FINAL REPORT
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SYNTHESIS AND CHARACTERIZATION OF PROCESSABLE POLYIMIDES WITH ENHANCED THERMAL STABILITY

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The following is a summary report of the research carried out under NASA Grant NAG-1-448. The work was divided into four major areas:

1. Enhanced polyimide processing through the use of reactive plasticizers
2. Development of processable polyhenylquinoxalines
3. Synthesis and characterization of perfluorovinylether-terminated imide oligomers.
4. Fluorosilicones containing perfuorocyclobutane rings.

Each of these areas are described in the following paragraphs.

1. Enhanced Polyimide Processing Through The Use of Reactive-Plasticizers

The objective of this research was to modify the reactive monomer approach used in the preparation of carbon-fiber reinforced polyimide composites to significantly enhance processability. In our approach a small amount of an unreactive diamine (5-15 mol %), i.e. a reactive plasticizer, was used in place of a portion of the major component diamine to prepare copolyimide precursor solutions of polyimides, which had previously been shown to be non-autoclave processable or processable only in low molecular-weight form. We postulated that these copolyimide precursor solutions could be coated onto reinforcing fibers and autoclave processed to give composites with mechanical properties equivalent to or better than non-autoclavable "parent" polyimides.

The research was divided into four parts. The first part of the study investigated neat resin properties of potential reactive plasticizer diamines when homopolymerized with the dianhydride BTDA and when incorporated as a comonomer into polyimide PI-2. The second part of the research involved the preparation and mechanical testing of compression molded composite parts to determine the most reactive plasticizer

candidates. In the third part of the research, 2,6-diaminopyridine (DAP) was found to be the most effective reactive plasticizer, yielding composite parts with equivalent or better mechanical properties than composites prepared from the equivalent homopolyimides. The versatility of the reactive plasticizer method was also established by the successful autoclave processing of a total of four polyimide resins, which had previously not been autoclave processed or processed only by limiting the ultimate molecular weight of the resin. The final part of the study involved the investigation of the possibility that transimidization participated in the success of DAP as a reactive plasticizer.

In the course of studying the polymerization of model imide and amide monomers it was observed that exchange reactions occurred rapidly not only in the melt, but even in the solid state when one reactant was able to plasticize the other. This suggested that transimidization and transimidization might be viable solvent-free method of rapidly producing thermoformable polyimides and polyamides. In fact, due to the rapidity of these exchange reactions at temperatures above 250 °C this polymerization route is well suited to producing polymers during reactive processing if the processing can accommodate the reaction by-products.

In conclusion, heterocyclic amines have been shown to be readily susceptible to transimidization at elevated temperatures. In the solid state pyrimidine amines were found to undergo transimidization starting at 100 °C, while the pyridine amines were found to undergo transimidization beginning at 150-200 °C. The susceptibility to exchange reactions coupled with low reactivity at low temperatures makes these amines and diamines useful and versatile processing aids. The diamines can be used to make copolyimides autoclavable copolyimides via the reactive plasticizer approach. They can

also be used to make reactive oligomers, which can be processed at temperatures and pressures below those of high-molecular-weight analogues.

2. Development of Processable Polyphenylquinoxalines (PPQs)

2.1. Development of Readily-Processable Thermoplastic PPQ Composite Resins

An improved synthetic route to a previously prepared self-polymerizable poly(phenylquinoxaline) (PPQ) monomer mixture, i.e., 2-(4-hydroxyphenyl)-3-phenyl-6-fluoroquinoxaline and 3-(4-hydroxyphenyl)-2-phenyl-6-fluoroquinoxaline, was developed. The monomer mixture was then polymerized in stages in N-methyl-2-pyrrolidinone/toluene and in N-cyclohexyl-2-pyrrolidinone at elevated temperatures in the presence of potassium carbonate. Polymer samples were obtained that had intrinsic viscosities as high as 1.64 dl/g in m-cresol at 30.0±0.1 °C and glass transition temperatures (T_gs) of 250-252 °C. Thin films of the PPQ had a room temperature (RT) tensile strength of 114 MPa, a RT Young's modulus of 3.7 GPa, and a RT elongation at break of 93%. The neat resin had a flexural modulus of 3.12 GPa, a fracture energy (G_{Ic})of 2170 J/m^2 and a titanium-titanium lap shear strength of 31.4 MPa at room temperature. The polymer melt underwent shear thinning at 320 °C. The melt viscosity decreased from 10^5 to 10^6 Pa s to less than 10^4 Pa s as the frequency was increased from 10^{-2} t 10^2 rad/s. Carbon-fiber (T650)®-reinforced composites of the PPQ were prepared and their mechanical properties determined.

In the second part of this work, a mixture of 3-(4-hydroxyphenyl)-2-phenyl-6-fluoroquinoxaline and 2-(4-hydroxyphenyl)-3-phenyl-6-fluoroquinoxaline was copolymerized with 4,4′-dichlorodiphenylsulfone and bisphenol A in NMP in order to

reduce the cost of PPQs. Single electron transfer reactions, which are prevalent in amide solvents at high temperatures, were minimized through copolymerizations under mild conditions. High molecular weight polymers were obtained, as evidenced by intrinsic viscosities of 0.88-1.25 dL/g. The T_gs of the copolymers ranged from 210 ° to 240 C. The copolymers exhibited tensile strengths of 87-98 MPa, tensile moduli of 2.2 to 2.9 GPa, and elongations of 15-20%. Attempts to copolymerize the mixture with 4,4′-dichlorobenzophenone and hydroquinone were unsuccessful.

In the third part of this research, a mixture of 3-(4-hydroxyphenyl)-2-phenyl-6-fluoroquinoxaline and 2-(4-hydroxyphenyl)-3-phenyl-6-fluoroquinoxaline (A-B-Cl) was synthesized in order to reduce the cost of PPQs. The synthetic route to this chloro-substituted mixture was modified from an earlier procedure in order to obtain high purity monomer. However, several attempts to polymerize this monomer only produced low molecular weight powders. Based upon electron density calculations, it appears that A-B-Cl may be impossible to polymerize via aromatic nucleophilic substitution reactions.

In the fourth part of this research, more reactive self-polymerizable quinoxaline monomers were synthesized. Electron density calculations showed that a mixture of 3-(2-(6-hydroxynaphthalenyl))-2-phenyl-6-fluoroquinoxaline and 2-(2-(6- hydroxy naphthalenyl))-3-phenyl- fluoroquinoxaline (A-B-N) and 2-(4-(4'-hydroxyphenyl))-3-phenyl-6-fluoroquinoxaline (A-B-B) should be more active than A-B. The synthetic route to A-B-N was similar to that previously developed for A-B except that 2-methoxynapthalene was used in the initial Friedel-Crafts acylation reaction rather than anisole. The synthetic route to A-B-B involved a coupling reaction of phenylacetylene with 4-(4-bromophenyl)phenol, followed by oxidation with $PdCl_2$ to afford 4-glyoxalyl-

4'-hydroxybiphenyl. Treatment of 4-glyoxalyl-4'-hydroxybiphenyl with 4-fluoro-1,2-phenylenediamine gave A-B-B.

Polymerization of A-B-N and A-B-B were carried out in NMP at 170 °C and 202 °C to afford high molecular weight polymers. Polymerization of A-B-N led to a PPQ with an intrinsic viscosity of 2.51 dL/g, a T_g of 278 °C, a tensile strength of 95 MPa, a tensile modulus of 3.0 GPa, and an elongation of 93%.

The polymerizations of A-B, A-B-N, and A-B-B also led to the formation of macrocycles as determined by MALDI-TOFMS. It is unknown what effect, if any, the presence of these macrocycles have on both the thermal and mechanical properties of the PPQs. Due to the high intrinsic viscosities of the PPQs and the low amounts of macrocycles determined by GPC, it is likely that the concentration of the macrocycles in the polymers is very low.

2.2. Phenylethynyl-Terminated, Star-Branched PPQ Oligomers

The known monomer mixture 2-(4-hydroxyphenyl)-3-phenyl-6-fluoroquinoxaline and 3-(4-hydroxyphenyl)-2-phenyl-6-fluoroquinoxaline (HPFQ) was prepared by an improved synthetic route. Thus, Friedel-Crafts acylation of excess phenol with phenylacetyl chloride gave 4-(phenylacetyl)phenol, which was oxidized to 4-hydroxybenzil with copper(II)bromide and DMSO. Condensation of 4-hydroxybenzil with 4-fluoro-1,2-diaminobenzene gave the monomer mixture. The overall yield of this route was 62%, compared to 38% overall yield obtained previously.

The end-capping agent, i.e., 4-fluoro-4'-phenylethynylbenzophenone (FPEB) was obtained by treating 4-bromobenzoyl chloride with excess fluorobenzene, followed by

coupling with phenylacetylene using a palladium catalyst. The reagent was used as the end-capping agent for the star-branched PPQ oligomers.

The preparation of phenylethynyl-terminated, star-branched PPQ oligomers was then attempted from HPFQ, FPEB, and 1,3,5-trihydroxybenzene (THB), which was used as the branching unit. The aromatic nucleophilic substitution reactions were carried out in an NMP/toluene mixture containing K_2CO_3. Although several different experimental procedures were employed, predominantly high-molecular-weight linear PPQs were obtained. This was attributed to the THB being consierably less reactive than the HPFQ, which allowed the HPFQ to homopolymerize. However, when 1,1,1-tris(4-hydroxyphenyl)ethane (THPE) was used as the branching unit, star-branched PPQ oligomers were obtained. In fact, the M_ns of the oligomers were 2900, 4190, 5980, and 13,600 g/mol, which were very close to the expected values based on the stoichiometry of the reactants used. The oligomer intrinsic viscosities and T_gs increased with increasing molecular weight ranging from 0.16 to 0.57 dL/g and from 181 to 233 °C, respectively. The temperatures at which the oligomers underwent an exothermic cure also increased from 377 °C to 433 °C as the molecular weight increased. Thin films were cast from 10% (w/v) chloroform solutions, but they were very brittle except for the one prepared from the oligomer with an M_n of 13,578 g/mol. The oligomers had melt viscosities considerably lower than those of the high-molecular-weight PPQs prepared in previous studies. The T_gs of samples that were heated to 480 °C and then rapidly quenched to room temperature, ranged from 259 °C to 284 °C, decreasing as the oligomer M_n increased. The oligomer with a calculated M_n of 13,578 g/mol was selected for more extensive study. The DSC thermogram of this oligomer showed an initial T_g of 233 °C

and an exotherm due to the chain extension reaction with a maximum at 433 °C. When the oligomer was cured at 350 °C for varying periods of time, the T_g increased from 263 to 280 °C, depending on the cure time. Isothermal TGA at 316 °C in air of the cured oligomer showed slightly better weight retention than displayed by an analogous linear PPQ. This suggests that the cured oligomer is slightly more thermooxidatively stable. The cured oligomer also exhibited improved solvent resistance and higher tensile strength (130 MPa) than the linear, high-molecular-weight PPQ. In conclusion, phenylethynyl-terminated, star-branched oligomers have been prepared that have wide processing windows. The oligomers have excellent melt processabilities and cure to thermally stable materials that display good mechanical properties.

2.3. PPQs Containing Pendant Phenylethynyl Groups

Two new A-B phenylethynyl-substituted PPQ monomer mixtures (PPEQs) were prepared. Thus, monomer mixtures of 2-(4-hydroxyphenyl)-3-(4-phenylethynylphenyl)-6-fluoroquinoxaline and 3-(4-phenylethynylphenyl)-6-fluoroquinoxaline) (HPEFQ) and 2-(4-hydroxyphenyl)-3-(4-phenylethynylphenyl)-6-chloroquinoxaline and 2-(4-hydroxyphenyl)-3-(4-phenylethynylphenyl)-6-chloroquinoxaline (HPECQ) were synthesized. The A-B PPEQ monomers HPEFQ and HPECQ were self polymerized in 1:1 (v/v) NMP/toluene mixture containing K_2CO_3. The activation conferred by the quinoxaline moiety was not sufficient for the displacement of a chlorine leaving group. No appreciable molecular weight build-up could be obtained from HPECQ. Although a phenylethynyl-substituted PPQ (PPEQ) with an intrinsic viscosity of 1.6 dL/g could be obtained from HPEFQ when the polymerization was carried out employing a 25% (w/v) solids content, the polymerizing mixture gelled affording considerable insoluble material.

In order to reduce gel formation, the solids content had to be reduced to 10%, and the polymerization run at 202 °C for 2 h. The PPEQ obtained under these conditions had an intrinsic viscosity of 1.03 dL/g and Tg of 272 °C. However, the chain extension reaction began immediately above the Tg, providing little flow before crosslinking. Tough, flexible films could be cast from 10% (w/v) chloroform solutions. Upon curing at 350 °C for 0.5 h in nitrogen. The films became brittle due probably to a high crosslink density.

Since the PPEQ homopolymer had a very narrow processing window, which was attributed to the high density of the pendant phenylethnyl groups, HPEFQ was copolymerized with HPFQ. The molar ratio of monomers was varied from 10:90 to 75:25. The copolymer intrinsic viscosities ranged from 1.02 to 2.03 dL/g. No clear correlation could be made between the Tgs of the copolymers, which ranged from 252 °C to 268 °C, and their HPEFQ contents. The thermal stabilities of the copolymers decreased as their HPEFQ contents increased. All the copolymers were soluble in $CHCl_3$, NMP and m-cresol. Tough, flexible films could be cast from 10% (w/v) chloroform solutions. Upon curing at 350 °C for 0.5 h in nitrogen, they displayed improved solvent resistance and a tensile strength of 86.4 MPa. It is postulated that the mechanical properties of the cured copolymer at elevated temperatures are also better than those of the analogous linear PPQ.

3. Synthesis and Characterization of Perfluorovinylether-Terminated Imide Oligomers

The objective of this research was to prepare high performance materials that exhibit a combination of the engineering properties of polyimides and the outstanding physical properties of fluorocarbon polymers. The approach involved the synthesis of

trifluorovinylether-terminated imide oligomers. The thermally induced ($2\pi + 2\pi$) cyclodimerization of the trifluorovinyl (TFV) functionality to form perfluorocyclobutane was used as a convenient pathway to chain extend the oligomers into the desired materials. The first task was to prepare a series of amine end-capping agents that contained the trifluorovinylether functional groups. Accordingly, the end-capping agents 3-amino-4(trifluorovinyloxy)biphenyl (3,4'P), 4-amino-4'-(trifluorovinyloxy)biphenyl (4,4BP) and 6-(3-aminophenyl)-2-(trifluorovinyloxy)naphthalene (3,6-NA) were synthesized. 3,3',4,4'-Benzophenonetetracarboxylic dianhydride (BTDA), 4,4'-oxydiphathalic dianhydride (ODPA), and 2,2-bis[3,4-dicarboxyphenoxy)phenyl]propane dianhydride (BisA-DA) were then treated with 2:1 molar excess of the end-capping agents to obtain trifluorovinylether end-capped imide oligomers. The oligomers were subsequently thermally chain extended to provide polyimides containing perfluorocyclobutane rings. The oligomers were soluble in common solvents such as acetone and chloroform and had melting points of 105 °C to 218 °C. The oligomer prepared by endcapping BisA-DA with 3,6-NA melted at 105 °C and underwent dimerization at 191 °C. Thus, the processing window was 86 °C. In fact, the melting point of the oligomer , and, thus, the width of the processing window, depended on the molecular structure of the end-capping agent as well as that of the dianhydride. The oligomer melting point could be depressed by using an equimolar ratio of two end-capping agents. The intrinsic viscosities of the polyimides obtained from the BisA-DA oligomers end-capped with 3,6-NA and 3,4'-BP were 0.66 dL/g and 0.58 dL/g, while their glass transition temperatures (T_gs) were 205 °C and 185 °C, respectively. Decomposition of the polymers in air and nitrogen occurred at temperatures above 450

°C when the polymers were subjected to thermogravimetric analysis with a heating rate of 10 °C/min. The polymer obtained from 3,6-NA and BisA-DA also displayed excellent thermo-oxidative stability, retaining over 99% of its weight after 100h at 300 °C. Thin films of the polymers exhibited coefficients of thermal expansion in the range of 49 x 10^{-6} C^{-1} to 5.8 x 10^{-6} C^{-1}. Fused discs of the materials displayed water absorptions in the range of 0.05% to 0.08%.

4. Fluorosilicones Containing Perfluorocyclobutane Rings

This work was directed towards developing elastomers that could lead to high temperature fuel tank sealants. Fuel tank sealants are urgently needed and are considered to be enabling technology for high speed civil transports (HSCTs). The sealant must exhibit a combination of properties such as high elongation, moderate peel strength, fuel resistance, and performance for 60,000 hours at 177 °C. No commercial sealant meets the requirement of the HSCT. The high temperature requirement is because aerodynamic heating while in flight at Mach 2.4 is projected to cause the fuel tank sealant (when the tank is empty) to reach temperatures approaching 177 °C. This work was carried out as part of the NASA funded High Speed Research (HSR) Program. The principal of the HSR Program was to develop technology to permit the Boeing Company to make a decision on HSCT g-head. The HSCT in this program was a commercial passenger airplane for transoceanic flight that could fly at speeds approaching Mach 2.4.

Two disilanol monomers containing perfluorocyclobuaten rings, 1,2-bis[4-dimethylhydroxysilyl)phenoxy]-1,2,3,3,4,4,-hexafluorocyclobutane and 1,2-bis[3-dimethylhydroxysilyl)phenoxy]-1,2,3,3,4,4,-hexafluorocyclobutane were prepared and self-polymerized by treatment with base. The glass transition temperatures (T_gs) of the

two high-molecular-weight polymers obtained were 27 °C and –12 °C, respectively. The two monomers were also copolymerized with an α,ω-silanol-terminated 3,3,3-trifluoropropylmethylsiloxane (fluorosilicone) oligomer to form copolymers with varying compositions. The Tgs of the copolymers, which ranged from –60 °C to –1 °C, increased as the amount of the perfluorocyclobutane-containing silphenylene repeat units increased. Copolymers containing more than 20 wt% of this repeat unit displayed less weight loss at elevated temperatures than a fluorosilicone homopolymer when subjected to isothermal gravimetric analysis. One of the copolymers, which contained about 30 wt % of the perfluorocyclobutane-containing repeat unit, was crosslinked with 2,4-dichlorobenzoperoxide. The crosslinked network displayed a volume swell of under 40 % in isooctane, similar to a crosslinked fluorosilicone.