Interfacial Modification in Silica-Siloxane Composites: Investigation by Ultra-Small-Angle X-ray Scattering

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Introduction

Polymers are typically reinforced by adding particulate fillers having high surface areas, such as carbon black or silica, as a second phase.[1] Poly(dimethylsiloxane) (PDMS) $[-Si(CH)_2O-]_x$ is a good example of an elastomer that requires considerable reinforcement from silica (SiO_2) in most of its applications.[2-4] The conventional method for obtaining such reinforcement is the simple blending of silica into the uncrosslinked polymers. This is a difficult procedure since the polymer has a very high bulk viscosity. Therefore, a good dispersion requires a great deal of time, energy, and patience. As an alternative, in the *in situ* technique, the hydrolysis reactions used in the sol-gel process are carried out within a polymeric matrix.[5-8] The silica is generated in the form of small, well-dispersed particles.[9]

Alkoxysilanes are the most widely used compounds in the modification of silica to improve the compatibility of these fillers with the elastomeric matrix.[10] These coupling agents form a durable chemical bridge between the organic polymers and the inorganic fillers. A molecule such as vinyltrimethoxysilane has methoxy groups that react with the silica surface and a vinyl group that can participate in crosslinking reactions with the elastomer.

A fundamental understanding of the mechanism of such reinforcement can lead to property enhancement in existing applications as well as the development of new ones. Questions regarding the mechanism of reinforcement include: What is the role of the interface? Should the two phases be bonded to form an extended network of the hard phase? Our goal is to modify such interfaces by using alkoxysilanes to bond the silica particles to the networks. Of primary interest is the effect of the coupling agents on the structures of the resulting materials.

Experimental

Preparation of the filled networks. Samples of vinyl-terminated PDMS having various number average molecular weights M_n were tetrafunctionally end-linked with tetrakis(dimethylsilyloxy)silane (TDSS) in the presence of vinyltrimethoxysilane (VTS) or vinylmethyldimethoxysilane (VMDS). These reactants were used in stoichiometric amounts, and the reaction was characterized by Fourier transform infrared spectroscopy (FTIR). The resulting network sheets were extracted using tetrahydrofuran followed by toluene.

The extracted PDMS strips were placed into tetraethoxysilane (TEOS) until swollen to equilibrium. Each swollen strip was then placed into a catalyst solution of diethylamine. The strips were dried under vacuum to constant weight, and the increase in dry weight gave the amount of SiO_2 precipitated within the polymer network.

Stress-strain measurements. Equilibrium stress-strain data were obtained in elongation in the usual manner[11,12] at 25°C.

USAXS. The structure of silica-siloxane composites was investigated using ultra-small-angle x-ray scattering.

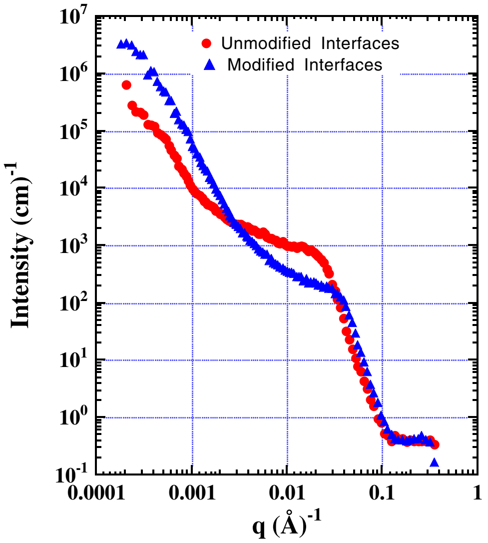

FIG. 1. SAXS data for the final materials with either vinyltrimethoxysilane modified interfaces or unmodified interfaces.

Results and Discussion

The ultra-small-angle x-ray scattering results are illustrated in Fig. 1. The data from Fig. 1 generated a Porod regime with slopes between -4 and -5, consistent with a diffuse interface. The domain size of phase separation (determined from the "knee" of the curve) of the filled elastomers having modified interfaces is smaller than those of the elastomers with unmodified interfaces.

The stress-strain isotherms are presented in Fig. 2. The data are displayed[11,12] as the dependence of the reduced stress or modulus on reciprocal elongation. The networks that have bonding between the silica particles and the networks are seen to have much higher values of the modulus.

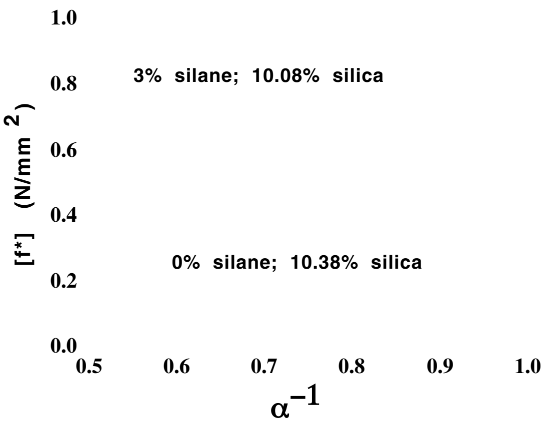

FIG. 2. Stress-strain curves in elongation at 25°C for the PDMS networks having a molecular weight of 9,430 g mol^{-1}.

Acknowledgments

We would like to thank the members of the UNICAT beamline at the Advanced Photon Source (APS) for support in collecting the SAXS data. The UNICAT facility at the APS is supported by the University of Illinois at Urbana Champaign, Materials Research Laboratory (U. S. Department of Energy), the State of Illinois-IBHE-HECA, and the National Science Foundation.

Use of the Advanced Photon Source was supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. W-31-109-ENG-38

It is pleasure to acknowledge the financial support provided JEM by the National Science Foundation through Grant DMR-9422223 (Polymer Program, Division of Materials Research).

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