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Developing predictive models for polycyanurates through a comparative study of molecular simulation and empirical thermo-mechanical data

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Abstract

Using a parameter set (RDA-DR2.21_Inv) previously published by our group, both the atom-to-atom connectivities and geometries and the physical and mechanical properties of poly[bis-4-(4-cyanatophenoxy)phenyl sulphone] have been simulated with remarkable accuracy. Molecular dynamics simulation, carried out on the polymer structure at a variety of experimental temperatures, yields a transition temperature of ca. 510–520 K, which can be equated with the empirical glass transition temperature (T_g) for the polycyanurate. The same dicyanate was prepared experimentally and characterised using dynamic mechanical analysis (yielding an empirical T_g of ca. 519 K) and thermo-mechanical analysis (yielding an empirical T_g of 508–528 K). The effect of incomplete cure of the monomer or development of structural defects in the network on the thermo-mechanical properties is also examined using molecular simulation.

Keywords: Cyanates; Molecular modelling; Glass transition

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1. Introduction

Cyanate ester resins (polycyanurates) are a family of thermosetting resins that are used within a variety of electronic and microelectronic applications. Once cured, polycyanurates offer high performance, including relatively high glass transition temperature ($T_g = 463$–563 K, depending on structure and degree of cure), high fracture toughness (typically $G_{IC} = 140$–225 J m^{-2}, although this can be raised significantly by blending with engineering thermoplastics) and good hot/wet performance [1]. Currently, the single largest application for polycyanurates is as lamination substrates for printed circuits and their assembly via prepreg adhesives into high-density, high-speed multi-layer boards, which are produced commercially for supercomputers, mainframes and high speed workstation mother units [2]. Polycyanurates also develop interesting dielectric properties (typically, the dielectric constant is 2.2–2.7 and the dissipation factor is 0.003 at GHz frequencies) that make them particularly attractive in these applications, for which epoxy resins and polyimides are market contenders.

Polyfunctional cyanate monomers cure via the formation of cyanurate rings (*sym*-triazine rings linked by aryl ether linkages to a polymer, correctly termed a polycyanurate) and a simplified reaction is depicted in Scheme 1 for bis-4-(4-cyanatophenoxy)phenyl sulphone (catalyst packages typically comprise a transition metal carboxylate or chelate and an alkyl phenol).

Although this reaction scheme predominates during the polymerisation, it is now recognised that the earlier claims for the exclusive formation of cyanurate rings [3] were somewhat optimistic and there is still debate about the exact nature of the polymerisation mechanism. Many routes have been proposed to acknowledge the effects of different catalysts and reaction intermediates—a fuller discussion of this aspect is outside the scope of the current paper although the reader is directed to other sources [4–8] in which this is dealt with in some detail.

For almost 15 years, research at Surrey has examined, with some success, how synthesis might yield polycyanurates (and indeed many other engineering polymers) with superior

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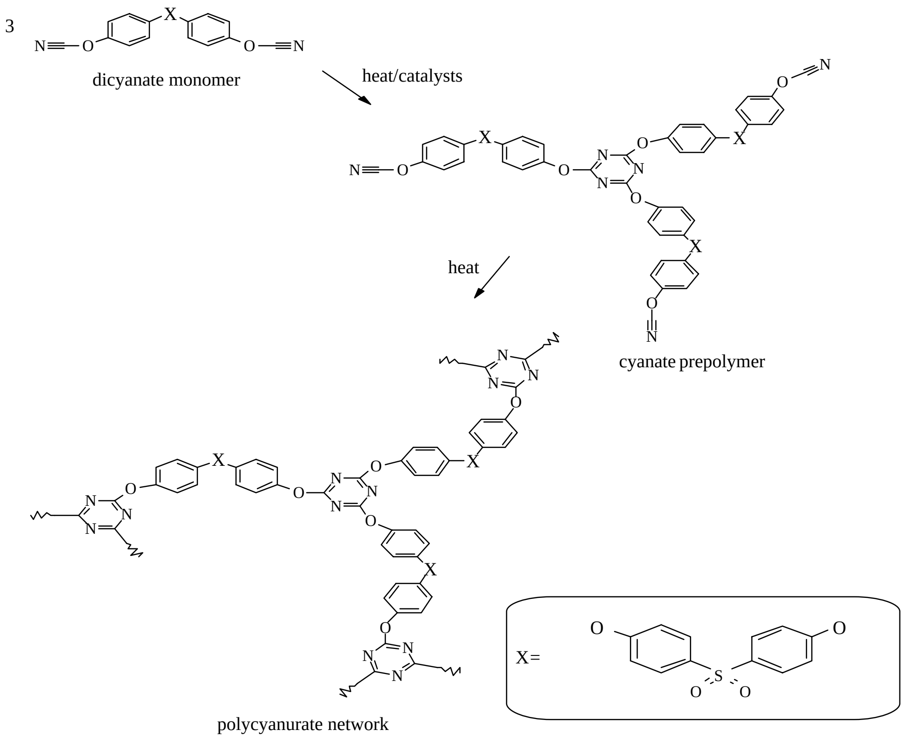

Scheme 1. Simplified cyclotrimerisation reaction to produce polycyanurate network (shown for bis-4-(4-cyanatophenoxy)phenyl sulphone).

properties to existing polymers, or how chemical modification might be employed to increase the utility of commercial dicyanates. During this time, many monomers, blends and copolymers have been prepared (on a variety of scales) through the efforts of a team of researchers, characterised and tested for their physical and mechanical properties. This effort has, of necessity, involved many chemicals, much analysis time and the involvement of many laboratory hours ‘at the bench’. In common with ‘traditional’ chemical synthesis involving the preparation of ‘small’ organic molecules, polymer synthesis brings many similar challenges and a few additional problems (e.g. limited solubility or reduced reactivity) arising from the extended chain structure. However, no matter what the nature of the preparation (whether fine chemicals, pharmaceuticals, agrochemicals or polymers), every synthesis will require that reaction conditions (e.g. temperature, solvent, pressure, reagents, and catalysts, etc.) are optimised. Furthermore, every preparation will consume energy and feedstock materials and generate waste (in the form of gaseous emissions, solvated (by)products or solid matter—the latter may be the desired product, but might also be accompanied by contaminants. It is self evident that energy requirements should be recognised for their environmental and economic impacts and to reduce them accordingly and that the prevention of waste is preferable to the treatment or clean-up of waste after it has formed.

Anastas and Warner have discussed, at length, the role that chemistry has in reducing the impact of chemicals and chemical processes on the environment and as a result have formulated their ‘12 principles of green chemistry’ [9]. Recently, a 13 principle was mooted [10] namely that ‘where possible, the reliable simulation or prediction of materials properties should be employed to optimize synthesis and reduce its impact on the environment’. The increasing advances made in computational power make the use of simulation techniques increasingly useful in the rational design of new materials. By adopting much of the methodology piloted with great success by the pharmaceutical industry to model the interaction of drug molecules with the active sites of proteins [11], molecular modelling has become generally accepted as a powerful technique for understanding some of the properties exhibited by materials. While still in its infancy in the field of polymer chemistry, computational chemistry has the potential to simulate the properties of novel materials, as yet unsynthesised. There is also the possibility of employing molecular simulation in a predictive capacity potentially offering savings in both labour and cost and reductions in chemical waste. Ultimately, this would allow the scientist or engineer to examine the potential of a novel structure to give him or her the required properties (e.g. heat resistance, bulk modulus or glass transition temperature) to fulfil a new application, without having to prepare the actual material in the laboratory. For although computation experiments do consume energy, the additional burdens, which synthesis places on the environment, would be largely avoided or dramatically reduced. At a later stage, the new monomer or polymer would be prepared in order to allow small scale testing, prior to scale up, but extensive exploratory syntheses to develop many potential monomers would be unnecessary.

A laudable aim, but how realistic is this aspiration? In 1996, Boyd published [12] a useful review detailing the state of the art (at that time) for the simulation of the glass transition from molecular dynamics simulations. He concentrated on