

Film Extrusion and Film Weldability of Poly(lactic acid) Plasticized with Triacetine and Tributyl Citrate

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ABSTRACT: Film extrusion and welding of biodegradable polymer films are important processes that must be considered in the development of compostable packaging materials. Film extrusion of poly(lactic acid) (PLA) has proved to be rather difficult because of its brittleness, but the flexibility of PLA can be improved by incorporation of a plasticizer in the material. PLA was plasticized with triacetine (TAc) and tributyl citrate (TbC). The blended materials and neat PLA were film extruded and the films were welded with constant heat (CH) welding. The films were analyzed by means of gas chromatography (GC), dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC), gel

permeation chromatography (GPC), contact angle measurements, and tensile testing. Storage of the plasticized films resulted in an increased crystallinity and changes in the film properties, rendering CH welding difficult. The welding process had no influence on thermal properties, such as cold crystallization temperature, melting temperature, crystallization temperature, and degree of crystallinity, of neat PLA but caused significant changes in the crystallinity of the plasticized materials. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 3239–3247, 2003

Key words: processing; welding; ageing; thermal properties

INTRODUCTION

In a society where garbage and waste are in abundance, the need to develop biologically degradable plastics and products that may be composted has come into focus. Poly(lactic acid) (PLA) is a biodegradable, semicrystalline polymer that can be manufactured from lactic acid produced by fermentation of renewable resources such as whey, corn, potato, or molasses. PLA is completely compostable and biodegrades to carbon dioxide, water, and biomass.¹

A very large fraction of the polymer materials consumed in industrialized countries is used for packaging and ends up on waste mountains, as landfill, or in incineration facilities. PLA is readily degradable, and as waste mountains continue to grow, landfill space continues to decrease, and incineration facilities are operating at full capacity, the community would have much to gain if PLA could be used for packaging materials,² thus rendering these products compostable. Even incineration would be considered en-

vironmentally friendly, given that PLA does not cause any net surplus of carbon dioxide. However, PLA is a comparably brittle material, and film extrusion has proved to be rather difficult.³

The flexibility of PLA can be improved by incorporation of a plasticizer in the material. PLA is a semicrystalline polymer and the plasticizers are incorporated primarily into the amorphous parts.⁴ An increase in the crystallinity over time could change the compatibility of the plasticizer with PLA and induce phase separation and segregation or migration of the plasticizer.⁵ Migration of additives within poly(ethylene) films⁵ and within poly(vinyl chloride) sheets⁶ have been studied. It was shown that small molecular substances migrated out of the polymer bulk as the crystallinity increased in the material. The rate of the migration process increased with temperature. Because packaging has become an indispensable element in the food manufacturing process,⁷ contamination of the food attributed to migration of the plasticizer is a major issue.

Two biodegradable, nontoxic plasticizers that have been successfully blended with PLA are triacetine (TAc) and tributyl citrate (TbC).^{8,9} At the concentrations used (up to 20%) these esters were shown to be compatible with PLA and to generate a significant decrease in glass-transition temperature, thereby enhancing the ductility of the material. However, the effect of aging on the material and the inclination of TAc and TbC to migrate have not been previously investigated.

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The weldability of a polymer film is another important property with regard to packaging materials. In the production of packages, especially for liquids, it is essential that the package can be tightly sealed, and that the weld is sufficiently strong to withstand handling during distribution. Welding or interdiffusion of miscible polymer materials starts out with both components being well separated from each other and no polymer chains crossing the interface. When the system is heated above the glass-transition or melting temperature of the polymer, chains start to diffuse across the interface with a reptation type of movement,¹⁰ which by the end produces a diffuse interphase and entangled chains.

Heat welding of semicrystalline polymer films, mainly low-density polyethylene (LDPE), has been investigated by Meka et al.^{11,12} The studies show that the interfacial temperature at the boundary between the films should be slightly higher than the melting point of the polymer film. Welding pressure does not affect the strength of the weld and should therefore be kept to a minimum to avoid distortion. In the case of polyethylene, a large amorphous phase fraction seems to cause a decrease in the minimum welding temperature required. Other studies that have been performed include the welding behavior of ultrahigh molecular weight polyethylene (UHMWPE)^{13,14} and hot-plate welding of thermoplastics.¹⁵ However, to our knowledge, no investigations have been done concerning the weldability of PLA.

In this study PLA was plasticized with TAc and TbC by means of continuous blending, followed by film extrusion. The films were welded by constant heat welding, and the behavior of the materials during processing and welding was investigated. Important issues were the effects of aging on the properties of the films and how the thermal properties of the materials, such as the degree of crystallinity, the melting temperature, and the crystallization and cold crystallization temperatures, were altered by film extrusion and welding.

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, Finland. The melting temperature (T_m) was 175°C and the glass-transition temperature (T_g) was 54°C. The plasticizers were triacetate (TAc) and tributyl citrate (TbC), provided from Acros Organics (Springfield, NJ). The surface energy for TAc was 36 dyn cm/cm² and for TbC, 30 dyn cm/cm², as measured by a surface balance according to Lecomte du Noüy. The boiling points were 259°C for TAc and 169°C for TbC according to the manufacturer. PLA and plasticizers were used as received.

Blending

PLA was swollen with 15 wt % TAc and the mixture was then blended in an Axon single-screw extruder (type BX-18; Axon, Nyvång, Sweden), with a screw diameter of 18 mm. The screw had an 80-mm slit to provide backmixing and thereby ensure that blending did take place. The L/D ratio of the screw was 30 and the screw speed was set to 18 rpm. The temperature was 160°C in the feeding zone and reached a maximum of 180°C. The die temperature was 165°C. Maximum cooling was used around the feeding zone. The molten polymer was formed into a strand by a single-filament die with a 5-mm diameter, and the strand was then cooled in a water bath before granulation. The granules were dried in a PIOVAN H31M drier with a PIOVAN DS403 control unit (Venice, Italy) at 27°C for 24 h.

PLA was blended with 15 wt % TbC in a Midi 2000 corotating twin-screw extruder from DSM Research (Heerlen, The Netherlands). The temperature profile ranged from 220°C in the feeding zone down to 185°C in the die and the screw speed was 100 rpm. The melt was extruded as a strand through a single-filament die. The strand was wound and cooled on a glass cylinder with a diameter of 15 cm, and then granulated.

Film extrusion

Film extrusion of neat PLA, PLA plasticized with TAc, and PLA plasticized with TbC was performed in a Haake Rheomex 254 extruder with a Rheocord 90 drive unit (Karlsruhe, Germany). During film extrusion of neat PLA the temperature was 160°C in the feeding zone, reached a maximum of 180°C, and was 175°C in the die. For PLA plasticized with TAc the temperature span was 100 to 175°C, with a die temperature of 165°C and for PLA/TbC it was 80 to 175°C, with a die temperature of 165°C. A 200-mm fishtail die with a 300–400 μ m split die-gap was used. The screw had a compression of 2:1, a diameter of 19.3 mm, and an L/D ratio of 25. The airgap was 15 mm.

The material was extruded onto a 36- μ m PET film with a screw speed of 50 rpm and the temperature of the water entering the chill roll was 20°C. By adjusting the speed on the rewind stand it was possible to control the thickness of the polymer films. Two film thicknesses were prepared from each material, 20 and 40 μ m. The films were stored as rolls in PE bags at ambient temperature.

Dynamic mechanical analysis (DMA)

Investigation of the glass-transition temperature was performed by DMA on a DMA 2980 from TA Instruments (New Castle, DE). The runs were conducted at

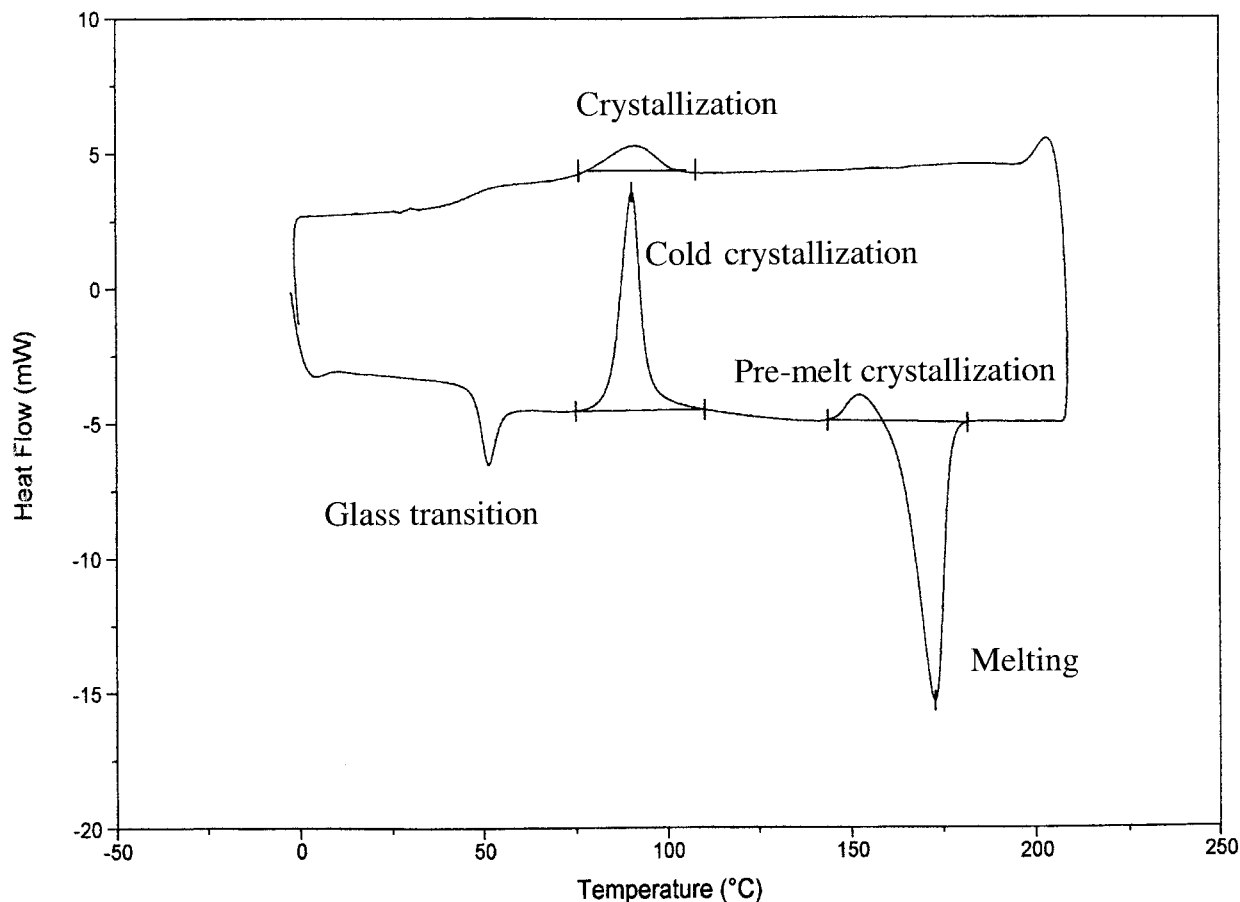


Figure 1 DSC trace for neat PLA displaying the glass transition, cold crystallization, premelt crystallization, and melting.

a heating rate of 3°C/min between -60 and 150°C under N₂ atmosphere in the tensile mode. The shape of the film samples was rectangular, approximately 15 × 6 × 0.03 mm. The amplitude was 5 μm and the autostrain was set to 115%. Curves displaying storage modulus, loss modulus, and tan δ versus temperature were obtained. The glass-transition temperature was taken to be the maximum of the loss modulus curve.

Gas chromatography (GC)

GC analysis was performed on granules from the blending and on samples from the film extrusion on a HP 6890. The column was from Hewlett-Packard (HP 5; Alto, CA) with a stationary phase of (5%) diphenyl-(95%) dimethylpolysiloxane. The length of the column was 30 m and the inner diameter was 0.32 mm. Samples (100 mg) were dissolved in 2 ml dichloromethane and PLA was precipitated with 10 ml of methanol. The clear solutions were injected on-column at 30°C, to prevent degradation reactions, and the temperature was ramped at 10°C/min up to 300°C.

Differential scanning calorimetry (DSC)

Differential scanning calorimetry was conducted on a DSC 2920 from TA Instruments. Two types of scans were performed: -60 to 210°C and -60 to 210 to -60°C, both at a heating/cooling rate of 10°C/min. The scans were carried out under N₂ atmosphere using approximately 10 mg of material. Values for glass-transition temperatures, fusion enthalpies, crystallization temperatures, and melting temperatures were evaluated from the scans. The crystallinity of the material after blending and film extrusion 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.¹⁶

Gel permeation chromatography (GPC)

GPC was carried out on film samples directly after extrusion and also after aging. The analyses were performed by the polymer manufacturer. The eluant was chloroform and the columns were Waters Styragel HT-6, HT-5, HT-4, and HT-3 (Waters Chromatography Division/Millipore, Medford, MA).

Tensile testing

Tensile testing of the films was conducted on an Instron 4502 tensile tester. The gauge length was 33 mm, the crosshead speed was 50 mm/min, and the load cell was 100 N. The shape of the film samples was rectangular, with a width of 15 mm. Ten tests were performed on each sample. Values for maximum stress and maximum strain were evaluated from the scans.

Constant heat (CH) welding

CH welding of the polymer films was conducted in the extrusion direction of the film on a Kopp Labour-Siegelgerät SGPE 20 (Reichenbach, Germany). The heat platens were flat with the dimensions 5×200 mm². The weldability of the material as a function of welding temperature was investigated by setting the welding time to 60 s, the pressure to 0.6 N/mm², and gradually increasing the temperature until a joint was achieved. Both platens were set at the same temperature. The joint was considered sufficiently strong when it could withstand manual peeling without delaminating. Films of varying age were used for this study.

To investigate the thermal properties of the welded material, welds were prepared with a welding temperature of 160°C, a welding time of 0.6 s, and a pressure of 0.6 N/mm². Welding was performed on a sandwich structure of the material, consisting of four layers: paper board, polymer film, polymer film, and paper board. Paper board was used as support for the film and was not integrated into the structure. However, although there was no adhesion between board and film, the structure simulated that of the actual welding process when packaging material is involved. Many packaging materials consist of paper board coated with a polymer film.

Contact angle measurements

Contact angle measurements of the extruded films were conducted on a Fibro 1100 DAT Mk11 (Stockholm, Sweden) according to the sessile drop method at 23°C/50% relative humidity. Nanopur water was used for the measurements. The measurements were performed on the air-facing surface of the films, from the vantage point of extrusion. However, because the material was stored as rolls, even the air-facing side had been in contact with the PET carrier film.

RESULTS AND DISCUSSION

Continuous blending and film extrusion

In a previous study⁸ PLA was blended with plasticizers in a batchwise process using a Brabender mixer

and films were prepared by heat pressing at 200°C. Under these conditions phase separation seemed to occur in the films at a certain plasticizer content, and insufficient processing could not be ruled out as a possible explanation for the phase separation. To obtain more reliable processing conditions and to achieve more reproducible results, continuous blending in an Axon extruder followed by film extrusion was chosen in the present work. PLA was mixed with 15 wt % TAc 2 days before blending and in this time the polymer was swollen with the plasticizer, leaving dry granules to be fed to the extruder. The extruder was fed by gravitational feeding from a feed hopper, and although the granules were dry they did not run as well as the nonswollen PLA granules. Thus, to make sure the screw was fed properly it was imperative that there was a sufficient amount of material in the hopper causing pressure on the feeding zone.

A similar mixing procedure was also tried for TbC. PLA and 15 wt % TbC were premixed but in this case no swelling took place. This was very unexpected, given that TbC has a solubility parameter close to that of PLA and TbC and TAc are very similar in density and viscosity. The premixing of PLA and TbC resulted in very sticky granules, which made blending in the Axon extruder impossible. The plasticizer separated from the PLA granules when fed to the extruder and accumulated in the feeding zone. Instead, blending was successfully performed in a small corotating twin-screw extruder. The extruder was mounted vertically and by means of a plunger the wet granules were pressed into the feed zone, ensuring that the plasticizer did not separate from the PLA granules. The material passed straight through the extruder without recirculation and the residence time was 40 s. The wet granules had to be continuously fed and pressed into the extruder and, because the extruder volume was only 15 cm³, the blending process was very time consuming. After extrusion the blended material was quickly cooled and granulated. The granules were dry on the surface, which indicated that the TbC had been properly incorporated into the PLA. Should there have been any variation in plasticizer concentration in the granules, this discrepancy would have been evened out once the material was film extruded.

Films of neat and plasticized PLA were extruded by means of a Haake film extruder equipped with a fish-tail die. The temperature profiles were practically equivalent for all three materials, except for the temperature in the feed zone. Neat PLA could tolerate a feed zone temperature of 160°C, whereas significantly lower temperatures had to be employed for the plasticized materials: 100°C for PLA/TAc and 80°C for PLA/TbC. Because of the lower T_g of the plasticized materials, the granules were caused to stick together and block the feed zone when the temperature was too high.

TABLE I
 T_g Measured by DMA and Plasticizer Content Measured by GC for PLA Plasticized with TAc in Continuous and Batchwise Processing

PLA/TAc	T_g (°C)	Plasticizer content (wt %)
Granules after continuous blending	—	14.5
Film after film extrusion	24	13.5
Granules after batchwise blending ^a	—	11.2
Film after film pressing ^a	29	11.2
Neat PLA	54	0

^a For details, see Ljungberg and Wesslén.⁸

Films with a width of 150 mm were produced. Because of the melt properties of the material, a film extruder with a vertical die was used. This extrusion equipment required the use of a carrier and a PET film was chosen because of its suitable release properties. By varying the speed of the rewind stand, two film thicknesses of each material were obtained, 20 and 40 μm . The thickness varied insignificantly across the film width, except for 15 mm at both edges of the film, where it was 50% thicker than desired.

DMA was used for measuring the T_g values of the extruded films and the values are displayed in Tables I and II. As shown in the tables, addition of TAc and TbC significantly lowered the glass-transition temperature of PLA. A similar decrease in T_g was observed in a previous study of plasticized PLA,⁸ in which batchwise blending and film pressing were carried out. For a comparison, the T_g values from that study are also given in Tables I and II. As clearly shown in the tables, continuous blending and film extrusion resulted in a larger depression of T_g than that of batchwise processing. An explanation for the low T_g values observed for the continuously blended samples is that continuous blending enables improved mixing of the substances and thus an increase in the homogeneity of the material compared to that of a batchwise process can be anticipated.

In the previous study⁸ it was noted that evaporation of the plasticizer seemed to occur during the blending process. To determine the actual amount of plasticizer present in the material after blending as well as after film preparation, GC analysis was performed. The GC measurements of PLA/TAc films showed that a significantly higher content of plasticizer was present in the continuously blended sample compared to that of the batch-processed one (see Table I). A possible explanation could be that the continuous processing required a shorter residence time for obtaining a homogeneous blend, thus leading to less evaporation of plasticizer. However, the amount of plasticizer present in the blends containing PLA and TbC was only fractionally higher in the continuously processed sample compared with that of the batch-processed

one, as can be seen in Table II. These findings suggest that swelling PLA with plasticizer, which was performed only for the continuously blended samples of PLA/TAc, decreased the plasticizer evaporation. Because swelling did not take place for either the continuously or the batchwise-blended samples containing TbC, the evaporation of plasticizer should be almost equal in both cases, which was also confirmed by the GC results.

In the packaging material industry, extruded material is often stored before it is shipped to customers. Because an earlier study⁸ revealed that plasticized PLA easily undergoes cold crystallization, even at low temperatures, an investigation of the effect of storage on the thermal properties of plasticized PLA was of great interest. The extruded films were analyzed by DSC after various storage periods and the results are shown in Table III. It should be noted that neat PLA did not show any change in thermal properties over the entire time period. However, on aging in room temperature, the plasticized films increased their crystallinity: from 14 to 33% for PLA plasticized with TAc, and from 19 to 32% for PLA plasticized with TbC (see Table III). Most of the crystallization took place within the first 30 days of storage, after which the crystallinity seemed to level out. The observed increase in crystallinity for the plasticized films is a consequence of the glass transition being close to room temperature. The increased molecular mobility of the PLA chains in the amorphous regions of the plasticized films allows the polymer chains to rearrange during storage and slowly crystallize. Compared with the pressed films investigated earlier,⁸ the extruded films displayed a lower crystallinity than that of the pressed ones directly after preparation, presumably caused by the faster cooling in the film-extrusion process.

The DSC results also indicate that the crystallization temperature, obtained on cooling the samples at 10°C/min, increased significantly with increasing age of the extruded plasticized films. The crystallization temperature for PLA plasticized with TAc remained constant at 80°C for 50 days, and then increased to 97°C after 123

TABLE II
 T_g Measured by DMA and Plasticizer Content Measured by GC for PLA Plasticized with TbC in Continuous and Batchwise Processing

PLA/TbC	T_g (°C)	Plasticizer content (wt %)
Granules after continuous blending	—	12.5
Film after film extrusion	24	12.5
Granules after batchwise blending ^a	—	12.2
Film after film pressing ^a	29	12.1
Neat PLA	54	0

^a For details, see Ljungberg and Wesslén.⁸

TABLE III
Thermal Data Obtained by DSC Measurements for Unwelded Films of Neat and Plasticized PLA
After Varying Storage Times at Room Temperature

Film	Time (days)	Cold crystallization (%)	Cold crystallization temperature (°C)	Melting temperature (°C)	Crystallization temperature (°C)	Crystallinity (%)
Neat PLA	1	31	92	174	93	10
	29	31	92	174	93	10
	52	31	92	174	93	10
	123	31	92	174	93	10
PLA/TAc	1	24	70	165	81	14
	28	13	65	165	80	28
	51	13	65	165	80	28
	123	13	69	164	97	33
PLA/TbC	1	21	66	168	83	19
	17	23	64	167	82	18
	28	19	71	168	84	28
	52	19	71	168	84	28
	123	17	74	163	98	32

days of storage. Films of PLA plasticized with TbC showed a similar increase in crystallization temperature from 83 to 98°C during the same time period, as shown in Table III. For neat PLA films the crystallization temperature remained unchanged after storage at similar conditions. An explanation for the increase in crystallization temperature with time can be a decrease in the

molecular weight of PLA over time attributed to hydrolytic degradation.^{17,18} Because the plasticizers are more hygroscopic than PLA the plasticized materials would tend to absorb a larger fraction of water than would neat PLA, thus rendering the plasticized PLA more susceptible to hydrolysis and chain cleavage. GPC measurements performed by the polymer manufacturer con-

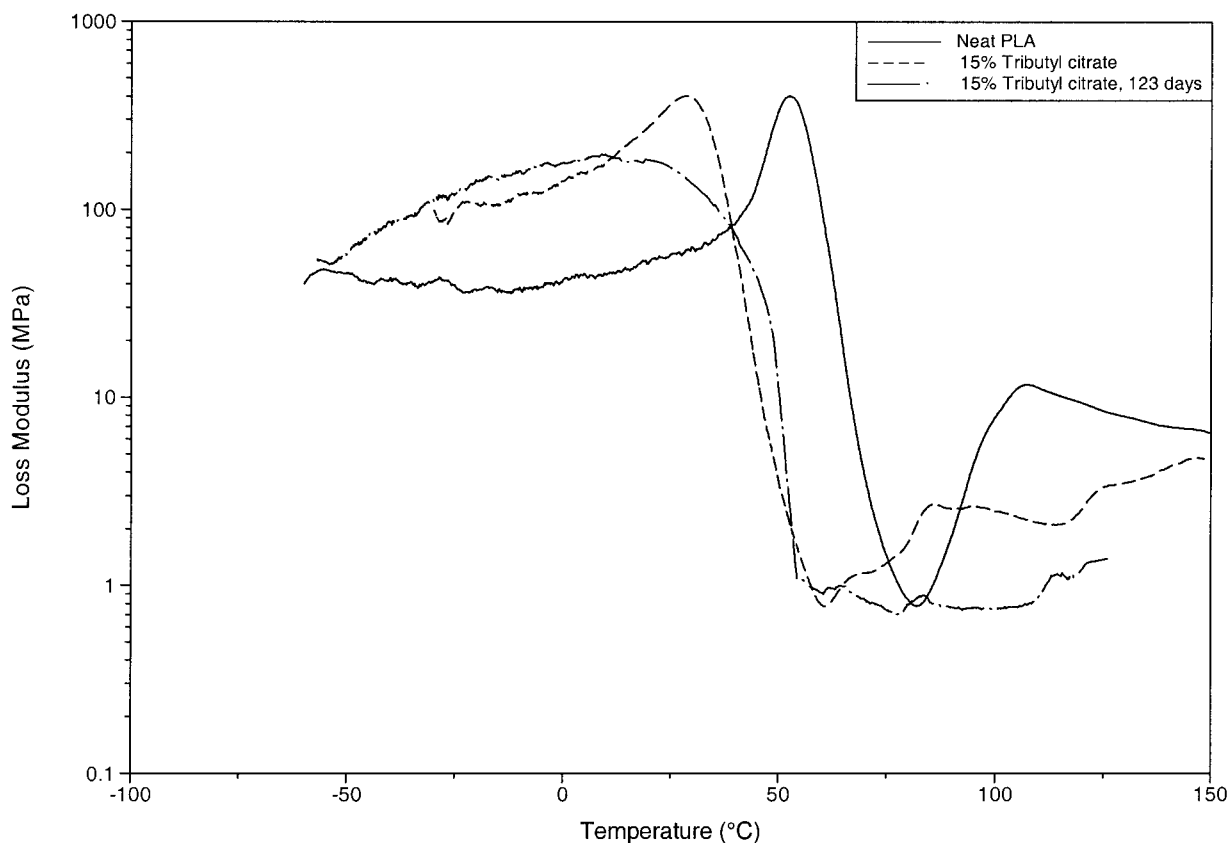


Figure 2 Loss modulus curves from DMA runs comparing neat PLA with blends containing 15 wt % TbC after 1 and 123 days of storage. Equivalent results were obtained for PLA/TAc.

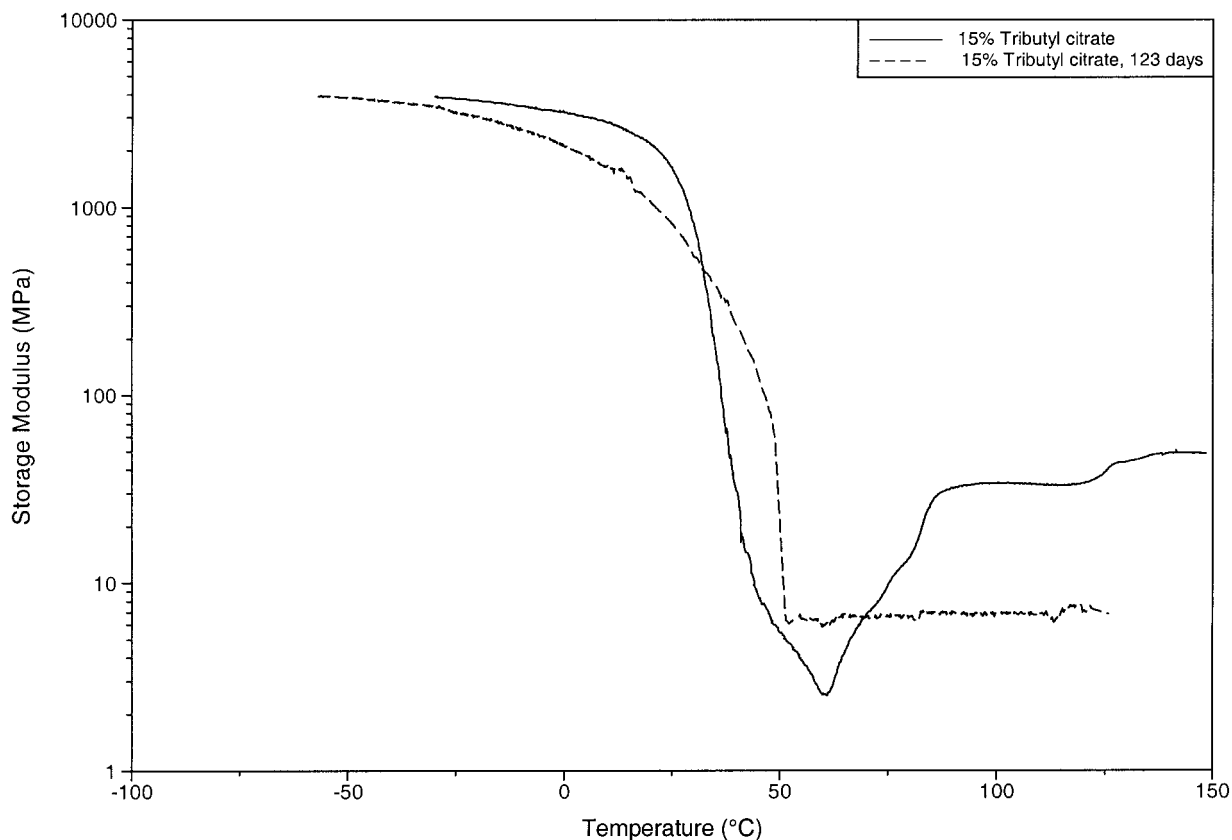


Figure 3 Storage modulus curves from DMA runs comparing blends containing 15 wt % TbC after 1 and 123 days of storage. Equivalent results were obtained for PLA/TAc.

firmed that degradation of the PLA indeed had occurred over time. After 123 days, the M_w for PLA plasticized with TAc was 21,500 g/mol and for PLA plasticized with TbC it was 24,000 g/mol compared to 100,000 g/mol for the nonplasticized PLA. The presence of this low molecular weight PLA provided an increase in the crystallization rate, thus allowing the crystallization of PLA to occur at a higher temperature (i.e., with less subcooling). This is in accordance with the crystallization behavior of PLA reported by Miyata et al.¹⁷

In our previous study⁸ we concluded that the plasticizer might phase separate at moderately high concentrations, as shown by DMA. In the present investigation we found that DMA curves of plasticized films stored for 123 days displayed significantly broadened loss modulus peaks, as clearly seen for

PLA/TbC in Figure 2. PLA plasticized with TAc showed equivalent results. The DMA curves also lacked the sharp increase in storage modulus that is generally observed after the glass transition as a result of cold crystallization, as shown in Figure 3. Again, equivalent DMA curves were obtained for PLA/TAc. These results are in accordance with the increase in crystallinity over time observed in the DSC measurements. It can also be noted, as depicted in Figure 2, that the loss modulus peaks shift toward a lower temperature for the 123-day-old films compared to the younger ones. This fact indicates that the T_g value has decreased after storage. The value is significantly lower than the T_g obtained for the younger films, and this is in line with the idea that plasticized PLA undergoes chain scission over long storage times.

The extruded films were tensile tested and the data obtained were compared with those for neat PLA. In Table IV it is shown that neat PLA film was approximately twice as strong as the plasticized films measured as stress at break. However, the plasticized films displayed considerable toughness and were able to withstand a strain of 350%, whereas the neat PLA film broke after a strain of only 6%. This increase in ductility is a good indication of the extent of the plasticizing effect provided by TAc and TbC.

TABLE IV
Data Obtained from Tensile Testing of Extruded Films After 1 Day of Storage

Film material ^a	Stress at break (N/mm ²)	Strain at break (%)
Neat PLA	62	6
PLA/TAc	30	355
PLA/TbC	35	350

^a All films were of the same thickness, 0.04 mm.

CH welding

In packaging applications the joining together of film materials by welding is a common process. To test the weldability of the PLA materials, neat and plasticized films were subject to constant-heat (CH) welding. It was found that welding of all three material types was possible, but seemed to be affected by the age of the films. The effect of storage on the weldability of the films is shown in Table V. The minimum weld temperature, as defined in the experimental section, for neat PLA remained constant at 65°C throughout the test period. This result was not unexpected, given that the T_g of neat PLA is 54°C and cold crystallization does not occur until the temperature reaches 92°C. Both plasticized films displayed lower welding temperatures than that of the neat PLA when welding was performed after 1 day of storage. At this storage time the crystallinity of the films was still quite low. However, after 6 days the minimum welding temperature for the plasticized films had increased to above 100°C and after 30 days it was 150°C. This increase in the minimum welding temperature can be explained by the fact that the plasticized materials undergo cold crystallization when stored as a result of their low glass-transition temperatures. As the crystallinity in the films increased, the temperature required for achieving a sufficiently strong weld had to exceed the cold crystallization temperature and approach the melting temperature of the material.

Another effect of the materials cold crystallizing during storage may be that the plasticizer is forced to migrate to the film surface. Even a slight increase in the amount of plasticizer present at the surface after merely a few days of storage is likely to cause the outmost surface of the film to crystallize because of increased molecular mobility. This would hinder the polymer chains from entangling during the welding process, thereby rendering welding more difficult.

TABLE V
Effect of Storage of the Films on Their Weldability

Material	Storage (days)	Minimum weld temperature ^a (°C)
Neat PLA	1	65
	6	65
	30	65
	160	65
PLA/TAc	1	46
	6	131
	30	150
	160	150
PLA/TbC	1	50
	6	104
	30	150
	160	150

^a Minimum weld temperature with a welding time of 60 s and a pressure of 0.6 N/mm².

TABLE VI
Contact Angles of Stored Films of Neat PLA and PLA Plasticized with TAc and TbC

Film	Storage (days)	Advancing contact angle (°)
Neat PLA	1	73
	>45	73
PLA/TAc	1	75
	>45	66
PLA/TbC	1	68
	>45	60

Welding is made increasingly difficult, given that the polymer chains that are mobile have a longer distance to diffuse because of the thin layer of plasticizer present on the surface. It was observed that the welding temperature reached its maximum value after approximately 30 days, where it remained despite further storage. At this time the crystallinity in the film had increased and reached an equilibrium value of around 30%.

The surface of the extruded films was also probed by measurements of contact angles with water to investigate possible changes in the surface energy of the films. The results of the measurements can be seen in Table VI. The advancing contact angles of the neat PLA films remained constant over time. However, the plasticized films displayed smaller advancing angles after having been stored longer than 45 days, which indicates an increase in hydrophilicity of the film surfaces over time. Again, migration of the plasticizer from the bulk to the film surface is a possible explanation for this phenomenon.

DSC measurements were performed on material that had been welded at 160°C after 1 day of storage and the thermal data can be found in Table VII. The melting temperature for welds of neat PLA was 173°C, the crystallinity was 9%, the crystallization temperature was 94°C, and the cold crystallization temperature was 91°C. These values were identical to the T_m , crystallinity, crystallization temperature, and cold crystallization temperature for the unwelded PLA films. Thus, constant heat welding did not affect the thermal properties of neat PLA.

The melting temperature for welds of PLA plasticized with TAc was 169°C, only slightly higher than that of the unwelded film. The crystallinity of the welds had increased to 42% after CH welding. This value is significantly higher than the original crystallinity in the unwelded film after 1 day of storage, which was 14%. The cause of the substantial increase in crystallinity after welding was a combination of the material's low T_g , promoting molecular mobility, and the increased temperature during the welding process (160°C for 0.6 s). The crystallization temperature for welds of PLA plasticized with TAc was 86°C, which is

TABLE VII
Thermal Data Obtained by DSC Measurements for Films of Neat and Plasticized PLA
Welded at 160°C After 1 day of Storage

Film	Cold crystallization (%)	Cold crystallization temperature (°C)	Melting temperature (°C)	Crystallization temperature (°C)	Crystallinity (%)
Neat PLA	33	91	173	94	9
PLA/TAc	1	70	169	86	42
PLA/TbC	1	73	168	86	43

an increase of 5°C compared to that of the unwelded film. The cold crystallization temperature, however, was maintained after welding.

The T_m for welds of PLA plasticized with TbC was 168°C and thus remained equal to that of the unwelded film. However, the crystallinity, compared to that of an unwelded film after 1 day of storage, increased from 19 to 43% after welding. Again, the increase in crystallinity was a result of a low T_g in the film and the increased temperature during the welding process. There was a slight increase in crystallization temperature for the welds compared to that of the unwelded film and the cold crystallization temperature for the welds was 7°C higher than that of the unwelded film.

CONCLUSIONS

Addition of TAc or TbC significantly lowered the T_g of PLA. Storage of the plasticized films resulted in an increase in crystallinity because glass-transition temperatures around room temperature allowed for rearrangement of the polymer chains. An increase in crystallization temperature was observed in the plasticized films after 123 days of storage, presumably because the PLA chains underwent chain scission. Both plasticizers migrated to the film surface after storage and seemed to cause an increase in the crystallinity and the hydrophilicity of the surface. These changes in the films' surface properties after storage along with the increased crystallinity in the bulk of the film rendered constant heat welding increasingly difficult.

Constant heat welding of neat PLA films had no effect on the T_m , crystallinity, or crystallization temperature of the material. However, the plasticized films displayed a significant increase in crystallinity after welding as a result of the low T_g of the material

and the increase in temperature during the welding process.

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