Reactive & Functional Polymers 72 (2012) 736–744

Contents lists available at SciVerse ScienceDirect

Reactive & Functional Polymers

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

Systematic examination of thermal, mechanical and dielectrical properties of aromatic polybenzoxazines

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ARTICLE INFO

Article history:
Received 24 May 2012
Accepted 2 July 2012
Available online 20 July 2012

Keywords:
Polybenzoxazines
Thermal analysis
Mechanical properties
Dielectric properties
Molecular simulation

ABSTRACT

A series of *bis*-benzoxazines, prepared in high yield and purity using two synthetic procedures, is reported. Differential scanning calorimetry reveals similar temperatures for the onset of polymerisation (162–180 °C); the higher values representing monomers containing polar bridges or rigid backbones. Dynamic viscoelasticity data reveal glass transition temperatures for the polybenzoxazines ranging from 187 °C to 235 °C; a fluorinated polybenzoxazine consistently yields the highest T_g of the polymers studied. The latter is interesting since it is superior to many commercial benzoxazines with a relatively high T_g (235 °C), flexural modulus (5.0 GPa) and flexural strength (146.7 MPa), but coupled with a breaking strain (3.06%) that is uncharacteristically high for polybenzoxazines. The incorporation of fluorine results in a low dielectric loss properties (D_k = 3.71–4.12 at 10 MHz, D_f = 0.0109 – 0.0980 at 10 MHz), which are comparable with commercial polybenzoxazines, FR4 and aerospace epoxy resins and superior to commercial bismaleimides.

1. Introduction

The field of thermosetting polymers has had a relatively brief but dramatic history. Barely 100 years have passed since Leo Baekeland synthesised and patented [1] the first thermosetting polymer (his eponymous phenol–formaldehyde resin, Bakelite), yet for instance thermoset-based composites now account for about 60% of the total composites market (*ca.* 7 Mt *p.a.* worldwide[1]) and they find application in a whole host of traditional and high performance applications, including general purpose electrical mouldings, heated appliance components and automotive parts, laminates, such as printed circuit boards, adhesives, bindings and surface coatings, to name but a few. Conventional phenolics are crosslinked products of their low molecular weight precursors, typically formed through a condensation reaction producing by-products such as ammonia and water. The versatility of their structures and that they often display very desirable properties such as good heat resistance, flame retardant properties, low dielectric constants and the production of these materials is relatively inexpensive [2]. However, there are some shortcomings associated with these materials in that they perform poorly under stress, i.e. they have poor toughness properties, they have a poor shelf life and the process of polymerisation of these materials produces by-products and requires, in many cases, the use of a strong acid or base catalyst to effect cure [3] and the highly corrosive medium has the potential to damage processing equipment. In the search for higher performance replacements for phenolic resins many materials have received attention and benzoxazines are perhaps the latest family to do so. Published reports of the preparation of polymers of aromatic oxazines, or benzoxazines, date back some sixty years [4]; although the preparation of their polymers and the commercial exploitation of these materials has only come about relatively recently and they are now receiving a great deal of academic and industrial interest with the publication of a comprehensive handbook [5].

Poly(*bis*-benzoxazine)s appear to incorporate the best properties from conventional phenolics, and may find application in a number of their traditional niches, whilst improving on shelf life and offering the potential for greater toughness properties through their greater molecular flexibility; the relative cheapness of the monomer is also an important factor influencing their adoption [6]. In electronics applications associated with printed circuit boards (PCBs), laminates produced from poly(*bis*-benzoxazine)s offer both high glass transition temperature (T_g) and reasonably good longevity in the demanding "pressure cooker test" which, as the name suggests, assesses the hot/wet properties under pressure. However, while poly(*bis*-benzoxazine)s display many benefits over conventional phenolics, the relatively low fracture toughness that is achieved by cured polymers (a K_{IC} value of *ca.* 0.51–0.54 MPa.m$^{0.5}$ for polybenzoxazines derived from monomeric

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[1] Figure supplied by Patricia Harrison, Director, Business Development, Cytec Engineered Materials, May 2011.

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http://dx.doi.org/10.1016/j.reactfunctpolym.2012.07.001

precursors is typical [7]) is still a problem in modern microelectronics applications when compared with competitor resins (although more recent polybenzoxazines based on side-chain polymeric precursors have potentially higher K_{IC} values). Furthermore, the drilling of small holes through the reinforced dielectric layer to accept small components or wires produces areas of concentrated stress, which may undergo stress fractures over time exacerbates this weakness. In our ongoing work programmes, the ultimate aim is to examine and increase our understanding of the influence of the benzoxazine monomer structure on reactivity, fracture toughness, and thermal stability. Consequently, a range of monomers has been produced in which the backbone and substituents were varied to cover a wide range of structural features. Thus, some of the structures e.g. poly(*bis*-benzoxazine)s based on bisphenol monomers might be anticipated to be very brittle materials, whereas others (bearing ether- and isopropylidene-bridges) might be expected to show greater toughness properties. In the present paper the influence of the backbone and substituent on the monomer reactivity and selected physical properties is discussed.

2. Experimental

2.1. Apparatus

Fourier transform infrared (FT-IR) spectra were recorded using a Perkin-Elmer (system 2000 FT-IR) spectrometer interfaced with a PC running PE-Spectrum v 2.00 software or a Nicolet Avatar 320 FT-IR spectrometer running Nicolet OMNIC ESP 5.1 software. The samples were presented in a variety of ways: on an ATR module, as liquid films or on KBr disks depending on physical state. In each case 16 scans, at a resolution of 4 cm^{-1}, were recorded and co-added to produce the final spectrum.

^1H nuclear magnetic resonance (NMR) spectra were obtained at 298 K using a Bruker DRX500 spectrometer operating at 500 MHz (for ^1H) and 125.7 MHz (for ^{13}C). Samples were prepared in $CDCl_3$, using tetramethylsilane (TMS) as an internal standard where applicable.

Elemental analysis was performed on samples (1–2 mg) using an Exeter Analytical EA440 CHN/O/S elemental analyser. Acetanilide was used to calibrate the instrument followed by a set of standards (*S*-benzyl thiouronium chloride and phenylthiourea); the accuracy with standard organic compounds is ±0.15% absolute plus ±0.15% relative.

Melting temperatures were determined using a Kopfler flat bed micro melting point (m.p.) apparatus and a heating rate of 5 K min^{-1}.

Differential scanning calorimetry (DSC) was undertaken using a TA Instruments 2920, controlled by TA Q series Advantage software, on samples of 3.5 ± 0.5 mg in hermetically-sealed aluminium pans. Experiments were conducted at a heating rate of 10 K min^{-1} from room temperature to 300 °C under flowing nitrogen (40 cm^3 min^{-1}). The sample was held isothermally for a further 5 min at this temperature to effect full cure before being cooled at 10 K min^{-1} from 300 to 20 °C. A rescan was run at 10 K min^{-1} (25–300 °C) to reveal glass transition temperature (T_g) for samples (taken as the midpoint of the transition).

Dynamic mechanical thermal analysis (DMTA) was undertaken using two instruments: a Polymer Labs PLII and a TA Instruments Q800 DMA. In the case of the former, samples (15 mg) were placed in steel powder clamps,[2] crimped and placed in a vacuum oven for 2 h to effect cure (the choice of cure temperature was informed by the DSC analyses). Samples were oscillated in a single cantilever clamp in a two-point flexural mode at a fixed frequency of 3 Hz while being scanned at 10 K min^{-1}. under nitrogen (40 cm^3 min^{-1}) over a temperature range of *ca.* 25 °C to a maximum temperature of 300 °C, dependent on the sample's degradation temperature (ascertained by Thermogravimetric analysis (TGA)).

Dynamic viscosity elasticity measurements were performed on samples (30 mm × 5 mm × 1 mm) in tensile mode using a DVE-V4 (Rheology Co., Ltd.) with the span of 20 mm at a frequency of 10 Hz, automated static loading, and a scan rate of 5 K min^{-1}.

Thermo-mechanical analysis (TMA) was undertaken using a TA Instruments Q400 Mfg-TMA. Samples (6.35 mm × 6.35 mm × 1 mm) were produced using a PTFE mould. Samples were run in standard mode with an expansion probe, the applied force being 0.02 N. The expansion of the samples was measured over a temperature range of *ca.* 25 °C to a maximum temperature of 250 °C (to prevent degradation of the sample damaging the probe) at a heating rate of 5 K min^{-1}. under nitrogen (50 cm^3 min^{-1}).

Flexural measurements were performed in triplicate at 25 °C on samples (50 mm × 25 mm × 1 mm) using an Instron Universal Testing Apparatus (span between the rollers = 20 mm, crosshead speed = 1 mm min^{-1}).

Dielectric properties (D_k and D_f) of the cured resins were analysed with an impedance material analyser using the IPC-TM-650 standard method [8] on samples (30 mm × 30 mm × 1 mm) between 1 MHz and 1 GHz at 25 °C. The permittivity of the sample was calculated using the capacitance of the sample and the effective surface area and the loss tangent calculated using the conductance.

2.2. Preparation and characterization of monomers

A range of monomers was prepared in the course of the present work (Table 1)[3] using two synthetic routes: the more widely reported and commonly used method from the seminal work in this field [9], hereafter denoted the 'standard route', and the 'solvent free' route [10]. The area of benzoxazine monomer synthesis has already been discussed in the literature and the reader is directed to detailed reviews for further information [11,12]. The synthetic procedures and analytical characterization data (FTIR spectroscopy, ^1H and ^{13}C NMR spectroscopy, and elemental analysis data) have been submitted as Supplementary Information.

2.3. Cure of polymer samples for thermo-mechanical analyses

Polymer samples to be subjected to thermal and mechanical analyses were prepared as follows. Monomers were dried (160 °C, 10 min) to remove volatiles and placed in an open mould (comprising two metal plates separated by a 50 mm × 40 mm × 1 mm PTFE shim). The mould was heated slowly *in vacuo* to 100 °C and held isothermally (2 h) followed by 180 °C (1 h). Samples were postcured at 200 °C (2 h) (1 MPa using a press moulding machine), to ensure full cure and machined to the appropriate size for the tests to be performed.

3. Results and discussion

3.1. Comparison of the synthetic methods used in this work

The most commonly reported and widely accepted route for polyfunctional monomer synthesis (which constitutes the 'standard' commercial preparation) can be considered a variant of the

[2] Supplied by John Gearing of Gearing Scientific Ltd., Leatherhead, Surrey, UK as flat sheet of steel with central groove that is pinched together around the sample to yield samples of approximate dimensions 20.7 mm × 9.5 mm × 0.7 mm.

[3] A smaller set of the monomers are presented in this paper and characterization data for the complete series are supplied as Supplementary Information.