Plasticization of Poly(lactic acid) with Oligomeric Malonate Esteramides: Dynamic Mechanical and Thermal Film Properties

Nadia Ljungberg, Didier Colombini, Bengt Wesslén

Department of Polymer Science and Engineering, Lund Institute of Technology, Lund, Sweden

ABSTRACT: Two oligomeric malonate esteramides and an oligomeric malonate ester were synthesized with the intention to plasticize poly(lactic acid), PLA. The synthesis was performed by reacting diethyl bishydroxymethyl malonate (DBM) with adipoyl dichloride and one of two diamines, that is, triethylene glycol diamine (TA) and polyoxypropylene glycol diamine (PA), or triethylene glycol (TEG), giving three platicizing agents denoted as DBMATA, DBMAPA, and DBMAT, respectively. The synthesis products were characterized by size exclusion chromatography and Fourier transform infrared spectroscopy, and blended with PLA at a concentration of 15 wt %. Dynamic mechanical analysis, differential scanning calorimetry, and tensile testing were used to investigate the physical properties of films from the resulting blends. All three plasticizers decreased the glass transition temperature of PLA, and the largest decrement was observed for PLA/DBMATA. Films of DBMATA and DBMAT showed enhanced flexibility in strain at break as compared to neat PLA. Subsequently, it was found that thermal annealing of the plasticized materials (4 h at 100°C) encouraged cold crystallization, inducing phase separation in the blends, and caused them to regain the brittleness of neat PLA. On the other hand, by aging (6 weeks) the blends at ambient conditions, cold crystallization could be avoided and the flexibility in the films maintained. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 96: 992–1002, 2005

Key words: poly(lactic acid); plasticization; esteramide; compatibility

INTRODUCTION

Biodegradable polymers from renewable resources are becoming more and more interesting in a society where a large part of the garbage and waste consists of polyolefins. Lactic acid, which can be obtained through fermentation of renewable resources,[1] is the main building block in the thermoplastic polymer poly(lactic acid), PLA. Among its many interesting properties are 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, the environment would benefit from PLA replacing polyolefins in these applications.

However, most packaging applications require the use of polymer film materials, and seeing as PLA has an inherent brittleness and thermal instability,[7] film extrusion of PLA is a difficult process. There is no tolerance for the PLA film tearing or cracking when subjected to forces during package manufacturing.

Nevertheless, there are means of improving the flexibility of PLA by modifying its physical properties. This can, for instance, be carried out through copolymerization.[8–15] Another possibility is to enhance the mechanical properties 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, for example, thermoplastic starch,[16] poly (ethylene oxide),[11,17,18] poly (ethylene glycol),[13,16,19,20] poly (ε-caprolactone),[11,12,20–26] poly (vinyl acetate),[27] poly (hydroxy butyrate),[28–30] cellulose acetate,[31] poly (butylene succinate),[32,33] and poly (hexamethylene succinate).[34] Low molecular weight compounds have also been used as plasticizers for PLA, for example, oligomeric lactic acid, glycerol,[16] triacetine,[35,36] and low molecular weight citrates.[35–37]

The packaging application has certain requirements that drastically limit the possible choices of polymers or plasticizers to be blended with PLA. It is of extreme importance that the substances are nontoxic and approved for food contact. The plasticizer should also be miscible, or at least compatible, with PLA, thus enabling a sufficiently homogeneous blend to be created. High volatility in the plasticizer is disadvantageous since this would cause it to evaporate at the elevated temperatures used during processing, and migration of the plasticizer is totally unacceptable in order not to

contaminate the food or beverage in contact with the plasticized PLA.

Earlier studies[35] showed that low molecular weight plasticizers such as tributyl citrate and tri-acetine drastically decreased the glass transition temperature of PLA, thus creating a homogeneous and flexible film material. Although it was also observed that the plasticizers migrated to the film surface after aging of the materials at ambient temperature for 1–4 months,[36] such a migration was successfully prevented[38] by increasing the molecular weight of the plasticizers. A trimer and a heptamer of tributyl citrate were synthesized by transesterification and by increasing the molecular weight in this way, the plasticizing agents became less inclined to migrate to the film surfaces.[38] In addition, it was reported that the higher molecular weight of the plasticizer caused phase separation to occur at lower concentrations.

Synthesis was also carried out to obtain oligomeric substances with a plasticizing effect on PLA where diethyl bishydroxymethyl malonate (DBM) was the main building block.[39] DBM was esterified with an acid dichloride, and it was found that increasing the hydrophobicity of the chains linking the DBM monomers together increased the compatibility of the resulting oligomer with PLA.[39] The glass transition temperature of PLA was decreased when blended with the DBM oligomers, and natural aging of the blends under ambient conditions left the material unchanged. This suggested that a stable plasticized system had been obtained, where the plasticizer was not inclined to migrate to the film surface at ambient temperature.[39]

Another possibility of increasing the compatibility could be by blending PLA with esteramides, thereby introducing polar amide groups that are able to interact with the PLA chains. This would allow for blends with esteramides of high molecular weights, thus enabling a reduced tendency for migration but at the same time preventing phase separation and the formation of a two-phase system.[40,41]

The present study describes the synthesis of oligomeric esteramide plasticizers for PLA. The oligomers were based on DBM, a substance that had previously proven successful as a plasticizer for PLA.[39] The polymerization was performed as a two-step reaction, where the first step was an esterification between DBM and excess adipoyl dichloride and the second step was an amidation between the –COCl terminated ester and a diamine. The study is mainly focused on the compatibility of the PLA/esteramide blends, and on the dynamic mechanical and thermal film properties of as-pressed, thermally annealed, and naturally aged blends.
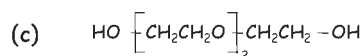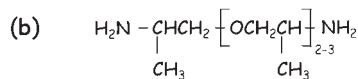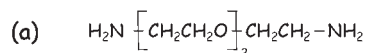
(a) $H_2N \left[CH_2CH_2O \right]_2 CH_2CH_2-NH_2$

(b) $H_2N-CHCH_2 \left[OCH_2CH \right]_{2-3} NH_2$
$\qquad\quad CH_3 \qquad\quad CH_3$

(c) $HO \left[CH_2CH_2O \right]_2 CH_2CH_2-OH$

Figure 1 Chemical structures of the two diamines, that is, (a) triethylene glycol diamine, TA, and (b) polyoxypropylene glycol diamine, PA, as well as of (c) triethylene glycol, TEG.

EXPERIMENTAL

Materials

Diethyl bishydroxymethyl malonate (DBM), adipoyl dichloride (AdCl), and triethylene glycol (TEG) were purchased from Aldrich (Steinheim, Germany). Triethylene glycol diamine (TA) with a molecular weight of 148 g/mol and polyoxypropylene glycol diamine (PA) with a molecular weight of 230 g/mol were kindly supplied by Huntsman Corp. (Rozenburg, The Netherlands). The chemical structure of the two diamines and of TEG can be seen in Figure 1. 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 Corp. (Keilaniemi, Finland). The melting temperature (T_m) and the glass transition temperature (T_g), as given by the supplier, were 175°C and 52°C, respectively. The polymer was dried for 30h at 40°C in a Piovan H31M drier with a Piovan DS403 control unit (Venice, Italy), and then stored in sealed PE-bags wrapped in aluminum foil in a desiccator at ambient temperature.

Synthesis

The esteramide syntheses were performed as two-step reactions. DBM was reacted with excess AdCl (molar ratio 4 : 5) for 8 h, after which the diamine was added. Chloroform (CHCl$_3$) was used as a solvent. The polymerization was performed in a reaction vessel equipped with a magnetic stirrer and an oil bath that kept 60°C. There was a constant flow of N$_2$-gas through the reaction vessel. Hydrochloric acid (HCl) was emitted from the reaction mixture

and collected in a trap device containing distilled water.

Three reactions were carried out to synthesize two oligomeric esteramides and an ester, defined as a reference material. In the first case, 13.2 g (0.06 mol) DBM was dissolved in 20 mL $CHCl_3$ and charged to the reaction vessel. 10.9 mL (0.075 mol) AdCl in 20 mL $CHCl_3$ was slowly added to the reaction mixture through a funnel. The reaction was run for 8 h at 60°C, after which 1.8 mL (0.013 mol) TA dissolved in 10 mL of $CHCl_3$ was slowly charged to the vessel. This second reaction step was allowed to run for 14 h. As a final step, 1.5 mL of ethanol was added to ensure that no –COCl groups were left unreacted. After an additional 2 h, the reaction was terminated, and the remaining chloroform and ethanol were then evaporated under vacuum (20 mm Hg) in a Rotavapor-R from Büchi (Flawil, Switzerland). Figure 2 displays the synthesis path for this reaction, where the product was denoted as DBMATA.

The second esteramide reaction was carried out in the same way as the first. The vessel was charged with 13.2 g (0.06 mol) DBM dissolved in 20 mL $CHCl_3$, and 10.9 mL (0.075 mol) AdCl in 20 mL $CHCl_3$ was slowly added to the mixture through a funnel. The reaction was run for 8 h at 60°C, after which 3.2 mL (0.013 mol) PA dissolved in 10 mL of $CHCl_3$ was slowly charged to the vessel. The reaction was continued for 14 h, and finally 1.5 mL of ethanol was added. After 2 h the reaction was terminated, and the remaining chloroform and ethanol were evaporated under vacuum (20 mm Hg) in a Rotavapor-R from Büchi. The product from this reaction was denoted as DBMAPA.

A third reaction was performed to obtain a reference material with the same chemical structure as DBMATA but without the amide groups, that is, an ester instead of an esteramide. The vessel was charged with 13.2 g (0.06 mol) DBM dissolved in 20 mL $CHCl_3$, and 10.9 mL (0.075 mol) AdCl in 20 mL $CHCl_3$ was slowly added to the mixture through a funnel. The reaction was run for 8 h at 60°C, after which 1.95 mL (0.013 mol) TEG dissolved in 10 mL of $CHCl_3$ was charged to the vessel. The reaction was continued for 14 h, and finally 1.5 mL of ethanol was added. After 2 h the reaction was terminated, and the remaining chloroform and ethanol were evaporated under vacuum (20 mm Hg) in a Rotavapor-R from Büchi. The product from this reaction was denoted as DBMAT.

Sample preparation

Blending

Blending experiments, with a blend composition of 15 wt % plasticizer and 85 wt % PLA, were performed in a Midi 2000 corotating twin screw extruder from DSM Research (Heerlen, The Netherlands). The extruder had a chamber volume of 15 cm^3 and was chosen because effective blending of small volumes was especially important since the syntheses only produced limited amounts of the oligomeric plasticizer. 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. The melt was blended for 2 min and then extruded as a strand through a single-filament die with the dimension 10mm × 1mm. 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.

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 9×10^5 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.

Thermal annealing and aging

To study the effect of storing the plasticized material, film samples of the blends were either thermally annealed in a circulating air oven at 100°C for 4 h or left to age at ambient conditions for 6 weeks. On the one hand, by performing a thermal treatment above the T_g of the blends, cold crystallization should be encouraged. On the other hand, the investigation of naturally aged samples was deemed of interest to reproduce the current storage conditions used in the packaging material industry.

Sample characterization

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 (Labscan Ltd, Ireland, concentration 1–2 wt %) on Waters' Styragel columns (10^5, 10^4, 10^3, 500 Å) or two Waters' Ultrastyragel linear columns, using differential refractive index and viscometry detectors (Dual detector, 250, Viscotek).
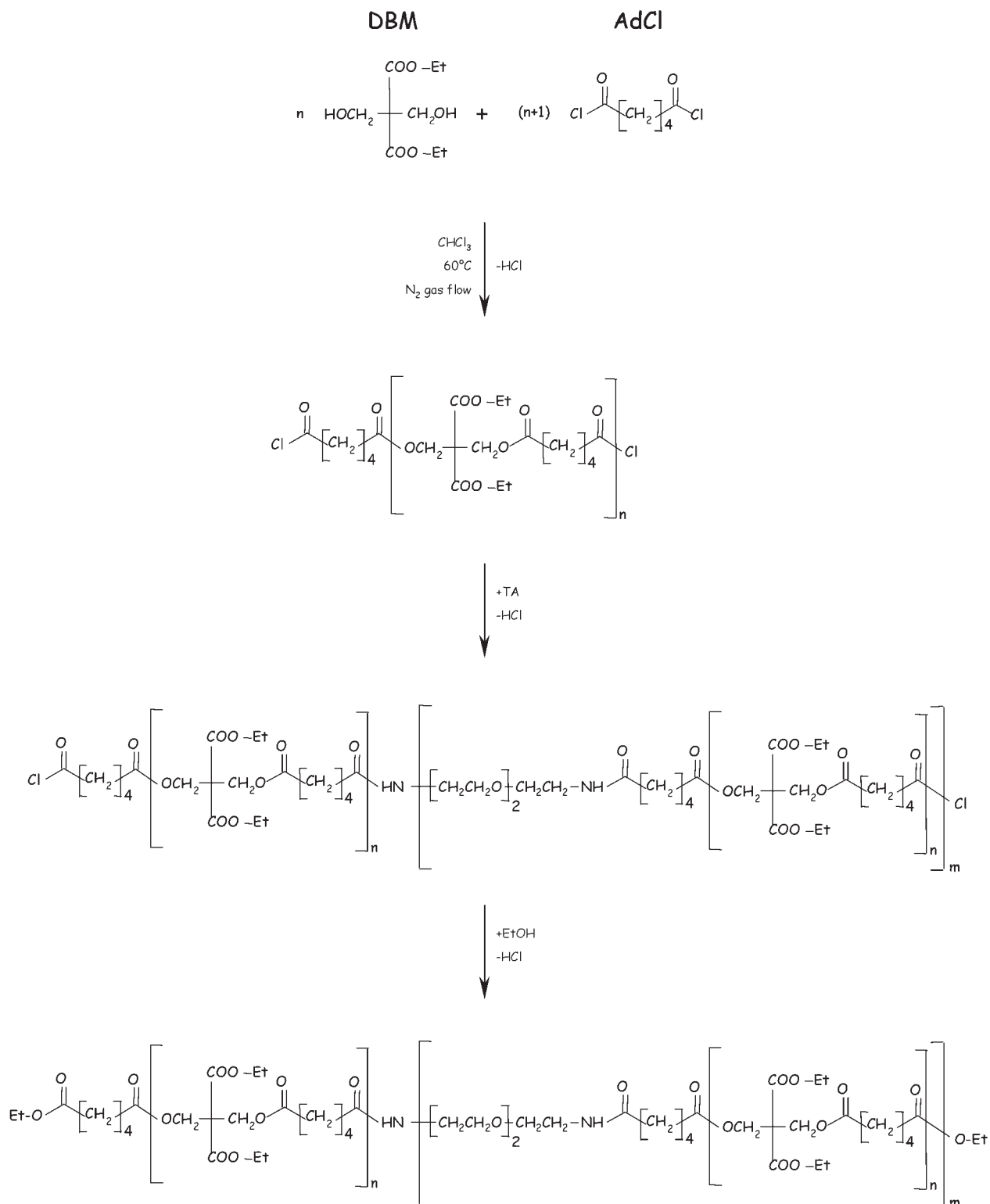
Figure 2 The synthesis path for the esteramide reaction between DBM, AdCl, and TA to obtain DBMATA.

Fourier transform infrared spectroscopy (FTIR)

To study the molecular structure of the oligomers, FTIR spectra were recorded using a Bruker IFS 66

FT-IR spectrometer (Ettlingen, Germany). Small droplets of the liquid esteramides were placed between two ZnSe crystals, and the samples were then analyzed in transmission mode. Each spectrum cor-

responds to the average of 32 scans at a resolution of 4 cm^{-1}.

Dynamic mechanical analysis (DMA)

Dynamic mechanical analysis (DMA) was performed on a DMA 2980 from TA Instruments (New Castle, Delaware, USA). The experiments were conducted in tensile mode under isochronal conditions at a frequency of 1 Hz. Curves displaying storage and loss moduli were recorded as a function of temperature between −60°C and 150°C at a heating rate of 3°C/min. The amplitude was chosen at 5 μm, a preload force of 0.010N was applied, and the autostrain was set to 115%. The shape of the film samples was rectangular, approximately 15mm ×5 mm × 0.35 mm.

The DMA 2980 was also used to perform tensile testing on the film material. The measurements were performed in controlled force mode on rectangular samples approximately 7.5mm × 3 mm × 0.08 mm under isothermal conditions at 30°C. The force was ramped at 10N/min from 0 to 17N, unless the sample broke before. Ten tests were carried out on each film sample, and average values of stress and strain at break were calculated.

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 on the pure plasticizing agents. All DSC scans were carried out under N$_2$ atmosphere on approximately 5 mg of material. The scans of the films were run from −60 to 210°C (10°C/min) and back down to −60°C (10°C/min). During the heating ramp the glass transition, cold crystallization, and melting of the material occurred, and during the cooling the crystallization of the material could be observed. The DSC traces of the pure plasticizing agents were recorded from −90 to 50°C at 10°C/min to observe their glass transitions.

RESULTS AND DISCUSSION

Synthesis and characterization

The objective of the syntheses was to prepare two oligomeric malonate esteramides (i.e., DBMATA or DBMAPA) of DBM, AdCl, and one of two diamines (i.e., TA or PA). An oligomeric ester was also synthesized as a reference material, DBMAT. The goal was for it to have the same chemical structure as DBMATA but without the amide groups.

The solubility parameter of any chemical substance can be calculated according to eq. (1):

TABLE I
The Molecular Weights (M$_n$ and M$_w$), Glass Transition Temperatures (T$_g$), and Solubility Parameters (δ) for PLA and three Plasticizing Agents

	M$_n$* (g · mol^{-1})	M$_w$* (g · mol^{-1})	T$_g$** (°C)	δ*** (J · cm^{-3})†
PLA	-	-	52	20.1
DBMATA	1600*	2300*	−53	20.0
DBMAPA	2700*	5300*	−67	19.8
DBMAT	1800*	3200*	−47	19.1

* Measured by SEC according to polystyrene standards.
** Measured by DSC at the inflection point of the change in the ΔC_p baseline.
*** As calculated with group molar attraction constants from the Hoy series.[42]

$$\delta = \frac{\Sigma F \cdot \rho}{M_0} \qquad (1)$$

where δ represents the solubility parameter, ρ the density, M$_0$ the molecular mass, and F the group molar attraction constants according to the Hoy series.[42] DBM was chosen as the monomeric unit for the synthesis since its calculated solubility parameter is close to that of PLA, thus suggesting that it should be an efficient plasticizer for PLA. It had also been observed in an earlier study[39] that oligomeric esters based on DBM and AdCl had successfully plasticized PLA while creating stable systems where the tendency for the plasticizer to migrate had been decreased. The solubility parameters for the esteramides were very close to those of PLA, as can be seen in Table I. There was only a slight decrease in the solubility parameter for the esteramide where PA was used instead of TA, whereas a somewhat larger difference in δ values was found between the TA-esteramide and the TEG-ester. As a matter of fact, exchanging the diamine for the corresponding dialcohol would lower the solubility parameter almost 1 unit (J cm^{-3})$^{1/2}$. These calculations suggest that DBMATA would be the most efficient as a plasticizer for PLA, but that all three substances should be compatible with PLA and have a plasticizing effect on the polymer.

The first step of the synthesis for both the esteramides and the ester was run for 8 h. At this time the carrier gas leading from the reaction vessel contained only small amounts of HCl. The decision was taken to continue with the next step to be sure that the –COCl groups on AdCl had not lost their reactivity. The diamine/TEG was added very slowly, and the second reaction step was then allowed to run for 14 h. The final step of the synthesis was to deactivate any remaining –COCl groups by adding an excess amount of ethanol and letting this react for 2 h.

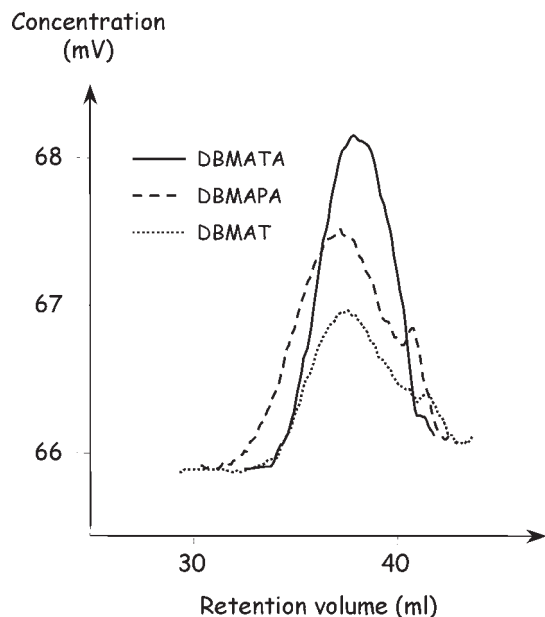Characterization of the obtained oligomers was performed by SEC, DSC, and FTIR analyses. SEC traces

Figure 3 SEC traces displaying DBMATA, DBMAPA, and DBMAT.

are presented in Figure 3, and Table I gives the main physical characteristics of the three oligomers as well as those of PLA.

The SEC traces clearly show that all oligomers had a broad molecular weight distribution. According to polystyrene standards, the apparent M_n values of the oligomers could be estimated. Thus, DBMATA had a molecular weight of 1600 g/mol (Table I), DBMAPA had an M_n value of 2700 g/mol, and for the ester, DBMAT, the molecular weight was 1800 g/mol. The plasticizers DBMATA and DBMAT could therefore be considered as of comparable size, while DBMAPA was somewhat larger.

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

FTIR analysis was carried out to verify that the amidation reaction had taken place. The IR-spectra that were recorded for the three oligomers are presented in Figure 4. They clearly display two amide bands for DBMATA and DBMAPA at the wave numbers 1647 cm^{-1} (¤) and 1545 cm^{-1} (*). The first band (¤) represented the C = O stretching and the second one (*) the *N*-H bending. Figure 4 also shows broad amide and amine bands between the wave numbers 3300–3600 cm^{-1} (◇). This was an indication that the amino groups had not been totally reacted in the synthesis. In addition, it should be observed that the IR-spectrum

for the reference DBMAT shows no bands for either amide or amine at the above-mentioned wave numbers.

Dynamic mechanical and thermal properties

DMA measurements

Figure 5 shows the temperature dependence of the viscoelastic storage (Fig. 5a) and loss (Fig. 5b) moduli for pressed films of neat PLA and blends containing 15 wt % of the synthesized oligomers. It can be seen that the drop in storage modulus (Fig. 5a) occurs at a lower temperature for the blends as compared with neat PLA. The loss modulus thermograms (Fig. 5b) show
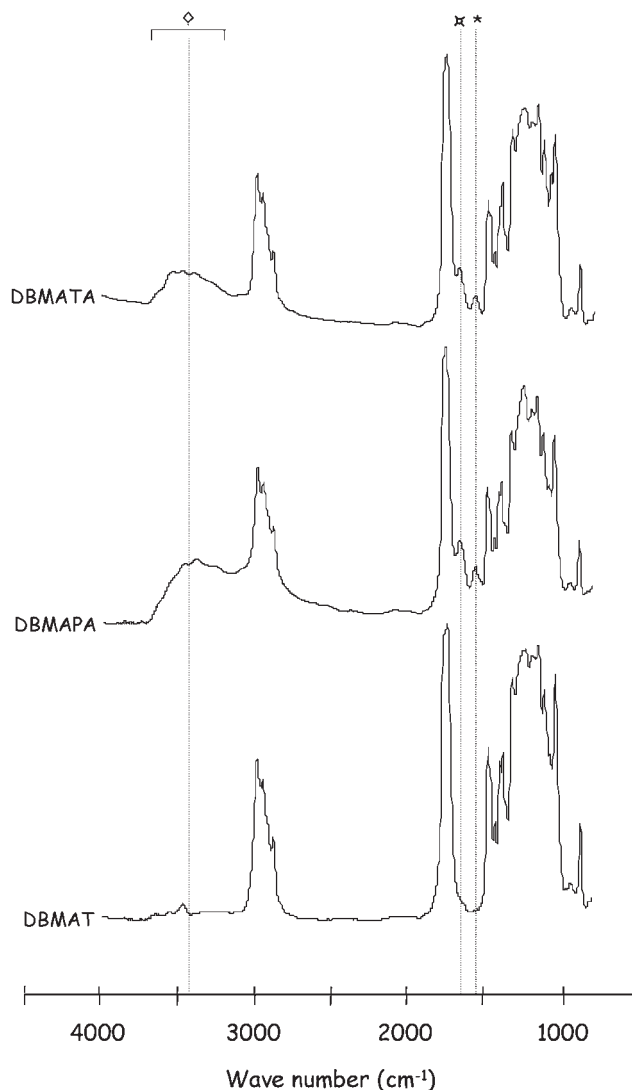

Figure 4 FTIR traces displaying DBMATA, DBMAPA, and DBMAT. The bands at 1647 cm^{-1} (¤) and 1545 cm^{-1} (*) represent the C = O stretching and the *N*-H bending of the amide groups, respectively, and the broad band centered at 3450 cm^{-1} (◇) shows the presence of amine and amide groups.
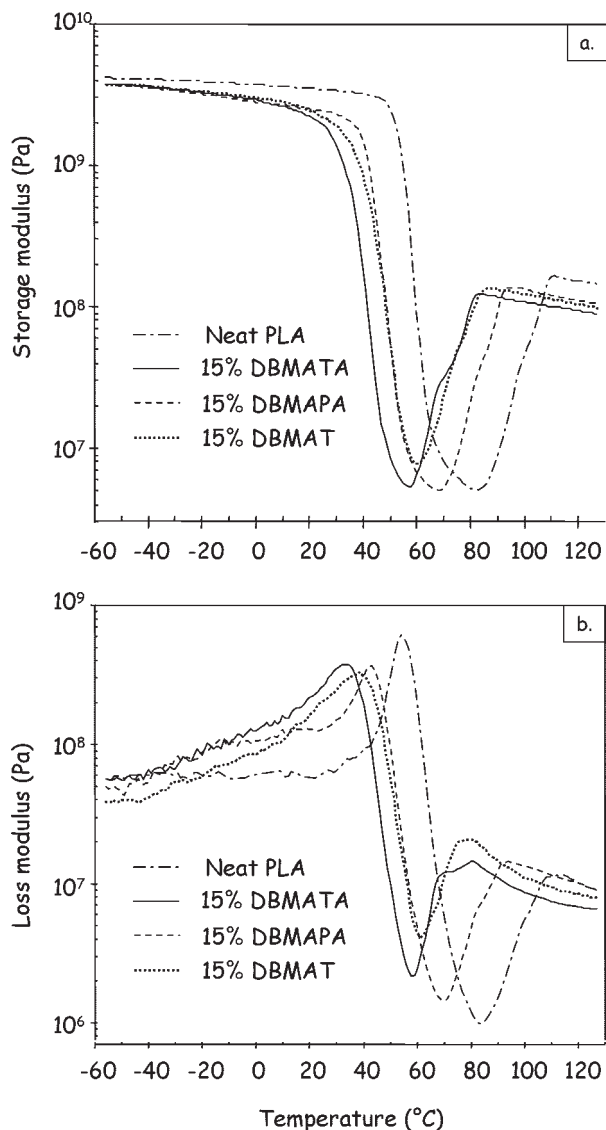
Figure 5 Storage (a) and loss (b) moduli curves as a function of temperature from DMA runs comparing blends containing 15 wt % DBMATA, DBMAPA, and DBMAT with neat PLA.

two peaks: one at low temperature, displaying the α-transition of PLA (associated with its glass transition), and one at high temperature portraying the cold crystallization. The T_α values of the films, defined as the temperature location of the maximum of the loss modulus obtained for the α-relaxation at 1 Hz, are given in Table II. Both esteramides and the ester had a plasticizing effect on PLA, which can be seen by the α-transition peak being shifted toward lower T_α values.

At the given blend composition (15 wt % plasticizer), the largest effect was seen with DBMATA, which portrayed a decrease in T_α from 54 to 33°C. Although DBMAT also showed a significant decrease in T_α, from 54 to 37°C, the effect was not as large as with DBMATA, suggesting that the amide groups in the esteramide improved the plasticization by increasing the solubility of PLA by polar interactions. The second esteramide showed the smallest decrement in T_α, which was likely because of the larger molecular weight of DBMAPA as compared to the other two oligomers. Other plausible explanations could be the lower flexibility of the polyoxypropylene chain as compared to TA and TEG or that the methyl side groups in PA prevented the oligomer molecules from coming close enough to the PLA chains for efficient hydrogen bonding to take place.

These decrements in T_α for the blends with the oligomers can be compared with those of PLA blended with the monomeric unit from the synthesis, DBM.[39] A blend of PLA and 15 wt % DBM had a T_α of 30°C, which was only slightly lower than that of the PLA/DBMATA blend. All the oligomers seemed compatible with PLA at the investigated concentration, seeing as no signs of phase separation were observed in the dynamic mechanical spectra.

The DMA was also used to investigate the tensile properties of the film materials. Average values for stress and strain at break of the films were calculated based on a series of ten tests for each sample. Figure 6 displays stress/strain curves for the samples, and it can be seen that there is a large difference between the blends containing DBMATA and DBMAT as compared to neat PLA and the blend with DBMAPA The blends with DBMATA and DBMAT were very flexible with strains at break above 200%, whereas the remain-

TABLE II
T_α Measured by DMA and Thermal Data Obtained by DSC Measurements for Films of Neat and Plasticized PLA

	Content (wt %)	T_α (°C)	T_g* (°C)	Cold crystallization temperature (°C)	Melting temperature (°C)	Crystallization temperature (°C)	ΔH_f (J/g)
PLA	100	54	52	91	173	95	17**
DBMATA	15	33	35	63	167	93	26
DBMAPA	15	42	41	80	172	89	20
DBMAT	15	37	39	71	170	93	22

* Measured by DSC at the inflection point of the change in the ΔC_p baseline.
** Corresponds to a degree of crystallinity of 18% assuming that ΔH_f for 100% crystalline PLA equals 93 J/g.[43]
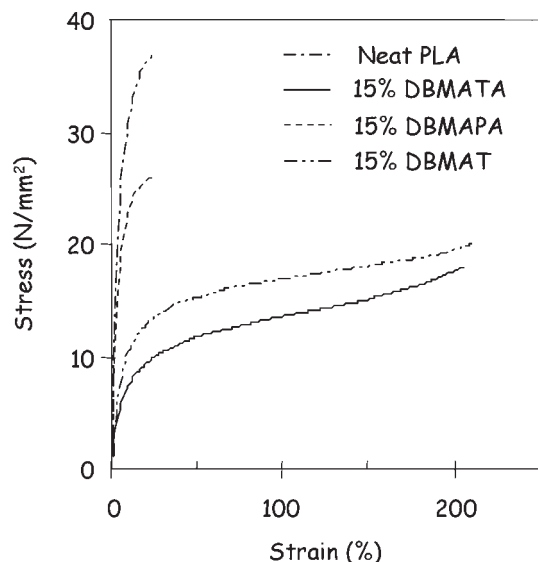
Figure 6 Stress/strain curves comparing blends containing 15 wt % DBMATA, DBMAPA, and DBMAT with neat PLA.

ing two materials only showed strain at break values around 20%. However, despite displaying a much more brittle behavior, neat PLA and the blend with DBMAPA could withstand much higher stress values before breaking, indicating that these two materials were stronger than the flexible ones. The enhancement of the flexibility of PLA by adding a plasticizer was therefore counterbalanced by a restriction in the strength of the material, and *vice versa*.

DSC measurements

DSC experiments were conducted to investigate the thermal properties of the blended materials. A DSC thermogram for neat PLA can be seen in Figure 7. All curves had a similar appearance, displaying glass transition, cold crystallization, and melting peaks as the temperature increased (Fig. 7). Values for glass transition temperatures, fusion enthalpies, crystallization temperatures, and melting temperatures, as well as the heat of fusion (ΔH_f), were evaluated from the scans and are given in Table II. The ΔH_f in the materials after film pressing was calculated by subtracting the enthalpies for cold crystallization and premelt crystallization from the melting enthalpy.

As noted for the T_α values, the T_g identified in the DSC traces occurred at lower temperatures in the blended materials than in neat PLA. The lowest T_g was noted for the PLA/DBMATA blend, which was in good agreement with the results from the DMA measurements. A shift in the cold crystallization and melting peaks was observed for the blended material. The more plasticized the material, the larger the shift to a lower temperature. There were also differences in the values for heat of fusion, ΔH_f, in the blended material

as compared to neat PLA. It was found that increasing the degree of plasticization in the material resulted in a higher ΔH_f in the film. This result can be explained by the fact that the low glass transition temperature allowed an additional crystallization to occur during cooling of the pressed film, as compared to the situation for neat PLA. It should also be mentioned that a slight shift was noticed in the baseline of the DSC traces, suggesting that crystallization occurred continuously between the cold crystallization and the premelt crystallization, that is, in the temperature region 80–150°C. However, this could not been taken into account when calculating the ΔH_f since it was very difficult to assess the baseline.

Thermal annealing and aging

Film samples of the blended materials as well as neat PLA were thermally annealed at 100°C for 4 h. Figure 8 shows the storage modulus as a function of temperature for annealed and as-pressed films of neat PLA and the blended materials. Performing a heat treatment above the glass transition temperature in this way allowed the material to cold crystallize because of the high segmental mobility. Consequently, the annealed samples all displayed storage modulus curves without a cold crystallization plateau.

In Figure 9 the temperature dependence of the loss modulus of the annealed and as-pressed samples are compared. The annealed sample of neat PLA displayed a small shift in T_α (Fig. 9a) toward a higher temperature caused by the increased crystallinity in
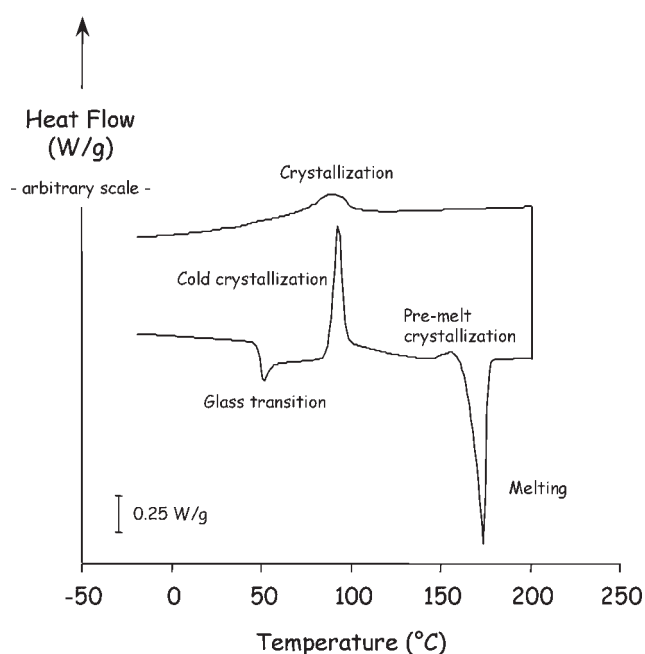

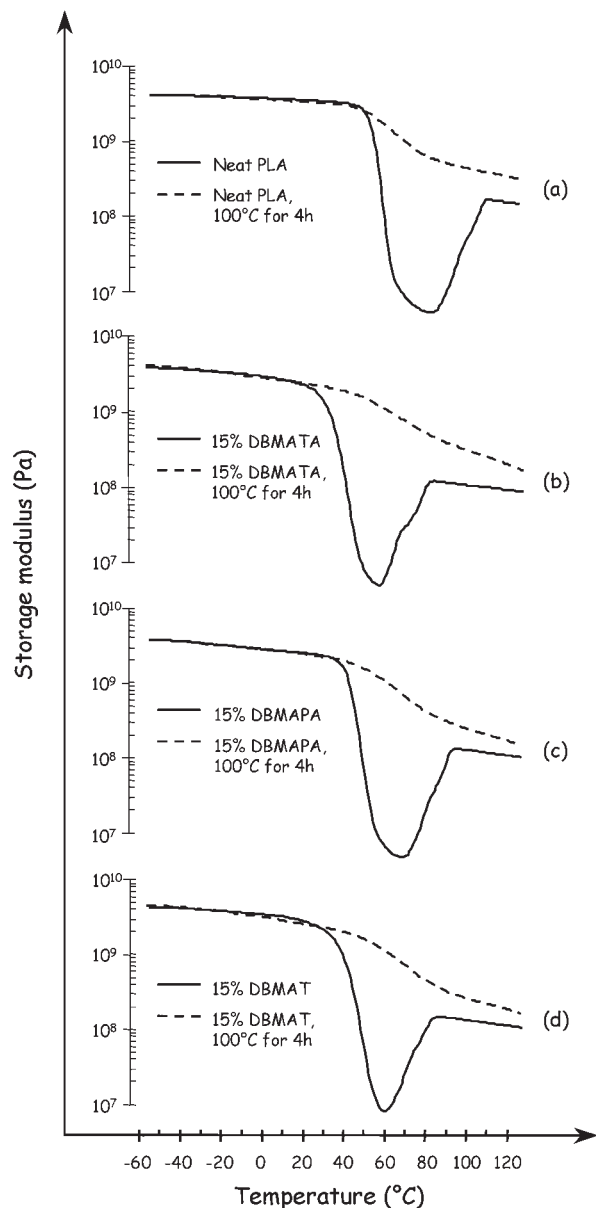**Figure 7** DSC trace for neat PLA displaying both the heating (10°C/min) and cooling ramp (10°C/min).

Figure 8 Storage modulus curves as a function of temperature from DMA runs comparing annealed (100°C for 4 h) and as-pressed films of (a) neat PLA, (b) 15 wt % DBMATA, (c) 15 wt % DBMAPA, and (d) 15 wt % DBMAT.

Tensile testing was performed on the annealed film samples, and the resulting stress/strain curves are presented in Figure 10. The strain at break value for neat PLA was depressed as a result of the increased crystallinity. In addition, it was seen that the induced phase separation in the blends after annealing caused them to regain the brittle properties of neat PLA. This resulted in strain at break values of around 10% for all three blends.

To imitate the storage conditions in the packaging material industry, film samples of the blends containing DBMATA and DBMAT were aged for 6 weeks at room temperature. Tensile testing was then performed, and Figure 11 presents the resulting stress/strain curves. A slight drop in the stress at break was
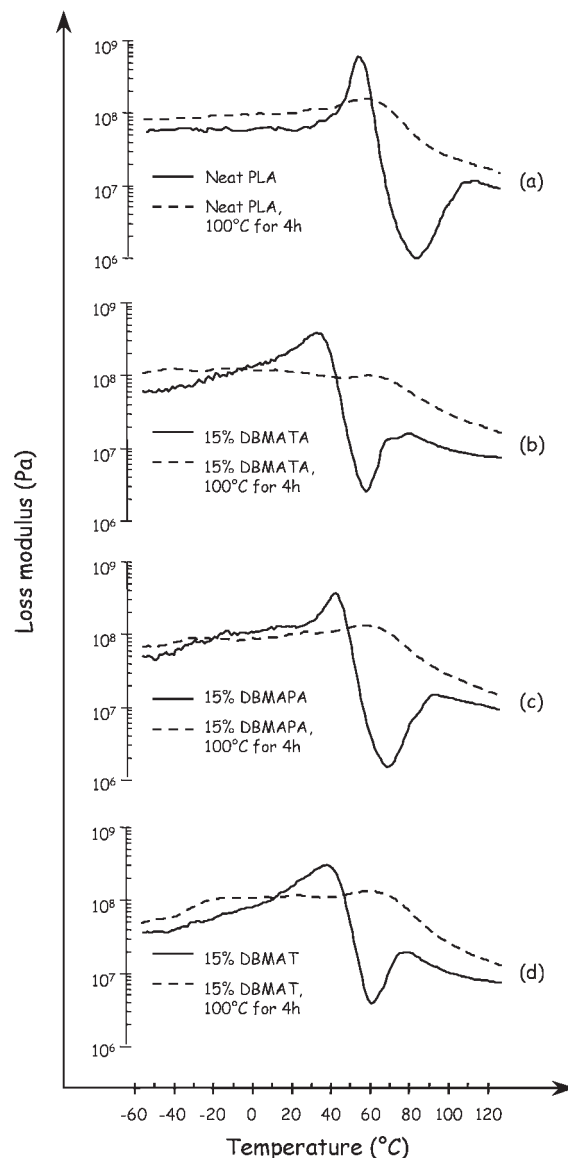

Figure 9 Loss modulus curves as a function of temperature from DMA runs comparing annealed (100°C for 4 h) and as-pressed films of (a) neat PLA, (b) 15 wt % DBMATA, (c) 15 wt % DBMAPA, and (d) 15 wt % DBMAT.
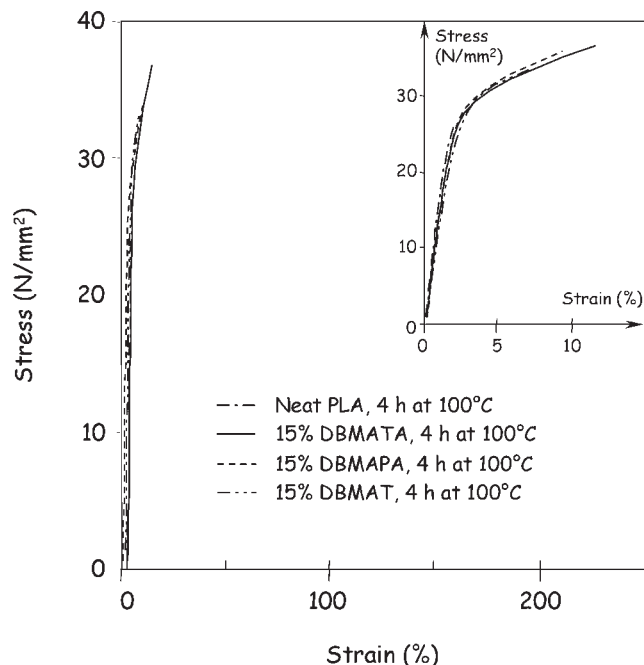
the material. The blended materials containing DBMAPA (Fig. 9c) and DBMAT (Fig. 9d) both showed signs of two relaxational peaks, indicating that phase separation had taken place in the systems. The α-relaxational peak of PLA in these two materials had also been shifted to higher temperatures, suggesting that the annealing caused them to regain the brittle properties of neat PLA. Although the PLA/DBMATA blend also showed signs of phase separation, it was to a lesser degree than for the other two blends (Fig. 9b), thus supporting the above-mentioned (Fig. 5, Table II) positive contribution of the amide groups in terms of polar interaction with the PLA chains.

Figure 10 Stress/strain curves of annealed (100°C for 4 h) samples comparing blends containing 15 wt % DBMATA, DBMAPA, and DBMAT with neat PLA. For easier comparison with Figures 6 and 11, this figure presents the same data in two different strain scales.

found for the two systems, whereas the strain at break values were equivalent to the values obtained before the aging. Since the temperature never passed the T_g of the materials, cold crystallization was prevented from occurring in the samples. Thus, natural aging resulted in the plasticized materials maintaining their initial flexibility.

CONCLUSION

Oligomeric malonate esteramides were synthesized by reacting diethyl bishydroxymethyl malonate (DBM) with adipoyl dichloride (AdCl) and then adding a diamine, either triethylene glycol diamine (TA) or polyoxypropylene glycol diamine (PA). An oligomeric polyester reference (DBMAT) with similar chemical structure as DBMATA but without any amide groups was synthesized by reacting DBM with AdCl and triethylene glycol (TEG).

Blending PLA with the oligomeric esteramides reduced the glass transition temperature of PLA significantly, the decrement in T_g being the largest with DBMATA. As compared to the corresponding polyester DBMAT, the esteramide DBMATA was more effective as a plasticizer, presumably because of stronger polar interactions and higher compatibility with PLA.

Large improvements of the strain at break values were noted for blends containing DBMATA and

DBMAT as compared to neat PLA. Despite the presence of amide groups, DBMAPA was less effective as plasticizer than DBMATA due to lower compatibility with PLA, which can be ascribed to the larger molecular weight of DPMAPA. Also, the side groups in the hydrophobic chain of DMAPA may prevent the oligomer molecules from approaching the PLA chains close enough for efficient hydrogen bonding through the amide groups.

Keeping PLA/oligomer blends above their glass transition temperatures for a limited time (4 h at 100°C) allowed for progressive cold crystallization to occur because of the high segmental mobility. The resulting size reduction of the amorphous domains in PLA decreased its ability to accommodate the plasticizer, resulting in phase separation in the blends, ultimately causing them to regain the brittle properties of neat PLA.

The materials were aged at ambient conditions, simulating the effects of current storage conditions in the packaging industry. By keeping the blends below their glass transition temperatures, cold crystallization was prevented from taking place and thereby the enhanced flexibility in the plasticized films was maintained.

So far, biodegradation of PLA containing oligomeric polyesteramides as plasticizers has not been investigated. However, it should be pointed out that the observed effects of the plasticizers on the PLA crystallinity may influence the degradation rate of PLA. Thus, further work should include biodegradation studies.
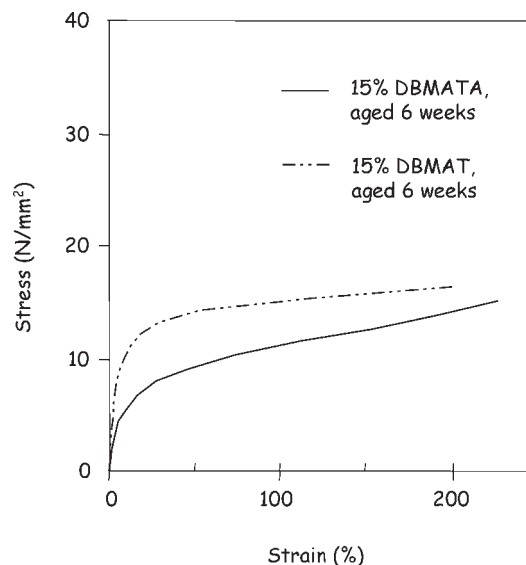
Figure 11 Stress/strain curves of naturally aged samples displaying blends containing 15 wt % DBMATA and DBMAT.

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