Available online at www.sciencedirect.com
ScienceDirect
ELSEVIER
Polymer Degradation and Stability 91 (2006) 2588–2594
Polymer Degradation and Stability
www.elsevier.com/locate/polydegstab

Silicon-containing flame retardant epoxy resins: Synthesis, characterization and properties

L.A. Mercado, M. Galià, J.A. Reina*

Departament de Química Analítica i Química Orgànica, Universitat Rovira i Virgili, Campus Sescelades, Marcel.lí Domingo s/n. E-43007 Tarragona, Spain

Received 29 March 2006; accepted 24 May 2006
Available online 10 July 2006

Abstract

Epoxy resins with different silicon contents were prepared from silicon-containing epoxides or silicon-containing prepolymers by curing with 4,4′-diaminodiphenylmethane. The reactivity of the silicon-based compounds toward amine curing agents was higher than that of the conventional epoxy resins. The T_g of the resulting thermosets was moderate and decreased when the silicon content increased. The onset decomposition temperatures decreased and the char yields increased when the silicon content increased. Epoxy resins had a high LOI value, according to the efficiency of silicon in improving flame retardance.

Keywords: Flame retardant polymers; Epoxy resins; Thermogravimetrical analysis; Limiting oxygen index

1. Introduction

A number of future industrial and commercial applications will require polymers with improved fire retardancy. Demands for flame retardant epoxy resins are extremely strong because they are widely used in adhesives, coatings and advanced composites in the aerospace and electronic industries. Traditionally, flame retardant polymers can be prepared by blending polymers with flame retardant additives, such as halogenated compounds [1]. This is the most economical way of promoting flame retardancy, but problems such as poor compatibility, leaching and reduced mechanical properties limit their application. The most effective way of improving flame retardancy in epoxy resins is the reactive approach: that is to say, the flame retardant compound is incorporated into the polymer backbone through the epoxide or the curing agent. Moreover, the use of halogenated compounds as flame retardants has clear disadvantages such as the toxicity and environmental impact of the decomposition products evolved during combustion. It is essential that flame retardant systems meet the requirements of new regulations and the development of new halogen-free epoxy resins is attracting considerable interest [2].

Research has shown that the addition of relatively small amounts of silicon compounds to various polymeric materials has a flame retardant effect. This is partly because these compounds dilute the more combustible organic components and partly because the silicaceous residues can form a barrier to an advancing flame [3]. Silicon, like phosphorus and nitrogen, is regarded as an environmentally friendly flame retardant because it can reduce the harmful impact on the environment more than the existing materials. Some approaches that prepare epoxy resins with silicon covalently bonded to the epoxy network have been reported. Hydroxyl-terminated siloxanes have been used directly in the epoxy resin formulation and diamino-terminated siloxanes can also be used as curing agents to effectively introduce silicon into an epoxy resin [4]. A more complicated approach is to synthesize silicon-containing epoxides, which can be cured on their own or blended with other epoxy comonomers. In this way, the synthesis of triglycidyloxyphenyl silane (TGPS), a silicon-based epoxy monomer has been described [5,6]. The monomer obtained was blended in various proportions with DGEBA and cured with

---

* Corresponding author. Tel.: +34 977559768; fax: +34 977558446.
E-mail address: joseantonio.reina@urv.net (J.A. Reina).

0141-3910/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymdegradstab.2006.05.007

diaminodiphenylmethane as hardening agent. Phase separation was not observed during the curing process and the materials obtained showed good thermal and flame retardant properties.

Epoxy-containing silsesquioxanes have also been used to prepare nano-reinforced epoxy networks [7,8]. In this approach, the most important concept is that a phase separation process may take place when a POSS-bearing organic group is used that is not compatible with the epoxy network. The results suggest that it should be possible to develop a formulation in which the phase separation process takes place in the course of the polymerization, leading to a dispersion of micro-particles in the thermosetting polymer and the *in situ* generation of a reinforced polymer.

The present study uses two different approaches to prepare silicon-containing epoxy resins. Silicon-containing glycidyl monomers (DGDPS, BGDMSB and TGPS, Scheme 1) were obtained and cured by 4,4′-diaminodiphenylmethane as hardening agent. We also examined the incorporation of silicon into the epoxy resin by reacting silanols and DGEBA to obtain prepolymers (EpSi 2-1 and EpSi 3-2, Scheme 2) that have been cured with DDM. The thermal stability of the final polymers was assessed by TGA and the flame retardant properties were evaluated by the limiting oxygen index.

2. Experimental part

2.1. Materials

Phenyltrimethoxy silane, dimethoxydiphenyl silane, allyl alcohol, titanium tetraisopropoxide and *m*-chloroperbenzoic acid (MCPBA) were supplied by Fluka. 4,4′-Diaminodiphenylmethane (DDM), glycidol, diphenylsilanediol, 1,4-bis(hydroxydimethyl silyl) benzene and tin (II) chloride were supplied by Aldrich. Diglycidylether of bisphenol A (Epikote 828; EEW = 192 g/equiv) was obtained from Shell Chemical Co. All solvents were purified by standard procedures.

2.2. Synthesis of diglycidyloxydiphenyl silane (DGDPS)

Dimethoxydiphenyl silane (10.0 g; 0.041 mol), allyl alcohol (40.0 g; 0.688 mol) and titanium tetraisopropoxide (0.3 g; 0.001 mol) were added to a 250-ml two-necked flask equipped with magnetic stirrer and condenser. The reaction was carried out in toluene at reflux temperature for 24 h. The progress of the reaction was monitored by thin-layer chromatography (5:3 hexane/ethyl acetate). The reaction mixture was washed twice with 5 wt% tartaric acid, three times with 5 wt% $NaHCO_3$, and with water and brine. The organic layer was dried over $MgSO_4$, filtered and then the solvent was evaporated at reduced pressure. The product obtained was used in the next step without purification.

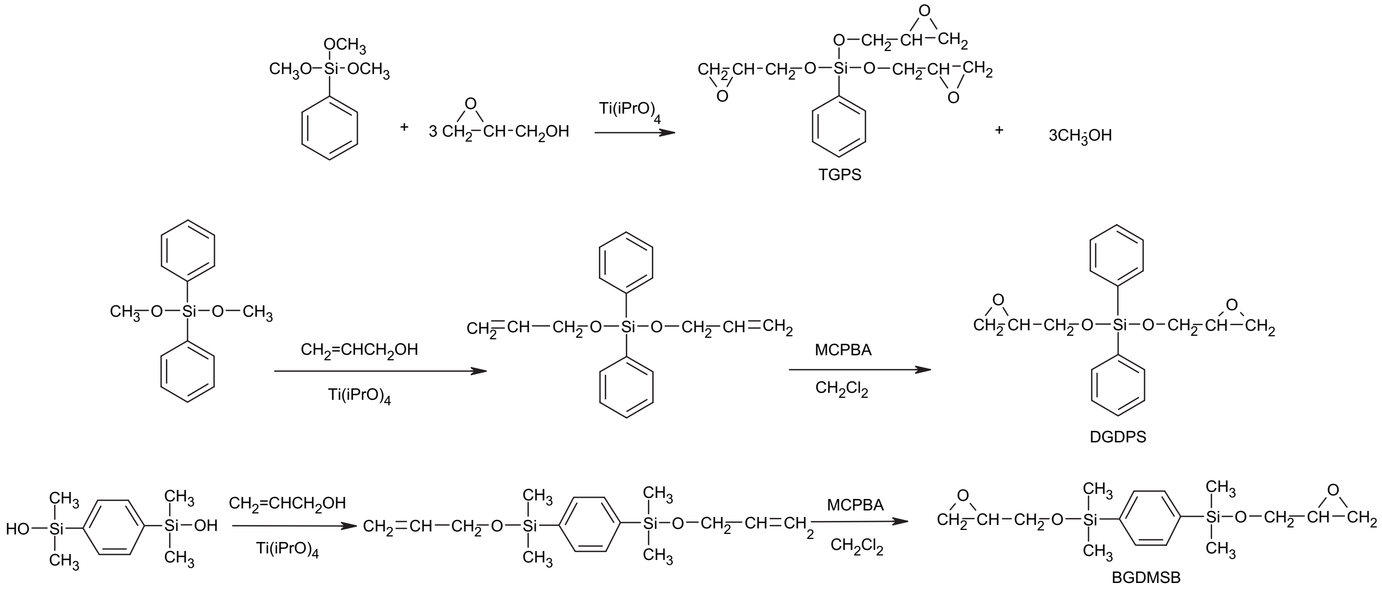
The allyloxy derivative (10 g; 0.034 mol) and MCPBA (30 g; 0.174 mol) were stirred with 250 ml of dichloromethane in a 500-ml two-necked flask at 50 °C for 48 h. The progress of the reaction was monitored by thin-layer chromatography (7:3 hexane/ethyl acetate). The reaction mixture was washed with 5 wt% Na_2SO_3, three times with 5 wt% $NaHCO_3$, and with water and brine. The organic layer was dried over $MgSO_4$, filtered and then the solvent was evaporated at reduced pressure. The product obtained was purified by flash chromatography (7:2 hexane/ethyl acetate). The final product was obtained in a 65% yield.

^{1}H NMR ($CDCl_3$/TMS, δ (ppm)): 7.65 (4H, m); 7.42 (6H, m); 4.03 (2H, dd, 12.0, 3.2 Hz); 3.75 (2H, dd, 12.0, 5.2 Hz); 3.15 (2H, m); 2.78 (2H, dd, 4.4, 2.8 Hz); 2.65 (2H, dd, 4.4, 2.8 Hz).

^{13}C NMR ($CDCl_3$/TMS, δ (ppm)): 134.9 (d); 132.2 (s); 130.6 (d); 127.9 (d) 63.8 (t); 52.0 (d); 44.5 (t).

2.3. Synthesis of 1,4-bis(glycidyloxydimethyl silyl)-benzene (BGDMSB)

1,4-Bis(hydroxydimethyl silyl) benzene (0.5 g; 0.002 mol), allyl alcohol (10.0 g; 0.170 mol) and titanium tetraisopropoxide



Scheme 1.