molecular weight data is consistent with the above IR data suggesting the occurrence of a chemical reaction between PEAA COOH groups and the LP amino groups with formation of primary amide groups. Thus PEAA, by reacting with the lignin-like biopolymer, yields a polyamide with 2–5× molecular weight increase relative to the pristine synthetic polymer and 6–16× higher than that of the neat biopolymer.

Thermal and Mechanical Behavior

Thermal gravimetric analyses (TGA) at 10°C/min scanning rate showed that the neat LP and SP undergo definite weight losses of about 12% at 220°C and 150°C, respectively, presumably due to the loss of residual moisture or solvents. At higher temperature broad loss extending from 250 up to 500°C was observed. By comparison, neat PEAA was stable up to 350°C. From this temperature up to 520°C, the sample weight loss was 100%. The blends thermal stability was found to decrease relatively to neat PEAA upon increasing the content of LP or SP. The blends containing the highest biopolymer concentration were stable up to 300°C.

DSC scans were performed from −65 to 140°C, at 10°C/min. The samples were first heated at 20°C/min from room temperature to 140°C in order to evaporate residual water or solvents. During this process the samples melted. They recrystallized on cooling to −65°C at 10°C/min. Finally, they were heated again to 140°C at the same rate. No thermal transitions were observed for neat LP and SP. On the contrary, for neat PEAA and the
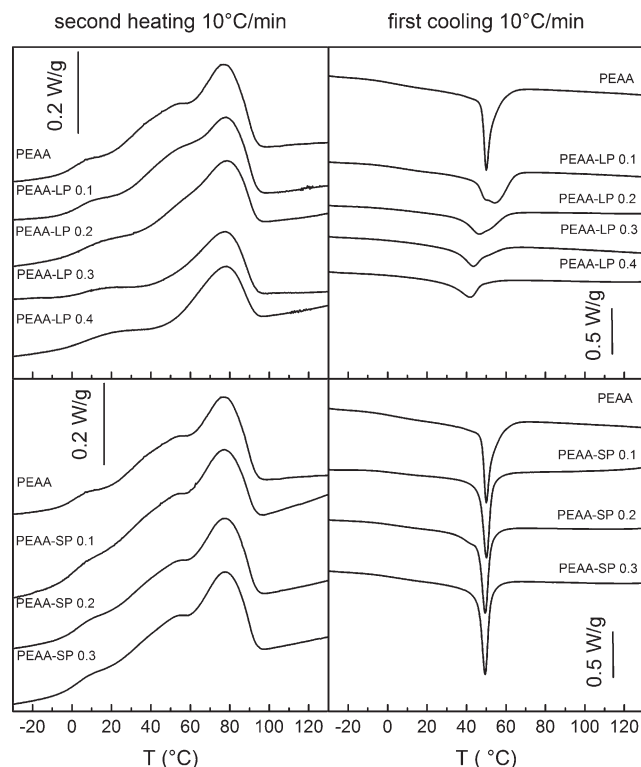
Figure 4. DSC second heating at 10°C/min (left panel; 0.2 W g^{-1} heat flow) and DSC first cooling at 10°C/min (right panel; 0.5 W g^{-1} heat flow) for PEAA-LP (upper panels) and PEAA-SP (lower panels) blends and PEAA.

PEAA-LP and PEAA-SP blends, their phase transition parameters were determined: i.e. the temperatures of glass transition (T_g) and melting (T_m), and the melting enthalpy (ΔH_m). Figure 4 shows the first cooling and the second heating scans of the neat PEAA and the PEAA-LP and PEAA-SP blends. On cooling, all the samples exhibit an exothermic peak due to the crystallization of the melt. In the second heating scan, the neat PEAA

sample exhibits a broad endothermic process which includes the glass transition at 2°C and two overlapping endothermic peaks, with maxima at about 50 and 77°C. The peak at 77°C has been associated[27] with melting of the primary crystallites. For the lower temperature peak, two explanations are available. According to Wakabayashi and Register,[28] this peak is attributed to melting of another crystallites' kind unable to pack into the primary crystal structure during initial crystallization. Other workers,[29] on the base of FT-IR spectra, assign the lower temperature peak to an endothermic transition involving dissociation of hydrogen bonds between carboxylic groups.

Table IV reports the relevant data determined from the DSC analysis. For the samples obtained at LP/PEAA w/w ratio increasing from 0.0 to 0.4, T_g increases from 2.2 to 9.8°C whereas no much effect on T_m is observed. For the SP blends at SP/PEAA w/w ratio increasing from 0.0 to 0.3, no effect is observed on T_g and T_m by the presence of SP in the blend compared with neat PEAA. Differences between the LP and SP blends are also observed on the ΔH_m and on the melting band shape. Figure 5 shows that only for the LP bends, as the biopolymer amount increases, the lower temperature endothermic component decreases in intensity and finally disappears corresponding to PEAA-LP 0.3 blend. The increasing amount of added LP also lowers significantly the crystallinity of the PEAA-LP blends as shown by the ΔH_m values in Table IV compared with the value for neat PEAA. No or much smaller effects of added SP on the melting features of the PEAA-SP blends are observed. The trends of the recrystallization temperature and enthalpy data are consistent with those observed for the melting transitions. Compared with the SP blends, the DSC results for the LP blends are more consistent with the formation of the new polymer II through reaction (5).

Neat SP and LP were not film forming. When cast from their aqueous solution they yielded products in powder form. Neat PEAA and all blends gave free standing flexible films which could be bent at 180° angle without breaking. All films were

Table IV. Thermal and Mechanical Data of PEAA and of Blend Films

Sample	T_g[a] (°C)	T_m[b] (°C)	ΔH_m[c] (J/g)	T_c[d] (°C)	ΔH_c[e] (J/g)	Young's modulus (MPa)	Stress at yield point (MPa)	Strain at break (%)	Stress at break (MPa)
PEAA	2.2	76.7	45.6	50.3	31.8	30.4 ± 2.5	4.7 ± 0.2	>300	10.6 ± 0.3
PEAA-LP 0.1[f]	2.8	78.0	41.3	54.8	28.1	76.6 ± 5.1	9.3 ± 0.5	280 ± 15	13.5 ± 2.3
PEAA-LP 0.2[f]	3.5	78.3	29.5	47.0	17.3	135.6 ± 4.3	13.7 ± 0.4	257 ± 7	19.3 ± 2.5
PEAA-LP 0.3[f]	5.8	77.9	24.1	43.6	13.0	172.2 ± 4.8	17.1 ± 0.3	55 ± 7	16.2 ± 2.5
PEAA-LP 0.4[f]	9.8	77.4	19.9	42.1	10.0	–	–	–	–
PEAA-SP 0.1[f]	2.3	76.5	40.0	50.4	28.8	23.9 ± 2.3	4.4 ± 0.3	>300	9.9 ± 0.8
PEAA-SP 0.2[f]	2.5	76.3	42.6	49.9	29.9	43.4 ± 2.7	6.7 ± 0.4	>300	15.1 ± 1.2
PEAA-SP 0.3[f]	2.1	76.5	43.2	49.9	30.5	23.8 ± 2.8	4.6 ± 0.4	>300	9.2 ± 1.1

[a] Glass transition temperature estimated at the midpoint.
[b] Melting temperature.
[c] Melting enthalpy.
[d] Crystallization temperature.
[e] Crystallization enthalphy.
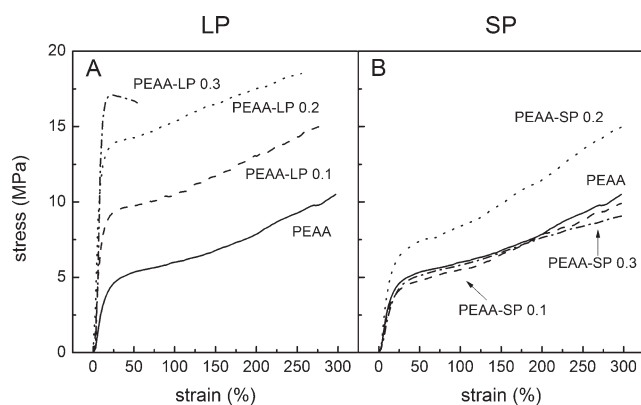[f] Raw materials weight ratio used in the films preparation.

Figure 5. Stress–strain curves for PEAA-LP (A) and PEAA-SP (B) blend film.

subjected to stress–strain analysis at low shear rate in order to investigate the effect of the nature and relative content of the biopolymers on the blended films mechanical properties compared with neat PEAA. The results are reported in Figure 5 and Table IV. It may be observed that for the PEAA-LP blends, the Young's modulus and the stress at yield point increase regularly, respectively from 30 to 172 MPa and from 4.7 to 17.1 MPa, as the LP amount increases, whereas a parallel decrease of strain at break from >300 to 55% is observed. On the contrary, the PEAA-SP blends show mechanical parameters values near to those for neat PEAA. The data show that the lignin-like biopolymer (LP) brings about strong Young's modulus and stress at yield point increases, respectively of 2–6× and over 3× the value for neat PEAA, but lowers the strain at break. By comparison the polysaccharide biopolymer (SP) does not seem to bring much change in the mechanical properties of neat PEAA. It is very interesting to observe from Figure 6 how the Young's modulus decreases regularly as the crystallization enthalpy of the blend films increases and approaches the value for neat PEAA. This trend clearly points out that the enhanced mechanical strength is directly proportional due to amount of the new amorphous phase formed as a consequence of the chemical reaction (5) between PEAA and LP.

The difference in the effects by the two biopolymers on mechanical properties is likely due to their different nature and reactivity versus PEAA. The LP, by virtue of its aromatic C moieties, keeps the memory of the chemical structure and mechanical strength of the parent lignin. In addition, the chemical reaction (5), bonding the mechanically flexible synthetic polymer to the hard lignin-like polymer, contributes more hardness and rigidity to the blend. Similar effects have been reported for lignin in blends with other synthetic polymers.[30,31] In the present work, the PEAA-LP films are shown capable to bear higher stress than PEAA and PEAA-SP before yielding and breaking, but have lower strain at break. Nonetheless at low relative content in the blends with PEAA, LP can contribute its mechanical strength without compromising critically the elasticity of the blend. For instance, the PEAA-LP film fabricated at 0.2 LP/PEAA w/w ratio exhibits 4.5× higher Young's modulus, 3× higher stress at yield point, and almost 2× higher stress at break than PEAA, while still achieving 257% strain. The same

lignin-like polymer (LP) blended with polyethylene-co-vinyl alcohol (EVOH),[14] has been found to exhibit very poor mechanical properties at LP/EVOH w/w ratio above 0.1. The materials prepared with 0.07 LP/EVOH w/w ratio could bear 70% higher stress than the synthetic polymer at the yield point, but exhibited 50% lower strain at break. Surprisingly, the samples fabricated at 0.03 LP/EVOH w/w ratio could bear 30 MPa stress at 150% strain at break against 25 MPa and 85% strain for the neat synthetic polymer. The results of the present work and of the previous work[14] point out that there is an optimum LP relative content for each blend type, where enhanced mechanical strength is attained while still keeping acceptable stain at break. Similar behavior has been reported for blended films of poly(4-vinylpyridine) and lignin.[30] The present data on the biopolymers-PEAA blends and the previously reported data on the biopolymers-EVOH blends[14] indicate a not yet fully explored potential in waste sourced soluble biopolymers to modify synthetic polymers. There is a wide range of available synthetic polymers and copolymers, and of obtainable waste sourced biopolymers, which can be blended to develop new high performance lower cost environmentally more compatible materials for human daily use.

Economic and Environmental Benefits

The results of this work demonstrate that it possible to use refuse derived biopolymers to fabricate blend materials with synthetic polymers having enhanced environmental compatibility, and enhanced or equal mechanical strength compared with the pristine synthetic polymer. This fact is important in relation to current several issues connected with replacing fossil sources with renewable sources of chemicals and materials, and with developing sustainable waste management practices. In relation to the first issue, as the biopolymers are sourced from negative cost refuse materials and their production cost is estimated 0.1 to 0.5 €/kg,[32] the partial substitution of PEAA with the cheaper more ecofriendly refuse derived biopolymers implies a significant reduction of the cost impact of the starting components in
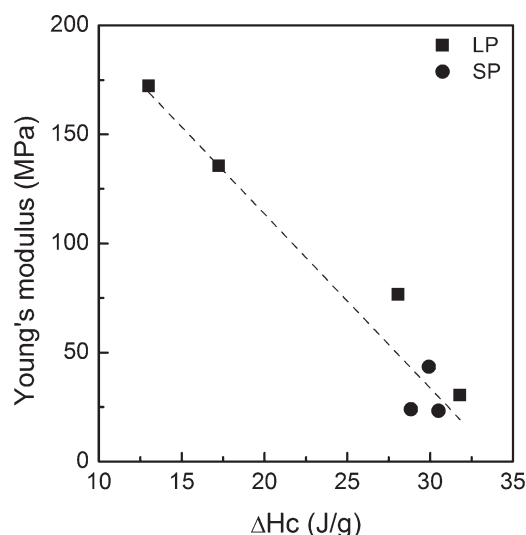

Figure 6. Trends of Young's modulus as a function of recrystallization enthalpy for PEAA-LP blend (square symbols) and PEAA-SP blend (round symbols).

the finished film product and the use of a more environmentally compatible product. In relation to the second issue, demonstration of the capacity of the above biopolymers to replace synthetic polymers opens wide opportunities for allocating the biopolymers in the chemical market and so prospecting new scenarios for improving the management of urban and agriculture residues either economically and environmentally. Additional value to this work stems from the fact that the LP biopolymers used for the manufacture of the blended films have been shown in previous work[15] to perform as biostimulants for use in cultivation practices. This fact prospect a virtuous scenario where mulch film fabricated with the above blends, at end of their service life, might contribute their beneficial properties to plants. For all these reasons, the present work is well in line with the EU calls for projects within the Horizon2020 program, with specific reference to the waste 2 and 7 calls. The results of this work are significant because they point out that the valorization of urban and agriculture residues as source of chemicals for the manufacture of biocompatible polymer blends is a realistic feasible goal from which economic and environmental benefits are expected for the chemical industry, agriculture and waste management practices.

Some important questions must however be answered in order to evaluate the feasibility of developing to industrial commercial scale the herewith proposed material recycling technology for agriculture and municipal bio-waste to be utilized as composite films. These are (i) the residual NMP solvent in the cast films, (ii) its environmental impact in the intended film application, (iii) the comparison of casting versus melting for the films fabrication, and (iv) the effects of the manufacture process on the film properties. To answer these questions, it should be considered first that NMP belongs to the class of dipolar aprotic solvents such as dimethylformamide and dimethyl sulfoxide. It is miscible with water and with most common organic solvents. Due to its good solvency properties NMP is used to dissolve a wide range of polymers.[33] It is widely used in the chemical industry. N-methyl-2-pyrrolidone is also an acceptable pharmaceutical solvent and its efficacy, toxicity, and side effects are comparable with other common solvent.[34] DuPont[35] reports that NMP is readily biodegradable, is not bioaccumulative in aquatic or terrestrial environments, and therefore is not likely to pose a risk to drinking water. The toxicological and ecotoxicological properties of this substance are of small concern regarding a hazard for humans via the indirect exposure route. Consequently all identified uses of the substance are assessed as safe for the environment. Nevertheless, NMP is on California's list of chemicals known to possess developmental toxicity.[33] In the face of increasing regulation, some manufacturers are considering alternative solvents for some applications, especially where worker exposure is difficult to control, such as in paint stripping, graffiti removal, and agriculture.[36] In the absence of alternative solvents, NMP can still be used safely. Technology at industrial level for film casting from organic solvents and solvent recovery, in compliance with safety regulations, is well developed.[37] In addition, to its solubility in water, residual solvent in the film should thoroughly be removed by optimizing the film water washing step. The other alternative is to replace solvent casting with hot-melt extrusion.

Solvent casting is ideal for manufacturing films containing heat sensitive substances because the temperature required for removing the solvent is usually lower than that for a hot-melt extrusion process.[38] In the case of NMP boiling at 202°C at atmospheric pressure, the solvent can be removed even at 85°C upon reducing the pressure to 13 mbar.[39] Preliminary data (not included in this article) has however indicated that LP composites can be obtained also by hot-melt extrusion at 200°C. This opens new technological perspectives. It offers worthwhile scope for research aiming to compare hot-melt extrusion versus solvent casting in relation to process and product cost, performance and environmental impact. Future work along these directions will also allow to address another important issue: i.e. the composite films obtained are biodegradable or not? There is no question that coupling the above shown film mechanical strengthening by LP with biodegradability would be mostly desirable. Data to answer this question has not been collected in the present work. Product biodegradability may be affected by the film fabrication technology. Thus, it will require a dedicated work, once both the cast and the extruded films will be available.

CONCLUSIONS

New materials are obtained starting from a synthetic polymer with carboxylic functional groups (PEAA) and biopolymers sourced from agriculture and municipal biowaste materials such as the soluble polysaccharide SP and the lignin-like polymer LP having acid and basic functional groups. The PEAA-SP and PEAA-LP blends have been found to have different solubility properties and/or molecular weight than the starting components. This suggests a chemical reaction occurring between PEAA and LP and/or SP. Strong support for a chemical reaction occurring between PEAA and LP with formation of new peptide bonds is provided by IR spectroscopy and DSC. No new functional groups could be identified for the reaction of PEAA with SP. The lignin-like biopolymer has been found to modify strongly the crystallinity and mechanical properties of the starting synthetic polymer. On the contrary the PEAA-SP blends behave more like the pristine PEAA. Similar effects have been reported previously for the reaction of LP with polyethylene-co-vinyl alcohol.[14] The results offer scope for further development work on these materials and investigation on biopolymers sourced from other biowastes to understand more the reasons of the observed effects and exploit their full potential to modify synthetic polymers. In this fashion, agriculture and urban biowastes may be promoted as source of renewable chemicals to replace or partially substitute synthetic chemical obtained from fossil sources and to obtain new eco-compatible materials for use in daily life. This in turn will generate relevant economic and environmental benefits[14,15] for waste management practices, agriculture, the chemical industry, and society.

ACKNOWLEDGMENTS

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