SYNTHESIS AND CHARACTERIZATION OF POLYESTERS MODIFIED WITH CITRIC ACID AND PDMS

Kamilė Vonžodaitė, Saulutė Budrienė

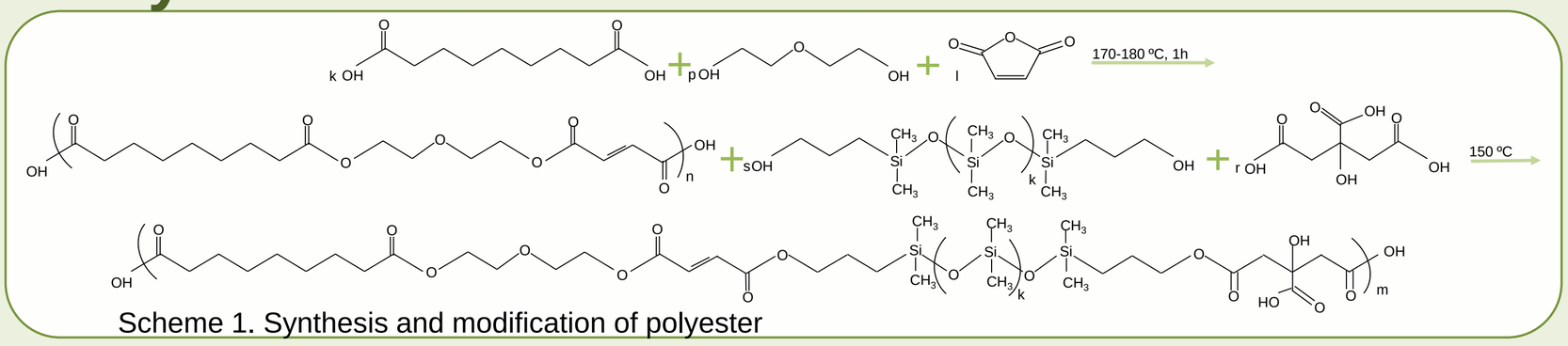
Department of Polymer chemistry, Vilnius University, Lithuania

E-mail: kamile.vonzodaite@chgf.stud.vu.lt

Introduction

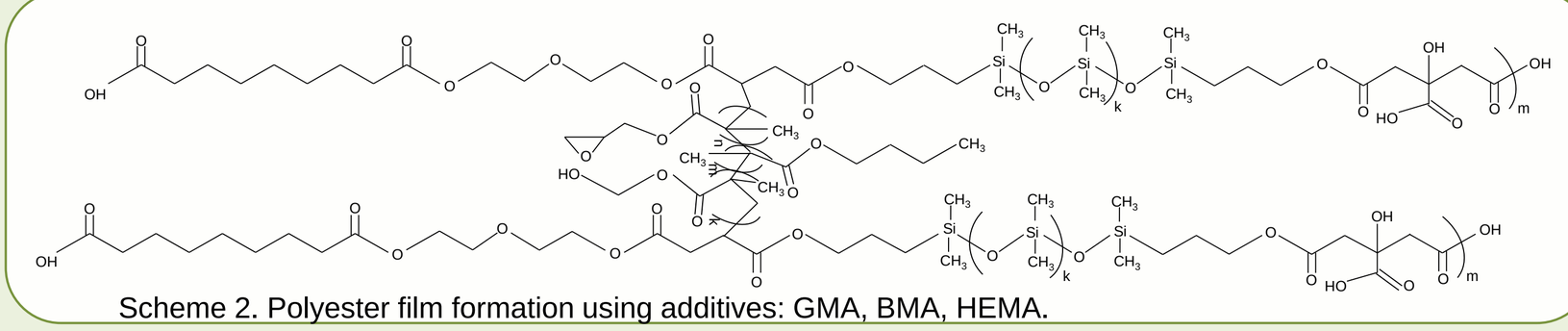
Tissue engineering is a rapidly evolving field of science that seeks to address the growing need for transplants and organ shortages. Materials used in tissue engineering must be biodegradable and biocompatible. They must also be easy to manufacture and comply with the mechanical properties of the tissue to be replaced [1]. To date, polydimethylsiloxane (PDMS) has been widely used in tissue engineering due to its good biocompatibility, transparency and gas permeability. PDMS, on the other hand, is very hydrophobic and does not posses good mechanical properties [2] . For these reasons PDMS can be modified with multifunctional biodegradable polyesters such as citric acid. Citric acid (CA) is non-toxic and easily extracted. Citric acid polyesters with different mechanical properties can be obtained by changing the synthesis conditions.

Synthesis and film formation



Scheme 1. Synthesis and modification of polyester

Polyesters were obtained by synthesis of pre-polymers from diethylene glycol (DEG), azelaic acid (AA) and maleic acid anhydride (MA). Pre-polymers were then modified with α,ω-dihidroksi-PDMS and CA (Scheme 1). Reactions were carried out in argon atmosphere under continuous stirring, until desired acid number of the reaction mixture was reached.



Scheme 2. Polyester film formation using additives: GMA, BMA, HEMA.

Three curing additives were used to form the films: glycidyl methacrylate (GMA), butyl methacrylate (BMA) and/or hydroxyethyl methacrylate (HEMA) (Scheme 2). Photo initiator used for film forming was IRG651. The films were cured in an UV oven for 30 min. and then dried to constant weight.

Results

Table 1. Degree of swelling and solubility of cured films in three solvents: hexane, ethanol and water.

[MA]:[AA]:[DEG]:[PDMS]:[CA]	Curing additives (amount corresponding to MA)			Degree of swelling, %		Solubility, %		
	[GMA]	[BMA]	[HEMA]	C_2H_5OH	H_2O	C_6H_{14}	C_2H_5OH	H_2O
0.60:0.3:1:0.05:0.10	1	2	-	44	5	1.5	9	1.0
	2	2	-	26	8	1.4	24	2.1
	2	2	2	57	8	1.4	5	3.3
0.50:0.3:1:0.05:0.20	1	2	-	29	7	0.6	11	0.3
	2	2	-	73	8	1.2	7	2.0
	2	2	2	44	12	0.1	4	1.9
0.45:0.3:1:0.05:0.25	1	2	-	38	7	2	12	1.7
	2	2	-	38	9	2.6	12	2.5
	2	2	2	57	9	1.3	16	2.0

Degree of swelling generally increased with increase in amount of curing additives. Low solubility in hexane showed that most of the PDMS was incorporated in the polyester (Table 1).

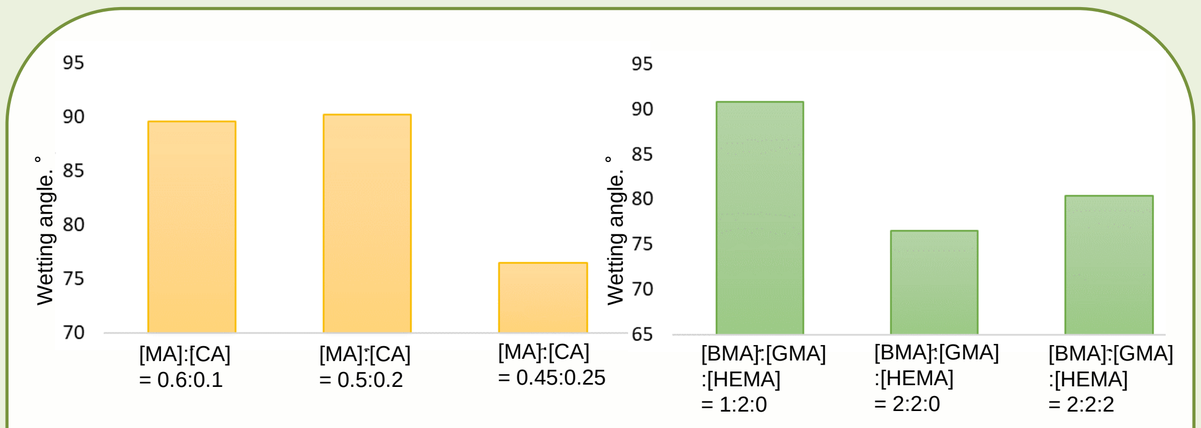


Fig. 1. Wetting angle dependance on different MA and CA molar ratios, when curing additives were [BMA]:[GMA]=2:2

Fig. 2. Wetting angle dependance on different BMA, GMA and HEMA molar ratios, when [MA]:[CA]=0.45:0.25

Water wetting angle of cured films was evaluated (Fig. 1, 2). Films with highest amount of CA had the lowest wetting angle (77˚). All films had lower contact angle than commercial PDMS (101˚) [3]. The lowest wetting angle was observed when curing additives [BMA]:[GMA]=2:2 were used.

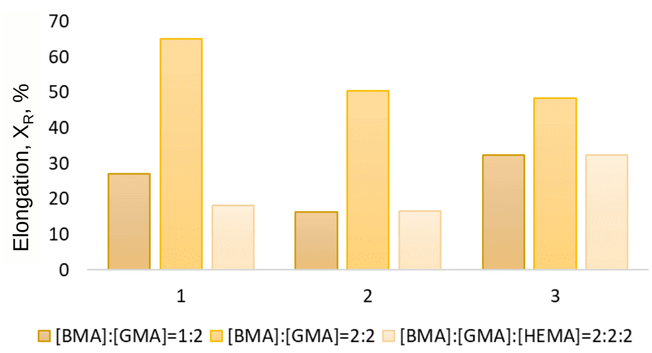


Fig 3. Elongation at break of films, when [MA]:[CA] were 0.6:0.1 (1), 0.5:0.2 (2) and 0.45:0.25 (3).

Table 2. Mechanical properties of polyester films ([BMA]:[GMA]=2:2).

[MA]:[CA]	X_R, %	E, M·Pa
0.6:0.1	65	26.3
0.5:0.2	50	10.5
0.45:0.25	48	5.8

Films with lowest amount of CA and highest amount of MA had the highest elongation at break X_R and Young's module (Table 2). Films with curing additives [BMA]:[GMA]=2:2 were more elastic than others (Fig 3).

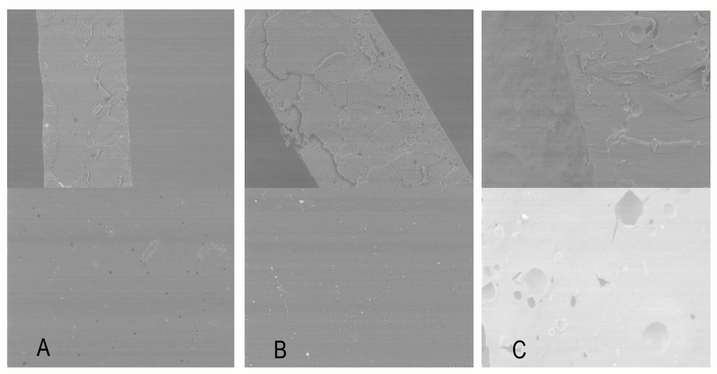


Fig. 4. SEM images of films cross-section (top) and surface (bottom) when [MA]:[CA] were 0.6: 0.1 (A); 0.5: 0.2 (B); 0.45:0.25 (C). ([GMA]:[BMA] = 2:2).

Table 3. Glass transition temperature of polyester films.

[MA]:[CA]	T_g, ºC	
	First heat cycle	Second heat cycle
0.6:0.1	11	15
0.5:0.2	-6	4

All produced films had small pores throughout the whole film (Fig 4.) Polyester films had a glass transition temperature lower than that of a human body. Increase in T_g after first cycle indicated additional crosslinking (Table 3).

References

1. Ye. H., Zhang, K. D. Kai, Z. Li, X. Loh. Chem. Soc. Rev. 47, 12 (2018) 4545–4580.
2. Y. Chuah, Y. Koh, K. Lim, N. Menon, Y. Wu, Y, Kang. Sci Rep 5 (2016) 18162.
3. T. Trantidou, Y. Elani, E. Parsons, O. Ces. Microsyst. Nanoeng. 3 (2017) 16091.

Conclusions

Increase of citric acid and decrease of maleic anhydride in polyesters resulted in less elastic films but improved water wettability. Using BMA and GMA as curing additives with molar ratio 2:2 resulted in films with overall better wettability and mechanical properties.