

POLYMER MATERIALS RESEARCH AT NASA AMES RESEARCH CENTER

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Research at NASA Ames to discover new polymers and the principles governing their physical and chemical behavior in severe environments has been organized to provide advanced materials for specific space applications such as reentry thermal protection heat shields (ref. 1), thermal coatings (ref. 2), and solar sails (ref. 3), as well as advanced components for service conditions encountered by aeronautical systems (ref. 4). This paper deals primarily with polymer activities that have led to new aeronautical materials that are providing significant improvements in both efficiency and safety for civilian transport aircraft and military combat aircraft. High strength to weight structures such as carbon fiber composites with long-term durability are requirements common to both classes of aircraft.

Aircraft safety improvements in fire resistance and crashworthiness of primary and secondary structures are long-term objectives for transport aircraft. Void filler ballistic foams (ref. 5), intumescent coatings (ref. 6), and radiation-resistant transparent plastics (ref. 7) are NASA Ames contributions to vulnerability reduction in combat military aircraft. As applied polymer research, the NASA Ames program is driven by aeronautical design requirements to improve both low- and high-velocity impact tolerance, fire resistance, thermal stability, and long-term durability of polymers and components derived therefrom.

Aerospace polymeric materials have several important constraints not usually encountered in usual commercial polymer applications. Most often, materials selection criteria are dominated by component weight minimization needs to achieve energy efficiency and operational capabilities. Neoprene fire-blocking layers (ref. 8) are perfectly adequate for ground-based applications, for example, but for cost-effective use in transport aircraft, a fire-blocking material with one-fourth the aerial density is required (ref. 9). This requirement has been met, surprisingly, with high-temperature-resistant, non-conductive fiber arrays and fabrics based on preoxidized PAN or PBI, so-called space age fibers (ref. 10). Weight constraints such as the specific stiffness requirements are typified by the extensive use of facesheet bonded honeycomb structures utilizing graphite and other organic fibers such as Kevlar, and high-performance polymeric film formers such as polyetheretherketone and matrix resins and adhesives based on polyimide technology.

The research at Ames has been concerned with the synthesis, characterization, and evaluation of new carbon fibers (ref. 11), new transparent self-supporting films derived from fluorenone monomers, and matrix resins derived from bismaleimide derivatives (ref. 12), new phenolics and stilbazole derivatives (ref. 13), and recently phthalocyanine (ref. 14) and phosphonitriles. These unusual polymers possess outstanding environmental properties that are not readily accessible with state-of-the-art polymers.

These polymers, although expensive by ordinary standards, have been designed to accommodate the kinds of environmental effects encountered in aerospace polymer applications. Here the environmental parameters often exceed the flux density and energy usually encountered in earthbound applications, such as temperature, photon energy and flux, creep-fatigue stress, impact energy, vacuum outgassing and chemical environments. Combined environmental effects are the rule. Hot wet strength is needed for supersonic applications of structural graphite composites. Impact- and fire-resistance properties are sought in the case of transport aircraft structure. High-energy particle and temperature resistance is generally required for new space structures. High-temperature- and impact-resistant turbine fan blades for jet engines would be economically useful.

There are few if any off-the-shelf standard tests that adequately simulate these aerospace environments needed to assess the time-dependent behavior of aerospace polymers. This is especially true in the case of thermal environments and impact effects. Analytical modeling, the development of special simulation facilities and often full-scale testing play a large role in most aerospace polymer research programs, and these test programs are generally long term and expensive.

Economically practical fabrication methods for large complex shapes such as composite structures for aircraft and spacecraft components impose inherent constraints on processing options. Spray molding of foams, tape, fabric, and fiber-wound lay-ups for composites; reaction injection molding (RIM); casting; and coatings are representative of some of these options. Particular classes of polymers are especially suitable. Reactive prepolymers which finally take the form of crosslinked binders and film formers satisfy these needs. The polymers discussed in this paper are concerned with these classes of materials.

AEROSPACE MATRIX RESINS FOR COMPOSITES

It is well known that aromatic polycyclic ring structures generally exhibit high-temperature and high-energy-radiation resistance due to high interchain bond strengths possible with such structures. Typically, polybenzimidazoles, "pyrones", polyphenylenes, and some polyimides exhibit these properties. All of these polymers have been examined in the NASA polymer program. Additional high-temperature stability, fire resistance, and thermochemical char formation for ablation efficiency may be obtained by elimination of processing solvents and introduction of crosslinked structures. Crosslink ability from a melt phase is constant with the processing requirements discussed previously, as well as with ultimate polymer properties.

A large part of the research at Ames is concerned with optimizing polymer properties for composite matrix resin binders by systematically manipulating the molecular structure of what may be conveniently described as crosslinked polycyclic aromatic structures in the form of liquid oligomers or fluid prepolymers. Inclusion of phosphorous and nitrogen heteroatoms in the basic ring systems is more the rule than not. As matrix resins these polymers must accommodate a substantial weight fraction of fiber for reinforcement such as glass, carbon, Kevlar, and hybrid blends. Often density reduction devices are included such as foaming gases, syntactic fillers and honeycomb structures. Formulation of aerospace components often include all of these elements. Combinations of widely diverse polymeric materials are necessary to obtain the combination of properties needed for cost-effective aeronautical applications.

It was clear from the outset of polymer research at Ames, that the development of weight-efficient ablative heat shields required that the chemist get control over the thermochemical rates of vapor and char formation to optimize heat shield design for different kinds of reentry environments. A significant observation was made at Ames in 1966 (ref. 15) which clearly demonstrated that in the one-dimensional heat transfer case, the pyrolysis vapor production rate was proportional to the applied cold-wall heating rate and inversely related to the number of multibonded aromatic rings in the neat resin. The generality of this result is shown in figure 1. Here the anaerobic thermochemical char yield (inversely related to the vapor production rate) is plotted as a function of the estimated concentration of multiply bonded aromatic rings. Linear polyphenylene is found to give the theoretical amount of residual carbon at 800°C in an inert atmosphere of 94 percent, epoxides are between 20-35, and phenolics and imides occupy an intermediate position of 60-65 percent.

Although this is a convenient relationship, a rather complete understanding of the bulk anaerobic thermochemical reactions is required to estimate the effective number of stable aromatic rings. Thermochemical decomposition temperature and glass or heat distortion temperatures follow similar trends but much less regularly than these char yield values. It follows intuitively from these relationships that if one is seeking the most thermally stable polymers, those polymers with more stable bonded aromatic ring systems such as those polycyclic aromatic structures which are bonded by relatively stable bridging linkages such as imides, imidazoles, sulfones, aromatic ethers, carbonyls, silicones, and even metal ligands should be examined. These thermochemical principles were first applied in the formulation of the fabrication of the Apollo reentry charring ablative heat shield which was based on an epoxy novolac-phenolic resin system, the starting point for polymer research at the Ames Research Center.

This reentry heat shield polymer technology was first exploited in technology transfer to explain and predict the fire resistance of polymeric materials (ref. 16). As shown in figure 2, it is possible to correlate many of the important flammability properties with this easily measured anaerobic char yield, measured thermogravimetrically at 800°C. It can be seen that those properties usually associated with flammability, such as flame spread, ignition and toxic gas emission, decrease linearly with increasing char yield where those thermal properties associated with fire containment, that is the ablation efficiency, reach a maximum value in the fire environment between 45-50 percent.

These results have been used to select polymers for the design and fabrication of a number of new fireworthy interior panel structures for transport aircraft of the generic type shown in figure 3, where the relatively flammable epoxy glass facesheets have been replaced with comparably processable aromatic bismaleimide or phenolic resins. This at present is the best available compromise of the desired fire containment and fire involvement characteristics. The phenolic system is in the form of a crushed-core configuration, as adopted for use in the new Boeing 757 and 756 interior panels (ref. 17). Although considerable improvement in the fire resistance of this class of panels has been demonstrated in both laboratory and full-scale simulations, further improvements in decorative films and bonding adhesives are possible. These represent other new project developments, and they will be discussed subsequently.

It is obvious from the results shown in figure 2 that flammability and fire containment can not be optimized in a given polymer. It is also common knowledge that highly crosslinked aromatic polymers are generally very brittle, with low strain to failure and high impact sensitivity. Current research at Ames on fire-resistant polymers is aimed at solving both of these problems. It has recently been found (ref. 18) that the virtually totally fire resistant matrix resins with anaerobic char yields greater than seventy-five percent are readily available from the condensation of alkyl-substituted pyridines such as collidone and lutidine with aromatic dialdehydes, as shown in figure 4. Carbon fiber composites formulated from this resin have been exposed to relatively severe fire environments (5 to 8 W/cm²) for periods of 5 minutes. They do not burn and they retain most of their mechanical integrity after such exposure. They exhibit no tendency to delaminate under severe high-speed impact. These are somewhat remarkable results. As shown in the figure, these new polystyrylpyridine polymers (PSP) have a "buried" thermochemically reactive functionality in the form of a conjugated stilbazole double bond. At modest temperatures, the stilbazole remains uncrosslinked providing some linear chain runs and points of flexibility. The stilbazole double bond appears to react thermally at temperatures in excess of 400°C in the thermal environment to crosslink,

giving an extremely fire resistant structure and retaining its mechanical integrity (ref. 19). The stilbene-like double bond has a high bond strength and meets the thermochemical requirements for a multiple bonding segment.

This matrix resin was first applied in the NASA Ames polymer program as a means of overcoming the phenomenon of accidental carbon fiber release to eliminate electrical hazards from carbon composites exposed to a crash fire environment (ref. 19). As shown in figure 5, the rate of carbon fiber release varies linearly with the increased anaerobic char yield. As expected, minimum fiber release was obtained under simulated fire impact conditions with carbon composites formulated from the PSP resin system. The long-term high-temperature stability of PSP-based carbon composites is apparent in comparing the effect of temperature on the dynamic modulus as measured by dynamic mechanical analysis (DMA). The results obtained for carbon composite formulated from PSP compared with conventional epoxides are compared in figure 6. Rapid loss of the epoxy-based composite occurs around 250°C whereas no change in the mechanical properties of the PSP composite is observed to occur up to 400°C. As should be expected, the application of these new PSP polymers requires special attention to the fiber sizing employed. Unsized fibers or those coated with polyimides in preliminary tests provide basic mechanical properties at least equivalent to standard aerospace epoxy composites.

Recent preliminary studies by the aircraft companies on vendor-prepared aircraft interior honeycomb sandwich panels have shown that these PSP composites withstand at least five minute exposure to simulated post-crash fire environments with virtually no loss in mechanical strength.

For the first time, a new matrix resin system has been developed for carbon fiber composites which clearly demonstrates the concept of using a stable, thermochemically reactive functionality which in the case of PSP has provided maximum fire resistance and adequate strength over a wide range of temperature conditions. Compound panels are being prepared wherein one sheet is derived from the highly ablatively efficient bismaleimide for fire containment, with PSP face sheets for complete interior resistance to fire involvement. Such systems are expected to provide optimum future designs for transport aircraft interiors and other aerospace vehicles.

Higher cure and post-cure temperatures are required for the basic PSP polymer shown in figure 4 than for those usually considered conventional for large aircraft parts. This concern has been overcome by altering the condensation cure to basic prepolymer reaction by means of vinyl end group termination through reaction with vinyl methyl pyridine, as shown in figure 7. The easily polymerized vinyl groups permit curing of these matrix resins under conventional epoxy curing conditions. In addition to providing low-temperature gelation of the matrix resin and cure, replacement of the condensation cure (elimination of water) with terminal vinyl groups gives low-void composites with acceptable mechanical properties with carbon fibers. It is interesting to note that these vinyl-modified PSP's still exhibit the same high char yields, that is, around seventy-five percent, due to high-temperature conversion of the stilbazole double bonds, and give the expected fire-resistant properties. It is clear that easy control of molecular weight of the divinyl PSP derivatives is possible by changing the concentration of the vinyl methyl pyridine to provide a series of stilbazole derivatives which can be used as reactive oligomers and reactive diluents for other matrix resins. Modification of bismaleimides and other unsaturated matrix resins of particular interest are currently under investigation. Sensitivity of high-modulus carbon fiber composites to the effects of both low- and high-speed impact and the potential limitations these responses

place on the use of such composites as primary aircraft structures are well known. The use of polyphase rubber dispersions in matrix resins has been examined in some detail (ref. 20). There are other important factors such as fiber resin interface adhesion and the nature of the fiber lay-up, orientation, and fabric weaves which also contribute to fracture toughness in such systems. Although high-strength properties of composites are largely influenced by matrix resin properties, composite tolerance to both low- and high-speed impact is controlled by the microstructural features of such compositions.

The effect of rubber modification of conventional aerospace-grade carbon fiber epoxy on the short beam shear strength as a function of low-speed impact is shown in figure 8. It can be seen that it requires as much as twenty-five percent addition of carboxy-terminated butadiene acrylonitrile elastomers to minimize the rate of change in short beam shear strength with impact energy. These modifications, although reducing the effect of low-speed impact, degrade the strength properties of the high-stiffness composites. The initial flexural strength is reduced by as much as ten to fifteen percent, the hot wet strength is reduced by as much as sixty percent, and the flexural modulus is reduced by as much as forty percent. This general degradation of mechanical properties through conventional rubber modification to improve impact tolerance may be sufficient to make this modification inappropriate. These results have been interpreted to mean that the controlling factor in rubber toughening, in addition to the well-known particle size and distribution of the rubber phase, is the phase distribution of rubber in resin and resin in rubber, the former plasticizing the resin phase and the latter reducing the dampening effectiveness of the dispersed elastic particle.

To examine this question, a trifunctional epoxy novolac, TEN, provided by the Dow Chemical Company, which is a much more aromatic matrix resin than the conventional TGMDA (shown in figure 9), was modified by addition of CTBN. The data is shown in Table 1. It is clear that the improvement in impact tolerance is maximized at a ten percent addition of CTBN elastomer with a three-fold increase in the shear strength after 10 in/lb impact with about a twenty percent improvement in the flexural strength over the control. Although the initial properties of the TEN/DDS control are somewhat lower than those obtained for the TGMDA/DDS control, in addition to higher impact tolerance possible with the ten percent modification of TEN/DDS, all of its mechanical properties are superior to both initial and any modification possible with the less aromatic TGMDA. Further improvements in impact tolerance, if required, may be possible by further tailoring the solubility parameters of the resin-elastomer system. Rubber modifications to provide large differences in solubility parameters of the resin-rubber system were examined by replacing the hydrocarbon by a fluorocarbon elastomer from preliminary results of rubber-toughening a standard EPON 828/DDS epoxy resin (ref. 21) in a glass laminate as shown in Table 2. As in the former case the improvement in retention of shear strength after impact goes through a maximum of eight percent addition of the fluoroelastomers of fluoropropylene oxide with a significant improvement of the impact tolerance and improvement of the mechanical properties as indicated. Since these fluoroelastomers have thermal stabilities in excess of 400°C as well as excellent fire resistance, they show considerable promise as fracture-toughening agents for high-temperature matrix resins such as the bismaleimides and PSP polymers described above.

It may be concluded from the brief overview of polymer research being conducted at the Ames Research Center with aerospace matrix resins for composites that liquid oligomers formulated from stilbazole derivatives alone or in combination with other

unsaturated imide monomers such as bismaleimides may be modified with selected elastomers to provide high-stiffness-molecule composites with an optimum combination of high-temperature, impact, and fire resistance required for many aerospace applications. It is believed that although these resin systems may be somewhat specialized for general commercial use, the principles that have been employed in their development have a broad range of applicability to the polymer industry at large.

Total polymer design as illustrated in the case of the stilbazole polymers probably offers the best route to effect the best combination of properties required for advanced aerospace applications. We have, however, investigated some simple modifications of conventional matrix resins which have improved both the thermal- and fire-resistant properties. Soluble phthalocyanine tetramines of copper, cobalt, nickel as shown in figure 9, are easily prepared (ref. 22). We have used these tetramines to prepare a variety of high-temperature imides with use temperatures in air in excess of 600°C. In addition, we have found that with borontrifluoride catalysis these organometallic tetramines react easily with conventional epoxides as shown in figure 10. The resulting polymers are useful as matrix binders for carbon-fiber composites with substantially improved fire resistance. Limiting oxygen index values in excess of 50 with anaerobic char yields corresponding to values greater than 70-75 percent have been obtained for carbon-fiber composites with acceptable mechanical and processing properties. Although the thermochemistry of these modifications is not well understood, the results may be very useful in conventional epoxy technology.

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TABLE I.- MECHANICAL PROPERTIES

Sample	Density	Shear Strength		Flexural Strength		Flex. Mod. 10 ⁶		Moisture abs
		Initial	10 in/lb impact	Dry	200°F Wet	Dry	200°F Wet	
DEN*/DDS	1.4886	6673	2866	83,265	78,146	9.4	8.8	2
DEN/DDS + CTBN								
2%	1.5418	5737	2303	80,643	71,862	9.5	9.8	1.3
5%	1.509	7137	3058	98,278	66,018	9.5	8.5	1.28
6%	1.555	8206	2587	113,825	85,362	9.5	7.4	0.71
10%	1.5373	9362	6302	105,838	89,430	7.6	8.2	0.30
15%	1.518	7919	4252	99,327	78,858	7.8	7.9	0.40
20%	1.4678	5404	3633	74,250	52,989	7.6	7.2	0.88

*
Trifunctional Epoxy Novolac
Composite fiber vol. 61.8±2.8

TABLE 2.- FLUOROETHER ELASTOMER MODIFIED EPOXY GLASS CLOTH COMPOSITES

	T _g (°C)	Flexural Toughness (ft. lbs/in ³)	Flexural Strength (psix10 ⁴)	Flexural Modulus (psix10 ⁶)	Retention of Shear Strength After 15 in. lbs impact (%)
EPON 828/DDS (DGEBA)	203	40.5	6.56	3.10	70.3
EPON 828/DDS 8% fluoroether	225	60.4	9.52	4.29	86.2
$\left\langle \text{CF}-\text{CF}_2-\text{O} \right\rangle$ $\quad \quad \quad \downarrow$ $\quad \quad \quad \text{CF}_3$					

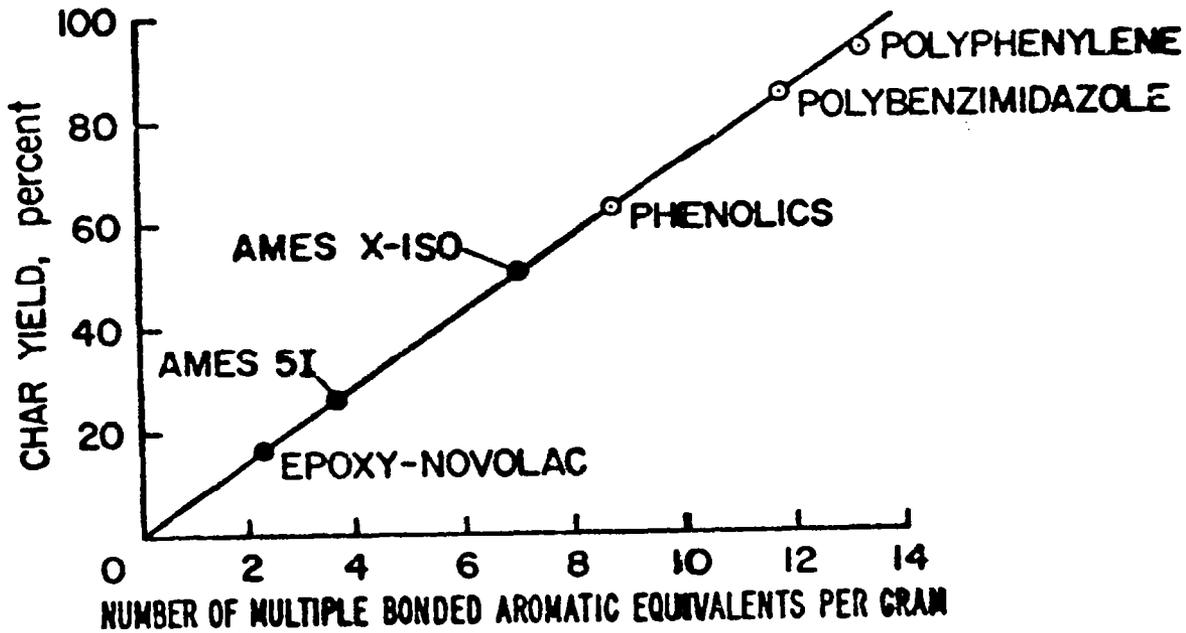


Figure 1.- Correlation of primary thermochemical char yield with molecular structure.

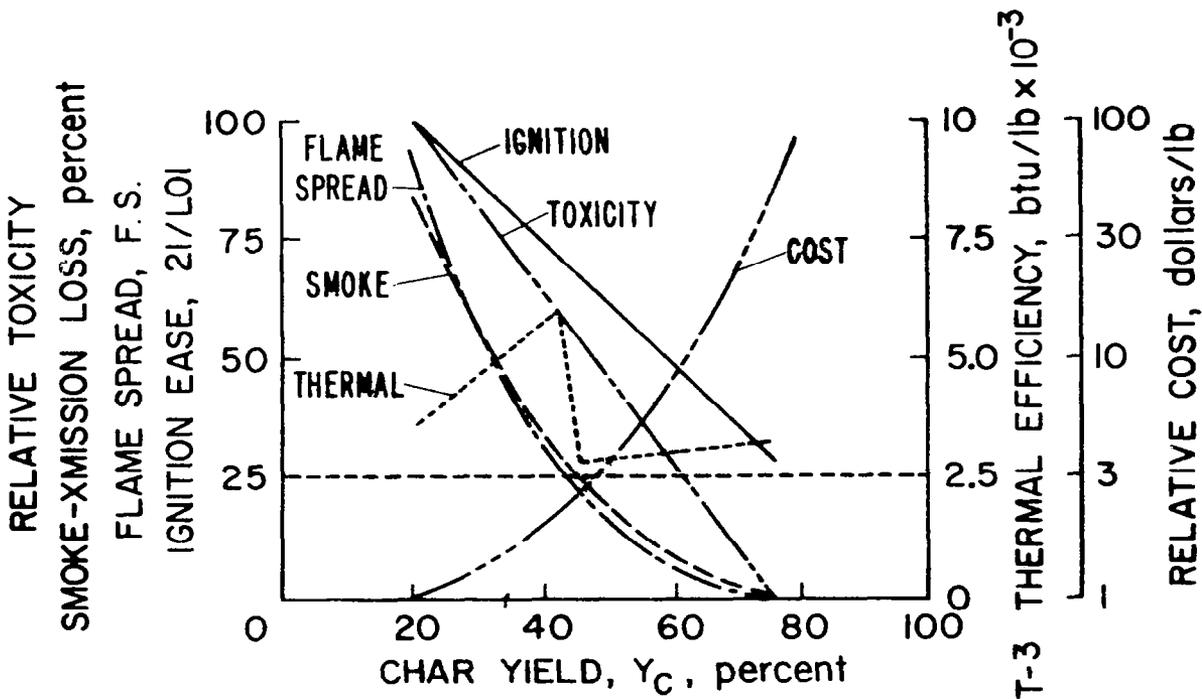
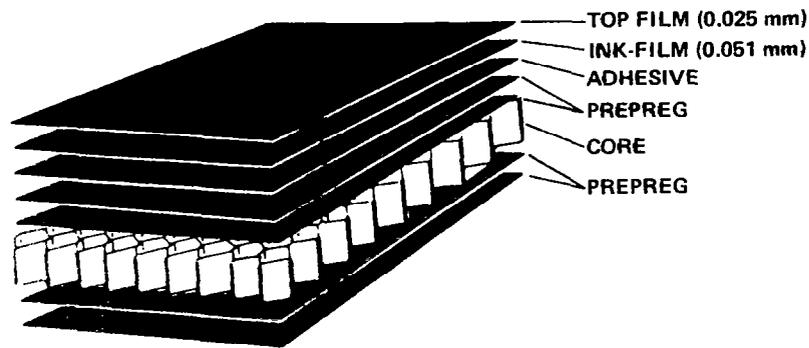


Figure 2.- Summary of properties of char-forming foamed polymers.



- CANDIDATE RESIN SYSTEMS FOR PREPREG
 - BASELINE EPOXY
 - BISMALIMIDE
 - PHENOLIC
 - POLYIMIDE
- TESTING MATRIX
 - FLAMMABILITY, SMOKE, AND TOXICITY
 - MECHANICALS AND AESTHETICS

Figure 3.- Sandwich panel configuration.

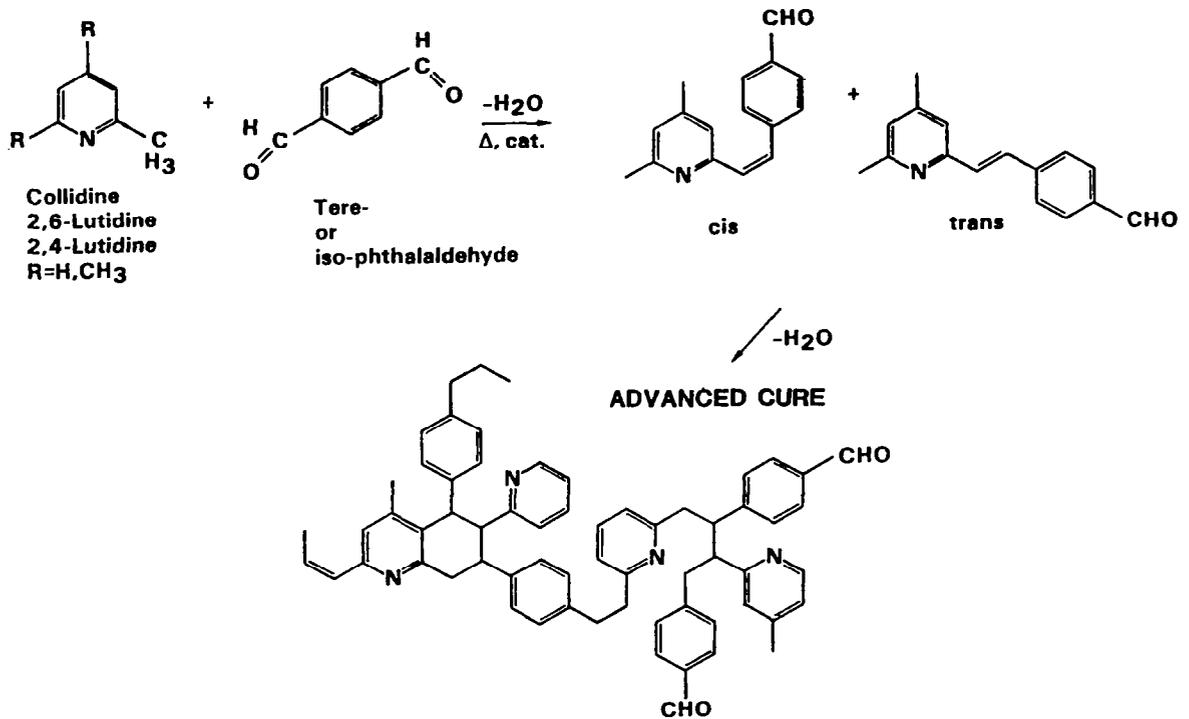


Figure 4.- Reaction scheme for linear or crosslinked polystyrylpyridine (PSP).

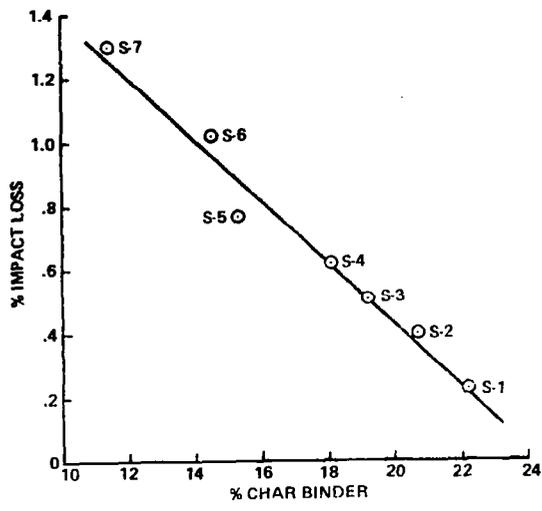


Figure 5.- Char versus impact loss after burn - satin weave.

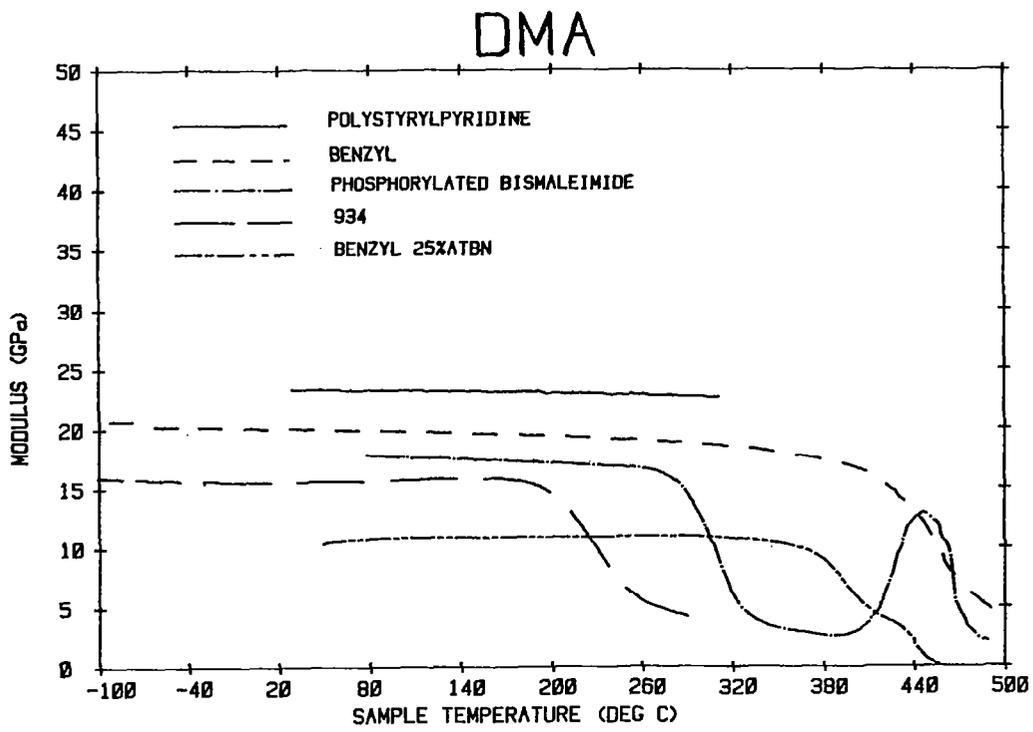


Figure 6.- Effect of temperature on dynamic modulus of carbon composites.

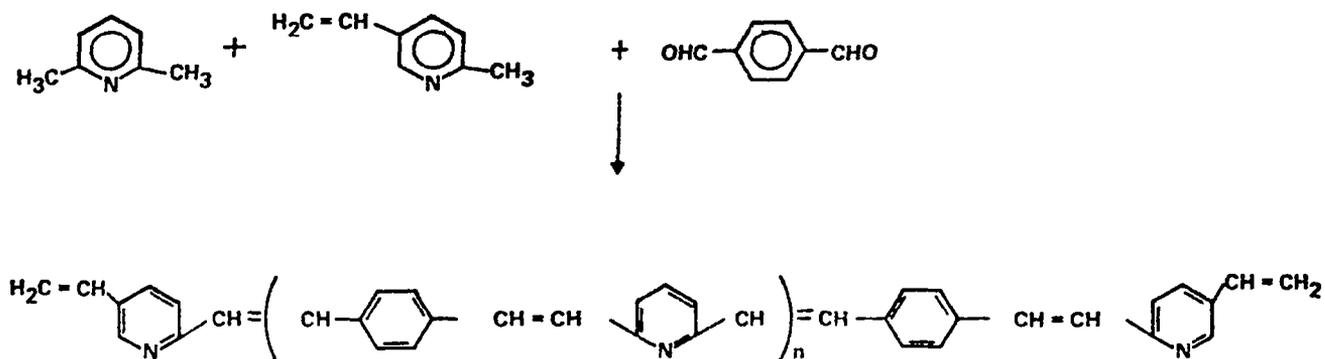


Figure 7.- Synthesis of PSP (vinyl-terminated polystyrylpyridine).

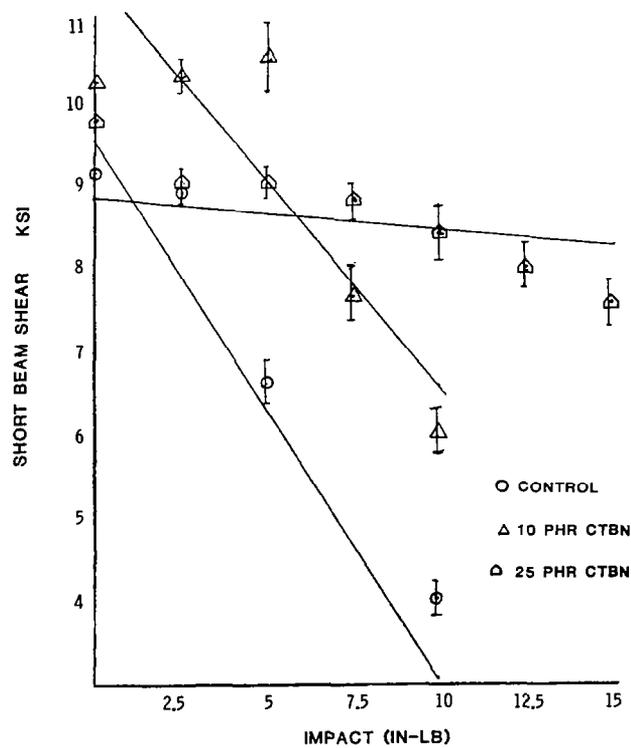


Figure 8.- Shear strength after impact.

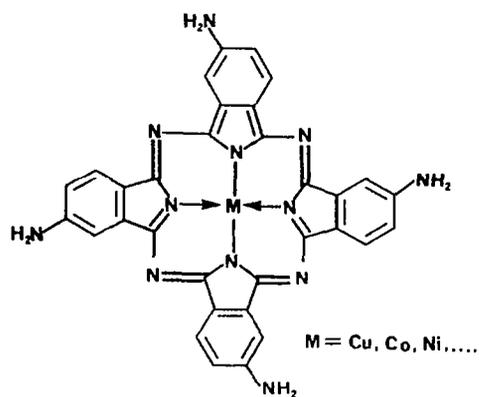


Figure 9.- Tetraminophthalocyanine monomer.

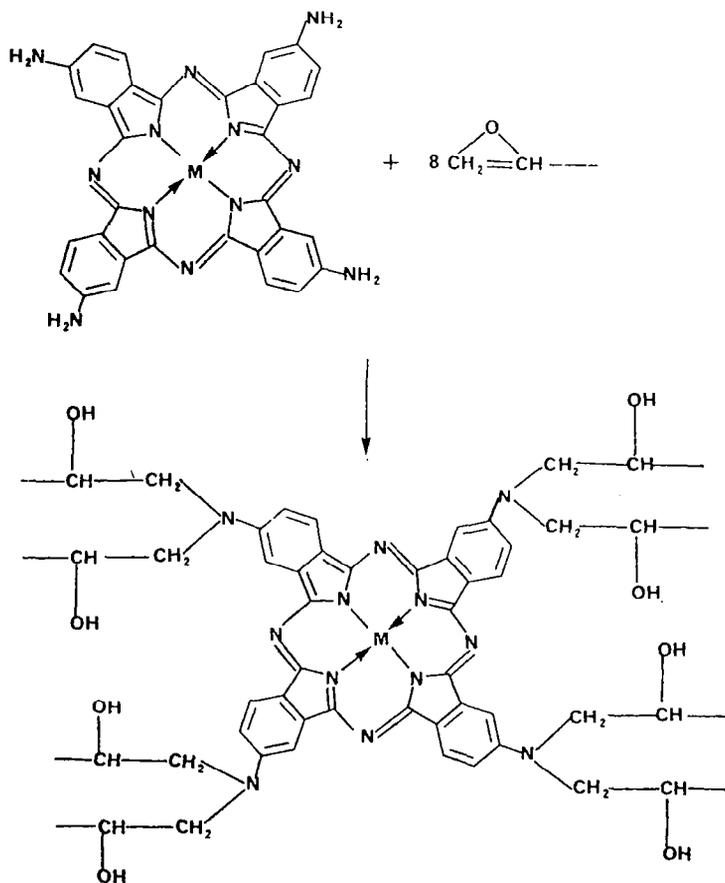


Figure 10.- Polymer structure of the reaction of tetraminophthalocyanine with conventional epoxides.