（ ※本報告書は英語で記述してください。ただし、産業利用課題として採択されている方は日本語で記述していただいても結構です。 ）

MLF Experimental Report	提出日 Date of Report
課題番号 Project No. 2014A0160 実験課題名 Title of experiment Effect of carbon black addition on silica particle's dispersion in fuel-efficient tire rubber 実験責任者名 Name of principal investigator Yohei NODA 所属 Affiliation Quantum Beam Science Center, JAEA	装置責任者 Name of responsible person Jun-ichi Suzuki 装置名 Name of Instrument/(BL No.) BL15 実施日 Date of Experiment 7 Nov 2014 – 11 Nov 2014

試料、実験方法、利用の結果得られた主なデータ、考察、結論等を、記述して下さい。（適宜、図表添付のこと）
Please report your samples, experimental method and results, discussion and conclusions. Please add figures and tables for better explanation.

1. 試料 Name of sample(s) and chemical formula, or compositions including physical form.

1. PS-b-PI block polymer (Standard sample)

2. Silica filled SBR rubber

3. Silica and CB filled SBR rubber

2. 実験方法及び結果（実験がうまくいかなかった場合、その理由を記述してください。）

Experimental method and results. If you failed to conduct experiment as planned, please describe reasons.

Proton's scattering length against fully polarized neutron (b_H) is largely dependent on the proton spin polarization (P) as shown in Figure 1. This effect can be utilized for contrast variation study in small angle neutron scattering (SANS). We have applied this "spin contrast variation technique" to polymer or rubber system, into which it is difficult to introduce deuterons. This technique is expected to be an ultimate solution for structural analysis of highly-functional composite-materials filled with several types of particles (silica, carbon black (CB) and so on).

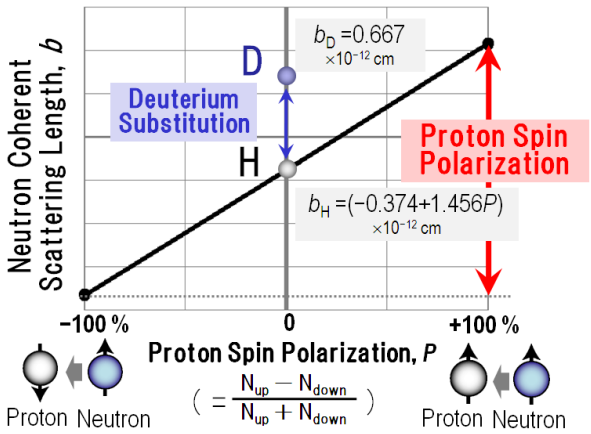

Figure 1: Neutron scattering length of proton as a function of proton spin polarization.

2. 実験方法及び結果（つづき） Experimental method and results (continued)

For achieving high *P*, in turn wide contrast variation, dynamic nuclear polarization (DNP) technique is usually used. DNP requires that samples should contain unpaired electrons. Stable radical TEMPO is known to work as an electron spin source. We doped ca. 30mM of TEMPO into particle-filled rubber samples by vapor permeation technique (40°C, 1 week). Figure 2 shows a cryostat for DNP experiment. 94GHz Microwave irradiation transferred spin polarization from unpaired electron spins to protons at 1.1 K and 3.35 T to achieve *P* around 30–40%.

Figure 2: Cryostat for DNP experiment on BL15 sample stage.

Figure 3a shows the observed SANS profile for silica/SBR, which can be assumed as a two-phase system. As a function of *P*, SANS intensity increased or decreased with keeping the shape of low-*q*-side coherent term. The observed intensity variation was well explained by the contrast between silica and SBR rubber phases. Whereas, for silica/CB/SBR (Figure 3b), in addition to the intensity variation, we can see the slight enhancement or reduction of the fringe at *P* = −31% or +31%, respectively. This fringe was due to the form factor of silica particle with small radius dispersion, and disappeared at *P* = +31% since the neutron scattering length density of SBR rubber matched with that of silica. The *P* = +31% profile (blue solid circle), which is the scattering contribution only due to CB, indicated the decaying power-law of −3.7, slightly deviating from that for silica (−4). The spatial distribution of CB dispersing with silica was successfully observed.

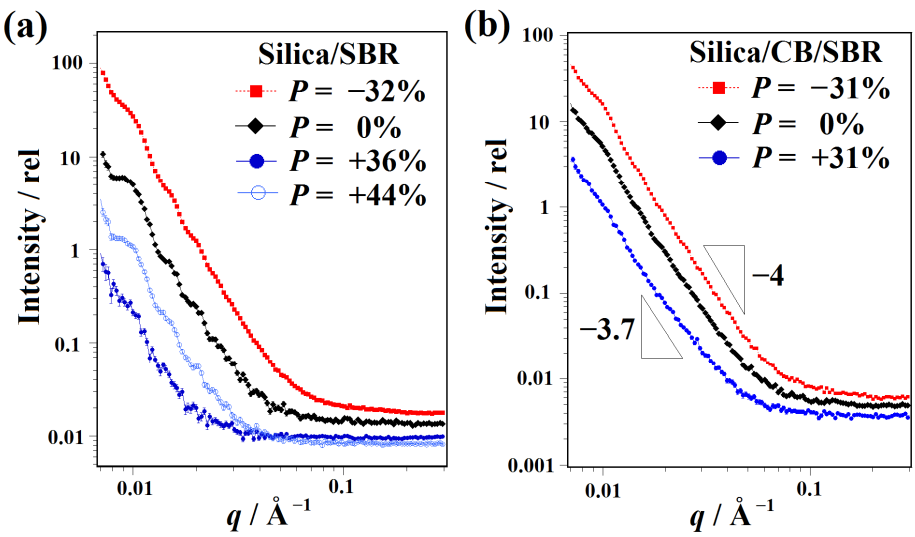

Figure 3: SANS profile as a function of proton spin polarization, *P*, for (a) silica-filled SBR rubber and (b) silica- and CB-filled rubber. Sample (a) contains silica particles with a radius of about 600Å introduced by 10%vol. Sample (b) contains silica with the same particles radius by 10%vol and CB by 2%vol.