CELLULOSE CHEMISTRY AND TECHNOLOGY

LDPE/GLUCURONOXYLAN BLENDS: PREPARATION AND STUDY OF THERMAL AND MECHANICAL PROPERTIES

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The continually growing utilization of non-degradable and environment-unfriendly polymeric materials stimulates further research on their possible applications. Estimates show that 2% of all plastics eventually reach the environment, extensively contributing to the currently acute ecological problem. The present study, concentrated on the preparation of natural and synthetic degradable polymers and of their blends, deals with the preparation of low density polyethylene (LDPE) and glucuronoxylan (LX) blends and of their laurate (LaCOLX) with DS = 1.9, in four different amounts (1, 3, 5, 10 wt%), with and without poly(ethylene-co-acrylic) acid (EAA) as a compatibilizer, in three different amounts (10, 25 and 50 wt%) with respect to polysaccharide. The compatibility of the LDPE/LaCOLX prepared blends has been studied by ATR (Attenuated Total Reflectance) spectroscopy and REM (Reflection Electron Microscopy). The presence of the LaCOLX filler and the effect of the compatibilizer have been studied *versus* the mechanical properties (tensile strength, elongation at break and Young's Modulus) of the blends. The prepared LDPE/LaCOLX blends, containing 25 and 50 wt% EAA, evidenced good mechanical properties. The increasing amount of LaCOLX and the presence of the compatibilizer had positive effects on the thermal stability of LDPE/LaCOLX blends.

Keywords: 4-O-methyl-D-glucurono-D-xylan, low-density polyethylene, blends, thermo-mechanical properties

INTRODUCTION

The replacement of some synthetic polymers by natural polysaccharides is very interesting, both economically and ecologically.[1-3] The application of polysaccharides in polymeric blends contributes to solving ecological problems, by partially substituting the environmentally unfriendly synthetic polymers. Considering the low price and wide availability of polysaccharides, their application in combination with polyolefins is of economic interest, as well.

Polysaccharides are natural polymers belonging to the most renewable sources on Earth, present in all organisms forming the plant life. Polysaccharides play an important role primarily as structural components of plants, animals, fungi or microorganisms (*e.g.* cellulose), and also as an energy source for various biochemical reactions (*e.g.* starch). Polysaccharides also have widespread utilization in the food and pharmaceutical industry. It is assumed that polysaccharides, such as cellulose, starch, xylans, chitin and hemicelluloses, will have an ever-rising industrial status.[4,5] The production of new polymeric blends is, however, impeded by the immiscibility that characterizes most of the polymers. Mutual immiscibility due to the different structure of the components has a negative influence on the properties of blended materials.[6,7] Immiscibility becomes evident by the phase separation of particular components. These characteristics have a negative influence on properties, such as toughness, tensile strength, elongation of the resulting material. The negative effects could be suppressed by a *compatibilizer*, which improves interfacial adhesion of the immiscible polymer blends, thus decreasing surface energy, improving and stabilizing the required morphology. The strategy of compatibilization is based on the addition of block/graft copolymers forming miscible blocks with one or another homopolymer. The compatibilizer is able to decrease interfacial tension and to create a more stable structure.[8,9]

The present work, continuing a previous investigation,[10] is focused on the possible application of Lenzing® (LX) xylan and of its more thermostable laurate (LaCOLX, DS 1.9) in polymeric blends. As a matrix material, low-density polyethylene (LDPE) was used, together with poly(ethylene-co-acrylic acid) (EAA) as a compatibilizer, for improving the interfacial adhesion of the prepared blends. All assumed structural changes caused by the above-mentioned ingredients are reflected on the measured tensile test curves.

EXPERIMENTAL

Materials

Low-density polyethylene (LDPE) BRALEN RB 2-62, the suitable EN 71 part 3 (Slovnaft Petrochemicals, Slovak Republic) appropriate for packing applications, was used. Poly(ethylene-co-acrylic acid) (EAA) containing 15 wt% acrylic acid was supplied by Aldrich (Germany). Water-insoluble glucuronoxylan (LX), a by-product of viscose production from beech sulfite pulp, was a gift from Lenzing AG (Austria): Xyl = 92.5% (of neutral sugars), 4-O-methylglucuronic acid (MeGUA) = 3.7%, M_w ~ 5000 g.mol^{-1}. Glucuronoxylan Lenzing laurate (LaCOLX) with a degree of substitution, *i.e.* average number of substituted hydroxyl groups per D-xylopyranose unit, DS = 1.9, was prepared by the reaction with lauroyl chloride.[11]

Melt blending

Lenzing glucuronoxylan and its laurate were melt-blended with LDPE in a Brabender Plasti–Corder PLE 331. Mixing was performed at 140 °C and 80 rpm for 15 min. For the LDPE/LaCOLX blends, four different amounts of polysaccharide were used, namely 1, 3, 5 and 10 wt%, and EAA was used as a compatibilizer in three different amounts, namely 10, 25 and 50 wt%, with respect to the polysaccharide.

Attenuated Total Reflectance (ATR) measurements

The ATR spectra were plotted on a NICOLET 6700 spectrometer (resolution 4 cm^{-1}), equipped with a DTGS detector and OMNIC 3.2 software. The samples occurred as thin, 7 μm thick films prepared by hot press moulding.

Mechanical properties

Measurements of the mechanical properties, such as tensile strength and elongation at break, were performed by the Instron Corporation Material Testing System 1.04, at 5 mm.min^{-1} crosshead speeds. Five measurements of each sample were performed, the average values obtained being reported in Figures 6 to 8. The maximum percentage error did not exceed 10%.

Thermogravimetric (TGA) measurements

TGA measurements were performed on a Thermobalance Mettler Toledo TGA/SDTA 851^{e} thermogravimetric analyzer, under nitrogen atmosphere, at a heating rate of 10 °C.min^{-1} up to 600 °C. The mass loss permits to estimate both the glucuronoxylan laurate content and the thermal stability of the blends.

REM (Reflection Electron Microscopy)

For taking micrographs of specimens after their fracture, a reflection electron microscope (Tesla BS300) was used, at an accelerating voltage of 20 kV, in an automatic sputter coater TESCA with software WinTip 3.1.

Differential Scanning Calorimetry (DSC) measurements

The DSC measurements were done on a Mettler Toledo DSC 821^{e}, over temperature ranges from -30 °C to 350 °C, or 5 °C to 160 °C, at a scan rate of 10 °C.min^{-1}, under nitrogen atmosphere.

RESULTS AND DISCUSSION

The compatibility of LDPE/LaCOLX blends was studied by means of ATR spectroscopy. 4-*O*-methylglucuronoxylan (GX) belongs to the standard types of xylan. Its main chain consists of D-xylopyranose units linked by a (1-4)-β-glycosidic linkage, as shown in Figure 1. 4-*O*-methylglucuronoxylan is found in hardwood and in other dicotyledonous plants. D-glucuronic acid, which is mostly present in 4-*O*-methylene form, is linked to the main chain by 1-2 (rarely 1-3)-α-glycosidic linkages. The presence of the α-D-glucuronic side chains increases the resistance of some (1-4)-β-glycosidic linkages in the xylan molecule against acid hydrolysis.[12]

The spectrum of the initial Lenzing glucuronoxylan (Fig. 2) shows bands at 894-1164 cm^{-1}, corresponding to the anhydroglucose unit of xylan. The band at 1635 cm^{-1} corresponds to the $\nu_{as}(COO^{-})$

vibration of the carboxylic group, while the characteristic band at 1733 cm^{-1} refers to the presence of ν(CO) vibration of the ester group. The lauroyl groups reduce the presence of OH groups, occurring as a broad absorption band of ν(OH) vibrations at 3355 cm^{-1}. The characteristic bands at 2955 and 1740 cm^{-1}, corresponding to ν(CH$_2$) and ν(CO) vibrations, respectively, increase in the laurate spectrum of Lenzing (LaCOLX) xylan. The band of ν_s(COO$^-$) vibration at 1467 cm^{-1} refers to the residual uronic acid in xylan. The high degree of LaCOLX substitution (DS 1.9) is explained by the fact that almost all OH groups of the xylan glucopyranose units are substituted with acyl residue of lauric acid. In the case of compatible blends, the spectrum is considerably shifted, compared to a pure polymer. In the case of incompatible blends, the characteristic absorption spectrum agrees with the spectrum of the pure polymer component.[13]

Figure 3 plots the ATR spectra of the pure LDPE, LDPE/LaCOLX blend containing 10 wt% LaCOLX and of the compatibilized LDPE/LaCOLX blend containing 10 wt% LaCOLX and 50 wt% EAA as a compatibilizer. The presence of the EAA compatibilizer in the blend is proved by the vibration band at 1701 cm^{-1}, corresponding to the free acid. The carboxyl group of the EAA compatibilizer forms hydrogen bonds with the hydroxyl groups of the polysaccharide. The higher the concentration of the compatibilizer, the higher is the concentration of carboxylic groups, leading probably to more hydrogen bonds at the interface. This phenomenon is one of the important factors affecting blend compatibility.[14] The intensity of the ν(CO) vibration band at 1740 cm^{-1}, in the case of LDPE/LaCOLX with 50 wt% EAA, is higher than in the case of LDPE/LaCOLX without the EAA compatibilizer.

For the LDPE/LaCOLX/EAA blends, the second derivatives of the ATR spectra have been used to detect the formation of hydrogen bonds of the carboxyl group of EAA compatibilizer with hydroxyl groups of the polysaccharide, analogously to the procedure used by Bastioli.[15]

To study this type of bonding, occurring also in our blends, the second derivatives of the ATR spectra were calculated (Fig. 4). In spectroscopy, they are used for the separation and identification of the overlapping absorption bands. The second derivative of the absorption spectrum of a molecule is defined as the second derivative – $d^2A/d\tilde{\nu}^2$ – of absorbance A, as a function of wavenumber, $\tilde{\nu}$. When LaCOLX is blended with LDPE using the EAA copolymer (50 wt%), the peak at 956 cm^{-1} shifts to lower values – of 954 cm^{-1}. This shift may be due to the ability of EAA to form hydrogen bonds with LaCOLX.

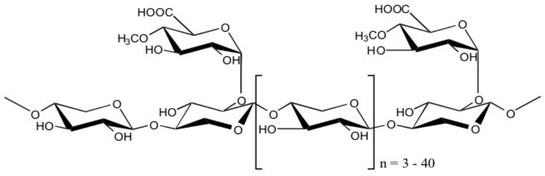

Figure 1: Structural unit of glucuronoxylan[12]

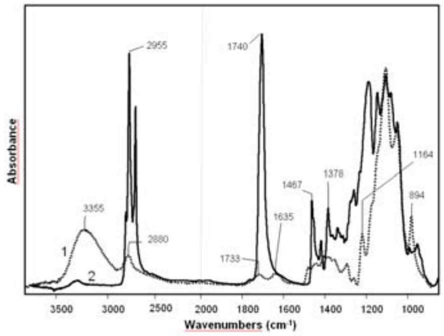

Figure 2: ATR spectra of pure Lenzing xylan (line 1) and laurate xylan of LX with DS 1.9 (line 2)

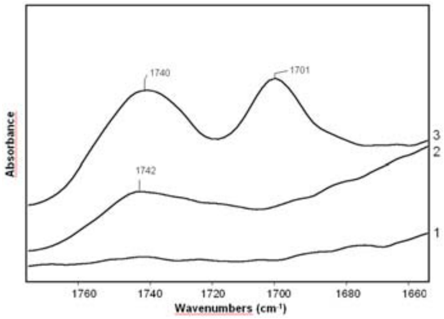

Figure 3: ATR spectra of pure LDPE (line 1) and LDPE/LaCOLX (10 wt%) blends with 50 wt% EAA (line 3) and without EAA (line 2) as a compatibilizer

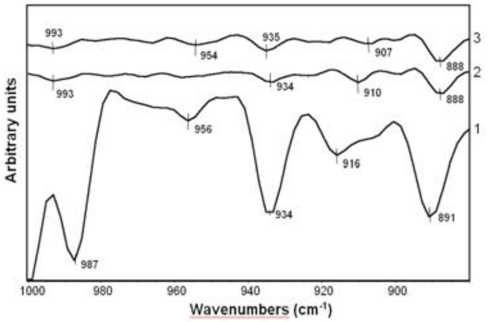

Figure 4: Second derivation of ATR spectra of LaCOLX, DS 1.9 (line 1), and LDPE + 10 wt% LaCOLX without EAA (line 2) and with 50 wt% EAA (line 3)

The modification of polysaccharides by incorporation of hydrophobic groups into the macromolecule caused the increase of interfacial adhesion with the synthetic polymer.[6,13] Figures 6-7 show the influence of xylan and of its LaCOLX derivative on the tensile strength and elongation at the break of the uncompatibilized blends. The tensile strength and elongation at break of the uncompatibilized blends decrease with increasing the amount of filler (LX or LaCOLX). The decrease is caused by the inhomogeneity of the LDPE/polysaccharide blends, as shown by microscopic observations (Fig. 5a).

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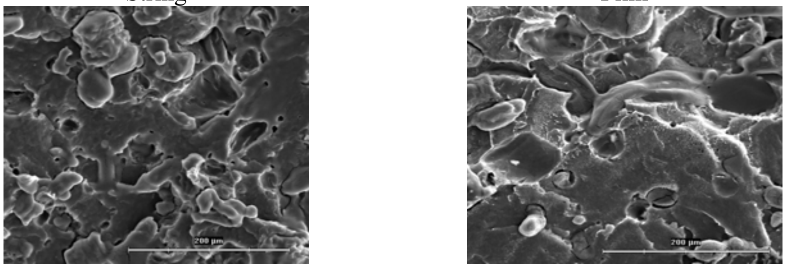
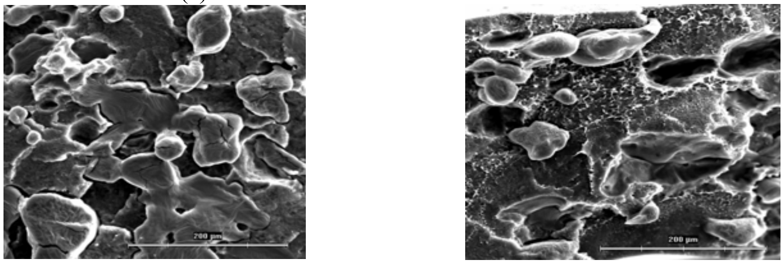
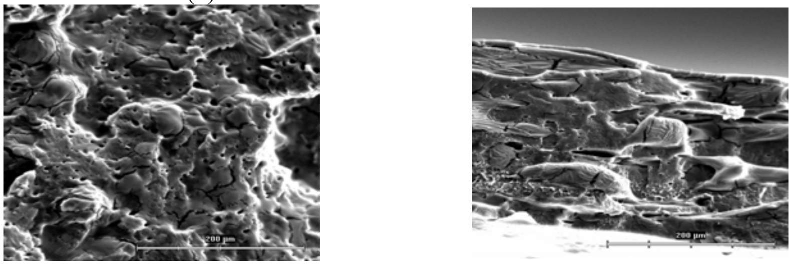


(a) LDPE/10 wt% LaCOLX/0 wt% EAA



(b) LDPE/5 wt% LaCOLX/10 wt% EAA



(c) LDPE/10 wt% LaCOLX/50 wt% EAA

Figure 5: REM photographs of LDPE/LaCOLX blends with different amounts of LaCOLX and EAA

LaCOLX is almost fully hydrophobicized; however, its glucopyranose units preserve their hydrophilic character, which has a negative effect on the mechanical properties of the prepared blends, because of the weak interfacial adhesion with polyethylene. The prevailing hydrophilicity of the glucoroxylan estherified with DS 1.9 (LaCOLX) prevents the formation of a continuous phase with the synthetic polymer (LDPE).

REM microscopy confirmed that the laurate of xylan LX is dispersed into larger domains with insufficient compatibility, as also visually confirmed during LaCOLX mixing with polyethylene (Fig. 5a).

Another possibility of improving the compatibility between two immiscible polymers is the utilization of a compatibilizer, meaning that the compound is able to form hydrogen bonds with the hydroxyl groups of the natural polymer or with its derivative. The EAA compatibilizer contains polyethylene segments and acrylic acid units, capable to form a stable complex with the polysaccharide as a result of the hydrogen bonds between the carboxylic groups of acrylic acid and the hydroxyl groups of polysaccharide.[16]

Hydrogen bonding was also recognized in polymeric blends consisting of poly(vinyl alcohol), poly(vinyl phenol), poly(vinyl acetate) or polymers containing carbonyl groups.[17-19] Also, improved compatibility between LDPE and LaCOLX was expected when using an EAA compatibilizer. Figure 6 shows the tensile strength of EAA compatibilized LDPE/LaCOLX blends. It is obvious that, with increasing the amount of LaCOLX, tensile strength decreases. The addition of an EAA compatibilizer (25 and 50 wt%) has a positive effect on tensile strength, especially in the case of the blend with 5 wt% LaCOLX content, comparatively with the uncompatibilized blends.

The compatibility degree of the polymeric blends is monitored over a range from totally miscible systems to phase separation. Compatibility, which is a function of polymeric molecule interactions in blends, can be studied by various methods, including mechanical and interfacial measurements.[20] In compatible blends, mechanical properties, such as tensile strength and Young's modulus, show linear functionality *vs.* blend composition. It is generally true that the negative deviation from the linear dependence is considered as a sign of poor compatibility between components, whereas a positive deviation is considered as a sign of improved compatibility.[21]

Figure 7 shows elongation at break of the samples of LDPE/LaCOLX blends with a varying amount of EAA compatibilizer. The addition of compatibilizer had a positive effect, especially in the case of blends with 3 and 5 wt% LaCOLX. The highest improvement was recorded in blends with 25 and 50 wt% EAA. Similarly, elongation at break decreases with increasing the content of LaCOLX at any amount of compatibilizer.

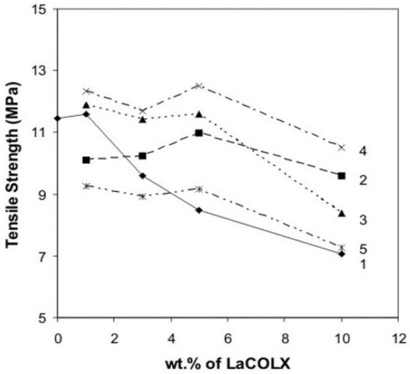


Figure 6: Tensile strength of EAA compatibilized blends of LDPE/LaCOLX with 0 wt% EAA (line 1); 10 wt% EAA (line 2); 25 wt% EAA (line 3); 50 wt% EAA (line 4) and LDPE/LX blend without EAA (line 5), as a function of LaCOLX (LX) content

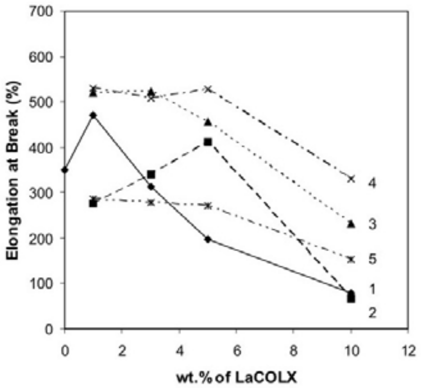


Figure 7: Elongation at break of EAA compatibilized blends of LDPE/LaCOLX with 0 wt% EAA (line 1); 10 wt% EAA (line 2); 25 wt% EAA (line 3); 50 wt% EAA (line 4) and LDPE/LX blend without EAA (line 5), as a function of LaCOLX (LX) content

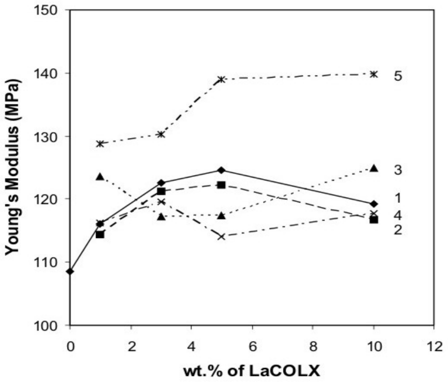


Figure 8: Young's modulus of EAA compatibilized blends of LDPE/LaCOLX with 0 wt% EAA (line 1); 10 wt% EAA (line 2); 25 wt% EAA (line 3); 50 wt% EAA (line 4) and LDPE/LX blend without EAA (line 5), as a function of LaCOLX (LX) content

Figure 7 plots some maxima (at least for LDPE/LaCOLX blends with 10 wt% EAA), a situation possibly caused by a measurement error.

The polysaccharide part of the synthetic polymer tends to affect polymer properties. In synthetic blends, the addition of another immiscible phase into the matrix causes a sharp decrease of elongation at break.[22] In such blends, elongation at break is affected by the interfacial interaction between matrix and filler. The reported[23] polysaccharide amount was of 15 wt%. At higher filler amounts, elongation at break and tensile strength dropped sharply. On the contrary, a slow decrease in tensile strength was noticed with increasing the polysaccharide content.[22] Elongation at break dropped sharply at 10 wt% polysaccharide. Several theories were proposed to express the dependence of composite properties on the volume fraction of the filler. One of the simplest is Nielsen's theory, which describes elongation providing an ideal adhesion between filler and the polymeric matrix.[24] Another is Nicolais-Nakri's theory, describing tensile strength.[24] Both theories, applied to LDPE/starch blends,[24] showed a good agreement with the theoretical assumptions. However, the application of these theories was not suitable in our case. The low agreement between theory and experimental data of tensile strength and elongation of break was ascribed to poor interfacial adhesion. As already mentioned, Nielsen's theory assumes an ideal adhesion of the two phases.

Young's modulus of the prepared LDPE/LaCOLX and LX blends with and without an EAA compatibilizer was measured by expressing the degree of material rigidity. According to Figure 8, Young's modulus decreases with increasing the amount of LaCOLX from 3 to 10 wt%, in blends with 25 and 50 wt% EAA. In the case of uncompatibilized blends containing 10 wt% EAA, Young's modulus rises slowly and moderately with increasing the content of LaCOLX and LX up to 5 wt%. Generally, Young's modulus is closely associated[25] with material rigidity. Blending of a natural polymer into polyethylene leads to higher standard deviations of Young's modulus, compared to monodispersive systems. This is caused either by the compatibilizer (EAA) or by the presence of filler (LaCOLX). Incompatibilized blends and blends with 10 wt% compatibilizer and more than 5 wt% LaCOLX filler show a decreasing tendency of Young's modulus, probably caused by a lower rigidity of xylan associates.

The thermostability (the quality of a substance to resist irreversible changes in its chemical or physical structure at a relatively high temperature) of LDPE/LaCOLX blends without an EAA compatibilizer, as well as of the initial LDPE, was observed by TGA. Lenzing xylan is thermostable up to temperatures of about 240-244 °C. Esterification of LX xylan by acylchlorides increases its thermostability. LaCOLX with a DS of 1.9 is stable at about 266-273 °C. The good thermostability of LaCOLX is caused by the lower OH group content in the polysaccharide. Polyethylene is thermostable at temperatures of up to 434 °C. The addition of 5-10 wt% LaCOLX influences the beginning of decomposition T_{onset}, which means that temperature rises up to 441 °C, in both cases. Thermal decomposition of LDPE and of its blends with both LX and LaCOLX (5 wt%) with varying amounts of EAA compatibilizer was observed by TGA. The prepared blends showed very good thermostability. LaCOLX decomposition was not observed[10,26] until 320-331 °C, while LDPE decomposition occurs at higher temperatures. The compatibilized LDPE/LaCOLX (5 wt%) blends exhibited better thermostability compared to the LDPE/LX (5 wt%) blends without EAA compatibilizer. LDPE/LX blend decomposition is a two-step process. The former, at 258-301 °C, is typical of the decomposition of Lenzing xylan, the so-called pyrolytic evaporation. As known, the process of thermal decomposition of polysaccharides releases CO_2, low aldehydes, methyl furans and ketones.[27] The better thermostability of the LDPE/LaCOLX blends, compared to that of the LDPE/LX ones, could be caused by the lower content of OH groups in LaCOLX, comparatively with initial xylan.

The thermostability of LDPE/LaCOLX blends was improved by the presence of the EAA compatibilizer. The two peaks observed in the LDPE/LX blend thermogram at 301 and 485 °C correspond to LX and LDPE, respectively. In the case of compatibilized blends, LDPE decomposition was shifted to higher temperatures with increasing the content of both LaCOLX and EAA in the blend, which is an evidence of the presence of molecular interactions between the synthetic polymer (LDPE) and the polysaccharide.[28] It can be concluded that the presence of compatibilizer and of an increasing amount of LaCOLX has a positive effect on the thermal properties of the LDPE blends.

The thermal properties of LDPE/LaCOLX blends with and without EAA compatibilizer were also tested by means of DSC, only small differences being recorded in the DSC thermograms of the tested blends, compared to those of pure PE (Fig. 9). With increasing the content of LaCOLX, the endothermic peak was slightly shifted to lower temperatures. The melting temperature (T_m) and enthalpy changes (ΔH) of LDPE/LaCOLX blends with various polysaccharide contents are listed in Table 1.

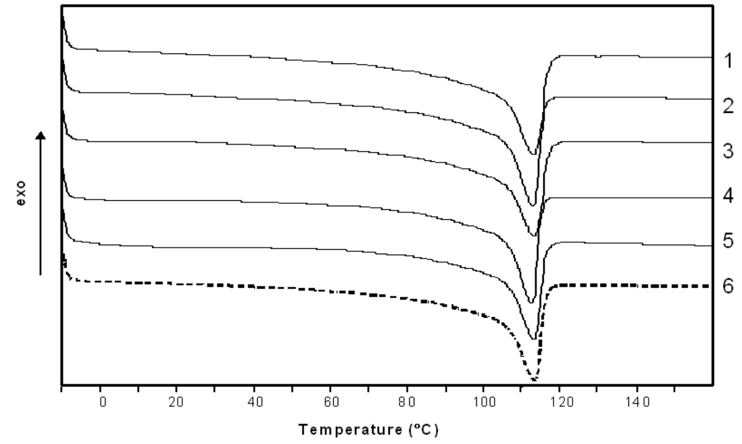


Figure 9: DSC thermograms (secondary melting) of LDPE (line 1) and uncompatibilized LDPE/LaCOLX blends with 1 wt% LaCOLX (line 2); 3 wt% LaCOLX (line 3); 5 wt% LaCOLX (line 4); 10 wt% LaCOLX (line 5) and LDPE/LX blend with 5 wt% LX (line 6)

The Flory-Huggins interaction parameter (χ_{12}) for polymeric blends containing a crystalline polymer is expressed by the difference of melting temperatures, according to the well-known Wang-Nishi equation:[29]

$$\frac{1}{T_m}-\frac{1}{T_m^0}=-\frac{R.V_2}{\Delta H_f^0.V_1}\chi_{12}(1-\varphi_2)^2$$

where T_m and T_m^0 are the melting temperatures of the crystalline polymer in blend and pure polymer, V_2 is the molar volume of the repeating crystal unit, ΔH_f^0 is the melting heat and ϕ_2 is the volume fraction of the crystal part. Negative values of χ_{12} are expected for miscible blends, therefore $T_m < T_m^0$ (the melting temperature decreases).

Table 1
Melting heat of LDPE depending on increasing filler (LaCOLX) concentration during primary and secondary heating

Amount of filler (wt%)	Tm_1 (°C)	ΔH_1 ($J.g_{PE}^{-1}$)	Tm_2 (°C)	ΔH_2 ($J.g_{PE}^{-1}$)
0	113.9	124.8	113.2	127.3
1	112.4	120.3	112.0	126.1
3	113.4	119.8	112.1	124.8
5	112.8	116.7	111.9	119.6
10	113.9	121.1	113.4	125.8
10*	113.3	126.6	113.1	127.4

*with 5 wt% EAA

Table 1 shows a small decrease of Tm, a rare phenomenon, depending on blend composition. This is probably due to the low (zero to negative) values of the interaction parameter between polymers.[29] It can be concluded that no distinct differences in the behaviour of LDPE/LaCOLX blends were observed during melting. LDPE is hardly miscible with LaCOLX, or the interactions between LDPE and LaCOLX are very poor. It is expected that pure LDPE will show a large amount of the crystalline phase. On the contrary, the addition of LaCOLX (10 wt%) causes a decrease of the crystalline phase, while the synergism of LaCOLX and EAA (5 wt%) influences the melting heat value, which is comparable with pure LDPE.

CONCLUSIONS

A series of LDPE/LaCOLX blends have been prepared and extensively studied as to their thermomechanical behaviour and the conclusions below were reached.

Tensile strength and elongation at break of uncompatibilized blends decrease with increasing the content of filler (LX or LaCOLX). The addition of 25 or 50 wt% EAA has a positive effect on tensile strength and elongation at break, especially in blends containing 3 and 5 wt% LaCOLX.

LDPE/LX blend decomposition is a two-step process. The former, occurring at 258-301 °C, is typical of the decomposition of Lenzing xylan, while the latter, appearing at higher temperatures, is due to LDPE decomposition.

The presence of a compatibilizer and of an increasing amount of LaCOLX has positive effects on the thermal properties of the blends.

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