1 Introduction to cyanate ester resins

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1.1 Historical perspective to the development of high performance polymers

High-temperature organic polymers have been described [1] as polymers that retain useful properties after thousands of hours of exposure at 200°C in air under static conditions. However, as Hergenrother [1] pointed out this definition is misleading and varies considerably depending upon the supplier and user of the material. In many instances, temperature is reported without regard to other important factors that influence the performance of the polymer, such as thermal cycling, stress and environmental factors like moisture, or chemical and electrical action. In addition, polymers that can survive high-temperature processing cycles, but are otherwise not exposed to high temperatures, are also referred to as high-temperature polymers.

The origins of high-temperature organic polymers can be traced back to the late 1950s [1-3] and at that time their development was stimulated primarily by the demands of the aerospace and electronics industries. In the intervening time the variety of high-temperature polymer systems has grown enormously so that a wealth of research literature is available to the reader, while many commercial polymer systems may be obtained to fill a range of technological applications. An indication of the diversity of these applications is outlined in the final chapter of this book, but it encompasses adhesives, coatings, composite matrices, fibres, films, foams, membranes and mouldings (and a host of electronic and microelectronic components).

To examine just one of these examples more closely, the growing need for high use-temperature matrix resins in fibre-reinforced composites has encouraged intensive research [4]. Resins from diacetylenes [5], polyimides [6] and epoxy resins [7] are among the most thoroughly investigated. Wright reported that the aerospace use of composites is expected to treble over the next decade [8]. Epoxy resins (epoxies) are currently by far the largest segment of addition-cured thermosetting polymers which are used to make structural composites in the aerospace industry. In 1987,
epoxy resins comprised the composite matrix in over 90% of these composites and the forecast for 2000 is that epoxies will still comprise about 80% of the total (the remainder being made up of 12–15% polyimides (including bismaleimides, BMIs) and 5–8% thermoplastics) [8]. Epoxies owe their wide usage to their ease of handling and processability: they can be cured at low temperatures and pressures (e.g. 121–177°C, 70–100 lb/in²), which means that currently available fixtures such as autoclaves suited to these conditions are usable. In most aerospace and other engineering applications, temperatures and pressures exceeding these values make it difficult to process composites.

The problem with epoxies lies with their hot/wet performance: their upper temperature range for structural performance is approximately 177°C, while exposure to moist environments limits this to 149°C [9]. This in turn limits the applications in which they may be used to those where relatively non-thermally critical structural parts are required. Recently, interest has developed in making parts that are to be used in close proximity to the thermally critical areas of aircraft, such as engines. In addition, considerable interest has developed in the use of higher performance composites in aircraft, where skin temperatures can be somewhat higher than epoxy resin capabilities. Similar conclusions are applicable to composite matrix resins. In circumstances where epoxies cannot be used, higher temperature performance resins are needed and several candidate resins (including polyimides and cyanate esters) are currently being investigated to fulfil this role.

1.2 Cyanate ester resins

The term ‘cyanate ester resin’ is used to describe both prepolymer and cured resins; the former containing reactive ring-forming cyanate (–O–C≡N) functional groups [10, 11]. Chemically this family of thermosetting monomers and their prepolymer are esters of bisphenols and cyanic acid and commercial monomers may be represented by the general structural model illustrated in Figure 1.1 (where R may be a range of functional groups, e.g. hydrogen atoms, methyl or allyl groups and the bridging group may be simply an isopropylidene moiety or an extended aromatic or cycloaliphatic backbone, etc.). Industrial cyanate ester producers have adopted a variety of synthetic approaches [12] to explore the resulting structure/property relationships in the poly(cyanurate) and some samples of the materials which are commercially available have been included in the Appendix.

Conversion, or curing, to thermoset plastics occurs via cyclotrimerization (an addition process) to form three-dimensional networks of oxygen-linked triazine (or cyanurate) and bisphenyl units, correctly termed