

SILICA SURFACE TREATMENT EFFECTS ON THE DYNAMICS OF POLY(DIMETHYL SILOXANE) BY TIME-OF-FLIGHT NEUTRON SPECTROSCOPY

A. I. Nakatani,* K. S. Kwan,[#] R. Ivkov,* P. Papanek,*[‡]

* - National Institute of Standards and Technology
Polymers Division and # - NIST Center for Neutron Research
Gaithersburg, MD 20899

[#] - Dow Corning Corporation, Midland, MI 48686

[‡] - Department of Materials Science, University of Pennsylvania

Introduction

A critical need in the fundamental understanding of reinforcement in filled polymers is the characterization of the polymer-filler interface and the dynamics of the polymer in this interfacial regime. The interactions between polymers and filler surfaces are also believed to be key in the development of more advanced nanocomposite materials. We have previously utilized inelastic neutron scattering methods to examine the variation of bound polymer dynamics as a function of carbon black type for various initial carbon black concentrations.¹ The results suggested that two types of dynamic behavior are observed above and below a critical cutoff concentration that may be related to the percolation threshold of the carbon black. These results indicate that instead of quantifying the amount of bound polymer present, the filler concentration at which the bound polymer is prepared may be a key variable in understanding the mechanism of reinforcement by fillers.

Controlling the specific number and type of interactions between carbon black and polymers is difficult to achieve, therefore, detailed results on local chain dynamics as a function of the quantity and strength of polymer-carbon black interactions are difficult to obtain. However, specific control of the surface chemistry of silicas is easier to accomplish. In this study we will examine the influence of the concentration of surface active groups on a colloidal silica on the dynamics of poly(dimethyl siloxane) (PDMS) chains by inelastic neutron scattering methods. The effects of curing (crosslinking) on the polymer dynamics will also be measured. Prior studies on silica filled PDMS by inelastic neutron methods have been performed,^{2,3} however, the detailed differences in the dynamics as a function of the silica surface chemistry have not been explored.

Experimental

We have compared the dynamics of PDMS in the presence of colloidal silica with different surface treatments by using inelastic neutron scattering measurements performed on a Fermi chopper time of flight (TOF) spectrometer. The data is presented in a "density of states" formalism, which gives the distribution of the vibrational energies, $g(\epsilon)$, in the sample over the accessible energy range of the instrument. The data is similar to that which can be obtained by infrared or Raman spectroscopy, however, the inelastic neutron method is not limited by quantum mechanical selection rules, and the penetrability of the incident radiation is much higher. The vibrational energy range covered by the neutron method can reach very low energies (i.e. frequencies) which are lower than the range accessed by infrared or Raman techniques, hence, longer wavelength, lower energy motions can be probed. We prepare samples with identical compositions in either the uncured or cured state and compare the spectra with the pure, unfilled polymer.

Materials. The PDMS for this study is vinyl terminated and has a mass average molecular mass, M_w ,⁴ of 103,000 g/mol, and a number average molecular mass, M_n , of 56,000 g/mol. The silica used in this study is a 20 nm diameter colloidal silica with a surface area of 150 m²/g as determined by nitrogen adsorption according to Brunauer, Emmett and Teller⁵ (BET) and with an approximate surface silanol group concentration of 5 to 8 silanol groups/nm² as determined in the literature.⁶ Three different surface treatments of the silica were examined: 1) Trimethyl functionalized, without vinyl functionality (hereafter, referred to as "no vinyl"); 2) 0.57 mass % vinyl functionalized (designated "low vinyl"); 3) 1.88 mass % vinyl functionalized (designated "high vinyl").

Colloidal silicas were surface treated according to a scheme described in an earlier publication.⁷ A dilute suspension of colloidal silica was added to a solution of concentrated HCl, isopropyl alcohol, and controlled amounts of

hexamethyldisiloxane and divinyltetramethyldisiloxane. The mixture was heated to 70 °C and held isothermally for 30 minutes. Upon cooling, the silica phase separated and the aqueous phase was decanted. The treated silica was then washed with water and the aqueous phase removed. Solvent was added and the mixture refluxed using a Dean Stark trap until all water was removed. The suspension of treated colloidal silica was then spray dried using a Büchi B191 Mini Spray Dryer ($T_{set} = 220$ °C, $T_{out} = 120$ °C -155 °C, pump setting = 55) to create a dry, fine powder.

The extent of surface treatment was determined by using a gas chromatographic technique. Samples of the silica were dissolved under basic conditions in the presence of excess tetraethoxysilanes. This converts the trimethylsilyl and dimethylvinylsilyl groups on the colloidal silica surface to ethoxytrimethylsilane and ethoxydimethylvinylsilane, respectively, that can be detected via GC. The yield of each alkoxysilane was quantified (~ 5 % error) by GC analysis and the concentration of SiO₂ was determined by difference. Higher molecular weight species containing trimethylsilyl or dimethylvinylsilyl groups were not observed in the GC chromatogram.

For all samples reported here, the mass fraction of silica is 60 %. Uncured samples were prepared by mixing the PDMS with the silica and a Si-H functional crosslinking agent (no catalyst). Cured samples were prepared by further addition of a trace amount of Pt catalyst and hot pressed at 5000 psi at 150 °C for 10 minutes and postcured at 200 °C for 60 minutes in an air circulating oven to produce 1 mm thick specimens. The T_g of the final cured materials is approximately -90 °C to -80 °C.

Instrumentation. The Fermi chopper time-of-flight spectrometer (TOF) instrument located at the NIST Center for Neutron Research (NCNR) was used for these experiments. For the uncured samples, approximately 2 g of sample are placed into a folded aluminum foil pouch, roughly 2 cm x 2 cm. The cured sheets are also put in an aluminum foil pouch with similar dimensions. The sample pouch is placed in a mounting bracket with indium wire seals to prevent sample leakage and to form a sandwich-type sample geometry. The samples are then mounted in a cryostat which is sealed under vacuum. The time-of flight spectrometer experiments were performed at 160 K. In the TOF spectrometer, a monochromatic beam is produced by monochromator crystals. A Fermi chopper is used to produce neutron bursts at well defined times. The scattered neutrons are detected in an array of 60 detectors as a function of time after the neutron burst produced by the Fermi chopper. The scattering function, $S(q, \omega)$ is integrated over all q to give, $S(\omega)$. An incident wavelength of 4.8 Å and instrument time channel width of 6 μ s was used, giving an energy resolution of 0.15 meV near zero energy transfer. The TOF technique measures $S(q, \omega)$, therefore, by integrating over all q at each ω , the so-called density of vibrational states, $g(\epsilon)$, is obtained. All data presented have been normalized over the energy range displayed (0 meV to 40 meV).

Results and Discussion

An example of the density of states comparison for the PDMS as it is filled and a function of cure is shown in Figure 1. The samples for the data in Figure 1 contain a mass fraction of 60 % of the high vinyl filler. The standard error estimates for each data point are smaller than the symbol sizes. The data are normalized so the area under the curve is unity for the energy range shown. Experiments on the low vinyl and no vinyl fillers are in progress and only preliminary results on the high vinyl filler are presented.

In all spectra, two peaks are present. The peaks and their positions are consistent with those reported by Henry and Safford.² The first peak occurs at about 22 meV (1 meV = 8.07 cm⁻¹) in the pure PDMS (we will refer to this peak as the "high energy peak") and the second peak occurs at approximately 8 meV (referred to as the "low energy peak") in the pure PDMS (O in Figure 1). The changes in these two peaks as filler is added to the polymer (■ in Figure 1) and as the sample is cured (Δ in Figure 1) are quite dramatic. As filler is added to the sample the intensity of both peaks increases. Upon curing, both peaks increase in intensity further, however, the high energy peak experiences a much stronger increase in intensity upon curing than the low energy peak. The high energy peak also appears to shift slightly to lower energies as the filler is added (peak position ca. 21.5 meV) and as the sample is cured (peak position ca. 21 meV). Finally, the high energy peak progressively narrows as filler is added to the PDMS and then the sample is cured.

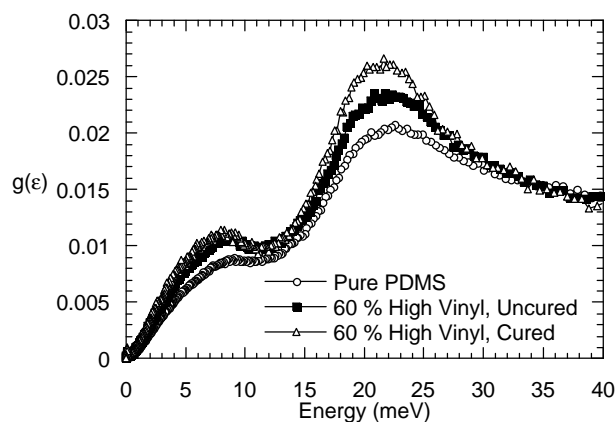


Figure 1. Density of states, $g(\epsilon)$, comparison for pure PDMS (○); PDMS filled with silica (mass fraction = 60%), high vinyl surface treatment, uncured (■); and PDMS filled with silica (mass fraction = 60%), high vinyl surface treatment, cured (△).

Based on prior work by Henry and Safford,² the high energy peak in the pure PDMS at 22 meV is related to threefold methyl group rotation as well as unhindered rotation and/or translation of the entire methyl group. The low energy peak at 8 meV is attributed to unspecified low frequency skeletal and interchain vibrations which are sensitive to chain conformation.

Upon addition of a filler (unmodified silica, surface area = 300 m²/g), Henry and Safford reported a broadening of the peaks, and concluded that the presence of filler disordered the PDMS chains but the disorder was counteracted by a decrease in chain flexibility due to attachment of the chains to the filler surface. While Henry and Safford observed a broadening and smearing of peaks on the addition of filler, we observe a sharpening of peaks through the addition of filler, indicating the presence of filler hinders the methyl group rotation and produces order in the chains.

In crosslinked samples, Henry and Safford observed that the high energy peak narrowed and shifted to lower energies and the low energy peak became more prominent. When the crosslinked samples were stretched, the low energy peak was observed to sharpen and intensify, indicating the effect of chain ordering on the spectra. These changes were attributed to a reduction of the methyl group freedom which is compensated by an enhancement of bending and torsional skeletal modes.

More recently Arrighi et al.³ have also examined the effect of reinforcing fillers on the local dynamics of PDMS. In these studies two different silicas were used (20 nm diameter, 90 m²/g surface area and 7 nm diameter, 300 m²/g, mass fraction = 40 %). No modification of the filler surfaces was performed in this study. While the study by Henry and Safford was performed at select temperatures (150 K and 298 K), the study by Arrighi et al. contains experimental data for a number of different temperatures between 4 K and 280 K. Relative to the measured glass transition temperature ($T_g = 151$ K), cold crystallization temperature ($T_c = 188$ K), and melting temperature (T_m endotherms at 227 K and 233 K) varying degrees of mobility in the PDMS are reported. With increasing temperature up to 235 K, Arrighi et al. reported a small effect due to the presence of fillers which indicated a slowing down of segmental motions. Above T_m , the effect was much more pronounced with the effect most obvious for the highest surface area filler, indicating the high surface area filler is the most effective at restricting chain mobility.

In our previous studies on carbon black filled polyisoprenes,¹ the density of states spectra of the bound polyisoprene showed an increase in the peak intensities due to methyl group librational motion as well as backbone motions. We originally attributed this increase to an apparent enhancement in local mobility of the bound polyisoprene. However, based on the interpretation of these spectra as well as work comparing the inelastic neutron spectra of amorphous and crystalline ethylbenzene,⁸ we believe a more plausible explanation may be the ordering of the bound polymer chains on the surface of the carbon black. This will be clarified in a future publication.⁹

Therefore, based on the interpretations of Henry and Safford, in our PDMS samples containing silica with a high degree of vinyl groups on the surface of the silica, addition of the filler hinders the methyl group rotations in

the PDMS and produces some order in the chains, possibly by forcing the chains to lie on the surface of the filler particles. When the samples are altered further by crosslinking, the degree of mobility of the methyl groups is restricted further with only a slight increase in order relative to the filled, uncured sample. While our study was only conducted at a single temperature, the results obtained are also consistent with those reported by Arrighi et al. The difference between our results and those of Henry and Safford may be attributed to the surface modification of the silica used in our experiments. Experiments on the other treated silicas are in progress to test this hypothesis.

Conclusions

We have presented some preliminary time-of-flight neutron spectroscopy results on poly(dimethyl siloxane) in the absence and presence of a colloidal silica filler and, for the filled samples, in the absence or presence of crosslinking. The results are consistent with the interpretation that the presence of filler restricts the local polymer dynamics. This result may depend on the strength of the interaction between the filler surface and polymer and will be tested with fillers having different surface treatments. As crosslinks are introduced into the filled sample, the mobility of the polymer chains is decreased further.

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