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Thermal Behaviour and Interaction Calculation of Polypropylene Blend with Poly (ε-Caprolactone) Obtained Using Bis(acac)$_2$Zr Catalyst

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Abstract

Polypropylene (PP) is a type of synthetic polymer that is non-biodegradable so it is difficult to degrade by microorganisms and causes environmental problems. One solution to overcome this problem is to mix PP with biodegradable polymers such as poly(ε-caprolactone) (PCL). This study aims to determine the thermal properties and study the interaction of PP mixtures with PCL obtained using bis(acetylacetonato)zirconium(IV) chloride (bis(acac)2Zr) catalyst. Mixing PP with PCL was carried out using blending and solvent evaporation techniques. The polyblend obtained was then analyzed using FTIR, XRD, DSC, and TGA. Based on the FTIR analysis, it can be seen that the PP/PCL polyblend has formed which is indicated by the absence of new functional groups outside PP and PCL. Furthermore, based on the XRD analysis, it can be seen that the resulting PP/PCL polyblend has a lower crystalline peak intensity than pure PP. In line with this, the melting point of PP/PCL polyblend is also lower than pure PP based on DSC analysis. Meanwhile, based on TGA analysis, it was obtained that the thermal decomposition of polyblend was higher than pure PP. These results indicate that there has been an interaction between PP and PCL as evidenced by changes in the crystalline properties and thermal properties of the resulting polyblend compared to pure PP and PCL. Based on the results of computational calculations, it was obtained that the interaction length of the hydrogen atoms of PP with the oxygen atoms of PCL were 3.6 Å and 3.04 Å, respectively. While the delta charge atoms between the hydrogen atoms of PP and the oxygen atoms of PCL were 0.213 and 0.499. These results indicate that there has been an interaction between PP and PCL.

Keywords: Poly(ε-caprolactone), polypropylene, PP/PCL polyblend, interaction, bis(acetylacetonato)zirconium(IV) chloride

1 Introduction

Petroleum-derived polymer products predominate in the global market due to their excellent characteristics. The advantages of these traits encompass mechanical characteristics, thermal attributes, lightweight composition, ease of processing, adaptability, and cost-effectiveness. Synthetic polymers are engineered to withstand photodegradation and biodegradation. A specific category of synthetic polymer is polypropylene (PP). [1], [2]. PP is extensively utilized in packaging applications, including dry food containers, beverage bottles, bottle caps, and plastic wrap for dishes. Polypropylene (PP) is frequently utilized for packaging due to its flexibility, high tensile strength, resistance to water and moisture, excellent chemical resistance, recyclability, and stability. Furthermore, polypropylene has been utilized in diverse applications such as military, construction, domestic goods, medical devices, and automobile components. [3]. Nonetheless, synthetic polymers such as polypropylene exhibit non-biodegradable properties and significant durability, resulting in severe environmental issues. The accumulation of polymer waste can contaminate the soil, so disrupting microbiological activity. [4]. Polymers in nature can experience progressive decomposition due to several elements, including light (photodegradation), humidity, air, temperature, wind (mechanical degradation), and macro or microbes (biodegradation). Nonetheless, the natural degradation rate of polymers is exceedingly protracted. [3].

Consequently, in recent decades, researchers have undertaken numerous studies to mitigate the issue of polymer waste accumulation, including polypropylene, to facilitate its decomposition in the environment. One method involves the synthesis of biodegradable polymers. Numerous biodegradable synthetic polymers that have been produced include aliphatic polyester poly-β-(hydroxybutyrate) (PHB).[5], poly(*β*-propiolactone), poly(lactic acid)(PLA) [6], poly(*δ*-valerolactone) [7],[8], poly(*β*-butyrolactone) and PCL [9], [10].

A prevalent way to expedite the disintegration of polypropylene (PP) is by combining it with biodegradable polymers like polycaprolactone (PCL). This technology is more economical than alternative approaches, including copolymer synthesis and polymer synthesis from natural sources. [11]. PCL can be produced through the ring opening polymerization (ROP) method using zirconium complex catalysts [12] [13]. Other catalysts that have been used in ε-CL polymerization are

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distannoxane [9], alkali metal salts [14], and zinc complex [15]. However, these catalysts have weaknesses, namely they are susceptible to water vapor and air, their Lewis acidity is also difficult to control, they are corrosive, and they are not suitable for use in tropical climates.

Numerous researchers have already investigated the PP/PCL polyblend by altering the makeup of PP and PCL. Our research group has done a biodegradation investigation of the PP/PCL polyblend in comparison to pure PP. The findings indicated that polyblend exhibited a more rapid biodegradation rate compared to pure polypropylene. PCL was selected as a biodegradable polymer due to its compatibility with numerous different materials, including PP. [16]. This amalgamation will address the deficiencies of PP and PCL. The resultant polyblend will exhibit enhanced physical, mechanical, and thermal qualities. Furthermore, the polyblend is readily biodegradable, hence mitigating the accumulation of polymer waste in the environment. The previously utilized PCL was a commercial substance. [2].

The biodegradation process in the PP/PCL polyblend is posited to progress through multiple stages. The preliminary phase entails disrupting the Van Der Waals forces between PP and PCL. Moreover, microbes will adhere to the PCL surface. Microorganisms will persist in proliferating and use PCL as a carbon source. Subsequently, the degradation of PCL will initiate at the ester group containing the carbonyl. [17]. Subsequently, PCL will disintegrate into monomers, specifically 5-hexenoic acid and carbon dioxide gas. In the concluding phase, methyl pentanoate, water, and carbon dioxide gas will be produced. [18]. Concurrently, PP will undergo degradation via two pathways. The initial pathway entails secondary radicals that provide the primary products: pentane, 2-methyl-1-pentene, and 2,4-dimethyl-1-heptene. The second pathway entails primary radicals, producing relatively minor products, specifically propane. [19].

This investigation will utilize PCL synthesized with the bis(acac)$_2$Zr catalyst. This research introduces the innovative application of synthetic PCL. Previously, numerous researchers have documented polyblends of polypropylene (PP) with polycaprolactone (PCL) obtained from commercial sources or synthesized by alternative complicated catalysts. The bis(acac)$_2$Zr catalyst employed in PCL synthesis is appropriate for tropical settings due to its insensitivity to water vapor and air. The created PCL will be combined with PP, anticipated to yield a polyblend with enhanced physical, mechanical, and thermal qualities, while also being readily biodegradable.

2 Experimental

2.1 Materials

The compounds utilized, including acetylacetone ligand, zirconium tetrachloride, and ε-CL, were procured from Sigma-Aldrich. PP was acquired from PT. Trinseo Indonesia. The computational analysis of the interaction between PP and PCL in the polyblend was conducted using HyperChem 8.0 software. The gear utilized comprised a computer using an Intel® Core (TM) i5-8265U CPU processor, operating at 1.6GHz, with 4096 MB of RAM, and running Windows v10 as the operating system. [21], [22].

2.2 Characterization Technique

This work employed FTIR instrumentation to analyse the functional groups of PP, PCL, and the PP/PCL polyblend. Whereas, the FTIR spectra measurements were conducted using a PerkinElmer Life spectrometer. Furthermore, crystallinity assessment and X-ray diffraction (XRD) measurements were carried out using a Shimadzu XRD-6100 diffractometer. While the radiation used was Cu-Kα.

On the other hand, the thermal properties were measured using Differential Scanning Calorimetry (DSC) and thermogravimetric Analysis (TGA) instruments. Then, the melting temperature and melting enthalpy were measured using a DSC instrument (Shimadzu DSC-60 Plus Series) at a heating rate of 10 °C/min in the temperature range of 40–550 °C. Subsequently, the decomposition temperature was analyzed using a TGA instrument model NETZSCH STA 449 F1 Jupiter, with a heating rate of 10 °C/min in the temperature range of 40–550 °C. Meanwhile, the instrumentation used in this study has similar specifications to those reported in our previous publications [7], [10], [20].

2.3 Method

2.3.1 Blends and Polyblend Films Preparation

In the initial stage, PP was dissolved in xylene at 120 °C, then PCL was added. In this study, PCL was obtained through a polymerization reaction using bis(acac)$_2$Zr catalyst. The ratio between PP and PCL is 10/4. This mixture ratio is considered the most optimal based on the results of tensile and elongation tests [23]. The mixture was refluxed and agitated for three hours. Upon completion of the process, the mixture was transferred to a container and subjected to an oven at 100 °C until the xylene evaporated, resulting in the formation of a PP/PCL polyblend plastic. The resultant sample was subsequently shaped in accordance with the prescribed dimensions of ASTM D368. In the concluding phase, the polyblend underwent analysis via FT-IR, XRD, DSC, and TGA. [4][24].

2.3.2 Computational Calculation of PP Interaction with PCL

Computational analyses were conducted to ascertain the interactions between PP and PCL within the PP/PCL polyblend structure. The calculations were conducted by initially depicting the PP and PCL molecules. The geometry optimization calculation was subsequently executed utilizing an RMS gradient setting of 0.1 kcal/(Amol). The employed method was the semi-empirical AM1. Single point calculations were conducted to illustrate hydrogen bonding. Subsequently, the option to recompute H bond was chosen from the display menu, resulting in the appearance of a dotted line. This circumstance signifies the establishment of interaction between PP and PCL. The optimum energy of PP, PCL, and the PP/PCL polyblend was also computed. [25][26].

3 Result and Discussion

3.1 Functional Group Analysis

Functional group analysis was conducted utilizing a Fourier Transform Infrared (FT-IR) instrument. The objective was to ascertain alterations in the functional groups of PP and PCL compounds following their incorporation into a PP/PCL polyblend, as illustrated in Figure 1.

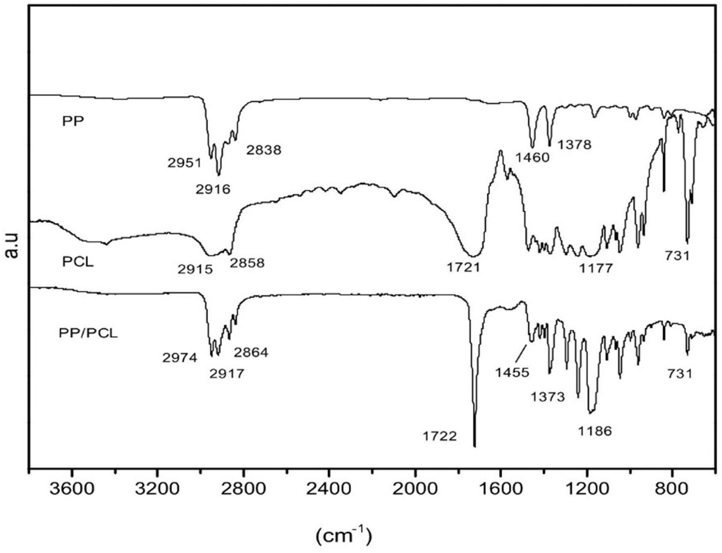

Figure 1: FTIR Analysis (a) PP; (b) PCL [20]; (c) PP/PCL Polyblend

The PP spectrum data reveals wave numbers at 2951 cm^{-1}, 2916 cm^{-1}, and 2838 cm^{-1}, signifying the existence of C-H stretching groups. Additionally, wave numbers at 1460 cm-1 and 1378 cm^{-1} corroborate the existence of CH$_2$ deformation and symmetric CH$_3$ deformation groups. [27]. Next, the PCL spectrum with wave number values of 2915 cm^{-1}, 2858 cm^{-1}, 1721 cm^{-1}, 1177 cm^{-1}, and 731 cm^{-1} indicates the presence of asymmetric CH$_2$, symmetric CH$_2$, C=O, C-O, and methylene rocking (C-H) groups [20]. The PP/PCL polyblend spectrum subsequently exhibits absorption wave numbers at around 2974 cm-1, 2917 cm^{-1}, and 2864 cm^{-1}, signifying the presence of C-H stretching groups. The presence of C=O and C-O groups was confirmed at 1722 cm-1 and 1186 cm^{-1}, respectively. The presence of CH$_2$ deformation at 1455 cm^{-1}, symmetric CH$_3$ deformation at 1373 cm^{-1}, and methylene rocking (C-H) at 731 cm^{-1} was confirmed. The spectrum data imply the formation of a polyblend, evidenced by the absence of additional functional groups other from those present in PP and PCL [4].

3.2 XRD Analysis

XRD examination of the PP/PCL polyblend was performed to examine its crystalline, amorphous, and diffraction characteristics. Most polymers possess both crystalline and amorphous areas, rendering them semicrystalline. The crystalline region of the polymer will have distinct peaks. The amorphous region of the polymer will exhibit large peaks on the XRD diffractogram, as illustrated in Figure 2.

The XRD diffractogram in Figure 2 reveals that the crystalline peaks of PP are located at 14.3°, 17°, 18.7°, 21.9°, 38.2°, 44.6°, and 64.9°. [28]. While the sharp PCL crystalline peaks were identified at 21.6°, and 23.9° [20]. Furthermore, the PP/PCL crystalline peaks were identified at 22°, 38.4°, 44.6°, and 64.9°. The XRD measurement of the PP/PCL polyblend indicated an interaction between PP and PCL. The resulting PP/PCL crystalline peak, which is a combination of the crystalline peaks of PP and PCL, illustrates this observation. PCL has a greater crystalline area compared to PP and the PP/PCL polyblend, as illustrated in Figure 2. The adaptable PCL chain structure enables its molecules to organize themselves more efficiently into a regular pattern, so forming a crystalline region. Conversely, PP possesses a more rigid structure and presents greater challenges in crystallization, resulting in a reduced crystalline region. Simultaneously, the PP/PCL polyblend comprises two distinct types of polymers. Consequently, the amalgamation of these two polymers typically diminishes the uniformity of the pristine PP and PCL structure. The formation of additional amorphous phases in the PP/PCL polyblend leads to a reduction in the overall crystalline region of the polyblend. [4].

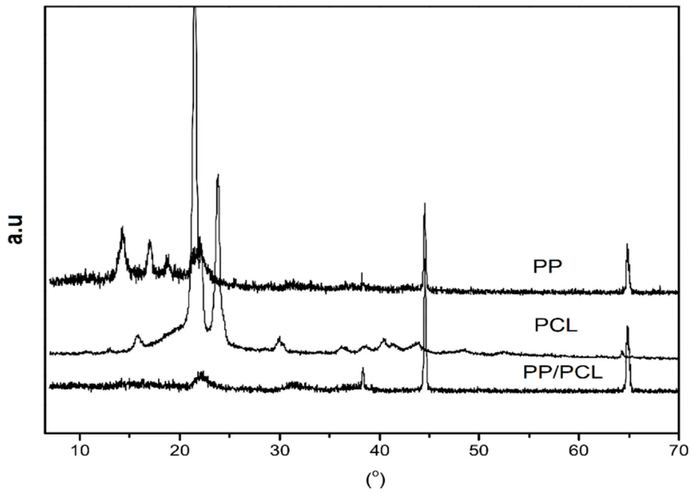

Figure 2: XRD Analysis (a) PP (b) PCL [20] (c) PP/PCL Polyblend

3.3 DSC Analysis

The objective of Differential Scanning Calorimetry (DSC) analysis is to ascertain the glass transition temperature (Tg), melting temperature (Tm), decomposition temperature (Td), and enthalpy. Tg denotes the temperature at which the polymer transitions from a glassy to a rubbery state. Conversely, the melting point (Tm) is the temperature at which a solid transitions into a liquid state. This state may arise when the temperatures of the solid and liquid phases are in equilibrium. Td is the temperature at which the polymer material commences degradation and breakdown. The DSC analysis of the PP/PCL polyblend is illustrated in Figure 3.

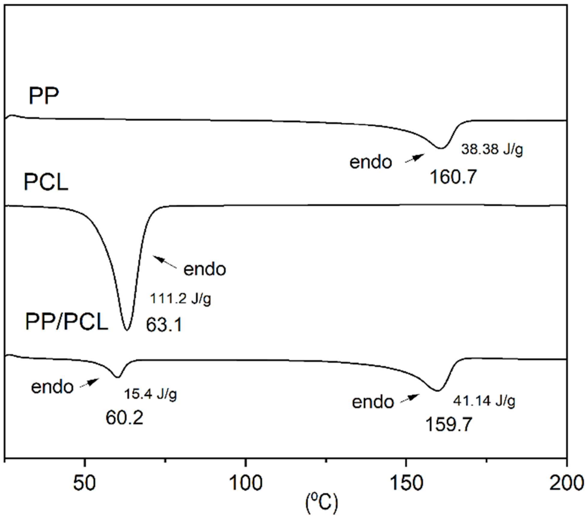

Figure 3: DSC Analysis (a) PP; (b) PCL[20]; (c) PP/PCL Polyblend

The DSC thermogram data exhibit an endothermic curve that signifies the melting points of polypropylene (PP), polycaprolactone (PCL), and the PP/PCL polyblend. The melting points are recorded at 160.7°C for polypropylene (PP) and 63.1°C for polycaprolactone (PCL), with enthalpies of 38.38 J/g for PP and 111.2 J/g for PCL. [4][17]. For the PP/PCL polyblend, the melting point was recorded at 159.7°C for PP and 60.2°C for PCL, with enthalpy values of 41.14 J/g for PP and 15.40 J/g for PCL. According to the data presented in Figure 3, the melting point (Tm) of PP has decreased from 160.79°C to 159.7°C following its amalgamation with PCL.

This reduction signifies that the crystalline phase in polypropylene diminishes due to the interaction with the polycaprolactone chain, which disturbs the molecular architecture of polypropylene. The inclusion of PCL may render the PP chain less uniform, hence reducing the energy (temperature) necessary to melt the PP component in the polyblend. PCL exhibited a reduction in Tm from 63.1 °C to 60.2 °C subsequent to its amalgamation with PP [4]. The reduction transpired as a result of the differing characteristics of PP and PCL, leading to the emergence of a mixed phase characterized by diminished crystallinity. The interaction with the PP chain disrupts the PCL chain's capacity for optimal crystallization. Consequently, the thermal stability of PCL diminishes, resulting in a reduced energy (temperature) need to melt the PCL component in the polyblend. Furthermore, during melting, the Van der Waals forces reduce, resulting in an increased distance between PP and PCL in the polyblend. Variations in the melting point of PP and PCL signify intermolecular interactions within the polyblend. The interactions that transpire may manifest as Van Der Waals forces, influencing the crystallinity and uniformity of each polymer. This interaction causes PP and PCL to modify by diminishing the regularity of their chains, leading to a reduction in the melting point.

3.4 TGA Analysis

Thermal analysis of PP, PCL, and polyblend was also carried out using TGA as shown in Figure 4. TGA is an instrument that can measure the mass change and decomposition temperature (Td) of polyblend.

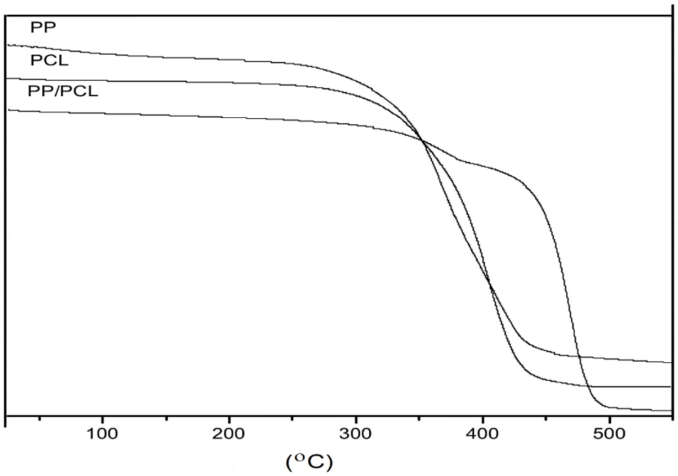

Figure 4: TGA Analysis (a) PP; (b) PCL [20] (c) PP/PCL Polyblend

The TGA curve for pure polypropylene exhibits a singular mass reduction trajectory. PP undergoes a mass loss of 5.5% within the temperature range of 0-250 °C. Subsequently, throughout the temperature range of 251-453 °C, a substantial mass drop occurs, with polypropylene (PP) diminishing by 92.3%. Moreover, the thermal breakdown of polypropylene persists at a temperature range of 454-550 °C, resulting in a mere 1.2% drop in mass. [1][19]. Conversely, the TGA curve for PCL has a singular mass reduction curve. Within the temperature range of 0-250 °C, the mass drop of PCL is gradual, amounting to only a 2% decrease. Subsequently, during the temperature range of 251-447 °C, a substantial mass reduction occurs, resulting in a 93% decrease in PCL. Moreover, the thermal degradation of PCL persists at 448 - 550 °C, resulting in a mere 2.5% drop in mass. [20].

Moreover, the PP/PCL polyblend exhibited a mass loss of merely 3.69% within the temperature range of 0-250 °C. Within the temperature range of 251-500 °C, a substantial mass reduction of 91.3% was seen in the polyblend. The thermal degradation of the polyblend persisted at 501-550 °C, resulting in a mass loss of 2.9%. The PP/PCL polyblend exhibited superior thermal breakdown relative to pure PP and PCL. This signifies that an interaction has occurred between PP and PCL in the polyblend, necessitating a higher temperature for degradation. Consequently, the thermal resistance of the polyblend will likewise augment. The thermal degradation process of PP/PCL transpires in multiple stages. In the preliminary phase, the Van der Waals interaction between PP and PCL will be disrupted. Subsequently, polypropylene will undergo degradation via two pathways. The initial pathway involves secondary radicals and yields principal products including pentane, 2-methyl-1-pentene, and 2,4-dimethyl-1-heptene [26]. The alternative pathway involves primary radicals and yields very minor products, specifically propane. PCL will undergo heat degradation into monomers. Subsequently, PCL will degrade into 5-hexenoic acid and carbon dioxide gas. In the concluding phase, methyl pentanoate, water, and carbon dioxide gas will be produced. [18].

(In Figure 4, it is recommended that authors provide the DTA associated with the TGA thermogram to accurately follow the thermal behavior of the measured samples and determine the main decomposition peaks and stages of weight loss for each sample.
Answer: Thank you for the review that has been given. In this article, we have presented DSC data as an additional thermal analysis. Previously, we have tested using DTA instrument but the device was broken. Therefore, we replaced it with DSC).

3.5 Study of the interaction of PP with PCL

The variations in crystallinity, melting point, and decomposition temperature of the PP/PCL polyblend relative to pure PP and PCL suggest an interaction between the two polymers. The interaction that transpires is characterized by Van der Waals forces. The calculations presented in Table 1 indicate that the interaction length between the H_1 atom of PP and the O_1 atom of PCL is 3.6 Å. The contact distance between the H_2 atom of PP and the O_2 atom of PCL is 3.04 Å (Figure 5). The charge disparity between the H_1 and O_1 atoms is 0.213. The charge disparity between the H_2 and O_2 atoms is 0.499. The significant charge disparity between the H_2 and O_2 atoms results in a reduced distance, hence intensifying the contact relative to that between the H_1 and O_1 atoms. The charge disparity between the hydrogen atom of PP and the oxygen atom of PCL induces a dynamic interaction between the PP and PCL molecules. The optimization energy of the PP/PCL polyblend differs from that of pure PP and PCL by -112.16 kJ/mol, as indicated in equation 1. The energy difference signifies an attractive contact between PP and PCL molecules within the polyblend mixing phase. Despite their distinct properties in the mixture, PP and PCL can interact to create optimal compatibility.

This suggests that PP and PCL molecules within the polyblend exhibit a propensity to converge, hence enhancing the intermolecular cohesion in the combination. Consequently, the phase distribution within the mixture attains more homogeneity, and the mechanical characteristics of the PP/PCL polyblend are enhanced due to the interactions that bolster cohesiveness. The favourable compatibility between PP and PCL can enhance mixture stability.

The attractive force generated mitigates significant phase deviations and yields a more uniform distribution. The interaction length and the disparity in optimization energy substantiate the conclusion that interactions between PP and PCL chains transpire. The interactions will influence the mixture's homogeneity, compatibility, mechanical characteristics, crystallinity, morphology, melting point, and decomposition point of the resultant polyblend.

The tensile test findings from prior research indicate that the mechanical qualities of the polyblend surpass those of pure polypropylene. The comparison of PP and PCL evaluated included compositions of 10/1, 10/2, 10/3, and 10/4. These four mixtures exhibit superior tensile strength compared to pure polypropylene. The results indicate that PP and PCL have been uniformly blended and are consistent with the findings of computational calculations. [23].

Table 1: The distance and energy interactions of PP with PCL

Poyiblend	R_1 (A)	Charge H_1	Charge O_1	Delta Charge H_1-O_1	R_2(A)	Charge H_2	Charge O_2	Delta Charge H_2-O_2	Energy (kcal/mol)
PP/PCL	3.6	0.020	0.233	0.213	3.04	0.010	0.509	0.499	-89427

R_1(A) : The distance between the H atom from PP and the O atom is in the position of the PCL hydroxy group
R_2 (A) : The distance between the H atom from PP and the O atom is in the position of the PCL carbonyl group
Charge H_1, H_2 : H atoms' charge from PP interacting with O atoms in the position of the hydroxy group (H_1) and the PCL carbonyl group (H_2)
Charge O_1, O_2 : O atomic charge from PCL in the position of the hydroxy group (O_1) and the PCL carbonyl group (O_2) that interacts with the H atom from PP

$$\begin{aligned}\Delta E = \text{Epoliblen} - (E_{PP} + E_{PCL}) &= -89427 - (-44100 + -45300)\\ &= -27 \text{ kkal.mol} \times 4.18\\ &= -112.16 \text{ kJ/mol}\end{aligned}$$

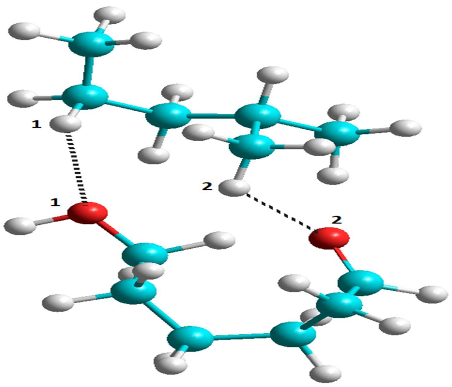

Figure 5: Optimized PP-PCL Interaction

Conclusion

The amalgamation of PP and PCL yields a PP/PCL blend exhibiting properties distinct from those of pure PP and PCL. The PCL utilized was acquired by a bis(acac)$_2$Zr catalyst. The resultant PP/PCL blend displays diffraction peaks that are unique compared to its individual polymers. Moreover, the polyblend has a diminished crystalline structure relative to pure PP and PCL. This situation results in a reduction of the melting point of the PP/PCL polyblend relative to its individual polymers. The interaction between PP and PCL in the mix has led to an elevated thermal breakdown temperature compared to that of PP and PCL individually. The findings suggest that a contact mediated by Van der Waals forces has occurred between PP and PCL, as demonstrated by alterations in the crystalline and thermal characteristics of the blend. The results align with computational models indicating an interaction between PP and PCL, with the distance between the hydrogen atom of PP and the oxygen atom of PCL measuring 3.6 Å and 3.04 Å, respectively. The PP/PCL polyblend, due to its crystallinity, thermal characteristics, and biodegradability, possesses potential for applications necessitating materials with robust mechanical qualities alongside biodegradability.

Conflicts of interest

The authors confirm no conflict of interest.

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