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The dynamic mechanical properties and fracture behaviour of phthalocyanine polymers

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The dynamic mechanical properties of a series of phthalocyanine polymers with varying aliphatic chain length linking stable phthalocyanine nuclei have been studied. Dynamic shear modulus and polymer loss factor were determined using a torsion pendulum. Polymer fracture energies were also determined using both the standard compact tension specimens and double-tapered cantilever beam specimens. The results showed that both the dynamic shear modulus and the glass transition temperature increased with decreasing molecular flexibility and increasing extent of cure. The fracture energies increased with increasing molecular flexibility. It was also shown that extended thermal treatment could greatly embrittle the thermosetting polymers and hence reduce the fracture toughness, even though such treatments usually promoted crosslinking leading to higher moduli and glass transition temperatures for these polymers.

1. Introduction

New high temperature organic polymers are in great demand due to the increasing need of such materials in aerospace applications as adhesives, sealant and coatings, and as matrix resins for fibre-reinforced composites. For such applications in hostile environments, it is specially desirable to have materials with improved resistance to moisture pick-up and chemical degradation and with better storage stability than the currently available epoxies. In recent years, research efforts at the Naval Research Laboratory have led to the development of a series of new resin systems called phthalocyanines that seem to provide these desired features [1, 2]. Briefly, 4–aminophthalonitrile is reacted with aliphatic diacid cholorides to form resin monomers having a diamide structure. Polymerization takes place via a "B" stage and a post-cure to develop stable phthalocyanine nuclei linked through aliphatic diamide linkages. These materials exhibited high temperature stability up to 245° C, and have the potential for advanced aerospace applications. The resin monomers and prepolymers are virtually inert at room temperatures for easy handling, in contrast with the cold storage requirements for epoxies and thermosetting polyimides. Furthermore, the monomers represent chemically simple and pure systems for easy quality control when compared with the complex formulations of conventional epoxies [3]. In this report, the dynamic mechanical properties and the fracture behaviour of a series of phthalocyanine polymers will be presented.

2. Experimental procedure

2.1. Resin monomers

The chemistry of resin synthesis and polymerization has been discussed elsewhere [1, 2]. Phthalocyanine cure behaviour was also examined [4]. In this study, four monomers were used which represented a systematic variation of the flexibility of molecular segments between phthalocyanine nuclei. These resins were designated as:

"C-6 Methyl diamide", or N,N′-bis(3,4) dicyanophenyl) 3-methylhexanediamide.

"C-10 diamide", N,N′-bis(3,4-dicyanophenyl) decanediamide.

"C-22 diamide", N,N′-bis(3,4-dicyanophenyl) docosanediamide.

"C-36 diamide", based on the EMPOL 1010 dimer acid of Emery Industries, Inc.

Resins were cured in an air-circulating oven by heating at temperatures above the resin melting temperatures. The resins melted to give a deep green viscous liquid and finally a black solid on continued heating.

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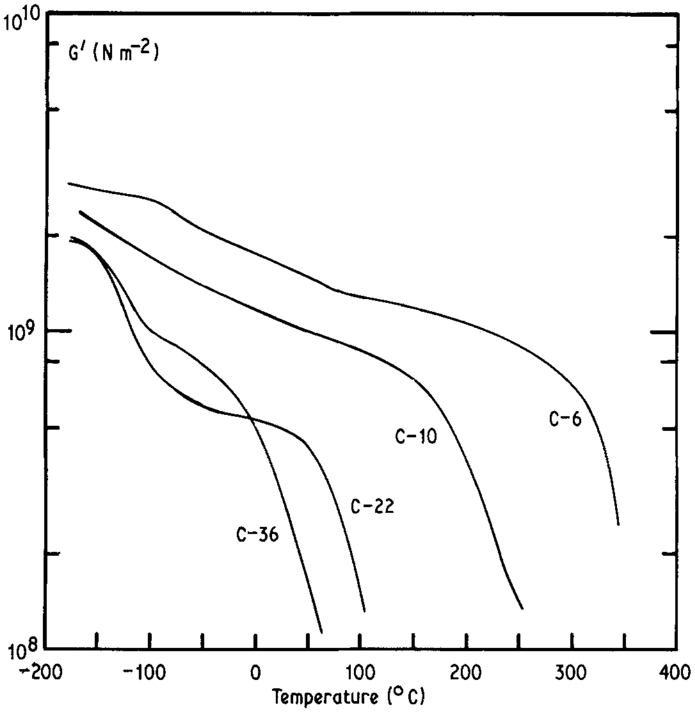

Figure 1 Dynamic shear modulus as a function of temperature for 1–day/220° C cured phthalocyanines, (C–36 resin cured 3 days).

2.2. Torsion pendulum analysis (TPA)

A freely oscillating torsion pendulum [5] operating at circa 1 Hz was used for all dynamic mechanical measurements. The experiments were carried out in a nitrogen atmosphere in accordance with the recommended ASTM procedure, D–2236–70. The sample size was 10 × 1.25 × 0.075 cm^3. The frequency of the freely damped wave and the logarithmic decrement $\Delta = \ln (A_i/A_{i+1})$, where A_i was the amplitude of the *i*th oscillation of the wave, were directly measured as the sample was heated at a rate of 1° C min^{-1}. These parameters led to the determination of the dynamic shear modulus and the loss factor of the sample as a function of temperature.

2.3. Fracture toughness evaluation

Sample fracture thoughness was determined by using standard one-inch compact tension specimens [6]. A precrack was introduced at the end of the saw-cut with a razor blade. Specimens were fractured in an Instron testing machine at a cross-head speed of 0.125 cm min^{-1} to measure the critical failure load, P_c. Polymer fracture energy was determined by using the equation [7]

$$\mathscr{G}_{\mathrm{I_c}} = Y^2 P_c^2\, a/\bar{W}^2\, b^2 E \qquad (1)$$

where $Y = Y(a/\bar{W})$ is a geometrical factor given as

$$Y = 29.6 - 186(a/\bar{W}) + 656(a/\bar{W})^2 - 1017(a/\bar{W})^3 + 639(a/\bar{W})^4 \qquad (2)$$

and a is the crack length, $\bar{W}$ the specimen width, b the specimen thickness, and E the Young's modulus.

The resins were also evaluated for their adhesive fracture toughness using double-tapered cantilever beam specimens, based on the method developed by Mosotovoy and Riplin [8]. Resins were applied to adhere two 5086 aluminum half-beams together with a bond thickness of 0.025 cm. After heat curing, the specimens were tested at room temperature in the Instron to detemined the fracture load P_c. Adhesive fracture energy was then calculated using the equation [8]

$$\mathscr{G}_{\mathrm{I_c}} = \frac{4P_c^2}{b^2E}\left(\frac{3a^2}{h^2} + \frac{1}{h}\right) \qquad (3)$$

where h is the beam height measured normal to the crack tip, and E in this case the Young's modulus for aluminum. The advantage of this specimen geometry is that the quantity in the bracket is a constant depending on the taper, and therefore $\mathscr{G}_{\mathrm{I_c}}$ becomes independent of the crack length, a. All adhesive fractures were centre-of-bond, so the measured fracture energy is the cohesive $\mathscr{G}_{\mathrm{I_c}}$ of the resin.

3. Results and discussion

Fig. 1 shows the effect of interaromatic molecular chain length on the dynamic shear modulus, G', of phthalocyanines cured at 220° C for one day,

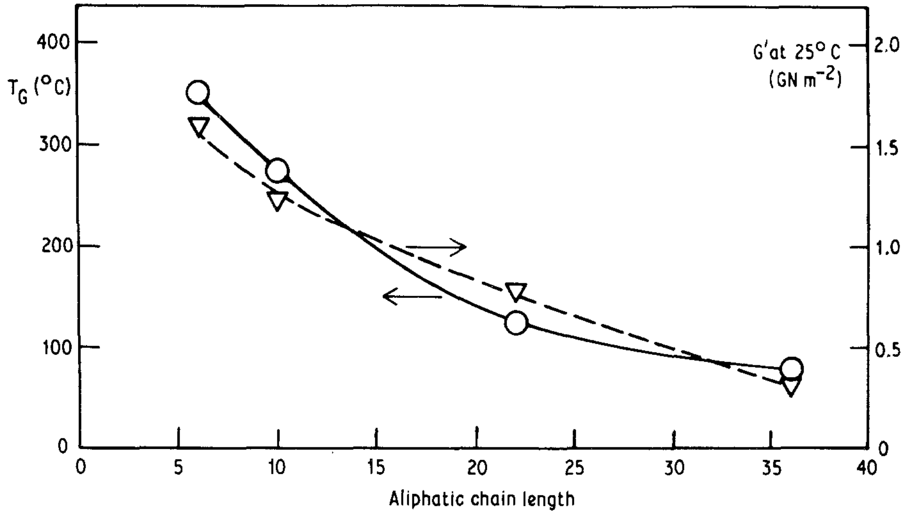

Figure 2 Glass transition and room-temperature shear modulus as functions of aliphatic chain length in number of carbon units.

(one exception was for the C–36 diamide resin which required a 3-day cure). As the length of the interaromatic chain linkage is reduced from 36 carbon atoms (C–36) to six carbon atoms (C–6), the polymer network became less flexible, and a progressive increase in both the shear modulus and the glass-to-rubber transition temperature, T_g, was observed. In a modulus–temperature plot, such as Fig. 1, the curves therefore systematically shifted toward the upper-right. During a TPA run, a temperature scan covering the complete glass-to-rubber transition could not be achieved because the sample softened as T_g was approached. Therefore, in this study T_g was estimated as the temperature where the dynamic shear modulus decreased rapidly with increasing temperature. This was usually the point where the TPA experiment has to be terminated. A plot of T_g and the room temperature shear modulus as a function of the aliphatic chain length is shown in Fig. 2. The number of carbon atoms in the diacid used to prepare the phthalocyanine resins is used here as an index of segmental molecular flexibility. The glass transition temperature decreases from 350° C for the C–6 phthalocyanine to 90° C for the C–36 compound. A similar decreasing trend of shear modulus with increasing polymer molecular flexibility is also observed.

Figs. 3 and 4 show some of the effect of post-cure on the dynamic mechnical properties of the C–10 phthalocyanine. When extended cure was carried out at 220° C for 5 days, it was found that the shear modulus remained the same as that of the sample with initial 1–day/220° C cure up to –25° C. Above this temperature an increase in modulus accompanied by an increase in T_g was observed. With a 10–day post-cure at 220° C, an overall increase in modulus for the C–10 phthalocyanine was found over the entire TPA temperature range, indicative of further crosslinking taking place. The glass transition temperature in this case reached 350° C. The dynamic loss curve for the C–10 phthalocyanine in Fig. 3 shows two low-temperature relaxation peaks: one at –130° C and the other at –60° C. These two relaxation processes seemed to be unaffected by the additional thermal treatment at 220° C. The origins of the relaxations have been examined by Gillham [9], who attributed the peak at –130° C to molecular motions of the amide linkages as well as the alkyl chain between them. The relaxation peak at –60° C was believed to be an induced water transition caused by absorbed water.

In Fig. 4, for a sample post-cured at 240° C for five days, the intensities of the low-temperature relaxation peaks were reversed. This indicated that the two relaxation processes were strongly coupled, showing that there were only a limited number of sites for interaction with water bonding to polar groups. Furthermore, a new relaxation peak appeared at about 100° C as a result of the 240° C post-cure. The origin of this relaxation is still unknown. Increases in shear modulus and glass transition temperature were similar to those

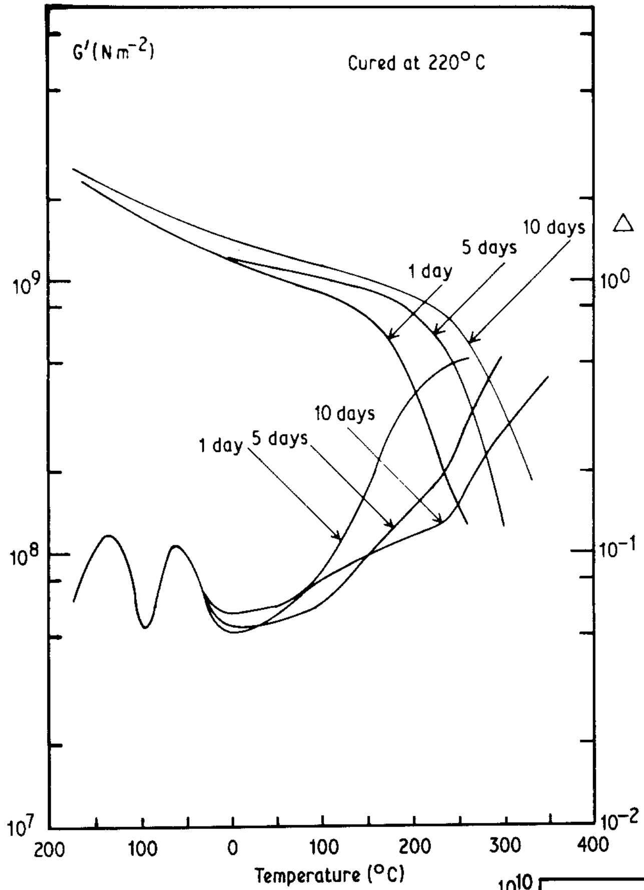

Figure 3 Effect of 220° C post-cure on the dynamic mechanical spectrum of C–10 phthalocyanine.

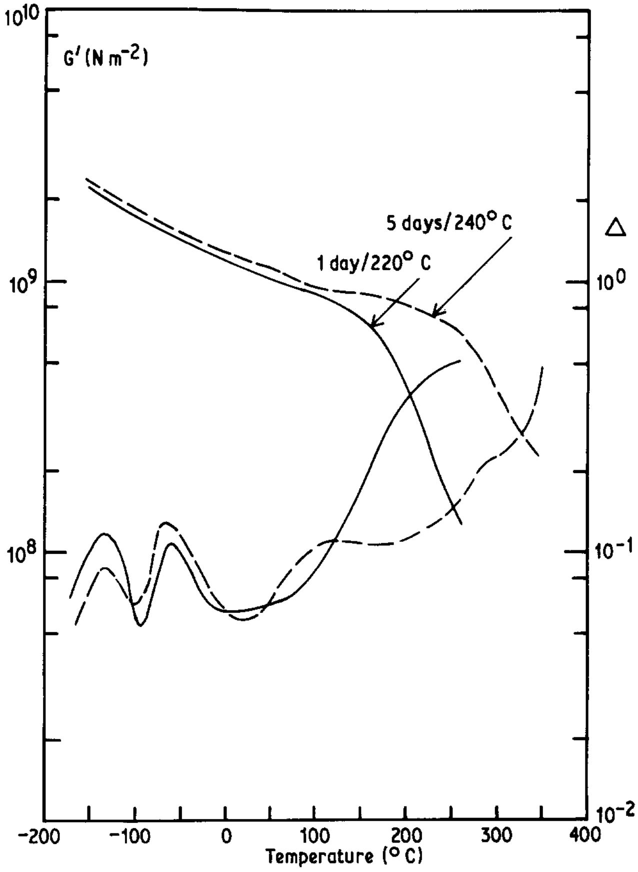

Figure 4 Effect of 240° C post-cure on the dynamic mechanical spectrum of C–10 phthalocyanine.

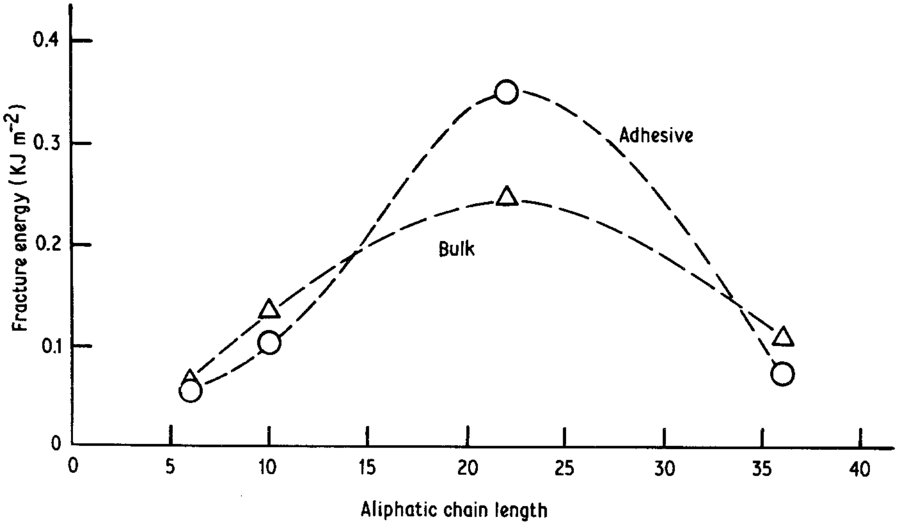

Figure 5 Effect of aliphatic chain length on the fracture energy of phthalocyanines.

found in the 10–day/220° C cured sample. No further change was observed when sample was post-cured at 240° C up to 10 days.

The results of the fracture evaluation is given in Fig. 5, where both the bulk and the adhesive fracture energy are plotted as functions of the aliphatic carbon chain length. The fracture energy increased initially with molecular flexibility as the interaromatic chain length increases from 6 to 22 carbon atoms. But, for the C–36 phthalocyanine polymer, the fracture energy was reduced. Originally it was expected that the C–36 diamide monomer, having a much longer interaromatic chain, would provide enhanced molecular flexibility and hence lead to a polymer with improved fracture toughness. However, as indicated earlier, the C–36 diamide was synthesized from the EMPOL 1010 dimer acid, which was produced by polymerization of unsaturated C–18 acids. Essentially the dimer acid is a long chain dicarboxylic with two alkyl side chains near the midpoint. This structure, although capable of entanglement and crosslinking upon cure, may reduce the free movement of the interaromatic carbon chain. Further-

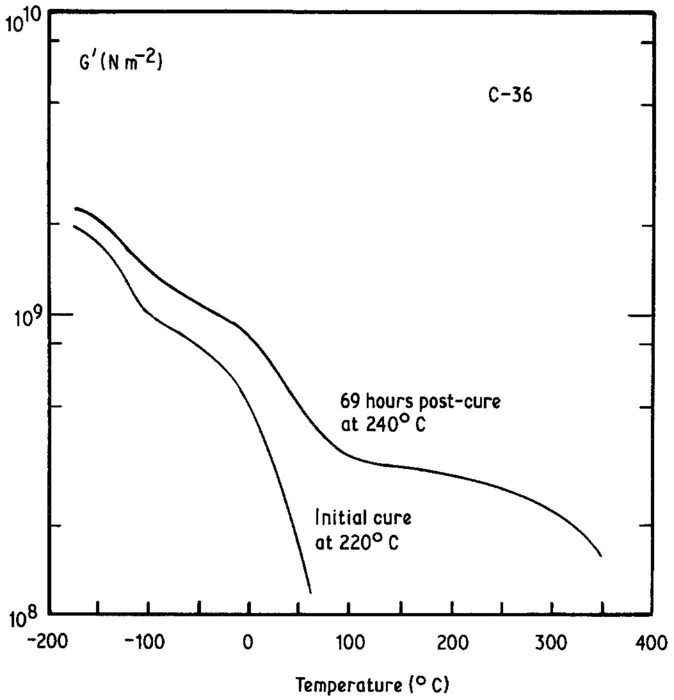

Figure 6 Effect of 240° C post-cure on the dynamic shear modulus of C–36 polyphthalocyanine.

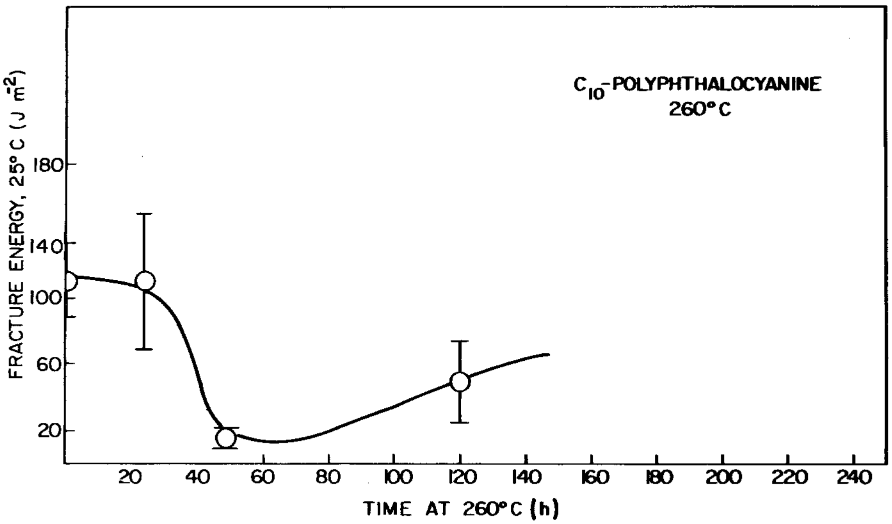

Figure 7 Effect of 260° C post-cure on the fracture energy of C–10 polyphthalocyanine.

more, the C–36 diamide was a liquid at room temperatures and an extended cure was needed in order to obtain a glassy polymer with reasonable modulus values for structural applications, (see Fig. 1). Such a thermal treatment clearly increased the crosslink density as manifested by the high shear modulus (~ $10^9\,\mathrm{N\,m^{-2}}$). But, at the same time, it reduced the capacity for plastic deformation in the polymer network, as reflected by the substantially low fracture energy value. Further cure of the C– 36 phthalocyanine sample at 240° C for 69 hours led to a polymer with $T_g \sim 320°$ C accompanied by increases in dynamic shear modulus, (see Fig. 6). Nevertheless, this treatment only caused the adhesive fracture energy to decrease to $25\,\mathrm{J\,M^{-2}}$ from the $80\,\mathrm{J\,M^{-2}}$ value shown in Fig. 5.

This effect of post-cure on polymer fracture toughness was further examined by using the C–10 phthalocyanine resin. Compact tension specimens were thermally aged at 220° C, 240° C and 260° C and then tested at room temperature. The fracture results showed that heating at 220° C and 240° C had little affect on the fracture energy, at least up to 240 hours. However, heating the C–10 polymer at 260° C definitely had a detrimental effect on its room temperature $\mathscr{G}_{\mathrm{I_c}}$ value. Fig. 7 shows that a sharp decline in the fracture toughness took place between 24 and 48 hours. The compact tension specimens could not be tested after 240 hours at 260° C because large internal blisters had developed and the specimens puffed up into the shape of pillows. Evidently, a vapour was evolved at that temperature which was not able to escape from the interior but forced open an internal pocket. Differential scanning calorimetry results for the thermally aged sample revealed an exotherm attributable to additional curing of the polymer. TPA data also indicated a progressive increase in the glass transition temperature. These results clearly demonstrated that prolonged thermal treatment, although promoting crosslinking in thermosetting materials, would greatly embrittle the polymer, reducing its fracture toughness to a value characteristic of a ceramic or silicate glass (10 to $20\,\mathrm{J\,m^{-2}}$).

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