

NEW HOMOGENEOUS BLENDS OF DIBUTYRYLCHITIN AND ALIPHATIC POLYESTERS

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Abstract

The results of physical modification of dibutrylchitin (DBCH) for the purpose of improvement of its imperfect mechanical properties are presented. Thus, the novel blends of DBCH and biodegradable aliphatic copolymer derived from ϵ -caprolactone, L-lactide and glycolide (PCLG) in various proportions were prepared and examined. DBCH/PCLG blends with PCLG contents between 6 - 50 wt% were successfully prepared in film form with the thickness in the range of 10 - 500 μm . The morphology of these blend films was studied by means of differential scanning calorimetry and infrared spectroscopy. DBCH was found to be able to form miscible blends with PCLG polyester within the whole composition range studied; revealed that blends were composed of an amorphous homogeneous phase as evidenced by the presence of a single glass transition temperature, that to decrease with increasing PCLG content in materials. Furthermore, physical modification of DBCH with 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.

Key words: *dibutrylchitin, blends, biodegradable polyester, poly(ϵ -caprolactone), polylactide.*

1. Introduction

Chitin is one of the most abundant natural polysaccharides. The interest in chitin and its derivatives mainly results from the fact that these materials possess specific properties such as biocompatibility, bioactivity and biodegradability, which makes them useful for biomedical purposes [1]. The poor solubility of chitin significantly limits its utilization. Therefore, different physical and chemical modifications have been studied widely in order to obtain chitin derivatives with considerably better solubility, while at the same time maintaining its biological activity [2].

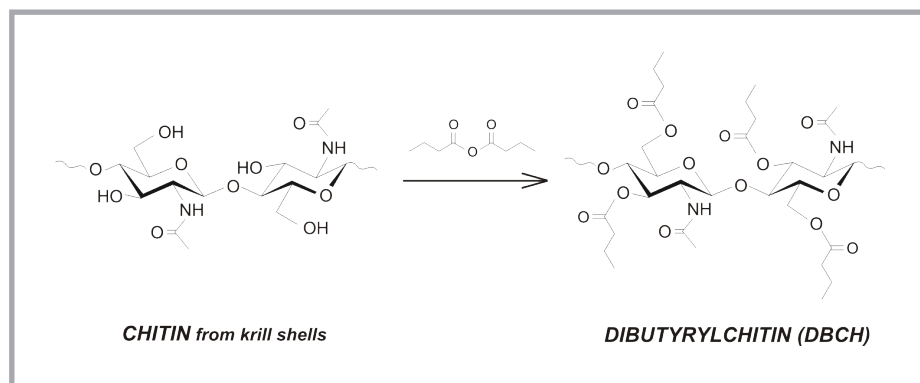
The interest has recently arisen over the use of an ester derivative of chitin - dibutylchitin (DBCH). DBCH is characterized by a good solubility in common organic solvents, which makes it possible to process them into many biomedical materials [3]. The excellent biomedical properties of DBCH have been confirmed by several clinical results which proved that DBCH is a biocompatible and biodegradable polymer, and stimulates regeneration of damaged tissues [4].

In this preliminary study, research on physical modification of DBCH was conducted for the improvement of its imperfect mechanical properties. By blending DBCH with aliphatic polyester, we expected to obtain novel materials with reduced brittleness and improved toughness and elasticity as compared to neat DBCH. An important aspect of this modification is also to preserve valuable biological properties of its products.

2. Materials and methods

2.1. Dibutylchitin (DBCH)

The polymer subjected to a physical modification is an ester derivative of chitin - dibutylchitin (DBCH) which was synthesized according to a procedure described in [5]. DBCH was additionally purified by a treatment of its acetone solution with an activated carbon. After filtering and evaporating to dryness, clear DBCH was obtained. Thus prepared DBCH having an intrinsic viscosity of 2.22 dL/g (measured in DMAc at 25 °C) was used for further studies.



2.2. Aliphatic polyester (PCLG)

In order to improve mechanical parameters, virgin DBCH was blended with high-molecular-weight aliphatic polyester. For this purpose, the copolymer of ϵ -caprolactone, L-lactide, and glycolide (PCLG) was synthesized in a ring-opening polymerization in melt using n-butanol and tin octoate as an initiating system. The copolymer was further purified from monomer and catalyst residues according to a procedure developed in our lab. The metal-free polyester is amorphous with a glass transition temperature of $-30\text{ }^{\circ}\text{C}$ and soluble in many organic solvents. The polyester composition was determined by $^1\text{H NMR}$ to be 50.3, 24.8, and 24.7 mol% of caproyl, lactyl, and glycolyl units, respectively. The intrinsic viscosity of the polyester was 1.60 dL/g, measured in chloroform at $25\text{ }^{\circ}\text{C}$.

2.3. Blends of DBCH/PCLG

The blends of DBCH and PCLG were prepared in a film form by casting the polymer solutions in dichloromethane onto Petri dishes and evaporating the solvent at ambient temperature. The blends varied in their compositions were thus obtained. The content of PCLG in blends ranged from 6 to 50 wt%. The prepared blend films possessed a uniform thickness ranging from about 10 to 500 μm , depending on the concentration of casted solutions.

2.4. Characterization

Fourier transform infrared spectra in attenuated total reflection mode (ATR-FTIR) were recorded on a Nexus spectrometer in $400 - 4000\text{ cm}^{-1}$ range with 32 scans per sample.

Thermal properties were examined by means of a DuPont 910 differential scanning calorimeter (DSC) in heating-cooling-heating cycles in the temperature range from $-50\text{ }^{\circ}\text{C}$ to $250\text{ }^{\circ}\text{C}$ at a scanning rate of $10\text{ }^{\circ}\text{C}/\text{min}$. Glass transition temperature (T_g) was estimated as the midpoint temperature of heat capacity change in the second heating run.

The thermogravimetry (TGA) experiments were performed in dynamic mode in nitrogen atmosphere using a Perkin-Elmer TGA7 analyzer. The experiments were carried out by placing film samples directly in thermobalance and subjecting to heating in the temperature range of $50 - 600\text{ }^{\circ}\text{C}$ at a constant heating rate of $10\text{ }^{\circ}\text{C}/\text{min}$.

The tensile properties of the specimens were obtained by using a tensile machine (Instron 4026). Rectangular strips with dimensions $70 \times 20\text{ mm}$ and thickness 0.1 mm were uniaxially drawn at a speed of $10\text{ mm}/\text{min}$ at room temperature. Each mechanical property value was an average of five measurements.

3. Results and discussion

Both the composition of the blends and the thickness had a predominant effect on transparency of the prepared films. Thin samples ($< 100\text{ }\mu\text{m}$) and those having the highest amount of PCLG component (50 wt%) were transparent, while the samples with the thickness of $100 - 500\text{ }\mu\text{m}$ became opaque if the amount of PCLG component did not exceed 25 wt%.

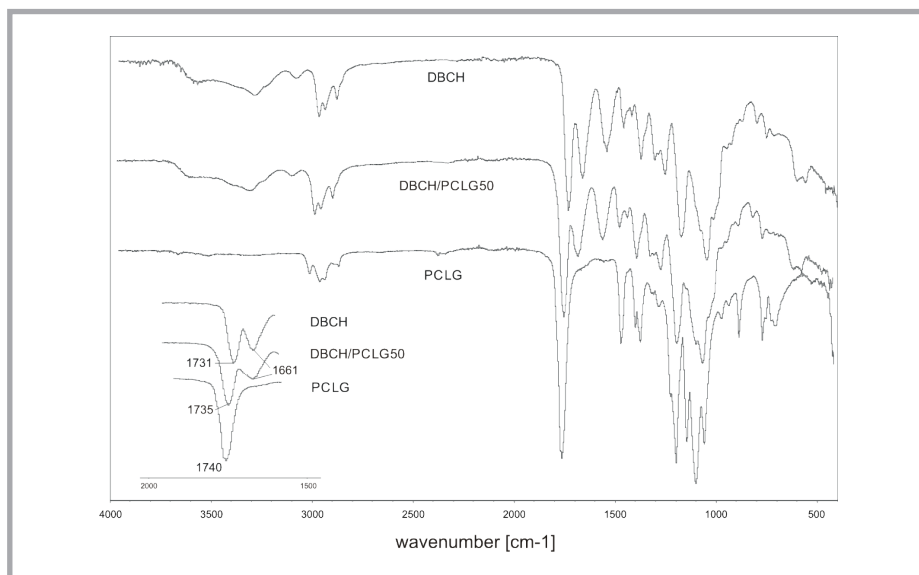


Figure 1. Infrared spectra of DBCH, PCLG, and their blend DBCH/PCLG50.

For further studies, the clear transparent films with thickness of 100 μm were chosen.

The FTIR transmission spectra of DBCH, PCLG and DBCH/PCLG50 blend (equal amounts of the components) are shown in **Figure 1**. The FTIR spectrum confirmed the chemical structure of DBCH, i.e. the total esterification of the hydroxyl groups with butyric anhydride, and the regularity of the film and its excellent transparency. A characteristic band for all systems is situated at 1730 - 1740 cm^{-1} which is assigned to ester carbonyl C=O stretching vibrations; in the case of DBCH, a peak is located at 1731 cm^{-1} . Addition of PCLG component into a DBCH matrix resulted in shifting the line towards higher wave numbers up to to 1735 cm^{-1} . There was no band with two distinct submaxima in this region as was often observed for many immiscible blends of polysaccharides (chitin or chitosan) and polyesters. This phenomenon may confirm the miscibility of the two components of blends, which would result in the formation of homogeneous systems. Furthermore, upon blending with PCLG, the band at 1730 - 1740 cm^{-1} was significantly broadened as compared to that of the neat DBCH. Hydrogen bonds were suggested to be formed between the carbonyl groups of PCLG polyester and the amide NH groups of DBCH.

The DSC thermograms of the studied materials are presented in **Figure 2**. To eliminate the thermal history of polymers, the properties were determined from the second heating cycle. The thermogram of DBCH showed no effects associated with any physical processes or phase transitions at a temperature range of -50 - 250°C; neither glass transition, nor melting of the crystalline phase were detected. On the thermogram of PCLG, characteristic inflection in the low-temperature region was visible due to endothermic

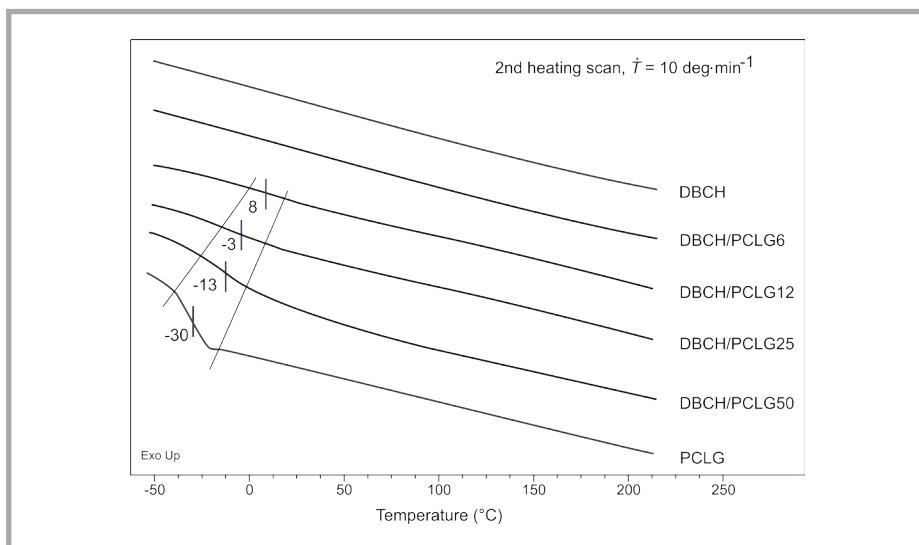


Figure 2. DSC thermograms of DBCH, PCLG, and blends from the second heating scan.

glass transition (T_g is -30 °C). There were no effects corresponding to phase transitions, *i.e.* crystallization and melting, thus PCLG is an amorphous polymer. As can be seen, the composition of the DBCH/PCLG blends affected the glass transition temperature of the systems. An increase of the PCLG content reduced glass transition temperature, while widening a temperature range and increasing a heat capacity change of the glass transition. This behavior evidenced the homogeneity of amorphous phases of the blend components.

Thermal resistance of blends and their components was examined by thermogravimetry (TGA). The curves from dynamic heat are presented in **Figure 3**. The TGA curves show that there is a small weight loss (about 5%) at $180 - 200$ °C for PCLG, which is probably related to ‘unzipping’ (depolymerization) reactions. The “unzipping” of the polyester macromolecules takes place from the hydroxyl ends leading to the formation of monomers and macrocycles. Interestingly, the TGA curves for the blends overlap with the curve for neat DBCH and do not differ significantly as a function of the composition of the blends. This phenomenon may be related with the formation of specific intermolecular interaction between polysaccharide and polyester chains, thus facilitating the miscibility of the components. In addition, there were no inflections observed on the curves for DBCH/PCLG blends at $180 - 200$ °C corresponding to the depolymerization reactions of PCLG in the systems, which additionally suggest that the interactions of the terminal hydroxyl groups of PCLG and DBCH chains, such as hydrogen bonds, may be formed.

Figure 4 compares the tensile data for studied blends. The apparent relationship between the mechanical parameters and the content of PCLG in blends was observed. As expected, with increasing amount of PCLG, the blend became more ductile. A significant increase of elongation at break (ϵ) was observed as the content of PCLG in blend increased.

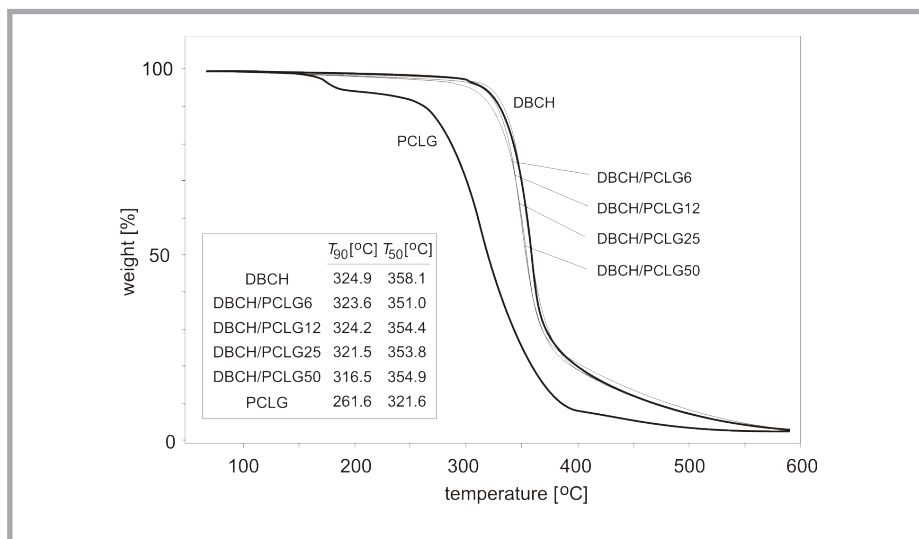


Figure 3. TGA curves of DBCH, PCLG, and blends.

When the amount of PCLG was 50%, the elongation at break increased up to near 40% while the ϵ for virgin DBCH was 7%. Conversely, the increasing content of PCLG reduced both tensile strength (σ) and modulus of elasticity (E). As can be seen in **Figure 4**, the trend of the decrease of the both parameters was the same. The films with the amount of PCLG above 10 wt% was tough and elastic. The test results indicated that the blending DBCH with PCLG polyester improved inherent stiffness and brittleness of DBCH.

4. Conclusions

The FTIR analysis indicated the occurrence of specific intermolecular interaction between polysaccharide and polyester components of the blends. DBCH was found to be able to form miscible blends with PCLG polyester within the whole composition range studied. The DSC thermal analysis revealed that blends were composed of an amorphous homogeneous phase as evidenced by the presence of a single glass transition temperature. Furthermore, the glass transition temperature was found to decrease with increasing PCLG content in materials confirming the plasticizing effect of PCLG on DBCH matrix. Physical modification of DBCH with biodegradable polyester resulted in superior mechanical properties as compared to neat DBCH. The blended materials exhibited a much higher toughness and elongation at break as well as a lower value of elasticity modulus.

5. References

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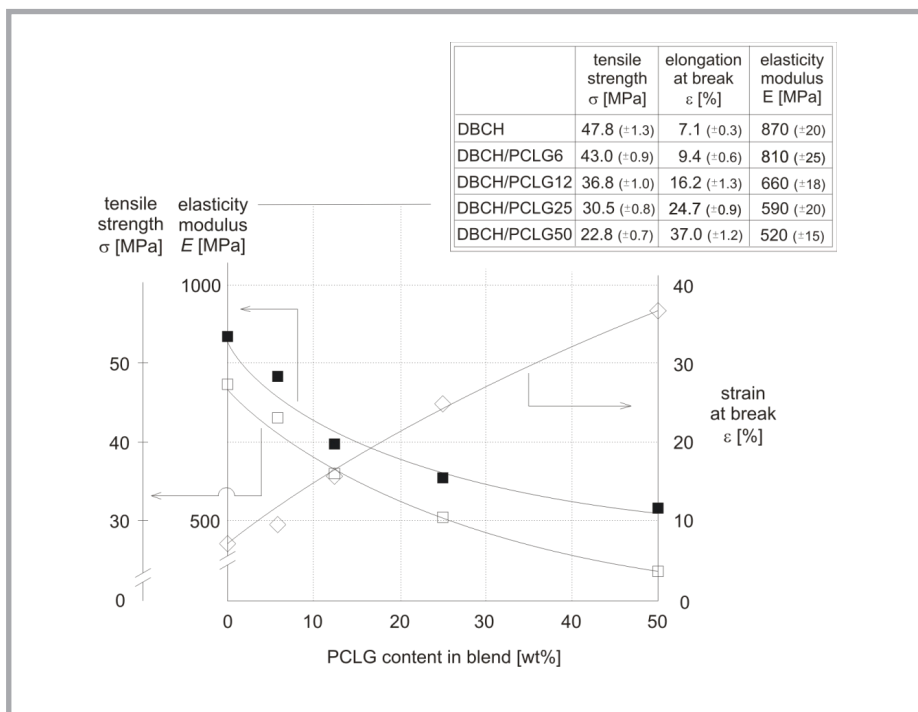


Figure 4. Tensile properties of the studied materials as a function of PCLG content in blend.

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