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NEAT RESIN PROPERTIES OF ACETYLENE TERMINATED SULFONE FORMULATED WITH COMMERCIAL ADDITIVES

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SECTION I

INTRODUCTION

Air Force development of acetylene terminated resin systems began in the early 1970's. After several materials had been synthesized and initially characterized, one material, 4,4'-bis (3 ethynylphenoxy) diphenylsulfone (acetylene terminated sulfone or ATS), was identified as the member of that family of resins most likely to have desired properties of a 350°F resin for structural composite fabrication. ATS also had the attribute of potential for low cost synthesis.[1]

In small quantities made in the laboratory, ATS was found to have excellent processing characteristics for hot-melt fabrication of prepreg and high retention of mechanical properties under high temperature, high humidity conditions.[2,3,4]

A larger quantity of ATS was delivered in 1980 under a contract with Gulf Research and Development Company for development of a low-cost synthesis. This material was found to differ from the laboratory version of ATS in an important aspect. The Gulf ATS contained approximately 37% oligomeric material, mostly dimer, but with some larger oligomers. While the lab synthesized material contained only 18% oligomer. Because of the oligomer content, Gulf ATS was lacking some of the processing attributes such as room temperature tack and drape in prepreg form which had made it attractive.[4]

In addition to this problem, it became apparent that some of the initial mechanical data on the neat resin had given a slightly inflated indication of resin toughness. Further, studies to improve the cure cycle to increase the resin's toughness at University of Dayton had not shown any significant improvement to be gained by that route.[5]

Therefore, the Air Force began efforts to identify an additive or additives that would alleviate the two major weaknesses of ATS, brittleness and lack of room temperature properties suitable for epoxy-like processing of unidirectional tape into laminates.

For purposes of toughening the material, two basic approaches were established. The first was to attempt to increase the distance between crosslinks. This was attempted by two approaches. One was to decrease the number of sites available for crosslinking by addition of monofunctional analogs of ATS. The second approach for decreasing crosslink density was through increase of the initial chain length by either increasing the oligomeric content of the base resin or by co-reacting the Gulf ATS with another material such as an epoxy or an amine.

Secondly, an attempt was made to increase the toughness by addition of a relatively more ductile second phase as is done by elastomeric additions to epoxies.

Except for the addition of some reactive plasticizers, the second problem, that of room temperature tack and drape, was not addressed as specifically as the toughening. Some of the plasticizers, added primarily in hopes of increasing chain length, had the desirable additional effect of improving the room temperature handling characteristics of the resin. This problem was felt to be of secondary importance.

The emphasis in this study was on a short-term empirical solution of the toughness problem, that is, additives were selected that were expected to be easily converted to large scale, not add substantially to the cost of the system and had an empirical rationale for contributing to resin toughness.

SECTION II

EXPERIMENTAL

1. All trial materials, with the exception of monofunctional analogs and elastomeric tougheners, were formulated at a level of 10 Parts Per Hundred parts resin (PPHR) additive. Differential scanning calorimetry was performed on each formulation on a DuPont 990 Thermal Analyzer at a heat up rate of 10°C/min. for sample sizes between 8 and 12 mgs. The general outline of all the curves was similar with minor fluctuations in peak exotherm and onset temperatures. DSC data is tabulated in Table 1.

2. Each formulation was evaluated for compatability under cure conditions microscopically. A sample was smeared onto a glass microscope slide, usually after heating to 180°F, and covered with a glass cover slip to form a thin film. Small segments of AS1 graphite fiber were included in the film. The graphite fiber serves at least two purposes. First, in an otherwise transparent medium, it furnishes a feature in the plane of the film to focus the microscope. Second, the inclusion of the fiber allows for preliminary evaluation of any

effects the fiber might have on the matrix behavior during cure. Some effects which have been observed are: evolution of gases at the fiber surface and preferential phasing out of ingredients on the fiber surface.

Another effect often seen adjacent to the included graphite fibers is the buildup of stresses (apparent under polarized light) in the resin. This phenomena is usually quite transient, appearing as cure shrinkage occurs and disappearing as the matrix material appears to relax, relieving the stresses.

The microscope slides were heated at a programmed rate, 2°C/min, to 300°C on a Mettler FP5 Hot Stage. Holds were incorporated into the cycle at 350°F and 400°F, the temperatures used for cure holds. Since the films are thin and small in volume, these holds were relatively brief, 15 minutes as opposed to two hours in curing resin castings.

The slides were observed during the cure cycle simulation with special attention over the range of the exotherm peak from DSC studies. The slides were then allowed to cool slowly to room temperature and again examined for signs of volatile evolution or phasing out of additives.

3. Each formulation was then fabricated into tensile dogbones. Closed silicone molds were preheated under vacuum to 200°-225°F and the formulated resin was vacuum debulked in a beaker at 160°-200°F until volatile evolution ceased. The debulked material was then poured into the molds. The molds were transferred to a circulating air oven and cured. The cure cycle used was to start in an oven preheated to 200°F, heat up at 2-4°F/min. to 350°F, hold one

hour; heat to 400°F at 2-4°F/min.; hold one hour at 400°F. The dogbones were then cooled at 2-4°F/min. to 200°F and removed from the molds at that temperature to prevent stress buildup due to the high thermal expansion coefficient of the silicone molding material.

The dogbones were then postcured 16 hours at 425°F between aluminum caul plates covered with a sheet of teflon coated glass cloth. After cooling to below 200°F, the dogbones were sanded lightly to smooth surface irregularities and tested.

4. Tensile testing was done on an Instron Model 1115 using air grips and a strain rate of 0.02 in./min. Elongation to break was measured with a 1" microextensometer with flat contacts to prevent stress buildups, which could arise with knife-edged microextensometers. Data was evaluated only for those specimens with failures within the gauge section.

Originally, tensile data was validated by testing strain gauged specimens as well as using the microextensometer. Since values for the strain gauged specimens were well within the scatter of the microextensometer data, strain gauging was discontinued. Tensile data is summarized in Table 2.

SECTION III

DISCUSSION AND RESULTS

1. Decreased Crosslink Density via Chain Lengthening

a. HR600. HR600 (Gulf Thermid 600) was one of the first acetylene terminated materials developed. Because of the greater length of the polyimide backbone, it was hoped that co-reaction of ATS and thermid through the acetylene end groups might result in a tougher material while retaining the high temperature performance of the material.

Microscopic studies showed the materials to be compatible. DSC showed a similar H value to neat Gulf ATS but the T_{onset} and T_{peak} of the exotherm were shifted about 30°C higher. Dogbone processing was not difficult. The mixture melted to a low viscosity at 100°C and was poured into the silicone molds. Dogbones were free of voids and inclusions but no improvement was realized as data mechanical properties were within scatter of neat ATS Gulf (Table 2).

b. Addition of Amines. Acetylenes are known to react with amines via a Michael addition reaction. The amines selected for this were: 1) the curing agent used in several current 350°F curing epoxy systems, diamino diphenyl sulfone (DDS), and 2) a hexafluoro bisphenol-A analog which was an experimental material obtained from TRW, Inc. called 4-BDAF. The DDS, because of the sulfone backbone, was expected to be most compatible chemically with the ATS. On the other hand, the 4-BDAF had demonstrated increased reactivity over DDS in epoxy cures, probably due to the electron withdrawing effect of the fluorines.

Both amines remained in solution during cure under microscopic examination and dissolved in readily below the cure temperature. DSC data was comparable to pure ATSGulf for the DDS mixture. However, the 4-BDAF amine showed a substantially lower heat of reaction. This was not unexpected since the 4-BDAF is a large molecule and addition of 10 pph would decrease the number of reactive groups available per weight of sample.

The 4-BDAF mixture showed some improvement in both ultimate tensile strength and % elongation at break. While the difference was evident, it was not of great enough significance to warrant further experiments, which would have been further complicated by the extremely limited availability of the 4-BDAF material.

DDS, although more easily processed into dogbones, showed little evidence of reaction and did not improve the properties of the ATSGulf with regard to tensile strength and elongation.

c. <u>Epoxies</u>. MY720, a current state-of-the-art 350°F curing epoxy, was also combined with the ATSG in an attempt to react the acetylene end groups with the tetrafunctional epoxy.

The materials combined homogeneously under microscopic examination and an increase in H measured by DSC gave evidence of some altered reaction mechanism. However, mechanical properties were again disappointing with no measurable improvement over Gulf ATS.

d. <u>Vinyl Terminated Resins</u>. The final approach to chain lengthening by co-reaction was the addition of vinyl terminated materials. The vinyl groups were expected to react in much the same manner as the acetylenes but would not have left over unsaturated sites where further crosslinking could take place. Two vinyl terminated additives were selected as representative of this class of compounds, Ebecryl 150 (Virginia Chemicals), a bisphenol A diacrylate, and dicyclopentenyl oxyethyl methacrylate or DOM (Rohm and Haas).

Both additives were extremely low viscosity fluids at room temperature and had the extra benefit of providing a mixture, with the ATSG, which had tack and drape at room temperatures. Under microscopic examination, they blended in readily and remained in solution through the reaction. No significant changes in the heat of reaction or peak exotherm temperature were observed on the DSC. Fabrication of tensile dogbones was quite easy due to the plasticizing effect of the vinyl terminated additives. Mechanical properties remained within the scatter of neat ATSG data.

2. Decreasing Crosslink Density by Limiting Reactive Sites

Monofunctional ATS and monofunctional ATP, an acetylene terminated phenylene oxide, were used as additives. The monofunctional ATS was added at the 1, 5, and 10 pph levels and, after 5 pph was identified as the most promising level, ATP was added at 5 pph.

Because of the nearly identical materials, these additives were compatible and co-reacted at all levels. Dogbones processed very similarly to neat ATSG but tensile properties showed no marked improvement at any level of monofunctional additive.

TABLE 1 Differential Scanning Calorimetry

Additive	H (cal./gm/)	T_{onset} (^{o}C)	T_{peak} (^{o}C)	$T_{complete}$ (^{o}C)
None[1]	107	110	219	326
HR600[2]	104	151	248	338
DDS[1]	103	129	221	309
4-BDAF[1]	69	154	225	314
DOM[1]	102	122	222	316
Ebecryl[1]	115	115	222	398
MY720[1]	128	121	222	352
None[2]	95	143	236	339
Mono ATS[2]				
5 pph	110	125	232	338
10 pph	109	156	237	338
Mono ATP (5 pph)[2]	121	83	190	302

[1] Heatup rate of 10°C/min.
[2] Heatup rate of 20°C/min.

TABLE 2: Neat Resin Tensile Dogbones Mechanical Properties

Additive	Ultimate Tensile Strength (ksi)	Tensile Modulus 10^6 psi	$\%\epsilon$ to break	No. of Specimens
None	7.09	0.525	1.43	2
HR600	5.82	0.782	0.98	3
DDS	4.82	0.753	0.75	4
4-BDAF	7.41	0.543	1.46	3
DOM	5.96	0.609	1.13	3
Ebecryl	6.09	0.635	1.19	3
MY720	5.16	0.563	1.01	5
Mono ATS				
1 pph	7.60	0.620	1.42	3
5 pph	8.00	0.685	1.49	3
10 pph	4.70	0.648	0.82	3
Mono ATP (5 pph)	7.20	0.508	1.60	3
PES (5 pph)	5.70	0.678	1.00	3
PS	7.31	0.467	1.67	3

3. Toughening by Elastomeric Additives

The addition of relatively elastomeric material to ATS was first reported by Hartness and Husman in 1980.[4] During their study, two molecular weights of polysulfone were added to the resin. Conventional polysulfone (M.W. 20,000) was found to phase out in large globules and did not improve the mechanical properties of the material. A lower molecular weight polysulfone (M.W. 5,000) was then obtained and added at levels of 10 and 15 pph. Examined under a transmission electron microscope, the 10 pph material gave a smaller particle size and more uniformly distributed second phase. Dogbones were fabricated and tested. The mechanical properties showed no significant improvement over Gulf ATS although the 10 pph mixture was more ductile than that with 15 pph.

It was theorized then that a more similar molecular structure might produce better properties by virtue of being able to be incorporated in larger amounts while retaining the smaller particle size. The material chosen for this purpose was polyethersulfone (PES). Unfortunately, a low molecular weight PES was not available nor was fractionation possible. The lowest molecular weight available was 14,000.

This material phased out significantly in large particles at levels above 5 pph. Dogbones were fabricated and tested, but the elongation of the mixture was not as good as neat ATSG.

SECTION IV

CONCLUSIONS

This work was performed to investigate the feasibility of a low-cost, easily incorporated additive which would dramatically improve the elongation of Gulf ATS, as well as the ultimate tensile strength, to make it comparable to SOTA epoxy systems.

However, none of the additives investigated showed significant potential towards achieving that goal. Although the amounts and types of additives to be explored is still probably quite large, representatives of many of the classes of compounds which might be expected to: 1) decrease the crosslink density; or 2) produce second phase toughening of the matrix material, have been examined.

The failure of additives to the ATS to effect elongation-to-break still leaves unanswered the question of which approach is the most promising to improve this property of ATS unanswered. Further investigation seems warranted into the following:

a. The relative importance of chain length between crosslinks, ultimate crosslink density and flexibility of the backbone structure in acetylene terminated systems.

b. The amounts and optimum particle size of elastomeric toughening to be incorporated into ATS.

c. The effect of varying stoichiometry in combining flexibilizing additives to ATS.

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