EFFECT OF PROTEIN ON PROPERTIES OF GLUTARALDEHYDE CROSSLINKED NATURAL RUBBER

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Abstract

In this work, Protein-free natural rubber was prepared by incubation of High ammonia natural rubber with urea, sodium dodecyl sulfate and acetone. This manuscript presents a continuation work a sample system to vulcanized high ammonia natural rubber (HANR) and protein-free natural rubber (PFNR) using glutaraldehyde as a cross-linking agent. Cross-linked rubber has been obtained by reacting natural rubber with pentane-1,5-diylidenediamine formed from the reaction between glutaraldehyde and ammonia. The cross-link density of the vulcanized rubber was determined from swelling experiments in toluene. The total nitrogen contents determined by means of Kjeldalh, were 0 wt% for PFNR prepared with urea acetone in the presence of SDS. Thus, be concluded that most proteins presence in natural rubber are attached just on the surface of the rubber particles with physical interactions, since all the proteins are removed by deproteinization with urea and acetone in the presence of SDS after centrifugation.

Keywords: protein-free natural rubber, nitrogen content, protein content, kjeldahl's method, glutaraldehyde, FT-IR, DSC

1. Introduction

Natural Rubber is an elastic substance obtained from the latex sap of trees, especially those trees which belong to the genera Hevea and Ficus. Technically speaking, natural rubber is an elastomer or an elastic hydrocarbon polymer. Natural rubber is one of the types of rubber that also include vulcanized rubber which is finished into a variety of rubber products. Natural rubber is also known by the names of India rubber, gum elastic. Natural rubber is extracted as a latex or 'milk', viz., an aqueous emulsion or dispersion of the natural polymer (~96 wt% of solids) and other substances, such as proteins (~1 %), lipids (~3 %) and traces of potassium, magnesium and copper. [1]

Removal of proteins from natural rubber is one of the important subjects in natural rubber science and technology, since some proteins present in the rubber causes a type I allergy with immunoglobulin E. The removal of the proteins has been, in most cases, performed in latex stage, since the proteins exist on a surface of natural rubber particles dispersed in water. [2]
In general, there are three main types of curing agents for rubber namely, sulphur, peroxide and phenolic compounds. Sulphur vulcanization is the most popular system for general purpose rubbers because it provides excellent properties together with low cost. However, this system needs high temperature together with various chemicals, activators and accelerators. [3]

In this work, an attempt has been made to optimize the amount of glutaraldehyde and ammonia to obtain a vulcanized natural rubber with better properties. High ammonia natural rubber (0.9 wt%) ammonia latex with amounts 12 mL of 10 wt% GA were used to prepare natural rubber vulcanizates. The mechanical and thermal properties and of the prepared elastomeric samples were investigated.

2. Experimental

2.1 Materials

High ammonia natural rubber (HANR) latex with approximately 60 % total solid content and urea (Nacalai Tesque Inc., 99.0%) and sodium dodecyl sulfate (SDS) (Chameleon Reagent., 98.0%) and acetone (Nacalai Tesque Inc., 95.5%) and 10% glutaraldehyde (GA) and ammonia (solution 28%) and toluene

2.2 Preparation of protein-free natural rubber (PFNR) latex

Natural rubber latex used in this study was commercial high ammonia natural rubber (HANR) latex 61.66 %TSC. The HANR latex was incubated with 0.1 wt% urea in the presence of 1.0 wt% sodium dodecyl sulfate (SDS) and 2.5 wt% acetone at room temperature for 1 hour followed by centrifugation at 30 min, at 9000 rpm. The cream fraction was redispersed in 0.5 wt% SDS solution and 2.5 wt% acetone and it was centrifuged again. Then the cream fraction was washed twice with 0.5 and 0.1 wt% SDS solution, respectively. [2]

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2.3 Determination of Alkalinity

Place approximately 5 g of latex into a glass weighing bottle of approximately 10-cm3 capacity, having a ground glass cap, and weigh to the nearest 1 mg. Pour the specimen into a beaker containing approximately 300 cm3 of distilled water, restopper quickly to prevent loss of ammonia, and set aside for reweighing. The specimen mass is equal to the difference between the two weighings. The transfer of the sample to the beaker shall be done in such a way that no latex runs down the outside of the weighing bottle**.** [3]

Alkalinity the free alkali content of the latex is determined volumetrically by titrating a known amount of latex which is diluted with water against standard hydrochloric acid using methyl red indicator

$$\text{Alkalinity (\%)} = \frac{1.7 \times N \times V}{W} \qquad (1)$$

where N = Normality of acid, V = Volume of acid and W = Weight of latex

2.4 Preparation of vulcanized natural rubber

A 10% glutaraldehyde solution was prepared by diluting in distilled water and added slowly to natural rubber latex with suitable amounts. The volume of natural rubber latex (60% dry rubber content) used was 30 mL throughout mixture. Then the solution was transferred to Petri dish and kept in hot- air oven at 45°C for 48 h. These casted samples were then peeled out, washed with distilled water, and dried in the oven. Samples were prepared with 10% glutaraldehyde. The resulting vulcanized rubber samples were then introduced for characterization.

2.4 Mechanical testing

The thermal properties of the samples was performed according to the differential scanning calorimetry (DSC) test. The protein content and nitrogen content of the samples performed according to the Kjeldalh method. And determination of peak protein by fourier-transform infrared spectroscopy (FTIR)

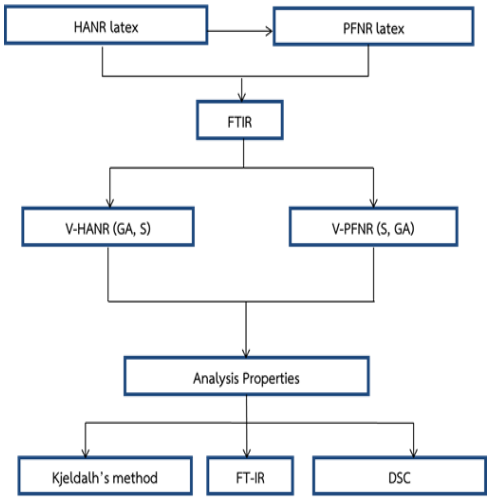

Fig. 1 Plan of this work3. Results and Discussion

3. Results and Discussion

3.1 Nitrogen content, water soluble protein

Total nitrogen content HANR and PFNR which is proportional to the amount of proteins present in the rubber latex., is show in Table 1. The total nitrogen content of HANR decreased from 0.45 wt% to 0.00 wt% after incubation with urea, SDS and acetone for 1 hours at room temperature. It may demonstrate the most proteins present in natural rubber latex are attractive forces, can be detached with urea.

The amount of water solution protein content of HANR was 4,215 µg/g which was very much higher than those of PFNR (0 µg/g) respectively. The result confirm that urea treatment is quite effective to prepare protein free rubber latex.

Table 1 Total nitrogen content, water soluble protein

Sample	Nitrogen content (wt%)	Water soluble protein (µg/g)
HANR	0.45	4,215
PFNR	0.00	0.00

3.2 Fourier-transform infrared spectroscopy (FT-IR)

Modern infrared spectrometers are usually Fourier transform infrared (FTIR) spectrometers. Their name originates from the fact that the detector signal of these spectrometers is related by a Fourier transformation to the measured spectrum. The heart of an FTIR spectrometer is an interferometer, like the Michelson interferometer [4]

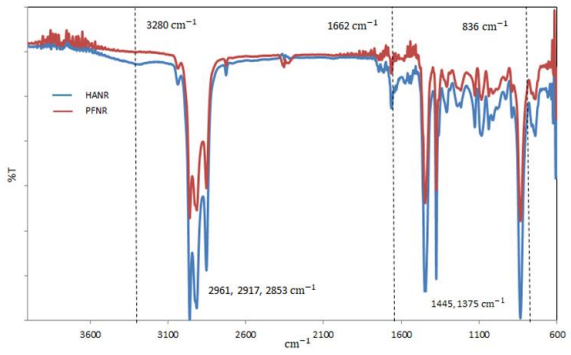

Fig. 2 Peaks of HANR and PFNR

A large panel of Natural Rubber (NR) samples was characterized using Fourier Transform Infrared (FT-IR) spectroscopy in Attenuated Total Reflection (ATR) configuration. The resulting PFNR was characterized by FT-IR spectroscopy. FT-IR spectra for HANR and PPNR prepared with urea and 2.5 wt% acetone, ranging from 3200 to 3400 Type equation here. The peak at 3280

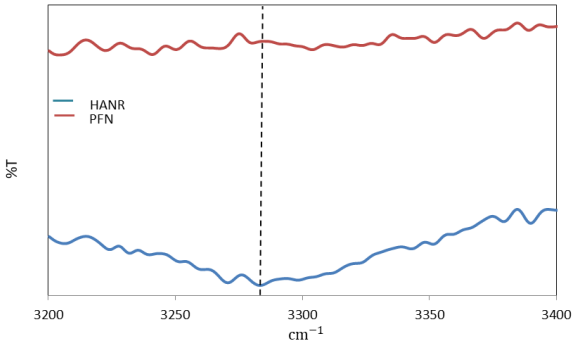

Fig. 3 Structure characteristics of HANR and PFNR after removal of protein

3.3 Differential scanning calorimetry

The Differential Scanning Calorimeter (DSC) detects changes in temperature and heat flow during thermal transitions of material by placing sample material in a furnace programmed with rising, declining, or constant temperatures and purged with constant ambient gas (liquid nitrogen). [3]

Table 2 Glass transition temperature and Specific heat capacity of NR

Sample	T_g (°C)	C_p (mJ/deg.mg)
HANR	72.1756	0.452404
GA-HANR	-71.7305	0.446453
PFNR	-72.1969	0.477779
GA-PFNR	-71.5557	0.407956

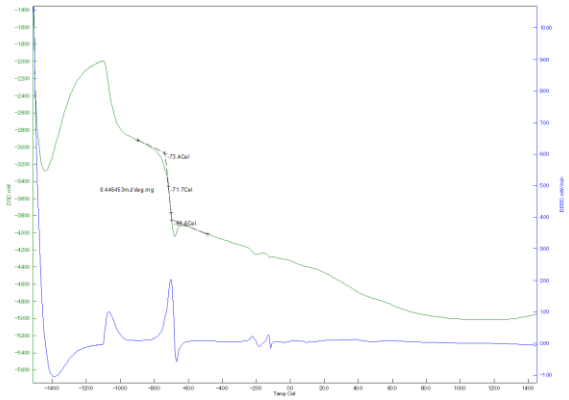

Fig. 4 Example graph of a DSC of HANR

4. Conclusion

Removal of protein from natural rubber latex using urea, SDS and acetone treatment was proved to be effective method to prepare vulcanized PFNR rapidly and efficiently. It was confirmed by nitrogen content and amount of charge even after remove protein. From the present study for vulcanized PFNR by using glutaraldehyde as a cross-linking agent. Cross-linked rubber has been obtained by reacting natural rubber with pentane-1,5-diylidenediamine formed from the reaction between glutaraldehyde and ammonia.

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