SOLID STATE POLYMERIZATION OF POLY(LACTIC ACID): CRITICAL PROCESS PARAMETERS

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INTRODUCTION

Solid state polymerization (SSP) comprises an eco-friendly polymerization technique and a standard step for molecular weight build-up of PET and of PA 6.6. It involves heating the prepolymer to a temperature above the glass transition point but below the onset of melting; polycondensation progresses through chain end reactions in the amorphous phase of the semicrystalline polymers and reaction by-products are removed by maintaining reduced pressure or through convection caused by passing inert gas[1-3]. Poly(lactic acid) (PLA) comprises one of the most promising materials from renewable resources, serving as an alternative for polymers on fossil basis[4-5]. The current work aims to apply SSP on PLA prepolymers so as to limit melt polymerization time. The process parameters herein studied were prepolymer initial molecular weight, reaction temperature and time, in order to establish an optimized SSP profile.

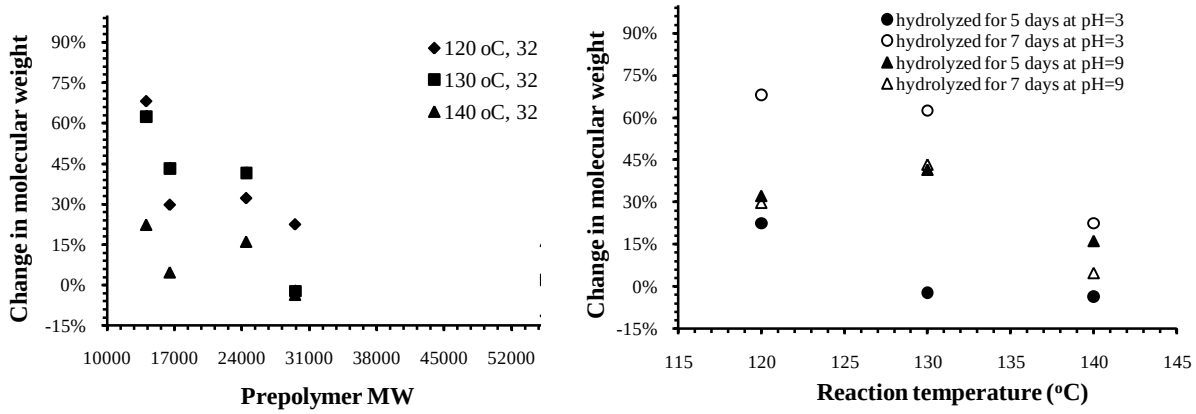
EXPERIMENTAL

Commercial PLA (NaturePlast) of 171500 g mol^{-1} was hydrolyzed at 60 ^{o}C under acidic (pH=3) and alkaline (pH=9) conditions for 3, 5 and 7 days in order to prepare suitable PLA prepolymers. The hydrolyzed grades were then submitted to SSP in a bench scale cylindrical stainless steel reactor at 120, 130 and 140 ^{o}C, for 16, 24 and 32 h under flowing nitrogen.

RESULTS AND DISCUSSION

PLA SSP under the studied conditions resulted in up to 68% increase of molecular weight. However, different trends were observed depending on the prepolymer starting molecular weight (MW), reaction temperature and time, as well as hydrolysis conditions.

In particular, it was found that PLA SSP at 120 and 130 ^{o}C occurred at a significant extent in the case of prepolymers with low MW, revealing a critical starting MW value at 30,000 g mol^{-1} for SSP efficiency (Fig.1a). On the other hand, at the highest SSP temperature of 140 ^{o}C, the SSP rate was kept low independently of starting MW, potentially due to accelerated side reactions.



(a) (b)

Fig.1. a) Change in molecular weight after 32 h of SSP of both grades, b) change in molecular weight vs. reaction temperature for prepolymers of MW<30,000 g mol^{-1}.

With regard to the influence of the reaction temperature (Fig. 1b), it was observed that the samples hydrolyzed under alkaline conditions (pH=9) showed the highest molecular weight change at 130 ^{o}C, while SSP at 120 ^{o}C was proved most efficient for the samples hydrolyzed under acidic conditions.

Finally, when comparing the prepolymers with the lowest starting MW, hydrolysis under acidic conditions favored post reaction compared to hydrolysis under alkaline environment.

REFERENCES

1. Papaspyrides C., Vouyiouka S., Solid state polymerization. N.J: John Wiley & Sons, 2009.
2. Vouyiouka S., Karakatsani E., Papaspyrides C., Prog. Polym. Sci. 30:10, 2005.
3. Papaspyrides C., Solid state polymerization. In The Polymeric Materials Encyclopedia, J. Salamone, Ed., CRC Press, Inc. 1996, pp.7819-7831.
4. Xu H., Luo M., Yu M., Teng C., Xie S. J. Macromol. Sci. Part B: Physics 45:681, 2006.
5. Moon S, Taniguchi I, Miyamoto M, Kimura Y, Lee Ch. High Perfor. Polym. 13:189, 2001.