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Review

Networks based on biodegradable polyesters: An overview of the chemical ways of crosslinking

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ABSTRACT

Biodegradable polymers have gained more importance due to growing concern of our society for the ecology and sustainable development. Among them, aliphatic polyesters, poly(ε-caprolactone) PCL, poly(lactic acid) PLA and poly(3-hydroxyalkanoate)s PHAs present the advantage to be both biodegradable and biocompatible. Nevertheless, their thermal and mechanical properties represent a major drawback limiting some engineering applications. As a result the design of novel structures such as networks based on polyesters is revealing as a great challenge for enhancing their mechanical and thermal properties. The networks can be obtained throughout several approaches. This review focuses on the different chemical methods of crosslinking by using radical mechanisms, condensation reactions of polyesters or functionalized oligoesters. Preparation of hybrid, interpenetrated or reversible networks are described. This review highlights the relations structure-properties of the resulted materials and their potential applications.

Contents

1. Introduction

Increasing uses of petrochemical based plastics have created environmental and ecological difficulties due to the non-degradability of these materials. As a consequence, aliphatic polyesters such as polylactide (PLA), poly(ε-caprolactone) (PCL) and poly(3-hydroxyalkanoate) (PHA) provide a more environmentally friendly alternative to their synthetic counterparts due to their biodegradability [1–12]. They have attracted more and more attentions aiming to at least partially replace the non-degradable plastics. These polyesters can be prepared by different methods, *i.e.* chemical polymerization or by biotechnology. PLA and PCL are obtained by ring opening polymerization (ROP) of lactide or ε-caprolactone respectively [13–18] whereas PHA were produced by enzymatic polymerization [19–24]. Although the most well-studied PHA is the poly(3-hydroxybutyrate) (PHB), over 140 constitutive monomer units have been investigated [25]. Three main types of PHAs are generally distinguished, the short-chain length PHAs (*scl*-PHAs) that possess alkyl side chains having up two carbon atoms, the medium-chain length PHAs (*mcl*-PHAs) that displays between three and eleven carbon atoms on their side chains, and unsaturated PHAs that contains alkene groups in the side chains (Fig.

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1). Concerning the degradability, PLA and PCL generally degraded by a backbone hydrolysis of the ester linkage and the degradation products are naturally occurring bioabsorbable metabolites [7,8,16,26–31]. A special interest of PHAs is their direct enzymatic biodegradability due to the presence of depolymerase able to entirely degrade natural PHAs into CO_2 and H_2O in aerobic conditions [32–41].

Many efforts have been recently made to improve the properties and make these linear thermoplastic polyesters more competitive against petroleum based polymers. For this, polymer blends, copolymerizations, composites and network formation have been extensively studied [42–62]. Among the different strategies, the formation of crosslinked structure is of much interest since it offers the possibility to increase both the mechanical and thermal properties of these polymers.

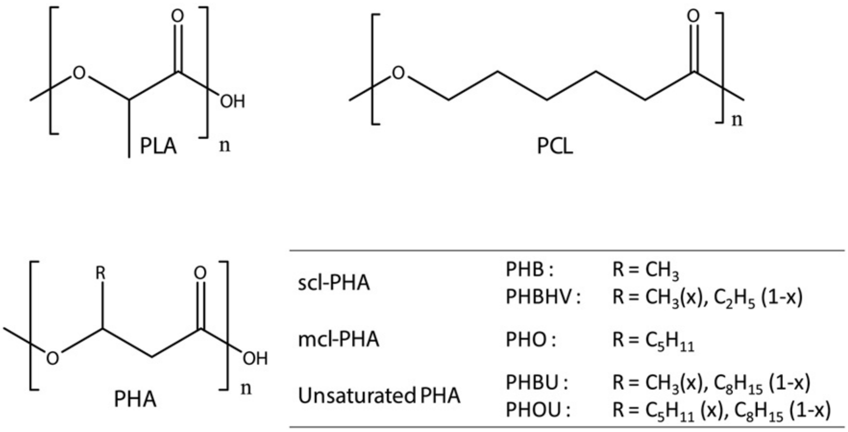
In this context, this chapter aims at reviewing the developments on the chemical crosslinking of polyesters. We can distinguish two different ways for designing the networks depending on the molar masses of the polyesters. Networks can be directly obtained from native polyesters (Fig. 2, way A). The way A describes the formation of networks in presence of a radical initiator (A1), a multifunctional co-agent as trithiol (A2) or the formation of semi interpenetrating network in which the polyester is embedded in a tridimensional network (A3). In the way B (Fig. 3), the formation of the networks first requires the synthesis of oligoesters with controlled architecture [63–67] that are further used in radical polymerization (B1), condensation reactions (B2) or sol-gel condensations (B3). The comparison of the different chemical strategies used to prepare networks based on PLA, PCL or PHA are detailed (Schema 1).

2. Networks based on native polyesters using radical initiator

Crosslinking reactions of polyesters in presence of radical initiators have been developed to create polymer radicals on the polymer backbone. The combinations of the radicals give branched or crosslinked materials with better physical and mechanical characteristics [68–71]. Among the different initiators (Table 1), dicumyl peroxide, DCP was the most efficient due to its relatively high hydrogen abstraction efficiency. The peroxide efficiency depends on two criteria [72,73]. The first criterion is the amount of peroxide required to the crosslinking reactions and the second is whether the free radicals cause more chain scissions than crosslinking reactions. The chain scissions are considered as a drawback because they are responsible of the loss of mechanical properties. In this context, the reactive extrusion process of polyesters using organic peroxides in the melt state is known to cause severe chain scissions [74,75]. An increase in the polymolecularity index from 2.8 to 6.0 was observed when PHBHV was cured with 0.3 wt% DCP at 160 °C [76]. To counteract this negative effect, crosslinking was conducted in the presence of multifunctional co-agent as a means to introduce long-chain branching (Table 1). Co-agent modified PLA and PHA materials showed strain hardening and high thermal stability [74,77].

Concerning the PHAs, the poly(3-hydroxyoctanoate-*co*-3-hydroxyundecenoate (PHOU) is an unsaturated polyester that contains double bonds in the side chains (Fig. 1). The addition of multifunctional co-agents such as ethylene glycol dimethacrylate and a triallyl cyanurate (Table 1) improved the crosslinking reactions and reduced the chain scission for the saturated or unsaturated polymers. However, the vinyl specific peroxides initiated the homopolymerization of the co-agent [78]. The choice of a proper initiator with favourable decomposition rate under the experimental conditions is important in the process of extrusion to improve the crosslinking degree of the materials.

The peroxide treatment was also successfully employed to enhance the compatibilization between polymers [79–81]. The role of DCP is to initiate free radical reactions between the different polymers to obtain grafted copolymers and crosslinked networks that significantly enhance the compatibility of the blends. Reactive blending of PHO/PLA has been performed to produce *in situ* compatibilized blends with improved properties [77] using DCP and a co-agent. The modified PHO/PLA blends had a finer morphology suggesting a compatibilization effect possibly arising from copolymer formation at the interface [77]. In addition, in order to improve the compatibilization between PCL and epoxidized natural rubber (ENR) (Table 1), Mishra et al. have synthetized PCL/ENR blends (70/30 or 50/50) by melt blending in presence of DCP. Biodegradable thermoplastic elastomers were obtained with higher tensile strength and elongation at break and fairly good elastic recovery as well as melt processability [82]. A compabilization between PHBHV, poly(butylene adipate-*co*-terephthalate) (PBAT) and ENR was also achieved during melt processing in the presence of DCP. Both, DCP and ENR play dual positive roles in the blend and composites, as they act as toughening agents and compatibilizers [83]. Using this process, green composites based on PHBHV, PBAT, ENR and Miscanthus fibers were prepared by reactive extrusion in presence of DCP to ensure good interfacial adhesion between the different phases of the biocomposites. Moreover, thiol-ene chemistry that involves the addition of a thiol group on a carbon — carbon double bond [84] has been employed in various applications. Ishida et al. prepared a novel material by combining the PHOU, a thiol functionalized polyhedral oligomeric silsesquioxane (POSS) and a tetrathiol crosslinker [85] (Fig. 4) to obtain an elastomeric material with excellent shape fixing and recovery. The crosslinking of poly(3-hydroxybutyrate-*co*-3-hydroxyundecenoate) (PHBU) was also accomplished by using a pentaerythritol tetrakis(3-mercaptopropionate) as crosslinker agent. The results have shown a unique combination of improved strength and flexibility of the polyester [86].



scl-PHA	PHB :	R = CH_3
	PHBHV :	R = CH_3(x), C_2H_5 (1-x)
mcl-PHA	PHO :	R = C_5H_{11}
Unsaturated PHA	PHBU :	R = CH_3(x), C_8H_{15} (1-x)
	PHOU :	R = C_5H_{11} (x), C_8H_{15} (1-x)

Fig. 1. Chemical structure of aliphatic polyesters.