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A Study of Mechanical and Thermal Properties Polymer Blend from Polystyrene with Poly(*ε*-Caprolactone) that Obtained Using Bis(Dibenzoylmethanato)Zirconium(IV) Chloride Catalyst

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ABSTRACT

Polystyrene (PS) is one form of the plastic that is most widely utilized for household application. However, plastics made from PS can pollute the environment. Hence, it is necessary to modify PS by mixing it with a biodegradable polymer like poly (ε-caprolactone) (PCL). The focus of this research was to determine the mechanical and thermal properties of PS/PCL polyblends. In this research, polyblend are prepared by mixing PS with PCL that acquired using the bis(dibenzoylmethanato)zirconium(IV) chloride bis(dibzm)$_2$Zr catalyst. The method employed is solvent casting with a ratio of PS/PCL of 10/0, 10/1, 10/2, 10/3, and 10/4 (w/w). The optimum mechanical properties were obtained in 10/2 mixing which had a tensile strength of 6.72 MPa with 1.01% in elongation. *Furthermore, the optimum PS/PCL polyblend was also characterized using DSC to determine its thermal properties.*

Keyword: Polystyrene, poly(*ε*-caprolactone), mechanical properties, thermal properties, and polyblend.

1. INTRODUCTION

One source of environmental pollution is polymer material which has been used for various purposes, especially as packaging. This is because most of the polymer do not have some ability to biodegrade. Then, to anticipate this problem, biodegradable polymers have been synthesized by numerous researchers like PCL, poly lactic acid, poly(*δ*-valerolactone), and bacterial cellulose.[1,2] PCL is one of the most well-known polymers because of its biodegradable properties and easily interacts with another polymer[2,3]. Now, PCL has been widely used in various fields such as surgical sutures, implants, composite, vascular grafts, bone screws, reinforcing agent, drug delivery system, and packaging.[4–6]

Meanwhile, PS is a polymer material that is widely used as packaging and household appliances such as disposable cutlery, bottle and caps, cups, trays, containers, and CD protectors.[7–9] Unlike PCL, PS is a material that is difficult to decompose so that it contributes to environmental damage.[10] Therefore, it is

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necessary to blend PCL with PS in order to produce polyblends that are easier to decompose in nature. The mixing of PS with PCL is also done in order to complement the lack of the polymer. PS has strong properties, high melting point, hard, and clear. But, this polymer is difficult to degraded.[11,12] Whereas, PCL has the good mechanical properties, semicrystalline, biodegradable, biocompatibility, nontoxic and permeability.[4] However, PCL has a disadvantage that is its low melting point. Besides to producing biodegradable polyblends, blending between PS and PCL is also carried out to produce strong, high melting point, and biocompatible polyblends.

Recently, several researchers had also conducted research on PS blending with PCL for various purposes. The PCL employed by earlier researchers was a commercial PCL. After that, they also observed the physical, thermal, chemical, and morphological properties of the resulting PS/PCL polyblends compared to pure PS.[11–14] On the other hand, our research group has also conducted a biodegradation test of PS/PCL polyblends on fungus media in a previous study. As a result, polyblend is more easily biodegradable than pure PS.[15]

In this investigation, PS and PCL will be combined to produce polyblend. The PCL employed in this study was produced by polymerizing ε-CL with bis(dibzm)$_2$Zr catalyst as we reported in a previous study.[4] Then, we will also report the mechanical and thermal properties of the PS/PCL polyblend compared to PS matrix. Meanwhile, the objective of this investigation was to determine the mechanical and thermal properties of PS/PCL polyblend. Last, the resulting PS/PCL polyblend is expected to have high mechanical and thermal properties compared to PS matrix.

2. EXPERIMENTAL

2.1. Chemicals, Equipment and Instrumentation

The PCL employed in this this investigation was produced by polymerizing ε-CL with bis(dibzm)$_2$Zr catalyst. Then, the materials used like ε-CL, zirconium tetrachloride, and dibenzoylmethane were supplied from Merck. Next, PS is supplied from PT Trinseo Materials Indonesia. Meanwhile, the characterization of the polyblend was tested using a tensile strength test (Gotech Al-7000M), and DSC (Shimadzu DSC-60 Plus 230V).

2.2. Research Procedure

2.2.1. ROP of ε–Caprolactone

ROP ε-CL lasts for four hours using a bis(dibzm)$_2$Zr catalyst at 100 °C. Meanwhile, the ε-CL monomer ratio with catalyst is 200:1 mmol. After polymer product formed, added chloroform and stirred for two hours. After that, the solution formed and then refluxed to get a clear solution. Next, the solution precipitated using diethyl ether. Finally, a white solid PCL was obtained.[4]

2.2.2. Polymer Blends Preparation

Polyblend specimen are prepared by mixing PS with PCL into xylene solvent at 120 ºC. Furthermore, PCL was added with ratio PS/PCL: 10/0, 10/1, 10/2, 10/3, 10/4. Then, the mixture refluxed for three hours and stirred. Next, the mixture was formed and placed in an oven to let the xylene solvent evaporate. Then, the created polyblend is imprinted based on ASTM D638 size. Last, the resulting polyblend was characterized for its mechanical and thermal properties.[3,16]

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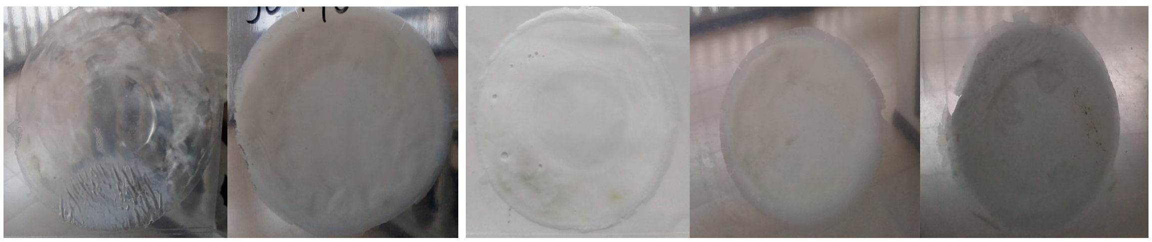
3. RESULT AND DISCUSSION

3.1. Preparation Plastic Film from PS/PCL Polyblend

The process of making plastic films was done by mixing PS and PCL. The process using blending technique that followed with evaporation of solvent (solvent casting). In this case, the PCL component will interact with the PS monomer in a physical way, but they won't form a chemical bond.

The addition of PCL to pure PS is done to get a plastic film that is strong, elastic, and its degradation can be accelerated in the presence of PCL.[6] To maintain the physical characteristics of the polyblend, the addition of PCL is limited to a maximum of only 40% w/w. Then, the plastic film prepared from the PS/PCL mixture consisted of only five ratios (10/0; 10/1; 10/2; 10/3; 10/4). The resulting plastic is a clear white film. Finally, all plastic films that have been successfully printed are presented in the Figure **1**.



(a) (b) (c) (d) (e)

Figure 1. Plastic Specimen: Pure PS (a); PS/PCL 10/1 (b); PS/PCL 10/2 (c); PS/PCL 10/3 (d); PS/PCL 10/4 (e)

3.2. Tensile Strength Test of PS/PCL Polyblend

Tensile strength testing is carried out with the purpose to identify a polyblend mechanical properties like tensile strength and strain that occur. The PS/PCL mixture's tensile strength test and elongation test are equally crucial in identifying a polymer's mechanical properties. Then, the determination of tensile strength can be done with giving a certain load of the specimen so that changes in length (strain) occur. As the result, the sample specimen will break up. The testing standard employed is ASTM D638. The results of the tensile and elongation tests with different compositional are presented in the following Table **1**.

Table 1. Tensile strength result data (σ_t) and elongation (ε) on mixing PS with PCL

PS /PCL (w/w)	σ (tensile strength) MPa	ε (elongation) %
10/0	3.724	0.41
10/1	5.978	0.70
10/2	6.762	1.01
10/3	2.156	0.42
10/4	0.882	0.29

The mixing of PS with PCL produces more biocompatible polyblend. This mixing is also improving mechanical properties of polyblends compared to pure PS. This is proven with increased tensile strength and flexural strength from polyblends that produced with ratio 10/1 and 10/2. However, the mechanical properties of the polyblends decreased further as the amount of PCL in the polyblends was further increased, as shown in Table 1 with ratios of 10/3 and 10/4. This is because PCL gets more brittle, which makes it difficult to form a homogeneous polyblend film with PS. As a consequence, a decrease in the interaction and

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miscibility between PS and PCL also occurred. Therefore, the polyblend that has good biocompatibility is at 10/2 mixing.

The most optimum mechanical properties were obtained at the ratio of PS/PCL 10/2 (%w/w) with 6.762 MPa in tensile strength and 1.01% in elongation, respectively (Table 1 number 3). Whereas, the tensile strength of PS matrix is 3.72 MPa with 0.41% in elongation (Table 1 number 1). In comparison to PS matrix, polyblends' tensile strength and percent elongation have risen with the addition of PCL up to 20%. This is due to an interaction between PS and PCL known as a Van der Wall interaction.[3]

3.3. The Differential Scanning Calorimetry (DSC) Analysis of PS/PCL Polyblend

DSC analysis is frequently used to examine polymeric materials' thermal transition. The goal of this analysis is to identify the thermal effects that come along with both the chemical and physical changes that occur in heated materials. During the DSC analysis, the heating rate is fixed. Meanwhile, melting temperature (T*m*) and glass transition temperature (T_g) are the results of this analysis. DSC test result are presented in the Figure **2**.

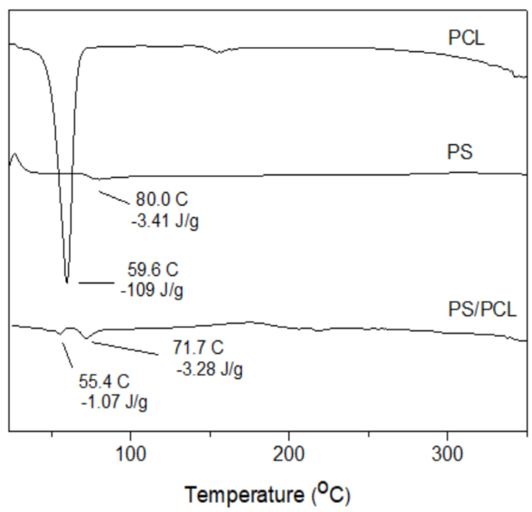

Figure 2. The results of DSC analysis of (a) PCL[4], (b) PS[6], and (c) polyblend PS/PCL (10/2)

In Figure **2** is presented the DSC analysis of PCL, PS, and also PS/PCL polyblend. The melting point (T_m) of PCL is 59.6°C[4]. Meanwhile, the glass transition temperature (T_g) of PS is 80.0 ºC. These T_g results are similar to those obtained by the Kadhim research group[17]. On the polyblend, two peak areas are shown. Both are PCL and PS peaks, respectively. In the polyblend thermograms, there was a decrease in Tm of PCL by 4.5 degrees, to 59.6 ºC. Likewise for PS, there was a decrease in Tg of 8.3 degrees to 71.7 ºC. Previously, Chun's research group also found that Tm and Tg were lower when the number of PS in the polyblend was higher than the number of PCL.[18]

On the other hand, the Tm peak of PCL in polyblend was shorter than the Tm peak of pure PCL. Whereas, the Tg peak of PS in the polyblend is sharper and wider compared to the Tg peak of pure PS. Furthermore, the enthalpy obtained for the PS/PCL polyblend was also different from that of pure PCL and PS. In the polyblend, there was a drastic decrease in the melting enthalpy of PCL by 107.93 to only 1.07 J/g. Likewise for PS, the glass transition enthalpy also decreased by 0.12 J/g to 3.29 J/g. Similar to the temperature changes, Chun's research group also found that the enthalpy of the polyblend will be lower when the proportion of PS in the polyblend is greater than that of PCL.[18] These results indicate that PS and PCL have interacted in a van der Wall manner. This is proven by the shift in the two peak regions of PS and PCL after being mixed into polyblend.

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4. CONCLUSION

The PS/PCL polyblends have been blended successfully in this research. The most optimum mechanical properties were obtained at the ratio of PS/PCL of 10/2 (%w/w). In this comparison, the polyblend obtained is also more biocompatible and stronger than other mixing variations. Meanwhile, the results of thermal analysis using DSC show that there has been a shift in the melting point of PS/PCL polyblends compared to pure PS and PCL. This indicates that there is a Van der Wall interaction between PS and PCL. Finally, the use of PCL in PS/PCL polyblend mixtures is also expected to accelerate plastic degradation.

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