

Summary

This PhD thesis deals with the systematic investigation of the phase transitions and molecular mobility of polymeric nanocomposite materials in relation to their structure and morphology as well as their final properties. Special attention was paid to the study of the thermodynamic glass transition and the dynamic glass transition (α relaxation), due to their interest from the point of view of basic research and of the applications of this class of materials.

Two types of polymer matrix were used, polydimethylsiloxane (PDMS) and natural rubber. The inclusions were silica nanoparticles which were prepared in situ in the polymer matrix using the sol-gel technique. Polydimethylsiloxane, having oxygen atoms in the main chain, interacts strongly with the silanol groups on the surface of the silica particle through hydrogen bonds, in contrast to natural rubber where there is no chemical interaction between the polymer matrix and the inclusions.

The morphology of the materials was studied using transmission electron microscopy. Phase transitions (melting and crystallization, glass transition) were studied using differential scanning calorimetry. Molecular mobility (both the main \sim relaxation and local secondary relaxations) were investigated in detail using two dielectric techniques, thermally stimulated depolarization currents and dielectric relaxation spectroscopy, while additional information regarding mechanical properties was provided by dynamic mechanical analysis as well as stress-strain measurements.

A general result, found with all experimental techniques used and for both types of polymer matrix, is that molecular mobility in a layer of polymer chains surrounding the filler particles is modified compared to that of the pure polymer. This modified interfacial layer has a thickness of a few nanometers, and its basic characteristics are common for the two polymer matrices. By studying two series of natural rubber / silica nanocomposites with different morphology of the dispersed silica phase, it was possible to study the effect of filler morphology on the molecular mobility of the polymer matrix. It was found that the modification of polymer dynamics close to the filler surface has a significant effect only when the silica particles are very small and well dispersed in the matrix.

The existence of the interfacial layer is detected in different ways using different experimental techniques. Regarding the thermal glass transition, as studied by differential scanning calorimetry, the chains in the interfacial layer are immobilized. On the other hand, using dielectric techniques the polymer in the interfacial layer shows an increase in relaxation times, having a glass transition temperature as much as 30 - 40 K higher than that of the pure polymer, but is not immobilized. Finally, using dynamic mechanical analysis the dynamics in the interfacial layer cannot be resolved separately, and what is observed is an overall shift of the glass transition of the material to higher temperatures.

Using thermally stimulated depolarization currents, in particular the thermal sampling technique, it was found that the molecular mobility in the interfacial layer cannot be described in terms of a discrete layer with lower mobility or a higher glass transition temperature, but rather as a continuous, gradual change of the glass transition temperature as a function of distance from the particle surface. However, dielectric spectra show, in addition to the main α relaxation (dynamic glass transition), an additional slower dielectric relaxation, called α' , which was attributed to the polymer chains in the interfacial layer. In the case of PDMS the polymer in the interfacial layer has a relaxation time 4 - 6 orders of magnitude larger than that of the pure polymer, compared to 2 - 3 orders of magnitude in the case of natural rubber. This difference was attributed to the existence of hydrogen bonds between the PDMS chains and the silica particles which further slow down the mobility of the interfacial layer.

The above situation, i.e. a continuous distribution of relaxation times close to the particles which causes a double _ peak in the dielectric spectrum, is an experimental verification of similar results which have been found in computer simulations of liquids close to a solid wall. The results obtained by dielectric spectroscopy in each series of samples was discussed in terms of the results of these simulations as well as theoretical and empirical models for the molecular mobility close to solid surfaces.

Based on the dielectric strength of the main α relaxation and the additional slow α' relaxation in the PDMS/silica samples, a characteristic length was calculated which corresponds to the effective thickness of the interfacial layer or, equivalently, the range of the polymer-filler interaction. This length is about 3 nm close to the glass transition temperature and decreases with increasing temperature. Its temperature dependence is well described by both an Arrhenius equation, which has been found to describe the range of the interaction in computer simulations, as well as an expression based on the concept of the cooperativity length, which is the sum of a constant value of the order of 1 nm (first layer) and a length with the temperature dependence of the cooperativity length.