

USAXS Structural Study of *In-situ*-generated Magnetic Filler Particles in Poly(dimethylsiloxane) Elastomers

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Introduction

In situ synthesis of nanostructured ceramics in organic elastomers has been well-studied over the last 20 years as an alternative to the separate synthesis of composite phases followed by energy-consuming mixing processes. The milling of reinforcing fillers into organic elastomers typically adds approximately 40% to the final cost of the elastomer. By swelling of the elastomer with ceramic precursors, such as sol-gel chemicals, this costly milling stage can be averted. Moreover, *in situ* generation of ceramic phases has led to novel filler morphologies, such as correlated spherical domains and tuned mass-fractal structures, that cannot be obtained with conventional *ex situ* synthesis. We have recently developed *in situ* methods for the production of magnetic particles in elastomers along the same lines as our previous work on reinforcing fillers (silica, zirconia and titania) for several reasons. Magnetic reinforcing filler particles offer a unique potential for alignment during formation/cross-linking. Also, after cure, magnetic particles may enable actuator functionality to elastomeric materials for several applications, including artificial muscles and microelectromechanical system (MEMS) devices. Moreover, in some cases, magnetic composites may be useful for control of optical properties through applied magnetic fields.

In this work, magnetic particles were generated in an elastomeric poly(dimethylsiloxane) (i.e., PDMS) network by an *in situ* process. The particles were generated by using either aqueous or nonaqueous systems and also from ferric acetoacetate [Fe(acac)]. The nonaqueous and Fe(acac) methods generated larger amounts of filler particles and were therefore judged the preferred approach. Magnetic studies using a vibrating sampling magnetometer (VSM) showed that the particles generated from the preferred approach were magnetic. Some studies of mechanical elongation were also carried out on these materials in order to determine the extent of reinforcement in these composites. Scanning electron microscopy (SEM) images were taken in conjunction with ultrasmall-angle x-ray scattering (USAXS) measurements at UNI-CAT 33-ID-D in order to understand the complex structure of these *in situ* composites.

Methods and Materials

Cross-linked PDMS networks were prepared from stoichiometric amounts of PDMS linear polymer with

hydroxyl end groups and tetraethoxysilane (TEOS) as a cross-linking agent. One percent stannous oleate was added as a catalyst. The unreacted sol content of these networks was extracted with a mixture of toluene and methanol, starting with 100% methanol and slowly increasing the fraction of toluene. The total sol content was about 5%.

Three similar synthetic protocols were used for the *in situ* production of iron oxide domains. The elastomer was swollen with (1) aqueous ferric chloride, (2) ferric chloride in toluene, and (3) Fe(acac). These protocols are described below:

In the first protocol, the cross-linked PDMS samples were swollen in a 10% solution of FeCl₃ in distilled water for 24 h. The swollen samples were then heated in 1M HCl for another day at 80°C. A yellowish precipitate formed in the PDMS elastomer. The samples were then heated at 80°C for another 24 h. The resulting PDMS changed to a reddish brown color with about 6% filler loading.

In the second protocol, other samples were swollen in a 10% FeCl₃ toluene solution by following the same procedure as that used for the aqueous solution. This led to a light brown precipitate before final heating and a reddish brown precipitate after heating. For the toluene samples, the final iron oxide loading was about 20%.

The third protocol, the Fe(acac) method, involved a similar procedure: swelling in a 10% solution of Fe(acac) in toluene for 24 h and heating in 1M HCl for 24 h at 80°C, yielding a reddish brown precipitate with about 27% filler loading.

Results

Figure 1 shows the magnetic hysteresis of the Fe(acac) sample by using a vibrating sampling magnetometer (VSM). The hysteresis indicates that the sample is magnetic. Figure 2 shows the behavior for the toluene-based ferric chloride sample.

Table 1 shows results for magnetic coercivity and remnant magnetization for the toluene (nonaqueous) and Fe(acac) samples. These preliminary results indicate that the toluene (nonaqueous) synthesis results in superior magnetic properties.

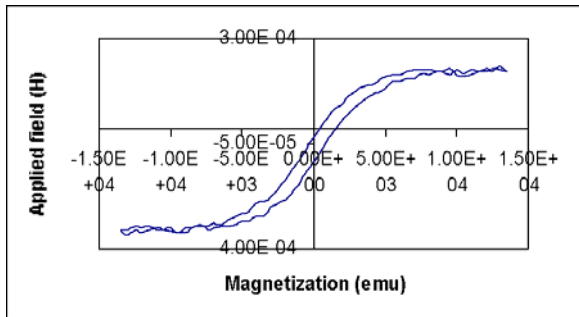


FIG. 1. Magnetic hysteresis of the Fe(acac) sample by using a VSM.

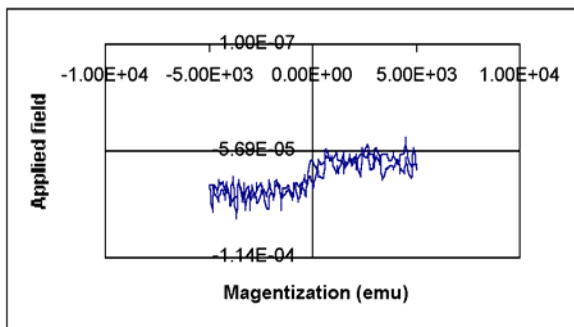


FIG. 2. Behavior of the toluene-based ferric chloride sample.

Table 1. Coercivity and remnant magnetization for the toluene and Fe(acac) samples.

Sample Type	Coercivity (O _e)	Remnant Magnetization (M _r)
Fe(acac)	588	2.78E-04
FeCl ₃ (Non aqueous)	5000	7.92E-06

The stress strain curves (stress in MPa vs. strain) for all three samples are shown in Fig. 3. The Fe(acac) sample shows higher modulus because of its higher loading but comparable toughness when compared with the nonaqueous sample, as seen in Table 2.

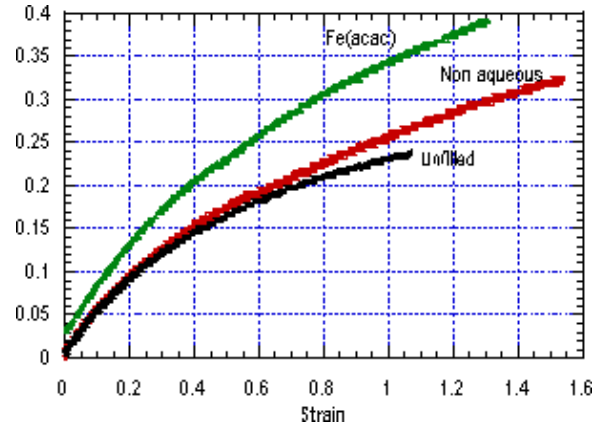


FIG. 3. Stress (MPa) versus strain for iron oxide composites.

Table 2. Amount of filler and toughness for iron oxide composites.

Sample	Amount of filler (%)	Toughness (MPa)
Unfilled	0	0.17
Fe(acac)	27	0.34
Nonaqueous	17	0.31

The USAXS data from these samples are complex and not amenable to a simple analysis. Two scattering curves (log scattered intensity vs. log q , scattering vector) for the Fe(acac) sample (light) and nonaqueous sample (dark) are shown in Fig. 4. Both synthetic protocols apparently lead to similar morphologies, which is surprising. Large-scale clusters on the order of 0.5 μm in size are seen at lowest- q . An unknown intermediate structure is reflected by an intermediate- q power law regime. At nanoscales, correlated domains (20-nm correlation distance) associated with the ionic nature of the iron oxide precursors are seen. The large-scale clusters have been verified in SEM micrographs from these samples, while the nanoscale structures have only a vague description and await further measurements for clarification of their origin. We plan to study further the relationships between magnetic, mechanical, and nanostructural features in these fascinating and technologically useful materials.

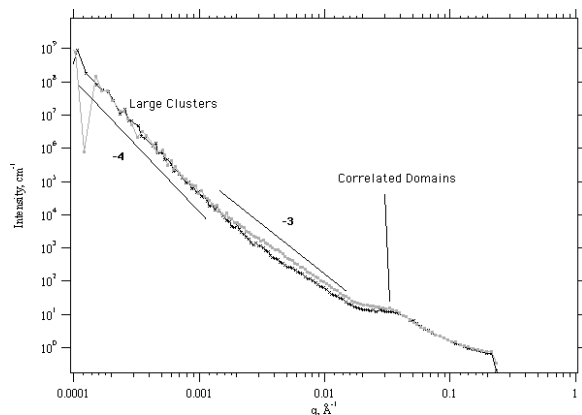


FIG. 4 USAXS data from $Fe(acac)$ (light curve), and iron chloride (dark curve) showing correlated nanodomains (20-nm correlation), intermediate structure, and large-scale clusters ($0.8 \mu m$) observable in SEM images.

Discussion/Conclusions

Magnetic particles were generated *in situ* in PDMS networks by using both aqueous and nonaqueous methods. The nonaqueous methods were very effective in generating higher amounts of filler particles in PDMS networks. Higher amounts of filler content lead to better magnetic activity. The mechanical properties of the samples show reinforcement due to the presence of iron oxide domains that scaled with loading. USAXS data and SEM images concur for microscale structures, but

nanoscale features in this system await further USAXS data and TEM images for elucidation of the growth mechanisms and structural details of these systems.

Several propositions can be made from the preliminary data presented here. First, the low filler content of the aqueous samples may be a result of the hydrophobic nature of the PDMS networks. This may also be the probable reason for no magnetic activity. Second, nonaqueous and $Fe(acac)$ samples had higher amounts of filler content. The higher generation may be a result of the penetration of the solvent into the networks. They had

weak magnetic activity because of the higher filler content. Weakness of the activity may be a result of mixtures of the Fe compound synthesized in the PDMS networks

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