



Preparation and characterization of poly(stearyl methacrylate) grafted natural rubber in latex stage



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ABSTRACT

An attempt to prepare graft copolymer of natural rubber, NR and poly(stearyl methacrylate), PSMA, was made to improve mechanical properties of NR, 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 deproteinized natural rubber (DPNR) was performed in latex stage with *tert*-butylhydroperoxide (TBHP)/tetraethylenepentamine (TEPA) as an initiator, after purifying the rubber with urea and sodium dodecyl sulphate followed by centrifugation. The optimal conditions for the graft-copolymerization were determined as follows: 3.3×10^{-2} mol/kg-rubber of initiator, 1.5 mol/kg-rubber of monomer and 30 w/w% of dry rubber content (DRC). The conversion and grafting efficiency of SMA were 95 mol% and 60 mol%, respectively. After graft-copolymerization, the melting temperature of PSMA increased from 304.1 K to 306.2 K. The morphology showed that the DPNR particles, which were about 1 μm in average diameter, were well dispersed in PSMA nanomatrix. The stress at break increased about three times, i.e. 13 MPa, as high as that of DPNR. The increase in the mechanical properties was promoted by the nucleating effect of stearyl group of PSMA.

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1. Introduction

Saturated fatty acid such as stearic acid is well known to play an important role as a nucleating agent in the crystallization of polymers. For instance, the crystallization of *cis*-1,4-polyisoprene is markedly promoted by the saturated fatty acid, since lattice mismatch between the saturated fatty acid and the *cis*-1,4-polyisoprene is very small on the basis of the same crystallography, i.e. orthorhombic [1–3]. A good pair of crystal planes is 001 plane of natural rubber (NR) and 110 plane of stearic acid: that is, 0.889 and 1.246 nm for NR [3] and 0.89 and 1.25 nm (0.25 nm \times 5) for stearic acid [4]. However, the nucleating effect of fatty acid on the strain-induced crystallization is considered to be small due to the fringed micelle structure of the strain-induced crystal. Therefore, it is necessary to prove the nucleating effect of fatty acid on the strain-induced crystallization of *cis*-1,4-polyisoprene, since it may be the origin of the outstanding mechanical properties of the polymer.

The nucleating effect of fatty acid on the strain-induced

crystallization is quite difficult to investigate, since the strain-induced crystallization occurs too rapidly [5,6]; that is, the nucleating effect is negligibly small. Therefore, an elaborate study is required to prove the nucleating effect on the strain-induced crystallization. In previous works, the effect of fatty acid on the strain-induced crystallization of NR in droplets, which were dispersed in styrene-butadiene rubber (SBR), was investigated, since the crystallization of the rubber was significantly suppressed in the droplets [7]. The tear energy was measured by the changing temperature and tear rate, and it was related to the strain-induced crystallization. The tear energy decreased after the removal of fatty acid [8], whereas it recovered to the original level after stearic acid was added to the rubber [9–11]. However, little nucleating effect was found in the strain-induced crystallization of synthetic *cis*-1,4-polyisoprene (IR). The difference in the nucleating effect between NR and IR may be attributed to the presence of the linked fatty acid of NR, which was reported in previous papers [12].

The chemical linkage between fatty acid and *cis*-1,4-polyisoprene, i.e. NR, may be formed by the graft-copolymerization of a suitable monomer, such as stearyl methacrylate (SMA) onto the rubber; that is, the stearyl groups may gather to form crystallites, and poly-methacrylate may link the crystallized stearyl groups to NR. The graft

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copolymerization must be carried out in the latex stage, since the stearyl groups are required to cover the NR particles, as reported in previous papers, whereby phospholipids and proteins are ensured to cover the NR particles [13]. In this case, it is necessary to achieve a high grafting efficiency to prepare the NR model in order to investigate the nucleating effect of the crystallized stearyl group on the strain-induced crystallization and the mechanical properties of NR.

There have been a few studies on the graft-copolymerization of stearyl methacrylate onto NR in solution. For instance, the graft-copolymerization of various alkylmethacrylates was performed in a toluene solution of NR and IR, respectively [14,15]. The grafting efficiency of SMA, in this case, was reported to be about 40 mol%. The low grafting efficiency was explained to be due to a chain transfer of radicals in the solution [16]. The grafting efficiency remained unimproved, even though the graft-copolymerization of SMA was carried out in the presence of divinylbenzene in toluene and chloroform solutions of the rubber [17]. Thus, in order to enhance the grafting efficiency, it is necessary to change the nature of the solution from hydrophobic to hydrophilic. However, no attempt has been made to perform the graft-copolymerization of SMA onto NR in water.

The strategy to prepare the NR model may be concerned with the method to increase the grafting efficiency of SMA in latex stage. It is necessary at least to remove the proteins from NR, since the proteins are known to be a radical scavenger. According to the previous work, high grafting efficiency was achieved for graft-copolymerization of vinyl monomers on NR when using purified latex, i.e. deproteinized natural rubber (DPNR) latex as a starting material instead of HANR latex [22]. A novel technique was developed to purify the NR in latex stage; that is, the proteins were removed from the NR, using urea as a denaturant in the presence of sodium dodecyl sulfate (SDS) [18,19]. After the removal of the proteins, the graft-copolymerization of SMA onto NR may be performed with an organic redox initiator in latex stage. In the previous work, a high conversion and high grafting efficiency were achieved under the optimal condition for the graft-copolymerization of styrene [20,21], methyl methacrylate [22], acrylonitrile [23], vinyltriethoxysilane [24,25] and so forth. The nanomatrix structure was formed in the resulting products, as in the case of NR. Therefore, the NR model may be prepared from NR through the graft-copolymerization of SMA in latex stage with an organic redox initiator.

In the present study, an attempt was made to prepare the NR model by the graft-copolymerization of SMA onto DPNR in latex stage in the presence of *tert*-butylhydroperoxide (TBHP)/tetraethylenepentamine (TEPA) as an organic redox initiator. The factors influencing the graft-copolymerization of SMA were investigated to determine the optimal conditions: for instance, the dry rubber content (DRC), the initiator concentration and monomer concentration. The resulting polymers were then characterized by particle size analysis, Fourier transform infra-red (FT-IR) spectroscopy, and differential scanning calorimetry (DSC). The images of graft-copolymers were observed by transmission electron microscope (TEM). The mechanical properties, such as tensile strength was measured to confirm the effect of the crystallized stearyl groups on the strain-induced crystallization of the NR model.

2. Materials and methods

2.1. Materials

High ammonia natural rubber (HANR) latex was purchased from Golden Hope Plantation, Malaysia. The SDS surfactant, TBHP - 68% and TEPA were from Kishida Chemicals (Japan) while the urea, potassium persulfate (KPS) and benzoyl peroxide (BPO) were from Nacalai Tesque (Japan). The SMA monomer was from Tokyo Kasei

Company (Japan). The α , α' -azobisisobutyronitrile (AIBN) was from Kanto Chemical Co. Inc. (Japan). The solvents used, such as acetone, tetrahydrofuran (THF), methanol, and toluene were from Nacalai Tesque (Japan).

2.2. Removal of proteins from NR latex

The HANR latex was diluted with distilled water from 60 to 30 w/w% of dry rubber content (DRC). The removal of the proteins from the NR was carried out by the incubation of the latex with 0.1 w/w% urea in the presence of 1 w/w% SDS at 303 K. The latex was then, centrifuged (ca, 10,000 g) 3-times at 288 K for 30 min. The cream fraction was collected after the second and third centrifugation and was re-dispersed in the solution with 0.5 w/w% SDS and 0.1 w/w% SDS, respectively. The procedure to remove the proteins is shown in Fig. 1. Prior to the graft-copolymerization, the DRC and the amount of SDS in the DPNR latex were adjusted to 30 w/w% and 0.1 w/w%, respectively.

2.3. Preparation of graft-copolymer

The graft-copolymerization of SMA onto DPNR was carried out in latex stage using various initiators. DPNR latex of 200 g with 20 w/w% DRC and 0.5 w/w% SDS was purged with N_2 gas for 1 h. Then, the initiator and SMA were added in turn to the latex. The graft-copolymerization was performed for 8 h with continuous stirring at 200 rpm under N_2 atmosphere at 333 K in a water bath. The unreacted SMA was removed with a rotary evaporator under reduced pressure for about 30 min at 353 K. The reacted latex was poured into a petri dish and dried in an oven at 323 K for about 2 days (until dry) and in a vacuum oven for 3 days at 323 K. The reacted rubber was subjected to Soxhlet extraction under nitrogen atmosphere in the dark for 24 h to remove homopolymer. The grafted rubber was obtained after the extraction and dried at 323 K. Then, the grafted rubber was characterized accordingly. The procedure for the graft-

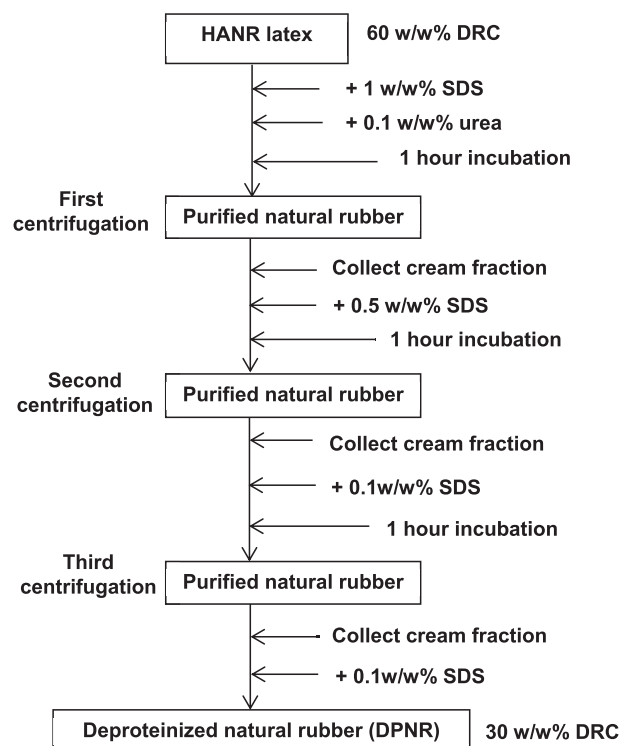


Fig. 1. Removal of proteins from NR latex.

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