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Thermal decomposition kinetics of thermotropic liquid crystalline *p*-hydroxy benzoic acid/poly(ethylene terephthalate) copolyester

Sunan Saikrasun*, Onanong Wongkalasin

Department of Chemistry, Faculty of Science, Mahasarakham University, Kantarawichai District, Mahasarakham 44150, Thailand

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Abstract

The nonisothermal and isothermal thermogravimetry (TG) in nitrogen and in air of thermotropic liquid crystalline poly(oxybenzoate-*co*-ethylene terephthalate), a copolyester consisting of 60 mol% of *p*-hydroxy benzoic acid (HBA) and 40 mol% of poly(ethylene terephthalate) (PET), known as Rodrun LC3000, was performed. The Friedman technique based on a single heating-rate method was used to calculate the kinetic parameters of the nonisothermal degradation and the Flynn technique was employed to calculate the kinetic parameters of isothermal degradation. The nonisothermal degradation of Rodrun LC3000 in nitrogen and in air occurred in two steps. In air, Rodrun LC3000 became degraded leaving very small residues within the range of experimental temperature whereas, in nitrogen, it left some residues which were found to increase in amount with increasing heating rate. The respective activation energy, order and ln(frequency factor) for nonisothermal decomposition of Rodrun LC3000 are 159 kJ/mol, 2.2 and 28 min^{-1} in nitrogen and 121 kJ/mol, 2.4 and 20 min^{-1} in air. The respective activation energy, order and ln(frequency factor) for isothermal degradation are found to be 110 kJ/mol, 2.2 and 17.1 min^{-1} in nitrogen and 103 kJ/mol, 2.3 and 15.9 min^{-1} in air. The kinetic parameters obtained from the two modes of decomposition indicate that the thermal stability of Rodrun LC3000 is substantially better in nitrogen than in air. The estimated lifetimes at various temperatures suggest a good thermal stability of Rodrun LC3000.

Keywords: Liquid crystalline polymer; Rodrun LC3000; Thermal degradation; Thermogravimetry; Thermal stability

1. Introduction

Thermotropic liquid crystalline polymer (TLCP) is one of the most advanced materials used in electronic devices and fibre composites due to its excellent mechanical properties, improved processability, good thermal, chemical, and dimensional stabilities. There has been an increasing application of TLCP, either alone, or as reinforcements or matrices for advanced composites. So far, numerous companies have made TLCPs available on a commercial or semicommercial basis. Among the first TLCPs to be discovered were the copolyesters formed from *p*-hydroxy benzoic acid (HBA) and poly(ethylene terephthalate) (PET), initially made by researchers at Eastman Kodak. One of the original Eastman products consisting of 60% HBA/40% PET was marketed under the code X7G but the polymer was not commercially developed. Similar product with the same composition is now produced using a new process by Unitika company [1–2]. The use of this new process results in material which has been commercialised by Unitika under the name Rodrun LC3000.

* Corresponding author. Tel./fax: +66 43754246.
E-mail address: sunan.s@msu.ac.th (S. Saikrasun).

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Rodrun LC3000 represents one of the most important aromatic polymers with low melt viscosity, excellent chemical resistance and mechanical properties. The semirigid rod-like aromatic chain structure of Rodrun LC3000 polyester is responsible for its relatively high-glass transition and melting temperature. Normally, the polymer must encounter elevated temperatures at almost every stage in manufacturing, compounding, and processing stages, in service and during repairing step. Therefore, the understanding of thermal stability and decomposition kinetics of the polymer is an essential information for development and extension of their applications. Thermal degradation and combustion process of X7G copolyester analysed by means of directly coupled thermal analysis-mass spectrometry (TA-MS) under inert and quasi-air atmospheres was investigated by Sato et al. [3]. In their report, the evolved gas products released from HBA and PET blocks were discussed in relation to the decomposition step. Crossland et al. [4] studied thermal degradation behaviour of fully aromatic polyester based on HBA by thermogravimetry (TG) and pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS). They explained that, during thermal degradation, the main breakdown route is scission in the ester group followed by hydrogen abstraction reaction. The thermal degradation of a series of TLCPs with different copolymer ratios of HBA, bisphenol (BP) by means of Py-GC/MS was examined by Sueoka et al. [5]. They clarified the origin of various aromatic degradation products and discussed the mechanisms for TLCPs. Moreover, a number of studies have been investigated on the thermal degradation behaviour of other TLCPs such as Vectra, Xydar, including other commercial and synthesized TLCPs [6–13]. However, to our knowledge, the thermal stability and degradation of Rodrun LC3000 have not been studied systematically. Recently, we have investigated the styrene–(ethylene-butylene)–styrene (SEBS) thermoplastic elastomer in situ reinforced with Rodrun LC3000. The rheological behaviour, mechanical properties and morphology of this blend have been reported [14–16]. From our previous work, the incorporation of Rodrun LC3000 into SEBS significantly enhanced the mechanical properties and improved processability of the blend. However, it is additionally necessary to examine the thermal stabilities and decomposition kinetics of the blend components and Rodrun LC3000/SEBS composite in order to fully elucidate the properties of the blend system.

In this article, we attempted to clarify the thermostability and decomposition kinetics of Rodrun LC3000 by performing nonisothermal and isothermal TG. To characterize the relative importance of pyrolytic and thermo-oxidative processes, the TG measurements were investigated in nitrogen and in air. For next communication, the thermal degradation behaviour of the Rodrun LC3000/SEBS composite will be reported in comparison with those of the blend components.

2. Experimental

The TLCP used in the present work was a semirigid copolyester composed of 60 mol% HBA and 40 mol% PET, known as Rodrun LC3000 from Unitika Co., Ltd. (Tokyo, Japan). It has a melting point of 220 °C and a density of 1.41 g/cm^3. The intrinsic viscosity was reported to be 0.65 dL/g [17]. The molecular weight for the TLCP was not obtainable, since no solvent was found to dissolve Rodrun LC3000. The material was dried in vacuum oven at 70 °C for at least 12 h before use. The TG analyses were carried out using TA instruments, SDT Q600 (Luken's drive, New Castle, DE, USA). The pellet of the sample of 8–10 mg was loaded in an alumina crucible. For nonisothermal method, the sample was heated from ambient temperature to 1000 °C at five different heating rates as 1, 3, 5, 7 and 10 °C/min. The isothermal tests were performed at 340 °C, 350 °C, 360 °C and 370 °C for 100 min. Prior to isothermal heating, the sample was heated at a rate of 20 °C/min from ambient temperature to the selected temperature of isothermal degradation. As soon as the system reached the selected temperature, the variations of sample weights with times were registered. Both nonisothermal and isothermal methods were performed in nitrogen and in air with the flow rate of 100 ml/min. The TG data were recorded online in TA instrument's Q series explorer software. The analyses of the TG data were done using TA Instrument's Universal Analysis 2000 software (version 3.3B).

2.1. Friedman method [18]

The analyses of thermal degradation of polymers by using Friedman technique based on single heating-rate method have been widely used. This method utilizes the following natural logarithmic differential equation:

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln\left(\beta\frac{d\alpha}{dT}\right) = \ln A + n\ln(1-\alpha) - \frac{E}{RT} \quad (1)$$

By plotting $\ln(d\alpha/dt)$ or $\ln(1-\alpha)$ against $1/T$ for a constant heating rate, a straight line could be obtained with a slope of $-E/R$. Additionally, the E/nR value could be calculated from the slope of the linear plot of $\ln(1-\alpha)$ versus $1/T$.

2.2. Flynn method [8]

Flynn technique has been used as the kinetic method to study the isothermal TG of thermal degradation. This