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# RADIATION GRAFT COPOLYMERIZATION OF A MIXTURE OF STYRENE AND *n*-BUTYL ACRYLATE ON NATURAL RUBBER LATEX

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## ABSTRACT

The radiation graft copolymerization of a mixture of styrene (St) and *n*-butyl acrylate (NBA) monomers on natural rubber (NR) latex has been studied. An irradiation dose of about 18 kGy was needed to attain a conversion of about 80%. The tensile strength of the grafted NR film increases with increasing irradiation dose. A film tensile strength of about 155 $kg/cm^2$ was attained by irradiation of a mixture of St, NBA, and NR latex with a dose of about 14 kGy. At low concentrations of monomer in the latex, the Mooney viscosity of the film increases with increasing irradiation dose. At higher monomer concentration, grafting and homopolymerization proceed more favorably than crosslinking, and thus the Mooney viscosity decreases with increasing dose. Thermal analysis of the film showed that the grafted NR was more heat resistant than ungrafted NR.

## INTRODUCTION

Radiation grafting of monomers on natural rubber (NR) latex has been studied by a number of investigators, but this technique of grafting was only successfully applied to grafting of certain monomers that are soluble in NR [1,2].

A number of monomers, such as acrylonitrile (AN) and *n*-butyl acrylate (NBA), are found to be difficult to dissolve in NR, and hence the grafting reaction is difficult to achieve. To make an insoluble monomer more soluble in NR, it must be mixed with another, more easily soluble monomer. For example, a mixture of styrene (St) and NBA monomer is expected to be easily soluble in NR. The possible irradiation products of a mixture of monomers and NR latex are crosslinked NR, grafted NR, and homopolymer.

Experimental results showed that the tensile strength of ST-NR graft copolymer vulcanizates was much higher than that of ungrafted NR vulcanizates, but the permanent sets were poorer [3]. On the other hand, the tensile strength of NBA-NR graft copolymer vulcanizates was poorer than that of ungrafted NR vulcanizates, but the permanent set was much better [4]. It is expected that St-NBA-NR graft copolymer will show better physical properties than ungrafted NR.

This paper presents experimental results for radiation grafting of a mixture of St and NBA monomers on NR latex.



## EXPERIMENTAL

Concentrated NR latex was obtained from Pasir Waringin Estate, West Java. The dry rubber content of the latex was about 60%, and the diameter of the NR particles was 0.5-1.0 μm, as measured by scanning electron microscopy. The NR particles form a number of small aggregates, each of which consists of hundreds of NR particles.

St and NBA monomers were purified by distillation under reduced pressure. A mixture of St and NBA monomers (weight ratio, 1:1) was emulsified, with Tween 20 as the emulsifier, to give the composition: 30 wt parts monomers, 70 water, and 3 Tween 20. The emulsion was mixed with NR latex to give 10, 20, 30, and 40 phr (per hundred rubber) of monomers in NR latex. The mixture was poured into glass tubes of about 150 mL volume, and irradiated at a dose rate of 4 kGy/h. The degree of conversion of monomer to polymer was determined gravimetrically by measuring the amount of monomer before irradiation and the total solids before and after irradiation. The total solids content was determined according to ASTM D-1076-77.

Films of St-NBA-NR graft copolymer were prepared by pouring the grafted latex onto a glass plate and drying at room temperature. Physical properties of the rubber film were determined as follows: Mooney viscosity by Shimadzu Mooney viscometer, according to ASTM 1646-1972; tensile strength, modulus, elongation at break, and tear strength with an Instron Tester Model 1122.

Grafted NR vulcanizates were prepared by mixing sulfur vulcanizing ingredients and the grafted film on a rubber mill and curing at 100°C for 60 min.

A Panoramic $^{60}Co$ irradiator of about 35 kCi was used to irradiate the sample. A Shimadzu infrared spectrophotometer, IR-435, was used to determine the IR spectra of the rubber films. A Shimadzu DT-30 thermal analyzer was used to determine the thermal behavior of grafted NR, and a JEOL scanning electron microscope JSM-T300 was used to study the form and size of the latex particles.

## RESULTS AND DISCUSSION

As Table 1 shows, the conversion increases with increasing irradiation dose and amount of monomer in the NR latex. A mixture of St and NBA is expected to be easily soluble in NR, and therefore, graft copolymerization should take place easily. The experimental results are in agreement with this theory. The increase in conversion with increasing monomer concentration may be due to the effect of dilution of the latex by mixing with a larger amount of monomer emulsion.

Scanning electron micrographs of grafted NR show that there are a number of particles with diameters of around 0.2 $\mu$m, which may be poly-St-NBA particles. It appears that polymerization takes place not only in the interior of the particles but also on the outside.

The infrared spectrum of St-NBA-NR graft copolymer film which had been extracted with acetone (Fig. 1) shows an absorption at 1727 $cm^{-1}$, which may be due to the C=O stretching vibration of the acrylic groups.

The latex viscosity increases with increasing irradiation dose or conversion (Table 2) as the solids content of the latex increases.

The modulus and tensile strength of the graft copolymer film increase with increasing conversion or irradiation dose (Table 2). Elongation at break is found not to differ much, but the permanent set decreases with increasing conversion. Even so, the permanent set of the graft copolymer film is still much poorer than that of sulfur-vulcanized NR film, which usually is less than 5%.

For monomer concentration of about 20 phr or less before irradiation, the Mooney viscosity of the grafted film increases monotonically with increasing irradiation dose; but for monomer concentration of 30 phr or more, it goes through a maximum (Table 1). The decrease in the Mooney viscosity after the maximum may be due to an increase in the true grafting and homopolymerization (Table 1).

TABLE 1. Influence of Irradiation Dose and Monomer Concentration on Conversion and Mooney Visc
of the Grafted NR Film[a]

| Irradiation | Conversion, % | | | | Mooney viscosity (ML 1 + 4) | | | |
|---|---|---|---|---|---|---|---|---|
| dose, kGy | 10 phr[b] | 20 phr | 30 phr | 40 phr | 10 phr | 20 phr | 30 phr | 40 |
| 0 | 0 | 0 | 0 | 0 | 106.6 | 103.9 | 98.6 | [illegible] |
| 2 | 7.7 | 3.2 | 1.8 | 3.0 | 123.3 | 121.1 | 112.8 | [illegible] |
| 4 | 18.6 | 17.1 | 17.5 | 24.7 | 137.5 | 135.2 | 122.5 | [illegible] |
| 6 | 33.8 | 31.6 | 28.8 | 44.2 | 146.0 | 143.2 | 128.1 | [illegible] |
| 8 | 41.8 | 43.7 | 50.6 | 60.0 | 152.0 | 147.6 | 124.0 | [illegible] |
| 10 | 39.8 | 66.6 | 59.7 | 60.9 | 155.3 | 150.7 | 121.6 | [illegible] |
| 12 | 49.1 | 58.8 | 68.5 | 75.7 | 158.0 | 150.0 | 118.4 | [illegible] |
| 14 | 53.5 | 65.5 | 73.9 | 79.5 | 161.5 | 150.9 | 114.9 | [illegible] |
| 16 | 57.8 | 68.7 | 77.4 | 83.9 | 163.6 | 151.9 | 110.5 | [illegible] |
| 18 | 67.7 | 73.0 | 80.1 | 86.1 | 166.8 | 150.3 | 106.6 | [illegible] |

[a]Irradiation dose rate, 4 kGy/h.

[b]Concentration of St-NBA monomer in the NR latex.

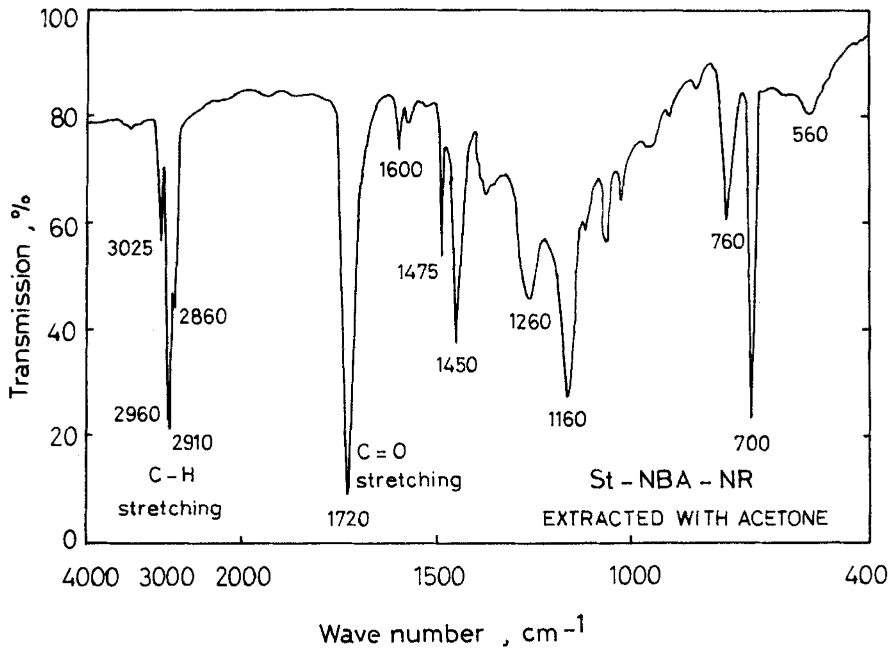


FIG. 1. Infrared spectrum of St-NBA-grafted NR that has been extracted with acetone.



Grafting and homopolymerization will take place more readily at the higher monomer concentration. Conversely, crosslinking will be easier at the lower monomer concentration. Our experimental results are in agreement with this: Increasing degree of grafting and homopolymer will decrease the Mooney viscosity, and an increase in the crosslink density should increase the Mooney viscosity of the grafted film.

The fraction of grafted NR film that is soluble in acetone increases with increasing irradiation dose or conversion (Table 3). The acetone-soluble fraction consists mainly of NBA homopolymer and other materials in the original NR that are soluble in acetone. The infrared spectrum of the acetone-soluble fraction shows that there is no poly-St in this fraction. Styrene homopolymer is known to be insoluble in acetone. It was found that on irradiation of a latex with 40 phr of St-NBA monomer, most of the reaction is homopolymerization. It can be concluded that the decrease of Mooney viscosity of the grafted film may be due to an increase in the homopolymer content in the grafted NR.

TABLE 2. Physical Properties of Grafted NR Latex and Film[a]

| | | | Film properties | | | |
|---|---|---|---|---|---|---|
| ion Gy | Conversion % | Latex viscosity, mPa·s | Modulus 500%, $kg/cm^2$ | Tensile strength, $kg/cm^2$ | Elongation at break, % | Perma set, % |
| | 0 | 16.1 | 4.7 | 14.2 | 960 | 90.3 |
| | 5.1 | 19.1 | 6.1 | 27.3 | 1130 | 79.2 |
| | 17.1 | 21.7 | 7.2 | 47.0 | 1160 | 70.7 |
| | 28.2 | 22.6 | 9.2 | 72.3 | 1120 | 59.5 |
| | 34.8 | 27.6 | 9.9 | 102.8 | 1180 | 49.0 |
| | 48.2 | 31.8 | 10.8 | 120.5 | 1160 | 43.3 |
| | 56.4 | 34.5 | 11.3 | 139.2 | 1160 | 39.7 |
| | 59.0 | 35.3 | 12.4 | 155.4 | 1190 | 37.0 |
| | 66.8 | 36.1 | 12.6 | 150.2 | 1150 | 33.5 |
| | 70.1 | 37.4 | 13.3 | 148.2 | 1110 | 31.0 |
| | 70.0 | 39.5 | 15.1 | 155.1 | 1090 | 27.3 |
| | 70.9 | 42.6 | 14.0 | 143.3 | 1080 | 30.3 |

ıcentration of St-NBA monomer in NR, 40 phr; total solid before irradiation, 45%; irradiation dose rate, 4 k

BLE 3. Influence of Irradiation Dose on the Fraction of St-NBA-Grafted NR Vulcanizates Soluble in Aceto

| diation , kGy | Conversion, % | Polymer loading, % | Fraction soluble in acetone, % | NBA homopolymer, % | St homopoly + St-NBA gra on NR, % |
|---|---|---|---|---|---|
| | 0 | 0 | 8.7 | 0 | 0 |
| | 5.0 | 2.0 | 8.7 | 0 | 2.0 |
| | 22.2 | 8.2 | 11.6 | 2.9 | 5.3 |
| | 44.6 | 15.1 | 15.1 | 6.4 | 8.7 |
| | 60.0 | 19.3 | 18.2 | 9.5 | 9.8 |
| | 67.4 | 21.1 | 18.9 | 10.2 | 10.0 |
| | 73.4 | 22.7 | 20.9 | 12.2 | 10.5 |
| | 72.2 | 22.4 | 20.4 | 11.7 | 10.7 |
| | 77.0 | 23.5 | 20.4 | 11.7 | 11.8 |
| | 76.8 | 23.5 | 20.9 | 12.2 | 11.3 |

Monomer concentration, 40 phr; irradiation dose rate, 4 kGy/h.

ABLE 4. Physical Properties of St-NBA-Grafted NR Vulcanizates for Various Grafting Conditions[a]

| Grafting conditions | | | Physical properties | | | | |
|---|---|---|---|---|---|---|---|
| ation kGy | Monomer concentration phr | Conversion, % | Modulus 300%, kg/cm² | Tensile strength, kg/cm² | Elongation at break, % | Permanent set, % | Hard Shore |
| | 10 | 0 | 14.1 | 133.0 | 740 | 3.3 | 45 |
| | 10 | 43.7 | 23.3 | 136.9 | 700 | 1.7 | 47 |
| | 20 | 0 | 14.2 | 156.7 | 720 | 1.7 | 46 |
| | 20 | 57.2 | 26.1 | 158.7 | 660 | 5.0 | 46.5 |
| | 30 | 0 | 14.9 | 178.7 | 750 | 3.3 | 46 |
| | 30 | 61.1 | 25.1 | 164.0 | 630 | 4.1 | 47.5 |
| | 40 | 0 | 14.2 | 139.7 | 740 | 3.5 | 43 |
| | 40 | 70.0 | 32.4 | 143.7 | 680 | 5.0 | 49 |

radiation dose rate, 4 kGy/h.

The tensile strength and elongation at break of the grafted NR film vulcanizates do not differ much from the ungrafted ones (Table 4). The tensile strengths of St-NBA-NR graft copolymer vulcanizates are much higher than those of NBA-NR graft copolymer vulcanizates [4]. Since NBA monomer is difficult to dissolve in NR particles, the grafting reaction and homopolymerization by irradiation may take place only in the outer layer of NR particles or in the water phase. This explains why the tensile strength was so poor at high conversion.

The DTA curves of St-NBA-NR graft copolymer vulcanizates with about 28% grafting (Fig. 2) show an endothermic peak around 407°C for a heating of 30°C/min. An endothermic peak is found at 391°C for 5°C/min. The activation energy for thermal degradation of St-NBA-NR graft copolymer vul-



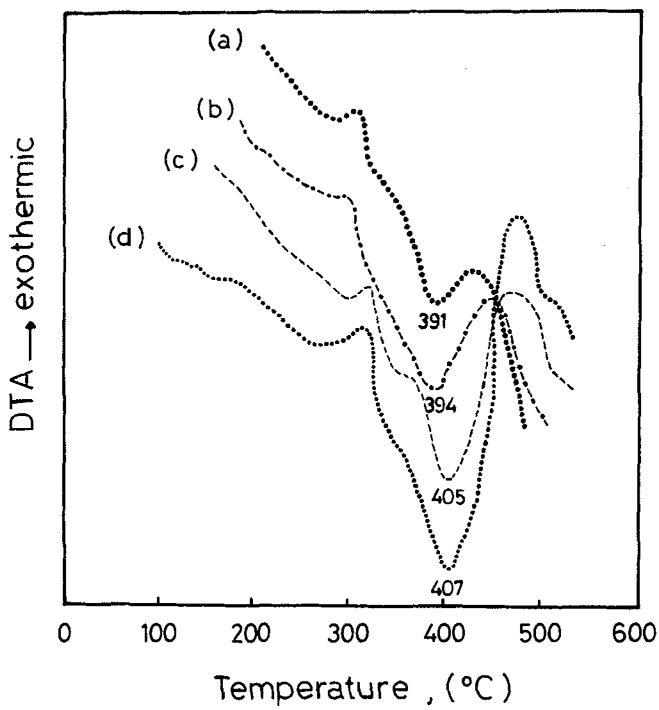


FIG. 2. DTA curves of St-NBA-grafted NR film. Heating rate: (a) 5°C/min, (b) 10°C/min, (c) 20°C/min, and (d) 30°C/min.

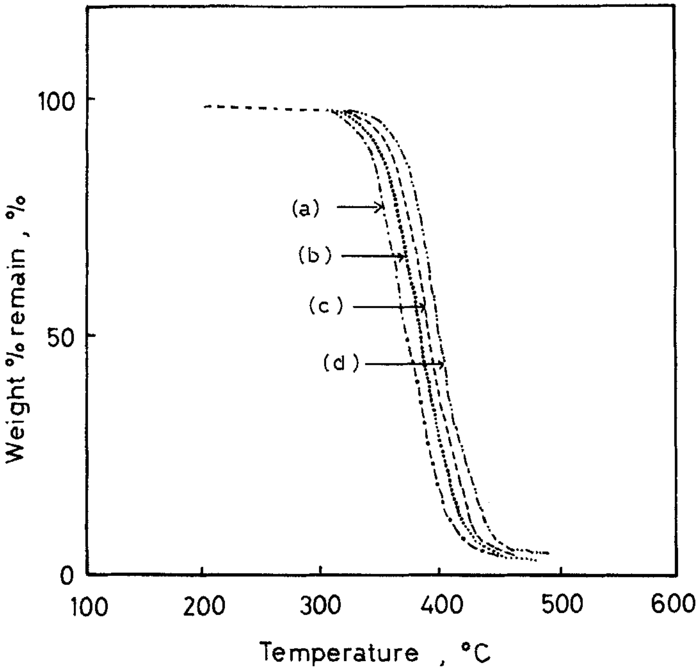


FIG. 3. TGA thermogram of St-NBA-grafted NR film. Heating rate: (a) 5°C/min, (b) 10°C/min, (c) 20°C/min, and (d) 30°C/min.

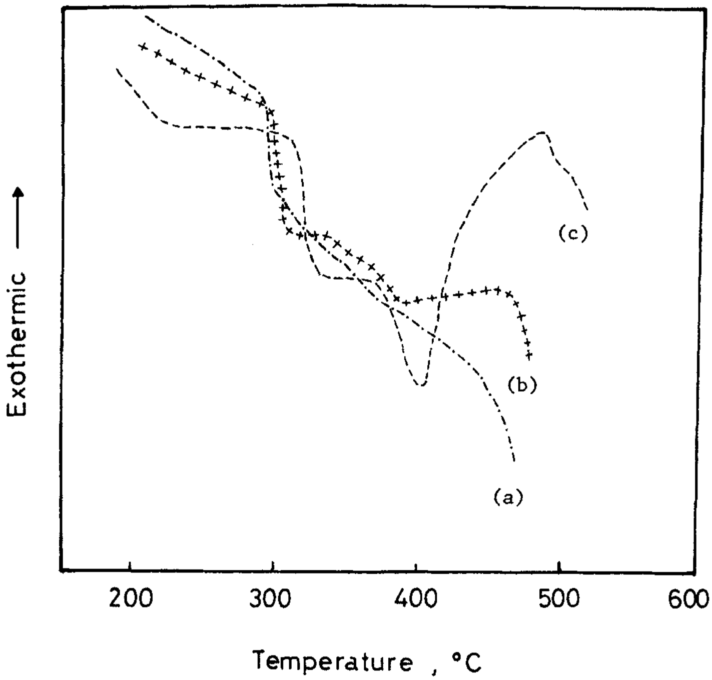


FIG. 4. DTA curves for ungrafted NR at various heating rates: (a) 5°C/min, (b) 10°C/min, and (c) 30°C/min.



canizates calculated by the method of Osawa and Flyn [7] was about 98 kcal/mol, which is much higher than that of the ungrafted one [8]. The TGA thermogram of St-NBA-grafted NR film is given in Fig. 3. The DTA curves of NR (Fig. 4) show an endothermic peak at about 400°C at a heating of 30°C/min.

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