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Preparation and compatibilization effect of β -cyclodextrin end-functionalized polystyrene for immiscible PCL/PS blends

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ABSTRACT

The compatibilizing effect of β -cyclodextrin end-functionalized polystyrene (β -CD-PS) on immiscible PCL/PS blends has been studied using 2D NOESY NMR and DSC techniques. The β -CD-PS was obtained via copper(I)-catalyzed azide-alkyne click reaction (CuAAC) of mono azide functional β -CD (β -CD-N₃) and low molecular weight PS as a compatibilizer. The preparation of inclusion complexes based on β -CD and PCL (equimolar ratio) was investigated, aiming to reduce the interfaces of PCL and PS and compatibilizer the immiscible PCL/PS mixture. Compatibilization was visually observed when turbid PCL/PS solutions became clear upon heating and extended stirring. Several solutions were prepared with PCL/PS contents ranging from 100/0, 70/30, 50/50, and 30/70 (wt%) with β -CD-PS contents (equivalent to PCL moles) by solution casting technique. The 30/70 PCL/PS blend containing stoichiometric 1:1 inclusion complex of β -CD and PCL showed significant changes in DSC analysis. Moreover, 2-fold and 4-fold β -CD-PS (stoichiometric 2:1 and 4:1 β -CD:PCL) were tested to 50/50 PCL/PS blends to observe the amount of compatibilizer for obtaining good miscibility.

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I. INTRODUCTION

Polymer blends have been used as a cost-effective, high-performance polymeric material and have become an essential science topic. Polymer blends are physical combinations of two or more polymers to form a new material with different physical properties. In these mixtures, most polymers do not mix homogeneously with each other and undergo phase separation [1, 2]. Compatibilizers can be used in the blending and stabilization of immiscible polymers. Compatibilizers create a homogeneous mixture by decreasing the interfacial tension in the mixture and increasing the adhesion between the two homopolymer phases. The compatibilizer is a block copolymer or graft copolymer of the monomers that make up the mixture. When such compatibilizers are used, one of the components is soluble in the co-solvent, and the other is insoluble and plays a surfactant-like role [3-5]. Polymer blends are generally prepared in two ways. The first way is the solvent-casting method, which is a method that is easily applied in the laboratory. According to this method, after the polymers are dissolved in a solvent in which both are soluble, they are mixed, the solvent evaporates, and the mixture is obtained as a film. The second method is the melt mixing method, usually done in extruders. In this method, all components are mixed by heating above their glass transition temperature (T_g) [6, 7].

Polystyrene (PS) is a standard thermoplastic polymer with atactic, amorphous, inexpensive, stiff, easily shaped, and good electrical and moisture resistance. Due to the benzene ring in its structure, its T_g is in the range of 90-100 °C. Due to this T_g value and its amorphous structure, it is considered a challenging and transparent material at

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room temperature. Above the softening temperature, it readily melts and is susceptible to processing by injection molding or extrusion [8, 9]. Polycaprolactone (PCL) is a hydrophobic and semi-crystalline biodegradable polyester. Its melting point is around 60 °C, and its glass transition temperature is around -60 °C. It is easily shaped and shows high mechanical strength [10, 11]. Kim et al. investigated the thermal and rheological properties of PCL/PS mixtures using differential scanning calorimetry and scanning electron microscopy. They explained that when low molecular weight PS is used in the mixture, the mixture is partially soluble in each other, and when high molecular weight PS is used, the mixture does not dissolve in each other [12]. Numerous combinations of immiscible PCL/PS mixtures have been made and investigated in the literature, focusing on their phase separation and separation morphology. These studies generally examined how the PS blocks are arranged within the crystal structure of PCL at low or high critical solution temperatures. By varying the composition of the mixture, the film's thickness (if applicable), the polydispersity of PS, and the molecular weight, researchers observed changes in the phase separation and surface morphology of the formed mixtures [13-16]. Ho et al. have proposed an exciting way to make PCL/PS blend as miscible blends. They said PCL mixed homogeneously when melted with PS-*b*-polyethylenepropylene (PEP) copolymer, not PS. Polarized light microscopy, transmission electron microscopy, and small-angle X-ray scattering were employed to study the morphology of the PCL/PS-PEP mixture [17].

Cyclodextrins (CDs) are a group of cyclic oligosaccharides comprising six to eight glucose units connected by glycosidic bonds. They are specified as α -, β -, and γ -CD, correspondingly. CDs exhibit a truncated cone shape, with primary hydroxyl groups on the narrower side and secondary hydroxyl groups on the wider side. It is known that these compounds form inclusion complexes with many molecules [18-20]. Harada et al. investigated for the first time the inclusion complex formation of polydimethylsiloxane (PDMS) with α -CD, β -CD, and γ -CD. As a result of the study, PDMS was observed to form complexes with β -CD and γ -CD, whereas no complexation occurred with α -CD. They explained that such complexes would create a new way to obtain new organic and inorganic materials and functional supramolecular structures [21]. The same working group investigated the formation of inclusion complexes with α -CD, β -CD, and γ -CD for polycaprolactone (PCL) and found that complex with β -CD in moderate yield [22]. Some papers proposed new types of compatibilizers based on CD-based polymers to form inclusion complexes [23-25]. For instance, Balik et al. used star polymers containing γ -CD core and PS arms as compatibilizers in the chloroform solution of PS/PDMS. Compatibilization was observed with the turbid solution becoming clear as CD-star was added. The coupling mechanism explained that the CD core complexed with PDMS, and the resulting complex increased its solubility with PS in the CD-star polymer. Thus, insoluble PDMS blocks were transformed into smaller, more stable micelles. 2D ROESY NMR demonstrated the complexation of the CD core with PDMS. To explore the impact of compatibilization, modifications were made to the PDMS molecular weight, concentration, and CD-star concentration, aiming to examine their effects [26].

Herein, we synthesized β -CD end-functionalized PS (β -CD-PS) to use it as a compatibilizer for immiscible PCL/PS blends. The 1:1 inclusion complexation was driven by β -CD and PCL by host-guest interaction and confirmed by 2D NOESY NMR. The miscibility behavior of resultant β -CD/PCL complexation occurring in PCL/PS blends reduced the interphase of polymers. This paper used morphological and thermal measurements and visual analysis to investigate the miscibility of PCL/PS blends.

II. EXPERIMENTAL METHOD

2.1 Materials

Polystyrene (PS) (average $M_n=35.000$ g/mol) and polycaprolactone (PCL) (average $M_n=45.000$ g/mol) homopolymers were purchased from Aldrich. β -cyclodextrin ($\geq 97\%$, Aldrich), tetrabutylammonium fluoride (TBAF, 1 M in THF, Aldrich), and CuBr (99.9%, Aldrich) were used as received. N,N,N',N'',N''' -pentamethyldiethylenetriamine (PMDETA, Aldrich) was distilled over NaOH prior to use. Dichloromethane (CH_2Cl_2) was purchased from Aldrich and used after distillation over P_2O_5 . Tetrahydrofuran (THF; 99.8%, J.T. Baker) and N,N -dimethylformamide (DMF, 99.8%, Aldrich) were all purchased from Aldrich and used as received. The mono-6-deoxy-6-azido- β -cyclodextrin (β -CD- N_3) was synthesized according to our previously published procedure [27]. 3-(Trimethylsilyl)prop-2-ynyl 2-bromo-2-methylpropanoate and α -silyl protected alkyne polystyrene (α -silyl-alkyne-PS) were prepared according to literature procedures [28].

2.2 Instrumentation

^1H NMR measurements at a frequency of 500 MHz were conducted using CDCl_3 as the solvent and $\text{Si}(\text{CH}_3)_4$ as the internal standard, employing an Agilent VNMRS 500 instrument. 2D NOESY measurement was performed on an Agilent VNMRS 500 instrument in DMSO-d_6 as the solvent. Conventional gel permeation chromatography (GPC) measurements were performed using an Agilent instrument (Model 1100) equipped with a pump, refractive index (RI), and ultraviolet (UV) detectors. The GPC system utilized a series of four Waters Styragel columns (guard, HR 5E, HR 4E, HR 3, HR 2) with dimensions of 4.6 mm internal diameter and 300 mm length, packed with 5 μm particles. The effective molecular weight ranges for the columns were 2000-4,000,000, 50-100,000, 500-30,000, and 500-20,000, respectively. Elution was carried out using THF as the mobile phase at a flow rate of 0.3 mL/min at 30 $^\circ\text{C}$, while toluene was employed as the internal standard. FT-IR spectra were obtained with an Agilent Technologies Cary 630 FTIR instrument over the range of 4000–500 cm^{-1} . DSC scans were carried out by using a Seiko DSC-7020 under a nitrogen atmosphere as the purge gas. The samples were heated from 25 $^\circ\text{C}$ to 300 $^\circ\text{C}$ (heating rate: 10 $^\circ\text{C}/\text{min}$) with a weight of about 3-5 mg. Optical microscope micrographs were taken by using YAMER at 10X magnification.

2.3 Preparation of Compatibilizer

2.3.1 Hydrolysis of α -silyl protected alkyne polystyrene (α -Silyl-Alkyne-PS) and preparation of alkyne-end functionalized PS (Alkyne-PS)

The protective silyl group of α -silyl-alkyne-PS (1.5 g, 0.75 mmol, $M_{n,\text{theo}}=2000$ g/mol) was removed using TBAF (1.1 mL, 3.75 mmol) dissolved in THF (20 mL). The reaction mixture was stirred at room temperature for 2 hours, followed by concentration under reduced pressure and precipitation in methanol. The resulting polymer was then dried under a vacuum at 40 $^\circ\text{C}$ for 24 hours. The ^1H NMR analysis (in CDCl_3 , δ) revealed peaks at 7.5–6.5 (ArH), 4.4 (CHBr), 4.1 (C[equiv]CCH₂O), and 2.0–0.9 (CH₂ and CH).

2.3.2 CuAAC click reaction of Alkyne-PS with β -CD- N_3 (β -CD-PS)

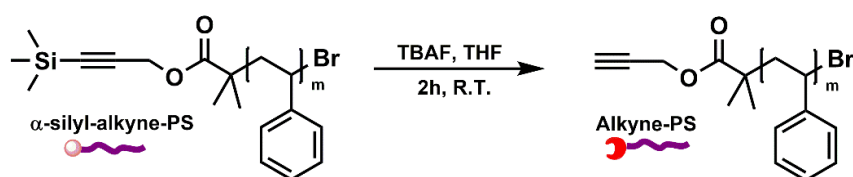
In a Schlenk tube containing a magnetic stirring bar, Alkyne-PS (1.3 g, 0.67 mmol, $M_{n,theo} = 1930$ g/mol) and β -CD- N_3 (1.16 g, 1.00 mmol) were dissolved in DMF (10 mL). To ensure protection from air, CuBr (0.143 g, 1.00 mmol) and PMDETA (195.0 μ L, 1.00 mmol) were added under a nitrogen flow. The reaction tube was degassed by three cycles of degassing using FPT (freeze-pump-thaw) method and was then placed in an oil bath set to a constant temperature of 60 °C for a period of 2 days. When the reaction was completed, it was dissolved in CH_2Cl_2 (no need to remove the DMF) and passed through an alumina column to eliminate copper catalysts. Next, the mixture was evaporated until completely dry, and then redissolved in CH_2Cl_2 , and precipitated in methanol. The blueish solid was subjected to washing with (10 mL x 2) and methanol (10 mL) to remove any excess β -CD- N_3 . Finally, the white precipitate was dried in a vacuum oven at 40 °C for 24 hours. Yield = 1.48 g (74 %). The 1H NMR spectrum (in $CDCl_3$, δ) displayed peaks at 7.79 (br, CH of triazole), 7.4–6.4 (ArH), 5.70 (br, 14H, OH-2,3), 5.01-4.83 (m, 6H, H-1), 4.55-4.48 (br, 6H, OH-6), 3.76-3.50 (br, 28H, H-3,5,6,6'), 3.49-3.23 (br, 14H, H-2,4 overlapping with H_2O), 2.0–1.1 (CH_2 and CH).

2.4 Preparation of Solution-Cast Films

Solutions containing PS (average $M_n = 35,000$ g/mol) and PCL (average $M_n = 45,000$ g/mol) both with and without β -CD-PS were prepared at a total solids concentration of 20% (w/v) in THF/DMF (4:1) mixture. The solutions were vigorously stirred using a Teflon-coated magnetic stir bar in an appropriately sized beaker, and the beaker was covered to minimize solvent evaporation. The magnetic stirring was conducted at 60 °C and 350 rpm for 1 day. Solution casting was performed in a glass petri dish. To establish controlled evaporation, a glass dish was placed over the films and sealed along the edges using a paper towel to prevent solvent evaporation and eliminate bubble formation. After controlled evaporation, the films were first dried in a fume hood for up to a week, followed by additional drying in a vacuum oven at 40°C for one day.

III. RESULTS AND DISCUSSIONS

To begin with, we synthesized and characterized the β -CD-PS to investigate its miscibility behavior in immiscible PCL/PS blends. Mono azide functional β -cyclodextrin (β -CD- N_3) was prepared according to our previously published paper [26]. The preparation of silyl protected polystyrene (α -silyl-alkyne-PS) was well described by Durmaz [27] and the same route was adopted to synthesize α -silyl-alkyne-PS via atom transfer radical polymerization (ATRP). Subsequently, the deprotection of α -silyl-alkyne-PS was successfully achieved using TBAF, resulting in the formation of the corresponding alkyne-PS as outlined in Scheme 1.



Scheme 1. Synthetic pathway for the deprotection of trimethyl silyl group ($(CH_3)_3Si-$).

The absence of the signal at 0.18 ppm, attributed to $(\text{CH}_3)_3\text{Si}$ -, provided confirmation of the structure of alkyne-PS, as depicted in Figure 1.

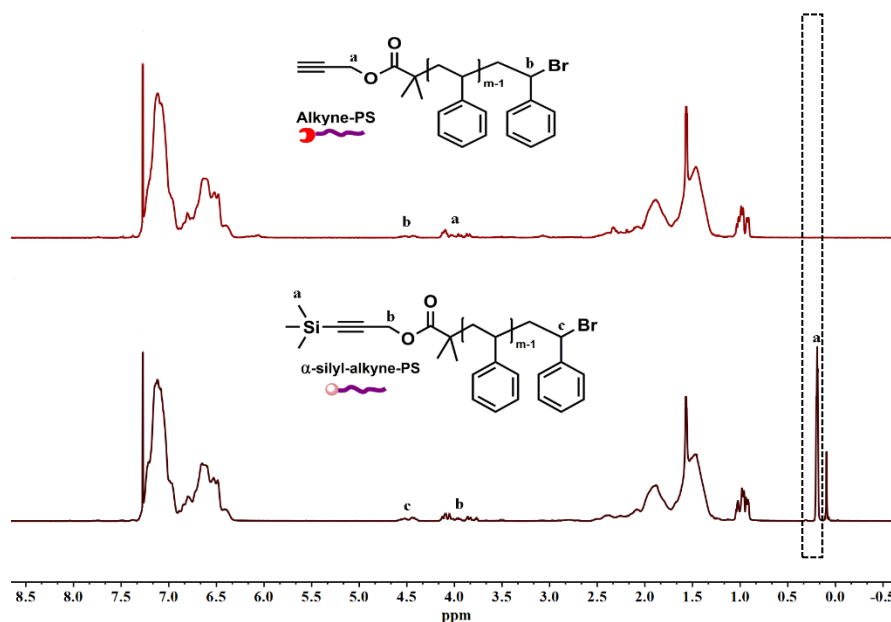


Figure 1. ^1H NMR spectra of α -silyl-alkyne-PS (bottom spectra) and alkyne-PS (upper spectra) in CDCl_3 .

A single-peaked GPC trace and a low-molecular-weight distribution were observed for α -silyl-alkyne-PS and alkyne-PS, which aligned with the theoretical molecular weight ($M_{n,\text{theo}}$) values as presented in Table 1.

Table 1. The results of polymers used in the synthesis of compatibilizer

| Polymer | $M_{n,\text{GPC}}^b$ (g/mol) | $M_{w,\text{GPC}}^b$ (g/mol) | M_w/M_n | $M_{n,\text{theo}}^c$ (g/mol) |
|--|---------------------------------|---------------------------------|-----------|----------------------------------|
| α-Silyl-Alkyne-PS^a | 2080 | 2310 | 1.11 | 2000 ^e |
| Alkyne-PS | 1450 | 1970 | 1.35 | 1930 ^d |
| β-CD-PS | 3060 | 4980 | 1.62 | 3090 ^e |

^a $[\text{M}]_0:[\text{I}]_0:[\text{CuBr}]:[\text{PMDETA}] = 200:1:1:1$; polymerization process was conducted at a temperature of 110 °C.

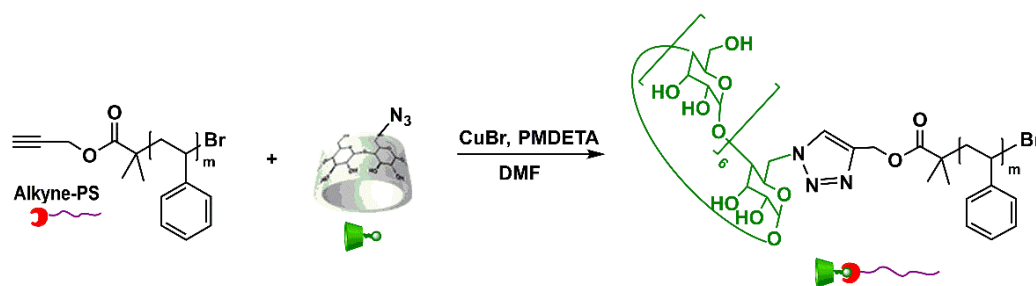
^b Determined through conventional GPC, calibrated with respect to linear PS standards in THF at 30 °C.

^c $M_{n,\text{theo}} = ([\text{M}]_0/[\text{I}]_0) \times \text{conversion \%} \times \text{molecular weight (MW) of monomer} + \text{MW of initiator}$.

^d $M_{n,\text{theo}} = M_{n,\text{theo}}$ of α -silyl-alkyne-PS (2000) – M_w of trimethyl silyl group.

^e $M_{n,\text{theo}} = \text{sum of ESI-MS of } \beta\text{-CD-N}_3 \text{ (1160 g/mol) and } M_{n,\text{theo}} \text{ of the alkyne-PS}$.

As a compatibilizer, β -CD-PS is simply prepared from copper(I) catalyzed azide-alkyne click reaction (CuAAC) of alkyne-PS with β -CD- N_3 concurrently in the CuBr/PMDETA in DMF at 60 °C for two days (Scheme 2). 1.5 equiv. of β -CD- N_3 to that of alkyne-PS was used in the reaction. Again, unreacted β -CD- N_3 was eliminated from the reaction mixture by employing a dissolution-precipitation method and washing with water and methanol, respectively.



Scheme 2. Synthetic route for the synthesis of β -CD-PS as a compatibilizer

The synthesized β -CD-PS was subjected to characterization using ^1H NMR and GPC techniques. In the ^1H NMR spectrum, distinctive signals corresponding to the PS and β -CD segments were observed at 7.4–6.4 (ArH) and 5.70–3.23 ppm (methylene protons and hydroxyl groups of the β -CD ring). The peak at 7.79 ppm was attributed to the proton of the 1,2,3-triazole ring. The integration ratio of these peaks, compared to the aromatic hydrogen protons of PS at 7.4–6.4 ppm and 1-positioned CH peaks of β -CD at 5.01–4.83 ppm, was found to be 16.86:1. This ratio indicates a high click efficiency (74%) in the formation of β -CD-PEG, as determined using the theoretical molecular weight ($M_{n,\text{theo}}$) value of alkyne PS for the calculation (Figure 2).

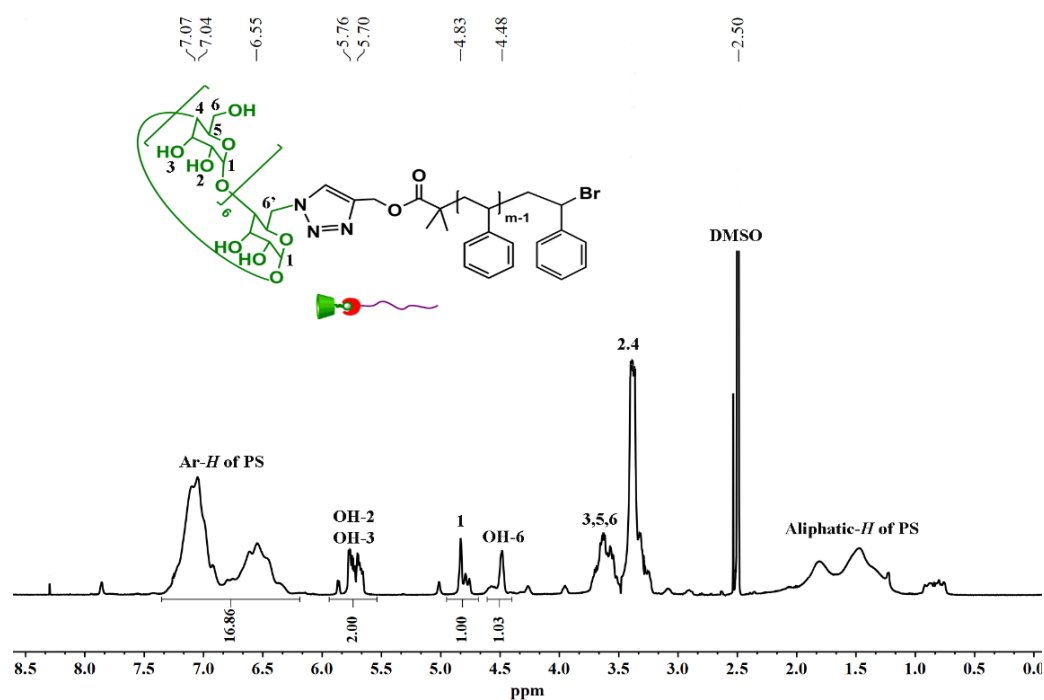


Figure 2. ^1H NMR spectrum of β -CD-PS in DMSO-d_6 at room temperature

GPC measurement was taken to see the change in molecular weight after the click reaction (Figure 3). According to GPC, M_n : 3060 g/mol (PDI: 1.62) was found, as listed in Table 1. The β -CD-PS exhibited a noticeable shift towards the higher molecular weight region; however, a necked chromatogram was obtained. It is more appropriate

to use DMF instead of THF in the analysis of such CD-based polymers. THF may not have shown steady flow through the column because it is not a suitable solvent for CDs.

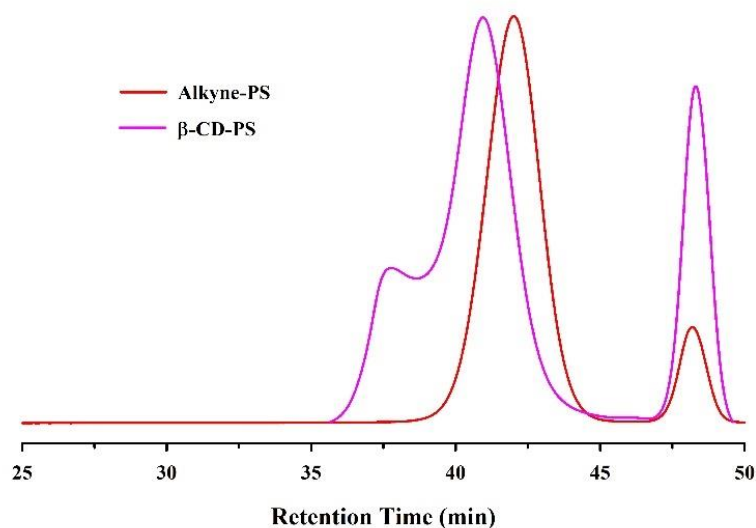


Figure 3. Evaluation of GPC traces of alkyne-PS and β -CD-PS, monitored using an RI detector in THF at 30 °C

Additionally, the efficiency of the click reaction was confirmed using FT-IR spectroscopy. From the FT-IR spectra taken before and after the CuAAC click reaction, it is seen that the azide peak of β -CD- N_3 (2100 cm^{-1}) disappeared after the click reaction (Figure 4). These FT-IR findings further prove the successful click reaction and the complete removal of the excess β -CD- N_3 .

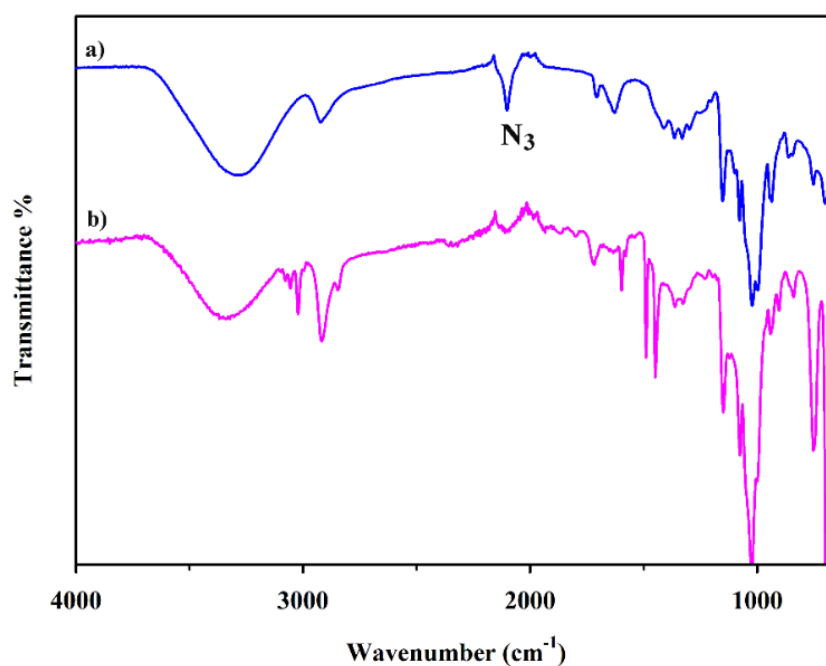


Figure 4. FT-IR spectra of β -CD- N_3 (blue) (a) and β -CD-PS (pink) (b)

Several solutions were prepared with PCL/PS contents ranging from 100/0, 70/30, 50/50, and 30/70 (wt%) with β -CD-PS contents (equivalent to PCL moles). Table 2 shows the compositions of PCL/PS blends with the compatibilizer (β -CD-PS) used in this work. The total solids concentration was 20% (w/v) in THF/DMF (4:1) mixture. The amount of β -CD-PS in the blends excludes the total mass of the PCL/PS amounts.

The compatibilizing effect of adding β -CD-PS to solutions of PCL and PS in the THF/DMF mixture can be seen in Figure 5. PCL and PLA were solubilized in THF (in different glass containers) and kept under stirring (350 rpm) and once completely dissolved, both solutions were mixed, and β -CD-PS in DMF was added by droplets during stirring. The blends with different compositions were carried out by magnetic stirring at 60 °C for one day. Upon preparation, all solutions exhibited turbidity; however, they gradually became clear (indicating compatibility) after being stirred for one day at 60 °C, as depicted in Figure 5.

Table 2. Composition of blends initially containing various amounts of β -CD-PS (equal moles of PCL to β -CD-PS)

| Composition of PCL/PS | β -CD-PS (mg) | PCL (g) | PS (g) |
|-----------------------|---------------------|---------|--------|
| 100/0 | 68.6 | 1.0 | - |
| 70/30 | 48.1 | 0.7 | 0.3 |
| 50/50 | 34.3 | 0.5 | 0.5 |
| 30/70 | 20.6 | 0.3 | 0.7 |

Polymer blends were performed in a glass petri dish by a solvent-cast technique. To control the evaporation process, the solutions were subjected to a controlled two-day evaporation by covering the films with a glass dish, which was sealed along the edges using a paper towel to slow down solvent evaporation and prevent bubble formation. Subsequently, the films were dried in a fume hood for a period of up to one week, followed by an additional drying step in a vacuum oven at 40 °C for one day. Photographs are shown in Figure 6 of the appearance of a polymer blend with and without β -CD-PS. As is easily observed, polymer blends without compatibilizers are white and opaque, and polymer blends with compatibilizers are yellowish and transparent. In addition, all blends which contain more PS are brittle and breakable. However, all blends which contain more PCL are flexible and easily removable from glass Petri dishes. The observed characteristics of the films suggest variations in their morphology.

The presence of an inclusion complex between β -CD and PCL was verified using 2D NOESY NMR, a technique commonly employed by researchers to investigate localized interactions within cyclodextrins. Figure 7 shows the 2D NOESY NMR spectrum of the 1:1 mixture of PCL and β -CD-PS, obtained using the same solution preparation steps to confirm the formation of the inclusion complex. The hydrophobic PCL block has gone through the hydrophobic cavity of β -CD to yield an inclusion compound. In this particular sample, the concentration of PCL and β -CD-PS is relatively low, leading to weak interactions between them, evident in the rectangular region of Figure 7a. Upon magnification of this region in Figure 7b, the proton signals of β -CD-PS can be discerned above the noise and exhibit cross-peaks with the methyl groups of PCL. Notably, cross-peaks arise from dipolar interactions between the signals at 4.5-5.9 ppm, assigned to protons located in the cavities of β -CD (such as C2, C3 secondary hydroxyl group, primary C6 hydroxyl group, and 1-H protons), and the signals at 3.8-3.5 ppm,

attributed to methylene protons adjacent to oxygen atoms on PCL. These cross-peaks confirm that methyl groups have been deeply embedded in the cavities of β -CD via host-guest interactions.

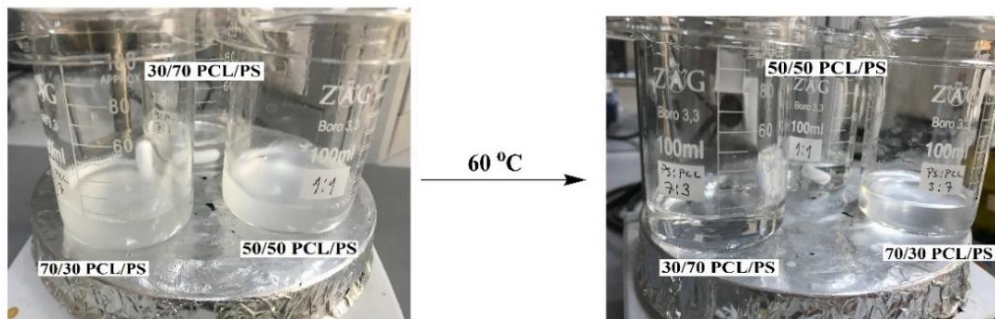


Figure 5. Three different solutions of PCL and PS in THF: DMF mixture with β -CD-PS before and after stirring at 60 °C for 1 day

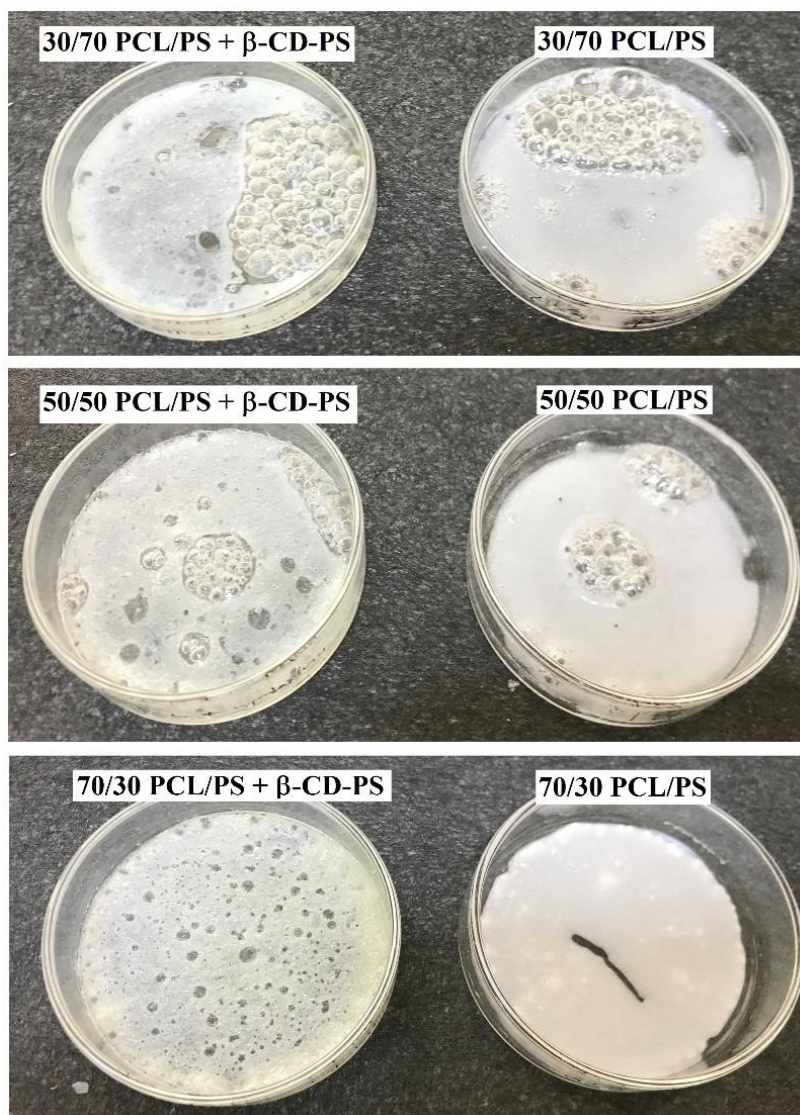


Figure 6. The appearance of solvent-cast films prepared with different ratios of PCL/PS with and without compatibilizer

Figure 8 presents the DSC thermograms of the individual components that constitute the solution-cast films. The homopolymer PCL (average $M_n=45.000$ g/mol) used in these samples shows a sharp melting point (T_m) 60.2 °C. The homopolymer PS (average $M_n=35.000$ g/mol) exhibits T_g of 17.9 and T_m 66.6 °C. The DSC analysis of β -CD-PS shows no distinctive features except for the T_g associated with the PS arms at 17.8 °C.

While the literature reports [5] the T_g of PCL to be around -61.5 °C, we did not measure the T_g of PCL in this particular experiment. Therefore, no crystallization peak associated with PCL is observed in our findings.

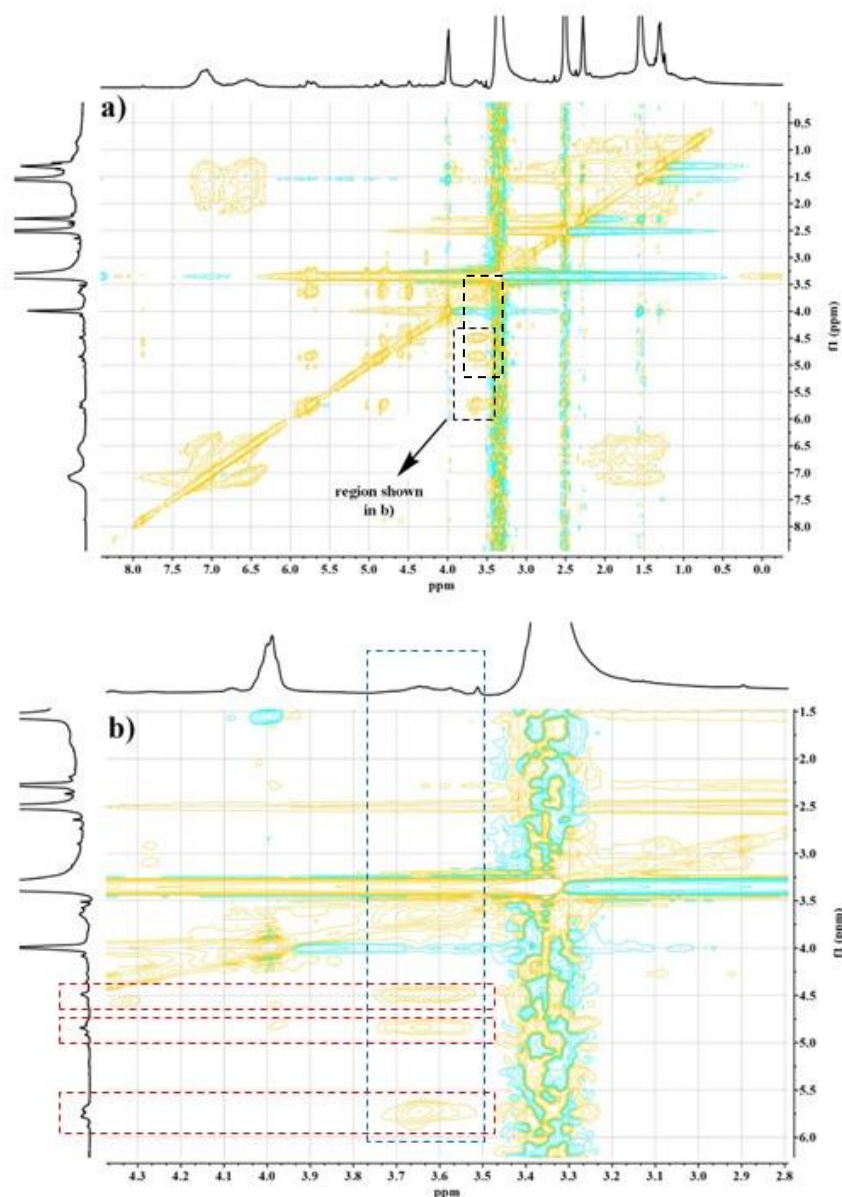


Figure 7. a) 2D NOESY NMR spectrum of 1:1 mol/mol of PCL/ β -CD-PS solutions in DMSO- d_6 at room temperature, b) Magnified view of the rectangular circle in a)

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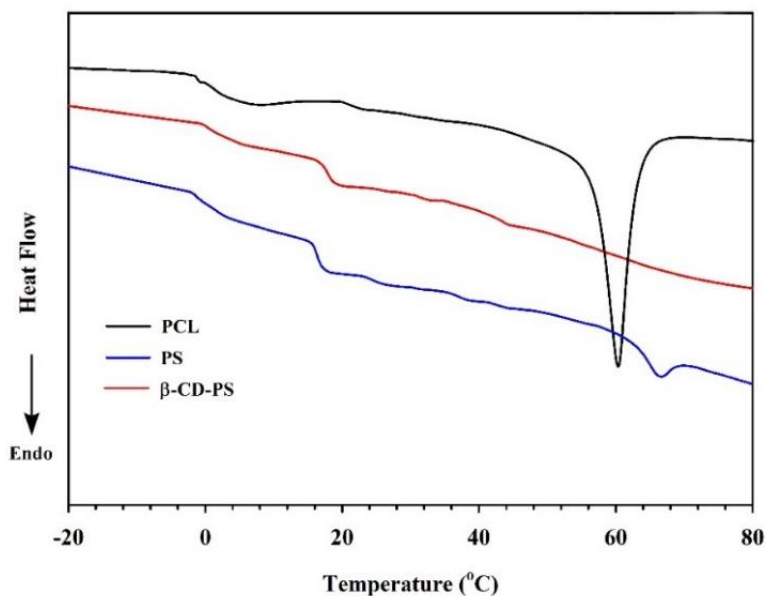


Figure 8. DSC thermograms of the constituent elements comprising the solution-cast films are depicted, with the curves being vertically displaced for better visibility

DSC scans of a series of PCL/PS (30/70, 50/50, and 70/30) blends with and without various amounts of β -CD-PS are shown in Figure 9. A significant change in the T_g value was observed for the 30/70 PCL/PS blend. The T_g of the 30/70 PCL/PS blend shifted to 21 °C and 30.5 °C (with β -CD-PS) (left graph (2)) from 18.8 °C (without β -CD-PS) (left graph (1)). In addition, in another series of PCL/PS blends, the T_g values were slightly changed. T_m s of PCL were observed to undergo slight alterations in the presence of β -CD-PS. This may be attributed to forming a crystalline structure that differs from the previous system. Figure 9, the right graph, shows the results of the cooling cycle from DSC analysis for all samples. The PCL crystallization of the β -CD-PS containing 30/70 PCL/PS blend significantly declined to 14 °C from 24.6 °C with an exothermic peak. It is possible to conclude that adding β -CD-PS as a compatibilizer causes changes in some of the thermal properties of the 30/70 PCL/PS blend. Specifically, the addition of β -CD-PS does not significantly impact the glass temperature or the melting temperature, as anticipated.

The amount of compatibilizer (β -CD-PS) added to PCL/PS blends for miscibility was also investigated. The films of 50/50 PCL/PS blends and 2-fold and 4-fold β -CD-PS contents are clearly in Figure 10a. When β -CD-PS is increased, more homogeneously mixed film is obtained. Moreover, from DSC cooling thermograms of 50/50 PCL/PS blends, show that T_c of PCL is remarkably decreased due to the inclusion complexation of β -CD:PCL (Figure 10b).

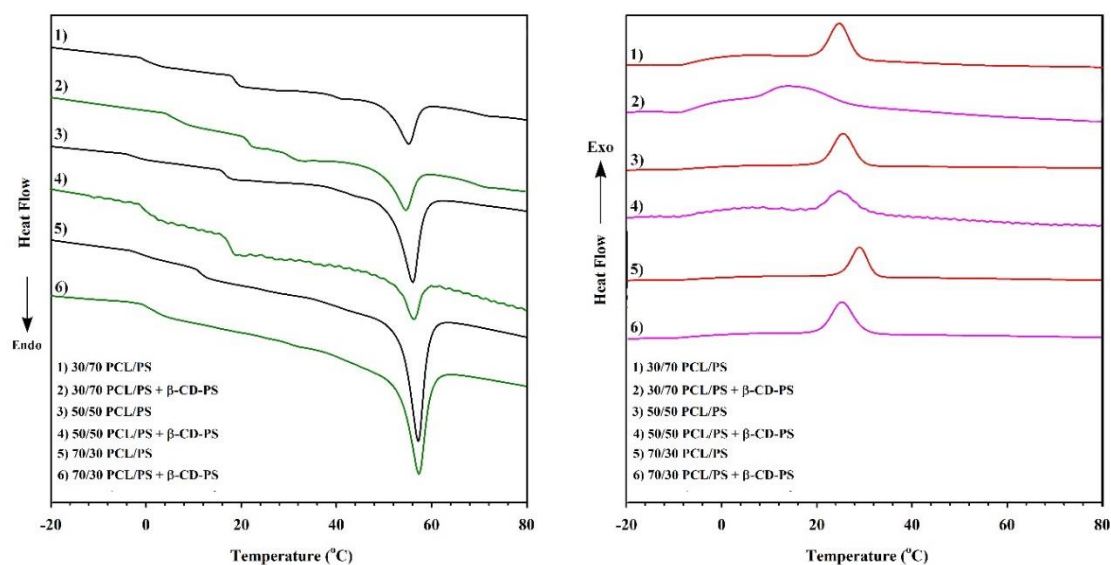


Figure 9. DSC thermograms of films containing different concentrations of β -CD-PS are presented, with the vertical shift applied to enhance clarity (left graph). The cooling cycle of the same samples (right graph)

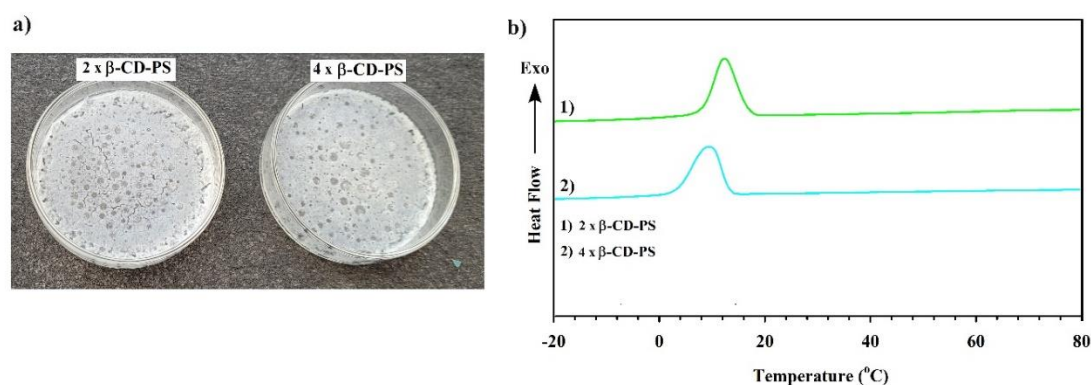


Figure 10. a) Appearance of solvent-cast films prepared with 50/50 PCL/PS blend with 2-fold and 4-fold β -CD-PS. b) DSC thermograms of 50/50 PCL/PS blend with 2 fold and 4 fold of β -CD-PS

The surface morphology of 50/50 PCL/PS blends containing various amounts of β -CD-PS was studied through an optical microscope to observe the miscibility of blends. The casting films were subsequently hot pressed for 3 min at 195 °C under the pressure of 5 Mpa between Teflon sheets to produce film samples of uniform thickness (~50 μ m). Figure 11 presents the optical microscope micrographs of 50/50 PCL/PS blends with different ratios of β -CD-PS at 10X magnification to evaluate the morphological surfaces of the blends. Figure 11a has significant phase separation on the surface. Figure 11d seems to have one uniform phase. Figure 11c showed better homogeneously dispersed droplets than Figure 11b. The morphologies of these binary blend films changed depending on the amount of β -CD-PS as compatibilizer. Additional techniques such as scanning electron microscopy (SEM) or atomic force microscopy (AFM) may be employed to get information about the nanoscale or detect slight phase separations for further studies.

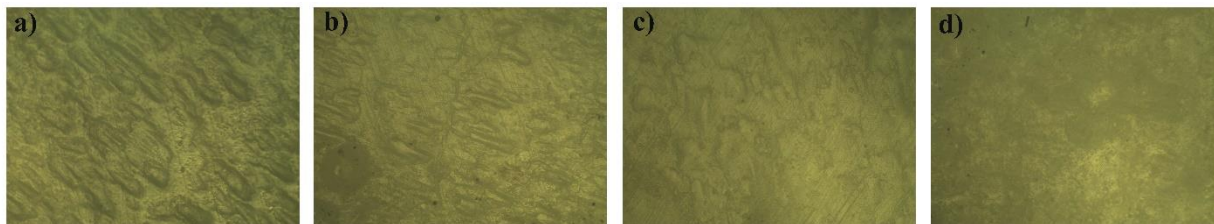


Figure 11. Optical microscopy micrographs of 50/50 PCL/PS blends **a)** without β -CD-PS, **b)** equimolar β -CD-PS to PCL, **c)** 2-fold of β -CD-PS to PCL, and **d)** 4 fold of β -CD-PS to PCL

IV. CONCLUSIONS

Compatibilization of PCL and PS in THF/DMF (4:1) is achieved by the addition of β -CD end-functionalized PS (β -CD-PS) (equimolar to PCL) by solution-cast technique. The β -CD-PS was obtained via CuAAC click reaction of mono azide functional β -CD (β -CD- N_3) and previously synthesized PS via ATRP. The 1:1 inclusion complexation was driven by β -CD and PCL by host-guest interaction. The process of compatibilization is visually evident as the initially cloudy solutions become clear when heated and stirred for an extended period. The mechanism underlying compatibilization is attributed to the threading of the β -CD-PS by PCL, which reduces the interfaces between different components. This threading phenomenon of the β -CD ring by PCL is supported by evidence obtained from 2D NOESY NMR analysis. A significant change in the T_g value was observed for the β -CD-PS containing a 30/70 PCL/PS blend. In addition, PCL crystallization was significantly shifted for the same blend. Moreover, the amount of compatibilizer (β -CD-PS) added to PCL/PS blends for miscibility was also investigated. The films of 50/50 PCL/PS blends with 2-fold and 4-fold β -CD-PS contents gave homogeneously mixed films via optical microscope observations. The morphological properties showed that the PCL/PS mixtures were miscible when the amount of β -CD-PS was increased. In conclusion, for inclusion complexation 1:1 β -CD:PCL mole ratio is enough; however, β -CD can be increased for good miscibility of blends.

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