

論文内容の要旨

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Graft-copolymerization of functional monomers onto natural rubber (NR) in latex may have a potential to achieve the outstanding properties indispensable for high performance natural rubber. It may lead to not only accomplishment of high conversion and grafting efficiency but also construction of the nanomatrix structure. The improved properties may be closely related to selection of suitable monomers for the graft-copolymerization. In the present study, various model graft-copolymers of NR were prepared from methyl methacrylate (MMA), vinyltriethoxysilane (VTES) and stearyl methacrylate (SMA), after removal of proteins from the rubber.

Removal of proteins was carried out by incubation of natural rubber latex with surfactant, denaturing agent and polar organic solvent, followed by centrifugation three times. The nitrogen content of the resulting rubbers was analyzed by the Kjeldahl method. The nitrogen content depended on the amount of urea, polar organic solvent concentration, amount of metal ions in the water and gel content. Distilled Malaysian water was found to be suitable to remove the proteins from natural rubber. Under suitable conditions, protein free natural rubber latex with 0.00 w/w% nitrogen content was prepared by incubation of fresh natural rubber latex (low gel content latex) and water with low amount of metal ions, with 1 w/w% SDS, 0.1 w/w% urea and 2.5 w/w% acetone. The green strength of the protein free natural rubber was slightly reduced compared to untreated natural rubber.

Graft-copolymerization of methyl methacrylate (MMA) onto urea-deproteinized natural rubber (U-DPNR) was performed in latex stage in order to improve some properties without sacrificing outstanding properties of natural rubber. Natural rubber was deproteinized by incubation of the latex with urea in the presence of sodium dodecyl sulfate (SDS). U-DPNR latex was graft-copolymerized with MMA at monomer feed of 0.5, 1.0, 1.5, 2.0 mol/kg-rubber. The monomer content, monomer conversion and grafting efficiency of the copolymerization reaction were determined. The resulting graft-copolymers were characterized by FT-IR spectroscopy and transmission electron microscopy (TEM). A suitable condition for the graft-copolymerization was determined: that is, 1.5 mol/kg-rubber of MMA, 6.6×10^{-2} mol/kg-rubber of initiator and 30 °C of temperature. The highest grafting efficiency of MMA was about 80 mol% under the suitable condition.

Natural rubber with filler nanomatrix structure was prepared by forming chemical linkages between natural rubber particles and filler nano-particles. The filler nanomatrix structure was formed by graft-copolymerization of vinyltriethoxysilane (VTES) onto natural

rubber particles in latex stage followed by casting the latex to prepare an as-cast film. The silica nano-particles were produced during the graft-copolymerization through hydrolysis and condensation, i.e. sol-gel reaction; hence, they linked to the natural rubber particles. The nanomatrix structure was observed by TEM, in which the natural rubber particles of about 1 μ m in diameter were well dispersed in the filler nanomatrix. Tensile properties were significantly improved by forming filler nanomatrix structure. The loss modulus and loss tangent of the natural rubber with the filler nanomatrix structure were almost independent of deformation frequency in the rubbery plateau region, which was explained to be due to energetic elasticity and entropic elasticity characteristic of the nanomatrix structure.

An attempt to prepare graft copolymer of deproteinized natural rubber and poly(stearyl methacrylate), DPNR-*graft*-PSMA, was made to improve mechanical properties of natural rubber, since the grafted PSMA was composed of crystallizable stearyl groups as a nucleating agent and methacrylate units. The graft-copolymerization of stearyl methacrylate (SMA) onto natural rubber was performed in latex stage with *tert*-butylhydroperoxide (TBHPO) / tetraethylenepentamine (TEPA) as an initiator, after purifying the rubber with urea and sodium dodecyl sulfate followed by centrifugation. After graft-copolymerization, the melting temperature of PSMA increased from 31.1 °C to 33.2 °C and the stress at break increased about three times as high as that of natural rubber. The mechanical properties were improved by the effect of stearyl group of PSMA.