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Mechanical Properties of PCL/PLA/PEG composite blended with different molecular weight (M_W) of PEG for Fused Deposition Modelling (FDM) filament wire.

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Abstract: In tnis study, Polycaprolactone/Polylactide (PCL/PLA) was plasticized by Polyethylene Glycols (PEGs) with three different molecular weights (Mw=400, 6000 and 10,000g/mol) with the objective to determine the effect of different molecular weight and percentage of PEG on the mechanical properties of PCL/PLA/PEG composites. The effects of content and molecular weight of PEG on the mechanical properties of PCL/PLA/PEG were studied by tensile and impact tests. The tensile test were carried out using Instron 5567 Universal Testing Machine meanwhile the impact test were carried out using Charpy Impact Testing Machine. The results revealed that, increasing in molecular weight of PEG could significantly improve the tensile and impact strenght of PCL/PLA. The results also shows that with increasing molecular weight of PEG, the tensile strength and modulus of elasticity of PCL/PLA/PEG composite were also increased. However, with the increasing of PEG content from 5phr to 15phr on PCL/PLA/PEG composites, it decreases the tensile strength and Young's modulus. Meanwhile from the Charpy impact test, it shows that the impact strength of PCL/PLA/PEG composites increased as the molecular weight of PEG increased from 400 to 10,000. The overall results demonstrated better mechanical properties of PCL/PLA/PEG composites can be achieved by optimizing the content and molecular weight of PEG. The introduction of PEG molecular weight increased the intermolecular force and enhanced the mobility of PCL/PLA chains, thus improving mechanical properties of PCL/PLA.

Keywords: PCL, PLA, PEG, FDM, tensile strength, impact strength, composite

1. Introduction

For past few years, there has been an intensive research on the development of biodegradable polymer as a suitable means for the uses of biomedical application. Polylactic acid (PLA) and Polycaprolactone (PCL) have been widely used for the application owing to excellent biocompatibility and biodegradable thermoplastic properties polymers.

In addition, PLA have a great mechanical properties, biocompatibility and offers unique features of biodegradability, thermo plasticity and eco-friendliness that offer potential applications as commodity plastics, as in packaging, agricultural products, disposable materials and medical textile industry [1][2]. PLA has been used as biological material as well as surgical implant material and drug delivery systems, and also as porous scaffolds for the growth of neo-tissue [3].

Meanwhile, PCL is one of the most eminent synthetic polymer that being researched for tissue engineering. This is because PCL is relatively inexpensive, highly elastic polyester that demonstrates a lack of toxicity with good mechanical properties and slow in degradation time [4]. PCL is a semi crystal-line polyester and highly processible as it is soluble in a wide range of organic solvents. It has a relatively low melting point and the more important that it has the ability to form miscible blends with a wide range of polymers. This has stimulated extensive research into its potential application in the biomedical field [5].

The blend of PLA/PCL has been focused on their compatibilization by many researchers. PCL exhibitions

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low glass transition temperature and high toughness, thus acting as a decent applicant for toughening PLA, PCL is degradable polyester, meaning that with blending this material with PLA it can result a totally degradable materials.

Plasticizers have been employed extensively to improve processability, flexibility, impact toughness, and reduce the glass transition temperature (Tg) of glassy polymers [9]. The molecular weight of plasticizer is an important factor that affects the crystalline and mechanical properties of polymer/ plasticizer blends. Yet surprisingly, there are only few researches on the effect of plasticizer molecular weight so far.

Previous researches stated that PCL and PLA are thermodynamically incompatible with each other and can only form a multiphase structure in their blended system, with poor interfacial adhesion, which restricts its further applications. In order to improve the PLA/PCL composition, PEG was added to the PLA/PCL as a cross linker to strengthen the mechanical properties.

2.0 Methodology of Research

2.1 Materials

The PCL (BGH600C) and PLA (PTG600C) was obtained from Shenzen Bright China Industrial Co, China. The PEGs with three different molecular weights were selected as plasticizers. The PEG used in this experiment were PEG 400, 6000 and 10,000 Mw. PEG 400 provided in colorless liquid form with a weight average molecular weight of 400 g/mol and density of 1.13 g/cm3. Meanwhile, PEG- 6000 and PEG-10,000 were in solid form at room temperature.

2.2 Sample preparation

The mixing was done using Barbender plastography machine with mixing temperature was set at 160 °C and the rotating speed is 30 rpm for all compositions. PEG granules was first pulverized before mixing with the PLA/PCL polymer. Figure 1 shows the bardender palstography machine used in this study.

Fig 1 Barbender machine use to mix the composition

Injection molding is a manufacturing process producing a part mostly from polymers that are melted and injected into a mold. Figure 2 below shows the injection moulding machine used in this study to produce samples from PCL/PLA/PEG composite for mechanical testing.

Fig 2 Injection molding machine used to produce samples

The blend composition of PCL/PLA/PEG composite are shown in Table 1.

Table-1: Composition of the PLA/PCL/PEG blends

PEG (Mw)	Sample Formulation	PCL (wt.%)	PLA (wt.%)	PEG (phr)
400	PLP-G41	70	30	5
	PLP-G42	70	30	10
	PLP-G43	70	30	15
6000	PLP-G61	70	30	5
	PLP-G62	70	30	10
	PLP-G63	70	30	15
10000	PLP-G101	70	30	5
	PLP-G102	70	30	10
	PLP-G103	70	30	15

2.3 Characterization- Fourier Transform Infrared (FTIR)

Fourier transform infrared spectroscopy (FTIR) is a technique which is used to obtain an infrared spectrum of absorption, emission, and photoconductivity. An FTIR spectrometer simultaneously collects high spectral resolution data over a wide spectral range. Fourier Transform Infra-red spectroscopy (FTIR) analyses were carried out to examine the spectrum of PCL/PLA/PEG composite.

Infrared (IR) radiation is electromagnetic radiation in the wavelength between the visible and microwave regions of the electromagnetic spectrum. The IR region can be divided into 3 small region which is near IR (14000-4000cm-1), mid IR (4000-400cm-1) and far IR (400-20cm-1).

Fig 3 Fourier transform infrared spectroscopy (FTIR) machine

2.4 Mechanical Tests

2.4.1 Tensile Test

The tensile test was carried out refering to the ISO 527-2A standard. For each blend, five specimens were tested. The test was conducted under ambient condition at the crosshead speeds of 5 mm/min by using an Instron 5567 Universal Testing Machine. Five specimens of each formulation were tested and the average values were reported. Figure 4 below shows the size of sample for the Tensile test.

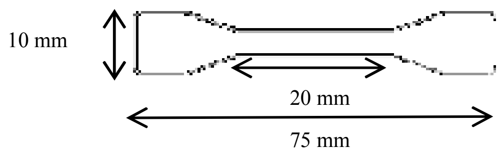

Fig 4 Dog bone sample for tensile testing [7]

2.4.2 Impact Test

The Charpy impact test is a standardized high strain-rate which determines the amount of energy absorbed by each composition of PLA/PCL/PEG during fracture. This test are applied in this study to evaluate the impact toughness of each formulation according to the ISO 179-1 standard. Figure 5 below shows the size of sample for impact test.

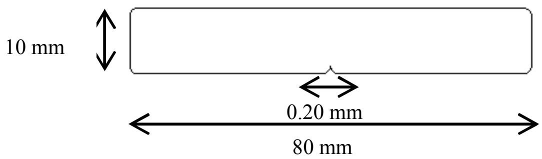

Fig 5 Sample for impact testing [8].

3.0 Results and Discussion

3.1 Fourier Transform Infrared (FTIR)

FTIR spectra of PCL/PLA/PEG blends are shown in Figure 6. The broad peaks at 3414.85 correspond to Intermolecular H bonds respectively as the molecular weight and content of PEG decreasing. Those at 2871.13 result from the asymmetric and symmetric CH2 stretching vibration. The third peaks at value 1719.85 indicates that the corresponding of C=O Stretching and Vibrations (Nonconjugated) and the fourth peaks state that it is correspond with CH Bending Vibrations (CH3). Lastly, peaks at 1108.37 origins from C-O-C vibrations in Esters (Formates).

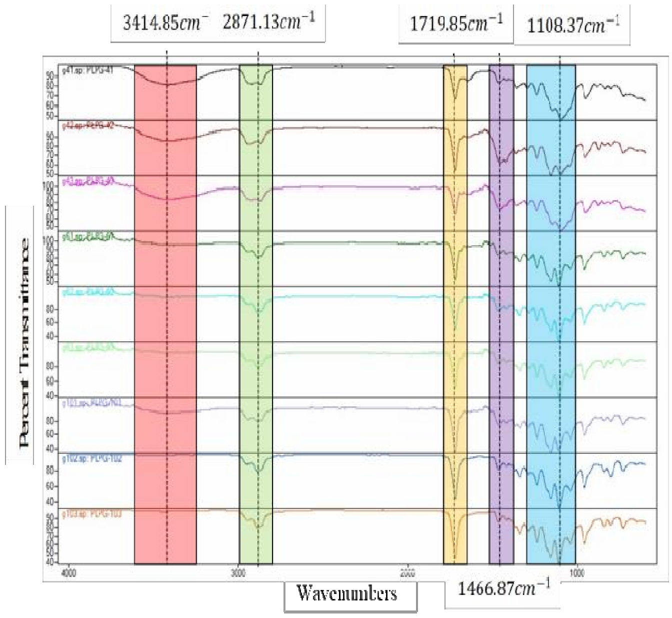

Fig 6 FTIR of PCL/PLA/PEG with different content and molecular weight.

3.2 Effect of PEG content on tensile strength of PCL/PLA/PEG blends

Tensile strength is an important parameter to characterize the largest stress limit of materials under tensile load. Figures 7 illustrates the effect of the PEG content on the tensile strength of the PCL/PLA/PEG composites. The figure shows that the tensile strength of the PCL/PLA/PEG composite with molecular weight of 400, 6000 and 10000 decreases with the increasing content of PEG from 5 to 15 phr. The highest values of tensile strength were recorded at 15.78Mpa for PLP-G101. Meanwhile the lowest value of tensile strength were recorded for PLP-G43 where the tensile strength is 12.93Mpa.

The tensile strength of the PCL/PLA/PEG composite decreases with the increasing of PEG content. This is mainly because the addition of PEG plays a dilution effect, which weakens the intermolecular forces among PCL/PLA chains and makes it more flexible and soft, resulting in a decline in tensile strength.

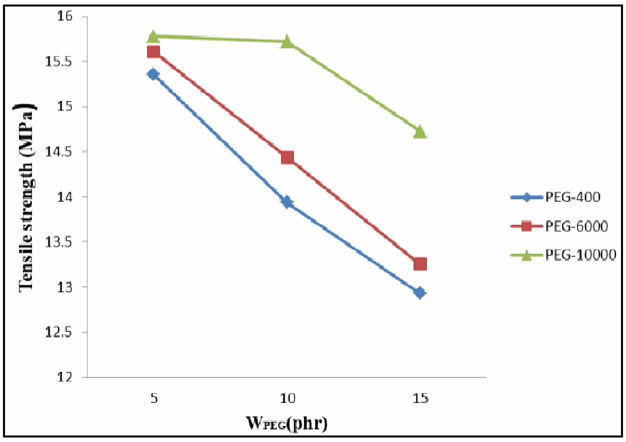

Fig 7 Effect of PEG400, PEG6000 and PEG10000 content on tensile strength of PCL/PLA/PEG blends.

Besides that, it also shows that composite that blended with PEG10000 shows better tensile strength compare to composites blended with PEG400 and PEG6000. The tensile strength of the blends largely depends upon the strength and molecular weight of PEG components. It is well-known that increased of molecular weight of PEG increases intermolecular forces and surface energy, and makes molecular chain entanglement easier, but simultaneously reduces the slippage of PCL/PLA molecular chains under tensile loading, resulting in an increase in tensile strength [10][11]. This reflect the result achived where higher Mw gives better result compare to low Mw PEG.

3.3 Effect of PEGs content on modulus of elasticity of PCL/PLA/PEG blends.

The modulus of elasticity for PCL/PLA/PEG composites blended with 5, 10 and 15 phr of PEG are shown in Figure 8. The modulus of elasticity is a very important parameter to characterize the stiffness of materials within the elastic range. The highest values of elastic modulus were recorded at 396.43Mpa for PLP-G101. Meanwhile the lowest values were recorded for PLP-G43 where the elastic modulus is 291.33Mpa. In overall pattern shows that the modulus of elasticity of the PCL/PLA/PEG blends with molecular weight of 400, 6000 and 10000 decreases with the increasing content of PEG from 5 to 15 phr.

The tensile modulus of the blends nonlinearly decreases with the increment of PEG content, indicating that the addition of PEG is prejudicial to improve the rigidity of the PCL/PLA/PEG composite. Generally, the addition of a plasticizer reduces the tensile modulus of rigid polymers. This is because that the interactions between plasticizer molecules and polymers weaken polymer–polymer intermolecular interactions, which is beneficial to improve the rearrangement between polymer chains under external force field, and impart flexibility, leading to tensile modulus declining with increase of PEG content [9].

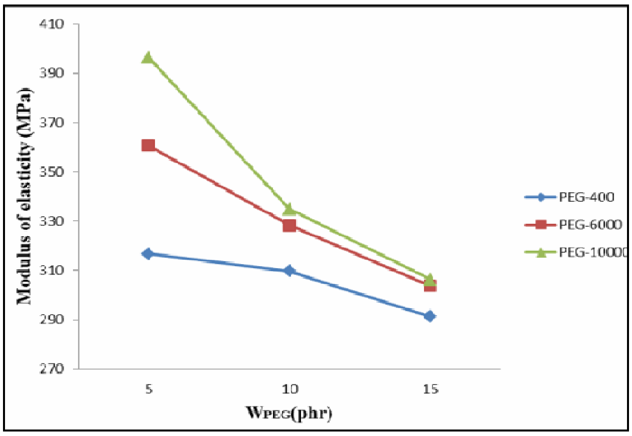

Fig 8 Effect of PEG content on modulus of elasticity of PCL/PLA/PEG blends

A part from that, the modulus of elasticity of the PCL/PLA/PEG composite increased as the molecular weight of PEG increase from 400 to 10000. This is mostly because higher molecular weight of PEG has smaller molecular size, which makes it easier to incorporate into the PCL/PLA chains and thereby exhibits a more efficient plasticizing effect than the higher molecular weight of PEG.

3.4 Effect of PEG content on impact strength of PCL/PLA/PEG blends.

Impact strength is a very important parameter to characterize the impact toughness and fracture resistance of materials under high-speed shock load. Figure 9 represent the dependence of Charpy impact strength of PCL/PLA/PEG blends on PEG content of 5phr, 10phr and 15phr. The highest values of impact strength were recorded at 0.14J for PLP-G103. Meanwhile the lowest value of impact strength were recorded when the weightage of PEG-400 is 5phr where the elastic modulus is 0.081J. Overall, the pattern shows that the impact strength of the PCL/PLA/PEG increased as the molecular weight of PEG increase from 400 to 10000.

The impact strength of the blends increased by increasing the PEG content. This indicates that the introduction of PEG can significantly improve the impact strengths of PCL/PLA in the case of relatively high PEG content. On the other hand, when PEG content is incresed further, it acts maily as a plasticizer and increases the free volume and movement ability of chain segments. As a result, the impact strengths of PCL/PLA/PEG increased significantly.

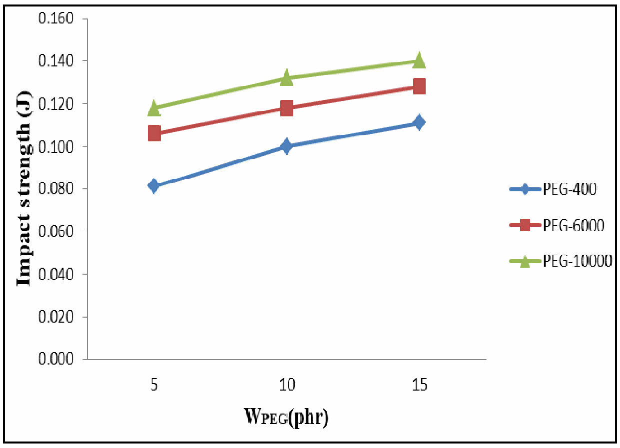

Fig 9 Effect of PEG content on impact strength of PCL/PLA/PEG blends.

Besides that, it also shows that the impact strength of the PCL/PLA/PEG blends that content 5, 10 and 15 phr increased as the molecular weight of PEG increased from 400 to 10000. This is attributed to increased molecular interactions between PEG and PCL/PLA when the molecular weight is higher. Generally, the length of PEG molecular chain increases with the increase of molecular weight, resulting in increasing the intermolecular forces. It also increases the entanglement between PCL/PLA and PEG molecular chains. Simultaneously, the relative slippage between molecular chains under impact loading decreases, resulting in an increase in impact strength [6].

4.0 Conclusion

To improve the PCL/PLA composite, it was blended with different molecular weight and content of PEG. The effects of different molecular weight and phr of PEG on the mechanical properties of PCL/PLA/PEG composite were explored. From the study, the following conclusions can be drawn:

i. Tensile strength and Young's modulus results showed that highest value for PCL/PLA/PEG composites that contain 5phr of PEG- 10,000 Mw. This is due to the increases intermolecular forces and surface energy, and makes molecular chain entanglement easier, but simultaneously reduces the slippage of PCL/PLA molecular chains under tensile loading, resulting in an increase in tensile strength and modulus of elasticity. It also can be said that as the molecular weight increase, the tensile strength and elastic modulus also increase. However, as the content of PEG increases, the tensile strength is decreased due to plasticizing effect of PEG.

ii. The highest value of impact strength was obtained for PCL/PLA/PEG composites that contain 15 phr of PEG-10,000 Mw. This is attributed to good molecular interactions between PEG and PCL/PLA when Mw is higher. Thus, the relative slippage between molecular chains under impact loading decreases, resulting in an increase in impact strength. The value of impact strength is largely depending on the molecular weight and content of PEG

iii. The results demonstrated that good mechanical properties of PCL/PLA/PEG blends could be achieved by optimizing the content and molecular weight of PEG. Besides having a better tensile strength and modulus of elasticity, it also demonstrate good result in impact strength.

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