Thermochimica Acta 605 (2015) 8–15

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Curing kinetics of nanostructured epoxy blends toughened with epoxidized carboxyl-terminated liquid rubber

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ARTICLE INFO

Article history:
Received 12 October 2014
Received in revised form 8 February 2015
Accepted 9 February 2015
Available online 11 February 2015

Keywords:
Epoxy resin
Curing kinetics
Non-isothermal DSC
Epoxidized CTBN

ABSTRACT

The curing kinetics of epoxy resin/rubber blends containing different contents of epoxidized carboxyl-terminated butadiene acrylonitrile (ECTBN) with different epoxidation degrees is studied using non-isothermal differential scanning calorimetry (DSC) at different heating rates. Kissinger method is used to calculate the apparent activation energies, and Málek method is used to determine the most suitable kinetic model characterizing the curing process. The results show that the curing reaction is catalyzed by the hydroxyl and carboxyl groups in ECTBNs, whereas hindered by the viscosity increment owing to addition of rubber. Within the chemical reaction control stage, the curing process could be well described by the two-parameter autocatalytic kinetic model of Šesták–Berggren, and the simulated curves calculated by Šesták–Berggren model show a good agreement with that experimentally determined.

1. Introduction

Epoxy resins have found a wide range of applications as surface coatings, adhesives, encapsulants and advanced composites due to their excellent mechanical, thermal and electrical properties and chemical resistance [1]. However, the use of epoxy resins can be greatly limited by their inherent brittleness and poor resistance to crack propagation [2–5]. In order to obtain high-performance cured epoxy resins, substantial efforts have been made in the last decades in toughening epoxy resins by incorporating toughening modifiers [6–16].

Phase separation takes place and a variety of morphologies can be generated during the curing reaction, which have a considerable effect on the properties of epoxy resins [17–21]. The morphology depends mainly on both thermodynamic and kinetic factors, such as the concentration, composition, and molecular weight of the modifier, curing conditions, and the change in viscosity of the systems during the phase separation [21,22].

The addition of fillers to the epoxy resin systems will alter their morphology and curing kinetics [23–27]. Vijayan et al. [26] have investigated the effects of nanoclay and carboxyl-terminated (butadiene-co-acrylonitrile) (CTBN) rubber on the reaction induced phase separation and curing kinetics of an epoxy/cyclic anhydride system using dynamic and isothermal differential scanning calorimetry (DSC), and found that nanoclay surfactant accelerated the cure reaction, whereas the phase-separated CTBN hindered the cure reaction. In another study investigating the effects of the epoxidation degree and content of epoxidized polystyrene-block-polybutadiene star copolymer on the final properties and curing behavior of nanostructured thermosetting system, Serrano et al. have shown that the final morphology was influenced by the competitive kinetics between phase separation and polymerization [28]. The cure kinetic parameters related to network formation can provide substantial information concerning the final structure, properties, and processability of epoxy resins. Thus, kinetic analysis of curing reaction of epoxy resin and its blends or composites is essential for a better understanding of the property–structure–processing relationship and preparation of high performance materials [29].

We have previously studied the effects of epoxidation degree and content of epoxidized CTBN (ECTBN) on the morphologies, the thermal and mechanical properties of epoxy/rubber blends, and the results showed that the epoxy resin/ECTBN blends outperformed the epoxy resin/CTBN blends and neat epoxy resins [30]. This study has extended our previous work by investigating the curing kinetics of epoxy resin/ECTBN and epoxy resin/CTBN blends under non-isothermal conditions using the dynamic DSC method. Thus, the purpose of this study is to investigate the effects

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http://dx.doi.org/10.1016/j.tca.2015.02.007
0040-6031/

Table 1
Characteristics of CTBN and ECTBNs.

Sample	Ev[a] [mol/(100 g)]	M_n[b] (g/mol)	M_w[b] (g/mol)	Polydispersity index (PDI)[b]	T_g[c] (°C)
CTBN	0.00	7755	12714	1.64	−62.9
ECTBN16	0.16	9597	17256	1.80	−48.8
ECTBN30	0.30	12832	24846	1.94	−37.1

[a] The epoxide value was determined by hydrochloric acid–acetone method in accordance with GB/T 1677–1981 (China).
[b] The average molecular weights and the PDI of the polymers were determined by gel permeation chromatography (GPC) using a Waters 1515 (WATERS, USA) equipped with a series of PS gel columns at 40 °C. The mobile phase was tetrahydrofuran at 1 ml/min flow rate.
[c] The T_gs of CTBN and ECTBNs were determined with an instrument DSC 2910 (TA Instruments, Inc., USA) calibrated with a high-purity indium standard, and an identical empty cell was taken as a reference. All of the samples were frozen to −120 °C, and then reheated to 25 °C at 10 °C/min.

Table 2
Formulations of different epoxy resin/rubber blends.

Sample ID[a]	Weight ratio of the components			
	Epoxy resin/504/554	CTBN	ECTBN16	ECTBN30
E51	1/0.8/0.02	–	–	–
E51/CTBN(10)	1/0.8/0.02	0.18	–	–
E51/CTBN(20)	1/0.8/0.02	0.36	–	–
E51/ECTBN16(10)	1/0.8/0.02	–	018	–
E51/ECTBN16(20)	1/0.8/0.02	–	0.36	–
E51/ECTBN30(10)	1/0.8/0.02	–	–	0.18
E51/ECTBN30(20)	1/0.8/0.02	–	–	0.36

[a] The Arabic numerals in parentheses represent the rubber content (wt%).

of ECTBN on the curing kinetics of epoxy resin, determine the kinetic parameters and the most suitable kinetic model characterizing the curing process using Málek method [31,32], and calculate the theoretical reaction rates for different epoxy resin/rubber systems. The results of this study may provide useful information for the practical applications of epoxy resin/rubber blends.

2. Experimental

2.1. Materials

The liquid rubber used in this study is a commercial CTBN (acrylonitrile content = 9.0 wt%) purchased from Zibo Qilong Chemical Industry Co., Ltd. (China) and used as received without any further purification. The epoxidized liquid rubbers (ECTBNs) were prepared by epoxidation of CTBN at several degrees as described in details elsewhere [33,34]. Throughout the present study, ECTBNs with different epoxidation degrees are denoted by ECTBN*x*, where *x* is the degree of epoxidation characterized by the epoxide value (Ev). For example, ECTBN16 indicates that the epoxide value of the ECTBN is 0.16 mol/100 g. In this study, ECTBNs with an epoxide value of 0.16 mol/100 g and 0.30 mol/100 g (ECTBN16 and ECTBN30) were prepared. The characteristics of CTBN and ECTBNs are shown in Table 1.

The epoxy resin E51 (618) used in this study is a diglycidyl ether of bisphenol A with an epoxy equivalent of approximately 185–210 g/eq., the curing agent 504 contains mainly methyl tetrahydrophthalic anhydride, and the accelerator 554 is a kind of aromatic tertiary amine. All of them were purchased from Shanghai Resin Co., China, and used as received. The weight ratio

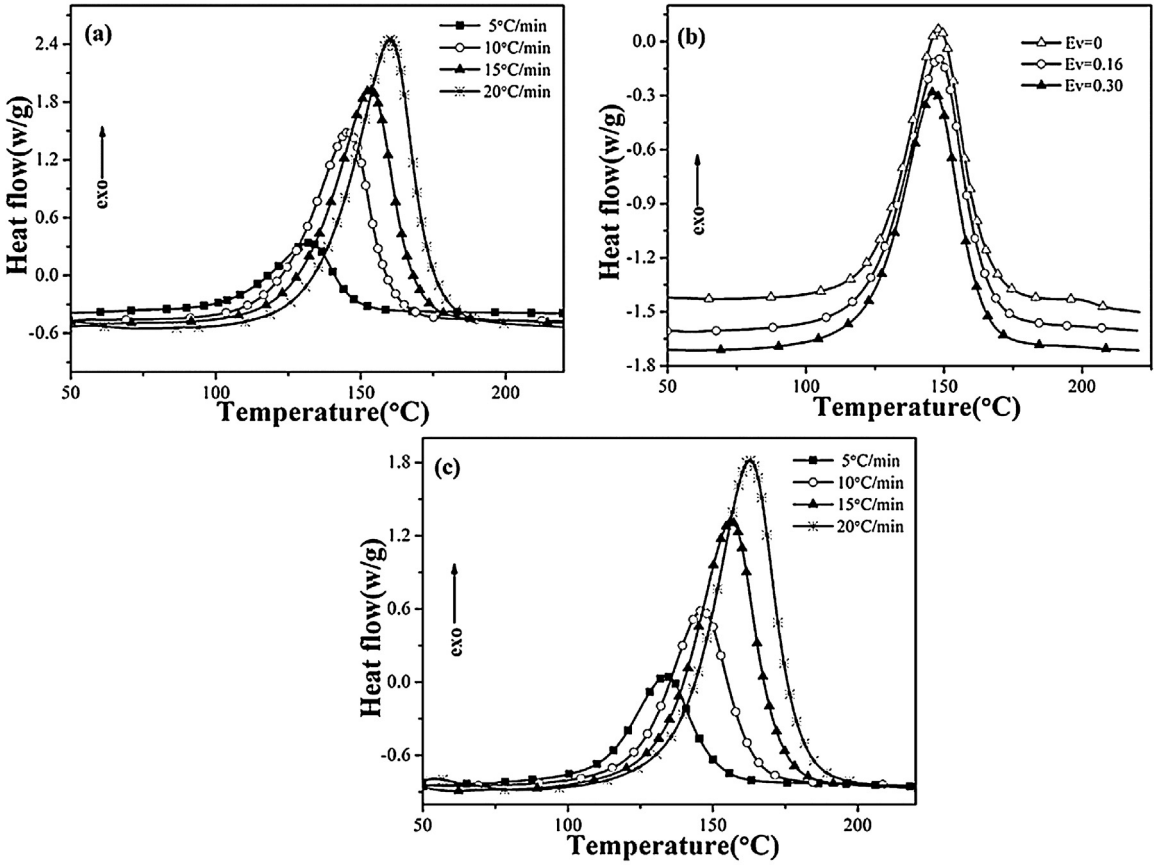

Fig. 1. Non-isothermal DSC thermograms for (a) E51 at different heating rates, (b) the systems with different epoxidation degrees at the same content (wt = 20%) with β = 10° C/min, (c) E51/ECTBN30(20) at different heating rates.