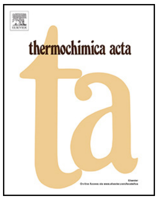
Thermochimica Acta 575 (2014) 21–28

Contents lists available at ScienceDirect

Thermochimica Acta

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



Curing behavior and thermal properties of TGDDM copolymerized with a new pyridine-containing diamine and with DDM or DDS

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ARTICLE INFO

Article history:
Received 11 February 2013
Received in revised form
10 September 2013
Accepted 11 September 2013
Available online 1 October 2013

Keywords:
Epoxy networks
Curing behavior
DMTA
TGA
Oxidation
Thermal decomposition

ABSTRACT

A new pyridine-containing diamine, 4,4′-(pyridine-2,6-diylbis(oxy)) dianiline (PDD) was used as curing agent for a tetra-epoxy resin, N,N,N′,N′-tetraglycidyl-4,4′-diaminodiphenylmethane (TGDDM). The chemical reactivity of the diamine was evaluated using Friedman's method, and compared with traditional diamine curing agents, 4,4′-diaminodiphenylmethane (DDM) and diaminodiphenylsulphone (DDS). PDD was found to be more reactive with the epoxy groups of TGDDM than DDS but less reactive than DDM. The dynamic mechanical thermal analysis showed all materials had T_gs above 250 °C and thermosets formed from TGDDM with blends of PDD with either DDM or DDS had T_gs which increased linearly with composition. Thermogravimetric analysis (TGA) of TGDDM/PDD under argon atmosphere gave a distinctive two-stage decomposition curve compared with the approximately single step observed when TGDDM was cured by the traditional amines. When carried out under air atmosphere, the TGA mass loss occurred in multiple stages and the rate of degradation for the PDD-cured TGDDM was slower than that for DDM- and DDS-cured epoxy resin. This suggests PDD enhances the flame retardancy of the cured thermosets when compared to the more traditional diamine curing systems.

1. Introduction

Epoxy resin thermosets have good chemical and corrosion resistance, high tensile strength and modulus, excellent dimension stability and adhesive properties [1]. These characteristics result in epoxy thermosets being widely used in a variety of industrial applications such as adhesives, coatings, laminating, electronic encapsulation and composites [2,3]. However, a major drawback which restricts their use as advanced materials is their flammability [2,4]. This can be overcome either by using flame retardant additives or by incorporating flame retardant materials into the backbone of the epoxy. In recent years, researchers have mainly focused on the latter strategy [2,4,5] because the flame retardants which are chemically incorporated cause less detrimental effects on the properties of the epoxy thermoset. Bromine-containing co-monomers are often used with epoxy resins for reduction in flammability [5,6]. However the evolution of toxic and corrosive halogenated gases as a result of combustion of these epoxy thermosets can cause serious threat to human health and the environment. Thus the development of non-halogen flame retardant epoxy systems has gained the interest of researchers in recently [2,3,5,7–9].

An improvement in the thermal properties of epoxy resins can also be achieved by introducing aromatic rings into crosslinked epoxy resins, either by use of aromatic epoxy monomers, such as N,N,N′,N′-tetraglycidyl-4,4′-diaminodiphenylmethane (TGDDM), triglycidyl p-aminophenol (TGAP), diglycidyl ether of bisphenol-A (DGEBA) or by using aromatic curing agents such as diaminodiphenylmethane (DDM) and diaminodiphenylsulphone (DDS). The second approach is more useful because a wide range of established, commercial epoxy resins used in various industries can be cured in this manner [10,11]. An alternative primary diamine, 4,4′-(pyridine-2,6-diylbis(oxy))dianiline (PDD), which contains an extra aromatic ring when compared with the conventional curing agents such as DDM and DDS, has been synthesized [12] which may provide better performance at high temperatures.

Thus the objective of the present work is focused on the properties of formulations obtained by the cure of TGDDM with PDD. For comparison, TGDDM was also cured with mixtures containing PDD and either DDM or DDS in varying ratios to investigate the effect of these blends on the properties of the cured samples. The curing kinetics of PDD with TGDDM was studied by dynamic DSC experiments. The thermal resistance and flame retardancy of these thermosets were studied by dynamic mechanical thermal analysis

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http://dx.doi.org/10.1016/j.tca.2013.09.018

(DMTA) and thermogravimetric analysis (TGA) under argon and air atmospheres.

2. Experimental

2.1. Materials

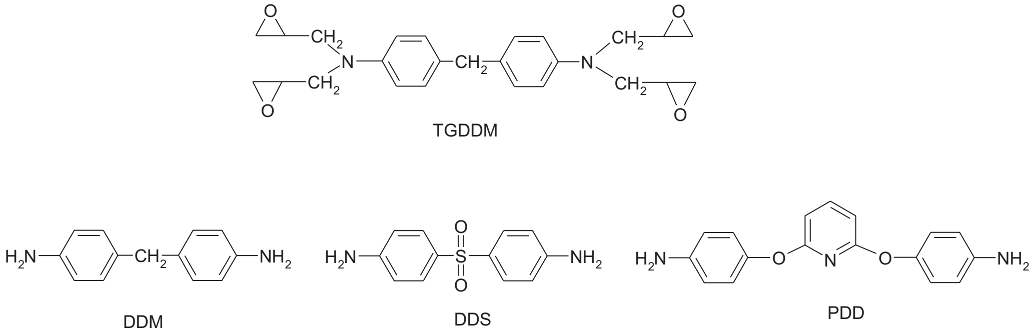
2,6-Dichloropyridine, 1-methyl-2-pyrolidone (NMP), 4-aminophenol and 4-4′-diaminodiphenylmethane (DDM), potassium carbonate and toluene were purchased from Sigma–Aldrich. N,N,N′,N′-tetraglycidyl-4,4′-diaminodiphenylmethane (TGDDM, Araldite MY 721) and diaminodiphenylsulphone (DDS) were obtained from Huntsman and Vantico, respectively. These chemicals were used as received. The structures of the amines and epoxy are shown in Scheme 1. All other reagents and solvents were obtained from Aldrich.

2.2. Synthesis and characterization of 4,4′-(pyridine-2,6-diylbis(oxy))dianiline)

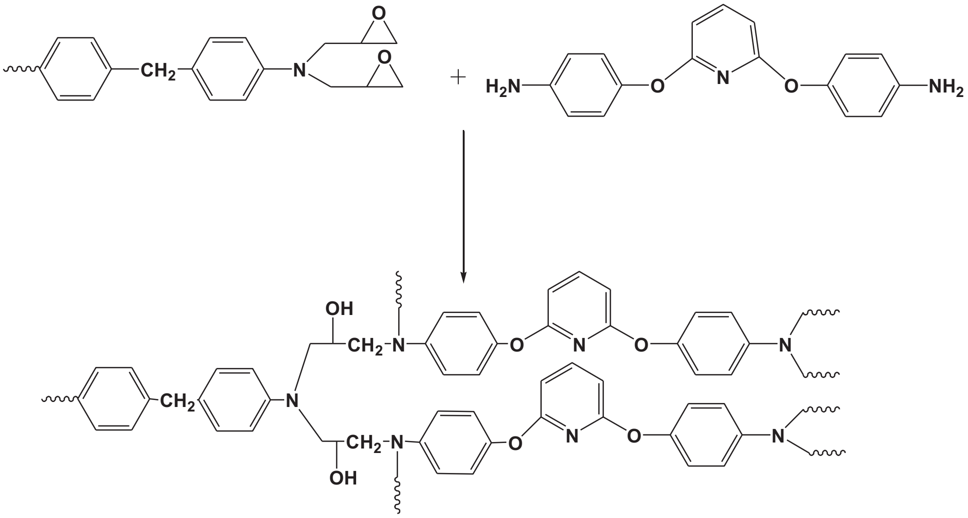
4,4′-(Pyridine-2,6-diylbis(oxy))dianiline (PDD) was synthesized according to the reported procedure [12]. Briefly, 2,6-dichloropyridine (3.0 g, 0.02 mol), 4-aminophenol (4.6 g, 0.04 mol), and K_2CO_3 (8.7 g, 0.06 mol), with N-methyl-2-pyrrolidone (NMP, 50 ml) and toluene (30 ml), was added to a 250 ml three neck round bottom flask equipped with a Dean–Stark apparatus. The reaction mixture was heated and stirred under nitrogen to 140 °C for 6 h, followed by 165 °C for 20 h, and the evolved water was removed from the reaction mixture by azeotropic distillation. During this time, the progress of the reaction was monitored by thin-layer chromatography (TLC). The resultant reaction mixture was cooled to room temperature and poured into 100 mL of cold water. PDD was precipitated out and washed with 100 mL of 3% NaOH to remove the traces of HCl produced in the reaction. The obtained diamine was dried in a vacuum oven at 60 °C and was recrystallized in toluene to give a yield of 80%. The melting point of PDD was 140 °C; the TLC R_f was 0.34 using ethyl acetate/silica gel; FTIR characterization gave 3215–3415 cm^{-1} (N—H stretching), 3036 cm^{-1} (C—H stretching), 1626 cm^{-1} (C=C stretching), 1578 cm^{-1} (N—H bending), 1429 cm^{-1} (C=N stretching), 1203 cm^{-1} (Ar—O—Ar stretching), 1148 cm^{-1} (C—N stretching); ^1H NMR (in DMSO-d_6 and referenced to the internal standard, tetramethyl silane): 4.95–5.1 ppm s(4H, amine), 6.33 ppm d(2H, pyridine), 6.59–6.56 ppm d(4H phenylene), 6.81–6.78 ppm d(4H phenylene), 7.66 ppm t(1H pyridine).

2.3. Sample preparation

TGDDM was mixed with combinations of PDD, DDM and DDS in stoichiometric amounts as shown in Table 1. The diamines were heated and stirred with TGDDM for 10 min at 90 °C, 100 °C or 120 °C for DDM, PDD or DDS, respectively. These temperatures were chosen to facilitate mixing with the more viscous TGDDM but reduce the chance of premature cure because the reactivity of the diamines with the epoxy is DDM > PDD > DDS. After mixing, the transparent and homogenous solutions were rapidly cooled to room temperature to prevent premature cure. Scheme 2 shows the chemistry of the curing process.



Scheme 1. Monomers used.



Scheme 2. Curing process of TGDDM with PDD.