The Modification of Secondary High Molecular Weight Guayule Rubber with Metachloroperoxybenzoic Acid

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SYNOPSIS

The epoxidation of secondary high molecular weight guayule rubber has been accomplished. The reaction is performed using metachloroperoxybenzoic acid as the epoxidation agent in various stoichiometric ratios including 5, 10, 20, and 50 mol %. The products were characterized by infrared spectroscopy, [1]H- and ^{13}C-nuclear magnetic resonance (NMR), differential scanning calorimetry, and elemental analysis. ^{1}H-NMR is used quantitatively to calculate epoxidation levels that are compared to stoichiometry. DSC results record a linear relationship between percent epoxidation and T_g. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Guayule, *Parthenium argentatum grey*, a shrub that grows in semiarid regions such as southwest Texas and northern Mexico, is known to provide polymeric fractions of high molecular weight natural rubber (HMWR), *cis*-1,4-polyisoprene.[1-4] HMWR is separated as a byproduct upon processing of the guayule shrub. It is an important strategic material due to its superior properties in comparison with synthetic rubber. Some of the application areas in which HMWR from guayule is used are truck and aircraft tires and as pads on tanks. However, the economics are not favorable to yield only HMWR.

In the HMWR separation process of guayule, secondary high molecular weight guayule rubber (SMWGR) precipitates as a usable fraction. SMWGR is unsuitable for high-performance applications due to lower molecular weight (10^5–10^6 g/mol). Therefore, the utilization of this coproduct fraction is important in establishing guayule as a source of natural rubber. Because of its lower molecular weight, SMWGR is easily reacted in solution.

Epoxy resin chemistry and its use in the coatings industry is well known.[5] Epoxidation of alkenes in the polymer backbone of rubber using peracids is known as the "Prilezhaev reaction" and is well es-

tablished.[6-8] The epoxidation of polymers such as polybutadiene and high molecular weight polyisoprene from Hevea (ENR) has been published.[9-12] Epoxy polybutadienes have use in the coatings industry as they possess good film-forming ability and yield excellent surface wetting. Chemically resistant coatings can be produced by baking with phenolic resins, whereas metal finishes can be produced by reaction of various nitrogen-containing resins. Esterification with fatty acids may be used to produce air-dry or baking resins.[13] However, little attention has been given to the possibility of incorporating epoxidized polyisoprene systems into coating applications. Epoxidized SMWGR, hereinafter EGR, will be studied in epoxy systems as a cross-linking agent with inherent flexibility and adhesion. The use of EGR in the above applications utilizes a natural rather than a synthetic precursor in the production of epoxy-coating systems.

In this paper, the formation and characterization of secondary molecular weight guayule rubber in various epoxidation levels is reported. Percent epoxidation has been determined using both NMR and elemental analysis; differential scanning calorimetry (DSC) has been used to support findings.

EXPERIMENTAL

Materials

Research-grade (50–60%) *m*-chloroperbenzoic acid (*m*-ClPOBA) in *m*-chlorobenzoic acid and toluene

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Figure 1 Epoxidation mechanism.

Table I Reaction Conditions and Results for EGR Synthesis

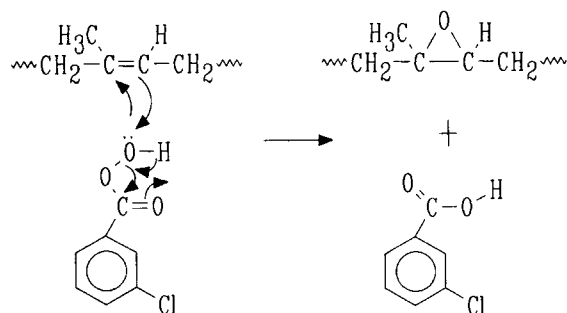| Rubber (g)	m-ClPOBA (g)	Theoretical % Epoxidation	Epoxidation % via NMR
2.1	0.53	5	5.6
2.1	1.34	10	12.3
2.1	2.65	25	22.8
2.1	5.3	50	48.6

were purchased from Aldrich Chemical Co., Milwaukee, WI, and were used as received. SMWGR was supplied by Dr. John Wagner and Daryl Parma at the Texas A&M Engineering and Bio-Sciences Research Center, College Station, Texas. The SMWGR is purified by dissolution in carbon tetrachloride, filtering with a 44 × 36 Gardco fine paint filter, and precipitation into 95% ethanol. The sample is then dried to constant weight under vacuum before reaction.

Epoxidation

A three-neck 250 mL round-bottomed flask fitted with a pressure-equalizing separatory funnel is

charged with a molar amount of SMWGR dissolved in toluene (5% solution) and placed on a magnetic stirring device. The funnel is charged with a molar amount corresponding to desired percentage epoxidation of m-ClPOBA dissolved in toluene (Table I). The flask is immersed in an ice bath to reduce undesired side reactions and allowed to stand for 15 min, after which dropwise addition of the m-ClPOBA is initiated. Upon addition, the reaction is allowed to proceed with high stirring for 30 min at 0°C. The sample is precipitated and washed with 95% ethanol. For the 50 mol % product, methanol is used as the precipitation medium due to the solubility of the product in a toluene/ethanol mixture.
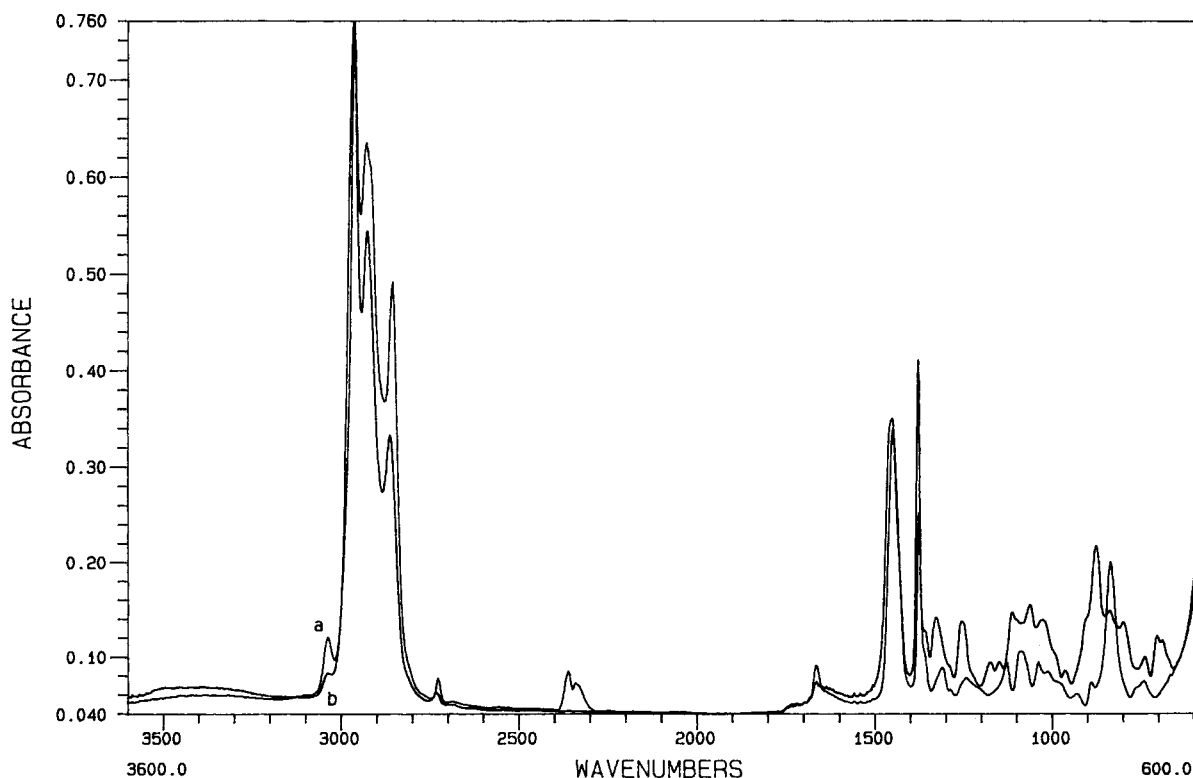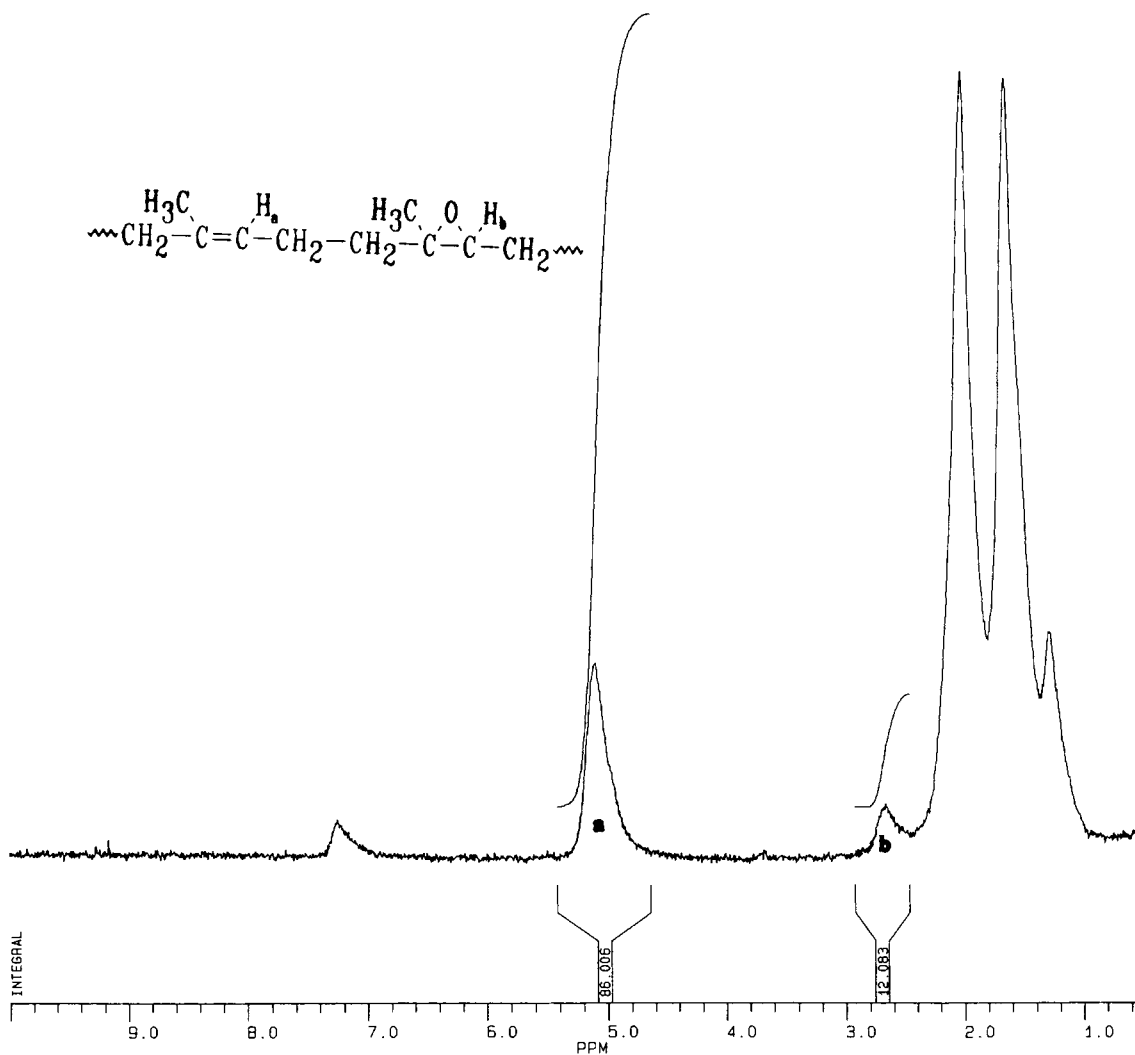

Figure 2 Infrared spectra of (a) SMWGR and (b) EGR 50.

Figure 3 ¹H-NMR spectrum of EGR 10 with relevant assignments. Integrals are shown under the spectrum.

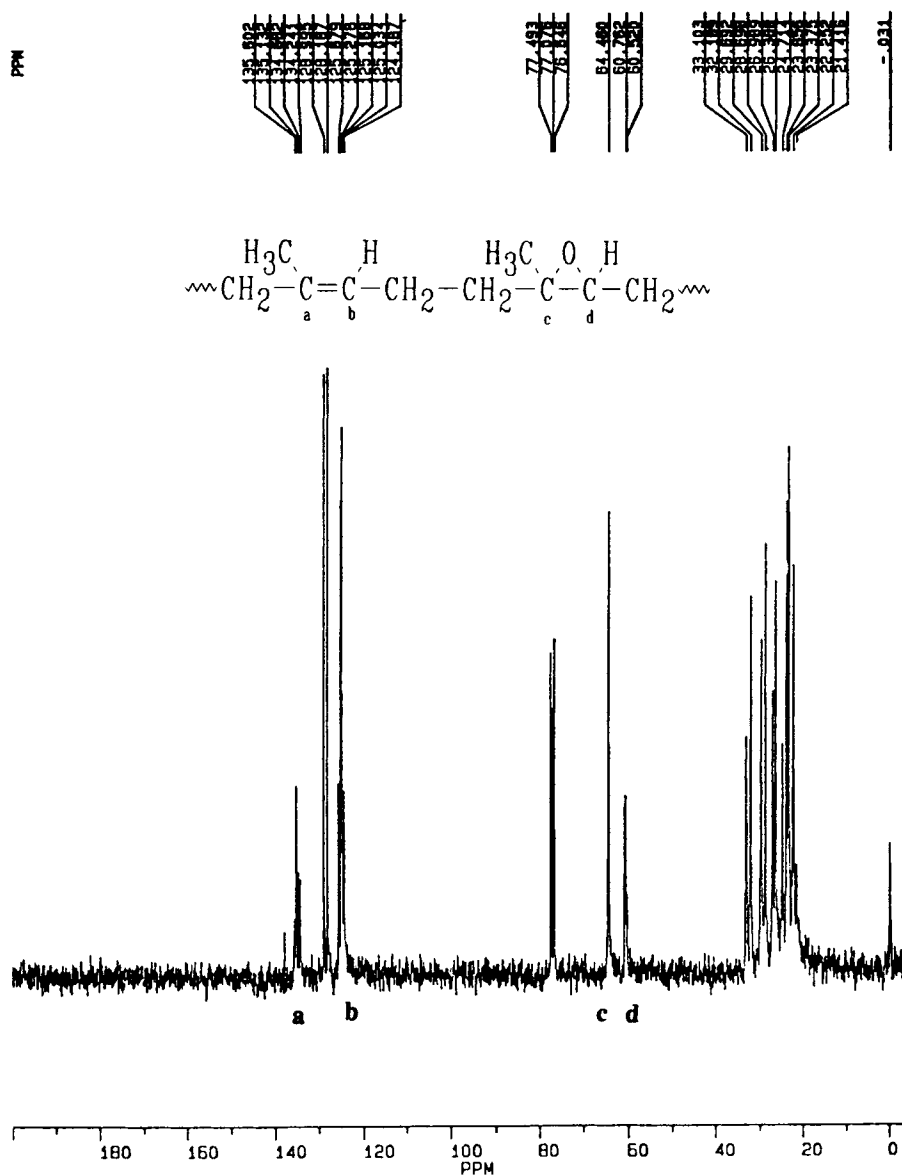The product is then dried to constant weight under vacuum.

Analytical

Infrared analysis was performed on a Nicolet Systems IR 42 FTIR spectrometer. Films were cast from toluene on sodium chloride-polished discs (Wilmad Glass Co., Buena, NJ) for analysis. ¹³C-NMR and ¹H-NMR were obtained on a Bruker 200 mHz nuclear magnetic resonance spectrometer using deuterated chloroform as solvent spiked with tetramethylsilane as internal reference. DSC was accomplished on a DuPont 9900 series DSC. Samples were tested at a heating rate of 10°C/min under a nitro-

gen atmosphere. Elemental analysis was performed by MHW labs, Phoenix, AZ.

RESULTS AND DISCUSSION

Although a variety of peracids may be used to perform the epoxidation, m-ClPOBA was chosen due to availability, reactivity, and economy. Among other methods, 3,5-dinitroperbenzoic and trifluoroperacetic are prominent reagents. The generally accepted mechanism of epoxidation[6] is shown in Figure 1. The mechanism involves a concerted reaction and the need for low ion formation is desired. The reaction is typically carried out in a solvent of low-ionization potential such as chloroform, xylene,

$$\underset{a}{\overset{H_3C}{\text{—}}}\text{CH}_2\text{—}\overset{H_3C}{\underset{a}{C}}=\underset{b}{\overset{H}{C}}\text{—CH}_2\text{—CH}_2\text{—}\underset{c}{\overset{H_3C}{\underset{}{C}}}\overset{O}{\text{—}}\underset{d}{\overset{H}{C}}\text{—CH}_2\text{—}$$

Figure 4 ^{13}C-NMR spectrum of EGR 25 with relevant assignments.

toluene, and benzene. The rubber dissolves slowly in toluene, but is soluble.

FTIR is used to verify the incorporation of epoxy rings into the natural rubber backbone. Evidence of the formation of epoxy groups can be seen from comparison of IR spectra in Figure 2, which shows an absorption decrease of the olefinic absorption bands at 3025 and 1660 cm^{-1}. These absorbances are due to vinylidene stretching frequencies: C — H stretching of olefinic protons and C = C stretching, respectively. Absorbances at 1255, 1067, and 874 cm^{-1} are indicative of internal epoxy groups.[14] The 874 cm^{-1} absorbance is due to C — C stretching dur-

ing contraction of the C — O bond. The appearance of the peak at 1255 cm^{-1} is due to stretching and contracting in phase[15] of the epoxy ring bonds.

The reaction is efficient as stoichiometric balance can be easily achieved. Only slight adjustments need be made in reaction conditions to achieve the desired percent epoxidation. The percent epoxidation can be calculated via ^{1}H-NMR. This permits the quantitative determination of percent epoxidation and, thus, reaction condition adjustments can be affected to achieve the desired percent epoxidation. The nature of the ^{1}H-NMR spectra is shown in Figure 3. If an assumption that no side reactions take place,

Table II   Elemental Analysis of EGR

	Theory			Found			
Material	% C	% H	% O	% C	% H	% O	Actual %
EGR 5	87.2	11.64	1.16	86.71	11.41	1.88	8.3
EGR 10	86.2	11.5	2.3	85.51	11.14	3.25	14
EGR 25	83.3	11.1	5.5	82.42	10.52	7.06	32
EGR 50	78.9	10.5	10.5	79.17	10.58	10.25	48.5

the percent epoxidation can be obtained via the ratio of the area under the epoxy proton peak (AE) to the sum of areas under the olefinic proton peak (AO) and the epoxy proton peak[16,17]:

$$\% \text{ Epoxidation} = \frac{\int AE}{\int (AE + AO)} \times 100 \quad (1)$$

In all cases, ^{1}H-NMR confirmed the percent epoxidation as expected [calculated from eq. (1); see Table I]. For instance, the ^{13}C-NMR spectrum shows absorptions at 64.46 and 60.76 ppm, representing the methine and quaternary carbon, respectively (Fig. 4). The epoxidation of SMWGR is a random process with the epoxy group placement showing no correlation to placement of other groups along the natural rubber backbone. In our hands, NMR analyses have fallen within 5% experimental
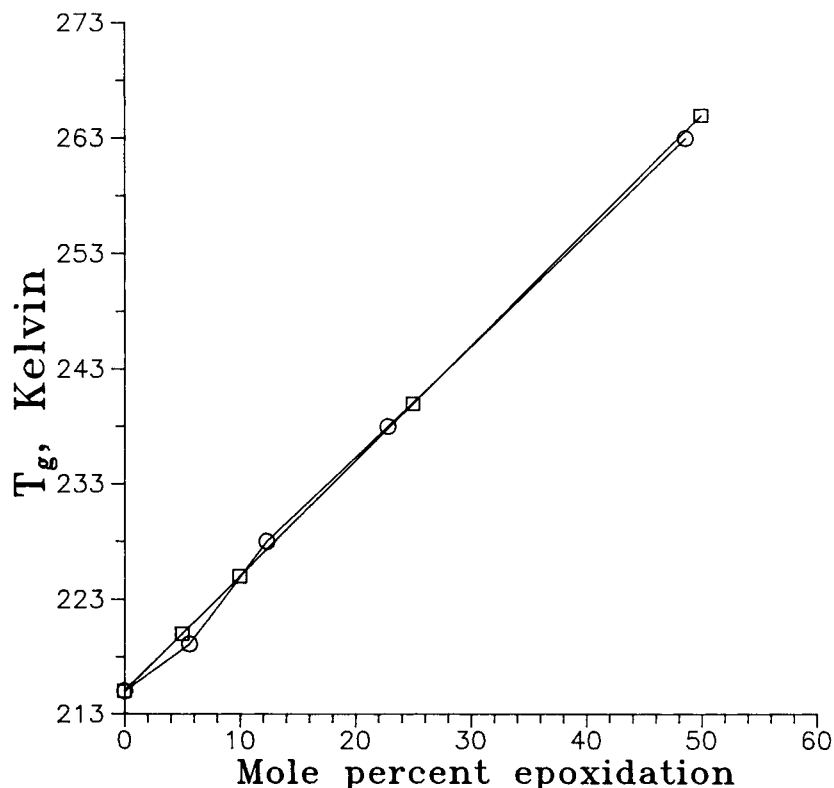
Figure 5   Graph depicting glass transition temperature in Kelvin vs mol % epoxidation. A linear relationship exists between mol % epoxidation and T_g: (□) theoretical plot from literature values; (○) experimentally found relationship between percent epoxidation from ^{1}H-NMR and T_g from DSC.
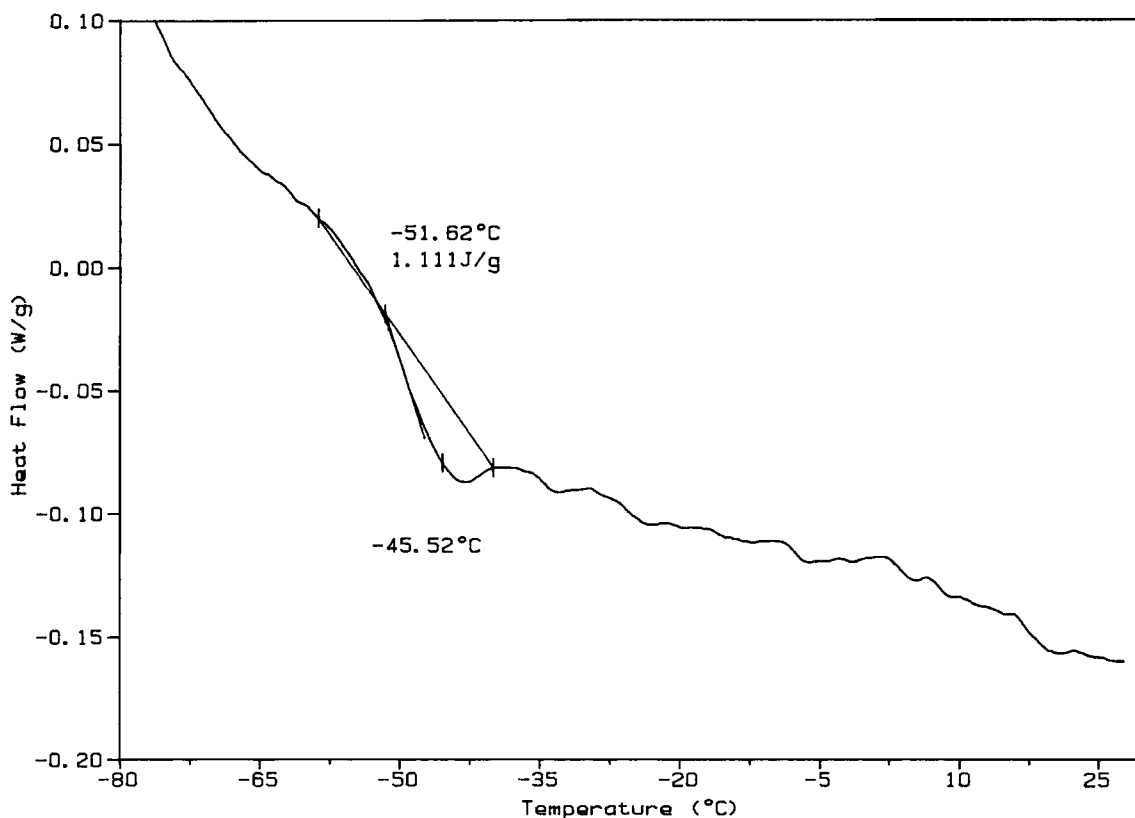
Figure 6 DSC trace of EGR 10.

error. For instance, NMR determinations show 5.6% epoxidation for EGR 5 stoichiometry, 12.3% epoxidation for EGR 10 stoichiometry, 22.8% epoxidation for EGR 25 stoichiometry, and 48.6% epoxidation for EGR 50 stoichiometry.

The desired epoxidation level is reached quickly as confirmed via ^{1}H-NMR. The need for low temperatures is important; otherwise, side reactions leading to undesirable compositions become significant. For instance, side reactions produce crosslinked systems as well as ring-opened structures.[9,12,18]

Elemental analysis is consistent with NMR findings (Table II) for values obtained with stoichiometrically balanced reaction conditions. Oxygen percent was performed by difference, explaining the apparent differences in elemental analysis of EGR 25 with the NMR data for the same system.

The T_g of SMWGR ($-58°C$) was determined by DSC analysis and is higher than that of high molecular weight NR ($-70°$) because of slight crosslinking due to storage hardening.[19] The material, although slightly cross-linked, remains soluble in common, organic, nonpolar solvents. The mol % epoxidation is reported to alter T_g in a linear fashion

(Fig. 5). For instance, values reported show a 1° increase in T_g for every 1% epoxidation.[9,10,19] Our findings are consistent with these results (Figs. 6 and 7, wherein EGR 5, 10, 25, and 50 refer to stoichiometric balances). Accordingly, DSC can be used as a quantitative measure for the extent epoxidation. Moreover, in all cases, the increase in T_g corresponded to the percent epoxidation as determined by NMR. For instance, DSC analyses showed T_g increases for the following stoichiometric variations as follows: EGR 5, a 5.1°C increase; EGR 10, a 13°C increase; EGR 25, a 23°C increase; and EGR 50, a 49°C increase. EGR remains rubbery after reaction, is soluble in common organic solvents and mixtures of solvents, and is a characteristic beige-colored product that darkens to brown with storage.

CONCLUSIONS

The formation and characterization of epoxidized secondary high molecular weight guayule rubber has
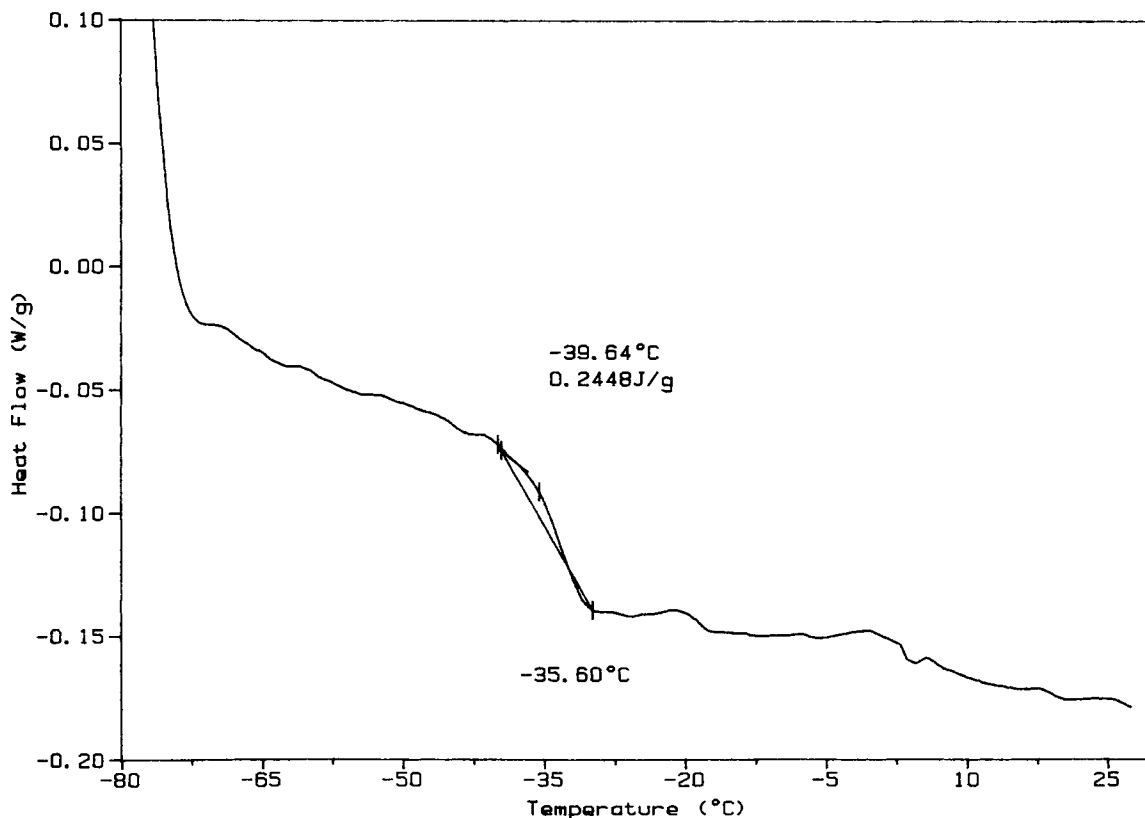
Figure 7 DSC trace of EGR 25.

been performed through reaction of olefinic bonds with m-chloroperoxybenzoic acid. The structure of the epoxidized rubber has been confirmed by NMR, IR, DSC, and elemental analysis. Quantification of the extent of epoxidation can be determined by DSC and NMR spectroscopy. The effects of epoxidation on T_g increases follow a linear relationship with mol % epoxidation. Epoxidized secondary molecular weight Guayule rubber is soluble in organic solvents and can be utilized as an additive for coatings that imparts flexibility to otherwise rigid epoxy systems.

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