Tensile and fracture properties of a phthalonitrile polymer

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The properties of a polymer prepared from an aromatic diether-linked phthalonitrile resin, 4,4′-bis(3,4-dicyanophenoxy)biphenyl, and cured with 1,3-bis(3-amino phenoxy)benzene are reported. The resin is easily processed from the melt of the monomer in a controlled manner as a function of the amine content and processing conditions. The resulting polymers show an excellent retention of mechanical properties following inert atmosphere post-cure to 375°C and oxidative ageing at 315°C for 100 h. Results are reported for the effects of cure, post-cure and ageing conditions on the tensile and fracture properties of these polymers.

(**Keywords: phthalonitrile; mechanical properties; fracture toughness; double torsion; elevated temperature; thermal stability**)

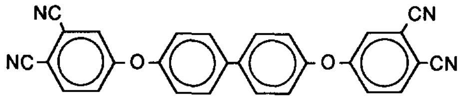
Introduction

Organic polymers that are both thermally and oxidatively stable above 315°C (600°F) are in demand as matrix materials for advanced composite applications, as adhesives for high temperature materials, and as weight-reducing replacement materials for metals. A new class of phthalonitrile-based polymers[1–8] with excellent thermo-oxidative properties has been under investigation for application in these areas. The phthalonitrile monomers are readily converted to crosslinked thermosetting polymers in the presence of thermally stable aromatic diamines[6]. The polymerization reaction occurs through the terminal phthalonitrile units which are interconnected by aromatic dioxy linkages, yielding heterocyclic crosslinked materials. Shaped components are easily processed by heating the polymerization mixture above its melting point or glass transition until gelation occurs. The prepolymers formed from these monomers are soluble in common solvents and indefinitely stable at room temperature.

Previous investigations of the properties of these materials have shown a high retention of weight and mechanical properties following exposure to elevated temperatures and oxidative conditions. Keller and others have reported the dynamic mechanical behaviour[1,2,5,7], the thermal and oxidative weight loss for various cure and ageing conditions[1–3,5–8], the network characteristics and glass transition behaviour[1,2,5], and the conductivity behaviour of phthalonitrile-based materials[3,4]. However, little information exists concerning the failure properties of these materials or the influence of post-cure and ageing conditions on these properties. The present work details the tensile failure and fracture properties of the phthalonitrile polymer following exposure to elevated temperature and oxidative conditions.

Experimental

Synthesis and polymerization. The synthesis and characterization of the monomer have been described previously[1–4,6–8]. The phthalonitrile resin was synthesized by the nucleophilic displacement of a nitro substituent from 4-nitrophthalonitrile by the dialkali salt of 4,4′-biphenyldiol in dry dimethyl sulphoxide. The phthalonitrile monomer (**I**) was melted at 240°C, cooled to 220–230°C, and 1,3-bis(3-aminophenoxy)benzene (APB, 1.5 wt%) was added with vigorous stirring. The resulting mixture was poured into aluminium or brass moulds and cured successively in air at 240°C for 6 h, 280°C for 16 h, and 315°C for 24 h. Free-standing samples were successively post-cured in an argon atmosphere at 350°C for 12 h and 375°C for 12 h. Samples previously post-cured at 375°C were oxidatively aged in an air-recirculating oven at 315°C for 100 h.



4,4′-bis(3,4-dicyanophenoxy)biphenyl (**I**)

Mechanical measurements. Tensile strength measurements were made on a minimum of five dogbone-shaped specimens for each cure, post-cure and ageing condition. Specimen dimensions, chosen to minimize material requirements, were 50 mm long overall with a gauge region of approximately 16 mm (L) × 3 mm (W) × 2 mm (T). All tensile strength specimens were abrasively ground and polished to final dimensions. Tensile modulus measurements were obtained on rectangular or dogbone-shaped specimens with a clip-on strain gauge mounted at a gauge length of 25.4 mm. The end tabs for all specimens were potted in Epon 828/Versamid 140

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(1:1 by weight) to allow firm gripping without premature fracture in the grips.

Tensile measurements at room temperature (22 ± 2°C) were carried out using an Instron 4206 instrument at a crosshead speed of 0.508 mm min^{-1}. A grip separation of 25.4 mm was used for the tensile strength specimens, producing an initial strain rate of $5.3 \times 10^{-4}\ \mathrm{s}^{-1}$ in the gauge region. The stress–strain response was recorded with a computer data collection and instrument control system which allowed calculation of the tensile modulus.

Fracture measurements. The concepts of linear elastic fracture mechanics, often applied to crack growth in brittle polymeric materials, have been extensively developed, both theoretically and experimentally[9–14]. The double torsion (DT) technique[9–14] was used for these studies due to the relative simplicity of specimen geometry and preparation, the stability of the crack growth, and the potential for studying variations in material and test conditions. The relation between the stress intensity factor in mode I fracture[9], K_{I}, specimen geometry, and load, P, for a DT specimen in plane strain is given by[9–14]:

$$K_{\mathrm{I}} = PW_{\mathrm{m}}\left[\frac{(1+\nu)}{Wt^3t_{\mathrm{n}}k_1}\right]^{1/2} \tag{1}$$

where W_{m} = moment arm (9.525 mm), W = specimen width, t = specimen thickness, t_{n} = web thickness (specimen thickness less the depth of the V-shaped groove), ν = Poisson's ratio, P = applied load, K_{I} = stress intensity factor or fracture toughness and k_1 = correction factor constant for finite specimen width[10].

The strain-energy release rate, or fracture energy, for a given crack velocity, G_{Ii}, is given by[10]:

$$G_{\mathrm{Ii}} = \frac{1}{2}\frac{P_i^2}{t_{\mathrm{n}}}\frac{\mathrm{d}C}{\mathrm{d}a} \tag{2}$$

where P_i = load at a given crack velocity and $\mathrm{d}C/\mathrm{d}a$ = derivative of the experimentally determined compliance, C, which varies with crack length, a. Alternatively, the critical strain-energy release rate, G_{Ic}, may be determined from[10]:

$$G_{\mathrm{Ic}} = \frac{K_{\mathrm{Ic}}^2}{E}(1-\nu^2) \tag{3}$$

where E is Young's modulus.

The average crack speed, $\dot{a}$, for a crosshead rate, $\dot{x}$, is given by[12]:

$$\dot{a} = \frac{\dot{x}}{P(\mathrm{d}C/\mathrm{d}a)} \tag{4}$$

DT specimens were prepared from moulded 10 cm × 10 cm plates. Specimen dimensions, selected in accordance with generally accepted dimensional ratios[10,14], were approximately 100 mm (L) × 38 mm (W) × 6 mm (T). All samples were abrasively ground, giving uniform dimensions and parallel faces. A grooving/scoring technique was used for the tensile face as an aid in specimen alignment and in control of the crack growth profile. A centred V-shaped groove was produced along the length of the specimen by using a 90° high-speed spiral fluted bit, held inverted to produce successively deeper cuts as the sample was passed over the cutter. The sample was held at an angle of 45° to the axis of the bit rotation by the use of a plexiglas jig. A final groove depth of 2.0 mm was produced by this method. The centre of the groove was then lightly scored with a razor blade along the length of the specimen, in the direction of crack growth, to a depth of 0.1 mm. A stress-relieved cut-crack was made by drilling a hole 0.6 mm deep perpendicular to the centre of the V-shaped groove at various lengths along the sample. The cut-crack was completed by using a 0.3 mm saw to cut the sample from the centreline of the V-shaped groove at the loading end of the specimen to the drilled hole. The cut was ground to remove score marks and a razor blade was used to introduce a pre-crack along the centreline of the V-shaped groove. By following this procedure, any overloading due to an initially blunt crack tip was minimized.

Fracture tests at room temperature (22 ± 2°C) were performed on an Instron 4206 at a displacement rate of 0.508 mm min^{-1}. A fracture test fixture was used to apply the load to the specimen, thereby propagating the crack in a stable and controlled manner. Test specimens were used to determine both the steady crack propagation load, P_{c}, and the compliance response at various initial crack lengths. A computer data collection and instrument control system was used to record the load–crosshead displacement response and calculate the compliance for each initial crack length. Specimens used to determine the compliance were successively cut to various lengths along the V-shaped groove and pre-cracked as described above prior to testing.

Results and discussion

Mechanical properties. Tensile strength values for the phthalonitrile polymer at room temperature are summarized in *Table 1* for various cure, post-cure and oxidative ageing conditions. These properties indicate a high retention of mechanical performance with only a small decrease following oxidative ageing for 100 h at 315°C. Compared with other state-of-the-art thermosetting materials, the neat phthalonitrile resin exhibits an excellent, if not superior, retention of mechanical strength. PMR resins, by comparison, have tensile strengths of 48–83 MPa[15] at room temperature. Other thermosetting polyimides exhibit similar or higher mechanical property values but, in certain cases, do not maintain the same degree of thermal and oxidative stability as is shown by phthalonitrile-based materials[15]. Materials formed from acetylene-terminated resin (ATR) precursors have also been shown to exhibit superior mechanical and thermo-oxidative properties[16]. The very brittle nature of ATR materials, however, limits their potential applications.

Preliminary tensile stress–strain measurements at room temperature indicate that the phthalonitrile

Table 1 Effect of cure conditions on the room temperature tensile strength of biphenyldiol-based phthalonitrile polymers

Temperature (°C)	Cure/post-cure[a] conditions Time (h)	Atmosphere	Tensile strength at break (MPa)
315	24	Air	94 ± 17
350	12	Argon	94 ± 21
375	12	Argon	80 ± 7
315	100	Air	72 ± 5

[a] All materials were initially cured at 240°C for 6 h and 280°C for 16 h. Tabulated conditions are successive thermal and oxidative treatments

polymers behave as brittle materials for cure/post-cure conditions at 315°C or above. Tensile moduli range from 3.6 to 2.4 GPa for specimens cured at 315 and 375°C, respectively. Previous results[1] have shown similar dynamic storage moduli with evidence of viscoelastic transitions to the rubbery state between 200 and 360°C for materials cured at 350°C or below. Phthalonitrile polymers post-cured at 375°C, as well as those aged at elevated temperatures following post-cure at 375°C, do not show any evidence of glass/rubber transitions up to 375°C. The maximum in the loss tangent also shifts to higher temperatures for cure temperatures below 375°C; glass transition maxima are observed at 290 and 332°C following cure for 16–24 h at 315°C and post-cure for 4 h at 350°C, respectively[1].

Fracture behaviour. The room temperature fracture behaviour of phthalonitrile materials cured at 315°C for 24 h has been studied. Stable crack growth was achieved under specimen and test conditions described previously, which allowed for a determination of crack propagation loads and specimen/test fixture compliance. As shown in *Figure 1*, for each cut-crack length a near linear load–displacement response was obtained until an initiated crack profile developed. At this point the load became nearly constant with the crack propagating at a steady rate along the length of the specimen. Occasionally, a slight overloading was observed prior to steady state crack growth (*Figure 1*, curve c); however, the overloading was apparently not sufficiently great to cause complete and unsteady failure in the specimens. The relatively small crack arresting potential of these specimens compared with thicker materials generally resulted in unstable crack growth for specimens with initial cut-cracks greater than 50 mm. For this reason, compliance calibrations were restricted to a cut-crack length of 10–50 mm. Since the stress intensity is generally constant over the length of the specimen, with the exception of the initial and final 15–20%[10], a determination of the compliance in this region allowed calculation of the fracture energy. *Figure 2* shows a linear

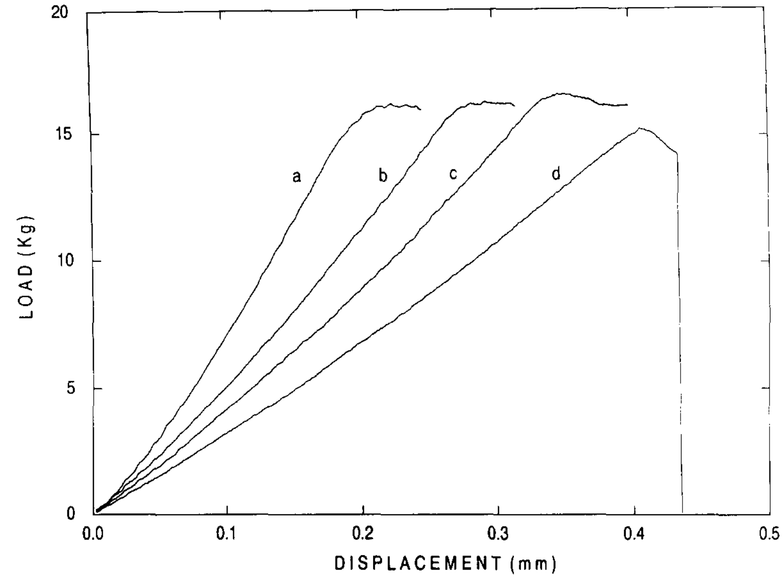

Figure 1 Load–displacement response at 22°C for the phthalonitrile polymer cured at 315°C for 24 h. The curves represent the compliance response for various initial cut-crack lengths: a, 10.1 mm; b, 20.7 mm; c, 31.4 mm; d, 44.0 mm

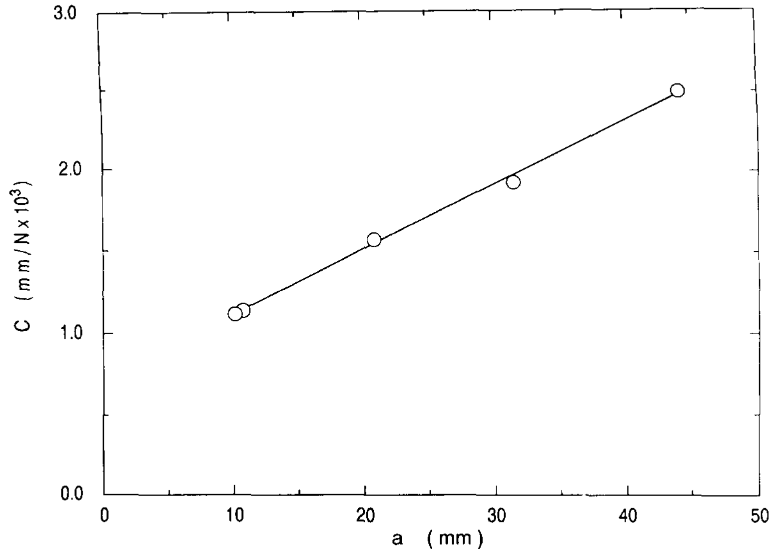

Figure 2 Compliance calibration at 22°C for the phthalonitrile polymer showing the linearity of specimen compliance variation with crack length

variation of the compliance with initial cut-crack length as is expected for brittle materials.

The fracture toughness and energy of the phthalonitrile materials were calculated using equations (1) and (2), respectively. Test results on five samples yielded a fracture toughness of 0.61–0.63 MN $m^{-3/2}$, and a fracture energy of 120–130 J m^{-2}. The corresponding crack speeds were 70–80 mm min^{-1}. Tests on similar poly(methyl methacrylate) (PMMA) specimens, performed as a means of comparison with published results, yielded K_{Ic} values of 1.2–1.3 MN $m^{-3/2}$. By comparison, values between 1.1 and 1.3 MN $m^{-3/2}$ are cited for the room temperature fracture toughness of PMMA at similar crack speeds[12]. A comparison of the fracture properties of phthalonitrile polymers with other thermosetting materials shows that the phthalonitrile materials are typical of highly crosslinked brittle resins at room temperature test conditions. Representative fracture toughness values for unmodified epoxy resins[9,13,17], for example, range from 0.5 to 0.8 MN $m^{-3/2}$.

Preliminary results obtained to verify the requirements of plane-strain conditions due to specimen thickness have also been made. Plate specimens, prepared without V-shaped grooves, with thicknesses ranging from 4.0 to 6.0 mm have been tested, yielding K_{Ic} values between 0.60 and 65 MN $m^{-3/2}$, and fracture energy values comparable to the grooved specimens. Limited testing was performed with ungrooved specimens, however, due to the difficulty in specimen alignment in the fracture jig, and the increased potential for crack wandering. According to ASTM E399-83, the minimum thickness required for plane-strain conditions is $2.5(K_{Ic}/\sigma_y)^2$, where σ_y is the tensile yield stress. Using a value of 94 MPa for σ_y, the minimum thickness required is approximately 0.1 mm. The observed insensitivity of the fracture toughness results to specimen thickness and groove geometry are therefore consistent with the existence of plane-strain conditions in these specimens.

Summary and conclusions

Phthalonitrile-based polymers prepared from 4,4′-bis(3,4-dicyanophenoxy)biphenyl, cured in the presence of a diamine and exposed to elevated post-cure and ageing conditions, have been shown to exhibit a high retention of mechanical strength. The thermo-oxidative properties of these polymers are excellent with very low weight loss and good mechanical properties obtained for cure conditions to 315°C, inert atmosphere post-cure to 375°C, and oxidative ageing at 315°C. The plane-strain fracture behaviour of the phthalonitrile polymers shows properties similar to unmodified epoxies, with brittle failure at room temperature observed. Due to the ease of processing and excellent mechanical properties evidenced by these materials it is anticipated that potential applications will include fabricated composites and structures subjected to elevated temperature and oxidative environments.

Acknowledgements

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