Physical properties of high molecular weight 1,3-trimethylene carbonate and D,L-lactide copolymers

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High molecular weight statistical copolymers of 1,3-trimethylene carbonate (TMC) and D,L-lactide (DLLA) were synthesized and characterized with the aim of assessing their potential in the development of degradable and flexible materials for application in the biomedical field. Under the applied polymerization conditions (130 °C, 3 days using stannous octoate as a catalyst) monomer conversion was high or almost complete, and high molecular weight polymers ($\bar{M}_n$ above 170 000) were obtained. Significant improvement of the mechanical performance of these materials was observed in comparison to results previously reported for TMC and DLLA based copolymers of lower molecular weight. For the entire range of compositions the polymers are amorphous with a glass transition temperature ranging between -17 °C for poly(TMC) and 53 °C for poly(DLLA). The polymers vary from rubbers to stiff materials as the content of TMC decreases. All polymers are hydrophobic with very low equilibrium water absorption (< 1.5 wt %). Thermal analyses and tensile tests were performed on polymer samples after water uptake. Due to a plasticizing effect of the water, the thermal properties, and consequently the mechanical performance, of the copolymers with higher content of DLLA were the most affected. After water absorption, the polymer mechanical behavior can change from glassy to rubbery, as observed for the copolymer with 80 mol % of DLLA. The obtained results suggest that these copolymers are promising candidates as biomaterials in the preparation of degradable medical devices and systems.

1. Introduction

Synthetic bioresorbable polymers have found application in different fields of medicine. Already in clinical use are sutures (Vicryl®), carriers for controlled drug release (Lupron Depot®) and several medical devices such as bone plates and screws (Lactosorb®). In the past few years much interest has risen in the use of degradable polymers for the preparation of three-dimensional scaffolds for tissue engineering [1, 2]. Studies involving bioresorbable polymers are numerous and deal with the synthesis and characterization of the polymer chemical structure, biocompatibility, degradation behavior and processing of the material into the desired device or system. Despite the extensive advances made in the biomaterial field, the number of polymers available for biomedical applications is still restricted. In particular, most attention has been given to polymers based on poly(lactic acid) (PLA) and poly(glycolic acid) (PGA), as well as their copolymers. This is largely due to their biocompatibility and to their resorbability through natural pathways but also because these polymers are approved by the Food and Drug Administration, provided that they are synthesized by ring-opening polymerization of the corresponding cyclic dimers, using stannous octoate as catalyst [3]. However, these materials, either crystalline or amorphous, are relatively stiff and brittle and can have too high degradation rates for certain applications [4]. For example, in soft tissue engineering applications, a flexible but relatively tough material with tunable degradation properties would be preferable [5, 6]. Amorphous polymers with glass transition temperatures below body temperature are expected to exhibit high permeabilities making them very suitable in drug delivery applications [7].

Copolymerization has been widely used to reach the desired material characteristics in the final polymer [8–10]. In the search for elastomeric degradable materials for biomedical applications, we have been using poly(1,3-trimethylene carbonate) (poly(TMC)) – an amorphous polymer with a glass transition temperature of approximately -15 °C [11, 12] – as a starting point in the design of alternative synthetic materials. The

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incorporation of other monomer units into the poly(TMC) chain proved to be a successful method of modulating the rate of polymer degradation as well as modifying its physical properties [13, 14]. We have previously reported on the synthesis and physical properties of poly(ester carbonate)s based on TMC and ε-caprolactone (CL) for the preparation of porous degradable nerve guides [12]. These materials are expected to degrade slowly [15] and are more suitable for long-term applications where the integrity of the system should be kept for relatively long periods of time. In order to further tune the physical properties and degradation profile of poly (TMC), TMC was copolymerized with D,L-lactide (DLLA). Poly(DLLA) is an amorphous polymer with a glass transition temperature around 54 °C [16], which degrades more rapidly than poly(CL) [17]. The copolymerization of TMC with DLLA yields amorphous materials with degradation rates that are expected to be faster than the ones of copolymers based on TMC and CL [14].

The physical properties of a polymer are directly dependent on its molecular weight. By preparing high molecular weight polymers one can obtain materials with good mechanical performance, even after the processing methods that can induce chain scission like melt processing [18, 19] or sterilization by gamma irradiation [20]. The control of the initial molecular weight of a degradable polymer is also a powerful way to control the time lag before the onset of mechanical properties and mass loss, as well as the total time for complete polymer resorption [21]. The synthesis and characterization of relatively low molecular weight TMC and DLLA based copolymers have been previously described [14, 22]. In the present study the effect of copolymerization on the physical properties of TMC and DLLA copolymers of much higher molecular weight was evaluated.

2. Materials and methods

2.1. Materials

Polymer grade TMC (1,3-dioxan-2-one) and DLLA (racemic mixture of D and L enantiomers of 3,6-dimethyl-dioxan-2,5-dione) were obtained, respectively, from Boehringer Ingelheim, Germany and Purac Biochem, The Netherlands. Stannous octoate ($SnOct_2$) (stannous 2-ethylhexanoate) was used as received from Sigma, USA. Solvents were of analytical grade (Biosolve, The Netherlands).

2.2. Polymer synthesis

In an argon atmosphere, a mixture of monomers was charged into dried freshly silanized (Serva, Boehringer Ingelheim Bioproducts Partnership, Germany) glass ampules and 2×10^{-4} mol of $SnOct_2$ per mol of monomer was added as a solution in sodium-dried pentane. The pentane was removed afterwards by evacuation. The ampules were purged three times with dry argon and heat-sealed under vacuum. The ampules were conditioned in an oil bath pre-heated to the polymerization temperature and vigorously shaken in order to obtain a homogeneous mixture of the monomers and the catalyst. All homo- and copolymerizations were carried out over a period of 3 days at 130 ± 2 °C. The ampules were then quenched to room temperature and the polymers were discharged. For purification, the obtained polymers were dissolved in chloroform (2–5 wt/vol %), filtered through a sintered glass filter, and subsequently precipitated into a ten-fold volume of isopropanol. The precipitated polymers were washed with fresh isopropanol and dried under reduced pressure at room temperature until constant weight.

2.3. Polymer analysis and characterization

The synthesized polymers were characterized with regard to the monomer conversion and chemical composition by nuclear magnetic resonance (NMR) spectroscopy. 300 MHz ^{1}H-NMR (Varian Inova 300 MHz, USA) spectra were recorded using polymer solutions in $CDCl_3$ (Sigma, USA).

Molecular weights, molecular weight distributions and intrinsic viscosities of the purified polymers were determined by gel permeation chromatography (GPC) using a Waters Model 510 pump (USA), a HP Ti-Series 1050 autosampler (USA), a Waters Model 410 Differential Refractometer and a Viscotek H502 Viscometer Detector (USA) with $10^5 - 10^4 - 10^3 -$ 500 Å Waters Ultra-Styragel columns placed in series. Chloroform was used as eluent at a flow rate of 1.5 ml/min. Narrow polystyrene standards were used for calibration. Sample concentrations of approximately 0.5 wt/vol % and injection volumes of 30 µl were used. All determinations were performed at 25 °C.

The thermal properties of the synthesized materials were evaluated by differential scanning calorimetry (DSC). Samples (5–15 mg) placed in aluminum pans were analyzed with a Perkin Elmer Pyris1 (USA) at a heating rate of 10 °C/min. All samples were heated to 40 °C above their glass transition temperature. The samples were then quenched rapidly (300 °C/min) until 40 °C below their glass transition temperature and after 5 min a second scan was recorded. Unless mentioned otherwise, the data presented were collected during the second heating scan. The glass transition temperature was taken as the midpoint of the heat capacity change. Under the applied conditions, the accuracy in the glass transition measurements is approximately 2 °C [16]. Indium, gallium and tin were used as standards for temperature calibration.

2.4. Mechanical properties

Tensile testing was performed on compression molded films. Purified polymer samples were compression molded in a 600 µm thick mold at 140 °C. All test specimens had dimensions in accordance to ASTM D882-91 specifications. Tensile tests were carried out at room temperature on a Zwick Z020 (Germany) universal tensile testing machine operated at a crosshead speed of 50 mm/min and a grip-to-grip separation of 50 mm. The specimen deformation was derived from the grip-to-grip separation, therefore the presented values of Young's modulus (calculated from the initial slope of the stress-strain curves) give only an indication of the stiffness of the different polymers. All data presented is the average

TABLE I Copolymerization of TMC and DLLA with $SnOct_2$ as a catalyst at 130 °C

TMC/DLLA charged (mol ratio)	TMC conversion (%)	DLLA conversion (%)	Polymer composition[a] TMC/DLLA (mol ratio)
100/0	99.5	—	100/0
85/15	99.7	99.6	79/21
75/25	99.3	99.0	72/28
50/50	97.8	98.3	50/50
30/70	98.4	96.5	34/66
22/78	93.6	98.0	20/80
0/100	—	97.4	0/100

[a] As determined by ^{1}H-NMR.

of triplicate measurements samples. The error in the average values of Young's modulus and stress (stress at yield – σ_{yield}; stress at break – σ_{break} and maximum stress – σ_{max}) was not larger than 10%, for the average strain values (strain at yield – ε_{yield} and strain at break – ε_{break}) the error was not larger than 20%.

2.5. Wettability and water uptake

Static contact angles of ultra-pure water (MilliQ Plus – Millipore, France) and water uptake in phosphate buffered saline (PBS, pH 7.4, NPBI, The Netherlands) were used to evaluate the wettability of the TMC and DLLA based (co)polymers.

Static contact angles of films spin-coated from chloroform solutions (2.1–2.5 wt/vol %) onto glass slips were measured with a Video-based Optical Contact Angle Meter OCA 15 (DataPhysics Instruments GmbH, Germany). The measurements were performed at room temperature on profiles of sessile drops and readings were taken within the first 10–15 s. Angles were measured on at least five different regions of each polymer surface and the results were averaged.

The water uptake was defined as the weight gain of the polymer specimen after conditioning, according to Equation 1:

$$\text{water uptake} = \frac{w - w_0}{w_0} \times 100 \ (\text{wt}\,\%) \qquad (1)$$

where w_0 is the initial specimen weight and w the weight of the specimen after conditioning. Compression molded specimens ($100 \times 50 \times 0.6\,\text{mm}^3$) were placed in PBS at 37 °C and the sample weight was evaluated for a period of 30 days. After 24 h of conditioning in PBS wet samples were subjected to thermal analysis and tensile testing.

3. Results and discussion

3.1. Polymer synthesis

Statistical copolymers of TMC and DLLA were synthesized by ring-opening polymerization in the melt using $SnOct_2$ as a catalyst (Fig. 1). Different examples of catalyst systems used for the copolymerization of these monomers can be found in literature [22–24]. $SnOct_2$ was selected, as it is highly efficient and frequently used in the preparation of polymers for biomedical applications [25].

A series of copolymers with a TMC content ranging from 20 to 79 mol % and the corresponding homopolymers were prepared (Table I).

The copolymer composition and monomer conversion could be determined by ^{1}H- NMR spectroscopy of the crude polymerization products, since the α-methylene resonances of monomeric (t, 4H, $\delta = 4.44$ ppm) and polymeric TMC (m, 4H, $\delta = 4.18$–4.26 ppm) as well as the methyl resonances of monomeric (d, 6H, 1.65 and 1.67 ppm) and polymeric (m, 2H, $\delta = 1.39$–1.63 ppm) DLLA are separated. Under the applied polymerization conditions the monomer conversion was high or almost complete. In some cases, the obtained compositions differ slightly from the ratio of monomers charged. This may be explained by a small loss of monomer that sublimated during the purging and evacuation of the ampules. In addition to the doublet corresponding to the DLLA monomer, another doublet (1.69 and 1.71 ppm) was identified downfield in the spectrum of the polymers with high content of DLLA. By comparison with values found in literature [22, 26], these peaks were assigned to methyl protons belonging to traces of mesolactide monomer.

^{1}H- NMR analysis of the crude polymerization products also allowed the determination of the monomer distribution in the copolymers as the methine portion of the spectrum is sensitive to sequence effects. The NMR signal of D,L-lactyl units (–CO–CH(CH_3)–O–) next to other D,L-lactyl units at $\delta > 5.08$ ppm can be distinguished from the signal of D,L-lactyl units next to TMC units (–CO–O–(CH_2)$_3$–O–) at $\delta < 5.08$, allowing the calculation of the average sequence length of lactyl units ($\overline{L}_{LA}$) from the relative intensity of these signals:

$$\overline{L}_{LA} = \frac{I_{(\underline{LA}-LA)}}{I_{(\underline{LA}-TMC)}} + 1 \qquad (2)$$

Table II shows the average sequence length of the lactyl

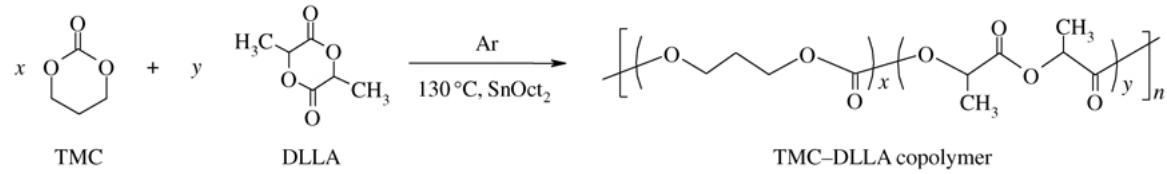

Figure 1 Synthesis of statistical poly(1,3-trimethylene carbonate-co-D,L-lactide).

TABLE II Average sequence lengths of lactyl units ($\overline{L}_{LA}$) and TMC units ($\overline{L}_{TMC}$) of TMC and DLLA copolymers based on ^{1}H-NMR analysis

Polymer composition TMC/DLLA (mol ratio)	$\overline{L}_{LA}$	$\overline{L}_{TMC}$
79/21	1.35	2.54
72/28	1.65	2.12
50/50	2.67	1.34
34/66	4.08	1.05
20/80	7.70	0.96

units determined this way, as well as the average sequence length of the TMC units ($\overline{L}_{TMC}$). The latter was determined from the average lactyl sequence length and the monomer ratio in the polymer. Previous reports confirm the correctness of this method by showing that the sequence lengths determined by ^{1}H-NMR are in accordance with those determined by integration of the carbonyl signals obtained by ^{13}C-NMR analysis [27].

For the copolymer containing 50 : 50 mol % of TMC and DLLA the average sequence lengths are 2.67 and 1.34 for the lactyl and TMC repeating units, respectively. A truly random monomer incorporation would yield average monomer sequence lengths equal to 4 for the lactyl units and 2 for the TMC units. An alternating incorporation of the monomers would result in average monomer sequence lengths of 2 for the lactyl units and 1 for the TMC units. The obtained values indicate a monomer distribution between random and alternating. This observation is in accordance with previous reports in which the product of the reactivity ratios of these monomers was found to be smaller than 1 [14]. Furthermore, these results show that copolymers with a TMC/DLLA mole ratio of 79/21 and 72/28 have single lactyl units connected to TMC on both sides, as the average lactyl sequence length is smaller than 2. The occurrence of TMC-lactyl-TMC sequences can only be explained by the occurrence of transesterification reactions, as the ring-opening polymerization of DLLA monomer could never yield such triad. This last observation is supported by the detection by ^{1}H-NMR analysis of mesolactide in the crude polymer. As no mesolactide contamination was detected in the DLLA monomer used in the polymerizations, such structure can only result from the transesterification of the racemic monomer or be a consequence of depolymerization.

In Table III, the values of the weight and number average molecular weight ($\overline{M}_w$ and $\overline{M}_n$ respectively), polydispersity ($\overline{M}_w/\overline{M}_n$) and intrinsic viscosity ([η]) of the prepared polymers are given. Under the applied polymerization conditions high molecular weight polymers were obtained. In previous work, molecular weights for these (co)polymers include: [η] values between 0.9–1.7 dl/g [22] and $\overline{M}_n$ in the range of 20 000 or lower [14]. The polydispersity values of all (co)polymers are approximately equal to two. This value has been reported before for lactone ring-opening polymerizations where transesterification reactions had occurred [28, 29].

TABLE III Molecular weights and intrinsic viscosity of TMC and DLLA (co)polymers determined by GPC

Polymer composition TMC/DLLA (mol %)	$\overline{M}_w \times 10^{-5}$	$\overline{M}_n \times 10^{-5}$	$\overline{M}_w/\overline{M}_n$	[η] (dl/g)
100	5.59	3.37	1.66	4.49
79	3.58	1.72	2.08	2.59
72	3.65	1.75	2.08	2.63
50	6.44	2.75	2.34	2.91
34	5.80	2.60	2.23	3.11
20	7.18	4.49	1.60	3.40
0	8.79	3.78	2.32	4.15

3.2. Thermal properties

The thermal properties of the TMC copolymers can be varied to a large extent by adjusting the quantity of comonomer used.

In the DSC scans no evidence of crystallinity was found. As the crystalline phase is poorly accessible to water and other permeants, an increase in crystallinity reduces the polymer permeability and the rate of biodegradation by chain scission due to a decrease in accessible hydrolyzable bonds. Concerning the use of these polymers for biomedical applications, one should further consider the fact that crystalline debris formed during degradation may cause an undesired late inflammatory response, negatively influencing tissue growth and normal function [30]. Therefore, little or no crystallinity is desired.

Almost for all polymers it was possible to observe an endotherm superimposed on the change of heat capacity at the glass transition temperature (T_g) in the first DSC scan. This endotherm is due to enthalpy relaxation, a phenomenon dependent on the thermal history of the samples [16]. In order to investigate the effect of monomer composition on the thermal properties of the polymers, the glass transition temperature was determined from the second heating scan. An increase in DLLA content resulted in an increase in T_g, with values ranging from 53 °C for poly(DLLA) to −17 °C for poly(TMC) (Fig. 2). At DLLA contents above 60 wt % all copolymers were in the glassy state at room temperature.

The Fox equation allows the estimation of the glass transition temperature of a copolymer based on the glass transition temperatures of the respective homopolymers [31]:

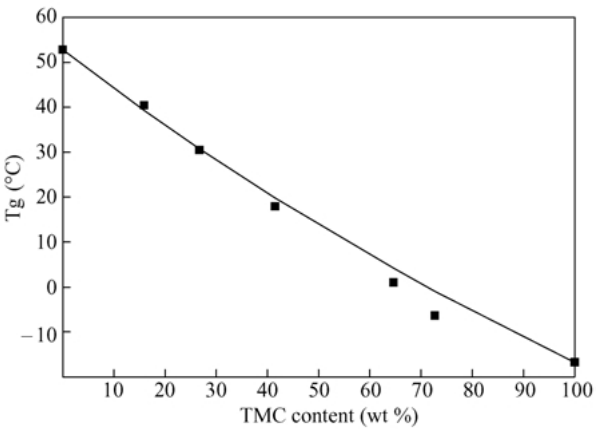

Figure 2 Thermal properties of TMC and DLLA (co)polymers as a function of the TMC content: (■) Experimental glass transition temperature (T_g); (—) Fox equation.

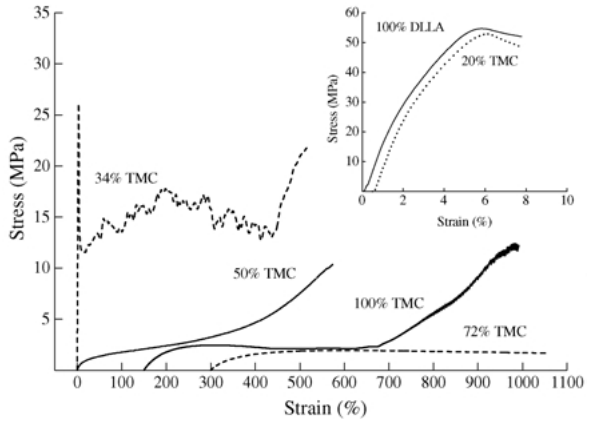

Figure 3 Stress–strain curves of TMC and DLLA (co)polymers (curves are offset for clarity).

$$\frac{1}{T_g} = \frac{w_1}{T_{g_1}} + \frac{w_2}{T_{g_2}} \tag{3}$$

where w_1 and w_2 refer to the weight fraction of the two comonomers and T_{g_1} and T_{g_2} refer to the glass transition temperatures of the two corresponding homopolymers. The close fit of the experimental values with the Fox equation (Fig. 2) indicates that for all compositions a single amorphous phase exists.

3.3. Mechanical properties

Considering the thermal properties of the synthesized TMC and DLLA (co)polymers one can expect a great effect of the polymer composition on the mechanical behavior of these materials.

Initially, specimens for tensile testing were obtained from films prepared by casting chloroform solutions of these polymers. However, for the polymers containing high contents of DLLA, the last traces of solvent were extremely difficult to remove from the films, requiring a series of time consuming extraction and drying steps. Even in small amounts, the presence of solvent in the films has a strong influence on the specimen mechanical properties due to the lowering of the polymer T_g, as a consequence of a plasticizing effect of the solvent [32, 33]. To ensure that the results were not affected by the possible presence of remaining solvent, tensile testing was performed on compression molded samples. Typical stress-strain curves are presented in Fig. 3.

The mechanical properties of the prepared TMC–DLLA copolymers are listed in Table IV. The $\overline{M}_n$ and [η] of the compression molded samples are also given. One can observe that especially for poly(DLLA) and the TMC–DLLA copolymer with 20 mol % of TMC heat processing resulted in extensive chain scission. This observation illustrates the previously mentioned need for high molecular weight polymers, to ensure good mechanical performance after heat processing.

The high modulus and strength, and the small elongations at break observed for the copolymer with 20 mol % of TMC and the DLLA homopolymer reflect the stiffness and relatively brittle character of these polymers in the glassy state at room temperature. The copolymer with 34 mol % of TMC is stiff but more ductile than the (co)polymers with lower TMC content, despite the fact that its T_g is above room temperature. The copolymer with 50 mol % of TMC ($T_g = 18°C$) shows highly flexible behavior but is still reasonably strong as its T_g is only slightly below room temperature. The copolymers with higher TMC content are highly flexible but rather weak, having low strength (tensile strength below 2 MPa) and deforming irreversibly at very low stresses. As previously reported [12], not only a high elongation at break but also a large upturn at high elongations in the stress–strain behavior of the TMC homopolymer were observed. The high value for the stress at break (corresponding also to the maximum stress) was found to be the result of strain-induced crystallization. This significantly improves the mechanical performance of this material at room temperature.

In comparison with the previously reported values for the TMC and DLLA-based copolymers of lower molecular weight [22], a significant improvement of mechanical performance of these polymers was observed. Strain-induced crystallization of poly(TMC) was also shown to be dependent on the molecular weight of the specimens [34].

3.4. Wettability and water uptake

The water uptake of a polymer can have important consequences for its thermal and mechanical properties. When designing a biodegradable material for use in the preparation of implantable biomedical devices and systems, the impact of the material's hydrophilicity extends further to other polymer properties. Protein–polymer interactions are particularly dependent on the hydrophilicity of the polymer surface [35] and directly affect the biocompatibility of the polymer and cell–material interactions [36]. Hydrophilicity will also influence the degradation rate of the material [37].

The static contact angles of the TMC and DLLA (co)polymers, which are a measure of the polymer surface hydrophilicity, are presented in Fig. 4. Although the values do not differ largely, the static contact angle decreases slightly with the increase of either monomer

TABLE IV Mechanical properties of TMC and DLLA (co)polymer compression molded films

TMC content (mol %)	$\overline{M}_n \times 10^{-5}$	[η] (dl/g)	Young's modulus (MPa)	σ_{yield} (MPa)	ε_{yield} (%)	σ_{break} (MPa)	ε_{break} (%)	σ_{max} (MPa)
100	3.24	4.34	6	2	130	12	830	12
79	1.71	2.63	5	2	160	2	270	2
72	1.76	2.66	5	2	300	2	730	2
50	2.56	3.24	16	1	54	10	570	10
34	2.58	3.25	1500	28	3	24	480	28
20	2.85	3.50	1900	51	5	46	7	51
0	2.91	3.85	1900	53	6	52	6	53

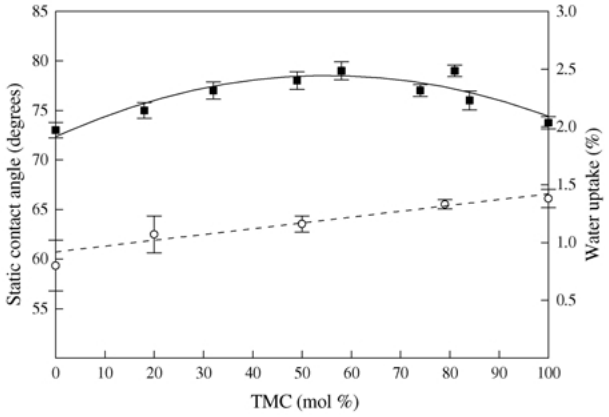

Figure 4 Wettability and water uptake of TMC and DLLA (co)polymers. Static contact angle (■) and water uptake of compression molded samples after 1 day (○).

content, reaching a maximum for the copolymers with 50 to 60 mol % of TMC. The values for the static contact angles of these polymers are high, indicating relatively hydrophobic surfaces [35, 38]. The water uptake of the TMC and DLLA (co)polymers in PBS at 37 °C was followed for a period of 30 days. In 24 h the water absorption had reached equilibrium and for all materials a very low (< 1.5 wt %) equilibrium water uptake was observed (Fig. 4). Despite the small differences one can observe that the water uptake slightly increases with TMC content. This can be explained by a decrease in T_g that increases polymer chain mobility and free volume, increasing water accessibility. Regardless of the described differences in water uptake and static contact angles, all (co)polymers can be considered hydrophobic.

The low water uptake observed for these materials is in accordance with the high values of the contact angle, which are characteristic of hydrophobic materials. Much lower static contact angles have been previously reported for TMC–DLLA based copolymers [14]. Copolymers with TMC contents ranging from 40 to 80 mol % respectively, possessed static water contact angles between approximately 15 and 50°. These values seem inconsistent with the water uptake values (< 5 wt %) reported in the same study.

Thermal analyses and tensile tests were performed on polymer samples after water uptake, in order to assess the effect of this parameter on the polymer thermal and mechanical properties (Table V). After water uptake the thermal properties of the copolymers with higher DLLA contents were the most affected (see Table IV for comparison). Related to this plasticizing effect of water a decrease in the Young's modulus and maximum stress were recorded for all samples with the exception of poly(TMC). In particular, the behavior of the copolymer containing 20 mol % of TMC is worth noticing. At room temperature, this material is in the glassy state ($T_g = 40$ °C) allowing easy processing and handling. After water uptake, T_g decreases to below body temperature and the material will show rubbery behavior under physiologic conditions.

4. Conclusions

High molecular weight statistical copolymers of TMC and DLLA were synthesized, characterized and compared with the parent polymers – poly(TMC) and poly(DLLA). The obtained results show that the thermal and mechanical properties of the polymers are strongly dependent on the composition. Furthermore, significant improvement of the mechanical performance of these materials was observed in comparison to results previously reported for TMC and DLLA based copolymers of lower molecular weight. All TMC and DLLA based (co)polymers are amorphous with T_g values varying between -17 °C for poly(TMC) and 53 °C for poly(DLLA). Therefore, the obtained materials vary from rubbers to stiff materials as the content of TMC decreases.

All materials are hydrophobic (water uptake $< 1.5\%$), although copolymers with higher TMC contents showed a slightly higher water uptake. The thermal properties, and consequently the mechanical performance, of the copolymers with higher content of DLLA were the most affected when evaluated in the wet state. After water absorption the mechanical behavior of the polymer can change from glassy to rubbery, as observed for the copolymer with 20 mol % of TMC.

The properties of the TMC and DLLA copolymers suggest their suitability as materials for resorbable biomedical devices. Copolymers with a high content of DLLA show good mechanical performance for application in the preparation of non-load bearing implants such as in soft tissue engineering. The highly elastic poly(TMC) and copolymers with high content of TMC seem more suitable for application as coatings or drug delivery systems.

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TABLE V Mechanical properties of TMC and DLLA (co)polymers after water uptake (in PBS, at 37 °C)

TMC content (mol %)	Water uptake (%)	T_g [a] (°C)	Young's modulus (MPa)	σ_{max} (MPa)
100	1.11	−19	6	18
79	1.32	−9	4	1
50	1.04	11	13	11
20	0.77	33	1100	38
0	0.69	46	1400	50

[a] First heating scan (DSC).

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