

PREPARATION AND CHARACTERIZATION OF TAPIOCA STARCH FILLED POLYCAPROLACTONE COMPOSITE FILMS

(Penyediaan dan Pencirian Filem Komposit Polikaprolakton Terisi Kanji Ubi Kayu)

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Abstract

This research was conducted to develop a new biodegradable polymeric packaging material to replace the current polymer packaging without changing the requirements properties. Polycaprolactone (PCL) was chosen as the matrix because of its biodegradability characteristics. Tapioca starch was used as filler from 10 to 40 wt% loading contents. The composite films were prepared using solvent casting technique and chloroform was used as solvent to dissolve the PCL pellets. The PCL matrix showed result of higher tensile strength which was 65.9 N/mm^2 with elongation at break at approximately 731%. The addition of starch in the PCL composite films increased the tensile modulus of the films. The tensile strength of the composite films decreased with increasing starch contents. Similar trends were also observed for elongation at break of the films.

Keywords: polycaprolactone (PCL), tapioca starch, casting films, biodegradable, polymer packaging

Abstrak

Kajian ini telah dijalankan bagi menghasilkan produk baru untuk menggantikan pembungkus plastik yang sedia ada dengan plastik mesra alam tanpa mengubah kriteria dan ciri-ciri yang diperlukan. Polikaprolakton (PCL) dipilih sebagai matrik kerana cirinya yang boleh terurai secara semulajadi. Kanji digunakan sebagai pengisi didalam komposit filem dari 10 hingga 40 wt%. Komposit ini telah disediakan dengan menggunakan teknik tuangan ke dalam acuan dan klorofom digunakan sebagai bahan pelarut untuk melarutkanpelet PCL. Matrik PCL menunjukkan kekuatan tegangan yang tinggi iaitu 65.9 N/mm^2 dengan pemanjangan pada ketika putus lebih kurang 731%. Penambahan kanji didalam PCL meningkatkan modulus tegangan komposit filem. Didapati kekuatan tegangan komposit filem semakin menurun dengan penambahan kanji. Corak yang sama juga dapat dilihat pada pemanjangan filem pada ketika putus.

Keywords: polycaprolactone (PCL), kanji ubi kayu, filem casting, biodegradasi, pembungkusan polimer

Introduction

Conventional plastics have been used in packaging applications for many years. Most of these plastics are non-biodegradable and are almost always discarded after a short period of usage. The use of these materials would induce a serious environmental problem if not controlled. Increase in environmental concern worldwide has highlighted the necessity to reduce and restructure the use of plastics, not only because their degradability characteristic but their production also requires large amount of petroleum supply which is very limited and non-renewable resources. Such awareness has drawn much attention in the development of biodegradable or environmentally sustainable packaging materials [1].

A biodegradable polymer is defined as one that breaks down into smaller fragments due to the action of bacteria and other microorganisms, leading to changes in its physical properties [2]. PCL is known to be a commercially biodegradable polymer with a rather low melting point about $60 \text{ }^\circ\text{C}$. It is biodegradable, hydrophobic and partially crystalline types of polyester with good mechanical properties [3-6] suitable for packaging application. A strong water-resistance PCL films can be produced when molar mass of the polymer is higher than $40,000 \text{ g/mol}$ [7].

However, due to the expensive price of PCL compared to others type of polymer, the use of PCL is limited in packaging applications. To reduce the cost of the matrix, PCL is often reinforced or blended with natural fiber or low cost polymer such as cellulose and starch. This will not only overcome the limitation of polymer in the industry but can also enhance the mechanical and physical properties of the composite itself [8].

Pure starch is white, odorless and tasteless powder that is insoluble in alcohol and water. It is a partially crystalline polymer composed of amylose and amylopectin [9,10]. In developing a product that have short period of usage, starch has been chosen as one of the potential material [11]. Furthermore, starch can be easily obtained from renewable resources at low cost and offers several natural advantages. Therefore, starch is widely used to be blended with synthetic thermoplastics polymers in producing many types of products [4,11,12]. Besides that, starch is completely biodegradable in soil and water and as such is environmental friendly material.

Previously in preparing the PCL/starch composite films, the common methods used by the researchers are blown films and extrusion [3-5,7]. The used of solvent casting technique in preparing the composite films is very rare. The aim of this work is to study the effects of starch in the PCL composite films by using solvent casting technique.

Materials and Methods

Materials and Sample Preparation

Polycaprolactone (PCL) pellets were purchased from Sigma Aldrich SdnBhd with average M_n 70,000 – 90,000. The solvent used in the experiment was chloroform purchased from Merck Sdn Bhd. Tapioca starch powder manufactured by Spion Product Sdn Bhd Malaysia. Chloroform was used as the solvent to prepare the PCL film by using solvent casting technique. Briefly, 10% (w/v) PCL solution were prepared. The PCL pellets were dissolved in the chloroform and continuously stirred until all of the PCL pellets dissolved completely. Then, the solution was cast onto the 20 cm square glass mold and it was then placed in the fume hood for slow rate of evaporation. The dried film was collected and dried for 48 hours. In preparing the PCL composite films, 10, 20, 30,40wt % of starch were added slowly into the dissolved PCL solution and continuously stirred for 1-2 hours before casting onto the mold. Composite films sample with approximately 1 mm in thickness were formed. The films prepared were then cut according to the standard dimension of specimen test and analyzed.

Attenuated Total Reflection Fourier Transform Infrared Spectroscopy (ATR-FTIR)

To characterize the composite films, the specimens in the dimension of 2 cm x 2 cm films were scanned directly by using Perkin Elmer 2000 Infrared Spectrometer. The spectra were obtained by accumulating 16 scans in the range of 600-4000 cm^{-1} with a resolution of 4 cm^{-1} .

Tensile Test

Tensile properties of the films were investigated using tensile machine Llyod LRX materials testing machine (Llyod Instruments Ltd, Fareham, UK) according to ASTM D882-10. The load and the constant crosshead speed were 2.5 kN and 10 mm/min respectively and the testing was carried out at room temperature. Five values of measurements were taken to evaluate the tensile strength, tensile modulus and elongation at break from the strain-stress curve.

Results and Discussion

FTIR Analysis

Figure 1 represents the spectra of PCL, starch and PCL composite films. All the characteristic peaks that are consistent with PCL structure were also present in the composite spectra. The broad peak at 3200 – 3600 cm^{-1} in the starch spectrum corresponds to the strong OH bonding in the chain. However, the spectra for all the PCL composite films showed no such peak although the amount of starch added increased in every formulation. This is probably due to poor interaction between starch and PCL matrix.

From the analysis, it can be concluded that the starch and PCL had different polarity, hydrophilic (starch) and hydrophobic (PCL). The same results were also reported by other researchers where they found that PCL and starch seemed too incompatible with each other due to the limited interaction [13,14].

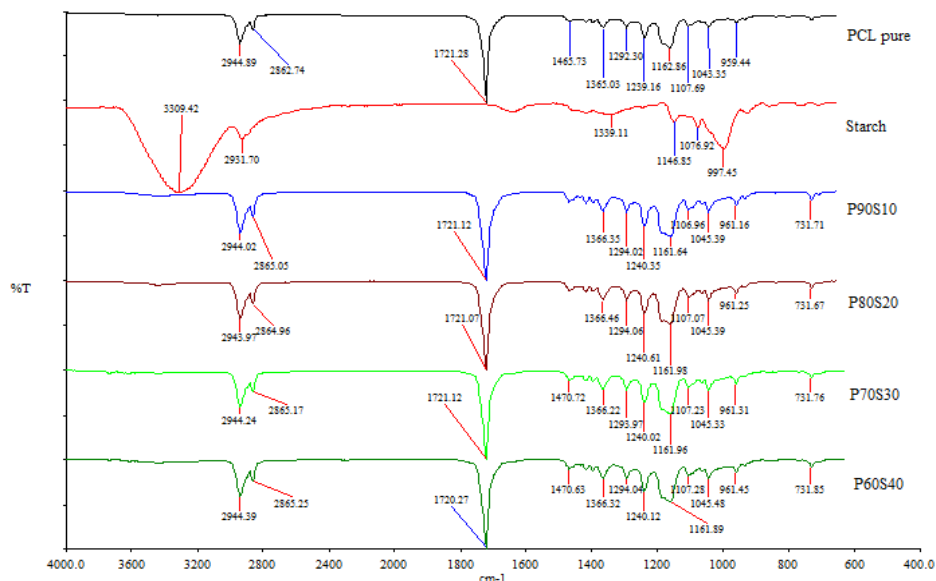


Figure 1. ATR-FTIR spectrum of PCL, starch and PCL composite films

Tensile Properties

Figures 2, 3 and 4 represent the tensile strength, elongation at break and the Young's Modulus of PCL and PCL composite films. From Figure 2, it can be seen that the tensile strength of pure PCL was initially high with the value of approximately 66 N/mm². However, this value dropped drastically to 27.5 N/mm² when starch was added and continue to decrease with increasing amount of starch. When the starch was added up to 40 wt%, the measured value dropped to 12.8 N/mm². Nonetheless, tensile strength value of the PCL/starch composite films up to 30 wt % of starch were quite high compared to tensile strength value of low density polyethylene (LDPE) which reported to be in the range of 9.7-17.2 N/mm² [15], suggesting that these films have great potential to replace LDPE as packaging material.

Similar research has been reported previously by using different methods. From the previous study [4], the tensile strength of the pure PCL prepared using blown films are reported to be 29 N/mm² but when the starch was added up to 40 wt%, the value obtained was 18.4 N/mm² which is higher than the value obtained in this research. There are several factors that cause the different in the measured value. As it was prepared using solvent-cast, the interaction of the starch filled in the composite films might be poor compared to blown films as the matrix and the starch was extruded together before blown.

The same trends seemed to appear in Figure 3. The elongation at break of pure PCL was quite higher before starch was added and dropped rapidly from 730% to 184% when 40 wt % of starch was added. When starch was added from 10 to 30 wt%, the values of the elongation at breaks was in the range of 498-419%. The different in the measured values was small.

From the tensile analysis, the well-known ductile polymer, PCL, was able to undergo large deformations. However the addition of starch in the composite films reduced the properties. From the FTIR analysis it was shown that there are poor interaction between the starch and PCL matrix. As such, the tensile strength and elongation at breaks of the films was decreased rapidly when the starch was added. Similar results were also reported [3-5] when natural biopolymer was blended together with polymer matrix. Besides that, good dispersion of starch in the composite films can also affect the results in the tensile analysis. According to Kim *et al.* [5], they claim that, although starch and PCL are immiscible with each other, to obtain good mechanical properties, it is essential for starch domain to be well dispersed within the PCL composite films.

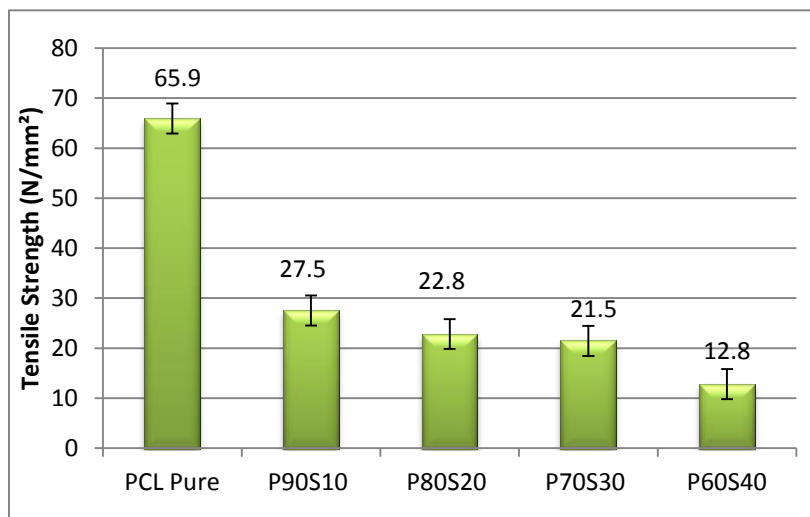


Figure 2. Tensile strength of PCL and PCL composite films

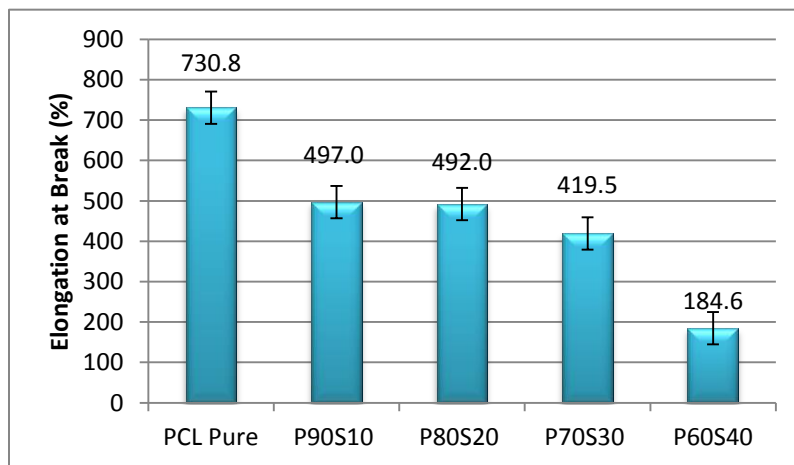


Figure 3. Elongation at break PCL and PCL composite films

The result in Figure 4 indicates that the Young's modulus of the pure PCL increased when the starch was added into the composite films. This is because starch has a high modulus compared to PCL [11]. Thus, the presence of starch in the mechanical blends can contribute to improve in modulus of the composite films. Increasing in the Young's modulus means increased in the stiffness of the composite films and affected the strength of the composite films. This is proven by previous researchers [3], when the starch added in the compositions all the mechanical properties of composite decreased.

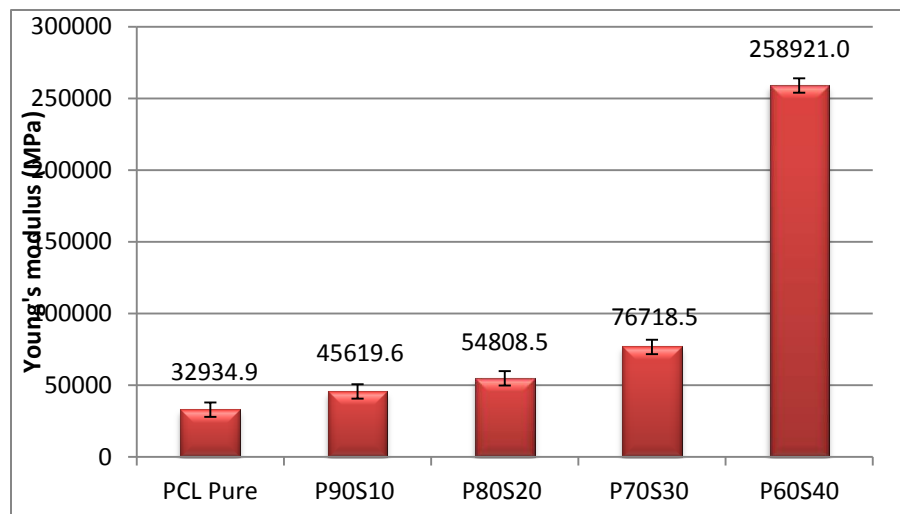


Figure 4. Young's Modulus of PCL and PCL composite films

Conclusion

The addition of starch as a filler in the composite films show improvement in the stiffness of the films. Although the tensile strength of the films decreased with increasing of the starch contents, the value are still acceptable for packaging application as the good tensile strength for starch contents up to 30 wt% was higher than LDPE strength value. The representative evidence for the presence of starch and PCL in the composite films was confirmed by ATR-FTIR.

Acknowledgement

The authors would like to express their appreciation to the Polymer Engineering Department, Universiti Teknologi Malaysia (UTM), Ministry of Education Malaysia (MOHE) and Research University Grant 4L028 for financial support.

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