Reactive & Functional Polymers 91-92 (2015) 11–18

Contents lists available at ScienceDirect

Reactive & Functional Polymers

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

Adamantane-based epoxy resin and siloxane-modified adamantane-based epoxy resin: Characterization of thermal, dielectric and optical properties

C.W. Tsai [a], K.H. Wu [b,*], C.C. Yang [c], G.P. Wang [d]

[a] School of Defense Science, Chung Cheng Institute of Technology, National Defense University, Taoyuan, Taiwan
[b] Department of Chemical and Materials Engineering, Chung Cheng Institute of Technology, National Defense University, Taoyuan, Taiwan
[c] Chemical Systems Research Division, Chung Shan Institute of Science and Technology, Taoyuan, Taiwan
[d] Office of Research & Development, Ming Hsin University of Science and Technology, Hsinchu, Taiwan

ARTICLE INFO

Article history:
Received 27 January 2015
Received in revised form 9 April 2015
Accepted 10 April 2015
Available online 18 April 2015

Keywords:
Epoxy
Adamantane
Thermal properties
Dielectric properties
Optical properties

ABSTRACT

An adamantane-based epoxy resin (ADEP) and a siloxane-modified adamantane-based epoxy resin (Siloxane-ADEP) were synthesized, and their chemical structures were confirmed from FT-IR, ^{1}H, ^{13}C and ^{29}Si NMR spectroscopy measurements. The morphological, thermal, dielectric and optical properties of ADEP and Siloxane-ADEP were studied. The introduction of the adamantane group into the chain of the epoxy resin resulted in improvements in the thermal, mechanical and dielectric properties. These results can be explained in terms of the tricyclic hydrocarbon of the adamantane in a diamond lattice structure and the movement of polymer chains being limited by chair-form cyclohexane rings, resulting in an immobile epoxy structure. Moreover, Siloxane-ADEP exhibited good thermal, mechanical and dielectric properties that were similar to those of epoxy resin, and its better processability may extend its application to electronic packing materials. The UV–Vis transmission spectra revealed that the adamantane-containing epoxy membranes exhibited novel ultraviolet light-filtering properties.

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1. Introduction

Epoxy resins, which are one of the most important classes of thermosetting polymers, have been widely applied in surface-coating and painting materials, matrices of composites, adhesives, insulating materials, encapsulating materials, and advanced materials. With the developments in the aerospace and automobile industries in the areas of structural composites and adhesives in microelectronic devices for encapsulating electrical circuit components and electronics packaging, excellent properties are required, including good processability, thermal and chemical resistance, moisture resistance, superior electrical and mechanical properties, and good adhesion to many substrates [1–4]. However, the brittle nature and fire risk of epoxy resins restrict their application in some advanced fields. To further improve the physical properties and thermal performance of epoxy resins, researchers have developed many additives and modifiers, such as calcium carbonate, adamantane, fullerene, silica, titania and carbon nanotubes [5–10].

Adamantane (tricyclo[3.3.1.13.7]decane) is a highly symmetric tricyclic hydrocarbon with three fused chair-form cyclohexane rings in a diamond lattice structure [11,12]. The effects of incorporating adamantane into backbones or as pendant groups on the physical, thermal, and mechanical properties of a number of polymer families have been investigated [13–17]. The incorporation of adamantane led to superior thermal stability, high glass transition temperatures (T_g) and decomposition temperatures, good mechanical strength, low dielectric constants, and good transparency. Although the feasibility of incorporating adamantane into the backbone of epoxy resins has been examined [18], investigations on the relationship of siloxane modification to physical properties based on adamantane-based epoxy resins are limited. Silicon-containing compounds can migrate to the surface of the material during the course of thermal degradation because of their low surface energy. Their products are silica carbons with high thermal stability [19]. Silicon carbide can form a protective silica layer and protect the polymer residue from further thermal decomposition at high temperatures. The inorganic components could suppress the production of toxic gases [20].

Epoxy resins are widely used in many fields, such as in the manufacturing of coatings, adhesives and matrix resins for

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* Corresponding author. Tel.: +886 3 3891716; fax: +886 3 3892494.
E-mail address: khwu@ndu.edu.tw (K.H. Wu).

http://dx.doi.org/10.1016/j.reactfunctpolym.2015.04.002
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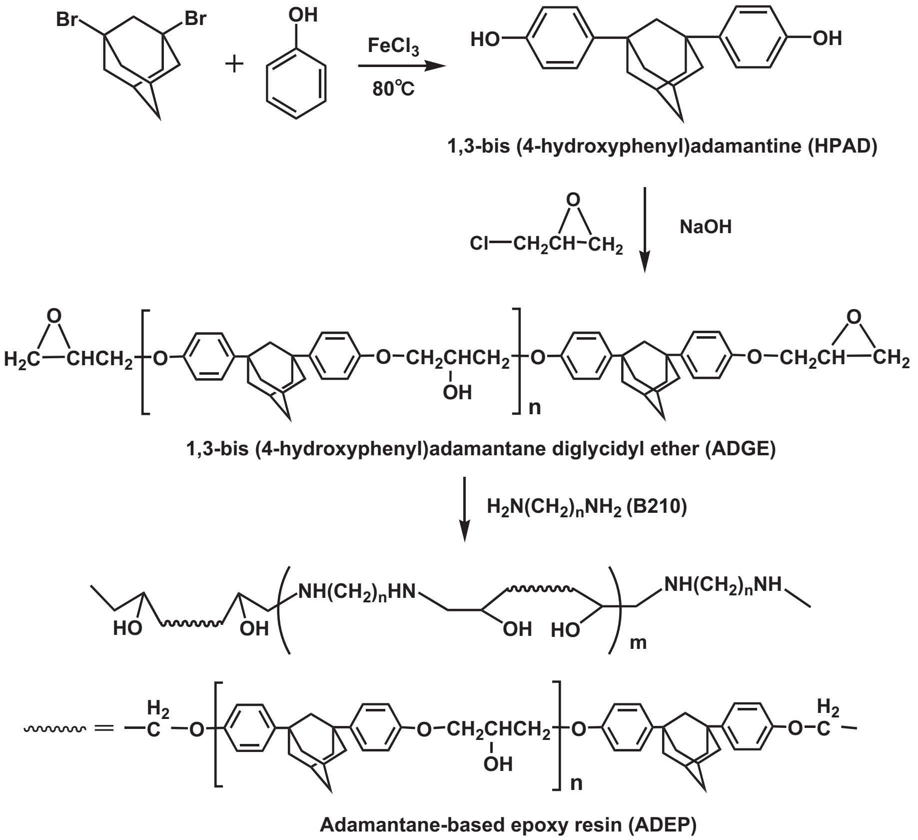

Scheme 1. Experimental procedure for the synthesis of HPAD, ADGE and ADEP.

advanced composites. Hence, the combinations of adamantane and polysiloxane with epoxy resins have broader application possibilities. To date, however, there have been few reports on adamantane-based epoxy resins with light-filtering properties. Fang et al. [7] prepared fullerene-containing epoxy membranes with tunable ultraviolet light-filtering properties. However, the thermal, dielectric and optical properties of siloxane-modified adamantane-based epoxy resins have not been investigated in detail. In this study, 1,3-dibromoadamantane and phenol were used as the starting materials to prepare 1,3-bis(4-hydroxyphenyl)adamantane (HPAD). Then, HPAD was reacted with epichlorohydrin to synthesize 1,3-bis(4-hydroxyphenyl)adamantane diglycidyl ether (ADGE). The synthesized adamantane-based epoxy resin (ADEP) was produced by curing ADGE with diamine (B210). A novel siloxane-modified adamantane-based epoxy resin (Siloxane-ADEP) was synthesized from 3-isocyanatopropyltriethoxysilane (IPTES), phenyltriethoxysilane (PTEOS) and ADGE using the sol–gel copolymerization technique. The chemical structures of ADEP and Siloxane-ADEP were confirmed using Fourier transform infrared, ^{1}H NMR, ^{13}C NMR and ^{29}Si NMR spectroscopy measurements. The morphological, thermal, dielectric and optical properties of ADEP and Siloxane-ADEP were studied and compared with those of the diglycidyl ether of bisphenol-A epoxy.

2. Experimental

2.1. Synthesis of 1,3-bis(4-hydroxyphenyl)adamantane (HPAD)

HPAD was prepared using a modification of a previously reported procedure [18]. A 150-mL round-bottom flask was filled with 1,3-dibromoadamantane (6.00 g), phenol (60.00 g) and iron(III) chloride (1.10 g). The flask was equipped with a reflux condenser and an outlet to a beaker containing a solution of NaOH to capture the HBr released from the reaction. The solution was stirred at 80 °C for 16 h under nitrogen. The excess phenol was removed by stirring the product in 500-mL portions of hot water 3 times, followed by drying under vacuum. The crude product was crystallized from methanol to afford 3.04 g (50.7 wt% yield) of white crystals of HPAD. The experimental procedure is shown in Scheme 1. Fig. 1 presents the ^{1}H and ^{13}C NMR spectra of HPAD. ^{1}H NMR (500 MHz, DMSO-d$_6$), δ 1.72 (s, 2H, H-3), 1.80 (m, 10H, H-1), 2.22 (s, 2H, H-2), 3.43 (s, HOD in DMSO-d$_6$), 6.75 (m, 4H, ArH), 7.22 (m, 4H, ArH), 9.18 ppm (s, 2H, H-6); ^{13}C NMR (500 MHz, DMSO-d$_6$), δ 29.58 (C-4), 35.83 (C-5), 36.36 (C-2), 42.28 (C-3), 49.70 (C-1), 115.21 (C-8), 125.78 (C-7), 141.41 (C-6), 155.50 ppm (C-9).

2.2. Synthesis of 1,3-bis(4-hydroxyphenyl)adamantane diglycidyl ether (ADGE) and ADEP

A 100-mL round-bottom flask was filled with 1 g of HPAD, 3.0 mL of isopropyl alcohol and 4.34 g of epichlorohydrin. The reaction temperature was controlled at 80 °C, and 0.625 g of 40 wt% aqueous NaOH was added dropwise over the course of 1 h. The mixture was reacted at this temperature for 6 h. After the reaction reached completion, the salt was filtered, and then the filtrate was washed three times with water. Then, the organic phase was separated from the mixture. Excess epichlorohydrin and the solvent were distilled using a rotary evaporator to afford 1.97 g of a yellow liquid of 1,3-bis(4-hydroxyphenyl)adamantane diglycidyl ether (ADGE). The mixture of ADGE and 10 wt% B210 diamine as a curing agent was homogeneously dissolved in THF as a solvent. The reaction solution was stirred for 12 h, evacuated for 5 min to remove the solvent from the solution, and then aged at 60 °C for 48 h to

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