RELAZIONE DI RICERCA STM

Il Fruitore: Riccardo Casalini

Istituto di afferenza : Chemistry Division, Naval Research Laboratory, 4555 overlook Avenue SW, Washington DC

con qualifica Ricercatore livello: Research Physicist, NP III

Descrizione dettagliata dell'Istituzione ospitante: Istituto per i Processi Chimico Fisici, Sede Secondaria di Pisa

Dipartimento di afferenza: Scienze chimiche e tecnologie dei materiali

Titolo del programma: Studio dell'effetto dell'interfaccia sulla dinamica segmentale dei polimeri nano strutturati usando misure locali di rilassamento dielettrico

Descrizione dell'attività svolta e dei risultati ottenuti:

During the research period at the Istituto per i Processi Chimico Fisici in Pisa, we investigated the effect of the interfacial interaction in polymer nanocomposites on the polymer segmental dynamics. In nanocomposites the presence of a relatively small amount of nanoparticles has been found to cause large changes in the physical properties of the polymer matrix (see for example [R. Casalini, R. Bogoslovov, S.B. Qadri, and C.M. Roland Polymer 53, 1282 (2012); R. Casalini and C.M. Roland Macromolecules 49, 3919 (2016)]). This large effect is due to the very large ratio of surface over volume which increases with decreasing of the nanoparticle size. Notwithstanding this large effect on some of physical properties, at present, it is not clear what is the effect of the nanoparticle/polymer interaction on the polymer segmental dynamics. Moreover, it is not clear over which distance the effect of the particle is felt into the polymer matrix. To this end we used the Local Dielectric Spectroscopy (LDS) method developed at the Processi Chimico Fisici in Pisa to measure the polymer segmental dynamics directly at the interface between polymer and nanoparticles. LDS makes use of an Atomic Force Microscope (AFM) to measure broadband dielectric properties with a high spatial resolution (around 20nm) allowing to directly investigate the dynamics in the vicinity of the nanoparticles. For the analysis of our results we took advantage of the recent development of this technique that allow us to measure quantitatively the local dielectric constant [J. Appl. Phys 118, 224104 (2015)] and thus the dielectric strength of the dielectric relaxation of polymers.

To obtain nanocomposites in which the nanoparticles are well dispersed it is necessary to choose a nanoparticle-polymer pair characterized by a strong interaction. For this project we used silica nanoparticles functionalized with hydroxyl groups at their surface to be mixed with poly-vinyl methyl ketone (PVMK). The ketone groups of the PVMK are able to hydrogen bond to the hydroxyl group on the functionalized silica particles allowing a good dispersion of the nanoparticles.

PVMK of Mw= 500,000 (glass transition T_g=38°C) was obtained from Aldrich and used as received. Silica nanoparticles of two sizes (10nm and 50nm) in suspensions in methyl ketone were obtained from Nissan Chemicals. The PVMK was dissolved in methyl ketone and mixed with the nanoparticle suspension. Thin films of the nanocomposite of different thickness (40-120nm) were then obtained by spin coating the suspension on metallized (gold/titanium) glass slides.

For the investigation a temperature range, above the polymer glass transition, in which the dielectric peak of the segmental motion was present in the frequency range of the LDS were chosen. While operating at a single frequency we were able to obtain spatial maps of the dielectric permittivity and the dielectric loss phase in the vicinity of the silica nanoparticles. Since the silica particles have a dielectric constant ($\varepsilon \sim 2$) much smaller than the polymer matrix ($\varepsilon \sim 14$), the presence of the silica particles was well resolved. These maps evidenced also the presence of a region around the nanoparticles were it is evident a difference in the phase between the "free" polymer and the polymer at the interface. Operating over a broad range of frequency in a single point we measured dielectric spectra in the vicinity of the nanoparticles compared them with those of the polymer farther away from the nanoparticle. We found that the spectra in the vicinity of the nanoparticles show an extra contribution at low frequency of the segmental peak. This extra peak at low frequency is the evidence that the segmental relaxation in the vicinity of the particles is slowed down of several orders of magnitude. From the LDS we found that the region over which evident changes in the permittivity are present has a size of about 20nm independently on the size of the particle, Interestingly this size is close to the radius of gyration (size of the polymer coil) for the used molecular weight of PVMK in agreement with recent molecular dynamics simulations.

The results obtained during the period allowed by the STM program are very encouraging and we are currently working on finalizing their analysis. We hope to present these results in a publication soon.

Firma del Proponente

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