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Plasticization of Poly(L-lactide) with Poly(propylene glycol)

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A new plasticizer for poly(L-lactide) (PLA)−poly(propylene glycol) (PPG) is proposed. The advantage of using PPG is that it does not crystallize, has low glass transition temperature, and is miscible with PLA. PLA was plasticized with PPGs with nominal M_w of 425 and 1000 g/mol. Poly(ethylene glycol) (PEG), long known as a plasticizer for PLA, with nominal M_w of 600 g/mol, was also used to plasticize PLA for comparison. The thermal and tensile properties of PLA and PLA with 5−12.5 wt % of the plasticizers were studied. In blends of PLA with PPGs the glass transition temperature was lower than that of neat PLA. Both PPGs enhanced the crystallizability of PLA albeit less than PEG. All of the plasticizers increased also the ability of PLA to plastic deformation which was reflected in a decrease of yield stress and in an increase of elongation at break. The effect was enhanced by the higher PPG content and also by lower molecular weight of PPG. A phase separation occurred only in the blend containing 12.5 wt % of PPG with higher molecular weight. The evidences of crazing were found in deformed samples of PLA with low plasticizer content, whereas the samples with higher content of plasticizers crystallized due to deformation.

Introduction

Poly(lactide), a biodegradable polymer which can also be produced from annually renewable resources, has gained recently a growing attention.[1]

The chiral center in the structure allows the enantiomeric compositions of poly(lactide) to vary. Although both optically pure poly(L-lactide) (PLA) and poly(D-lactide) are the crystallizable polymers, dimers of different chirality in the polymer chain lower its ability to crystallize.[2] Poly(lactide)s could be quenched below the glass transition temperature without crystallization and crystallize during subsequent heating.[3] In contrast, PLA and poly(D-lactide) cocrystallize into a stereocomplex which melts at a temperature higher than that of crystals of both enantiomers.[4]

Below glass transition temperature (T_g), in the range of 50−60 °C, amorphous PLA is rigid and brittle having the elastic modulus about 3−3.5 GPa and low ability to plastic deformation. Crystallinity, if developed, increases slightly the modulus of elasticity and further decreases drawability.[5] Poly(3-methyl-1,4-dioxan-2-one),[6] poly(ethylene oxide),[7] citrate esters,[8,9] triacetine,[9] and poly(ethylene glycol)s (PEGs)[10−14] were found to be efficient plasticizers for PLA. The transition from brittle to ductile behavior in the plasticized polylactide occurs when T_g is shifted to 35 °C. Recent studies of PLA plasticized with PEGs have demonstrated an increase in the efficiency of plasticization with a decrease of PEG molecular weight resulting from increased miscibility with PLA and more efficient reduction of T_g. The cold-crystallization temperature of PLA is also shifted down in parallel with the shift in T_g.[12] The plasticization effect is enhanced by PEG higher content; however, blends of PLA with PEG undergo phase separation at a certain PEG content, dependent on its molecular weight. Blends of PLA of low stereoregularity with 30 wt % of PEG having molecular weight of 8000 g/mol are unstable due to slow crystallization of PEG that depletes the amorphous phase of the plasticizer.[13] Blends of PLA of high stereoregularity with 30% of the same PEG underwent phase separation before either constituent crystallized, whereas blends with 20% of this plasticizer followed the process of PEG crystallization from the homogeneous blend.[15] The PEG rich phase was also found in PLA with 20% of PEG having a molecular weight of 1000 g/mol.[16] Separation of PEG increases stiffness and decreases an elongation to fracture of plasticized PLA.

Cold crystallization of PLA reduces the ability of PLA blended with PEG to plastic deformation.[14] On the other hand, blends containing 10 wt % of PEG with relatively low molecular weight of 400−750 g/mol crystallize during deformation.[14]

The search for new plasticizers drove us toward other polyglycols. Good candidates appeared to be oligomers and polymers of propylene glycol.

Poly(propylene glycol)s (PPGs) are viscous liquids with a molecular weight of 150−4000 g/mol and T_g of −60 to −75 °C.[17] They can be supercooled to the glassy state without crystallization. A low T_g and an inability to crystallize make them attractive potential plasticizers for PLA; however, their miscibility with PLA is unknown. In the past, PPGs were blended with another biodegradable polymer, poly(3-hydroxybutyrate)−poly(3-hydroxyvalerate), but immiscibility was found.[18] In this paper, we attempt to plasticize PLA by blending with PPGs and to study the structure and the thermal and mechanical properties of plasticized PLA. We also intended to compare the properties of PLA plasticized with PPGs with those of the same PLA plasticized with PEG with a molecular weight similar to that of one of the PPGs.

Experimental Section

The study utilized PLA (HM1) manufactured by Hycail BV (The Netherlands), with a residual lactide content of 0.5%, according to the producer, with a DLA content of 6.2% as determined by the specific optical rotation measurement,[19] and M_w of 108 kg/mol, $M_w/M_n = 1.6$ as determined by a GPC method in methylene chloride. Two PPGs with nominal M_w equal to 425 g/mol (PPG4) and to 1000 g/mol (PPG1), purchased from Sigma-Aldrich, were used as plasticizers. PEG with nominal M_w of 600 g/mol (PEG6), purchased from Loba-Chemie, was

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also applied to plasticize PLA for comparison. MALDI time-of-flight (MTOF) method applied in the same way as in ref 14 enabled us to establish that M_w and M_w/M_n were equal to 530 g/mol and 1.03 for PPG4 and 1123 g/mol and 1.05 for PPG1. M_w and M_w/M_n of PEG6 were 578 g/mol and 1.08, respectively.[14] These values are close to those specified by suppliers. Molecular weight of PEG6 is also close to that of PPG4, so their activities as plasticizers can be compared. T_gs of PPG4 and PPG1 were at −72 and −70 °C, respectively, as measured by a DSC method during heating at 10 K/min. PEG6 exhibited only melting with a peak temperature at 20 °C.

Prior to blending, the polymers were vacuum-dried at 100 °C for 4 h. Melt-blends containing 5, 7.5, 10, and 12.5 wt % of plasticizers were prepared using a Brabender mixer operating at 190 °C for 20 min at 60 rpm, under the flow of dry gaseous nitrogen. Neat PLA was also processed in the same way in order to obtain a reference material. The blends will be referred to through the paper as PLA/PPG4, PLA/PPG1, and PLA/PEG6 with a number indicating percentage of plasticizer, for instance, PLA/PPG4-5 for the blend of PLA with 5 wt % of PPG4.

Differential scanning calorimetry (DSC) was carried out with a TA Instrument 2920 DSC. Specimens of neat PLA and all of the blends weighing 10−12 mg were heated and cooled at the rate of 10 K/min. All of the materials were amorphous after the processing. Cooling at the rate of 10 K/min was sufficiently fast to prevent PLA crystallization in all of the systems studied. According to the above findings, 0.4−0.5 and 1 mm thick entirely amorphous films of PLA and plasticized PLA were prepared by compression molding at 180 °C for 3 min in a hydraulic hot press followed by quenching between thick metal blocks kept at room temperature. Care was taken to ensure the same thermal history of all films. All materials and molded films were then stored in dry atmosphere in desiccators at ambient temperature.

Samples of the films were heated in the DSC at 10 K/min. T_gs of all of the materials were measured as the temperature corresponding to the midpoint of the heat capacity increment. The crystallinity level was calculated based on the enthalpy of crystallization and/or melting, assuming the enthalpy of fusion of 106 J/g.[20] In addition, measurements at the heating rate of 1 K/min, amplitude 0.106 K, and frequency 1/40 Hz were conducted in a TA Instruments Modulated DSC 2920 (MDSC).

Dynamic mechanical properties were measured in the three point bending mode in a DMTA Mk III, Rheometric Scientific Ltd. apparatus at the frequency of 1 Hz, at the heating rate of 2 K/min, on rectangular samples, 14 mm × 32 mm, cut from 1 mm thick films.

Oar-shaped specimens, conforming to ASTMD639, with 9.53 mm gauge length, and width of 3.18 mm, were cut from 0.5 mm thick films for tensile tests which were performed on an Instron tensile testing machine at the rate of 0.5 mm/min, in a temperature chamber with circulating air, at 25 °C. At least three samples of each type were drawn to fracture. To study the effect of elongation on thermal behavior, additional specimens were drawn to the predetermined strain; blends with the plasticizer content of 7.5 wt % to 100%, and blends with the plasticizer contents of 10 and 12.5 wt % to 100% and 400%.

Both, DMTA measurements and Instron tests were performed on specimens cut from freshly molded films 1 day before the tests.

The gauge region of deformed samples was examined under a polarized light microscope with crossed polarizers, rotated by 45° with respect to the drawing direction.

Specimens cut from the gauge regions of selected samples were studied in the DSC, at the heating rate of 10 K/min. The fracture surfaces of all materials were studied under a JEOL 5500LV scanning electron microscope (SEM). To have an insight into blend morphology prior to deformation, 0.4−0.5 mm thick films of the blends with 10 and 12.5 wt % of PPG1 and also films of the blends with 12.5 wt % of PPG4 and PEG6 were submerged in liquid nitrogen and broken; the fracture surfaces were studied under the SEM. Prior to the SEM examination all surfaces were sputtered with gold.

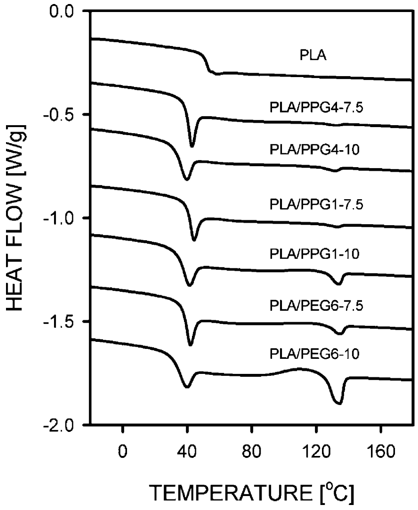

Figure 1. DSC thermograms recorded during heating at the rate of 10 K/min for neat PLA and the blends of PLA with 7.5 and 10 wt % of PPG4, PPG1, and PEG6. Thermograms shifted vertically.

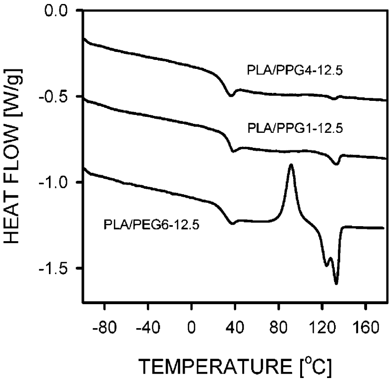

Figure 2. DSC thermograms recorded during heating at the rate of 10 K/min for PLA blends with 12.5 wt % and of PPG4, PPG1, and PEG6. Thermograms shifted vertically.

Results

DSC and MDSC. Exemplary heating thermograms of the films of PLA and plasticized PLA are collected in Figures 1 and 2. The plasticizers decreased T_g from about 55.7 °C for neat PLA to 43−45, 38−39, 31−34, and 27−32 for the blends with 5, 7.5, 10, and 12.5 wt % of plasticizers, respectively, as is listed in Table 1. T_g of PLA/PPG4 and PLA/PEG6 blends was similar and lower than T_g of PLA/PPG1 blends with the corresponding plasticizer content. The glass transition of the blends with 10 wt % of plasticizers began at about 20 °C, whereas an increase of the plasticizer content to 12.5 wt % decreased the onset of the transition even further. A trace of the second glass transition, around −77 °C, was detected only in the PLA/PPG1-12.5 blend. All of the blends exhibited single glass transitions. No separate melting of PEG6 crystals was found in the PLA/PEG6 blends.

Above the glass transition, only traces of crystallization, at 119 °C, and subsequent melting, at 134 °C, were detected on the thermogram of neat PLA; the enthalpy of each transition was equal to 0.1 J/g only. With the increase of plasticizer content in a blend, the crystallization peak temperature decreased, although not below 104 °C, and the crystallization enthalpy increased, at best to 2−3 J/g. The melting temperature also decreased but remained above 130 °C. In the PLA/PEG6-10 blend, the crystallization peak, centered at 111 °C, was associated with the larger enthalpy of 5 J/g. The PLA/PEG6-

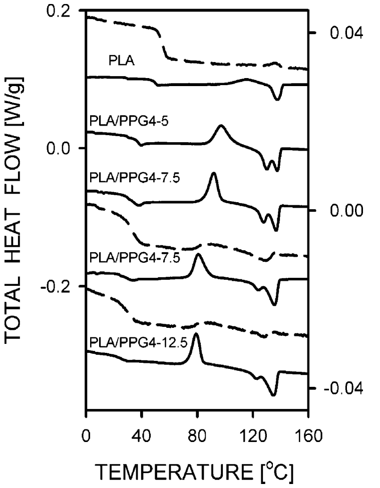

Figure 3. MDSC thermograms recorded during heating at the rate of 1 K/min for: PLA, PLA with 5, 7.5, 10, and 12.5 wt % of PPG4. Total heat flow, continuous line; reversing heat flow, dashed line. Thermograms shifted vertically.

Table 1. T_g Measured by a DSC Method, and Temperature of log E'' Peak (T_E) and tan δ Peak (T_δ) for Neat PLA and Plasticized PLA

plasticizer type	plasticizer content [wt %]	T_g, DSC [°C]	T_E [°C]	T_δ [°C]
none	0	55.7	58.5	63.8
PPG4	5.0	44.5	45.7	54.7
	7.5	38.5	41.7	51.6
	10.0	33.1	35.0	46.3
	12.5	26.8	30.4	42.7
PPG1	5.0	44.8	47.6	57.4
	7.5	39.0	44.0	53.9
	10.0	34.0	41.4	52.3
	12.5	32.0	39.5	50.4
PEG6	5.0	42.8	46.5	55.4
	7.5	37.8	41.0	50.9
	10.0	31.3	35.2	46.5
	12.5	28.0	28.0	43.6

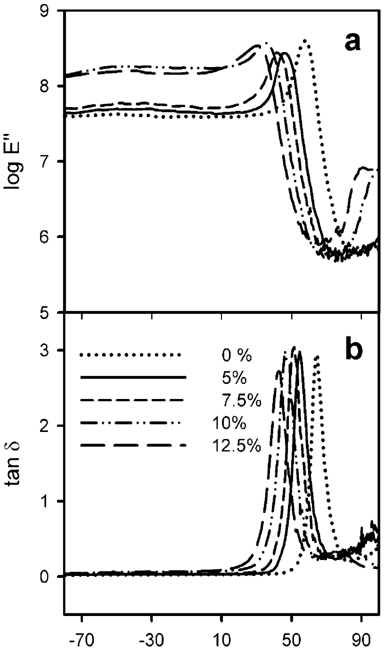

Figure 4. Temperature dependence of dynamic mechanical properties of PLA and PLA/PPG4 blends: log E'' (A) and tan δ (B), PPG4 content indicated in the figure.

12.5 blend was exceptional: the pronounced crystallization peak at 92 °C and two melting peaks, at 124 and 133 °C, were recorded for this blend; the crystallization enthalpy and corresponding melting enthalpy were equal to 25 J/g.

The effect of both PPGs on cold crystallization behavior of PLA was weaker than that of PEG6 despite a similar influence of PPG4 and PEG6 on glass transition; however, more detailed studies are required to explain this difference.

T_g values measured from the MDSC reversing signal (Figure 3) although slightly diverged from those obtained from ordinary DSC measurements due to different thermal conditions of measurements exhibited the same tendency: all of the plasticizers efficiently decreased T_g and the decrease was enhanced by a higher plasticizer content. For the same content of a plasticizer, T_g values were similar for PLA/PPG4 and PLA/PEG6 blends, whereas they were higher for the PLA/PPG1 blends. The slower heating rate employed in the MDSC experiment enhanced the crystallization of PLA. The total heat flow thermogram of neat PLA exhibited a rather broad and flat crystallization peak centered around 117 °C followed by a sharper melting peak at 138 °C; the transitions were associated with the enthalpy of 8 J/g. For the plasticized PLA, pronounced crystallization peaks were observed on the total heat thermograms and the crystallization temperature decreased with the increase of plasticizer content. The PLA/PEG6 blends crystallized at the lowest temperature, and the peaks were sharper than those recorded for PLA/PPG blends with a corresponding plastizer content. This result is consistent with the DSC results pointing out that both PPGs accelerated crystallization of PLA less efficiently than PEG6. The crystallization enthalpy of blends was about 22−23 J/g, which corresponds to the crystallinity level of 21%. The melting enthalpy of the blends exceeded slightly, by 1−2 J/g, the crystallization enthalpy, especially for the blends with a higher content of the plasticizer. The PLA melting behavior in blends changed with an increase of the plasticizer content in a similar way independently of a plasticizer type. In addition to the main melting peaks at 135−139 °C, low-temperature melting peaks appeared on the total heat thermograms. With an increase of the plasticizer content, those peaks diminished and shifted to even lower temperature, whereas flat and broad endothermic peaks appeared on the reversing heat flow thermograms (Figure 3). Thus, PLA crystals in the blends with a higher plasticizer content, formed at lower temperature, exhibited a decreased stability and underwent reorganization during heating, beginning with about 100 °C. This could contribute also to the excess of melting enthalpy over the crystallization enthalpy estimated from a total heat flow.

DMTA. Figures 4 and 5 show temperature dependencies of the loss modulus E'' and tan δ for PLA/PPG4 and PLA/PPG1 blends; PLA/PEG6 blends behaved in a similar way. The glass transition reflected in the E'' peaks and tan δ peaks is clearly visible for all of the materials studied. The temperatures of both peaks, shown in Figure 6 and listed in Table 1, decreased with the increase of plasticizer content for all of the plasticizers used, although less for PPG1. The temperatures of the log E'' peak exceeded by few degrees the T_g values determined from DSC; it is known that 1 Hz DMTA data may correspond to a DSC heating rate in the 20−40 K/min range.[21] The temperatures of log E'' peaks and tan δ peaks recorded for the PLA/ PEG6 and PLA/PPG4 blends were nearly equal and lower than those

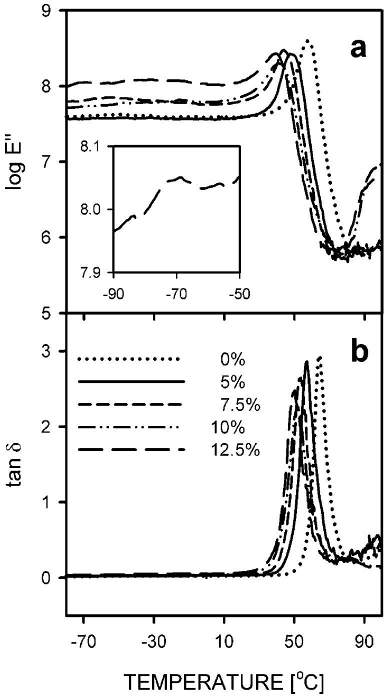

Figure 5. Temperature dependence of dynamic mechanical properties of PLA and PLA/PPG1 blends: log *E*″ (A) and tan *δ* (B). PPG1 content indicated in the figure.

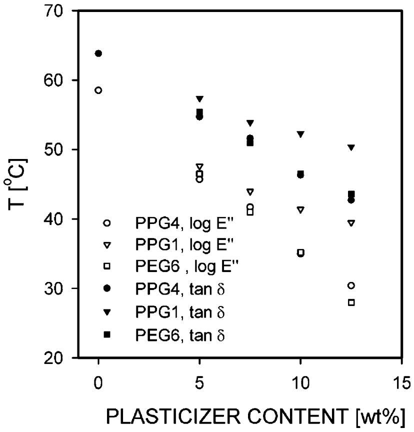

Figure 6. Temperature of log *E*″ (empty symbols) and tan *δ* peaks (filled symbols) for neat PLA and PLA plasticized with PPG4, PPG1, and PEG6 vs plasticizer content.

measured for the PLA/PPG1 blends with a corresponding plasticizer content. Only a trace of a low-temperature peak appeared at about −72 °C on the log *E*″ plot recorded for the PLA/PPG1-12.5 blend as it shown in the insert in Figure 5.

Tensile Properties. Stress−strain dependencies for the materials studied are plotted in Figure 7, panels a and b, whereas the average values of the yield stress, elongation, and stress at break are collected in Table 2 and shown in Figure 8. Neat PLA yielded at the deformation of about 5% and the stress of 41 MPa and exhibited some ability to plastic flow; the average elongation and stress at break were around 64% and 26 MPa, respectively. Beyond a yield, the stress dropped again before it leveled off, as it is illustrated in Figure 7a. The yield stress of all of the blends was lower than that of neat PLA. The elongation at break exceeded that of neat PLA beginning with the plasticizer content of 7.5 wt % and reached 500−700% for the plasticizer content of 12.5 wt %. The stress at break of the blends, in the range of 17.5−22.8 MPa, was generally lower than that of neat PLA, 25.5 MPa; its relatively high values for the blends with

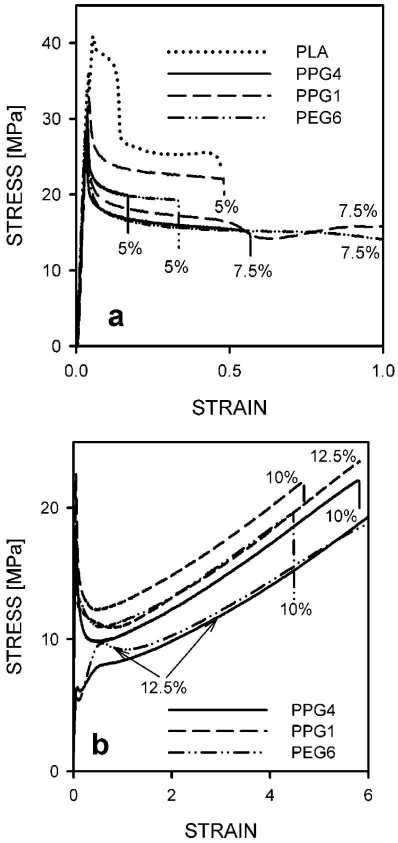

Figure 7. Examples of stress−strain dependencies for neat PLA and PLA plasticized with 5 and 7.5 wt % of PPG4, PPG1, and PEG6 (A) and for PLA plasticized with 10 and 12.5 wt % of PPG4, PPG1, and PEG6 (B).

Table 2. Tensile Properties of Neat PLA and Plasticized PLA

plasticizer type	plasticizer content [wt %]	yield stress [MPa]	stress at break [MPa]	elongation at break [m/m]
none	0	41.4 ± 1.5	25.5 ± 0.4	0.64 ± 0.42
PPG4	5.0	31.3 ± 1.2	20.7 ± 0.9	0.19 ± 0.08
	7.5	29.0 ± 2.1	17.7 ± 2.9	1.07 ± 0.50
	10.0	17.4 ± 2.0	21.0 ± 1.5	5.24 ± 0.66
	12.5	6.0 ± 0.4	21.0 ± 1.4	7.02 ± 0.31
PPG1	5.0	32.3 ± 1 8	22.2 ± 1.5	0.44 ± 0.03
	7.5	28.4 ± 1.3	22.6 ± 1.6	3.29 ± 2.0
	10.0	23.1 ± 0.9	22.8 ± 2.8	4.73 ± 1.11
	12.5	16.1 ± 1.6	21.6 ± 1.6	4.96 ± 0.70
PEG6	5.0	30.3 ± 1.8	19.3 ± 3.5	0.67 ± 0.33
	7.5	25.7 ± 0.2	17.5 ± 3.1	3.60 ± 0.25
	10.0	17.5 ± 1.7	18.5 ± 1.2	4.27 ± 0.42
	12.5	5.4 ± 0.8	19.7 ± 1.4	6.22 ± 0.75

10 and 12.5 wt % of plasticizers resulted from the strain hardening, clearly visible in the respective stress−strain dependencies. The appearance of strain hardening is an indisputable sign of very significant plastic deformation of the amorphous phase and straining of the chain entanglement network. The presence of strain hardening indicates a very intense plasticizing effect of PPGs and increased segmental mobility of PLA chains.

The elongation at break of all of the blends increased with the plasticizer content. The PLA/PPG4-5 and PLA/PPG4-7.5 blends exhibited rather small elongation at break. On the contrary, the PLA/PPG4-10 and PLA/PPG4-12.5 fractured at elongation of approximately 500 and 700%, respectively,

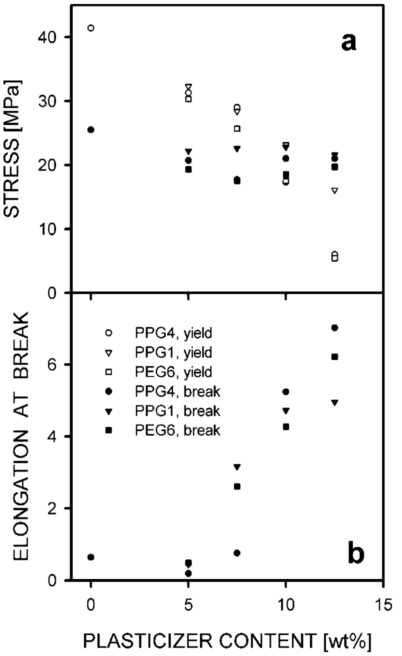

Figure 8. Yield stress and stress at break (A) and elongation at break (B) of neat PLA and PLA plasticized with PPG4, PPG1, and PEG6 vs plasticizer content.

exceeding those of the other blends with a corresponding plasticizer content. The increase of PEG6 and PPG4 content from 10 to 12.5 wt % resulted in a change of behavior; a double yield of unknown origin appeared on stress–strain dependencies, as it is illustrated in Figure 7b.

Polarized Light Microscopy of Deformed Samples. In the micrographs of PLA and PLA/PPG4-5 specimens strained to fracture, shown in Figure 9, panels a and b, a relatively uniform distribution of whitened craze zones is visible. Crazes were already visible in neat PLA specimens at yield; however, a neck was formed after the second drop of stress visible in Figure 7a. The specimen of PLA/PPG4-7.5 (Figure 9c) revealed cavities elongated perpendicularly to the drawing direction, whereas PLA/PPG4-10 and PLA/PPG4-12.5 (Figure 9, panels d and e) showed uniform brightening. These features are also typical of the PLA/PPG1 and PLA/PEG6 blends. The necking was observed during deformation of all of the blends with 10 wt % of plasticizers and also the PLA/PPG1-12.5 blend. In the PLA/PEG4-12.5 and PLA/PEG6-12.5 specimens, the deformation began within the gauge but then spread over the entire portion of the sample between the grips. The gauge regions of specimen of neat PLA with 5 and 7.5 wt % of plasticizers exhibited some stress-whitening due to cavitation. The specimens of blends with higher plasticizer content became less transparent but no stress-whitening was observed in unpolarized illumination indicating that no light scattering cavities were formed.

SEM. The structure of the blend films fractured in liquid nitrogen is demonstrated in Figure 10. The PLA/PPG1-12.5 blend reveals emptied voids of submicron size where PPG1 has been accumulated during phase separation. Surfaces of PLA/PPG1-10 and PLA/PPG4-12.5 blends (Figure 10, panels a and c) and also PLA/PEG6-12.5 blends (not shown) revealed only features typical of brittle fracture of a glassy polymer, without any evidences of heterogeneities. Typical micrographs of the fracture surfaces of drawn specimens are shown in Figures 11 and 12. The SEM studies of PLA, PLA/PPG4-5 (Figure 11, panels a and b), and PLA/PPG4-7.5 (not shown) revealed rather brittle fracture surfaces with little plastic deformation and a few long threads of a deformed material occasionally discernible. On the contrary, a large amount of plastically deformed material was visible on the entire fracture surfaces of the specimens of PLA/PPG4-10 (Figure 11c) and PLA/PPG4-12.5 (not shown). Similar features were found in the blends with PEG6 and PPG1 except that plastically deformed polymer was also visible on the fracture surfaces of blends with 7.5 wt % of these plasticizers (Figure 12a). In the specimen of the PLA/PPG1-12.5 blend, strained to fracture, in addition to intense plastic deformation, visible in Figure 12b, cavities of about 0.2 μm size were detected, shown in Figure 12c. Such cavities were not found on the fracture surfaces of the other blends.

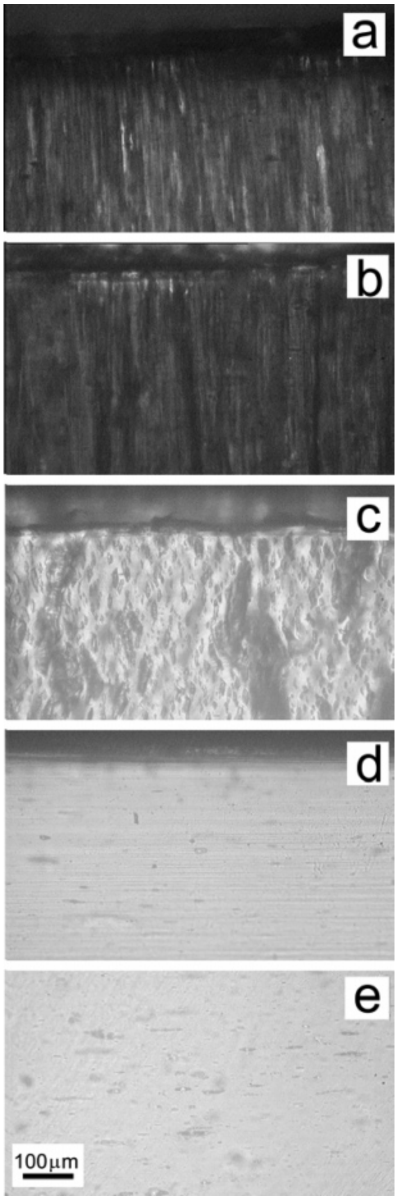

Figure 9. Polarized light micrographs of the gauge regions of specimens strained to fracture: neat PLA (A), PLA/PPG4-5 (B), PLA/PPG4-7.5 (C), PLA/PPG4-10 (D), PLA/PPG4-12.5 (E). Crossed polarizers. Drawing direction, horizontal.

DSC of Deformed Samples. Heating scans, at the rate of 10 K/min, of the samples cut from gauge regions of the specimens, differed from the scans of the respective films prior to deformation, as it is shown in Figure 13. On each thermogram, the pronounced glass transition associated with a very intense enthalpy relaxation, a cold-crystallization peak, and, at higher temperature, a single melting peak was observed.

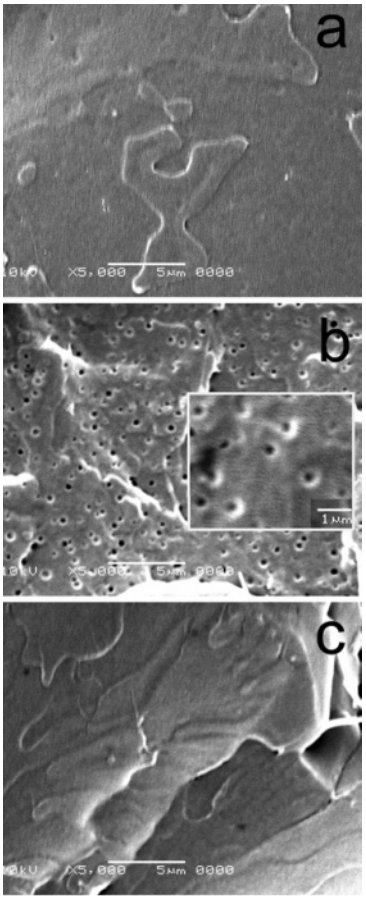

Figure 10. SEM micrographs of fracture surfaces of the blends: PLA /PPG1-10 (A), PLA/PPG1-12.5 (B), and PLA/PPG4-12.5 (C).

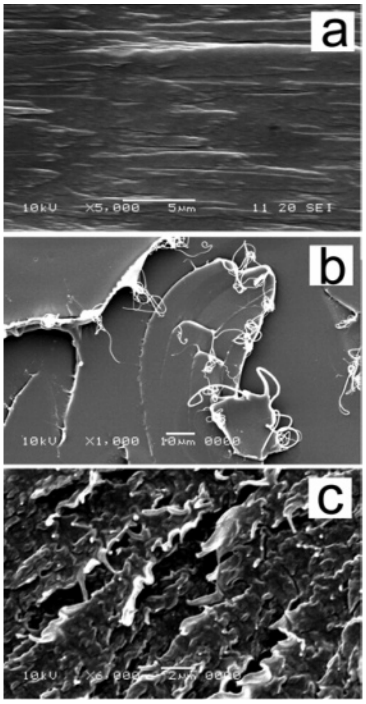

Figure 11. SEM micrographs of fracture surfaces of tensile specimens deformed to fracture: neat PLA (A), PLA/PPG4-5 (B), and PLA/PPG4-10 (C).

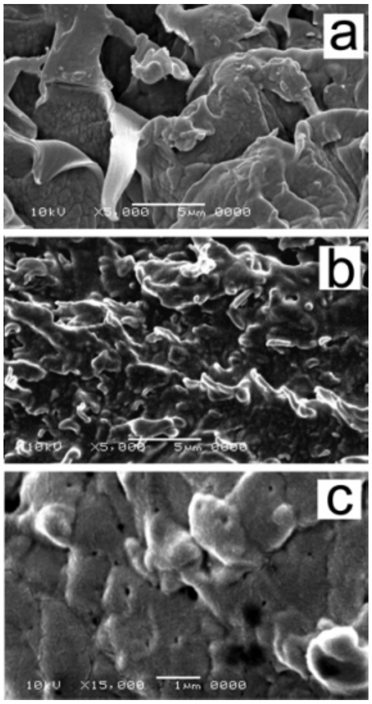

Figure 12. SEM micrographs of fracture surfaces of tensile specimens deformed to fracture: PLA/PPG1-7.5 (A) and PLA/PPG1-12.5 (B and C).

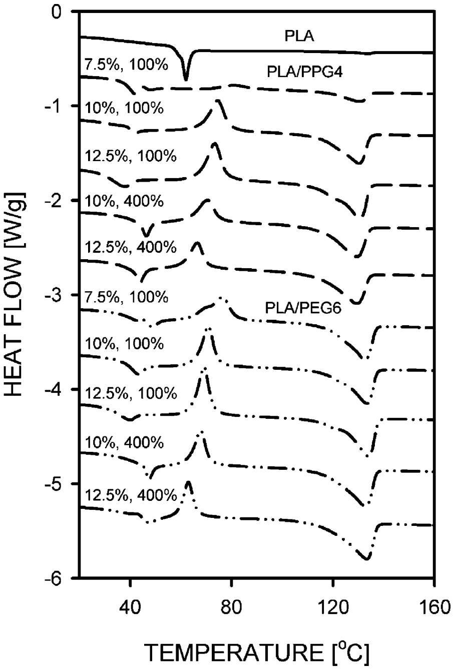

Figure 13. DSC heating thermograms recorded at the rate of 10 K/min for tensile specimens of neat PLA deformed to fracture (solid line) and specimens of plasticized with 7.5−12.5 wt % of PPG4 (dashed line), and PEG6 (dotted-dashed line) deformed to 100 and 400%. Plasticizer content and strain indicated in the Figure. Thermograms shifted vertically.

The crystallization of neat PLA after deformation to fracture was slightly enhanced; the flat and broad exotherm, was followed by melting peak at 132 °C; the enthalpy of both transitions was about 0.5 J/g. The effect was stronger in the blends with 5 wt % of plasticizers despite smaller elongation at break. The crystallization temperature decreased to 84−90 °C; however, the melting temperature decreased only by 1 K. The crystallization enthalpy and the melting enthalpy increased up to 3 J/g.

With the increase of plasticizer content, hence also the elongation at break, the crystallization peaks shifted to 63−80

°C. The melting enthalpy associated with peaks centered at 127−131 °C exceeded significantly the crystallization enthalpy which indicated that the specimens with a higher plasticizer content crystallized during deformation. The crystallization continued in the DSC but at a lower temperature than the cold crystallization in the same materials prior to deformation. Figure 13 shows thermograms of the PLA/PPG4 and PLA/PEG6 specimens strained to 100 and 400%. PLA/PPG1 blends (not shown) behaved similarly. The cold-crystallization temperature of samples strained to the same elongation decreased with the increase of plasticizer content, although was higher for samples strained to 100%. Crystallization temperature was always the lowest for PLA/PEG6 blends.

The precise determination of the crystallization enthalpy of strained samples encounters difficulties due to shapes of thermograms above T_g. However, the DSC data show that for samples strained to 100% the enthalpy increased with the plasticizer content, whereas for samples strained to 400%, it was at the same level for the plasticizer content of 10 and 12.5 wt %.

The excess of melting enthalpy over the crystallization enthalpy, corresponding to crystallinity developed during drawing, depended primarily on elongation, being below 8J/g and in the range of 12−15J/g, for samples strained to 100 and 400%, respectively. For specimens with the same elongation this enthalpy excess increased with the plasticizer content, being the largest for PLA/PPG6 blends.

Discussion and Conclusions

Both the DSC and DMTA data for PLA plasticized with PPGs show clearly a decrease of T_g due to enhanced segmental mobility of PLA chains caused by the presence of plasticizers, increasing with the plasticizer content. The blends, except for the PLA/PPG1-12.5 blend, were homogeneous. PPG1 decreased T_g less than PPG4 despite nearly the same T_g of both PPGs. The effect of PPG4 was practically the same as the effect of PEG6. In the PLA/PPG1-12.5 blend, the PPG1 separation was evidenced by SEM, that indicates that the miscibility of PPGs with PLA decreases with the increase of PPG molecular weight. T_g of the PLA/PPG1-12.5 blend was still below that of PLA/PPG1-10 blend which pointed out that only a minor fraction of PPG1 formed separate droplets, hence significant separate glass transition showed up neither in DSC nor in DMTA experiments conducted for this blend. The relative abundance of emptied cavities visible on SEM micrographs of the PLA/PPG1-12.5 blend resulted most probably from the preferred propagation of fracture through interfacial surfaces at liquid nitrogen temperature. Only a trace of the second glass transition was detected by a DSC method in the PLA/PPG1−12.5 blend. We attribute this to the glass transition of PPG1, despite a T_g lower than that of pure PPG1. The lower T_g of PPG1 inclusions dispersed in a glassy matrix is caused by negative pressure generated during cooling due to the mismatch of thermal expansion coefficients of glassy PLA and liquid PPG1. A similar effect was reported in the past for a system of polystyrene with polybutadiene.[22] The plasticizers increased the ability of PLA to crystallize, which was manifested by a decrease of cold crystallization temperature and an increase of the crystallization enthalpy during heating in the DSC at the rate of 10 K/min. The enhancement of the crystallizability was already reported for PLA plasticized with triacetine,[9] citrate esters,[9,12] glycerol,[23] and PEG.[12,14,23−25]

It should be noted that both PPGs influenced less the crystallization behavior of PLA than PEG6 did, although PPG4 and PEG6 had practically the same effect on the glass transition. This is of importance because the thermal crystallization has a negative effect on the drawability of plasticized PLA.

Both the crystallization and melting behavior of the materials studied depended on their composition but also on the heating rate. The additional melting peaks appearing on DSC thermograms of plasticized PLA were already explained by others as related to the reorganization of the crystal structure.[7] The MDSC heating scans carried out in the present study confirmed the lamellae reorganization in the plasticized PLA reflected in the MDSC reversing signal

The plasticizers enhancing the segmental mobility of PLA chains increased the ability of amorphous PLA to the plastic deformation, decreasing the yield stress and increasing the elongation at break, the latter beginning with the plasticizer concentration of 7.5 wt %. The sign of increased segmental mobility and straining the network of chain entanglements is a strain hardening stage achieved in tensile drawing. In PLA and in the blends with 5 wt % of plasticizers, where the T_g was still well above room temperature, the plastic deformation was due to crazing, similarly as in other glassy polymers, including neat PLA and PLA plasticized with 5 wt % of PEG.[14] The increase of chain mobility due to plasticizers decreases obviously the stress required for craze initiation and growth which was reflected in a lower yield stress and craze flow stress.

Neat PLA and the blends with 5 wt % of plasticizers strained to fracture exhibited increased ability to crystallize due to macromolecule orientation within craze tufts. Beginning with 7.5 wt % of PPGs and PEG6, the blends crystallized during deformation, similarly as was reported for PLA plasticized with 10 wt % of PEGs.[14] Due to higher stereoregularity of PLA used in ref 14, a larger crystallinity degree was reached during deformation despite nearly the same elongation to fracture. The strain induced crystallization also contributed to strain hardening observed in the plasticized PLA, as crystallites play a role of physical knots. However, the crystallization of PLA in the blend leads also to an increase of plasticizer content in the amorphous phase and to further decrease of T_g.

The cavities detected on the fracture surface of PLA/PPG1-12.5 tensile specimen which were much smaller than those found in the blend prior to deformation resulted probably from phase separation caused by a local increase of PPG1 concentration in the amorphous phase of the blend during strain induced crystallization of PLA. Hu et al.[13,15] demonstrated that only PLA/PEG blends with T_g lower than ambient temperature phase separated, and the separation essentially ceased when T_g of the PLA rich phase reached ambient temperature. Therefore, the PLA/PPG1-12.5 blend with T_g at 32.5 °C should be stable at room temperature and static conditions. Aging of PLA/PPG blends requires, however, further studies.

Phase separation that occurred in the PLA/PPG1-12.5 prevented a further decrease of T_g but did not reduce the drawability of the material. However, enhancement of diluent conductance in glassy polymers undergoing plastic flow was observed in the past.[26] Argon and Cohen[27] reported the local plasticization of polystyrene by low molecular weight polybutadiene droplets. Thus, although solid inclusions of crystallizable plasticizers, like PEGs, are undesirable as they degrade the blend drawability, tiny liquid pools of PPG may locally plasticize PLA during plastic flow and have a positive effect on drawability.

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