May 1969

Brief 69-10118

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NASA TECH BRIEF

New Rapid-Curing, Stable Polyimide Polymers With High-Temperature Strength and Thermal Stability

Polyimide resins are noted for their high temperature thermal stability and high temperature strength. Polyimides, thus, have found numerous applications in fields of advancing technology. While these outstanding high temperature properties make the polyimides attractive for many applications, processing problems have limited their full technical and economic potential.

Normally, polyimides are produced by the reaction between a dianhydride and a diamine. Reaction of the starting constituents at low temperature produces high molecular weight polyamic-acid by chain extension or polymerization requiring a period of 30 minutes for some varieties to as much as 4 hours for others. When this polyamic-acid formation has been completed, the material must be kept in solution, hermetically sealed and refrigerated if application is not anticipated within a few hours to prevent hydrolytical degradation. Thus, special packaging for subsequent storage is an expense which is passed on to the users. In the final product form, the polyamic-acid must be cured by heat treatment for a period of 5 to 16 hours at elevated temperatures to produce the polyimide, which process is accompanied by the evolution of an appreciable amount of volatile matter.

The problems of processing thermally stable polymer systems arise principally from the nature of the condensation polymerization reaction. The solution to this difficulty lies in preparing thermally stable polymer precursors which polymerize by an addition-type reaction, thereby eliminating the volatile matter attendant with the condensation reaction.

A new addition-type polymerization reaction has been discovered which is suitable for forming thermally stable polyimide polymers and is based on utilization of reactive alicyclic rings positioned on the ends of polyimide prepolymers having relatively low molecular weights (1000–2000).

Reinforced structural plastics can be made by impregnating sheets of fibrous materials (glass, graphite, metals, cloth fabrics) with suspensions of these polyimide prepolymers. Amic acid precursors are prepared which are soluble in common laminating solvents. Reinforcement materials are impregnated with this varnish, and, following removal of excess solvent, the amic acid groups are converted to imide groups. The fully imidized prepolymer is stable for long durations at ambient conditions without special handling or storage requirements. Subsequently, the impregnated reinforcement is stacked and molded together at 600°F and modest pressure (100–200 psi) and time (30–60 minutes), depending on specimen thickness. Under these conditions, the reactive alicyclic rings at the terminal positions of the prepolymer coreact, causing resin flow, chain extension, and cross-linking to form a coherent, compact high molecular weight thermally stable polyimide reinforced structure. This basic polymer system, called A-type polyimide, has been designed to (1) cure with the evolution of minimal volatile matter; (2) form from precursors that are oxidatively, thermally, and hydrolytically stable, and (3) require no post cure.

As a varnish, the A-type polyimide resin system permits processing by two different means; either using dry, tack-free fully imidized prepregs, or tacky, partially advanced prepregs which have drape. The first approach provides a process which has essentially no

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volatile matter evolving during cure, and requires relatively short processing times. The second approach provides a prepreg which is easier to lay-up but requires a separate imidization step prior to molding to insure low void products. In either case, the polyimide differs from conventional commercial polyimide resin systems in that initially, imidization is performed on relatively low molecular weight prepolymers, while during final molding at 600°F, the chains extend and cross-link by a pyrolytic polymerization addition-type reaction that simultaneously fuses the plies together to form a coherent, compact, void-free product.

Notes:

1. Specific applications of this resin system include ablative materials, supersonic aircraft structures, jet engine components, circuit boards, high temperature structures, flexible electrical cable insulation, and adhesive formulations.
2. Plastic molding powders with or without fillers or reinforcers can be prepared from these polyimide prepolymers. Molded items prepared from this class of resin show promise for use in ablative and high temperature applications, cryogenic applications, and as a self-lubricating bearing material. Items, such as seals, bearings, valve seats, and bushings, can be prepared by standard methods of compression and transfer moldings.

Patent status:

Title to this invention has been waived under the provisions of the National Aeronautics and Space Act [42 U.S.C. 2457(f)], to TRW Inc., One Space Park, Redondo Beach, California 90278 (Attention: Mr. Ernest R. Boller).

Source: Hyman R. Lubowitz, John F. Jones,
Eugene A. Burns, William R. Kendrick,
Richard S. Thorpe, and Edgar R. Wilson
of TRW Inc.
under contract to
Lewis Research Center
(LEW-10576)