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LIQUID OXYGEN-COMPATIBLE FILAMENT-WINDING MATRIX RESIN

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16. Abstract

Polyurethanes derived from hydroxy terminated polyperfluoropropylene oxide prepolymers were evaluated as matrix resins for filament wound composites which would be exposed to liquid (and 100% gaseous) oxygen environments. A number of structural modifications were brought about by variations in prepolymer molecular weight, and alternative curing agents which allowed retention of the oxygen compatibility. Although satisfactory performance was achieved at sub-ambient temperatures, the derived composites suffered considerable property loss at ambient or slightly elevated temperatures. To attain overall effectiveness of the composite system, upgrading of the polymer thermomechanical properties must first be achieved.

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FOREWORD

This report was prepared by Whittaker Corporation, Research and Development Division (WRD), under Contract No. NAS3-15832, entitled "Liquid Oxygen-Compatible Filament-Winding Matrix Resin", for the NASA Lewis Research Center. The work was performed during the period 3 April to 3 December 1972. The work was administered under the direction of the Materials and Structures Division with Dr. Tito T. Serafini acting as Project Manager.

The research work was conducted in WRD's Polymer Research Department under the direction of Chadwick B. Delano, Acting Manager. Mr. Edward S. Harriso was the principal investigator. Also contributing to the program was Mr. William D. Warner, Senior Technician. Analytical work was carried out by Dr. William G. Stevens.

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SUMMARY

Polyurethanes derived from difunctional hydroxyl terminated polyperfluoropropylene oxide (PFPOH) prepolymers were evaluated as matrix resins for E-glass filament wound composites which would be exposed to liquid (and 100% gaseous) oxygen environments.

Urethane extension (end-capping) was brought about by reaction of the basic PFPOH with 6-chloro-2,4,5-trifluoro-m-phenylene diisocyanate. The thus formed isocyanate terminated prepolymer (PFPOI) was cured by a number of alternative curing agents. These curing agents were selected primarily on the basis of their nonflammability characteristics in oxygen atmospheres, both individually and in combination with PFPOI. A second consideration was in the requirement of attenuated reactivity with the very reactive haloaromatic isocyanate moiety.

The effect of variation in prepolymer molecular weight was established when PFPOI was cured with the various curing agents which included the following: cyanoguanidine, bis-guanamines derived from lower molecular weight telomers of difunctional polyperfluoropropyleneoxide, di-amines derived from the same, and urethane extended hydroxyl terminated PFPOH, as well as combinations of these.

Although sub-ambient temperature performance was satisfactory for the derived composites, the strength at elevated temperatures was insufficient for the desired application. In order to attain overall effectiveness of the composite system the inadequate inadequate elevated temperature performance much be up-graded with no corresponding loss in the excellent oxygen inertness. Experimental details of prepolymer(s), curing agents, and polymer(s) are included.

TECHNICAL DISCUSSION

A. INTRODUCTION

The approach to the development of a liquid oxygen-compatible matrix resin for filament-wound composite systems involves selected modification of the basic poly(perfluoropropylene oxide) urethane system (PFPO) which has been extensively developed in adhesive and conformal coating application, during previous contracts at Whittaker Corporation, Research and Development Division (WRD) under NASA sponsorship (NAS8-11086 and NAS8-27087, Marshall Space Flight Center). The resultant state-of-the-art PFPO resin has demonstrated remarkable resistance to flammability and impact with gaseous- and liquid-oxygen at pressures up to 1030 N/cm^2 at 10 kg-m impact loading levels.

The basic PFPO polymer is obtained by the following multistep synthesis, shown in Figure A.

Cure of the resulting isocyanate-terminated PFPOI prepolymer has been previously accomplished with various functional reagents, resulting in extension/crosslinking modes incorporating urethane/allophanate, urea/biuret, urea and semi-carbazide linkages, derived from polyfunctional amines, hydrazides, and related systems.

The previous programs have been directed toward elastomeric systems which exhibit useful performance from cryogenic temperatures up to ca. 370°K (200°F).

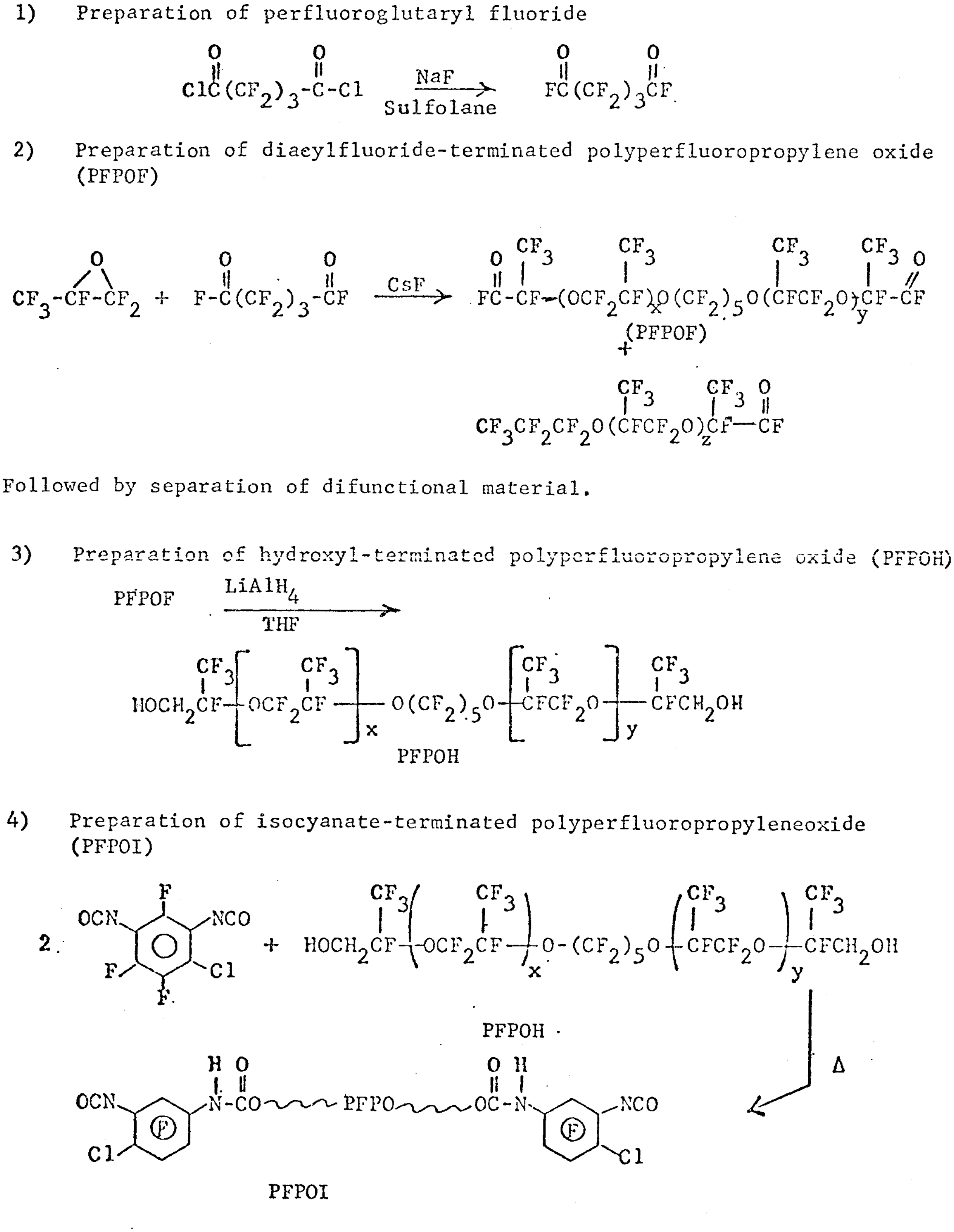
The elastomeric character, as well as the useful upper thermomechanical limit, of the cured resin systems is profoundly affected by such factors as: the nature of the particular curing agents; the degree and type of crosslink; and, in particular, the molecular weight level of versatile glycol-terminated PFPOH prepolymer segment.

B. PREPARATION OF PFPOH PREPOLYMERS

It was felt that, to impart enhanced support resin character to the cured system, as well as to significantly raise its upper thermomechanical limit, the effective length of the perfluoro-ether inter-urethane chain length must first be reduced. The decrease in molecular weight of this non-bonding segment was expected to impart higher bulk modulus and tensile strength to the system without deleterious effect on its nonflammability and impact resistance in 100% oxygen environments.

1. Preparation and Fractionation of Acid Fluoride-Terminated PFPOF Prepolymer

Efforts during the early phase of the program were directed toward developing techniques (primarily stoichiometry variations) to obtain lower molecular weight glycol-terminated PFPOH prepolymer. This prepolymer is formed by hydride-reduction of the corresponding di-acyl fluoride-terminated PFPOF prepolymer (Eq. 3 in Figure A below).



1) Preparation of perfluoroglutaryl fluoride

$$ClC(O)(CF_2)_3C(O)Cl \xrightarrow[\text{Sulfolane}]{\text{NaF}} FC(O)(CF_2)_3C(O)F$$

2) Preparation of diacylfluoride-terminated polyperfluoropropylene oxide (PFPOF)

Followed by separation of difunctional material.

3) Preparation of hydroxyl-terminated polyperfluoropropylene oxide (PFPOH)

$$PFPOF \xrightarrow[\text{THF}]{\text{LiAlH}_4}$$

4) Preparation of isocyanate-terminated polyperfluoropropyleneoxide (PFPOI)

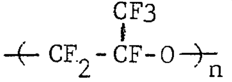
Figure A. Synthesis of Perfluoropropylene Oxide (PFPO) Prepolymers

Small-scale synthesis of the PFPOF proceeded in high yield, with a predominance of lower molecular weight material in the product. The reaction particulars, showing the stoichiometry used, are summarized in the Experimental Section.

Separation of the various oligomeric PFPOF products is best accomplished by fractional distillation under vacuum, providing relatively pure, oligomeric fractions. End-group analysis of the PFPOF has likewise proven much more reliable, based on titration techniques, than end-group analysis of the hydroxyl-terminated PFPOH prepolymer. Because of the very low order of reactivity of the fluoro-alcohol,end-group analysis of the PFPOH is far less reliable.

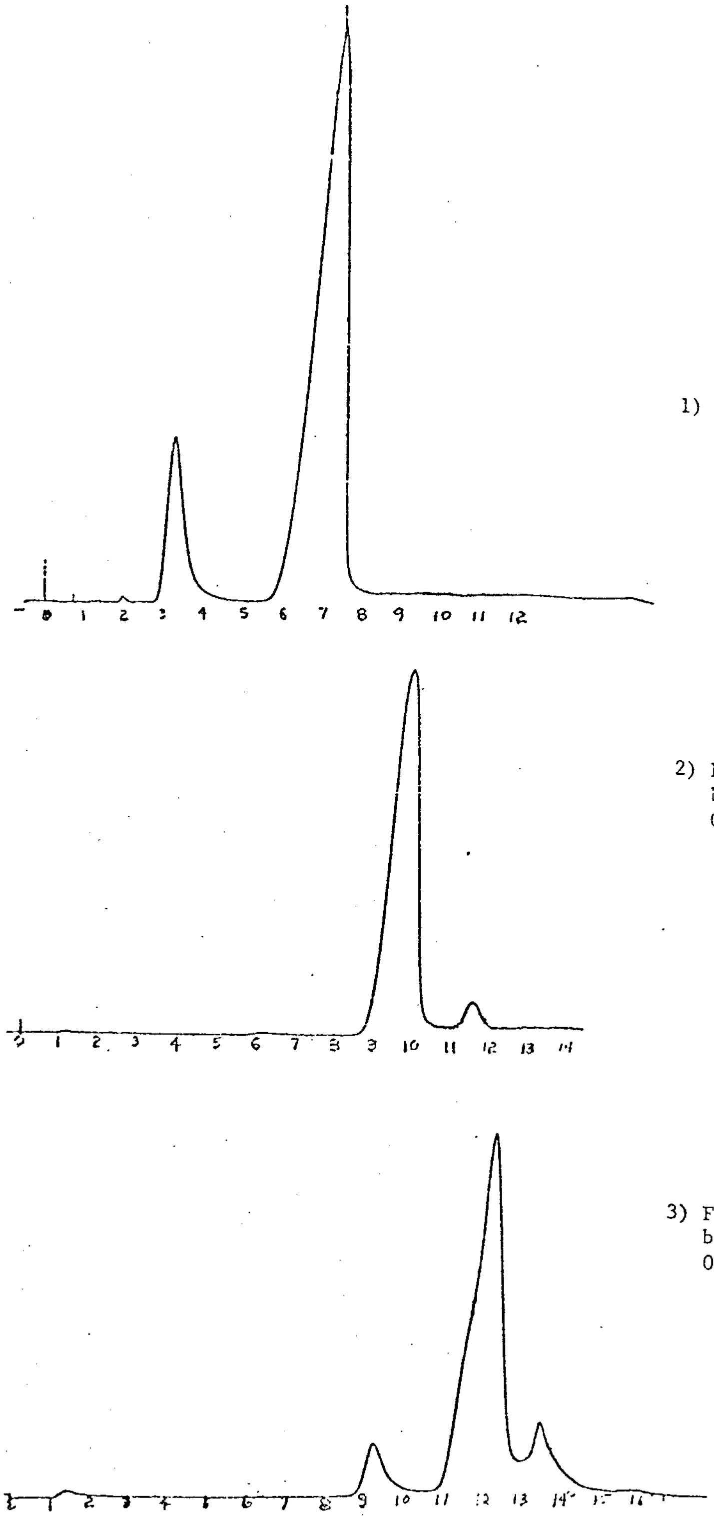
Molecular weight determinations of PFPOF were determined by vapor pressure osmometry (VPO) using Freon TF solvent and have routinely been carried out in the past both in our laboratory and also at the Galbraith Laboratories.

Figure B shows replicates of the vapor-phase chromatograms (VPC) obtained for the crude (isolated) PFPOF, and for the various fractions.

The discrete boiling points of the various homologs provides identification of the component peaks as obtained by VPC. Since the molecular weight increment must be 166 (molecular wt. of perfluoropropylene oxide mer-component,  $\left(CF_2-\overset{CF_3}{\overset{|}{C}}F-O\right)_n$ the molecular weight of a mixture may be closely approximated by simple integration of the relative peak areas and performing a weighted summation of the totals. The final identification of the various peaks is most readily accomplished using a combination of vapor pressure osmometry and end-group analysis data.

End group analysis of the isolated fractions yielded the following results:

Fraction No.	Acid Fluoride Analysis
2	497
4	557
6	657



1) Fraction No. 2
bp 136°-138°C at
3 torr

2) Fraction No. 4
bp 73°-74°C at
0.01 torr

3) Fraction No. 6
bp 96°-123°C at
0.2 torr

Figure B. Vapor-Phase Chromatograms of Acyl Fluoride-Terminated PFPOF Fractions*

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* 6 meter W-96 silicone gum column, 5 min hold at 80°C followed by 10°C/min program to 250°C.

Calculation of molecular weight by VPC (based on rationale previously described) yields the following molecular weights:

Cut 2 - 984
Cut 4 - 1094
Cut 6 - 1297

Molecular weight determinations by vapor pressure osmometry (VPO) of these same fractions are included in Table I below.

TABLE I

ACYL FLUORIDE-TERMINATED PFPOF FRACTIONATION RESULTS

Fraction No.	End Group Analysis(1)	Vapor Phase Chromatography(2)	Vapor Pressure Osmometry(3)
2	996	984	1010
4	1114	1094	1170
6	1304	1297	1410

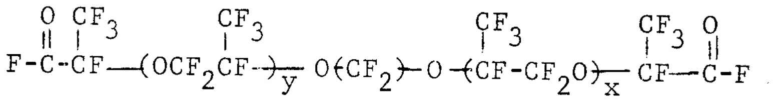
---

(1) Acid fluoride number times 2

(2) 2 meter W-96 silicone gum column used

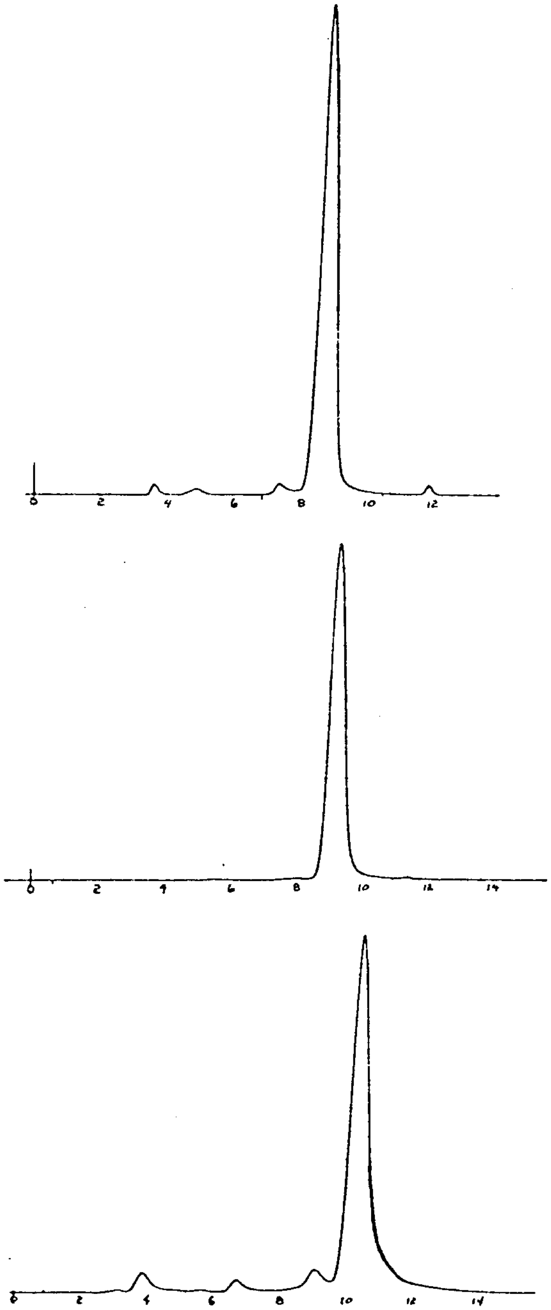
(3) In Freon TF solvent

The excellent agreement among the three measurement modes is apparent. All results agree within the limits of experimental error (±7% in VPO technique). Hence, the parent VPC peaks may therefore be assigned the following values in the PFPOF structure:



$$F-\overset{O}{\overset{\|}{C}}-\overset{CF_3}{\overset{|}{C}F}-(OCF_2\overset{CF_3}{\overset{|}{C}F})_y-O(CF_2)-O-(\overset{CF_3}{\overset{|}{C}F}-CF_2O)_x-\overset{CF_3}{\overset{|}{C}F}-\overset{O}{\overset{\|}{C}}-F$$

Cut No.	Peak at Elution Time (minutes)	Mol. Wt.	x + y Values
2	3	742	1
	6	908	2
4	9	1074	3
	11	1240	4
6	9	1074	3
	11	1240	4
	13	1486	5



1)* Fraction No. 3 of PFPOH obtained from reduction of PFPOF Fraction No. 2 (Figure B,1)

2)*Fraction No. 2 of PFPOH obtained from reduction of PFPOF (Figure B.2)

3)* Fraction No. 2 of PFPOH obtained from reduction of PFPOF Fraction No. 6 (Figure B.3)

Figure C. Hydroxyl-Terminated PFPOH VPC Analyses

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* W-96 silicone column 2 meter
140° to 250°C at 10°C/min with 3 minute hold at 250°C.

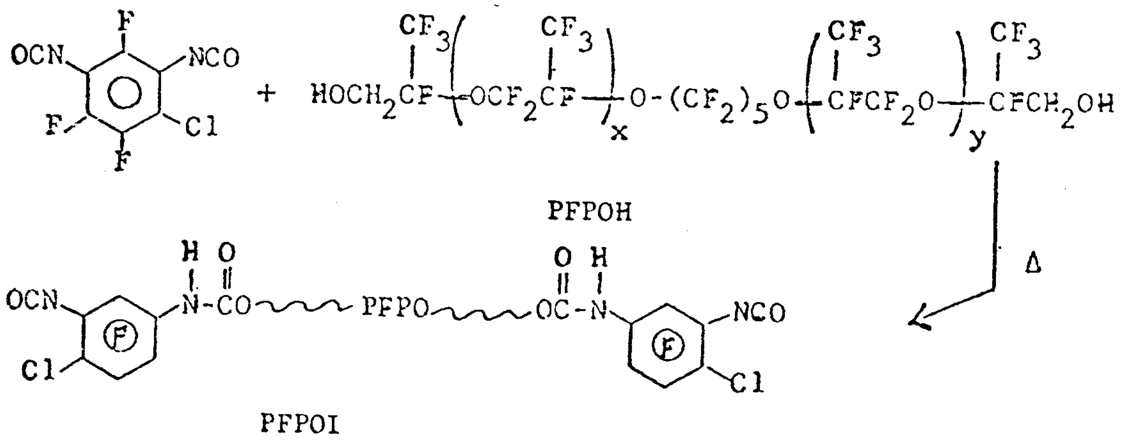
2. Reduction of PFPOF to Hydroxyl-Terminated PFPOH Prepolymer

The three separate PFPOF fractions were individually reduced with lithium aluminum hydride to provide the corresponding PFPOH derivatives. Following isolation of the crude product, purification by fractionation under reduced pressure was again employed. The VPC chromatograms of the major component fractions (difunctional PFPOH) are shown in Figure C (with annotated identification). Infrared analysis indicated complete hydroxyl termination with no residual acidic functionality or olefinic termination.

3. Capping of the Hydroxyl-Terminated PFPOH Prepolymer

The "capping" of the three respective fractions was carried out by the following reaction:

2.



The progress of the reaction has been monitored by infrared spectroscopy, using the disappearance of the absorbtion at 3400 cm^{-1} (OH stretch) and the corresponding appearance of absorptions at 3305 cm^{-1} (NH stretch) and 1745 cm^{-1} ($-C{=}O$ stretch). The reactions were carried out between 90°-100°C for 2-3 hours.

A larger batch of the acyl fluoride-terminated PFPOF prepolymer was prepared using similar reaction conditions to those of the previous preparation. Essentially the same product oligomeric molecular weight distribution was obtained as on the smaller scale. The crude acyl fluoride product was fractionated under reduced pressure with isolation of the following fractions:

PFPOF Fraction	b.p. °C/mm Hg	Total (g)	Molecular Weight By End Group Analysis	Molecular Weight By Vapor Phase Chromatography
4	87-101/2.5-3.0	38	788	
5	64-67/0.01-0.02	136	1017	1060
6	86-93/0.02	83	1156	1164
7	94-103/0.02	98	1275	1265
8	97-128/0.02-0.1	38	1420	1370

The close agreement of these molecular weight values provides accurate definition of complete difunctionality of the derived prepolymer.

Portions of each isolated oligomeric PFPOF prepolymer were individually reduced using the same lithium aluminum hydride techniques described above. Redistillation of the crude material yielded the following PFPOH hydroxyl terminated prepolymer fractions:

PFPOF Fraction (grams)	PFPOH Recovered (grams)	b.p. °C/mm Hg	Mol.Wt. by VPC
5 (90.0)	55.0	126-130/0.1-0.2	1030
6 (75.4)	36.0	128-130/0.1-0.05	1110
7 (89.7)	56.5	122-130/0.8-0.4	1220

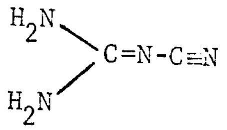
"Capping" of the PFPOH with chlorotrifluoro-m-phenylene diisocyanate was accomplished as before, yielding the versatile isocyanate-terminated PFPOI prepolymer in three corresponding molecular weight ranges.

C. CURE STUDIES

1. Cyanoguanidine Curing Agent

It had been anticipated that an increase in apparent T_g of the cured polymer, and the concurrent elevation of the upper thermomechanical limit could be readily produced by reduction of the inter-urethane distance in the PFPO chain growth. It was likewise hoped that the resulting polymer would not suffer an appreciable loss in toughness with the corresponding increase in bulk modulus. Hence, thermomechanical measurement of the T_g variation with change in PFPOH molecular weight using the various derived PFPOI telomers, with cyanoguanidine as curing agent, was carried out.

Significant improvement in elevated temperature (93°C) performance of the PFPO resin system has been attained by utilizing cyanoguanidine as a curing agent.



The utility of this agent is predicated on its lack of the labile (oxidatively) carbon-hydrogen bonds. In addition, the reactivity of the amine functionality is greatly attenuated by resonance-stabilization and by the multiplicity of the possible tautomeric forms. Reduced reactivity is essential due to the extremely reactive nature of the derived fluoroaryl isocyanate.

Cure of the PFPOI (isocyanate-terminated polyperfluoropropylene oxide) prepolymer proceeds at a reasonable rate only at temperatures in excess of 160°C. The same latency of cyanoguanidine at lower temperatures has long been noted in epoxy resin technology, and has generally been ascribed to the essential insolubility of this curing agent in the various resin systems. A corresponding lack of reactivity has currently been noted in the current PFPOI system. Thus, no significant degree of reaction is apparent after several hours at 121°C. The finely-divided curing agent obviously remains particulate and not appreciable dissolved.

Initial studies were concerned with cure schedule. The PFPOI (molecular weight 1540) and finely ground, dried cyanoguanidine were thoroughly admixed in stoichiometric amounts, warmed to ~66°C and degassed. Films of ca. 1 mm thickness were cured by the following techniques:

(1) Placing the mixture in an ambient oven and heating to 175°C at 10°C/minute. Cure was then continued for one hour at 175°C; and,

(2) Placing the mixture in a preheated oven for one hour at 175°C.

Cured samples from both techniques were brittle with a slight haze. The film prepared by the second procedure was slightly superior, with respect to brittleness and opacity. Consequently, the preheated oven approach was utilized in subsequent cure studies.

It was felt that the milky appearance in the film samples was probably due to stoichiometric imbalance. In other words, the curing agent was not being completely consumed, due to competitive reactions undergone by the extremely reactive isocyanate to form such side products as a biuret, an allophanate and/or a cyclic trimer.

Hence, a series of castings were prepared using various NCO/NH_2 ratios to determine the effect of same on the T_g. Table II lists these results, along with similar results of the other PFPOI oligomers, also cured with cyanoguanidine.

TABLE II

EFFECT OF STOICHIOMETRY AND MOLECULAR WEIGHT ON PFPO GLASS TRANSITION TEMPERATURE

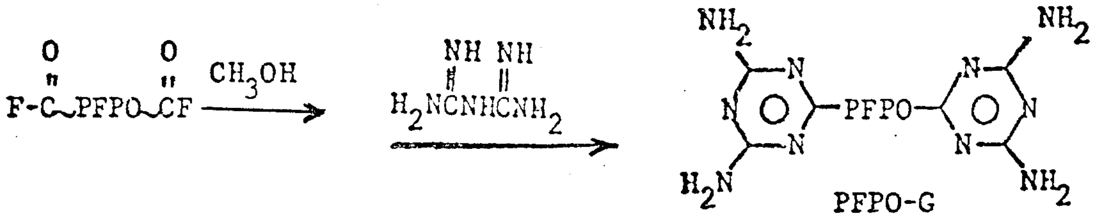
Sample No.	Mol. Wt. PFPOI	NCO/NH_2	T_g by Thermomechanical Analysis
25-2	1540	10/10	33°C
25-3	↓	10/9	30°C
25-4		10/8	35°C
25-5		10/7	34°C
25-6		10/6	34°C
27-1	1380	10/10	30°C
27-2	↓	10/8	32°C
27-3		10/6	31°C
27-4		10/5	31°C
28-1	1710	10/10	26°C
28-2	↓	10/8	30°C
28-3		10/6	24°C
28-4		10/5	24°C

In all cases a somewhat milky casting was obtained. The systems also exhibited a slightly brittle character.

The T_g of the cured polymer has thus been found to be essentially independent of both inter-urethane chain length and, even more surprising, NCO/NH2 ratio. Previous work on similar systems which were evaluated as adhesives indicated a maximum lap shear strength at an NCO/NH_2 ratio of 10/6.7. These results were tentatively ascribed to a complex heterocycle formation which was based on complete disappearance of both isocyanate absorption at 2270 cm^{-1} and also the cyanoguanidine nitrile doublet at 2240-2280 cm^{-1}.

2. Bis-guanamines Derived from Lower Molecular Weight Telomers of PFPOF

The preparation of the derived bis-guanamines from Fraction No. 5 (1020 mol.wt.) from the large scale synthesis of PFPOF was carried out, in accordance with the reaction shown below:



The rationale for the suitability of PFPO-G is based on a consideration of the multiplicity of amine-extension-cure sites (four), coupled with the total absence of oxidatively-labile carbon-hydrogen bonds. Use of such a system was expected to result in a superior cure and enhanced thermal capability for the derived polymer, inasmuch as all extension/crosslink bonds formed are urea linkages in a 1/1 NH_2/NCO ratio as in Figure D. Such linkages are of known higher thermal stability than the normal carbamate/allophanate crosslink.

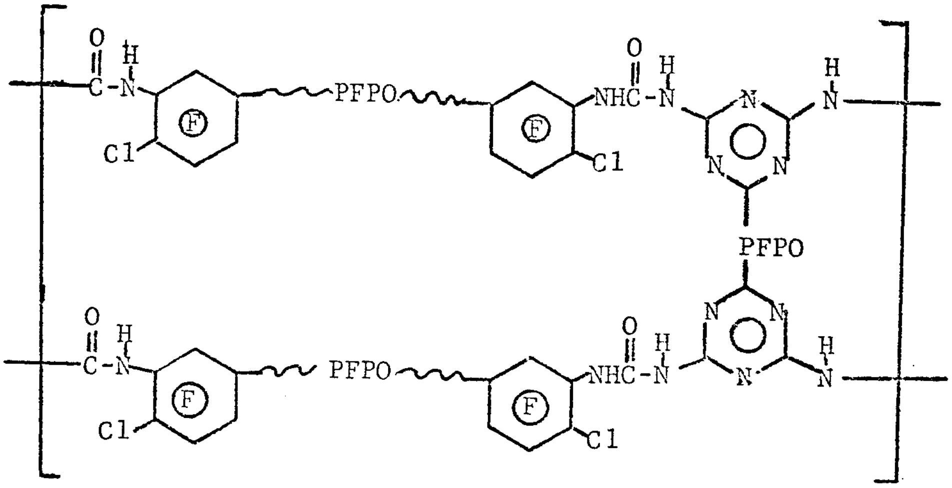


Figure D. Idealized Extended/Cured Polyurea from PFPO-I/PFPO-G

The high density of rigid aromatic rings in this structure, coupled with the efficient hydrogen-bonding capability of the urea and urethane moieties was expected to produce a tougher system. The two-step synthesis was carried out by first preparing and isolating the dimethyl ester followed by reaction with the biguanide.

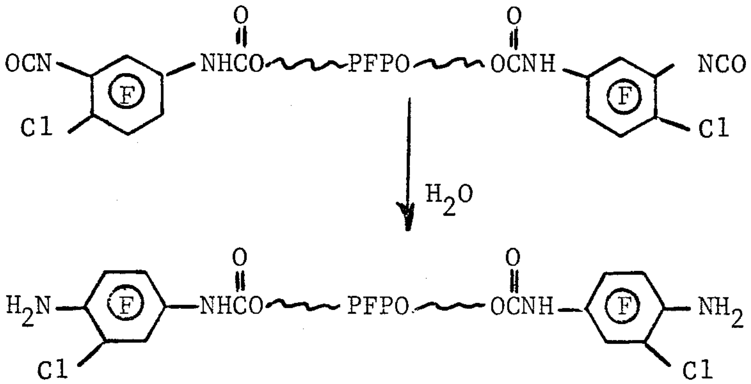
The isolated product (PFPOG) was a brittle solid at room temperature which softened sufficiently at 85°C to allow admixture with PFPOI (mol. wt. 1530). This requisite elevated mixing temperature markedly reduced the pot life. In attempting to de-gas the mixture, the system gelled and became unusable.

The admixing was repeated, with omission of the degassing step, and a specimen was cast for thermomechanical testing. Curing was monitored by infrared spectroscopy. Complete cure is apparently achieved in 40 minutes at 177°C as indicated by disappearance of the IR bands for the isocyanate group.

The T_g of the cured material, which exhibits minimal improvement in room temperature-flexibility, relative to the cyanoguanidine cured system, was determined by thermomechanical (TMA) measurement using a Du Pont No. 741 Thermomechanical Analyzer. The major transition temperature was found to be 34°C, with a second transition at <u>ca</u>. 90°C. At this higher temperature, the system had become significantly softer and less elastomeric. Although elevations of T_g have been achieved by the use of this curing agent the systems displayed two disappointing characteristics: (1) the elevation of T_g was insufficient, and (2) the material showed a marked decrease of toughness with both increase in crosslink density and decrease in inter-urethane distance. The lack of significant toughness is considered too large a detriment to proper matrix resin performance.

3. Amine Terminated Polyperfluoropropylene Oxide PFPOA

A third alternative curing agent prepared by hydrolysis of the isocyanate terminated PFPOI to yield the corresponding amine terminated telomer (II) labelled PFPOA was then evaluated.



PFPOA

A few samples of the PFPOI/PFPOA system were prepared. Table III shows the results of free NCO/NH2 variation using PFPOI of 1850 molecular weight and PFPOA of 1950 molecular weight cured one hour at 82°C plus a postcure of 2.5 hours at 135°C.

TABLE III

PFPOA CURED PFPOI

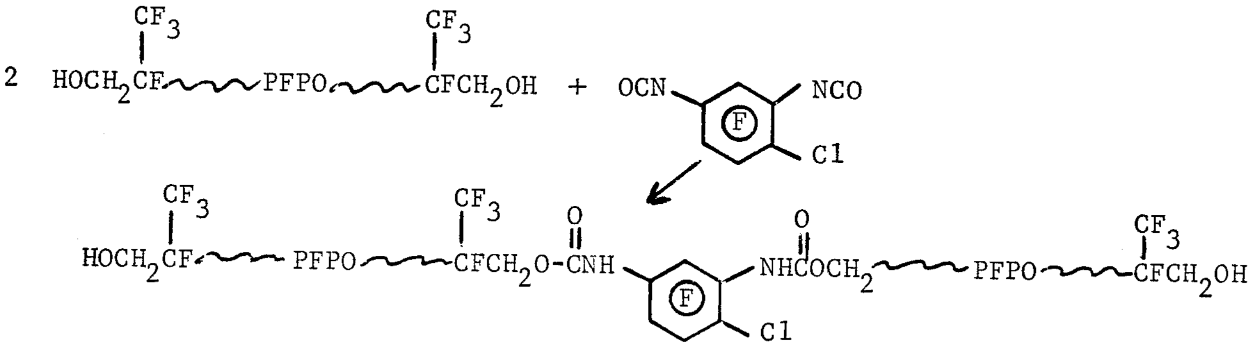
NCO/NH2	Tg, °C
1.4/1	6°
1.6/1	10°
1.8/1	13°

The resulting polymer was quite tough with good tear resistance.

A significant drawback to the PFPOA system is the very short pot life, which was in the order of 5 minutes at 66°C. That temperature is necessary for appreciable flow and mixability of the two components. This short pot life considerably influenced future usage as a potentially attractive curing agent.

4. Combination Curing Agents

Attention was then turned to a combination curing agent; namely cyanoguanidine in conjunction with the urethane extended glycol terminated system UPFPOH.



UPFPOH

The use of this UPFPOH curing agent had been developed during previous programs (NASA-Huntsville Contract No. NAS8-27087) for liquid oxygen compatible adhesive applications. Its use is predicated on solubility requirements, in that the simple polyperfluoropropyleneoxide (glycol terminated) telomer PFPOH is surprisingly insoluble (at room temperature) in the derived PFPOI (isocyanate terminated) system. The urethane extension provides solubility of the two components at room temperature.

It had similary been previously established that an overall NCO/OH ratio of 1.8/1 provided the best overall adhesive performance. Account must be taken of the OH and NCO "content" of the urethane segments of both PFPOI and UPFPOH in arriving at the overall NCO/OH ratio.

In the system under evaluation it was decided to hold the overall NCO/(NH_2+OH) ratio at 1.6/1. The ratio of "free" amine (from cyanoguanidine) to "free" hydroxyl (from UPFPOH) was then varied as shown in Table IV.

TABLE IV

PFPOI CURED WITH DUPLEX CURING AGENT

Free NH_2/Free OH	T_g (°C) (At fixed Overall NCO/NH_2+OH ratio of 1.6/1)	
	Air Cure	N_2 Cure
4/1	-2	-4
1.5/1	-10	-12
1/1	19	10
2/3	5	10

The cure schedule followed in all cases was:

30 minutes at 75°C plus
30 minutes at 100°C plus
15 minutes at 125°C plus
15 minutes at 150°C plus
20 minutes at 177°C

Duplicate cures were accomplished both in air and dry nitrogen atmospheres.

The results indicate inconsistencies which are not readily explainable. In any case only minor improvements in T_g elevation and apparent toughness, as determined by a qualitative evaluation, were forthcoming, hence further investigation was discontinued.

D. OXYGEN FLAMMABILITY STUDIES

All prepolymers and cured polymer systems (from all four curing agents in conjunction with PFPOI) were routinely tested for flammability characteristics in 100% oxygen environment at one atmosphere pressure.

In all instances the characteristics were the same, i.e., the material melted and burned while the gas igniter flame was impinged on it but immediately self-extinguished upon removal of the flame. Under these same conditions Teflon (TFE) film was burned to insure reasonable consistency in the test (i.e., >94% oxygen).

E. LAMINATE FABRICATION AND TESTING

The fabrication of a unidirectional filament wound glass-reinforced laminate was accomplished to allow evaluation of the perfluorourethane system in this particular end-use configuration. These studies were carried out primarily to ascertain cryogenic performance and capability.

The most reproducible results were obtained using PFPOI in conjunction with cyanoguanide as curing agent. Hence this combination was utilized in preparation of the laminate. Standard filament winding technology was utilized in preparation of the laminate.

An aluminum winding mandrel 25.4 cm in length with a 1.27 cm radius at either end and a width of two inches was used. The mandrel was released with GS-3 fluorocarbon release agent. E-glass 40-end continuous roving was heat cleaned (16 hours at 345°C) and continuously fed to the revolving mandrel using an average 2 pound tension. Resin pickup was accomplished by dip/brush techniques. Total resin pickup was 40%/w.

Following the winding operation the wound mandrel was vacuum bagged and cured in an autoclave (under vacuum) at 177°C under 69 N/cm^2 for 90 minutes using a bleeder ply of 1581 fabric and a perforated Teflon separator.

The cured laminate had a specific gravity of 2.242 at a resin content of 35.5%/w. Calculated void content was <1% at a resin density of 1.68 g/cm^3. Table V lists the various strength/modulus values obtained at temperature.

TABLE V

LAMINATE PERFORMANCE OF CYANOGUANIDE CURED PFPOI
($NCO/NH_2 = 1.67/1$)

Temp °C	Flexural Strength N/cm^2 (psi x 10^3)	/	Modulus MN/cm^2 (psi x 10^6)	Short Beam Shear Strength N/cm^2 (psi x 10^3)
25	12,100 (17.5)	/	0.814 (1.18)	7,860 (11.4)
0	43,400 (62.9)	/	2.97 (4.32)	3,060 (4.43)
-20	42,800 (62.3)	/	2.82 (4.10)	3,630 (5.28)
-50	57,200 (83.0)	/	3.60 (5.21)	4,210 (6.11)
-90	66,600 (95.8)	/	3.09 (4.49)	4,440 (6.44)
-180	35,400 (51.3)	/	2.22 (3.22)	16,450 (23.9)

Figure E is a representation of the performance of PFPOI/cyanoguanidine system as measured by torsional braid analysis (TBA). The left-hand ordinate plots the normallized square of the frequency of the torsional pendulum formed by coating a glass fabric braid with the resin under investigation. The right-hand ordinate plots flexural strength values of the laminate. The abscissa represents the temperature in degrees centigrade.

Laminate flexural strengths closely parallel the TBA curve, with extrapolated inflection points for the laminate in the general temperature region as those obtained by TBA. The T_g of this resin was found to be 34°C by thermomechanical analysis (intersection thermal expansion curves of the glassy and rubbery states). The surprisingly close correlation of these two measurement modes of resin performance is noteworthy.

Flammability testing of the laminate in 100% oxygen led to very good results. Flame was evident, while the igniter flame was unpinged, but there was no dripping or melting apparent. The decomposed resin volatilized as apparently nonflammable products. The heat sink effect of the glass fiber apparently removed enough heat from the resin to immediately reduce it below the flammability temperature. At no time was there any indication of a propagating flame below the molten glass.

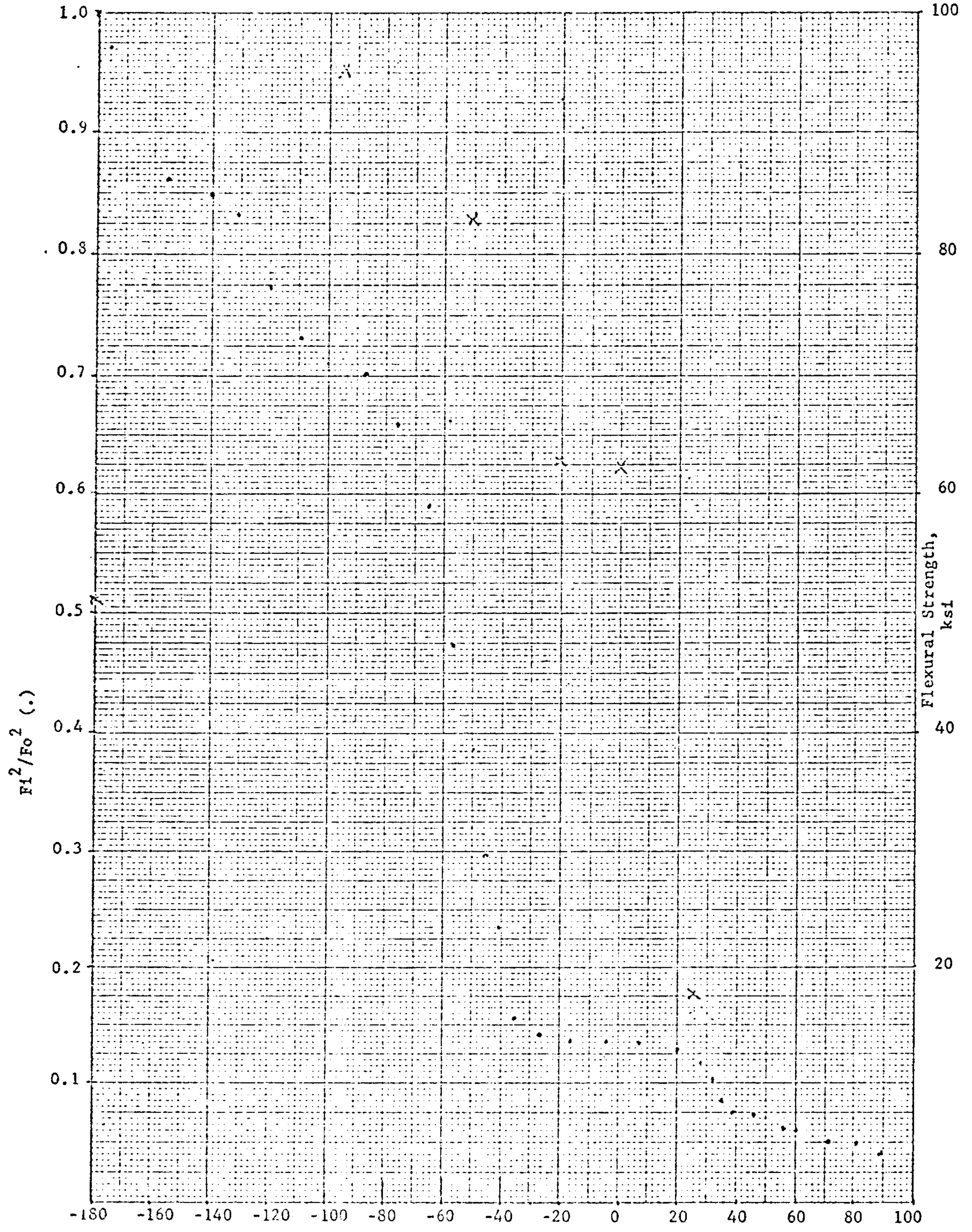


Figure E. TBA Curve of Cyanoguanidine Cured PFPOI

CONCLUSIONS

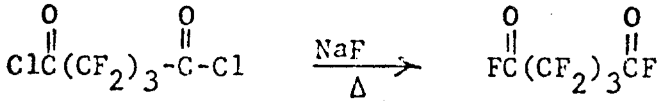
The development of a laminating resin with oxygen compatibility has been accomplished but the system as presently constituted suffers from insufficient elevated temperature performance. The insensitivity of the polyperfluoropropylene oxide based polyurethane to significant modification by alternate curing agents (and modes) as well as the inadequate elevation of polymer T_g by variation in crosslink density continue to be a significant barrier to exploitation of the remarkable stability of the polymers to gaseous and liquid oxygen.

The cryogenic performance of the various systems provides adequate performance as a laminating resin. For such applications as filament wound liquid oxygen bottles there is a definite utility. However, exposure to temperatures near to the polymer T_g causes a very significant drop-off in laminate performance, reducing the composite to a less than useful status. The upper thermomechanical limit may be increased significantly but the results of this program indicate that such improvement is accompanied by a concurrent decrease in cured resin toughness to the point where again the system loses useful properties.

EXPERIMENTAL

TYPICAL PREPARATION OF HYDROXYL-TERMINATED POLYPERFLUOROPROPYLENE OXIDE (PFPOH)

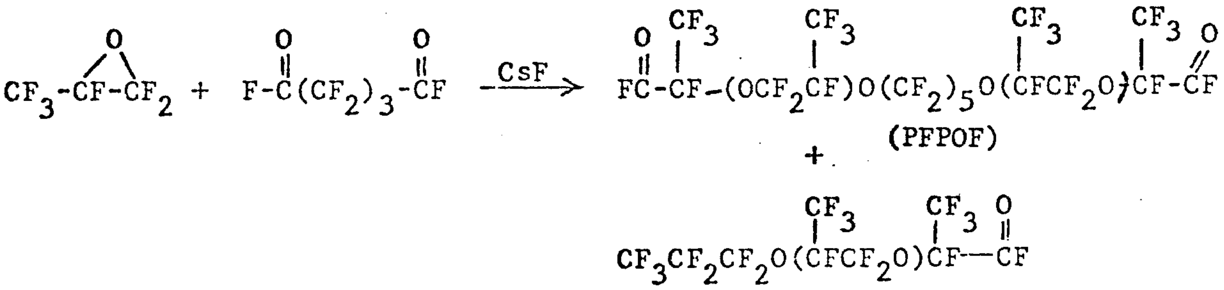
A. Preparation of Perfluoroglutaryl Fluoride



$$\mathrm{Cl\overset{O}{\overset{\|}{C}}(CF_2)_3\text{-}\overset{O}{\overset{\|}{C}}\text{-}Cl \xrightarrow[\Delta]{NaF} F\overset{O}{\overset{\|}{C}}(CF_2)_3\overset{O}{\overset{\|}{C}}F}$$

Sodium fluoride (276 g, 6.6 mole) was dried 72 hours at 316°C in a five-liter flask. The flask was removed from the oven and allowed to cool under a dry nitrogen flow. Redistilled sulfolane (800 ml) was added and stirring begun. Perfluoroglutaryl chloride (500 g, 1.85 mole) was added over a period of three hours. The temperature was kept below 35° during the addition. Heat was applied and the reaction mixture allowed to reflux (48°C) for 3 hours. After standing (under nitrogen) overnight, the volatile material (<49°C bp, 305 g) was isolated by distillation and then distilled through a helices-packed, 96-cm vacuum-jacketed column. The fraction boiling at 45°-46°C was collected. Purity (by VPC) was >99%, and the yield was 236 g.

B. Polymerization of Perfluoropropylene Oxide



$$\mathrm{CF_3\text{-}CF\text{-}CF_2(O) + F\text{-}\overset{O}{\overset{\|}{C}}(CF_2)_3\text{-}\overset{O}{\overset{\|}{C}}F \xrightarrow{CsF} F\overset{O}{\overset{\|}{C}}\text{-}\underset{}{\overset{CF_3}{\overset{|}{C}}}F\text{-}(OCF_2\overset{CF_3}{\overset{|}{C}}F)O(CF_2)_5O(\overset{CF_3}{\overset{|}{C}}FCF_2O)\overset{CF_3}{\overset{|}{C}}F\text{-}\overset{O}{\overset{/\!/}{C}}F}$$

(PFPOF)

$$\mathrm{+\ CF_3CF_2CF_2O(\overset{CF_3}{\overset{|}{C}}FCF_2O)\overset{CF_3}{\overset{|}{C}}F\text{—}\overset{O}{\overset{\|}{C}}F}$$

Cesium fluoride (14.9 g, 0.11 mole) was dried in a one-liter reaction flask at 315°C for 5 days. The dried material was allowed to cool under dry nitrogen. The partially solidified mass was broken up into small lumps and doubly distilled diglyme (bp 162°-163°C, 55 ml) was added. The mixture was then stirred for 30 minutes. Perfluoroglutaryl fluoride (38.5 g, 0.158 mole) was added over a 20-minute period, with the temperature of the stirred reaction mixture maintained at 4°-9°C with a dry ice/acetone bath. The finely dispersed slurry was stirred an additional 30 minutes at 10°-11°C. The mixture was cooled to -13°C and perfluoropropylene oxide (8.5 g, 0.051 mole) was added over a 25-minute period at this temperature. The reaction mass was allowed to warm to 10°C and the remainder of the epoxide (200 g, 1.09 mole) was added (T = 9°-10°C) over a four-hour period. Stirring was continued overnight at ambient temperature. Filtration through fine fritted glass funnels produced 179.3 g of a clear, colorless mobile liquid. Fractional distillation under reduced pressure yielded the following cuts:

	Boiling Range, °C	Pressure Torr	Weight Recovered
Cut 1	54-81	10-11	24.0
Cut 2	72-74	3.3-3.5	30.7
Cut 3	67-96	2.0-2.2	5.0
Cut 4	73-74	0.01-0.02	62.2
Cut 6	96-123	0.04-0.20	28.4

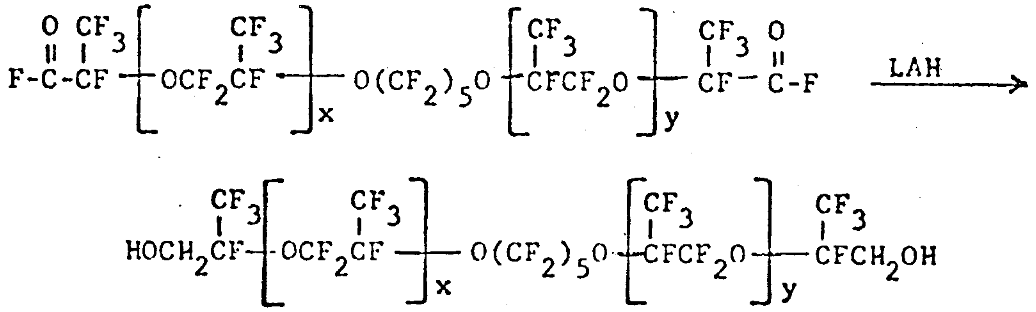
23.0 g of material was collected in the pre-pump dry ice/acetone traps.

Acid fluoride number was determined by the following procedure:

Place 75.00 ml of standardized 0.1N NaOH in a 250 ml flask. Add 10 ml of 5% pyridine in water solution. Weight in 3 to 4 milli-equivalents of PFPO acid fluoride. Stopper the flask and shake for at least 2 hours and until clear. Titrate with standardized 0.1N hydrochloric acid to the phenol phthalein end point.

$$\text{EW} = \frac{(2000)\ (\text{Sample Weight})\ (\text{grams})}{(\text{ml Base} \times \text{N Base}) - (\text{ml acid} \times \text{N acid})}$$

C. Reduction of Acyl Fluoride-Terminated Polyperfluoropropylene Oxide



$$\mathrm{F{-}\overset{O}{\overset{\|}{C}}{-}\overset{CF_3}{\overset{|}{C}}F}\left[\mathrm{OCF_2\overset{CF_3}{\overset{|}{C}}F}\right]_x \mathrm{O(CF_2)_5O}\left[\mathrm{\overset{CF_3}{\overset{|}{C}}FCF_2O}\right]_y \mathrm{\overset{CF_3}{\overset{|}{C}}F{-}\overset{O}{\overset{\|}{C}}{-}F} \xrightarrow{\text{LAH}}$$

$$\mathrm{HOCH_2\overset{CF_3}{\overset{|}{C}}F}\left[\mathrm{OCF_2\overset{CF_3}{\overset{|}{C}}F}\right]_x \mathrm{O(CF_2)_5O}\left[\mathrm{\overset{CF_3}{\overset{|}{C}}FCF_2O}\right]_y \mathrm{\overset{CF_3}{\overset{|}{C}}FCH_2OH}$$

PFPCH

Lithium aluminum hydride (5.7 g, 0.212 mole) was carefully added to dry tetrahydrofuran (100 ml) in a 250 ml Morton flask and stirred for 30 minutes. Polyperfluoropropylene oxide (Cut 2 above, 24.0 g) was added over a 45 minute period using external cooling to maintain the temperature between 5-10°C. The gray slurry was vigorously stirred throughout the addition and then for an additional 30 minutes. Wet (20%, 100 ml) THF was cautiously added over a one-hour period and stirred for an additional 30 minutes. The gray emulsion was then cautiously poured into 500 ml of 5% sulfuric acid with stirring and allowed to stand overnight. The clear fluorocarbon layer was isolated, washed with water, dissolved in ether (200 ml) and dried 24 hours (MgSO4). The ether was then removed from the filtered solution, yield 21.3 g of crude product. Vacuum fractionation resulted in the following fractions:

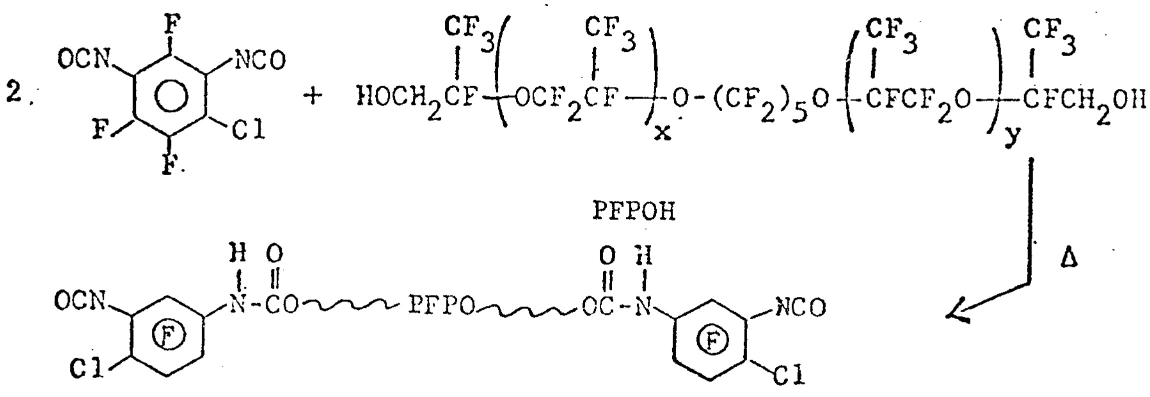
Fraction	Boiling Range	mm Hg	Total Weight
1	64-68	0.1-0.2	1.2 g
2	68-96	0.1-0.2	2.0 g
3	110-111	0.1-0.2	15.1 g

In addition, 2.6 g of low boiling material was caught in the dry ice/acetone traps.

Similar procedures with adjustment in amount of LAH and solvent were followed for the reduction of the other two partially purified PFPOF cuts. The following fractions were obtained from the various reduced cuts of PFPOF.

Precursor (PFPOF) Cut No.	Crude (PFPOH) Weight (g)	(PFPOH) Cut No.	Wt. (g)	b.p. °C @ mm Hg
4	43.6	1	2.2	130°-134°/0.9
		2	37.9	136°-137°/0.9
6	22.4	1	3.2	142°-157°/0.5
		2	14.2	157°-178°/0.5
		3	3.7	179°-186°/0.5

TYPICAL PREPARATION OF PFPOI



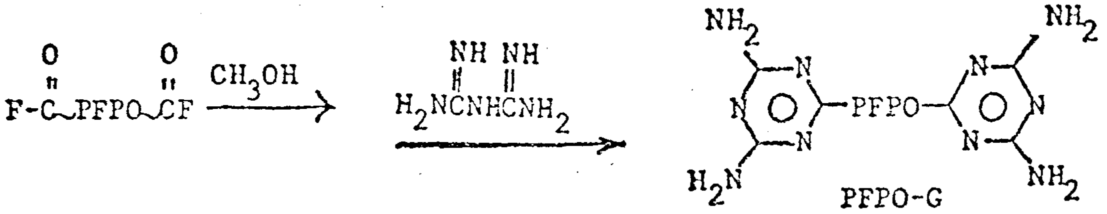
PFPOH

PFPOI

Hydroxyl terminated polyether (PFPOH) (52.3 g, 0.0507 mole) was placed in a micro resin kettle equipped with stirrer, dry nitrogen inlet and thermometer. Addition of 6-chloro-2,4,5-trifluoro-m-phenylene diisocyanate (26.65 g, 0.107 mole) was added all at once at room temperature. Stirring was initiated and the temperature increased slowly ($\sim$5°C/min) using an oil bath. The two phase mixture began to clear at $\sim$95°C. After 15 minutes at 104° the mixture was completely clear. Periodic checks on the progress of the reaction were made by infrared spectroscopy, observing the decrease of the OH stretch absroption at 3390 cm^{-1}, with concurrent increase in the NH stretch at 3300 cm^{-1} at carbamate carbonyl absorption at 1760 cm^{-1}.

Stirring was continued for 2-3/4 hours at 100° to 110°C when the reaction was terminated. The system was degassed hot and the PFPOI prepolymer stored in a vacuum dessicator at 5°C.

PREPARATION OF PFPOG



A. Preparation of the Dimethyl Ester of PFPOF

PFPOF (30.8 g, 0.039 mole) was added to bone-dry methanol (300 ml, which had been dried over 3A molecular sieves) in a polyethylene beaker under a dry nitrogen blanket. Stirring (may-bar) was carried out overnight when silica gel (4.0 g) was added to destory residual hydrofluoric acid. After filtration, the major portion of the solvent was removed under reduced pressure and the remaining material fractionated under reduced pressure.

The fraction boiling at 87°-107°C at 0.05-0.1 torr (22.9 g) was collected and utilized in the subsequent preparation of PFPOG. The infrared spectrum showed complete conversion to methyl ester with no residual acyl fluoride present.

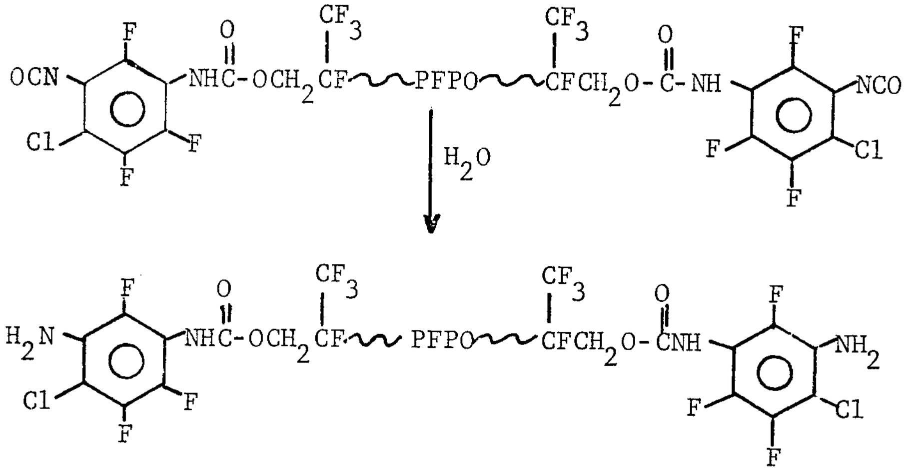
B. Preparation of PFPOG

Biguanide (6.43 g, 0.0636 mole) was added to bone-dry methanol (250 ml) and the slurry stirred. The dimethyl ester above (22.6 g, 0.0289 mole) was added over a 45 minute period. The temperature was increased to reflux where the system became clear. Reflux was continued overnight under dry nitrogen. The volume was reduced to $\sim$30% under reduced pressure.

The water white solution was then poured into distilled water in a rapidly stirred Waring blender. The white suspension settled only very slowly, consequently the centrifuge was used with good results. The wet sticky precipitate was washed again in the blender and allowed to settle overnight. The slightly cloudy supernatent liquid was decanted and the white product taken up in acetone, dried over magnesium sulfate, filtered and stripped of solvent under reduced pressure at 96°C.

The glassy product (melting range ~82°-88°C) was recovered in 50% yield (12.7 g).

PREPARATION OF PFPOA



Isocyanate Terminated Prepolymer

Isocyanate terminated prepolymer (PFPOI, 18.5 g, 0.01 mole) was dissolved in dry tetrahydrofuran (250 ml) in a 1000-ml beaker. The clear solution was rapidly stirred and 50% THF/H_2O (50 ml) was added at once. There was an immediate evolution of carbon dioxide from decomposition of the rapidly formed carbamic acid. Stirring was continued for 15 minutes. Water (500 ml) was added to completely precipitate the polymer. The aqueous layer was decanted and the product taken up in Freon TF (100 ml), washed with water (3x100) and dried over anhydrous magnesium sulfate. After filtration the clear solution was freed of solvent under full vacuum at 85°C. 14.6 grams of semi-solid product was obtained. Infrared spectroscopy showed no residual isocyanate (4.5 μ). Molecular weight (by VPO in Freon TF) was determined to be 1950 ±20.

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