

Hydrogenation of Epoxidized Natural Rubber

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SYNOPSIS

The thermal properties of epoxidized natural rubber (ENR) have been found to improve upon hydrogenation in a solution phase, in the presence of a homogeneous catalyst, at 50°C. The hydrogenated ENR shows higher T_{max} values in the DTG scan and, upon aging, the change in carbonyl concentration is less as compared to that of ENR, as detected by IR spectrophotometry. The hydrogenated product was characterized by IR and 1H -NMR spectroscopy. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The feasibility of chemical modification of various commercially available polymers has attracted attention for altering and optimizing their physical and mechanical properties. The chemical modification of diene elastomers has attained special significance, because of (i) the ease of conversion, due to the reactivity of double bonds, (ii) the retention of major properties of parent polymer, and (iii) the improvements achieved in some other properties upon modification. Thus, hydrogenated nitrile rubber (HNBR) and epoxidized natural rubber (ENR) are two technocommercially accepted chemically modified elastomers. HNBR has very good aging resistance and high temperature performance and oil resistance. ENR, being derived from natural rubber (NR), has excellent strength and acquires solvent and oil resistance and property of gas impermeance upon epoxidation. The primary drawback of ENR, like NR, is its poor aging properties.¹⁻³ The hydrogenation of ENR is expected to yield a product with improved aging behavior, due to a reduction in the unsaturation level.

A variety of chemical methods, as well as the more usual direct catalytic processes for hydrogenation, have been described in the literature, which has been reviewed by Schulz et al.⁴ Burfield et al.⁵ reported

successful hydrogenation of NR and synthetic Cis, 1,4-polyisoprene in solution, using nickel and cobalt salts in conjunction with trialkyl ammonium compounds. Shahab and Basheer⁶ described the use of the palladium catalyst, with calcium carbonate support, for the solution hydrogenation of cis- and trans-polyisoprene. Burfield⁷ further described a dry process for the hydrogenation of NR and synthetic polyisoprene with a nickel catalyst and an aluminum cocatalyst. He mixed the catalyst system in dry rubber in a two-rolled mill to yield a 50% hydrogenated product.

The objective of the present work is to hydrogenate ENR with a homogeneous catalyst system, and to evaluate the aging property of the products by TGA and IR spectrophotometry. The analysis of the hydrogenated product has been performed with IR and 1H -NMR spectrometry.

EXPERIMENTAL

Materials

ENR, with 50 mol %/epoxidation level (ENR50), was prepared in our laboratory using an *in-situ* generated performic acid, as per the method described in our previous publication.^{8,9} The catalyst for hydrogenation, viz. palladium acetate, was obtained from M/s. Aurora-Mathey, Ltd., Calcutta, India. All other solvents and chemicals were supplied by M/s. E. Merck, Ltd., India.

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Instrumental Analysis

The IR analysis of the product was performed with a Perkin-Elmer, model 843, IR spectrophotometer. The hydrogenated product was dissolved in spectroscopic grade chloroform and the film cast on the KBr plate was analyzed in the IR spectroscopy.

A $^1\text{H-NMR}$ study was carried out with a Jeol JNM $F \times 100$ FT-NMR instrument; CDCl_3 was used as the solvent, and TMS was used as the standard.

Thermogravimetric analysis was done in a Dupont 9000 thermal analyzer with a 951 TGA attachment.

The Reaction

The catalyst tried for hydrogenation of ENR was palladium acetate, which was used successfully by Bhattacharya et al.¹⁰ for hydrogenation of NBR.

ENR was milled in a two-rolled mill and was sheeted out. The thin film was cut into small pieces and was kept in a measured amount of ethyl acetate for 48 h to make a 2% solution. However, complete dissolution of the rubber did not take place. Microgels were visible under strong light. The solution was transferred to a high pressure autoclave with a glass reactor without separating the gels. Palladium acetate catalyst, in the concentration of 1.8×10^{-4}

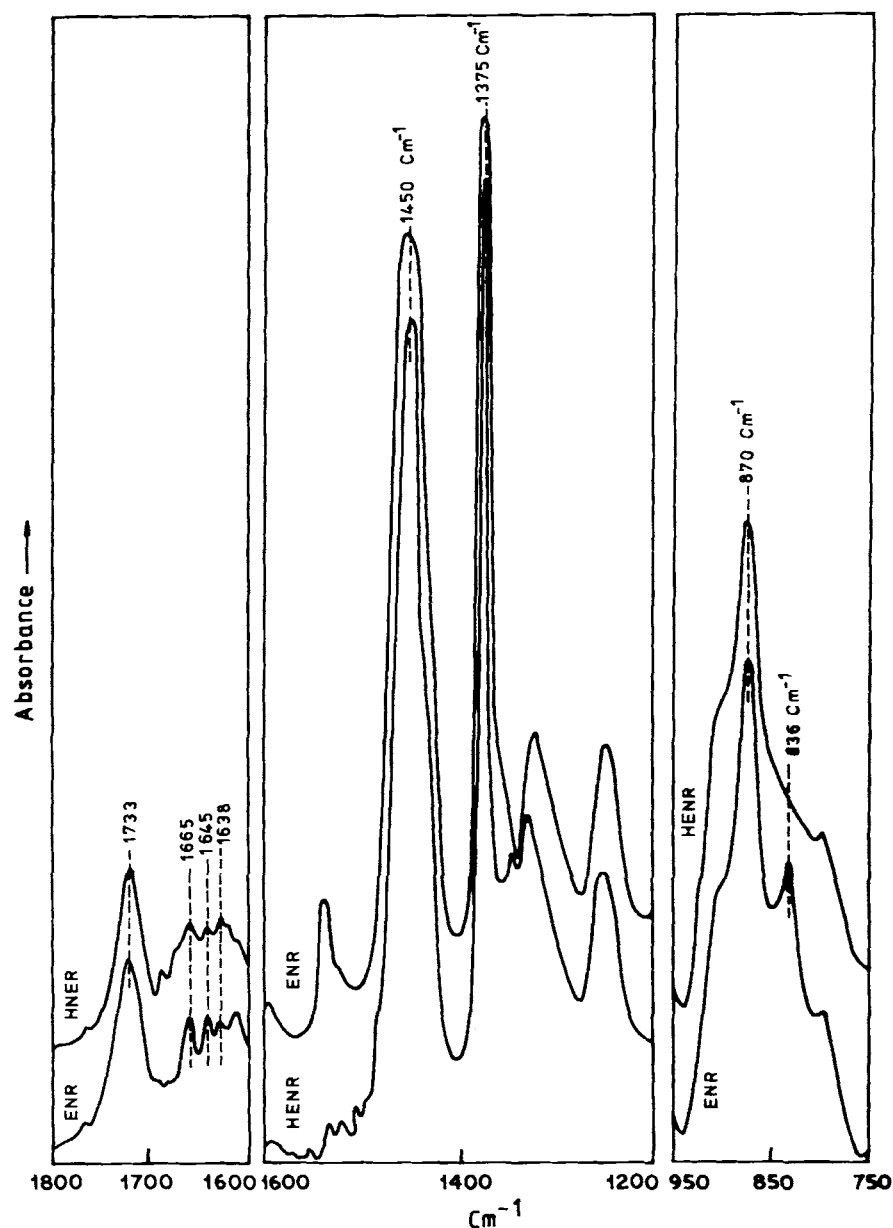


Figure 1 IR spectra of ENR and HENR.

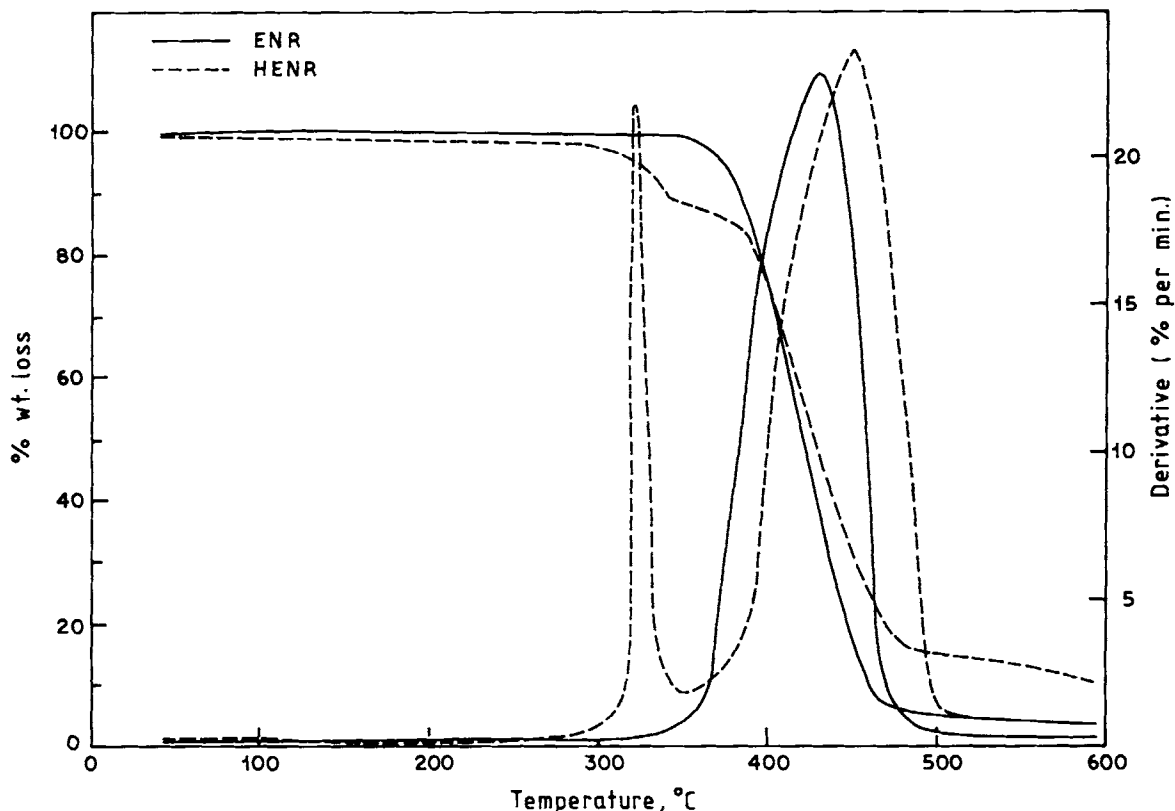


Figure 3 TGA and DTG traces of ENR and HENR.

thoroughly with methanol and was dried under vacuum for 48 h. The color of the hydrogenated sample was dark brown, presumably due to the presence of the catalyst.

Determination of Gel Content

The gel content of the samples was determined by keeping 0.4–0.5 g of samples in measured volume of chloroform for three days at room temperature. The solution was filtered and % sol was determined from the concentration of the filtrate by evaporating an aliquot portion. The gel content was determined by the difference.

Mechanical Properties

Mechanical properties of raw rubber samples were determined with a Zwick 1445 universal testing machine with a strain rate of 20 cm/min.

RESULTS AND DISCUSSIONS

Figure 1 shows the IR spectra of both hydrogenated ENR (HENR) and ENR. The spectra of ENR shows distinct peaks for the epoxy group at 870 cm^{-1} and

for the 1:4 Cis-isoprene unit at 836 cm^{-1} . The latter peak is absent in the spectra of HENR. However, the broad width of this band of HENR in this region indicates that some residual double bonds are still present. This is more prominent in the $1900\text{--}1600\text{ cm}^{-1}$ region, where the 1665 cm^{-1} peak, due to 1,4 >C=C< moiety, is reduced for HENR. But the peaks for 3,4 and 1,2 structures, at 1645 cm^{-1} and 1638 cm^{-1} , respectively, have almost vanished in the case of HENR. This signifies that the 1,2 and 3,4 isomer units are more reactive towards hydrogenation. The spectra in the $1600\text{--}1200\text{ cm}^{-1}$ region shows a relative increase in the height of the 1450 cm^{-1} peak, corresponding to the >CH_2 group for HENR, as compared to ENR. However, the epoxy peak height at 870 cm^{-1} remains unchanged. The absorbance ratio (with reference to the methyl deformation band at 1375 cm^{-1}) of the epoxy-band, determined as per ASTM method (ASTM D3677),¹¹ both for ENR and HENR, is found to be of the same value.

Figure 2 represents the $^1\text{H-NMR}$ spectra of ENR and that of HENR. The increase in the 1.28 ppm signal for HENR signifies an increase in methylene groups. Also, there is a prominent reduction in the

5.14 ppm signal for HENR, which is due to the ole-

finic methine proton ($\begin{array}{c} \text{H} \\ | \\ \text{C}=\text{C} \\ | \end{array}$). Interestingly,

the small signal at 3.67 ppm for ENR, due to tetrahydrofuranly methine proton, disappeared in the case of HENR and a small hump appeared at 3.88 ppm instead. This signal may be assigned to the proton α - to an ester group. However, no change of signal intensity is detectable at 2.72 ppm, due to the

epoxy methine proton ($\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{C} \quad \text{C} \\ | \quad | \\ \text{H} \end{array}$) for HENR.

The epoxy content is calculated by the formula, % epoxy = $A_{2.72}/(A_{2.72} + A_{5.14})$, as described by Davey and Loadman,¹² where A represents the area under the respective signals. By analogy, percent double bond = $A_{5.14}/(A_{2.72} + A_{5.14})$. The difference in double bond contents for ENR and HENR, calculated with this formula, shows a 24% reduction in HENR. Thus, percent hydrogenation is found to be 24%.

Figure 3 represents the superimposed TGA thermogram and derivatigrams of ENR and HENR. The T_{max} values for ENR and HENR are 428 and 455°C, respectively. This clearly indicates the improvement in thermal stability of HENR over ENR. The sharp peak in the derivatigram of HENR, at around 310°C, is due to the decomposition of palladium acetate.

Both ENR and HENR were aged at 70°C for 48 h in an oven. The IR spectra of aged and unaged ENR and HENR, at 1900–1600 cm^{-1} (Fig. 4) reveals that the increase in carbonyl peak height at 1733 cm^{-1} of the aged HENR is much less as compared to that of aged ENR.

Physical Properties of Gum Rubbers

The gel content, green strength, modulus at 300% elongation, and elongation at break have been determined for both the modified and the unmodified rubbers. It has been found that the gel content of both ENR and hydrogenated ENR is more or less same (60 to 62%), showing that hydrogenation does not add to the gel content of the rubber. However, the gel content of ENR shows a considerable increase upon aging (from 62 to 77%), but in the case of HENR, the increase is relatively small (60 to 66%). This observation may be explained on the basis of the low amount of oxygenated group formation, due to the reduced level of unsaturation in the hydrogenated product (Fig. 4 shows the reduced amount of carbonyl group formation for HENR upon aging).

Hydrogenation of ENR reduces both the green strength (0.65 to 0.57 MPa) and the modulus at

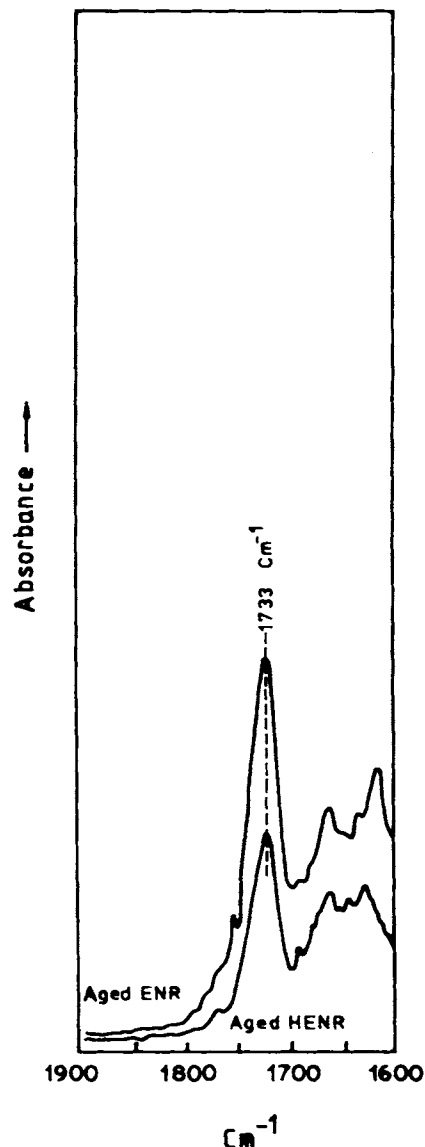


Figure 4 IR spectra of aged ENR and HENR.

300% elongation (from 0.26 to 0.22 MPa), whereas the elongation at break is increased marginally (from 403% to 417%). These effects are the consequence of increased chain flexibility, due to the reduction in double bond content of the polymer backbone.

CONCLUSIONS

Hydrogenation of ENR in solution phase has been successfully performed with a homogeneous catalyst, such as palladium acetate, at a temperature of 323 K. The product has been characterized by IR, NMR, and TGA. HENR shows better thermal stability and aging resistance.

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