Thermochimica Acta 600 (2015) 20–27

Contents lists available at ScienceDirect

Thermochimica Acta

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

# Curing kinetic, thermal and adhesive properties of epoxy resin cured with cashew nut shell liquid

Pornnpa Kasemsiri [a], Arthit Neramittagapong [a,**], Prinya Chindaprasirt [b,*]

[a] Sustainable Infrastructure Research and Development Center and Department of Chemical Engineering, Faculty of Engineering, Khon Kaen University, Khon Kaen 40002, Thailand
[b] Sustainable Infrastructure Research and Development Center and Department of Civil Engineering, Faculty of Engineering, Khon Kaen University, Khon Kaen 40002, Thailand

ARTICLE INFO

*Article history:*
Received 13 September 2014
Received in revised form 28 November 2014
Accepted 29 November 2014
Available online 2 December 2014

*Keywords:*
Cashew nut shell liquid
Epoxy resin
Curing agent
Adhesive

ABSTRACT

The curing kinetic, thermal and adhesive properties of epoxy resin cured with cashew nut shell liquid (CNSL) were investigated. The CNSL was used as a curing agent for epoxy resin. The epoxy resin cured with 10, 20 30, 40 and 50 wt% of CNSL showed two-stages curing process between 165–170 °C and 230–235 °C. The solvent extraction experiment indicated that the CNSL content should not exceed 40 wt% to avoid the presence of unreacted CNSL. The apparent activation energy ($E_a$) of 60/40 epoxy resin/CNSL copolymer was obtained from Friedman's model-free method for both stages of curing process. The kinetic model and kinetic parameters were determined by Málek's method and the reaction processes was simulated favorably by Sestak–Berggren (SB ($m$, $n$)) model. In addition, silica powder was used to improve the adhesion and thermal properties of copolymer. The epoxy resin/CNSL copolymer with 0.5 wt % silica showed a substantial increase in the lap shear strength and thermal stability tended to increase with increasing silica content. The epoxy resin/CNSL composite showed a great potential for use as a high performance adhesive with good thermal stability.



## 1. Introduction

Epoxy resins are the most important thermosetting polymers which have been extensively used as adhesives in various applications such as aerospace and surface coating industries [1]. This is due to their outstanding properties viz., good adhesion to various substrates, high modulus, high temperature performance, low shrinkage and good corrosion resistance [2,3]. However, the application of this polymer is limited to certain areas due to its rather high rigidity and brittleness. In principle, toughness of epoxy resin can be enhanced by incorporating a rubber or a thermoplastic polymer [4–6].

Recently, the development of epoxy resin-based renewable organic material has attracted a lot of attention [7,8]. Cardanol-based novolac resins have been also studied as modifiers and curing agent for commercial epoxy resins to improve the toughness and other mechanical properties [8]. Cardanol is the main component of cashew nut shell liquid (CNSL) obtained as a by-product during the process of removing cashew kernel from its nut [9]. The major components of CNSL are anacardic acid, cardanol, and traces of cardol and 1-methylcardol.

From previous work, Mathew et al. [10] investigated the curing behavior of epoxy resin with a conventional amide-type hardener and CNSL and showed that the presence of multifunctionalities such as OH, COOH and aliphatic unsaturations in CNSL's molecule provides the chemical reaction with epoxy resin. Generally, CNSL has various applications in different industries such as friction linings, paints and varnishes, laminating resins, rubber compounding resin, urethane based polymer, surfactant, modifier agent of benzoxazine resin for wood composite production and intermediate for chemical industries [11–18]. Consequently, CNSL is an excellent candidate material to modify the properties of epoxy resin and to reduce the adhesive cost.

In order to optimize the final product of epoxy resin modified with CNSL, it is important to understand its curing process and kinetic parameters [19]. The curing of a resin system is a major controlling step for fabrication and thermosetting of matrix composites. The curing process of epoxy resin is the crosslinking of linear macromolecules with complicated mechanism [20]. To monitor the curing process, kinetic models obtained from reliable

* Corresponding author. Tel.: +66 4 336 2240; fax: +66 4 4336 2142.
** Corresponding author.
*E-mail addresses:* artyner@kku.ac.th (A. Neramittagapong), prinya@kku.ac.th (P. Chindaprasirt).

http://dx.doi.org/10.1016/j.tca.2014.11.031
0040-6031/

methods are crucial for the process control, optimization of the polymer network processing and analysis of kinetic parameters. Kinetic analysis of non-isothermal resin cured system can be performed by multiple heating rates [21]. A multiple heating-rate method provides good reliable kinetic parameters and is suitable for evaluating both simple and complex chemical reactions [22,23]. Currently, there is a lack of information about the properties of adhesive based epoxy resin cured by hardener based on renewable organic material, without conventional or synthesized hardener. Therefore, the objective of this work is to investigate the effects of epoxy resin cured with CNSL on the curing process by isoconventional method. Furthermore, the thermal properties and adhesion performance of epoxy resin/CNSL copolymer reinforced with silica are also examined.

## 2. Experimental details

### 2.1. Materials

Epoxy resin based on Bisphenol A diglycidyl ether (DGEBA) was supplied by Dow Chemical (Thailand) Co., Ltd. Cashew nut shell liquid (CNSL) from Maboonkrong Sirichai 25 Ltd., was used as the curing agent. Amorphous silica powder HDK T40 from Wacker Chemie AG was used as filler. The specific gravity of silica powder is 2.20 and its particle size is less than 10 nm.

### 2.2. Chemical characterization of CNSL compositions

The CNSL's fractions were analyzed by gas chromatography–mass spectrometry (GC–MS) 2010: DB capillary column (30m × 0.25 mm, 0.25 μm film thickness). The initial oven temperature of GC was 40 °C for 2 min and then programmed to increase at a rate of 5 °C/min to 270 °C. Helium was used as the carrier gas with a rate of 0:7 ml/min. The percent of area was obtained electronically from GC–MS response without the use of internal standard.

### 2.3. Preparation of epoxy resin–cashew nut oil matrix

Mixtures were prepared with epoxy resin/CNSL mass ratios of 10/90, 20/80, 30/70, 40/60 and 50/50 by blending with magnetic stirrer at 80 °C for 30 min. They were for the curing behaviors and kinetic tests.

### 2.4. Preparation of epoxy resin–CSNL reinforced with silica adhesives

The quality of preparation of the epoxy resin–CSNL reinforced with silica was important factor affecting the adhesives properties. Therefore, the epoxy resin/CSNL reinforced with silica adhesives were prepared following the preparation process used successfully by a number of researchers [24,25]. The adhesive samples were prepared by compounding epoxy resin–CSNL matrix with 0–1.5 wt % silica. Silica was added into epoxy resin and it was dispersed using ultrasonic instruments for 30 min at 80 °C. After that, CNSL was mixed with the epoxy resin and silica mixture using ultrasonication for another 30 min at 80 °C. The mixture was continuously stirred until homogeneous compound was obtained. The compound was placed in a vacuum chamber at 80 °C to remove bubbles trapped in the mixture during the stirring and sonicating steps. The obtained compound was applied uniformly onto both sides of the overlapped area of aluminum substrates and then cured at 200 °C under a constant pressure of 0.05 MPa for 1 h. The thickness of the adhesive layers after curing was 0.3 mm.

### 2.5. Measurements and characterizations

The curing behavior and kinetic parameters of epoxy resin/CNSL copolymers were evaluated using a differential scanning calorimeter (DSC) pyris diamond model from PerkinElmer. The heating rates were 3, 5, 10 and 20 °C $min^{-1}$ from 30 to 300 °C under nitrogen gas purging. The overlapping exothermic peaks were separated and analyzed by PeakFit v4.11 software.

Attenuated total reflection infrared (FTIR-ATR) spectra of all epoxy resin/CNSL samples after curing were acquired by Bruker Tensor 27 spectrometer. All spectra were taken as a function of time with 64 scans at a resolution of 4 $cm^{-1}$ and a spectral range of 4000–650 $cm^{-1}$. The selected intensity data was normalized using the C=C of benzene ring at 1507 $cm^{-1}$ and was used as internal standard to compensate for the variation in mass and thickness of sample after curing at 170 °C for 1 h and 200 °C for 1 h.

The gel content or insoluble fraction produced by crosslinking was determined by measuring the weight loss after extracting at room temperature for 24 h in accordance with ASTM D 2765-95 standard using test method C. The percent extraction was calculated as follows:

$$\%\text{Extraction} = \frac{W_o - W_d}{W_o} \times 100 \quad (1)$$

where $W_o$ is the original polymer weight and $W_d$ is the weight of dried gel.

The experiment was done strictly in accordance with ASTM D 2765-95 standard using test method C to evaluate gel content or insoluble fraction produced by crosslinking after placing the samples in chloroform. After removal of sample from chloroform solution, some part of the solution still penetrated in the gel sample and needed to be evaporated before the percent extraction could be calculated. Therefore, the total amount of chloroform solution could not be collected to evaluate exactly the composition of extractive substances.

The adhesive behavior was evaluated for mechanical tests using single-lap shear joint. The adhesion test was carried out according to ASTM D 1002-01 employing a Universal Testing Machine, Instron, Model 5567 equipped with a 10 kN load cell. Aluminum (alloy 2024) was used as metal for adhesive test.

The thermal degradation of adhesives was studied using a TGA-50, Shimadzu. The testing temperature program was ramped at a heating rate of 20 °C $min^{-1}$ from room temperature to 700 °C under nitrogen atmosphere. The purge nitrogen gas flow rate was maintained at 20 ml $min^{-1}$. The sample mass used was 10–20 mg. Degradation temperature of each specimen was evaluated from the temperature at 5% weight loss.

## 3. Results and discussion

### 3.1. Characterization of CNSL's compositions

CNSL is a by-product of the cashew nut industry waste. CNSL contains several phenolic compounds such as cardol, anacardic acid, cardanol, and methyl cardol. The CNSL's compositions were analyzed by gas chromatography–mass spectrometer as shown in Fig. 1. CNSL contained mainly cardol (36.16%), cardanol (31.53%), anacardic acid (24.59%), and traces of methyl cardol.

### 3.2. Curing reaction and thermal properties of epoxy resin/CNSL

The results of dynamic DSC measurements of the epoxy resin/CNSL mixtures are shown in Fig. 2. Two overlapped exothermic peaks were observed and the peaks became more distinct when the CNSL content was higher than 20 wt%. The two overlapped exothermic peaks were between 165–170 °C and 230–235 °C.