

Synthesis and Properties of Natural Rubber Modified with Stearyl Methacrylate and Divinylbenzene by Graft Polymerization

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ABSTRACT: The graft polymerizations of stearyl methacrylate (SMA) and divinylbenzene (DVB) onto natural rubber (NR) were carried out in a solution process using benzoyl peroxide (BPO) as an initiator in toluene or chloroform. The main products of the grafted NR include an uncrosslinked (sol) part [sol(SMA-NR-DVB): s-SNRD] and a crosslinked (gel) part [gel(SMA-NR-DVB), g-SNRD]. s-SNRD was obtained by extraction using tetrahydrofuran. It was identified by IR and ¹H-NMR spectroscopies. The glass transition temperature (T_g) and thermal properties of s-SNRD and g-SNRD were studied by DSC and TGA. The glass transition temperature and thermal decomposition temperature of s-SNRD and g-SNRD were higher than were those of NR. The light resistance and weatherability of s-SNRD were measured with a Weather-o-Meter. The light resistance and weatherability of s-SNRD are better than are those of NR. The effects of the initiator concentration, mol ratio of SMA to DVB, reaction time, temperature on grafting ratio, and crosslinking ratio were investigated. The highest grafting ratio and crosslinking ratio in the graft polymerization of SMA and DVB onto NR were obtained when the mol ratio of SMA to DVB and BPO were 4.0 and 2 wt %, at 80°C for 48 h, respectively. Following several studies on oil-absorptive polymers in our laboratory,⁹ the oil absorptivity of g-SNRD was examined using crude oil. The oil absorptivity of g-SNRD was 600% when the immersion time was 10 min. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 2464–2470, 2001

Key words: graft polymerization; g-SNRD; s-SNRD; thermal property; light resistance; grafting ratio; oil absorptivity

INTRODUCTION

Natural rubber (NR) is an unsaturated elastomer having some good properties such as high

strength, outstanding resilience, and high elongation at break.^{1,2} However, it is very sensitive to heat and oxidation because of the existence of double bonds in its chains.^{3,4} It has low tensile strength, tensile modulus, and poor creep characteristics unless highly vulcanized. These disadvantages of NR have limited its application in industry. Some methods are known to improve the disadvantages of elastomers: modification of the elastomer by graft polymerization with vinyl

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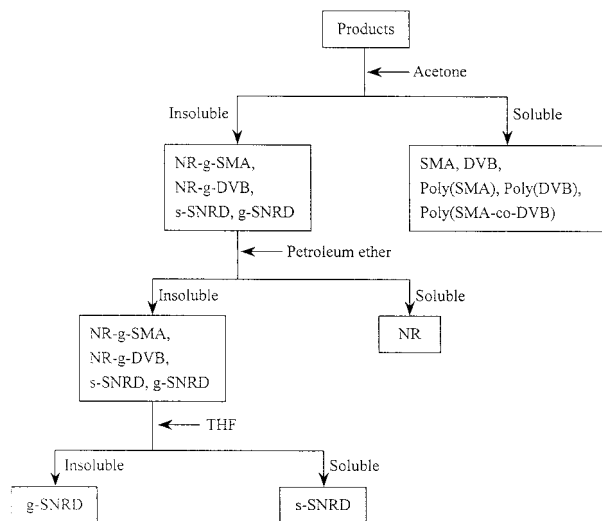


Figure 1 Scheme of separation of s-SNRD and g-SNRD.

monomers in a solution or solid state using initiators and crosslinkers^{5–8} and blending elastomers with other polymers.^{9,10}

The aim of this study was to improve the thermal-oxidative stability, physicochemical properties, and oil absorptivity of NR. The graft polymerizations of stearyl methacrylate (SMA) and divinylbenzene (DVB) onto NR were carried out by a solution process using benzoyl peroxide (BPO) as an initiator in toluene. The main products of the grafted NR include an uncrosslinked (sol) part [sol(SMA–NR–DVB): s-SNRD] and a crosslinked (gel) part [gel(SMA–NR–DVB), g-SNRD]. s-SNRD was obtained by extraction using tetrahydrofuran (THF). It was identified by IR and ¹H-NMR spectroscopies. The glass transition temperature (T_g) and thermal properties of s-SNRD and g-SNRD were studied by DSC and TGA. The light resistance and weatherability of s-SNRD were measured with a Weather-o-Meter. The effects of initiator concentration, mol ratio of SMA to DVB, reaction time, and temperature on the total grafting ratio and crosslinking ratio were investigated. Following several studies on oil-absorptive polymers in our laboratory,¹¹ the oil absorptivity of g-SNRD was examined using crude oil.

EXPERIMENTAL

Materials

NR (SMR type, Malaysia) was purified by precipitating a toluene solution of NR into methanol.

SMA (Aldrich Chemical Co., Milwaukee, WI) and DVB (Fluka Chemical Co., Tokyo, Japan) were purified by standard procedures.¹² BPO (Aldrich) was purified by recrystallization from methanol. Toluene, THF, acetone, methanol (MeOH), chloroform, *n*-hexane, and petroleum ether (Junsei Chemical Co., Tokyo, Japan) were distilled prior to use.

Graft Polymerization

A typical example for the graft polymerization of SMA and DVB onto NR is as follows: The solutions such as 15 wt % (1 g) of NR, 4.5 g of SMA (13.2 mmol) dissolved in 20 mL toluene, 0.45 g DVB (3.3 mmol) in 10 mL toluene, and 0.12 g BPO (2 wt % based on monomers + NR) in 20 mL toluene were introduced into a 250-mL demountable four-neck flask equipped with a condenser, a thermometer, a nitrogen gas inlet and outlet, and a stirrer.^{13,14} The reaction was performed at 80°C for 48 h. After finishing the graft polymerization, the reaction mixture was precipitated in excess MeOH. To remove the poly(SMA), poly(DVB), and poly(SMA-co-DVB) formed during the graft polymerization, the mixture was extracted with acetone using a Soxhlet apparatus for 16 h. Non-grafted NR was separated from the mixture by extraction with petroleum ether for 12 h. s-SNRD was obtained by extracting the graft polymers with THF using a Soxhlet apparatus. The obtained s-SNRD and g-SNRD were dried in a vacuum oven at room temperature to a constant weight. The separation of s-SNRD and g-SNRD is schematically shown in Figure 1. The graft polymerizations were carried out under various experimental conditions (see Table I).

The grafting ratio (percent) and grafting efficiency (percent) of the graft polymerization were estimated from the following equations^{15,16}:

$$\text{Grafting ratio (\%)} = \frac{\text{weight of the grafted polymers (SNRD)}}{\text{weight of substrate}} \times 100 \quad (1)$$

Table I Reaction Conditions for Graft Polymerization in This Study

Condition	Description
Reaction time (h)	24, 48, 72, 96
Mol ratio ([VAc]/[St])	1.0, 2.0, 3.0, 4.0, 5.0
Reaction temperature (°C)	60, 70, 80, 90

^a The concentration was based on the total weights of the monomers and NR.

Crosslinking ratio (%)

$$= \frac{\text{Weight of the crosslinked graft polymers after extraction with THF}}{\text{Weight of the grafted polymers (SNRD)}} \times 100 \quad (2)$$

Measurement

Infrared Spectroscopy

The IR spectra of s-SNRD and g-SNRD were obtained with a Jasco FTIR-5300 spectrophotometer in film and solid forms, respectively.

Nuclear Magnetic Resonance Spectroscopy

The $^1\text{H-NMR}$ spectrum of s-SNRD was determined by an FT-300 MHz Varian Gemini 2000 spectrophotometer. The measurement was done using chloroform (CDCl_3) as the solvent and tetramethylsilane (TMS) as the internal reference.

Ultraviolet Spectroscopy

The UV spectrum of s-SNRD was recorded using a Varian CM 300 UV-visible spectrophotometer in chloroform (CDCl_3) as a solvent using a quartz cell at ambient temperature.

Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) of NR, s-SNRD, and g-SNRD was carried out with a Perkin-Elmer DSC7 (Shimadzu Co.). First, the temperatures of the samples were increased from 30 to 150°C at a rate of 20°C/min to erase their thermal history. The cooling rate from 150 to -100°C is 80°C/min. Then, the second scanning was heated from -100 to 200°C at a rate of 10°C/min to determine the glass transition temperature of the samples.

Thermogravimetric Analysis

The thermal properties of NR, s-SNRD, and g-SNRD were also examined with a thermogravimetric analysis instrument (Shimadzu DT 30A TGA) at a scanning rate of 15°C/min in nitrogen air.

Light Resistance

The color differences of NR and s-SNRD were determined by a color-difference meter (Minolta Co., Japan). First, the film specimens were cast from a chloroform solution (0.5 wt %) on a non-

yellowing urethane-coated hiding paper. Then, they were dried slowly at room temperature and kept under a vacuum to a constant weight. The thickness of the film was 35 μm . The color difference (ΔE) of the samples was calculated using the Hunter-Schofield equation.¹⁷

Weatherability

The weather resistance (ASTM G53) of the samples was measured by using a Q-panel ultraviolet (UV) B 313 weathering tester coupled with a UV lamp of 313–280 nm in wavelength. The film specimens were prepared by the same method as described for the determination of the color difference.

Oil-absorption Test

First, g-SNRD was immersed in crude oil at room temperature for given time periods. Then, the sample was lifted from the oil, tapped with filter paper to remove excess oil from the sample surface, and weighted. The weight ratio, $(W_s - W_p)/W_p$, was used to evaluate the swelling ratio of the sample, where W_s is the weight of the polymer and the absorbed oil and W_p is that of the dried polymer sample (ASTM F726-81).

RESULTS AND DISCUSSION

Characterization

s-SNRD was identified by IR and $^1\text{H-NMR}$ spectroscopies.^{18–21} The IR spectrum of g-SNRD (Fig. 2) exhibited characteristic absorption bands at 3065 cm^{-1} (stretching vibration of aromatic C—H bond), 2920 cm^{-1} (stretching vibration of aliphatic C—H bond), 1730 cm^{-1} (stretching vibration of aliphatic C=O bond in the SMA moiety), 1465 cm^{-1} (scissoring of CH_2), 1375 cm^{-1} (bending of CH_3), 1240 cm^{-1} (stretching vibration of aliphatic C—O), and 760 cm^{-1} (out-of-plane bending vibration of aromatic C—H bond in the DVB moiety). The $^1\text{H-NMR}$ spectrum of s-SNRD showed the methyl protons of NR at 0.8 ppm, the methine and methylene protons of NR at 1.1–2.5 ppm, the O— CH_2 protons of the SMA moiety at 3.7 ppm, and the phenyl protons of the DVB moiety at 7.2–7.3 ppm (Fig. 2). The UV spectrum of s-SNRD showed a characteristic absorption peak at 270 nm, which is due to the phenyl group of the DVB moiety in s-SNRD. Therefore, we were able to confirm that SMA and DVB were grafted randomly onto NR. From the results of FTIR and

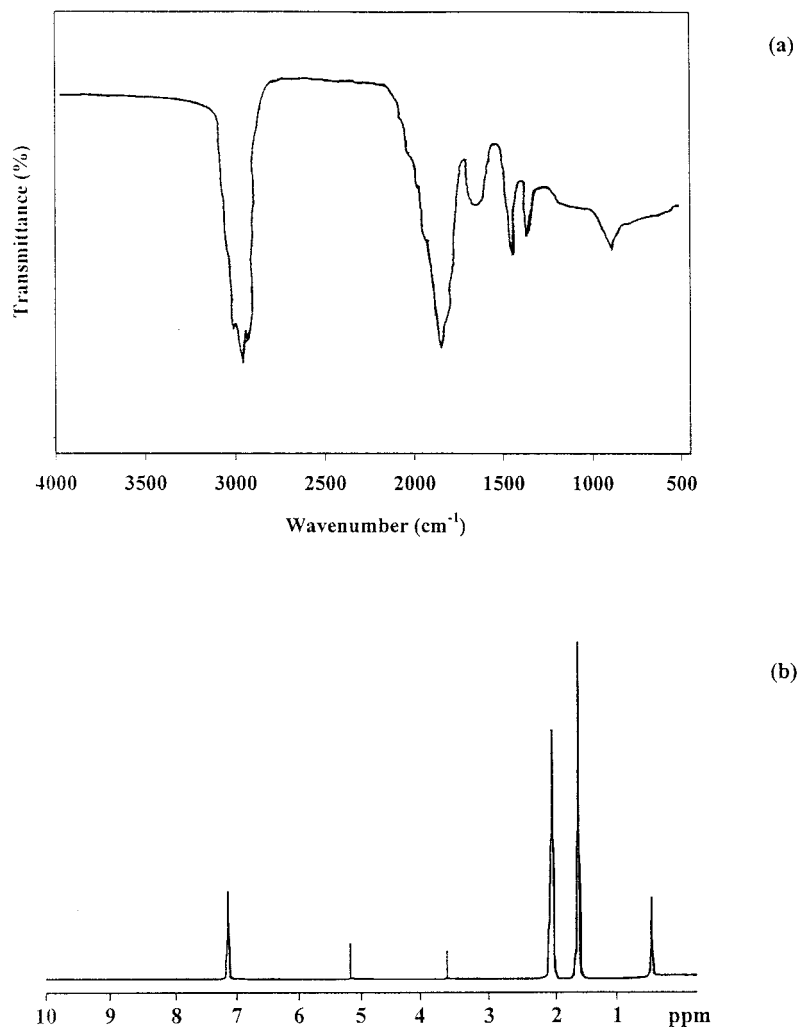


Figure 2 (a) IR and (b) $^1\text{H-NMR}$ spectra of s-SNRD.

$^1\text{H-NMR}$ spectra, the structure of the obtained graft polymer was SMA-NR-DVB (SNRD).

Effect of Reaction Conditions

Effect of Reaction Time

The effect of reaction time on the grafting ratio is showed in Figure 3. The reaction was carried out in toluene with an NR concentration of 15 wt %, BPO (2.0 wt %) as an initiator, and a mol ratio of SMA to DVB of 4.0 at 80°C. In this case, the grafting ratio increased with an increasing reaction time up to 48 h and then it leveled off with a further increasing reaction time. After 48 h, the level-off result may be caused by the decrease of the unreacted monomer concentration as well as by the increase of viscosity of the reaction medium during the graft polymerization.²²

Effect of Mol Ratio

Table II presents the effect of the mol ratio of SMA to DVB on the graft polymerization. The reaction was performed in toluene with an NR concentration of 15 wt % and BPO (2.0 wt %) as an initiator at 80°C for 48 h. The grafting ratio and crosslinking ratio increased with an increasing mol ratio of SMA to DVB up to 4.0 and then they decreased. From the results, to obtain the highest grafting ratio and crosslinking ratio, the most suitable mol ratio of SMA to DVB was 4.0 in the graft polymerization.

Effect of Reaction Temperature

The effect of the reaction temperature on the graft polymerization is shown in Figure 4. The reaction was carried out in toluene with an NR concentra-

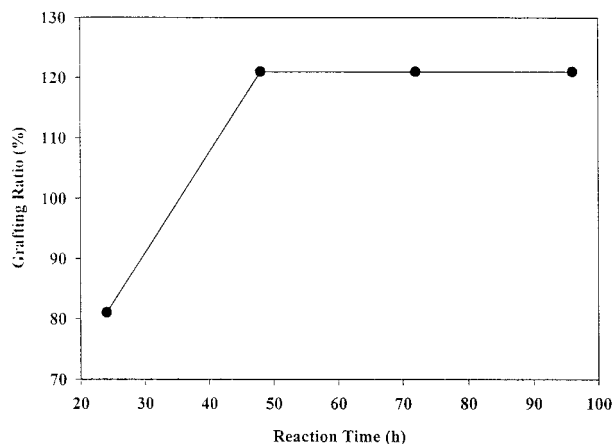


Figure 3 Effect of reaction time on the grafting ratio of SMA and DVB onto NR.

tion of 15 wt %, BPO (2.0 wt %) as an initiator, and a mol ratio of SMA to DVB of 4.0, for 48 h. The grafting ratio increased with an increasing reaction temperature up to 80°C and then it decreased with a further increasing reaction temperature. In general, the graft polymerization depends on the number of active sites available. An increased reaction temperature is expected to improve the rate of graft polymerization.^{23–26} However, with increase of the temperature, the rate of homopolymerization of SMA, as well as that of DVB, also increases. As a result, the grafting ratio only increases initially (up to 8°C), but on further increasing of temperature, it decreases.

Glass Transition Temperature

Table III shows the glass transition temperatures (T_g 's) of s-SNRD and g-SNRD obtained from the DSC diagram. It is clear that the T_g values of both s-SNRD and g-SNRD were higher than were those of NR. This can be explained by the exist-

Table II Effect of the Mol Ratio of SMA to DVB on the Graft Polymerization

[SMA]/[DVB]	Grafting Ratio (%)	Crosslinking Ratio (%)
1.0	42	7
2.0	43	8
3.0	51	1.6
4.0	121	25
5.0	98	23

NR, 15%; reaction time, 48 h; BPO, 2.0 wt %; reaction temperature, 80°C; solvent, toluene.

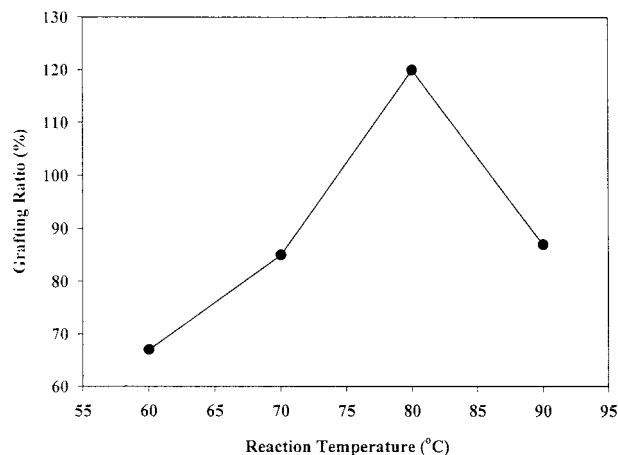


Figure 4 Effect of reaction temperature on the grafting ratio of SMA and DVB onto NR.

tence of poly(SMA) and poly(DVB) having high T_g values in s-SNRD and g-SNRD as well as a crosslinked structure in g-SNRD.

Thermal Properties

The thermal properties of NR, s-SNRD, and g-SNRD were based on their decomposition temperature and weight residue at 450°C (Table III). In this table, they were synthesized in toluene with an NR concentration of 15 wt %, BPO (2.0 wt %) as an initiator, and a mol ratio of SMA to DVB of 4.0 at 80°C for 48 h. It is clear that both s-SNRD and g-SNRD show better thermal properties than those of NR. As shown in Table III, the initial decomposition temperature of NR, s-SNRD, and g-SNRD were 354, 373, and 380°C, respectively. The weight residue of NR, s-SNRD, and g-SNRD at 450°C were 91, 72, and 70%, respectively. s-SNRD and g-SNRD had improved thermal properties as compared with NR because of the presence of poly(SMA) and poly(DVB) having higher T_g 's than that of NR as well as a crosslinked structure in g-SNRD.²⁷

Table III Thermal Properties of NR, s-SNRD, and g-SNRD

Sample	T_g (°C)	Initial Decomposition Temperature (°C)	Residual Weight at 450°C (%)
NR	-70	354	91
s-SNRD	-42	373	72
g-SNRD	71	380	70

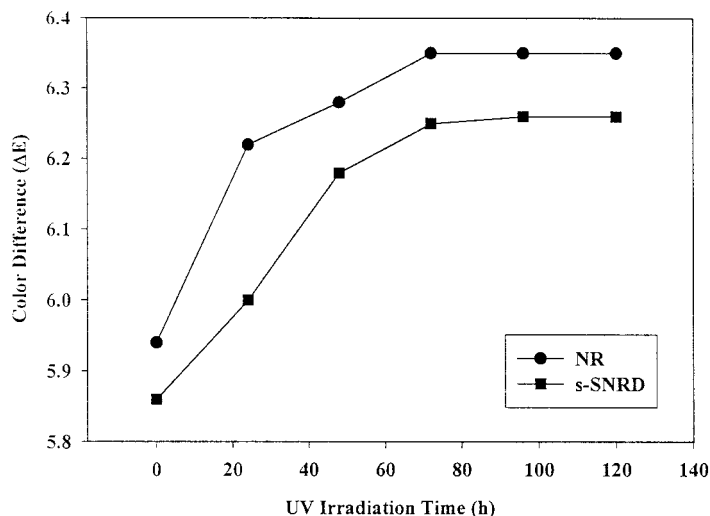


Figure 5 Color differences of NR and s-SNRD on UV irradiation time.

Light Resistance and Weatherability

The light resistance and weatherability were semiquantitatively expressed in terms of ΔE with the National Bureau of Standards Unit. The smaller ΔE means better light resistance and weatherability.²⁸ The samples were tested in a Weather-o-Meter for the measurements of light resistance and weatherability according to the time of UV irradiation. Figure 5 shows the ΔE data of NR and s-SNRD as a function of UV irradiation. s-SNRD and g-SNRD were synthesized in toluene with an NR concentration of 15 wt % and BPO (2.0 wt %) as an initiator at a mol ratio of 4.0 of SMA to DVB of 4.0 at 80°C for 48 h. The

dependence of the light resistance and weatherability of s-SNRD on the reaction conditions was not significant. It should be noted that the s-SNRD obtained in this work shows better light resistance and weatherability than those of non-modified NR, which is easily degraded by UV irradiation because of the existence of a double bond in its molecule.

Oil Absorption

The oil absorption of g-SNRD increased with an increasing immersion time (Fig. 6). The high oil absorption of g-SNRD was 600% when the immersion time was 10 min. g-SNRD showed oil absorp-

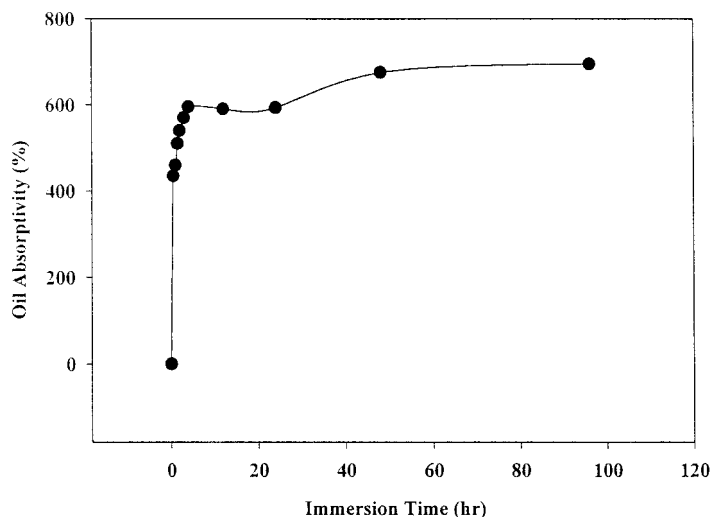


Figure 6 Oil absorption of the g-SNRD.

tion because of the presence of PSMA having a long alkyl chain and a crosslinked structure in g-SNRD. However, NR could not be measured for oil absorptivity because it dissolved in crude oil.

CONCLUSIONS

Modified NR with SMA and DVB was synthesized by the graft radical polymerization technique. The dependence of the various reaction conditions was examined on the graft polymerization of SMA and DVB onto NR. The properties of s-SNRD and g-SNRD were determined. The main results are summarized as follows:

1. The highest grafting ratio and crosslinking ratio in the graft polymerization of SMA and DVB onto NR were obtained when the mol ratio of SMA to DVB and BPO were 4.0 and 2 wt % at 80°C for 48 h, respectively.
2. The glass transition temperature and thermal decomposition temperature of s-SNRD and g-SNRD were higher than were those of NR.
3. The light resistance and weatherability of s-SNRD are better than are those of NR.
4. The oil absorptivity of g-SNRD was 600% when the immersion time was 10 min.

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