Final Report

Development of Star-shaped Copolymers for Toughening and Optical Transparency of Polylactic Acid

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1. Abstract

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Project Title : Development of Star-shaped Copolymers for Toughening and Optical Transparency of Polylactic Acid

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Abstract:

Considering enhancement toughness of PLA including retaining its optical transparency, star-shaped copolyester was investigated. The star-shaped polycaprolactone-co-polylactide (stPCL-co-PLA) with a different number of arms was synthesized using star-shaped initiators. Number of arms was independent to thermal properties and crystallinity of stPCL-co-PLA. However, number of arms of stPCL-coPLA affected to crystallinity of PLA in the blend of PLA/stPCL-co-PLA. The glass transition temperature of the blend was decreased as resulted of stPCL-so-PLA plasticizers. The stPCL-co-PLA with 2-arms and 4-arms provided increasing of crystallinity of PLA in the blends but 3-arms resulted in decreasing of crystallinity due to their steric hindrance. Moreover, the toughness of PLA was enhanced with mixed stPCL-co-PLA up to 3 phr; for example, 4-arms of stPCL-co-PLA provided increasing of toughness as 61% compared to neat PLA. The results revealed that an improvement in toughness may be obtained from shear-yielding deformation which is provided from rubber-toughened amorphous plastics accompanied with extensive orientation of the semicrystalline portion. Moreover, it was found that at 3 phr of stPCL-co-PLA, the compound retained its optical transparency comparable to neat PLA.

Keywords : polycaprolactone; polylactide; star-shaped polyester; toughness; optical transparency

บทคัดย่อ

งานวิจัยเพื่อปรับปรุงสมบัติความแข็งเหนียวของพอลิแลคติกแอซิด (PLA) โดยยังคงความใสของ PLA ไว้ได้ด้วยการใช้โคพอลิเอสเทอร์รูปร่างคล้ายดาว การสังเคราะห์โคพอลิเอสเทอร์ของพอลิคาร์โปรแลคโทนกับแลคไทด์ (stPCL-co-PLA) ให้มีจำนวนแขนต่างๆกัน สามารถเตรียมได้โดยการใช้ตัวริเริ่มปฏิกิริยาที่มีรูปร่างคล้ายดาวและมีจำนวนแขนที่ไม่เท่ากัน ผลการวิจัยแสดงให้เห็นว่าสมบัติทางความร้อนและความสามารถในการเกิดผลึกของ stPCL-co-PLA ไม่ขึ้นกับจำนวนแขนของโคพอลิเมอร์ แต่เมื่อนำไปผสมกับ PLA จะพบว่า stPCL-co-PLA มีสมบัติเป็นพลาสติไซส์เซอร์ โดยสามารถลดอุณหภูมิเปลี่ยนสภาวะคล้ายแก้วของ PLA ลง นอกจากนั้น stPCL-co-PLA ที่มีจำนวนแขนเท่ากับ 2 และ 4 มีผลต่อความสามารถในการเกิดผลึกของ PLA ในของผสมระหว่าง PLA และ stPCL-co-PLA เพิ่มขึ้น แต่กรณีของ 3 แขนนั้น พบว่าความสามารถในการเกิดผลึกลดลง จากการผสม stPCL-co-PLA ร่วมกับ PLA ความเหนียวของ PLA เพิ่มขึ้น เช่น กรณีผสม 4 แขน stPCL-co-PLA สามารถเพิ่มความเหนียวของ PLA ได้ 61%เมื่อเทียบกับ PLA เปล่า จากการวิเคราะห์พบว่าการเปลี่ยนรูปของขผงผสม คาดว่าจะเกิดในรูปของ shear-yielding ผ่านส่วนที่เป็นยางได้แก่ stPCL-co-PLA และส่วนที่เกิดผลึกขึ้น ส่งผลให้ความเหนียวของ PLA สูงขึ้น นอกจากนี้ความใส โปร่งแสงของ PLA ยังคงอยู่ เมื่อผสมกับ stPCL-co-PLA ที่ 3 phr

คำสำคัญ: พอลิคาร์โปรแลคโทน; พอลิแลคไทด์; โคพอลิเอสเทอร์รูปร่างคล้ายดาว; ความแข็งเหนียว; โปร่งใส

2. Executive summary

This research investigated on effect of polycaprolactone-co-polylactide copolyesters' arms to toughening transparent PLA. Although there have been several reports concerning the synthesis of star-shaped copolymers with 3-, 4-, 6- and multi- arms, they have investigated effect of a star-shaped structure on the polymerization of high molecular weight PLA, crystallinity, and thermal properties. They did not investigate using these copolymers as an impact modifier or toughening agent. Here, the number of arms of copolyesters were different from star-initiators. Not only chemical structure and thermal properties of stPCL-co-PLA were investigated, but also the blend of PLA/stPCL-co-PLA were investigated including effect of number of arms. The results showed that Number of arms was independent to thermal properties and crystallinity of stPCL-co-PLA. However, number of arms of stPCL-co-PLA affected to crystallinity of PLA in the blend of PLA/stPCL-co-PLA. It was found that stPCL-co-PLA could plasticized PLA by lowering its glass transition temperature (T_g). The 2-arms and 4-arms of stPCL-co-PLA provided increasing of crystallinity of PLA in the blends. In contrast, 3-arms stPCL-co-PLA provided decreasing. These resulted to toughness of PLA. For instance, 4-arms of stPCL-co-PLA could enhance toughness of PLA to 61% comparing to neat PLA when it was mixed at 3 phr. The results revealed that an improvement in toughness may be obtained from shear-yielding deformation which is provided from rubber-toughened amorphous plastics accompanied with extensive orientation of the semicrystalline portion. Moreover, the blend of PLA/stPCL-co-PLA showed optical transparency comparable to PLA.

This research finds star-shaped copolyester of polycaprolactone-co-lactide could enhance toughness of PLA including retain its optical transparency. The number of arms affect to crystallinity of PLA which related to deformation of PLA from brittle to shear-yielding deformation.

3. Objective:

In this work, I investigated effect of polycaprolactone-co-polylactide (stPCL-co-PLA) copolyester's arms to toughening transparent PLA.

4. Research methodology

4.1. Materials

ε-Caprolactone (CL), star-shaped initiators: 4 arms of pentaerythritol, 3 arms of 1,1,1-tris (hydroxymethyl) propane, and 2 arms of 2,2-diethyl-1,3-propanediol were purchased from Merck Millipore, Germany. Tin (II) 2-ethylhexanoate (SnOct2) was purchased from Sigma-Aldrich, USA. L-lactide (LA) was purchased from Asst. Prof. Winita Punyodom's Laboratory, Department of Chemistry, Faculty of Science, Chiang Mai University, Thailand. PLA pellets (IngeoTM Biopolymer 2003D) were a gift from PTT Public Company Limited, Thailand. HPLC grade chloroform, analytical-grade chloroform, and analytical-grade methanol were purchased from Lab-scan, Thailand.

4.2 Synthesis of star-shaped poly(ε-caprolactone) (stPCL)

The st4PCL200 was synthesized by ring-opening polymerization (ROP) of CL with a molar ratio between CL and Pent of 200:1 and 2M of SnOct2 was used as the catalyst according to our previous report with a molar ratio of 1,000 compared to the CL monomer. The reaction was carried out overnight in an oil bath at 160°C, and stopped by quenching in an ice bath. The crude product was dissolved in chloroform and precipitated in cold methanol. The product (st4PCL200) was filtered and dried under vacuum. The st3PCL and st2PCL were synthesized using 1,1,1-tris (hydroxymethyl) propane and 2,2-diethyl-1,3-propanediol as the respective initiators.

4.3 Star-shaped copolymers stPCL-co-PLA by using stPCL as macroinitiator

Polymerization was carried out in bulk by ROP of LA. The molar ratio between LA and st4PCL was 100:1 and 2M of SnOct2 was used as the catalyst with a molar ratio of 1:1000 compared to the LA monomer. The reaction was carried out overnight in an oil bath at 160°C and stopped by quenching in an ice bath. Crude product was dissolved in chloroform and precipitated in cold methanol. The product (st4PCL-co-PLA) was filtered and dried under vacuum. The st3PCL-co-PLA and st2PCL-co-PLA were synthesized using same procedure with st3PCL and st2PCL as the respective macroinitiators.

4.4 Compounding of PLA/stPCL-co-PLA

Prior to melt blending, the PLA pellets were dried for 1 day to remove moisture. A Brabender mixer was used to melt mix the stPCL-co-PLA at 1, 3, and 5 phr with PLA pellets at 190ºC and a speed of 45 revolutions min-1 for 10 min. For tensile testing, the dumbbell-shaped specimen was prepared by compression molding. The sample size followed ASTM D1822 type L.

4.5 Measurements

Proton and carbon nuclear magnetic resonance (NMR) spectra were obtained using a Brüker

AVANCE 400 spectrometer, with chloroform-d as the corresponding solvent. The number-average molecular weight (Mn) of the obtained polymers was measured using size-exclusion chromatography (SEC) with two Waters Styragel columns (HR3 and HR4, each 300 mm × 7.8 mm, providing a molecular mass range of 5×102 – 6×105 g/mol) equipped with a Waters 2414 refractive index detector. The eluent was chloroform with a flow rate of 1.0 mL/min at an operating temperature of 40°C and a sample injection volume of 75 μL. Differential scanning calorimetry (DSC) was conducted using Mettler-Toledo equipment (Schwerzenbach) where nitrogen gas was purged into the DSC cell at a flow rate of 50 mL/min. Measurements were carried out by using 5–7 mg of samples in a sealed aluminum pan. The samples were first heated from -70ºC to 170ºC at a heating rate of 10ºC/min and were annealed for 10 min at 170ºC to erase any previous thermal history, followed by cooling to -70ºC at a rate of 10ºC/min. The second heating was subsequently made to 170ºC at a heating rate of 1ºC/min. The glass-transition temperature (T_g) was taken as the temperature at the midpoint of the corresponding heat-capacity jump in the second heating run. The degrees of crystallinity (χ_c) of PLA in the blends of PLA/stPCL-co-PLA were calculated following equation:

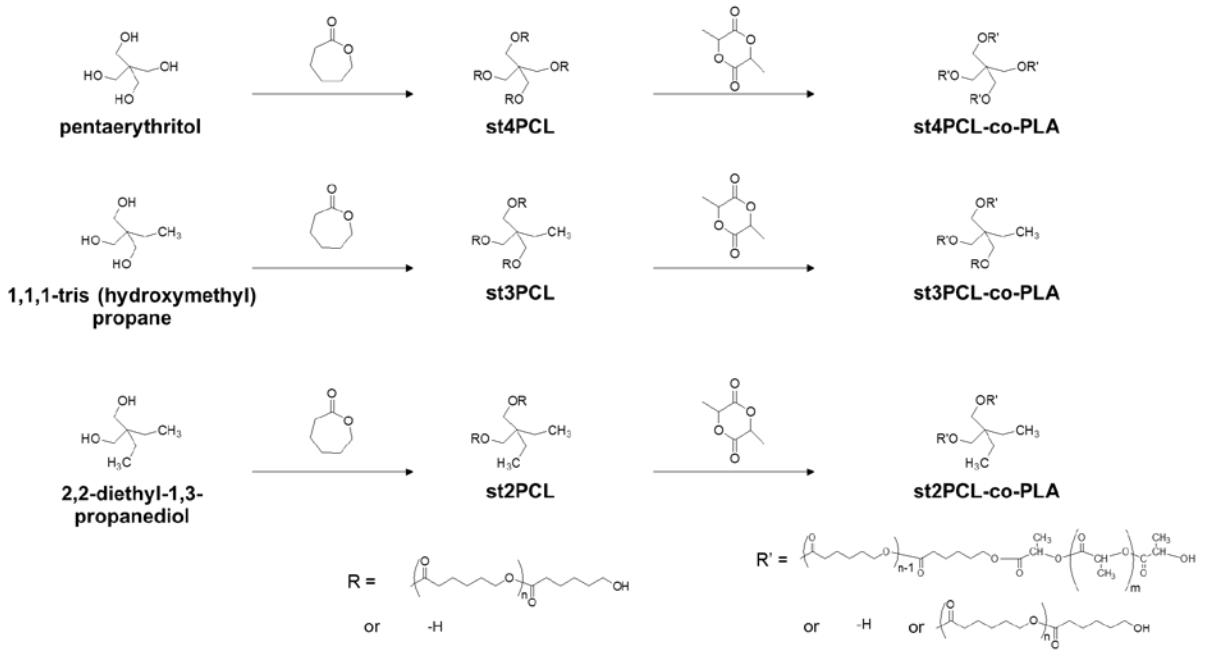
$$\chi_c = (\Delta H_m / \Delta H^0_m) \times 100$$

where ΔH^0_m of PLA is 93.6 J/g. The surface of tensile testing specimens was observed using a JEOL (JSM-5410LV) scanning electron microscope (SEM). The transparency of compound specimens was measured at a thickness of 0.4 mm using a PerkinElmer Lambda 650 unit with a scan wavelength from 400 to 750 nm. The tensile properties of the compound specimens were tested using a 5965 Universal Testing Machine (Instron).

5. Results and Discussion

5.1. Synthesis of star-shaped polycaprolactone (stPCL)

ROP of CL was carried out with different numbers of arm initiators, namely 4 arms from pentaerythritol, 3 arms from 1,1,1-tris (hydroxymethyl) propane, and 2 arms from 2,2-diethyl-1,3-propanediol (Scheme 1).



Scheme 1 Synthesis of stPCL and stPCL-co-PLA

Table 1 Results of stPCL with different numbers of arm initiators

stPCL	Initiator (In)	[CL]:[In]	%yield	Mn (g/mol) (PdI)	DPn*
st4PCL200	pentaerythritol	200:1	78	22,840 (1.66)	34
st3PCL200	1,1,1-tris (hydroxymethyl) propane	200:1	81	20,000 (1.56)	32
st2PCL200	2,2-diethyl-1,3-propanediol	200:1	76	14,480 (1.47)	30

* calculated from ^{1}H NMR

^{1}H NMR was applied to confirm the chemical structure of stPCL (Figure 1). All samples showed characteristic peaks of polycaprolactone such as 3.87-4.25 ppm (-CH_2-, **4**), 2.12-2.46 ppm (-CH_2-, **3**), 1.67 ppm (-CH_2-, **2** and **2'**), and 1.37 ppm (-CH_2-, **1**). The hydroxyl in the terminated chain was confirmed by the methylene proton at 3.63 ppm (-CH_2-,**4'**). In addition, the degree of polymerization (DPn) was calculated from the ratio of the integrated peak of **4** and **4'** and the results are reported in Table 1. The ^{13}C NMR spectra also confirmed the hydroxyl termination of stPCL by the existence of methine (**4'**) at 64.57 ppm (Figure 1) which corresponded to methine at the chain end adjacent to

the hydroxyl-terminated group. However, the ^{1}H NMR spectra (δ 3.5 ppm, -C**H**$_2$-OH) indicated that not all hydroxyls of initiators were converted to the PCL arms.[14]

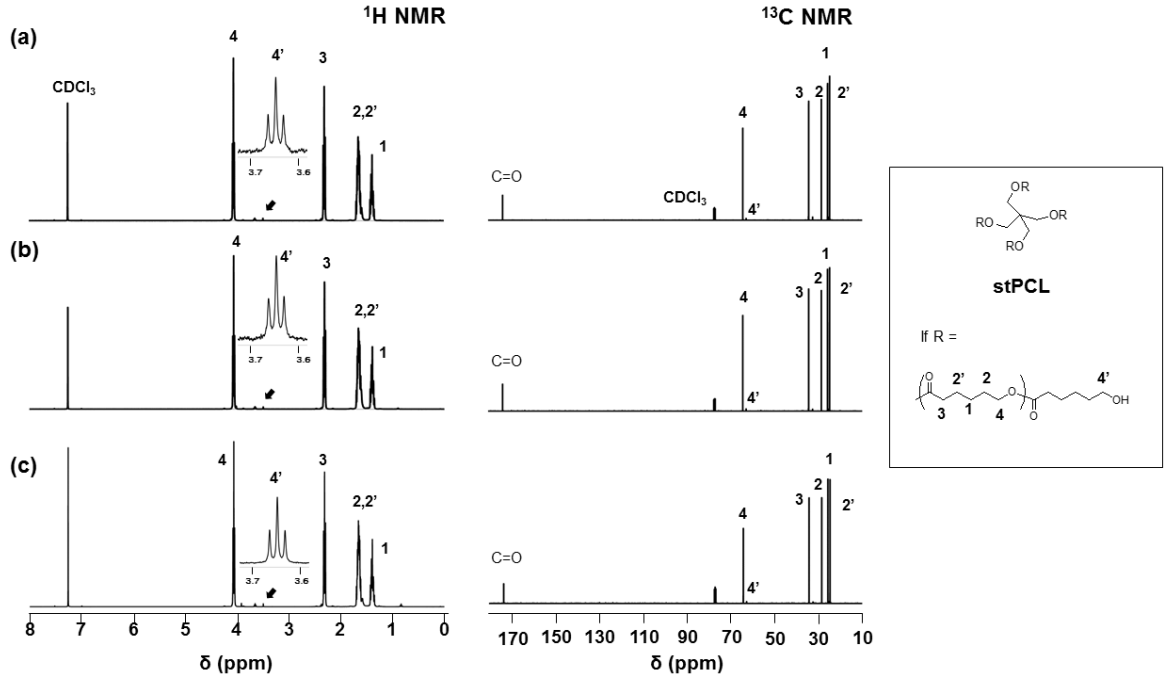


Figure 1. ^{1}H NMR and ^{13}C NMR spectra of stPCL: (a) st4PCL, (b) st3PCL, and (c) st2PCL in $CDCl_3$.

5.2 Ring-opening polymerization of LA via stPCL marcoinitiator

The stPCL with the hydroxyl-terminated group was used as a macroinitiator to open the ring of LA using $SnOct_2$ as a catalyst. Table 2 shows the molecular weight and degree of polymerization of stPCL-co-PLA. On the basis of the SEC data, the ring opening of LA by the hydroxyl-terminated stPCL caused some chain breakage of PCL arms.

Table 2 Results of stPCL-co-PLA with stPCL as macroinitiator

stPCL-co-PLA	[LA]:[stPCL]	%yield	Mn (g/mol) (PdI)	DPn* of PLA
st4PCL200-co-PLA100	100:1	68	17,450 (1.5)	7
st3PCL200-co-PLA100	100:1	65	14,560 (1.3)	18
st2PCL200-co-PLA100	100:1	73	11,500 (1.3)	27

*calculated from ^{1}H NMR

^{1}H NMR showed characteristic peaks of PLA (Figure 2) such as 5.0-5.2 ppm (-CH-, **5**) and 1.46-1.5 ppm (-CH_3-, **6**) Furthermore, DPn of the PLA segment was calculated from the integral ratio of the methine proton (-CH-, **5**) and the methylene proton at the chain end of PCL (-CH_2-, **4"**) (Table 2).

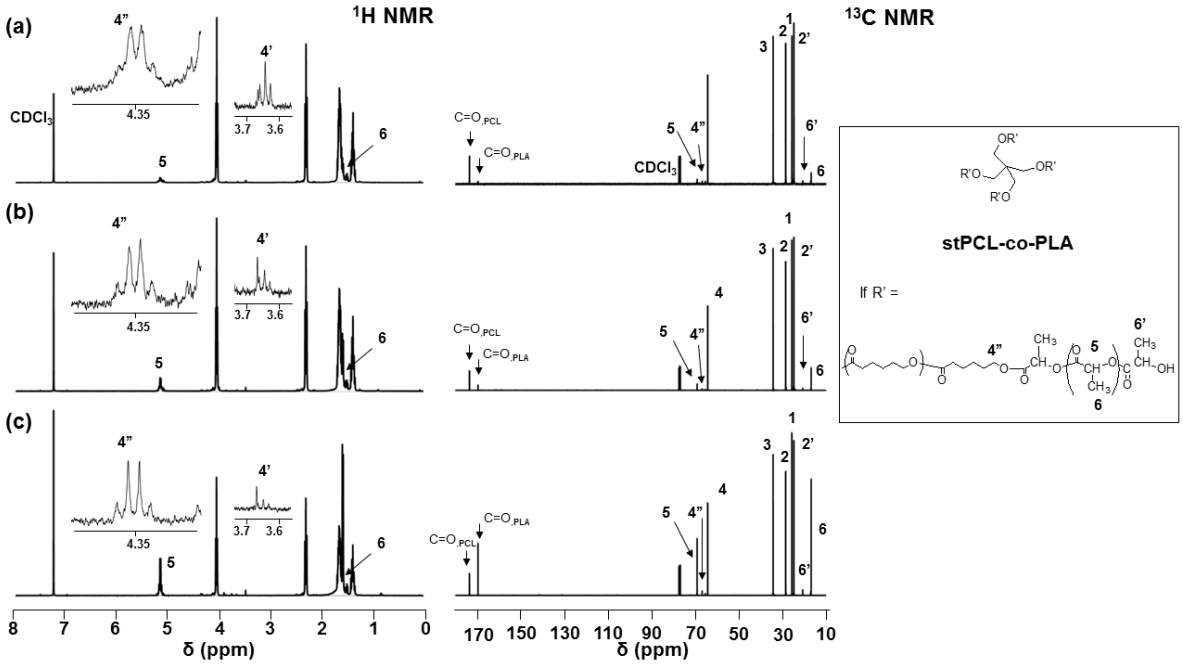


Figure 2. ^{1}H NMR and ^{13}C NMR spectra of stPCL-co-PLA (a) st4PCL-co-PLA, (b) st3PCL-co-PLA, and (c) st2PCL-co-PLA in $CDCl_3$.

The success in opening the ring of lactide by the macroinitiator stPCL was confirmed by the peak shift which belonged to the adjacent methylene proton to the lactide segment. The peak shifted from 3.87-4.25 (**4**) to 4.35 (**4"**) ppm. However, the methylene proton at the chain end of PCL (-CH_2-, **4'**) still remained. This implied that not all hydroxyl-terminated groups on stPCL could open the ring of the lactide. This might have been due to the high viscosity of reaction and the high molecular weight of the macroinitiators. In addition, ^{13}C NMR confirmed the ring opening of the lactide by the peak at 66.8 ppm (-CH_2-, **4"**) corresponding to the methine carbon that linked to the PLA.

5.3 Thermal properties of stPCL and stPCL-co-PLA

The crystallization temperature (T_c) was obtained from the cooling run and the melting temperature (T_m) and the degree of crystallinity (χ_c) were obtained from the second heating run. The results are listed in Table 3 and the DSC thermogram of T_m is shown in Figure 3. The T_m of stPCL showed a single peak in the range 52-54ºC for all samples. In the case of stPCL, the results showed that number of arms was independent of T_c, T_m, and χ_c with comparable molecular weights. In contrast, 6-arms of stPCL had an approximate similar molecular weight that provided lower values for T_c, T_m,

and χ_c.[12] This might have been due to the packing structure of stPCL with 6-arms being more complicated than with lower numbers of arms. In this study, the T_g value of stPCL was too low to be detected in the temperature range.

Table 3 Melting and crystallization behavior of PCL in stPCL and stPCL-co-PLA

Sample	T_c (°C)	T_m (°C)	ΔH_m (J/g)	χ_c (%)
st4PCL	31.0	54.2	76.39	56.1
st3PCL	29.1	52.3	80.50	59.1
st2PCL	30.5	52.6	72.65	53.4
st4PCL-co-PLA	19.5	44.5, 49.4	58.92	43.3
st3PCL-co-PLA	14.3	42.7, 48.4	54.70	40.2
st2PCL-co-PLA	20.8	45.0, 50.9	67.32	49.5

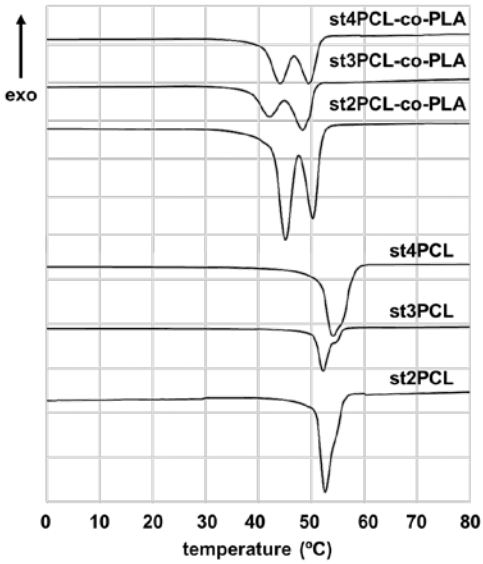


Figure 3. DSC thermogram of stPCL and stPCL-co-PLA.

For stPCL-co-PLA, the T_c shifted to a lower temperature. This implied a restriction of the PLA outer shell due to the mobility of the PCL core. This was also supported by the decrease in T_m and χ_c. The value for T_m presented as a double melting peak (Figure 3). This phenomenon referred to the presence of two different crystalline phases. The lower melting peak is attributed to the melting of the imperfect crystalline structure and the higher melting peak is attributed to the melting of the perfect crystalline structure based on lamellae thicknesses.[15] While thermal transitions of PCL could

be detected in stPCL-co-PLA, it was difficult to detect PLA as the PLA block had a very short chain length.

5.4 Compounding of PLA with stPCL-co-PLA

Thermal properties of the blends

Neat PLA had a T_g at 61°C and T_m at 151°C (Figure 4). After compounding with stPCL-co-PLA at 1, 3, and 5 phr, a change in the glass transition behavior of the blends could be observed. The T_g of the blends at 1 phr showed a shift to a lower temperature (ca. 55°C), presumably because the stPCL-co-PLA enhanced the flexibility of the PLA matrix or increased the free volume of the compound from the star-shaped architecture of stPCL-co-PLA. Therefore, the star-shaped structure of PCL and PLA copolymers responded to plasticize PLA.

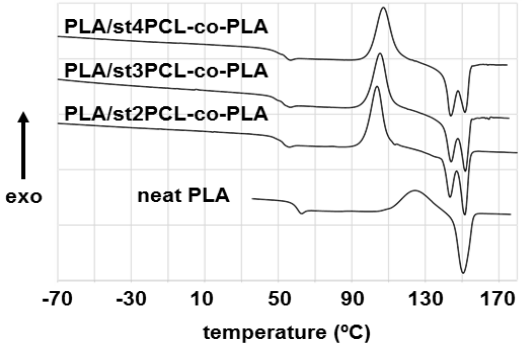


Figure 4. Second heating scan of PLA and the blends of PLA/stPCL-co-PLA at 1 phr.

For T_ms of PLA in the blends (Table 4), they were found that the T_m of PLA in the blends were related to neat PLA. These were similar to the blends of PLA with linear PCL-co-PLA[17] and interpenetrating network of PCL[18] which were also showed unchanged T_m of PLA in the blends. However, characteristic of melting peak was changed from single broad peak to multiple peaks. The multiple melting peaks could be attributed to different crystalline structures involving size and perfection. Lorenzo et al.[16] reported that the less stable α' crystal form had a lower T_m than the α-form within PLA. The cold crystallization temperature (T_c) was observed during second heating scan. The T_c of neat PLA was 124°C and was displayed as a broad peak (Figure 4). After compounding with stPCL-co-PLA, the T_c of the blends shifted to a lower temperature.

The χ_c of PLA in the blends was calculated as reported in Table 4. The χ_c of the blends showed a slight increase compared to the neat PLA. This implied that stPCL-co-PLA may perform as a nucleating agent. Yupin et al. reported that the multi-branches of polylactic acid also performed as a nucleating agent of PLA.[15] However, the imperfection of the crystalline structure remained as evidence of multiple melting peaks. In this work, the χ_c of 2-arms and 4-arms stPCL-co-PLA

provided higher value than 3-arms stPCL-co-PLA. This may be due to steric hindrance of 3-arms obstructed folded chain of PLA around st3PCL-co-PLA. It should be noted that crystallinity was a key that related to energy dissipation of the blends that will be mentioned in the next section.

Table 4 Melting and crystallization behavior of PLA in the blends of PLA/stPCL-co-PLA

Samples	phr	T_c (ºC)	T_m (ºC)	ΔH_m (J/g)	χ_c (%)
PLA/st4PCL-co-PLA	1	105.5	145.0, 151.6	32.4	34.6
	3	107.2	144.0, 151.0	27.8	29.7
	5	109.0	144.5, 151.1	27.3	29.0
PLA/st3PCL-co-PLA	1	108.6	145.0, 152.0	27.2	29.0
	3	105.4	145.0, 151.8	23.7	25.4
	5	107.6	145.0, 151.8	29.5	31.5
PLA/st2PCL-co-PLA	1	113.5	146.2, 152.0	34.7	37.0
	3	103.6	144.0, 150.7	30.3	32.0
	5	102.6	143.0, 151.4	30.5	32.5
Neat PLA		123.6	151.0	22.6	24.0

Tensile properties of the blends

Table 5 shows the results of tensile testing. Young's modulus of the neat PLA was 143 MPa. When mixed with stPCL-co-PLA, Young's modulus of the blends showed a tendency to decrease as the stPCL-co-PLA increased. These results implied that the toughness of the blend increased and was related to the lower T_g as mentioned previously. Therefore, this provided support that stPCL-co-PLA could plasticize the PLA matrix. The elongation at break of the blends was also increased as the stPCL-co-PLA increased. With st2PCL-co-PLA and st3PCL-co-PLA, the results showed that 3 phr was the optimum concentration to increase the %elongation at break. For st4PCL-co-PLA, the %elongation at break was increased up to 6.6% at 5 phr compared to neat PLA (4.4%).

Table 5 Results of tensile testing of the blends

Sample	Young's modulus (MPa)			Elongation at break (%)			Toughness (MPa)*		
Neat PLA	143±8.0			4.4±0.7			74.2±16		
PLA/stPCL-co-PLA	**Content (phr)**								
	1	**3**	**5**	**1**	**3**	**5**	**1**	**3**	**5**
PLA/st4PCL-co-PLA	125±6.4	134±3.1	131±3.7	3.5±0.5	5.8±1.0	6.6±2.2	44.2±9	119.8±21	103.0±15
PLA/st3PCL-co-PLA	138±2.4	135±2.4	133±8.0	4.1±1.0	5.8±2.0	4.0±0.2	54.7±6	60.0±7	54.3±5
PLA/st2PCL-co-PLA	133±3.5	128±3.4	129±5.7	3.6±0.2	5.4±1.2	3.2±2.4	48.0±5	80.8±12	35.2±3

*calculated from area under stress-strain curve from a tensile test

The toughness of the blends was calculated from the area under the stress-strain curve obtained from tensile testing. At 1 phr of stPCL-co-PLA, surprisingly, the toughness decreased compared to the neat PLA. However, the toughness increased with blended stPCL-co-PLA at 3 phr. Moreover, this was the optimum composition of stPCL-co-PLA to improve the toughness of the blends (Table 5). For example, the toughness of PLA/st4PCL-co-PLA at 3 phr was 119.8±21 J cm^3 which was 61% higher than neat PLA. Interestingly, 3-arms of stPCL-co-PLA provided slightly decreased toughness of the blends. This might have been due to obstruction of the 3-arms which was a difficult arrangement compared to 2-arms and 4-arms as the χ_c of st3PCL-co-PLA was the lowest (Table 4).

The fracture surface of the tensile testing samples was observed using SEM. The neat PLA shows a smooth surface (Figure 5) which is characteristic of a brittle specimen. For the blends, the SEM images showed a rough surface for all samples. At 3 phr (Figure 5b) the rough surface with fibers might have been the effect of rubbery PCL and resulted in enhanced toughness of the blends.

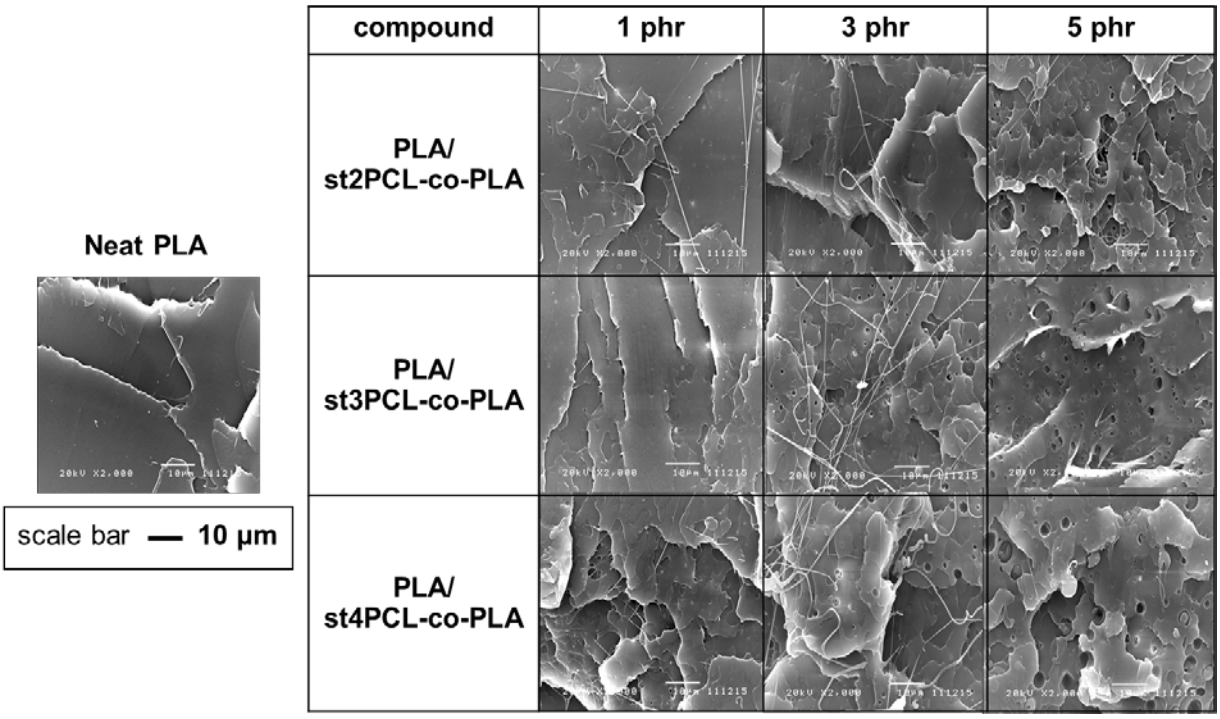


Figure 5. SEM images of fracture surface of neat PLA and PLA/stPCL-co-PLA (a) 1 phr, (b) 3 phr, and (c) at 5 phr (magnification x2,000 for all samples).

Stoclet et al.[19] reported that deformation of PLA occurred through a localized crazing mechanism which responded to brittleness. In order to improve the toughness of the PLA, either rubber-modified PLA or extending its crystallinity can be used as energy-dissipative toughening mechanisms.

In the present work, the stress-strain curve showed the behavior of a cold drawing (Figure 6). There are two basic causes for this phenomenon. One is rubber-toughened amorphous plastics. The region of cold drawing is where extensive orientation of the chains take place. The other is semicrystalline polymers with an amorphous portion above T_g, so that cold drawing rearrangement of the chain results in shear-yielding deformation.[20] Therefore, stPCL-co-PLA not only provided rubber-toughened amorphous (decreased T_g of PLA) but also created semicrystalline (increased χ_c of PLA) to establish crystalline in PLA matrix for effective energy absorption and resulted in stress propagation via shear-yielding.

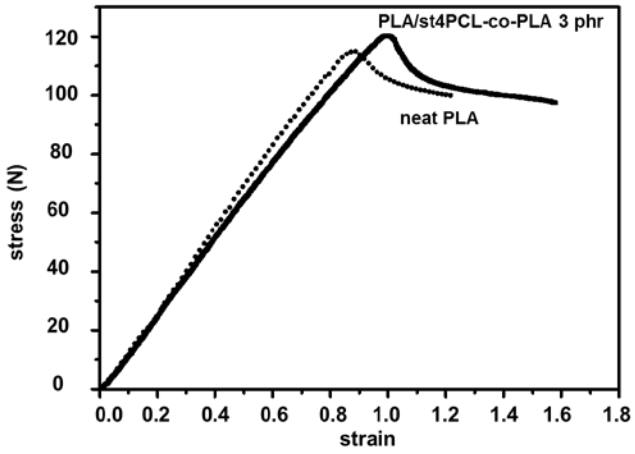


Figure 6. Stress-strain curve of neat PLA (dotted line) and the blend of PLA/st4PCL-co-PLA at 3 phr (bold solid line).

5.5 Optical transparency of the blends

The optical transparency of PLA occurs because of the transmittance of light without the inhibition of crystals, or the size of the crystals is smaller than the wavelength of light.[21] In this work, the optical transparency was investigated by measuring the %transmittance of the visible light (400-750 nm) as shown in Figure 7. The blends of PLA/st2PCL-co-PLA were comparable in the %transmittance to the neat PLA in all contents. For the blends of st3PCL-co-PLA and st4PCL-co-PLA, the %transmittance diminished when the content of stPCL-co-PLA was up to 5 phr. The appearances of the blend with thickness of 0.4 mm were shown in Figure 8. In addition, the optical transparency of the blends provided indirect evidence to clarify the miscibility between the two compounds. If the compound was immiscible, it would show opaqueness or translucence. In our case, the results showed transparent blends at the optimum of 3 phr.

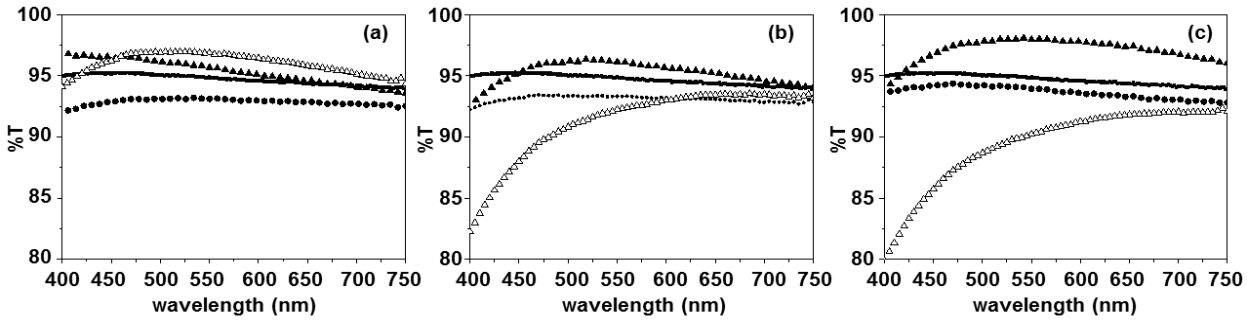


Figure 7. %Transparency of compounds PLA/stPCL-co-PLA: (a) st2PCL-co-PLA, (b) st3PCL-co-PLA, and (c) st4PCL-co-PLA at different compositions: (●) 1 phr, (▲) 3phr, and (Δ) 5 phr compared to neat PLA (—) at the wavelength of visible light from 400 to 750 nm.

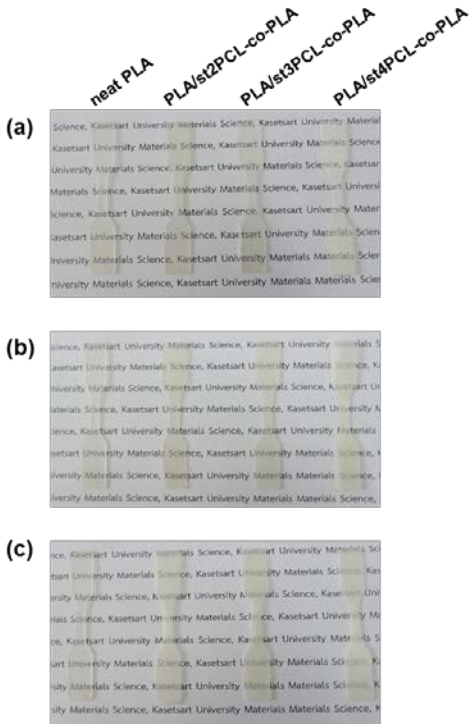


Figure 8. The transparency appearance of the blends and neat PLA obtained from compression molding with thickness of 0.4 mm: (a) at 1 phr, (b) at 3 phr, and (c) at 5 phr.

6. Conclusions

Star-shaped copolyesters of stPCL-co-PLA were synthesized with different numbers of arms and consisting of a rubbery PCL core. The short segment of PLA was grown for miscibility to the PLA matrix. The thermal properties of stPCL-co-PLA revealed that Tc, Tm, and χc were independent of the number of arms of the star-structure. However, number of arms belonging to stPCL-co-PLA affected to the blends of PLA/stPCL-co-PLA. All stPCL-co-PLA showed plasticized PLA as decreased T_g, although, the χ_c of the blends with 2-arms and 4-arms of stPCL-co-PLA provided increasing of crystallinity compared to neat PLA. For 3-arms stPCL-co-PLA provided decreasing in crystallinity of PLA.

Both of rubber-toughened amorphous (lower T_g) and semicrystalline (increased χ_c) affected to toughness and energy dissipation of PLA. The blend of st4PCL-co-PLA at 3 phr resulted in enhanced toughness of the PLA up to 61%. In addition, st4PCL-co-PLA increased the %elongation by up to 6.6% at 5 phr compared to neat PLA. Here, the toughening of PLA may be obtained from rubber-toughened amorphous plastics accompanied with extensive orientation of the semicrystalline portion which provides shear-yielding deformation. Furthermore, the optical transparency of the blends revealed that the %transparency was comparable to neat PLA when mixed with stPCL-co-PLA up to 3 phr.

7. Output

7.1 International Journal Submitted

Submitted to Maromolecular Research entitle of “Effect of Polycaprolactone-co-polylactide Copolyesters’ Arms in Enhancing Optical Transparent PLA Toughness”. The submission id is: MARE-D-16-00188.

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Macromolecular Research

Effect of Polycaprolactone-co-polylactide Copolyesters' Arms in Enhancing Optical Transparent PLA Toughness

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Abstract:	Considering enhancement toughness of PLA including retaining its optical transparency, star-shaped copolyester was investigated. The star-shaped polycaprolactone-co-polylactide (stPCL-co-PLA) with a different number of arms was synthesized using star-shaped initiators. Number of arms was independent to thermal properties and crystallinity of stPCL-co-PLA. However, number of arms of stPCL-coPLA affected to crystallinity of PLA in the blend of PLA/stPCL-co-PLA. The glass transition temperature of the blend was decreased as resulted of stPCL-so-PLA plasticizers. The stPCL-co-PLA with 2-arms and 4-arms provided increasing of crystallinity of PLA in the blends but 3-arms resulted in decreasing of crystallinity due to their steric hindrance. Moreover, the toughness of PLA was enhanced with mixed stPCL-co-PLA up to 3 phr; for example, 4-arms of stPCL-co-PLA provided increasing of toughness as 61% compared to neat PLA. The results revealed that an improvement in toughness may be obtained from shear-yielding deformation which is provided from rubber-toughened amorphous plastics accompanied with extensive orientation of the semicrystalline portion. Moreover, it was found that at 3 phr of stPCL-co-PLA, the compound retained its optical transparency comparable to neat PLA.
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16 May 2016

Professor Dong Hoon Choi,
Editor-in-Chief of *Macromolecular Research*
Department of Chemistry
College of Science, Korea University,
Seoul, Korea

Dear Professor Choi,

For the past several years, I have been carrying the research on synthesis and modification of polymers based on polylactide (PLA). Our approach is to develop copolymers to improve toughness of PLA including retain its optical transparency (*J. Ind. Eng. Chem.* **2012**, 18, 993), (*Eur. Polym. J.* **2013**, 49, 957).

Here, I investigated effect of polycaprolactone-co-polylactide (stPCL-co-PLA) copolyester's arms to toughening transparent PLA. Number of arms was independent to thermal properties and crystallinity of stPCL-co-PLA. However, number of arms of stPCL-co-PLA affected to crystallinity of PLA in the blend of PLA/stPCL-co-PLA. The blends of PLA/stPCL-co-PLA were increased in toughness. The results revealed that an improvement in toughness may be obtained from shear-yielding deformation which was provided from rubber-toughened amorphous plastics accompanied with extensive orientation of the semicrystalline portion. Crystallinity of PLA in the blends were dependent on number of arms.

The 'Keywords' of the work are polycaprolactone; polylactide; star-shaped polyester; toughness; optical transparency

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Attachment

Please find the manuscript attached, consisting of 13-pages-text, including 8 Figures, 1 scheme, 5 Tables, and Table of contents.

No prior publication

We hereby give our assurance the manuscript has not been published, or simultaneously submitted for publication elsewhere.

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If you, or the editorial group, require more information, please let me know. I look forward to hearing from you.

Yours sincerely,

Chantiga Choochottiros, Ph.D.

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Effect of Polycaprolactone-co-polylactide Copolyesters' Arms in Enhancing Optical Transparent PLA Toughness

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Abstract: Considering enhancement toughness of PLA including retaining its optical transparency, star-shaped copolyester was investigated. The star-shaped polycaprolactone-co-polylactide (stPCL-co-PLA) with a different number of arms was synthesized using star-shaped initiators. Number of arms was independent to thermal properties and crystallinity of stPCL-co-PLA. However, number of arms of stPCL-coPLA affected to crystallinity of PLA in the blend of PLA/stPCL-co-PLA. The glass transition temperature of the blend was decreased as resulted of stPCL-so-PLA plasticizers. The stPCL-co-PLA with 2-arms and 4-arms provided increasing of crystallinity of PLA in the blends but 3-arms resulted in decreasing of crystallinity due to their steric hindrance. Moreover, the toughness of PLA was enhanced with mixed stPCL-co-PLA up to 3 phr; for example, 4-arms of stPCL-co-PLA provided increasing of toughness as 61% compared to neat PLA. The results revealed that an improvement in toughness may be obtained from shear-yielding deformation which is provided from rubber-toughened amorphous plastics accompanied with extensive orientation of the semicrystalline portion. Moreover, it was found that at 3 phr of stPCL-co-PLA, the compound retained its optical transparency comparable to neat PLA.

Keywords: polycaprolactone; polylactide; star-shaped polyester; toughness; optical transparency

1. Introduction

Polylactic acid (PLA) is the most significant biodegradable polymer among thermoplastic biodegradable polyesters. It has excellent properties which allow it to compete with petroleum-based polymers as it is eco-friendly and biocompatible and has good processability and can save energy in the production process.[1] However, PLA has high strength and a high modulus, which results in limitations in its application due to its inherent brittleness as well as poor toughness and low impact strength.[2] The literature has reported methods to improve the toughness of PLA such as plasticization,[3-4] copolymerization,[5] and blending with flexible polymers or rubbers.[6]

The approaches to enhance the toughness or impact resistance of PLA tend to result in opaque or translucent blends. Although they present excellent impact strength, their opacity makes such blends unsuitable for applications in which clarity is important. There have been attempts to overcome opacity by matching the refractive index of the impact modifier with that of the PLA resin (1.454).[7] Recently, our group attempted to prepare a transparency impact modifier based on amorphous poly(methy methacrylate) (PMMA) copolymers. Conceptually, in this work PMMA was introduced, which has a refractive index (1.49) close to PLA in order to retain the transparent property. Polylactide-PMMA copolymers were synthesized and were successful in retaining the transparency of PLA but the impact strengths of the blends were rarely increased.[8] We added rubbery polymers such as butyl acrylate and butadiene rubber as another component in the copolymers via free radical polymerization. Poly(butadiene-co-methyl methacrylate-co-butyl methacrylate-co-hydroxyethyl methacrylate), poly(butadiene-co-methyl methacrylate-co-butyl acrylate-co-hydroxyethyl methacrylate), and poly(butadiene-co-lactide-co-methyl methacrylate-co-butylmethacrylate) showed a translucent appearance and the copolymer with the butadiene component showed a 25% increase in the impact strength compared to neat PLA.[9]

The synthesis of an impact modifier needs to not only be concerned with retaining transparency but also with the biodegradable properties to maintain the complete biodegradability of the new compound. With regard to this consideration, ε-caprolactone which has a glass transition temperature (T_g) of -60°C is an attractive rubbery polymer for preparation in toughening copolymers in the rubbery phase. Odent et al.[10] reported on a random copolyester of poly(caprolactone) and polylactide (P[CL-co-LA]) via the ring-opening polymerization method. The results showed that copolymers containing 28 mol% of lactide provided a 4-fold increase in impact strength and transmission electron microscopy showed rubbery particles of copolyeseters with a size of 0.9 μm that were regularly dispersed within the PLA matrix. An interesting feature was that the transparency of the blends was moderately affected by P[CL-co-LA]. Furthermore, star-shaped copolymers are attractive from our point of view. From the literature survey, there have been several reports concerning the synthesis of star-shaped copolymers with 3-, 4-, 6- and multi- arms.[11-13] Most previous reports studied the effect of a star-shaped structure on the polymerization of high molecular weight PLA, crystallinity, and thermal properties, but they did not investigate using these copolymers as an impact modifier or toughening agent.

In this work, rubbery polycaprolactone was synthesized as the core part of star-shaped polymers and grown with a polylactide segment to obtain toughening copolymers with different numbers of arms depending on the star-shaped initiators. The chemical structure and composition including thermal properties of the star-shaped polycaprolactone-co-polylactide (stPCL-co-PLA) were evaluated. The effect of stPCL-co-PLA on toughening PLA including tensile properties were investigated by comparing to neat PLA.

2. Experimental

2.1. Materials

Ɛ-Caprolactone (CL), star-shaped initiators: 4 arms of pentaerythritol, 3 arms of 1,1,1-tris (hydroxymethyl) propane, and 2 arms of 2,2-diethyl-1,3-propanediol were purchased from Merck Millipore, Germany. Tin (II) 2-ethylhexanoate (SnOct2) was purchased from Sigma-Aldrich, USA. L-lactide (LA) was purchased from Asst. Prof. Winita Punyodom's Laboratory, Department of Chemistry, Faculty of Science, Chiang Mai University, Thailand. PLA pellets (IngeoTM Biopolymer 2003D) were a gift from PTT Public Company Limited, Thailand. HPLC grade chloroform, analytical-grade chloroform, and analytical-grade methanol were purchased from Lab-scan, Thailand.

2.2 Synthesis of star-shaped poly(Ɛ-caprolactone) (stPCL)

The st4PCL200 was synthesized by ring-opening polymerization (ROP) of CL with a molar ratio between CL and Pent of 200:1 and 2M of SnOct2 was used as the catalyst according to our previous report with a molar ratio of 1,000 compared to the CL monomer. The reaction was carried out overnight in an oil bath at 160°C, and stopped by quenching in an ice bath. The crude product was dissolved in chloroform and precipitated in cold methanol. The product (st4PCL200) was filtered and dried under vacuum. The st3PCL and st2PCL were synthesized using 1,1,1-tris (hydroxymethyl) propane and 2,2-diethyl-1,3-propanediol as the respective initiators.

2.3 Star-shaped copolymers stPCL-co-PLA by using stPCL as macroinitiator

Polymerization was carried out in bulk by ROP of LA. The molar ratio between LA and st4PCL was 100:1 and 2M of SnOct2 was used as the catalyst with a molar ratio of 1:1000 compared to the LA monomer. The reaction was carried out overnight in an oil bath at 160°C and stopped by quenching in an ice bath. Crude product was dissolved in chloroform and precipitated in cold methanol. The product (st4PCL-co-PLA) was filtered and dried under vacuum. The st3PCL-co-PLA and st2PCL-co-PLA were synthesized using same procedure with st3PCL and st2PCL as the respective macroinitiators.

2.4 Compounding of PLA/stPCL-co-PLA

Prior to melt blending, the PLA pellets were dried for 1 day to remove moisture. A Brabender mixer was used to melt mix the stPCL-co-PLA at 1, 3, and 5 phr with PLA pellets at 190ºC and a speed of 45 revolutions min-1 for 10 min. For tensile testing, the dumbbell-shaped specimen was prepared by compression molding. The sample size followed ASTM D1822 type L.

2.5 Measurements

Proton and carbon nuclear magnetic resonance (NMR) spectra were obtained using a Brüker AVANCE 400 spectrometer, with chloroform-d as the corresponding solvent. The number-average molecular weight (Mn) of the obtained polymers was measured using size-exclusion chromatography (SEC) with two Waters Styragel columns (HR3 and HR4, each 300 mm × 7.8 mm, providing a molecular mass range of 5×102 – 6×105 g/mol) equipped with a Waters 2414 refractive index detector. The eluent was chloroform with a flow rate of 1.0 mL min−1 at an operating temperature of 40°C and a sample injection volume of 75 μL. Differential scanning calorimetry (DSC) was conducted using Mettler-Toledo equipment (Schwerzenbach) where nitrogen gas was purged into the DSC cell at a flow rate of 50 mL/min. Measurements were carried out by using 5–7 mg of samples in a sealed aluminum pan. The samples were first heated from -70ºC to 170ºC at a heating rate of 10ºC/min and were annealed for 10 min at 170ºC to erase any previous thermal history, followed by cooling to -70ºC at a rate of 10ºC/min. The second heating was subsequently made to 170ºC at a heating rate of 1ºC/min. The glass-transition temperature (T_g) was taken as the temperature at the midpoint of the corresponding heat-capacity jump in the second heating run. The degrees of

crystallinity (χ_c) of PLA in the blends of PLA/stPCL-co-PLA were calculated following equation:

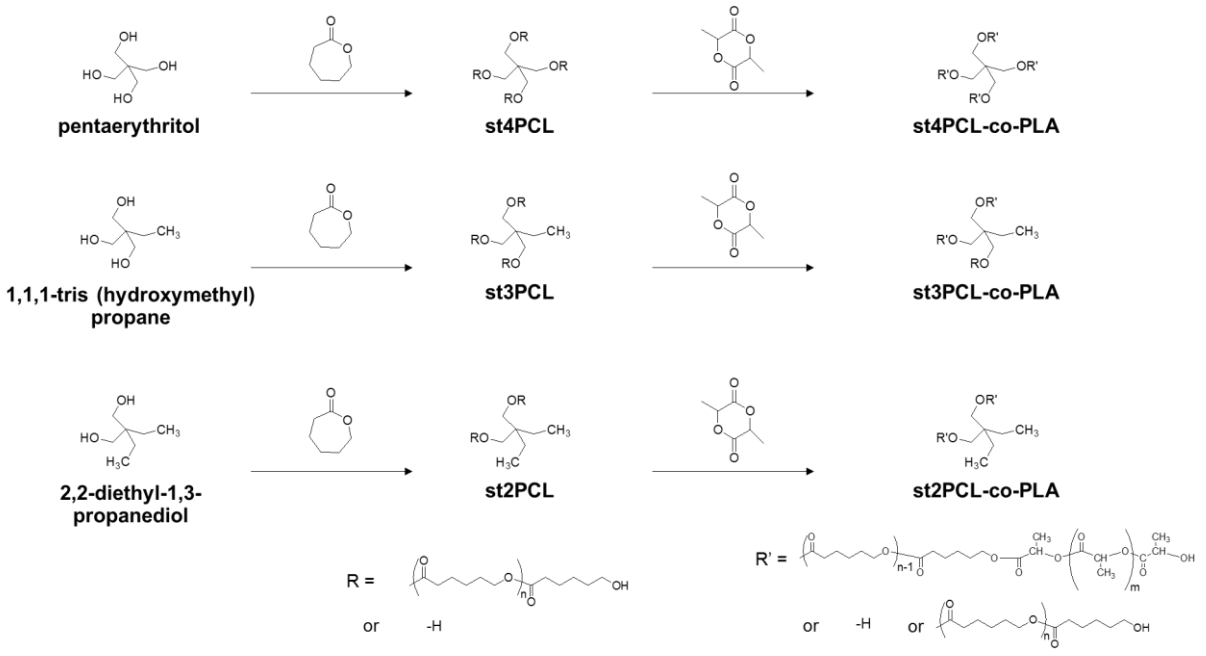
$$\chi_c = (\Delta H_m / \Delta H^0_m) \times 100$$

where ΔH^0_m of PLA is 93.6 J/g. The surface of tensile testing specimens was observed using a JEOL (JSM-5410LV) scanning electron microscope (SEM). The transparency of compound specimens was measured at a thickness of 0.4 mm using a PerkinElmer Lambda 650 unit with a scan wavelength from 400 to 750 nm. The tensile properties of the compound specimens were tested using a 5965 Universal Testing Machine (Instron).

3. Results and Discussion

3.1. Synthesis of star-shaped polycaprolactone (stPCL)

ROP of CL was carried out with different numbers of arm initiators, namely 4 arms from pentaerythritol, 3 arms from 1,1,1-tris (hydroxymethyl) propane, and 2 arms from 2,2-diethyl-1,3-propanediol (Scheme 1).



Scheme 1 Synthesis of stPCL and stPCL-co-PLA

Table 1 Results of stPCL with different numbers of arm initiators

stPCL	Initiator (In)	[CL]:[In]	%yield	Mn (g/mol) (PdI)	DPn*
st4PCL200	pentaerythritol	200:1	78	22,840 (1.66)	34
st3PCL200	1,1,1-tris (hydroxymethyl) propane	200:1	81	20,000 (1.56)	32
st2PCL200	2,2-diethyl-1,3-propanediol	200:1	76	14,480 (1.47)	30

*calculated from ^{1}H NMR

^{1}H NMR was applied to confirm the chemical structure of stPCL (Figure 1). All samples showed characteristic peaks of polycaprolactone such as 3.87-4.25 ppm (-CH_2-, **4**), 2.12-2.46 ppm (-CH_2-, **3**), 1.67 ppm (-CH_2-, **2** and **2'**), and 1.37 ppm (-CH_2-, **1**). The hydroxyl in the terminated chain was confirmed by the methylene proton at 3.63 ppm (-CH_2-,**4'**). In addition, the degree of polymerization (DPn) was calculated from the ratio of the integrated peak of **4** and **4'** and the results are reported in Table 1. The ^{13}C NMR spectra also confirmed the hydroxyl termination of stPCL by the existence of methine (**4'**) at 64.57 ppm (Figure 1) which corresponded to

methine at the chain end adjacent to the hydroxyl-terminated group. However, the ^{1}H NMR spectra (δ 3.5 ppm, -C**H**$_2$-OH) indicated that not all hydroxyls of initiators were converted to the PCL arms.[14]

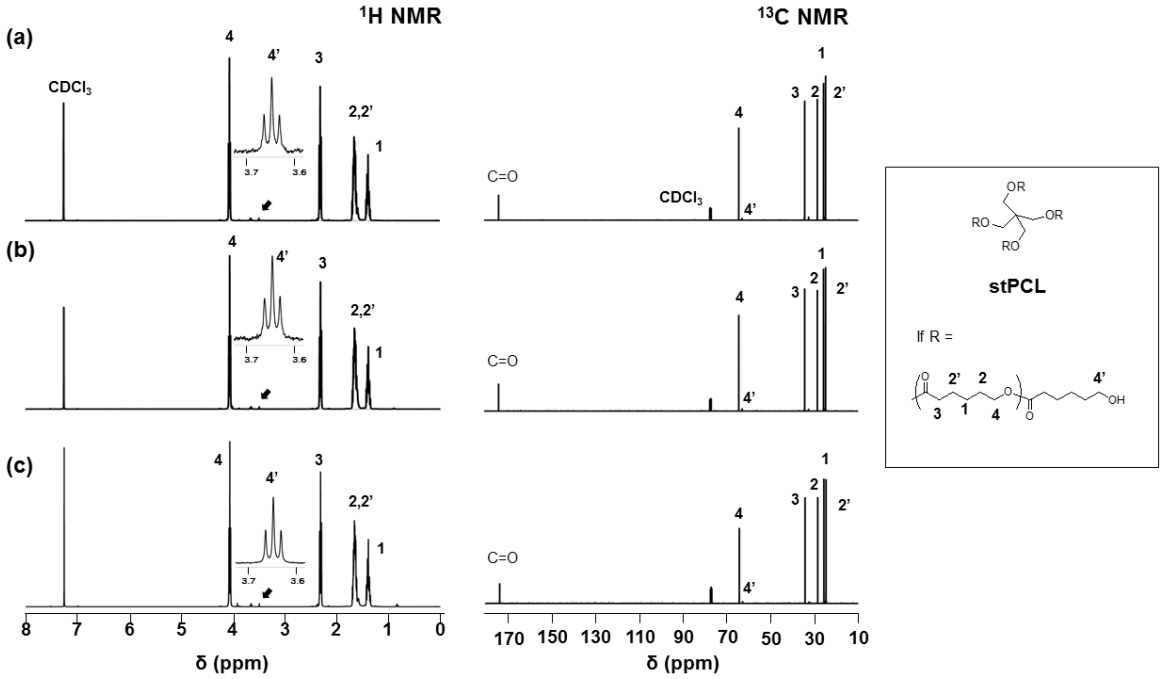


Figure 1. ^{1}H NMR and ^{13}C NMR spectra of stPCL: (a) st4PCL, (b) st3PCL, and (c) st2PCL in $CDCl_3$.

3.2 Ring-opening polymerization of LA via stPCL marcoinitiator

The stPCL with the hydroxyl-terminated group was used as a macroinitiator to open the ring of LA using $SnOct_2$ as a catalyst. Table 2 shows the molecular weight and degree of polymerization of stPCL-co-PLA. On the basis of the SEC data, the ring opening of LA by the hydroxyl-terminated stPCL caused some chain breakage of PCL arms.

Table 2 Results of stPCL-co-PLA with stPCL as macroinitiator

stPCL-co-PLA	[LA]:[stPCL]	%yield	Mn (g/mol) (PdI)	DPn* of PLA
st4PCL200-co-PLA100	100:1	68	17,450 (1.5)	7
st3PCL200-co-PLA100	100:1	65	14,560 (1.3)	18
st2PCL200-co-PLA100	100:1	73	11,500 (1.3)	27

*calculated from ^{1}H NMR

^{1}H NMR showed characteristic peaks of PLA (Figure 2) such as 5.0-5.2 ppm (-CH-, **5**) and 1.46-1.5 ppm (-CH_3-, **6**) Furthermore, DPn of the PLA segment was calculated from the integral ratio of the methine proton (-CH-, **5**) and the methylene proton at the chain end of PCL (-CH_2-, **4"**) (Table 2).

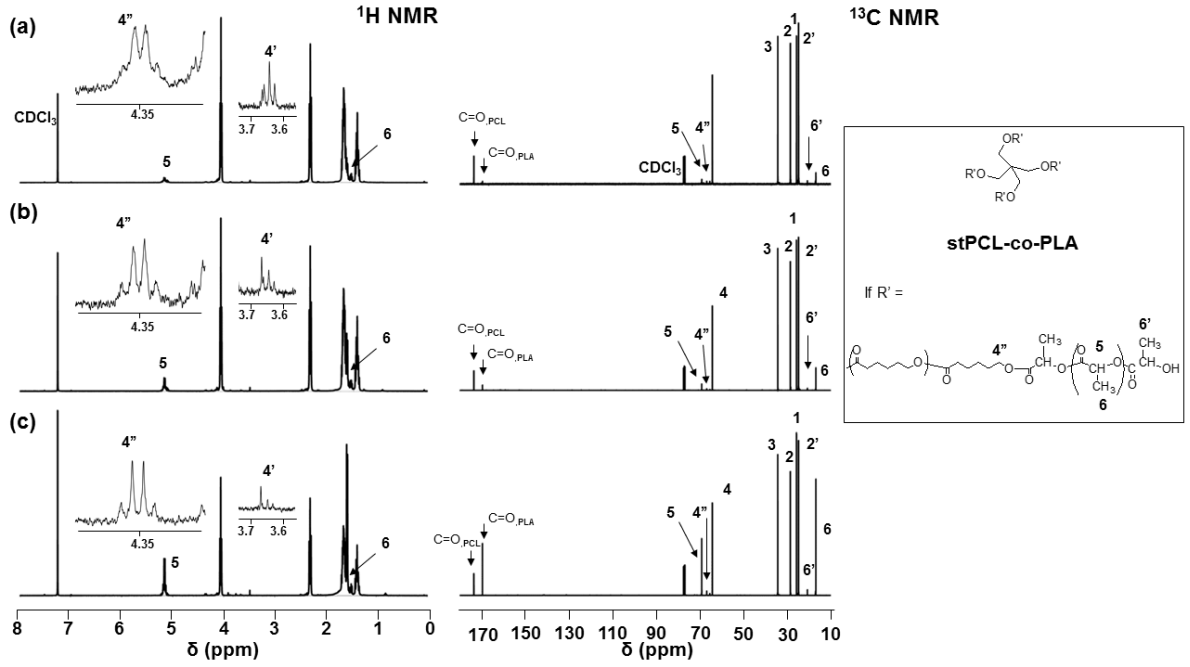


Figure 2. ^{1}H NMR and ^{13}C NMR spectra of stPCL-co-PLA (a) st4PCL-co-PLA, (b) st3PCL-co-PLA, and (c) st2PCL-co-PLA in $CDCl_3$.

The success in opening the ring of lactide by the macroinitiator stPCL was confirmed by the peak shift which belonged to the adjacent methylene proton to the lactide segment. The peak shifted from 3.87-4.25 (**4**) to 4.35 (**4"**) ppm. However, the methylene proton at the chain end of PCL (-CH_2-, **4'**) still remained. This implied that not all hydroxyl-terminated groups on stPCL could open the ring of the lactide. This might have been due to the high viscosity of reaction and the high molecular weight of the macroinitiators. In addition, ^{13}C NMR confirmed the ring opening of the lactide by the peak at 66.8 ppm (-CH_2-, **4"**) corresponding to the methine carbon that linked to the PLA.

3.3 Thermal properties of stPCL and stPCL-co-PLA

The crystallization temperature (T_c) was obtained from the cooling run and the melting temperature (T_m) and the degree of crystallinity (χ_c) were obtained from the second heating run. The results are listed in Table 3 and the DSC thermogram of T_m is shown in Figure 3. The T_m of stPCL showed a single peak in the range 52-54ºC for all samples. In the case of stPCL, the results showed that number of arms was independent of T_c, T_m, and χ_c with comparable molecular weights. In contrast, 6-arms of stPCL had an approximate similar molecular weight that provided lower values for T_c, T_m, and χ_c.[12] This might have been due to the packing structure of stPCL with 6-arms being more complicated than with lower numbers of arms. In this study, the T_g value of stPCL was too low to be detected in the temperature range.

Table 3 Melting and crystallization behavior of PCL in stPCL and stPCL-co-PLA

Sample	T_c (°C)	T_m (°C)	ΔH_m (J/g)	χ_c (%)
st4PCL	31.0	54.2	76.39	56.1
st3PCL	29.1	52.3	80.50	59.1
st2PCL	30.5	52.6	72.65	53.4
st4PCL-co-PLA	19.5	44.5, 49.4	58.92	43.3
st3PCL-co-PLA	14.3	42.7, 48.4	54.70	40.2
st2PCL-co-PLA	20.8	45.0, 50.9	67.32	49.5

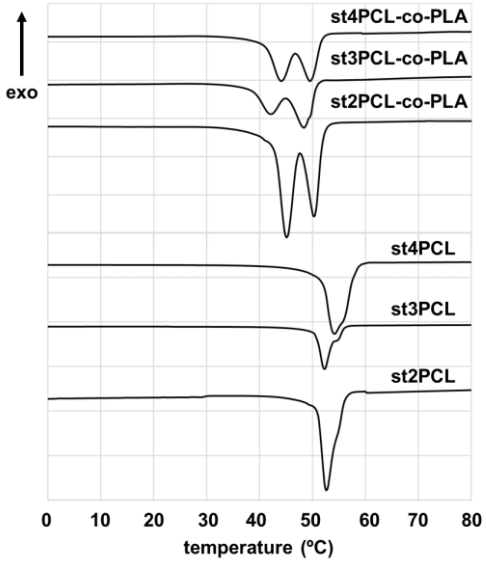


Figure 3. DSC thermogram of stPCL and stPCL-co-PLA.

For stPCL-co-PLA, the T_c shifted to a lower temperature. This implied a restriction of the PLA outer shell due to the mobility of the PCL core. This was also supported by the decrease in T_m and χ_c. The value for T_m presented as a double melting peak (Figure 3). This phenomenon referred to the presence of two different crystalline phases. The lower melting peak is attributed to the melting of the imperfect crystalline structure and the higher melting peak is attributed to the melting of the perfect crystalline structure based on lamellae thicknesses.[15] While thermal transitions of PCL could be detected in stPCL-co-PLA, it was difficult to detect PLA as the PLA block had a very short chain length.

3.4 Compounding of PLA with stPCL-co-PLA

Thermal properties of the blends

Neat PLA had a T_g at 61°C and T_m at 151°C (Figure 4). After compounding with stPCL-co-PLA at 1, 3, and 5 phr, a change in the glass transition behavior of the blends could be observed. The T_g of the blends at 1 phr showed a shift to a lower temperature (ca. 55°C), presumably because the stPCL-co-PLA enhanced the flexibility of the PLA matrix or increased the free volume of the compound from the star-shaped architecture of stPCL-co-PLA. Therefore, the star-shaped structure of PCL and PLA copolymers responded to plasticize PLA.

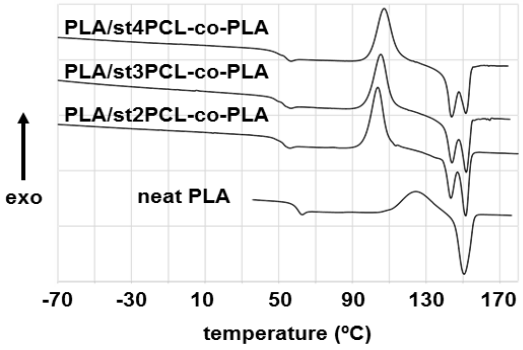


Figure 4. Second heating scan of PLA and the blends of PLA/stPCL-co-PLA at 1 phr.

For T_ms of PLA in the blends (Table 4), they were found that the T_m of PLA in the blends were related to neat PLA. These were similar to the blends of PLA with linear PCL-co-PLA[17] and interpenetrating network of PCL[18] which were also showed unchanged T_m of PLA in the blends. However, characteristic of melting peak was changed from single broad peak to multiple peaks. The multiple melting peaks could be attributed to different crystalline structures involving size and perfection. Lorenzo et al.[16] reported that the less stable α' crystal form had a lower T_m than the α-form within PLA. The cold crystallization temperature (T_c) was observed during second heating scan. The T_c of neat PLA was 124°C and was displayed as a broad peak (Figure 4). After compounding with stPCL-co-PLA, the T_c of the blends shifted to a lower temperature.

The χ_c of PLA in the blends was calculated as reported in Table 4. The χ_c of the blends showed a slight increase compared to the neat PLA. This implied that stPCL-co-PLA may perform as a nucleating agent. Yupin et al. reported that the multi-branches of polylactic acid also performed as a nucleating agent of PLA.[15] However, the imperfection of the crystalline structure remained as evidence of multiple melting peaks. In this work, the χ_c of 2-arms and 4-arms stPCL-co-PLA provided higher value than 3-arms stPCL-co-PLA. This may be due to steric hindrance of 3-arms obstructed folded chain of PLA around st3PCL-co-PLA. It should be noted that crystallinity was a key that related to energy dissipation of the blends that will be mentioned in the next section.

Table 4 Melting and crystallization behavior of PLA in the blends of PLA/stPCL-co-PLA

Samples	phr	T_c (ºC)	T_m (ºC)	ΔH_m (J/g)	χ_c (%)
PLA/st4PCL-co-PLA	1	105.5	145.0, 151.6	32.4	34.6
	3	107.2	144.0, 151.0	27.8	29.7
	5	109.0	144.5, 151.1	27.3	29.0
PLA/st3PCL-co-PLA	1	108.6	145.0, 152.0	27.2	29.0
	3	105.4	145.0, 151.8	23.7	25.4
	5	107.6	145.0, 151.8	29.5	31.5
PLA/st2PCL-co-PLA	1	113.5	146.2, 152.0	34.7	37.0
	3	103.6	144.0, 150.7	30.3	32.0
	5	102.6	143.0, 151.4	30.5	32.5
Neat PLA		123.6	151.0	22.6	24.0

Tensile properties of the blends

Table 5 shows the results of tensile testing. Young's modulus of the neat PLA was 143 MPa. When mixed with stPCL-co-PLA, Young's modulus of the blends showed a tendency to decrease as the stPCL-co-PLA

increased. These results implied that the toughness of the blend increased and was related to the lower T_g as mentioned previously. Therefore, this provided support that stPCL-co-PLA could plasticize the PLA matrix. The elongation at break of the blends was also increased as the stPCL-co-PLA increased. With st2PCL-co-PLA and st3PCL-co-PLA, the results showed that 3 phr was the optimum concentration to increase the %elongation at break. For st4PCL-co-PLA, the %elongation at break was increased up to 6.6% at 5 phr compared to neat PLA (4.4%).

Table 5 Results of tensile testing of the blends

Sample	**Young's modulus (MPa)**			**Elongation at break (%)**			**Toughness (MPa)***		
Neat PLA	143±8.0			4.4±0.7			74.2±16		
PLA/stPCL-co-PLA	**Content (phr)**								
	1	**3**	**5**	**1**	**3**	**5**	**1**	**3**	**5**
PLA/st4PCL-co-PLA	125±6.4	134±3.1	131±3.7	3.5±0.5	5.8±1.0	6.6±2.2	44.2±9	119.8±21	103.0±15
PLA/st3PCL-co-PLA	138±2.4	135±2.4	133±8.0	4.1±1.0	5.8±2.0	4.0±0.2	54.7±6	60.0±7	54.3±5
PLA/st2PCL-co-PLA	133±3.5	128±3.4	129±5.7	3.6±0.2	5.4±1.2	3.2±2.4	48.0±5	80.8±12	35.2±3

*calculated from area under stress-strain curve from a tensile test

The toughness of the blends was calculated from the area under the stress-strain curve obtained from tensile testing. At 1 phr of stPCL-co-PLA, surprisingly, the toughness decreased compared to the neat PLA. However, the toughness increased with blended stPCL-co-PLA at 3 phr. Moreover, this was the optimum composition of stPCL-co-PLA to improve the toughness of the blends (Table 5). For example, the toughness of PLA/st4PCL-co-PLA at 3 phr was 119.8±21 J cm^3 which was 61% higher than neat PLA. Interestingly, 3-arms of stPCL-co-PLA provided slightly decreased toughness of the blends. This might have been due to obstruction of the 3-arms which was a difficult arrangement compared to 2-arms and 4-arms as the χ_c of st3PCL-co-PLA was the lowest (Table 4).

The fracture surface of the tensile testing samples was observed using SEM. The neat PLA shows a smooth surface (Figure 5) which is characteristic of a brittle specimen. For the blends, the SEM images showed a rough surface for all samples. At 3 phr (Figure 5b) the rough surface with fibers might have been the effect of rubbery PCL and resulted in enhanced toughness of the blends.

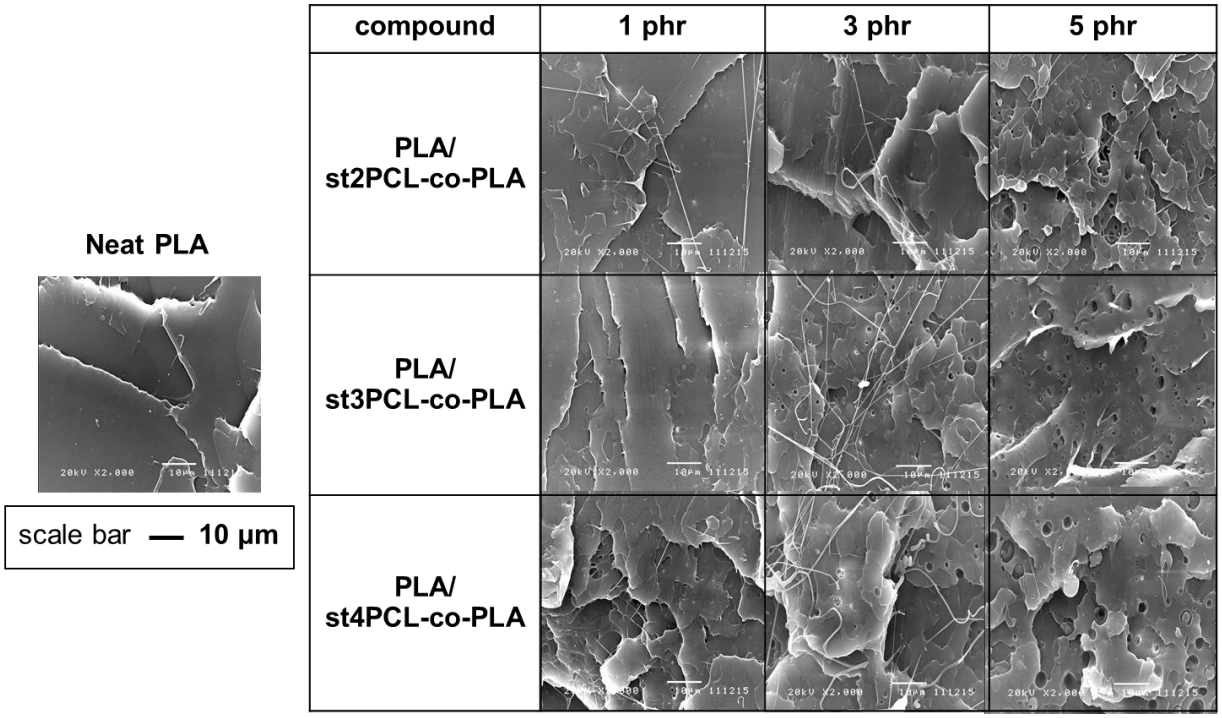


Figure 5. SEM images of fracture surface of neat PLA and PLA/stPCL-co-PLA (a) 1 phr, (b) 3 phr, and (c) at 5 phr (magnification x2,000 for all samples).

Stoclet et al.[19] reported that deformation of PLA occurred through a localized crazing mechanism which responded to brittleness. In order to improve the toughness of the PLA, either rubber-modified PLA or extending its crystallinity can be used as energy-dissipative toughening mechanisms.

In the present work, the stress-strain curve showed the behavior of a cold drawing (Figure 6). There are two basic causes for this phenomenon. One is rubber-toughened amorphous plastics. The region of cold drawing is where extensive orientation of the chains take place. The other is semicrystalline polymers with an amorphous portion above T_g, so that cold drawing rearrangement of the chain results in shear-yielding deformation.[20] Therefore, stPCL-co-PLA not only provided rubber-toughened amorphous (decreased T_g of PLA) but also created semicrystalline (increased χ_c of PLA) to establish crystalline in PLA matrix for effective energy absorption and resulted in stress propagation via shear-yielding.

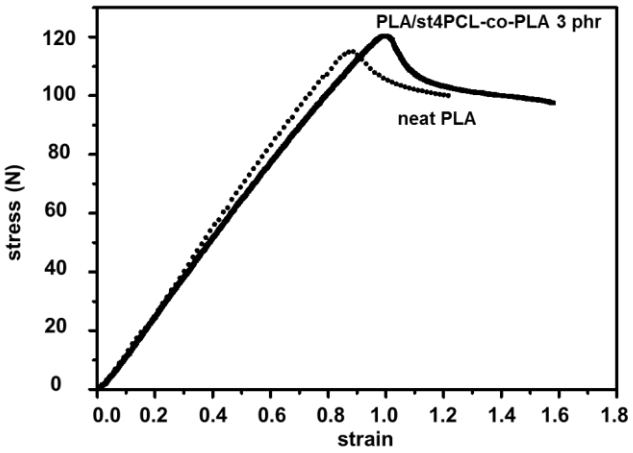


Figure 6. Stress-strain curve of neat PLA (dotted line) and the blend of PLA/st4PCL-co-PLA at 3 phr (bold solid line).

3.5 Optical transparency of the blends

The optical transparency of PLA occurs because of the transmittance of light without the inhibition of crystals, or the size of the crystals is smaller than the wavelength of light.[21] In this work, the optical transparency was investigated by measuring the %transmittance of the visible light (400-750 nm) as shown in Figure 7. The blends of PLA/st2PCL-co-PLA were comparable in the %transmittance to the neat PLA in all contents. For the blends of st3PCL-co-PLA and st4PCL-co-PLA, the %transmittance diminished when the content of stPCL-co-PLA was up to 5 phr. The appearances of the blend with thickness of 0.4 mm were shown in Figure 8. In addition, the optical transparency of the blends provided indirect evidence to clarify the miscibility between the two compounds. If the compound was immiscible, it would show opaqueness or translucence. In our case, the results showed transparent blends at the optimum of 3 phr.

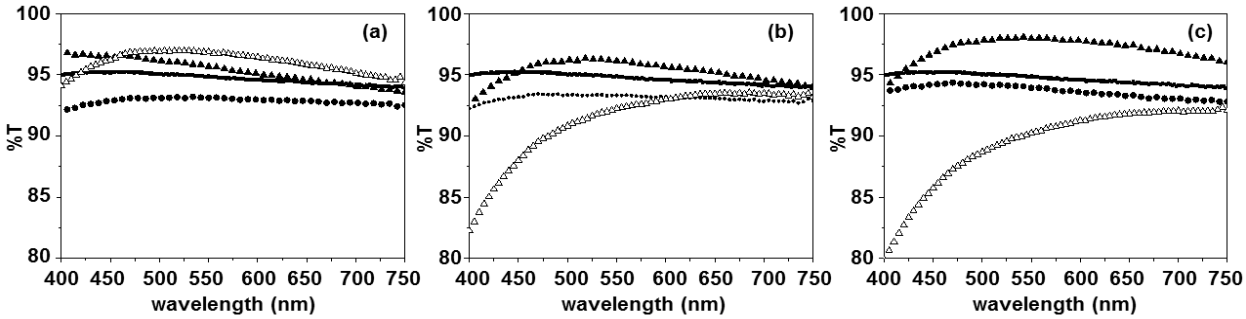


Figure 7. %Transparency of compounds PLA/stPCL-co-PLA: (a) st2PCL-co-PLA, (b) st3PCL-co-PLA, and (c) st4PCL-co-PLA at different compositions: (●) 1 phr, (▲) 3phr, and (Δ) 5 phr compared to neat PLA (—) at the wavelength of visible light from 400 to 750 nm.

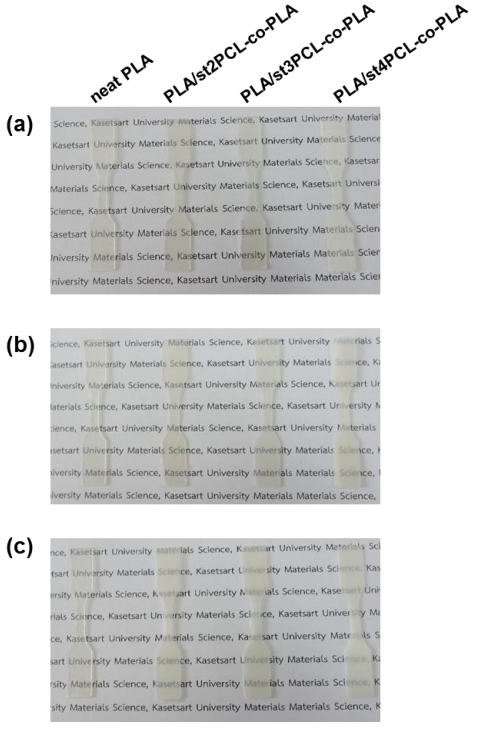


Figure 8. The transparency appearance of the blends and neat PLA obtained from compression molding with thickness of 0.4 mm: (a) at 1 phr, (b) at 3 phr, and (c) at 5 phr.

4. Conclusions

Star-shaped copolyesters of stPCL-co-PLA were synthesized with different numbers of arms and consisting of a rubbery PCL core. The short segment of PLA was grown for miscibility to the PLA matrix. The thermal properties of stPCL-co-PLA revealed that Tc, Tm, and χc were independent of the number of arms of the star-structure. However, number of arms belonging to stPCL-co-PLA affected to the blends of PLA/stPCL-co-PLA. All stPCL-co-PLA showed plasticized PLA as decreased T_g, although, the χ_c of the blends with 2-arms and 4-arms of stPCL-co-PLA provided increasing of crystallinity compared to neat PLA. For 3-arms stPCL-co-PLA provided decreasing in crystallinity of PLA.

Both of rubber-toughened amorphous (lower T_g) and semicrystalline (increased χ_c) affected to toughness and energy dissipation of PLA. The blend of st4PCL-co-PLA at 3 phr resulted in enhanced toughness of the PLA up to 61%. In addition, st4PCL-co-PLA increased the %elongation by up to 6.6% at 5 phr compared to neat PLA. Here, the toughening of PLA may be obtained from rubber-toughened amorphous plastics accompanied with extensive orientation of the semicrystalline portion which provides shear-yielding deformation. Furthermore, the optical transparency of the blends revealed that the %transparency was comparable to neat PLA when mixed with stPCL-co-PLA up to 3 phr.

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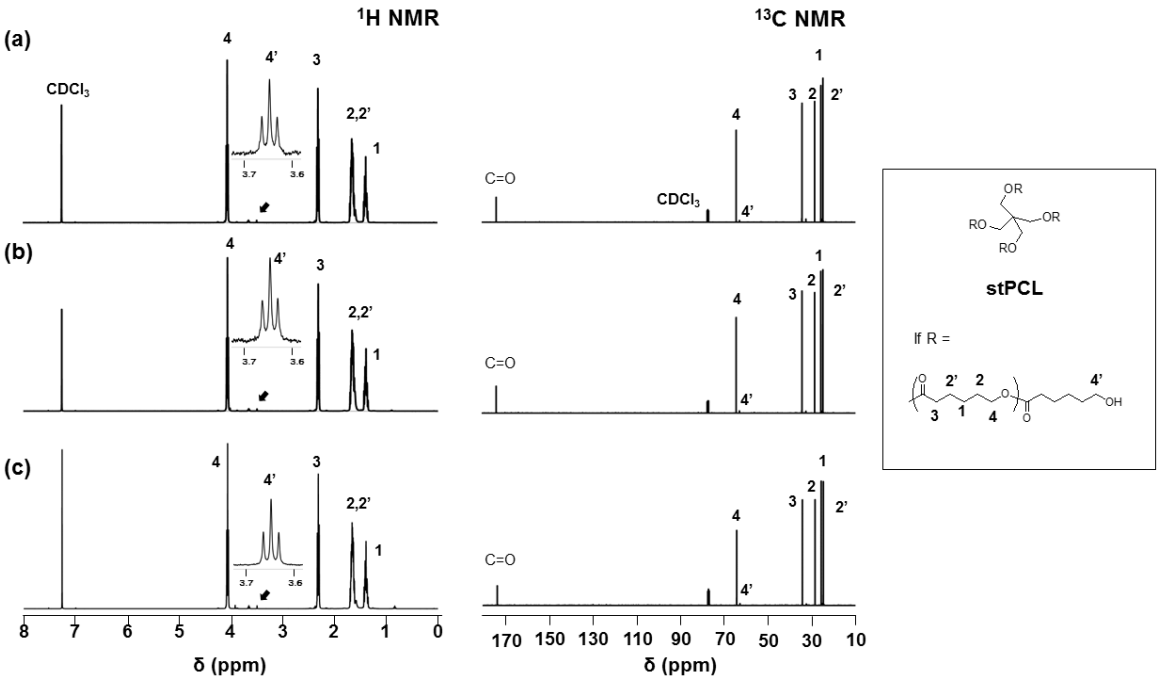

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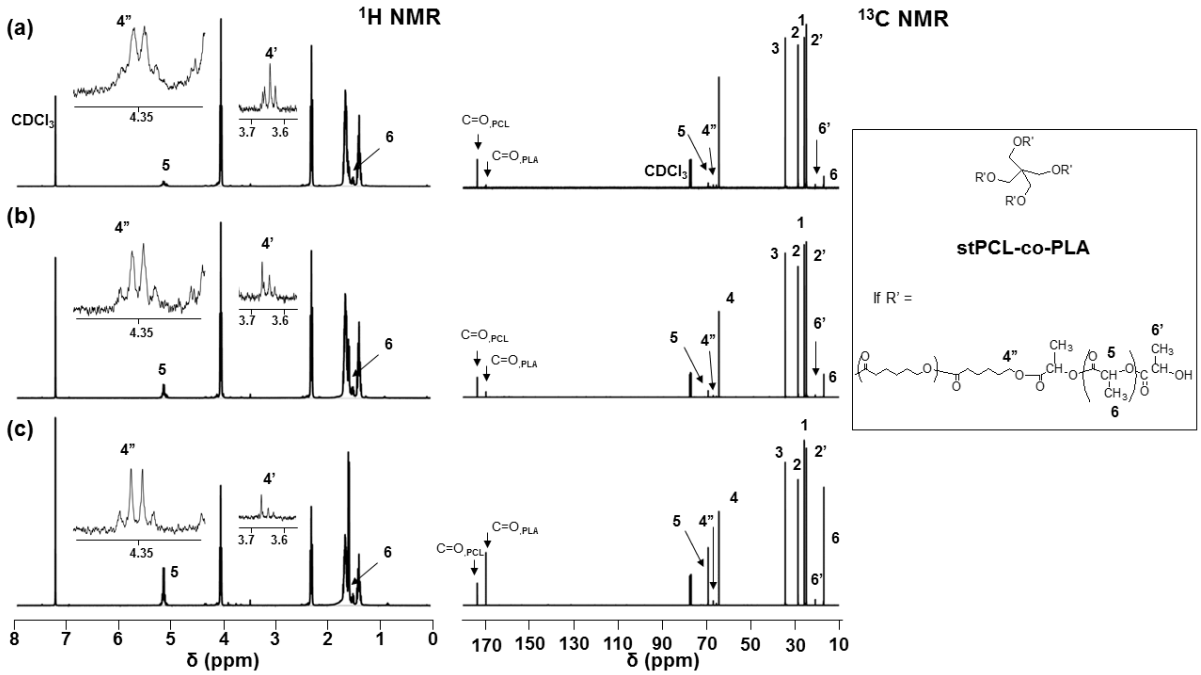

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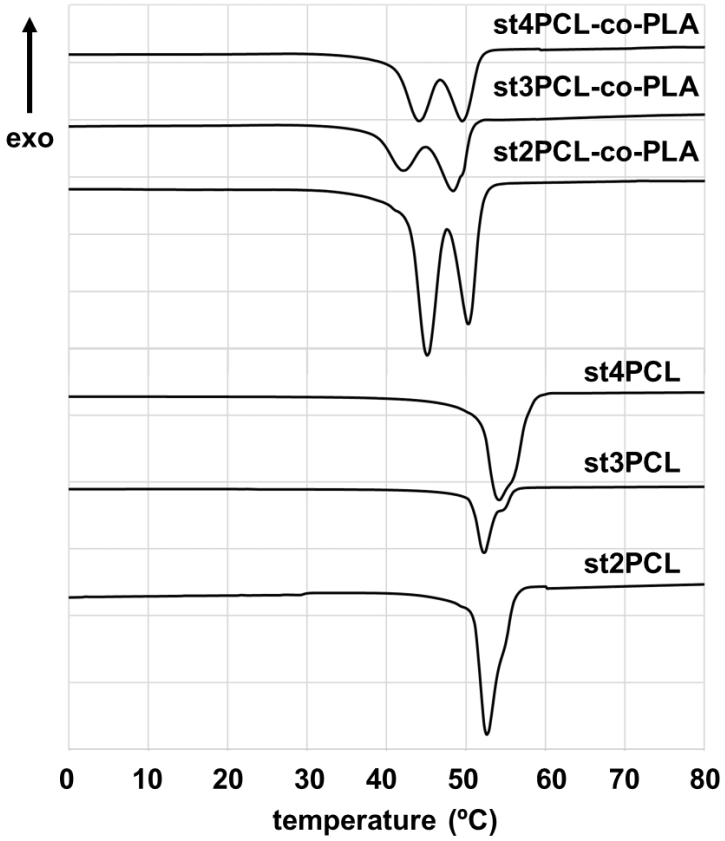

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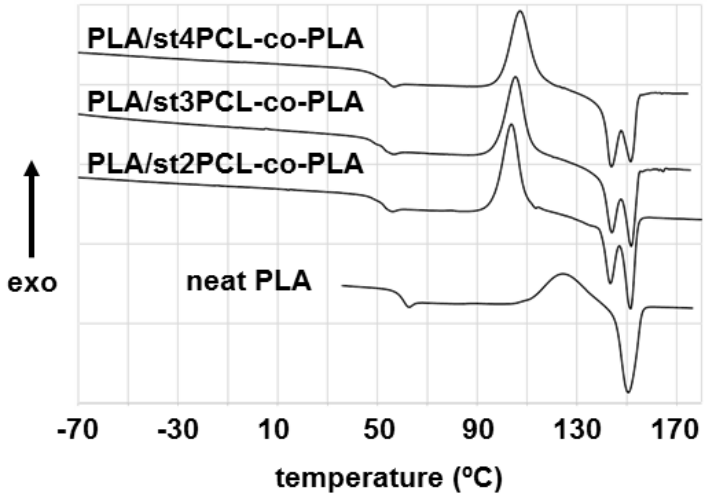

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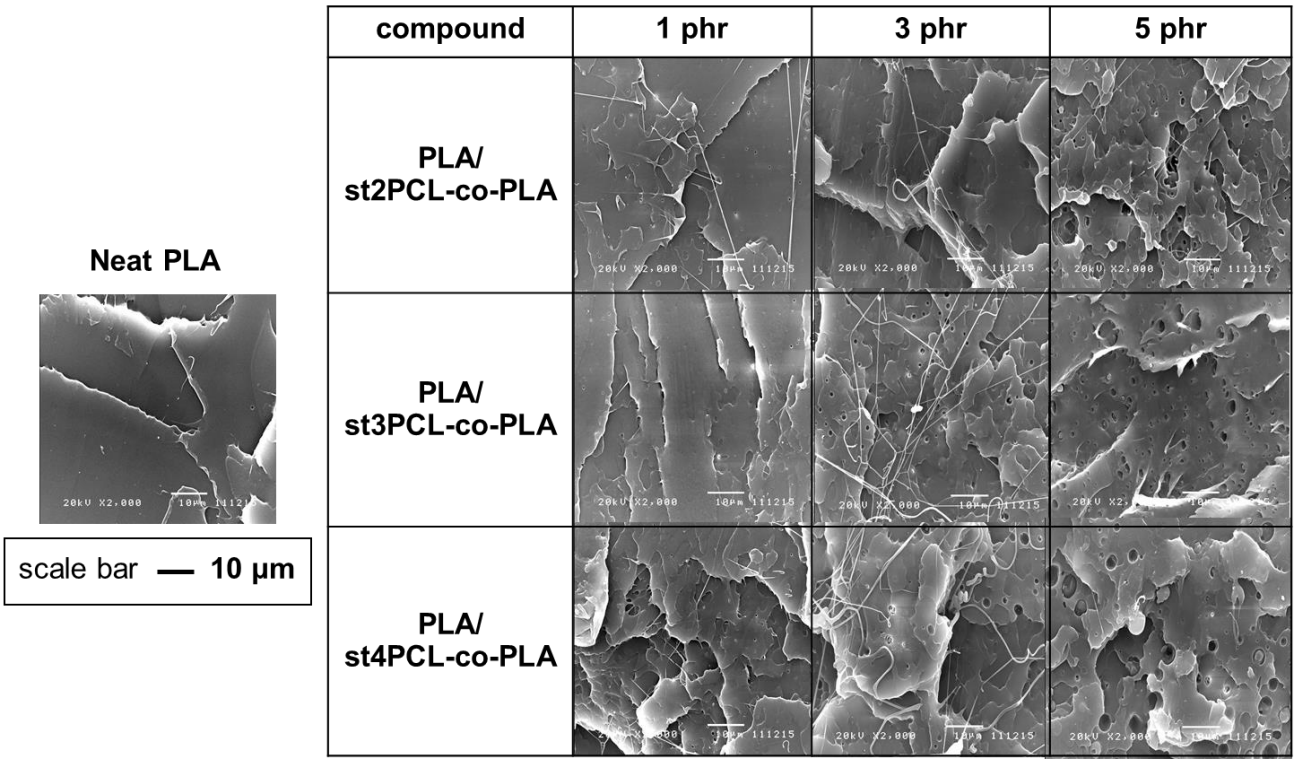

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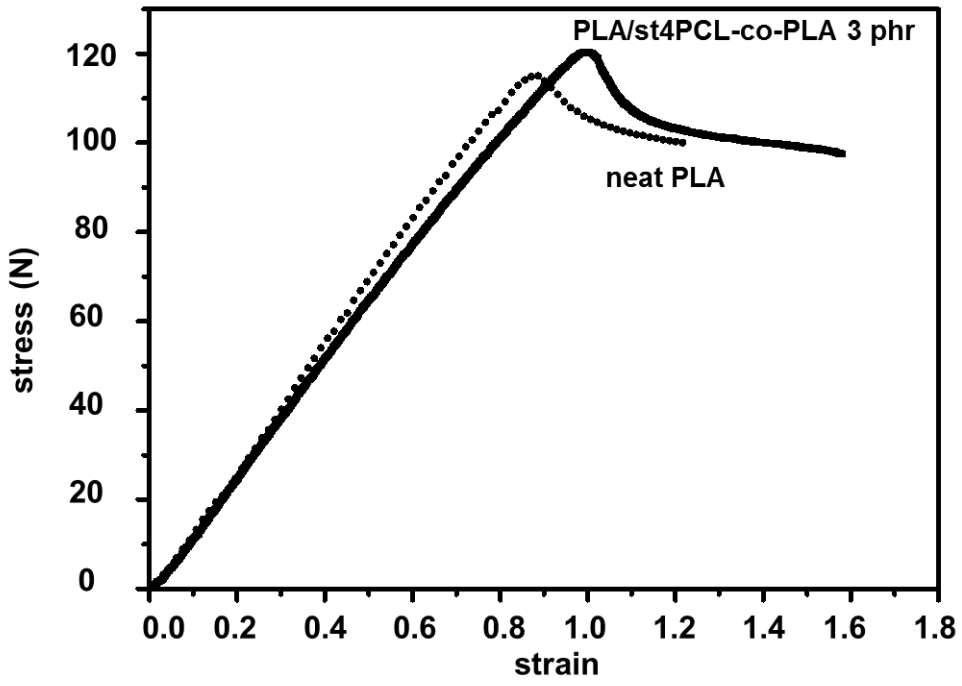

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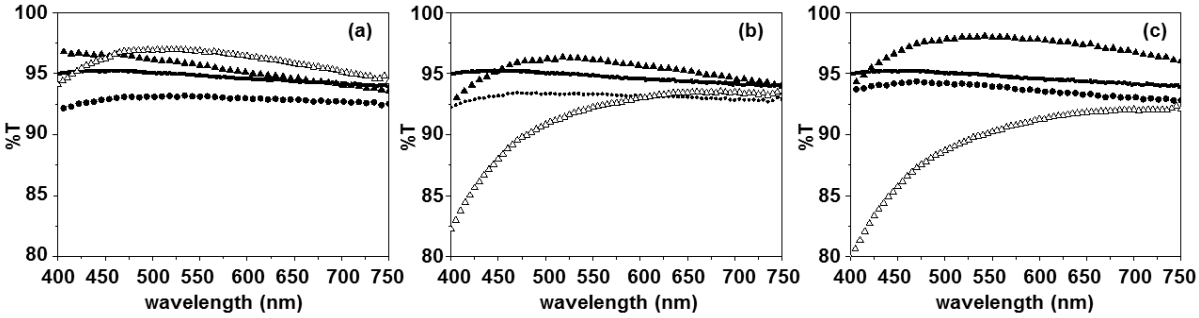

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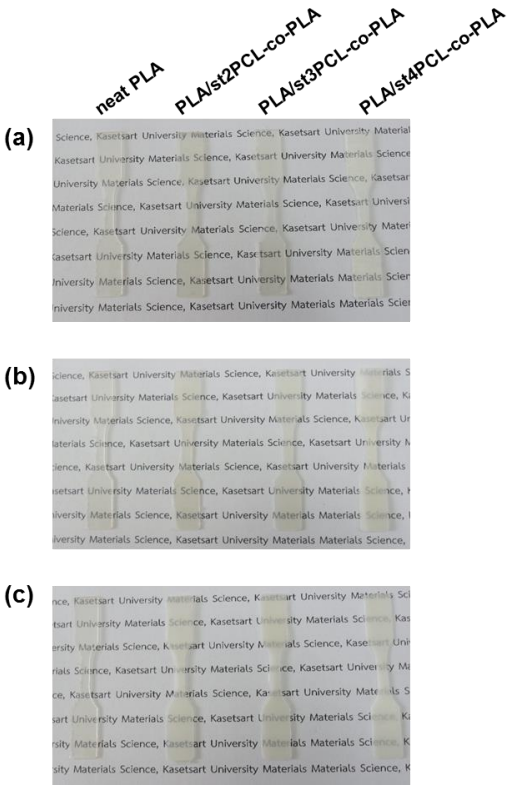

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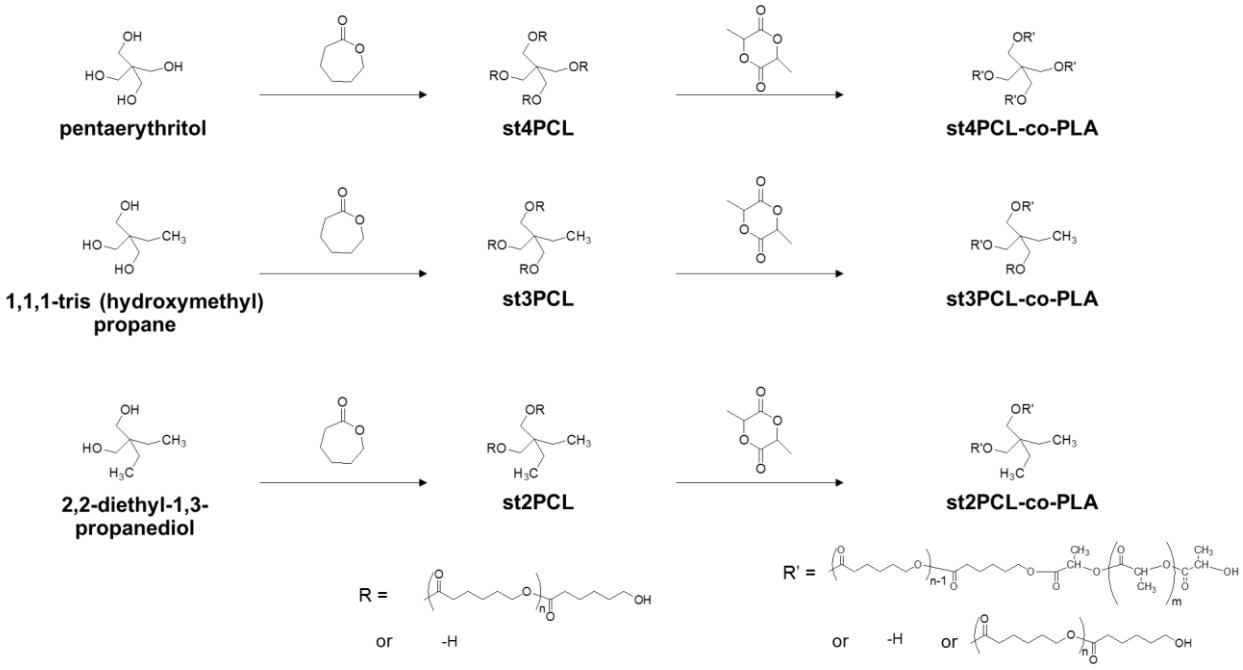

Scheme 1 Choochottiros C.