NASA Technical Memorandum 81918

NASA-TM-81918 19810005568

CROSSLINKING OF AROMATIC POLYAMIDES VIA PENDANT PROPARGYL GROUPS

ANNE K. ST. CLAIR, TERRY L. ST. CLAIR,
JOHN D. BARRICK, AND FRANCIS J. CAMPBELL

DECEMBER 1980

National Aeronautics and
Space Administration

Langley Research Center
Hampton, Virginia 23665

INTRODUCTION

The use of thermoplastics such as polyamides as matrix resins for composite or laminate fabrication has one major drawback. They must be processed at and have a softening temperature of at least 50°C above the temperature at which they are to be used so that their stiffness properties will be acceptable. This problem becomes compounded when an organic fiber is the reinforcing agent with such a polymer, because the fiber has a characteristic temperature at which it begins to irreversibly lose its stiffness properties. This is generally due to a relaxation phenomenon occuring in a highly oriented fiber.

Attractive organic fibers for structural composite applications are of the aromatic polyamide class such as Kevlar^{R} which has a relaxation slightly below 300°C. In order to fabricate a structural laminate with this fiber reinforcement a processing temperature of 280°C should not be exceeded in order to assure retention of fiber stiffness. This thermal restriction must now in turn be imposed on the resin or polymer, meaning it should be processable at a temperature lower than 280°C.

In an effort to improve the applicability of wholly aromatic polyamides as matrix resins for Kevlar^{R} fiber composites, methods for crosslinking N-methyl-substituted aromatic polyamides have been investigated. The approach used to reach this goal was to take advantage of the low processing temperature (154-160°C) of methyl-substituted polyamides; and, in addition, incorporated a propargyl crosslinking agent at various points along the polymer backbone causing the polymer to "set-up" when treated at a higher temperature (280°C).

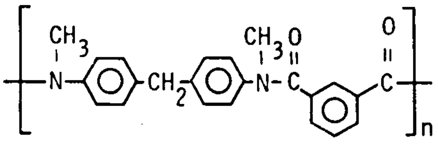
N81-~~8~~14080#

N-METHYL-SUBSTITUTED AROMATIC POLYAMIDES

Attempts to produce a polymer system which would be thermally and chemically compatible with polyamide (Kevlar^R) fibers led to the development of an aromatic secondary polyamide shown below (Ref. 1). The substitution of amide hydrogens with methyl groups did much to improve the processability of an all aromatic polyamide. The glass transition temperature (Tg) of the unsubstituted polyamide was reduced from 257°C to 159°C by incorporation of N-methyl groups. Methyl substitution also caused a reduction in the degree of crystallinity, and significantly improved the solubility and thermal stability of the polymer.

Although the processability of the polyamide was improved by lowering the Tg, a problem existed in that the material behaved as a thermoplastic, which made use of the full thermal potential of the fiber virtually impossible. A need still remained for a crosslinking mechanism to convert this polymer to a thermoset without exceeding 300°C. Latent propargyl groups were therefore incorporated into the polymer to produce crosslinks at approximately 280°C.

N - METHYL - SUBSTITUTED AROMATIC POLYAMIDES *



CH_3 - SUBSTITUTION:

- LOWERED T_g (257°C TO 159°C)
- REDUCED DEGREE OF CRYSTALLINITY
- IMPROVED SOLUBILITY IN CHLORINATED SOLVENTS
- IMPROVED THERMAL STABILITY

DISADVANTAGE:

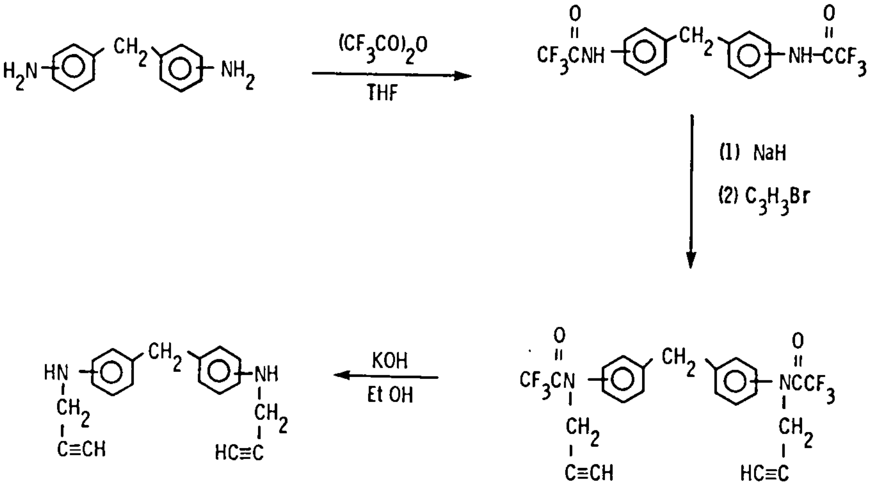
USE AT HIGH TEMPERATURES WAS LIMITED BY LOWERED T_g

* Greenwood, Kahley, Wolfe, St. Clair, Johnston; J. Polym. Sci: Polym. Chem. Ed., Vol. 18, 1047-1059 (1980).

PREPARATION OF THE PROPARGYL-CONTAINING DIAMINE MONOMER

The propargyl-containing diamine monomers used in the preparation of propargylated polyamides were synthesized by the N,N'-dialkylation of primary methylene dianiline (MDA) (Ref. 2). According to the reaction scheme below, the reaction of trifluoroacetic anhydride with 3,3'- or 4,4'-MDA produced a 99% yield of bis(trifluoroacetamido)diphenylmethane. This compound was then propargylated by adding propargyl bromide to a NaH/dimethylformamide solution of the alkylated diamine. After stirring at room temperature, the mixture was neutralized and the product dried to produce an 84% yield. The propargyl-containing diamine was made by the reduction of the bispropargyl alkylation product in KOH/ETOH for 1 hour at room temperature. On recrystallization in 95% ETOH, a 92% yield of the bispropargyl diamine was obtained.

PREPARATION OF N, N' - BISPROPARGYL DIAMINES *



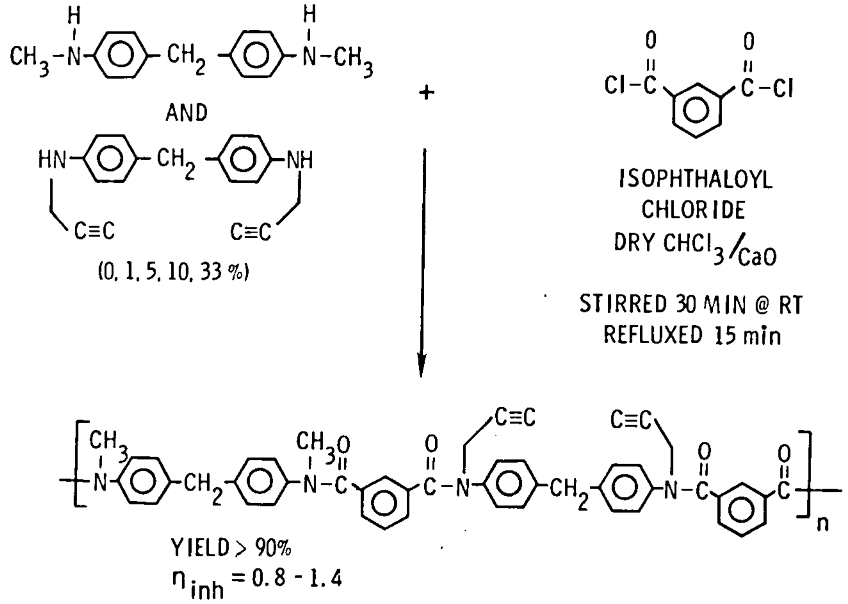
m, m' - 67% YIELD
p, p' - 77% YIELD

* Armistead, Wolfe, Greenwood; 31st SE-ACS, Roanoke, Va, October 1979.

PREPARATION OF METHYL-SUBSTITUTED POLYAMIDES CONTAINING PROPARGYL GROUPS

Polymers were prepared according to the reaction scheme below. Several polyamides were made with varying percentages (0, 1, 5, 10 and 33%) of the propargyl diamine incorporated into the polymer backbone. Appropriate molar portions of the propargylated and methyl-substituted diamines were dissolved in dry $CHCl_3$ containing powdered CaO. As this mixture stirred, a solution of isophthaloyl chloride in $CHCl_3$ was added dropwise. The solution was stirred for 1/2 hour at room temperature and refluxed for 15 minutes to produce a colorless, viscous polymer solution. The polyamide was precipitated by pouring into rapidly stirring petroleum ether or hexane. The resulting white, fibrous polymer was then filtered and dried *in vacuo* at 100°C overnight.

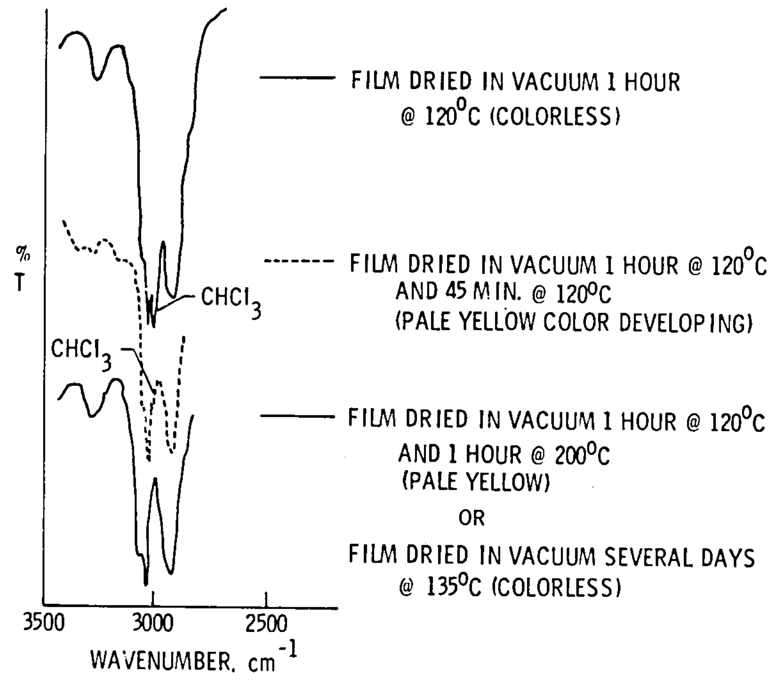
METHYL - SUBSTITUTED POLYAMIDES CONTAINING PROPARGYL CROSSLINKING GROUPS



PREPARATION OF POLYAMIDE FILMS

In order to characterize these new propargyl-containing polyamides, thin films were prepared from solutions of the polymers (10% solids by weight in $CHCl_3$). Films were cast onto glass plates and cured in vacuum at elevated temperature. After one hour in vacuum at 120°C (a conventional cure for polyamides), the films were colorless but still contained a significant amount of solvent as evidenced by the infrared spectrum. The difficulties associated with the removal of chlorinated solvents from high-temperature polymers have been reported elsewhere (Refs. 1 and 3). To remove all traces of $CHCl_3$, the films were heated: (1) in vacuum 1 hour each at 120°C and 200°C; or (2) several days in vacuum at 135°C. For the remainder of this study, the latter cure was employed so as not to confuse the effects of crosslinking with other factors such as thermal degradation.

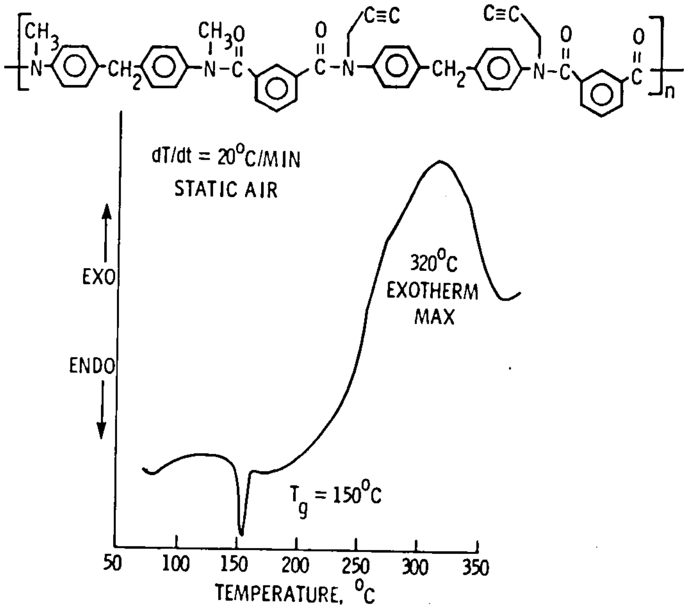
INFRARED SPECTRA OF POLYAMIDE FILMS PREPARED FROM $CHCl_3$ SOLUTIONS



CHARACTERIZATION BY DIFFERENTIAL SCANNING CALORIMETRY

Differential scanning calorimetry (DSC) was used as a characterization tool for studying the thermal crosslinking behavior of the polyamide films. The apparent Tgs of films containing various amounts of propargyl diamine were determined by DSC in a nitrogen atmosphere using a 20°C/min. temperature program. The thermal crosslinking of the polyamide film containing 33% propargyl diamine is represented by the DSC scan displayed below. After a sharp Tg at 150°C, the polymer exhibits a broad exotherm centered around 320°C. This exotherm, which begins between 200° and 250°C is indicative of crosslinking brought about by the added latent propargyl groups.

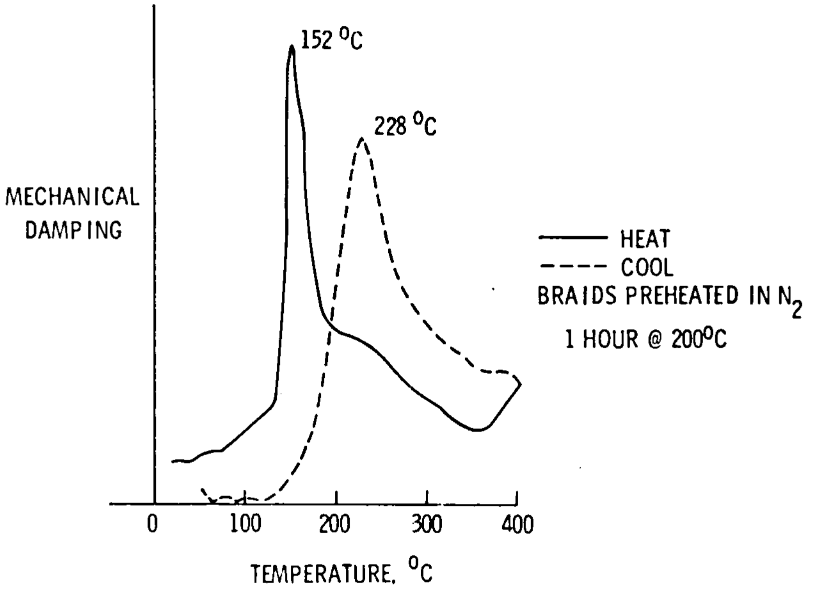
DSC SCAN OF POLYAMIDE CONTAINING 33% PROPARGYL DIAMINE



CHARACTERIZATION BY TORSIONAL BRAID ANALYSIS

The thermal crosslinking of the polyamide propargyl groups was also observed by torsional braid analysis (TBA). TBAs were performed in a nitrogen atomosphere on glass fiber braids coated with 10% $CHCl_3$ solutions of the polyamides containing 0% and 33% propargyl diamine. After a pretreatment in nitrogen for 1 hour at 200°C, the braids were heated at 3°C/min. to 400°C. Spectra were recorded both on heating and cooling the braids. The Tg (154°C) of the control polymer containing 0% propargyl diamine remained unchanged after the polymer was heated to 400°C. The Tg of the polymer containing 33% propargyl diamine, however, increased from 152°C to 228°C as shown in the spectrum below. The added propargyl groups caused an increase in the Tg of this polyamide indicating that crosslinking had occurred.

TORSIONAL BRAID ANALYSIS OF POLYAMIDE CONTAINING 33% PROPARGYL DIAMINE



THERMAL CROSSLINKING

Crosslinking was observed after several types of thermal treatment to polyamide powders, films and TBA braids. Initial Tgs of the polymers ranged from 150°-165°C depending upon the effects of varying degrees of crystallinity (Ref. 1). After heating the polyamide powders 1/4 hour at 280°C in air, the Tgs determined by DSC increased in the order of increasing propargyl content. Similar behavior was observed by thermomechanical analysis (TMA) and TBA. Thermal crosslinking of the propargyl-containing polyamide films was monitored by the disappearance of the acetylenic carbon-hydrogen infrared stretch at 3290 cm^{-1}. The once soluble films were found to be totally insoluble in such solvents as $CHCl_3$ and cresol after thermal crosslinking.

From the data shown below, it is evident that these polymers can be thermally crosslinked below 300°C. Their use as matrix resins for polyamide fiber composites is therefore made feasible.

THERMAL CROSSLINKING OF PROPARGYL - CONTAINING POLYAMIDES

% PROPARGYL DIAMINE	INITIAL T_g[a] (°C)	T_g AFTER 1/4 HR @ 280° C[a] (°C)	T_g AFTER 1 HR @ 300° C[b] (°C)	T_g AFTER HEATING TO 400° C[c] (°C)
0	165	165	163	154
1	151	171	Films yellowed after thermal exposure 3290 cm^{-1} IR peak disappearing Solubility in $CHCl_3$ and cresol lost	
5	165	193		
10	160	200		
33	150	206	248	228

[a] DETERMINED ON POWDER BY DSC @ 20° C/MIN IN AIR

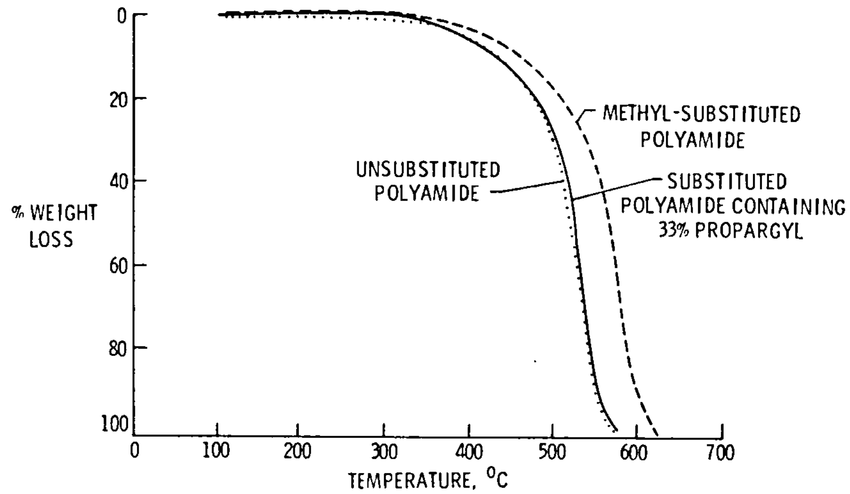
[b] DETERMINED ON FILM BY TMA @ 10° C/MIN IN AIR

[c] DETERMINED ON TBA BRAIDS BY COOLING 3° C/MIN IN N_2

DYNAMIC THERMOGRAVIMETRIC ANALYSIS OF AROMATIC POLYAMIDES

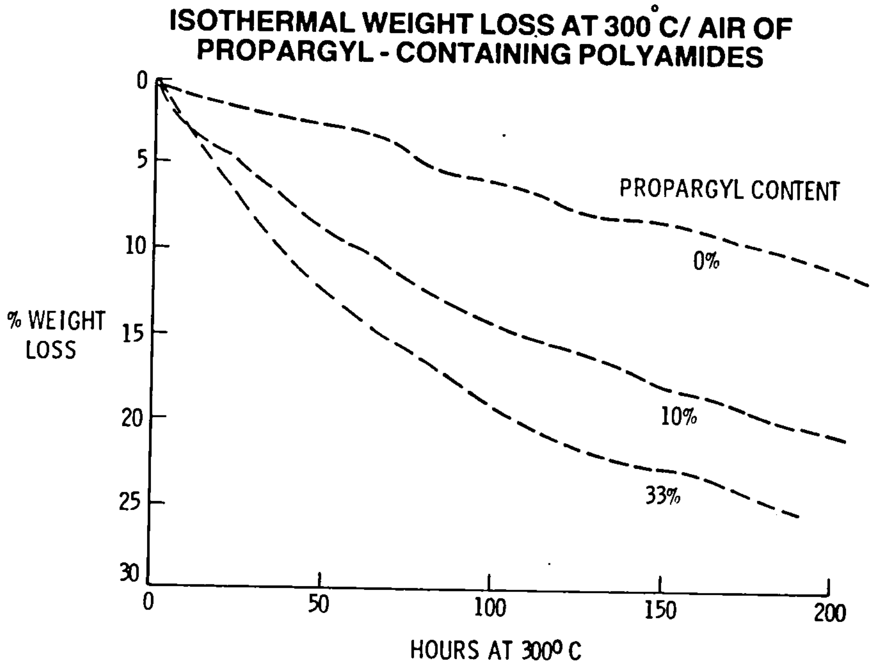
Thermogravimetric analyses (TGAs) of polyamide films were performed in static air at a heating rate of 2.5°C/min. As stated earlier, methyl-substituted polyamides showed an improvement in thermal stability compared to the unsubstituted polymer (Ref. 1). As shown by the graph below, however, this enhanced thermal stability of the methyl-substituted polymer was lost upon incorporation of propargyl groups. In fact, the dynamic TGA curve of the methyl-substituted polymer containing 33% propargyl diamine was very similar to that of the original unsubstituted polyamide.

TGA's COMPARING THERMAL STABILITIES OF SUBSTITUTED POLYAMIDES



ISOTHERMAL AGING

Isothermal TGAs were performed at 300°C in static air on polyamide films containing varying amounts of propargyl diamine. After 200 hours at 300°C, the weight loss of the films was found to increase with increasing propargyl content. Although 300°C aging is considered a harsh treatment for polyamides, it should provide an accelerated view of the long-term aging properties of these polymers.



RADIATION EXPOSURE

In an attempt to crosslink latent propargyl groups, polyamide films containing 0-33% propargyl diamine were exposed to ultraviolet, electron beam, and cobalt-60 gamma radiation. The Tgs of the polyamide films were monitored by thermomechanical analysis before and after irradiating. Exposure to a 40-W UV lamp for 300 hours in air caused a reduction in the Tgs of polyamide films containing propargyl groups. The UV-exposed films which were yellow and extremely brittle were obviously degraded by the combination of both UV and humid air. However, exposure to radiation from an electron beam (2 MeV electrons from Van de Graaff accelerator) and cobalt-60 (1.2, MeV gamma rays) had relatively no affect on the Tgs of the polyamide films. After irradiation by electron beam and cobalt-60, the films were still colorless and soluble indicating that no crosslinking had occurred.

RADIATION EXPOSURE TO PROPARGYL - CONTAINING POLYAMIDES

% PROPARGYL DIAMINE	INITIAL T_g OF FILM (^{o}C)	UV[a] 300 HRS/AIR T_g (^{o}C)	ELECTRON BEAM[b] 25Mrad	51Mrad	COBALT-60[b] 51Mrad T_g ^{o}C
			T_g (^{o}C)		
0	163	158	160	162	161
1	157	153	147	–	–
5	158	154	161	–	–
10	160	145	160	–	–
33	154	127	155	153	156

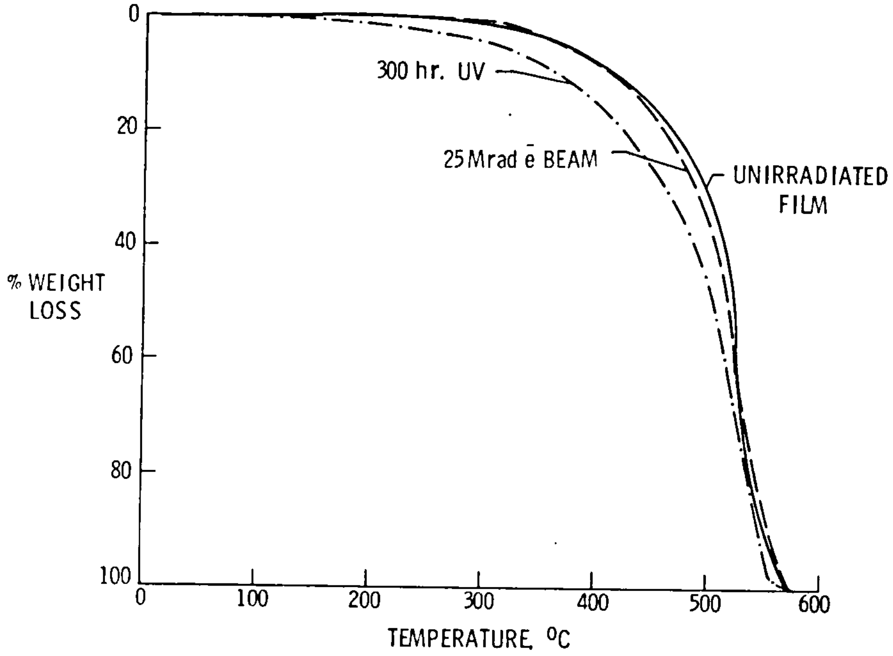
[a] FILMS YELLOWED AND BECAME BRITTLE

[b] FILMS REMAINED ESSENTIALLY COLORLESS AND SOLUBLE

TGA CURVES OF IRRADIATED FILMS

Thermogravimetric analyses (TGAs) were performed on polyamide film containing 33% propargyl diamine before and after irradiation. When compared to the unirradiated and electron beam-irradiated films, the UV-exposed film showed an early weight loss at temperatures below 200°C. This loss in thermal stability confirms the degradation of this polymer as observed earlier by TMA.

TGA CURVES OF 33% PROPARGYL - CONTAINING POLYAMIDES



INFRARED ANALYSIS OF FILMS

The polyamide films were analyzed by infrared (IR) spectroscopy before and after thermal crosslinking and irradiating. The IR spectrum of unirradiated film containing 33% propargyl diamine displayed distinct peaks at 3290 cm^{-1} and 2120 cm^{-1} due to the presence of the propargyl triple bond. No changes in the IR spectrum of this polymer were observed upon irradiation with an electron beam (or cobalt-60). UV irradiation, however, caused a weakening of the propargyl triple bond-related bands and the appearance of a broad hydroxyl peak at 3500 cm^{-1} (acid formed due to decomposition) and a carbonyl peak at 1725 cm^{-1} (photo-oxidation of -CH_2-hydrogens, Ref. 4). Thermal crosslinking of the film in air at 300°C resulted in a diminishing of the triple bond carbon-hydrogen stretch, complete disappearance of the triple bond peak, and the appearance of a carbonyl "shoulder" at 1725 cm^{-1}.

INFRARED SPECTRAL ANALYSIS OF 33% PROPARGYL-CONTAINING POLYAMIDES

FILM HISTORY	≡C-H 3290 cm^{-1}	C≡C 2120 cm^{-1}	HYDROXYL 3500 cm^{-1}	C=O 1725 cm^{-1}
Vac. 135°C (UNIRRADIATED)	SHARP	SHARP	NONE	NONE
ē BEAM 25 Mrad	SHARP	SHARP	NONE	NONE
UV 300 HRS	WEAKENED	WEAKENED	BROAD	SHOULDER (PHOTO OXIDATION)
THERMALLY CROSSLINKED AIR/300 °C	DIMINISHING	NONE	NONE	SHOULDER

CONCLUSIONS

A study was conducted to crosslink methyl-substituted polyamides via pendant propargyl groups for the purpose of improving the applicability of this resin as a matrix for polyamide fiber composites. Films of the polyamide containing 1-33% propargyl diamine were successfully crosslinked by heating in air at 280°-300°C. The thermal crosslinking of the latent propargyl groups was evidenced by a rise in the glass transition temperatures of the films with increasing propargyl concentration, a loss in solubility, and disappearance of the propargyl-related peaks from the infrared film spectra. Thermal crosslinking was accomplished with a slight loss in thermooxidative stability.

Other crosslinking methods investigated include exposure of the propargyl-containing polyamide films to ultraviolet, electron beam, and cobalt-60 radiation. UV exposure in the presence of humid air caused the films to degrade. Exposure to an electron beam and cobalt-60 gamma rays had no effect on the polyamide films.

From the results of this investigation, propargyl-containing polyamides are feasible matrices for polyamide fiber (Kevlar^R) composites. These materials are processable at advantageously low temperatures and thermally crosslinkable at temperatures below the relaxation temperature of the fiber. Compatibility of these resins with aromatic polyamide fibers gives them high potential for success as matrix resins for Kevlar^R composites.

REFERENCES

1. Greenwood, T.D.; Kahley, R. A.; Wolfe, J. F.; St. Clair, A. K.; and Johnston, N. J.: J. Polym. Sci. - Polym. Chem. Ed., Vol. 18, 1047 (1980).
2. Armistead, D. M.; Wolfe, J. F.; and Greenwood, T. D.; "N-Propargylated Derivatives of Benzanilides and N,N'-Bisbenzoyl Aromatic Diamines As Model Compounds For Thermosetting Aromatic Polyamides", 31st Annual Southeastern Regional Meeting, American Chemical Society, Roanoke, VA (1979).
3. St. Clair, A. K. and Johnston, N. J.; J. Polym. Sci. Polym. Chem. Ed., Vol. 15, 3009 (1977).
4. Kato, Masao and Yoneshige, Yasuo; J. Polym. Sci.- Polym. Lett. Ed., Vol. 17, 79 (1979).

1. Report No.
NASA TM-81918

2. Government Accession No.

3. Recipient's Catalog No.

4. Title and Subtitle
CROSSLINKING OF AROMATIC POLYAMIDES VIA PENDANT PROPARGYL GROUPS

5. Report Date
December 1980

6. Performing Organization Code

7. Author(s)
Anne K. St. Clair, Terry L. St. Clair, John D. Barrick, and*Francis J. Campbell

8. Performing Organization Report No.

9. Performing Organization Name and Address
NASA-Langley Research Center
Hampton, VA 23665

10. Work Unit No.
505-33-33-02

11. Contract or Grant No.

12. Sponsoring Agency Name and Address
National Aeronautics and Space Administration
Washington, D.C. 20546

13. Type of Report and Period Covered
Technical Memorandum

14. Sponsoring Agency Code

15. Supplementary Notes
This paper was presented at the 1980 Southeast-Southwest Regional Meeting of the American Chemical Society, December 10-13, 1980, New Orleans, LA.
*Francis J. Campbell, Naval Research Laboratory, Washington, DC 20375.

16. Abstract

Methods for crosslinking N-methyl substituted aromatic polyamides have been investigated in an effort to improve the applicability of these polymers as matrix resins for Kevlar^R fiber composites. High molecular weight polymers were prepared from isophthaloyl dichloride and 4,4'-bis(methylamino)diphenylmethane with varying proportions of the N,N'-bispropargyl diamine incorporated as a crosslinking agent. The propargyl-containing diamines were crosslinked thermally and characterized by infrared spectroscopy, differential scanning calorimetry, and thermogravimetric analysis. Attempts were also made to crosslink polyamide films by exposure to ultraviolet light, electron beam, and gamma radiation.

17. Key Words (Suggested by Author(s))
Polyamides
Crosslinking
Propargyl

18. Distribution Statement
Unclassified-Unlimited
Subject Category - 27

19. Security Classif. (of this report)
Unclassified

20. Security Classif. (of this page)
Unclassified

21. No. of Pages
15

22. Price*
A02

N-305

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