



Investigation of cure kinetics in a system with reactant evaporation: Epoxidized soybean oil and maleic anhydride case study



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ABSTRACT

Cure kinetics of epoxidized soybean oil (ESO) with maleic anhydride (MAH), which evaporates during the curing process, is studied quantitatively considering MAH evaporation. Since MAH is commonly applied as a hardener for epoxy systems, it has been used also for ESO curing. As catalyst 4-amino-3-hydrazino-5-mercapto-1,2,4-triazole in different amounts was used. Data necessary for modeling purposes were obtained by means of differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The two-parameter Šesták–Berggren autocatalytic model was successfully applied in the mathematical modeling. The reaction orders n and m were found to be 2.275 and 0.420, respectively, and pre-exponential factor was found to be $3.91 \times 10^6 \text{ s}^{-1}$. The apparent activation energy decreased from 69.1 to 67.8 kJ/mol with increasing the amount of applied catalyst from 0.5 to 2.5 wt.% of catalyst per hundred parts of ESO/MAH mixture. The use of combination of DSC and TGA techniques revealed as a useful tool for kinetics investigations and predictions of reaction systems involving evaporation of one or more compounds.

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1. Introduction

Epoxy resins are known as important thermosetting polymers widely used as matrices in coatings, adhesives and composite materials [1]. Today, due to growing economic, environmental and sustainability concerns, the research and development activities in polymer science and engineering are focused also on replacing synthetic polymeric materials, which are produced from limited petroleum resources, with materials from renewable resources [2]. Lately a great attention has been paid to potential use of pristine or chemically modified vegetable oils as raw materials for production of novel or modified thermosetting materials.

Common vegetable oils are triglycerides containing five major fatty acids: oleic (C18:1), linoleic (C18:2), linolenic (C18:3), palmitic (C16:0), and stearic (C18:0). Double

bonds in unsaturated fatty acids offer the possibility for chemical modifications, such as epoxidation by the *in situ* performic acid procedure [3]. Epoxidized vegetable oils have been largely utilized for different non-structural applications [4–8]. Traditionally, they are used as plasticizers and stabilizers for polyvinylchloride (PVC), but also in the painting and coating formulations [5]. Unfortunately, because of the low reactivity of epoxy groups and their tendency for intramolecular bonding, all epoxidized oils lead to poorly crosslinked materials with limited thermal and mechanical properties [7]. Low reactivity of epoxy groups is caused by steric hindrance induced by saturated fatty acids (FA). Therefore, the poorer thermal and mechanical properties result from both partially unreacted ESO and self-plasticization effect of saturated FA chains [9,10].

To promote the crosslinking and therefore obtain a more densely crosslinked material with higher mechanical properties amines, anhydrides and acids are used. One of the most commonly used vegetable oils, which has been

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crosslinked with various anhydrides to obtain bio-thermosets, is commercially available epoxidized soybean oil [11–20], whose triglycerides contain an average of about five unsaturated bonds per molecule. Most of the published researches dealing with application of epoxidized vegetable oils crosslinked with anhydrides for thermosets are focused on mechanical and other applicative properties of already crosslinked materials. The curing kinetics, which is fundamental in understanding structure/property/processing relationships for manufacturing and utilization of high-performance composites [21] has been investigated less often. Lately, Tan et al. [19] and Liang and Chandrashekhara [22] used Kamal's equation to model the cure kinetics of soy-based epoxy resin system with anhydrides. Tan et al. [19] thermally cured epoxidized soybean oil (ESO) resin using methylhexahydrophthalic anhydride (MHHPA) curing agent, in the presence of 2-ethyl-4-methylimidazole (EMI) at different temperatures and studied the curing kinetics using Fourier Transform Infrared Spectroscopy (FTIR). It was observed that EMI-catalyzed ESO/MHHPA system showed autocatalytic behavior in the isothermal curing reaction. Liang and Chandrashekhara [22] used differential scanning calorimetry (DSC) and rheology techniques in their kinetics investigation and found an overall reaction order of their system was approximately two. On the other hand, Boquillon and Fringant [23] modeled the cure kinetics of epoxidized linseed oil with tetrahydrophthalic anhydride (ELO/THPA) system catalyzed with 2-methylimidazole (2MI). They employed DSC and the n th-order rate equation. It was observed, that the curing reaction of their system followed the first-order kinetics law also at extents of cure above 0.7. However, maybe the most popular method for cure predictions of epoxidized vegetable oil/anhydride systems in isothermal conditions remains the so-called model-free (or iso-conversional) kinetic method, which relies on conversion-dependent, non-constant apparent activation energy [24–26]. Since maleic anhydride (MAH) is one of several anhydride type curing agents applied as a hardener for epoxy systems [2,23,27], it has been used also for ESO curing. Nevertheless, the cure kinetics involving MAH as hardener has not been extensively studied, most likely due to MAH evaporation during the process and resulting difficulties in quantitative data analysis.

Fourier transform infrared spectroscopy (FTIR) and differential scanning calorimetry are two commonly used

techniques for investigation of cure kinetics of thermosetting resins. In the present work, the cure kinetics of ESO with MAH is studied quantitatively using DSC and thermogravimetric analysis (TGA), as additional and supporting method in the case of evaporating compound from the curing system. 4-amino-3-hydrazino-5-mercapto-1,2,4-triazole in different amounts was used as catalyst. The two-parameter Šesták–Berggren autocatalytic equation [28], the use of which was confirmed by Malék kinetic analysis [29], was successfully applied in the mathematical modeling of non-isothermal curing process. To our knowledge, this is the first study, where the combination of DSC and TGA techniques was used for kinetic investigation and prediction of reaction system in the case of evaporating compound during the curing reaction.

2. Materials and methods

2.1. Materials

Epoxidized soybean oil (ESO, Drapex 39, Galata Chemicals, Southbury, CT, USA) with 6.5% epoxy oxygen content (epoxy equivalent weight 246 g/eq) and maleic anhydride (MAH, 99.5% purity, Navast, China) were used in this study. 4-amino-3-hydrazino-5-mercapto-1,2,4-triazole (AHMT, $\geq 97\%$ purity, Fluka AG, Switzerland) was applied as catalyst.

2.2. Curing Investigation by DSC and TGA

The samples used for the DSC and TGA experiments were prepared as follows: The epoxidized soybean oil (ESO) was mixed with the hardener (MAH) (ESO/MAH molar ratio was 1). Mixing of the components was carried out using a magnetic stirrer at a temperature of 50 °C to melt and dissolve the MAH powder in the ESO. After the mixing process, different amounts of 4-amino-3-hydrazino-5-mercapto-1,2,4-triazole (AHMT) were added to the mixture to act as catalyst for the chemical reaction, maintaining the temperature at 50 °C and it was stirred for 5 additional minutes until the mixture was homogenized. The mentioned catalyst was used due to its high number of reactive amino groups per molecule.

Compositions of reaction mixtures under investigation and list of performed DSC and TGA experiments are collected in Table 1. Samples containing ESO, MAH and cata-

Table 1

Compositions of reaction mixtures used in DSC and TGA experiments.

Sample	MAH/epoxy group molar ratio (I)	ESO (wt.%)	MAH (wt.%)	AHMT (wt.%) ^a	DSC and TGA heating rate (°C/min)
MAH	/	0	100	0	20
MAH/2.0	/	0	100	2.00	20
ESO	0.00	100	0	0	20
ESO/2.0	0.00	100	0	2.00	20
EM/0.0	1.00	72	28	0	20
EM/0.5	1.00	72	28	0.50	20
EM/1.0	1.00	72	28	1.00	20
EM/1.5	1.00	72	28	1.50	20
EM/2.0	1.00	72	28	2.00	10, 15, 20
EM/2.5	1.00	72	28	2.50	20

^a Parts of AHMT per 100 parts of ESO/MAH mixture.

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