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Effect of γ-radiation on crystallization of polycaprolactone

Guangming Zhu[a,*], Qianyong Xu[b], Ruifeng Qin[a], Hongxia Yan[a], Guozheng Liang[a]

[a]*Department of Applied Chemistry, Northwestern Polytechnical University, 127 West Friendship Road, Xi'an 710072, PR China*
[b]*Northwest Institute of Nuclear Technology, Post Box 69, Xi'an 710024, PR China*

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Abstract

The crystallization behavior of radiation cross-linked poly(ε-caprolactone) (PCL) was studied by DSC at different cooling rates. The crystallization process was analyzed by the Ozawa equation and the Mo–Zhishen method that is developed from combining the Avrami equation and the Ozawa equation. It was concluded that the crystallization of radiation crosslinked PCL is governed by heterogeneous nucleation and single-dimension growth; the crystal fraction and rates of crystallization are related to the radiation dose and degree of cross-linking; the relationship between relative crystallinity and time follows the Ozawa equation: The higher the degree of crosslinking, the less the crystal velocity constant. The activation energy of crystallization for irradiated PCL is between 65 and 54 kJ/mol.

Keywords: Poly(ε-caprolactone); Radiation crosslinking; Non-isothermal crystallization; Ozawa equation

1. Introduction

Poly(ε-caprolactone) (PCL), as an aliphatic polyester, has received much attention because of its possible application as both a biocompatible and a biodegradable material. PCL-based products can be used as soil degradable films or containers, which could contribute to the reduction of "white pollution" (Iannace et al., 1999; Cyras et al., 2001). For biomedical purpose, it may be used for drug delivery systems to the human body or tissue engineering scaffolding material (Pitt et al., 1981; Pitt and Schinder, 1984; Bei et al., 1995; Kweon et al., 2003). Radiation cross-linked PCL can be used as bioabsorbable sutures, orthopedics fixing materials etc because of its shape-memory effects at lower temperature (Zhu et al., 2003). However, PCL is a semi-crystalline polymer, and its final properties, such as strength, modulus, biodegradability and shape-memory effect, depend to a great extent on the crystalline fraction, which is affected in turn by conditions of crystallization. Therefore, investigation of the crystallization kinetics of PCL is of considerable practical significance. Although the isothermal crystallization kinetics has been reported in literature (Peter and Ake, 1996), practical processes, such as extrusion molding and film forming usually proceed under dynamic, non-isothermal conditions. In order to obtain material with better physical properties, it is especially necessary to study the dynamic, non-isothermal crystallization process. On the other hand, it is also of great interest to study the effect of radiation cross-linking on the limited crystallization.

In this work, the crystallization process of radiation cross-linked PCL was studied under non-isothermal conditions at different cooling rates. The Ozawa

*Corresponding author. Fax: +86 2988474080.
E-mail address: nwpuzgm@vip.sina.com (G.M. Zhu).

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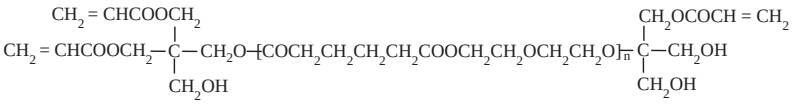
(Ozawa, 1971) equation and a new method developed by combining the Avrami equation (Avrami M) and the Ozawa equation were employed to explain the non-isothermal crystallization data. By using the Kissinger (An et al., 1998) method, the activation energies of cooling crystallization process have been evaluated.

2. Experimental

2.1. Materials

PCL-H5 (M_W 50000) was obtained as a commercial product from Nippon Daicel Company (Japan). Trifunctional polyester acrylate (PEA), bought from Tianjin Tianjiao Chemical Industry Co. Ltd, was blended with PCL to improve its degree of radiation cross-linking. The structure of PEA is showed as follows:



$n = 2$–5, molecular weight between 700 and 1200. The reason to select PEA as cross-linking agent is that the double bond in the molecule is sensitive to radiation and can promote radiation cross-linking; moreover, its structure is similar to PCL and has maybe better miscibility with PCL.

2.2. Preparation of samples

PEA was gradually added to PCL in a blender at 70 °C and roll milled for 15 min to ensure complete mixing. Then the blend was compression molded in a press at 60–70 °C for 5 min to give 2 mm thick sheets. The composition of the blend was 98/2 (PCL/PEA, mol ratio), and this blend was named T2.

2.3. Radiation

Samples were enclosed in a polyester bag with limited air and irradiated by a cobalt-60 source with dose rate 20 kGy/h in Xi'an Radiation Research Center (China). The doses were 0, 50, 100, 300 kGy. For example, T2, irradiated with 100 kGy, would be marked as T2-100.

2.4. Measurement of degree of cross-linking

The degree of cross-linking was characterized by gel content (G%) which was determined using Soxhlet extractor with toluene (refluxing for 30–40 h) and it was defined as the ratio of insoluble material dried to constant weight in a vacuum oven after extraction to its original mass.

$$G\% = \frac{\text{mass of residue (g)}}{\text{original mass (g)}} \times 100\%.$$

The gel content of samples with different dose is as following:

Samples	H5-0	T2-50	T2-100	T2-300
G%	0	28.3	36.5	45.8

2.5. DSC analysis

The non-isothermal crystallization characteristics of the radiation cross-linked PCLs were measured by differential scanning calorimetry (DSC, TA Instrument, 2910model). The temperature and energy readings were corrected with indium and water at the cooling rates employed in the measurements. The sample size was between 8–10 mg. The environment for measuring samples was purged with high pure nitrogen gas followed by quenching with liquid nitrogen. Each sample was heated first to 80 °C and then kept at that temperature for 5 min to avoid the differences in thermal history. DSC was carried out over a temperature range from 80 °C to −40 °C with cooling rates of 2.5 °C, 5 °C, 10 °C and 20 °C/min. The exothermic crystallization peak was recorded as a function of temperature. The relative degree of crystallinity (X_t) and absolute degree of crystallinity (X_c) as a function of crystallization temperature T are defined as

$$X_t = \int_{T_0}^{T} (dH_c/dT)\, dT \Big/ \int_{T_0}^{T_\infty} (dH_c/dT)\, dT,$$

$$X_c = \int_{T_0}^{T_\infty} (dH_c/dT)\, dT \Big/ \Delta H_{m,c},$$

where T_0 and T_∞; are the onset and end of crystallization temperature, respectively. $\Delta H_{m,cc}$ is the heat of fusion of 100% crystalline PCL. In this work, the reported fusion enthalpy of 139.5 J/g was adopted (Pitt et al., 1981).