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Review article

Nanocomposites of aliphatic polyesters: An overview of the effect of different nanofillers on enzymatic hydrolysis and biodegradation of polyesters

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ABSTRACT

In the present review the findings concerning the effect of nanofillers to biodegradation and enzymatic hydrolysis of aliphatic polyesters were summarized and discussed. Most of the published works are dealing with the effect of layered silicates such as montmorillonite (unmodified and modified with organic compounds), carbon nanotubes and spherical shape additives like SiO_2 and TiO_2. The degradation of polyester due to the enzymatic hydrolysis is a complex process involving different phenomena, namely, water absorption from the polyesters, enzymatic attack to the polyester surface, ester cleavage, formation of oligomer fragments due to endo- or exo-type hydrolysis, solubilization of oligomer fragments in the surrounding environment, diffusion of soluble oligomers by bacteria and finally consumption of the oligomers and formation of CO_2 and H_2O. By studying the published works in nanocomposites, different and sometimes contradictory results have been reported concerning the effect of the nanofillers on aliphatic polyesters biodegradation. Most of the papers suggested that the addition of nanofillers provokes a substantial enhancement of polyester hydrolysis due to the catalyzing effect of the existed reactive groups (−OH and −COOH), to the crystallinity decrease, to the higher hydrophilicity of nanofillers and thus higher water uptake, to the higher interactions, etc. However, there are also some papers that suggested a delay effect of nanofillers to the polyesters degradation mainly due to the barrier effect of nanofillers and the lower available surface for enzymatic hydrolysis.

1. Introduction

1.1. Aliphatic polyesters

Aliphatic polyesters are a growing research subject, since due to their biodegradability they appear as a solution to the emerging environmental concerns that have risen in recent years. They represent an interesting alternative to synthetic non-biodegradable polymers for a short-life range of applications. Aliphatic polyesters are biopolymers in which repeating units are bonded via ester linkages; many kinds of esters are present in nature and the enzymes that degrade them, esterases, are also ubiquitous in nature [1]. In fact, a number of synthetic polyesters has been found to be biodegradable, and several polyesters like aliphatic, are now produced on a semi-commercial scale by a number of companies that make biodegradable plastics. Polylactide (PLA), polyglycolate (PGA), polycaprolactone (PCL), poly(3-hydroxybutyrate) (PHB), polyhydroxyvalerate (PHV) and their copolymers poly(butylene succinate) (PBSu), poly(ethylene succinate) (PESu), poly(propylene adipate) (PPAd), etc., are the most used aliphatic polyesters (Table 1) for a wide variety of applications such as packaging materials and mulch films, in an effort to solve the problems related to plastic waste accumulation. Furthermore, since these aliphatic polyesters are biocompatible they can be used as biomaterials in drug release formulations, tissue engineering, implants, etc. An additional advantage of these polyesters is that almost all monomers that are used for their preparation can be produced from monomers derived from renewable resources [2,3]. Thus, these polyesters could replace petroleum-based plastics in many fields such as packaging, agricultural, and biomedical applications.

1.2. Aliphatic polyester nanocomposites

The application of aliphatic polyesters may be limited because of their low mechanical strength, thermal stability, gas permeability, solvent resistance, hydrophobic character, and slower resorption/degradation kinetics as compared to other polymers. These drawbacks could be overcome by enhancing their thermomechanical

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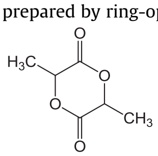
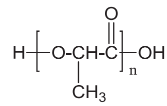
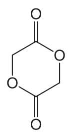
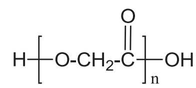
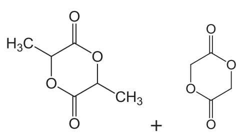
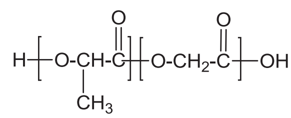
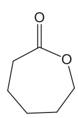
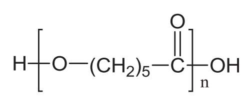
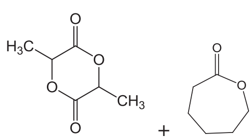
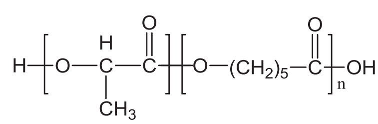
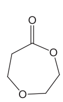
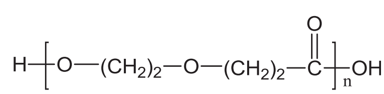
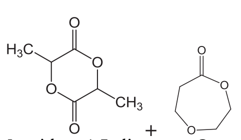
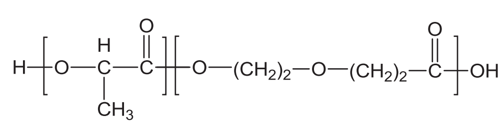
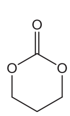
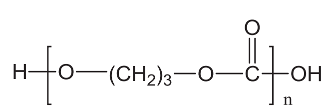
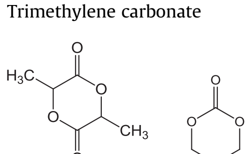
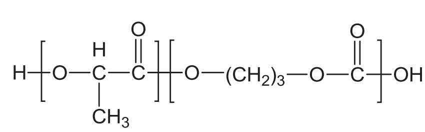
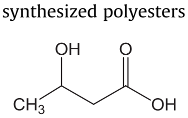
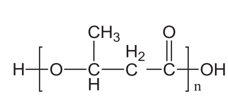
Table 1
Monomers and chemical structures of the most important aliphatic polyesters used for several applications.

a/a	Monomer	Polyester
Polyesters prepared by ring-opening polymerization		
1	 Lactide	 Polylactide (PLA)
2	 Glycolide	 Polyglycolide (PGA)
3	 Lactide + glycolide	 Poly(lactide-*co*-glycolide) (PLGA)
4	 *ε*-caprolactone	 Polycaprolactone (PCL)
5	 lactide + *ε*-caprolactone	 Poly(lactide-*co*-caprolactone) [P(LA-*co*-CL)
6	 1,5-dioxepan-2-one	 Poly(1,5-dioxepan-2-one) (PDXO)
7	 Lactide + 1,5-dioxepan-2-one	 Poly(lactide-*co*-1,5-dioxapan-2-one) [P(LA-*co*-DXO)
8	 Trimethylene carbonate	 Poly(trimethylene carbonate) (PTMC)
9	 Lactide + trimethylene carbonate	 Poly(lactide-*co*-trimethylene carbonate) [P(LA-*co*-TMC)]
Microbial synthesized polyesters		
10	 3-hydroxybutyric acid	 Polyhydroxybutyrate (PHB)

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