

The Fabrication and Properties of Biodegradable PHB/PEG Fiber Blend

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Introduction

In today's scientific community, biodegradable and eco-friendly materials produced by renewable sources are of particular interests to many researchers. One of such materials that has been extensively studied is poly (3-hydroxybutyrate), or PHB, a natural polyester of the poly (3-hydroxyalkanoates) family. PHB can be produced by various microorganisms as a means of energy storage. Because of its biological origin, natural PHB is extremely pure and easily renewable. More importantly, PHB is recognized as a biodegradable and biocompatible thermoplastic that is potentially suitable for such applications as implant scaffolds and drug delivery. This particular experiment will seek the possibility of fabricating PHB fibers for synthetic tendon and ligament tissues.

Despite its excellent properties, PHB has many drawbacks that limit its processability and effectiveness as an implant material. Research has shown that due to PHB's highly crystalline and hydrophobic nature, the rate of its biodegradation *in vivo* is much slower than desired. Furthermore, PHB displays exceptional thermal instability at temperatures beyond its melting point, which poses great difficulty in processing PHB using conventional methods. One possible solution for these problems is to blend PHB with another polymer to improve the properties of the system. Poly (ethylene glycol), or PEG, a hydrophilic polymer, is chosen for this purpose. PEG is believed to be able to accelerate the degradation process by reducing the crystallinity of PHB. Conventionally, PHB/PEG blends are prepared in films by solution-casting. This method is generally inconvenient for industrial production and the film blend is incompatible with the ultimate application of this project.

The objectives of this experiment are to examine the difference, if any, in reducing the degree of crystallinity of PHB between linear (LPEG) and star-shaped (SPEG) PEG, and to evaluate the feasibility of fabricating PHB/PEG fiber blend using extrusion, rather than solution-casting.

Experimental

The materials examined in this experiment included unpurified PHB (MW = 300,000 g/mol), linear PEG, and star-shaped PEG (each MW = 20,000 g/mol). Pure PHB was first extruded in a Thermo-Hakke Micro-Extruder at various temperatures 5-20° C above its melting point (~ 170° C) in the presence of nitrogen gas. Since severe degradation was observed during extrusion after alternating various parameters, solution-casting in chloroform was employed as the blending mechanism instead. PHB and PEG were blended at three different compositions: 80 (wt%) PHB/20 (wt%) PEG, 50 PHB/50 PEG, and 20 PHB/80 PEG. Each composition was prepared on a 35.0 mg basis and dissolved in 10 mL of CHCl₃. Sonication and solvent reflux were used as means of dissolving the blend in CHCl₃. Reflux enabled the PHB to be dissolved at a much higher temperature than the boiling point of chloroform, which produced a more homogeneous solution. The resulting solution was cast onto Teflon sheet to form thin films. Differential scanning calorimetry (DSC) tests for each blend sample were carried out in a TA Instrument DSC machine. The sample size was 5.55 mg ± 5% and the heating and cooling rate was set at 10° C/min.

Results and Discussion

As described above, the blended polymers were obtained via solution casting instead of extrusion, which was the original intent of the experiment. After repeatedly attempting to process pure PHB at several different temperatures and external conditions, e.g. inert gas environment, severe odor and discoloration were still observed. More importantly, the melted (and degraded) PHB was not viscous enough to be extruded, i.e. the final product turned into liquid rather than fiber. Therefore, given the amount of time permitted for this project and the goal to test the effects of LPEG versus SPEG, solution casting was carried out to produce blended films.

Phase Crystallinity of PHB and PEG as a Function of Composition

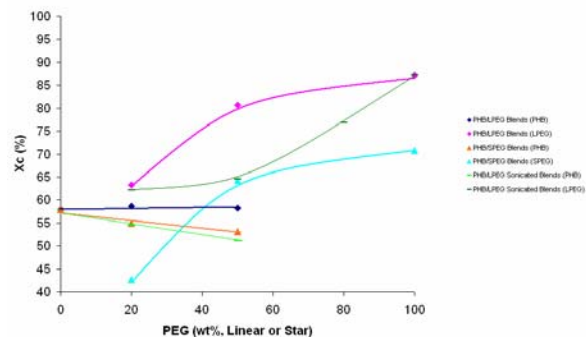


Figure 1: DSC analysis on the composition of PEG and the percent crystallinity of each of the component in the blend. The navy, orange and light green colored markers represent the crystallinity of PHB in various blends.

Figure 1 suggests that as the amount of SPEG increased in the blend, the X_c (% crystallization) of PHB decreased slightly, while increase in LPEG component increased the X_c of PHB. This is an indication that the star-shaped PEG is slightly more effective in reducing the amount of crystalline region in PHB. However, further experiments are needed to validate the statement since the difference between the two is small. On the other hand, as the amount of PHB increased in the blends, the X_c of PEG, linear and star, was largely suppressed, especially in the case of the SPEG blends. The reason could be that the numerous branches of the star polymer inhibited close packing of the individual particles, which would otherwise organize themselves into ordered crystals upon cooling. One other reason why the effect of linear versus star PEG in reducing the X_c of PHB needs to be further validated is that the reduction in crystallinity did not lead to a lower T_m for the blends (Table 1), which normally is not the case.

Table 1: Melting and Crystallization Temperatures of PHB/PEG Blends (prepared by reflux) and Neat Polymers

Sample	PHB		PEG		
	T_m (°C)	T_c (°C)	T_m (°C)	T_c (°C)	
PHB/LPEG	80/20	170.82	81	58.8	18.87
	50/50	171.06	80.57	62.58	38.07
PHB/SPEG	80/20	166.25	91.38	50.31	-25.91
	50/50	169.8	95.79	50.76	27.83
Neat PHB	100/0	166.23	92.37	N/A	N/A
Neat LPEG	0/100	N/A	N/A	64.38	39.06
Neat SPEG	0/100	N/A	N/A	55.89	31.81

Many irregularities such as the observation of double peaks in PHB's melting during 2nd heating and the appearance of a 3rd "crystallization peak" among the 50 PHB/50 PEG blends were noticed and need to be studied more carefully in the further experiments.

Conclusion

The effect of linear and star-shaped PEG in reducing the degree of crystallinity of PHB was examined by DSC. Though SPEG showed a slight trend in reducing X_c of PHB, further experiments are needed to reach a conclusive result. Due to the time limitation and failures in using extrusion to fabricate PHB fibers, solution-casting using chloroform proved to be an easier method to produce small quantity of PHB/PEG blended films in the laboratory.

