IL-08

Vibrational Spectroscopy Investgations on the Molecular Mechanism of H_2O Diffusion in Polyimides and Polyimide/Silica Hybrids

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Polyimides (PI's) represent an important class of high-performance polymers that exhibit very high T_g, ductility, thermal oxidative stability, and solvent resistance, coupled with relatively low permittivity and dielectric losses up to very high temperatures. For these reasons polyimides find extensive use in microelectronics, photonics, optics and aerospace industry, as well as in separation membrane technology [1]. More recently, they have been proposed as matrices for organic/inorganic (O-I) hybrid systems prepared by the sol-gel route [2]. Hybrid systems are an interesting class of new-generation materials which combine the relevant properties of a ceramic phase (heat resistance, high-temperature mechanical performances, low thermal expansion) and those of organic polymers (toughness, ductility and processability).

In the present study the diffusion of water vapor in a polyimide and in a polyimide-silica hybrid having a nanoscale morphology has been investigated in detail by use of *time-resolved* FTIR spectroscopy. Despite the obvious implications of water sorption on the performances of such materials as insulators, as well as on their aging behavior, the details of the diffusion process at a molecular level are still poorly understood. Of particular relevance, in this respect, is the state of aggregation of the absorbed H_2O molecules and the molecular interactions they form with the polymeric matrix and/or with the inorganic phase in the case of the hybrid system. These issues have been addressed by employing several vibrational spectroscopy techniques, namely difference spectroscopy, two-dimensional FTIR correlation spectroscopy (2D-FTIR) and curve fitting analysis. In particular, difference spectroscopy has been successfully employed to isolate the spectrum of the penetrant, thus allowing a quantitative determination of its concentration and the precise measurement of the diffusion coefficients. Furthermore, the interacting sites onto the polymer backbone (imide carbonyls) have been identified and a method has been proposed to quantify their population. The 2D-FTIR results allowed us to investigate in detail the dynamic behavior of the different water species present in the systems, thus providing important clues towards their identification.

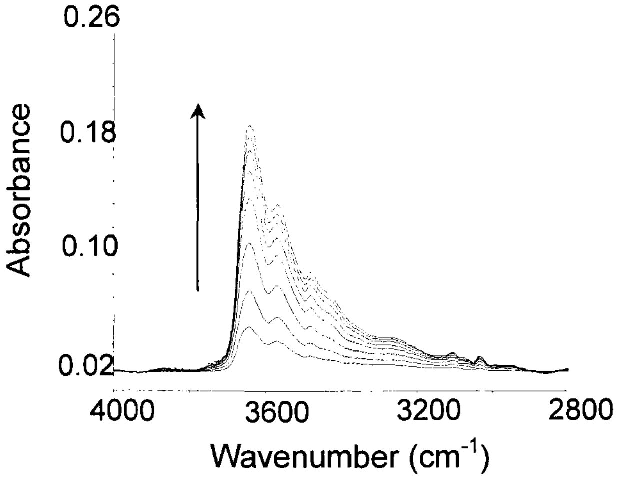

Figure 1. FTIR difference spectra in the 4000-2800 cm^{-1} range, collected at different time intervals during the sorption of H_2O in neat polyimide (a = 0.4, T = 30°C). Collection time increases as indicated by the arrow.

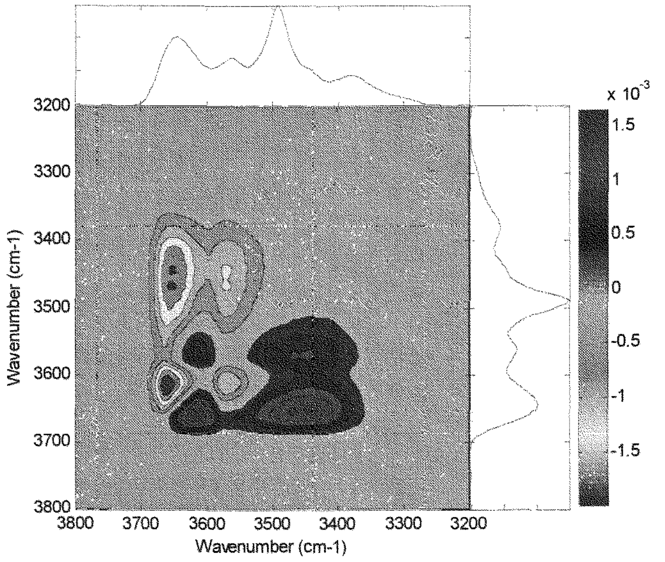

Figure 2. Asynchronous 2D-IR correlation spectrum in the 3800 3200 cm^{-1} range, obtained from the *time-resolved* FTIR spectra relative to the sorption of H_2O in neat polyimide (a = 0.4, T = 30°C).

References

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2. Mascia L. Trends Polym. Sci. **3**, 61 (1995)