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Preliminary Study on the Preparation of Poly(D,L-Lactide/Propylene Glycol) Triblock and Cross-Linked Copolymers

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Abstract: This study aims to improve the properties of poly(D,L-lactide) (PDLLA)through copolymerization with poly(propylene glycol)(PPG) followed by cross-linking process. Cross-linked copolymer poly(D,L-lactide/propylene glycol) with strong and elastic properties wasobtained in two steps. First step wasthe synthesis of PDLLA-PPG-PDLLA triblock copolymer via melt polymerization method. The second step was the cross-linking process where the triblock copolymers reacted with hexametylenediisocyanate (HMDI) as chain extender and glycerol as cross-link agent. The formation of triblock copolymer was identified from the presence of a signal at 4.3 ppm in the^{1}H NMRspectrum which belongs to the PDLLA repeating unit bonded to PPG block.Gas Permeation Chromatography indicated an increase in the number average molecular number (M_n)of PPG from 4000g/mol to 4600g/mol (PDI = 1.52). The cross-linked copolymer was identified using Fourier-Transform infrared spectroscopy.Absorption at 1690cm^{-1} indicates the presence of urethane carbonyl group and supported the existence of urethane links. The product was also characterized by Scanning Electron Microscope (SEM). SEM micrograph showedthat the cross-linked copolymer contains macro pores, which is typical from reaction employing glycerol as the cross-linking agent.

Keywords: Cross-link; poly(D,L-lactide); poly(propylene glycol); triblock copolymer.

Introduction

Polylactide (PLA) is biodegradable thermoplastic aliphatic polyester derived from renewable sources such as corn starch, tapioca roots or sugarcane. PLA can decompose into lactic acid which is not harmful. Thus, PLA have been used in medical implants. Polymerization of racemic mixture of L- and D-lactides produces poly(D,L-lactide) (PDLLA). The formation of PDLLA into irregular polymer chains and contributes to its amorphous property[1].A lot of polymers which can decompose are rigid and not suitable in many applications, such as in clinical and packaging fields. Therefore, many studies have been carried out in improving the mechanical properties of polymers to expand their applications. Environmentally friendly elastomer was produced to satisfy different needs. Cross-link can be used to produce materials which can maintain the shape very well. High density of the cross-links tends to make materials stronger and gives rubbery properties. The cross-link term used in synthetic polymer field refers to the use of cross-link to encourage the changes in physical properties of polymers. For example, Han and Hubbell have reported the preparation of polylactide-based hydrogel to be used as support in tissue engineering[2]. Generally, cross-link improves mechanical properties especially at high temperatures. Cross-link can also cause lack of flexibility. The characteristic of cross-linked polymers varies depending on the degree of cross-links. The degree of cross-links influences the degree of swelling, pore size, surface area and mechanical strength of polymer[3].

In this study, triblock copolymer with poly(D,L-lactide) and poly(propylene glycol) was synthesized through the ring opening of D,L-lactide via melt polymerization, followed by cross-linking process. Cross-linked copolymer was synthesized by mixing the triblock with HMDI as the chain extender and glycerol as the cross-link agent. The resulting polymer with improved properties is reported in this paper.

Experimental

Materials:

D,L-lactide and poly(propylene glycol) (PPG) weresupplied by Sigma Aldrich (M) Sdn Bhd. The PPG used has a number average molecular weight, $M_n$of 4,000 g/mol. Glycerol which was used as cross-link agent was supplied by R&M Marketing, Essex, UK. Tin(II)2-etylhexanoate ($Sn(Oct)_2$) (~ 95 %) and 1,6-hexamethylene diisocyanate (HMDI) which actas catalyst and chain extender, respectively, were obtained from Sigma Aldrich (M) Sdn Bhd. Dichloromethane supplied from Classic Chemicals SdnBhd was the solvent used in this study.

Cross-linked copolymer was synthesized through two steps. The first step was the formation of triblock copolymer and the second step was the cross-linking process.

Synthesis of PDLLA-PPG-PDLLA triblock copolymer:

Triblock copolymer with two hydroxyl groups at the ends of the chain was synthesized through ring opening of D,L-lactidevia melt polymerization (Figure 1).D,L-lactide (12.08 g, 8.4×10^{-2}mol) and PPG (12.21 g, 3.0×10^{-3}mol) were added into the two necked flask. Then, the mixture was dried under vacuum for 1 h. After purging with nitrogen gas, $Sn(Oct)_2$catalyst (50 µL, 1.7×10^{-4}mol) was added into the flask using a micropipette. Magnetic bar was also introduced into the flask to help the mixing process. Nitrogen gas was supplied into the reactor for about one hour. The flask later was connected to the oil bubbler and the polymerization reaction was performed at a temperature of 120°C for 14 h.

Synthesis of PDLLA-PPG cross-linked copolymer:

Cross-linked copolymer was synthesized by mixing 1.0 g of triblock copolymer, 1.0 g of glycerol and 2.0 g of HMDI into the 50mL beaker with weight ratio of 50:50:100. $Sn(Oct_2)$ (0.05 g) was added into the beaker together with 5mL of dichloromethane. Then, the mixture was stirred for 5 min. until homogeneous. Finally,the mixture was poured into a mould and left overnight for excess solvent to dry. The reaction scheme is shown in Figure 2.

Characterization:

The characterization of triblock copolymer was carried out using^{1}H Nuclear Magnetic Resonance (^{1}H NMR) model JEOL JNM-ECP 400 (400 MHz). Approximately 30 mg of the sample was dissolved in 560 µL chloroform-*d*. The molecular weight of triblock was determined using Gas Permeation Chromatography (GPC)of model Waters 1515 Isocratic Pump with Waters 2424 refractive index detector by dissolving 30 mg of sample in 5 mL of tetrahydrofuran. The molecular weight values were compared against polystyrene standards. Meanwhile, the cross-linked copolymer was characterized by ATR-FTIR Spectrum 400 Perkin Elmer GX Spectrometer. The prepared samples were analyzed with infrared ranged from the frequency of 4000 to 650 cm^{-1}.The surface of the cross-linked copolymer was observed using Scanning Electron Microscope (SEM) model Leo 1450VP SEM.

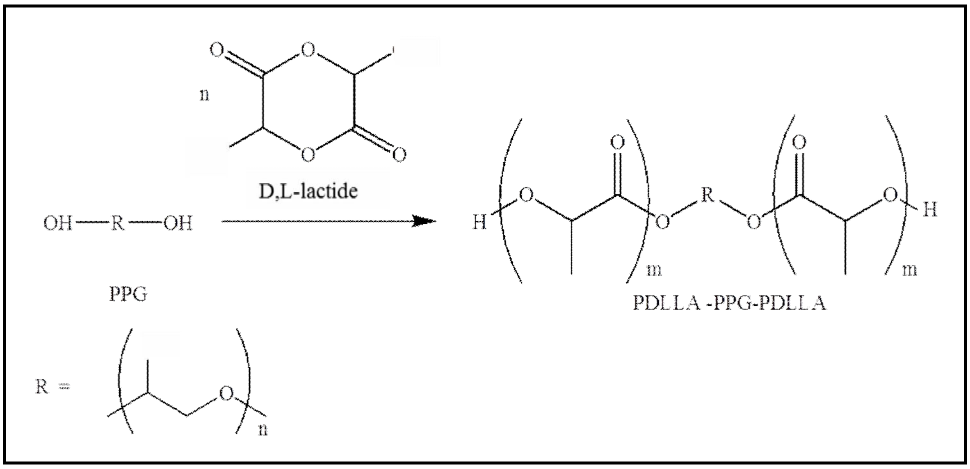

Figure 1:Ring opening polymerization of lactide

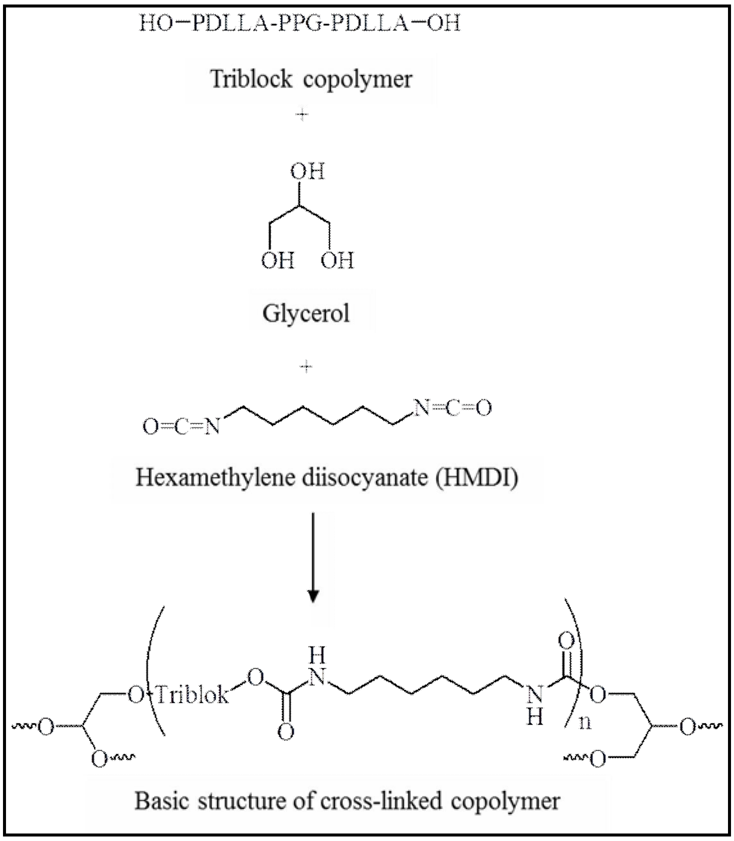

Figure 2: Cross-linking process of the triblock copolymer

Results and Discussion

Synthesis of PDLLA-PPG-PDLLA triblock copolymer:

The melt ring-opening polymerization of D,L-lactide initiated by the two hydroxyl terminals of PPG with the presence of $Sn(Oct)_2$ catalyst has not yet been reported. However, analogous reactions employing various other soft polymers such as poly(ethylene glycol) and polydimethylsiloxane as the initiator have been widely reported[4,5,6].PPG of M_n 4,000 g/mol was used. The molecular weight of PDLLA blocks was controlled by using the appropriate mol ratio of D,L-lactide. For this preliminary study, PDLLA-PPG-PDLLA with theoretical segmental M_n of 2,000-4,000-2,000 (50 % PDLLA, 50 % PPG) was synthesized. The resulting product was sticky and highly viscous. The triblock copolymer was characterized using ^{1}H NMR, GPC and FTIR.

Characterization by ^{1}H NMR:

NMR spectroscopy was used to determine the structure of the triblock copolymer and its number average molecular weight. The ^{1}H NMR spectrum of the triblock copolymer is shown in Figure 3. The signal at chemical shift of5.1-5.2ppmbelongs to the methyneprotonin the PDLLA repeating units ($H_b$and$H_{b'}$) and suggests triblock copolymer formation. There was asmall signalat4.3ppm, which refers to themethyne proton of terminal lactyl unit ($H_a$and$H_{a'}$) adjacent to hydroxyl ends of the triblock. The signals around chemical shifts of 3.5and 3.4 ppm belong to the protons of methylene (H_c) and methyne(H_d) group of PPG segment, respectively. There was also asignalaround1.5-1.6ppm ($H_e$and $H_{e'}$), which refers to methylprotons ofPDLLA segment. The signal slightly overlaps with another signal at 1.4-1.5 ppm that can be assigned to the methylprotons of PDLLA terminallactyl unit (H_f and $H_{f'}$). The signalat1.1ppmchemical shift belongs to the methylprotons of PPG segment(H_g).

The M_n of the triblock copolymer can be calculated using NMR by comparing the intensity of signals at 5.1-5.2 ppm (H_b and $H_{b'}$) and 1.1 ppm (H_g). The combined M_n of two PDLLA blocks was calculated as 4250 g/mol, which gives a total M_n value of 8,250 g/mol (^{1}H NMR) for the synthesized PDLLA-PPG-PDLLA triblock copolymer.

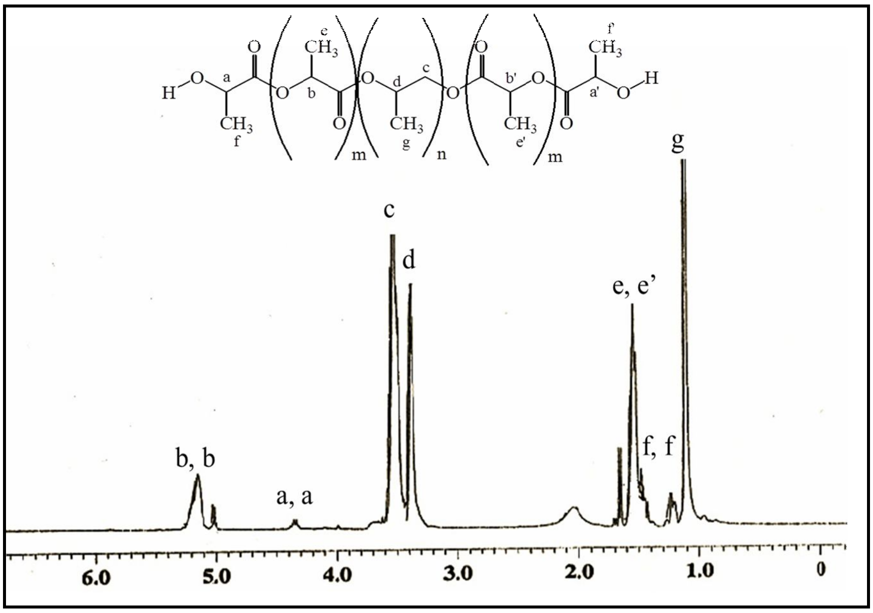

Figure 3: NMR spectrum of triblock copolymer

Characterization by GPC:

The number average molecular weight, $M_n$of triblock copolymer recorded by GPC was 4,600 g/mol while the weight average molecular weight, M_w was 7,000 g/mol. This showed that the PPG initiator(M_n 4,000)experienced an increase of length to form triblock copolymer. The value of polydispersion index (PDI) was 1.5, indicating that living polymerization has occurred. Living polymerization is a form of growth of the polymer chain which termination step does not exist[7,8].

Synthesis of PDLLA-PPG cross-linked copolymer:

Cross-linking of PDLLA-PPG-PDLLA was carried out using glycerol as cross-linker and HMDI as chain extender. The hydroxyl ends from the triblock copolymer and glycerol react with isocyanate group from HMDI to form urethane links and subsequently forming a large cross-linked network. The product obtained was strong, elastic and insoluble in all solvents tested, indicating that the cross-linking was successful. However, it can be observed that the cross-linked copolymer contained significant-sized pores. This is due to the stirring process during the mixing of reactants, as well as the use of dichloromethane that acts as blowing agent. The cross-linked copolymer was analysed using FTIR and SEM.

Characterization by FTIR:

The FTIR spectra of triblock copolymer (Figure 4) and cross-linked copolymer (Figure 5) were compared. The stretching of OH group at the end of the triblock copolymer was observed at 3500cm^{-1}. There was a strong absorption produced at 1000cm^{-1} which indicates the stretching of C-O bond. Cross-linked copolymer has been identified by the absorption at 3320 cm^{-1} which indicates the NH stretching of urethane group. The bending of NH bond can be seen at 1500cm^{-1}. The observation of strong band at 1600cm^{-1} represents the carbonyl of urethane group. This analysis showed that the reaction between OH group and N=C=O had beena success.

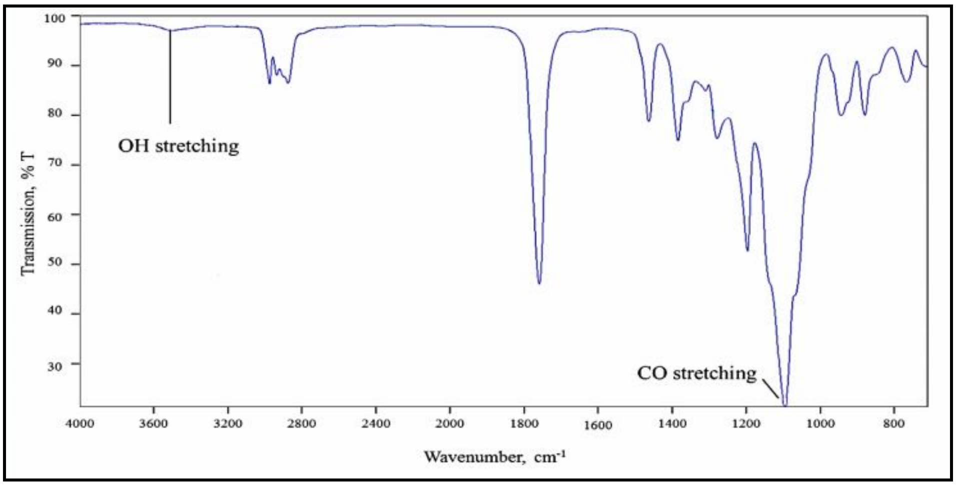

Figure 4: FTIR spectrum of PDLLA-PPG-PDLLA triblock copolymer

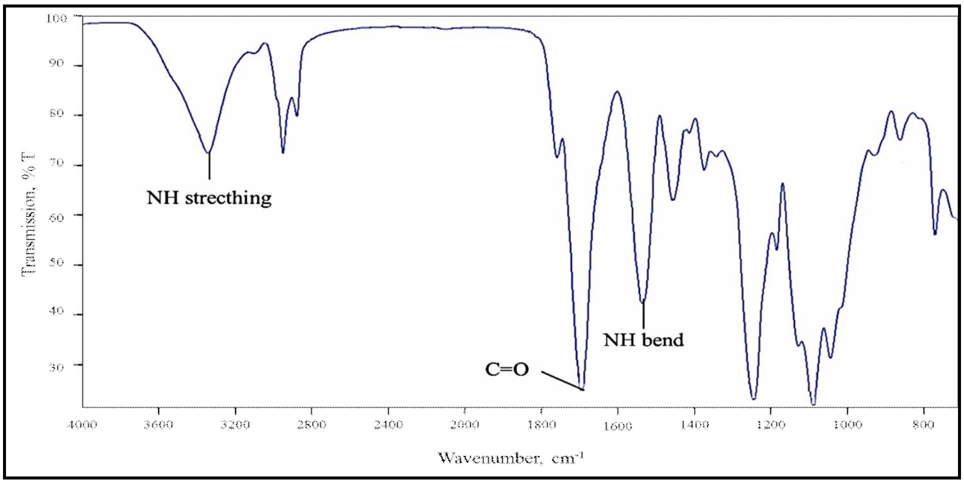

Figure 5: FTIR spectrum of cross-linked copolymer

Characterization by SEM:

The SEM micrograph of cross-linked copolymer was shown in Figure6.The formation of macro pores can be seen in Figure6(a). Dichloromethane was used as the solvent for the cross-linking reaction. After the mixing process, the mixture was left to cure and for the dichloromethane to evaporate. The two processes occurred simultaneously, resulting in the trapping of dichloromethane and formation of the macro pores when dichloromethane evaporates. Overall, the surface of the sample was smooth, indicating homogeneity of polymers. Moreover, no crystal formation was seen because the polymer formed was amorphous.

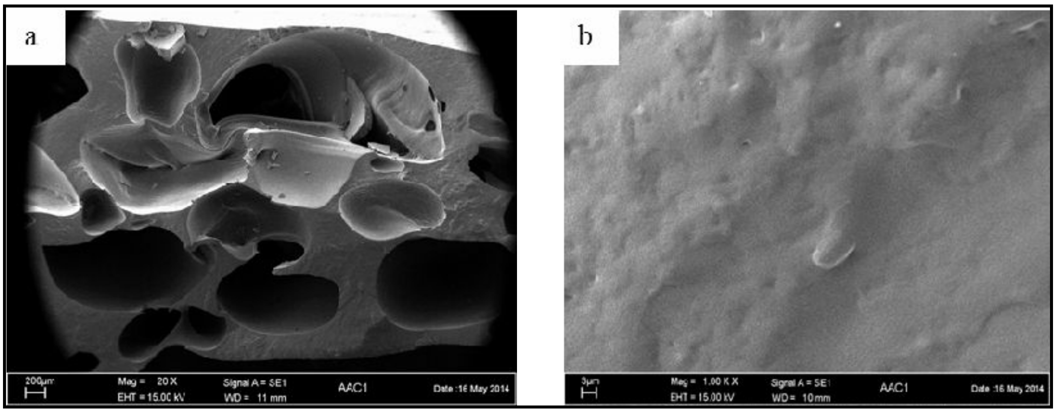

Figure6: SEM micrograph of (a) macro pores and (b) smooth surface of the PDLLA-PPG cross-linked copolymer

Conclusion

Triblock and cross-linked poly(D,L-lactide/propylene glycol) copolymer were successfully synthesised. The properties of poly(D,L-lactide) improved after the copolymerization with poly(propylene glycol) and cross-linking process. The appearance changed from sticky and highly viscous triblock into elastic and tough cross-linked copolymer. Some experimental parameters for the cross-linking process still need to be optimised in order to control the pore size and density of the resulting copolymer. It would also be interesting to explore the variation in the properties of the cross-linked copolymer when compositions of PDLLA and PPG are used.

Acknowledgements

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