Preparation of Low Molecular Weight Natural Rubber by Ozonolysis of High Ammonia Latex

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Depolymerisation of natural rubber (NR) by bubbling ozone into high ammonia latex was attempted in order to prepare liquid natural rubber. NR was found to depolymerise at a faster rate with increasing ozone generation. Addition of hydrogen peroxide to the latex accelerated the depolymerisation of NR. Regardless of added hydrogen peroxide concentration, when the pH of latex was above 8 at the initial stage of reaction, the rate of depolymerisation was remarkably rapid. However, subsequently, the reaction abruptly slowed when the pH fell below 8. The decrease in pH was due to the formation of levulinic acid during reaction. These results suggested that the main reaction of the depolymerisation in latex was not direct oxidation by ozone through the formation of ozonide, but radical oxidation by hydroxyl and hydroperoxyl radicals formed by reaction between ozone and hydroxyl ion under basic conditions. It seemed that the very slow depolymerisation below pH 8 was due to the formation of levulinic acid from a terminal of a polymer chain, by direct oxidation of ozone. The minimum weight-average molecular-weight of the depolymerised NR achieved was about 50 000.

Key words: depolymerisation; ozone; high ammonia latex; hydrogen peroxide; levulinic acid; weight-average; molecular-weight; liquid natural rubber

Depolymerised natural rubber (NR) with weight-average molecular-weight ($M_w$) below 20 000 is termed liquid natural rubber (LNR). LNR is used for adhesives, binders, sealants and plasticizers, and has been prepared by mechanical, thermal or chemical depolymerisation of NR in latex or solution. Recently, because of convenience for quality control, LNR is produced by the redox depolymerisation of NR latex. Tanaka et al. reported a new method of preparing LNR from deprotonised natural rubber latex by the oxidative depolymerisation in the presence of $K_2S_2O_5$ and propanal.

Theoretically, it is possible to prepare LNR by ozonolysis of NR in latex. However, there has been no report for this process.
In this study, the depolymerisation of NR by bubbling ozone into high ammonia latex (HAL) was investigated to prepare LNR.

MATERIALS AND METHODS

Ozone Generator

A silent discharging type of ozone generator (TADA Electric Co., Japan) was used in this work. This generator was operated at a constant gas flow rate of 0.2 Nm$^3$/h. The ozone-generating rate was controlled by discharging voltage, and was monitored by an EG-2001 ozone concentration meter (Ebara Jitsugyo Co., Japan). The maximum rate was 4 g/h using dry air as a feeding gas.

Depolymerisation Procedure

200 mL of commercial high ammonia latex (HAL), dry rubber content (DRC) 60 %w/v, was charged into a 1 L separating flask, and diluted to 400 mL with distilled water. After addition of 8 g (2 %w/v) of dodecyl sodium sulphate and 0.4 g (0.1 %w/v) of a silicone defoamer, ozonised air was bubbled into the latex at 20°C. The defoamer was Shin-etsu Silicone KM72 (Shin-etsu Chemical Industry Co., Japan). The bubbling rate of ozonised air was 0.2 Nm$^3$/h. Excess ozone was exhausted through a glass column filled with activated carbon for ozone decomposition. The molecular weight distribution was determined using a Shodex-101 gel permeation chromatograph (Showa Denko Co., Japan). Measurements were made using THF as an eluent monitored with a refractometer at 30°C. Calibration was done using commercial standard polystyrenes. The molecular weights of the sample were expressed as polystyrene equivalent values. The FT-IR measurements were performed using a Spectrum 2000 FTIR spectrometer (Perkin-Elmer Inc.). The viscosity of depolymerised rubber was measured using a MR-500 visco-elastic rheometer (UBM Co., Japan) equipped with a cone plate rotor.

Analysis of Levulinic Acid

The detection and the determination of levulinic acid were done using a JMS-AUTOMASS 20 gas chromatograph-mass spectrometer (JEOL Inc. Japan). The process of analysis is shown in Scheme 1. The BF$_3$-methanol complex (Tokyo Kasei Co.) was used for methylation. Calibration was done using reagent grade levulinic acid methyl ester (Tokyo Kasei Co.). The analytical conditions of GC-MS are shown in Table 1. The retention time of levulinic acid methyl ester was 15.6 min under the conditions employed.

RESULTS AND DISCUSSION

Depolymerisation of NR by Ozone Bubbling

Figure 1 shows the change in the weight-average molecular-weight ($M_w$) of the coagulum. Since $M_w$ decreased with reaction time, it is
Clear that the NR can be depolymerised by ozone in latex. $M_w$ decreased remarkably in the first 1 h of reaction, and then decreased gradually subsequently. This result seems to be the same as that of ozonolysis of NR in chloroform solution reported by Nor and Ebdon. They considered that the drastic increase in the degradation rate was due to initial rapid diffusion controlled ozonolysis, by which polymeric ozonides and peroxides were formed; and subsequent cleavage reactions were slow because they were relatively stable. However, since an ozonide could quickly decompose via hydrolysis in water, it is unlikely that abrupt change of the depolymerisation rate should take place in latex.
It is well known that hydroxyl and hydroperoxyl radicals are formed by the reaction between ozone and the hydroxyl ion. Scheme 2 shows the reaction mechanism proposed by Weiss. There are many studies on the effect of pH on the decomposition rate of ozone in water. Gurol and Singer investigated it under dynamic conditions (ozone bubbling process), and it concurred that the decomposition rate increased in proportion with \([{O_3}][{OH}^-]^{0.55}\) above pH 4, while it was insensitive to pH below 4. They also indicated that the decomposition of ozone was remarkably accelerated above pH 8. Their results indicate that not only direct oxidation by ozone, but also reaction by hydroxyl and hydroperoxyl radicals occur under basic conditions.

As shown in Figure 2, pH of HAL fell from its initial value of 9.9, with prolonged reaction time. Since levulinic acid was detected in the serum by GC-MS analysis, the drop in pH must be due to the formation of levulinic acid.

Comparing Figure 1 to Figure 2, it is apparent that the depolymerisation of NR by ozone bubbling was very fast above pH 8, and became abruptly slow after the pH fell to below 8. Therefore, it is likely that the rapid chain scission in the initial period of reaction was due to oxidative reaction by hydroxyl and hydroperoxyl radicals, and direct oxidation by ozone was very slow in aqueous systems.

Effects of Hydrogen Peroxide on Depolymerisation Reaction

It is apparent that NR can be depolymerised by bubbling ozone into HAL. However, the lowest \(M_w\) is about 100 000 with the most severe conditions of the ozone generating rate of 4 g/h and a reaction time of 8 h, as shown in Figure 1. This result indicates that further reaction is necessary to prepare lower \(M_w\) of NR, when only ozone is used. Moreover, long reaction time is not practical.

Staehelin and Hoigne reported that the decomposition of ozone in water was accelerated by addition of hydrogen peroxide under basic conditions, since \(HO_2^-\) has greater effect than \(OH^-\). The decomposition mechanism is shown in Scheme 3. Therefore, in this study, the depolymerisation of NR by ozone bubbling was done in the presence of reagent grade \(H_2O_2\), varying from 2% to 10%. As shown in Figure 3, it is obvious that the rate of \(M_w\) reduction in the initial period of reaction could be accelerated by the addition of \(H_2O_2\), and the increase depended on the amount of \(H_2O_2\). The rate subsequently became abruptly slow. It is evident that this remarkable decrease of rate was due to the fall of pH as in the case of non-addition of \(H_2O_2\).

The molecular weight distribution curves with respect to reaction time are given in Figure 4 (without addition of \(H_2O_2\)) and Figure 5 (with addition of \(H_2O_2\), 10%). The ozone generating rate was 4 g/h in both cases. It was clear that the addition of \(H_2O_2\) had an effect on the change of molecular weight distribution, too. With no \(H_2O_2\) addition, as shown in Figure 4, the fraction of high molecular weight decreased, and the distribution broadened with reaction time. The distribution patterns till 3 h were bimodal. After 5 h, the high molecular weight fraction was found to exist only as a shoulder peak, and after 8 h the distribution was unimodal. On the other hand, the peak of the high molecular weight fraction decreased remarkably in the initial period of reaction by addition of \(H_2O_2\). Distribution patterns were unimodal during reaction, and the peak was sharper than those in the case of no \(H_2O_2\)-addition.
Yield of Degradation Products

*Figure 6* shows the yield of depolymerised NR, compared with the amount of levulinic acid formed. It is likely that the abrupt decrease in the yield of depolymerised NR in the first hour of reaction was due to the formation of the fraction which could not be coagulated because it was of very low molecular weight. The fraction was formed by random chain scission with radicals. After one hour, the yield decreased slowly and linearly with prolonged reaction time. On the other hand, the amount of levulinic acid also increased linearly as a function of reaction time. The total yield of the degradation products, depolymerised NR and levulinic acid, was above 90% during reaction. These results and very slow decrease of $M_n$ after its rapid fall in initial period of reaction indicated that the formation of levulinic acid occurred from a terminal of a polymer chain with direct oxidation by ozone.

**FTIR Spectra**

IR spectra of original and depolymerised NR are shown in *Figure 7*. If NR was degraded by the direct oxidation of ozone in the same way as that in organic solvent, three peaks at 3440, 1720 and 1084 cm$^{-1}$ assigned
Figure 1. Weight average molecular weight of depolymerised NR as a function of reaction time.

Figure 2. Change of pH of latex with reaction time.
**Figure 3.** Weight average molecular weight of depolymerised NR in the presence of \( \text{H}_2\text{O}_2 \) as a function of reaction time.

*Ozone generating rate: 4g/h.*

**Figure 4.** Molecular weight distribution curves in the absence of \( \text{H}_2\text{O}_2 \).

*Ozone generating rate: 4g/h.*
Figure 5. Molecular weight distribution curves in the presence of $\text{H}_2\text{O}_2$.
Ozone generating rate: 4g/h; amount of addition of $\text{H}_2\text{O}_2$: 10%.

Figure 6. Yield of depolymerised NR and levulinic acid with reaction time.
to hydroxyl, carbonyl and ether group respectively, were expected to appear, and increase with reaction time. However, as shown in Figure 7, only one peak (at 1720 cm\(^{-1}\)) was found to appear and increase with reaction time. Therefore, it is suggested that the terminal group of depolymerised NR is ketone or aldehyde, and hydroxyl and carboxyl group were not formed.

**Viscosity**

It is known that melt viscosity (\(\eta\)) of a polymer is dependent on its \(\overline{M}_w\), and a log-log plot of \(\eta\) vs. \(\overline{M}_w\) is linear. Therefore, the relationship between viscosity and \(\overline{M}_w\) is expressed by the following equation

\[
\eta = K\overline{M}_w^\alpha
\]

where \(K\) is a function of temperature and dependent on the chemical structure of a polymer. Fox and Loshaek\(^8\) showed that a log-log plot of \(\eta\) vs. \(\overline{M}_w\) covering a very wide range of \(\overline{M}_w\) showed two lines which intersected at a critical value of \(\overline{M}_w\) (\(\overline{M}_c\)) for many types of polymers, and the value of \(\alpha\) was 3.4 for all kinds of polymers when the \(\overline{M}_w\) is above \(\overline{M}_c\), while \(\overline{M}_c\) was dependent on the chemical structure of a polymer. They also showed that polymer molecules entangled with other if the \(\overline{M}_w\) is above \(\overline{M}_c\), and disentangled below \(\overline{M}_c\). As shown in Figure 8, a log-log plot of \(\eta\) vs. \(\overline{M}_w\) is one line, and \(\alpha\) is 3.5. Therefore, it appeared that NR had not degraded enough to disentangle under conditions of this study.

![Figure 7. IR spectra of original and depolymerised NR.](image-url)
CONCLUSION

NR could be depolymerised by bubbling ozone into commercial HAL. The formation of levulinic acid caused pH of latex to fall during reaction. While the pH of latex was above 8 in the initial period of reaction, decrease in $M_w$ was very fast, but abruptly slow after pH fell below 8. The initial depolymerisation was accelerated by the addition of $H_2O_2$. However, the amount of levulinic acid increased and the yield of depolymerised NR decreased linearly with prolonged reaction time. Only carbonyl groups were found in IR spectra of depolymerised NR, and the intensity increased with prolonged reaction time. These results indicated that most of the chain scission of NR occurred via oxidative degradation reaction of hydroxyl and hydroperoxyl radicals at the initial stage, and the subsequent slow decrease in $M_w$ was due to the formation of levulinic acid from the terminal of a polymer chain with direct oxidation by ozone. Although the minimum $M_w$ of depolymerised NR was about 50 000 in this study, it appeared that a lower $M_w$ of NR could be prepared by increasing the generation rate of ozone.

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REFERENCE


