

Hydrolytic stability of polycarbonate/poly(lactic acid) blends and its evaluation via poly(lactic) acid median melting point depression



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ABSTRACT

The hydrolytic degradation of polycarbonate (PC)/poly(lactic) acid (PLA) blends in deionized water media first time was studied in this research. Effects of degradation on mechanical properties and elasticity of the blends was presented and evaluated. Median PLA melting point depression approach is proposed for determination of degree of degradation. The proposed technique allowed true degree of degradation estimation not subjected to numerous phenomena affecting mechanical properties like moisture absorption and crystallization. The use of median melting point of PLA allowed accounting for numerous effects of PLA degradation resulting in its asymmetric melting curve. The presence of the acrylic impact modifier in blend significantly decreased the rate of moisture absorption rate and properties deterioration at later stages of degradation. This phenomenon was attributed to limited propagation of degradation areas due to the presence of acrylic modifier droplets having hydrophobic nature. It was found that degradation of PC/PLA blends due to hydrolysis may proceed in two distinctive stages: a) water diffusion and pit formation and b) hydrolytic degradation in PLA phase where degradation was supported by water transport via pits. The second stage is accompanied by accelerated water absorption due to the hydrolysis reaction and rapid properties deterioration. It was also found that PC phase also subjected to degradation due to pH decrease caused by PLA degradation. The PC degradation by-products like bisphenol A were not detected in degraded polymer samples which was attributed to their continuous removal into surrounding water media.

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1. Introduction

The use of bio-based polymers for various application attracted attention of researchers for many years. Most of the research was aimed for application of bio-based polymers for disposable and compostable applications of such polymers [1]. As the use of bio-sourced polymers continued to grow more and more research was aimed on studies of the polymer blends for durable applications [2,3]. Poly(lactic acid) (PLA) is the most promising polymer for

durable applications requiring high mechanical properties exceeding in that aspect all bio-based polymers. That is why PLA remains in focus of research of polymer blends for durable applications. A number of blends of PLA with engineering thermoplastics were studied in recent years: PTT/PLA [4], PP/PLA [5,6], ABS/PLA [7] and many others. PC/PLA blends are considered as one of the most promising polymer systems for durable applications [8,9]. Recent advances in polymer compatibilization allowed creating blends having mechanical properties sufficient for most advanced durable applications like automotive industry, machinery etc. Potentially, PC/PLA blends could replace PC/ABS blends without compromise in properties but with significant cost savings and lower environmental impact. Therefore, it is a matter of importance to establish durability of the PC/PLA blends since it is the durability of bio-based polymers becomes a limiting factor for actual industrial applications.

The degradation of PLA was studied by many researchers.

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Summarizing many studies, it was found that hydrolytic PLA degradation occurs primarily through hydrolysis of the ester bond followed by decrease of PLA molecular weight and carboxylic acid formation [10,11]. Many studies confirmed that the rate of hydrolysis, i.e. degradation depends on numerous factors [12,13]. Most influential factors for PLA hydrolysis are temperature, access to moisture, sample's thickness and its geometry, microstructure, and the presence of basic or acidic environments [14,15]. In addition, degradation in a composting environment has been studied for applications such as packaging [16]. In these types of applications a controlled degradation rate is needed. The water uptake in PLA was found to be obey Fick's law at relatively low temperatures deviating from it at higher temperatures due to secondary reactions [17,18].

Many aspects of PC durability also studied well since PC is an important thermoplastic for durable applications including biomedical and food industries. Bair et al. [19] conducted a comprehensive study of PC degradation at different temperatures ranging from 60 °C to 125 °C. They found that hydrolytic degradation of PC leads to formation of by-products containing up to 70% of bisphenol A and higher molecular weight oligomers of bisphenol A. These observations were confirmed later by Haghghi-Yazdizet al [20] as well as other studies [21–24]. Mishra et al. [25] studied PC degradation in buffer solutions for up to 52 weeks at different temperatures. They observed an accelerating decrease of molecular weight of PC with increasing exposure temperature. PC molecular weight dropped 47% after 52 weeks of exposure at 80 °C. The PC hydrolysis was well described by Arrhenius equation with some degree of deviation at higher temperatures due to additional thermal degradation. Significant research was done in the field of poly(carbonate)-based thermoplastic polyurethanes for biomedical applications [26–30].

There are relatively few studies of effects of biodegradation on PLA blends with durable materials and very few studies on durability of PC/PLA blends. Phuong et al. [31] studied biodegradation of PC/PLA blends prepared via reactive extrusion in presence of triacetin (TA) and tetrabutylammonium tetraphenylborate (TBATBP). They found that in the PC/PLA blends, the final degradation degree is proportional to the PLA content in the blend. Depending on the PC content, the onset of degradation was delayed and the final biodegradation percentage was reduced. It was found that the presence of TA and TBATBP initially increase the speed of degradation, but decrease the final biodegradation percentage.

Durability of PC itself in PC/PLA blends is dependent on pH of the media and significantly accelerates in acidic media. Harris et al. [32] conducted an extensive study of commercially available PC/PLA blends to test their environmental durability at accelerated degradation conditions. It was found that at 70 °C and 90% of relative humidity all tested PC/PLA blends experience significant flexural strength drop after only 5 days of exposure regardless of PLA content. Researchers also established that degradation of PC in PC/PLA blends clearly accelerated by acidic by-products of PLA degradation with formation of bisphenol A leached to the surface which was confirmed by FT-IR studies.

In this study we set several goals: first, to characterize hydrolytic degradation of impact modified and non-modified PC/PLA blends and compare the degradation process with durable PC/ABS blends; second, develop a technique allowing reliably evaluate degree of degradation of PLA in complex polymer blends; third, reach better understanding of mechanisms of degradation and water transport in polymer blends. This study may become an important step for development of durable high performance biobased blends.

2. Materials and methods

2.1. Materials

The hydrolytic degradation studies were performed using two PC/PLA blends. One blend was non-impact modified PC/PLA blend containing 32 wt% PLA and 68 wt% PC. The second blend was an impact modified high performance PC/PLA blend containing 32 wt% PLA, 62 wt% PC and 6 wt% of poly(ethylene *n*-butylene acrylate glycidyl methacrylate) (EBA-GMA) ethylene terpolymer. The chemical structure of the EBA-GMA is given in Fig. 1. Since only these two compositions were used in further references and notations the studied blends are referred as PC/PLA and PC/PLA/EBA-GMA blends. High performance PC/ABS blend for automotive applications was PULSE 2000EZ produced by Trinseo was used in this study as comparison and referred in this manuscript as PC/ABS.

Low viscosity general purpose polycarbonate was used in this study to prepare PC/PLA blends. PC Hylex P1025L1HB (MFI = 25 g/10 min at 300°C/1.2 kg according to manufacturer) was produced and supplied by Entec Polymers. An injection grade PLA Ingeo 3251D is a product of Nature Works LLC (USA). The mechanical properties and heat resistance data of neat materials and blends used in this study are given in Table 1. Poly(ethylene *n*-butylene acrylate glycidyl methacrylate) (EBA-GMA) ethylene terpolymer was manufactured and supplied by DuPont company under the trade name Elvaloy PTW. Elvaloy PTW is a terpolymer consisting from 66.75 wt% ethylene, 28.00 wt% butyl acrylate and 5.25%wt glycidyl methacrylate [33]. A Melt Flow Index of Elvaloy PTW was 12 g/10 min(190 °C/2.16 kg) as measured according to ASTM method D1238. The melting point of 72 °C and glass transition temperature (T_g) of –55 °C were determined using DSC.

To avoid degradation during the blending at high temperatures a 0.3 phr of chain extender was used. Commercially available chain extender Joncryl ADR-4368C is a BASF product. Joncryl ADR-4368C is supplied in form of a glassy brittle semi-transparent pellets and consists of a multi-functional reactive polymer having epoxy equivalent weight of 285 g/mol and T_g of 54 °C according to manufacturer's data. Joncryl ADR-4368C is typically used as additive for thermal degradation mitigation in a number of polymers including PLA and PC. The chemical structures of the EBA-GMA terpolymer, Joncryl ADR-4368C have significant similarities but these terpolymers have different role in polymer blending. PC and PLA for immiscible blends and EBA-GMA is also immiscible in both PLA and PC. After reactive blending EBA-GMA forms fine droplets in preferentially PLA phase which explains its high toughening efficiency.

2.2. Sample preparation and conditioning

The dry mix of polymer pellets was prepared by premixing with powdered chain extender in hand mixer. The blend then was extruded in Leistritz extruder at a screw speed of 100 rpm at temperature of 265 °C. The extruder was equipped with co-rotating twin screws with a screw diameter of 27 mm and L/D ratio of 48. The extruded strands were pelletized and dried in an oven at 80 °C

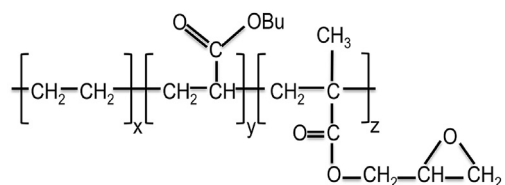


Fig. 1. A chemical structure of poly(ethylene *n*-butylene acrylate glycidyl methacrylate) (EBA-GMA) ethylene terpolymer.

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