（ ※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。 ）

CROSS TOKAI **Experimental Report** J-PARC

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実験課題名 Title of experiment
Slow dynamics in rubber crosslinked by metal acrylate as studied by quasielastic neuron scattering

実験責任者名 Name of principal investigator
Rintaro Inoue
所属 Affiliation
Kyoto University

装置責任者 Name of responsible person
Kaoru Shibata

装置名 Name of Instrument/(BL No.)
BL-02

実施日 Date of Experiment
2014/6/12～2014/6/20

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.

Polybutadiene rubbers (−(C4H6)n−) crosslinked with zinc diacrylate (C6H6O4Zn) as a function of concentration of zinc diacrylate (volume fraction of 0, 0.05, 0.1.0.15) were used for sample and the thicknesses of prepared sample were at around 0.2mm.

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.

It is well known that an introduction of crosslinking by zinc diacrylate (ZDA) into polybutadiene (PB) exhibited a dramatic improvement of elastic modulus called the “reinforcement effect” (refer to Fig.1), however the detailed mechanism of “reinforcement effect” is still far from understanding despite of vigorous researches. It is considered that dynamical studies on such rubber materials would offer the better opportunity for understanding the mechanism of “reinforcement effect”. We then tried to study the dynamics of PB crosslinked with ZDA through quasielastic neutron scattering.

As a first step we performed elastic window scan from 10K to 323K at the heating rate of 1 K/min for rubber materials and mean square displacement ($\langle u^2 \rangle$), was evaluated for PB rubber crosslinked by ZDA. The temperature dependence of $\langle u^2 \rangle$ for crosslinked PB rubber at different ZDA concentrations is plotted in Fig. 2. Below about 110K $\langle u^2 \rangle$ increased linearly with temperature, implying that the motion below 110K is harmonic. On the other hand $\langle u^2 \rangle$ started to increase steeply above about 110 K, which is below T_g. It is considered that an onset of anharmoic motion must be originated from

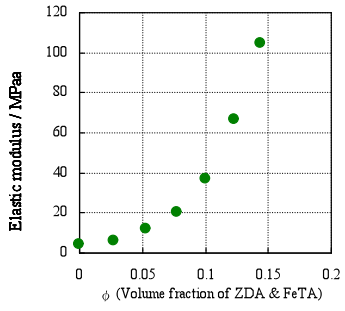

Fig. 1 Elastic modulus of PB rubber as a function of concentration of ZDA.

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

local process or so-called fast process based on our former works. With further increasing temperature we again observed the onset of relaxation process or anharmonic motion at around 170K. From preliminary DSC measurements T_gs of PB crosslinked with ZDA were estimated to 170K, hence it is considered that the onset of another relaxation process must be attributed to detection of T_g with DNA spectrometer. At 230K, which is about 60K above T_g the other steep increase of $\langle u^2 \rangle$ was found. To find out the plausible physical origin for steep increase at 230K we paid attention to dynamic scattering laws ($S(Q, \omega)$) from matrix PB, which is not crosslinked by ZDA as shown in Fig. 3. Above 230 K we could clearly observe the broadening on central component, hence it is supposed that steep increase of $\langle u^2 \rangle$ is ascribed to the broadening of alpha process, which is responsible for glass transition with an energy resolution of 3 μeV measurements. From the temperature dependence of $\langle u^2 \rangle$ at least three characteristic different temperatures were seen. Interestingly we could not observe noticeable shift of onset temperatures of fast process, alpha process and broadening of alpha process regardless of concentration of ZDA. Furthermore decrease of $\langle u^2 \rangle$ with increasing the amount of ZDA was observable at the temperature above 230 K. That is to say, ZDA has a little effect on local motion of present rubber material. In other words it seems only the alpha process was affected by an addition of ZDA within in present energy resolution.

Taking into account the experimental facts: T_g is constant independent of the concentration of ZDA and $\langle u^2 \rangle$ drastically deceased with increasing the concentration of ZDA at the temperature above 230K. It is expected that the dynamics in matrix PB rubber must be heterogeneous by the addition of ZDA. Namely there coexists mobile and immobile component under present energy resolution and only the mobile component is responsible for the observable dynamics in present QENS measurements. In order to confirm such an idea we tried to fit dynamics scattering law at 310 K. As for curve fitting observed dynamics scattering laws we used a model function consisting of the sun of a delta function and Havriliak-Negami function (Fourier transformed KWW function). The results of fit with a model function is shown in Fig. 4 and all of the observed spectra as a function of concentration of ZDA were well fitted with above model function. From the results of fit it was found that distribution of relaxation time (=beta) is not dependent on the volume fraction of ZDA. On the other hand clear increase of EISF (=immobile component) was observed with ZDA concentration. Hence an increase of mobile component seems to be related to the decrease of $\langle u^2 \rangle$ above T_g and such an increase of immobile part might be related to the increase of elastic modulus. Contrary to our expectation we also observed a slight increase of relaxation time with increasing the concentration of ZDA. The detailed analysis, which can connect the microscopic dynamics and elastic modulus, is still on progress.

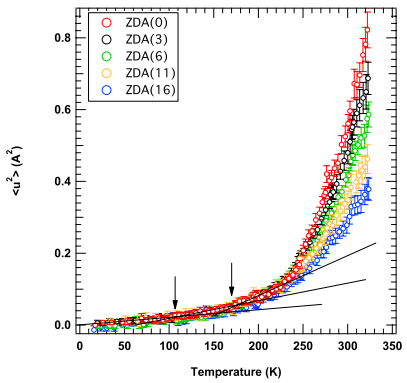

Fig. 2 Temperature dependence of $\langle u^2 \rangle$ for PB crosslinked by ZDA at different ZDA concentrations.

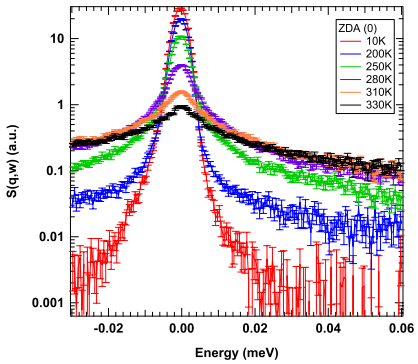

Fig. 3 Temperature dependence of $\langle u^2 \rangle$ for PB crosslinked by ZDA at different ZDA concentrations.

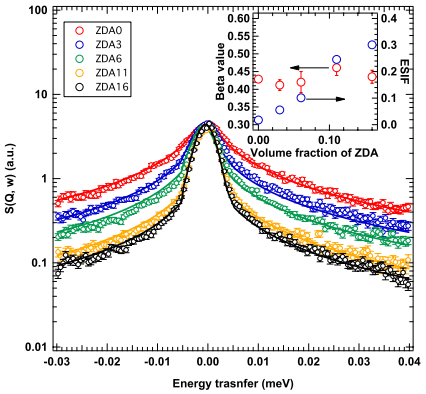

Fig. 4 Results of fits with a model function and inset indicates the distribution of relaxation time and EISF as a function of volume fraction of ZDA.