Polymer Degradation and Stability 127 (2016) 44–55

Contents lists available at ScienceDirect

Polymer Degradation and Stability

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

Fire behaviour and morphology of epoxy matrices designed for composite materials processed by infusion

Suzanne Laik [a, b], Jocelyne Galy [a, b, *], Jean-François Gérard [a, b], Marco Monti [c], Giovanni Camino [c, d]

[a] Université de Lyon, F-69003, Lyon, France
[b] INSA Lyon, CNRS, UMR 5223, Ingénierie des Matériaux Polymères, F-69621, Villeurbanne, France
[c] Proplast Consortium, Strada Comunale Savonesa 9, 15057 Rivalta Scrivia, AL, Italy
[d] Politecnico di Torino - Sede di Alessandria, V.le T. Michel 5, 15121 Alessandria, Italy

ARTICLE INFO

Article history:
Received 21 July 2015
Received in revised form
10 November 2015
Accepted 25 November 2015
Available online 9 December 2015

Keywords:
Flame-retardancy
TGDDM
Epoxy
POSS
Morphology
Reactivity

ABSTRACT

The present work is about the investigation of the fire behavior of epoxy networks designed for structural composite materials used in aeronautics. Two high-Tg, infusion-suitable epoxy systems were studied. A model system was based on tetraglycidyl(diaminodiphenyl)methane (TGDDM) as an epoxy prepolymer, and 4,4′ methylene bis(2,6-diethylaniline) (MDEA) as a curing agent. A second system was based on a commercial aeronautic formulation specially designed for the infusion process. The triSilanolPhenyl POSS (POSSOH) was chosen as an additive due to the presence of phenyl groups and silanol functions that could possibly react with the network compounds. In this perspective, an aluminium salt (aluminium tri(acetylacetonate)) was introduced in presence of POSSOH in order to enhance the reaction of the additive with the epoxy monomer. The study of the morphology revealed intricate structures, with an overall good dispersion of the POSSOH in the epoxy networks. In terms of fire behaviour, same tendencies were observed for both epoxy networks, i.e. the combined presence of POSSOH and the aluminium-based additive brought significant improvements with a substantial and effective intumescent-like behaviour.

1. Introduction

Polymer materials are now part of most of the consumer goods but also find applications in very specific domains. Among them, thermosetting epoxy polymers are particularly interesting as they can be suitable for a wide range of applications. For certain structural polymer composite parts for aeronautics, TGDDM-based matrices are preferred, as they possess better mechanical and thermal properties. However, epoxy polymers suffer from a high flammability that is detrimental for some of the applications, in terms of human safety, material damage, and psychological impact on public.

Solutions to overcome this main drawback have been found that include introducing halogenated fire retardant compounds in a conventional epoxy polymer, or modifying the chemical structure of the epoxy prepolymer (e.g. brominated epoxy resins). Such compounds tend nowadays to be subjected to drastic regulations due to the evolution of European directives such as REACH [1]. The research community has been looking for alternatives, among which the phosphorus-based compounds, phosphorus-modified resin backbones and/or hardeners have attracted great interest [2–5]. In many cases though, those compounds need to be used in high proportions, which can sometimes bring detrimental changes to other material properties [6]. More recently, inorganic flame retardants, such as silicate clays or carbon nanotubes, have been investigated and a great emphasis has been put on their nanostructuration and influence on the thermal stability and fire retardancy of the organic/inorganic synthesized networks [7–9].

In the last decade, incorporation of Polyhedral Oligomeric Silsesquioxanes (POSS) in polymeric materials has been intensively studied. The enhancement of a wide range of properties has been targeted, such as thermal and thermomechanical properties [10–13], surface features (adhesion and wettability) [14,15],

---

* Corresponding author. Université de Lyon, F-69003, Lyon, France.
E-mail addresses: suzanne.laik@insa-lyon.fr (S. Laik), jocelyne.galy@insa-lyon.fr (J. Galy), jean-francois.gerard@insa-lyon.fr (J.-F. Gérard), marco.monti@proplast.it (M. Monti), giovanni.camino@polito.it (G. Camino).

http://dx.doi.org/10.1016/j.polymdegradstab.2015.11.027
0141-3910/

electrical properties [16], and combustion performance [17–22]. POSS are organic/inorganic materials made of a silica core surrounded by organic ligands. The POSS-T_8 is a type of POSS with a cubic-shaped cage and of general formula $(RSiO_{1/2})_8$, where R are organic ligands on the silicon atoms. The versatility of such a compound comes then from the ability to tailor the properties of the synthesized networks by selecting the appropriate organic ligands. In particular, phenyl-bearing POSS have been found to have a beneficial effect on fire retardancy of epoxy networks over other types of ligands [23]. The morphologies of synthesized networks can be controlled through the POSS ligand nature [24–27]. POSS can be incorporated as non-reactive nano-objects or they can be grafted to the polymer backbone as pendant units or inserted to the polymer network or chains, depending on their functionality.

In the present work, two high-Tg, infusion-suitable epoxy systems were studied. Only the behaviour of epoxy matrices was investigated at this stage of the study, but not that of their carbon fibre composites. Indeed, the potential of POSSOH as fire retardant must be demonstrated at first in epoxy matrices. A model system was based on tetraglycidyl(diaminodiphenyl)methane (TGDDM) as an epoxy prepolymer, and 4,4′ methylene bis(2,6-diethylaniline) (MDEA, Lonza) as a low-reactive curing agent. A second system was based on a commercial aeronautic formulation specially designed for the infusion process, the MVR444 epoxy system from Cytec. Those networks were modified introducing 4 wt% of triSilanolPhenyl POSS (POSSOH), which is an incompletely-condensed POSS with 3 silanol functions and 7 phenyl ligands. POSSOH were introduced in the epoxy networks either alone or in combination with aluminium triacetylacetonate, as silanol functions were reported to react with the hydroxyl and the oxirane ring of the epoxy prepolymer under the action of metal catalysts [20,22,28]. POSSOH is a versatile molecule as it can be included into the network via four different ways, depending on how many silanol functions react. Without any covalent bond with the epoxy, the POSSOH are potentially dispersed as molecular nano-objects; the reaction of one silanol leads to free POSSOH-terminated chain ends; POSSOH acts as a chain extender or a crosslinker when two or three silanols react, respectively. In addition, the silanol groups of POSSOH could undergo auto-condensation in between them. All these reactions can be in competition with the epoxy-amine reactions. Investigation of the reactivity of the systems was carried, before focusing on morphology analyses, thermal stability measured via thermogravimetry, and fire behaviour of the hybrid networks as compared to the neat epoxy matrices.

2. Experimental part

2.1. Materials

Two different epoxy systems were selected: a commercial bicomponent formulation (MVR444, supplied by Cytec), and a simplified binary system of known composition for the sake of understanding. The MVR444 system is suitable for structural composite materials, and allows low infusion temperatures – *ca.* 70 °C – and good performances before and after hot/wet conditioning. Its two parts were mixtures of several epoxy prepolymers and several hardeners, among which tetraglycidyl(diaminodiphenyl)methane (TGDDM) and 4,4'-methylenebis(2-isopropyl-6-methylaniline) (MMIPA), respectively. The binary model system was based on a TGDDM prepolymer and 4,4′ methylene bis(2,6-diethylaniline (MDEA) a low-reactive, primary aromatic diamine as curing. The TGDDM (MY9512 from Huntsman), has an epoxy equivalent weight between 117 and 134 g/eq. The hardener MDEA (Lonza) is a crystalline powder at room temperature and has an amine equivalent weight of 77.6 g/eq. TrisilanolPhenyl POSS (POSSOH) was purchased from Hybrid Plastics. It was a crystalline powder (T_m = 219 °C) at room temperature. Aluminium acetylacetonate was a 99%-purity reactant obtained from Sigma–Aldrich. All products were used as received. The structure of all the materials and abbreviations used for simplification concerns are reported in Table 1.

2.2. Processing

2.2.1. Reference epoxy networks

The neat MVR444 network was produced by mixing the hardener and the epoxy resin components in a weight ratio of 58:100, respectively, as advised by the material supplier, at 90 °C under vacuum in a glass reactor. For the binary model system, a stoichiometric amount of TGDDM was mixed together with MDEA under vacuum and mechanical stirring at 90 °C for about 20 min – until complete dissolution of MDEA. The mixture, called MVR or TM, respectively, was then cast into closed moulds and cured in oven according to the curing cycle given in Table 2.

2.2.2. POSS-modified epoxy networks

The desired amount of POSSOH was dispersed in the resin component of the MVR 444 system or in TGDDM at 130 °C for 45 min, under vacuum and mechanical stirring. The mixture was then slowly cooled to 90 °C before addition of a stoichiometric amount of MDEA and further stirred for 30 min until complete dissolution of MDEA. For some of the networks, the addition of the aluminium salt was carried on at this stage and the mixture was stirred at 90 °C for 5 min until complete dissolution of the additive. The mixture was then cast in closed moulds and cured in oven. Compositions and curing cycles of all systems are detailed in Table 2. The first dwell temperature was lowered in the curing cycle of the aluminium salt-containing networks, which will be discussed in the ‘Results and Discussion’ part below.

2.3. Experimental techniques

2.3.1. Differential scanning Calorimetry

DSC analyses were performed using a Q20 or Q30 from TA Instrument under inert atmosphere, the scan rate being of 10 K. min^{-1}. The reactive mixtures were scanned from 25 to 350 °C, and the first ramp up revealed the exotherm of reaction. The crosslinked networks were scanned in the temperature range of 25–250 °C and the middle point of the glass transition domain, as given by the analysis tool of Universal Analysis (TA Instruments software), was considered as the value of glass transition temperature, T_g.

2.3.2. Gel times

The gel times of the reactive systems were determined via chemorheology (parallel-plates method) using a Rheometric Dynamic Analyser (RDAII). Six frequencies were implemented (1, 5, 10, 20, 30 and 40 Hz); the gelation time was given by the point of crossing of the tanδ-vs-time curves at the different frequencies according to Chambon & Winter criteria, [29]. The gel time were measured either at 90 °C or 135 °C.

2.3.3. Viscosity measurements

An Anton Paar rheometer Physica MCR 301 was used to determine the viscosity of reactive systems. The configuration used was the cone-plate geometry (50 mm in diameter, 4°) with a constant shear rate of 5 s^{-1} and at a given temperature, controlled by the heating plate.