

Probing polymer nanocomposite morphology by small angle neutron scattering

PUYAM S SINGH^{1,*} and VINOD K ASWAL²

¹RO Membrane Division, Central Salt and Marine Chemicals Research Institute (CSIR),
G.B. Marg, Bhavnagar 364 002, India

²Solid State Physics Division, Bhabha Atomic Research Centre,
Mumbai 400 085, India

*Corresponding author. E-mail: puyam@csmcri.org

Abstract. Polyamide nanocomposite films were prepared from nanometer-sized silica particles having particle radius of gyration (R_g) of about 66 Å and trimesoyl chloride-*m*-phenylene diamine-based polyamides having macromolecular units of about 100–140 Å. The nanoscale morphology of the samples was characterized using small angle neutron scattering (SANS). SANS reveals that silica nanoparticles interact well with the polyamide units only at limited silica loading.

Keywords. Small angle neutron scattering; silica nanoparticles; polyamide nanocomposite films.

PACS Nos 82.35.Np; 61.12.Ex; 81.05.Qk

1. Introduction

The use of inorganic nanoparticles as additives to enhance polymer performance is now commercially realized; however, to optimize property enhancement of the nanocomposite with respect to neat polymer, a precise control of nanocomposite nanostructural morphology is required [1]. Polymer nanocomposite morphology can be an ordered arrangement of organic polymer chain size and inorganic nanoparticles or a random distribution of the nanoparticles in the polymeric structure [2]. One synthesis approach to generate the nanocomposite system in which the polymer unit and silica nanoparticles interacted at nanometer length scale with reduced silica particle agglomeration is emulsion polymerization, where the silica particle is encapsulated *in situ* in the polymer structure [3]. Spherical polymer particles are obtained from the polymerization at the interface of stable emulsion controlled by micelle formation using a surfactant. The interfacial polymerization reaction system is commonly applied to prepare trimesoyl chloride-*m*-phenylene diamine-based polyamide membrane films which are largely used in desalination, waste water treatment and food and chemical industry [4]. In this case, the emulsion is not a droplet-like but a spreading absorbed aqueous layer containing *m*-phenylene

diamine monomers on a flat support which is then dipped in a continuous organic phase containing trimesoyl chloride monomers so that polymer film is formed at the surface of the support by interfacial polycondensation of *m*-phenylene diamine and trimesoyl chloride monomers. We are interested to prepare polyamide nanocomposite membrane films with enhanced properties from nanometer-sized silica particles and trimesoyl chloride-*m*-phenylene diamine-based polyamides using the interfacial polymerization process and we have chosen LUDOX[®] HS-40 colloidal silica aqueous solution of $R_g \sim 66 \text{ \AA}$ as the silica source for the nanocomposite synthesis. We report here characterization of the physical structure of silica particles encapsulated in the polyamide structure by probing the physical structure of the nanocomposites at the nanometer length scale (20–350 \AA) using SANS.

2. Experimental section

The polyamide membrane was prepared by initially immersing a glass plate in 2% (w/v) solution of *m*-phenylenediamine (Atul Chemicals, India) in water, followed by immersing into *n*-hexane solution of 0.1% (w/v) trimesoyl chloride (Aldrich), which resulted in lamination of sub-micrometer thick skin layer of polyamide over the glass surface. Immediately, the nascent polyamide films were washed off from the surface of the glass plate and collected in water. The colloidal-like polymer (2% w/v) aqueous solutions were made for the neutron scattering measurements. LUDOX[®] HS-40 colloidal silica (40 wt% suspensions in alkaline water) was used as silica source for the silica incorporation in the polyamide structure. Appropriate amount of silica was added into the 2% (w/v) solution of *m*-phenylenediamine in water; and the above preparation procedure of membrane films was followed. The SANS measurements from the sample solutions over the wave vector range (Q) of 0.018–0.35 \AA^{-1} were taken at room temperature or higher on the SANS instrument [5] at the Dhruva reactor, BARC, Mumbai, India. Throughout the data analysis, corrections were made for instrumental smearing. The measurements from the sample aqueous solutions with 60% D₂O–40% H₂O and 90% D₂O–10% H₂O solvent mixtures were used for extracting separate information on the polyamide and the silica.

SANS data analysis. An expression of the scattering law for two-phase system in the case of perfectly random form and distribution of phases, as developed by Debye *et al* [6] is shown below:

$$I(Q) = \frac{I(0)}{(1 + Q^2\xi^2)^2}, \quad (1)$$

where ξ is known as the Debye–Bueche correlation length. In the case of the core–shell structure morphology of various systems, the scattering profile can be examined by the following equation.

$$I(Q) = \frac{A}{V_t} \left[\frac{3V_c(\rho_c - \rho_s)J_1(QR_c)}{QR_c} + \frac{3V_t(\rho_s - \rho_{\text{solv}})J_1(QR_s)}{QR_t} \right]^2 + Bkg \quad (2)$$

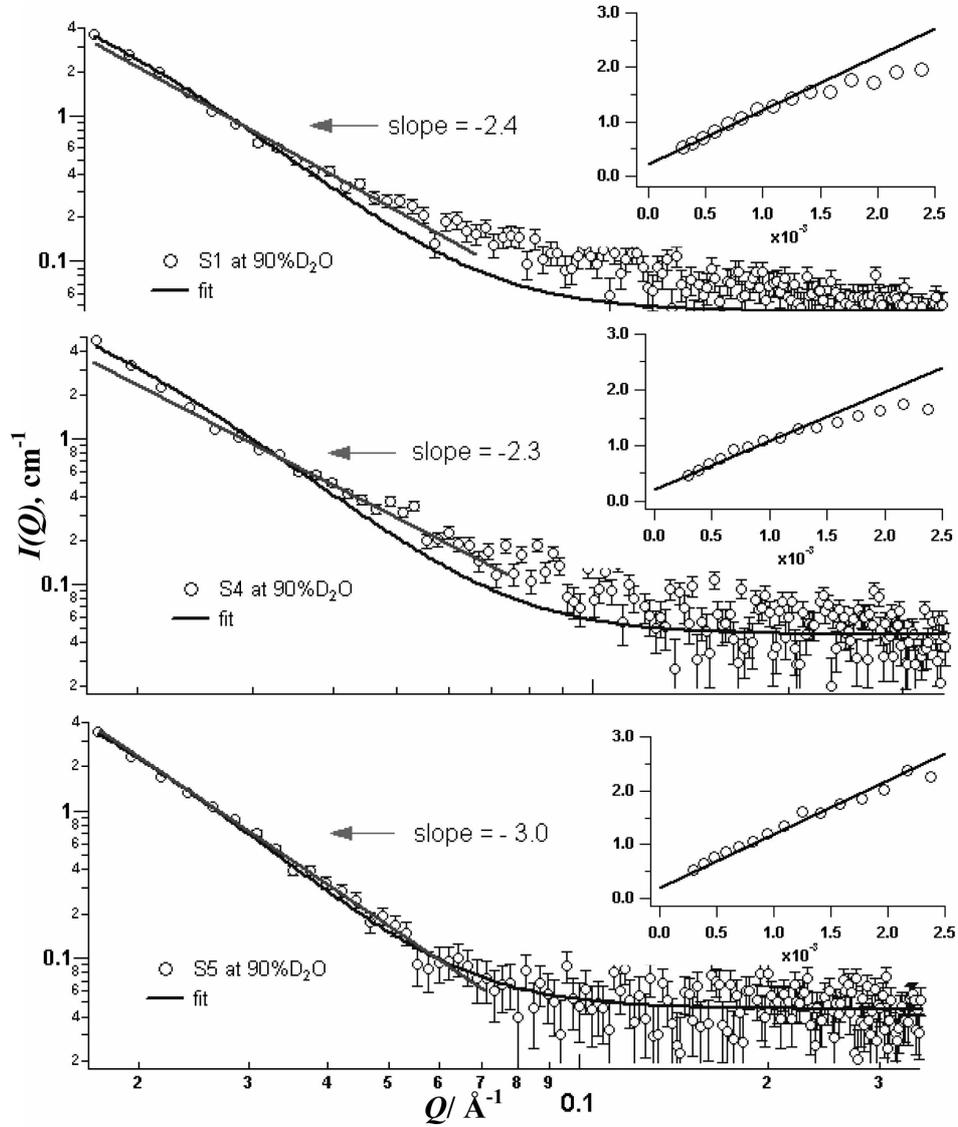


Figure 1. The Debye–Anderson–Brumberger model fits of the selected nanocomposite samples (S1, S4, S5) measured at 90% D₂O–10% H₂O. Inset: $1/\sqrt{I(Q)}$ vs. Q^2 plot.

where $J_1(x) = (\sin x - x \cos x)/x^2$ and A is a scale factor; ρ_c , ρ_s and ρ_{solv} are respectively, the scattering length densities of the core, shell and solvent.

Table 1. Silicon content of the silica–polyamide samples.

	S1	S2	S3	S4	S5
%Si (w/w)	2.2	2.6	4.1	4.5	10.3

3. Results and discussion

SANS measurements were taken separately on the initial silica and polyamide samples to first examine the size of initial silica particles and polymer macromolecular units. The results (data not shown) indicate that R_g of silica nanoparticles is about 66 Å while R_g of polymer macromolecular unit is about 100–140 Å. Series of samples from this organic polymerization reaction system containing various amounts of silica nanoparticles were made. The silica content of the samples as determined by inductively coupled plasma atomic emission spectroscopy are given in table 1. Figure 1 displays the SANS profiles of the samples with low (S1, 2.2%) and high (S4, 4.5%) silica content, along with the S5 sample containing excess silica (10.3%) measured at 90% D₂O–10% H₂O solvent mixture. The scattering curves are shown as log–log plot of the scattered intensity $I(Q)$ vs. the scattering vector Q . $I(Q)$ decays with a power-law of the form $I(Q) \sim Q^{-(2.3-2.4)}$ for sample S1 and S4 and $I(Q) \sim Q^{-3}$ for sample S5 over the Q range of 0.03–0.05 Å⁻¹. The exponent values are smaller from either the power law of the form $I(Q) \sim Q^{-4}$ in the case of initial neat silica or $I(Q) \sim Q^{-3.3}$ in the case of the neat polymer. The changes in the exponent values of the power-law relation, from -2.3 to -3 , can be explained by the changes in scattering domains consisting of locally different structural units. The scattering profiles are fitted with the scattering law developed by Debye *et al* [6]. As shown in figure 1, there is a good fit using this model, as well as a linear $1/\sqrt{I(Q)}$ vs. Q^2 plot over the 0.018–0.05 Å⁻¹ Q range for sample S5. This may be indicative of a two-phase system with a perfectly random form and distribution of silica and polymer phases in sample S5. In the case of samples S1 and S4, the above model fit is poor and there is deviation from the linearity in $1/\sqrt{I(Q)}$ vs. Q^2 plots over similar Q range. In order to figure out the differences between the structures directed by the amount of silica incorporation, the SANS data of the sample was corrected after removing the bulk polyamide scattering (figure 2). In the case of the extracted SANS profiles of samples with 2.2% and 4.5% silica content, there are clearly two types of scattering signatures, one is from a population of larger sized particles at lower Q range (0.018–0.035 Å⁻¹) and the other is from a population of smaller sized particles at higher Q range (0.035–0.08 Å⁻¹). These profiles may be interpreted in terms of core–shell particle morphology, where the core and the shell have different sizes and scattering length densities and fitted well with the core–shell sphere model. However, the hard sphere model is more suitable for the profile of S5 sample having excess silica content of 10.3%.

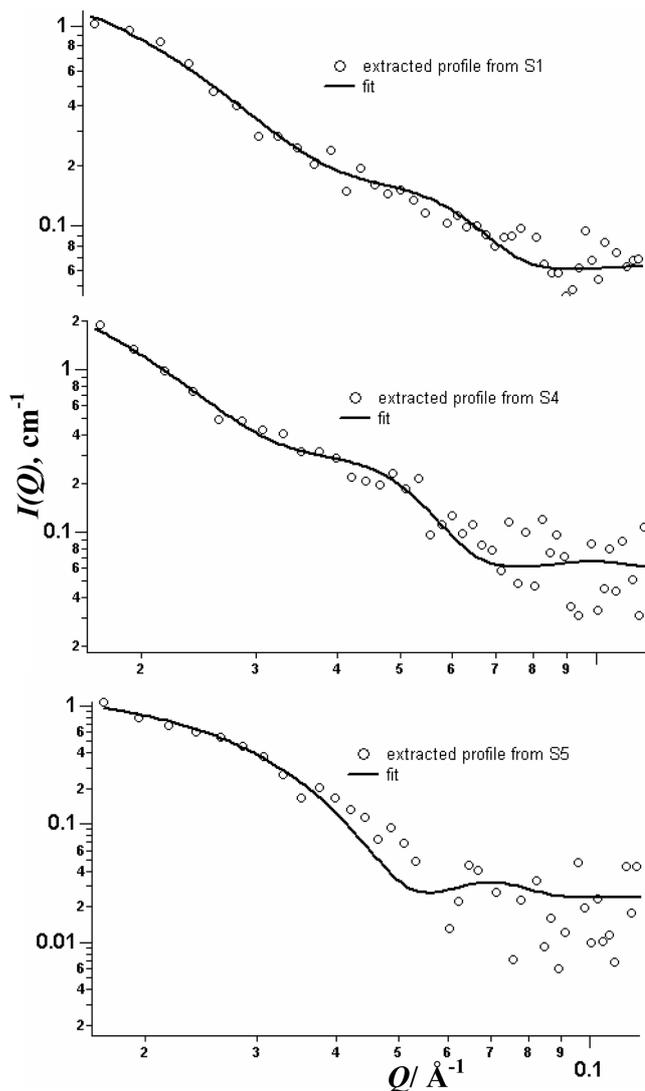


Figure 2. Extracted SANS profiles along with fits S1, S4: core-shell spherical form factor fit; S5: hard spherical form factor fit.

4. Conclusions

Characterization of physical structure of silica (LUDOX[®] HS-40) nanoparticles encapsulated in polyamide film using small angle neutron scattering study on the silica-polyamide (trimesoyl chloride-*m*-phenylene-diamine-based-) nanocomposites reveal that the nanocomposite structure is directed by the amount of silica incorporation. For the nanocomposite sample with silica content up to 4.5%, the surface

of the silica particle is well interacted with the polyamide chains and the surface-coated silica takes the form of core-shell sphere morphology. The polymer does not interact well with silica in the sample having excessive silica content (10.3%). In this case, the silica size is not appreciably bigger indicating thin coating and the silica scattering profile is fitted well with original hard sphere morphology of silica.

Acknowledgments

The authors gratefully acknowledge guidance and encouragement from Dr P K Ghosh, Director, CSMCRI (CSIR) and Dr P S Goyal, Former Director UGC-DAE (Mumbai Branch). Financial assistance to carry out SANS experiments from UGC-DAE CSR (CRS-M-121) is also acknowledged.

References

- [1] E P Giannelis, *Adv. Mater.* **8**, 29 (1996)
- [2] R A Vaia and J F Maguire, *Chem. Mater.* **19**, 2736 (2007)
- [3] S Boutti, E Bourgeat-Lami and N Zydowicz, *Macromol. Rapid Commun.* **26**, 1860 (2005)
- [4] R J Petersen, *J. Membr. Sci.* **83**, 81 (1993)
- [5] V K Aswal and P S Goyal, *Curr. Sci.* **79**, 947 (2000)
- [6] P Debye, H R Anderson and H Brumberger, *J. Appl. Phys.* **28**, 679 (1957)