NASA Technical Memorandum 89829

Ethynylated Aromatics as High Temperature Matrix Resins

(NASA-TM-89829) ETHYNYLATED AROMATICS AS HIGH TEMPERATURE MATRIX RESINS (NASA) 12 p CSCL 11D

N88-18640

Unclas

G3/24 0128796

Frances I. Hurwitz
Lewis Research Center
Cleveland, Ohio

Prepared for the
18th National SAMPE Technical Conference
Seattle, Washington, October 7-9, 1986

E-3480

ETHYNYLATED AROMATICS AS HIGH TEMPERATURE MATRIX RESINS

Frances I. Hurwitz
National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135

Abstract

Di- and trifunctional arylacetylenes were used as monomers to form thermoset matrix resin composites. Composites can be hot pressed at 180°C to react $\sim$80% of the acetylene groups. Crosslinking is completed by postcuring at 350°C. The postcured resins are thermally stable to nominally 460°C in air. As a result of their high crosslink density, the matrix exhibits brittle failure when uniaxial composites are tested in tension. Failure of both uniaxial tensile and flexural specimens occurs in shear at the fiber matrix interface. Tensile fracture stresses for 0° composites fabricated with 60 v/o Celion 6K graphite fiber were 827MPa (120ksi). The strain to failure was 0.5%. Composites fabricated with 8 harness satin Celion cloth (Fiberite 1133) and tested in tension also failed in shear at tensile stresses of 413MPa (60ksi).

1. INTRODUCTION

4,4'-diethynyldiphenylmethane (DEDPM) was first proposed as a matrix resin by Bilow et al.(1) and Austin and Bilow.(2) The monomer polymerizes exothermically by a free radical mechanism. It also will form copolymers with other arylacetylenes. Two such trifunctional acetylenes, 1, 3, 5-triethynyltriphenylbenzene (TETPB) and 4,4'4''-triethynytriphenylmethane (TETPM), are shown in Figure 1a. Because of their high aromatic content, these polymers are of exceptional thermal stability and, on heating above 600°C, form carbon chars with yields of >90%.(2)

The present study addresses the applicability of these monomers for fabrication of high temperature resin matrix composites stable in the 370°-400°C temperature regime, just above the useful operating temperature of polyimides. Reaction kinetics were determined by isothermal and scanning differential scanning calorimetry (DSC) techniques. Composites fabricated with DEDPM and copolymers of DEDPM with TETPB or TETPM were characterized by dynamic mechanical spectroscopy, thermogravimetric analysis (TGA), thermomechanical analysis (TMA), three and four point flexure and tensile testing.

2. EXPERIMENTAL

4, 4'-diethynyldiphenylmethane, 1, 3, 5-triethynyltriphenylbenzene and 4,4',4'' -triethynyltriphenylmethane were purchased from Chem. Biochem. Research Inc., Salt Lake City, Utah, and used without further purification. Reaction kinetics of the homopolymers, as well as of copolymers formed between DEDPM and 10 and 20 w/o of the trifunctional arylacetylenes, were determined by isothermal differential scanning calorimetry using the relationship:

$$\int_0^{\alpha} d\alpha = \frac{1}{\Delta H_t} \int_0^{t} \frac{dH}{dt}\, dt \qquad (1)$$

where:

ΔH_t is the total heat of reaction,

$\frac{dH}{dt}$ is the rate heat evolution

and α is the extent conversion ($0<\alpha<1$).

For homopolymerization of DEDPM, ΔH_t is the total heat evolved as determined by scanning DSC at 10°C/min to 400°C. In the case of the copolymers, a heat of reaction per mole of acetylene was determined from ΔH_t for DEDPM, and the total heat for the mixed acetylenes calculated on the basis of total moles of acetylene per gram.(3)

Composites were fabricated with DEDPM and unsized Celion 6K graphite fiber (CCF, Inc.) as well as with 8 harness satin Celion cloth (Fiberite 1133). Composites of DEDPM with 10 w/o trifunctional monomers (either TETPB or TETPM) were fabricated with continuous filament only. Both 12 ply 0° and 10 ply balanced ±45° laminates were prepared. Continuous filament was wound at 4.7 turns/cm (12 turns/in). The resin was partially polymerized by staging at 120°C for 16h in the case of DEDPM homopolymer, or 10h for the dry mixed DEDPM and TETPB or TETPM powders (see RESULTS and DISCUSSION). Fiber (or cloth) was preheated using an array of heat lamps, and the resin applied as a hot melt. After cooling and accompanying crystallization of the resin, the prepreg was removed from the drum, cut and stacked in a matched metal die and pressed at 180°C for 1.5h at a pressure of 1.38MPa.

Composites were characterized both as fabricated and after postcuring for 1h at 350°C. Dynamic mechanical studies were conducted on specimens 63.5 x 6.35 x 1.70mm in forced torsion using a Rheometrics RMS 7700 spectrometer at a frequency of 1Hz. Coefficients of expansion and glass transition temperatures were measured using a Perkin-Elmer thermomechanical TMS-2 analysis system (TMA) equipped with a 725°C furnace. Measurements were made in helium. Thermogravimetric analysis (TGA) was carried out both in nitrogen and in air at a heating rate of 10°C/min using composite samples nominally 17.0 x 20.3 x 20.3mm.

Flexural specimens nominally 101 x 6.35 x 1.70mm 6.35mm wide were tested in both three and four point bending at a span to depth ratio of 32 to 1. Crosshead speed was 1.27mm/min for three point loading, and .5mm/min in four point loading of the fabric reinforced composites. Tapered fiberglass epoxy tabs were bonded to straight-edged tensile specimens 203 x 12.7 x 1.70mm in dimension. Strain was measured by gauges bonded to both sides of the composite. Loading was at a crosshead rate of 1.27mm/min.

3. RESULTS AND DISCUSSION

3.1 Reaction Kinetics

DEDPM melts at 60°C to a low viscosity fluid, and polymerizes exothermically at 120°C and above. A typical DSC scan is shown in Figure 2. The heat of reaction, as determined by the area under the exotherm, is 1116 J/g, or 127.2kJ per mole of acetylene. On heating to 350°C virtually all the acetylene groups are reacted, as indicated by the disappearance of the 3294cm^{-1} infrared band attributable to acetylene hydrogen stretching.(4) On polymerization at 180°C, slightly more than 80% reaction of acetylene end groups is achieved (Figure 3). At this extent of conversion and temperature vitrification occurs, and higher temperatures are needed to achieve crosslinking. This further crosslinking on "postcuring" can be demonstrated by the increase in shear modulus seen in forced torsion of a Celion/DEDPM composite cured at 180°C for 1.5h when that composite is heated beyond the initial cure temperature (Figure 4).

The polymerization kinetics obtained at 170-200°C have been shown(4) to follow the relationship for an autocatalyzed reaction proposed by Kamal and Sourour(5):

$$\frac{d\alpha}{dt} = k\alpha^m(1-\alpha)^n \tag{2}$$

where α is the extent of conversion and t is time

$$k = k_0 e^{-E/RT} \qquad (3)$$

with:

$k_0 = 1.942 \times 10^{11}\ \mathrm{sec}^{-1}$

E = 126.2kJ/mole (activation energy)

m = .106

n = 1

R = 8.3144 J deg^{-1} mole^{-1}, and

T = temperature, K

On copolymerization of DEDPM with trifunctional monomers at 180°C, the rate of conversion is decreased slightly when TETPB is the second monomer, and more substantially with addition of TETPM (Figure 3). The decreased rate of polymerization may be attributed to the increase in viscosity which accompanies the introduction of trifunctional crosslinking sites. The smaller size of the TETPM molecule relative to that of TETPB may introduce steric hindrance to reaction of the third ethynyl group, which could account for the further decrease in reactivity. At low temperature (120°C) the relative rates of reaction for the copolymerization and homopolymerization are reversed (Figure 5). The kinetics no longer can be described by equation (2), and the rate of reaction is greater on copolymerization with TETPB than with TETPM. The low temperature polymerization reactions are discussed in greater detail elsewhere.(3)

Because the melt viscosity of the monomers is extremely low, attempts to fabricate composites by solvent casting the monomers and then hot pressing resulted in excessive loss of resin from the mold and high void content. Therefore the resins were first partially polymerized by heating at 120°C. (Staging at higher temperatures is difficult due to the large heat of reaction and leads to runaway exotherms).

It was determined empirically that the viscosity at nominally 20% conversion is suitable for hot melt fabrication; this corresponds to a polymerization time of 16h for DEDPM, or 10h for the 10% copolymers, as shown in Figure 5. (Heating of the copolymers at 120°C for 16h takes them beyond their gel point). Scanning DSC of TETPB and TETPM alone produces heats of reaction of 59% and 81%, respectively, of those calculated based on the total number of ethynyl groups present. Therefore, in fabricating composites, only 10% additions of trifunctional reactants were studied so as to avoid the influence of unreacted end groups.

3.2 Composite Physical Properties

The as-fabricated composites (hot pressed at 180°C, but not post-cured) have glass transition (T_g) temperatures, as determined by TMA at a heating rate of 10°C/minute in helium, of 320°C for DEDPM and the .90 DEDPM/.10 TETPM copolymer, and 333°C for the .90 DEDPM/.10 TETPB copolymer. The copolymers are not fully cured at this stage; considerable variation is seen from sample to sample for the copolymers, though not for the homopolymer. On heating to higher temperatures, a second peak T_g appears at >460°C following one hour postcure at 350°C. The T_g continues to shift upward on further heating. TGA shows that the composites all lose ∿0.4% of their weight on postcuring at 350°C, and this weight loss occurs on first heating to 350°C; there is no further decrease on holding at this temperature for 1h. Further heating in inert atmosphere (nitrogen) shows the onset of more significant weight loss occurs at >500°C for all composites (Table I), and above 470°C for DEDPM composite heated in air (Figure 6), corresponding to the oxidation of carbon. Total weight loss to 950°C in inert atmosphere is <6%.

3.3 Composite Mechanical Properties

Uniaxial composites having nominally 60 v/o fiber content were screened in three point flexural loading. At a span to depth ratio of 32 to 1, all samples tested failed in shear at mid-plane. Stresses at fracture, including the shear stress at midplane, are summarized in Table II. All three resin compositions share a low shear strength; the DEDPM and 10% TETPB resins seemed slightly more resistant to shear than did the 10% TETPM composition.

In uniaxial tension all three resins again failed in shear within the gripping region one or two plies below the laminate surface. Examination of the fracture surface by optical microscopy showed that fracture occurred at the fiber matrix interface, and not within the matrix. All samples failed at approximately 827MPa (120ksi) at a strain of 0.5%.

Balanced 10 ply ±45° laminates were fabricated in an attempt to measure shear strength.(6) These showed evidence of delamination prior to testing and were not evaluated further. Measurement of the coefficient of thermal expansion along the principal composite axes (Figure 7) showed essentially zero expansion in the fiber direction, and marked anisotropy in the 2 and 3 directions. The expansion in the 2 direction was significantly greater than that through the thickness, suggesting that these composites delaminate as a result of high residual thermal stress ($\alpha = 3.0 \times 10^{-5}$ along the 2 axis, and 2.2×10^{-5} along the 3 axis for the DEDPM matrix composite as fabricated; these values changed on further heating).

Fabric reinforced composites also failed by delamination at approximately half the stress level determined for the unidirectional laminates. Flexural testing of the fabric composites resulted in delamination one ply below the surface under compression.

4. CONCLUSIONS

Composites of poly (4,4'-diethynyldiphenylmethane) and copolymers of DEDPM with 1, 3, 5-triethynyltriphenylbenzene and 4,4',4'' -triethynyltriphenylmethane are easily formed by hot pressing at low temperatures (180°C). Postcuring at 350°C is required to increase crosslink density. The resins are thermally stable to ∿460°C in air, and thus are candidate materials for use at ∿400°C, above the current use temperatures of polyimides. The laminates produced from these arylacetylenes all show a tendency to fail in shear under both flexural and tensile loadings. Because of their high extent of crosslinking the matrices behave in a brittle manner. Uniaxial tensile specimens all failed at 0.5% strain by delamination. The poor shear strength and low strain to failure combine to limit load bearing capabilities. The matrices themselves appear to be anisotropic as evidenced by the differences in coefficient of expansion along the 2 and 3 composite axes. This results in high residual thermal stresses, and poor laminates when a cross-ply lay-up is employed. However fabric reinforced composites demonstrate reasonable tensile properties. In bending the fabric reinforced laminates all failed by debonding just below the compressive surface; this might be attributed to the low strain capability of the matrix, or to the poor bond between matrix and fiber. The ease of fabrication and temperature capabilities render these resin systems of interest for further study despite their mechanical strength limitations.

5. REFERENCES

1. N. Bilow, A. L. Landis, W. B. Austin, and D. D. Wooley, "Arylacetylenes as High Char Forming Matrix Resins," SAMPE J., vol. 18, no. 3, May-June 1982, pp. 19-24.

2. W. B. Austin, and N. Bilow, "Diethynyl Aromatic Hydrocarbons Which Homopolymerize and Char Efficiently After Cure," U.S. Patent 4,284,834, Aug. 1981.
3. F. I. Hurwitz, L. Hyatt, L. D'Amore, H. X. Nguyen, and H. Ishida, "Copolymerization and Di- and Trifunctional Aryl Acetylenes," to be submitted to Polymer, 1987.
4. H. X. Nguyen, H. Ishida, F. I. Hurwitz, L. D'Amore, and L. Hyatt, "Polymerization of Diethynyldiphenylmethane: DSC, FTIR, and NMR Characterization," to be submitted to J. Polym. Sci., Polym. Phys. Ed., 1987.
5. M. R. Kamal, and S. Sourour, "Kinetics and Thermal Characterization of Thermoset Cure," Polym. Eng. Sci., vol. 13, no. 1, Jan. 1973, pp. 59-64.
6. B. W. Rosen, "A Simple Procedure for Experimental Determination of the Longitudinal Shear Modulus of Unidirectional Composites," J. Compos. Mater., vol. 6, Oct. 1972, pp. 552-554.

6. ACKNOWLEDGMENTS

The author wishes to thank L. Hyatt, R. Phillips and P. Addante for their assistance, and A. Calomino for helpful discussions.

TABLE I

THERMAL STABILITY AS DETERMINED BY TGA AT 10°/MIN. IN N_2

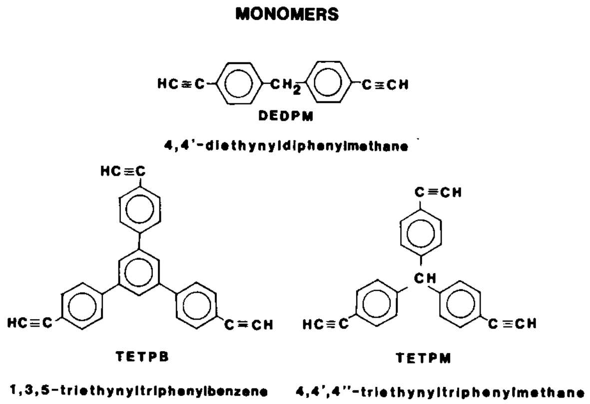
Matrix	Onset, °C
DEDPM	520
.90 DEDPM/.10 TETPB	540
.90 DEDPM/.10 TETPM	550

TABLE II

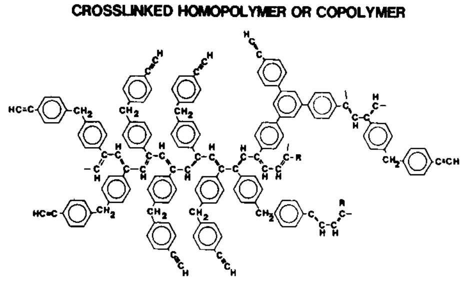
THREE POINT FLEXURAL STRENGTH
32:1

Matrix	Fracture Stress* MPa	Fracture Stress* ksi	Shear Stress at Fracture MPa	Shear Stress at Fracture ksi
DEDPM	1116	162.2	17.3	2.51
.90 DEDPM/.10 TETPB	1185	171.7	18.4	2.68
.90 DEDPM/.10 TETPM	992	144.3	15.3	2.22

*All specimens failed in shear



(A) MONOMERS.



(B) PROPOSED POLYMER STRUCTURE.

FIGURE 1. - MOLECULAR STRUCTURES.

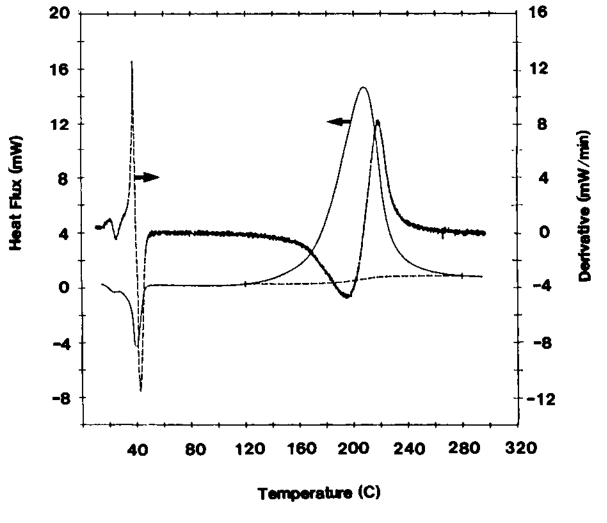


FIGURE 2. - TYPICAL DSC SCAN OF DEDPM AT 10 ^{o}C/MIN SHOWING MELTING FOLLOWED BY EXOTHERMIC POLYMERIZATION.

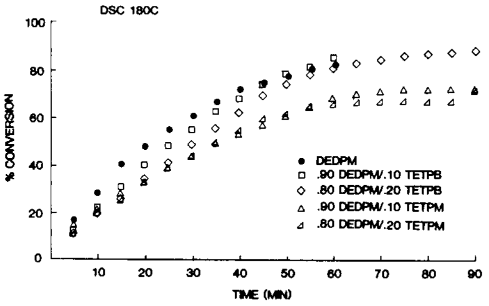


FIGURE 3. - EXTENT OF CONVERSION, α, WITH TIME FOR DEDPM AND COPOLYMERS HEATED ISOTHERMALLY AT 180 ^{o}C, AS DETERMINED BY DSC.

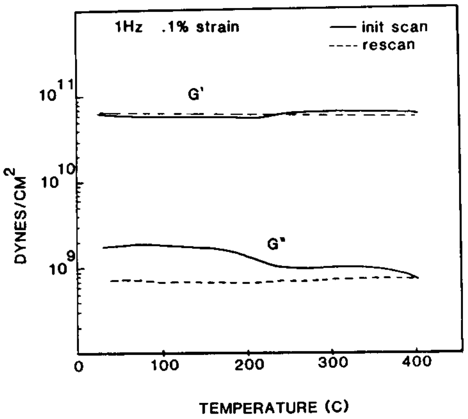


FIGURE 4. - SHEAR MODULI G' AND G'' AS MEASURED IN FORCED TORSION AT 1 Hz FOR AS-FABRICATED CELION/DEDPM COMPOSITE.

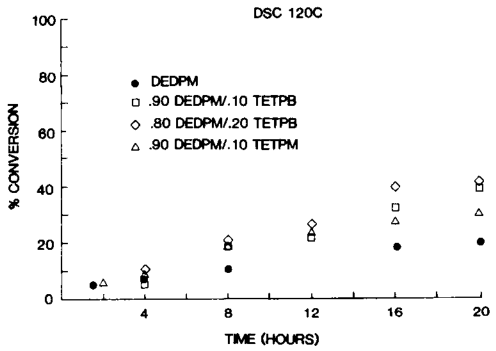


FIGURE 5. - EXTENT OF CONVERSION, α, WITH TIME FOR DEDPM AND COPOLYMERS HEATED ISOTHERMALLY AT 120 °C, AS DETERMINED BY DSC.

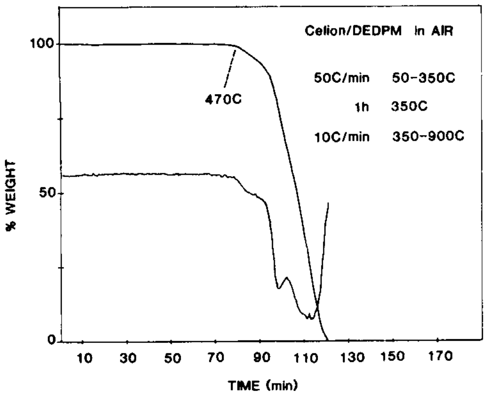


FIGURE 6. - WEIGHT LOSS ON POSTCURING AT 350 °C FOR 1 HR FOLLOWED BY HEATING AT 10 °C/MIN FROM 350 TO 900 °C FOR CELION/DEDPM COMPOSITE HEATED IN AIR.

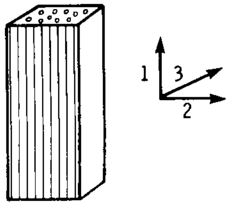


FIGURE 7. - COMPOSITE PRINCIPLE AXES.

1. Report No. NASA TM-89829	2. Government Accession No.	3. Recipient's Catalog No.

4. Title and Subtitle

Ethynylated Aromatics as High Temperature
Matrix Resins

5. Report Date

6. Performing Organization Code

506-43-11

7. Author(s)

Frances I. Hurwitz

8. Performing Organization Report No.

E-3480

10. Work Unit No.

9. Performing Organization Name and Address

National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135

11. Contract or Grant No.

13. Type of Report and Period Covered

Technical Memorandum

12. Sponsoring Agency Name and Address

National Aeronautics and Space Administration
Washington, D.C. 20546

14. Sponsoring Agency Code

15. Supplementary Notes

Prepared for the 18th National SAMPE Technical Conference, Seattle, Washington, October 7-9, 1986.

16. Abstract

Di- and trifunctional arylacetylenes were used as monomers to form thermoset matrix resin composites. Composites can be hot pressed at 180 °C to react ~80 percent of the acetylene groups. Crosslinking is completed by postcuring at 350 °C. The postcured resins are thermally stable to nominally 460 °C in air. As a result of their high crosslink density, the matrix exhibits brittle failure when uniaxial composites are tested in tension. Failure of both uniaxial tensile and flexural specimens occurs in shear at the fiber matrix interface. Tensile fracture stresses for 0° composites fabricated with 60 vol % Celion 6K graphite fiber were 827 MPa (120 ksi). The strain to failure was 0.5 percent. Composites fabricated with 8 harness satin Celion cloth (Fiberite 1133) and tested in tension also failed in shear at tensile stresses of 413 MPa (60 ksi).

17. Key Words (Suggested by Author(s)) Acetylene terminated resins Diethynyldiphenylmethane Composites	18. Distribution Statement Unclassified - unlimited STAR Category 24

19. Security Classif. (of this report)	20. Security Classif. (of this page)	21. No. of pages	22. Price*
Unclassified	Unclassified	11	A02

*For sale by the National Technical Information Service, Springfield, Virginia 22161