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Material properties

A model study on effect of glucose on the basic characteristics and physical properties of natural rubber

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ABSTRACT

Glucose at various concentrations was incorporated into sugar free purified natural rubber (PNR) latex to model the effect of carbohydrate on the basic characteristics and physical properties of natural rubber (NR). PNR samples treated with various concentrations of glucose were characterized for the basic properties of unvulcanized NR, i.e., gel content, molecular weight distribution and Mooney viscosity to evaluate the effect of sugar on these parameters. In addition, the effect of glucose on the physical properties of vulcanizates derived using sulfur and peroxide vulcanization was investigated. Glucose was shown to affect the viscosity of unvulcanized NR and the discoloration of vulcanized NR. Moreover, glucose was found to have a strong effect on crosslink density, as well as tensile and dynamic properties of sulfur vulcanizates, while those properties of peroxide vulcanizates was not much affected by glucose.

1. Introduction

Over 2000 species of plants can produce aqueous dispersions or latices of rubber hydrocarbon. However, rubber from *Hevea brasiliensis*, widely known as natural rubber (NR), has been established as a practically essential rubber source due to its high yield of rubber along with excellent properties of the rubber product. NR latex is present as a colloidal dispersion with 94% *cis*-1,4 polyisoprene and about 6% non-rubber components such as proteins, lipids, carbohydrates and inorganic salts in an aqueous serum [1]. NR exhibits properties that are superior to other naturally occurring polyisoprenes and synthetic analogues such as high green strength [2,3] in the un-vulcanized state, high tensile strength [4], high crack growth resistance [5,6] and low heat buildup in the vulcanizate. A long standing question is why only NR exhibits these outstanding properties. Some biomolecules, particularly proteins and lipids, are believed to bring about the characteristic network structure as well as the outstanding properties of NR. The fundamental structure of NR consists of ω-terminal, two *trans*-1,4 isoprene units connected with a long-chain of *cis*-1,4 polyisoprene units andan α-terminal group containing mono- or di-phosphate linked with phospholipids. The ω-terminal contains a modified dimethylallyl group that associates with proteins through intermolecular hydrogen bonding. Thus, the interaction between proteins and lipids at terminal ends of the rubber molecules allows for the formation of the naturally occurring three-dimensional network that is a characteristic structure in NR [7,8]. This naturally occurring network was proposed to be the origin of strain-induced crystallization in unvulcanized NR that contributes to its very high green strength [9]. Furthermore, proteins and lipids in NR have long been considered to be essential components governing several properties of NR, such as mechanical [10,11] and ageing properties [12–14].

However, carbohydrates are also present in NR latex consisting of quebrachitol (1-methyl inositol), glucose,

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fructose, galactose, pentose and sucrose [15–17]. Currently, there is no evidence of the effect of carbohydrate on properties of NR. In this study, the role of carbohydrate on the basic characteristics and physical properties of NR was examined for the first time. Purified NR (PNR) latex lacking endogenous sugar was incorporated with glucose as a model of naturally occurring sugar. The reasons for using glucose are based on the fact that glucose is one of endogenous sugars obtained from NR latex. It is the most common carbohydrate as a simple sugar (monosaccharide) involved in the biosynthesis pathway of latex from a *Hevea* tree and other plants [18,24].

The aim of present work is to investigate the effect of carbohydrate on the basic characteristic of unvulcanized NR, i.e., gel content, molecular weight distribution and Mooney viscosity, as well as the physical properties of both sulfur and peroxide vulcanizates. These studies should provide novel information for improving the properties of NR.

2. Experimental section

2.1. Materials

Fresh NR (FNR) latex (ca. 30% dry rubber content (DRC)) purchased from Thai Rubber Latex Co. Ltd was freshly tapped from *Hevea* trees and preserved with 0.6% of NH_3. All chemicals were purchased from Sigma-Aldrich and used without further purification. Analytical and HPLC grade solvents were purchased from RCI Labscan.

2.2. Preparation of PNR treated with various concentrations of glucose

PNR treated with various concentrations of glucose was prepared by the following method. FNR latex was stabilized with 1% w/v of sodium dodecylsulphate (SDS), followed by centrifugation at 13,000 rpm for 30 min. The cream fraction was dispersed in distilled water and this procedure was repeated 3 times. The resulting latex, termed PNR latex, was adjusted to 30% DRC and then incorporated with 0, 0.5, 1, 2 and 3 parts of glucose per hundred of rubber (phr) at room temperature (RT) with stirring for 1 h. Each preparation of rubber latex was cast into thin film and dried at 70 °C for 24 h.

2.3. Preparation of vulcanized samples

Both sulfur and peroxide vulcanization systems were used in these experiments. Sulfur vulcanization was based on a sulfur-accelerator recipe containing zinc oxide (6 phr), stearic acid (0.5 phr), *N*-cyclohexylbenzothiazole-2-sulfenamide (CBS) (0.5 phr), and sulfur (3.5 phr). The peroxide vulcanization contains only dicumyl peroxide (DCP) (1 phr). Vulcanized rubber samples were prepared by mixing the PNR treated with various concentrations of glucose and rubber chemicals in an internal mixer (Haake Plasticorder®) at 40 °C for 15 min with a rotor speed of 40 rpm. The optimum cure time (t_{c90}) used in preparation of vulcanized samples was the time required for the torque of the rheometer to increase to 90% of total torque at 155 °C.

2.4. Characterizations

The composition of sugar in latex samples was analyzed by high-performance liquid chromatography (HPLC) (Waters® e2695) with refractive index detector (Waters® 2414). Shodex™ Asahipak NH2P-50 4E was used as a column. The mixture of acetonitrile and water was used as mobile phase with a flow rate of 1 mL/min at 40 ± 0.01 °C. For a quantitative analysis, a six-point calibration curve was made for each sugar.

The PNR samples and the brownish products were characterized by Fourier transform infrared (FTIR) measurements (Jasco FT/IR 4100). The spectra were obtained from an average of 100 scans.

The nitrogen content of rubber samples was determined using a LECO Nitrogen Analyzer (Model FP 528) with a detection limit of 0.001%. Rubber samples of approximately 0.25 g were accurately weighed and used in each of the triplicate analyses.

Gel content was determined by swelling measurements. A small piece of each rubber sample was dissolved in dried toluene at 0.1% w/v without stirring and sunlight for one week at RT. The solution was then centrifuged at 10,000 rpm for 30 min to separate the gel fraction. The weight of the gel fraction against the total sample weight was determined as percent gel content.

The molecular weight distribution (MWD) of rubber samples was determined by size exclusion chromatography (Jasco-Borwin) with two crosslinked polystyrene gel columns with exclusion limits of 2.0×10^7 and 4×10^5. The refractive index was utilized to detect NR species. A 0.05% w/v rubber solution was prepared by dissolving rubber samples in tetrahydrofuran (THF) (High performance liquid chromatography grade) and filtered through a Millipore prefilter and 0.45 μm membrane filter (Alltech). THF was used as the eluent with a flow rate of 0.5 mL/min at 35 ± 0.01 °C. Calibration was carried out using synthetic a poly(*cis*-1,4-isoprene) standard (Polymer Standard Service GmbH, Germany).

Mooney viscosity (ML1 + 4) was determined using a TECHPRO Mooney Viscometer based on ISO 289-1. The temperature of die and groove rotors was set at 100 °C and rubber samples were pre-heated for 1 min followed by a 4 min period of continuous shear at a strain rate of about $1\ s^{-1}$ to measure the Mooney viscosity. The decay of torque was subsequently measured after stopping the rotor.

Analysis of glass transition temperature (T_g) for rubber samples was performed using differential scanning calorimetry (Perkin-elmer DSC7). Rubber samples were cut into small pieces (ca. 1 mm^3) and placed in a standard aluminum pan without mechanical stress with a heating rate of 10.0 °C/min, from −70 °C to 120 °C. This cycle was followed by cooling from 120 °C to −70 °C with a rate of 10.0 °C/min.

Non-enzymatic browning reaction products of vulcanizates were monitored using a UV–VIS spectrophotometer (Jasco V-530). Small pieces of samples were swollen in toluene at RT for 24 h and then refluxed in distilled water at 10% w/v for 48 h at 80 °C with stirring to extract the water-soluble brownish compound. After that, water fractions were dialyzed through 0.45 μm of nylon dialysis