

AN IMPROVED PROCESSIBLE ACETYLENE-TERMINATED POLYIMIDE
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HR600P is the newest member of a family of thermosetting acetylene-substituted polyimide oligomers. This oligomer is the isoimide version of the oligomer known as HR600P and Thermid 600.* Although both types of material yield the same heat resistant end products after cure, HR600P has much superior processing characteristics. This is attributed to its lower melting temperature ($160 \pm 10^\circ\text{C}$, $320 \pm 20^\circ\text{F}$) in contrast to 202°C (396°F) for Thermid MC-600, its longer gel time at its processing temperature (16-30 minutes vs 3 minutes), and its excellent solubility in low boiling solvents such as tetrahydrofuran, glymes, or 4:1 methyl ethyl ketone/toluene mixtures. These advantages provide more acceptable coating and impregnation procedures, allow for more complete removal at lower temperatures, provide a longer pot life or working time, and allow composite structure fabrication in conventional autoclaves used for epoxy composite curing. The excellent processing characteristics of HR600P allow its use in large area laminated structures, structural composites, and molding compositions. The HR600P and HR60XP, where X is the degree of polymerization of the oligomer, materials will be produced in the future by National Starch and Chemical Company, Bridgewater, New Jersey.

DISCUSSION

In 1961, research was initiated, under U.S. Air Force Material Laboratory sponsorship (reference 1), aimed at the development of high temperature resins for composites which cure by addition reactions. A unique system of resins was developed based on the homopolymerization of an acetylene end group by heat alone. These oligomers were difunctional acetylene-terminated polyimides, sufficiently low in molecular weight and having the necessary structural features to impart solubility and fusibility during their processing.

Polyimides in general tend to be insoluble, intractable materials. Even as low molecular weight prepolymers special consideration had to be given to the polymer backbone to impart fusibility and solubility to the acetylene-terminated polyimide prepolymer. Numerous combinations of aryldiamines, difunctional aromatic acid anhydrides and 3-aminophenylacetylene finally gave a composition of an oligomer depicted by Figure 1 which had reasonably good processibility.

*Gulf Oil Chemical Company Trade Mark

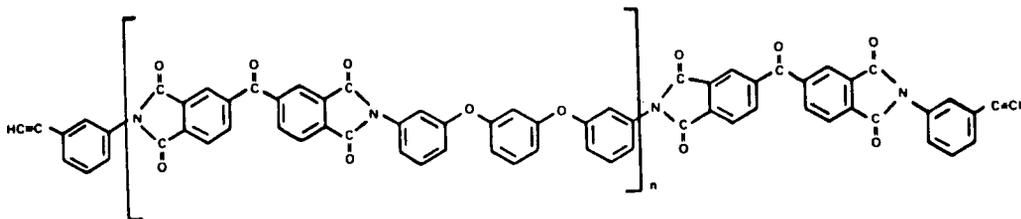


Figure 1. Specific designations: Thermid 600 when $n = 1$,
HR-60X when $n = X$.

This oligomer was prepared by the reaction of benzophenonetetracarboxylic dianhydride (BTDA), 1,3-bis(3-aminophenoxy)benzene (APB) and 3-aminophenylacetylene (APA) in molar ratios of 2:1:2. By varying the molar ratio of the reactants, the value of n , also called the degree of polymerization DP, could be varied. The oligomer with a DP of one was found to be very promising both as a molding and as a matrix resin and was initially licensed to Gulf Oil Chemical Company and marketed under the trade name Thermid 600. It has found utility as matrix resin for glass and graphite reinforced composites, chopped graphite reinforced molding compounds, adhesives for titanium, self-lubricating composites, bearing retainers, adhesives for other polyimides such as Kapton, and matrix resin for printed wiring boards. Thermid 600 has the proven ability to meet both long term (under 550°F) and short term exposure (over 550°F) with minimal degradation of mechanical properties. In the past, these resins have had limited acceptability because their high melting point and rapid cure allow a very limited time at viscosities acceptable for processing.

Also, the resins have a relatively limited solubility in common solvents. The processing window becomes even smaller with higher DP oligomers. In the past, a number of approaches have been tried to improve the processibility of these oligomers. For example, the incorporation of acetylene-terminated reactive diluents met with limited success because of the lack of mutual solubility of the oligomer and diluent.

A new approach was tried several years ago to improve the processibility of these oligomers. It was found that, under specific conditions, an isomeric form of these oligomers can be made which has a lower melting temperature and is soluble in a wide variety of common solvents when compared to the imides. This isomeric form is the iminolactone or isoimide form and is depicted by the structure shown in Figure 2.

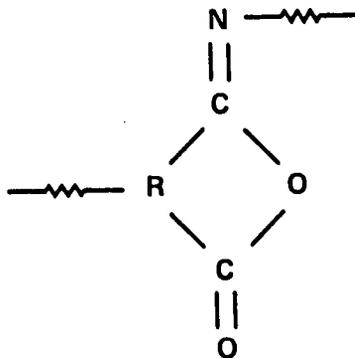


Figure 2. - Isoimide form of oligomer.

This structure is metastable and readily converts irreversibly to the imide form, either by heat or by catalysis. There are numerous references in the literature to this phenomenon (reference 2 and 3). The formation of the isoimide structure is through the cyclodehydration of the amic acid precursor by selected dehydrating agents. Thus, depending upon the cyclodehydration method used, the imide or isoimide structure is formed. This is depicted in Figure 3.

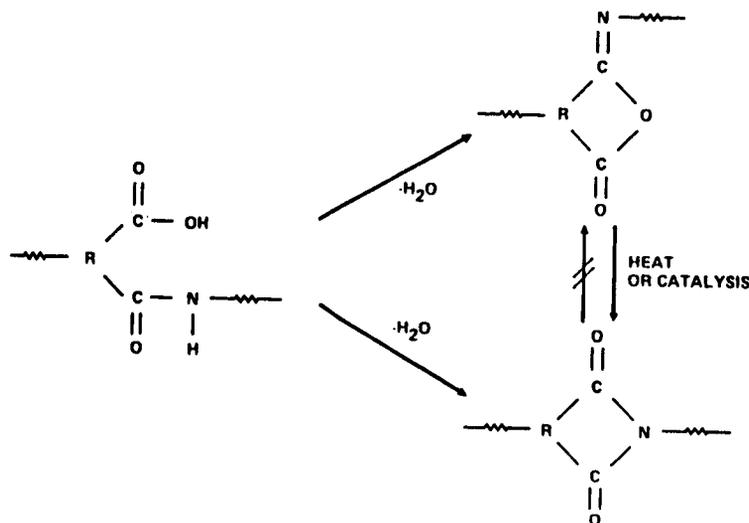


Figure 3. - Imide-Isoimide formation and conversion.

Because of the number of isomers possible for the isoimide compared to the imide and due to its asymmetry, the isoimide version of the Thermid 600 is known as HR600P oligomer. It is prepared by chemical rather than thermal cyclodehydration of the amic acid precursor. Generally, the HR600P has an isoimide content greater than 80 percent. The theoretical structure is depicted in Figure 4.

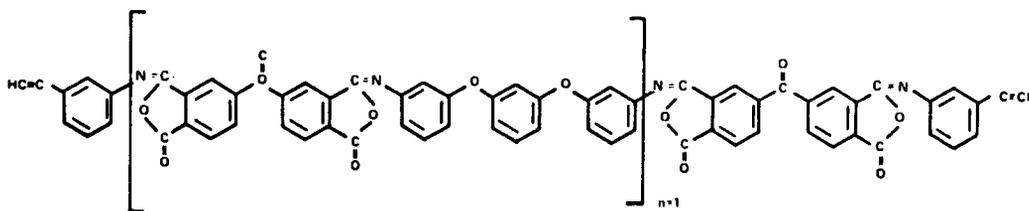


Figure 4. - HR600P Acetylene-terminated polyisoimide oligomer.

The spectrum for the imide form is depicted in Figure 5 and that of the isoimide version in Figure 6. The I.R. spectrum of the imide form shows the expected C=O (sym 1707-1730 cm^{-1} , asym 1776-1794 cm^{-1}). The I.R. spectrum of the isoimide shows C=O at 1789-1841 cm^{-1} , C=N at 1680-1730 cm^{-1} , and a characteristic broad band base at 900-950 cm^{-1} which can be attributed to the lactone ring with an exo-double bond.

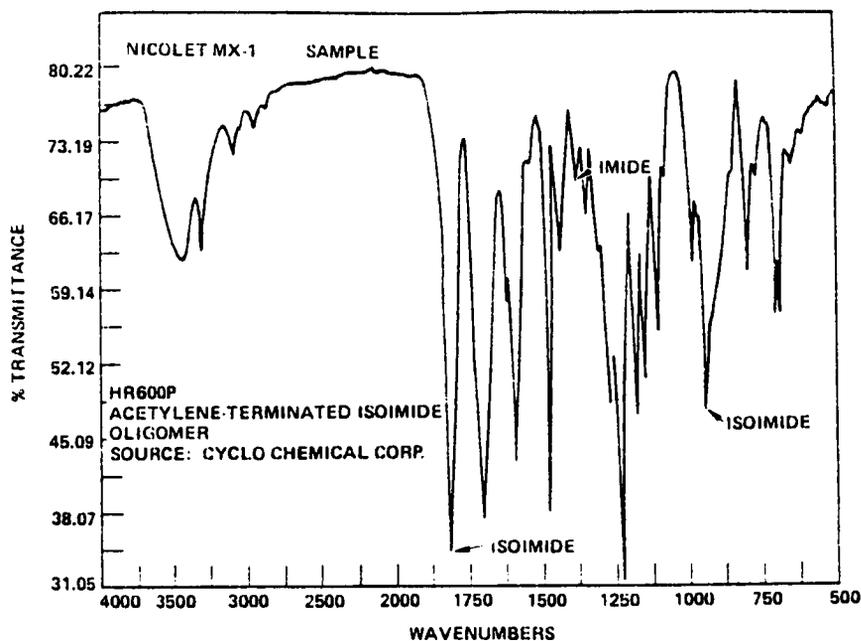


Figure 5. - HR600P Acetylene-terminated isoimide oligomer.

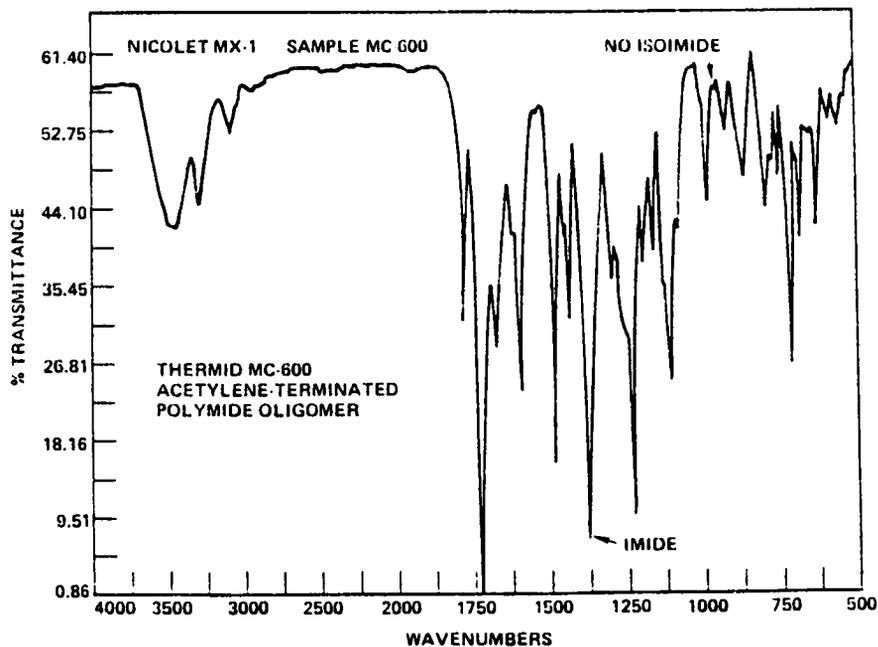


Figure 6. - Thermid MC-acetylene-terminated polyimide oligomer.

A study reported in the literature with N-substituted phthaloisimide, Figure 7,

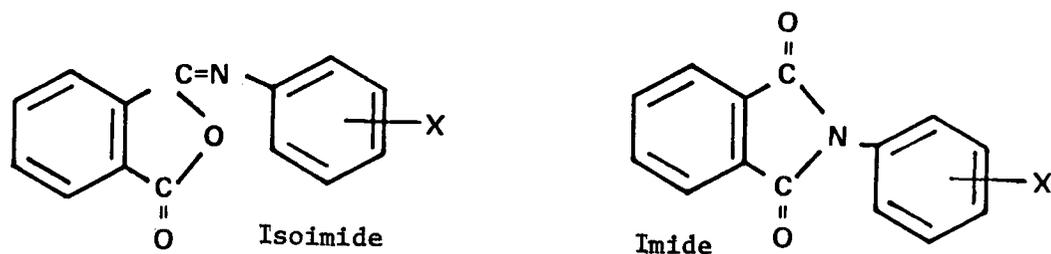


Figure 7. - Configurations of isoimide and imide forms of N-substituted phthaloisimide.

shows a significant difference in melting point of the isoimide form over that of the imide. Table I depicts this difference. The dramatic decrease in melting point is very significant. Also, the solubility of the isoimide form in a number of common solvents in which the imide version is sparingly soluble is greatly increased.

TABLE I - Melting Points Of Comparable Imides and Isoimides (reference 3)

N-Substituted Phthaloisimide	M.P. °C	
	Imide	Isoimide
C ₆ H ₅ -	207-8	110-2
o-CH ₃ C ₆ H ₄ -	180-1	135-6
p-CH ₃ OC ₆ H ₄ -	203-4	112-4
o-CH ₃ OC ₆ H ₄ -	158-9	116-7

The structure of the acetylene-terminated isomeric oligomers differs from that of the corresponding imide oligomers only in the arrangement of atoms in the functional heterocycle formed. Thus, the preparation of both oligomers requires the same stoichiometry of the reacting monomers but different reaction conditions. The acetylene-terminated polyisoimide analogous to Thermid MC-600, and having a degree of polymerization of 1 (DP=1), is referred to as HR600P in this discussion. The DP and DP_x materials are referred to as HR602P and HR60XP, respectively. The HR600P oligomer melts at about 150-160°C, whereas Thermid MC-600 melts at 195-205°C. Also, HR600P has excellent solubility in such solvents as tetrahydrofuran, glyme, N,N-dimethylacetamide, N-methylpyrrolidone and other amide or ketone solvents.

Upon heating and curing the HR600P converts to a thermally and oxidatively stable polymer having good physical properties. Figure 8 compares the infra-red spectra of molded and cured specimens of HR600P and MC-600. The similarity of the spectra is striking. The enhanced processibility permits the use of a wider range of DP's than has been possible with acetylene-terminated polyimides. Oligomers with high DP's are still very processible and have been particularly useful for coatings where flexibility and toughness are important. The fabrication of good quality composites using conventional autoclaving techniques (starting with a cold mold and curing at moderate temperatures) has been demonstrated. Sharp angular shapes were molded from graphite fiber composites. Such shapes are very difficult to produce with other high performance polyimides.

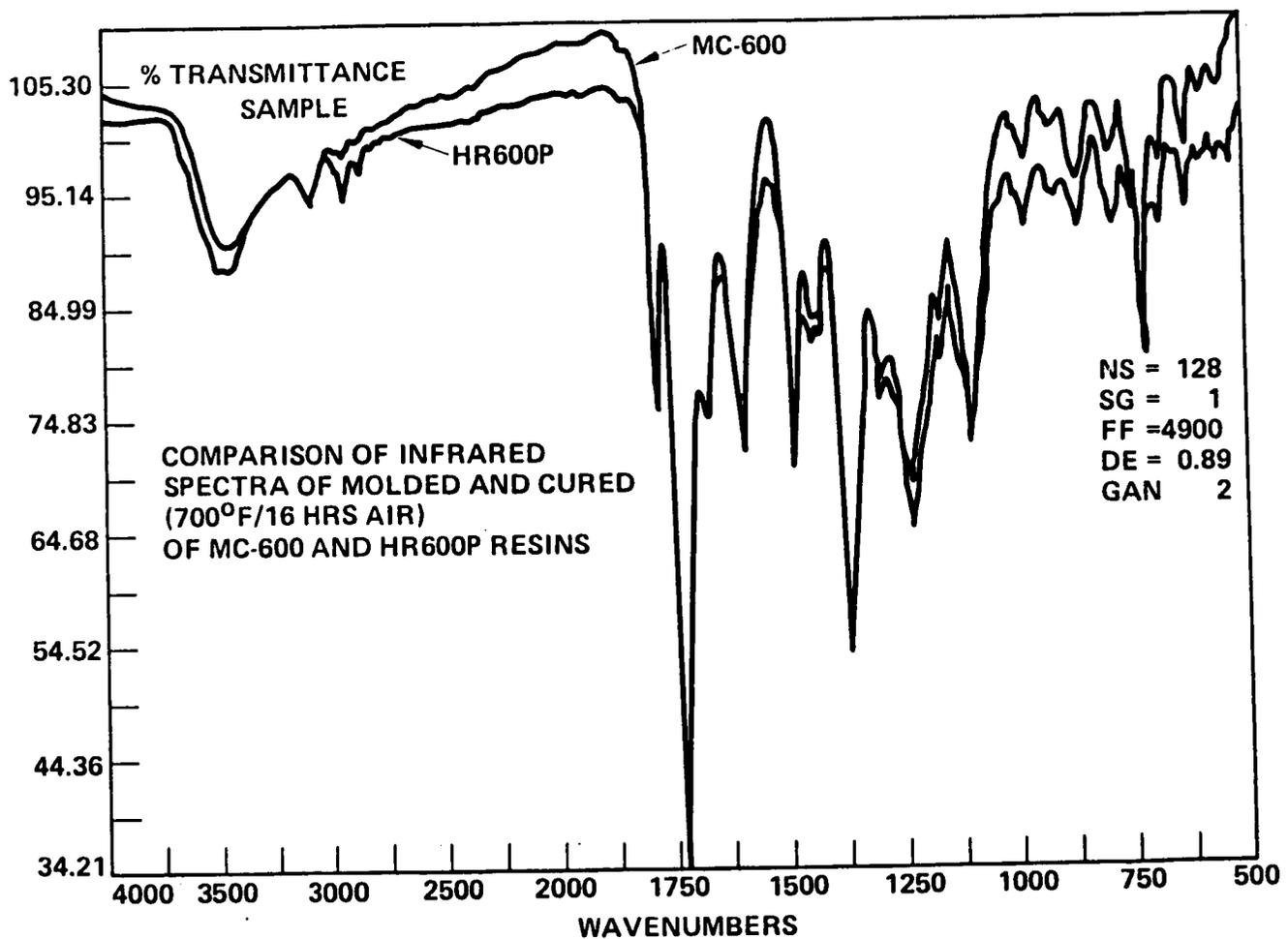


Figure 8. - Comparison of infrared spectra of molded and cured (700 °F/16 hrs air) of MC-600 and HR600P resins.

Properties and Processibility of HR60XP Oligomers

The uncured resin is a dry, free flowing, yellow powder. Its properties are shown in Table II.

TABLE II - Properties of HR600P

Melting Range	320 ± 20°F (160 ± 10°C)
Gel Time (see Figure 9)	<p>Traditional Method</p> <p>6-7 minutes @ 190°C 6 minutes @ 218°C</p> <p>Rheometrics</p> <p>30 minutes @ 190°C 8 minutes @ 210°C</p>
Solubility	<p>tetrahydrofuran dimethylformamide 4:1 methyl ethyl ketone/toluene N-methylpyrrolidinone Cellosolve</p>
Molecular Weight	<p>M_w ~ 2600 M_n ~ 1100</p>
Viscosity (Rheometric)	<p><u>Minimum</u> 2.3 x 10⁴ poise @ 190°C 3.6 x 10³ poise @ 210°C <u>Time to reach 10⁵ poise</u> 8 minutes @ 190°C 8 minutes @ 210°C</p>

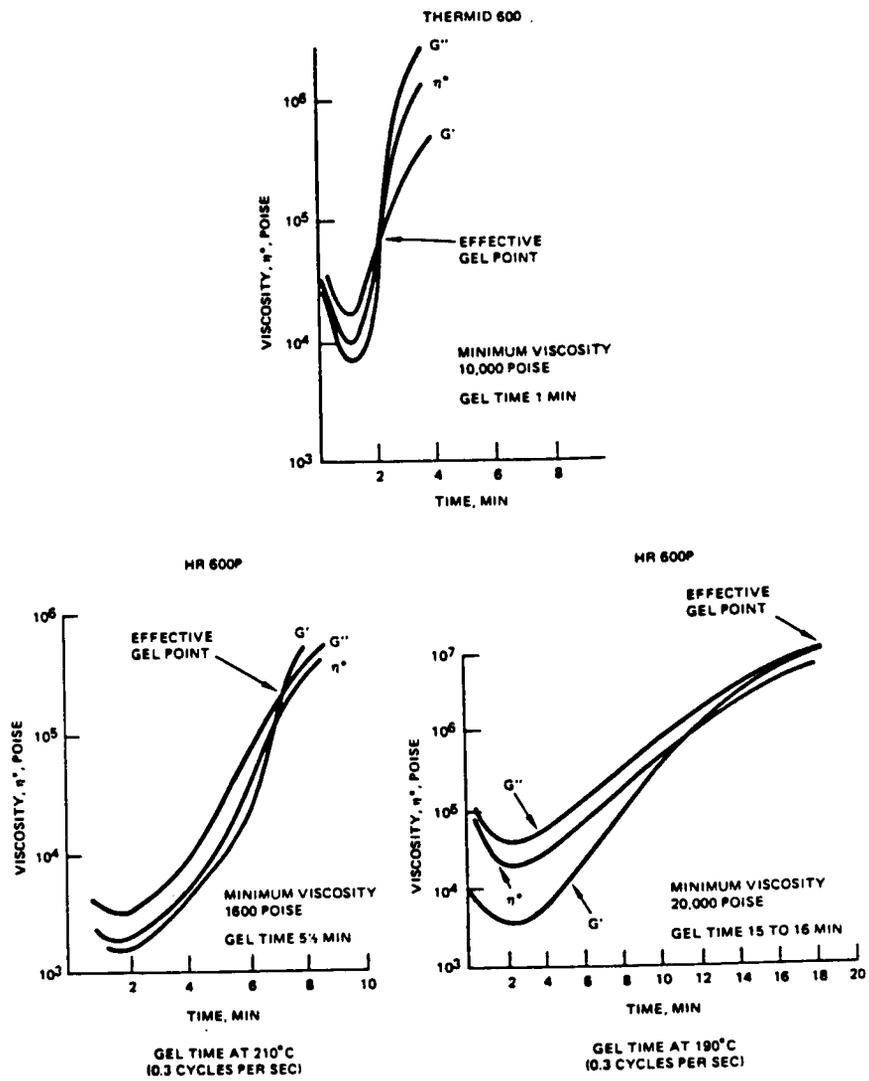


Figure 9. - Gel times of Thermid 600 and HR600P.

Figure 10 depicts a comparison of the differential scanning calorimetric curves (DSC) for HR600P and Thermid MC-600. The increase in the width of the HR600P curve over the MC-600 indicates a wider processing window. The neat resin can be molded below 400°F (210°C) by compression molding. By postcuring through a controlled temperature cycle up to 600°F (316°C) and then at 700°F (371°C) for approximately eight hours in air, a Tg of approximately 662°F (350°C) can be achieved, which is approximately that obtained for Thermid MC-600.

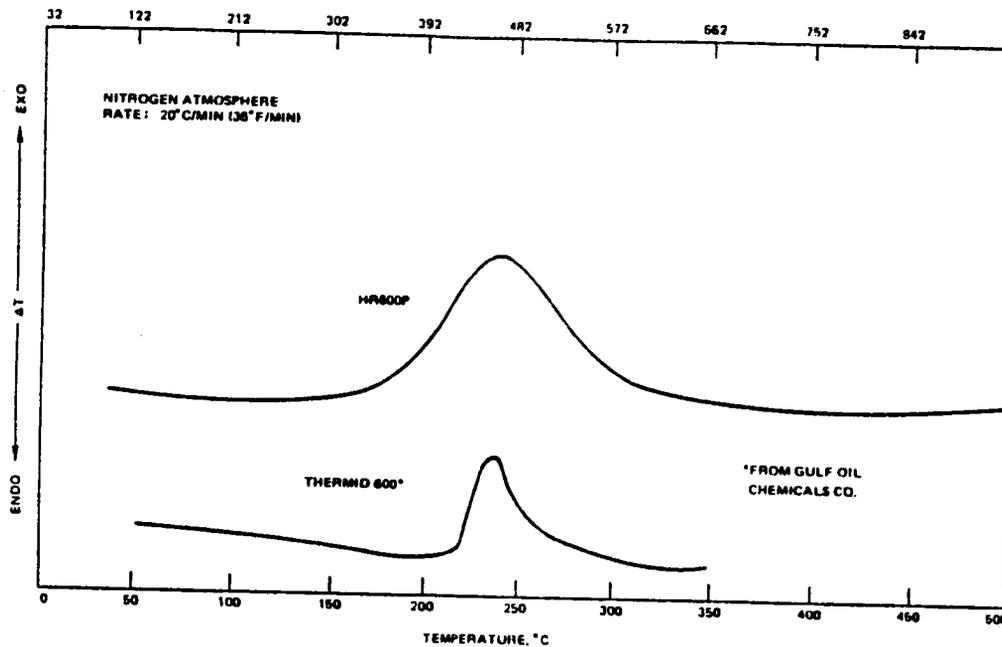


Figure 10. - Differential scanning calorimetry curves for Thermid MC-600 and HR600P resins.

Some select thermal mechanical properties for the molded HR600P oligomer are shown in Table III.

TABLE III - Select Thermal Mechanical Properties of Molded HR600P Oligomer

Neat Resin Properties	Values
Tensile Strength (Specimen size, 2 in. gauge length) (Rate at loading, .05 in./min.)	8500 psi at 21°C (70°F) 4000 psi at 316°C (600°F)
Tensile Modulus	730,000 psi at 21°C (70°F) 180,000 psi at 316°C (600°F)
Elongation at Break	1.2% at 21°C (70°F) 4.2% at 316°C (600°F)
Glass Transition Temperature, T _g by TMA	300°C after 8 hrs. @ 370°C air postcure 350°C after 15 hrs. @ 370°C air postcure 330°C after 4 hrs. @ 400°C air postcure 354°C after 8 hrs. @ 400°C air postcure
Density	1.34 g/cc

Composites

The high processibility of the HR600P oligomer makes this oligomer particularly amenable to the state-of-the-art autoclaving molding techniques. The processibility is compared to two other high temperature, high performance resins, namely LARC-160 and NRC-150 in Figure 11. It should be noted that with the HR600P oligomer, the part can be easily formed at 375°F starting with a cold mold. After several hours, the part can be removed from the autoclave and postcured in an oven. This cannot be easily accomplished with the other two resins.

Typically, a glass cloth prepreg is prepared by coating the cloth with a lacquer containing 25 percent by weight of HR600P resin in tetrahydrofuran containing one percent of N-methylpyrrolidinone. In the case of graphite, the tow is coated with the same lacquer using a dip tank and a collimation drum. The prepreg is placed between Mylar film to preserve tack and drape. Tetrahydrofuran is used to reactivate the tack and drape. The bulk may be reduced every fourth ply by vacuum bagging for thirty minutes. After the final ply, the layup is oven dried at 140°F for 16 hours under vacuum. The debulked preform is then molded using the cycle shown in Figure 11. A typical postcure involves 150°F to 450°F in 2 hours, hold at 450°F

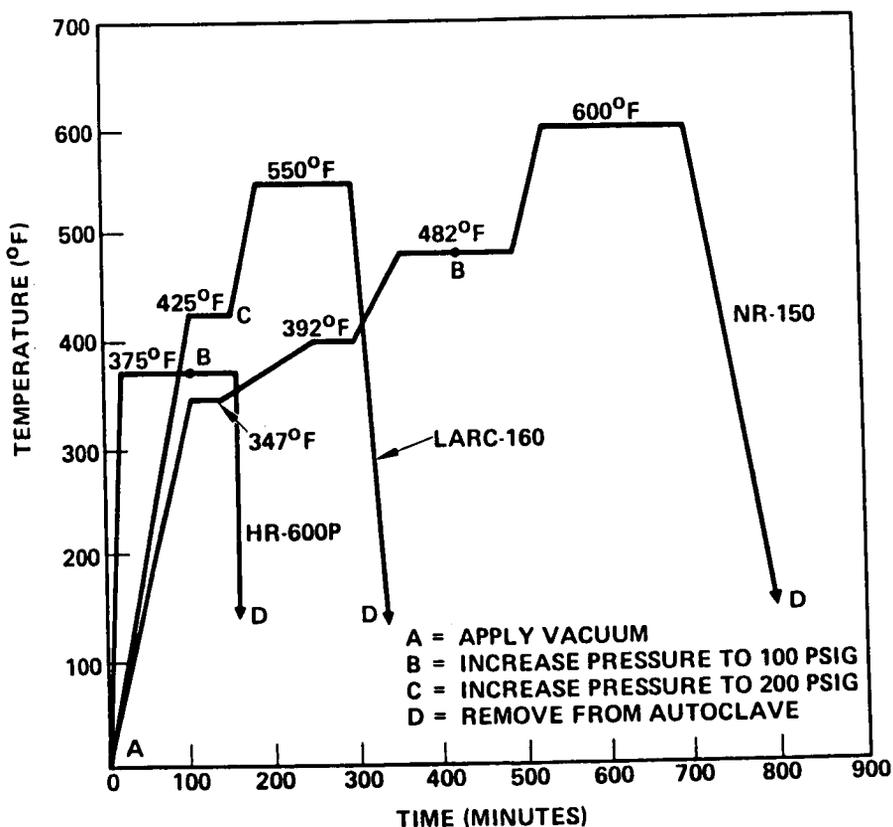


Figure 11. - Comparison of autoclave cycles of HR600P with high performance resins LARC-160 and NR-150.

for 1 hour, 450°F to 600°F in 2 hours, hold at 600°F in 3 hours, 600°F to 700°F in 1.5 hours, and hold at 700°F for 6 hours. In the case of compression molding, it is necessary to introduce about 5 percent by weight of Cab-O-Sil to the resin to prevent excessive squeeze-out of the resin or to advance the resin to a suitable viscosity for molding.

Recent test results of HR600P HTS unidirectional graphite laminates show that the strength retention properties are good. It is difficult to compare this data with that of Thermid 600 since those laminates were made by compression molding techniques whereas HR600P laminates were made by vacuum bag autoclaving techniques. Figures 12 and 13 depict the change in flexural strength and shear strength as a function of heat aging in air at 550°F up to 1000 hours. Most noteworthy is the small change in these values when measured at room temperature. It should be noted that these measurements were made on samples prepared by an unoptimized process.

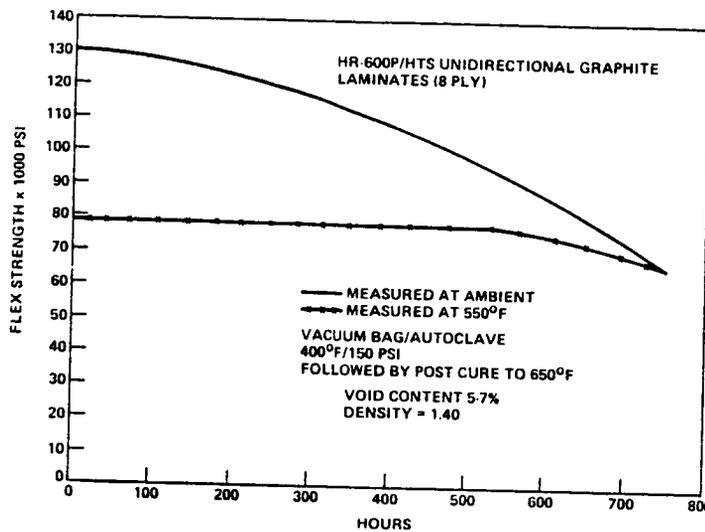


Figure 12. - Change in flexural strength as function of air aging at 550 °F.

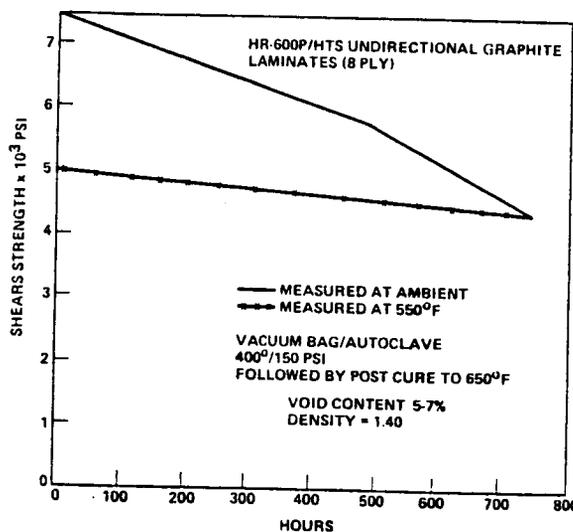


Figure 13. - Change in shear strength as function of air aging at 550 °F.

Coatings and Films

Good quality films and coatings could be made from the HR60XP oligomers having DP's of five or greater. High solid content resins can be formulated in a solvent mixture containing tetrahydrofuran and N-methylpyrrolidone. After drying, these coatings can be cured at the usual cure temperature where homopolymerization of the acetylene group takes place (500-600°F). Steel test specimens coated with HR605P oligomer and cured at 600°F had excellent corrosion and moisture resistance. Good quality films could be cast from lacquers formulated from HR605P and HR610 oligomers.

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