Elaboration and Characterization of Bioblends Based on PVC/PLA

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ABSTRACT: With the aim to develop new biomaterials (bioblends) to be used in the field of waste elimination, this contribution focuses on the elaboration and characterization of new materials based on poly (vinyl chloride) (PVC) and poly (lactic acid) (PLA). The bioblends based on PVC/PLA were prepared by melt mixing in the absence and presence of maleic anhydride (MAH). The binary blends were first characterized in terms of thermal (glass transition temperature) and mechanical properties (tensile and micro-hardness). Their thermal stability was investigated by thermogravimetric analysis (TGA). The results showed that this pair of polymers is not miscible and exhibited lower properties than those of the separated polymers. The *in situ* compatibilization was then performed using MAH and dicumyl peroxide (DCP) as an initiator. The presence of MAH enhanced the processability of the bioblends by decreasing the temperature of mixing. The properties of subsequent PVC/PLA bioblends were investigated through tensile and micro-hardness testing, thermal analysis (DSC and TGA), and SEM. From the mechanical results, high level of compatibility was found when introducing MAH. The TGA studies indicated that the incorporation of PLA in PVC (matrix) increased thermal stability of the bioblend. Microscopic observations revealed uniformly dispersed PLA in the PVC matrix, confirming that phase separation has disappeared in the presence of MAH. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40045.

INTRODUCTION

The consumption of plastic materials is increasing day-by-day. Annually, a large quantity of non-biodegradable industrial and domestic plastics is disposed of. The quantity of municipal solid waste (MSW) is a significant problem. Although plastics account only for a few part of such wastes, since they are very visible they are subject to harsh criticism. Wastes are also considered as valuable secondary raw materials in the perspective of developing industrial ecology and circular economy.

Recycling is one of the routes to reduce this pollution. But the properties of the recycled materials, mostly mechanical ones are poor due to the incompatibility between the different polymers.[1] Thus one of the major concerns of using synthetic polymers is disposal after end the product life cycle.

Another way to solve that problem is replacing commodity synthetic plastics with biodegradable plastics.

The development of biodegradable plastics can play a crucial role in helping to solve the waste disposal problems. Since the waste reduction is important for future MSW, a number of important issues need to be addressed to ensure that new bio-

degradable plastics industry develops.[2] The products that will be discarded by the consumer after use will become wastes and these products do break down naturally by the air, moisture, climate, or soil and disintegrate in the surrounding land.

Polymer blending is one of the most important contemporary ways for the development of new polymeric materials which often exhibit properties that are superior to any individual component polymer.[3]

Blends allow to combine the useful properties of different molecular species and can provide a wide range of physical or chemical properties and morphological states.[4]

Polymer blends comprising at least one biodegradable polymer with other polymers are referred to as bioblends. Biodegradable polymer bioblends are of interest in the development of a variety of products for use in packaging materials, medical devices, drug delivery systems etc. Successful development of bioblends requires that the biodegradable polymers be compatible with other component polymers.[5]

It has been found that the products of degradation of one polymer can influence the degradation behavior of the other. The

structure and composition of various products formed during the degradation process and their mutual interactions in the ultimate degrading mechanism depends on the compatibility of polymers components in the blend.[6,7]

Among the biodegradable polymers, polylactic acid is the thermoplastic polymer with excellent mechanical properties. It is now produced on a large scale from fermentation of corn to lactic acid and subsequent chemical polymerization. Pure PLA can degrade to carbon dioxide, water and methane in the environment over a period of several months to 2 years, compared to other petroleum plastics which need 500–1000 years.[2] However, its cost remains higher than petroleum polymers. However the plastics industry continually looks for cost savings in some cases, where an expansive polymer may be over-engineered for an application blending with a less expensive polymer or filler using a corresponding compatibilizer reduces cost. To satisfy the market expectation and achieve technical specifications, some fundamental basics must be challenged, for example competitive prices and similar or improved mechanical properties. The prefix "bio" can only be attractive if material costs are moderate and consumer acceptance can be guaranteed.[8]

Indeed PLA has biodegradability, annually renewable availability and processability following standard melt processes it is melt blended with different elastomeric polymers like: poly(ε-caprolactone),[9] poly (hydroxyl butyrate),[10] poly(butylenes succinate), poly butylenes adipate-co-terephthalate)[11]appears a sustainable effective approach to improve the thermomechanical behavior of PLA-based material, while mainly the biodegradability.[12] PLA was also melt blended with non-biodegradable polymers like PP,[13] ABS,[14] PS,[7] PET,[15,16] PMMA,[17] PVA,[18] and PE but no article dealing with poly (vinyl chloride) (PVC) was found.

The low cost and high performance of PVC products combined with the wide range of properties that can be obtained from different formulations has contributed to its widespread use.[19] To modify a less expensive polymer like PVC using additives or blend components so that competes with highly end biomaterial.

Not only because of the poor availability, but also due to difficulties in processing, no articles concerning the PVC /PLA based blends have been published.

The prime focus of this study is to elaborate bioblends based on PVC/PLA. Fundamental aspects of these bioblends were measured using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) under inert atmosphere. The morphological description and the information about the compatibility for different bioblends composition have been studied through scanning electron microscopy (SEM). The mechanical properties of the blends in terms of tensile modulus, stress, elongation at break, and micro-hardness were investigated.

EXPERIMENTAL

Bioblends Preparation
Commercial PVC (K value = 65) from ENEOS was used as received while PLA (2002D) obtained from NATUREWORKS was grinded and then heated at 90°C at least 12 h before using. The blends of PVC/PLA were premixed manually at ratios of 95/5, 90/10, 85/15, 80/20 and 75/25 (wt%) in the presence of 6% of Ca/Zn complex from BETAQUIMICA, 5% soya bean oil from HENKEL, 3% stearic acid from HENKEL, and 25% dioctyl phthlate (DOP) from LG based on the total PVC weight content in all composition. Maleic anhydride (MAHs) (BAYER) concentration was fixed at 4% and DCP's (BAYER) concentration fixed at 0.2% based on the total polymers weights for the *in situ* compatibilization.[20]

The bioblends were prepared by melt mixing in a Haake Rheomix Polydrive R 600/610 at 200°C and rotors speed 150 rpm for 5 min and at 160°C and 150 rpm for 6 min for the *in situ* compatibilization.

The blended hot samples were compression molded in an electrically heated hydraulic press. Hot press procedures involved preheating at 175°C for 10min, followed by compressing for 4 min (optimum time to have excellent sample without affecting visual degradation) at the same temperature.

Samples Characterization
Tensile Testing. Dumbbell specimens were cut from molded sheets with a Wallace die cutter S6/1/4A.

Tensile testing was carried out on an Inston tensile test machines model MTS 2/M according to the ASTM D882-91, with a crosshead speed of 30 mm/min. Young's modulus, stress and elongation at break were measured. The results of the tensile test were obtained by averaging the results of at least five measurements following the standard cited above.

Micro-Hardness Analysis
Vickers micro-hardness (Hv) measurements were carried out with a load of 50 g maintained for 15s using a Zwick 3212 micro-hardness tester. At every point, the average micro-hardness was determined from five separate measurements clustered uniformly around the selected position.

DSC Analysis
DSC was performed using a 240 F1NETZSCH apparatus. Each sample (6 ± 0.5 mg) was equilibrated at 0°, and then the temperature increased at 10°C/min to 200°C. At this temperature, an isotherm was maintained for 1min, then the sample was cooled at the same rate to 0°C and heated again from 0 to 200°C at 10°C/min. The glass transition temperatures (T_gs) were determined from the second heating scan. The first scan was meant to discard thermal history of the sample.

Thermo-Gravimetric Analysis
TGA was performed using a NETZSCH STA 449 instrument with a heating rate of 10°C/min from room temperature to 600°C under nitrogen atmosphere.

Scanning Electron Microscopy Characterization
Morphological studies were conducted using a scanning electron microscope JEOL (model JFM-6360 LV). Specimens were sputter-coated with gold to a thickness of ~10 nm before surface characterization to prevent charging. The SEM was equipped with a lanthanum hexaboride (LaB6) crystal as
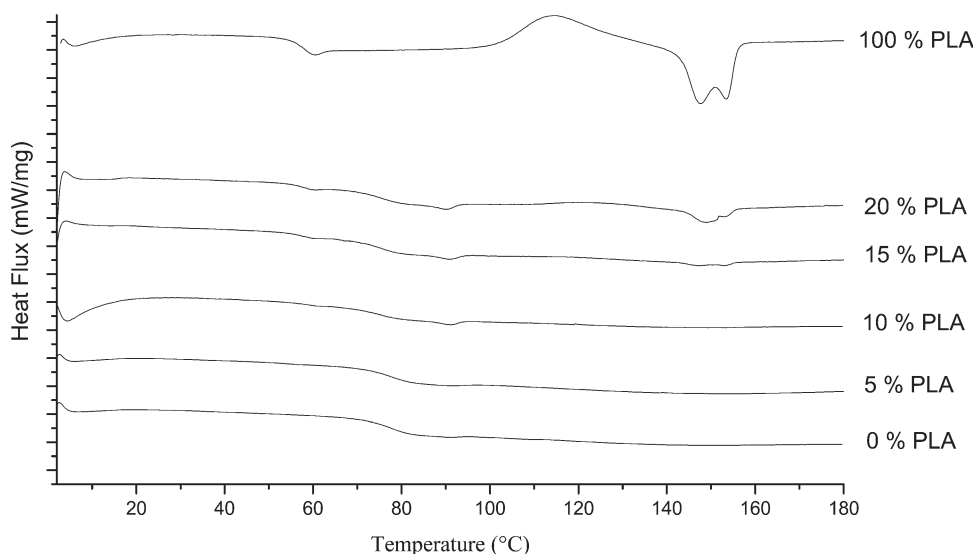
Figure 1. DSC thermograms of PVC/PLA blends.

electron emitter source. An accelerating voltage of 13 kV was used to collect the SEM image.

RESULTS AND DISCUSSION

Characterization of PVC/PLA Blends

DSC Analysis. The determination of the glass transition temperature allows to obtain indications about the miscibility of blends. Immiscible blends will retain the glass transition temperature of the original components, whereas miscible blends will show only one glass transition temperature. In our case, as could be expected, two glass transition temperatures were observed for our entire blends PVC/PLA (Figure 1 and Table I). So, in a first approach, our binary system exhibits the behavior expected for immiscible and incompatible blends. The incompatibility between the two polymers based blend PVC/PLA is due to the shrinkage of both PVC and PLA coil dimensions.

Mechanical Properties. Table II shows the effect of blends composition on the Young's modulus, stress and elongation at break and micro-hardness of PVC/PLA blends. As expected for the incompatible blends, the mechanical properties of the considered blends decreased with addition of PLA. This can be attributed to lack of interfacial interaction between the PLA dispersed phase and the PVC matrix. As the ratio of the PLA dispersed phase increased, the effective cross-sectional area of the PVC continuous phase was reduced subsequently, resulting in a decrease in tensile properties. Especially in 85/15 PVC/PLA blend which shows drastically decrease in results and this is may be due to the intensive agglomeration of PLA cross the PVC matrix.

In term of micro-hardness, the material is subjected to a compression stress that induces structural rearrangement on lamellar material. At small applied stresses, bonds rotations and lamellar shearing are envisaged, higher stresses could lead to chain scission and lamellae fracture. Micro-hardness values have a tendency to increase with increasing degree of crystallinity.[21] In our case, the increase in micro-hardness in the bioblends was due to the incorporation of PLA which is harder than the plasticized

PVC due to its semi-crystallinity. The value improved up to 10 wt % PLA beyond that the value decreased. The improvement was due the decrease in mobility of the intercalated polymer chains. At high PLA content, migration of PVC to the interface of the blends and poor interfacial adhesion between the two polymers at the surface might decrease the hardness.

SEM Analysis. Besides the mechanical measurements, phase separation is confirmed by SEM pictures as depicted in Figure 2. For immiscible blend, when one component is present in the blend at low concentration, a dispersed phase–matrix morphology is found, for which the shape of the dispersed particle can be spherical or fibrillar.[22] In our case the eggs particles of PLA are incorporated in a continuous phase which is the PVC matrix (intrusion). This confirms low adhesion between phases giving rise to poor stress across the interface.

TGA Analysis. The main use of TGA is to evaluate the thermal stability of polymers and their blends. The higher the decomposition temperature, the more stable the polymer or blend.

The influence of PLA in PVC matrix on the thermal stability of PVC/PLA blends was investigated by TGA analysis from room temperature to 600°C. The thermograms are given in Figure 3. Except for PLA, the thermal decomposition involved at least three steps of the degradation as measured from the peaks observed from the first derivative of the thermogravimetric (TG) curves. The corresponding data are given in Table III. The results showed that thermal decomposition of PLA occurred at

Table I. Glass Transition Temperature

PVC/PLA blends (wt %)	T_g1 (°C)	T_g2 (°C)
100/0	76.8	
90/10	76.8	57.2
85/15	76.8	57.5
80/20	76.2	57.4
0/100	58.2	

Table II. Mechanical Properties of PVC/PLA Blends

PVC/PLA blends	Modulus (MPa)	Stress at break (MPa)	Elongation at break (%)	Micro-hardness
100/0	183 ± 8	29 ± 1	433 ± 10	4.70 ± 0.09
95/5	168 ± 12	26 ± 1	448 ± 9	4.86 ± 0.08
90/10	160 ± 14	24 ± 1	424 ± 14	5.32 ± 0.15
85/15	114 ± 18	19 ± 1	295 ± 11	4.66 ± 0.10
80/20	162 ± 12	15 ± 1	178 ± 12	5.40 ± 0.14
75/25	229 ± 12	15 ± 1	253 ± 15	4.58 ± 0.15

358°C by statistical chains scissions followed by depolymerization and liberation of pure monomer. A 100% weight loss is attained.[6] Concerning PVC, the first stage corresponds to dehydrochlorination (DHC) of the polymer and the most abundant volatile product is HCl. The free volume induced by the presence of DOP allows a better diffusion of the produced HCl and leads to an increase of its autocatalytic effect on PVC DHC which results in more rapid consumption of the heat stabilizer. As the DHC of PVC results in the formation of conjugated double bonds, the second step of the thermal degradation represents the oxidation of polyenes to compounds of lower molecular masses. It is accompanied by the evaporation of the DOP plasticizer which leads to the creation of voids around the chlorine atoms, making their release and diffusion easier. A weight loss of 63.60% was measured at the end of this step. The second and third steps are parallel. Cracking of some carbon–carbon bonds of the previous polyene structures occurs where monocyclic and polycyclic aromatics compounds like benzene, toluene and naphthalene derivatives obtained by cyclization of the conjugated olefin intermediate structures are found and are formed rather than aliphatic structures.[23]

The thermal degradation of the blends appeared to be a cumulative phenomenon of the thermal degradation of the matrix (PVC) and the filler (PLA).

During the stages 1, 2, 3, and 4, PLA exerted a stabilizing effect on the blend which is confirmed by the increase of T_{max} (Table III). The weight loss of the blend at 280°C relative to both PVC and PLA components was different, i.e., 100% PVC degradation was 39.35% ($W_1 + W_2$), 10% PLA was 37.23%, 20% PLA was 30.21%, 100% PLA was 2.08%. This is another way to show that PLA increases the thermal stability of PVC.

Characterization of PVC/PLA/MAH Blends
DSC Analysis. Two glass transition temperatures were observed for the blends PVC/PLA/MAH (Figure 4 and Table IV). So, in a first approach, this system exhibits the behavior expected for immiscible blends.

MAH is used as a reactive compatibilizer with DCP, it has an extremely low tendency to homopolymerize in radical polymerization condition; on the contrary, it copolymerizes with variety of donor monomers.[24]

MAH grafted on PLA and leads to decrease the T_g of PLA compared to that of pure blend. It is known that plasticizer decreases the glass transition of polymer. Though MAH was introduced as a reactive compatibilizer, MAH might act as a

plasticizer as well in this blend.[25] Hwang et al. found that grafting of MAH on PLA decreases also the glass transition temperature and the crystallinity of PLA.[26]

On the other hand, the glass transition temperature of PVC increased. This cannot be attributed to the crosslinking of PVC since the blends became absolutely soluble in THF.[27] It is probably due to the formation of MAHgPVC. The incorporation of MAH as a side group on PVC chains decreases the free volume by expanding the polymer chains and therefore the rigidity and
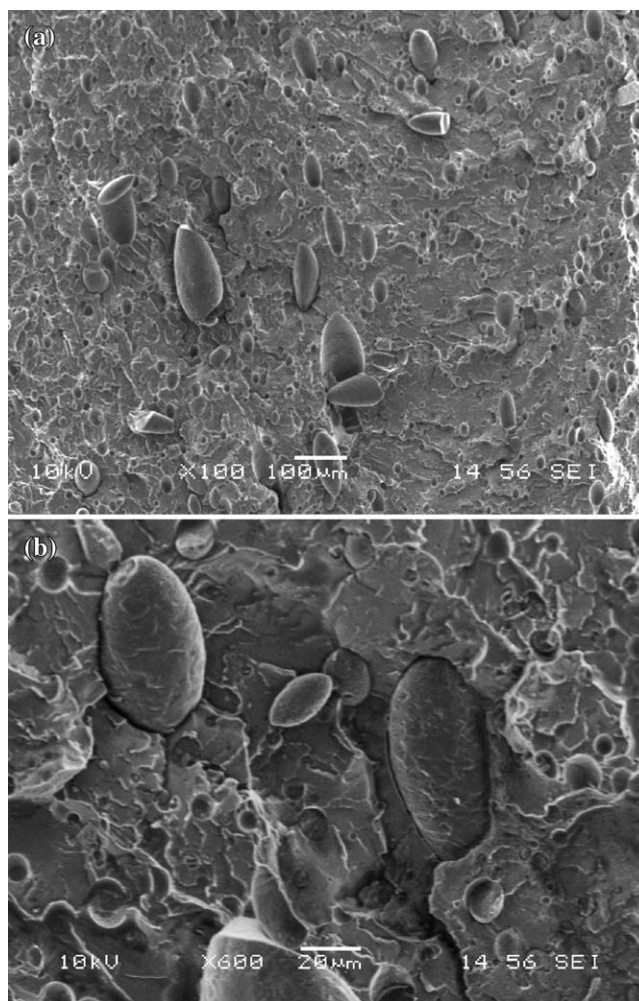

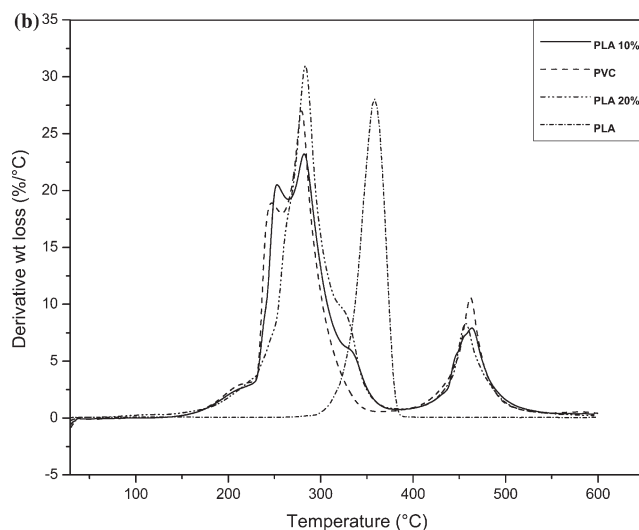**Figure 2.** Scanning micrographs of the fractured surfaces for PVC/PLA blends (80/20).
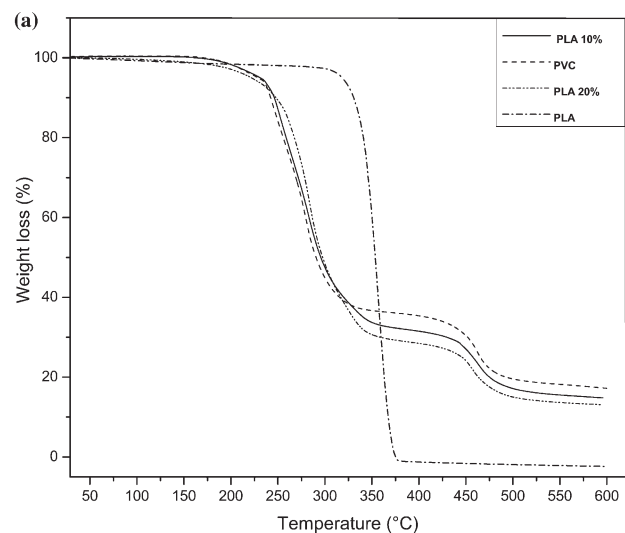
Figure 3. TG and DTGA curves of PVC/PLA blends.

Figure 4. DSC Thermograms of PVC/PLA/MAH blends.

Table IV. Glass Transition Temperature

PVC/PLA/MAH blends	T_g1 (°C)	T_g2 (°C)
90/10	48.0	103.6
80/20	48.1	104.5

adhesion between PVC and PLA. This phenomenon can be explained in terms of strong interfacial interaction of PLA with PVC matrix. In fact the introduction of PLA which is a brittle material leads to early breaks at lower elongations and stress at break (high modulus and low strain are the shortages of PLA[28]). As the inclusion of PLA increases, the stiffness and brittleness of the blends increase with an associated decrease in stress at break and elongation at break. In the first case (absence of MAH), PLA was introduced as non-treated charges which decreased the mechanical properties of the blends. However, when introducing MAH, it behaves as dispersing agent among the polymers resulting in improved interfacial adhesion and making PLA acts as a reinforcement agent in PVC matrix.

One can see very clearly that MAH increased the hardness of the blends due to the improvement of the interfacial adhesion between the two polymers. The maximum micro-hardness is achieved at 10% PLA.

stiffness increased which leads to the increase of the glass transition temperature of PVC.

Mechanical Properties. At a similar blend composition (Table V) and when introducing MAH as compatibilizer, the blends show higher Young's modulus but lower stress and elongation at break. This is due to the enhancement in interfacial
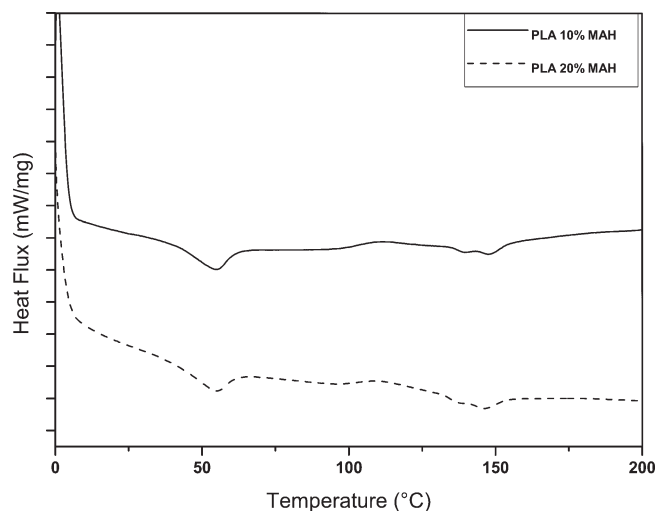
Table III. Thermogravimetric Data of PVC/PLA Blends

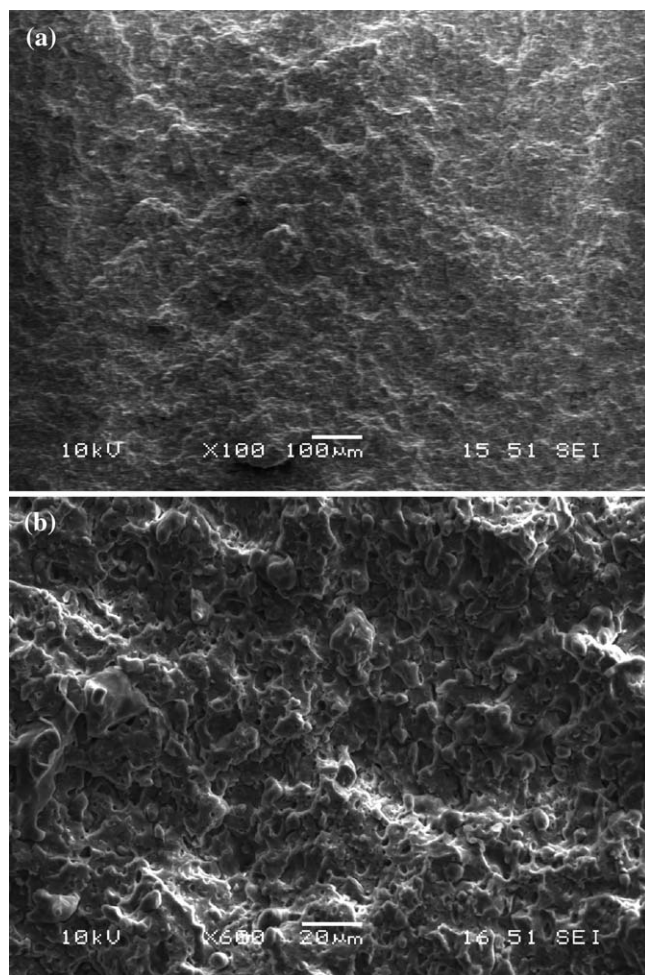|	Stage 1		Stage 2		Stage 3		Stage 4		Stage 5		
PVC/PLA	W_1	T_{max}	W_2	T_{max}	W_3	T_{max}	W_4	T_{max}	W_f	T_f	W_{total}
100/0	12	243	27	280		–	35	463	9	600	82
90/10	16	254	23	283	21	323	17	464	8	600	85
80/20	0	–	37	283	29	329	13	459	8	600	87
0/100			0		67	358			33	600	100

W: weight loss (%).

T_{max}: temperature of maximum weight loss, W_{total}: total of weight loss in stages 1, 2, 3, 4 and 5 (%).

Table V. Mechanical Properties of PVC/PLA/MAH Blends

PVC/PLA/MAH blends	Modulus (MPa)	Stress at break (MPa)	Elongation at break (%)	Micro-hardness
95/5	181 ± 23	27 ± 2	404 ± 22	5.20 ± 0.14
90/10	333 ± 13	25 ± 1	335 ± 25	7.32 ± 0.19
85/15	338 ± 35	17 ± 2	223 ± 29	7.16 ± 0.05
80/20	354 ± 24	16 ± 1	228 ± 13	6.24 ± 0.44
75/25	415 ± 23	13 ± 1	183 ± 12	5.60 ± 0.14

SEM Analysis. Figure 5 shows that the eggs particles disappeared and a more homogeneous rough surface can be observed. It means that with the presence of MAH there is better dispersion of PLA in PVC matrix indicating improvement in compatibility between PLA and PVC. In other terms this solubility of PLA in the PVC matrix indicates the effect of increased interaction between phases, thus improving compatibility and enhancing the mechanical properties in terms of tensile modulus.

TGA Analysis. The influence of PLA in the PVC matrix on the thermal stability of PVC/PLA blends in the presence of MAH was investigated by TG analysis. The thermograms are given in Figure 6.

The profile of the blends showed four degradation steps representing the components of the blends (three steps for PVC and one for PLA).

Montrikool et al.[29] found that by mixing MAH with PVC prior the pyrolysis, the DHC of PVC was retarded. This is confirmed by the increase in T_{max} with the presence of MAH for example for 90/10 PVC/PLA blend T_{max} were at 263, 286, and 335°C in presence of MAH instead of 254, 283, and 323°C in the absence of MAH.
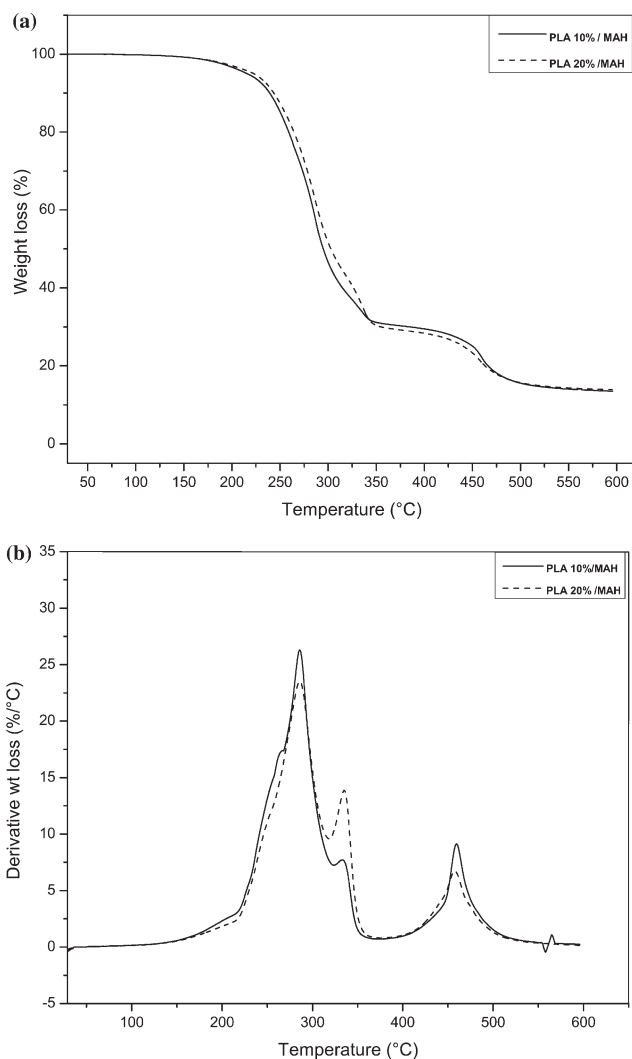

Figure 5. Scanning micrographs of the fractured surfaces for PVC/PLA/MAH blends (80/20).

Figure 6. TG and DTG of PVC/PLA/MAH blends.

Table VI. Thermogravimetric Data of PVC/PLA/MAH Blends

PVC/PLA/MAH	Stage 1		Stage 2		Stage 3		Stage 4		Stage 5		
	W_1	T_{max}	W_2	T_{max}	W_3	T_{max}	W_4	T_{max}	W_f	T_f	W_{total}
90/10	25	263	18	286	22	335	12	459	9	600	86
80/20	0	–	36	286	27	335	15	457	8	600	86

W: weight loss (%).
T_{max}: temperature of maximum weight loss, W_{total}: total of weight loss in stages 1, 2, 3, 4, and 5 (%).

MAH exerted a stabilizing effect on the blends by increasing interactions between PVC and PLA which were confirmed by the decrease in weight loss of the blends at 286°C relative to both PVC and PLA components which was different, i.e., 100% PVC percent degradation was 48%, 10% PLA was 43%, 20% PLA was 36%, 100% PLA was 2%. This is another way to show that PLA increased the thermal stability of PVC.

CONCLUSIONS

This study focuses on the elaboration and characterization of new bioblends based on PVC/PLA. PLA was added as a charge on PVC matrix without exceeding the amount of 25 wt %. The binary blends are not miscible and exhibited lower properties than those of separated polymers. PLA exerted a stabilizing effect on thermal degradation of PVC in stages1 and 2 by increasing T_{max}. However A better compatibility was found when introducing MAH. Young's modulus increased with PLA while micro-hardness showed an optimum value at 10% PLA. Microscopic observations revealed uniformly dispersed PLA in the PVC matrix, confirming that phase separation has disappeared in the presence of MAH. Formation of MAHgPVC is confirmed by the increase of glass transition temperature of PVC. The incorporation of MAH has expanded the coil dimension among PVC and PLA due to the strong intermolecular interaction that made them compatible. PVC/PLA/MAH blends showed better thermal stability than PVC/PLA blends.

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