Formation of Metallic Nanophases in Polymeric Matrices for Space Applications

Final Report

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FORMATION OF METALLIC NANOPHASES IN POLYMERIC MATRICES FOR SPACE APPLICATIONS:

1. SYNTHESIS OF FLEXIBLE AND LIGHT WEIGHT OPTICALLY REFLECTIVE POLYMERIC HYBRID MATERIALS

2. ENHANCEMENT OF DIMENSIONAL STABILITY AND SOLVENT INSOLUBILITY OF INORGANIC-POLYMERIC HYBRID FILMS

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There are a select number of polyimides which are soluble in organic media. Incorporation of hexafluoroisopropylidene groups is a route to achieving solubility. Such fluorinated polyimides have desirable properties for processing and electronic purposes; however, they often have linear coefficients of thermal expansion (CTE) which are well above those for metals and inorganic oxides or ceramics with which they might be bonded. We have developed a synthesis of composite inorganic-polyimide films using diaquatris(2,4-pentane-dionato)lanthanum(III) as the inorganic precursor and two soluble polyimides formed from 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane (6FDA) and 1,3-bis(3-aminophenoxyl)benzene (APB) or 2,2-bis[4-(4-aminophenoxyl)phenyl]hexafluoropropane (4-BDAF). A primary goal of our work was to control the linear CTE in these fluorinated polymer composites without adversely affecting mechanical or other thermal properties. The polyimides, 6FDA/3,3’-APB and 6FDA/4,4’-BDAF, are representative of a growing class of fluorinated polyimides which for space and electronic applications have several desirable properties including low dielectric constants, low moisture absorptivity, resistance to UV and electron radiation in nitrogen and in vacuo, enhanced processibility, and transparency in the visible region of the electromagnetic spectrum (colorlessness) while maintaining the thermal-oxidative stability associated with traditional polyimides.
Our work focused on attempts to lower the linear CTE while maintaining the visual clarity of 6FDA/APB and 6FDA/4-BDAF films via the addition of the hydrolytically and thermally labile eight coordinate diaqoctris(2,4-pentanedionato)-lanthanum(III) complex, La(acac)\textsubscript{3}(H\textsubscript{2}O)\textsubscript{2}, to dimethylacetamide (DMAc), N-methyl-pyrollidinone (NMP), and 2-methoxyethyl ether (diglyme) solutions of imidized 6FDA/APB and 6FDA/BDAF. [La(acac)\textsubscript{3}(H\textsubscript{2}O)\textsubscript{2}] was chosen as the inorganic precursor to a metal-oxo phase within the polymer for several reasons. Lanthanum(III) is a metal ion which has a single stable tervalent oxidation state with a very large crystal radius. Also, La(acac)\textsubscript{3}(H\textsubscript{2}O)\textsubscript{2} is transformed, with the loss of 2,4-pentanedione and water, by mild heating to a tetranuclear 2,4-pentanedionate complex, [La\textsubscript{4}(O)(acac)\textsubscript{10}] with a polynuclear tetrahedral La\textsubscript{4}(μ\textsubscript{4}-O) core. Our expectation was that La(acac)\textsubscript{3}(H\textsubscript{2}O)\textsubscript{2} would give nanometer-sized metal-oxo clusters in polyimides, which due to high surface area, would give tailored lowerings of CTEs.

The addition of the eight coordinate diaqoctris(2,4-pentanedionato)lanthanum(III) complex at very low weight percents to solutions of the soluble polyimides gave, after curing to the standard 300 °C, lowerings of the linear CTE up to a maximum of \(\sim 40\%\) while maintaining essential mechanical and thermal properties and the visual clarity of the parent polymers. It was also observed that there is substantial CTE lowering when the cure temperatures are relatively low, e.g., 220°. Based on a crystallographic structure of the product of the thermal hydrolysis of [La(acac)\textsubscript{3}(H\textsubscript{2}O)\textsubscript{2}] which shows formation of an La\textsubscript{4}(μ\textsubscript{4}-O) core, the TGA curve for [La(acac)\textsubscript{3}(H\textsubscript{2}O)\textsubscript{2}], and TEM data, it is reasonable that some type of lanthanum-oxo cluster is being formed with particle sizes on the nanometer level. The CTE lowerings are much greater than those observed with silica-polyimide hybrids and on the order of those of exfoliated montmorillonite (silicate) sheets incorporated into PMDA/4,4'-ODA.

Optically reflective and electrivally conductive composite polyimide films have been prepared by casting a DMAc solution of silver(I) acetate, trifluoroacetylacetone, and the poly(amic acid) derived from 3,3',4,4'-benzophenone tetracarboxylic acid dianhydride (BTDA) and 4,4'-oxydianiline (ODA) onto glass plates. Thermal curing of the silver(I)-containing poly(amic acid) topcoat led to imidization with concomitant silver(I) reduction followed by silver(0) migration/aggregation yielding a reflective and conductive silver surface similar to that of native silver metal. The metallized films exhibited outstanding metal-polymer and polymer-polymer adhesion, with the strong adhesion attributable to mechanical interlocking. The bulk of the polymer was not conductive. X-ray diffraction shows crystalline fcc silver in the films after thermal curing.

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