PLA GRAFTING PROCESS WITH MALEIC ANHYDRIDE

Nikica Baričević, Ena Miletić, Karla Stražičić, Lucija Vlahović, Roko Blažic, Dajana Kučić Grgić, Vesna Ocelić Bulatović
University of Zagreb Faculty of Chemical Engineering and Technology, Trg Marka Marulića 19, 10 000 Zagreb

INTRODUCTION

Poly(lactic acid), PLA, is a biodegradable polymer with potential application in the packaging industry. However, the commercialization of such packaging materials is still not acheaved due to the brittleness and lack of flexibility and hygroscopic nature of PLA. Therefore, considerable effort is put into developing biodegradable mixtures based on PLA with good mechanical properties, the disadvantage of which is the poor miscibility of the polymer, which can be improved by using compatibilizers. A possible compatibilizer of polymer mixtures based on PLA are graft copolymers that contain PLA as the basic chain. An example of such a copolymer is PLA grafted with maleic anhydride (PLA-g-MA). It ensures the dispersion of one polymer phase in another and improves the interphase adhesion of polymers in the mixture. Steric interference and possible unwanted reactions such as cross-linking of PLA or polymerization of MA in the presence of initiators reduce the efficiency of the grafting process. In order to prepare a graft copolymer with a high degree of grafting, it is necessary to optimize the preparation process.

SYNTHESIS

The samples were prepared by the process of reactive polymerization in a Brabender mixer. In order to optimize the PLA-g-MA preparation process, different reaction conditions were used. The process was carried out at 175 °C or 165 °C with a stirring speed of 60 rpm, using different precursor addition sequences and different mass fractions of maleic anhydride and initiator (benzoyl peroxide, BPO) shown in *Table 1*. For PLAGMA **N** samples, PLA was first mixed for two minutes, then BPO was added and mixed for one minute, after which MA was added and mixed for three minutes. For samples PLAGMA **Z**, after mixing PLA for two minutes, BPO and MA were added simultaneously and mixed for three minutes.

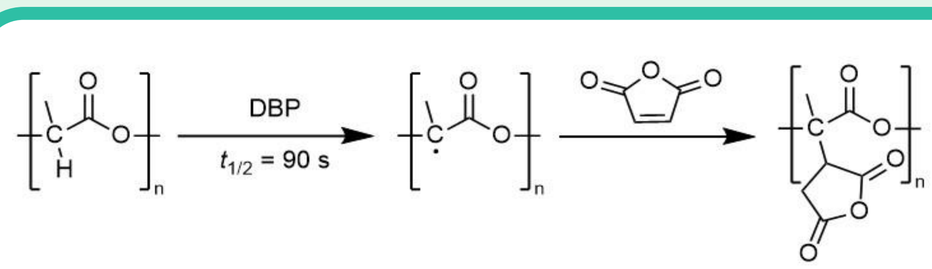
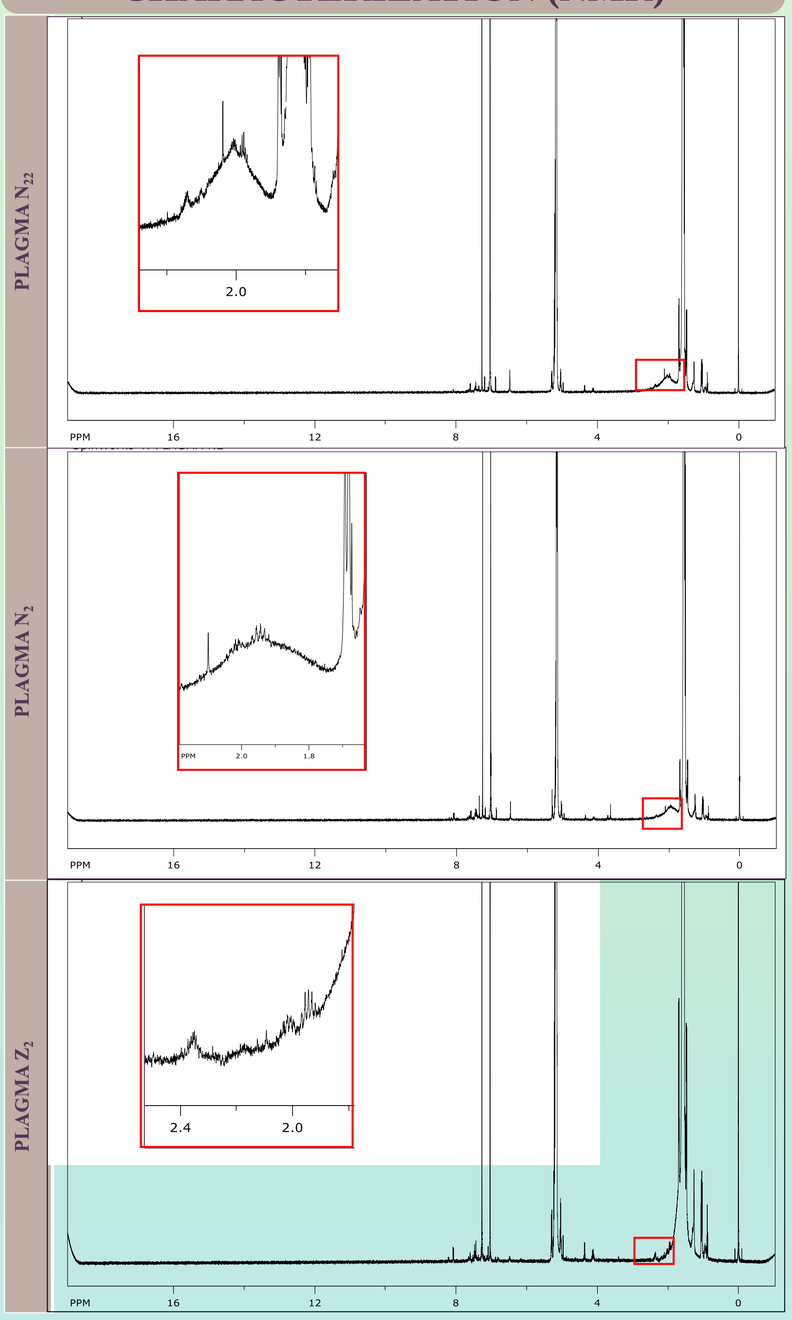


Table 1. Grafting components

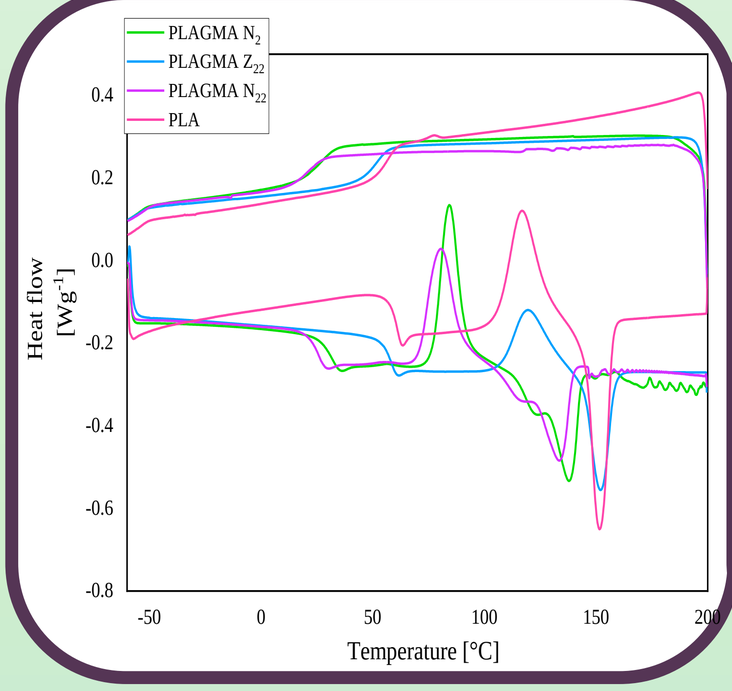
SAMPLE	w(PLA), %	w(MA), %	w(initiator), %
PLAGMA N_1	88	10	2
PLAGMA N_2	76	20	4
PLAGMA N_{11} (165 °C)	88	10	2
PLAGMA N_{22} (165 °C)	76	20	4
PLAGMA Z_1	88	10	2
PLAGMA Z_2	76	20	4

RESULTS

SPECTROSCOPIC CHARACTERIZATION (NMR)



DSC & TG ANALYSIS



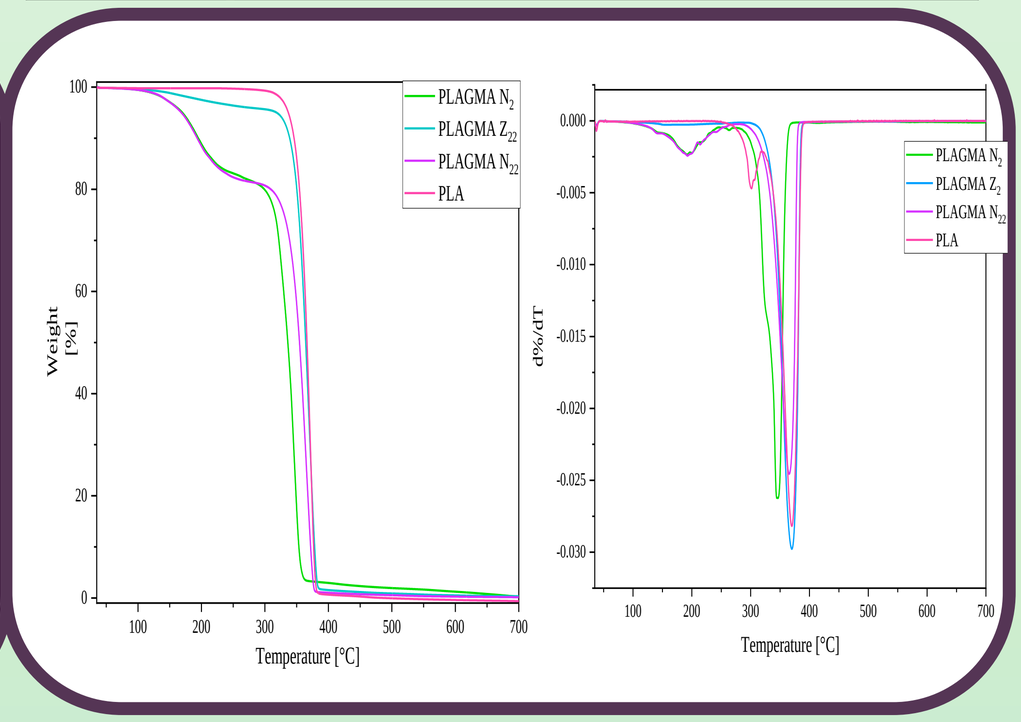


Table 2. DSC results

SAMPLE	T_g [°C]	T_{cc} [°C]	T_m [°C]	ΔH_m [Jg^{-1}]	ΔH_{cc} [Jg^{-1}]	χ_c [%]	T_{max} [°C]	grafting
PLAGMA N_1	55,54	113,69	150,32	-25,24	26,86	26,94	369,21	no
PLAGMA N_2	31,09	84,26	137,90	-22,23	26,33	23,72	381,81	yes
PLAGMA Z_2	57,41	119,75	152,07	-13,43	18,95	14,33	410,48	no
PLAGMA N_{11}	51,08	119,44	148,86	-17,79	18,89	20,16	391,76	no
PLAGMA N_{22}	25,08	80,52	133,50	-21,14	24,47	26,12	429,59	yes
PLA	60,49	116,88	151,38	-24,64	28,74	26,29	370,52	/

GAS PHASE CROMATOGRAPHY (GPC)

SAMPLE	*M*n	*M*w	*Đ*
PLA	90889	168690	1,9
PLAGMA N_1	101530	179300	1,8
PLAGMA Z_2	86124	161600	1,9

CONCLUSION

Grafting of MA onto PLA for samples N_2 and N_{22} was confirmed by observing a signal on the NMR spectra at 2 ppm. For succesful grafting, it is necessary to ensure the temperature and amount of initiator used are high enough. The results of GPC indicate that the molecular mass of ungrafted samples changed. Slight decrease or increase in molecular mass for ungrafted samples might be caused by side reactions such as cross-linking or PLA degradation.
The reduction of T_g and lower thermal stability of grafted samples could be caused by chain branching due to a grafting reaction between PLA and MA, resulting in an increase in the segmental mobility of PLA chains.

LITERATURE:

[1] S. Farah, D. G. Anderson, R. Langer, Adv. Drug Deliv. Rev., 107 (2016) 367-392.

[2] H. Jang., S. Kwoon, S. Jong Kim, S. Park, Int. J. Mol. Sci., 23 (2022) 13.

[3] S. W. Hwang et al., Polym. Test., 31 (2012) 2.

Financira Europska unija NextGenerationEU

This research was conducted as part of the project „Production and development of compostable packaging from waste biomass for the packaging of industrially processed food products” (**NPOO.C3.2.R3-I1 .04.0059**) funded by National Recovery and Resilience Plan (funded by the European Union, NextGenerationEU).