Structure and mechanical properties of biodegradable triblock thermoplastic elastomers based on L-lactide and ε-caprolactone

Vitali T. Lipik[1], Subramanian S. Venkatraman[1] & Marc J.M. Abadie[1, 2]

[1] School of Materials Science & Engineering, Block N4.1, 50 Nanyang Avenue, Nanyang Technological University, 639798, Singapore.

[2] Laboratory of Polymer Science & Advanced Organic Materials, Université Montpellier II, Place Eugène Bataillon, 34095 Montpellier, France. vitali@ntu.edu.sg, assubbu@ntu.edu.sg, marc@ntu.edu.sg

Series of elastomeric ABA triblock copolymer has been synthesized by sequential addition of the comonomers in toluene. The aim of research is to reveal the influence of polymer structure on mechanical properties and to receive triblock copolymer with good elastic properties. Stannous octoate and 1,4-butanediol were used as catalyst and initiator of polymerization. Coordinated anionic ring opening polymerization was realized in two steps. Soft block based on ε-caprolactone was polymerized at the first step of polymerization followed by hard block polymerization which was made of L-lactide. Poly(ε-caprolactone) (PCL) and poly(L-lactide) (PLA) are known as semicrystalline polymers, that does not promote elastic behavior of polymer. Usually elasticity of block copolymer is achieved by reducing the crystalinity of middle soft block (PCL), randomizing it as random by copolymerization with another monomer. Trying to disrupt the crystallinity of PCL and reduce the crystallinity of PLA, we added some quantity of L-lactide during ε-caprolactone polymerization and some quantity of ε-caprolactone during L-lactide polymerization. Syntheses have been planned according to the design of experiment based on finite Galois field. Targeted molar weight of the soft block (B) was 40,000 Da for all syntheses. Quantity of L-lactide added to the soft block, quantity of ε-caprolactone added to the hard block and molar weight of hard block (PLA) have been varied at three levels. Quantity of L-lactide added at the first step of polymerization has been varied as 10, 25 and 50% mol. Quantity of ε-caprolactone added at the second step of synthesis has been changed as 0, 10 and 25%. Molar weight of PLA (A) has been varied as 10,000, 20,000, 40,000 Da. Totally 9 polymer have been synthesized. Mixing two monomers at the first and second steps of synthesis we receive polymers with multiblock structure. Bigger segments in the soft block (B) are made of PCL and bigger segments in the hard blocks (A) are made of PLA. Different multyblock structures with majority of PCL in the soft block and PLA in the hard block has revealed a variety of mechanical properties of polymers. Structure of polymers and their mechanical properties were studied by DSC, NMR, SEC, tensile and cyclic tests. Polymers composition and structural properties of polymers are presented in table 1.

Table 1 – Polymers composition and structural properties

N	PLA targeted M_n kDa	% LA in PCL, mole	% CL in PLA, mole	*PLA crystallinity, %	*PCL crystallinity, %	*PLA segment length, monomer unit	*PCL segment length, monomer unit	*M_n, Da; (M_n/M_w)
1	10	10	0	27.9	39.10	18.0	12.8	53025 (1.58)
2	20	10	10	47.1	25.61	20.1	11.2	56821 (1.78)
3	40	10	25	31.6	25.58	16.1	9.9	61490 (1.40)
4	10	25	10	20.8	-	6.9	5.9	46295 (1.61)
5	20	25	25	1.3	-	8.9	6.7	84190 (1.53)
6	40	25	0	50.4	-	35.6	7.4	86730 (1.58)
7	10	50	25	34.8	-	8.3	3.6	50471 (1.44)
8	20	50	0	47.9	-	20.6	4.3	58564 (1.60)
9	40	50	10	45.6	-	23.5	3.7	83577 (1.67)

*Crystallinity of PCL and PLA was calculated based on DSC data, PCL and PLA segment lengths were calculated by ^{13}C NMR analysis, molar weights of polymers was measured by SEC.

Young's modulus of the received polymers ranges from 1-330 MPa. Elongation at break varies from 7% to 2000%. Shape recovery property is different for different polymer structure, the lowest measured shape recovery property is 32% and the best one is 87% after 100% of stretching. For example polymer with structure 10-40-10 kDa (PLA-b-PCL-b-PLA) with 10% of L-lactide in the soft block and homopolymer PLA hard block shows very large deformation. It has high elongation at break (more than 1200%) but shape recovery property is bad. Polymers with 25% of L-lactide in PCL and 25% of ε-caprolactone in PLA have quite good shape recovery characteristic and rubbery behavior. Polymer with structure 40-40-40 kDa (PLA-b-PCL-b-PLA), 50% of L-lactide in PCL, 10% ε-caprolactone in PLA has the highest modulus 237 MPa and very low elongation at break – only 42%. Mechanical properties of synthesized polymers are presented in table 2.

Table 2 – Mechanical properties of polymers

N	PLA targeted M_n, kDa	% LA in PCL, mole	%CL in PLA, mole	Elongation at break, %	Young's Modulus, MPa	Shape recovery property, %
1	10	10	0	1268	19.2	57
2	20	10	10	1483	33.9	61
3	40	10	25	1106	14.9	70
4	10	25	10	1187	3.4	83
5	20	25	25	1954	9.2	87
6	40	25	0	186	26.1	32
7	10	50	25	700	14.7	80
8	20	50	0	283	58.3	73
9	40	50	10	42	237.0	45

Correlations (R) between polymer structure parameters and mechanical properties were calculated. Elongation at break correlate in biggest degree with PLA crystallinity (R=-0.71). Young's modulus has revealed the closest relationship with %LA in PCL (R=0.52). Shape recovery correlates more with PLA segment length (R=-0.93).
Equations describing relationships between polymers structure and mechanical properties have been built based on the received data. Dependence of elongation at break (E), Young's modulus (M) and shape recovery property (S) from PLA molar weight (M_{PLA}), quantity of L-lactide in PCL soft block (%LA) and quantity of ε-caprolactone in PLA hard blocks (%CL) were described by quadratic and pair multiplication equations with correlation coefficients equal 0.983, 0.976 and 0.993 accordingly.

$$E=513.25+77.28\times M_{PLA}+4.86\times\%LA+36.18\times\%CL-1.95\times M_{PLA}^{2}-0.47\times\%LA^{2}-0.36\times\%CL^{2}$$

$$M=88.91-4.73\times M_{PLA}-2.99\times\%LA-4.98\times\%CL+0.21\times M_{PLA}\times\%LA+0.16*M_{PLA}\times\%CL+0.074\times\%LA\times\%CL$$

$$S=60.70-1.21\times M_{PLA}+0.76\times\%LA+2.86\times\%CL-6.44\times10^{-4}\times M_{PLA}\times\%LA-5.58\times10^{-3}\times M_{PLA}\times\%CL-6.04\times10^{-2}\times\%LA\times\%CL$$

Based on the received data and modeling, polymers with defined mechanical properties can be designed and obtained. For example, we can use the equations and calculate the ratio of monomer in the blocks which allow to reach the best shape recovery property (46% L-lactide in the soft block and 12.5% ε-caprolactone in the hard block). Elongation at break, Young's modulus, hardness and softness of polymer can be designed by the same way. Using equations we can predict which structural parameters is more critical for defined polymer mechanical properties. Knowing the influence of ε-caprolactone:L-lactide ratio on degradation, it is possible to create polymers with defined mechanical properties and programmed biodegradation behavior.