



Effect of Chain Extension on Thermal Stability Behaviors of Polylactide Bioplastics

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<http://dx.doi.org/10.13005/ojc/310204>

(Received: January 22, 2015; Accepted: March 12, 2015)

ABSTRACT

The influences of chain extension and blending temperature on the thermal properties of poly(L-lactide) (PLL) were investigated. Joncryl[®] ADR 4368, a styrene-acrylic multifunctional oligomeric agent, was used as a chain extender. Differential scanning calorimetry and thermogravimetry were used to determine the thermal transition properties and thermal stability of the chain extended PLL, respectively. The chain extension reaction occurred at a blending temperature of 190 °C better than at 170 °C. The molecular weights of the chain extended PLLs increased and melt flow indices decreased when the Joncryl[®] ADR 4368 ratio was increased. The addition of Joncryl[®] ADR 4368 had an effect on the glass transition temperature, crystallizing temperature and crystallinity of the PLL for the blending temperature of 190 °C. The chain extended PLLs with branched structures showed lower thermal stability than the linear PLLs. The content of branched PLLs increased with the Joncryl[®] ADR 4368 ratio and blending temperature. The chain extension reaction was complete when 2% Joncryl[®] ADR 4368 and a blending temperature of 190 °C were used. The results indicated that the chain extension improved the PLL's melt strength and it has an effect on the thermal stability of the PLLs.

Key words: Biodegradable polymer, Polylactide, Chain extender, Melt flow index, Thermal stability.

INTRODUCTION

Poly lactides including semi-crystalline poly(L-lactide) (PLL) and amorphous poly(D,L-lactide) (PDLL) are biodegradable polyesters that have attracted much interest for medical and packaging applications because of its

biodegradability and biocompatibility¹⁻⁵. The PLL and PDLL have widely used in packaging and drug delivery applications, respectively.

For packaging applications, the properties of PLL can be tailored to meet specific applications by copolymerization and additive compounding.

The later method is low cost and convenient for used at an industrial scale. It is well known that the linear PLL has a low melt strength⁵⁻⁶. The melt strength of PLL has been improved by reactive blending with a styrene-acrylic multifunctional oligomeric agent, under the trade name Joncryl[®], to form the branched structures of PLLs⁷. Joncryl[®] ADR 4368 has been shown to be the most efficient chain extender to restore the molecular weight of PLLs during melt processing⁸⁻⁹.

However, to the best of our knowledge, the effect of chain extension on the thermal stability behaviors of PLL has not been reported so far. Thus, the purpose of this study is to investigate the effect of the chain extender on the thermal properties of PLL. For this purpose, pure PLL was synthesized. Then, the chain extender/PLL blends were prepared by melt blending with different chain extender ratios (0.5 – 2.0 wt.%) and blending temperatures (170 and 190 °C). The resulting PLLs were characterized by the use of melt flow index analysis, differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). In addition, the obtained results were also compared with those of the chain extender-free PLLs.

EXPERIMENTAL

Materials

The L-lactide monomer was prepared using well-established procedures, from L-lactic acid (88%, Purac, Thailand). The lactide monomer was purified by re-crystallization four times from ethyl acetate before drying in a vacuum oven at 55 °C for 24 h. 1-Dodecanol (98%, Fluka, Switzerland) was purified by distillation under reduced pressure before use. Stannous octoate (Sn(Oct)₂, 95%, Sigma, USA) was used without further purification. All reagents used were analytical grade. A styrene-acrylic multi-functional-epoxide oligomeric agent (Joncryl[®] ADR 4368, supplied by BASF, Thailand) with a molecular weight of 6,800 g/mol (an epoxy equivalent weight of 285 g/mol) was used as a chain extender.

Methods

The poly(L-lactide) (PLL) was synthesized by ring-opening polymerization in bulk at 165 °C for 2.5 h under a nitrogen atmosphere using stannous

octoate (0.01 mol%) and 1-dodecanol (0.14 mol%) as the initiating system. The obtained PLL was then granulated before drying in a vacuum oven at 110 °C for 3 h to remove un-reacted lactides. The intrinsic viscosity ($[\eta]$) and viscosity-average molecular weight (M_v) of the obtained PLL were 2.53 dL/g and 104,700 g/mol, respectively.

The PLL and Joncryl[®] ADR 4368 were dried in a vacuum oven at 60 °C for 24 h before melt blending. The PLL with different Joncryl[®] ADR 4368 ratios (0.5, 1 and 2 wt.%) were melt blended to prepare the chain extended PLL in an internal mixer (HAAKE PolyLab OS system) for 4 min at different blending temperatures (170 °C and 190 °C). A rotor speed of 100 rpm was used. The PLL without the addition of Joncryl[®] ADR 4368 (0 wt.%) was also melt blended in an internal mixer under the same conditions for comparison.

Measurements

The intrinsic viscosity, $[\eta]$, of PLL was determined from flow-time measurements on a diluted series of solutions in chloroform, as the solvent, at 25 °C using viscometrically. The viscosity-average molecular weight (M_v) was calculated from the $[\eta]$ using equation (1)¹⁰.

$$[\eta] = 5.45 \times 10^{-4} M_v^{0.73} \quad \dots(1)$$

The melt flow index (MFI) of the PLL was determined using a Tinius Olsen MP1200 melt flow indexer. The temperature of the melt was kept at a uniform 190 °C and a 2.16 kg load was applied to extrude the molten PLL. A 100 g rod was used as a plunger. The MFI was averaged from at least five determinations.

The thermal transition properties of the PLL were determined with a Perkin-Elmer Pyris Diamond differential scanning calorimeter (DSC) under a nitrogen flow. For DSC, samples of 3 – 5 mg in weight were heated at 10 °C/min over a temperature range of 0 to 200 °C. The crystallinity (X_c) of the PLL was determined from the heat of melting using equation (2).

$$X_c (\%) = [(\Delta H_m - \Delta H_c) / 93.7 \text{ J/g}] \times 100 \quad \dots(2)$$

where the ΔH_m and ΔH_c were the heat of

melting and heat of crystallizing, respectively, that were obtained from the DSC method. The heat of melting for 100% crystallinity of PLL was 93.7 J/g¹¹.

RESULTS AND DISCUSSION

The chain extension is usually used to adjust the melt strength of PLLs for specific melt processing. Joncryl[®] ADR 4368, a styrene-acrylic multifunctional oligomeric agent, has been widely used as a chain extender for this purpose by the formation of branched PLLs. The $[\eta]$, M_v and melt flow index (MFI) of PLLs with and without Joncryl[®] ADR 4368 addition are summarized in Table 1. For Joncryl[®]-free PLLs, the higher blending temperature (190 °C) induced lower $[\eta]$ and M_v values and higher MFI. This was due to the large

thermal degradation and chain scission that occurred during melt blending at 190 °C.

The $[\eta]$ and M_v of the PLLs increased and the MFI decreased when the Joncryl[®] ADR 4368 ratio was increased. This indicates that the chain extension between the Joncryl[®] and PLL molecules was formed. The branched structures of PLLs obtained from chain extension increased the melt strength and decreased the MFI of the PLLs. The MFI values of the chain extended PLLs largely decreased as the blending temperature increased from 170 °C to 190 °C for the same Joncryl[®] ADR 4368 ratio. The results suggested that the larger Joncryl[®] ADR 4368 ratio and higher blending temperature induced more chain extension accorded to the literature^{7, 12-14}.

Table 1: $[\eta]$, M_v and MFI of chain extended PLL

Blending temperature (°C)	Joncryl [®] ratio (wt.%)	$[\eta]$ (dL/g)	M_v^* (g/mol)	MFI (g/10 min)
170	0	1.4	47,900	132
	0.5	1.5	50,100	78
	1.0	1.7	58,900	34
	2.0	2.1	81,300	6
190	0	1.2	38,000	148
	0.5	1.7	61,700	33
	1.0	1.9	70,800	11
	2.0	2.2	87,100	0.7

* calculated from equation (1)

Table 2: Thermal transition properties of chain extended PLL

Blending temperature(°C)	Joncryl [®] ratio(wt.%)	T_g (°C)	T_c (°C)	ΔH_c (J/g)	T_m (°C)	ΔH_m (J/g)	X_c^* (%)
170	0	57	94	8.0	175	36.8	31
	0.5	59	94	25.3	174	47.3	24
	1.0	59	97	27.2	174	49.9	24
	2.0	58	95	32.3	174	57.4	27
190	0	50	99	30.2	171	36.6	7
	0.5	49	95	30.9	170	37.0	6
	1.0	49	91	32.8	169	48.6	17
	2.0	48	88	34.1	169	57.0	24

* calculated from equation (2)

Table 3: $T_{d, \max}$ of chain extended PLL

Blending temperature (°C)	Joncryl® ratio (wt.%)	$T_{d, \max 1}$ (°C)	$T_{d, \max 2}$ (°C)
170	0	310	367
	0.5	313	363
	1.0	313	365
	2.0	314	368
190	0	312	374
	0.5	316	370
	1.0	319	369
	2.0	333	-

Thermal transition properties

Fig. 1 shows the DSC thermograms of the chain extended PLLs when they reacted with different Joncryl® ADR 4368 ratios for blending temperatures of 170 °C and 190 °C. They showed crystallizing peaks because they solidified quickly from the melt state in the internal mixer. The results of the thermal transition properties of the PLL obtained from the DSC thermograms are summarized in Table 2. The Joncryl® ADR 4368 addition did not significantly change the glass transition temperature (T_g) of the PLLs. The T_g of the PLLs blended at temperatures of 170 °C and 190 °C were in the ranges 57 – 59 °C and 48 – 50 °C, respectively. It can be seen that the T_g decreased as the blending temperature increased. This may be explained by the higher blending temperature enhancing the chain extension. The branched structures of chain extended PLLs contained a higher free volume. The T_g of the PLLs was then reduced.

The Joncryl® ADR 4368 did not affect the crystallizing temperature (T_c) of chain extended PLLs for the blending temperature of 170 °C. However, for the blending temperature of 190 °C, the T_c decreased as the Joncryl® ADR 4368 ratio increased. This may be explained by the longer branched PLLs having higher free volumes that were more easily rearranged for crystallization. From Table 2, the T_m of the chain extended PLLs blended at temperatures of 170 °C and 190 °C were in the ranges 174 – 175 °C and 169 – 171 °C, respectively. The T_m slightly decreased as the blending temperature increased. The heat of crystallization (ΔH_c) and heat of melting (ΔH_m) of the

PLLs increased when the Joncryl® ADR 4368 ratio and blending temperature were increased. The crystallinity (X_c) of PLL did not significant change when the PLL was blended with the Joncryl® ADR 4368 at 170 °C. However, the X_c of PLL significantly increased as the Joncryl® ADR 4368 ratio increased up to 1% and 2% for the blending temperature of 190 °C. This may be explained by the longer chains of branched PLLs inducing larger crystallites of PLLs. The DSC results supported that the chain extension reaction between the Joncryl® ADR 4368 and PLL molecules occurred at 190 °C better than at 170 °C.

Thermal stability

Thermal stability of the chain extended PLLs prepared with different Joncryl® ADR 4368 ratios and blending temperatures was determined from the TG thermograms, as shown in Fig. 2. The weight losses of PLLs started at approximate 300 °C. The thermal decompositions completely finished at approximate 400 °C. The PLLs with and without Joncryl® ADR 4368 addition showed two thermal decomposition stages in the ranges 300 – 350 °C and 350 – 400 °C. The weight loss behaviors of the PLLs depended on the Joncryl® ADR 4368 ratio.

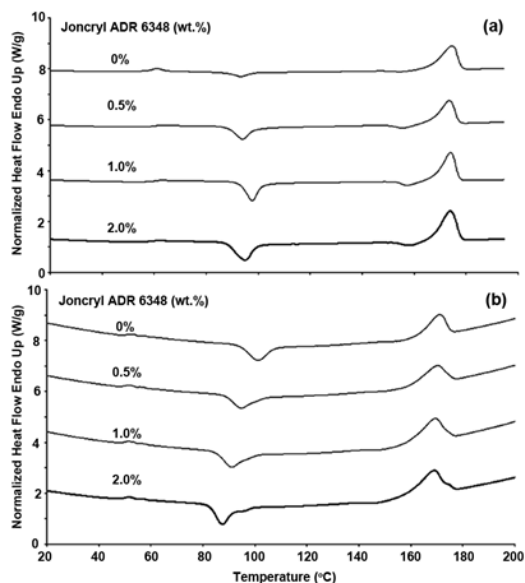


Fig. 1: DSC thermograms of chain extended PLL prepared with different Joncryl® ADR 4368 ratios at blending temperatures of (a) 170 °C and (b) 190 °C.

The weight losses of the first decomposition step, in the range 300 – 350 °C, increased slightly with the Joncryl® ADR 4368 ratio.

Thermal stability results can be clearly investigated from the derivative TG (DTG) thermograms, as shown in Fig. 3. The peak of the DTG thermogram indicates the temperature of the maximum decomposition rate ($T_{d, \max}$). The DTG thermograms of PLLs exhibited two peaks of two decomposition stages accorded to their TG thermograms. From Fig. 3, it was found that the area of the lower $T_{d, \max}$ peaks of Joncryl®-free PLLs (0% Joncryl® ADR 4368) increased when the blending temperature was increased from 170 °C to 190 °C. The results suggested that the higher blending temperature (190 °C) induced more PLL chain scissions to form as shorter linear PLL chains. The shorter linear PLL chains had lower thermal stability (lower $T_{d, \max}$ peaks) than the longer linear PLL chains.

It can be clearly seen that the intensities of the lower $T_{d, \max}$ peaks steadily increased and higher $T_{d, \max}$ peaks significantly decreased as the Joncryl® ADR 4368 ratio increased for both blending temperatures. It may be proposed that the branched PLLs from chain extension degraded at the lower $T_{d, \max}$. Therefore the lower $T_{d, \max}$ peak could contribute to the thermal decompositions of both shorter linear PLLs and branched PLLs. While the higher $T_{d, \max}$ peak could attribute to thermal decomposition of the longer linear PLLs. The DTG results suggested that the thermal stability of the PLLs decreased when the PLLs were reacted with the Joncryl® ADR 4368. The increasing Joncryl® ADR 4368 ratio also decreased the thermal stability of the PLLs.

The resulting $T_{d, \max}$ values from the DTG thermograms are summarized in Table 3. The lower $T_{d, \max}$ values of chain extended PLLs slightly increased with the Joncryl® ADR 4368 ratio. This

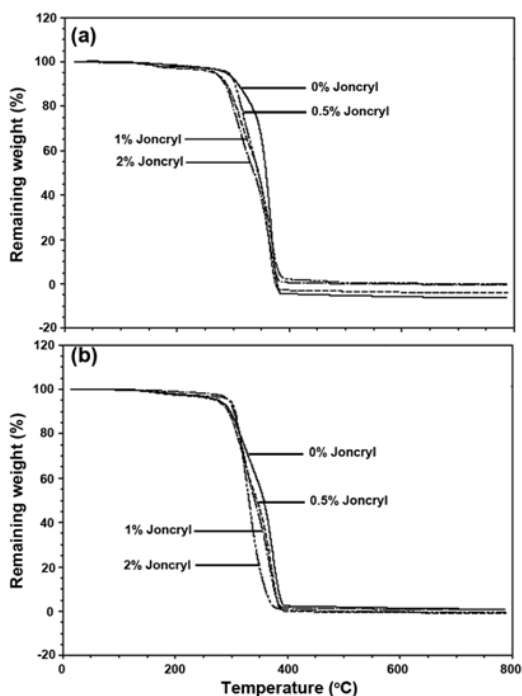


Fig. 2: TG thermograms of chain extended PLL prepared with different Joncryl® ADR 4368 ratios at blending temperatures of (a) 170 °C and (b) 190 °C

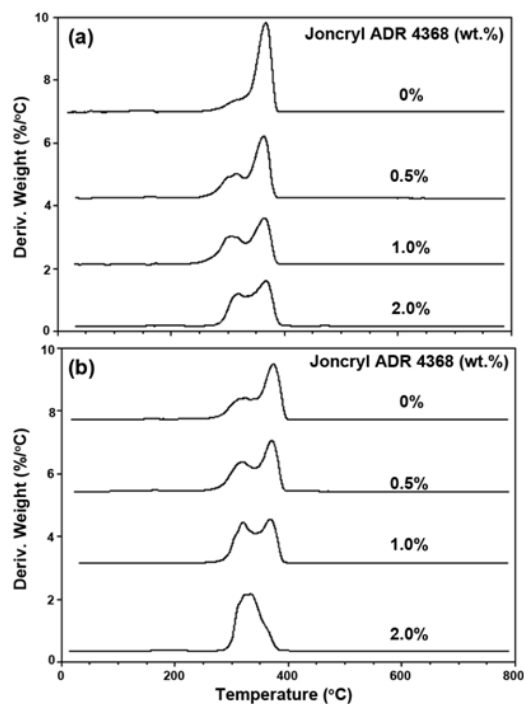


Fig. 3: DTG thermograms of chain extended PLL prepared with different Joncryl® ADR 4368 ratios at blending temperatures of (a) 170 °C and (b) 190 °C

may be explained by the longer branched PLLs from larger Joncryl® ADR 4368 ratio having higher thermal stability than those of the shorter branched PLLs. In addition, the PLL reacted with 2% Joncryl® ADR 4368 at the blending temperature of 190 °C and exhibited only a single lower $T_{d, max}$. This may indicate that the chain extension reaction was complete. The thermal decomposition of the longer linear PLLs then disappeared.

CONCLUSIONS

The addition of Joncryl® ADR 4368 can increase the molecular weight and decrease the MFI of PLLs by forming branched structures. The blending temperature of 190 °C was better than that of 170 °C for the chain extension reaction. The T_g and T_c values of PLLs decreased and X_c increased as the Joncryl® ADR 4368 ratio increased for the blending temperature of 190 °C. The thermal stability behaviors of PLLs depended upon the architectures (linear or branched structures) and lengths (short or long chains) of the PLLs. The shorter linear and branched PLLs showed lower

thermal stability than the longer linear PLL. The investigation indicates that the chain extension reaction reduced the thermal stability of PLL by the formation of branching structures. The influence of chain extension on the thermal properties of the PLL from this work could be used for determining the optimum content of chain extender in actual industrial applications. The effects of chain extension and blending temperature on the mechanical and thermo-mechanical properties of the PLLs will require further investigations.

ACKNOWLEDGEMENTS

This work was supported by the Higher Education Research Promotion and National Research University project of Thailand and the Center of Excellence for Innovation in Chemistry (PERCH-CIC), Office of the Higher Education Commission, Ministry of Education, Thailand. The Office of the National Research Council of Thailand (NRCT) is also acknowledged.

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