

論文内容の要旨

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Naturally occurring crosslinking junctions of natural rubber may have a potential to play an important role in the outstanding mechanical properties of the rubber. However, no comprehensive research work has been carried out on the role of naturally occurring crosslinking junctions, since the non-rubber components such as proteins and phospholipids present in natural rubber as an impurity, as well as abnormal groups such as epoxy groups, formyl groups and *trans*-1,4-isoprene units, prevented the study on the effect of the naturally occurring crosslinking junctions on the mechanical properties. In the present study, nuclear magnetic resonance (NMR) spectroscopy was applied to the structural characterization of natural rubber, which was purified by removal of proteins, lipids and fatty acids / their esters. First, assignments of all signals in ^1H -NMR and ^{13}C -NMR spectra were performed with rubber obtained from *Lactarius Volemus* (LV rubber) as a model. Second, commercial natural rubbers were characterized by NMR spectroscopy on the basis of the assignments of the signals of ^1H -NMR and ^{13}C -NMR spectra for LV rubber. The damage to commercial natural rubbers was found to reduce the mechanical properties, since it generated abnormal groups. Third, effect of the naturally occurring crosslinking junctions on mechanical properties of natural rubber was investigated in conjunction with the effect of the non-rubber components by using rubbers obtained from *Parthenium argentatum* Gray as a model. Outcomes, achieved in the present study, are described in detail, as follows.

Assignments of small signals appearing in ^1H - and ^{13}C -NMR spectra of naturally occurring *cis*-1,4-polyisoprene isolated from LV rubber were made through 2D-NMR spectroscopy. The LV rubber was collected as a latex by tapping mushroom basidiocarp followed by purification. The resulting LV rubber was characterized by NMR spectroscopy such as hetero-nuclear multiple quantum coherence (HMQC) and hetero-nuclear multiple bond correlation (HMBC). A signal, found in ^1H -NMR spectrum, was assigned to the methylene proton of carbon (C1) of *trans*-1,4-isoprene unit and three ^{13}C signals in ^{13}C -NMR spectrum were assigned to methine carbons (C3) of terminal units of the LV rubber. Consequently, all small signals were assigned successfully to terminal units of LV rubber as a model compound.

Damage to various commercial natural rubbers (NR) such as Pale Crepe (PC), Ribbed Smoked Sheet (RSS3), Technically Specified Sheet (TSS8[®]), Standard Thai Rubber (STR5L) and Standard Malaysian Rubber (SMR20) was investigated through liquid state NMR spectroscopy. As-cast films of the rubbers were prepared by solution casting method and

followed by acetone extraction. Chemical structures of the rubbers were analyzed through ^1H and ^{13}C -NMR spectroscopy. The signals at 60.8 and 64.5 ppm appeared for PC, STR5L, RSS3, TSS8® and SMR20, while the signal at 40 ppm appeared for TSS8® and SMR20. The signals at 60.8 and 64.5 ppm were assigned to C2 and C3 of *cis* epoxy group and the signal at 40.0 ppm was assigned to the *trans*-1,4-isoprene unit in the *cis-trans* sequence. The intensities of these signals for TSS8® and SMR20 were higher than those for PC, STR5L and RSS3; however, the green strength of TSS8® and SMR20 was lower than that of PC, STR5L and RSS3. The mechanical properties depended in part on the damage of the rubbers during processing.

Effect of the naturally occurring crosslinking junctions on green strength of natural rubber isolated from *Hevea brasiliensis* was investigated by using a rubber extracted from *Parthenium argentatum* Gray (Guayule) as a model. Guayule rubber and natural rubber were characterized through NMR spectroscopy and size exclusion chromatography. The non-rubber components were characterized by Kjeldahl method and FT-IR spectroscopy. It was found that Guayule rubber contained much amount of fatty acids and their esters, while it contained no proteins. The gel content, determined by swelling method, was related to number of naturally occurring crosslinking junctions. The outstanding mechanical properties of natural rubber were found to be due to the effect of naturally occurring crosslinking junctions, when stress-strain curve and tensile properties of unvulcanized Guayule rubber were compared with those of unvulcanized natural rubber.