Modification of hydrolytic stability of high molecular weight poly(ε-caprolactone) by addition of medium molecular weight poly(ε-caprolactone) aggregated in the presence of CaO (*Rapid Communication*)

Melania Bednarek[1),*], Michał Cichorek[1)]

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Abstract: Medium molecular weight poly(ε-caprolactone) containing three carboxyl groups at one chain end (PCL5000) and the same polymer but aggregated in the presence of CaO (PCL5000/CaO) were used as an additive for modification of hydrolytic stability of high molecular weight poly(ε-caprolactone) (PCL80000). Thermal and mechanical properties of PCL80000 and its composites together with their molecular weight changes upon hydrolysis were investigated. The composite obtained using PCL5000/CaO showed higher tendency to hydrolytic degradation than unmodified PCL80000 with the preservation of mechanical properties.

Keywords: biodegradable polyester, poly(ε-caprolactone) modification, composites, hydrolytic degradation.

Modyfikacja stabilności hydrolitycznej poli(ε-kaprolaktonu) o dużym ciężarze cząsteczkowym za pomocą zagregowanego w obecności CaO poli(ε-kaprolaktonu) o średnim ciężarze cząsteczkowym

Streszczenie: Poli(ε-kaprolakton) o średnim ciężarze cząsteczkowym (PCL5000) zawierający trzy grupy karboksylowe na jednym końcu łańcucha oraz ten sam polimer zagregowany w obecności CaO (PCL5000/CaO) zastosowano jako domieszki w celu modyfikacji stabilności hydrolitycznej wielkocząsteczkowego poli(ε-kaprolaktonu) (PCL80000). Zbadano właściwości termiczne i mechaniczne PCL80000 oraz jego kompozytów, a także zmiany ciężaru cząsteczkowego w wyniku ich hydrolizy. Kompozyt otrzymany z dodatkiem PCL5000/CaO wykazał większą podatność na hydrolizę niż niemodyfikowany PCL80000, bez pogorszenia właściwości mechanicznych.

Słowa kluczowe: poliester biodegradowalny, modyfikacja poli(ε-kaprolaktonu), kompozyty, degradacja hydrolityczna.

An important property of degradable polymers is their ability to undergo hydrolytic or enzymatic degradation to low molecular weight compounds [1, 2]. For diverse potential applications different degradation rates may be advantageous. Thus, there are numerous studies in the literature concerning factors affecting the degradation rate. The most important class of degradable polymers is aliphatic polyesters [1]. Among them, polylactide (PLA) is most extensively studied as a prospective degradable polymer in packaging, agriculture and biomedical applications. One of the approaches to modifying its properties, including the degradation rate, is based on blending it with inorganic compounds (mainly calcium salts) [3, 4]. Studies of such systems revealed their complexity [3, 4], which may be partly due to the physical form of the added inorganic salt. Much less is known of the effect of inorganic additives on the degradation rate of another degradable polyester, namely poly(ε-caprolactone) (PCL).

We have previously reported [5] that medium molecular weight PCL containing different numbers of carboxyl groups at one chain end interacts with calcium cations (introduced as calcium oxide) forming aggregates in solution, as evidenced by dramatic increase in solution viscosity (from 150 cP up to about $1 \cdot 10^6$ cP). Finally, viscous solutions turned into transparent gels. After solvent evaporation, solid PCL material was obtained, in which long cylindrical structures (formed probably on aggregate templates) were present as it was found on the basis of SEM analysis [5]. By the incorporation of CaO in aggre-

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[1)] Center of Molecular and Macromolecular Studies, Polish Academy of Sciences, ul. Sienkiewicza 112, 90-363 Łódź, Poland.

[*)] Author for correspondence; e-mail: bednarek@cbmm.lodz.pl

gate structures via ionic interactions with -COOH groups, calcium ions were uniformly dispersed in PCL matrix.

PCL is a degradable polymer but the rate of its hydrolytic degradation is rather low, which may be a limitation if biomedical applications are considered. Hydrolysis is catalyzed by acids, thus blending the high molecular weight PCL with small amount of PCL oligomers containing relatively higher fraction of terminal -COOH groups should enhance the rate of hydrolysis. The presence of -COOH groups, however, may have a detrimental effect to mechanical properties of material due to possible degradation during processing. We speculated that blending PCL-$(COOH)_3/Ca^{2+}$ aggregates with high molecular weight PCL should enhance the rate of hydrolytic degradation of material when exposed to water without a deterioration of mechanical properties during preparation. To check this hypothesis, preliminary investigation of properties of blends of high molecular weight PCL with medium molecular weight PCL containing Ca^{2+} ions dispersed and bounded by ionic interactions was conducted and its results are reported in this communication.

EXPERIMENTAL

Materials

ε-Caprolactone (CL, Aldrich, 99 %) was dried over molecular sieves and distilled on a vacuum line. Poly(ε-caprolactone) (PCL80000, $\overline{M}_n$ = 80 000, Aldrich) and citric acid (Aldrich) were dried in vacuum before use. Triflic acid (98 %, Aldrich) and calcium oxide (p.p.a., POCh, Poland) were used as received. 1,2-Dichlorobenzene (Aldrich, 99 %) was distilled.

Preparation of aggregated PCL5000

Poly(ε-caprolactone) containing three carboxyl groups at one chain end [PCL-$(COOH)_3$] with $\overline{M}_n \approx 5000$, denoted as PCL5000, was synthesized according to the procedure described earlier [5], by applying cationic ring-opening polymerization of CL, using citric acid as an initiator and triflic acid as a catalyst.

An aggregated PCL5000/CaO was prepared by mixing 10 wt % solution of PCL5000 in 1,2-dichlorobenzene with CaO used with 2-fold excess with respect to -COOH groups [5].

Preparation of PCL80000/PCL5000 (PCL5000/CaO) composites

Composites PCL80000/PCL5000 and PCL80000/PCL5000/CaO were prepared using ZAMAK EHP-5CS conical twin-screw extruder. PCL80000 was mixed with 6 wt % of PCL5000 or with 6 wt % of PCL5000/CaO for 10 min at 80 °C and 50 rpm.

Hydrolysis of PCL80000 and its composites

0.5 g of polymer film was placed in 5 cm^3 of distilled water in vials closed with a lid. The vials were placed in a thermostated oven at 60 °C for 20 days. The vials content was then cooled to the room temperature, water was removed by decantation and the polymer was dried in vacuum before analysis.

Methods of testing

^1H NMR spectra were recorded in $CDCl_3$ using a Bruker DRX500 spectrometer operating at 500 MHz.

Size exclusion chromatography (SEC) was performed using an Agilent Pump 1100 Series with an Agilent G1379A degasser and a set of two PL-Gel 5 μm mixed-C columns. Wyatt Optilab Rex interferometric refractometer and multi-angle laser light scattering (MALLS) Dawn Eos laser photometer (Wyatt Technology Corp., Santa Barbara, CA) were used as detectors. Dichloromethane was used as an eluent at the flow rate of 0.8 cm^3/min at the room temperature. The system was calibrated according to polystyrene standards. Because of the discrepancy between molar mass of PCL determined by SEC (M_{SEC}) using polystyrene calibration and real $\overline{M}_n$ value [6], molar masses presented as results (Table 1 and 3) were calculated using a correcting coefficient equal to 0.7 ($\overline{M}_n$ or $\overline{M}_w = 0.7 \cdot M_{SEC}$)

Differential scanning calorimetry (DSC) analysis was performed under nitrogen at the heating and cooling rate of 10 °C/min on DSC 2920 Modulated TA Instrument. Both temperature and heat flows were calibrated with indium. Enthalpy and temperature of melting (ΔH_m and T_m, respectively) were calculated from DSC traces for the second run.

Mechanical properties were analyzed using Linkam TST 353 micro-tensile tester with environmental chamber. For measurements, 0.5 mm thick films were made by compression molding at 80 °C for 3 min using a hydraulic press and then rapidly cooled to 15 °C between metal blocks. Oar shaped specimens complied with the ASTM D638 (type V) standard with 2× reduced dimensions (3.81 and 1.50 mm gauge width and length, respectively). All specimens were uniaxially drawn with 50 %/min (3.20 mm/s) rate until the break point or slip out from the machine jaws.

RESULTS AND DISCUSSION

In order to check how the presence of aggregated medium molecular weight PCL containing CaO influences the properties of PCL with $\overline{M}_n$ sufficient for application as a material, the composite of PCL80000 and 6 wt % of PCL5000 aggregated in the presence of CaO (PCL5000/CaO) was prepared by melt mixing of both components in a counter-rotating twin screw extruder. The influence of CaO-containing medium molecular weight component on PCL physical properties was investigated by comparative studies including SEC and DSC analysis, tensile tests and susceptibility to hydrolysis performed for PCL80000 alone, PCL80000 containing unaggregated PCL5000 (PCL80000/PCL5000) and PCL80000 composite containing aggregated PCL5000 (PCL80000/PCL5000/CaO). Table 1 presents the results of SEC and DSC analyses.

T a b l e 1. Characterization of analyzed PCL composites

Material	$\overline{M}_n$ b)	$\overline{M}_w$ b)	$\overline{M}_w/\overline{M}_n$	ΔH_m (DSC) J/g	T_m (DSC) °C
PCL80000a)	81 270	134 500	1.65	62.3	58.2
PCL80000/PCL5000	23 450	57 430	2.44	80.6	57.5
PCL80000/PCL5000/CaO	73 080	134 400	1.85	67.3	57.3

a) PCL80000 was also processed in an extruder in order to provide comparable processing conditions.

b) Molar mass is given only for the main peak (elution volume 11—17 cm^3) which corresponds to macromolecules of PCL80000 overlapping slightly with higher fraction of PCL5000 (PCL5000 alone gives a broad signal at elution volume 16—24.5 cm^3).

The blend of PCL80000 with PCL5000 containing free carboxyl groups undergoes a significant degradation in the applied mixing conditions (80 °C, 50 rpm, 10 min) as evidenced by the decrease in $\overline{M}_w$ and $\overline{M}_n$. This may be attributed to relatively high content of carboxyl groups catalyzing the degradation. In contrast, blending of PCL80000 with PCL5000 containing Ca^{2+} ions does not cause any detectable degradation.

All three PCL samples were subjected to tensile test on Instron instrument. Strain-stress profiles are presented in Fig. 1, and determined values of yield stress (σ_y), stress at break (σ_B) and elongation at break (ε_B) are listed in Table 2.

T a b l e 2. Mechanical properties of the studied samples (presented values are calculated as an average of three measurements)

Material	σ_y, MPa	σ_B, MPa	ε_B, %
PCL80000a)	15.0	24.8	1436
PCL80000/PCL5000	—	18.1	20
PCL80000/PCL5000/CaO	15.4	27.8	1704

a) PCL80000 was also processed in an extruder in order to provide comparable processing conditions.

Different behaviors of starting PCL80000 and PCL80000 with additives can be observed. PCL 80000 is a material which during uniaxial drawing attains high elongation (the limit in the tests was in the range of 1100—1600 % when a specimen slipped out from the machine jaws). The addition of PCL5000 containing free carboxyl end groups causes degradation during processing which leads to molecular weight decrease and thus decrease of mechanical strength, so that the sample breaks at relatively low strain and does not achieve the yield point. Effects of degradation of semi-crystalline polymers on the degree of crystallinity and brittleness of partly degraded polymers are discussed in detail in a review paper [7]. The addition of aggregated PCL5000/CaO did not significantly change the PCL80000 tensile properties — similar values of σ_y and slightly higher σ_B were observed for both materials. The presence of aggregates caused a slight increase of elongation at break in comparison with the value for PCL80000. Thus, the involvement of -COOH

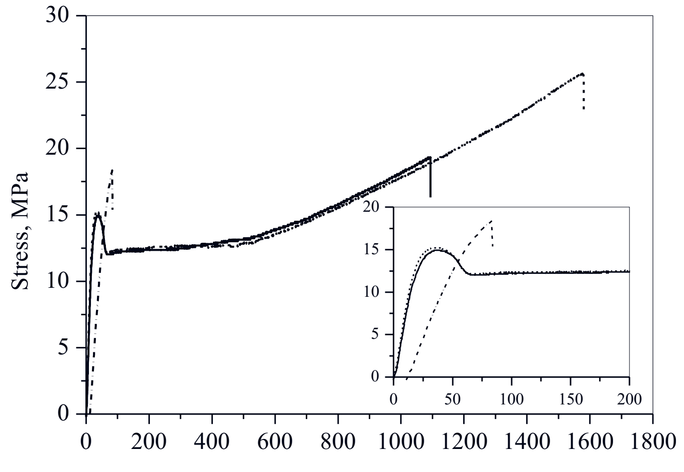

Fig. 1. Exemplary stress-strain profiles for the analyzed PCL materials; solid line — starting PCL80000, dashed-dotted line — PCL80000/PCL5000, dashed line — PCL80000/PCL5000/CaO

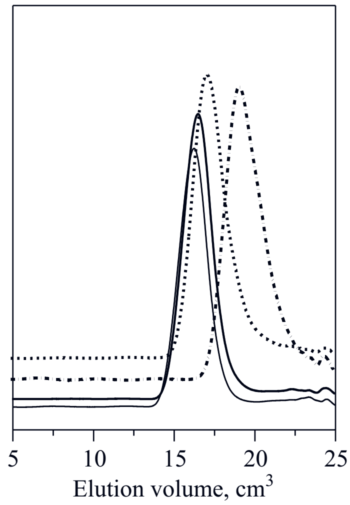

Fig. 2. SEC curves of PCL polymers after hydrolysis: solid line — starting PCL80000, dashed-dotted line — PCL80000/PCL5000, dotted line — PCL80000/PCL5000/CaO (SEC trace of PCL80000 before hydrolysis is shown for comparison, solid thin line)

groups of low molecular weight PCL in ionic interactions with Ca^{2+} cations prevented the composite from deterioration of its mechanical properties which could be caused by the presence of free carboxyl groups.

At the same time small improvement of elongation at break was observed which was due to the presence of medium molecular weight PCL5000/CaO with carboxyl groups (neutralized with Ca^{2+} cations) which acted as a plasticizer.

All prepared PCL samples were subjected to hydrolysis (60 °C for 20 days). Fig. 2 presents SEC curves of the three analyzed samples and of the starting PCL80000. Determined by SEC analysis values of $\overline{M}_n$, $\overline{M}_w$ and $\overline{M}_w/\overline{M}_n$ are collected in Table 3.

Table 3. Molecular weights of polymers after hydrolysis (20 h at temp. 60 °C)

Material	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$
PCL80000	60 980	104 150	1.71
PCL80000/PCL5000	3640	11 660	3.20
PCL80000/PCL5000/CaO	22 440	55 930	2.04

As it may be expected, the presence of PCL5000 containing free carboxyl groups led to a significant increase of the hydrolysis rate. At the same time, however, the addition of PCL5000 caused a molecular weight decrease and thus the decrease of mechanical strength. On the other hand, the addition of PCL5000/CaO led to a noticeable increase of the hydrolysis rate without affecting the mechanical properties. Apparently, in bulk, neutralized carboxyl groups do not catalyze the degradation during processing while in the presence of water the catalytic effect is restored. Thus PCL5000/CaO may be treated as a reservoir of „dormant" carboxyl groups which may, however, display a catalytic effect in the presence of water. As a result, the composite material is stable during processing but undergoes enhanced hydrolysis.

CONCLUSIONS

The formation of aggregates upon addition of CaO to medium molecular weight PCL containing carboxyl end groups provides a possibility of blending this material with high molecular weight PCL. The resulting composite shows an enhanced rate of hydrolysis while its mechanical properties do not deteriorate.

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