Thermochimica Acta 521 (2011) 18–25

Contents lists available at ScienceDirect

Thermochimica Acta

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

Curing behaviors and kinetics of epoxy resins with a series of biphenyl curing agents having different methylene units

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ARTICLE INFO

Article history:
Received 23 December 2010
Received in revised form 28 March 2011
Accepted 30 March 2011
Available online 8 April 2011

Keywords:
Curing agent
Epoxy resin
Kinetics
Liquid crystal

ABSTRACT

A series of curing agents (LCCAn) bearing biphenyl group and *n*-methylene units (*n* = 2, 4 and 6) were synthesized. The curing behaviors of epoxy resin based on diglycidyl ether of bisphenol A (DGEBA) with LCCAn were investigated in comparison with commercial biphenyl type curing agent 4,4′-diaminobiphenyl (DABP) by dynamic DSC. The results indicated that LCCAn curing systems showed higher chemical reactivity and lower glass transition temperatures than DABP system. The kinetics was studied under isothermal and non-isothermal conditions using isoconversional methods, and the isothermal DSC data can be fitted reasonably by an autocatalytic curing model. POM studies revealed that the cured samples of DGEBA/LCCAn systems showed liquid crystalline transitions while DABP curing system displayed an isotropic state, which indicated that methylene units played a key rule for the formation of liquid crystalline phases.

1. Introduction

Epoxy resins are the most important thermosetting polymers which are finding increasing use in the industry due to their excellent properties, such as good adhesion to various substrates, high modulus and high temperature performance, low shrinkage, good corrosion resistance, and so on [1–3]. However, they also have low fracture toughness, and the incorporation of liquid crystalline structure is one of effectual way to make a modification. So recently, many studies have been focused on the subject of liquid crystalline thermosets due to their prior properties compared with ordinary epoxy resins, but most of these reports give the emphasis on the studies of liquid crystalline epoxy resins (LCERs) [4–10]. Well, as is known that curing agents can influence the structure of the networks, and the formation of LC phase in the networks can also be affected (even be determined) by the structure of the curing agents to crosslink the epoxy monomers. However, there are only a few reports concerning the importance of the curing agent [11–14].

In this article, the synthesis of a homologous series of curing agents LCCAn bearing biphenyl and *n*-methylene units (*n* = 2, 4 and 6) was described. The curing behaviors of epoxy resin DGEBA with LCCAn were investigated compared to commercial curing agent 4,4′-diaminobiphenyl (DABP) system. Their kinetics was analyzed based on the isoconversional method and Kamal model. The liquid crystalline properties of DGEBA systems cured with LCCAn and DABP were further discussed.

2. Experimental

2.1. Materials

1,2-Dibromo ethane, 1,4-dibromo butane, 1,6-dibromo hexane, potassium hydroxide, phthalimide, and hydrazine hydrate were analytical grade products from Third Chemical Fractory, Tianjin, China. 4,4′-Dihydroxybiphenyl and the curing agent 4,4′-diaminobiphenyl (DABP), analytical reagent grade, were both obtained from Beijing Chemical Fractory, Beijing, China, and used without further purification. The epoxy resin was a liquid diglycidyl ether of bisphenol A (DGEBA), W_{ep} = 196 (Tianjin Industrial Research Institute of Synthetic Materials, China).

2.2. Synthesis of curing agents LCCAn

The curing agents (LCCAn) bearing biphenyl type mesogenic groups and *n*-methylene units (*n* = 2, 4 and 6) were synthesized according to Ref. [15]. *n* = 2: Yield: 31%; mp: 178 °C; ^{1}H NMR (D-DMSO; δ, ppm): 2.86 (t, 4H, –CH_2–), 3.97 (t, 4H, –CH_2–), 6.98 (d, 4H, aromatic), 7.52 (d, 4H, aromatic). IR (KBr; υ, cm^{-1}): 3316 (–NH_2), 2938, 2870 (–CH_2), 1566, 1498 (–Ar–), 1246 (Ar–O–C), 825 (C–H). *n* = 4: Yield: 42%; mp: 146.8 °C; ^{1}H NMR (D-DMSO; δ, ppm): 1.48 (m, 4H, –CH_2–), 1.82 (m, 4H, –CH_2–), 3.66 (t, 4H, –CH_2–), 4.05 (t, 4H, –CH_2–), 6.98 (d, 4H, aromatic), 7.56 (d, 4H, aromatic). IR (KBr; υ, cm^{-1}): 3292 (–NH_2), 2930, 2854 (–CH_2), 1566, 1948 (–Ar–), 1250

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0040-6031/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2011.03.036

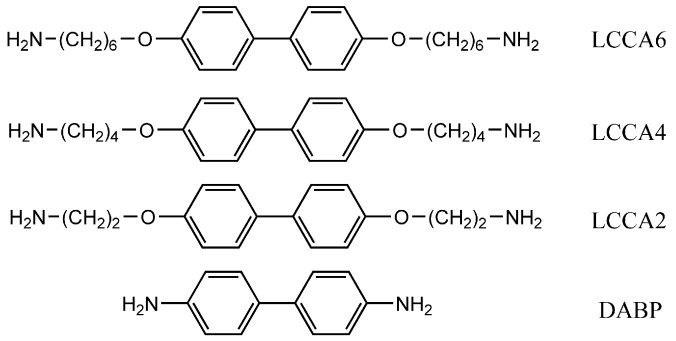

Fig. 1. Structures of curing agents.

(Ar–O–C), 824 (C–H). $n = 6$: Yield: 38%; mp: 135 °C; ^{1}H NMR (D-DMSO; δ, ppm): 1.42 (m, 4H, –CH_2–), 1.69 (m, 4H, –CH_2–), 1.81 (m, 4H, –CH_2–), 3.52 (t, 4H, –CH_2–), 3.96 (t, 4H, –CH_2–), 6.95 (d, 4H, aromatic), 7.48 (d, 4H, aromatic). IR (KBr; υ, cm^{-1}): 3308 (–NH_2), 2930, 2853 (–CH_2), 1567, 1948 (–Ar–), 1242 (Ar–O–C), 817 (C–H). The structures of LCCAn and commercial curing agent 4,4′-diaminobiphenyl (DABP) which also has biphenyl group without methylene units are exhibited in Fig. 1.

2.3. Structural of characterization of curing agents LCCAn

IR spectra of curing agents LCCAn is shown in Fig. 2. It can be found that LCCA2, LCCA4 and LCCA6 have similar spectra. As the number of methylene increases, the characteristic peaks around 2938 and 2870 cm^{-1} increase obviously.

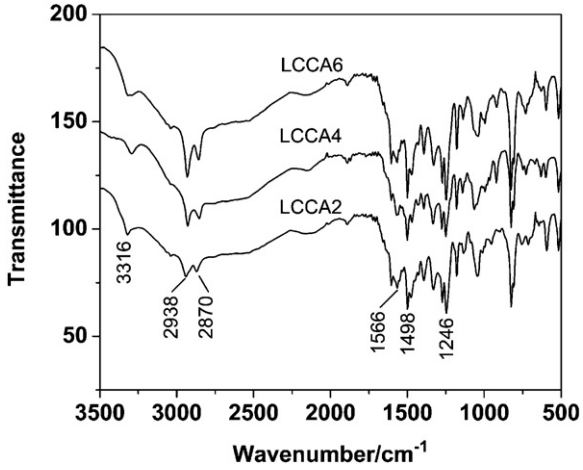

Fig. 2. IR spectra of LCCAn.

2.4. Measurements

IR spectra were recorded on a Bio-Rad FTS-6000 Fourier transform infrared (FTIR) spectrometer. ^{1}H NMR spectra were obtained with a UNITY Plus-400 (400 MHz) spectrometer with D-DMSO as the solvent and tetramethylsilane (TMS) as the internal standard. Thermal kinetic studies were carried out on a NETZSCH DSC 200 F3 thermal analyzer with N_2 as a purge gas by isothermal and non-isothermal scanning. The isothermal DSC curves of DGEBA/LCCAn systems were investigated at different temperatures respectively. The non-isothermal experiments were performed at different scanning rates of 5 °C/min, 10 °C/min, 15 °C/min, 20 °C/min. The textures

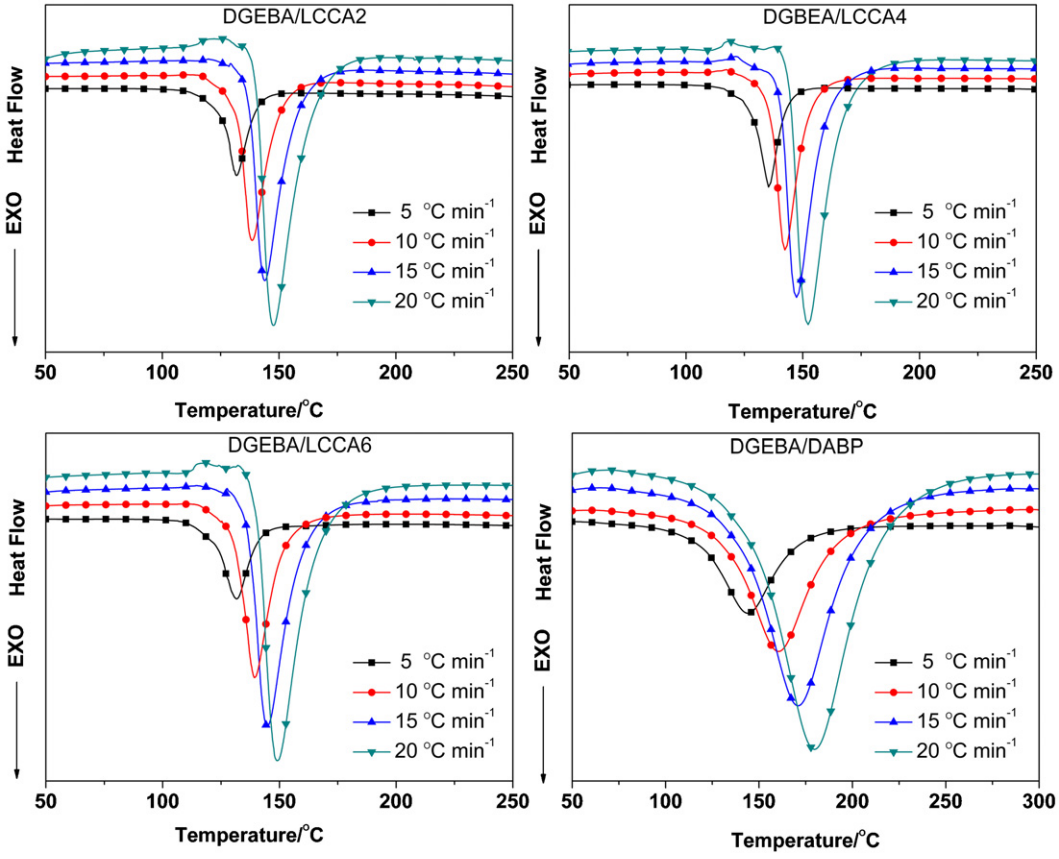

Fig. 3. Non-isothermal DSC curves of DEGBA/LCCAn and DGEBA/DABP systems with different scanning rates.