THERMAL AND MECHANICAL PROPERTIES OF POLY(METHACRYLATE) NETWORKS WITH COOLIGO(LACTONE) BRANCHES

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SUMMARY: Poly(methacrylate) networks with cooligo(lactone) branches are obtainable by free radical copolymerization of cooligo(lactone) macromonomers and tri(ethyleneglycol) dimethacrylate (TEGDMA). These cooligo(lactone) macromonomers were prepared by ring-opening cooligomerization of (S,S)-3,6-dimethyl-1,4-dioxane-2,5-dione (L-lactide) with δ-valerolactone and ε-caprolactone, respectively, initiated by Bisphenol-A-bis(2-hydroxypropyl methacrylate) (BisGMA). Partially biodegradable composites with a potential application as bone implant material have been received by cross-linking copolymerization of the macromonomers in the presence of 45 wt.% hydroxy apatite. Thermal and mechanical properties of the composites were studied in dependence on the structure of the polymer matrix. Copolymers from certain macromonomers contain crystalline domains of oligo-L-lactide branches as proved by wide angle X-ray scattering. The formation of the crystalline domains will be promoted if the oligo-L-lactide branches are linked via the flexible spacer δ-valerolactone to Bis-GMA. The partial crystallinity results in higher Young´s moduli in the temperature range between glass transition and melting of the composites. Furthermore it gives rise to a higher compressive strength and to a decreasing rate of hydrolytic degradation.

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Introduction

New biocompatible composites were described based on partially biodegradable copolymers and the bioactive filler hydroxy apatite [1]. The partially biodegradable copolymers consist of a hydrolytically stable poly(methacrylate) network and degradable oligo(lactide) branches. The composites were prepared by free-radical copolymerization of an oligo(lactide) methacrylate macromonomer and a diluting monomer, like tri(ethyleneglycol) dimethacrylate (TEGDMA), in the presence of hydroxy apatite.

 CCC 1022-1360/00/$ 17.50+.50/0

2,2-bis[4-(2-hydroxy-3-methacryloyloxy propoxy) phenyl] propane (BisGMA) has been proved as a suitable initiator of the ring-opening oligomerization of various lactones [1-3]. This reaction results in a macromonomer including two degradable oligo(ester) side-chains and two polymerizable methacrylate groups.

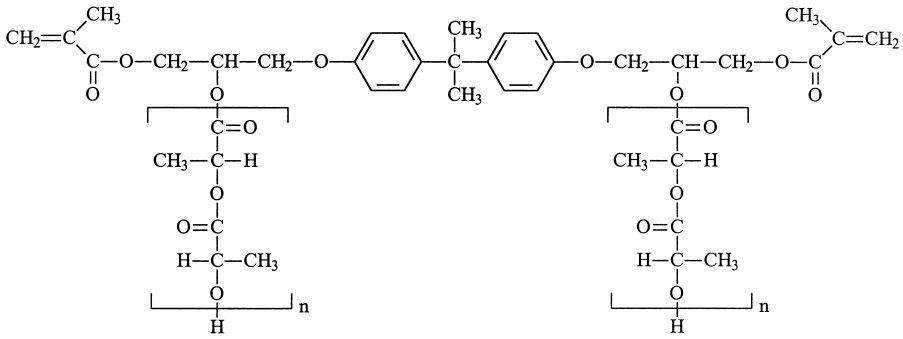

Figure 1: Macromonomer obtained by ring opening oligomerization of lactide, initiated by BisGMA

Composites made from these macromonomers can be of interest for some medical applications especially in osteosynthesis. In the primary state the composite guarantees the mechanical solidity of the implant. The hydrolytic degradation of the material, started by the aqueous body fluid, and the following resorption of the degradation products by the human metabolism yield free volume in the composite as a supposition for the ingrowth of new bone tissue.

As already described [2], the ring-opening oligomerization of lactide and lactones proceeds according to an insertion mechanism with living character. Taking advantage of these conditions, two different reaction procedures can be used to prepare cooligo(lactone) macromonomers of different structure: the parallel reaction and the step reaction. Products of the parallel reaction exhibit a random distribution of the comonomer units in the cooligo(lactone) branches. The step reaction results in macromonomers with block-like structures [3]. These variations in the structures should cause different properties of the obtained copolymers. The goal of this work is to investigate the influence of the microstructure on the thermal and the mechanical properties of the copolymers and composites as well as on the degradation behaviour of the latter.

Experimental

Materials

BisGMA was prepared as described [4]. L-lactide (Boehringer Ingelheim) was purified by recrystallization from ethyl acetate and dried in vacuum. δ-valerolactone (Fluka), ε-caprolactone (Fluka) and N,N-dimethyl-p-toluidine (Aldrich) were distilled under reduced pressure. Magnesia oxide, stannous(II)-octoate (Sigma Chemical), 2,6-di-(1,1-dimethylethyl)-4-methylphenol (Merck), tri(ethyleneglycol) dimethacrylate (TEGDMA) (Roehm) and hydroxy apatite (Osprovit®, Cerasiv) were used as received. Dibenzoyl peroxide (Merck) was dissolved in chloroform and filtered. After precipitation in cold methanol and filtration dibenzoyl peroxide was dried in vacuum.

Synthesis of cooligo(lactone) macromonomers

L-lactide, δ-valerolactone and ε-caprolactone, repectively, the initiator BisGMA, the catalyst $Sn(oct)_2$ and the inhibitor 2,6-di-(1,1-dimethylethyl)-4-methylphenol (0.1 wt.% rel. to BisGMA) were mixed in the reaction vessel under stirring and heating at 130°C for accomplishing the parallel reaction procedure. The typical ratio of catalyst to initiator was 0.02 mole/mole. The reaction time was varied from six to eight hours dependent on the concentrations of lactone and lactide. The step reaction procedure works as follows. First the less reactive lactone was oligomerized by the initiator BisGMA catalysed by MgO in the presence of the inhibitor Ionol at 130°C. After attaining the limiting conversion of δ-valerolactone and ε-caprolactone, repectively, (e. g. after a reaction time of four hours), the more reactive L-lactide was added. In this case the typical ratio of catalyst to initiator was 0.1 mole/mole. The reactions of both described cooligomerization procedures were stopped, when no further increase in the degree of oligomerization was detected by size exclusion chromatography.

Copolymerization and preparation of composites

The copolymers were prepared by free radical polymerization of the macromonomers with the diluting monomer TEGDMA in a weight ratio of 7 to 3. The redox system dibenzoyl peroxide / N,N-dimethyl-p-toluidine was used for the initiation of the free radical polymerization. The initiator dibenzoyl peroxide was added to one part of the comonomer mixture (0.4 wt.%), and the activating substance N,N-dimethyl-p-toluidine was given to a second part of the comonomer mixture in an equimolar ratio relative to the concentration of the peroxide in the first part. Thus, the copolymerization was started by

intensive mixing of equivalent parts of the two comonomer mixtures. Composites were received by admixture of 45 wt.% hydroxy apatite to the monomer mixtures and mixing of equal parts per weight of the resulting pastes.

Analysis

The thermal properties of the copolymers and composites were determined by DSC using a Perkin Elmer DSC 7 device. The heating rate was 10 K/min. The dynamic mechanical-thermal analysis was performed on a Perkin Elmer DMA-7 thermal analysis system using the dual cantilever mode (specimen size 22 mm x 12 mm x 2 mm) at a heating rate of 2 K/min and a frequency of 1 Hz. The shear viscosities of the pastes were determined on a TA-instruments CSL-rheometer carri 20 device (coin-plate) at 25°C. The compressive strength of the composites were determined on a Zwick Z020 device. The specimen had a length of 12 mm and a diameter of 6 mm (ISO/DIS 5833-1E). The constant cross-head speed was 20 mm/min. Wide angle X-ray scattering was performed on a X-ray diffractometer URD 65 operating in the reflection mode. For monitoring of the *in vitro* degradation, the samples were stored in a citric acid/sodium dihydrogen phosphate buffer solution (pH = 7.4) at 37°C. The released acid was determined by potentiometric titration with aqueous 0.05 N KOH solution. The amount of released acid is referred to the theoretical quantity after total degradation.

Results and discussion

As already described the macromonomers consisting of L-lactide and BisGMA in a molar ratio lower than 15 to 1 are amorphous [3]. The cooligo(lactone) macromonomers indicate an almost similar crystallizability. The amorphous cooligo(lactone) macromonomers are able to form crystallites after mixing with the diluting monomer TEGDMA (weight ratio 7:3). The process of crystallization slowly occurs at room temperature and occasionally lasts a couple of days. It is dependent on the sequence length of the L-lactide units in the cooligo(lactone) branches. The effect of crystallinity on the thermal behaviour of copolymers and composites is shown in Table 1. The macromonomers prepared by step reaction are amorphous. The addition of TEGDMA has a softening effect and gives rise to a lower T_g of the macromonomer mixture and to a high mobility of the cooligo(lactone) side-chains promoting their crystallization.

Table 1: Glass transition temperature (T_g), melting temperature (T_m) and heat of fusion (ΔH_m) of macromonomers prepared by step reaction, of the comonomer mixtures (macromonomer:TEGDMA = 7:3 g/g), of the corresponding copolymers (redox-initiated) and of the composites containing 45 wt.% hydroxy apatite

Composition/Material	**T_g [°C]**	**T_m [°C]**	**ΔH_m [J/g]**
Macromonomer BisGMA:δ-valerolactone:L-lactide 1:2:10 mole/mole	14	-	-
Comonomer mixture with TEGDMA	-44	59	5.6
Copolymer	32	91	4.2
Composite	28	89	2.1
Macromonomer BisGMA:δ-valerolactone:L-lactide 1:2:8 mole/mole	10	-	-
Comonomer mixture with TEGDMA	-46	49	3.2
Copolymer	21	87	7.0
Composite	24	86	2.0
Macromonomer BisGMA:ε-caprolactone:L-lactide 1:2:10 mole/mole	12	-	-
Comonomer mixture with TEGDMA	-47	70	6.0
Copolymer	25	93	4.7
Composite	37	93	2.5

The partial crystallinity of the pastes influences their viscosities. The crystallinity gives rise to an increasing shear viscosity and a shear dependence of the viscosity. The amorphous paste containing the macromonomer BisGMA:δ-valerolactone:DL-lactide = 1:2:10 mole/mole has a lower shear viscosity (Fig. 2), because the block-like DL-lactide sequences are unable to form crystalline phases.

The redox-initiated copolymerization of the semi-crystalline monomer mixtures results in the formation of a network and in the subsequent increase of T_g and T_m. The softening ranges of the received copolymers and composites are almost identical.

The DSC thermograms of the comonomer mixtures as well as the copolymers and composites show explicit melting endotherms with maxima in the DSC thermograms (Table 1).

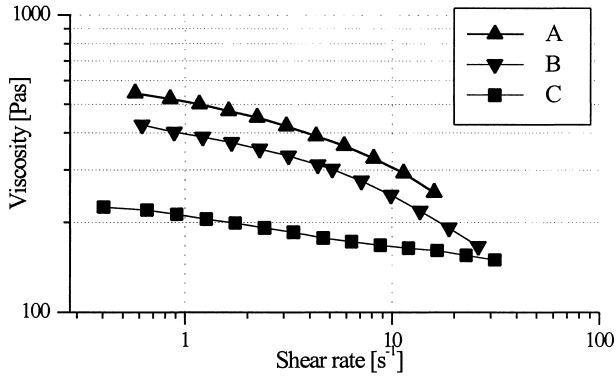

Figure 2: Shear viscosity of pastes consisting of macromonomer/TEGDMA/hydroxy apatite at 25°C; macromonomers:
A: ▲ BisGMA:δ-valerolactone:L-lactide = 1:2:10 mole/mole (semi-crystalline)
B: ▼ BisGMA:ε-caprolactone:L-lactide = 1:2:10 mole/mole (semi-crystalline)
C: ■ BisGMA:δ-valerolactone:DL-lactide = 1:2:10 mole/mole (amorphous)

The crystallinity is caused by the block-like oligo-L-lactide sequences, which is proved by wide angle X-ray scattering (Fig. 3). The position of the crystalline reflexes of the comonomer mixture, the copolymer and a high molecular semi-crystalline poly-L-lactide are identical at 2θ = 14,7° (d = 0,599 nm); 16,6° (d = 0,532 nm); 19,0° (d = 0,467 nm) and 22,3° (d = 0,399 nm). The copolymers consisting of TEGDMA and the macromonomers with the same compositions but prepared by parallel reaction do not show any crystalline reflexes, they are amorphous. The characterization of composites by WAXS is not helpful, because the reflexes of the copolymer-matrix are covered by several reflexes of the inorganic filler hydroxy apatite.

If the curing temperature of the sample surpasses the melting temperature of the oligo-L-lactide crystallites during the exothermic copolymerization, the cross-linking reaction will yield an amorphous copolymer. Thus, the copolymerization initiated by the

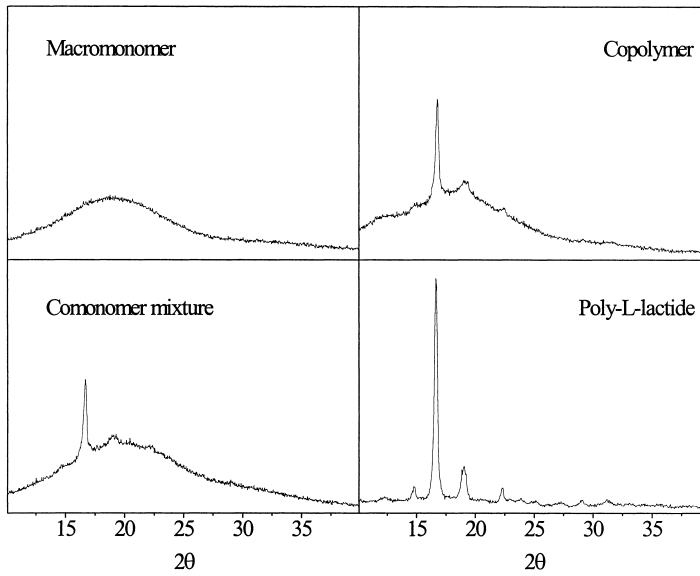

Figure 3: X-ray diffraction diagram of the macromonomer with the composition BisGMA:δ-valerolactone:L-lactide 1:2:10 mole/mole prepared by step reaction, of the comonomer mixture with TEGDMA (7:3 g/g), of the corresponding copolymer (redox-initiated) and of poly-L-lactide

thermal decomposition of dibenzoyl peroxide at 90°C results in an amorphous copolymer, although the comonomer mixture is partially crystalline. Recrystallization of the block-like oligo-L-lactide units is impossible during the cooling procedure of the sample, because of the relatively high T_g of the formed network. Thermal analysis by DSC precisely demonstrates this behaviour (Fig. 4). The second heating scan showed no recrystallization and no melting, even if very slow cooling rates (2.5 K/min.) were applied in the cooling scan before. Additionally the annealing of the sample at temperatures above T_g did not succeed in crystallization.

DMTA is another possibility for analysing the thermal behaviour. Furthermore it is simultaneously possible to determine the influence of the crystalline phase on the mechanical characteristics. In Fig. 4 the storage moduli of a composite during the first and the second heating scan are given as a function of temperature and are compared with the course of the corresponding DSC scans of the composite. The course of the DMTA curves

may be subdivided in three parts. The first part is the glassy state. In both runs the storage moduli are nearly identical. However, significant differences appear in the softening range. In the first heating scan the composite with the semi-crystalline copolymer-matrix displays a slighter decrease in the storage modulus. The softening range reaches from the glass transition point to the end of the melting process related to the DSC thermogram. The

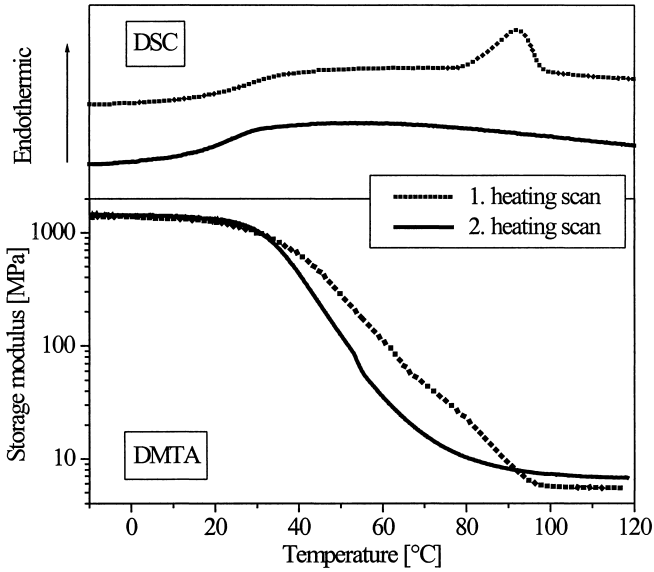

Figure 4: DSC- and DMTA-plots of the composite from BisGMA:δ-valerolactone:L-lactide 1:2:10 mole/mole (step reaction) /TEGDMA/hydroxy apatite

second heating scan shows a sharper slope and a narrower softening range. The storage modulus of the composite with the semi-crystalline copolymer-matrix is higher in the range between the softening point and the melting point of the copolymer-matrix. This difference is caused by the presence of crystalline domains which act as physical network points and yield an advancing network density. The melting process destroys these physical network points, reduces the network density and softens the material. In the second heating scan the higher storage modulus in the elastic state may be caused by a post-curing reaction during the first heating scan. A higher content of residual monomers in the composite before the first heating scan may also be the reason, that the storage modulus of the composite in the glassy state is not higher for the first heating scan than for the second one.

Furthermore the stiffening effect of the crystalline domains in the network could be verified by determination of the compressive strength of the composites. Table 2 shows the compressive strengths of the composites with the composition BisGMA:δ-valerolactone:L-lactide 1:2:10 mole/mole /TEGDMA/hydroxy apatite and BisGMA:δ-valerolactone:L-lactide 1:2:8 mole/mole /TEGDMA/hydroxy apatite. The semi-crystalline copolymer matrices contain units of the macromonomers prepared by step-reaction. The macromonomers of the amorphous copolymer matrices were prepared by parallel reaction.

Table 2: Compressive strength σ_d of composites made from various macromonomers, TEGDMA and hydroxy apatite

Composite	σ_d [MPa]
BisGMA:δ-valerolactone:L-lactide 1:2:10 mole/mole (step reaction) redox-cured (partially crystalline)	90±12
BisGMA:δ-valerolactone:L-lactide 1:2:10 mole/mole (parallel reaction) thermally cured at 90 °C (amorphous)	92±11
BisGMA:δ-valerolactone:L-lactide 1:2:10 mole/mole (parallel reaction) redox-cured (amorphous)	67±4
BisGMA:δ-valerolactone:L-lactide 1:2:8 mole/mole (step reaction) redox-cured (partially crystalline)	85±6
BisGMA:δ-valerolactone:L-lactide 1:2:8 mole/mole (parallel reaction) redox-cured (amorphous)	65±6

The composites with the amorphous copolymer matrices exhibit lower compressive strengths. This fact is another proof for the stiffening effect of the crystalline phases. Otherwise a thermally cured (90°C) composite has a compressive strength of 92 ± 11 MPa, but it is amorphous as mentioned before. The compressive strengths of the semi-crystalline, redox-cured composite and of the amorphous, thermally cured composite are almost similar. Taking into account that high curing temperatures also increase the network density, both effects improve the mechanical properties.

Besides the influence of the partial crystallinity on the thermal and the mechanical behaviour of the composites also the influence on the degradation behaviour was studied.

Fig. 5 demonstrates the difference in the release of acid from an amorphous and a semi-crystalline composite. Again the amorphous copolymer-matrix contains a macromonomer prepared by parallel reaction and the partially crystalline copolymer-matrix includes the macromonomer prepared by step-reaction. Obviously the amorphous composite exhibits a faster release of acid, i. e. the crystallinity retards the hydrolytic degradation.

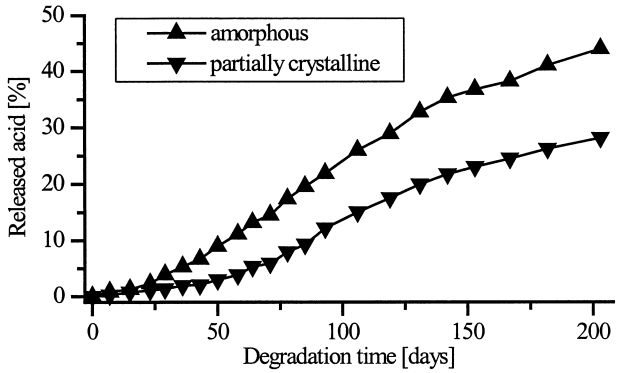

Figure 5: *In vitro* degradation of the composite with the composition BisGMA:δ-valerolactone:L-lactide 1:2:10 mole/mole /TEGDMA/hydroxy apatite (redox-cured) stored in buffer solution at 37°C

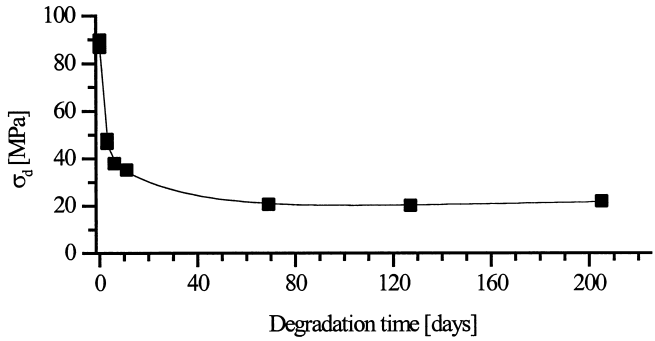

Figure 6: Decrease in compressive strength σ_d of the composite with the composition BisGMA:δ-valerolactone:L-lactide 1:2:10 mole/mole (step reaction)/TEGDMA /hydroxy apatite (redox-cured) during degradation in buffer solution at 37°C

The loss of the compressive strength σ_d during the degradation is shown in Fig. 6. This decrease is not caused by the hydrolytic degradation. The water-uptake and the swelling of the composite soften the material and this softening is the reason for the rapid loss of strength after a few days. At this time the degradation is in an originate state, which can be verified by regarding Fig. 5. After 60 days of incubation the compressive strength remains at a nearly constant level. Further storing of the samples in buffer solution did not succeed in a decrease in σ_d and all the samples retained their coherence. The remaining strength is induced by the hydrolytically stable poly(methacrylate) network and the filler hydroxy apatite. The glass transition temperatures of the stored and dried samples (determined by DMTA at the temperature of the maximum of the loss factor) increase with advancing incubation time, because of the loss of the biodegradable phase, which expands and softens the network in the initial dry state [5].

Conclusions

Amorphous cooligo(lactone) macromonomers prepared by a step reaction of δ-valerolactone and ε-caprolactone, respectively, and then of L-lactide with BisGMA will be able to form a crystalline phase by diluting with TEGDMA if the oligo(L-lactide) reach a minimum block length. By the redox-initiated copolymerization of these semi-crystalline monomer mixtures, partially crystalline copolymers and composites with a partially crystalline copolymer matrix, respectively, can be received. The polymerization temperature must not exceed the melting temperature of the macromonomer in the mixture with TEGDMA. Recrystallization of the oligo(L-lactide) units is impossible after the polymerization reaction because the formation of the network raises T_g and decreases the mobility of the oligo(lactone) branches. The crystallinity has a stiffening effect on the copolymers and composites. Furthermore it reduces the rate of hydrolytic degradation.

Acknowledgement

We like to thank the Innovationskolleg "Neue Polymermaterialien" constituted by the Deutsche Forschungsgemeinschaft for financial support.

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