The Effects of Plasticizers on the Dynamic Mechanical and Thermal Properties of Poly(Lactic Acid)

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ABSTRACT: Poly(lactic acid) (PLA) was blended with five plasticizers in a batchwise mixer and pressed into films. The films were analyzed by means of dynamic mechanical analysis and differential scanning calorimetry to investigate the properties of the blends. Triacetine and tributyl citrate proved to be effective as plasticizers when blended with PLA. The glass transition temperature of PLA decreased linearly as the plasticizer content was increased. Both plasticizers were miscible with PLA to an extent of ∼ 25 wt %. At this point, the PLA seemed to be saturated with plasticizer and the blends tended to phase separate when more plasticizer was added. There were also signs of phase separation occurring in samples heated at 35, 50, and 80°C, most likely because of the material undergoing crystallization. The presence of the plasticizers induced an increased crystallinity by enhancing the molecular mobility. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 1227–1234, 2002

Key words: poly(lactic acid); plasticizers; thermal properties; dynamic mechanical properties; films

INTRODUCTION

In today's society, the rapid growth of municipal waste has come more and more into focus. Because polymeric materials constitute a large part of the waste, consumer awareness in conjunction with strict laws and regulations have emphasized the need to develop biologically degradable plastics and products that may be composted.

Biodegradable polymers that are produced from renewable raw materials have many advantages. On degradation, they do not give any net contribution to the carbon dioxide emissions in the atmosphere. Also, because they are based on agricultural products such as whey, corn, potato, and molasses, crude oil resources are saved. Biodegradable polymers offer new possibilities for use of agricultural products which, especially in the developed countries, suffer from overproduction.

Poly(lactic acid) (PLA) is a biodegradable thermoplastic that can be produced from renewable resources. Because of its good mechanical properties and processibility as well as biocompatibility,[1] PLA can be used for producing packaging materials[2] and hygiene products. For example, milk cartons and diapers are consumer products that constitute a huge part of the household waste. Today, polyolefins are used for these products. Consequently, the environment would benefit greatly if PLA could be used in these applications.

In many packaging materials as well as in the outer layers of diapers, polymer film materials are used. To replace the polyolefins in these applications with PLA, film extrusion of the polymer has to be performed, but because of the brittleness and thermal instability of PLA, this is a difficult process.[3] Another disadvantage with PLA is that the barrier properties (e.g., the water vapor barrier) are not as good as for the traditional polyolefins. The brittleness of the PLA film, however, constitutes the major problem. Packaging materials as well as diapers require flexible polymer films, and in the industrial production line, there is no tolerance for the film cracking or tearing when folded or subjected to force during manufacturing.

The physical properties of PLA may be modified by blending the polymer with a plasticizer or with a second polymer, and the flexibility of PLA can thereby be improved. Examples of polymers that have been blended with PLA are thermoplastic starch,[4] poly(ethylene oxide),[5] poly(ethylene glycol),[6] poly(ε-caprolactone),[7–9] and poly(hydroxybutyrate).[10,11] As plasticizers for PLA, oligomeric lactic acid, glycerol,[4] and low molecular weight esters such as citrates[12] were investigated.

The choice of polymers or plasticizers to be used as modifiers for PLA is limited by the requirements of the application. For packaging and hygiene applications, only nontoxic substances approved for food
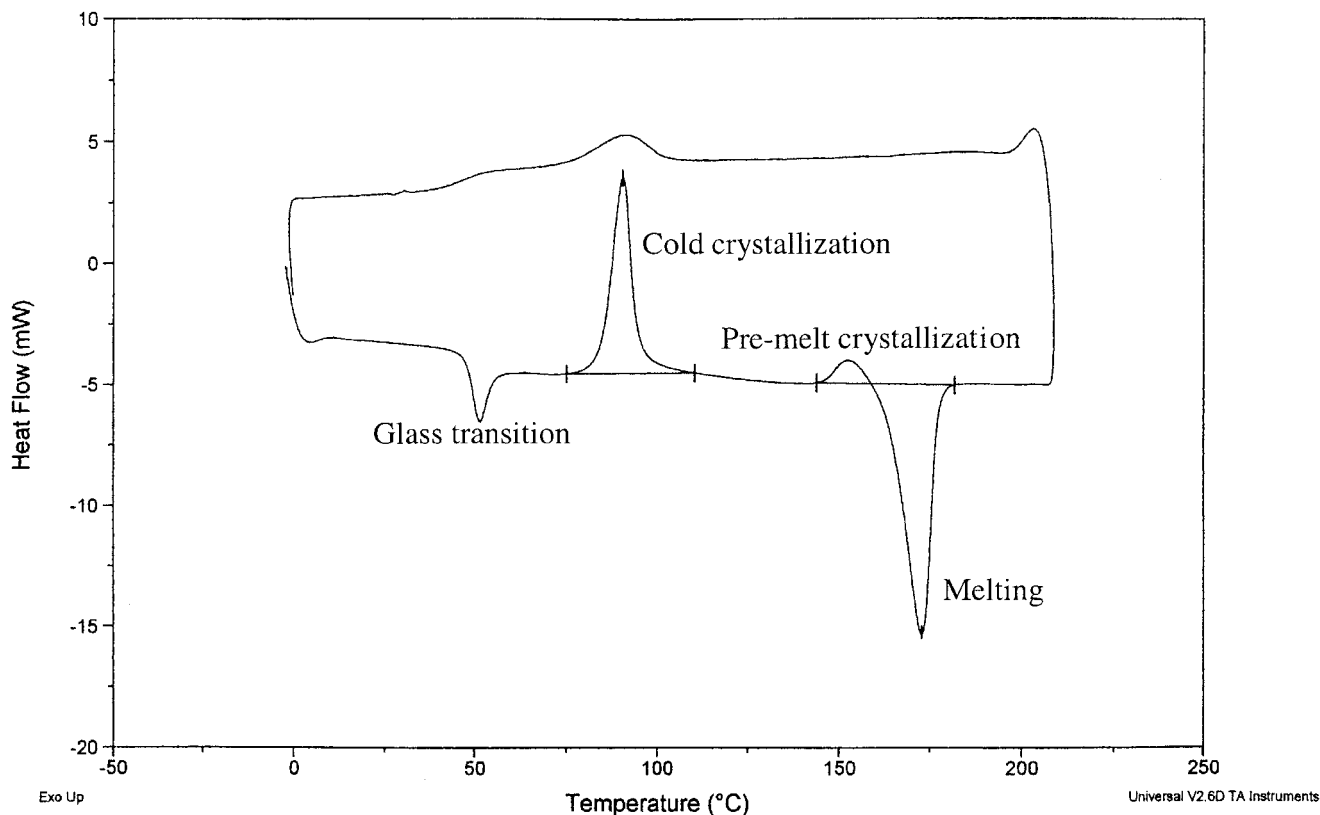
Figure 1 A DSC trace for neat PLA displaying the glass transition temperature, cold crystallization, premelt crystallization, and melting.

contact and personal care can be considered as plasticizing agents. There are numerous other demands put on the plasticizers, but the following ones are especially important. The plasticizer should be miscible with PLA, thus creating a homogeneous blend. The plasticizer should not be too volatile because this would cause evaporation to occur at the elevated temperatures used at processing. Furthermore, the plasticizer should not be prone to migration because this would cause contamination of the materials in contact with the plasticized PLA. It would also cause the blended material to regain the brittleness of pure PLA.

The present study focused on the use of plasticizers as modifiers for PLA and their effects on the dynamic mechanical and thermal properties of the polymer.

The aim of the study was to build a platform for further research concerning oligomeric plasticizers for PLA.

EXPERIMENTAL

Materials

PLA with a molecular weight (M_w) of approximately 100,000 g/mol and a polydispersity of 2.4 was supplied by Fortum, Helsinki, Finland. The melting temperature (T_m) was 175°C and the glass transition temperature (T_g) was 54°C. The polymer was used as received. The plasticizers used were triacetine, tributyl citrate, acetyl tributyl citrate, triethyl citrate, and acetyl triethyl citrate, provided by Scientific Polymer Products Inc., Ontario, NY, USA. All plasticizers were used as received.

Blending

PLA was blended with the plasticizers in a Brabender plastograph equipped with a measuring mixer W50 EHT. The temperature was 190°C and the blending time 5.0 min. To minimize the risk of degrading the PLA, blending was performed under N_2 atmosphere. After blending, the melt was dumped directly onto an

TABLE I
Densities and Solubility Parameters for PLA and Five Plasticizers as Calculated with Group Molar Attraction Constants from the Hoy Series[14]

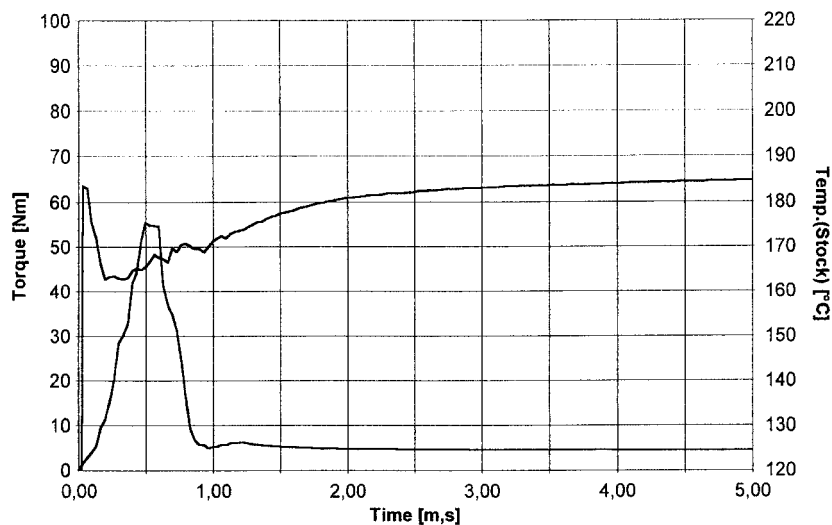| Substance	Bp (°C)	ρ (g cm^{-3})	δ (J cm^{-3})$^{1/2}$
PLA		1.26	20.1
Triacetine	259	1.15	19.1
Tributyl citrate	169	1.10	19.6
Triethyl citrate	126	1.14	19.7
Acetyl tributyl citrate	173	1.05	18.0
Acetyl triethyl citrate	131	1.14	18.9

Figure 2 The stock temperature (upper curve) and the torque (lower curve) as measured during blending of PLA and 20 wt % triacetine in a Brabender mixer.

aluminum plate, which caused it to cool very quickly. The material was then cut into granules (5 × 5 mm) with pliers.

In the first blending series, all five plasticizers were individually blended with PLA at a ratio of 15 wt % plasticizer and 85 wt % PLA. In the second blending series, blends were prepared from PLA and triacetine and PLA and tributyl citrate in amounts of 20 and 25 wt % plasticizer, and for PLA and triacetine also in amounts of 30 wt %.

Film preparation

Films were prepared from the blends by heat pressing at 200°C. Granules of the blends were placed in a template frame to ensure a constant film thickness and covered with aluminum foil sheets to prevent sticking to the press plates. This assembly was then placed between the press plates for 3.5 min, without applying pressure, until the material was properly melted, and then pressed for 30 s at a pressure of 9 bar. The samples were removed from the press plates and cooled in air until they reached ambient temperature

(~ 20 s). The specimens where then stored in sealed plastic bags in air, awaiting analysis.

Dynamic mechanical analysis (DMA)

DMA was performed on a DMA 2980 from TA Instruments. The runs were conducted at 3°C/min between −30 and 150°C or −60 and 150°C under N_2 atmosphere. The analyses were run in tensile mode with film samples ~ 15 × 6 × 0.3 mm. The amplitude was 5 μm and the autostrain was set to 115%. The curves displayed storage modulus, loss modulus, and tan δ versus temperature. The T_g was taken to be the temperature for the maximum of the loss modulus curve.

TABLE II
T_g **Values as Measured by DMA for Blends with PLA and 15 wt % Plasticizer**

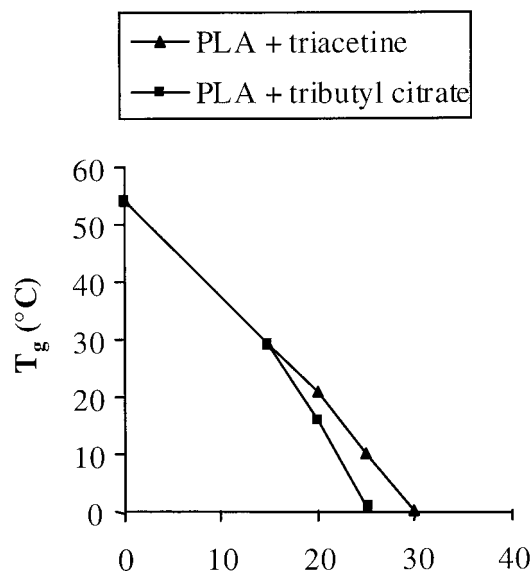| Plasticizer	Content (wt %)	T_g (°C)
Triacetine	15	29
Tributyl citrate	15	29
Triethyl citrate	15	31
Acetyl tributyl citrate	15	30
Acetyl triethyl citrate	15	34
Neat PLA		54

Figure 3 T_g for the PLA + triacetine and PLA + tributyl citrate blends as a function of the plasticizer content.

TABLE III
Average[a] T_g Values as Measured by DMA for Blends with PLA and Different Contents of Triacetine or Tributyl Citrate

Plasticizer	Content (wt %)	T_g (°C)
Triacetine	15	29
Triacetine	20	21
Triacetine	25	10
Triacetine	30	0
Tributyl citrate	15	29
Tributyl citrate	20	16
Tributyl citrate	25	1

[a] The average values for T_g are based on three to five measurements.

Differential scanning calorimetry (DSC)

Two series of DSC scans were conducted on a Mettler DSC 30. In the first series, the samples were heated from −60 to 210°C at a rate of 10°C/min. In the second series, the temperature was increased from −60 to 210°C, where the temperature was kept constant for 5 min, and then decreased to −60°C. The heating and cooling rates were 10°C/min. All scans were run under N_2 atmosphere using ∼ 10 mg of material. Values for T_g, fusion enthalpies, crystallization temperatures, and melting temperatures were evaluated from the scans. The crystallinity of the material after blending and film preparation was determined by subtracting the enthalpies for premelt crystallization and cold crystallization from the enthalpy for melting (see Fig. 1). The calculations are based on ΔH_m for 100% crystalline PLA being equal to 93 J/g.[13]

Heat treatment

Three samples of a blend containing 20 wt % triacetine were heat-treated in air at temperatures of 35, 50, and 80°C for 1 and 3 days. After the heat treatment, the samples were analyzed with DSC and DMA as above.

RESULTS AND DISCUSSION

Blending

The choice of the plasticizers was made to meet the criteria mentioned earlier. The miscibility of plasticizers and polymers can be estimated by comparing the solubility parameters of the materials. In the present study, the solubility parameters for PLA and the five plasticizers were calculated according to the equation
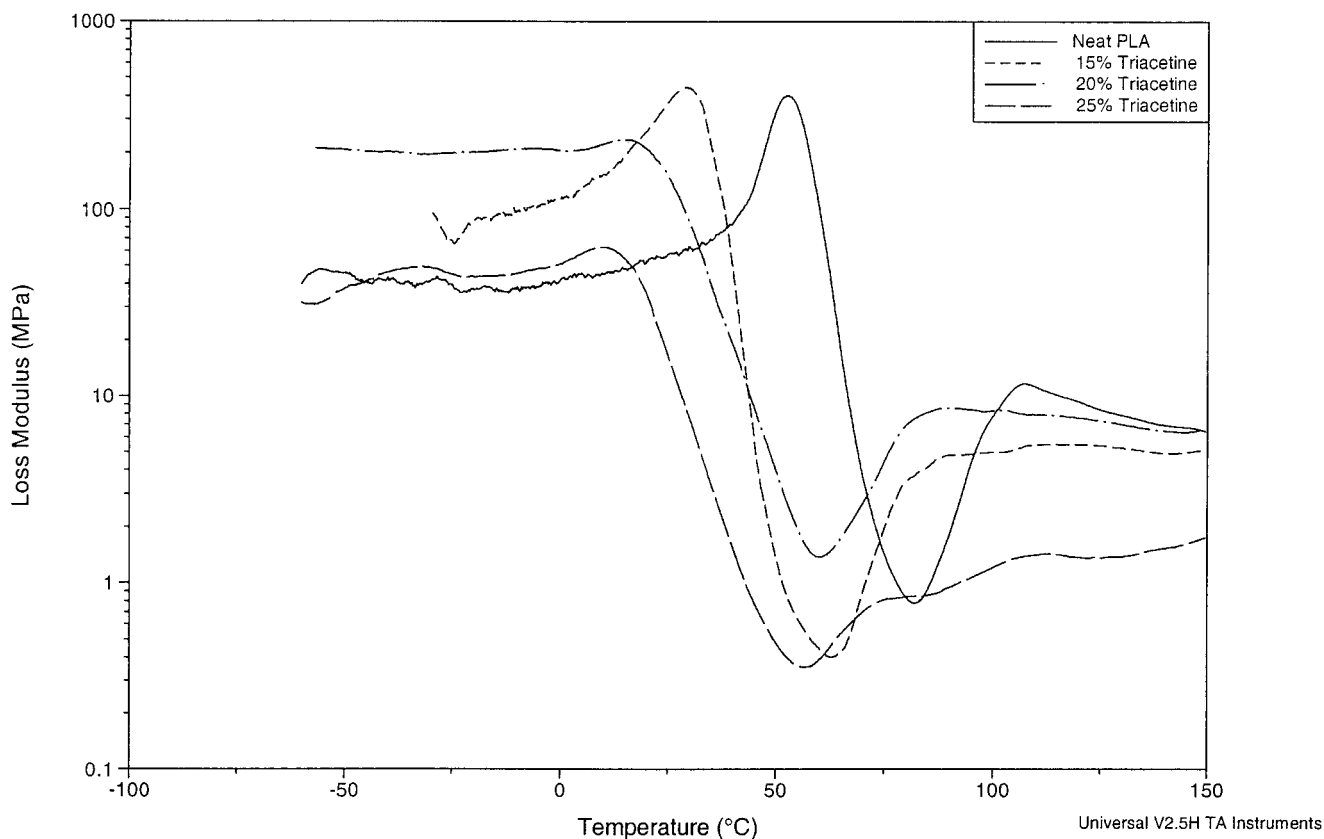
$$\delta = \frac{\sum F \rho}{M_0}$$

Figure 4 Loss modulus curves from DMA runs comparing blends containing 15, 20, and 25 wt % triacetine with neat PLA.
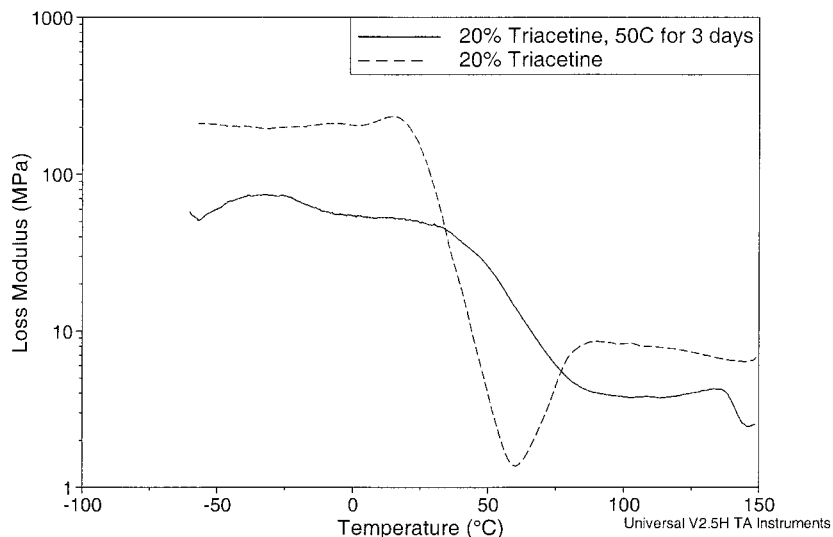
Figure 5 Loss modulus curves from DMA runs comparing untreated and heat-treated (3 days at 50°C) blends containing 20 wt % triacetine.

where δ represents the solubility parameter, ρ is the density, M_0 is the molecular mass, and F is the group molar attraction constants according to the Hoy series.[14] As shown in Table I, all five plasticizers had calculated solubility parameters close to that of PLA, which indicated that they should be miscible. The boiling points of the plasticizers (see Table I) confirmed that they should not be too volatile for blending experiments carried out at 190°C. Their tendency to migrate from the plasticized material, however, is one aspect that must be investigated further on.

According to the manufacturer, the degradation temperature (T_d) for PLA is 315°C, and because the blending temperature was much lower, there was lit-

tle risk for thermal degradation. However, PLA is prone to oxidative degradation, and to avoid this phenomenon, blending was performed in N_2 atmosphere. Visual comparison of samples blended in N_2 and preliminary samples blended in air, at otherwise identical conditions, revealed that the ones blended in air had a much darker color. It was concluded that blending thus should be performed in N_2 atmosphere to minimize the risk of oxidative degradation.

In the blending operation, the torque on the mixer's rotors was measured as a function of time. As seen in Figure 2, the torque increased sharply as the material was added to the blender, after which it eventually decreased and leveled out. After 5 min, the blend was considered homogeneous.
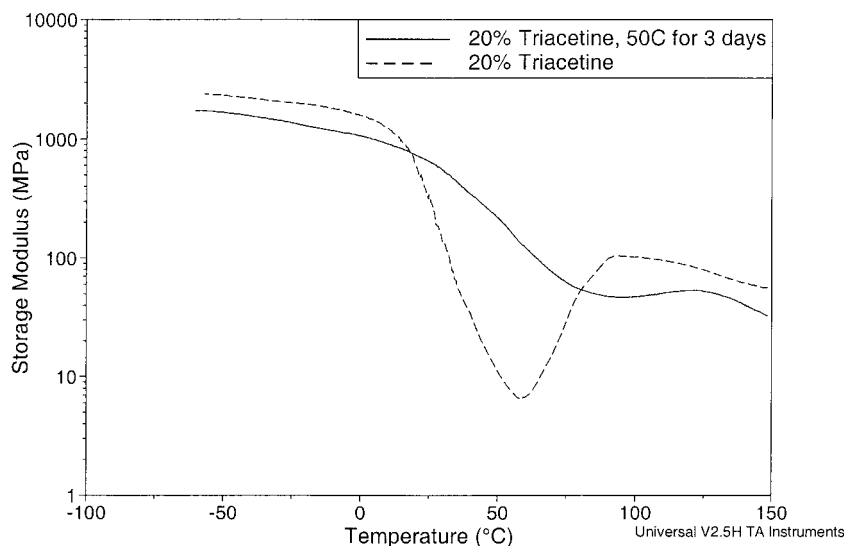

Figure 6 Storage modulus curves from DMA runs comparing untreated and heat-treated (3 days at 50°C) blends containing 20 wt % triacetine.
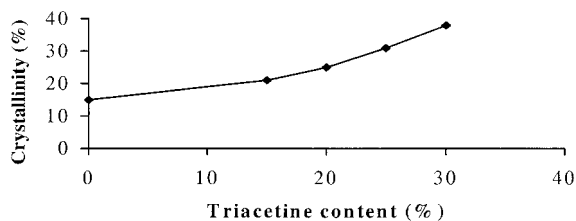
Figure 7 Crystallinity after heat pressing for PLA + triacetine blends as a function of the triacetine content.

DMA

The T_g values obtained from the loss modulus curves in the DMA measurements of the first blending series are shown in Table II. Triacetine and all four citrates significantly decreased the T_g for PLA, and the values obtained for the citrates correlate well with those reported by Labrecque et al.[12] The results given in Table II indicate that triacetine and tributyl citrate were the most effective plasticizers of the five tested. It is noted that both these plasticizers had solubility parameters close to that of PLA [a difference of <1 $(J\ cm^{-3})^{1/2}$]. Triethyl citrate has a δ value even closer to that of PLA, but in this case, evaporation of the low-boiling plasticizer on processing might yield a lower concentration than calculated and thus a too low T_g value.

Additional blending experiments were carried out with triacetine and tributyl citrate. In these experiments, the plasticizer content was further increased from 15 wt % to 20 and 25 wt %. One experiment was also attempted with 30 wt % triacetine, but the blending proved to be difficult because the melt was sticky and would barely release from the mixer walls. No further blends were prepared with this plasticizer content. As in the first test series, films were prepared from the blends by heat pressing, and the films were then analyzed by DMA. The average T_g values obtained from the DMA measurements of these blends are given in Figure 3 and Table III.

As evident from Figure 3, an increasing plasticizer content decreased the T_g of PLA almost linearly. A slight difference in the plasticizing effects between triacetine and tributyl citrate was observed, tributyl citrate seemingly being somewhat more effective as a plasticizer based on the T_g values. It can also be noted that both triacetine and tributyl citrate seem to be more efficient than the plasticizers investigated by Martin and Avérous.[4]

Figure 4 shows loss modulus curves from DMA runs on blends containing 0, 15, 20, and 25 wt % triacetine, respectively. For neat PLA, the loss modulus curve showed only one sharp peak at 54°C. Similarly, there was only one peak at 29°C for the blend containing 15 wt % triacetine. For the blend containing 20 wt % triacetine, a plateau at low temperature leading up to a single peak at 21°C was observed, whereas

the blend containing 25 wt % triacetine showed a broad loss modulus curve displaying two peaks: a narrow peak at 10°C and a much broader one at -30°C. The peak at -30°C may be regarded as an indication of phase separation in the sample at high loadings of plasticizer and was thus assigned to a separate plasticizer phase. Seemingly, the plasticizer was only partially miscible with PLA. At a concentration of 25 wt %, PLA was saturated with plasticizer and further addition created a new phase. Blends with tributyl citrate behaved similarly to those containing triacetine, and for both plasticizers, saturation seemed to occur at a content of $\sim$ 25 wt %.

There is, however, a possibility that the batchwise blending and film pressing did not create a homogeneous blend and film, thereby causing the phase separation. Further investigations must be performed on material that has been continuously blended and film-extruded to rule out that the phase separation was due to insufficient processing.

Neat PLA is a semicrystalline polymer and investigation of the crystallization behavior of plasticized PLA can thus be considered of interest. The presence of the plasticizer influences the mobility of the PLA molecules, as evidenced by the depression of the T_g, and consequently, the kinetics of the crystallization are affected.[4] Cold crystallization and changes in the crystalline content with time are of great importance for the storage of the material and for the long-term mechanical properties. A study of these parameters was carried out by performing a series of heat treatments on the plasticized PLA films. Changes in the mechanical properties were followed by DMA measurements. Figure 5 displays the difference between the loss modulus curves for two samples plasticized with 20 wt % triacetine, where one sample was run directly after processing and the other after heat treatment at 50°C for 3 days. The nontreated sample showed a single loss modulus peak, whereas the sample subjected to heat treatment showed two peaks, indicating phase separation, as discussed above. In Figure 6, the storage modulus curves for the two samples are given. The untreated sample displays a sharp increase in storage modulus between 60 and 100°C, which is an indication that cold crystallization occurs in this temperature region. No such increase was observed for the heat-treated sample, presumably because crystallization had already taken place during the 3-day heat treatment.

It seems plausible that the driving force for phase separation in the heat-treated sample is the crystallization occurring during storage at the elevated temperature. Crystallization should cause a decrease in the amorphous content of the PLA, and because the plasticizer is only miscible with the amorphous phase, this phase should become supersaturated and force the plasticizer to create its own phase (cf. synerisis).

TABLE IV
Thermal Data Obtained by DSC Measurements for PLA with Different Contents of Triacetine and Tributyl Citrate

Plasticizer	Cold crystallization temperature (°C)	Melting temperature (°C)	Crystallization temperature (°C)
20 wt % Triacetine	67	164	97
25 wt % Triacetine	—	163	98
30 wt % Triacetine	—	165	98
20 wt % Tributyl citrate	70	164	92
25 wt % Tributyl citrate	68	165	96
Neat PLA	95	175	95

Heat treatments were also performed at 35 and 80°C. Similar results as those obtained at 50°C were acquired. However, the separation of the plasticizer occurred at a slightly lesser degree at the lower temperature and at a slightly larger degree at the higher temperature.

DSC

The thermal properties of all blends were studied by DSC. All samples showed crystalline melting peaks, but T_g's were very difficult to identify and evaluate from the DSC thermograms because the transition took place over a very broad temperature span. The ones that could be evaluated, however, correlated well with the T_g values obtained from DMA measurements.

The crystallinity of the samples after blending and film preparation was evaluated from the DSC thermograms according to the procedure given in the Experimental section. Most plasticized samples showed cold crystallization above T_g, followed by crystalline melting at ~ 165°C (cf. Fig. 1). The crystallinity of neat PLA granules was determined to be 15%, and on cooling, crystallization occurred at a temperature of 95°C. The blends with triacetine had higher crystallinity. At a level of 15 wt % triacetine, the crystallinity was 20% and increased with increasing amounts of triacetine, as illustrated in Figure 7. Cold crystallization occurred at temperatures around 67°C for blends containing up to 20 wt % triacetine, but for samples containing higher amounts, cold crystallization was no longer visible. The final degree of crystallinity was approximately the same in all the samples, whereas the cold crystallization decreased with increasing amounts of plasticizer.

The heat-treated samples had 45% crystallinity regardless of the time and temperature the heat treatment had been performed. None of the heat-treated samples showed any cold crystallization peaks in the DSC traces, corroborating the results obtained from DMA, which indicated that crystallization took place during the heat treatment, thereby causing phase separation to occur.

The increasing crystallinity of the blends having increasing contents of triacetine, as shown in Figure 7, gives a clear indication that the presence of the plasticizer facilitates the crystallization process of PLA. As noted previously, the increased molecular mobility increases the rate of crystallization, which allows PLA to crystallize to a higher degree during cooling after film preparation.[4] The PLA samples plasticized with tributyl citrate showed a crystallinity of 30% for all the three different tributyl citrate contents examined, and cold crystallization occurred around 70°C, according to DSC thermograms. Again it was found that the presence of the plasticizer enhances the crystallization of the PLA.

The significant decrease in cold crystallization temperature and the depression of T_g indicate that both triacetine and tributyl citrate are more efficient plasticizers than the ones used by Martin and Avérous.[4]

Crystallization of PLA and plasticized PLA melts was studied by DSC by cooling the melts from 210°C. Crystallization occurred at ~ 95°C for all samples. It was observed that for all of the plasticized samples there was a depression of the melting temperature of 10°C, compared to neat PLA. This depression seemed to be independent of the plasticizer content.[4] Table IV shows a collection of data obtained by DSC measurements of the different samples.

CONCLUSIONS

By plasticizing PLA with triacetine or tributyl citrate, it is possible to obtain a significant decrease in T_g for PLA. T_g decreases almost linearly with plasticizer content down to ~ 10°C at 25 wt %, at which point phase separation seems to occur. There is also a tendency toward phase separation of the plasticizer after heat treatment at 50°C of the samples. The reason for this is presumably the increase in crystallinity, which occurs during the heat treatment. Increasing amounts of plasticizer give increased crystallinity of the blends, whereas the melting temperature of the blends decreases by 10°C, regardless of plasticizer concentration.

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