

Curing kinetics of epoxy cured by cardanol-based phenalkamines synthesized from different polyethylenepolyamines by Mannich reaction

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Received: 23 December 2016 / Accepted: 2 June 2017 / Published online: 6 June 2017
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Abstract Phenalkamines with different structures are expected to affect the curing reaction of epoxy, yet the exact mechanism remains to be elucidated. In this study, four cardanol-based phenalkamines (named PK1, PK2, PK3, and PK4, respectively), synthesized from ethylenediamine, diethylenetriamine, triethylenetetramine, and pentaethylenehexamine, were used as curing agents in diglycidyl ether of bisphenol A (DGEBA) epoxy system. The phenalkamines were characterized by Fourier transform infrared spectroscopy, nuclear magnetic resonance, and time-of-flight secondary ion mass spectrometry. The curing behaviors and kinetics were investigated by non-isothermal differential scanning calorimetry, and the activation energies of the reactions (E_{α}) were determined using Kissinger–Akahira–Sunose (KAS) and Starink methods. The results indicate a similar curing mechanism for all four phenalkamines. All E_{α} values remain almost constant in the range of $0.05 \leq \alpha \leq 0.6$, and increase dramatically after $\alpha > 0.6$ due to greater viscosity of the reaction systems. The diffusion of reactive groups plays an increasingly important role in determining the curing kinetics. In addition, DGEBA/PK1 and DGEBA/PK2 have lower initial E_{α} values than DGEBA/PK3 and DGEBA/PK4, because PK1 and PK2 have lower viscosity than PK3 and PK4. When α is high, DGEBA/PK1 and DGEBA/PK2 have higher E_{α} values than DGEBA/PK3 and DGEBA/PK4, because more tertiary amine groups can be formed in the

reactions between the epoxy and secondary amine groups in the DGEBA/PK3 and DGEBA/PK4 systems, which catalyze the curing reaction and it thus lowers energetic barrier.

Keywords Cardanol · Phenalkamines · Thermal analysis · Curing kinetics · Epoxy

Introduction

Epoxy is one of the most important polymers with a wide range of applications, such as coatings, adhesives, insulating materials, electronic encapsulation, and polymeric composite materials, due to its excellent chemical resistance, good adhesive, mechanical, and electrical properties, and easy handling [1–5]. However, low molecular weight epoxy needs to be converted into three-dimensional crosslinked thermoset networks using suitable curing agents in order to achieve better performance [6, 7]. Thus, many novel curing agents have been synthesized over the past years [8, 9].

Although ethylenediamine, diethylenetriamine, triethylenetetramine, and pentaethylenehexamine can be used to cure epoxy, their applications are limited due to toxicity and irritation. Thus, they are often modified with a variety of compounds to reduce the volatility. One of the most common methods is to prepare phenalkamines by Mannich reaction [1]. Phenalkamines are shown to be promising curing agents that combine the unique properties of aliphatic amines and polyamides, thereby making them applicable to humid conditions. Traditionally, phenalkamines are synthesized using phenol or its derivatives by the condensation reaction with formaldehyde and amines. A potential problem is that phenol originates from non-renewable petroleum resources, and thus it is imperative to utilize renewable resources as a result of the high cost and the depletion

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