# Moisture-Sorption Properties and Studies on the Dilute Solution Behavior of Epoxidized Natural Rubber ENR 50

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ABSTRACT: Studies of the dilute solution capillary viscosity and moisture sorption of commercial samples of epoxidized natural rubber (ENR 50) were carried out. Dilute solution viscometry of ENR 50 solutions was conducted in xylene, tetrahydrofuran, and methyl ethyl ketone solvents and the degradation due to shearing and oxidation for this rubber was followed. At average elevated temperatures and high relative humidities, epoxidized natural rubber ENR 50 shows high moisture sorption. Moisture sorption measurements at 100% RH and 34°C followed by desorption show near equilibrium moisture intake of 3.402–3.661 g H<sub>2</sub>O/100 g rubber, which agrees reasonably well with the estimated value of 4.108 g H<sub>2</sub>O/100 g ENR 50. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1633–1644, 1999

**Key words:** moisture sorption; dilute solution viscometry; epoxidized natural rubber; shear degradation; oxidative degradation

# **INTRODUCTION**

Epoxidation of unsaturated hydrocarbon polymers provides a means of introducing polarity along the polymer. For example, controlled epoxidations of natural rubber (NR) in solution<sup>1</sup> or latex<sup>2,3</sup> enable the conversion of *cis*-1,4-isoprenyl units to predominantly 2-methyl-2,3-oxybutyl units. In latex modification, *a priori* expectation of the nonuniformity of the reaction between peroxy acid and isoprenyl repeat units is not evident; the rate of epoxidation and the extent of epoxidation are reported not to be affected by the change in the average particle size of the unmodified latex.<sup>4</sup>

Gelling has published a great deal on his studies of NR latex modification to obtain epoxidized natural rubbers.<sup>5–8</sup> It has been confirmed that the epoxidation of NR in solution gives a random copolymer.<sup>9</sup> In industrial practice, NR latex is epoxidized and the extent of epoxidation is cut short to avoid loss of useful rubbery properties. Of the existing commercial grades, ENR 50 and ENR 25 are nearly 50 and 25 mol % epoxidized NR latices, respectively.

From the point of view of market demand, a hydrocarbon-based polymer modification such as that from NR to ENR has excellent scope for a variety of applications. Given the low cost of NR latex and the simple nature of the setup for ENR rubber production, not only could commodity elastomers be upgraded with ENR rubbers but also added value elastomers could be replaced. Examples of the latter are polychloroprenes, poly(butadiene-co-vinylpyridine),  $\alpha, \omega$ -dihydroxypolybutadienes, polypentenamers, and carboxyl-terminated rubbers. The control over the reaction, the glass transition temperature  $(T_g)$  that follows it to  $T_g \approx$  ambient temperature makes modified NR latex attractive for indoor paints and coatings

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Table I Gel Fraction of ENR 50 (1G)

Solvent	Samples of ENR 50 <sup>a</sup>	Gel Fraction <sup>b</sup>
Xylene	NM	0.49-0.68
Xylene	Μ	None
THF	NM	0.43 - 0.46
THF	Μ	None
MEK	NM	0.25 - 0.46
MEK	Μ	None
NMP	NM	0.77 - 0.85
NMP	Μ	None
1,2-Dimethoxyethane	NM	0.86 - 0.94
1,2-Dimethoxyethane	Μ	0.23 - 0.28
Dimethylformamide	NM	0.43 - 0.47
Dimethylformamide	Μ	0.11 - 0.14
Dimethylacetamide	NM	0.82 - 0.90
Dimethylacetamide	Μ	None

<sup>a</sup> M, masticated; NM, nonmasticated.

<sup>b</sup> Retained on 0.3-mm screen.

applications. ENR 50 is reinforcible with silica<sup>10</sup> and may be pigmentated with a variety of colors.

Among the applications that have been proposed for ENRs, oil-resistant tubing, footwear soling, adhesives, and vibration isolation devices are noted.<sup>8</sup> The latter is proposed based on the high damping nature of ENRs.<sup>10</sup> The oil resistance of ENR 50 is noted to be comparable to that of medium grades of NBR rubber.<sup>10</sup> In terms of both air permeability and the temperature coefficient of air permeability, ENR 50 is considered equivalent to butyl rubber.<sup>10</sup>

In latex form, ENRs or their mixtures may well prove useful as film formers for sound damping applications in the audible frequency range. A thorough study of the properties of PVC–ENR blends was accomplished.<sup>11</sup> The toughening properties of ENR 50 in epoxy matrices has recently been reported.<sup>12</sup> In sealing applications like underground wire and cable sheathing, the use of rubbery particles of water-swellable polymers provide containment of water in case of leakage reaching the cable.<sup>13</sup> In similar applications, the use of ENRs as fillers is not inconceivable. Here, studies on the dilute solution behavior and the moisture sorption of commercial samples of ENR 50 are reported.

# **EXPERIMENTAL**

Epoxidized NR bales were obtained from Kumpulan Guthrie Berhad, Seremban, Negeri Sembilan. ENR 50 contains a fraction of 0.48 (by mole) of methyl-2,3-butyleneoxy repeat units. The *cis*-1,4polyisoprene (NR) used was Standard Malaysian Rubber (SMR-L), supplied by the Rubber Research Institute of Malaysia, Sungai Buloh, Selangor. The designations of 1G, 2G, and 3G trace the supply of the ENR 50 to its respective bale.

Xylene, tetrahydrofuran (THF), and methyl ethyl ketone (MEK) were Analar grade, supplied by BDH, Poole (England). 1-Methyl-2-pyrrolidone, 1,2-dimethoxyethane, dimethylformamide, and dimethylacetamide were purchased from Fluka AG (Buchs, Switzerland) and dried over 5 Å molecular sieves before use.

#### **Mastication of ENR 50**

Typically, 8-g quantities of ENR 50 were masticated at a low kneading speed of 20 rpm in the 40-mL capacity mixing chamber of a Brabender<sup>™</sup> Plasticorder (Duisburg, Germany). This way, frictional heat within the material was kept at 37– 45°C. Kneading times were 8, 12, 16, and 20 min. For studies of the solution properties, chopped bits of the rubber were placed after mastication immediately into 1-dL volumetric flasks and dissolved by gentle swirling. Samples referred to as "masticated" in the text are those with an 8-min history unless otherwise stated.

#### **Sol-Gel Fractions**

Samples, 1.0 g, of ENR 50 (1G) were left to dissolve for 24 h at room temperature by swirling at 15 rpm on a shaker table (Gerhardt, Bonn, Germany). Their solutions were then filtered through a 0.3-mm stainless-steel screen and centrifuged using a Biofuge 17S (Heraeus GmbH, Germany). Gel fractions were determined by evaporation of the solvent and gravimetry of the samples dried to a constant weight after filtration.

#### **Dilute Solution Capillary Viscometry**

Differently treated samples were left to dissolve in appropriate solvents in 1-dL calibrated volumetric flasks. Initial rubber concentrations were in the range of 0.3 and 0.5 g dL<sup>-1</sup>. These concentrations were corrected for any gel deposition upon centrifugation. Measurements of the dilute solution viscosity were made using a direct dilution Ubbelohde viscometer at 30.00°C  $\pm$  0.02°C. Flow times for each dilution were within 0.2 s. The samples containing



**Figure 1** Plots of viscosity number versus concentration for xylene solutions of epoxidized NR ENR 50 (2G).

0.10% (w/w on rubber) 2,2,4-trimethyl-1,2-dihydroquinoline (TMQ) antidegradant were prepared from a stock of this antidegradant in the appropriate solvent. Solutions designated as "oxygenated" were obtained without TMQ addition, by bubbling air at a rate of 0.5 L min<sup>-1</sup> for 18 h using a gas dispersion tube (Pyrex fritted glass tip #1). Viscosity numbers were obtained in the usual manner; shear rate corrections were omitted as the calculated maximum shear rates in the capillary were  $<1500 \text{ s}^{-1}$ .



**Figure 2** Plots of viscosity number versus concentration for xylene solutions of epoxidized NR ENR 50 (2G).

# Fourier Transform Medium IR (FtmIR) Spectroscopy

Films of ENR 50 (3G) were cast from xylene solutions by evaporation. Aliquots, 1.5 mL, of a 5% w/v solution of the rubber were poured into  $30 \times 25$ -mm PE molds after straining through a 0.3-mm screen. Films were cast from three fractions: (a) masticated sol and microgel in xylene, (b) gel fraction retained on the 0.3-mm screen, and (c) dispersion of unmasticated ENR 50. Evaporation of the solvent took 3

days under a stream of sweeping air at ambient temperatures. The films obtained were placed as windows on the sample mounts and kept in the dark. Thicknesses varied between 0.1 and 0.2 mm. The spectra were recorded monthly using an FTIR spectrometer (1600 Perkin–Elmer) up to 5 months.

#### **Moisture Sorption**

Typically, 0.4000 g of a rectangular ENR 50 (3G) sample was hooked, suspended in a protective cup



**Figure 3** Plots of viscosity number versus concentration for xylene solutions of NR SMR L.

from a wire, and placed in a constant humidity chamber (LEEC Model SFC3, Nottingham, England) at 34°C and 100% RH up to 900 h. No checks were undertaken to gauge contributions from oxidative aging. The moisture absorbed by the samples was determined gravimetrically. Desorption experiments were conducted in a desiccator over potassium hydroxide and silica gel as desiccants.

# **RESULTS AND DISCUSSION**

# Gel Content in ENR 50

The insoluble fractions of the commercial samples obtained from various solvents are shown in Table I. Insoluble weight fractions for a typical nonmasticated NR (SMR-L) reference are shown to be



**Figure 4** Plots of viscosity number versus concentration for THF solutions of epoxidized NR ENR 50 (2G).

<0.02. Prior to mastication, the gel-weight fraction of the samples of the ENR 50 (1G) used were found to be high, up to 0.68 in xylene. The formation and prevention of crosslinking in NR latex has been well researched and documented.<sup>14</sup> The prevention of crosslinking appears to have remained unchallenged. Nevertheless, the solubilities of the ENR 50 samples are much improved after mastication of this rubber under mild shearing. Among the solvents considered, *N*-methylpyrrolidone (NMP) was found to be most suitable for masticated samples of this rubber.



**Figure 5** Plots of viscosity number versus concentration for MEK solutions of epoxidized NR ENR 50 (2G).

It has long been known that the epoxidation of unsaturated hydrocarbon polymers (UHP) leads to secondary reactions besides oxirane-ring formation.<sup>1</sup> Whether conducted in a dilute solution of a UHP or with UHP in latex form,<sup>3</sup> the reaction conditions may lead to the following secondary reactions:

(a) Aside from oxirane ring closure, modification of the unsaturated hydrocarbon poly-



Figure 6 Typical FTmIR spectrum of unaged ENR 50 film.

mer backbone also gives  $\mathcal{M}(H_2C=)C$ — CH(OH) $\mathcal{M}$  an allylic moiety,<sup>1</sup> hydroxyesters,<sup>1,5</sup> diols,<sup>5</sup> and cyclization of the modified backbone with closure to form substituted furans and pyrans.<sup>5,6</sup>

- (b) Chain scission of the UHP backbone;<sup>1</sup> chain scission is reported to be higher, the higher the extent of epoxidation.<sup>4</sup>
- (c) Interchain linkages and gel formation via ether crosslinks<sup>1,7</sup> besides well-established free-radical mechanisms involving hydroxy free radicals.

# Dilute Solution Capillary Viscometry of ENR 50 Solutions

Apparent viscosity number versus concentration plots for differently treated NR 50s are shown in Figures 1–5. The behavior of ENR 50 in dilute solution was different in the THF and MEK solvents. From measurements made in the xylene solvent (Fig. 1), no difference is notable for differently treated samples that had an 8-min mastication history. Mastication between 8 and 20 min did not cause significant additional lowering of  $[\eta]_{app}$  (see Fig. 1). Based on the results obtained

(Fig. 2), ENR 50 does appear to have chain degradation under mild conditions of kneading/ shearing at 20 rpm for over 8 min. The fact that under identical treatment NR shows similar  $[\eta]_{app}$ 's in xylene solutions before and after mastication (see Fig. 3) points to the absence of chain scission. In fact, in a previous mechanodegradation study,<sup>15</sup> the rate of breakdown of NR was reported to be lowest up to 115°C; it can be argued that up to that temperature shearing forces are insufficient to cause substantial "physical" chain scission and, yet, the temperature is not high enough to bring about an efficient chemically induced breakdown. Here, nevertheless, lower limiting viscosity numbers are notable for mastication periods up to 20 min (see Fig. 3).

The results for the THF solutions of the ENR 50 samples (Fig. 4) show the following:

- (a) The difference in the  $[\eta]_{app}$  values for nonmasticated and masticated versions of ENR 50 (2G) is not appreciable.
- (b) In contrast to the behavior in xylene, a marked lowering in  $[\eta]_{app}$  for the THF solution that has been aerated for 18 h is a

Vibration (cm <sup>-1</sup> )	Assignment
$\nu$ 700	st cis CR—CH
ω 737	С—Н
v 800–840	cis CR=CH
$\nu 840 - 870$	st cis Oxirane (1,2 epoxide)
$\nu 840$	st $-CH_2$ (methylene)
$\nu 860$	st $C = CH_2$
$\nu 880$	st C—O—C (ether)
	cis Oxirane
$\nu$ 1030–1150 asym	st C—O—C
	Furan (Saturated acyclic 1,4-epoxid
	Pyran (Saturated acyclic 1,5-epoxid
$\nu 1125 - 1260$	st C—O—C
	Saturated acyclic epoxides
ω 1375–1380	d —CH <sub>3</sub> in —C (Me)
v 1385–1390	st C—O in —C—OH
$\omega$ 1440–1465	d C—H
	(methylene)
	$-CH_3$ in $-C$ (Me)
$\nu 2750-2960$	st C—H
	(methylene)
v 2860–2980	st C—H
	$-CH_3$
$\nu 3100$	st C—H in <i>cis</i> -alkane

Table II mIR Absorption Peaks in ENR 50

result of oxidative chain degradation from peroxidation.

(c) The extent of degradation is highest for the ENR 50 sample that has had the longest history of shearing.

As shown in Figure 5, the ENR 50 samples show severe degradation on aging in the MEK solvent (compare the  $[\eta]_{app}$ 's for solutions whose viscosity numbers were determined well after their preparation). The effect of the degradation is most severe in MEK than in any other solvent thus far reported.

#### FTmIR Spectroscopy of ENR 50

A typical FTmIR spectrum  $(4400-650 \text{ cm}^{-1})$  of ENR 50 is shown in Figure 6. The films were stored in the dark under ambient conditions. The frequency assignments for the material in the range of  $3200-700 \text{ cm}^{-1}$  are given in Table II. Over the 5-month storage period, there was no noted change in the relative absorbances at any of the frequencies, with the exception of that of  $\nu$  $(3200-3600 \text{ cm}^{-1})$  for all samples over the same period (see Fig. 7). The increase in absorbance is attributed to the absorption of moisture based on the following:

- (a) Absence of any significant carbonyl absorption  $\nu$  (1640–1780 cm<sup>-1</sup>), which would correspond to the expected ultimate product of peroxide decomposition over the period of the experiment; this also excludes hydroperoxide formation whose absorption frequency range  $\nu$  (3150–3750 cm<sup>-1</sup>) falls within that of hydroxyl absorption.
- (b) Moisture sorption is reversible, that is, appreciable desorption is inferred from decreases in  $\nu$  (3200–3600 cm<sup>-1</sup>). This was observed for the films that have been heated at 40°C for over 24 h after their storage for 150 days at RT.
- (c) The possibility for structures like  $m(CH_2 =)$  C—CH(OH) massigned to  $\nu$  (3450 cm<sup>-1</sup>) and  $\nu$  (1055 cm<sup>-1</sup>) and diols to have appeared over the storage period is excluded; if any appeared, it would only have been at the expense of
  - (i) A decrease in any of the epoxy absorptions;
  - (ii) Increase of the C=CH<sub>2</sub> absorption at  $\nu$  (860 cm<sup>-1</sup>); or



**Figure 7** FTmIR spectra  $\nu$  (1200–4400 cm<sup>-1</sup>) of epoxidized NR ENR 50 taken over 150 days of storage at ambient conditions.

(iii) Appearance of a more important etheroxygen absorption at  $\nu$  (1125 cm<sup>-1</sup>).

#### Moisture Sorption Behavior of ENR 50

At a given point in time in the material, the moisture level is a complex function of temperature, thermal history of the material, the environment, material properties, for example, composition, and other factors like purity. Water ingress into ENR 50 could not be described by the Fickian processes of diffusion. However, in this case, moisture sorption can be expressed by an equation of the form

Moisture (%) = 
$$A - Be^{-t}$$
 (1)

where A and B are constants for a given set of experimental conditions and t is the time. Equation (1) has been found to be applicable up to fractional moisture intake of 0.7. For ENR 50, moisture intake increases exponentially in time up to  $\approx 120$  h and then on tends toward a plateau value. However, under the conditions of these experiments, an equilibrium value in moisture intake has not been reached even up to 900 h. Moisture intake is plotted versus  $\log_{10} (t, h)$  as shown in Figure 8. A linear portion is noted, corresponding mostly to a 0.3 < fractional moisture



**Figure 8** Plots of moisture intake (%) versus  $\log_{10}(t, h)$  for ENR 50 that were conditioned at 100% RH and 34°C.

intake < 0.9. It is recognized that differences in sample size and shape would introduce differences in the surface to volume ratios, which, in turn, would affect the rate of intake; the rates of intake are similar within the exposure time of these experiments.

Desorption experiments where wet samples are conditioned over desiccants provided dryness to a constant weight. Near equilibrium values for moisture intake was determined from these experiments by the weight difference. For the samples that have been predried at 60°C over 48 h, the moisture intake of ENR 50 was found to fall within the range 3.402-3.661 g H<sub>2</sub>O/100 g rubber.

A thermodynamically determined value would constitute a "reference value" for a material property like moisture-absorption capacity; in this respect, "the group contribution approach"<sup>16</sup> in the estimation of the equilibrium moisture content of ENR 50 at 100% RH and 34°C indicates a value of 4.108 g  $H_2O/100$  g rubber. This value was obtained by taking the molar fractions of the repeat unit structures for epoxidized NR to consist of 0.50 (isoprenyl), 0.48 (2-methyl-2,3-butyleneoxy), and 0.02 (2-methyl 2,3-dihydroxybutylene).

# CONCLUSIONS

The effect of mechanochemical degradation by mastication is exacerbated for solutions of ENR 50 in polar solvents like THF and MEK. This worsening in solution is attributed to oxidative degradation. The processes of mastication for ENR 50 remain essential if this rubber is to be mixed, dispersed, or dissolved. For dissolution, mastication is necessary and recommended in cases where this rubber is to be incorporated into hydrocarbon solvents like toluene or xylene. ENR 50 has a high propensity to absorb moisture and requires thorough drying and air-tight storage, particularly in the moisture-intense tropical climates where this rubber's production is most profitable.

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