Dramatic Improvements in Strain Hardening and Crystallization Kinetics of PLA by Simple Reactive Modification in the Melt State

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Poly(lactic acid) (PLA) is chemically modified by radical mediated solvent-free, peroxide-initiated grafting of triallyl trimesate (TAM) coagent in the melt state. When compared with the parent material and with PLA samples treated with peroxide alone, coagent-modified materials demonstrate higher molar mass and improved melt rheological properties, including substantial improvements in melt elasticity and strain hardening under uniaxial extension. Although similar rheological modifications are obtained by PLA chain extension using a multifunctional epoxide oligomeric chain extender, the coagent-modified material demonstrates significantly enhanced crystallinity and crystallization rates. The appearance of a distinct crystallization exothermic peak and the disappearance of the cold crystallization temperature point to a nucleation effect in the coagent modified PLA, which together with the rheological enhancements can promote the processability of this material in conventional thermoplastics operations.

1. Introduction

Poly(lactic acid) (PLA) is a bio-derived, biodegradable thermoplastic polyester, which can be processed using conventional thermoplastics processing equipment, including injection molding, blow molding, film casting, and blowing. However it has a very narrow processing window, because of the lack of melt strength and its slow crystallization rates. Additionally its poor engineering properties, including impact strength and heat resistance...
have mainly confined its applications to food packaging, as well as biomedical applications, such as drug delivery, where biocompatibility and biodegradability are desired. The properties of PLA depend significantly upon its molecular weight and the stereochondrical makeup of the backbone, which is controlled by polymerization with \( \delta \)-lactide, \( L \)-lactide, or \( DL \)-lactide, to form random or block stereopolymers. Minimizing the amount of \( \delta \)-lactide is required to obtain PLA with higher crystallinity; however most commercial grades have low crystallinities and low crystallization rates, unless nucleating agents are used. The rheological properties of PLA depend on the molecular weight and molecular weight distributions (MWD), presence of branching, as well as its stereochondemochemical makeup. Strain hardening has been reported in melts containing a high molecular weight tail, and in amorphous PLA containing mixtures of the \( \delta \) and \( L \) isomers at low temperatures, but otherwise it is generally accepted that commercially available linear PLA lacks the level of strain hardening, and therefore melt strength, needed for normal processing operations. This restricts its processability in operations involving high stretch rates, such as film blowing, thermoforming, foaming etc. Given these shortcomings, approaches have been proposed to achieve chain extension and/or branching in PLA, with which generally considered more beneficial. Compared to the various synthetic routes that exist to synthesize branched PLA, methods that employ reactive modifications in the melt state are generally considered to be more convenient and industrially relevant. Various modification approaches to improve processability have been summarized by Pilla et al. and Yu et al. These include chain extension in the presence of glycido and long chain branching via functional group reactions of pyromellitic dianhydride and triglycidyl isocyanurate. Furthermore chain extenders, such as tris (nonylphenyl) phosphate, polycarboximide, and multi-functional epoxy compounds have been used to counteract degradation in polyesters, such as PLA and to achieve chain extension.

Reactive extrusion of PLA using organic peroxides has been undertaken to increase the molecular weight, viscosity, and melt strength with limited success, as the resulting branching is often counter-balanced by severe chain scission. Radiation induced cross-linking in the presence of multi-functional coagents has been suggested as an alternative, but generally resulted in physical properties reduction. Peroxide-initiated reactive extrusion in the melt state, assisted by coagents is frequently employed as a means to introduce long-chain branching in linear polyesters, such as polypropylene. However there are only two reports, employing this approach in PLA. Yang et al. used triallyl isocyanurate as a crosslinking agent together with dimethyl peroxide (DCP), to obtain compounds with different levels of cross-linking. More recently, You et al. reported that PLA prepared through reaction with DCP and pentaerythritol triacrylate (PETA) coagent had enhanced viscoelastic properties, attributed to branching. The resulting product had faster crystallization rates under isothermal conditions. However in these publications there was no mention about the properties of the resulting materials under uniaxial extension and the non-isothermal crystallization behavior of the polymers, which is relevant to processing, was not reported.

The present communication reports substantial improvements in the melt strength and non-isothermal crystallization kinetics, upon employing a simple chemical modification method in the melt state using solvent-free, peroxide-initiated grafting of a multi-functional co-agent (triallyl trimesate, TAM). To the best of our knowledge this is the first time that simultaneous improvements in all these properties upon reactive modification are reported for PLA. These attributes are expected to facilitate use of these materials in operations such as foaming, injection moulding, film processing etc.

2. Experimental Section

PLA (grade 3251D, MFI 35 g/10 min at 190 °C/2.16 kg) was obtained from Natureworks. Triallyl trimesate (TAM, 98%, Monomer Polymer Inc.), DCP (98%, Sigma–Aldrich) and Tetrahydrofuran (Sigma–Aldrich) were used as received. Joncryl™ 4368 a multi-functional epoxide styrene-acrylic oligomeric chain extender, containing glycidyl methacrylate (GMA) functions was supplied by BASF. It has a functionality of 9 with epoxy equivalent weight 285 g mol⁻¹, and molecular weight 6,800 g mol⁻¹.

PLA was dried in a vacuum oven at 100 °C for 3 h to remove moisture. Peroxide-degraded PLA (PLA/DCP) was prepared by coating ground PLA powder (15 g) with an acetone solution containing DCP (0.045 g) and allowing the solvent to evaporate. The resulting mixture, containing 0.3 wt.-% DCP, was charged to a DSM micro-compounder, equipped with twin-co-rotating screws, at 180 °C at 100 rpm for 6 min. Coagent-modified PLA was prepared as described for PLA/DCP from a mixture of PLA (14.8 g), DCP (0.045 g), and TAM (0.15 g), yielding PLA/TAM containing 0.3 wt.-% DCP and 1 wt.-% TAM. A compound containing 1.2 wt.-% of GMA, which was the amount required to yield a similar zero shear viscosity as the PLA/TAM, was also prepared and used for comparison. Neat PLA was processed under the same conditions outlined above, to provide a suitable basis for comparison. After compounding, the strands were quenched in cold water before chopping into pellets for further characterization.

Samples were prepared for SEC analysis by dissolving 10 mg of polymer in 1 mL of distilled THF overnight to ensure complete dissolution, and filtered through a 0.2 μm nylon filter. The molecular weight distributions (MWD) of the polymers MWD were determined with respect to polystyrene standards using a Viscotec 270max separation module with triple detection by differential refractive index (DRI), viscosity (IV), and light scattering (low angle LALS and right angle RALS), which was...
maintained at 40 °C and contained two porous PolyAnalytik columns in series. Distilled THF was used as the eluent at a flow rate of 1 mL·min⁻¹.

The linear viscoelastic (LVE) properties were measured in the oscillatory mode using a stress controlled rheometer (Visco Tech by Reologica). Frequency sweeps were conducted at 180 °C using 20 mm parallel plates, under nitrogen purge. Samples were further characterized in uniaxial extension using an SER-2 universal testing platform from Xpansion Instruments hosted on an MCR-301 Anton Paar rheometer. Measurements were conducted at 180 °C at Hencky strain rates ranging from 0.10 to 10 s⁻¹. The LVE oscillatory measurements obtained at 180 °C were used to calculate the LVE stress growth curve, \( \eta^* \), and to check the consistency of the extensional measurements. The curve corresponding to 3\( \eta^* \) represents the LVE envelope in uniaxial extension, according to Trouton’s law.

Differential scanning calorimetry (DSC) was conducted using a DSC Q 100 by TA Instruments. Samples were scanned between 0 and 200 °C at a heating rate of 5 °C·min⁻¹. After the first heating, each sample was held isothermally at 200 °C for 3 min before cooling at rates between 2.5 and 20 °C·min⁻¹, to determine the crystallization onset and peak temperatures according to ASTM D3418. The % crystallinity of PLA, was estimated using Equation (1):

\[
X_c = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_{100}} \times 100
\]  

where \( \Delta H_m \) is the apparent fusion enthalpy, \( \Delta H_{cc} \) is the exothermic enthalpy that is absorbed by crystals formed during the heating scan and \( \Delta H_{100} \) is the theoretical fusion enthalpy of a 100% crystalline polymer, which is 93 J·g⁻¹ for PLA.

Isothermal studies involved heating the sample to 200 °C and holding it for 3 min, followed by cooling at 50 °C·min⁻¹ to temperatures ranging from 135 to 155 °C, and held isothermally until completion of crystallization. The analysis included evaluations of the relative crystallinity as a function of time and standard Avrami kinetics.[33]

3. Results and Discussion

3.1. Rheological Characterization

The linear viscoelastic properties of neat PLA, PLA reacted with 0.3 wt.-% DCP (PLA/DCP) and with 0.3 wt.-% DCP/1 wt.-% TAM (PLA/TAM) are summarized in Figure 1. PLA/DCP had essentially unaltered flow characteristics compared to the unmodified PLA (Figure 1a) and linear architecture, as revealed by the Van Gurp-Palmen plots of Figure 1b, which tend to the limit of 90°. This suggests that peroxide-induced degradation was compensated by chain extension, without branching. This is corroborated by the minimal differences in the molar mass distributions between these two compounds (Table 1).

On the contrary, PLA/TAM demonstrated a substantial increase in molar mass (Table 1) and melt viscosity (Figure 1a). It is well-known that solvent-free processing with multi-functional coagents involves simultaneous chain scission and cross-linking, the balance of which controls the molecular weight and branching distributions of the final product. In general, reaction with coagents bearing multiple acrylate, allylic or styrenic groups results in bimodal molecular weight and branched distribution, comprised of a linear chain population of relatively low molecular weight, and a high molecular weight hyper-branched chain population, which can progress above the gel point.[27,28] Furthermore it has been reported that systems containing polypropylene reacted with coagent and peroxide can undergo a precipitation polymerization, which results in the formation of a separate phase of highly cross-linked, coagent-rich sub-micron sized particles.[27,31] The resulting products possess a creamy appearance in the melt state, owing to the presence of these cross-linked nano-particles.[27]

In the present case, treatment with 0.3 wt.-% DCP and 0.1 wt.-% TAM produced a creamy (as opposed to the transparent PLA and PLA/DCP), gel-free product with increased melt elasticity, and shear thinning, as observed in Figure 1, consistent with the presence of branching.[29]
We compared the properties of PLA/TAM to those of PLA chain extended using a multi-functional epoxide styrene-acrylic oligomeric chain extender, containing GMA functions (trade name Joncryl from BASF). The chain extended (PLA/GMA) was prepared by reacting PLA with 1.2 wt.% Joncryl, which was the amount needed to match the low shear viscosity of PLA/TAM. The epoxy functions contained within multi-functional epoxies can react with the —OH and —COOH end groups of PLA, resulting in random branching and/or cross-linking. The low levels of Joncryl used herein, produced a gel-free product with higher molar mass than the parent PLA (Table 1), accompanied by increased viscosity and deviations from the terminal flow behaviour (Figure 1).

The different shear thinning characteristics and shapes of the Van Gurp-Palmen plots of PLA/GMA compared to PLA/TAM point to different branching levels and chain topologies. PLA/TAM presumably contained small amounts of a hyper-branched population, which are characteristic of this coagent modification, whereas reaction with multi-functional epoxies produces random branching. In spite of the different mechanisms of chain extension/branching, the ultimate strain hardening characteristics of PLA/TAM and PLA/GMA were very similar, as shown in Figure 2. Pronounced strain hardening was present in both materials, providing evidence of long chain branching. Note that the viscosities of the parent PLA and PLA/DCP were below the threshold needed to support extensional viscosity experiments.

### 3.2. Thermal Properties

Detailed DSC data are presented in Table 1 and Figure 3. The glass transition temperature of PLA was 62°C and remained unchanged in all modified materials. PLA had a cold crystallization peak, $T_{cc}$, at 109°C, and a melting peak, $T_m$, at 173°C (Table 1 and Figure 3a). PLA/DCP had reduced cold crystallization temperature and increased crystallinity. These findings are commonly associated with PLA degradation.[18,26] Neither of these two materials crystallized during the cooling cycle. On the contrary, the branched PLAs showed exothermic crystallization peaks. PLA/GMA had a weak crystallization peak, $T_c$, around 105°C, suggesting a moderate effect of this modification on the ability of the chains to crystallize. On the other hand, co-agent modified PLA had a clear and sharp crystallization peak at 133°C (Figure 3b). This was accompanied by the disappearance of the cold crystallization peak, and a significant increase in crystallinity by 117% with respect to neat PLA and 50% with respect to PLA/DCP. Even though changes in the cold crystallization of PLA upon modification with a PETA co-agent have been mentioned previously[26] this is the first time that the presence of an exothermic crystallization peak arising during the cooling cycle, which is indicative of the capability of the material to crystallize upon cooling during normal polymer processing operations, is reported.

The ability of our modified materials to crystallize was evident not only by the appearance of an exothermic crystallization peak, but also by their isothermal and non-isothermal crystallization kinetics (Figure 4). The PLA and PLA/DCP formulations did not crystallize and therefore are

### Table 1. Material characterization.

<table>
<thead>
<tr>
<th>Material</th>
<th>$\mathcal{M}_w$ a) [g mol$^{-1}$]</th>
<th>PDI b)</th>
<th>$T_m$ [°C]</th>
<th>$T_c$ [°C]</th>
<th>$T_{onset}$ [°C]</th>
<th>$T_{cc}$ [°C]</th>
<th>Crystallinity [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA</td>
<td>98 140</td>
<td>1.7</td>
<td>173</td>
<td>N/A</td>
<td>N/A</td>
<td>109</td>
<td>24</td>
</tr>
<tr>
<td>PLA/DCP</td>
<td>90 000</td>
<td>1.8</td>
<td>170</td>
<td>N/A</td>
<td>N/A</td>
<td>94</td>
<td>35</td>
</tr>
<tr>
<td>PLA/TAM</td>
<td>143 020</td>
<td>2.0</td>
<td>169</td>
<td>133</td>
<td>149c), 142d)</td>
<td>N/A</td>
<td>52</td>
</tr>
<tr>
<td>PLA/GMA</td>
<td>115 000</td>
<td>1.7</td>
<td>168</td>
<td>105</td>
<td>124c), 123d)</td>
<td>95</td>
<td>34</td>
</tr>
</tbody>
</table>

a) $\mathcal{M}_w$: Weight average molar mass; b) PDI: polydispersity index; c) at cooling rate of 2.5°C; d) at cooling rate of 5°C.

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![Figure 2](https://www.mme-journal.de/)

Figure 2. Tensile stress growth coefficient ($\eta_E^+$) of TAM and GMA modified PLA as a function of strain rate and time at Hencky strain rates of 0.1, 1 and 10 s$^{-1}$ at 180°C. Curves are shifted by an arbitrary factor for the sake of clarity. Solid lines represent the LVE envelop ($\eta_E^+$) for each sample.

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not included in this comparison. Plots of the evolution of relative crystallinity as a function of time revealed a crystallization half-time of 9.3 min at 135 °C for PLA/GMA, whereas the half-time of PLA/TAM at this temperature was only 0.6 min. The results of the Avrami analysis for temperatures ranging from 135 to 155 °C are presented in Table 2. The Avrami exponents suggest similar crystal growth habit in all cases. Introduction of branching in polymers such as polypropylene has been associated previously to changes in the crystallization kinetics.[32]

The relative crystallinity as a function of time, recorded during non-isothermal crystallization experiments is shown in Figure 4b. While cooling from the melt state, PLA/TAM started to crystallize significantly earlier, with crystallization half times, \( t_{1/2} \) of 2.6 and 1.8 min at cooling rates of 2.5 and 5 °C·min\(^{-1} \), respectively as compared to 8.4 and 3.9 min for PLA/GMA. Furthermore PLA/TAM had \( t_{1/2} \) of 0.96, 0.73 and 0.66 min at cooling rates of 10, 15 and 20 °C.

**Figure 3.** DSC (a) 2nd heating scan at rate of 5 °C·min\(^{-1} \) (b) cooling scan at the rate of 5 °C·min\(^{-1} \).

**Figure 4.** Relative degree of crystallinity as a function of time (a) isothermal crystallization experiments; (○) PLA/TAM at 135 °C, (●) PLA/TAM at 140 °C, (■) PLA/TAM at 150 °C, (▲) PLA/GMA at 135 °C and (b) non-isothermal crystallization experiments; (●) PLA/TAM at 2.5 °C·min\(^{-1} \), (○) PLA/TAM at 5 °C·min\(^{-1} \), (▲) PLA/TAM at 20 °C·min\(^{-1} \), (▲) PLA/GMA at 2.5 °C·min\(^{-1} \), (△) PLA/GMA at 5 °C·min\(^{-1} \).

**Table 2.** Isothermal Avrami constants and crystallization half time for PLA/GMA and PLA/TAM at various temperatures.

<table>
<thead>
<tr>
<th>Temperature [°C]</th>
<th>n</th>
<th>( K ) [min(^{-1} )]</th>
<th>( t_{1/2} ) [min]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA/GMA</td>
<td>135</td>
<td>2.9</td>
<td>0.001</td>
</tr>
<tr>
<td>PLA/TAM</td>
<td>135</td>
<td>3.0</td>
<td>4.27</td>
</tr>
<tr>
<td>PLA/TAM</td>
<td>145</td>
<td>3.4</td>
<td>0.14</td>
</tr>
<tr>
<td>PLA/TAM</td>
<td>150</td>
<td>3.3</td>
<td>0.02</td>
</tr>
<tr>
<td>PLA/TAM</td>
<td>155</td>
<td>2.6</td>
<td>0.01</td>
</tr>
</tbody>
</table>
respectively whereas PLA/GMA did not crystallize at these conditions.

The findings reported above point to a nucleating effect, which occurred in spite of the absence of a nucleating agent. As explained earlier, a nucleating effect attributed to the formation of a separate phase of coagent-rich particles that forms upon reactive modification,[30] was reported recently in co-agent modified polypropylene. We suggest that a similar nucleation effect is responsible for the enhancements in crystallinity and crystallization rates in the reactivity modified PLA/TAM product.

4. Conclusion

PLA with long chain branching was produced by a simple radical mediated peroxide-initiated grafting of triallyl trimesate (TAM) coagent in the melt state. The resulting product demonstrated strain hardening, consistent with its long chain branched characteristics, and significantly enhanced crystallinity and crystallization rates, suggesting that this is a promising approach to enhance the processing characteristics and properties of PLA.

Acknowledgements: Funding from the Natural Sciences and Engineering Council of Canada (NSERC) and Xerox Corporation is greatly appreciated.

Received: March 3, 2014; Revised: May 16, 2014; Published online: DOI: 10.1002/mame.201400078

Keywords: coagent; crystallization; melt strength; peroxide; poly(lactic acid)