MULTIPLE SIZE SCALE STRUCTURES IN SILICA/SILOXANE COMPOSITES STUDIED BY SMALL-ANGLE SCATTERING*,
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INTRODUCTION

The physical properties of *in-situ* produced composites, such as the TEOS-polysiloxane based systems, are directly related to the complex interaction of structural features from the nano- to macro-scopic scales. The nature of these structural interactions are a key element in understanding and controlling mechanical properties in these systems. We believe that the smallest scale structures, in the nanometer range, correlate with properties such as the modulus while large-scale structures on the micron scale effect failure in these materials. In this paper we discuss techniques for the analysis of structural features and the interrelation of structural features over these wide ranges of size using small-angle light, x-ray and neutron scattering. The combination of data from a number of different instruments allows for characterization of the interaction between these different size scale features.

RESULTS AND DISCUSSION

Complex systems present a formidable challenge to morphologists. These systems often display structural features on length scales ranging from Angstroms to millimeters. Scattering patterns are characteristically featureless, displaying, at best, broad shoulders on monotonic backgrounds. The application of fractal concepts has lead to some relief in dealing with these monotonic scattering profiles, but local fits to power-law functions are dangerous when self-similar structures exists in narrow size limits[1]. A main area of application for the fractal approach has been in structural studies using small-angle scattering. As an example, the mass and surface dimensions for combustion aerosols, such as carbon black and fumed silica, obtained from small-angle x-ray (SAXS) and neutron scattering (SANS) have been related to their growth mechanisms.

By combining absolute intensity measurements from ultra-low angle [2] and conventional SAXS[3], SANS [4], small-angle light scattering (SALS), with diffraction instruments we wish to describe morphologies from the tens of microns to Angstroms using a general unified approach. Although several authors, have developed semi-empirical equations to fit length-scale-limited power-law scattering, none are adequate over five decades in length-scale. Beaucage[5], on the other hand, has developed a general equation that we find capable of describing scattering functions containing multiple length-scales (Guinier regimes) separated by power-law scaling regimes. In this paper, we apply this methodology to silica/siloxane composites.

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1) A UNIFIED EQUATION FOR SMALL-ANGLE SCATTERING

Beaucage [5], describes how Guinier's law and structurally limited power-laws can be derived from mutually exclusive scattering events. In the simplest case, the observed scattering is a summation two components,

$$I(q) \approx G \exp\left(-\frac{q^2 R_g^2}{3}\right) + B \left[\frac{(\text{erf}(q R_g/\sqrt{6}))^3}{q} \right]^P \quad (1),$$

where $G = N_p \rho^2 V^2$ is the classic Guinier prefactor and B is a prefactor specific to the type of power-law scattering, specified by the regime in which the exponent P , falls. The momentum transfer, q , has the units $(\text{length})^{-1}$ so large- q scattering probes small length-scales. For Porod's law (scattering from sharp interfaces), for example, $P=4$ and $B=2\pi\rho^2 S$.

For a Gaussian polymer, $P=2$, and $B = \frac{2G}{R_g^2}$. In general, for surface fractals $4 > P > 3$, for mass fractals $P < 3$ and for diffuse interfaces $P > 4$ [2]. The error function (erf) is available in a number of fitting programs [6] or can be calculated using an empirical expansion given in the footnotes [7].

Since the crossover error function incorporates the same parameter (the Guinier Radius, R_g), as the exponential term, no new parameters are generated by eq. 1 compared to local Guinier and power-law fits. Equation 1 is a good approximation for model systems (spheres, disks, rods) that display a single length-scale, and are rotationally and translationally random. In order to consider multiple-size-scale structures, however, the high- q , small-size limit to power-law scattering must also be considered.

2) MULTIPLE SIZE SCALE PHENOMENA AND THE UNIFIED APPROACH

We have used an exponential prefactor to describe the high- q structural limit for fractal scaling [5]. The two size limits to power-law scattering ($qR_{gi} = 1$ and $qR_{g(i+1)} = 1$) can be described through an extension of equation 1,

$$I(q) \approx \sum_{i=1}^n G_i \exp\left(-\frac{q^2 R_{gi}^2}{3}\right) + B_i \exp\left(-\frac{q^2 R_{g(i+1)}^2}{3}\right) \left[\frac{(\text{erf}(q R_{gi}/\sqrt{6}))^3}{q} \right]^{P_i} \quad (2)$$

where n is the number of structures observed in the scattering pattern. The first term describes a large-scale structure of size R_{gi} composed of small-scale structures of size $R_{g(i+1)}$. The second term allow for mass-, surface-fractal or diffuse-interfacial power-law regimes for the large structure. Using eq. 2 we can parameterize scattering from a system with multiple-size-scale features. It should be noted that, although equation 2 appears cumbersome, no new parameters have been introduced over local fits using exponentials and power laws. Equation 2 can be extended to describe an arbitrary number of interrelated structural features at different size-scales. Such extensions, however, can only be justified when data extends over many decades in q .

Fig. 1 is an example of the use of equation 2 in a silica/siloxane composite material. The material displays structural features on three size scales and has fairly well behaved mass scaling behavior which separates these size scale regimes. The solid line in fig. 1 is a fit using equation 2 for $n=3$ and $G_1=2 \times 10^8$, $R_{g1}=0.91\mu\text{m}$, $B_1=6 \times 10^{-8}$, $P_1=4.15$, $G_2=80$, $R_{g2}=115\text{\AA}$, $B_2=0.015$, $P_2=1.55$, $G_3=1.2$, $R_{g3}=12\text{\AA}$, $B_3=0.00027$, $P_3=4$.

Fig. 1 Scattering profile for an insitu-filled composite in which three size scales and two regimes of constant mass/size scaling are observed. Low- q data is light scattering, mid- q is Bonse-Hart x-ray scattering data and high- q is from the 10-meter Oak Ridge Pinhole Camera. The low- q data indicates a weakly diffuse interface while the power law between 115 and 12Å reflects a polymeric or network like structure.

The micron sizes structure in figure 1 has a diffuse interface with the matrix as determined by a power law greater than 4 at higher q . The size regime between 115 and 12Å reflects a regime of mass fractal scaling as might be expected from a network. The network is composed of 12Å structures.

3) CORRELATED SYSTEMS

The case of weakly correlated particles will be briefly considered. The scattered intensity for this case is given by [5],

$$\overline{I(q)} = A F(q)^2 S(q) \quad (3)$$

where $A F(q)^2$ corresponds to the scattered intensity for non-correlated domains discussed above and $S(q)$ is a structure factor which accounts for weak correlations of the domains. As an example, we have previously used a semi-empirical function for $S(q)$ which describes damped spherical correlations of colloidal particles [8], [9],

$$S(q) = \frac{1}{1 + k \theta} \quad (4)$$

where θ is the "form factor" for spherical interactions correlated over a distance ζ [10],

$$\theta = 3 \frac{\sin(q\zeta) - q\zeta \cos(q\zeta)}{q\zeta^3} \quad (5)$$

and k describes the degree of correlation ($0 < k < 6$). For application of equations 1 and 2, k must have a low value, $k < 3$, consistent with weak correlations. Weakly correlated systems are sufficiently random that concepts discussed above with regard to uncorrelated systems are adequate, especially in the high- q power-law regime. Weakly correlated particles are expected to display two size scales, ζ and the radius of gyration, R_g , for the particles. In general $R_g \leq \zeta$.

Figure 2. Fit of equation 3 to SANS data from insitu-filled siloxane rubber with a precursor PDMS molecular weight of 18 kg/mole. The correlation distance is $\zeta=532\pm1\text{\AA}$, degree of correlation $k=1.99\pm0.01$, $R_g=166.1\pm0.2\text{\AA}$, $G=1508\pm4\text{ cm}^{-1}$, $P=4.24$, $B=2.23\text{e-}6\text{ cm}^{-1}$. The weak knee in the data at $q=0.025\text{\AA}^{-1}$ corresponds to the average radius of gyration for the filler particles in this interpretation.

We have recently investigated *in-situ* filled siloxane rubber systems in which there is evidence for weakly correlated particulate fillers. Equation 3 was used to determine the correlation distance and the average size of the filler particles as well as the surface characteristics of the filler. Figure 2 shows a typical fit to data from one of these systems.

The power law exponent less than -4 indicates that the interface between the filler and the matrix is diffuse as might be expected for filler particles produced in a viscous medium by chemical reaction. Silicone NMR also supports incomplete reaction of the *in-situ*-produced filler precursor which might lead to a diffuse interface. Fits without the unified approach fail to match the curve in the vicinity of the proposed R_g . Attempts to fit the knee as a second order peak failed since the position does not correspond to $2q_{\text{max}}$ peak. Finally, it should be noted that, in this system, the buried R_g has been observed to scale with the molecular weight of the precursor polymer.

SUMMARY

The unified approach to small-angle scattering [5] is useful in examining multiple-size-scale structures in silica/siloxane composites. We demonstrated that the concepts developed for random structures are applicable to weakly correlated systems as well. The unified approach is flexible enough to extract useful information from data in which micro-

and nano-structures overlap. This approach is the first to simultaneously account for Guinier scattering and power-law scattering of arbitrary type, i.e. mass-, surface-fractal, Porod or diffuse-interfacial scattering.

REFERENCES

1. see for example the review by Schmidt, P.W. *J. Appl. Cryst.* **15**, 567-69, 1992 for a general survey of power-law scattering and Korberstein, J. T., Morra, B., Stein, R.S., *J. Appl. Cryst.* **13**, 34-45 (1980) for particular reference to diffuse interfacial scattering. Also see Debye, P. Henderson, H. R., Brumberger, H., *J. Appl. Phys.* **28**, 679 (1957) and Fischer, M. E., Burford, R. J. *Phys. Rev.*, **156**, 583 (1967) for references to models of complex systems.
 2. National Institute of Standards and Technology beam-line at Brookhaven National Laboratory's National Synchrotron Light Source. G. Long, D. Fischer, G. Beaucage, D. Schaefer.
 3. 10-meter small angle x-ray camera at Oak Ridge National Laboratory.
 4. SANS measurements were performed at Oak Ridge National Laboratory's High Flux Isotope Reactor, National Institute of Standards and Technology's Neutron Scattering Facility and at Los Alamos National Laboratory's LANSCE facility.
 5. G. Beaucage, submitted *J. Appl. Cryst.*
 6. For example, "Igor" by WaveMetrics Inc., P.O. Box 2088, Lake Oswego, Oregon 97035. Also the error function is available in some versions of C.
 7. For example an empirical function which described the error function is given in "Numerical Recipes in C, the Art of Scientific Computing", W. H. Press, B. P. Flannery, S. A. Teukolsky, W. T. Vetterling, Camb. U. Press., NY NY, p.176
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Function erf(x)
 z=abs(x)
 t=1.0/(1.0+0.5*z)
 ans=t*exp{-z*z-1.26551223+t*[1.00002368+t*[0.37409196+t*(0.09678418
 +t*{-0.18628806+t*[0.27886807 +t*(-1.13520398+t*[1.48851587
 +t*[-0.82215223+t*0.17087277])])])])])
 if(x>=0)
 return(1-ans)
 else
 return(ans-1)
 endif
End

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- This returns the error function with fractional error less than  $1.2 \times 10^{-7}$ .
8. G. Beaucage, D. W. Schaefer, T. Ulibarri and B. J. Olivier, in preparation and short summary of some of this work in *MRS Bulletin* April 1992 T. Ulibarri, G. Beaucage, D. W. Schaefer.
  9. Guinier, A and Fournet, G., "Small-Angle Scattering of X-rays", John Wiley and Sons Inc., New York, NY, 1955, p. 42-65. also see Porod, G. in *Small Angle X-ray Scattering* ed. Glatter, O. and Kratky, O. Academic Press New York, 1982 as well as Feigin, L.A., Svergun, D. I., "Structural Analysis by SAXS and SANS", Plenum Press, New York, 1987.
  10. Guinier, A and Fournet, G., "Small-Angle Scattering of X-rays", John Wiley and Sons Inc., New York, NY, 1955, p. 55.

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