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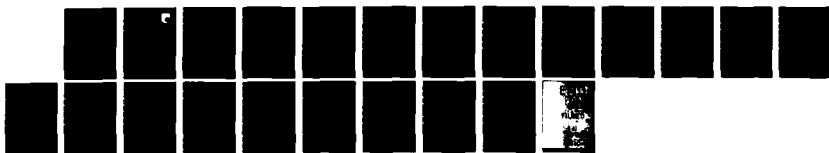
AN EVALUATION OF AN ACETYLENE TERMINATED SULFONE  
OLIGOMER(U) AIR FORCE WRIGHT AERONAUTICAL LABS  
WRIGHT-PATTERSON AFB OH S R EDDY ET AL. JAN 83  
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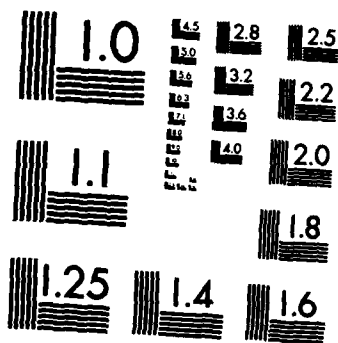
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AN EVALUATION OF AN ACETYLENE TERMINATED SULFONE OLIGOMER

Composites, Adhesives and Fibrous Materials Branch  
Nonmetallic Materials Division

January 1983

Final Report for Period June 1977 - December 1979

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) This paper describes the initial characterization and evaluation of a novel acetylene terminated oligomer 4,4'-bis(3-ethynylphenoxy)diphenylsulfone (ATS). The approach uses a scientific interdisciplinary team concept to generate material properties. The result is an initial characterization of the reactive oligomer (ATS) and the crosslinked polymer that results from its thermal cure. This quantitative characterization includes the consideration of cure rheometry, cure kinetics, volume change, secant modulus, tensile properties, dynamic shear		

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modulus and surface energetics. From the data generated, initial material characteristics have been judged to be of sufficient interest to warrant further material development. Of the properties measured, the polymer is noteworthy in its ease of processing, high temperature (177°C and above) mechanical properties, favorable surface properties for moisture resistance, and inherently low moisture pick-up.

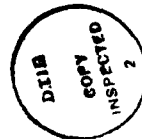
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FOREWORD

The work reported here was performed in the Composites, Adhesives, and Fibrous Materials Branch, Nonmetallic Materials Division, Materials Laboratory, Air Force Wright Aeronautical Laboratories, Wright-Patterson AFB, Ohio. The work was accomplished in WUD 44, under the leadership of Dr. T. W. Haas. The investigators in this task were Lt. Steven R. Eddy, Dr. Thaddeus E. Helminiak, Airman Michael A. Lucarelli, Dr. William B. Jones, Jr., and Lewellyn G. Picklesimer. The author would also like to thank Dr. Fred Arnold, Dr. Ivan Goldfarb, Dr. Fred Hedberg, and Dr. Charles Lee of the Polymer Branch (AFWAL/MLBP) for their contributions in synthesis, kinetics, and processing. Additionally, the author would like to acknowledge Dr. Lawrence T. Drzal for his expertise in the surface energetics work.

This report was released by the author in December 1979 and covers the time period of June 1977 to December 1979.



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## SECTION I

## INTRODUCTION

The initial approach to evaluating a newly synthesized material for resin application is crucial to the ultimate success or failure of the material. Consequently, an interdisciplinary team at the Air Force Wright Aeronautical Laboratories Materials Laboratory focused on this problem. The result was an experimental method based on the team's experience and on recommendations from authoritative specialists. Using the developed method, an acetylene terminated sulfone oligomer was characterized and evaluated for possible use as a composite matrix resin and/or a structural adhesive.

To properly characterize a polymer for structural application, a number of scientific disciplines should be utilized. The multidisciplinary approach, subscribed to by several investigators (References 1 and 2) has many advantages. The interrelation of polymer science, surface physical chemistry, and engineering mechanics provides a formulation for understanding adhesion. This integral relation is illustrated in Figure 1. This pattern was followed, and a team of investigators with experience in the three primary disciplines applied scientific methods to characterize the material. This understanding was focused to allow a maximum generation of scientific data from a minimum amount of polymer.

The plan for obtaining the material characteristics is the result of the team discussions. The plan is illustrated in Figure 2 and shows the important measurements to be gathered in this initial characterization. The early steps of the plan provide data to allow subsequent experiments to be made. The results of all the experimentation provide a data base to screen for further materials development.

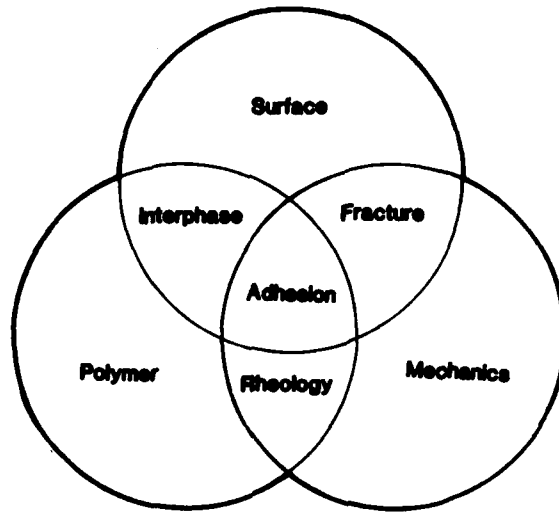


Figure 1. Areas of Investigative Interaction

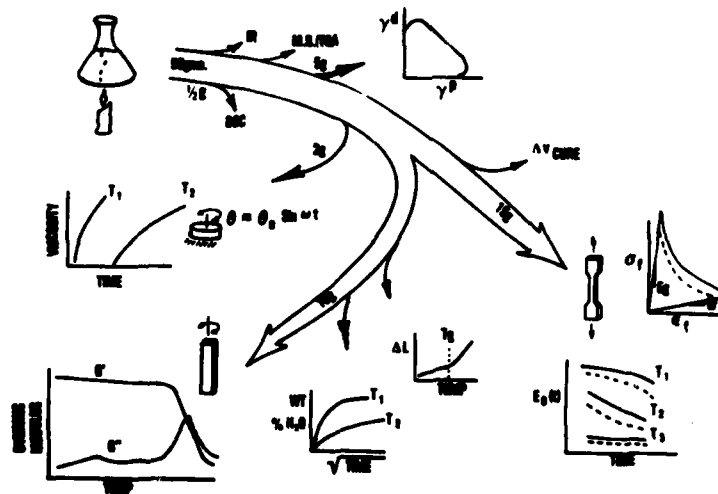


Figure 2. Schematic of the Material Evaluation Method

## SECTION II

## THE MATERIAL

Fifty grams of an addition curing acetylene terminated sulfone oligomer (ATS) with a molecular structure as shown in Figure 3 was synthesized (Reference 3). Infrared spectra were measured using solvent cast films in order to verify the material identity. In addition, mass spectroscopy and thermogravimetric analysis were conducted to quantify residual solvents and/or volatiles. Physically, the material at room temperature is a waxy reddish-brown compound.

## 1. CURE KINETICS

In order to define phase transitions, cure energetics, cure kinetics, and decomposition kinetics, a series of differential scanning calorimeter (DSC) (Reference 4) tests were run at five different scanning rates. The results for one such test on ATS are shown in Figure 4. This DSC experiment was run at 20°C in nitrogen and shows onset of the polymerization exotherm at 170°C. The series of five scans were analyzed and plotted in Figure 5. The parametric diagonal lines on the graph indicate advancement of the ATS to cure completion. The lines are extrapolated using first-order kinetic theory and, therefore, do not include consideration of phase transitions and rheological constraints on mobility during the advancement of cure. Given these caveats, the graph should be an accurate description of the polymer early in the cure and progressively less accurate later in the cure. This data was also used for cure rheometry temperature selection.

## 2. CURE RHEOMETRY

Samples of ATS (0.5 grams) were placed between preheated parallel plates in a Rheometrics RMS-7200 mechanical spectrometer, and were subjected to low frequency (0.16 Hz) (sinusoidal shearing rate) viscosity measurements at constant temperature. The temperatures were chosen using the kinetics data. The first temperature is 5°C above onset of polymerization and the second temperature is about 20°C higher.

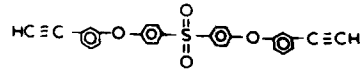


Figure 3. Molecular Structure of ATS

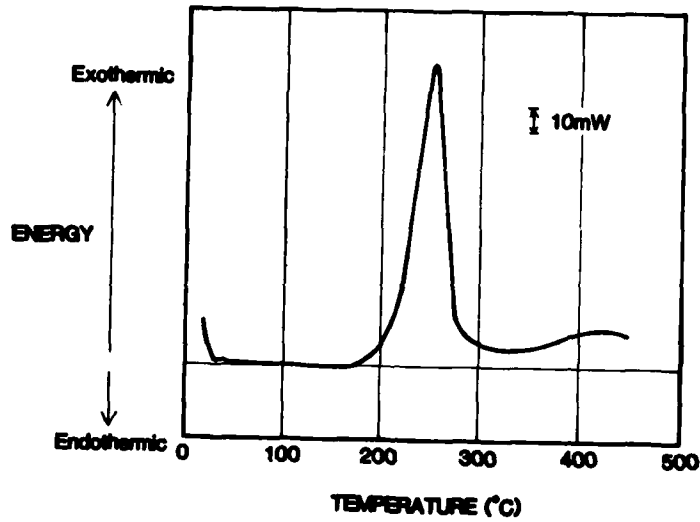


Figure 4. DSC for ATS

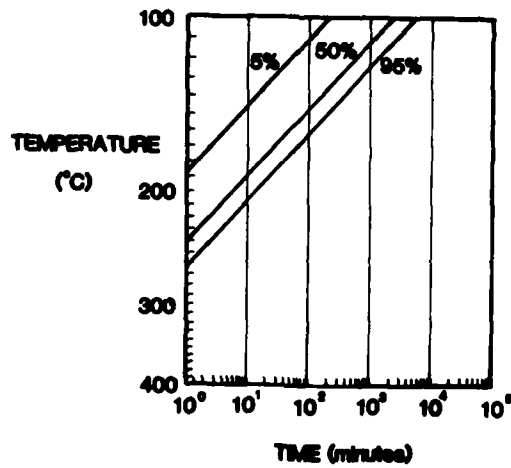


Figure 5. Reaction Window for ATS

The results of these runs are shown in Figure 6. These data illustrate the processing window for the polymer and suggest guidelines on fabrication methods. ATS has water-like viscosity around the cure temperature so fabrication was possible by pouring the material into molds.

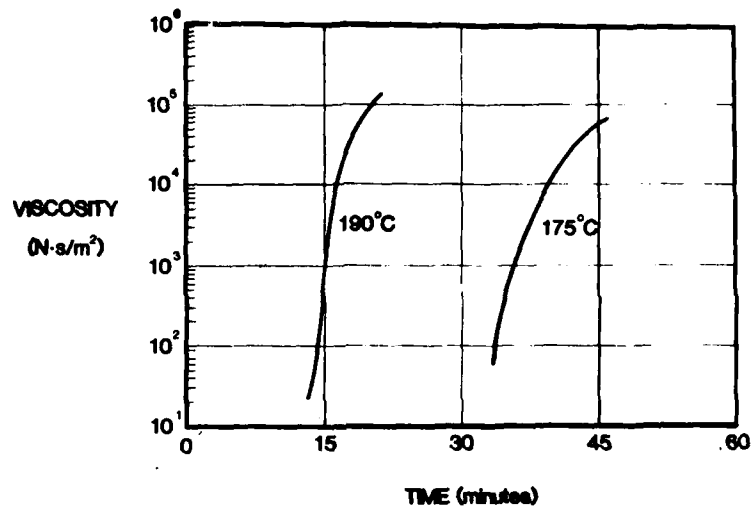


Figure 6. Cure Rheometry for ATS Parallel Plates, Isothermal, 160mHz

## SECTION III

## SPECIMEN FABRICATION

RTV 664 silicone molds were used to fabricate 20 dogbone tensile specimens (25mm gauge length and two torsion bars (36mm x 12mm x 2mm)). The molds were degassed at cure temperatures prior to polymer casting. The ATS was heated to 125°C and evacuated for 15 minutes. The ATS was then poured into the mold and cured at 125°C for 16 hours. At this point the specimens were removed from the molds. The temperature was then raised to 288°C at a rate of 28°C per half hour. The ATS was then held at 288°C for one hour. The ATS was surrounded by dry nitrogen gas during all stages of cure. These conditions were more than required by the kinetics data yet well below decomposition kinetics. The resulting test specimens were sorted into two equal groups; one kept dry and the other conditioned wet (95°C, 95% R.H.) for approximately 30 days. The specimens intended for surface characterization were cast in the manner of the torsion bar specimens. Those specimens were cured in a glass reactor vessel using the previously annotated cure cycle.

## SECTION IV

### MECHANICAL PROPERTIES

The dry and wet conditioned test specimens were tested and their mechanical properties measured. The dogbone tensile test specimens were tested at constant strain rate (0.02/min) to failure. Load vs. time diagrams were recorded continuously. Figure 7 schematically describes the recorded data and the resulting data reduction process. Since the specimens were tested at constant strain rate, the strain is directly proportional to time. The secant moduli vs. time data is thus obtained for the dry and wet ATS and shown in Figure 8.

The stress at failure and strain at failure data points determined from the constant strain rate testing are plotted in Figure 9 as suggested by Smith (Reference 5). These graphs are useful to convey the locus of stresses and strains at failure. Data taken at ambient temperatures are shown in the upper left-hand region of the graph, while data taken at high temperatures appear in the lower right-hand region. The tensile strength ranged from  $6.1 \times 10^7 \text{ n/m}^2$  (8.8 ksi) at  $25^\circ\text{C}$  to  $5.5 \times 10^6 \text{ n/m}^2$  (0.8 ksi) at  $315^\circ\text{C}$ . The failure strain was around 4%. This data is shown in Figure 9 with the solid line representing the dry specimens and the dashed line being the humidity conditioned specimens. The test chamber was dry, however, so some opportunity for drying out during the test did occur. This effect may be more pronounced at high temperatures because of increased time for specimen equilibrium. The wet data shows little effect from the moisture in these tests.

#### Dynamic Modulus Spectra

The ATS bar specimen was tested in torsion using the Rheometrics RMS-7200 spectrometer. In the test one end of the bar is subjected to a sinusoidally varying (0.16 Hz) angular displacement, while the other end is immobilized by an instrumented torque grip. The ratio between the torque and angular displacement and their phase angle are used to calculate the real ( $G'$ ) and loss ( $G''$ ) components of the dynamic shear modulus ( $G^* = G' + iG''$ ). These properties were measured over the temperature range of  $+100^\circ\text{C}$  to  $380^\circ\text{C}$ . The results for the rest are shown in Figure 10. The data shown are for the dry specimen. Missing is the data for

the environmentally conditioned bar. From this data we can note that the glass transition temperature is above 380°C which is the upper limit of the heating chamber.

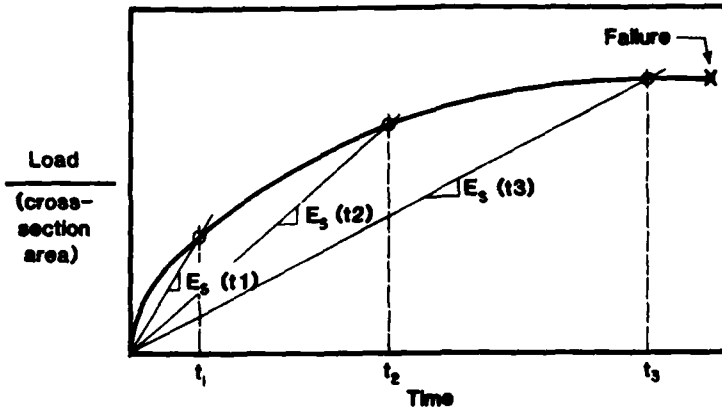


Figure 7. Schematic of Constant Strain Rate Test Results

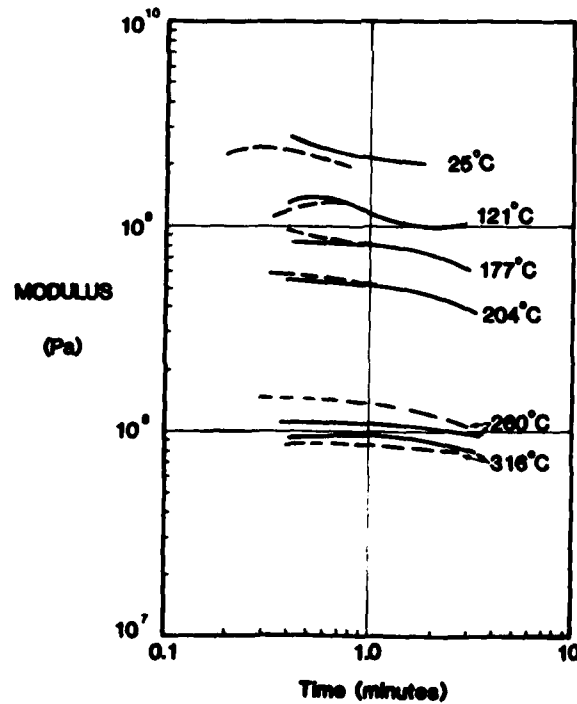


Figure 8. Secant Modulus for ATS

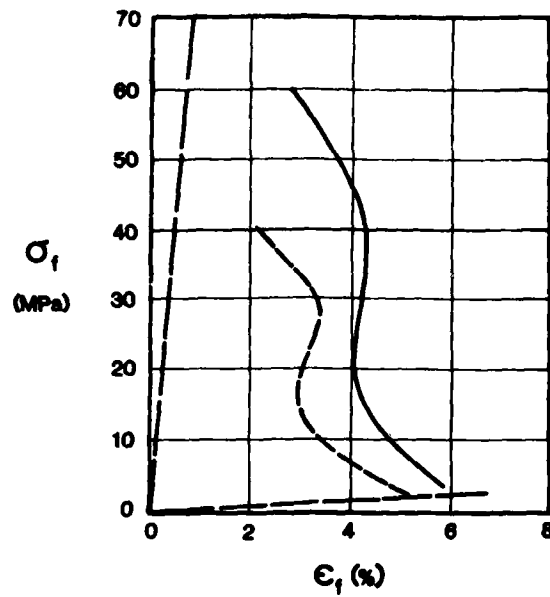


Figure 9. Smith Plot for ATS

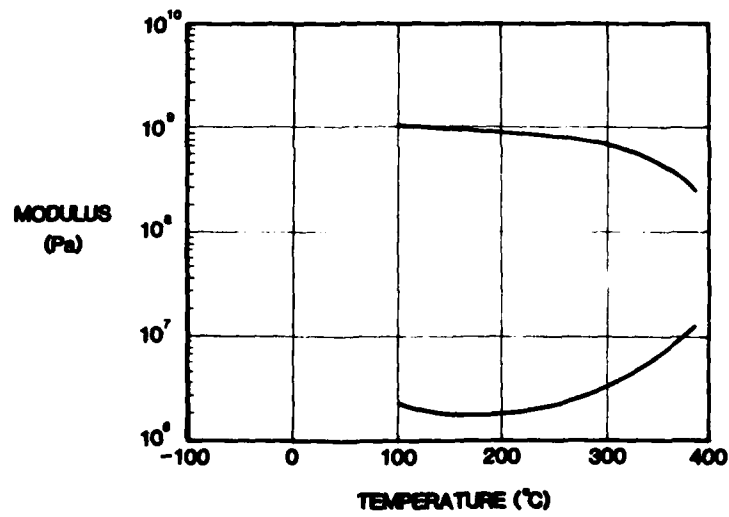


Figure 10. Dynamic Shear Modulus for ATS

SECTION V  
VOLUME CHANGE

The volume change of a polymer during temperature and moisture excursions and cure is an important material characteristic. Unfortunately, cure shrinkage is not available at the present time. The dimensional changes of cured ATS were measured using a Dupont 943 Thermomechanical Analyzer attached to a Dupont 990 Controller. The dimensional change or coefficient of thermal expansion below glass transition temperature is  $5 \times 10^{-5}/^{\circ}\text{C}$ . Volume change during moisture conditioning ( $95^{\circ}\text{C}$ , 95% R.H.) was not measured directly, but inferred from weight gain. These data are somewhat scattered and are shown in Figure 11.

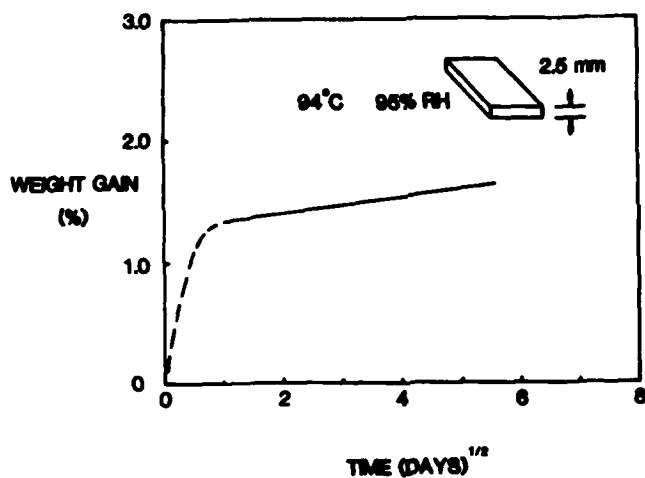


Figure 11. Moisture Uptake for ATS

SECTION VI  
SURFACE ENERGETICS

To quantify surface energetics, contact angle measurements were made following the methods of Drzal and Kaelble (References 6 and 7). Contact angles were measured (in a clean room at 22°C, 40% R.H.) using the Rame'-Hart goniometer. The bar specimen was cooled in liquid nitrogen and cleaved to create a contaminant-free surface. Sessile drops of 0.005 ml were used for nine different reference liquids (Table 1). The contact angle data were reduced using the equation:

$$\frac{W_a}{2(\gamma_l^d)^{1/2}} = (\gamma_s^d)^{1/2} + (\gamma_s^p)^{1/2} \frac{(\gamma_l^p)^{1/2}}{(\gamma_l^d)^{1/2}}$$

where  $\gamma_l^p, \gamma_l^d$  = polar and dispersive forces of known liquids

$\gamma_l^p, \gamma_s^d$  = polar and dispersive forces of polymer

$W_a = \gamma_L (1 - \cos\theta)$  work of adhesion

A linear least squares fit gave the polar and dispersive components of the polymer. The results are shown in Figure 12. The total surface energy is close to that of an epoxy (DGEBA-mPDA). The notable difference is the reduced polar component of 9.0 mJ/m<sup>2</sup> vs. 11.6 mJ/m<sup>2</sup> for the epoxy. These results predict, thermodynamically, the wetting of graphite, aluminum, and titanium surfaces. In addition, the reduced polarity should increase the moisture resistance and durability of the van der Waals bonding forces between the polymer and the adhered surface.

TABLE 1  
SURFACE TENSIONS OF KNOWN LIQUIDS

LIQUID	$\gamma_L^p$ mJ/M <sup>2</sup>	$\gamma_L^d$ mJ/M <sup>2</sup>	$\gamma_L$ mJ/M <sup>2</sup>
FORMAMIDE	26.12	32.38	58.1
PG-1200	6.88	24.5	31.8
METHYLENE IODIDE	2.34	48.58	50.8
WATER	51.12	21.8	72.0
ETHYLENE GLYCOL	19.27	29.38	48.2
n-OCTANE	0	21.62	21.62
HEXA DECANE	0	27.2	27.2
1-BROMO NAPHTHALENE	0	44.4	44.4
GLYCERIN	30.0	54.0	64.0

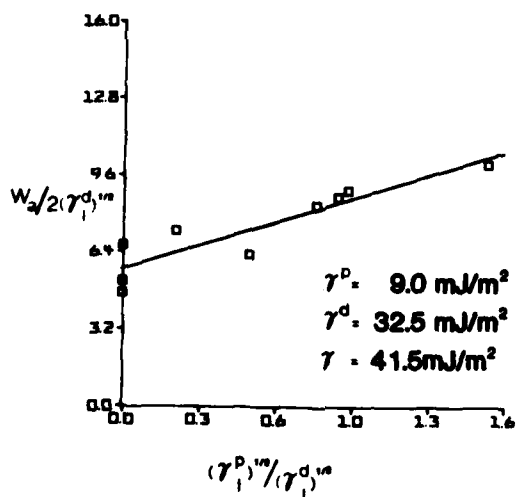


Figure 12. Surface Energetics for ATS

## SECTION VII

## CONCLUSIONS

As the method developed and data was collected, several experiments were suggested as being necessary to this evaluation. The first involves gathering data involving material mechanical durability for time at temperature properties. Secondly, fracture energy data also is an important material parameter. Both of these experiments are under development and will be included in later work. Underlying all the work involving fabricated specimens implies a state of cure advancement (completion). Although a cure cycle was chosen as previously mentioned, the final state of cure for this and other similar acetylene terminated systems is not well understood and is the subject of investigation within this laboratory. This lack of knowledge has not precluded fabrication of engineering specimens nor the garnering of useful mechanical property data.

The scientific method and interdisciplinary relationships provide the opportunity for a unique understanding of material characteristics. This understanding will serve to simplify the subsequent steps in material assessment. In addition, the data generated on the polymer can be fed back to the synthesis chemist for improvements in molecular design. Optimally, the risks have been minimized before increasing investment of manpower and material.

ATS has been shown to have many desirable features. The material has good properties to  $\sim 177^{\circ}\text{C}$ , while being easy to process. ATS shows exceptional moisture resistance. Consequently, ATS has entered the next evaluation phase which involves studying ATS impregnation of graphite and fabrication and testing of graphite composite structures.

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