

Studying the effect of the chloral group on the thermal and physical properties of aromatic cyanate esters



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ABSTRACT

Two cyanate ester monomers: 2,2-bis(4-cyanatophenyl)propane (**1**) and 1,1-dichloro-2,2-(4-cyanatophenyl)ethylidene (**2**) are formulated with copper(II) acetylacetonate (200 ppm) in dodecylphenol (1% w/v active copper suspension) and cured (2 K/min to 150 °C + 1 h; 2 K/min to 200 °C + 3 h) followed by a post cure (2 K/min to 260 °C + 1 h). The polymerisation enthalpy for the thermal polymerisation of monomer (**2**) was recorded as 87.6 ± 0.75 kJ/mol. OCN (75.0 ± 0.80 kJ/mol. OCN following catalysis) and 99.4 ± 1.86 kJ/mol. OCN, 85.8 ± 4.03 kJ/mol. OCN following catalysis for (**1**). Formulated monomers show little advancement in cure during storage at a several temperatures (ambient, -5 °C and -20 °C) over a period of 2 months. TGA measurements conducted on cured 'puck' sample3s reveal char yields of 38% at 800 °C in the case of (**1**) and 54% for (**2**). Pyrolysis-GC shows only minor similarities in the species detected implying that the two polymers undergo significantly different degradation pathways under the analysis conditions, but the low incidence of polynuclear aromatics present (aside from substituted fluorenes, biphenyls and anthracenes) is probably due to the rapidity of heating a short residence times involved.

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1. Introduction

Thermoset polymers have an established history in civil aviation, in applications involving decorative panels, secondary composite structures and adhesives – around 90% of the interior furnishings of a typical civil airliner will contain thermoset composites [1]. Cyanate ester (CE) polymers constitute a family of addition cured high performance, thermosetting polymers, which occupy a niche intermediate between high glass transition temperature (T_g), tetrafunctional epoxy resins and bismaleimides (BMIs) [2] and, whilst they are not currently widely used in civil aviation, they are used increasingly in military aerospace applications [3,4]. Cured CEs offer a combination of favourable thermal and mechanical performance (e.g. dry T_g values of 270–300 °C are common with a strain at break of over 5–8%) coupled with low dielectric loss properties (a low dielectric constant of ca. 2.7 with a loss tangent of 0.003 (at 25 °C and 1 MHz) is typical) that gives a unique property profile. Although requiring toughening for some

engineering applications, cyanates can be combined with inherently tough engineering thermoplastics (HexPly 954-2A, $G_{IC} = 250$ J/m²) [5,6] or elastomers (HexPly 953-3, $G_{IC} = 450$ J/m²) [7] to yield impressive enhancements. In this form they typically find application as matrices in advanced composites (either in combination with epoxy resins in aerospace applications [8,9]) or with BMIs as dielectric polymers in the microelectronics industry [10].

The preparation of bisphenol C (1,1-dichloro-2,2-(4-hydroxyphenyl)ethylidene) was first reported in 1874 [11], but the first reports of useful polymers based on bisphenol C (i.e. polycarbonates and epoxy resins) were published during the 1960s and Union Carbide and Carbon Corporation obtained a patent covering the composition and preparation of such epoxy blends [12]. The blends exhibited improvements in physical and mechanical properties, e.g. both tensile strength and hardness remained stable even at the point of charring and epoxies based on bisphenol C were reported to be self extinguishing and of potential interest for aerospace and similar applications [13]. During the next decade bisphenol C was investigate in more depth within several research programmes to identify non-burning plastics yielding patents [14,15]. In parallel with the extensive work with thermoset

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polymers, a considerable body of work was produced reporting the influence of the chloral moiety on commodity thermoplastics such as polycarbonate [16–18]. Korshak and Rusanov produced a thorough review of the preparation of thermostable and fire-resistant polymers based on chloral and its derivatives in 1989 [19].

During the 1980s the Federal Aviation Administration (FAA) and Ciba worked together on the CE based on bisphenol C, particularly through the work of Lyon et al., who stated [20] that Ciba had produced bisphenol C based cyanate esters which displayed the lowest heat release capacity of any thermoset polymer tested at that time. This was timely, for during the following decade the FAA brought in new regulations limiting the rate of heat release and smoke emissions from interior panels in flaming combustion; the most widely used polymers for this application at the time, epoxies, failed under the new regulation. In 2001 the FAA, together with the Dow Chemical Company, worked on scale up of bisphenol C polycarbonates (in which the bisphenol A unit was replaced directly by bisphenol C), which demonstrated significantly higher char yield and limiting oxygen index, coupled with a heat release capacity that was 1/12 that of the parent polymer.

In 2001 a patent [21] emerged covering composition of matter and preparation for bisphenol C cyanate esters exhibiting improved heat release and curing properties; a continuation-in-part was approved the following year [22]. The two patents together are aimed at polymers for use in aircraft interior due to the materials low peak heat release rates and low total heat release rates; the following year the US Navy tested and approved bisphenol CEs for use in submarines. Lyon and/or Ramirez working for the FAA have published several studies on this material [23–26] and the degradation of bisphenol C based polymers was elucidated by Ramirez [27] in a Masters project supported by the FAA [18]. The self-extinguishing behaviour in flame tests of bisphenol C based polymers is the main reason for the interest expressed in them. Yet it must also be noted that the mechanical properties of these polymers remain equivalent to the bisphenol A analogues, so processing is unaffected.

In the current study, we are particularly interested in examining the processability of the cyanate monomer and the influence on cure conditions on the thermal stability of the resulting polymer. We report, for the first time, the analysis of the products of the degradation of aryl cyanate esters following exposure to extremely high heating rates (20,000 K/s).

2. Materials

The dicyanate ester monomer 2,2-bis(4-cyanatophenyl)propane (**1**) was supplied by Lonza AG (Visp, Switzerland) and, having confirmed its purity using ^1H NMR and elemental analysis, was used as received without further purification. Copper(II) acetylacetonate, $\text{Cu}(\text{acac})_2$ (97%), cyanogen bromide (97%) and dodecylphenol (mixture of isomers) were obtained from Sigma Aldrich. 1,1-Dichloro-2,2-(4-hydroxyphenyl)ethylidene (97%) was obtained from Wilshire Technologies, Inc. (USA). Following characterisation to verify purity, all reagents were used as received without further purification (Fig. 1).

2.1. Characterisation of 1,1-dichloro-2,2-(4-hydroxyphenyl)ethylene (2)

The cyanate ester was prepared using a well-used route (originally reported by Bayer AG) [28]. ^1H NMR analysis. ^1H NMR analysis was performed following recrystallisation before samples were combined to ensure consistency of batch quality (examples of spectra are presented in the following sections) before scale up was performed. To a solution of 1,1-dichloro-2,2-(4-hydroxyphenyl)ethylidene (acetone, 0 °C) was added CNBr (2 molar equivalents),

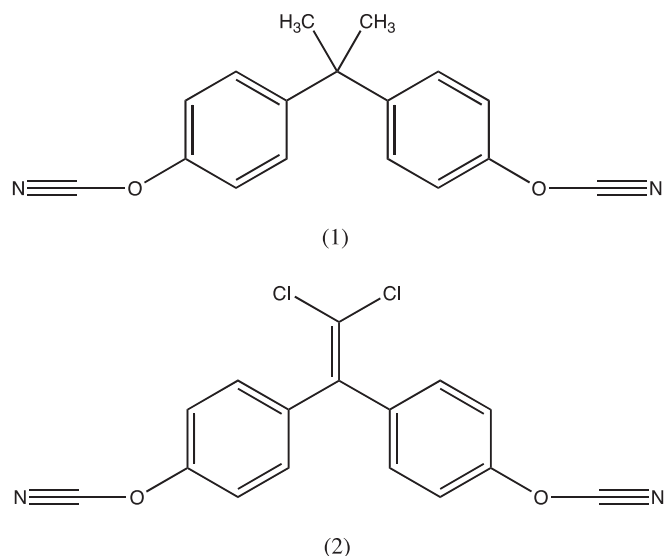


Fig. 1. CE monomers studied in this work.

then triethylamine (2.1 molar equivalents) was introduced to the reaction vessel (rapid stirring, dropwise addition, ~30 min, whilst maintaining the temperature at $-10\text{ }^\circ\text{C}$ with a card ice/acetone/methanol bath). The resulting triethylammonium hydrobromide salt was filtered from the solution. Yields ca. 85–90% (crude); the product (**2**) was recrystallised from a dichloromethane/hexane mixture (70:30). Calculated for $\text{C}_{16}\text{H}_8\text{Cl}_2\text{N}_2\text{O}_2$, wt. %: C 58.00, H 2.42, N 8.46, found: C 57.86, H 2.20, N 8.03; IR (ATR, cm^{-1}): 2273, 2235 (OCN stretch), 3000–3100 (Ar–H stretch), 1595 (Ar, C=C stretch), 975 (C–Cl stretch), 900–1000 (out-of-plane = C–Cl deformation), 835 (out-of-plane C–H deformation characteristic of *para*-disubstituted phenyl), 600–800 (C–Cl stretch), and 656 (in-plane C–H deformation characteristic of *para*-disubstituted phenyl). ^1H NMR δ_{H} (500 MHz, CDCl_3 , ppm from TMS): 7.39 (4H, *ortho*-to the alkene); 7.32 (4H, *ortho*-to the cyanate); ^{13}C NMR δ_{C} (75 MHz, D_6 -DMSO, ppm from TMS): 152.32 ($2 \times \text{C}_2$); 137.52 (C_6); 136.95 (C_6); 131.65 ($2 \times \text{C}_5$); 122.10 (C_7); 115.61 ($2 \times \text{C}_4$); 108.28 ($2 \times \text{C}_1$); 77.00 (C from CDCl_3 solvent).

2.2. Blending and cure of polymer samples for thermo-mechanical analyses

The $\text{Cu}^{\text{II}}(\text{acac})_2 \cdot \text{C}_{18}\text{H}_{30}\text{O}$ initiator suspension (1% w/v) was made up by mixing $\text{Cu}^{\text{II}}(\text{acac})_2$ with dodecylphenol, heating to 80 °C for 30 min then ramping to 120 °C for a further 30 min, stirring throughout. Good homogenisation was achieved. $\text{Cu}^{\text{II}}(\text{acac})_2$ (200 ppm) was added to the monomer/s and heated to 90 °C whilst stirring to yield a homogenous suspension with uniformly dispersed initiator after 15 min. The monomer/initiator solution was decanted into aluminium dishes (55 mm diameter, depth 10 mm) and cured in a fan-assisted oven heating at 2 K/min to 150 °C (1 h isothermal) + heating at 2 K/min to 200 °C (3 h isothermal) then post cured – heating at 2 K/min to 260 °C (1 h isothermal) followed by a gradual cool (3 K/min) to room temperature. Cured samples were cut to correct size for analysis.

2.3. Instrumentation

^1H nuclear magnetic resonance (NMR) spectra were obtained at 298 K using a Bruker AV-300 NMR spectrometer operating at 300 MHz and a Bruker DRX-500 spectrometer operating at 500 MHz. ^{13}C NMR spectra were obtained by Bruker AV-300

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