



# Tributyl citrate oligomers as plasticizers for poly (lactic acid): thermo-mechanical film properties and aging

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## Abstract

Poly (lactic acid), PLA, is a biodegradable thermoplastic that can be produced from renewable resources. The polymer is of interest for production of films for packaging applications. However, plasticization of PLA is required in order to obtain films with sufficient flexibility. PLA was blended with tributyl citrate (TbC) and two oligomers of TbC that were synthesized by transesterification of tributyl citrate (TbC) and diethylene glycol (DEG). Dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC) were used to investigate the dynamic mechanical and thermal properties of the blends. All the plasticizers investigated decreased the glass transition temperature of PLA, and the reduction was the largest with the plasticizer having the lowest molecular weight. The PLA matrix became saturated with plasticizer at a certain concentration and phase separation occurred; the higher the molecular weight of the plasticizer, the lower the saturation concentration. Aging of the blends at room temperature for several months induced partial phase separation in the material. It was observed that the morphological stability of the blends was enhanced when the plasticizer concentration was reasonably low, i.e. 10–15 wt%.

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## 1. Introduction

Poly (lactic acid), PLA, is a thermoplastic polymer that can be produced from lactic acid obtained through fermentation of renewable resources [1]. The polymer has a number of interesting properties including biodegradability [1], biocompatibility [2,3], good mechanical properties and processability [4,5]. For these reasons PLA is an interesting candidate for producing packaging materials [3, 6], an area in which, today, mainly polyolefins are used. Consequently, it would be of great benefit to the environment if PLA could replace polyolefins to some extent in these applications.

In many packaging applications polymer film materials prepared by film extrusion are used. For PLA this is a difficult process due to the inherent brittleness and thermal instability of the polymer [7]. One important requirement for packaging materials is high flexibility at room temperature, and consequently, there is no tolerance for the polymer film tearing or cracking when subjected to

forces during package manufacturing. Other requirements include transparency and low crystallinity. A major issue is long-term stability since it is often the case that packaging material is stored during longer periods of time before use. Thus it is imperative that the shelf life of the material is acceptable, i.e. that the mechanical properties of the polymer film remain unchanged during the storage time.

The flexibility of PLA can be improved by modifying its physical properties, e.g. through copolymerization [8–15]. The mechanical properties can also be affected by blending PLA with a plasticizer or a second polymer. A large number of investigations have been performed on the blending of PLA with various polymers. Examples of such polymers are thermoplastic starch [16], poly (ethylene oxide) [9,17,18], poly (ethylene glycol) [10,16,19–23], poly ( $\epsilon$ -caprolactone) [8,9,20,24–29], poly (vinyl acetate) [30], poly (hydroxy butyrate) [31–34], cellulose acetate [35], poly (butylene succinate) [36,37] and poly (hexamethylene succinate) [38]. Low molecular weight compounds have also been used as plasticizers for PLA, e.g. oligomeric lactic acid, glycerol [16], triacetine [39,40] and low molecular weight citrates [39–41].

Crystallization properties, phase structure and

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morphology are aspects of great importance for the performance of PLA and its copolymers or blends. Neat PLA only crystallizes at temperatures above the glass transition temperature, i.e. around 50–60 °C, where the chain mobility is sufficiently high to allow reorganization [9]. Thus, heat treatment or annealing of amorphous PLA leads to crystallization of the polymer [42]. In addition, the presence of lower molecular weight polymer or oligomers contributes to a more complete crystallization because of the increased chain mobility [42]. It has been reported [43] that neat high molecular weight PLA that is cooled from the melt at a cooling rate lower than 10 °C/min will crystallize, and the degree of crystallinity increases with decreasing cooling rate. The same authors also reported that it seems to be difficult to achieve a degree of crystallinity in neat PLA higher than 45–50%.

The choice of polymers or plasticizers to be used as modifiers for PLA is limited by the requirements of the application. Only non-toxic substances approved for food contact can be considered as plasticizing agents in food packaging materials. For a low molecular weight plasticizer an important demand is that it should be miscible with PLA, thus creating a homogeneous blend. The plasticizer should not be too volatile so as not to evaporate at the elevated temperatures used during processing. Nor should the plasticizer be prone to migration as this would be a source of contamination of the food or beverage in contact with the plasticized PLA. Migration would also cause the blended material to regain the brittleness of neat PLA.

It has been reported that plasticizing PLA with 30 wt% PEG resulted in a material with a  $T_g$  below room temperature [21–23]. As a consequence the blends were not stable over time and an increase in modulus accompanied by a decrease in the elongation at break could be observed [23]. This was attributed to the crystallization of PEG which caused phase separation in the blend, gradually enriching the amorphous phase in PLA and increasing its  $T_g$  [22]. Cooling the blend from the melt state at a rate of 5 °C/min or less caused crystallization of both PLA and PEG to occur [21]. This also resulted in a gradual increase of the  $T_g$ . However, both the aging and the crystallization ceased when the  $T_g$  reached ambient temperature.

We have previously reported [40] that low molecular weight plasticizers such as tributyl citrate and triacetine drastically lowered the glass transition temperature of PLA, thus creating homogeneous and flexible materials. The reason for the good solubility of PLA in the plasticizers would be the polar interactions occurring between the ester groups in the plasticizer and PLA. However, it was observed that upon aging of the plasticized film materials the plasticizers had a tendency to migrate to the film surface. This was explained by the materials undergoing cold crystallization because the glass transition temperature was close to room temperature, which would allow large-scale chain movements to occur. The volume of the

amorphous phase decreased on crystallization thus forcing the plasticizer to migrate. A possible way to prevent the migration would be to increase the molecular weight of the plasticizers. In this way solubility could be maintained through the polar interactions, whereas the higher molecular weight would decrease the tendency for migration. However, increasing the molecular weight too much would eventually decrease the solubility causing phase separation and the formation of a two-phase system [44,45].

The objectives of the present study were to determine means of plastifying PLA and thereby obtaining films of increased flexibility for potential use in packaging material applications. The study describes the synthesis of oligomeric plasticizers for PLA. The oligomers were based on tributyl citrate; a substance that had previously proven successful as a plasticizer for PLA [39,40]. The polymerization was performed as a transesterification reaction with diethylene glycol. The study is mainly focused on the miscibility of PLA and the oligomeric citrates, and the dynamic mechanical and thermal properties of the blends. The effects of aging were also investigated.

## 2. Experimental

### 2.1. Materials

Tributyl citrate (TbC) was purchased from Acros Organics (Springfield, NJ). Diethylene glycol (DEG), and the catalyst tetrabutyl titanate were obtained from Aldrich (Milwaukee, WI). All reactants, along with other chemicals and solvents, were used as received.

PLA, with a molecular weight ( $M_w$ ) of approximately 100,000 g/mol and a polydispersity index of 2.4, was supplied by Fortum, Finland. The melting temperature ( $T_m$ ) was 175 °C and the glass transition temperature ( $T_g$ ) was 52 °C. The enantiomeric form of the PLA was 100% L. The polymer was dried for 30 h at 40 °C in a Piovon H31M drier with a Piovon DS403 control unit and then stored in sealed PE-bags wrapped in aluminum foil in a desiccator at ambient temperature.

### 2.2. Synthesis

A transesterification based on the plasticizer TbC was performed. The two main reactants were TbC and DEG and they were added to achieve 20 g of the polymerization product. Fig. 1 shows the synthesis path for the transesterification. The polymerization was performed in a reaction vessel with a magnetic stirrer in an oil bath that kept 130 °C. Butanol (BuOH) was distilled from the reaction mixture and collected in a trap device. There was a constant flow of N<sub>2</sub>-gas through the reaction vessel.

The aim of the first synthesis was to produce a short oligomer. TbC and DEG were added with a mol ratio of 2:1. To the reaction vessel 20.8 ml (0.06 mol) TbC and 2.8 ml

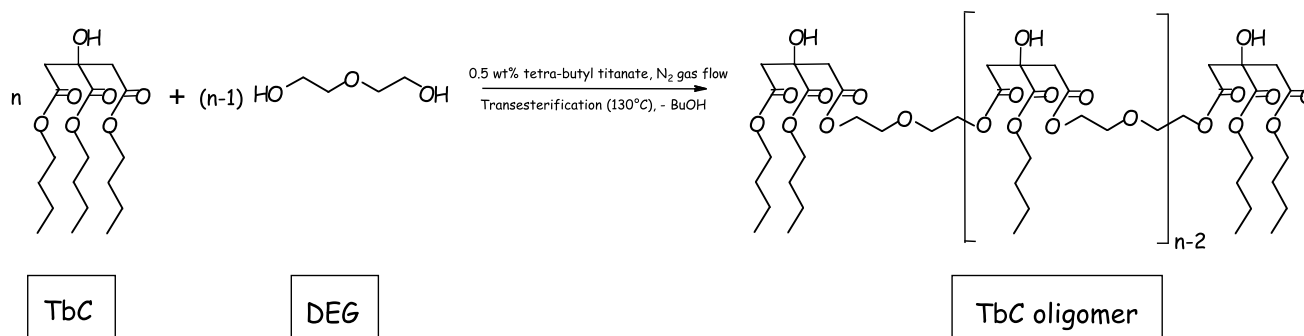


Fig. 1. Synthesis path for the transesterification of TbC and DEG.

(0.03 mol) DEG were charged and 0.06 g of the catalyst tetrabutyl titanate was added. The temperature was kept at 130 °C for 9 h after which the reaction was stopped.

The second product in the series was intended to be a long oligomer. The mol ratio between TbC and DEG was 1.02:1. The reaction vessel was charged with 21.7 ml (0.063 mol) TbC and 5.9 ml (0.062 mol) DEG along with 0.15 g tetrabutyl titanate. The reaction was run for 10 h at 130 °C. The crude oligomeric citrate esters were then used in the blending experiments without further purification.

### 2.3. Sample preparation

#### 2.3.1. Blending

Blending experiments were performed in a Midi 2000 co-rotating twin screw extruder from DSM Research (Heerlen, The Netherlands). The temperature profile ranged from 220 °C in the feeding zone down to 180 °C in the die, and the screw speed was 100 rpm. Fig. 2 shows the screw assembly and profile. The melt was blended for 2 min and

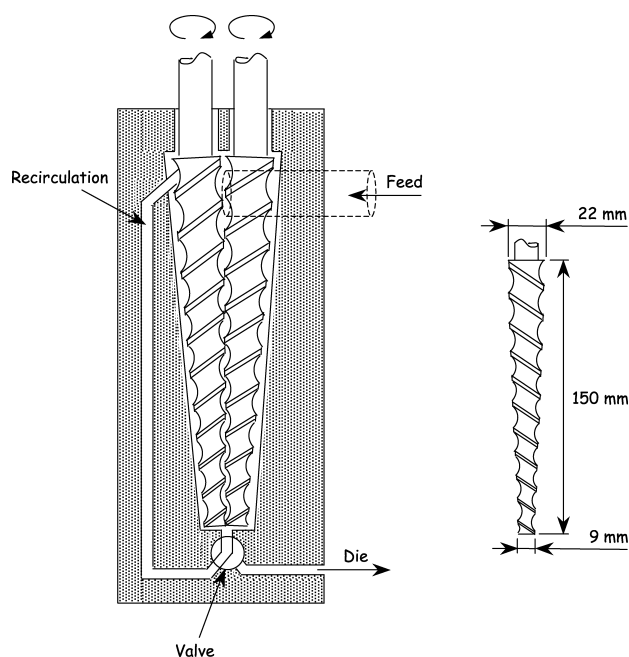


Fig. 2. Assembly and profile of the screws in the twin screw extruder.

then extruded as a strand through a single-filament die with the dimension 10 × 1 mm<sup>2</sup>. The strand was wound and cooled on a glass cylinder with a diameter of 15 cm and stored at ambient temperature in sealed PE-bags.

#### 2.3.2. Film preparation

Films were prepared from the blends by heat pressing at 200 °C. Short strands 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 × 10<sup>5</sup> Pa. The samples were removed from the press plates and cooled in air until they reached ambient temperature (approximately 20 s). The specimens were then stored in sealed plastic bags in air awaiting analysis.

#### 2.3.3. Aging

The plasticized PLA films were aged at ambient conditions for 4 months. The films were then characterized with DMA in order to investigate the stability of the blends.

### 2.4. Sample characterization

#### 2.4.1. Size exclusion chromatography (SEC)

The oligomers from the synthesis were characterized by means of size exclusion chromatography (SEC). SEC analyses were run at room temperature in THF (Labs scan Ltd, Ireland, concentration 1–2 wt%) on Waters' Styragel columns (10<sup>5</sup>, 10<sup>4</sup>, 10<sup>3</sup>, 500 Å) or 2 Waters' Ultrastaygel linear columns, using differential refractive index and viscometry detectors (Dual detector, 250, Viscotek).

#### 2.4.2. Dynamic mechanical analysis (DMA)

Investigation of the α-relaxational process associated with the glass transition was performed by dynamic mechanical analysis (DMA) on a DMA 2980 from TA Instruments (New Castle, Delaware, USA). The runs were conducted at a heating rate of 3 °C/min between –60 and 150 °C. Tensile mode was used under isochronal conditions at a frequency of 1 Hz. The shape of the film samples was rectangular, approximately 15 mm × 5 mm × 0.35 mm.

The amplitude was chosen at 5  $\mu\text{m}$ , a pre-load force of 0.010N was applied and the autostrain was set to 115%. Curves displaying storage modulus ( $E'$ ), loss modulus ( $E''$ ) and loss factor ( $\tan \delta$ ) were recorded as a function of temperature.

#### 2.4.3. Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) was conducted on a Q1000 from TA Instruments (New Castle, Delaware, USA) on the film materials as well as the pure plasticizing agents. The scans on the films were run from  $-60$  to  $210$   $^{\circ}\text{C}$  and back down to  $-60$   $^{\circ}\text{C}$ . Fig. 3 shows a DSC thermogram of neat PLA. During the heating ramp (10  $^{\circ}\text{C}/\text{min}$ ) the glass transition, cold crystallization and melting of the material occurred and during the cooling (10  $^{\circ}\text{C}/\text{min}$ ) the crystallization of the material could be observed. The scans on the pure plasticizing agents were run from  $-90$  to  $50$   $^{\circ}\text{C}$  at 10  $^{\circ}\text{C}/\text{min}$  in order to observe the glass transition. All scans were carried out under  $\text{N}_2$  atmosphere on approximately 10 mg of material. Values for glass transition temperatures, fusion enthalpies, crystallization temperatures and melting temperatures were evaluated from the scans. The degree of crystallinity in the materials after film pressing was calculated by subtracting the cold crystallization and pre-melt crystallization from the melting (c.f. Fig. 3).

### 3. Results and discussion

#### 3.1. Synthesis of TbC oligomers

The aims of the syntheses were to prepare one short-chain and one long-chain oligomer from TbC and DEG through transesterification. DEG was chosen as the second reactant since it has a successful history as a plasticizer. It should contribute to increased flexibility and at the same time retain the polar interactions with PLA. Table 1 gives

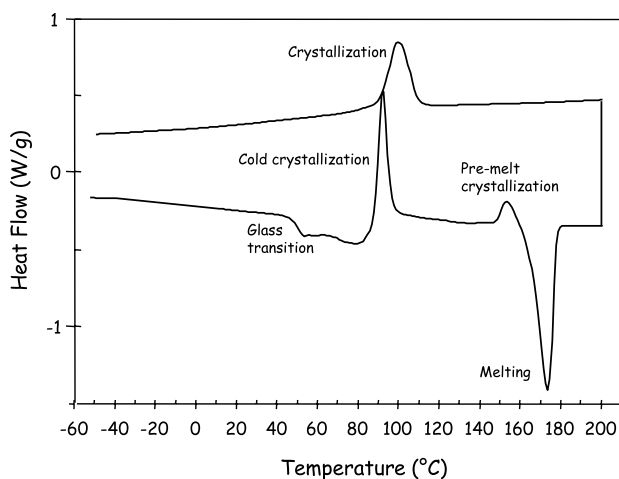


Fig. 3. DSC trace for neat PLA displaying both the heating and cooling ramp as well as the glass transition, cold crystallization, pre-melt crystallization, melting and crystallization.

the solubility parameters of the materials. The calculations were made according to Eq. (1):

$$\delta = \frac{\sum F\rho}{M_0} \quad (1)$$

where  $\delta$  represents the solubility parameter,  $\rho$  the density,  $M_0$  the molecular mass and  $F$  the group molar attraction constants according to the Hoy series [46]. It can be shown that TbC, its oligomers and neat PLA have similar solubility parameters, which indicates that they should be miscible and therefore that the oligomers should be efficient as plasticizers. Pure DEG has a solubility parameter that is higher than that of PLA, but by increasing the number of DEG-links in the oligomers their solubility parameters decrease. This decrease in the solubility parameter is caused by the esterification of the hydroxyl groups, since the polarity of the ester groups is lower than that of OH-groups.

The synthesis of the short-chain oligomer was run until no more BuOH distilled off from the reaction mixture. In the case of the long-chain oligomer, the viscosity increased drastically after 10 h and the reaction was terminated in order to avoid gelling of the polymer. In order to characterize the synthesized oligomers SEC and DSC experiments were performed. Fig. 4 shows SEC traces of the two oligomers and Table 1 gives their main physical characteristics, as well as those of TbC and neat PLA.

The presence of TbC and DEG peaks in the SEC traces (Fig. 4) clearly shows that all of the reactants had not been polymerized. The  $M_n$  value for the short oligomer was calculated with polystyrene standards to 980 g/mol (Table 1) representing an oligomer with three repeating units (c.f. Fig. 1). Hence, the short oligomer is referred to as TbC-3. The  $M_n$  value for the long oligomer was calculated to 2240 g/mol, corresponding to an oligomer with seven repeating units. The long oligomer is therefore referred to as TbC-7. It should be noticed that the determination of  $M_n$  by the use of linear PS standards is not entirely accurate and thus, the molecular weights obtained from the SEC analyses should not be taken as true values but as rough indications of the sizes of the oligomers. The results were, however,

Table 1

The molecular weights ( $M_n$  and  $M_w$ ), no of repeating units ( $n$ ), glass transition temperatures ( $T_g$ ) and solubility parameters ( $\delta$ ) for PLA and four plasticizing agents

	$M_n$ (g mol $^{-1}$ )	$M_w$ (g mol $^{-1}$ )	$n$	$T_g^a$ ( $^{\circ}\text{C}$ )	$\delta^b$ (J cm $^{-3}$ ) $^{1/2}$
PLA	—	—	—	52	20.1
DEG	106	—	—	—	23.5
TbC	360	—	1	-89	19.6
TbC-3	980 <sup>c</sup>	4550 <sup>c</sup>	3	-62	18.6
TbC-7	2240 <sup>c</sup>	63,600 <sup>c</sup>	7	-32	18.6

<sup>a</sup> Measured by DSC at the inflection point of the change in the  $\Delta C_p$  baseline.

<sup>b</sup> As calculated with group molar attraction constants from the Hoy series [46].

<sup>c</sup> Measured by SEC according to polystyrene standards.

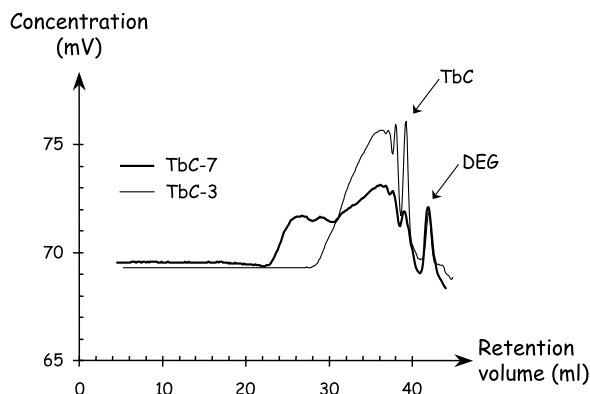


Fig. 4. SEC traces displaying TbC-3 and TbC-7.

sufficient in order to obtain a qualitative characterization of the synthesis products and to be able to compare the oligomers to each other.

The reactants were added assuming that the tertiary hydroxyl group on TbC would be quite unreactive and not participate in the transesterification reaction. It was also assumed that out of the three ester groups present in TbC, two would be transesterified and the third one would be less reactive because of sterical hindrance after the first two had reacted. Thus, a more or less linear oligomer should be produced. However, seeing as TbC-7 seemed to be close to gelling without  $M_n$  being especially high, it seems probable that the tertiary OH-group as well as the third ester group would have participated in the reaction to some extent, causing uncontrolled branching and a molecular weight increase to occur.

### 3.2. Dynamic mechanical and thermal properties

#### 3.2.1. Blending

The blending was performed in a small co-rotating twin screw extruder (MIDI-2000) with a chamber volume of 15 cm<sup>3</sup>. Since the syntheses only produced limited amounts of the oligomeric plasticizers, effective blending of small volumes was especially important. In a previous study [36] blending was performed in a Brabender Plastograph with counter-rotating screws. In comparison the MIDI-2000 was considered more suitable because of the smaller volume and the simpler handling of the melt after the blending operation. The extruded strands could be used directly for film pressing, producing homogeneous films. Blending in the MIDI-2000 was also considered more effective since co-rotating screws induce larger shear forces than counter rotating ones.

#### 3.2.2. DMA measurements

Figs. 5(a) and (b) give the evolution of the viscoelastic storage and loss moduli, respectively, as a function of the temperature for pressed films of neat PLA and blends containing 15 wt% plasticizer. The thermograms show the  $\alpha$ -relaxation (between 30 and 60 °C) of the materials and the

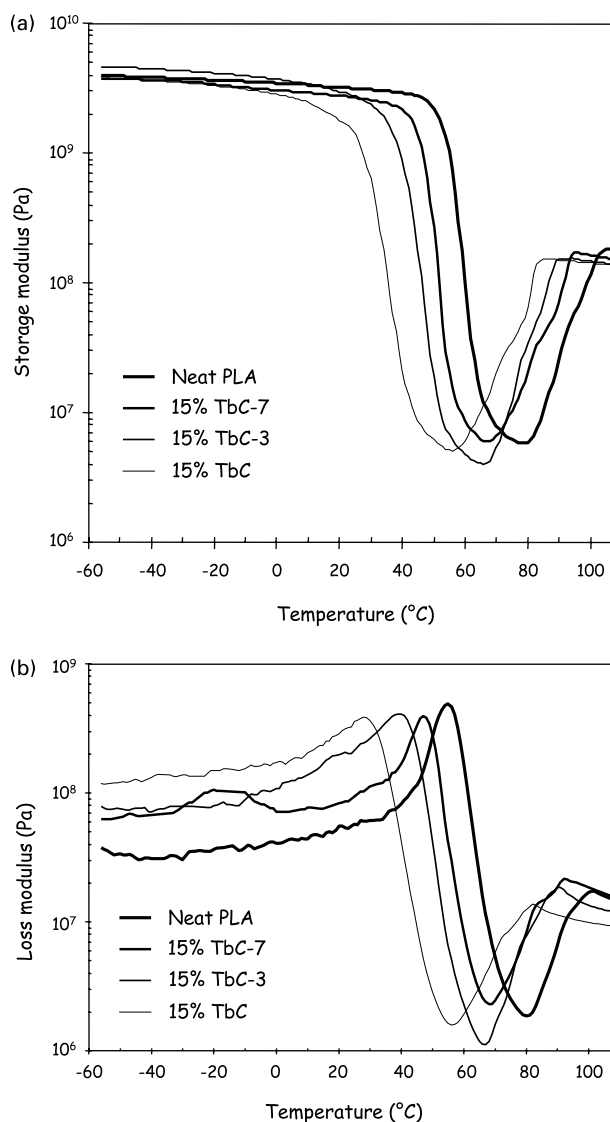


Fig. 5. (a) Storage modulus curves as a function of temperature from DMA runs comparing blends containing 15 wt% TbC, TbC-3 and TbC-7 with neat PLA. (b) Loss modulus curves as a function of temperature from DMA runs comparing blends containing 15 wt% TbC, TbC-3 and TbC-7 with neat PLA.

effects of cold crystallization (between 80 and 100 °C). The  $T_\alpha$  values of the films, here defined as the temperature location of the maximum of the loss modulus,  $E''$ , obtained for the  $\alpha$ -relaxation (associated with the glass transition) at the frequency of 1 Hz are given in Table 2. It is clearly shown in Fig. 5(a) that the drop in storage modulus following the  $\alpha$ -relaxation was found at a lower temperature for the plasticized materials as compared to neat PLA. The same trend can be observed in Fig. 5(b) where  $T_\alpha$  was significantly decreased for all the plasticized materials, the plasticizer having the lowest molecular weight, i.e. TbC, being the most effective. At 15 wt% both TbC and TbC-3 were seemingly compatible with PLA, while TbC-7, however, displayed an additional loss peak at -20 °C (Fig. 5(b)). Since the  $T_\alpha$  of the PLA/TbC-7 blend was

Table 2

 $T_{\alpha}$  measured by DMA and thermal data obtained by DSC measurements for films of neat and plasticized PLA

	Content (wt%)	$T_{\alpha}$ (°C)	$T_g$ (°C)	Cold crystallization temperature (°C)	Melting temperature (°C)	Crystallization temperature (°C)	Degree of crystallinity <sup>d</sup> (%)
PLA	100	54	52	91	173	95	16
TbC	15	28	25	68	166	91	22
TbC-3	10	42	38	78	171	95	18
	15	37	33	76	168	96	20
	20	36	30	75	168	96	20
TbC-7	15	47	43	78	170	86	19

<sup>a</sup> Calculations are based on  $\Delta H_m$  for 100% crystalline PLA being equal to 93 J/g [47].

depressed relative to the value obtained for neat PLA the additional loss peak indicated that a partial phase separation had occurred. These results are consistent with a study on block copolymers of PLA and polycaprolactone [9], where the depressed  $T_g$  of the copolymer as compared to neat PLA indicated that the segments were partially miscible despite the crystallization-induced phase separation.

As was observed in the SEC traces, there are minor amounts of unreacted TbC present in the two oligomers that could contribute to the decrement in  $T_{\alpha}$ . Both TbC-3 and TbC-7 contain approximately 10% of pure TbC, which means that 1.5 wt% pure TbC is present in a blend of PLA and 15 wt% oligomer. Thus, the depression of  $T_{\alpha}$  caused solely by TbC would, according to previous investigations [39,41], only amount to 1–2 °C which is far less than observed.

The TbC-3 oligomer showed a reasonably good performance at 15 wt%. In order to investigate the concentration dependence, films were pressed from blends of PLA with 10, 15 and 20 wt% TbC-3, and the films were analyzed with DMA. Figs. 6(a) and (b) shows the evolution of storage and loss moduli, respectively, as a function of temperature of the blends compared with neat PLA. The drop in storage modulus observed in Fig. 6(a) is found at a lower temperature with an increasing concentration of TbC-3. In addition, as can be seen in Fig. 6(b) and as previously observed for TbC,  $T_{\alpha}$  decreased with increasing amount of plasticizer. However, at 20 wt% the loss modulus curve showed an additional peak, as previously noted for TbC-7, again suggesting that the TbC-3 oligomer formed a separate phase at the higher concentration. These results correspond well with those on PLA/TbC blends reported on earlier [39], in which case phase separation started to occur around 20 wt%.

The amorphous domains of the semi-crystalline PLA seem to be able to incorporate a certain amount of plasticizer through swelling. Since the crystalline domains act as crosslinks, swelling equilibrium may be reached and the excess plasticizer will be left as its own phase. As a comparison, blends of PLA and poly (ethylene glycol), PEG, have shown signs of phase separation when the PEG concentration exceeded 30 wt% [19]. This investigation was, however, performed with a PLA consisting of 96%

L-form, thus leading to a system with a larger amorphous phase.

A high molecular weight plasticizer, such as TbC-7, will reach swelling equilibrium of the amorphous phase at a

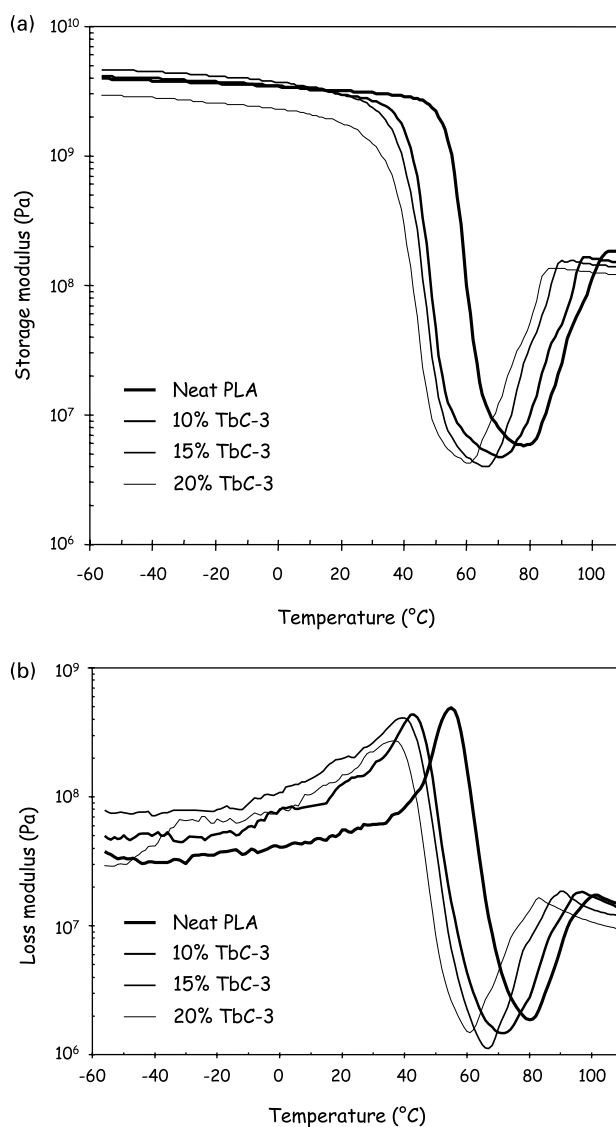


Fig. 6. (a) Storage modulus curves as a function of temperature from DMA runs comparing blends containing 10, 15 and 20 wt% TbC-3 with neat PLA. (b) Loss modulus curves as a function of temperature from DMA runs comparing blends containing 10, 15 and 20 wt% TbC-3 with neat PLA.

relatively low concentration as compared to lower molecular weight plasticizers. This is due to less entropy of mixing. However, seeing as the molecular weight distribution of TbC-7 was very broad, segregation had likely occurred, i.e. the lower molecular weight species may have been incorporated in the amorphous part while species with a higher molecular weight may have formed a separate phase.

### 3.2.3. DSC measurements

DSC experiments were conducted to investigate the thermal properties of the blended materials. Fig. 7 shows DSC traces comparing neat PLA with the various PLA/TbC-oligomer blends. The shapes of the curves are similar, displaying glass transition, cold crystallization and melting peaks. The thermal characteristics are summarized in Table 2. Fig. 8 shows  $T_g$  as a function of plasticizer content for the blends. As noted for the  $T_\alpha$  values, the glass transitions identified in the DSC traces occur at lower temperatures in the blended materials than in neat PLA, the lowest  $T_g$  value being noted for the plasticizer having the lowest molecular weight. The  $T_g$  values are in good agreement with those reported in a previous investigation of the effects of plasticizing PLA with citrates, conducted by Labreque et al. [41].

The effects of blending PLA with TbC and TbC-3 can be compared with the results from a study [16] where PLA was

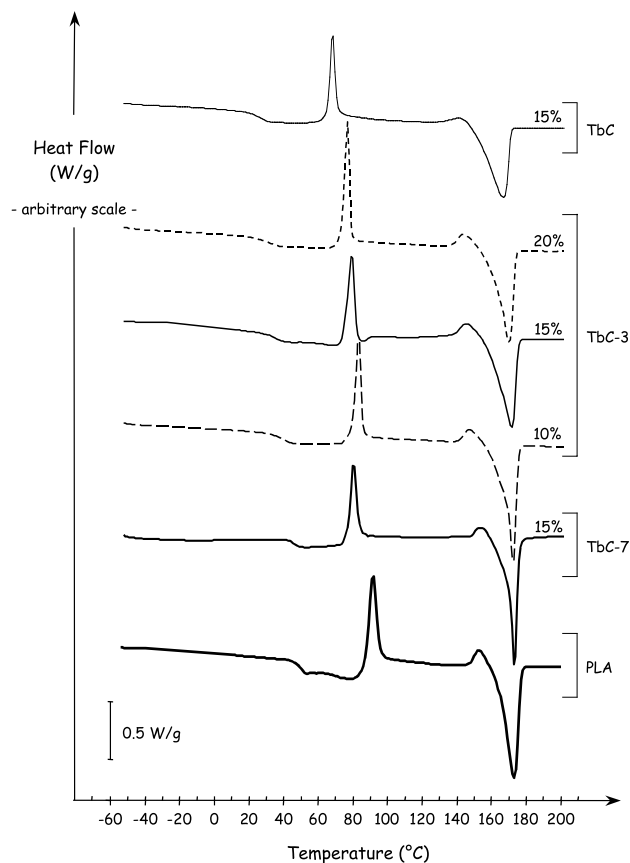


Fig. 7. DSC traces showing glass transitions, cold crystallization, pre-melt crystallization and melting for neat and plasticized PLA materials.

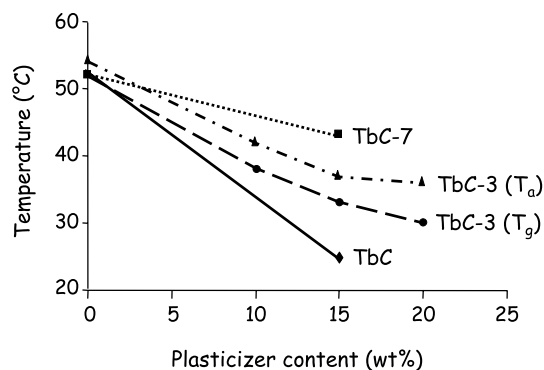


Fig. 8.  $T_g$  as a function of plasticizer content for blends of PLA with TbC, TbC-3 and TbC-7.

plasticized with PEG. PLA was there blended with PEG of two molecular weights corresponding to the molecular weights of TbC and TbC-3 and it was observed that the decrease in  $T_g$  obtained by blending with PEG was in the same vicinity as for the citrates.

It should be noted that the materials that were phase separated according to the DMA measurements, i.e. those containing 15 wt% TbC-7 and 20 wt% TbC-3, respectively, did not show any signs of a thermal transition connected to the plasticizer phase around  $-20$  °C in the DSC traces. It seems likely that the volume of the second phase was too small to be detected with DSC.

Lowering the molecular weight of the plasticizer caused a shift to lower temperature for both the cold crystallization and melting peaks, as displayed in the DSC traces (Fig. 7). The size of the shift increased as the molecular weight of the plasticizer decreased. Similar observations have been presented in a study concerning PLA/PEG blends [21]. Within the TbC-3 blend series there was also a decrease in glass transition, cold crystallization and melting temperatures with increasing amount of oligomer (Table 2).

The degree of crystallinity (Table 2) of the materials obtained after blending and film pressing was determined by subtracting the enthalpies for pre-melt crystallization and cold crystallization from the melting enthalpy (c.f. Fig. 3). It was found that the degree of crystallinity in the films was higher in the more plasticized materials, although the differences were small. This result can be explained by the fact that a low glass transition temperature allows an additional crystallization to occur during cooling of the pressed film, as compared to the situation for neat PLA. The values (Table 2) obtained in the present study correspond well with those reported in our previous study [39]. However, there was a shift in the baseline of the DSC traces, which suggests that crystallization occurred continuously in the temperature region 80–150 °C, i.e. between the cold crystallization and the pre-melt crystallization. This effect has not been taken into account when calculating the degrees of crystallinity since it was very difficult to assess the baseline.

### 3.2.4. Aging

The morphological stability of polymer/plasticizer blends is of great importance in most applications. We have previously reported on progressive phase separation and migration of TbC on annealing and aging of plasticized PLA. In the present investigation the effects of molecular size on the morphological stability of PLA plasticized with oligomeric TbC was one of the key issues.

PLA/TbC and PLA/TbC-3 samples were naturally aged at ambient temperature (approximately 22 °C) for 4 months to investigate the morphological stability of the materials. Figs. 9(a) and (b) show curves of the storage and loss moduli, respectively, as a function of temperature for four blend systems of aged and unaged material. A shift to higher temperature for the drop in storage modulus can be seen in Fig. 9(a) for all the aged samples as compared to the unaged ones. Fig. 9(b) shows a broadened loss modulus peak for the

aged blend containing 15 wt% TbC and a shift to higher temperature for the increase in modulus connected to the cold crystallization. It can be assumed that the low molecular weight of TbC and the low glass transition temperature of the blend significantly facilitate the migration of the plasticizer from the bulk of the material to the film surface. Previous investigations by contact angle measurements [40] strongly pointed toward this assumption and it was further corroborated by the film attaining a sticky surface after aging. The character of the material that remained after TbC had migrated to the surface resembled that of neat PLA, which means that the aged material regained the brittle properties of the unplasticized polymer. These results correspond well with those from aging of PLA/PEG blends [22,23], where the aging caused phase separation and crystallization in the system, resulting in an increased rigidity of the material.

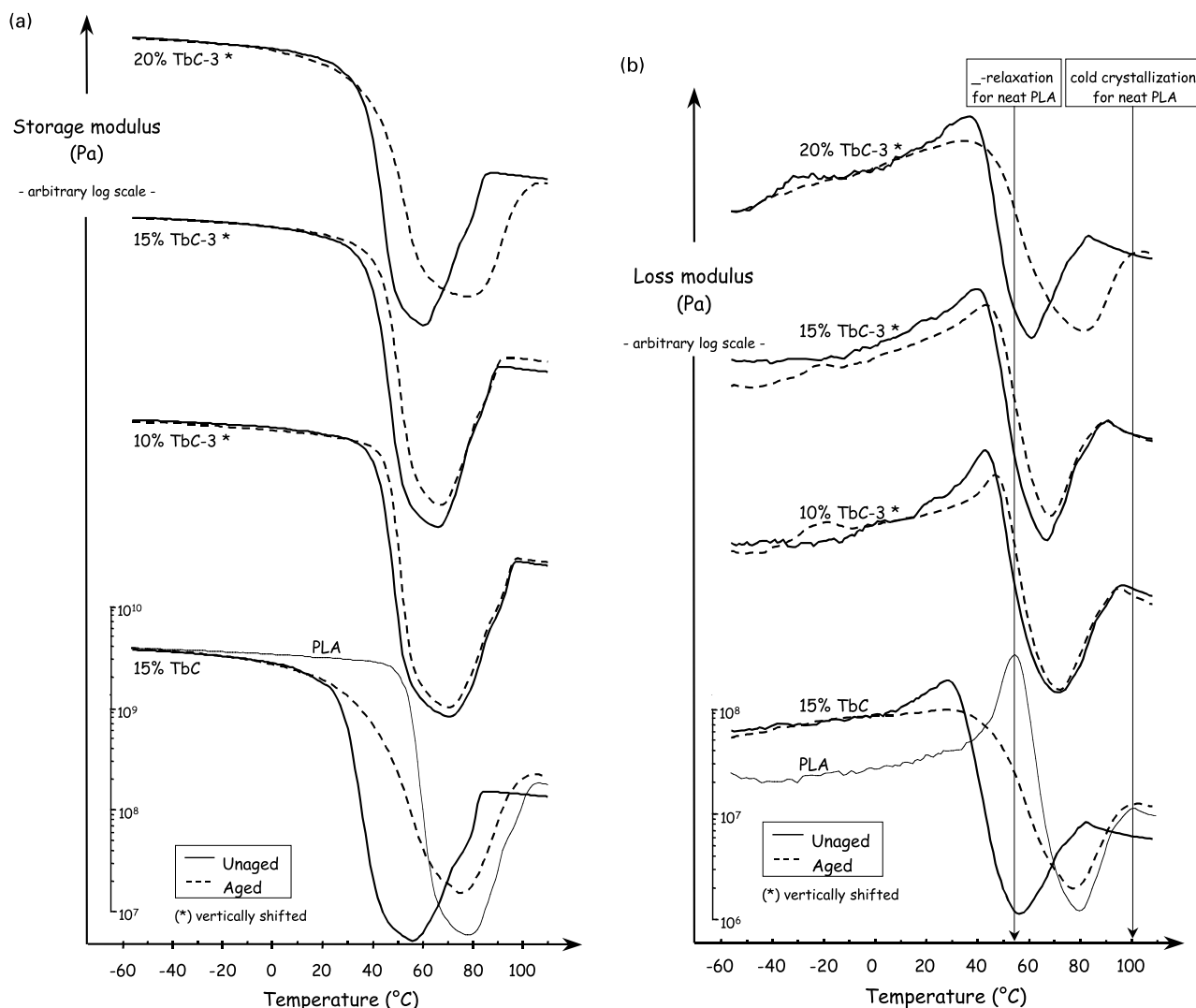


Fig. 9. (a) Storage modulus curves as a function of temperature from DMA runs comparing aged (4 months) and unaged PLA blends containing TbC or TbC-3. The thermograms for the PLA/TbC-3 blends have been vertically shifted for a clearer overview. (b) Loss modulus curves as a function of temperature from DMA runs comparing aged (4 months) and unaged PLA blends containing TbC or TbC-3. The thermograms for the PLA/TbC-3 blends have been vertically shifted for a clearer overview.



Aged samples of blends containing 10 and 15 wt% TbC-3 (Fig. 9(b)) displayed an additional peak at low temperature in the loss modulus curve that suggested that both materials underwent phase separation to some extent. However, the modulus increase caused by cold crystallization remained at the same temperature as that of the unaged materials. This fact would indicate that even though a phase separation had occurred the plasticizer was probably still more or less incorporated in the material and did not migrate to the surface. A further indication was that the surfaces of these aged films were not sticky. An explanation for this behavior is that the higher molecular weight of TbC-3 decreased its inclination to migrate, especially when the concentration was reasonably low. On the other hand, the 20 wt% blend already displayed the low temperature peak in the loss modulus curve in the unaged material. When the material was aged the peak broadened significantly and the increase in modulus caused by cold crystallization was shifted to a higher temperature. Again this would indicate a larger-scale phase separation causing migration of the plasticizer to the film surface, which was also supported by the fact that the aged 20 wt% PLA/TbC-3 film had a sticky surface.

#### 4. Conclusions

Two oligomeric plasticizers, one trimer (TbC-3) and one heptamer (TbC-7), were prepared by transesterification of TbC and DEG. The tertiary hydroxyl group on TbC seemed to have participated in the reaction, causing uncontrolled branching.

Blending PLA with the oligomeric plasticizers lowered the glass transition temperature. The plasticization effect was larger with low molecular weight plasticizers. TbC-3 was compatible with PLA at concentrations up to 20 wt% after which phase separation occurred. Materials containing 10 and 15 wt% TbC-3 that were aged at ambient temperature for 4 months displayed an additional peak in the loss modulus curves indicating phase separation. The cold crystallization temperature of the aged material remained the same as for the unaged one, suggesting that even though there was progressive phase separation the plasticizer remained in the bulk instead of migrating to the film surface. Aging of the 20 wt% TbC-3 film in the same manner generated further phase separation but also forced the plasticizer to migrate to the film surface. Thus the morphological stability of the PLA/TbC-3 blends was better when the plasticizer concentration was reasonably low.

Blends of PLA plasticized with TbC-7 displayed phase separation already at a concentration of 15 wt%, due to its higher molecular weight. The results indicate that PLA can only incorporate a certain amount of plasticizer before becoming saturated and the higher the molecular weight of the plasticizer, the lower the saturation concentration.

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