Hydrolytic Degradation Behaviors of Poly(p-dioxanone) in Ambient Environments*

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Abstract The effects of temperature and relative humidity on the hydrolytic degradation of poly(p-dioxanone) (PPDO) were investigated. The hydrolytic degradation behaviors were monitored by tracing the changes of water absorption, mechanical and crystalline properties, molecular weight and its distribution, surface morphologies, as well as infrared absorption peaks and hydrogen chemical shifts during the degradation. It is found that the water absorption increases whilst the intrinsic viscosity, tensile strength and elongation at break decrease as the temperature or relative humidity increases. With degradation time growing, the molecular weight drops and its distribution broadens. The crystallinity of PPDO has a tendency to increase at first and then to decrease, while the crystalline structure is not significantly changed. At the same time, some cracks are observed on the surface and keep growing and deepening. All results show that temperature plays more significant roles than relative humidity during the degradation. The analyses of Fourier transform infrared spectroscopy and hydrogen nuclear magnetic resonance spectroscopy reveal that the degradation of PPDO is a predominant hydrolysis of ester linkages.

Keywords: Poly(p-dioxanone); Hydrolytic degradation; Temperature; Relative humidity.

INTRODUCTION

Poly(p-dioxanone) (PPDO) has good biocompatibility, bioresorbability, degradability and excellent mechanical properties[1-3]. In 1970s, it was manufactured as absorbable monofilament suture PDS® by Ethicon Inc, and now PDS® is still commonly used in surgery[4]. Recently, due to the successful use of a highly active dehydrogenation catalyst for the preparation of p-dioxanone (PDO) monomer from diethylene glycol, the cost of PDO decreased significantly[5-7]. Furthermore, PPDO is also a feedstock recyclable polymer, which can be decomposed into PDO with a high yield of more than 90% by means of pyrolysis[8, 9]. This can give rise to the further cost reduction of PPDO. Therefore, it becomes possible for the extensive applications of PPDO, such as films, molded products, unwoven materials and shape memory devices[10-12].

The hydrolytic degradation of PPDO has played a key role in biomedical materials applications and has been investigated in previous reports[13-15]. Most of the researches were only conducted in the phosphate buffer solution (PBS) of pH 7.4 at 37 °C in order to simulate the degradation of PPDO in vivo[13, 15]. Generally, with the process of the hydrolytic degradation, the retention weight decreases; the molecular weight reduces; and the

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mechanical properties deteriorate. The degradation of PPDO proceeds in a two-stage process: the chain segments located in the amorphous regions are broken down randomly at first, and then those located in the crystalline regions are attacked gradually\[^{16}\]. These aforementioned research results have an important guiding significance for the applications of PPDO \textit{in vivo}.

With the great progress in the research and development, PPDO can also be widely used as general materials in ambient environments\[^{11, 12, 17}\]. In fact, the hydrolytic degradation of PPDO not only occurs \textit{in vivo}, but also takes place in ambient environments. It is well known that the degradation behaviors of materials are seriously dependent on the degradation medium\[^{18}\]. For example, the degradation behaviors of polylactic acid (PLA) in ambient environments with different temperatures and relative humidities (RH) showed that both of the temperature and relative humidity had significant effects on the degradation of PLA\[^{19, 20}\]. Moreover, the degradation behaviors in ambient environments are quite different from those in PBS, such as mechanical properties changes, surface morphologies changes\[^{21-23}\]. The degradation behaviors of materials in ambient environments are more close to the actual situation for processing and application environment of polymers\[^{20}\]. However, there have been few reports on the hydrolytic degradation of PPDO in ambient environments up to now. This is not in favor of PPDO material development, extending its applications, predicting its life time and so on. In the meantime, the research concerning the degradation in ambient environments also has a vital guiding significance for the transportation and storage of PPDO. Therefore, a detailed description of the degradation behaviors occurring in ambient environments with different temperatures and relative humidities is very necessary.

In the present paper, the hydrolytic degradation behaviors of PPDO were investigated in ambient environments with different temperatures and relative humidities. The changes of water absorption, mechanical and crystalline properties, molecular weight and its distribution, surface morphologies of PPDO were monitored by weight loss measurement, tensile test, differential scanning calorimetry, wide-angle X-ray diffraction, Ubbelohde viscosimeter, gel permeation chromatography, and scanning electron microscopy. The process of degradation was traced by the Fourier transform infrared spectroscopy and hydrogen nuclear magnetic resonance.

\textbf{EXPERIMENTAL}

\textbf{Materials}
\(p\)-Dioxanone, provided by the Pilot Plant of the Center for Degradable and Flame-Retardant Polymeric Materials (Chengdu, CHN), was dried over CaH\(_2\) for 48 h and distilled twice under reduced pressure of 30 Pa at 80 °C before use. Stannous octoate (AR grade) was purchased from Sigma (USA) and used as received. After diluted with anhydrous toluene, stannous octoate solution was stored in the glass ampoules under nitrogen. Phenol, 1,1,2,2-tetrachloroethane, acetone and other chemicals with AR grade were procured from Kelong Chemical Corporation (Chengdu, CHN) and used without further purification.

\textbf{Preparation of PPDO}
PPDO was synthesized by ring-opening polymerization of PDO with stannous octoate as catalyst. Predetermined amount of PDO and stannous octoate with a molar ratio of 10000:1 were charged into a pre-dried 3 L reaction kettle (Weihai Automatic Control Reaction Kettle Co. Ltd., CHN) under nitrogen atmosphere. The reaction was performed at 120 °C for 6 h, and then the unreacted monomer was removed by vacuum distillation at 30 Pa and 120 °C for 1 h. The obtained crude polymer was milled into powder and then further purified by removing the unreacted monomers in Soxhlet extractor with acetone for 8 h. The purified PPDO was dried to constant weight under vacuum at 40 °C and stored in a desiccator over silica gel.

\textbf{Sample Preparation}
PPDO bars with the slice of 25 mm \(\times\) 4 mm \(\times\) 0.5 mm were prepared by platen vulcanizing press (Qingdao Ya Dong Rubber Machinery Group Co., Ltd., CHN) at a pressure of 10 MPa and 130 °C for 3 min, and then cooled at room temperature.