

PHYSICO-CHEMICAL CHARACTERISTICS OF CHITIN-POLYESTER SYSTEMS IN DEPENDENCE ON THEIR COMPOSITION

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Abstract

In order to improve the properties of their individual components, the compositions of dibutylchitin (DBC) and aliphatic polyesters (PCLG) were prepared and examined. The studied systems are homogeneous in a wide range of composition and molar masses of their components. The homogeneities of the blends made it possible to form smooth and transparent films, which were investigated by mechanical testing. It was found that the chemical structure and molar mass of a polyester component had an effect on mechanical properties of the systems. The films were subjected to hydrolytic degradation in media of various pH values (4.0, 7.4 and 13.0) at 37 °C. Furthermore, it was found that the molar mass and composition of the PCLG component clearly affected the rate of hydrolysis of the studied systems. The effect of hydrophilicity of the DBC/PCLG blends on degradation rate was also investigated. Consequently, by an appropriate choice of the components it is possible to control the profile of hydrolytic degradation of the DBC/PCLG systems.

Key words: *dibutylchitin, biodegradable, polyesters, blends, poly(ϵ -caprolactone), polylactide.*

1. Introduction

The natural polymers are a diverse and versatile class of materials that are produced by living organisms. They represent the most abundant reserves of organic compounds on Earth. Some of them may be used in their natural form without changing the structure of their molecules. However, the majority is subjected to various types of modifications to improve their functional properties for wider use. The properties of biopolymers can be significantly improved by blending (mixing) them with synthetic polymers because of its simplicity and efficiency [1].

Among the biopolymers, chitin and chitosan are suitable functional materials due to their excellent properties such as biocompatibility, biodegradability, non-toxicity and unique ability to form films. A wide variety of biomedical applications for chitin and chitosan have been reported in the last few years [2, 3]. They are used extensively as wound dressings, drug delivery systems, tissue engineering scaffolds, separation membranes, stent coatings and many more. Recently, there has also been a growing interest in chitin and chitosan nanofibers obtained by electrospinning.

The main disadvantage of natural chitin application is its insolubility in common solvents and hence causing significant difficulties in chitin processing. The interest has increased in the use of an ester derivative of chitin - dibutylchitin (DBC) which, in comparison to chitin, is characterized by a good solubility in organic solvents. Therefore, dibutylchitin can be processed in the form of fiber or film which is essential for manufacturing of biomaterials. Many investigations revealed that DBC is biocompatible, bioactive, bacteriostatic and enzymatically degradable [4, 5].

This work is a continuation of our research presented in [6 - 8], concerning the physical modification of dibutylchitin for overcoming the drawback of its brittle nature and poor mechanical properties. It was shown that amorphous aliphatic polyesters of ϵ -caprolactone, L-lactide and glycolide (PCLG) exhibited a profound effect on mechanical and physical properties of DBC. Physical modification of DBC with PCLG polyester resulted in superior mechanical properties – the blended materials exhibited a much higher toughness and elongation at break as well as a lower value of elasticity modulus as compared to original DBC.

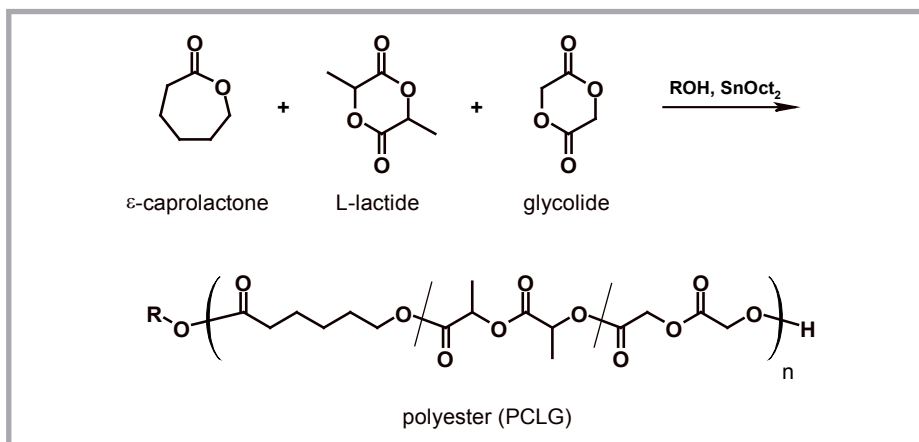
2. Materials and methods

2.1. Dibutylchitin (DBC)

Dibutylchitin was synthesized by the reaction of krill chitin with butyric anhydride according to [9 - 11] and additionally purified (decolorized) with an activated carbon. The degree of esterification was close to two as confirmed by elemental analysis. Intrinsic viscosity of the studied DBC was 2.2 dL/g (dimethylacetamide, 25 °C).

2.2. Aliphatic polyesters (PCLG)

The copolymers of ϵ -caprolactone (C), L-lactide (L), and glycolide (G) were synthesized *via* ring-opening polymerization in melt using 1,4-butanediol and tin octoate as an



Scheme 1. Synthesis of PCLG polyesters via ring-opening polymerization

initiating system (**Scheme 1**). The products were further purified from monomer and catalyst residues by a dissolution-precipitation procedure using dichloromethane and methanol as a solvent and non-solvent, respectively.

The prepared polyesters are amorphous (except PC₁₀₀LG4k which is semicrystalline) and readily soluble in chlorinated organic solvents such as chloroform and dichloromethane. The glass transition temperature of PCLG varied in a broad range, from -50 °C to 40 °C, depending on the composition and molar mass of the polyester. The increasing content of caproyl moieties (from C monomer) in PCLG reduces the T_g value of the resulting polymer.

The syntheses of PCLG polyesters are summarized in **Table 1**.

2.3. Blends of DBC and PCLG

Solution blending was used in this study. The DBC/PCLG blends were prepared by mixing constant percentages (50:50 wt%) of 10% w/w solutions of the components in

Table 1. The PCLG polyesters used for the study.

Polyester	C/L/G - composition, mol%	M_n - molar mass, g/mol
PC ₅₀ LG4k	50/25/25	4 000
PC ₅₀ LG10k		10 000
PC ₅₀ LG20k		20 000
PC ₅₀ LG50k		50 000
PC ₁₀₀ LG4k	100/0/0	4 000
PC ₇₅ LG4k	75/12.5/12.5	
PC ₅₀ LG4k	50/25/25	
PC ₂₅ LG4k	25/37.5/37.5	
PC ₀ LG4k	0/50/50	

dichloromethane. The homogeneous solutions were casted on Petri dishes. After evaporation of the solvent at ambient temperature, the films were removed and thoroughly dried at 45 °C in vacuum. The thickness of the films was adjusted to $200 \pm 10 \mu\text{m}$.

2.4. Characterization

The tensile properties of the specimens were obtained by using a tensile machine (Instron 4026). The dumbbell-shaped specimens (50 mm in length with a nominal gage section of 4 mm width and 0.2 mm thickness) were uniaxially drawn at a speed of 10 mm/min at 25 °C. Each mechanical property value was an average of five measurements.

Thermal properties were examined by means of a TA Instruments DSC 2920 differential scanning calorimeter in heating-cooling-heating cycles in the temperature range from -100 °C to 150 °C at a scanning rate of 10°C/min. The glass transition temperature (T_g) was determined at the inflection point of heat capacity change in the second heating run.

The water contact angle measurements were conducted at room temperature in air using the sessile drop technique. A NRL CA goniometer (Ramé-Hart Inc., Model No. 100-00-230) equipped with a digital camera (JVC KY-F70B) and image analysis software (Drop ver. 2.1) was utilized. The static contact angle was measured from the profiles of 10 μL droplets of deionized water placed on the sample surface. The contact angle was calculated from the mean value of three measurements at three different places on the film.

For water absorption measurements, the samples, in triplicate for each system, were immersed in deionized water at 37 °C for 72 h. The samples were then recovered and after wiping off the excess surface water with a filter paper, were weighed. The water uptake was calculated as the difference between hydrated and original mass of the sample and expressed as a percentage of the original mass of the sample.

For the degradation study, the films were cut into 15 mm diameter discs. Fifteen discs of each film were divided into three groups (five samples per group). The samples were placed individually in test plates containing 10 ml of the buffer solution. The specimens were regularly withdrawn from the test media, washed with distilled water, wiped by the absorbent paper and weighed. The experiment was performed at 37 °C in buffer solutions with different pH values (4.0, 7.4 and 13.0).

3. Results and discussion

Following our previous studies [6 - 8], in this work we present a further research on modification of dibutylchitin (DBC) by its blending with aliphatic polyesters (PCLG) synthesized from ϵ -caprolactone, L-lactide and glycolide monomers.

The mechanical properties such as tensile strength (σ), elongation at break (ϵ) and elasticity modulus (E) of a series of films as a function of the molar mass (M_n) of PCLG component in equimass DBC/PCLG blends is shown in **Figure 1**. As can be seen, the molar mass of PCLG does not significantly affect the elasticity modulus of the materials. Within the whole range of M_n studied, the modulus is almost unchanged ($E = 530 - 540 \text{ MPa}$). The

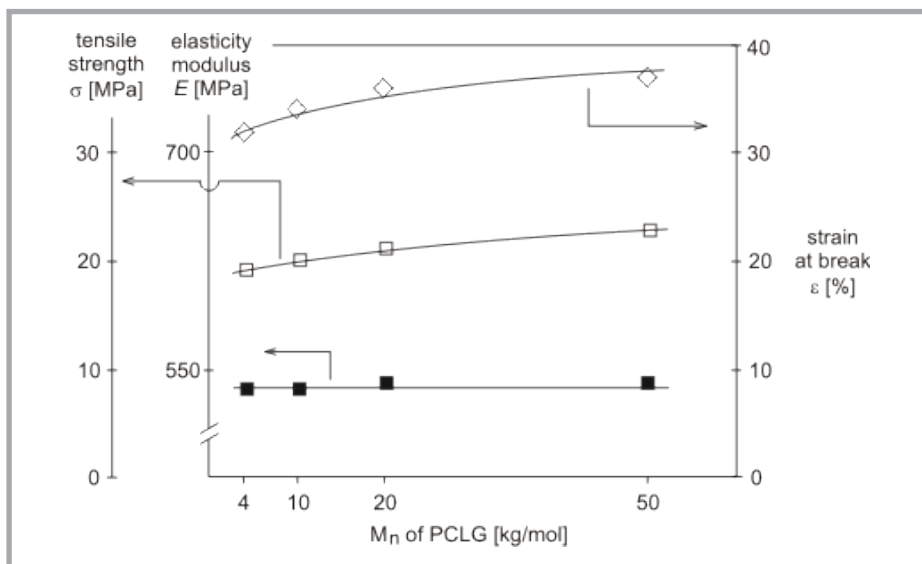


Figure 1. Tensile properties of the blends with various molar masses of the PCLG component

elasticity moduli of the blends are significantly lower than that of original DBC (870 MPa [6]). Tensile strength and strain at break slightly increase with increasing M_n of the PCLG in blends. The results indicate that the PCLG polyester component exhibits a good plasticizing effect on the DBC matrix, which efficiently reduces brittleness and low toughness of the latter.

Considering the small effect of the molar mass of PCLG on mechanical parameters of the examined blends, we synthesized a series of copolyesters of constant $M_n = 4000$ g/mol but variable composition. An increase in the content of the caproyl moieties (from C monomer) in PCLG macromolecules results in significant decrease in the glass transition temperature (T_g) of the copolyester (for PCL homopolymer, here denoted as PC₁₀₀LG4k, $T_g = -65$ °C).

Figure 2 presents the changes of mechanical properties of DBC/PCLG films as a function of PCLG composition. The plot demonstrates that the higher content of C units in the polyester led to an improved flexibility of the materials, i.e. reduced the elasticity modulus and tensile strength, and simultaneously increased the strain at break. It is clearly seen from the figure that the materials exhibit good mechanical properties if PCLG used for blending with DBC contains at least 50 mol% of C.

The DBC/PCLG materials were subjected to hydrolytic degradation in buffer solutions with different pH values (4.0, 7.4 and 13.0) at 37 °C. After three weeks of incubation, it was found that the hydrolytic degradation of samples proceeds at a rate depending on pH of the environment as well as the chemical structure and molar mass of the polyester component (**Table 2**).

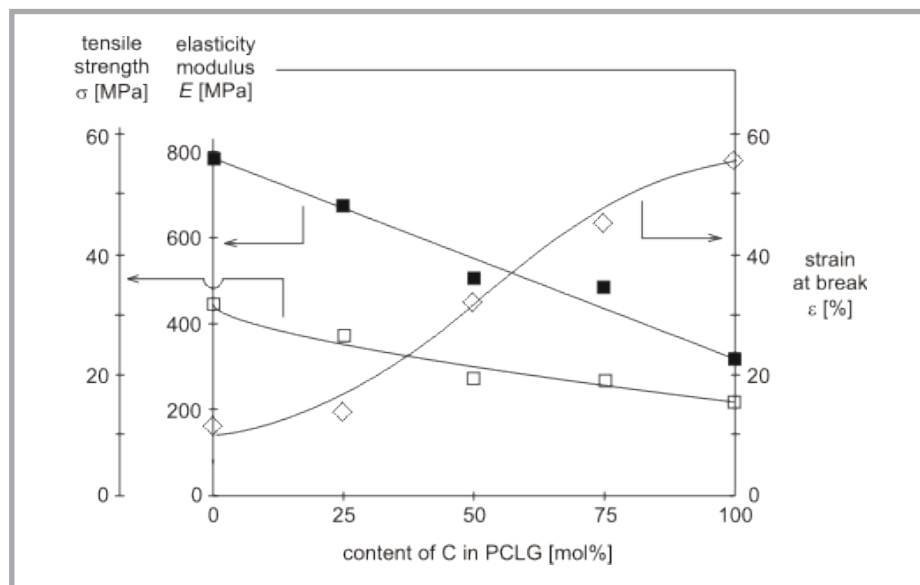


Figure 2. Tensile properties of the blends with various composition of the PCLG component.

Table 2. Hydrophilicity and hydrolytic degradation at different pH of the blends.

Material	Contact angle Θ , °	Water uptake, %	Mass loss after 3 weeks, %		
			pH		
			4.0	7.4	13.0
DBC	87	21.0	-	-	-
DBC/PC ₅₀ LG4k	66	3.9	4.7	6.9	26.6
DBC/PC ₅₀ LG10k	66	3.7	3.4	5.0	22.4
DBC/PC ₅₀ LG20k	68	2.9	3.2	3.9	19.6
DBC/PC ₅₀ LG50k	69	2.8	2.1	2.6	15.4
DBC/PC ₁₀₀ LG4k	74	10.0	3.4	4.6	7.1
DBC/PC ₇₅ LG4k	69	9.4	4.7	6.5	19.9
DBC/PC ₅₀ LG4k	66	3.9	5.5	6.9	26.6
DBC/PC ₂₅ LG4k	66	2.5	4.3	6.4	23.3
DBC/PC ₀ LG4k	65	0.5	2.8	3.8	12.4

The higher pH value of the solution caused a significant mass loss of all tested materials. The hydrolysis rate among the homologous series of the blends with the polyester component of variable molar mass increases with decreasing chain length of PCLG, irrespective of pH. Shorter chains of PCLG with high mobility around chain ends reduce the glass transition temperature of the system which may enhance water uptake and hence accelerates the degradation. The composition of PCLG component plays a key role in terms of the degradation rate of the blends. In a series of blends containing PCLG with a constant molar mass but different composition, hydrolysis rate increases, goes through a maximum at the caproyl content of 50 mol% (DBC/PC₅₀LG4k), and then decreases. This phenomenon

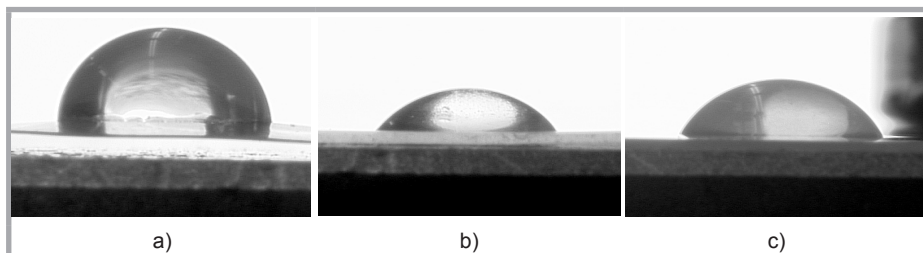


Figure 3. Water droplets on surfaces of: (a) DBC, (b) DBC/PC₅₀LG4k, and (c) DBC/PC₁₀₀LG4k.

is observed for all studied pH values. The mass loss in buffer at pH 7.4 (simulating the pH of human blood plasma) of the DBC/PC₅₀LG4k blend was near 7% after 3 weeks.

The effect of hydrophilicity of the DBC/PCLG blends on degradation rate was also investigated. The material hydrophilicity expressed by the contact angle of a water droplet on a surface (surface hydrophilicity) and water uptake (bulk hydrophilicity) is presented in **Table 2**. The contact angle of the DBC film ($\Theta = 87^\circ$) indicates that its surface is rather hydrophobic. According to the results, the value of the contact angle decreased as the DBC was blended with PCLG. **Figure 3** presents photographs of water droplets of original DBC (a) as well as DBC blended with PC₅₀LG4k (b) and PC₁₀₀LG4k (c). The Θ value among both series of blends decreased as the molar mass (series I) or the content of caproyl moieties (series II) in PCLG decreased.

An enormously high water absorption observed for DBC may have been due to many small visible cracks formed on the polymer surface during the film preparation.

It is worth noting that the incorporation of hydrophobic caproyl moieties into PCLG macromolecules would reduce hydrophilicity of both PCLG polyester and its blend with DBC. Indeed, the higher content of caproyl units in PCLG is, the more hydrophobic surface the blend has. However, the opposite trend was found for water absorption of the systems. The water uptake in this series of films was highest if the PCL homopolymer (PC₁₀₀LG4k) was blended with DBC. This behaviour may be explained by the fact that an increasing content of caproyl units in PCLG rapidly reduces its T_g , from +39 °C for PC₀LG4k to -65 °C for PC₁₀₀LG4k. A low T_g of caproyl-rich DBC/PCLG blends enhances mobility of polymer chains at 37 °C, which in turn facilitates the penetration of water molecules and promotes the absorption of water.

4. Conclusions

The blending of DBC with aliphatic PCLG polyesters is an effective means for improving the mechanical properties of the former. Excellent compatibility between both components resulted in the formation of the elastic and tough materials. The molar mass of the PCLG component has slight effect on mechanical parameters of the blends while the composition of PCLG strongly affects the tensile characteristics. The higher content of caproyl units in PCLG led to an increased flexibility of the materials which was associated

with the low glass transition temperatures of the caproyl-rich systems. The studied materials are hydrolytically degradable. The hydrolysis rate of the blends depends on pH of the environment as well as the chemical structure and molar mass of the polyester component. The fastest mass loss among the examined blends was observed for the material containing the caproyl content of 50 mol% (DBC/PC₅₀LG4k). The hydrophobic nature of DBC was significantly reduced after blending with PCLG. The more caproyl-content in PCLG, the greater the water uptake of the blend.

5. References

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