	Experiment title: Small angle X-ray scattering study of nanoparticle structure in PDMS based composites for nanodielectrics in high voltage applications	**Experiment number**: MA-564
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Introduction

Commercially available SiO_2 particles which have specific surface areas from 50 to 300 m^2/g were mixed into a PDMS monomer of an addition cure system with a DAC (dual assymetric centrifuge) for several minutes. Cured samples were investigated with small angle X-ray (SAXS) measurements to characterize particle dispersion detecting primary particle, aggregate and agglomerate sizes, mass fractal dimension as well as silica volume fraction. SAXS measurements were compared to BET measurements and TEM images of cryostate-microtome thin sectioned rubber foils. This reports only covers the discussion of the SAXS/USAXS measurements while no comparison to mechanical measurements in the PDMS monomer suspension or in cured rubbers will be shown. Nevertheless, SAXS/USAXS results will be used to explain the mechanical properties of such composite systems in a publication which is about to be submitted soon.

Experimental

For the investigation of primary particle, aggregate and agglomerate size as well as particle morphology in cured rubbers SAXS at the ESRF (high brilliance beam line ID02, pinhole camera)[1,2] was used. Monochromatic X-rays ($\lambda = 1$ Å) with a beam cross-sectional area of 200 x 200 μm^2 were focused on a thin rubber piece (thickness: 100-200 μm). Scattered X-rays were collected on the SAXS detector inside the 12 m long detector tube.[2] The position of the detector was at 10 m to cover a scattering wave vector q-range (0.001–0.05 Å^{-1}). The exposure time of the charged-coupled-device camera was from 1 s for unfilled rubbers down to 0.1 s for highly filled rubbers (11.7 vol%) and duration was adjusted to get sufficient high detector counts. Background subtraction was carried out using unfilled rubbers. A wider size range of scattering objects in the range of 1 μm to 0.05 μm was obtained with the USAXS (Bonse-Hart camera)[3] than the 100 to 1 nm for the SAXS configuration (pinhole camera). However with the USAXS camera longer measurement time in the order of 5–10 min was needed instead of the fast SAXS measurements (0.1 to 1 s). The USAXS setup allows detection of a broader q-range especially at lower q (10^{-4}–0.02 Å^{-1}). SAXS/USAXS data were combined to cover a q-range of (10^{-4}–0.05 Å^{-1}) and particle, aggregate and agglomerate characteristics were determined from SAXS/USAXS scattering spectra analysis following the unified fit model:[4,5] aggregate and agglomerate radii of gyration (R_{g2}, R_{g3}), mass fractal dimension (D_f), primary particle diameter ($d_{v/s}$) and number of primary particles per aggregate (n_p). The silica volume fraction (ϕ_v) was also extracted. The primary particle diameter ($d_{v/s}$) is obtained by the moment ratio, volume-to-surface[6,7] as measured by BET. Additionally to filled PDMS rubbers, small amount of dry powders were placed between two adhesive tapes (Scotch, Magic, 3M).[7-9] Particle-free adhesive tapes were used for background subtraction.

Results & Discussion

Figure 1 shows the combined USAXS and SAXS intensities (solid lines, open symbols) as a function of the scattering vector q of (a) 6.2 vol% A150 and (b) A300 filled rubbers. Scattering intensities for three different mixing durations (circles: 10, triangles: 20 and diamonds: 30 minutes) are shown. Dry SiO_2 particle were placed between two scotch tapes as reported elsewhere[7-9] and scattering intensity (open butterflies) was measured with the Pinhole setup (SAXS).

Figure 1 shows that at high q (0.01–0.04 Å^{-1}), the power law (Porod's law)[10,11] decays with a slope equal to -4, which indicates a smooth primary particle surface.[11] Towards lower q values, first a knee-like decay follows (Guinier's law, G_1)[10,11] depicted by $q \propto 2\pi/R_{g1}$, a proportionality to the reciprocal of the scattering size (hence here the primary particle size).

For OX50 (not shown here) the calculation of the surface-to-volume equivalent primary particles size ($d_{v/s}$) resulted in 41 nm which is lower than the $d_{BET} = 55$ to which it should be comparable according to literature.[6,7] The second Porod regime (0.002–0.01 Å^{-1}) depicts the mass fractal dimension ($D_f = 1.74$),[10,11] and above that, in the 2nd Guinier regime (G_2), the characteristic larger size structure, the aggregate size ($R_{g2} = 130$ nm), is depicted. Increasing the mixing duration from 10 minutes to 30 minutes did not affect primary particle and aggregate size or morphology (mass fractal dimension, D_f). An aggregate size $2 \cdot R_{g2} = 260$ nm is in good agreement with a dispersion study where OX50 was defragmented down to sizes in the order of 250 nm (measured by DLS, d_{DLS}) in a high pressure dispersion apparatus.[12]

However, above the 2nd Guinier regime (G_2) a third one (G_3) is detected, distinctive by a knee-like increase with a power law (Porod's law) decay of -3 which is some what less steep than one would expect (instead of -4) which depicts that these agglomerates show a broad size distribution. While increasing the mixing duration, variations in the 3rd Guinier regime (G_3) were detected. The agglomerate size (R_{g3}) varied from 262 up to 362 nm. This increase depicts that with applied DAC mixing conditions the agglomerate size rather increased due to mixing induced agglomeration. Although the changes above 20 minutes of mixing were minor. The dry OX50 placed between two scotch tapes (open butterlies) showed in the first two Guinier (G_1, G_2) and Porod regimes (P_1, P_2) similar scattering intensity evolution but a steeper 2nd Porod slope than in the filled PDMS rubber sample which is comparable to reported values for OX50 of $D_f = 1.6 \pm 0.1$[13] resulting from similarly measurements between two scotch tapes or measured in PDMS rubbers $D_f = 1.8 \pm 0.2$.[14] Moreover, a distinct 3rd Guinier regime was not detectable meaning that in case of the dry particles a distinctive aggregate or agglomerate size was not detectable a drawback of the scotch tape method as here dry particle are not dispersed in a polymeric matrix forming large agglomerates (> 1 μm).

In Figure 1a three rubbers samples filled with 6.2 vol% of A150 are presented (circles: 10, triangles: 20, diamonds: 30 minutes). Also a scotch tape sample (butterflies) is shown. The 1st Porod showed a decay of -4 and the 2nd one a similar decay as OX50 ($D_f = 1.75$) but also here the first and the second regimes were not affected by increasing mixing duration. The calculated primary particle size $d_{v/s} = 14.5$ nm was slightly smaller than $d_{BET} = 18$ nm. However the 3rd regime showed a steeper power law decay of -4 than in case of OX50 indicative of a narrower agglomerate size distribution. The variation of mixing duration from 10 minutes up to 30 minutes did not affect the aggregate size ($R_{g2} = 92$ nm) nor the agglomerate size (seen from G_3, doted lines, or $R_{g3} = 219$-231 nm) significantly. The particles stitched between scotch tapes (open butterflies) showed a similar evolution but as already seen in the case of OX50 with less distinct separation of the three regimes (primary particles, aggregates and agglomerates). At low q vector range (< 0.002 Å^{-1}) the slope of the 3rd Porod regime is rather towards -3 than compared to -4 in the filled PDMS rubber samples again an indication of agglomerate size polydispersity.

For the 6.2 vol% A200 filled rubbers (not shown here) also increased mixing duration had no influence on primary particle ($d_{v/s} = 12$ nm), aggregate size ($R_{g2} = 75$ nm) nor morphology ($D_f = 1.82$). The primary particle size $d_{v/s}$ is in agreement with $d_{BET} = 14$ nm also the size of the aggregate ($2 \cdot R_{g2} = 184$ nm) compared to TEM images[7] or by DLS in high pressure mixing with sizes in the order of $d_{DLS} = 200$ nm were reached.[12] The mass fractal dimension was smaller or equal than reported in literature where $D_f = 2.0$[7] or 2.2 ± 0.2[13] with scotch tape method or $D_f = 1.8 \pm 0.2$[14] in PDMS rubber were observed. However, no good agreement to literature where A200 particles were placed between scotch tapes was found regarding to the aggregate size (R_{g2}) results as they reported huge aggregates sizes ($R_{g2} > 1$ μm)[7] which might be attributed to the scotch tape method which fails to predict the aggregate size and rather detects an agglomerate size. However, variations in the 3rd Guinier regime were detected similar as in case of OX50 and A150 but with a distinct difference at 10 minutes of mixing. The scattering intensity at $q < 0.002$ Å^{-1} did not show the power law slope of -4 rather showed a slope comparable to the one of the 2nd Porod (-1.82). No agglomerate size ($R_{g3} > 1$ μm) was detectable due to scattering vector limitation at small q. This emphasizes that incase large agglomerates (> 1 μm) are present in the rubbers, similar scattering curves are detected as found in the case when particles are placed between scotch tapes.[7] Above 10 minutes of mixing, the power law slope in the 3rd regime was similar to the A150 sample equal to -4, indicative of narrow agglomerate size distribution. Increasing the mixing duration resulted in agglomerate sizes in the order of $R_{g3} = 174$-180 nm.
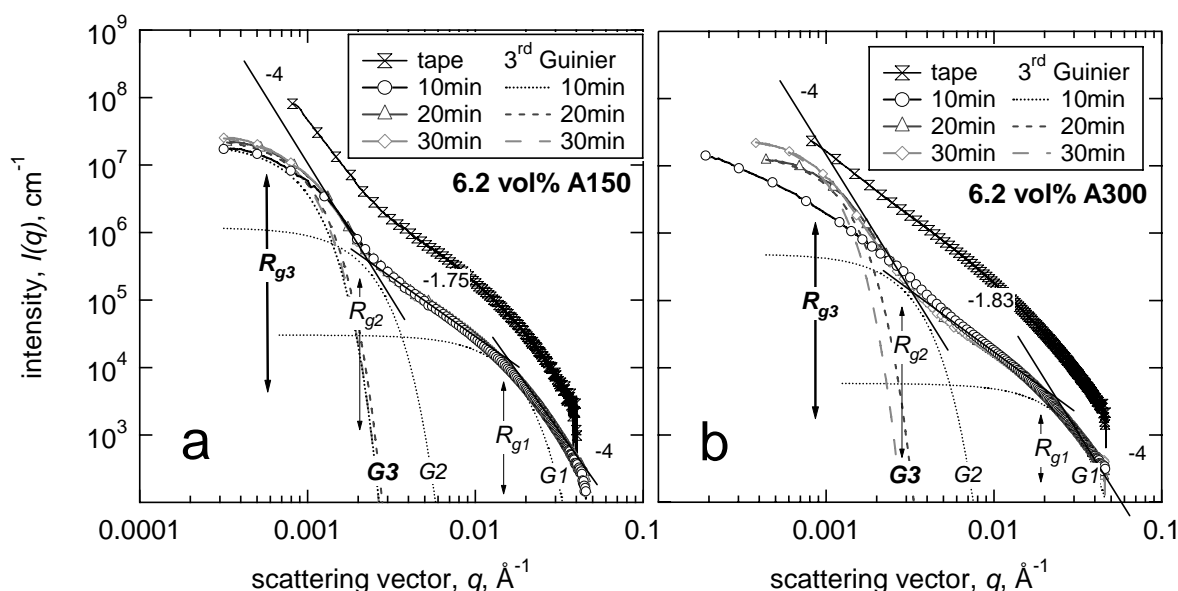
Fig. 1 Combined USAXS and SAXS spectra as a function of scattering vector q of dry particles between scotch tape (butterfly) and filled rubbers (a) 6.2 vol% A150 and (b) A300 mixed for different durations (10: circle, 20: triangles, 30 minutes: diamonds). Unified fit (thin lines) for Guinier (G_1, G_2) and Porod (P_1, P_2) regimes, showing (a) $D_f = 1.75$ and (b) 1.83, and smooth primary particle surface (-4), R_{g2} and R_{g1}, which correspond to aggregate and primary particle sizes, all non-affected by increasing mixing duration.

For 6.2 vol% A300 filled rubbers and particles stitched between two scotch tapes mixing duration has no influence on primary particle ($d_{v/s} = 9$ nm), aggregate size ($R_{g2} = 70$ nm) nor morphology ($D_f = 1.83$). Here the $d_{v/s}$ is in good agreement with d_{BET} (= 9 nm) while no significant changes in the D_f nor R_{g2} compared to A200 was found. A300 consists of smaller primary particles than compared to A200 and as morphology nor aggregate size is changing an increase of number of primary particles in case of A300 compared to A200 is expected where an increase from $n_p = 40$ (A200) to almost 90 (A300) was detected. In the 3rd Guinier regime the same trend as seen in case of A200 was found. After 10 minutes of mixing an agglomerate size bigger than 1 μm was detected accompanied with a Porod slope different from -4 and more close to the mass fractal value of -1.83. The slope looks similar to the scotch tape filled with A300 (open diamonds) in all three regimes and especially at low q (< 0.003) which indicates that after 10 minutes of mixing rather big agglomerates were still present. Increasing the mixing duration to 20 and 30 minutes resulted in changes in the 3rd regime with a Porod decay of -4 and smaller R_{g3} in the range of 179-220 nm.

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