

Structure and Dynamics of Nanocomposites Consisting of Block Copolymer-Grafted Silica Particles by Synchrotron Radiation X-ray Scattering/Spectroscopy

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論 文 名 : Structure and Dynamics of Nanocomposites Consisting of Block
Copolymer-Grafted Silica Particles by Synchrotron Radiation X-ray
Scattering/Spectroscopy
(放射光 X 線散乱・分光法によるブロック共重合体修飾シリカ粒子ナノ
コンポジットの構造とダイナミクスに関する研究)

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論 文 内 容 の 要 旨

In recent years, the nanocomposites assembled by the polymer-grafted nanoparticles without additional polymer matrices have attracted great attention. This kind of materials can form a periodically ordered structure by self-assembly of these hairy particles. However, increasing the strength of these matrix-free nanocomposites with a suitable extensibility is still a challenge. For adjusting the mechanical properties of materials, it is crucial to realize the structural responses and dynamics to mechanical deformation. The purpose in this thesis is to investigate the effect of the block copolymer on the enhancement of the mechanical properties. Furthermore, another purpose in this thesis is to investigate the structure and dynamics of the matrix-free nanocomposites under mechanical deformation through different methods of the synchrotron radiation.

In this thesis, Chapter 1 described the introduction of the background, purpose, and the structure of this thesis.

In Chapter 2, the poly(methyl methacrylate)-*b*-poly(*n*-butyl acrylate)-*g*-silica nanoparticles (PMMA-*b*-PnBA-*g*-SiNPs) were prepared with different weight ratios of PnBA and PMMA. A flexible and strong nanocomposite elastomer was prepared by the assembly of PMMA-*b*-PnBA-*g*-SiNPs. The PMMA-*b*-PnBA-*g*-SiNPs formed paracrystal-like structures and exhibited structural color depending on the particles size. The PMMA-*b*-PnBA-*g*-SiNPs exhibited two different glass-transition temperatures (T_g s), indicating the microphase-separated state existed in the PMMA-*b*-PnBA-*g*-SiNPs. The atomic force microscope observation revealed that two layers of PnBA inner layer and PMMA outer layer formed in the particles.

In Chapter 3, the heat-pressed PMMA-*b*-PnBA-*g*-SiNPs nanocomposite exhibited the mechanochromic properties under the uniaxial and biaxial elongation. Through the *in-situ* ultra small-angle X-ray scattering (USAXS), the PMMA-*b*-PnBA-*g*-SiNPs nanocomposite was found to behave more rubber-like as the PnBA weight ratio increased. The distance between the SiNPs decreased in the direction perpendicular to elongation, causing mechanochromic behavior. By biaxial stretching, the distance between the SiNPs increased isotropically because the polymer surrounding the SiNPs was elongated isotropically toward the in-plane direction.

In Chapter 4, the X-ray photon correlation spectroscopy (XPCS) was utilized to analyze the dynamics of a PMMA-*b*-PnBA-*g*-SiNPs nanocomposite during the heating, uniaxial elongation and stress relaxation processes. When the temperature approached the T_g of PMMA, the SiNPs velocity increased rapidly because the restriction of SiNPs motion from the glassy PMMA decreased. During the uniaxial elongation, the dynamics of the SiNPs in the direction perpendicular to elongation were faster than those parallel to elongation. The anisotropic dynamics might be caused by the *trans* rich state of the polymer chains which could potentially induce the restriction of SiNPs motion in the stretching direction. During the stress relaxation process, the decrease of SiNPs velocity was also observed with decreasing stress at a strain of 0.2. Since the plastic deformation at a high strain of 0.2 lead to a long relaxation time, the change in SiNPs velocity was obvious in the XPCS at a strain 0.2.

In Chapter 5, the dynamic X-ray scattering measurement was carried out to investigate the responses of SiNPs in the nanocomposite under minor cyclic strain. The loss modulus (E'') from the dynamic X-ray scattering revealed that the responses of SiNPs in PMMA-*b*-PnBA-*g*-SiNPs under a cyclic strain behaved more viscous as the weight ratio of PnBA/PMMA increased. The structural responses to the rheological measurements were different between the SiNPs core and the bulk material in the PMMA-*b*-PnBA-*g*-SiNPs nanocomposite. The results obtained by the dynamic X-ray seem to be governed by PnBA.

Finally, Chapter 6 concluded the fabrication, structure, dynamics, and microscopic rheological behaviors of the PMMA-*b*-PnBA-*g*-SiNPs nanocomposite in this thesis. These results are considered to be a valuable contribution to understanding the mechanism of matrix-free nanocomposites under mechanical deformation to optimize their design.