Better End-Cap Processing for Oxidation-Resistant Polyimides
Cross-linking in an inert atmosphere (as opposed to air) yields better results.

John H. Glenn Research Center, Cleveland, Ohio

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 processability 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, for example, in order to enable norbornene-end-capped polyimide matrices to last for lifetimes up to 1,000 hours, it is necessary to limit their use temperatures to ≤315 °C.

Like NE, these end caps are also subject to oxidation at high temperatures, but they oxidize in a different manner, such that the long-term stability of a polymer made with one of these end caps exceeds the long-term stability of the corresponding polymer made with NE. Hence, use temperatures and/or lifetimes can be increased. The approach taken in formulating these end caps is to seek derivatives that preserve the desirable processing properties of NE while exploiting one of the modes of the thermo-oxidative degradation of the nadi end cap in such a way as to retard the overall thermo-oxidative degradation of the affected polymers. 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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