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An Investigation of the Functional Groups and Structure Characteristics of a Polymer Blend of Polystyrene and Poly(ε-Caprolactone) Produced by Using Bis(Dibenzoylmethanato)Zirconium(IV) Chloride Catalyst

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ABSTRACT

Although polystyrene (PS) finds widespread use in household applications, its non-biodegradable nature raises concerns about its environmental impact. Therefore, modifying PS by blending it with a biodegradable polymer such as poly(ε-caprolactone) (PCL) is essential. This study focuses on investigating the functional groups and structural characteristics of PS/PCL blends. In this study, we produce polyblend using the solvent casting method. On the other hand, the PCL employed in this study was synthesized using the bis(dibenzoylmethanato)zirconium(IV)chloride (bis(dibzm)$_2$Zr) catalyst. Next, the FTIR analysis indicates a Van Der Wall's interaction between PS and PCL. Therefore, we did not find any absorption of new functional groups outside of the PS and PCL functional groups. Next, the XRD analysis revealed that polyblend has a more crystalline structure than PS. Meanwhile, PCL has a more crystalline structure than PS/PCL polyblend and pure PS.

Keyword: Polystyrene, poly(ε-caprolactone), functional groups, structure, and polyblend.

1 INTRODUCTION

One major cause of environmental pollution stems from the widespread use of polymer materials, particularly in packaging. The issue lies in the fact that many of these polymers lack the ability to biodegrade. To address this concern, researchers have been actively developing biodegradable polymers, such as PCL, polylactic acid, poly(δ-valerolactone), and bacterial cellulose.[1,2] PCL stands out as a widely recognized polymer due to its notable biodegradable properties and its good compatibility with other polymers.[2,3] As a result, PCL has been extensively utilized in a range of areas, including vascular grafts, surgical sutures, composite materials, reinforcing agents, bone screws, drug delivery systems, implants, and packaging.[4–6]

On the other hand, PS is a type of polymer that is extensively utilized for household appliances and packaging purposes like bottles and caps, disposable cutlery, trays, containers, CD protectors, and cups.[7–9] However, PS is unlike PCL. PS lacks the ability to biodegrade, thereby negatively impacting the environment.[10] Therefore, blending PCL with PS is essential to creating polyblends that decompose more easily in natural environments. PS possesses strong tensile strength, high durability, a high melting point, and is clear and hard. However, it exhibits resistance to degradation.[11,12] In contrast, PCL has the biodegradable properties of being semicrystalline, biocompatibility, permeability, and nontoxicity.[4] Nevertheless, one drawback of PCL is its relatively low melting point. In addition to creating biodegradable polyblends, blending PS with PCL is also conducted to produce materials with enhanced strength, are more biocompatible, and have a have a higher melting point.

In recent times, numerous researchers have explored the blending of PS with PCL for a variety of purposes. Previously, researchers utilized commercial PCL in their studies. Subsequently, they also investigated the chemical, thermal, physical, and morphological properties. They also examined the characteristics of the resulting PS/PCL polyblends in comparison to pure PS.[11–14] Meanwhile, our research team has also undertaken a biodegradation assessment of PS/PCL blends on fungus media.[15]

In this study, we aim to create a polyblend by combining PS and PCL. The PCL used here was synthesized by polymerizing ε-CL with a bis(dibzm)$_2$Zr catalyst, as detailed in our prior research.[4] Additionally, we will analyze the functional groups and structure characteristics of the PS/PCL polyblend in comparison to the pure PS matrix.

2 EXPERIMENTAL

2.1 Chemicals, Equipment and Instrumentation

In this study, the PCL utilized was synthesized through the polymerization of ε-CL with a bis(dibzm)2Zr catalyst. The raw materials, including ε-CL, zirconium tetrachloride, and dibenzoylmethane, were obtained from Merck. Additionally, PT Trinseo Materials Indonesia supplied the PS. The polyblend was characterized using a FTIR (Perkin Elmer Life spectrometer) and XRD (Shimadzu MAXIMA-XRD-7000).[16]

2.2 Research Procedure

2.2.1 Polymer Blends Preparation

Previously, the PCL used here was synthesized by polymerizing ε-CL with a bis(dibzm)$_2$Zr catalyst. The next step is polymer blend preparation by blending PS with PCL in xylene solvent at 120°C. Next, the mixture was refluxed and stirred for three hours. Afterward, the mixture was formed and then placed in an oven to allow the xylene solvent to evaporate. Subsequently, the formed polyblend was molded based on ASTM D638 specifications. Finally, the resulting polyblend was subjected to characterization for its functional groups and structural properties.[3, 17]

3 RESULTS AND DISCUSSION

Polyblend plastic films are produced through a process involving the mixing of PS and PCL. This blending technique is followed by the evaporation of the solvent. In this instance, the PCL component will engage with the PS monomer in a physical manner.

3.1 Infrared Spectrum Analysis of PS/PCL Polyblend

FT-IR analysis aims to determine the absorption of PS component functional groups and PCL component functional groups in the polyblend specimen. Additionally, this analysis can determine whether the formed polyblends have interacted physically or chemically. The spectrum result of the polyblend FT-IR analysis can be seen in Figure **1**

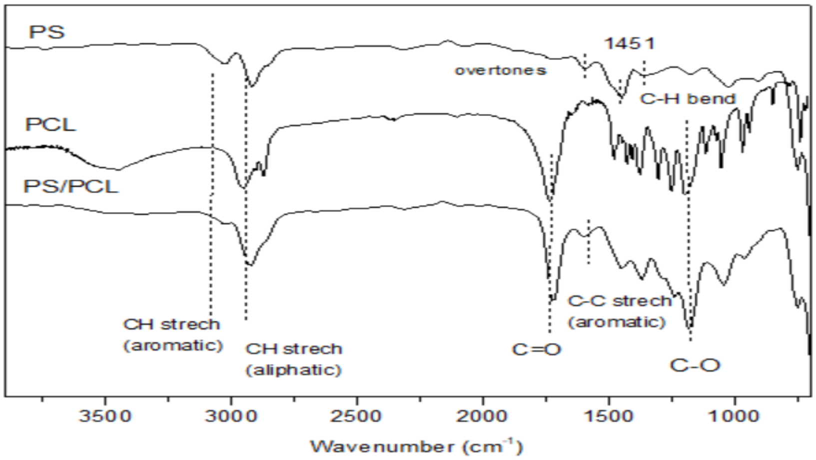

Figure 1. FT-IR Spectrum of (a) PS and (b) PS/PCL Polyblend

In Figure **1**, the FT-IR spectrum of PS and PS/PCL polyblends is presented. In the PS spectrum, a peak at 3029 cm^{-1} indicates the presence of CH-strech (aromatic). The peak at 2917 cm^{-1} indicates the presence of CH-strech (aliphatic). Aromatic C-H combination frequency overtones are shown at around 1663-2071 cm^{-1}. [11] The peak at 1353 cm^{-1} indicates the presence of C-H bending vibration. The peak is at 1593 cm^{-1} and 1451 cm^{-1} according to the benzene ring framework on PS (C-C stretch in the ring). The peak at 1593 cm^{-1} is also the peak of adsorption vibrations of methylene and methylene substituted mono in the benzene ring.[12]

On the other hand, the PCL FT-IR spectrum has been reported by our research group in previous reports, where the peak at 2949 cm^{-1} and at 2865 cm^{-1} indicate the presence of CH_2- asymmetric and CH_2-symmetrical. Then, the peak at 732 cm^{-1} indicates the presence of the rocking movements of methylene (CH-). Furthermore, the peak at 1724 cm^{-1} indicates the presence of an ester group (C=O). Last, the peak at 1248 cm^{-1} indicates the presence of a strain of C-O ester. [4,5]

Meanwhile, the PS/PCL blending spectrum shows the most typical absorption values at the wavelength of 1717 cm^{-1}. This peak is the typical peak of the C=O groups in PCL. PS does not have a significant band in the carbonyl region. However, the small peak that was observed in the area is related to the overtone peak of the aromatic PS group.[11] The decrease in the absorption band of the PCL carbonyl group in the area occurred due to overlapping with the overtone peak of PS.

Furthermore, at the 1179 cm^{-1} wavelength, according to the C-O groups of PCL, The peak at 3019 cm^{-1} indicates the presence of CH-stretch (aromatic). The peak at 2928 cm^{-1} indicates the presence of CH-stretch (aliphatic). Last, the peak at 1593 cm^{-1} indicates the presence of a benzene ring on the PS (C–C stretch in the ring). These results indicate that PS and PCL have interacted in a van der Wall manner. Hence, no absorption of new functional groups outside of the PS and PCL functional groups was found. Furthermore, the proposed Van der Wall's interaction between PS and PCL is shown in Figure **2**.

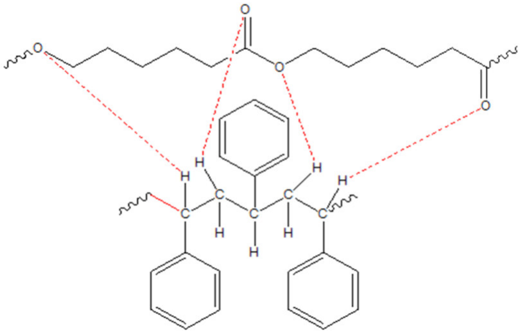

Figure 2.Interaction of PS/PCL that proposed

3.2 X-Ray Diffraction (XRD) Results of PS/PCL Polyblend

XRD analysis aims to determine the polymer structure. In general, polymer properties are semicrystalline, which means they have an amorphous and crystalline part. XRD diffractograms of crystalline polymers tend to produce sharp peaks. Whereas amorphous polymers produce wide peaks. [18] The amorphous and crystalline parts would show specific scattering intensities. XRD diffractograms of PCL, PS, and PS/PCL polyblends are shown in Figure **3**.

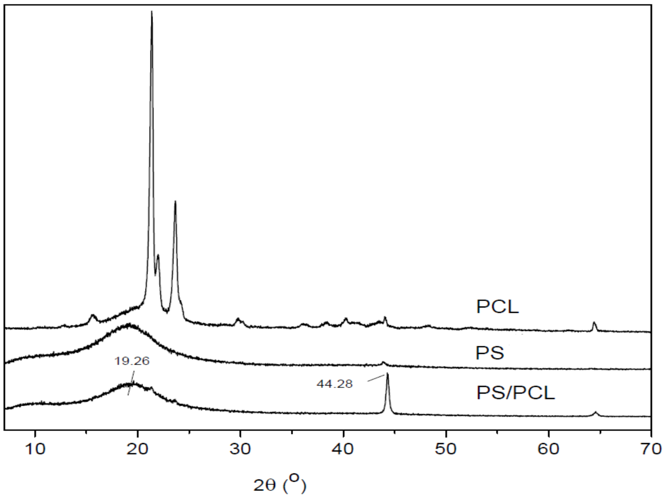

Figure 3. XRD diffractograms of (a) PCL [4], (b) PS, (c) PS/PCL polyblend

The XRD specimen diffractogram in Figure **3** shows that there has been a change in peak shape in the resulting polyblend compared to pure PCL and PS. In the PS/PCL polyblend, a peak was identified at 2θ = 19.26°. These peaks are narrower than pure PS and wider than pure PCL crystal peaks.[4, 5] This peak is the combined diffraction peak of pure PS and PCL. The resulting polyblend diffraction pattern was different from the diffraction patterns of pure PS and PCL. Meanwhile, the crystalline peak of the polyblend appears at 2θ = 44.28°. At this position, the polyblend peaks were sharper than those of the pure PCL and PS peaks. On the other hand, the PCL crystalline peak was identified at 2θ = 21.36°; 22.02°, and 23.66°.[4]

On the other hand, the change in the shape of the diffractogram and the crystallinity of the polyblend may be related to Van der Wall's interaction between PS and PCL, as shown in Figure **2.**[19] Moreover, the presence of crystalline polyblend peaks in the 44.28° region indicated that the resulting polyblend was more regular compared to pure PS.

4 CONCLUSION

The results of the FTIR analysis show that there is no absorption of additional functional groups beyond those contained in the PS and PCL functional groups. These results indicate that PS and PCL interact via Van Der Wall forces. Meanwhile, XRD analysis revealed that the polyblend has a more crystalline structure than PS. These results indicate that PS/PCL polyblend has a more regular structure than PS. Conversely, PCL exhibited a higher degree of crystallinity compared to both the PS/PCL polyblend and pure PS.

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