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# Preparation and characterization of natural rubber dispersed in nano-matrix

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**Abstract**

Preparation of a model nano-matrix-dispersed polymer was investigated in terms of graft-copolymerization of deproteinized natural rubber latex with styrene, using *tert*-butyl hydroperoxide/tetraethylenepentamine as an initiator. The products were characterized by $^1$H-NMR spectroscopy and size-exclusion-chromatography after ozonolysis. The grafting efficiency of styrene was found to be more than 90% under the best condition of the graft-copolymerization. The morphology of the film specimens, prepared from graft-copolymers, was observed by transmission electron microscopy after staining the films with $OsO_4$. Natural rubber particle of about 0.5 μm in diameter was dispersed in polystyrene matrix of about 15 nm in thickness.

*Keywords:* Natural rubber; Nano-matrix; Graft-copolymerization

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## 1. Introduction

A polymeric material composed of thin matrix of several nano-meter in thickness and dispersoid of a micro-meter in diameter will be proposed to be a novel, multi-functional soft-material, namely 'nano-matrix-dispersed polymer'. It is expected to achieve both mechanical properties that depend upon quantity of a polymer in multi-component system and functional properties that come from matrix formed in the system. For instance, high strength and outstanding elasticity may be compatible with ionic or electric conductivity and oil resistance; hence, it may provide a superior functional-soft-material that ever appeared. In this regard, natural rubber, isolated from *Hevea brasiliensis*, is worthy of note as a component, because it is well-known to be the most excellent rubbery material, having outstanding mechanical properties while it is weak in oil-resistance, whether-resistance, ozone-resistance and so forth. To make up for the defects without loss of the outstanding properties, the concept of nano-matrix-dispersed polymer may be of importance, because natural rubber is improved with a small amount of functional polymer when the polymer forms matrix.

The nano-matrix-dispersed polymer may be prepared by graft-copolymerization of natural rubber in latex form, since the rubber consists mainly of *cis*-1,4-isoprene units [1], having carbon–carbon double bonds useful for graft-copolymerization. For instance, a dispersoid of about 1 μm in diameter in latex is covered with the polymer, when the graft-copolymerization proceeds on the surface of the dispersoid. If a thickness of the graft-copolymerized layer is less than 20 nm, a coagulation of the graft-copolymerized latex may result in nano-matrix-dispersed polymer. However, in the previous work [2–5], side reactions that occurred during the graft-copolymerization were reported to be due to non-rubber components present in natural rubber, such as protein [6]. Thus, removal of the protein would be the most important for the graft-copolymerization of natural rubber

Deproteinization of natural rubber has been made in latex form because almost all proteins exist on a surface of the rubber particle [7]. In the last decade, an enzymatic depronization of the latex in the presence of surfactant followed by washing was proposed to be effective to remove proteins from natural rubber [8], because whole proteins were decomposed with proteolytic enzyme and, then, they were removed. In fact, nitrogen content of the rubber was significantly reduced from 0.38 to 0.02 w/w%. Using the deproteinized natural rubber (DPNR), it may be possible to

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achieve not only high conversion but also high grafting efficiency of monomer for graft-copolymerization of natural rubber in latex form.

In the previous work [9], we investigated the graft-copolymerization of the DPNR swollen with styrene as a monomer, and found that *tert*-butyl hydroperoxide/tetraethylenepentamine was a suitable initiator for the copolymerization proceeding in the dispersoid. Both the conversion and grafting efficiency for DPNR were found to be higher than those for untreated natural rubber. In the present study, the graft-copolymerization of DPNR with styrene was carried out on a surface of the dispesoid. The model nano-matrix-dispersed polymer was prepared from the graft copolymer.

## 2. Experimental

Natural rubber latex used in the present study was a commercial high-ammonia natural rubber latex. Enzymatic deproteinization of natural rubber latex was carried out by incubation of the latex diluted to 30 w/w% dry rubber content (DRC) with 0.04 w/v% proteolytic enzyme (Novo Alcalase 2.0T) and 1 w/v% sodium dodecyl sulphate (SDS) for 12 h at 38 °C followed by centrifugation at 10,000 rpm. The cream fraction was redispersed in 1 w/v% SDS to make 30 w/w% DRC and centrifuged again to prepare DPNR latex. The DPNR latex was diluted with distilled water to make 10 w/w% DRC and SDS was added up to 0.1 w/v%.

Graft-copolymerization of the DPNR latex was carried out with styrene as a monomer, using *tert*-butyl hydroperoxide with tetraethylene pentamine as an initiator. The DPNR latex was charged with $N_2$ gas for 1 h at 30 °C. The initiator of $3.3 \times 10^{-2}$ mol/kg-rubber and monomer were added to the latex, respectively. The reaction was carried out by stirring the latex at about 400 rpm for 2 h at 30 °C. The unreacted styrene was removed by using a rotary evaporator under reduced pressure. The as-prepared graft copolymer (gross polymer) was obtained by dipping the glass tube into the reacted latex and dried under reduced pressure at ambient temperature for more than a week. The gross polymer was extracted with acetone/2-butanone 3:1 mixture in a Soxhlet apparatus for 24 h under nitrogen atmosphere in the dark and dried under reduced pressure for about one week, in which the removal of almost all free-polystyrene, isolated from natural rubber, was completed by the extraction for 24 h.

Ozonization was carried out by blowing an equimolar amount of ozone in ozonated oxygen through a 0.4 w/v% methylene chloride solution of the extracted graft-copolymer at −30 °C. Reductive degradation of the resulting ozonide was performed by reaction with lithium aluminum hydride ($LiAlH_4$) in diethyl ether followed by decomposition of residual $LiAlH_4$ with water. After reductive degradation, grafted polystyrene, thus isolated from graft copolymer, was dissolved in a small amount of chloroform. The chloroform solution was centrifuged, and the polymer was precipitated with methanol.

Measurements of molecular weight and molecular weight distribution of the rubbers were made with a TOSOH GPC, consisting of a TOSOH CCPD pump, RI-8012 Differential Refractometer and UV-8011 UV detector. The measurement was made at 30 °C and the flow rate of the mobile phase, THF, was 0.5 ml/min.

$^1$H-NMR measurements were carried out at 50 °C by a JEOL EX-400 NMR spectrometer at the pulse repetition time of 7 s.

The volume mean particle diameter was determined using a Coulter LS230 equipped with a small volume module.

Observation of morphology for the graft-copolymer was made with a transmission electron microscope (TEM), Hitachi H-800 at accelerating voltage of 120 kV. The ultra thin sections of the graft-copolymer were prepared by a Sovall Instruments MT6000 Ultra-microtome at a temperature lower than $T_g$ of NR. The thin sections were stained by $OsO_4$ after annealing the blends at 80 °C for 30 min.

## 3. Results and discussion

### 3.1. Characterization

Graft-copolymer was characterized through $^1$H-NMR spectroscopy. A typical $^1$H-NMR spectrum of the graft-copolymer, i.e. DPNR-St3, is shown in Fig. 1, in which signals characteristic of *cis*-1,4-isoprene units appeared at 1.76, 2.10 and 5.13 ppm, assigned to methyl, methylene and unsaturated methyne protons of isoprene units, respectively. Broad signals at 6–7 ppm were assigned to phenyl proton of styrene units, whose intensity was dependent on the feed of styrene as a monomer. Thus, we estimated a content of styrene units in the graft-copolymer and conversion of styrene from a ratio of signal intensity of phenyl to methyl proton and the feed of styrene. The estimated content of styrene units and conversion of styrene are shown in Fig. 2.

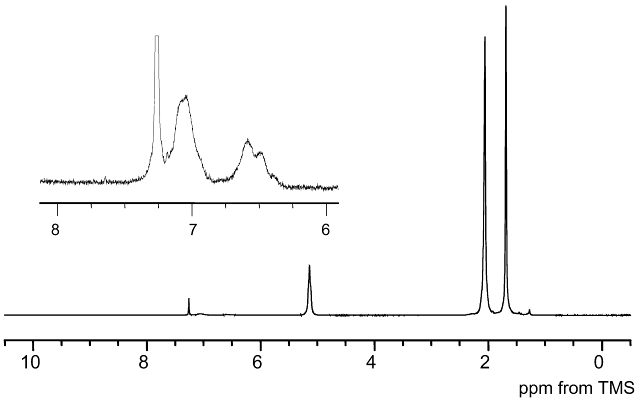

Fig. 1. A typical $^1$H-NMR spectrum for DPNR-St3.

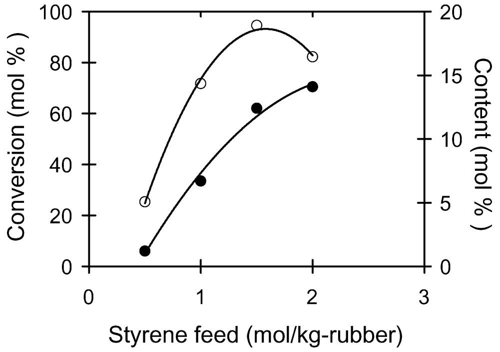

Fig. 2. Conversion and content of styrene for DPNR-St.

Both of the content and conversion were dependent on the feed of styrene. For instance, the higher the feed of styrene, the higher is the content of styrene units. On the other hand, for the conversion, a locus of convex curve was drawn with a maximum at styrene-feed of 1.5 mol/kg-rubber. This suggests that the most significant feed of styrene is 1.5 mol/kg-rubber in the case of graft-copolymerization of DPNR initiated by *tert*-butyl hydroperoxide of $3.3 \times 10^{-5}$ mol/g-rubber with tetraethylene pentamine at 30 °C.

To estimate the grafting efficiency, free polystyrene, which was a mixture present in the graft-copolymer, was removed by extraction with acetone/2-butanone 3:1 mixture. The grafting efficiency, $\nu$, was estimated as follows:

$$\nu = \frac{\text{Mole of polystyrene linked to natural rubber}}{\text{Mole of polystyrene produced during graft-copolymerization}}$$

The estimated value of grafting efficiency of styrene is shown in Fig. 3. The efficiency was significantly dependent on the feed of styrene and showed a maximum at 1.5 mol/kg-rubber feed of styrene, as in the case of conversion of styrene. This may be attributed to a deactivation and chain transformation of the radicals due to less and large amount of styrene, respectively. At 1.5 mol/kg-rubber feed of styrene, almost all polystyrene, thus produced, was proved to link up to natural rubber as a grafting polymer without homo-polymer.

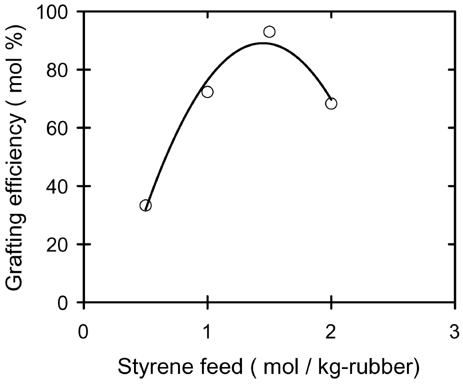

Fig. 3. Grafting efficiency for DPNR-St.

To characterize the grafting polymer, size-exclusion-chromatography after ozonolysis of DPNR-Sts was made, since all of carbon–carbon double bonds were cleaved by ozonization followed by reduction. Chromatograms for the products are shown in Fig. 4. A unimodal, symmetrical peak was shown in the chromatograms for all of the grafting polymers. From elution volume and height of the peak, number average molecular weight, $M_n$, weight average molecular weight, $M_w$, and polydispersity, $M_w/M_n$, were estimated, using a calibration curve drawn for polystyrene as a standard. Table 1 shows values of $M_n$, $M_w$ and $M_w/M_n$. The $M_n$ and $M_w$ were dependent on the feed of styrene, and they were the highest at 1.5 mol/kg-rubber feed of styrene, while $M_w/M_n$ was independent. The highest molecular weight for the grafting polymer, extracted from DPNR-St3, may be explained to be due to the most effective graft-copolymeriztion of styrene on DPNR.

### 3.2. Morphology and mechanical strength

TEM photographs for DPNR-St1, DPNR-St2, DPNR-St3 and DPNR-St4 are shown in Fig. 5, in which a gloomy domain is natural rubber and a bright domain is polystyrene. As for DPNR-St1, few bright domains was scattered in the gloomy matrix. As the feed of polystyrene increased, the bright domain segregated together to cover the gloomy spheres. To characterize the gloomy spheres, we estimated an average diameter of gloomy sphere for DPNR-St3 and DPNR-St4, and these are tabulated in Table 2. The average diameter of gloomy sphere was a similar to the volume mean particle diameter of the dispersoid present in natural rubber latex, which is about 0.7 μm in diameter. Since the

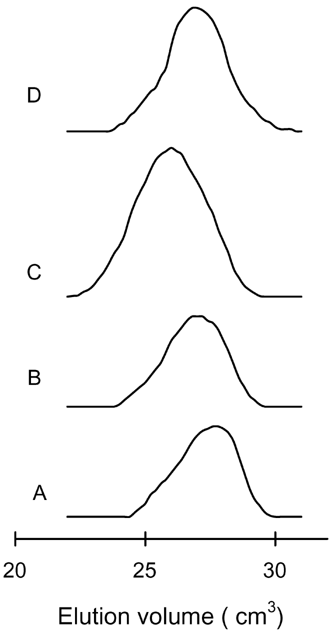

Fig. 4. Size exclusion chromatogram for polystyrene linking up to DPNR, measured after ozonolysis of (A) DPNR-St1, (B) DPNR-St2, (C) DPNR-St3 and (D) DPNR-St4, respectively.

Table 1
$M_n$, $M_w$ and $M_w/M_n$ for polystyrene linking up to DPNR

| Specimen | Feed of styrene (mol/kg-rubber) | $M_n/10^3$ | $M_w/10^3$ | $M_w/M_n$ |
|---|---|---|---|---|
| DPNR-St1 | 0.5 | 8.4 | 11.9 | 1.4 |
| DPNR-St2 | 1.0 | 10.8 | 15.4 | 1.4 |
| DPNR-St3 | 1.5 | 15.3 | 24.7 | 1.6 |
| DPNR-St4 | 2.0 | 9.7 | 14.8 | 1.5 |

Table 2
Average diameter and average thickness for DPNR-St3 and DPNR-St4

| Specimen | $D$ (μm) | $t$ (nm) |
|---|---|---|
| DPNR-St3 | 0.5 | 15 |
| DPNR-St4 | 0.6 | 25 |

$D$ : average diameter, $t$ : average thickness.

film specimens were prepared by coagulation of the latex, the gloomy sphere, observed in the photograph, may be attributed to the dispersoid present in the latex.

The thickness of the bright domain is also shown in Table 2. The thickness was about 15 nm for DPNR-St3, while it was about 25 nm for DPNR-St4. This bright domain would be a matrix, that is, a continuous phase. To confirm the fact that polystyrene was the matrix, a volume fraction of polystyrene for DPNR-St3 was estimated by image-analysis of the photograph. The estimated volume fraction of polystyrene was about 10 v/v% for DPNR-St3, which corresponded to 11 v/v%, estimated from styrene unit content shown in Fig. 2. This demonstrates that natural rubber particle of about 0.5 μm in diameter is dispersed in polystyrene matrix of about 15 nm in thickness. Since the grafting efficiency of styrene for DPNR-St3 is more than 90 mol%, as shown in Fig. 4, almost all polystyrene may link up to DPNR. Thus, a crack growth must be suppressed for DPNR-St3.

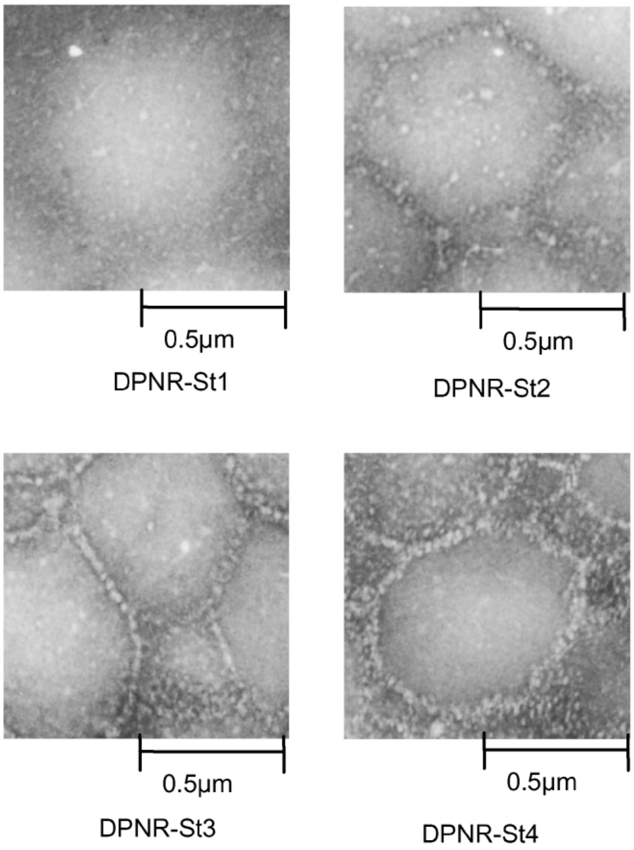

Fig. 5. TEM photograph for DPNR-St1, DPNR-St2, DPNR-St3 and DPNR-St4, respectively.

Fig. 6 shows stress–strain curve for unvulcanized graft-copolymers, that is, DPNR-St1, DPNR-St2, DPNR-St3 and DPNR-St4. A stress at strain of 1 increased as the styrene content increased, reflecting an increase in Young's modulus. On the other hand, the highest stress at break was shown for DPNR-St3. This may be attributed to not only nano-matrix of polystyrene but also the highest grafting efficiency. As the results, DPNR-St3 was proved to be the model nano-matrix-dispersed polymer.

## 4. Conclusion

Graft-copolymerization of DPNR was carried out with *tert*-butyl hydroperoxide/tetraethylenepentamine as an initiator. The highest conversion and grafting efficiency were achieved at styrene feed of 1.5 mol/kg-rubber to be 50% and 93 mol%, respectively. For DPNR-St3, natural rubber particle of about 0.5 μm in diameter was dispersed in polystyrene-matrix of about 15 nm in thickness. The stress at break for DPNR-St3 was found to be the highest, due to not only nano-matrix of polystyrene but also the highest grafting efficiency. It is, thus, concluded that the 'nano-matrix-dispersed polymer', having outstanding mechanical strength, is prepared in terms of graft-copolymerization of DPNR in latex foam.

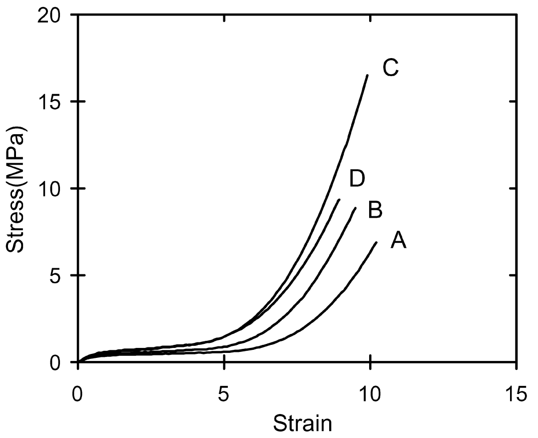

Fig. 6. Stress–strain curve for unvulcanized DPNR-St: A, DPNR-St1; B, DPNR-St2; C, DPNR-St3; D, DPNR-St4.

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