

# CROSSLINKING OF STAR-SHAPED POLYLACTIDE AND ITS CURING BEHAVIOR

S. Chang<sup>1</sup>, C. Zeng<sup>1</sup>, J. Ren<sup>1,2\*</sup>

<sup>1</sup> Institute of Nano and Bio-Polymeric Materials, Tongji University, Shanghai, China, <sup>2</sup> Key laboratory of Advanced Civil Engineering Materials, Ministry of Education, Tongji University, Shanghai, China

\* Corresponding author ([renjie6598@163.com](mailto:renjie6598@163.com))

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## 1. INTRODUCTION

Much attention has been paid to biobased polymers used as matrix in natural fiber composites, not only because they are from renewable sources but also have comparable mechanical properties compared to conventional petroleum-based polymers as well as the positive environmental benefits. Poly (lactic acid) (PLA) is a typical biobased polymer that can be synthesized by direct condensation polymerization of lactic acid (LA) and can be completely degraded into CO<sub>2</sub> and H<sub>2</sub>O in natural environment. So far, many kinds of natural fiber/PLA composites have been produced including ramie fiber, jute fiber, flax fiber, kenaf fiber, hemp fiber, bamboo fiber, sugarcane fiber, etc. However, the hardness and brittleness of PLA and its thermal sensitivity at compounding processes limit their further development and practical application.

Crosslinking provides polymers with properties differing from those of thermoplastic biopolymers and new synthetic routes to biodegradable materials are opened [1]. Among the several techniques to produce crosslinked PLA [2-5], the use of a star-shaped oligomer becomes the first priority due to its low melt viscosity, which is a major advantage when producing composites, and its crosslinking density and thermal and mechanical properties can be adjusted by changing the arm length or using a reactive diluent such as styrene, divinylbenzene, etc.

In this study, the effect of star architecture, e.g. different average arm length, on the thermal properties of crosslinked polylactide was studied, and its non-isothermal and isothermal curing was investigated with expectation to obtain accurate prediction and characterization of the curing behavior of the thermoset PLA since the curing kinetics of the resin has a direct impact on process variables. In fact, the synthesis of pentaarmed star-shaped PLA (4sPLA) could also be realized by direct condensation polymerization of LA as confirmed by our laboratory experiments, but the ring opening process gives a

better controlled chemistry which is essential to this work. In order to achieve a relatively high biomass content (>75 wt%), the theoretical average arm length of the star-shaped oligomers are always kept above 5 LA units.

## 2. EXPERIMENTAL

### Materials

*L*-lactide (TJL Biomaterials, China) was purified by twice recrystallization from ethyl acetate solution. Tin 2-ethylhexanoate (SnOct<sub>2</sub>; 95%, Aldrich, USA), hydroquinone (99%, Sinopharm Chemical Reagent, China), pentaerythritol (PENTA; 98%, Sinopharm Chemical Reagent, China), *tert*-butyl peroxybenzoate (TBPB; 98%, Aldrich, USA) and methacrylic anhydride (MAAH; 94%, Sigma-Aldrich, USA) were used as received without further purification.

### Synthesis of 4sPLA

Monomer, appropriate amount of co-initiator and 0.01 wt% of SnOct<sub>2</sub> were added into a glass reactor immersed in an oil bath. The reaction was conducted in bulk at 160 °C for 3 h under nitrogen atmosphere with continuous magnetic stirring. The resulting oligomers were labeled with the theoretical average arm length. For example, 4sPLA polymerized with 10:1 mole ratio of *L*-lactide to PENTA will have a theoretical arm length of 5 LA units and is designated as 4sPLA-5 as presented in Table 1.

### End functionalization of 4sPLA

After the ring opening polymerization, the oil bath temperature was cooled down to 120 °C, then 0.2 wt% hydroquinone and a 20 mol % excess of stoichiometric amount of MAAH were added into the reactor. The end-functionalization modification was carried out at 130 °C for 3 h under nitrogen atmosphere with continuous magnetic stirring. The final product, methacrylated pentaarmed star-shaped PLA (M4sPLA), was purified by distillation under reduced pressure at 140 °C.

### Characterization

<sup>1</sup>H NMR spectra were obtained using a Bruker DMX-500 NMR spectrometer with CDCl<sub>3</sub> as solvent at 25 °C. The intrinsic viscosities were measured by a NCY2 automatic Euler viscometer. Crystalline morphology of the 4sPLAs and M4sPLAs was observed using a Leica DMLP polarized optical microscope (POM). DSC measurements were conducted using a DSC-Q100 thermal analysis system with a constant nitrogen flow of 50 mL/min. The isothermally cured products were characterized by Soxhlet extractions. Samples were extracted with CHCl<sub>3</sub> for 20h. Thermogravimetric analysis (TGA) was performed on a NETZSCH STA449C instrument at a heating rate of 10 °C/min with a constant nitrogen flow of 80 mL/min over a temperature range from room temperature to 600 °C.

## 3. RESULTS AND DISCUSSION

### Characterization of 4sPLAs

As shown in Table 1, four kinds of 4sPLAs with theoretical average arm length of 5, 10, 15 and 20 LA units, respectively, were synthesized by ring opening polymerization of *L*-lactide with PENTA as the co-initiator. An increase in the mole ratio of *L*-lactide/PENTA causes longer arm length as well as increased molecular weight, and the average arm length of the resulting 4sPLA becomes closer to the theoretical value and more OH groups in the co-initiator have participated in the polymerization. This could be attributed to a relatively low initiation activity of OH groups in PENTA due to the steric hindrance effect, but the situation will be much improved when more monomer is added into the reaction system and when the arm length has propagated long enough.

With increasing arm length, the intrinsic viscosity increases gradually. For comparison, we synthesized a linear PLA with the number average molecular weight of about 4000 g/mol by ring opening polymerization of *L*-lactide. The linear PLA exhibits higher intrinsic viscosity ( $[\eta]_{\text{linear}}=0.172$ ) than that of 4sPLA-15 ( $[\eta]_{\text{star}}=0.127$ ) at similar molecular weight. This is ascribed to the more severe coiling character of the linear polymer [6]. Generally, there is a useful parameter  $g'$  to give a picture of branched polymers:

$$g' = [\eta]_{\text{star}} / [\eta]_{\text{linear}} \quad (1)$$

The experiment data calculate the value of  $g'$  to be 0.74. It agrees well with Douglas's empirical model expressed as follows [7]:

$$g' = \left( \frac{3f-2}{f^2} \right)^{0.58} \frac{1-0.276-0.015(f-1)}{1-0.276} \quad (2)$$

where  $f$  is the number of arms.

A polarized optical microscope was used to observe the crystalline morphology of these 4sPLAs. From Fig.1, we can see that 4sPLA-10, 4sPLA-15 and 4sPLA-20 showed a spherulitic morphology with apparent Maltese cross patterns. But the morphology became irregular and the diameter of the spherulites along with the isothermal crystallization rate was much decreased when decreasing the arm length. For 4sPLA-5, spherulite growth even cannot be observed. Possible reason is that the shorter PLA arm length and constrained geometry restricted regular rearrangement and molecular chain packing.

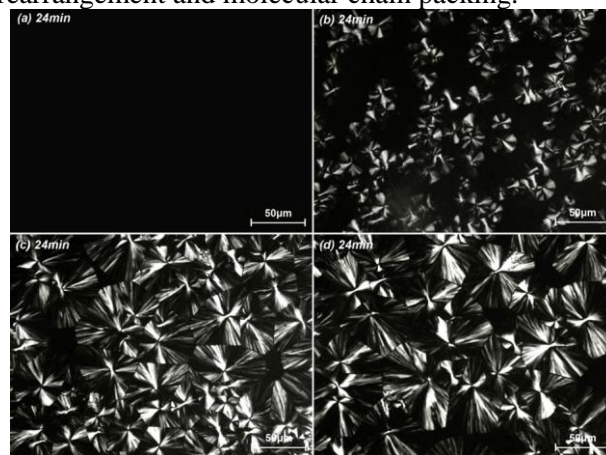


Fig.1. POM micrographs of (a) 4sPLA-5, (b) 4sPLA-10, (c) 4sPLA-15 and (d) 4sPLA-20 at an isothermal crystallization temperature of 100 °C.

### Characterization of M4sPLAs

End functionalization introduces C=C to the star-shaped oligomers through esterification reaction of MAAH with the terminal OH groups of 4sPLA, thus its resonances at 4.35 and 3.09 ppm are dramatically weakened (Fig. 2). A comparison of the integration of chain methane protons (d, 5.18 ppm) and terminal methane protons (d', 4.36 ppm) before and after the modification could provide us the degree of substitution (DS) of terminal OH groups in PLA arms by the methacrylate group. They are 82.6%, 85.1%, 86.3% and 88.5% for M4sPLA-5, M4sPLA-10,

Table 1. Properties of 4sPLA with different average arm length.

| Sample   | [L-lactide]/<br>[PENTA] | Theoretical                   | <sup>1</sup> H NMR                   |                        |                                | Viscometer    | Crystallization rate       | DSC                                 |
|----------|-------------------------|-------------------------------|--------------------------------------|------------------------|--------------------------------|---------------|----------------------------|-------------------------------------|
|          |                         | M <sub>n, th</sub><br>(g/mol) | L <sub>LA</sub> <sup>a</sup><br>(LA) | N <sup>b</sup><br>(OH) | M <sub>n, NMR</sub><br>(g/mol) | [η]<br>(dl/g) | G <sup>c</sup><br>(μm/min) | T <sub>g</sub> <sup>d</sup><br>(°C) |
| 4sPLA-5  | 10:1                    | 1570                          | 4.03                                 | 3.65                   | 1190                           | 0.069         | --                         | 21                                  |
| 4sPLA-10 | 20:1                    | 3010                          | 9.33                                 | 3.71                   | 2620                           | 0.099         | 1.19                       | 46                                  |
| 4sPLA-15 | 30:1                    | 4450                          | 14.50                                | 3.94                   | 4240                           | 0.127         | 3.15                       | 50                                  |
| 4sPLA-20 | 40:1                    | 5890                          | 19.76                                | 3.96                   | 5770                           | 0.157         | 3.21                       | 51                                  |

<sup>a</sup> Average arm length of 4sPLA.<sup>b</sup> The number of initiating OH groups in PENTA (Bruker DMX-500 NMR spectrometer).<sup>c</sup> Determined by POM at an isothermal crystallization temperature of 100 °C.<sup>d</sup> Determined in the second heating run at a heating rate of 10 °C/min.

M4sPLA-15 and M4sPLA-20, respectively. Considering the presence of free OH groups in PENTA, actual DS for these M4sPLAs will be a little higher than that from the calculation. Besides, though purification process was conducted, we still can find a residue of methacrylic acid (MAA) in the functionalized product, while the characteristic resonances of MAAH are negligible. In addition, spherulitic morphology with Maltese cross patterns still can be observed by POM for M4sPLA-15 and M4sPLA-20 at an isothermal crystallization temperature of 100 °C, but the morphology became irregular and indistinct and the isothermal crystallization rate (2.00 and 2.45 μm/min for

M4sPLA-15 and M4sPLA-20 respectively) was much decreased compared to that of 4sPLA-15 and 4sPLA-20 (Fig. 3). The results can be attributed to the presence of terminal methyl methacrylate in the star-shaped oligomers interfering with the natural growth of the spherulite.

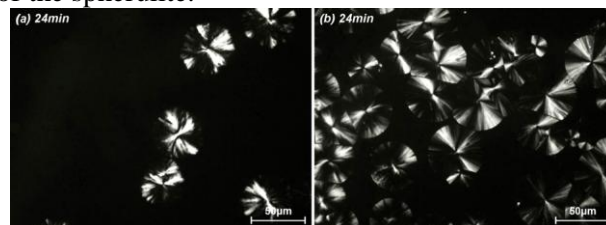


Fig.3. POM micrographs of (a) M4sPLA-15 and (b) M4sPLA-20 at an isothermal crystallization temperature of 100 °C.

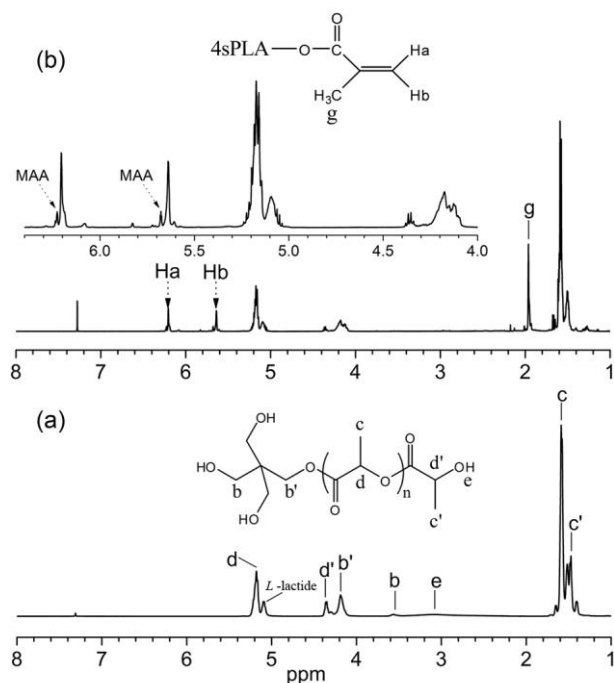


Fig.2. <sup>1</sup>H NMR spectra of (a) 4sPLA-5 and (b) M4sPLA-5.

### Curing behavior of M4sPLAs

In order to characterize the curing behavior of M4sPLA, a total amount of 1.0 wt% of TBPB was blended into the oligomer with CHCl<sub>3</sub> as solvent at room temperature to avoid premature curing. The solution was then kept at 30 °C in vacuum for a week to eliminate CHCl<sub>3</sub>. For isothermal curing, samples were heated to the setting temperature at a heating rate of 200 °C/min.

Fig. 4 shows the plots of curing rate dQ/dt versus time obtained from DSC measurements. All curves are asymmetrical bell-shaped with right-tails on the side of higher curing times. At higher temperatures, the curing times of M4sPLA are lower and the reaction rates as well as the heat release during the isothermal curing are higher. For M4sPLA-5, we even can't obtain a complete heat flow curve at 125 °C as its curing reaction almost finished during the stabilization of the calorimeter, while for M4sPLA-20, we have to change the isothermal curing temperature to 110-130 °C as the reaction heat



can hardly be detected at 105 °C. This is because the melt viscosity of M4sPLAs is lower at higher temperatures and with shorter arm length so as to facilitate the diffusion of the reactive groups (C=C) and a higher degree of conversion of the curing reaction could be expected. However, at the same curing temperatures, the total isothermal curing reaction heat and the reaction rate also decrease with increasing arm length. Taking into account of the reduced molecular mobility due to chain entanglement and decreasing content of C=C in M4sPLA with increasing arm length, these phenomena are not difficult to understand.

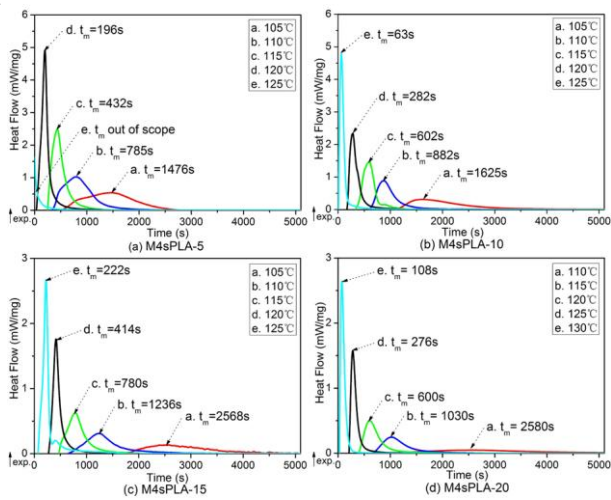


Fig. 4. Isothermal curing of (a) M4sPLA-5, (b) M4sPLA-10, (c) M4sPLA-15 and (d) M4sPLA-20 at various temperatures.

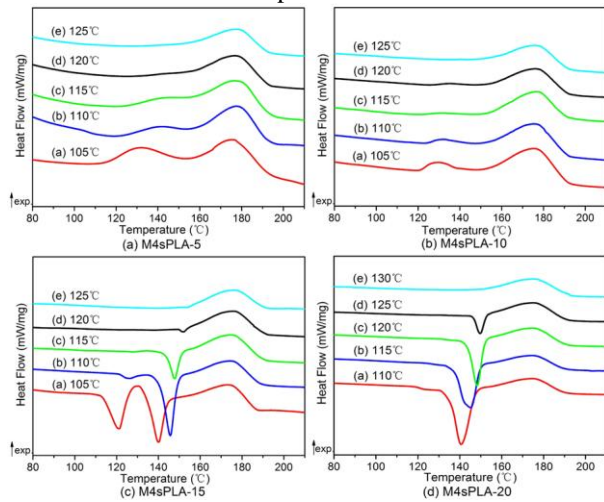


Fig. 5. Post curing of (a) M4sPLA-5, (b) M4sPLA-10, (c) M4sPLA-15 and (d) M4sPLA-20 after the isothermal curing at various temperatures.

After the isothermal curing, we performed immediately a dynamic scan at a heating rate of 10 °C/min on each

sample (Fig. 5). The existence of a residual heat on the heat flow curves indicates that at the experimental conditions the curing reactions are not completed. This may be because the movement of the existing reactive groups in the reaction medium is restricted in the partly cured network [8]. Once being heated to a higher temperature, these groups become movable and reactive again.

For M4sPLA-5 and M4sPLA-10, the residue exotherm occurred mainly at about 175 °C with a side peak at around 130 °C corresponding to the thermal homopolymerization of residual MAA and copolymerization of M4sPLA with MAA or the bulk polymerization of M4sPLA, respectively. Because Young [9] has found that the reaction rate of the latter is faster than that of the former. Interestingly, a melting endothermic peak was observed in the dynamic scan of M4sPLA-15 together with M4sPLA-20 and the exothermic peak at around 130 °C could hardly be seen. These endothermic peaks shifted to higher temperatures and the total absorbed melting heat decreased, even disappeared, when increasing the isothermal curing temperature. Note that longer arm length incorporates less methacrylates and produces less cross-link points. It is not surprise that though isothermal curing was conducted, M4sPLAs with relatively long arm length still could melt due to incomplete cure and low crosslinking density. But the situation will be improved when the isothermal curing temperature is increased. Besides, all of these endothermic or exothermic peaks disappeared when a third heating run was performed after the dynamic scan indicating a high degree of conversion of the curing reaction was obtained after the post curing.

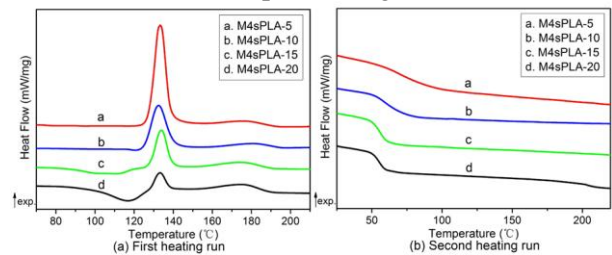


Fig. 6. Non-isothermal curing of M4sPLAs.

Apart from isothermal curing, non-isothermal curing was also conducted at a heating rate of 10 °C/min to measure the total heat of the curing reaction as shown in Fig.6 and relevant data are listed in Table 2. Similar with the post curing (Fig. 5), the TBPB-initiated reaction shows a main exothermic

peak at about 135 °C and a residual heat at around 175 °C. After the first heating run, all samples are fully cured as no peaks can be observed in Figure 6b. Crosslinking brings about a significant increase of  $T_g$ , and it increases along with decreasing arm length due to a higher crosslinking density.

Table 2. Characteristic data of non-isothermal curing.

| Sample    | $\Delta Q_{dyn}^a$<br>(mJ/mg) | $T_g^b$<br>(°C) | Extraction gel<br>content <sup>c</sup> (wt%) |
|-----------|-------------------------------|-----------------|--|
| M4sPLA-5  | 106.2                         | 75              | 99.0   |
| M4sPLA-10 | 74.8                          | 66              | 98.7   |
| M4sPLA-15 | 56.1                          | 54              | 96.3   |
| M4sPLA-20 | 42.2                          | 54              | 91.5   |

<sup>a</sup> Calculated from the first heating run of the non-isothermal curing by integration of the heat flow curves.

<sup>b</sup> Determined by the second heating run of the non-isothermal curing.

<sup>c</sup> Determined by Soxhlet extraction.

An integration of the heat exotherm in the isothermal curing (Fig. 4) divided by the total reaction heat obtained from the non-isothermal curing ( $\Delta Q_{dyn}$ ) provides us the degrees of conversion of the curing reactions after isothermal curing (Fig. 7). It can be seen that the higher the isothermal curing temperature, the higher the degree of conversion of the reaction. At the same curing temperature, M4sPLA with shorter arm length shows a higher degree of conversion (Figure 7). The highest value (80.1%) is obtained for M4sPLA-5 at 120 °C, and it is only 34.1% for M4sPLA-20 at 110 °C. However, when post curing was performed, the degrees of conversion are significantly increased (Table 2). Therefore, post curing is essential in practical applications.

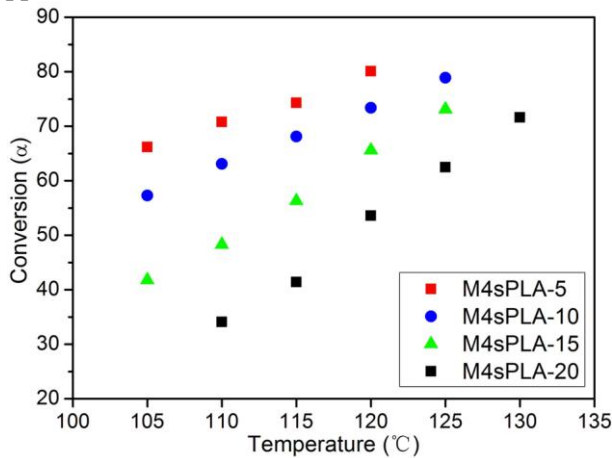


Fig. 7. Maximum degrees of conversion of the curing reaction obtained after isothermal curing.

### Thermal stability of crosslinked M4sPLAs

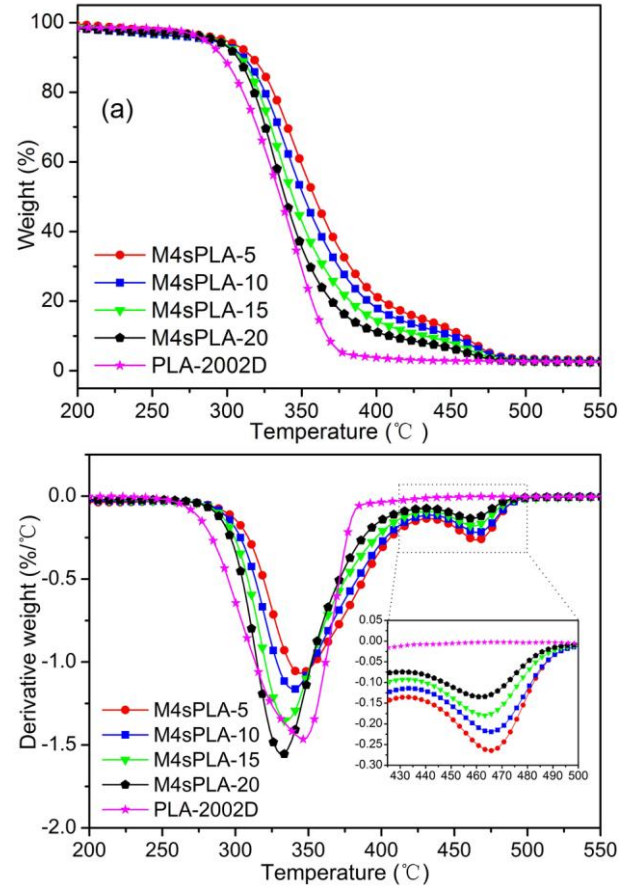


Fig. 8. TGA results of crosslinked M4sPLAs.

The crosslinked M4sPLAs were finally characterized by TGA (Fig. 8) and related data are listed in Table 3. Here,  $T_{10}$  ( $T_{50}$ ) is defined as the temperature when 10% (50%) weight loss occurs and  $T_{max}$ , the temperature at maximum weight loss rate. All of the samples are relatively stable up to 300 °C. The thermal degradation of all cured M4sPLAs experience a two-stage weight loss corresponding to the decomposition of PLA network and homopolymer of MAA, respectively, as confirmed by DSC measurements. For comparison, commercial PLA (2002D, Melt index=5-7g/min (210 °C/2.16kg), extrusion/thermoforming grade) from NatureWorks was used in this work. The introduction of crosslinking improves the thermal stability of PLA with an increase of both onset thermal degradation temperature and complete degradation temperature. Especially, these values have a tendency to increase with decreasing arm length of the star-shaped oligomers indicating a higher crosslinking density will play a more important role on improving the heat

resistance of PLA. The cured M4sPLA-5 has the most superior thermal stability since its  $T_{10}$  and  $T_{50}$  are about 20 °C higher than that of the PLA-2002D.

Table 3. Characteristic data of TGA results.

| Sample    | $T_{10}$ (°C) | $T_{50}$ (°C) | $T_{max}$ (°C) |
|-----------|---------------|---------------|----------------|
| M4sPLA-5  | 316           | 358           | 343            |
| M4sPLA-10 | 311           | 351           | 340            |
| M4sPLA-15 | 309           | 343           | 333            |
| M4sPLA-20 | 309           | 338           | 331            |
| PLA-2002D | 298           | 336           | 346            |

#### 4. CONCLUSIONS

Pentaarmed star-shaped polylactides with different average arm length were successfully synthesized by ring opening polymerization of *L*-lactide with pentaerythritol as the co-initiator. An increase in the feeding mole ratio of *L*-lactide/PENTA causes longer arm length and the average arm length of the resulting 4sPLA becomes closer to the theoretical value and more OH groups in the co-initiator have participated in the polymerization. The intrinsic viscosity, isothermal crystallization rate and glass transition temperature of these oligomers increase with increasing arm length.

Methacrylated 4sPLA was prepared by end functionalization of 4sPLA with MAAH. Details of the curing behavior of M4sPLAs were obtained and elucidated through the utilization of DSC in the presence of the free radical initiator TBPB. The thermal stability of the cured products was investigated by thermogravimetric analysis. Experimental results indicate that the crosslinking density and thermal stability of the cured samples increase with decreasing arm length of the oligomers. Due to better chain mobility, M4sPLA with shorter arm length shows a faster curing rate. The degree of conversion of the curing reaction of M4sPLA-5 can reach 80.1% at 120 °C and 99.0% after post curing and the final cured resin has a glass transition temperature of 75 °C, while they are only 53.6%, 91.5% and 54 °C for M4sPLA-20, respectively.

Compared to conventional thermoplastic PLA, the star-shaped oligomer has a low melt viscosity and its crosslinking density can be adjusted by adjusting the arm length or using a reactive diluent such as styrene, divinylbenzene, etc., thus is fit for composite production.

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