Better End-Cap Processing for Oxidation-Resistant Polyimides

Cross-linking in an inert atmosphere (as opposed to air) yields better results.

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A class of end-cap compounds that increase the thermo-oxidative stability of polyimides of the polymerization of monomeric reactants (PMR) type has been extended. In addition, an improved processing protocol for this class of end-cap compounds has been invented.

The class of end-cap compounds was described in “End Caps for More Thermo-Oxidative Stability in Polyimides” (LEW-17012), *NASA Tech Briefs*, Vol. 25, No. 10 (October 2001), page 32. To recapitulate: PMR polyimides are often used as matrix resins of high-temperature-resistant composite materials. These end-cap compounds are intended to supplant the norbornene end cap (NE) compound that, heretofore, has served to limit molecular weights during oligomerization and, at high temperatures, to form cross-links that become parts of stable network molecular structures. NE has been important to process-ability of high-temperature resins because (1) in limiting molecular weights, it enables resins to flow more readily for processing and (2) it does not give off volatile byproducts during final cure and, therefore, enables the production of void-free composite parts. However, with respect to ability of addition polymers to resist oxidation at high temperature, NE has been a “weak link.” Consequently, in order to enable

![End Caps of These Molecular Structures](https://ntrs.nasa.gov/search.jsp?R=20110020457)

End Caps of These Molecular Structures are alternatives to previously reported end caps for increasing the thermo-oxidative stability of polyimides. R1 through R4 can be any of a variety of substituents (for example, alkyl, alkoxy, aryl, halogen, or nitro), the inclusion of which reduces the cross-linking temperature.

The figure depicts the generic molecular structures of the prior version and the present extended version of this class of end caps. Each end cap is a 1,2,3,6-tetrahydrophthalic anhydride, substituted in such a way as to lower the cross-linking temperature. The end cap maintains its stability during imidization (at 200 °C) and cross-linking.

If the imidization is carried out in air, then the end cap subsequently aromatizes in competition with cross-linking. This aromatization is undesirable. Therefore, the improved processing protocol specifies that the process be carried out in an inert atmosphere, wherein cross-linking is the predominant, if not the exclusive, reaction path. Following cross-linking, the end cap is spontaneously converted, upon aging in air, to a thermally stable capping group.

This work was done by Wenhong Fan, Jun Li, and Jie Han of *Ames Research Center*. Further information is contained in a TSP (see page 1).

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