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13. ABSTRACT (Maximum 200 words) This is a summary of work performed in the late 1970's when author was employed in Code 6120, Naval Research Lab., Washington, DC 20375. This encyclopedia was put together by Dr. Stuart M. Lee, Editor, SAMPE Journal who invited author to prepare this article. The chemistry and mechanical properties of phthalocyanine resins were described. The structure-property relationship leads to the selection of C-10 resin for matrix application in fiber-reinforced composites. The development of C-10/graphite composites was briefly described, and composite properties were summarized.			
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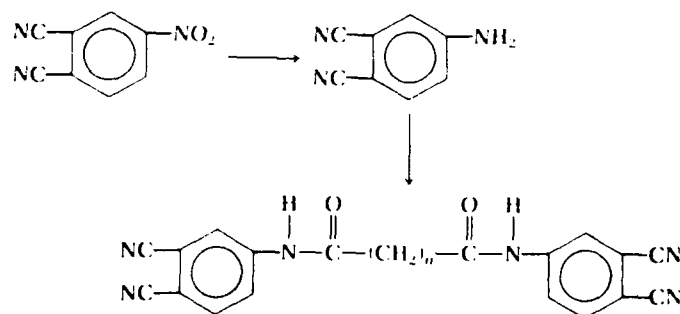
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(V/STOL) aircraft, many of the metallic structural components must be replaced with organic composites for weight-saving purposes in order to compensate for the large and heavy propulsive systems required for vertical lift. By incorporating the superior properties of fiber-reinforced composites, such as high strength-to-weight ratio and fatigue resistance, the designer may successfully develop a V/STOL aircraft with extended range and/or increased payload. The proposed design calls for a matrix resin that can meet operational temperatures in excess of 200°C. In addition, the resin needs to have a very low moisture sensitivity. Unfortunately, conventional epoxy resins can only offer a maximum use temperature of about 135°C, and the moisture absorption in these resins is normally quite high. The room temperature storage stability of the epoxies is also very poor.

In order to meet the requirement for a wide range of high temperature applications, such as adhesives, sealants, coatings, and matrix resins, research efforts of Griffith and coworkers [1,2] at the Chemistry Division, Naval Research Laboratory in the 1970s have led to the development of a new class of resins called phthalocyanines. These materials have been demonstrated to be promising candidates for advanced composite applications. In this article, the structure and properties of phthalocyanine resins will be discussed. The development of a selected phthalocyanine resin for fiber-reinforced composites will also be described. Test results on the mechanical properties of composite samples will be presented and compared with those of other popular composite systems.

Material

The chemistry of phthalocyanine resin synthesis and polymerization was first reported by Griffith, O'Rear, and Walton [1]. Briefly, the reaction of 4-aminophthalonitrile with aliphatic diacid chlorides forms resin monomers that have a diamide structure:



Phthalocyanine Matrix Resins and Composites

Fiber-reinforced composite materials are being considered for many advanced structural applications in order to achieve a substantial weight saving in the structures. Many of these applications involve a high temperature requirement that cannot be met by conventional matrix resin systems such as epoxy. For instance, in the design of advanced vertical and short takeoff and landing

aircraft, many of the metallic structural components must be replaced with organic composites for weight-saving purposes in order to compensate for the large and heavy propulsive systems required for vertical lift. By incorporating the superior properties of fiber-reinforced composites, such as high strength-to-weight ratio and fatigue resistance, the designer may successfully develop a V/STOL aircraft with extended range and/or increased payload. The proposed design calls for a matrix resin that can meet operational temperatures in excess of 200°C. In addition, the resin needs to have a very low moisture sensitivity. Unfortunately, conventional epoxy resins can only offer a maximum use temperature of about 135°C, and the moisture absorption in these resins is normally quite high. The room temperature storage stability of the epoxies is also very poor.

Abbreviated names are used to identify these compounds. For example, if $n = 8$, the compound is called C-10 diamide because it was made from a diacid chloride containing 10 carbon atoms. Polymerization occurs upon thermal reaction of the diamide monomers at temperatures above their melting temperatures. The B stage and postcure at about 200°C lead to the development of

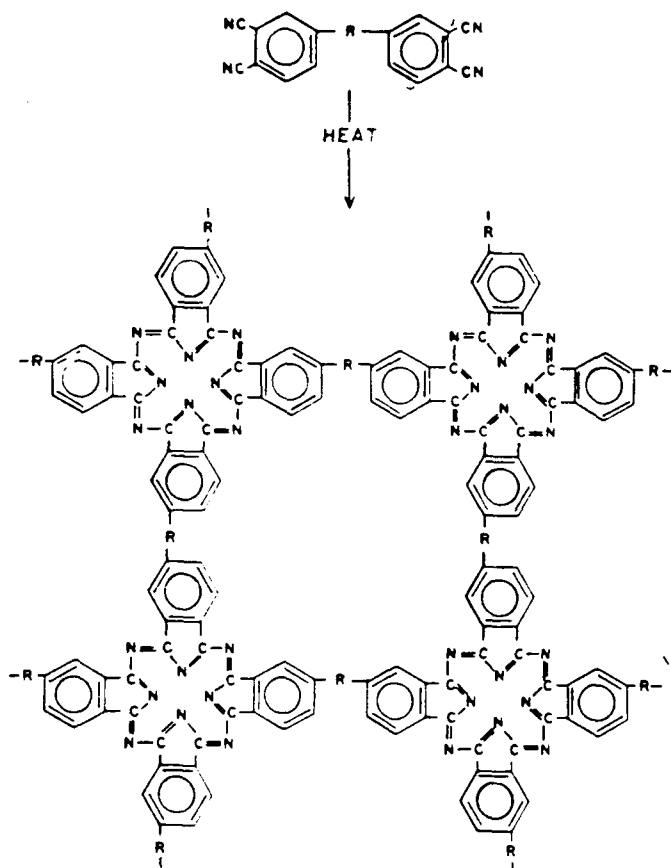


FIGURE 1 A schematic representation of the polymerization of phthalocyanine resins.

stable phthalocyanine nuclei linked through aliphatic diamide linkages. Figure 1 shows schematically the proposed phthalocyanine network structure. The figure suggests a two-dimensional network, but the more likely situation is a three-dimensional structure produced by numerous out-of-plane reactions of the phthalonitrile end groups.

Four resin monomers were developed to represent a systematic variation of the flexibility of molecular segments between phthalocyanine nuclei. They were designated as:

- C-6 methyl diamide, or *N,N'*-bis(3,4-dicyanophenyl)-3-methylhexanediamide
- C-10 diamide, or *N,N'*-bis(3,4-dicyanophenyl) decanediamide
- C-22 diamide, or *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. The compounds with short aliphatic chain lengths ($n \leq 8$) require

a high temperature cure, and thus offer high temperature stability up to 260°C [2]. 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 compared with the complex formulations of conventional epoxies [3].

Dynamic Mechanical Properties

A freely oscillating torsion pendulum [4] operating at approximately 1 Hz was used for 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 $10 \times 1.25 \times 0.075$ cm³. 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. Figure 2 shows the effect of interaromatic molecular chain length on the dynamic shear modulus G' of cured phthalocyanines. 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

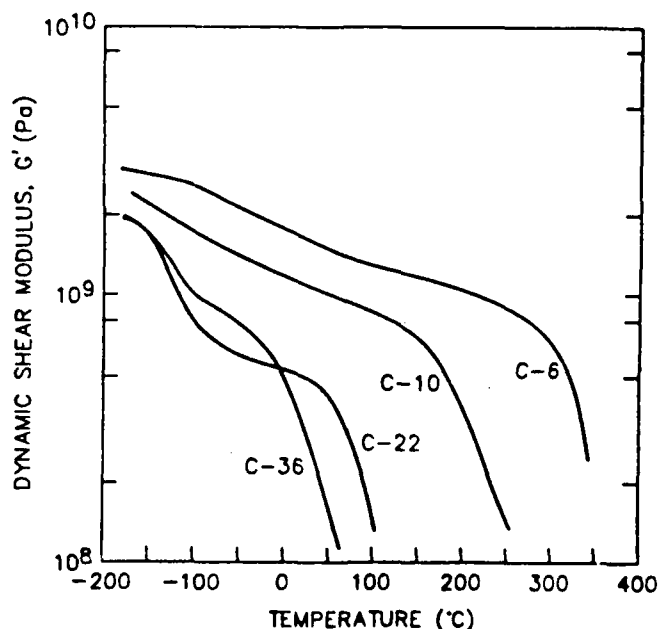


FIGURE 2 Dynamic shear modulus as a function of temperature for 1 day 220°C cured phthalocyanines (C-36 resin cured 3 days).

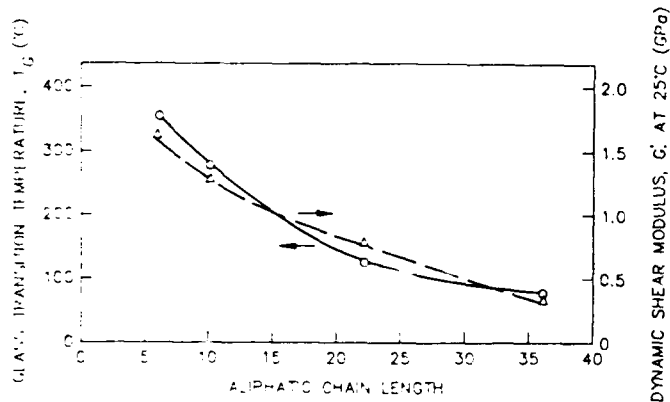


FIGURE 3 Glass transition temperature and room temperature shear modulus as functions of aliphatic chain length in number of carbon units.

T_g was observed. A plot of T_g , estimated as the temperature where the dynamic shear modulus decreased rapidly with increasing temperature, and the room temperature shear modulus as a function of the aliphatic chain length is shown in Figure 3. 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. An extended postcure at 220°C for 10 days led to an overall increase in modulus for the C-10 phthalocyanine, indicative of further cross-linking taking place. The glass transition temperature in this case reached 350°C. The dynamic loss curve shows two low temperature relaxation peaks, one at -130°C and the other at -60°C. The origins of the relaxations have been examined by Gillham [5], who attributed the peak at -130°C to molecular motions of the amide linkages as well as the alkyl chain between them. The small relaxation peak at -60°C was believed to be an induced water transition caused by absorbed water.

Fracture Toughness

It is recognized that structural composites and adhesives are relatively brittle and stiff materials [6]. Their failure mode is characterized by flaw growth from internal cracks and microvoids, which are inherently present as a result of the methods employed for processing the structural parts. The fracture toughness of the phthalocyanine resins was therefore of concern, and the evaluation of this property was carried out using standard compact tension specimens [7]. Polymer fracture energy was determined by the equation:

$$\mathcal{G}_i = \frac{Y^2 P_c^2 a}{W^2 b^2 E}$$

where $Y = Y(a/W)$ is a geometrical factor given as:

$$Y = 29.6 - 186 \left(\frac{a}{W} \right) + 656 \left(\frac{a}{W} \right)^2 - 1017 \left(\frac{a}{W} \right)^3 + 639 \left(\frac{a}{W} \right)^4$$

where a is the crack length, W the specimen width, b the specimen thickness, E the Young's modulus, and P_c the critical failure load. The resins were also evaluated for their adhesive fracture toughness using double-tapered cantilever beam specimens [8]. Adhesive fracture energy was calculated using the equation:

$$\mathcal{G}_i = \frac{4P_c^2}{b^2 E} \left[\frac{3a^2}{n^3} + \frac{1}{h} \right]$$

where h is the beam height measured normal to the crack tip, and E in this case is the Young's modulus for aluminum substrate. All adhesive fractures were center-of-bond, so the measured fracture energy is the cohesive \mathcal{G}_i of the resin.

The results of the fracture evaluation are given in Figure 4. The fracture energy initially increased with molecular flexibility as the interaromatic chain length increased from 6 to 22 carbon atoms. But, for the C-36 phthalocyanine polymer, the fracture energy was reduced. This unexpected reduction was believed to be due to the fact that 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, which is capable of entanglement and cross-linking upon cure, may reduce the free movement of the interaromatic carbon chain. Furthermore, the C-36 diamide was a liquid at room temperatures, and an extended cure was needed. The extended cure clearly reduced the capacity for plastic deformation in the polymer network. Similar reductions in the fracture toughness of the C-10 phthalocyanine were also observed when extended postcure was carried out [9]. The results clearly demonstrated that

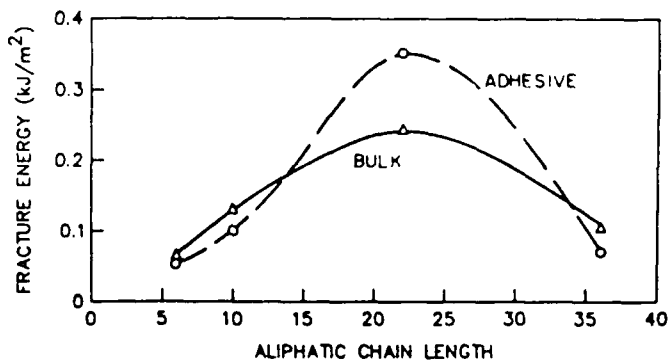


FIGURE 4 Effect of aliphatic chain length on the fracture energy of phthalocyanines.

TABLE 1
Properties of Composite Matrix Materials

Polymer	Fracture Toughness* (J/m ²)	Glass Transition Temperature (°C)
Tetrafunctional epoxy	82	160
Addition polyimide	104	260
C-10 phthalocyanine	110	280

* Room temperature test result

prolonged thermal treatment, although promoting cross-linking in phthalocyanines, would greatly embrittle the polymer, reducing its fracture toughness to a value characteristic of a ceramic or silicate glass (10–20 J·m⁻²). This observation has serious implications in the design of cure cycles for fiber-reinforced phthalocyanine composites and their high temperature use. Postcure cycles must be designed to achieve the desired good mechanical properties (i.e., strength, modulus, and so on) of the composites without adversely affecting their interlaminar fracture properties. Table 1 shows the fracture toughness and glass transition temperature of the C-10 resin in comparison with those of a tetrafunctional epoxy and an addition polyimide system.

Prepreg Preparation

The results in Figure 3 show that the glass transition temperature of the cured C-10 phthalocyanine is about 280°C. Its shear modulus remains fairly constant at the level of 1 GPa in the glassy state. Figure 3 thus suggests that if a resin is sought to meet operational requirements at temperatures in excess of 200°C, one is limited to resins with interaromatic chain length of no more than 14 carbon atoms. The C-10 diamide resin was therefore selected for study as a composite matrix resin. Thornel 300 graphite fibers (T-300, Union Carbide) with an UC-309 epoxy finish were selected for the preparation of unidirectional prepreg tapes in collaboration with commercial sources. Both the hot-melt prepregging and a resin-solvent slurry technique were demonstrated to be capable of successfully producing 30 cm wide prepreg taps. The hot-melt method yielded a product containing about 32% resin with less than 1% residual volatiles. On the other hand, the slurry technique using dimethylformamide as the solvent yielded an average resin content of about 40%. The final product also contained about 6% volatiles. When the resin was staged at about 200°C, the precured resin passed through a liquid intermediate state, and the fiber reinforcements were easily impregnated. As a result of the staging operation, the prepreg had a dark green color, and its general appearance was dry and brittle. However, the material could be briefly heated at 110°C to develop sufficient amounts of tack for easy layup.

Cure of C-10/T-300 Composites

Differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and dynamic dielectric analysis (DDA) were performed, and the thermal and dielectric analysis results were used for the development of cure cycles for C-10/T-300 composite samples. Typical DSC scans showed multiple endotherm peaks, which were related to the melting of resin oligomers of separate entities. The highest melting peak was at about 190°C, while no exotherm was evident up to 230°C. The TGA data for the prepreg sample showed a rapid weight loss beginning near 275°C. These results therefore defined the initial cure temperature "window" for the C-10/T-300 system to be above 230°C, but not to exceed 260°C. The DDA results showed that at temperatures within this "window," the prepregged resin quickly melted and polymerization of phthalocyanine was activated thermally. The gelation reaction followed an Arrhenius relationship with an activation energy of about 62.8 kJ/mole, higher than that reported for epoxy resins [10]. Hence, the cure of C-10 phthalocyanine would require higher temperatures and longer times than that of the epoxies. The final cure cycle developed included heating the samples under pressure at 250°C for over 3 hours. The details of the development were given in Ref. 11. The postcure requirement was established to be 245°C for 72 hours.

Prepreg Aging

A 28 week prepreg aging study was carried out by exposing the prepreg materials at room temperature in two separate environmental chambers, controlled at 16 and 95% relative humidity, respectively. At the end of every 4 week period, sufficient material was removed to fabricate a 16-ply laminate and its flexural and shear properties were evaluated. The short beam shear strength of unidirectional C-10/T-300 composites, a resin-dominated property, was found to remain unchanged over the 28 week period. This result suggested that room temperature aging had caused no chemical degradation in the C-10 phthalocyanine resin. Further results from chemical analysis indeed confirmed this [12]. This observation is in contrast to a similar aging study previously carried out for polyimide-graphite prepregs, in which room temperature aging was shown to greatly affect the processibility and, consequently, the laminate mechanical properties of that material [13].

Mechanical Properties of Composites

Sixteen-ply angle plies consisted of the orientations of $\pm 15^\circ$ and $\pm 45^\circ$, and quasi-isotropic laminates (90° , $\pm 45^\circ$, 0°) were prepared. Tensile tests were carried out using $10 \times 1.25 \times 0.2$ cm specimens. For angle plies, the specimens were machined in such a way that the loading direction bisected the included angle between fiber orientations. A three-point flexural test was also performed in accordance with ASTM-D730.

TABLE 2
Laminate Mechanical Properties at Room Temperature

Orientation	Property (GPa)	5208/T-300	F-178/T-300	C-10/T-300
Quasi-isotropic	Strength: tensile	0.48	0.39	0.47
	flexural	—	0.52	0.46
	Modulus: tensile	48.3	62.8	75.2
	flexural	—	37.3	33.8
$2\theta = 30^\circ$	Strength: tensile	0.75	0.61	0.56
	flexural	1.03	0.81	0.66
	Modulus: tensile	104.9	97.3	93.2
	flexural	107.0	91.1	75.2
$2\theta = 90^\circ$	Strength: tensile	0.16	0.13	0.11
	flexural	—	0.28	0.18
	Modulus: tensile	26.9	40.7	37.3
	flexural	—	17.3	9.7
$2\theta = 150^\circ$	Strength: tensile	0.041	0.035	0.031
	Modulus: tensile	10.4	26.2	22.8

All test results are given in Table 2, where the data for the Narmco 5208/T-300 (epoxy-graphite) and Hexcel F-178/T-300 (polyimide-graphite) composites are also included. It can be seen that the C-10/T-300 system exhibited tensile and flexural moduli similar to those of the F-178/T-300 material. In all cases, the 5208/T-300 showed higher strength than the F-178/T-300 and C-10/T-300 samples, particularly when the fiber orientation was $2\theta = 30^\circ$. The tensile moduli of angle-ply laminates were plotted as a function of the included angle in Figure 5 to show the strong dependence on fiber orientation. For small θ , the tensile properties are dominated by the fiber strength. As the included angle increases, the role of the matrix becomes increasingly important in its contribution to the distribution of the load. In those cases, the data clearly showed that the three composite systems were similar. For the popular quasi-isotropic design of

laminates, the C-10/T-300 composite exhibited good strength properties, with an even higher tensile modulus than the other two systems. The fracture behavior of the C-10/T-300 laminates under complex in-plane loading has also been studied [14]. The onset of crack propagation under various combinations of in-plane loading conditions was determined both at room temperature and at 232°C . The results again showed that the C-10/T-300 composites exhibited a similar performance in both cases to the epoxy and polyimide systems. Physical characterization of the laminates showed that all laminate thicknesses were in the range of 0.0125–0.014 cm/ply. The resin contents ranged from about 30% for the 5208/T-300 laminates to approximately 38% for the C-10/T-300 and the F-178/T-300 laminates.

Concluding Remarks

The C-10 phthalocyanine resin has been demonstrated to be a potential matrix material for advanced composites. This polymer exhibited long-term stability at temperatures up to 245°C , and its moisture uptake is less than that in epoxies or polyimides [1]. The phthalocyanine reaction can be induced to proceed simply by heating the resin at temperatures above the melting temperature without any curing agent or catalyst. The resin monomer represents a chemically simple and pure system for easy quality control when compared with the complex formulations of other systems such as epoxies. The resin monomers and prepolymers are also virtually inert at room temperature, so that no cold storage is required. Upon melting, the resin flows readily, and successful prepregging has been demonstrated. The processibility of C-10 phthalocyanine was comparable to that of conventional epoxies, but at higher temperatures. The processing was also shown to be unaffected by room temperature aging of the prepregs of up to 28 weeks. Mechanical properties have been determined in both

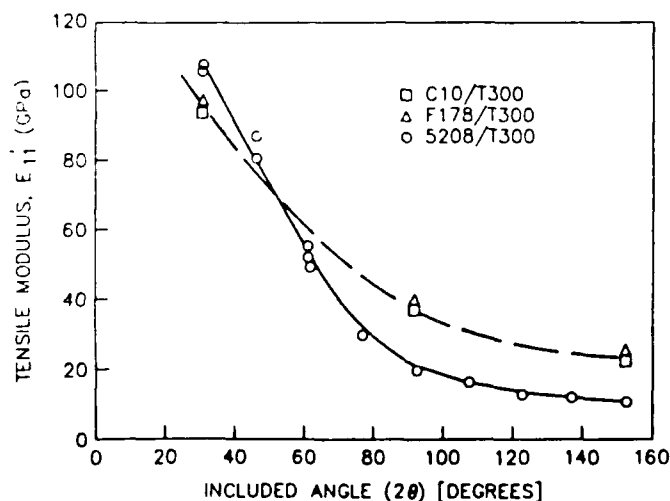


FIGURE 5 Laminate tensile modulus as a function of fiber included angle.

tensile and flexural tests for the C-10/T-300 system. The results were compared with those of the 5208/T-300 and the F-178/T-300 composites to show that the C-10/T-300 samples exhibited similar properties.

Robert Y. Ting

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