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Dynamics of Interfacial Polymers in Composites

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Introduction

Much experimental and theoretical work has been done on the behavior of adsorbed polymers. However, not much work has focused on the dynamics, especially segmental dynamics, of the adsorbed polymers. This is especially true of filled polymer or composite systems as the interfacial layers in these systems are difficult to study with most techniques. NMR is not restricted to use in optically clear samples and its use in the characterization in surface polymers has been reviewed. (1-4)

In our laboratory, we have found that deuterium NMR could be used to probe the segmental dynamics of adsorbed polymers. The position of the deuterium label (selective deuteration) ensured that information on only certain moieties will be obtained. We have used solid-state deuterium NMR to probe the behavior of block copolymers (5) and homopolymers (6-8) on surfaces. We have suggested that for poly(vinyl acetate)- d_3 (PVAc- d_3) and poly(methyl acrylate)- d_3 (PMA- d_3) homopolymers at the silica-polymer-air interface that a motional gradient exists. This motional gradient includes regions where the segmental mobility was lower and higher than that of the bulk polymer. The lower mobility segments were identified to be due to segments at or near the polymer-silica interface, while those with the higher mobility were assigned to the polymer segments at the polymer-air interface.

In the present study, we report the effect of a polymer overcoat on the segmental dynamics of PMA- d_3 adsorbed on silica. We believe that this situation is very similar to that found in a filled polymer composite. We find that the presence of the polymer overlayer changes the dynamics of the original layer on the surface. The advantage of these experiments is that the originally adsorbed polymers are deuterated while the overcoat polymers are hydrogenated. Since deuterium NMR "sees" only the deuterated polymer, we directly probe the interfacial material.

Experimental

Methyl acrylate- d_3 was synthesized using methanol- d_4 and acryloyl chloride as starting materials. The monomer was then used to make poly(methyl acrylate)- d_3 . A high molecular weight (HMw) PMA was made via emulsion polymerization, and a low molecular weight (LMw) PMA was made via solution polymerization. The details of the monomer and polymer synthesis can be found elsewhere, (7,8) as can the detailed procedures for the adsorption experiments, line shape simulations, and the ^2H NMR experiment. These are only briefly described below.

The PMA- d_3 had a M_w of 1.10×10^6 g/mol and a polydispersity of 2.22, as measured by gel permeation chromatography (GPC). The surface sample at the solid-air interface was prepared by adsorption of the PMA- d_3 onto silica from toluene. The adsorbed sample with PMA- d_3 was prepared at saturation coverage, 2.61 mg/m^2 . The composite samples were prepared by hot pressing the surface sample in an 8 mm glass tube with different polymers, by hand, at 100°C for one minute. The ratio of the mass of the polymer overlayer to that in the interfacial adsorbed layer was about 1000.

The NMR spectra were obtained on a Varian VXR-400/S spectrometer equipped with a wideline probe (Doty Scientific, Columbia, SC), a high power amplifier and fast digitizer. The ^2H resonance frequency was 61.395 MHz. The pulse sequence was $\text{delay} - 90^\circ_x - \tau - 90^\circ_y - \tau - \text{acquisition}$. The 90° pulse width was $2.7 \mu\text{s}$ and $\tau = 30 \mu\text{s}$. The number of scans ranged from 3,000 to 100,000, depending upon the concentration of deuterium in the sample.

Results and Discussion

The ^2H spectra of PMA- d_3 at 52°C are shown in Figure 1 for the polymer in three environments. These spectra show a trend that was similar to that obtained at other temperatures (not shown). In bulk, the powder spectrum observed at lower temperatures had collapsed to a partially motionally averaged spectrum. The spectra for the bulk polymers were homogeneous in that all segments appeared to have the same mobility regardless of their location in the sample.

For the polymer at the silica-polymer-air interface, the presence of a powder pattern suggests that some segments were not motionally averaged

and are static on the deuterium NMR timescale (in this case on the order of 40 kHz). In addition, there was also the presence of a motionally averaged component that was even narrower than that of the bulk sample. Thus this polymer had segments which were *more* and *less* mobile than those of the bulk polymer. We have proposed that a continuous distribution of mobilities existed in the surface sample. Those near the silica were restricted and those near the air were more mobile. The use of deuterium NMR resulted in a filter through which the segments of intermediate mobility had reduced intensity. Thus the rigid and narrow features tended to dominate the spectra

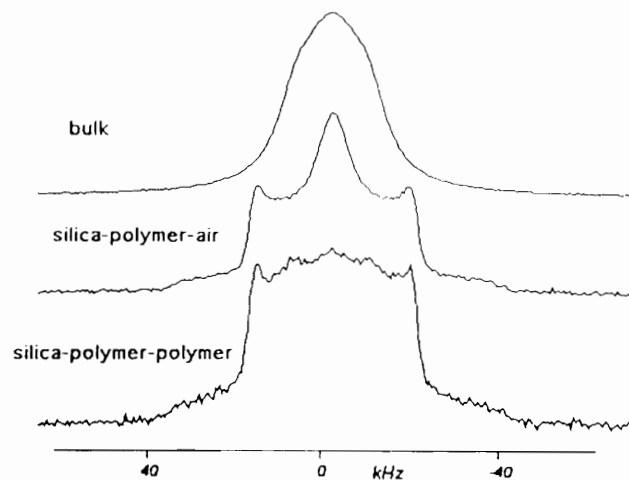


Figure 1. ^2H NMR spectra of PMA- d_3 at 52°C for the polymer in *bulk*, at the *silica-polymer-air* interface, and at the *silica-polymer-polymer* interface.

For the composite spectrum (silica-polymer-polymer), the presence of the powder pattern was noted, as was the *absence* of a narrow central resonance. We believe that this was due to the presence of the overlayer of polymer, reducing the mobility of the interfacial polymer. In this case, the high mobility of the polymer that was at the air interface was eliminated by the overlayer.

Conclusions

Deuterium NMR was shown to be a powerful technique for studying the behavior of surface-bound labelled polymer segments. While the bulk polymer segments were heterogeneous with respect to motion, the surface polymer in the silica-polymer-air system was graded in mobility. A region of enhanced mobility in the polymer-air region existed. The addition of an overlayer of unlabelled polymer eliminated the region of enhanced mobility.

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