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Process for Preparing Polyimide Adhesives

Bonded structures are advantageous to aerospace vehicles due to their lightness of weight and excellent resistance to fatigue and corrosion. Advanced aircraft experience skin temperatures approaching 300° C, and future spacecraft could require adhesives for use at that temperature and above.

A process has been developed for preparing aromatic polyimides for use as adhesives in bonding metals and fiber-reinforced organic resin composites. High bonding strengths are obtained with no resultant significant loss in thermo-oxidative stability of the adhesive resin, and these polyimide adhesives retain a high proportion of their adhesive strength when formulated with various additives and when used at elevated temperatures.

Producing polymers for use as adhesives involves the addition of an equimolar quantity of a suitable aromatic dianhydride to a stirred solution of an appropriate aromatic diamine (or equivalent mixture of two or more diamines) in certain water-miscible or alcohol-miscible ether solvents. In certain instances, when a highly-viscous polyamic-acid intermediate polymer precipitates from the ether solvent, the addition of very small amounts of water or alcohol generally leads to redissolution of the polyamic-acid to give a viscous polymer solution. At other times, depending upon the choice of monomers, the polyamic-acid intermediate polymer does not become insoluble, and a smooth viscous polymer solution is formed directly. The choice of diamines and dianhydrides inappropriate for this process is signaled by failures, such as the following:

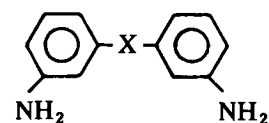
- One or both monomers fail to dissolve in the ether solvents.
- A mismatch between the rate of polymerization of the reactants and the rate of precipitation of the polymer causes the incompletely-reacted insoluble

monomer to become coated by precipitating polymer and, thus, inactivated before the completion of polymerization.

- The polyamic-acid intermediate polymer is precipitated from the solution, usually as a powder, before a suitable degree of polymerization has been reached.

The solvents useful for this process are of the aliphatic acyclic and cyclic ether types, such as tetrahydrofuran, m-dioxane and p-dioxane, monoglyme, diglyme, triglyme, and tetraglyme. These solvents have a high affinity for the polar chemical groups of the aromatic polyamic-acid intermediates.

The diamines which are most suitable for use with ether solvents are those of the dianilino variety, usually with both of the amino groups situated meta to the divalent X groups (e.g., methylene, carbonyl, or oxy) joining the two aromatic rings as follows:



Two specific examples of such diamines are 3,3'-diaminobenzophenone and 3,3'-diaminodiphenylmethane. The most useful dianhydrides for use in the synthesis of the resins by the ether process are those of the bisdiphthalic anhydride variety, where the two phthalic anhydride functions are also separated by a divalent group, such as carbonyl or oxy. Two specific examples of appropriate dianhydrides are 3,3'-benzophenone tetracarboxylic dianhydride and 4,4'-oxydiphthalic anhydride.

The polyamic-acid solutions are applied to suitably-prepared substrate surfaces, either as pure adhesive resins or in various formulations with fillers, thickeners, or the like, with or without supports such

(continued overleaf)

as glass fabric. The substrates are allowed to stand to permit some or all of the solvent to evaporate. To be bonded, the treated surfaces are assembled together by means of clamps or in a press, and heat is applied to complete the evaporation of the solvent. This leads to conversion of the intermediate polyamic-acid to the more thermally-resistant cyclic polyimide, during the course of which the bonding of the substrate occurs. Although the bonding cycle can be varied over a wide range of time, temperature, and pressure, a typical bonding operation would initially involve the drying of the primed surfaces in air at room temperature. This would be followed by bonding of the joint at pressures from 30 to 200 psi (0.2×10^6 to 1.38×10^6 N/m²), with thermal treatment, under pressure, up to temperatures of 200° to 300° C. Times of 1 hour or more, at the required temperature and pressure, are sufficient to post-cure the bonded joint.

This process is different from the usual procedure for polyimide preparation in the necessity of using ether solvents. This is in contrast to the usually used solvents of the N,N-dialkylcarboxylamide class. The use of the proper ether solvents leads to molecular weights of the polyamic-acid prepolymers which result in superior bonding properties. Also, the ether solvents are more readily volatilized from the polymer at the optimum states of cyclization of the polyamic-acids to the polyimides.

Note:

Requests for further information may be directed to:

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