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FIXATION OF α-NAPHTHYL ACETIC ACID ONTO EPOXIDIZED LIQUID NATURAL RUBBER IN MICROWAVE REACTOR (MONOMODE SYSTEM)

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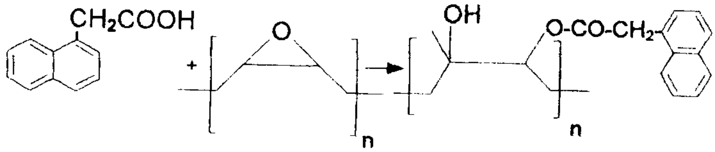
ABSTRACT

The fixation of α-naphthyl acetic acid (NAA) onto epoxidized liquid natural rubber (ELNR) obtained by deploymerization of natural rubber macromolecules in the latex phase using the phenylhydrazine-H_2O_2-O_2 system followed by $HCOOH$-H_2O_2 treatment (in situ) has been investigated in a microwave reactor (Monomode system). This paper reports on the effect of some parameters such as: power of the reactor, amount of quaternary ammonium salts (TEBA), and reaction time on the fixation between ELNR via the epoxy functions and NAA.

α-Naphthyl acetic acid (NAA) is a plant growth stimulator that is widely used in agriculture. In order to prolong its active period on plants, some authors have tried to fix α-NAA onto polymeric carriers, e.g., polyisoprene rubber [1], polyesters [2], amylose [3], polyacrylate [4], poly(methacrylate glycidyle) [5], and poly(acid methacrylic) [6].

Using polyisoprene as polymeric carrier, Brosse and coworkers [1, 7] have carried out the expoxidation of polyisoprene or liquid rubber and then the oxirane ring opening reaction by α-NAA in the presence of naphthyl acetate tetraammonium salt in $CHCl_3$. According to Ref. 1 the reaction is second-order and the conversion of this system is quite low (23.7% for 24 h, at 120°C and molar ratio of catalyst/reagent = 0.1).



This research aimed at improving the conversion and shortening the reaction time.

EXPERIMENTAL

Materials and Apparatus

- 58% natural rubber latex was obtained from SongBe Rubber Company.
- α-NAA, from CICA, was twice recrystallized from water, m.p. = 129°C.
- Nonionic surfactant: Arkopal N-300 from Hoechst.
- Microwave monomode: Maxidigest MX-350 (Prolabo).
- Infrared spectrometer: Shimadzu IR-470, film on NaCl tablet.
- ^{1}H-NMR spectra were recorded on a Brucker-AC 200 spectrometer in $CDCl_3$ or CCl_4 with TMS as internal standard.
- ^{13}C-NMR spectra were recorded on a Brucker-AC 200 spectrometer in $CDCl_3$ or C_6D_6 with TMS as internal standard.
- Gel permeation chromatography: the average molecular weights of liquid natural rubber and ELNR were indicated in THF (debit 1 mL/min), 4 microstyragel columns (100, 500, 1000, and 10^4 Å), detector: Shimadzu RID-6A, compared with polyisoprene standard.

Degradation of Natural Rubber

Natural rubber was depolymerized by a phenylhydrazine-H_2O_2-O_2 system in the latex phase (stabilized by nonionic surfactant Arkopal N-300) at 60°C for 10 h.

The molecular weight of the liquid natural rubber (LNR) obtained was M_n = 15,100, M_w = 32,300.

IR: 3036 cm^{-1} (=CH), 2961 cm^{-1} (C—H, aliphatic), 1719 cm^{-1} (—CH=O), 1664 cm^{-1} (C=C); 1451 cm^{-1}, 1376 cm^{-1} (C—H aliphatic), 836 cm^{-1} (=C—H, cis), 700 cm^{-1} (aromatic monosubstituted phenylhydrazine).

H-NMR (CCl₄: δ = 5.24 (—CH=C—, 1H); 2.18 (—CH_2—C=C, 4H); 1.84 (CH_3—C=C, cis, 3H).

Epoxidation of Liquid Natural Rubber

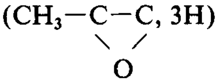
The epoxidation of LNR was carried out simultaneously, without isolation, by the HCOOH-H_2O_2 system (in situ) at 60°C, for 17 h (where the molar ratio of HCOOH/rubber = 0.2, H_2O_2/rubber = 0.8). The reaction mixture was then neutralized with $NaHCO_3$ 5%. The product was coagulated in methanol, washed several times with H_2O, precipitated 3 times in $CHCl_3/CH_3OH$, and dried under vacuum at 50°C.

The epoxy content of ELNR is 38% (based on ^{1}H-NMR).

Molecular Weight: $M_n = 22{,}000$; $M_w = 35{,}000$.

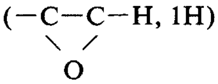
IR: 3460 cm^{-1} (—OH, from oxirane ring opening reaction); 1064 cm^{-1} (C—O, tetrahydrofuran); 1245, 872 cm^{-1} (C—O, oxirane).

^{1}H-NMR (CCl_4): $\delta = 1.4$



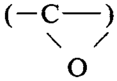
$(CH_3{-}\underset{\diagdown\;O\;\diagup}{C{-}C},\ 3H)$

and 2.73



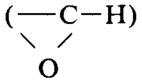
$({-}\underset{\diagdown\;O\;\diagup}{C{-}C}{-}H,\ 1H)$

^{13}C-NMR ($CDCl_3$): $\delta = 60.5$



$({-}\underset{\diagdown\;O\;\diagup}{C{-\!-}})$

and 64.1



$(\underset{\diagdown\;O\;\diagup}{{-\!-}C}{-}H)$

Fixation of α-NAA onto ELNR

ELNR38, NAA, TEBA, and chlorobenzene were mixed in a Teflon vessel. The mixture was shaken to form a homogeneous system. The Teflon vessel was put into a focused open-vessel Maxidigest Mx-350 microwave reactor. Microwave radiation was carried out with incident power between 150 and 240 W, reaction time: 5–15 min, molar ratio of catalyst/ELNR38: 0.012–0.100. The conversion of the fixation was calculated based on titration of the residual NAA with hydroxide tetrabutyl ammonium in CH_3OH using a pH meter. The reaction mixture was precipitated in methanol, reprecipitated in $CHCl_3/CH_3OH$, and dried in a vacuum oven. The conversion was also determined based on ^{13}C-NMR spectrum analysis.

IR: 3452 cm^{-1} (O—H), 2963-2763 cm^{-1} (C—H, aliphatic), 1729 cm^{-1} (C—O, ester); 1599-1512 cm^{-1} (C=C, aromatic), 1440-1375 cm^{-1} (C—H, aliphatic), 783 cm^{-1} (C—H, aromatic).

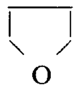
^{1}H-NMR (*$CDCl_3$*: $\delta = 7.50$–8.3 (naphthyl, 7H), 4.17 (—CH_2— naphthyl, 2H)

TABLE 1. Dependence of the Conversion *H*% on the Incident Power of Microwave Reactor

Power, *P* (W)	Conversion, *H*%	Temp. at the end[a] (°C)
120	38	109
150	44	111
210	29	111
240	38	111
270	gel	–

Note. ELNR 38 = 2.5 mmol, NAA = 2.5 mmol, TEBA = 0.083 mmol, chlorobenzene = 1.2 mL, reaction time 10 min.

[a] Temperature was determined at the end of the reaction by thermometer.

^{13}C-NMR (C_6D_6): δ = 171 (O—CO), 124.3-135.2 (naphthyl), 73-86 (—C—OH,COOAr, )

RESULTS AND DISCUSSION

Influence of Incident Power of Microwave Reactor on the Conversion

The conversion of the fixation was followed in the range of incident power 120-270 (Table 1).

At high power of 270 W, the product was gelled and insoluble in $CHCl_3$. At *P* = 150 W, the highest conversion can be obtained.

TABLE 2. Dependence of the Conversion *H*% on the Reaction Time

Reaction time, *t* (min)	Conversion, *H* %	Temp. at the end[a] (°C)
05	33	109
08	35	109
10	44	111
15	44	111

Note. ELNR 38 = 2.5 mmol, NAA = 2.5 mmol, TEBA = 0.083 mmol, chlorobenzene = 1.2 mL, *P* = 150 W.

[a] Temperature was determined at the end of the reaction by thermometer.

TABLE 3. Dependence of the Conversion $H\%$ on the Amount of Catalyst (TEBA)

TEBA (mmol)	Conversion, $H\%$	Temp. at the end[a] (°C)
0.030	27	109
0.083	44	111
0.150	44	111
0.250	44	111

Note. ELNR 38 = 2.5 mmol, NAA = 2.5 mmol, chlorobenzene = 1.2 ml, P = 150 W.

[a] Temperature was determined at the end of the reaction by thermometer.

Influence of Reaction Time

The conversion was increased with the reaction time and almost unchanged at $t \geq 10$ min (Table 2).

Influence of Catalyst TEBA

The conversion of the reaction is almost unchanged at the content of TEBA ≥ 0.0083 (Table 3). From the above results, a satisfactory yield (44%) can be obtained in the following conditions:

- Incident power = 150 W
- Reaction time = 10 min
- Molar ratio of TEBA/ELNR38 = 1/30

Comparison of the Conversion of Fixation Reaction Carried Out by Traditional Method and in Microwave

The fixation of NAA onto ELNR performed in the microwave reactor Monomode Maxidigest MX-350 shows the better results in comparison with the traditional (in flask) method (Table 4).

TABLE 4. Comparison of Traditional and Microwave Methods

Method	Reaction time	Conversion ($H\%$)
Traditional[a]	24 h	33
Microwave	10 min	44

[a]ELNR 38 = 10.2 mmol, NAA = 10.2 mmol, TEBA = 0.34 mmol, chlorobenzene = 20 mL, at 110°C.

CONCLUSION

The fixation of NAA onto ELNR 38 in the microwave reactor Monomode Maxidigest MX-350 has been investigated. This method shows better results in comparison with the traditional procedure:

- Higher conversion
- Shorter reaction time

NAA will be released slowly by hydrolysis from the polyisoprene carrier to exert its effect on the plant.

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