

VIII- II -1. Project Research

Project 7

PR7 Project Research on Development of Scattering Spectrometers Utilizing Small and Medium Class Neutron Source

M. Sugiyama

Research Reactor Institute, Kyoto University

Objectives and Allotted Research Subjects:

Small-angle neutron scattering is again recognizing to one of the most powerful tools to investigate nanoscale structures in variety of materials. Under this circumstance, the most serious problem is shortage of machine time and to solve this, utilization of compact neutron source is crucial. This project proves it through showing the feasibility and upgrade of KUR-SANS.

ARS-1: Challenge for Development of Analyzer for Particle-Size Distribution with Small-Angle Scattering. (M. Sugiyama and Y. Oba)

ARS-2: Upgraded Compact $d=7\text{nm}$ Monochromator for KUR-SANS. (M. Hino, Y. Oba, T. Oda and M. Sugiyama)

ARS-3: Modification of KUR-SANS for Metallic Materials. (Y. Oba, M. Hino, T. Oda, M. Ohnuma, N. Sato, M. Sugiyama)

ARS-4: Surfactants' Nano-Structural Observations by Utilizing KUR-SANS. (K. Hara, T. Miyazaki, Y. Hidaka, H. Okabe, N. Sato, Y. Oba and M. Sugiyama)

ARS-5: Small-Angle Neutron Scattering Analysis of the Nanostructure of Wheat Proteins. (R. Urade, A. Matsu-miya, Y. Higashino, N. Sato, M. Sugiyama and Y. Oba)

ARS-6: Thermoresponsive Structural Change of Radiation-Fabricated Porous Binary Polymer Gels as Revealed by Small-Angle Scattering. (N. Sato, Y. Oba, R. Inoue and M. Sugiyama)

ARS-7: Application of SANS in Compact Neutron Source for Quantitative Analysis of Precipitates in Steels. (M. Ohnuma, Y. Oba, and M. Sugiyama)

ARS-8: Nano Structure of Metal Hydride by Neutron Small Angle Scattering. (K. Iwase, K. Mori, S. Tomihira, Y. Onodera, T. Fukunaga, M. Sugiyama)

Main Results and Contents of This Project:

ARS-1: Sugiyama et.al. have continued to develop software to analyze the size-distribution of nano-particles with small-angle scattering. This challenge will open the further application of SAS and help the new SAS researchers.

ARS-2: Hino et.al. developed a new monochromator mirror for dedicating to 1 MW power of KUR. Compared with the old one, this new monochromator gives us 2.5 times neutron beam at 3nm wavelength neutron.

ARS-3: Oba et.al. are working to utilize KUR-SANS to metallic material researches. The important point is to avoid Bragg cut-off effect from crystallite in the metallic materials. Therefore, they made and estimated a performance of monochromator with 0.46nm.

ARS-4: Hara et.al. investigated nano-scale structures of hydrogels with KUR-SANS. They investigated the nano-structure of Sodium Oleate (NaOl, surfactant) in heavy water (D_2O) in the floatation process, which demonstrated the performance usable for practical SANS research.

ARS-5: Urade et.al. investigated nano-structure of gliadin gel, which is one of basic unit of wheat origin food. They performed SANS analysis of hydrated gliadins and, from the results, attempted to establish a model of the hydrated gliadin nanostructure.

ARS-6: Sato et.al. studied γ -radiation - fabricated thermo-responsive binary hydrogels. As a result of investigation of swelling behavior of those gels, it was suggested that porous gels are less shrinkable due to the localization of the PNIPAm component in the pore space of the PEG matrix gel. To confirm this consideration more directly in the nanoscopic level, they have performed SANS with KUR-SANS.

ARS-7: Ohnuma et.al. are trying to use SANS in relatively small scale facilities, i.e., KUR or HUNS (Hokkaido University Neutron Scattering). For this purpose, they are measuring series of steel samples which are used as the structural materials using different facilities to see which facilities are suitable for certain q -range and whether it can be used in the front line of materials development.

ARS-8: Iwase et.al. developed an *in situ* sample holder and used the well-known hydrogen-absorbing alloy LaNi_5 to evaluate its basic performance in SANS under a deuterium atmosphere at room temperature during the first absorption-desorption cycle. Using D enabled us to clearly observe SANS profiles even in the high- q region because of the low $\sigma_{\text{inc}}(D)$.

M. Sugiyama

Research Reactor Institute, Kyoto University

INTRODUCTION: Clarification of particle-size distribution in nano-scale is one of the most important issues in improvement of performance of materials. Small-angle scattering (SAS) is a promising technique to give us this required structural information. However, there still remains the difficulty to derive the structural information from the SAS data.

Applying Guinier approximation is an easy and powerful technique to derive the size of the particle in the system. However, it is difficult to extend the Guinier technique to poly-dispersed system, such as particles with the size-distribution. One possible answer is to assume that the particle size has Gaussian distribution. However, there is no promise that the size distribution is Gaussian. Therefore, more flexible analysis method, which can analyze the more general size distribution.

In addition, recently, it has been focused to control the size of precipitates in steel because of adding the functionality. For this purpose, to know the size distribution of the precipitates in steel is very important. In some cases, it is supposed that the size distribution of the precipitates does not have the Gaussian. In this industrial demand, it is important to analyze the SAS data without any assumption easily.

Following the above mentioned requirements, I have started to develop the size distribution analyzer from SAS data, namely, one-click analyzer; “one click” means “easy”, which gives us the reasonable result even an operator does not have a lot of knowledge about small-angle x-ray and/or neutron scattering. Here, I report the present status the developing program, one click analyzer.

PROGRAM: “One click analyzer” has graphical user interface (GUI) as shown in Fig 1. The black dots in the left panel show the SANS profile of the Cu precipitates in the steel. By clicking the “Generate Initial”, the program generates the Gaussian particle size distribution by analyzing the inputted scattering curve (blue line in the right panel) and calculates the SAS curve (blue line in the left panel). Then, by clicking the “iteration”, the program starts the iteration by utilizing a Monte Carlo algorithm: the program randomly picks up the size of the particle and change its number slightly, next, calculates its SAS curve and compare the coincident ratio with χ between before and after the iteration, adopts the size-distribution with the lower χ , then goes back the first step and repeats this until χ becomes low enough.

The red line in the left panel of Fig.2 shows the final fitting SAS curve with $\chi=0.05$ at iteration of 50000 and well-reproduces the experimental SAS curve. The red line in the right panel of Fig.2 shows the final size-distribution of the Cu precipitates. The result indicates there are mainly particles with two sizes of 12 Å and 18 Å. This result is well agreement with that obtained by atom-probe method.

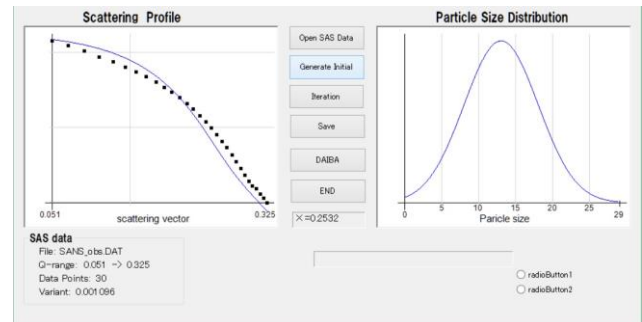


Fig. 1. Initial state of the fitting.

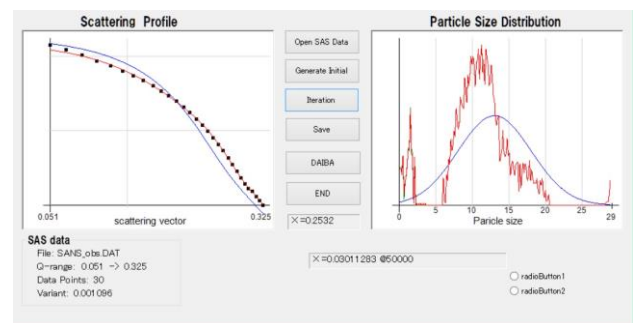


Fig. 2. Final state of the fitting.

M. Hino, Y. Oba, T.Oda¹ and M. Sugiyama

Research Reactor Institute, Kyoto University

¹Department of Nucl. Eng., Kyoto University

INTRODUCTION: Small angle neutron scattering (SANS) technique is very powerful to investigate of structure of complex material with size of 1-100 nm. The scope of application is very wide and there are a lot of interesting sample with strong scattering intensity. Thus KUR-SANS [1] is still very useful and popular spectrometer even with 1MW reactor operation. There are three monochromators in which average wavelength is 0.28, 0.41 and 0.55 nm in the KUR-SANS [1-3]. These monochromator are double reflection type as shown in Fig.1 and they change average incident wavelength to sample without change of the beam line. The maximum neutron intensity of CN2 beam line was about 0.28 nm and the average d-spacing of the monochromator for 0.28 nm was 7 nm since the incident angle was 20 mrad in Fig.1. The acceptable beam width of d=7nm monochromator was limited in 8 mm and the intensity reflected by the d=7nm monochromator was only 1.8 times larger than that by the d=11.8 nm one for 0.47 nm [3]. Thus we upgraded d=7nm monochromator. In this study, we show the performance of new d=7nm monochromator for the KUR-SANS.

EXPERIMENTS: The d=7nm multilayer mirrors were deposited on both surface of silicon substrates in which size of 64x32x0.6 mm. The total number of mirrors was 34 and acceptable beam width was 20 mm. They were fabricated by using ion beam sputtering machine at KURRI. The reflectivity and SANS measurement was carried out at CN3 and CN2 beam lines, respectively. The maximum neutron intensity of new d=7nm monochromator was 0.3 nm. The average incident wavelength was slightly shifted due to the slightly change of angle between the mirrors.

RESULTS: We used a glassy carbon as a standard sample to estimate the performance of the new monochromator. The slit width and divergent angle were 5 mm and 2.7 mrad, respectively. It was suitable condition for the old monochromator. Figure 2 shows SANS data with these old and new monochromator. Even in small beam size, the new monochromator was much better than old one and the gain factor was estimated to be 2.5. As a next step, we will enlarge beam size and try to obtain gain factor 10.

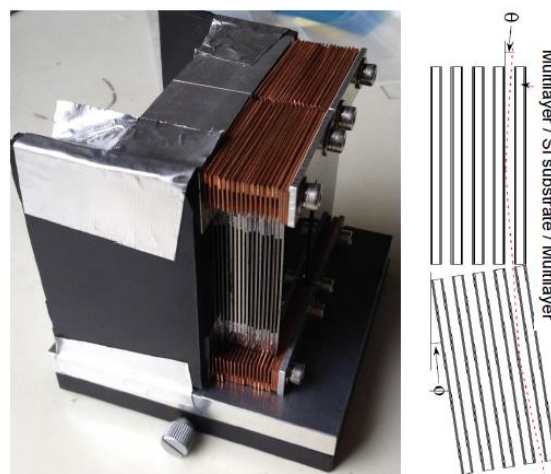


Fig.1 The photograph of new d=7nm monochromator and layout of the two set of NiC/Ti multilayer mirrors for KUR-SANS. Here ϕ is equal to 2θ .

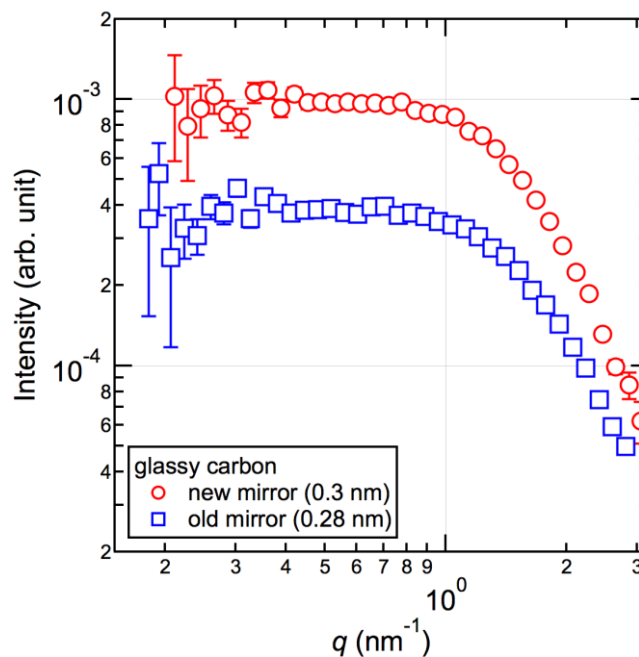


Fig.2 The scattering neutron intensities by a glassy carbon as a function of scattering vector q with old(\square) and new(\circ) monochromator.

REFERENCES:

- [1] M. Sugiyama, *et al.*, JAP, **33** (1994) 6396.
- [2] H. Sunohara, M. Hino, *et al.*, Physica B, **350** (2004) 869.
- [3] M. Hino, *et al.*, KURRI Progress report (2012) 179.

Y. Oba, M. Hino, T. Oda¹, M. Ohnuma², N. Sato and M. Sugiyama

Research Reactor Institute, Kyoto University

¹Graduate School of Engineering, Kyoto University

²Faculty of Engineering, Hokkaido University

INTRODUCTION: Small-angle neutron scattering (SANS) is a powerful technique to characterize nanostructure. One of the biggest advantages of SANS over the other methods like electron microscope is that SANS can quantitatively measure the nanostructure. This is essential for advanced research and development of new materials. However, the application of SANS especially to metallic materials does not make much progress. This is mostly caused by a limited number of SANS instruments. Thus each SANS user gets little beamtime. To make a breakthrough, effective use of small and medium neutron sources is needed. A SANS instrument KUR-SANS is a typical example of the instrument installed at such small neutron source [1,2]. Due to the decrease in thermal power of research reactor and shutdown of cold neutron source, incident neutron flux of KUR-SANS is weak compared with general SANS instruments, but still useful for materials science.

KUR-SANS now focuses on the application of SANS to steel research because a lot of steel researchers expect easy access to SANS. For this purpose, a new monochromator and magnet were prepared last year [3,4]. In this study, we investigated the performance of these new components.

EXPERIMENTS: The experiments were conducted at KUR-SANS [1,2]. Its monochromator consists of NiC/Ti multilayer mirrors. The thickness of layers is changed to change wavelength of neutron λ . For the steels, $\lambda > 0.41$ nm is required to avoid multiple Bragg scattering. Hence, a new monochromator was prepared.

In addition, the steels are often ferromagnetic and show strong magnetic scattering as well as nuclear scattering. To separate the magnetic and nuclear scattering, a permanent magnet for sample was prepared.

RESULTS: Figure 1 shows the I - q profile of a silver behenate, which is a standard sample for q . Here, q is a momentum transfer and equal to $4\pi\sin(2\theta/2)/\lambda$ where 2θ is the scattering angle. A clear peak is observed in Fig. 1. Since the peak position of the silver behenate is known, λ can be evaluated from the scattering angle using the above equation. The estimated λ is 0.46 nm. This value is larger than 0.41 nm and almost agrees with designed value. The effective intensity (incident neutron intensity \times detection efficiency) of this new mirror estimated

from a transmission monitor is 80% of conventional monochromator with $\lambda=0.28$ nm. This value of the effective intensity is fairly high compared with the intensity expected from the incident neutron spectrum [1]. This gain is probably attributed to the improvement of the quality of the multilayers.

Using this new monochromator, the SANS measurements of several steel and other metallic samples were performed. The measurement for about 6-10 hours provided good statistical accuracy. The scattering profiles obtained are almost good and consistent with the result obtained in the other instruments. However, a part of the results do not show proper scattering profile. This probably arose from the direction or magnitude of the magnetic field applied to the sample. In the future plan, the permanent magnet will be improved. Furthermore, a focusing device targeting more intensity is in the planning stage.

A part of this work was supported by JSPS KAKENHI Grant number 23360428 (Principal investigator: Masahiro Hino).

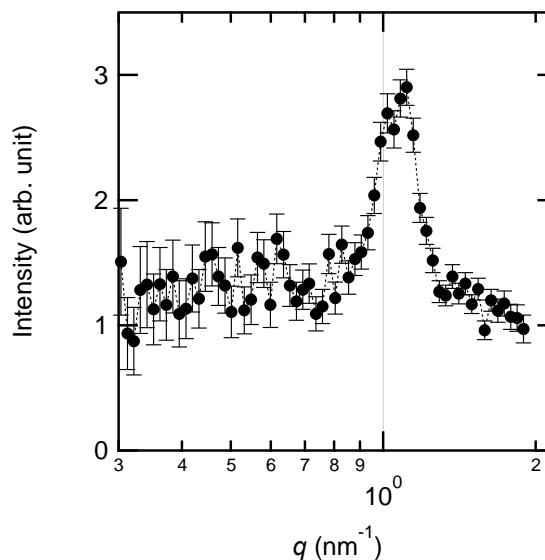


Fig. 1. I - q profile of silver behenate.

REFERENCES:

- [1] M. Sugiyama and Y. Maeda, Jpn. J. Appl. Phys., **33** (1994) 6396-6402.
- [2] H. Sunohara *et. al.*, Physica, **350** (2004) e869-e871.
- [3] M. Hino, *et. al.*, KURRI Progress Report 2012 (2013) 179.
- [4] M. Ohnuma, *et. al.*, KURRI Progress Report 2012 (2013) 177.

K. Hara, T. Miyazaki, Y. Hidaka, H. Okabe,
N. Sato¹, Y. Oba¹ and M. Sugiyama¹

Department of Applied Quantum Physics and Nuclear
Engineering, Kyushu University

¹Division of Quantum Beam Material Science, Research
Reactor Institute, Kyoto University

INTRODUCTION:

Hydrocolloids such as hydrogels and surfactants show very useful as well as interesting properties, for which the structures in the scale of nano-meters often have decisive influences. Therefore, the authors have been investigating them by utilizing the Small Angle Neutron Scattering (SANS) method. In addition, the characteristic features of many hydrocolloids often result from the change in the interactions between their solid-ingredient and solvent, which usually induce drastic changes in their nano-structures. Therefore, the nano-structural investigation can be usable for the examination of the performance the KUR-SANS system installed at Research Reactor Institute, Kyoto University. For this purpose, in the present investigation, the authors investigated the nano-structure of Sodium Oleate (NaOl, surfactant) (Fig. 1) in heavy water (D_2O) in the floatation process (Fig. 2), which demonstrated the performance usable for practical SANS research works.

EXPERIMENTS:

Utilized were the KUR-SANS system installed at Kyoto University Reactor, Kumatori, Japan for the SANS experiments. Several 30 mM Sodium Oleate (NaOl) D_2O solutions were prepared, and then the Cu-ion capturing and subsequent Cu-captured-solution bubbling (for 10 min) treatments were performed to the NaOl D_2O solutions at pH=7 and 8. After then, the processed-solutions were poured into quartz cells for the SANS measurements. The SANS profiles were observed at room temperature.

RESULTS:

Figure 3 shows the SANS profiles of the NaOl D_2O (pH7(a) and pH8(a)), after capturing Cu-ion (pH7(b) and pH8(b)) and after the floatation process (pH7(c) and pH8(c)) at pH=7 and 8, which were calculated with the 2-dimensional scattered-neutron intensity-distribution (from these NaOl solutions) measured by the KUR-SANS system. As is shown in the figures, the SANS profiles obtained with the KUR-SANS system could distinguish the change in the nano-scale structure in a quality usable for the practical research works.

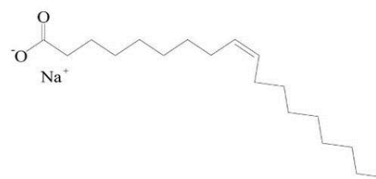


Fig. 1 Sodium Oleate

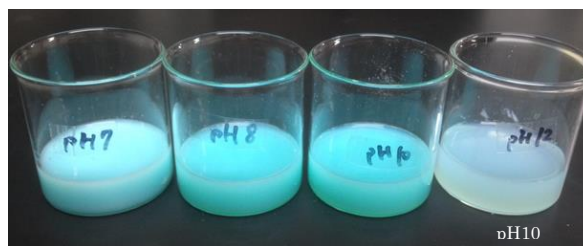


Fig.2 30mM Sodium Oleate in heavy water after capturing Cu at pH=7, 8, 9 and 10.

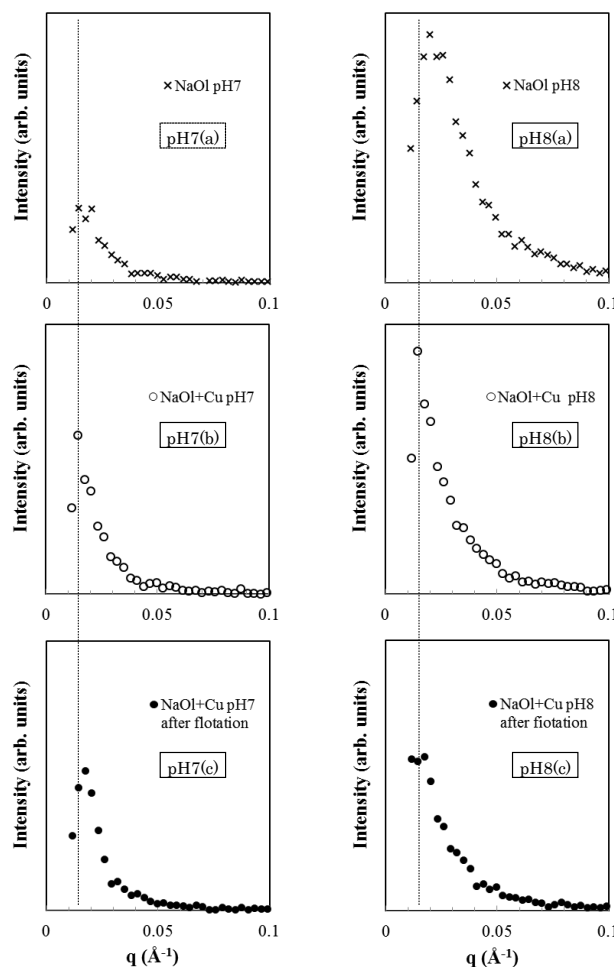


Fig. 3 SANS Profiles of 30mM Sodium Oleate (NaOl) in D_2O in the floatation processes at pH=7 and 8.

PR7-5 Small-Angle Neutron Scattering Analysis of the Nanostructure of Wheat Proteins

R. Urade, A. Matsumiya, Y. Higashino, N. Sato¹, M. Sugiyama¹ and Y. Oba¹

Graduate School of Agriculture, Kyoto University
¹Research Reactor Institute, Kyoto University

INTRODUCTION: The rheological properties of wheat flour dough are dependent on the physical properties of gluten. Gluten consists mainly of two types of proteins: glutenins and gliadins [1]. Among them, gliadins are responsible for the viscosity of dough [2]. Gliadins are monomeric proteins; therefore, the gliadin nanostructure formed by noncovalent intermolecular associations is thought to be responsible for the viscoelastic properties. Hence, detailed analysis of the nanostructure of gliadins is essential to understand the rheological properties of hydrated gliadins at the molecular level. In this study, we performed SANS and SAXS analyses of hydrated gliadins. From the results, we attempted to establish a model of the hydrated gliadin nanostructure.

EXPERIMENTS: Gliadins were prepared by a previously established method [3]. The nanostructure of gliadins dissolved in distilled water at a wide of range concentrations was investigated by SANS and SAXS analyses. The SANS experiments were carried out at the CN-2 beam line of the Kyoto University Research Reactor Institute (KURRI). The SAXS experiments were carried out at beam line BL-10C of the Photon Factory, a synchrotron radiation facility of the Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK). Diluted solution samples were measured in an aluminum cell with 20- μm thick quartz windows, while viscous hydrated solids-concentrated solutions were measured in a PTFE sandwich cell with windows of 7.5- μm thick Kapton film (TORAY-DuPont).

RESULTS: Gliadins became a transparent solution in distilled water below 10 wt%; however, their monomers were only isolated below 0.5 wt% and interparticle interference appeared above that concentration. Guinier and cross-section Guinier analyses of SANS and SAXS data proved that gliadins in water were larger in size than those in 70% ethanol [4]. At greater than 15 wt%, gliadins became insoluble in water but formed gel-like pastes. In the marginal concentration range, the solutions and pastes showed similar SAXS profiles with a shoulder peak at 0.13 nm^{-1} . Fig. 1 shows SANS profiles of gliadins in D_2O (10 wt%) measured after different periods of time from solution preparation. The result of a SAXS measurement for an H_2O solution is also displayed. The scattering curve of the solution stored for 4 days in D_2O showed a profile similar to the SAXS profile of the solution stored 4 days in H_2O , but the slope in the low- q re-

gion ($< 0.2 \text{ nm}^{-1}$) became more flat. This fact indicates that the associated gliadin molecules became smaller. The reason for this phenomenon is accounted for by the exchange of hydrogen with deuterium. Hydrogen atoms bonded to such as amide groups can be exchanged by deuterium atoms of solvent heavy water. Outer hydrogens are exchanged more readily than inner hydrogens. Therefore the contrast of the outer region becomes lower and apparent size observed by SANS gets smaller. The low- q profile became more flat when the stored time was extended to 10 days, indicating that more inner hydrogens were exchanged. The curve in the high- q region ($> 1 \text{ nm}^{-1}$) was also different from the 4-day solution. This may be due to growing aggregation of dispersed small gliadin associates. However, with increasing concentration, there appeared to be a steep rise in the low- q region owing to the large aggregation.

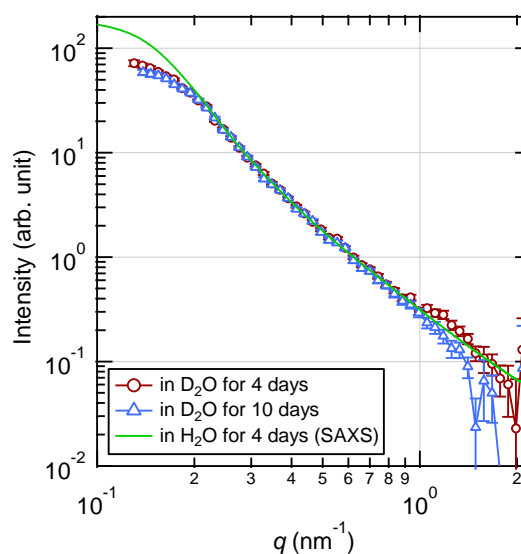


Fig. 1. SANS profiles of gliadins stored in different periods in heavy water at a concentration of 10 wt% . The curves are vertically shifted for comparison. The profiles were similar to the SAXS profile in H_2O except in the low- q region.

REFERENCES:

- [1] F. MacRitchie and P. L. Weegels. Structure and functional properties of gluten. "Wheat, 4th ed." AACC International Press, 2009.
- [2] M. Cornec *et al.*, J. Cereal Sci., **19** (1994) 131-139.
- [3] T. Ukai *et al.* J. Agric. Food Chem. **56** (2008) 1122-1130.
- [4] N. Thomson *et al.* Biochim. Biophys. Acta, **1430** (1999) 359-366.

PR7-6 Thermoresponsive Structural Change of Radiation-Fabricated Porous Binary Polymer Gels as Revealed by Small-Angle Scattering

N. Sato, Y. Oba, R. Inoue and M. Sugiyama

Research Reactor Institute, Kyoto University

INTRODUCTION: Polymer hydrogels are widely used as various biocompatible materials because of their softness and moistness. Extensive studies have been reported not only aiming at the application of polymer hydrogels for novel functional materials, but also a lot of attention has been attracted to the three-dimensional network structure of crosslinking polymer chains of the polymer gels. We have been studying so far the radiation-induced fabrication of porous binary hydrogels. This method has an advantage of reduced impurity and suppressed structural disordering of the final product gels. In this study, a well-known thermoresponsive polymer, poly(N-isopropylacrylamide) (PNIPAm) was incorporated as an additional gel component into nonporous and porous matrix gels of a common polymer, poly(ethylene glycol) (PEG). As a result of investigation of swelling behavior of those gels, it was suggested that porous gels are less shrinkable due to the localization of the PNIPAm component in the pore space of the PEG matrix gel [1]. To confirm this consideration more directly in the nanoscopic level, we have employed the small-angle X-ray and neutron scattering methods (SAXS and SANS). Here we report the SAXS and SANS analyses of PEG/PNIPAm nonporous and porous binary hydrogels on temperature change.

EXPERIMENTS: The PEG matrix gel was prepared by γ -irradiation to a deoxygenated 10 wt% PEG aqueous solution for a dose of 60 kGy. A PNIPAm monomer solution was impregnated into the matrix gel. After the γ -irradiation to the gel for a dose of 3 kGy, binary gels were finally obtained. Pores were made by mixing silica microparticles in the PEG solution followed by the decomposition of silica with hydrofluoric acid. SAXS experiment were carried out at the beamline BL-10C of Photon Factory, KEK. SANS experiments were conducted at the KUR-SANS of Research Reactor Institute, Kyoto University.

RESULTS AND DISCUSSION: The PEG/PNIPAm binary gels prepared by the above-mentioned γ -irradiation method shows the same thermoresponsive behavior as pure PNIPAm gels, but the property of these gels are softer and more elastic like the PEG gel. When the ambient temperature becomes higher than 34 °C, the binary gels greatly shrinks but the soft and elastic prop-

erty is still kept unlike the pure PNIPAm gel.

Figure 1 shows the temperature-dependent SAXS profiles of PEG/PNIPAm binary hydrogels with pores of 1000 nm in diameter.

When the temperature is raised to 40 °C, a steep rise with a relationship of $I \propto q^{-4}$ appears while the slope value is smaller for the nonporous binary gels. The -4 th power relationship called Porod's law is known to offer evidence for clear interface of two domains. Thus, this fact indicates the clear phase separation between PEG domains and PNIPAm domains in the porous gel, proving that PNIPAm chains are prone to be localized in pore space. The result of SANS also shows the similar profile.

When the PNIPAm chains localized in the pores are shrinking at higher temperature, voids in the pores become larger. Therefore these porous binary gels have a potential application for temperature-controlled substance capture and release. It is expected that a novel drug delivery system can be developed using this feature.

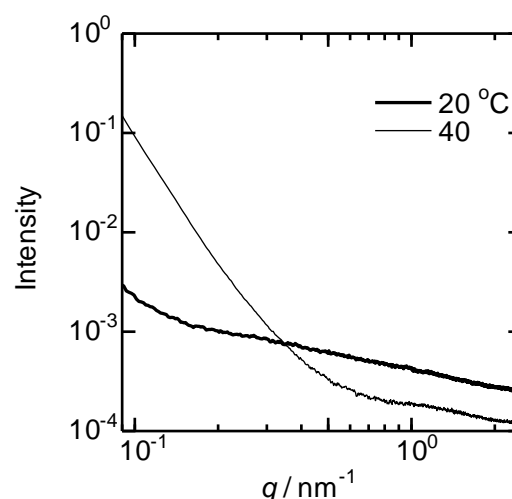


Fig. 1 SAXS profiles of PEG/PNIPAm binary gel with pores of 1000 nm in diameter. A steep rise following Porod's law can be observed in the low- q region at 40 °C.

REFERENCES:

[1] N. Sato, M. Ueda, T. Matsuyama, and M. Sugiyama, *Trans. Mater. Res. Soc. Jpn.*, **37** (2012) 127-130.

PR7-7 Application of SANS in Compact Neutron Source for Quantitative Analysis of Precipitates in Steels

M. Ohnuma, Y. Oba¹ and M. Sugiyama¹

Hokkaido University

¹Research Reactor Institute, Kyoto University

INTRODUCTION: Small-angle neutron scattering (SANS) is useful technique to obtain statistical representative microstructural parameters. However, machine times are quite limited especially in Japan. Therefore, we are trying to use SANS in relatively small scale facilities, i.e., KUR or HUNS (Hokkaido University Neutron Scattering). For this purpose, we are measuring series of steel samples which are used as the structural materials using different facilities to see which facilities are suitable for certain q -range and whether it can be used in the front line of materials development.

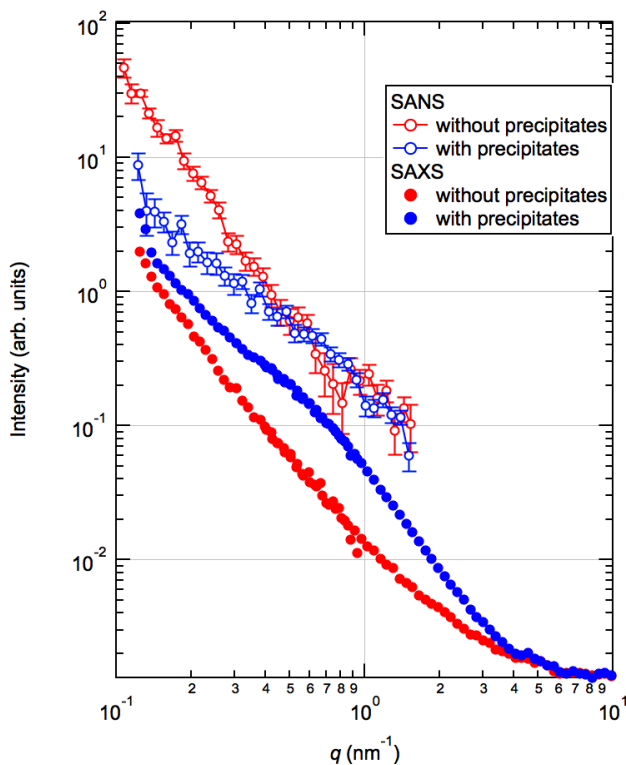


Fig. 1. SANS and SAXS profiles of steel with and without precipitates

EXPERIMENTS: The series of samples are the steels with precipitates which are formed by annealing. SANS measurements have been performed under the magnetic field about 0.6 T using NdFeB permanent magnet at room temperature. All of the samples are planned to be measured both HUNS and HANARO in Korea Atomic Energy Institute in 2014.

RESULTS: Figure 1 shows SANS profiles measured in KUR. They are normalized by thickness. Clear difference observed between samples with and without precipitates. Figure 1 also shows SAXS profiles of same samples. They are also normalized by thickness. The profile shapes are almost same in both samples, however, the intensity level is opposite between them.

We will measure these sample using HUNS and HANARO. Meanwhile, we plan to convert the intensity scale to absolute units and discuss about the composition of matrix and precipitates from the intensity ratio between SAXS and SANS.

K. Iwase¹, K. Mori, S. Tomihira², Y. Oba, T. Fukunaga and M. Sugiyama

Research Reactor Institute, Kyoto University

¹Department of Materials Science and Engineering, Ibaraki University

²Graduate School of Science, Kyoto University

INTRODUCTION: Hydrogen-absorbing alloys are key materials for modern industrial applications; La₂Ni₇-based intermetallic alloys are used as cathodes in Ni/metal-hydride batteries, and Ti-Cr-V-based solid-solution alloys are promising candidates for application to high-pressure metal-hydride tanks in fuel-cell vehicles [1]. It is very important to comprehensively understand the hydrogenation properties, crystal structures, and surface structures of particles of hydrogen-absorbing alloys in order to further improve the hydrogen storage capacities (i.e., hydrogen-to-metal ratio, H/M), residual hydrogen contents, rates of hydrogen absorption and desorption, and reliabilities of such alloys.

It is also necessary to characterize the hydrogenation (or deuteration) properties of hydrogen-absorbing alloys by assessing the morphology of the surface of alloy particles. Numerous scanning electron microscopy (SEM) and transmission electron microscopy (TEM) investigations of the microstructure and morphology of such alloys have previously been reported, although there is insufficient information on the surfaces of hydrogenated-alloy particles. Small-angle neutron scattering (SANS) has recently attracted much attention as a powerful tool for observing the particle surface of hydroxides [2]. The fractal dimension of a particle surface (DS) can be extracted from the slope of a SANS profile, $I(q)$, in the Porod region, where q represents the magnitude of a scattering vector. The SANS technique would be applicable to hydrogen-absorbing alloys; however, almost all of them (e.g., LaNi₅) require a hydrogen (or deuterium) atmosphere during *in situ* SANS experiments. Hence, we developed a sample holder for *in situ* SANS experiments on hydrogen-absorbing alloys (*in situ* sample holder, hereafter).

We developed an *in situ* sample holder and used the well-known hydrogen-absorbing alloy LaNi₅ to evaluate its basic performance in SANS under a deuterium atmosphere at room temperature (RT) during the first absorption-desorption cycle. Using D enabled us to clearly observe SANS profiles even in the high- q region because of the low $\sigma_{\text{inc}}(\text{D})$. Pressure-composition (P-C) isotherms and XRD patterns were simultaneously measured.

EXPERIMENTS: the *in situ* sample holder is composed of a rectangular parallelepiped stainless-steel body (SS304, 25 mm × 25 mm × 55 mm), a stainless-steel flange (SS304, 25 mm × 25 mm), and two 3-mm-thick, 20-mm-diameter disk-shaped quartz windows. A 1-mm-diameter indium wire was used between the stain-

less-steel body and the quartz window (each side wall), and an O-ring was used between the stainless-steel body and the stainless-steel flange (upper part) to seal the *in situ* sample holder. Additionally, the *in situ* sample holder was equipped with an inlet and outlet gas pipeline (SS304, 6.35 mm (1-quarter-inch) in diameter), high-pressure diaphragm valves (Swagelok®), and a pressure gauge for constantly monitoring gas pressure. A 0.5-mm-thick cadmium plate was used as a neutron-shielding material and was placed on the front wall to direct the incident neutron beam in order to reduce the intensity of the background signals during the SANS experiments.

RESULTS: Figure 1 shows the SANS profiles, $I(q)$, for LaNi₅D_{6.3} (D/M = 1.05) measured at 1 MPa during absorption (Fig. 2), LaNi₅ during desorption, and undeuterated LaNi₅. It is noteworthy that the intensities attributed to the *in situ* sample holder have already been excluded from the SANS intensities. We used the *in situ* sample holder and high-purity D₂ gas to eventually clearly observe the SANS profiles for LaNi₅ over the wide q region. The surface morphology of the undeuterated LaNi₅ was first assessed through DS, which was obtained from the least-squares fit in the q range 0.17–1.45 nm⁻¹ using equations $I(q) \propto q^{-k}$ and DS = 6- k , where k represents the slope of the SANS profile. As a result, DS was estimated at 2.8 ($k = 3.2$), meaning that the particle surface of undeuterated LaNi₅ was quite rough.

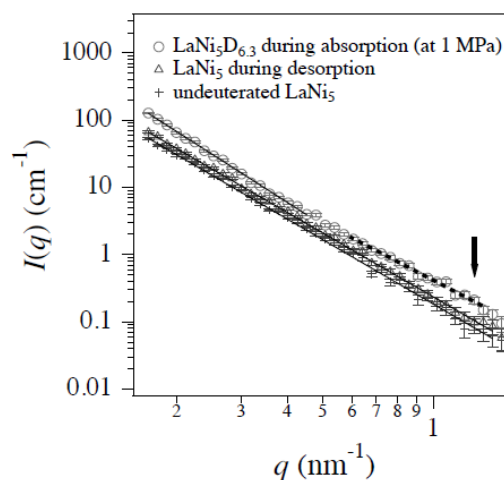


Fig. 1 SANS profiles, $I(q)$, for LaNi₅D_{6.3} (D/M = 1.05) measured at 1 MPa and at RT (~299 K)

REFERENCES:

- [1] Schlapbach *et al.*, Hydrogen-storage materials for mobile applications. *Nature* **414** (2001) 353–361.
- [2] R. Livingston R, Fractal nucleation and growth model for the hydration of tricalcium silicate. *Cem. Concr. Res.*, **30** (2000) 1853–1860.