Hierarchic Structures and Propeties of Natural Rubber

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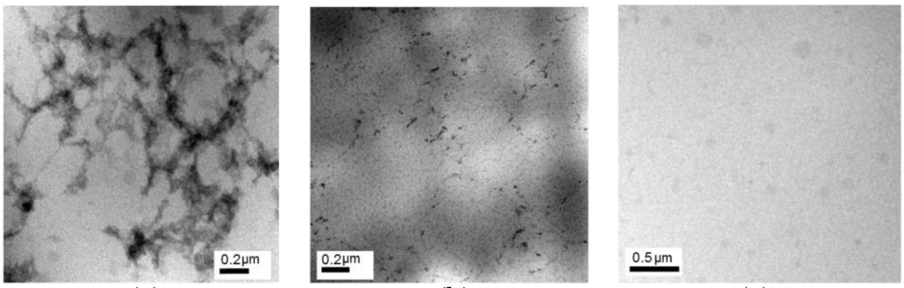
Natural rubber is well-known to be superior in mechanical properties such as tensile strength, tear strength, green strength and so forth. In the last century, therefore, attempts to analyse a primary structure of natural rubber were made to elucidate a relationship between the structure and properties. For instance, a fundamental structure of natural rubber is known to consist of ω-terminal, 2 *trans*-1,4-isoprene units, about 5,000 *cis*-1,4-isoprene units and α-terminal, aligned in this order. Furthermore, the α-terminal is composed of phospholipids linking to fatty acids and the ω-terminal is a modified dimethylallyl group linking to a functional group, which is associated with the proteins. Thus, the branching structure is inherently formed in natural rubber. The outstanding properties of natural rubber is partly associated to the branching structure. However, in order to understand an origin of the outstanding properties of the rubber, we are required to analyse hierarchal structure of natural rubber, since the proteins and the phospholipids are immiscible with natural rubber. In the present study, the relationship between the structure and mechanical properties was investigated in relation to the nanomatrix structure, which was discovered in this century.

Natural rubber particles in latex are covered with the proteins and phospholipids. Therefore, the proteins and phospholipids of the particles may merge into each other to form a dispersion medium, when the latex is coagulated. Natural rubber may, thus, possess the nanomatrix structure[1], which consists of natural rubber particles of about 1 μm in diameter as a dispersoid and the nanomatrix of the proteins and phospholipids as a medium. Figure 1 shows TEM images for fresh natural rubber, natural rubber and DPNR, which were stained with phosphotungstic acid. In the TEM images, phase separated structure was found for fresh natural rubber and natural rubber, in which bright domains represent natural rubber and gloomy domains represent non-rubber components. The rubber particles of various sizes were well dispersed in the nanomatrix of the proteins and phospholipids. The thickness of the matrix was dependent upon the protein contents. For example, total nitrogen contents were 0.777 w/w% for fresh natural rubber (Figure 1a) and 0.251 w/w% for natural rubber (Figure 1b). This implies that the natural rubber particles are covered by a membrane layer, i.e. protein-lipid complex; hence, the proteins and phospholipids may essentially form the nanomatrix after coagulation of the latex. On the contrary, no phase separated structure was found for DPNR (Figure 1c). This may be explained to be due to the removal of the proteins from natural rubber: The nanomatrix structure was associated to the outstanding properties of natural rubber.

[1] S. Kawahara, *et. al. Macromolecules*, **41** (2008) 4510-4513.



(a) (b) (c)

Figure 4 TEM images for fresh natural rubber, natural rubber and DPNR.