ABSTRACT

The development of new and more complex polymeric materials involves challenging problems to basic sciences. The relationship between structure and molecular dynamics assumes great importance for the future development of novel technologies based on such polymers. Thus, the understanding of how small changes in the chemical structure affect the properties of the material is essential to progress in the technological and scientific area. An in-depth analysis of the molecular mobility leads to establish the structure-properties relationships. On this basis, the main aim of the present work is to study the molecular mobility of two different families of polymeric materials. For this purpose, the experimental techniques mainly used were Differential Scanning Calorimetry (DSC) and Dielectric Relaxation Spectroscopy (DRS) (Chapter 3).

The first family of polymers characterized was a series of chemically cross-linked copolymers composed by Vinylpyrrolidone (VP) and Butyl Acrylate (BA) monomers. The study was divided in two parts, which are collected in Chapter 4 and 5.

In the first place, Chapter 4 contains the influence of the monomer molar ratio (XVP/YBA) on the copolymer properties. Thus, a Fourier Transform Infrared Spectroscopy (FTIR) analysis verified dipole-dipole interactions between amide groups. The influence of these interactions on several parameters related to the molecular mobility was evidenced by the DSC, DRS and Dynamic Mechanical Analysis (DMA) techniques. The glass transition temperature (T_g) was found to increase with the VP content due to a reduction of the molecular mobility. The dielectric and mechanical spectra showed γ, β and α relaxations in increasing order of temperature, followed by conductive contributions in the dielectric spectrum. The γ process was related to the local motions of the butyl units, and the β process was a Johari–Goldstein (JG) secondary relaxation related to the local motions of the pyrrolidone group together with the motion of polymer backbone segments. Finally, the dc conductivity (σ_{dc}) was observed to increase with VP content. The conductivity was found to decouple from segmental dynamics at temperatures near glass transition.

Secondly, Chapter 5 presents the analysis of the effect of the cross-link density on the molecular dynamics of 60VP/40BA copolymers using DSC and DRS. One single glass transition was detected by DSC measurements. The dielectric spectra exhibited, for all the samples, conductive processes and three dipolar relaxations labeled as α, β and γ in decreasing order of temperatures. An increase of the cross-linking produced a typical effect on the α process dynamics. However, the β process, which possessed typical features of pure JG relaxation, unexpectedly lost the intermolecular character for the highest cross-linker content. The fastest γ process was relatively unaffected.

The second family of polymeric materials studied was a series of segmented polycarbonatediol polyurethane (PUPH) modified with different amounts of expanded graphite (EG) conductive filler. The results are presented and discussed in Chapter 6. Scanning Electron Microscopy (SEM), X-ray diffraction measurements and FTIR analysis demonstrated a homogeneous dispersion of the EG filler in the matrix. DRS was used to study the dielectric properties of the PUPH/EG composites. The dielectric permittivity of the composites showed an insulator to conductor percolation transition with the increase of

the EG content. Significant changes in the dielectric permittivity took place when the weight fraction of EG is in the range of 20–30 wt%. The addition of expanded graphite to the matrix caused a dramatic increase in the electrical conductivity of ten orders of magnitude, which is an indication of percolative behavior.

Finally, the general conclusions are summarized in Chapter 7.