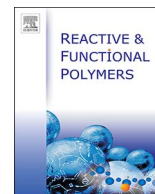




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Influence of backbone structure, conversion and phenolic co-curing of cyanate esters on side relaxations, fracture toughness, flammability properties and water uptake and toughening with low molecular weight polyethersulphones

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ABSTRACT

The effect of backbone structure and conversion of polycyanurate networks on solid state properties has been studied and compared to co-curing with bisphenol-A. Dynamic mechanical behaviour, density, flammability properties, fracture toughness and long-term water uptake were investigated. The intensity of the γ -relaxation increases, room temperature density decreases with increasing conversion, both due to increasing free volume with increasing conversion. A brittle-ductile transition was detected by precise fracture toughness measurements; above a critical conversion the fracture toughness rises suddenly from extremely low values to a plateau or maximum: Networks with higher toughness show a maximum, those with lower toughness a plateau. Bisphenol-A modification causes intrinsic toughness variations. Toughening of two different cyanate esters with polyethersulphones synthesized with various molecular weights between 3000 and 10,500 (M_n) was investigated. Significant toughening effects can be achieved already with intermediate molecular weights lower than those of commercially-available high- T_g amorphous thermoplastics. Long-term water uptake measurements at 28 °C, 50 °C and 70 °C over two years show a non-Fickian part of the water uptake for all cyanate esters even at temperatures as low as 28 °C. The effects of backbone structure, conversion and storage temperature are discussed in detail.

1. Introduction

Cyanate ester resins are high performance thermosetting polymers. In the cured state they are also called polycyanurates. A unique combination of properties such as high temperature stability, low moisture uptake and low dielectric constant in the cured state, plus low viscosity in the uncured state (lowest viscosity of all high temperature resins) has led to their use in low-volume high-performance applications [1]. In such applications, the use of these high-priced materials is justified by their excellent performance as well as a lack of alternatives. This lack of alternatives is one reason why their price remains high, and confines their application to a few low-volume applications such as space satellites, microelectronics, and radomes or airducts in aircraft.

Recently, the authors received requests from civil air and ground

transportation companies to investigate the use of cyanate ester resins for higher-volume applications as composite parts in civil aircraft interiors and in motors at high temperature. There is also an increased interest in the use of new cyanate ester types in high-speed telecommunications. This move is driven by new trends: The number of cyanate ester resin producers has increased recently (and may increase even further), which may lead to reductions in price. Perhaps even more importantly, there is an increasing concern about health issues, mainly during production but also when thermoset materials are used in vehicles or aircraft. For instance, there are indications that the toxicity of phenolic resins might not be acceptable under future European regulations. There are also concerns about epoxy resins regarding allergic reactions to epoxy compounds, and the carcinogenicity of aromatic amine curing agents. New and stricter health and safety

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regulations will drive the search for less-toxic thermosetting resins. Cyanate esters seem to be the best existing alternative to both epoxy and phenolic resins. There are no concerns at all regarding toxicity of cyanates. Like epoxy resins they are addition-curing and exhibit comparable or superior thermal and mechanical properties, whereas for flammability properties they are far superior to epoxies and in the same range as phenolic resins.

Another driver for higher-volume use of cyanate esters is the need for high-throughput technologies for fibre composite production, such as high pressure resin transfer moulding (RTM). If properly formulated with co-monomers, cyanate ester resins combine the lowest viscosity of all resins possessing high glass transition temperatures (only vinyl ester resins or unsaturated polyester resins have lower viscosities) with an extremely high reactivity. There are also technologies available to combine latency and high reactivity [2]. All these factors justify the assumption that cyanate esters are ready to move from the specialty low-volume applications of the past to high-volume applications in the near future.

There are already a large number of publications on cyanate ester resins. These works were either motivated by fundamental scientific considerations, since cyanate esters are an interesting model system for networks due to their uniform trifunctional network structure, or aspects which are relevant mainly in high-performance applications. However, aspects which are relevant in higher-volume applications have not been considered in sufficient detail, and this work addresses these gaps.

The maximum glass transition temperature (T_g) for the fully cured state (i.e. for maximum conversion, denoted $T_g(\text{max})$) of nearly all commercially-available cyanate esters is much higher than that required in applications such as ground or air transport vehicles. The question is then: Do cyanate ester resins need to be fully cured for such applications? Further, phenolics, which are the current resins used for aircraft interiors, are not fully cured in most cases. If a conversion lower than the maximum is acceptable then the effect of conversion on the properties becomes highly relevant. This effect has been briefly reported in [3–7], but this work covers a broader range. Whereas in [3–7] the effect of conversion is investigated only for one cyanate ester monomer, two different cyanate ester monomers are compared here to show the effect of backbone structure. In the first part of this work high precision thermomechanical data (measured using a custom-built torsional pendulum) and precise measurements of conversion form the basis of an analysis over an extended range of conversion. A small part of these data has already been published in [8], but only in the context of analysing the formation of irregular structures in polycyanurate networks. The present work concentrates on networks from 2,2-bis(4-cyanatophenyl)propane (B10) and bis(4-cyanato-3,5-dimethyl)methane (M10) with regular structures, and an analysis of the influence of backbone structure and conversion on thermophysical properties is given.

This work also shows an interesting fracture phenomenon: a brittle-ductile transition which occurs within a narrow region of conversion and was not reported before. During the course of these investigations an improved technique to measure fracture toughness has been developed [9]. Using this new optical crack tracing (OCT) technique, this brittle-ductile transition has been investigated in more detail for five different cyanate ester resins. To the authors' knowledge there are no publications with such a broad range of high accuracy fracture toughness data for cyanate esters.

The fire-smoke-toxicity (FST) properties (i.e. flammability) of cyanate esters have been investigated using cone calorimetry [10–13], but the effect of conversion has not previously been studied. This work reports the effect of conversion on heat release rate as determined by cone calorimetry for four different cyanate ester resins.

The effect of the modification of cyanate esters with phenolics such as bisphenol-A on network structure comes closest to that of conversion [14–16]. The practical importance of phenolic modification lies in the

fact that $T_g(\text{max})$ of the network (and thus the curing temperatures needed to achieve $T_g(\text{max})$) can be dramatically reduced and the curing reaction is highly accelerated. However, no significant deterioration in flammability properties would be expected since the structural elements are nearly identical, and only the network density is reduced by phenolic modification. In this work the effects of modification of cyanate esters with bisphenol-A on both fracture and flammability properties have been studied and compared to the effect of conversion on these properties.

As will be shown, the fracture toughness of unmodified cyanate esters is relatively high in relation to their T_g . However, for their use as matrix resins for structural composites an increase in toughness would still be required. High- T_g amorphous thermoplastics (TPs) have been shown to toughen cyanate esters [17–36]. Commercial types of polysulphone or polyetherimide can be used, but due to the high molecular weight of all commercial TPs, this is at the expense of a large increase in viscosity of the cyanate-TP blend. Cyanate esters are especially suitable for manufacturing fibre composites using infusion processes such as vacuum infusion or resin transfer moulding (RTM) because of their low viscosity. Therefore it would be of practical interest if toughening can be achieved using lower molecular weight grades of such thermoplastics that do not increase the viscosity so much. For applications where low flammability is required, polyethersulphone (PES) seems to be the best choice as the toughening agent. There are a number of publications on polyethersulphone toughening of cyanate esters [17–36]. However, the present work investigates the low molar mass range of PES in more detail than any other study so far. Moreover, whereas other works have mainly concentrated on toughening of the bisphenol-A dicyanate, the present work compares polyethersulphone toughening for bisphenol-A dicyanate (B10) and a multifunctional novolac-type cyanate ester (PT-resin). As will be shown below, novolac-type cyanate esters are much more interesting for applications requiring low flammability. Furthermore, their toughness in the unmodified state is lower than that of bisphenol-A dicyanate, and therefore toughening of the PT-resins is of particular interest for many applications.

The sensitivity of polycyanurates to hydrolytic attack is well known [37]. Various aspects of moisture diffusion and degradation in water at elevated temperatures and at long times have been presented for pure and formulated cyanate ester resins [7,38–47]. In some of these reports accelerated ageing conditions have been used. However, extrapolations from severe conditions of storage in water down to mild conditions cannot be made, since processes such as hydrolytic degradation are threshold processes which cannot be described by Arrhenius laws. Therefore, in the last part of the present work a detailed study on the long-term water uptake behaviour (up to 2.2 years) is presented for five different cyanates with different conversions. The effect of conversion and backbone structure on Fickian and non-Fickian water uptake is discussed. To investigate the realistic long-term behaviour in the typical range of operating temperatures, 28 °C, 50 °C and 70 °C were chosen as the isothermal water bath temperatures.

2. Experimental

2.1. Materials

The cyanate ester resins used are listed in Table 1 together with their chemical structures, trade names, producers and alternative designations in literature. In this work the former trade names of Rhone-Poulenc (now Huntsman USA) are used for the di-functional cyanate esters. For the cyanate ester resins of higher functionality the respective trade names of DOW and Lonza are used. For a better understanding abbreviations referring to structure are used additionally in case of two monomers (B10 (DCBA) and M10 (TMDCBF)). Bisphenol-A (BA) used as co-monomer for cyanate esters was obtained from Sigma Aldrich (purity > 99%).

For the synthesis of linear bisphenol-A polyethersulphone (PES)

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