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Use of inorganic materials to enhance thermal stability and flammability behavior of a polyimide

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ABSTRACT

While a great variety of high temperature polyimide materials exist, these materials are being subjected to higher and higher use temperatures in oxidative and environmentally aggressive environments. There is a limit to the extent one can take a polyimide before it will oxidize and subsequently suffer property degradation, thermal decomposition, and structural failure. Therefore, we instead sought to use materials which do not oxidize (inorganic materials) to enhance the polyimide composition and perhaps move the properties of the organic polymer more into the realm of ceramics while maintaining polyimide composite weights and processing advantages. In this paper we present results of the combination of inorganic micron sized particles with and without carbon nanofibers to produce a variety of highly inorganic particle filled polyimides. These polyimides were tested for thermal stability and flammability in resin pellet form and as a protective coating for a carbon–fiber composite structure. Our results demonstrate that the resin with inorganic particles exhibited significant reductions in flammability by themselves, but minimal flammability reduction when used as a thin coating to protect a carbon–fiber composite. Further, the gains in thermal stability are limited by the thermal stability of the polyimide matrix, suggesting that more work is needed in measuring the limits of inorganic fillers to improve thermal stability. Still, the results are promising and may yield polyimide systems useful for providing resistance to damage from high heat flux exposures/fire risk scenarios.

1. Introduction

One of the most common material replacements in aircraft structures today is the replacement of metal or ceramic with a fiber reinforced polymeric composite. This is primarily done to achieve weight savings for improved fuel efficiency/flying range for an aircraft, but sometimes is also put in place to avoid corrosion issues encountered with metals or to yield complex structures which cannot be easily made from ceramic. However, the insertion of polymeric materials into places where metals and ceramics had originally been used means that these polymers must survive extremes of temperature (heat, flame). Therefore there is an increasing desire to combine the most advantageous features of metals and ceramics into a polymeric material and create a hybrid of the two materials. In this paper we discuss recent developments in polyimide + ceramic hybrids to provide enhanced thermal stability.

When considering which inorganic/ceramic filler to use in a polyimide composite, some background is needed to explain the choices that were made in this study as well as what we hoped to achieve. While polyimides can be used to replace metals and ceramics, they still suffer from thermal oxidative damage which causes the polyimide to slowly ablate away resulting in microcrack and structural failure of the composites [1–10]. Since polyimides will always oxidize when exposed to enough heat and oxygen, the best protective scheme for this material is to either help assist the thermally decomposing polymer form into glassy carbon char [11–13], or use materials which cannot oxidize further to form a ceramic shield *in situ* as the polymer decomposes [14–20]. Since polyimides are pre-disposed to form carbon chars upon exposure to high levels of heat and/or flame, we added finely dispersed inorganic particles in the polyimide matrix to improve thermal oxidative stability. The reason for this approach comes from the polymer nanocomposite literature, where the use of finely dispersed nanoscale inorganic particles (such as montmorillonite clays, aluminas, other metal oxides) delays the onset of thermal decomposition in a polymer and slows down the mass loss rate of the pyrolyzing polymer once thermal decomposition temperatures are reached

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[21–24]. Nanomaterials such as vapor grown carbon nanofibers (CNF), multi-wall carbon nanotubes (MWNT), or exfoliated graphite flake (EXGF) were focused on as these nanomaterials have shown significant reductions in mass loss rate under polymer decomposition temperatures [25–27]. These nanomaterials may also provide thermal and electrical conductivity enhancements to the composite for multifunctional performance [28–32]. However these commonly studied nanomaterials at their typical loading levels (0.1–10 wt%) cannot provide all of the needed thermal protection by themselves and so the chemistry of ceramics must be considered as well.

When it comes to thermal protection provided by ceramics the two chemistries most appropriate are silica (SiO_2) and alumina (Al_2O_3), both of which are widely and commercially available. These materials are available in a wide range of forms, especially as very fine (small size) particles appropriate for mixing into a fiber reinforced composite. If the inorganic particles are too big then they will filter out on the carbon fiber fabric during composite manufacture or worse, create defect sites for micro-cracking and mechanical failure. Therefore particle sizes of 5 μm or smaller are needed and silica and alumina are both available in this particle size. Fumed silica was chosen due to known effects of reducing mass loss and helping to form char in some polymer systems under thermal decomposition temperatures [15,18,19,33,34]. Alumina represents an inert filler and bulk ceramic shield, and so was chosen as a relatively inexpensive filler to do most of the thermal protection and work in a potentially synergistic manner with the other nanofillers described above. If alumina is calcined (heat treated to remove hydroxyls) and finely ground, then it should have very little effect on polyimide processing/resin viscosity since its typical surface chemistry (Al–OH) that would interact with polyimides will have been minimized. This point is important since nanomaterials used to produce polymer nanocomposites often increase resin viscosity to the point that the material is difficult to process, [35–37] and it is essential in this project to maintain ease of processing/composite quality while providing thermal protection. So for this project a calcined alumina used to produce larger high performance ceramic parts was chosen as a potential filler for the formation of polyimide + inorganic hybrids.

To produce a polyimide + inorganic hybrid with enhanced thermal durability, we focused on the development of a polymer formulation with more ceramic than polymer content. We achieved this by focusing on high loadings (>50 wt%) of inorganic material so that as the polymer decomposed, there would be high potential to form a ceramic rich layer which would protect the underlying (undamaged) material. This filler approach to producing a polymer + inorganic hybrid is admittedly simplistic and avoids other known polymer + inorganic hybrids such as sol-gel and ceramer (pre-ceramic monomers) chemistry, but this is done for two key reasons. The first reason is that co-reactive inorganic materials are very likely to interfere with polyimide polymerization chemistry and may in turn make thermal stability for the resulting composite worse, not better. The second reason is that combining fillers into a resin system is much more cost effective and easier to implement/commercialize than development of new polymer chemistry. Interestingly for commercial polyimide systems, most fillers are actually cheaper per kilogram than the polyimides and so by pursuing a filler approach, we may improve polyimide composite thermal damage resistance properties while lowering cost at the same time.

With all of these criteria in mind, we combined inorganic fillers with an aerospace grade resin transfer molding (RTM) polyimide to produce several different nanocomposites which were studied for thermal stability improvement and lowered flammability.

2. Experimental section

2.1. Materials

Polyimide monomers (MVK-10) in methanol solution used in this report was a Resin Transfer Molding (RTM) grade material provided by Maverick Corporation (Blue Ash, OH). Carbon fiber used to make the composites was T650-35 3K 309NT, Fabric Style 998, purchased from Fabric Development, Quakertown, PA. Dry Ball Milled Low Soda Alumina (99.75% purity – lot# BL6662) was purchased from Baikowski Malakoff (http://www.baikowskimalakoff.com/) through Brenntag Specialties. Fumed silica was purchased from Sigma–Aldrich. Vapor grown carbon nanofibers (PR-25-HHT) were provided by Applied Sciences Inc. (Cedarville, OH), and were heat treated at UDRI (UDRI Lot #181). Exfoliated graphitic flake was prepared by UDRI in the labs of Prof. Khalid Lafdi (UDRI Lot #219). Multi-wall carbon nanotubes (Nanocyl 7000) were obtained from Nanocyl S.A. (Belgium). All additives were dried in a vacuum oven at 100 °C for 24 h before use unless indicated otherwise below.

2.2. Resin and additive mixing & filming

The MVK-10 resin varnish was weighed into a container and the alumina added. This mixture was stirred manually with a spatula for 15 min. A 20 cm (8 in) 3-roll mill was pre-heated to 50 °C. The resin mixture was then rolled on the mill for 4 passes thru a gap spacing of 3 mil. On the fourth pass the material was collected into a Teflon lined tray placed in a sealed bag and then frozen at −23 °C. Films were made on an 18 inch wide roll film line. The fully dispersed resin was placed between the rolls and filmed onto release paper so that the film thickness was 9 mil. The rolls were heated to 48 °C. The films were cut to the appropriate size, bagged and frozen at −23 °C.

2.3. Polymer pellet processing

MVK-10 was dried at 105 °C under full vacuum until the solvent was removed (∼4 h). The resulting material was ground into a powder using a mortar and pestle. This powder was imidized for 2 h at 232 °C and allowed to cool. The sample was reground and placed in a pellet mold. The pellet mold was placed in a press and heated at 5 °C/min to 232 °C under minimal pressure. Pressure was applied at 232 °C and the press was allowed to continue heating to 316 °C and held for 3 h. The press was allowed to cool to room temperature and the mold removed. If the resin contained only alumina the pressure was minimal (kiss pressure), for other filled system with silica, nanofiber, etc. the pressure was 3.44 MPa (500 psi). Once the pellets were removed, they were wafer-saw cut into small pieces for thermomechanical analysis (TMA), as well as for other small scale thermal tests mentioned in this paper.

2.4. Composite layup and autoclave processing

The composite panels were made one of two ways. The first way was made using dry fabric then inserting MVK-10 resin films between each ply with the nano-modified film being on the tool surface. The second way was made using MVK-10 prepreg with the nano-modified material also being on the tool side. In the second case excess resin was bleed off. The panels were bagged and cured in the autoclave using a typical MVK-10 autoclave cycle as recommended by the manufacturer.