

Synthesis and Characterization of Pendent Hydroxy Fluoroesters of Secondary High Molecular Weight Guayule Rubber

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Received 30 January 1996; accepted 27 June 1996

ABSTRACT: The epoxidation of secondary high molecular weight guayule rubber (SHMWGR) and subsequent ring opening with fluoroacids to give hydroxyfluoroesters (FGR) is reported. Structural characterization was performed with FTIR; ^1H -, ^{13}C -, and ^{19}F -NMR; and DSC. The percent epoxidation was quantitatively determined by ^1H -NMR. It was noted that the glass transition temperatures (T_g) of the FGR polymers increased with increasing fluoro acid content; however, reactions with longer chain, highly fluorinated acids lowered the T_g . © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **63**: 1077–1089, 1997

INTRODUCTION

Guayule, *Parthenium argentatum gray*, is a shrub that grows in the semiarid regions of the southwestern United States and northern Mexico. During shrub processing, five major components are produced: high molecular weight guayule rubber (HMWGR), low molecular weight guayule rubber (LMWGR), organic soluble resins, water soluble extracts, and bagasse.^{1–4} In an effort to establish a domestic guayule industry and optimize potential revenues, it is important to utilize all of its coproduct fractions.

In the process of separating and isolating HMWGR (molecular weight $> 10^6$ g/mol), SHMWGR (molecular weight = 4×10^5 – 6×10^5 g/mol) is precipitated as a by-product. SHMWGR is soluble in organic solvents, and synthetic modifications can be performed at the *cis*-1,4-polyiso-

prene repeat unit. Thus, fluorine modification was performed to determine its effect(s) on performance properties.

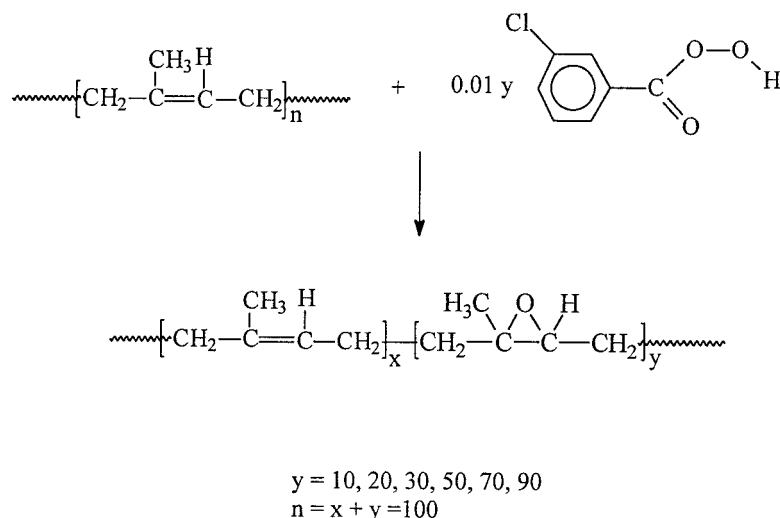
Fluoropolymers are typically characterized by high heat resistance, chemical and weather resistance, water and oil repellency, low flammability, and low surface energy. These properties can be attributed to fluorine's high electronegativity and small atomic radius.⁵ Similar property enhancements were anticipated with the fluorination of GR derivatives. Of particular interest were fluorine's surface properties, that is, low surface energy^{6–9} and nonstick behavior,¹⁰ which results in low critical surface tension, high adhesive energy, and high contact angle.

EXPERIMENTAL

Materials

m-Chloroperbenzoic acid (MCPBA) was purchased from Aldrich Chemical Company, and its

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Scheme 1 Synthesis of epoxidized secondary high molecular weight guayule rubber (EGR).

percent purity was determined via titration.¹¹ 1,2-Dichloroethane, dichloromethane, methyl ethyl ketone (MEK), trifluoroacetic acid, pentafluoropropionic acid, heptafluorobutyric acid, and nonafluoropentanoic acid were purchased from Aldrich and were used as received. High-solids polyester resin 57-5776 and Desmodur aliphatic polyisocyanate N-3300 were obtained from McWhorter Technologies, Inc. and Miles, Inc., respectively. SHMWGR was supplied by Texas A&M Engineering and Bio-sciences Research Center. SHMWGR was dissolved in 1,2-dichloroethane and filtered through a Gardco medium filter to remove any gelled rubber. The purified rubber was obtained by precipitation in 95% ethanol followed by drying in a vacuum oven. The purity of the SHMWGR was confirmed by ¹³C-NMR.

Table I Reaction Conditions and Results for EGR Synthesis

SHMWGR (mol)	MCPBA (mol)	Expected % Epoxidation	Achieved % Epoxidation (via NMR)
0.147	0.0147	10	9.5
0.147	0.0294	20	19.8
0.147	0.0441	30	29.0
0.147	0.0735	50	48.0
0.147	0.1029	70	65.0
0.147	0.1323	90	87.0

Synthesis of Epoxidized SHMWGR (EGR)

A solution of MCPBA in dichloromethane was added dropwise to a stirring solution of purified SHMWGR in 1,2-dichloroethane maintained at 0–5°C.¹² The molar ratios of MCPBA and SHMWGR were adjusted to give the desired level of epoxidation. As the level of epoxidation increased to 50% and above, it was necessary to buffer the reaction mixture with sodium carbonate to prevent gelation. The EGR formed was precipitated by pouring the reaction mixture into 95% ethanol. The precipitated beige-colored product was filtered and dried under reduced

Table II Stoichiometry for FGR Syntheses

Guayule Rubber Compound	EGR Used (%)	Fluoroacid Used	Acid Equiv. Based on EGR
Trifluoroester			
TFGR 1	30	Trifluoroacetic	1.0
TFGR 2	50	Trifluoroacetic	1.0
Pentafluoroester			
PFGR 1	30	Pentafluoropropionic	0.75
PFGR 2	50	Pentafluoropropionic	0.75
Heptafluoroester			
HFGR 1	30	Heptafluorobutyric	0.50
HFGR 2	50	Heptafluorobutyric	0.50
Nonafluoroester			
NFGR 1	30	Nonafluoropentanoic	0.25
NFGR 2	50	Nonafluoropentanoic	0.25

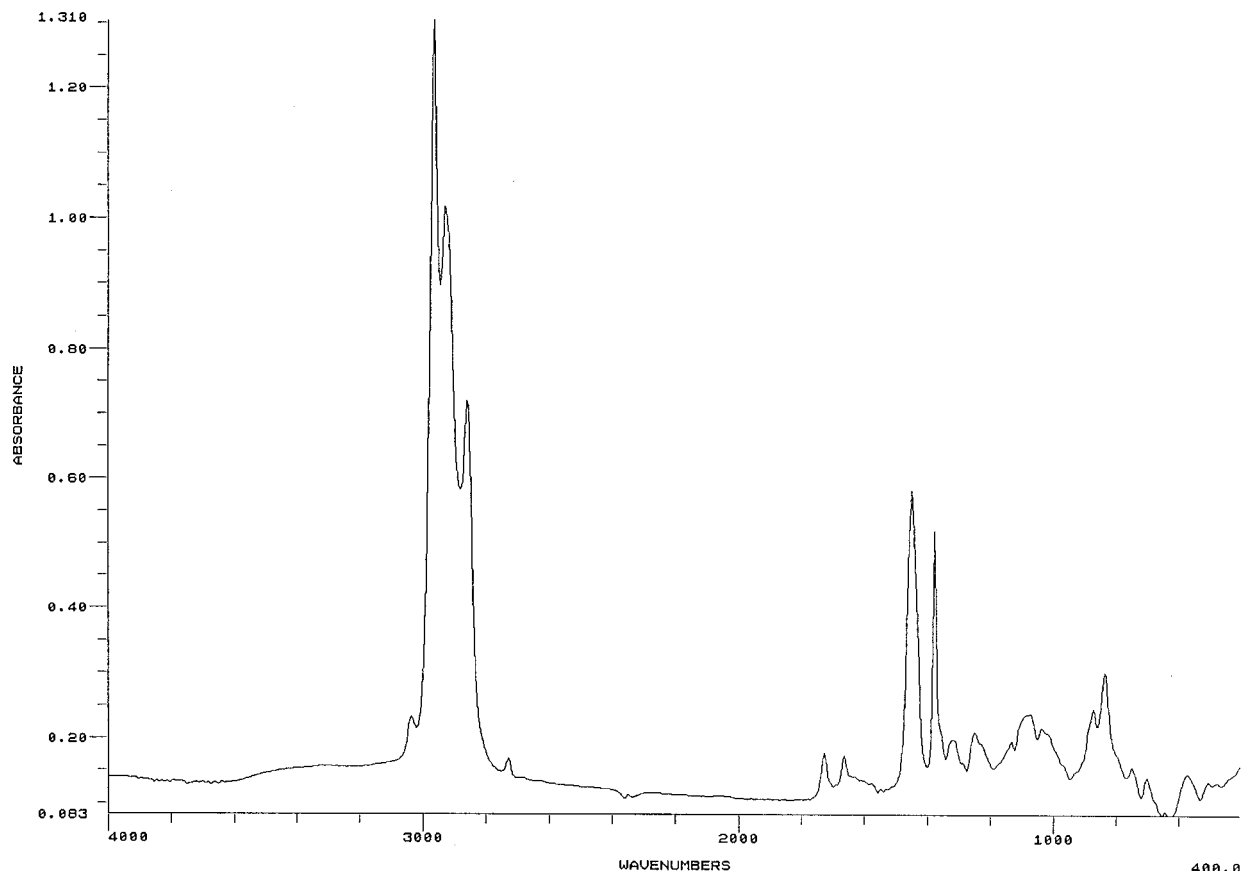


Figure 1 FTIR spectrum of epoxidized secondary high molecular weight guayule rubber (EGR).

pressure to constant weight giving an 85–90% yield.

Synthesis of Hydroxy Fluoroesters of SHMWGR (FGR)

The desired fluoroacid was slowly added via a glass syringe to a stirring solution of EGR in 1,2-dichloroethane, under nitrogen, at 0°C. The reaction was continued for 2 h after which FGR was precipitated by pouring the reaction mixture into methanol. The precipitated product was filtered and dried under reduced pressure to a constant weight giving a 90–95% yield.

Synthesis of FGR Based Polyurethane Coatings (PUFGR)

Trifluoroacetic acid ester of SHMWGR (TFGR 1; 40% solution in MEK), polyester resin (57-

5776), and polyisocyanate (Desmodur N-3300) were blended using a high-speed stirrer. The isocyanate : hydroxyl (NCO : OH) ratio was maintained at 1 : 1. Using a drawdown bar, 4 mil (100 μm) thick wet film coatings were applied on steel panels and cured at 150°C for 30 min.

Analytical

Infrared analysis was performed with a Nicolet IR/42 FTIR spectrometer. Samples were cast from dichloromethane onto sodium chloride polished disks and analyzed after solvent evaporation.

^{13}C -NMR and ^1H -NMR were performed with a Bruker 200-MHz NMR spectrometer with deuterated chloroform and tetramethylsilane as the internal references, respectively. ^{19}F - and solid-state ^{13}C -NMR were performed with a Bruker

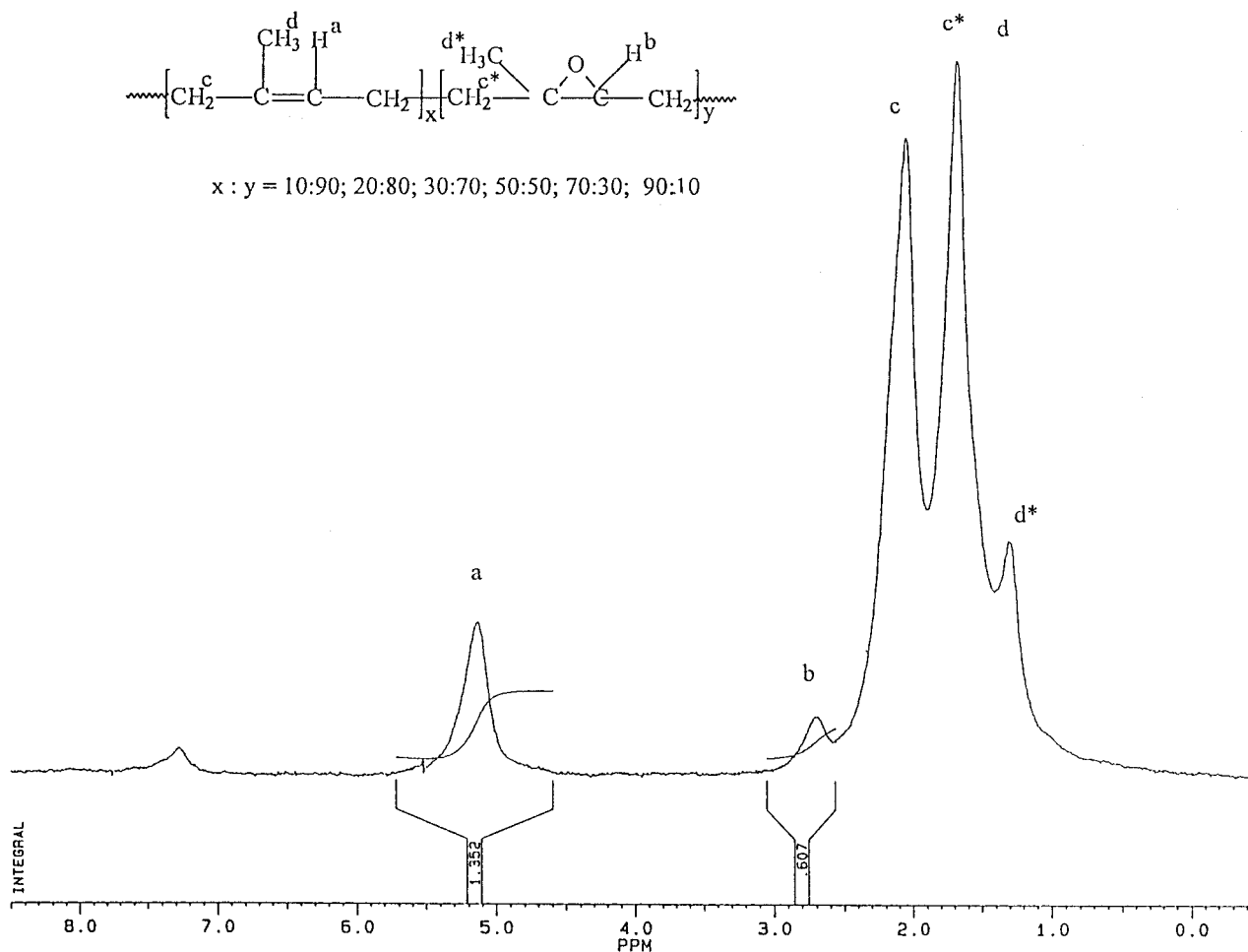


Figure 2 $^1\text{H-NMR}$ spectrum of epoxidized secondary high molecular weight guayule rubber (EGR).

400-MHz NMR spectrometer. Thermal analysis was accomplished with a Mettler DSC 30 under nitrogen at a heating rate of $10^\circ\text{C}/\text{min}$.

Contact angles were measured on a Helix International L09 goniometer. Solutions of SHMWGR, EGR, FGR, and PUFGR were applied on steel panels with a drawdown bar and dried in a desiccator under nitrogen prior to evaluation. Precautions were taken to minimize the surface roughness.

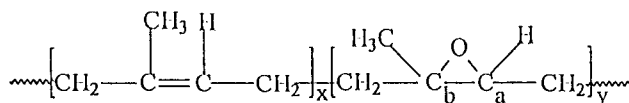
RESULTS AND DISCUSSION

The synthesis of EGR was effected by peracid epoxidation of the olefinic bonds in the SHMWGR (Scheme 1).¹³⁻¹⁶ The epoxidation of SHMWGR is reported as a random process

wherein the epoxy group placement shows no correlation to a substituent location in the rubber backbone.¹⁷ The molar ratios of SHMWGR and peracid used and the results of the EGR synthesis are listed in Table I.

FGR derivatives were synthesized via the fluoroacid catalyzed ring opening of EGR.^{18,19} Consequently, four different fluoroacids were used: trifluoroacetic acid, pentafluoropropionic acid, heptafluorobutyric acid, and nonafluoropentanoic acid. The $\text{p}K_a$ values of the acids dictate their reactivity with EGR.²⁰ It was necessary to reduce the equivalents of the higher homologue fluoroacids due to their strong acidity and the increasing perfluoroalkyl chain length. Table II includes the stoichiometric ratios of EGR and fluoroacid used in the FGR syntheses.

All FGR derivatives were soluble in chloro-



$$x : y = 10:90; 20:80; 30:70; 50:50; 70:30; 90:10$$

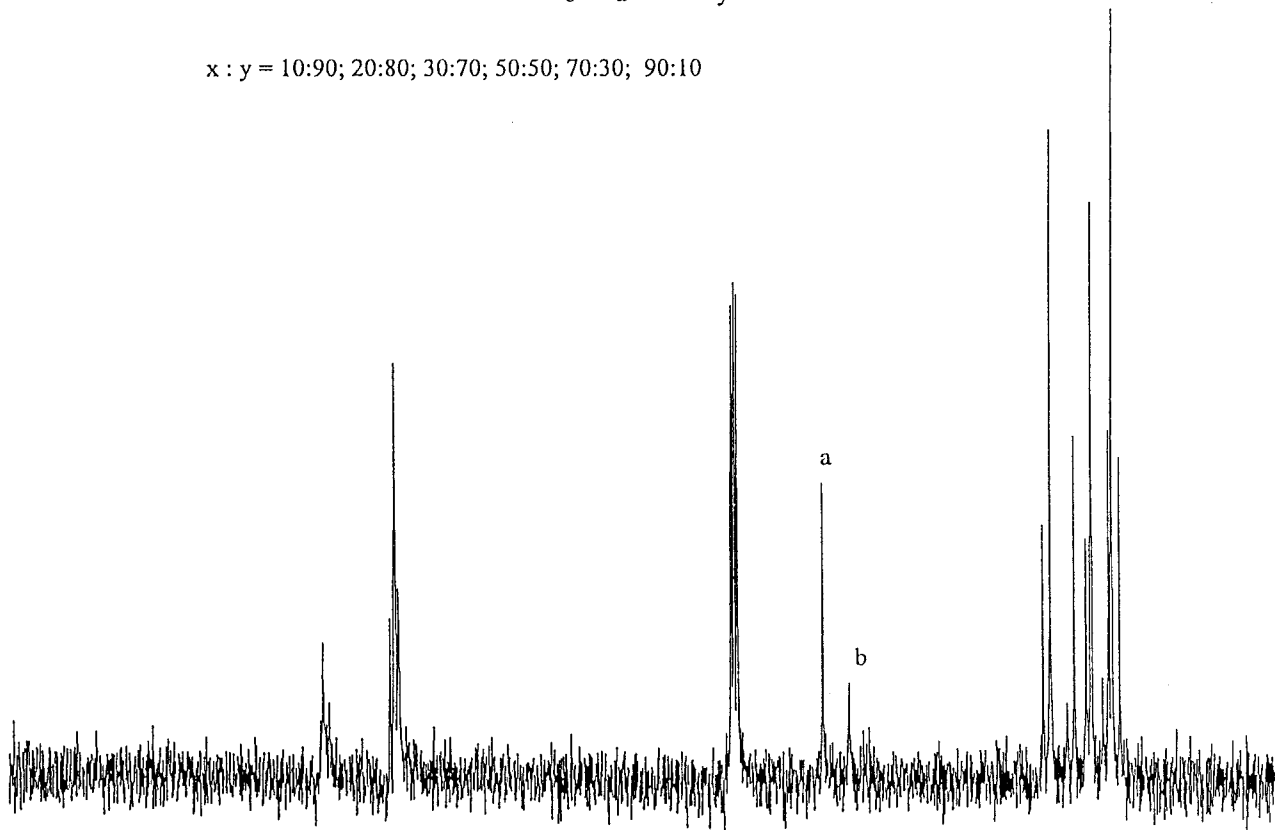


Figure 3 ^{13}C -NMR spectrum of epoxidized secondary high molecular weight guayule rubber (EGR).

form, methylene chloride, and MEK. Upon initial precipitation, the FGR derivatives were soft and light brown in color; however, they hardened and darkened upon storage, a possible consequence of the oxidation of the remaining double bonds in the isoprene units to by-products and a crosslinked network.^{22,23} In fact, DSC measurements of the hardened rubber showed a glass transition temperature (T_g) increase of 10°C. Storage under anaerobic conditions or in solution with 2,6-di-*t*-butyl-*p*-cresol (BHT) as an antioxidant effectively preserved the integrity of the FGR products.

Characterization of EGR

The structure of EGR was confirmed via FTIR, ^1H -NMR, and ^{13}C -NMR studies. Absorptions at 1255, 1067, and 874 cm^{-1} in the FTIR analysis

confirmed the presence of internal epoxy moieties (Fig. 1). The ^1H -NMR spectrum (Fig. 2) exhibited characteristic absorptions at 5.13, 2.71, 2.06, 1.68, and 1.30 ppm corresponding to vinyl (H_a), epoxy (H_b), methylene (H_c), isoprene methyl (H_d), and epoxy methyl protons (H_{d^*}), respectively. Methylene proton (H_{c^*}) absorption merged with the absorption of methyl protons (H_d) at 1.68 ppm.²² There were no absorptions between 3.0 and 4.0 ppm, indicating the absence of furan ring structures or diol formation.²² The percent epoxidation was determined from the ratio of the area under the peak of the epoxy proton (H_b) to the sum of areas under the vinyl proton peak (H_a) and epoxy proton peak (H_b ; Fig. 2).^{24,25}

$$\% \text{ epoxidation} = \frac{\int H_b}{\int H_a + H_b} \times 100.$$

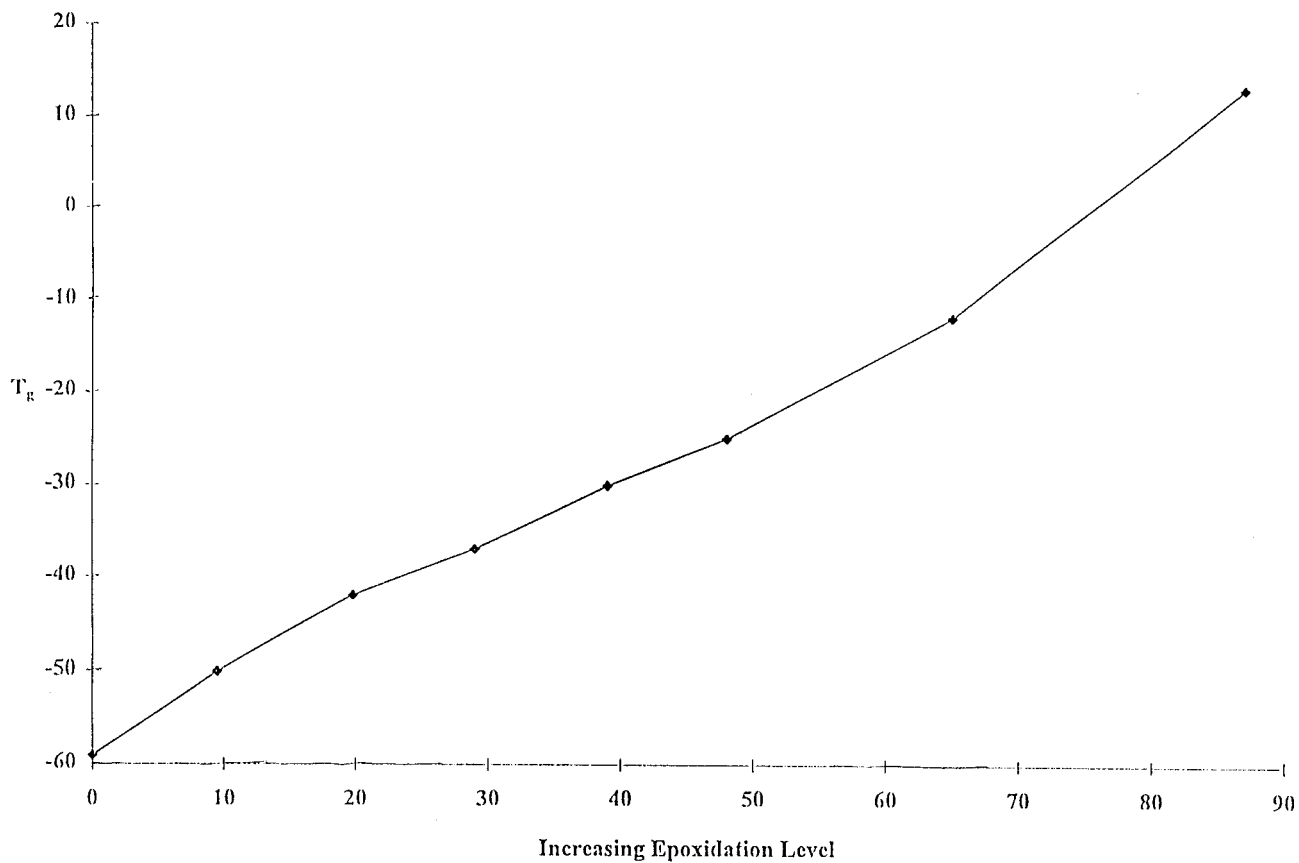
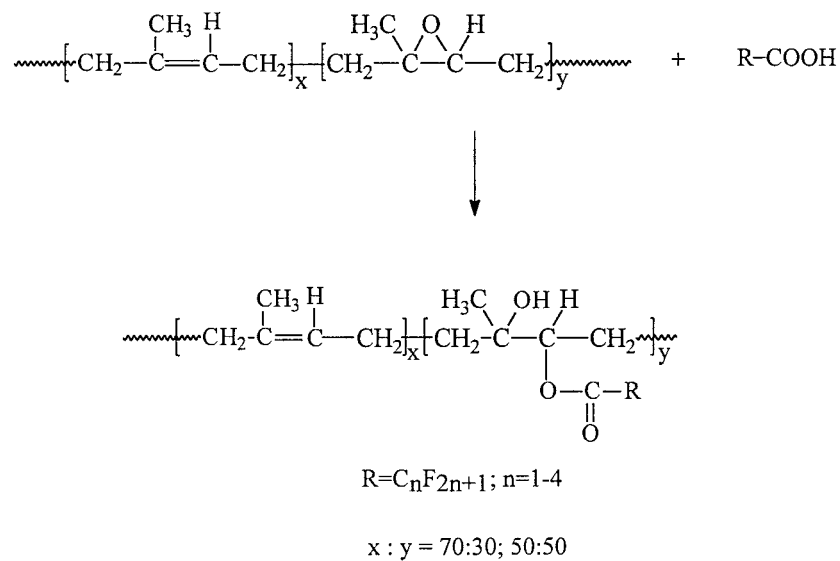


Figure 4 Graph depicting relationship of T_g with increasing epoxidation level.



Scheme 2 Synthesis of hydroxyfluoroesters of secondary high molecular weight guayule rubber (FGR).

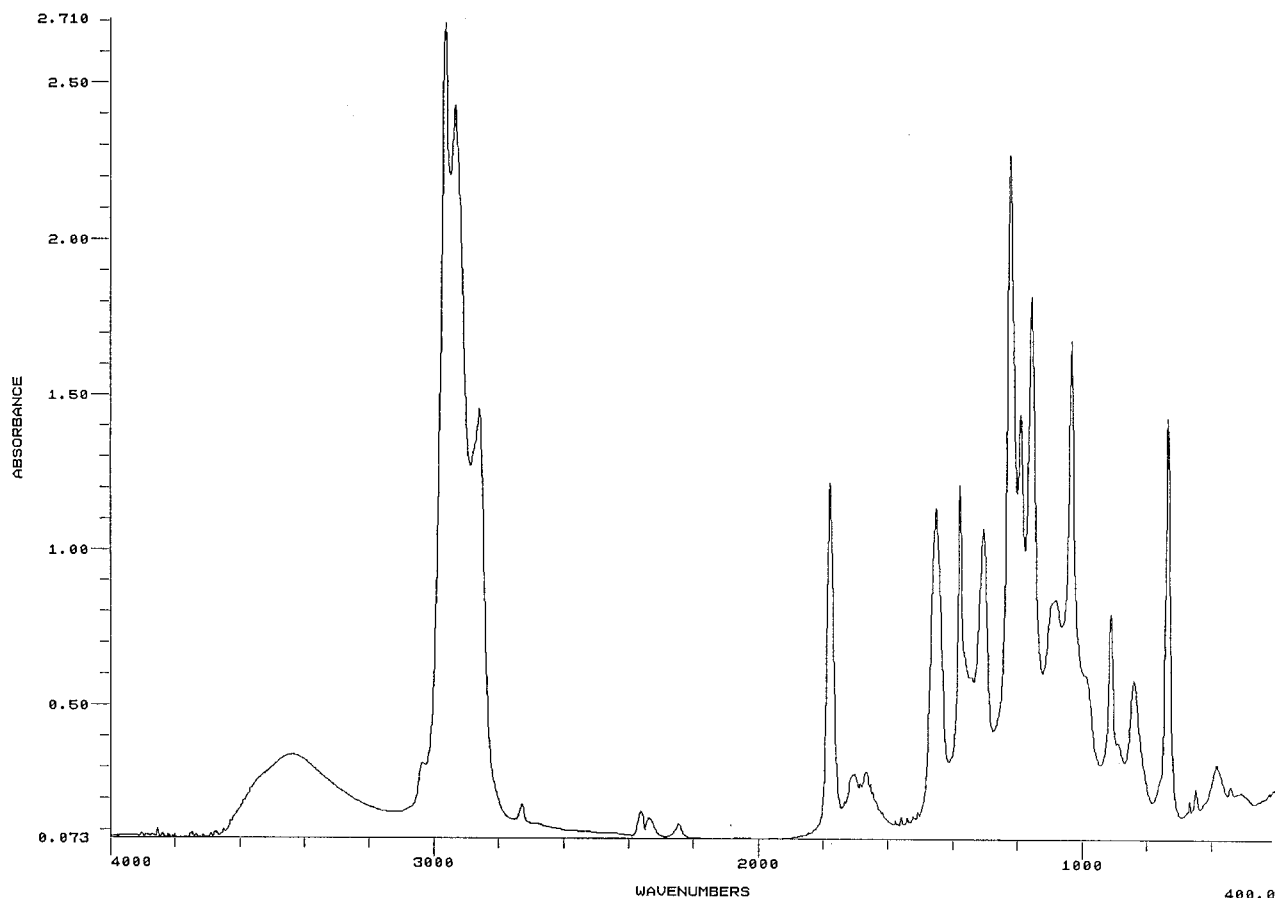


Figure 5 FTIR spectrum of hydroxyfluoroester of secondary high molecular weight guayule rubber (FGR).

The ^{13}C -NMR spectrum (Fig. 3) displayed absorptions at 64.75 and 61.03 ppm, corresponding to the methine (C_a) and tertiary carbons (C_b), respectively. The absence of absorptions between 80.00 and 90.00 ppm confirmed the absence of the five-membered cyclic ethers (furan rings).

DSC analysis revealed a T_g of -59.9°C for SHMWGR. The T_g increased with the degree of epoxidation (Fig. 4). This data is consistent with reported values for rubber epoxidation.^{22,26,27}

Characterization of FGR

Several studies have been reported on acid catalyzed ring opening of epoxides.^{18-20,28-32} The FGR polymers were obtained by acid catalyzed ring opening of EGR via protonation of the epoxide ring followed by nucleophilic attack by the carbox-

ylate anion (Scheme 2).^{22,33} The FGR polymers were characterized using FTIR, ^1H -NMR, and solid state ^{13}C -NMR and ^{19}F -NMR.

FTIR analysis (Fig. 5) showed absorptions at 3500 and 1795–1800 cm^{-1} for the hydroxyl and ester moiety, respectively. Strong CF_3 and CF_2 absorptions were noted in the 1100–1350 cm^{-1} region, and the CF stretching was observed in the 730–1400 cm^{-1} region.²⁵

The ^1H -NMR spectrum was devoid of absorptions characteristic of the epoxy proton at 2.8 ppm, indicating that all epoxy groups had reacted. The ^1H -NMR of FGR polymers (Fig. 6) exhibited absorptions at 5.12, 3.72, 2.03, 1.67, and 1.24 ppm, corresponding to vinylic (H_a), methine (H_b), methylene (H_c), isoprene methyl (H_d), and fluoroester methyl (H_{d*}) protons, respectively. Methylene proton (H_{c*}) absorption merged with the absorption of methyl protons (H_d) at 1.67 ppm. ^{19}F -NMR

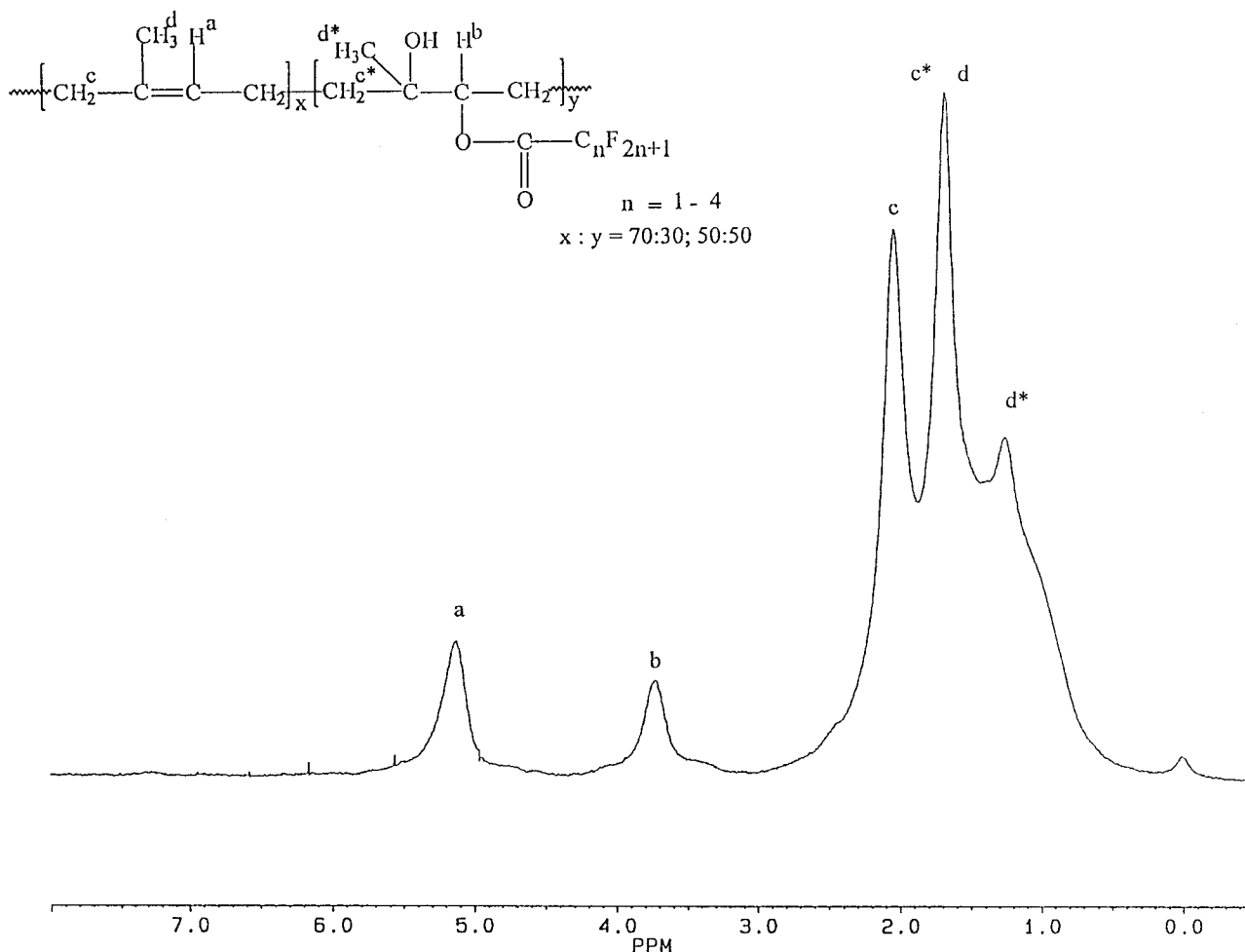


Figure 6 $^1\text{H-NMR}$ spectrum of hydroxyfluoroester of secondary high molecular weight guayule rubber (FGR).

analysis confirmed the presence of fluorine in the polymers.

Solid-state $^{13}\text{C-NMR}$ (Fig. 7) confirmed the presence of methyl (C_a), methine carbon (C_b), tertiary carbon (C_c), and ester moiety (C_d) at 23.0, 74.7, 84.9, and 157.00 ppm, respectively.

Due to their acidity and increasing chain length, the fluoroacids reacted almost instantaneously; therefore, the epoxide ring opening with stoichiometric amounts of fluoroacids was difficult to control.

As the acid content of the polymers increased, so did the T_g values. For instance, when 39% EGR was reacted with pentafluoropropionic acid at 0.25, 0.50, and 1.00 equivalents based on EGR epoxide content, the T_g increase in FGR polymers was proportional to the fluorinated acid content (Table III, Fig. 8).²⁸ Thermogravimetric analysis

(TGA) studies confirmed that fluorination increased thermal stability; however, the thermal stability was not a function of the fluorinated acid content (Table III).

A series of four fluoroacids was selected in order to study the effect of increasing fluorine content on polymer properties. DSC showed a decline in the T_g of the FGR polymers in the series from trifluoroester to nonafluoroester, a likely consequence of the plasticizing effect of the longer chain length (Tables IV, V, Fig. 9). However, the T_g s of all FGR polymers were higher than EGR and can be attributed to the polar hydroxyl moiety and the introduction of inter- and intramolecular hydrogen bonding. It is noteworthy that the DSC data of EGR and FGR gave only a single T_g , suggesting random placement of epoxide moieties and conse-

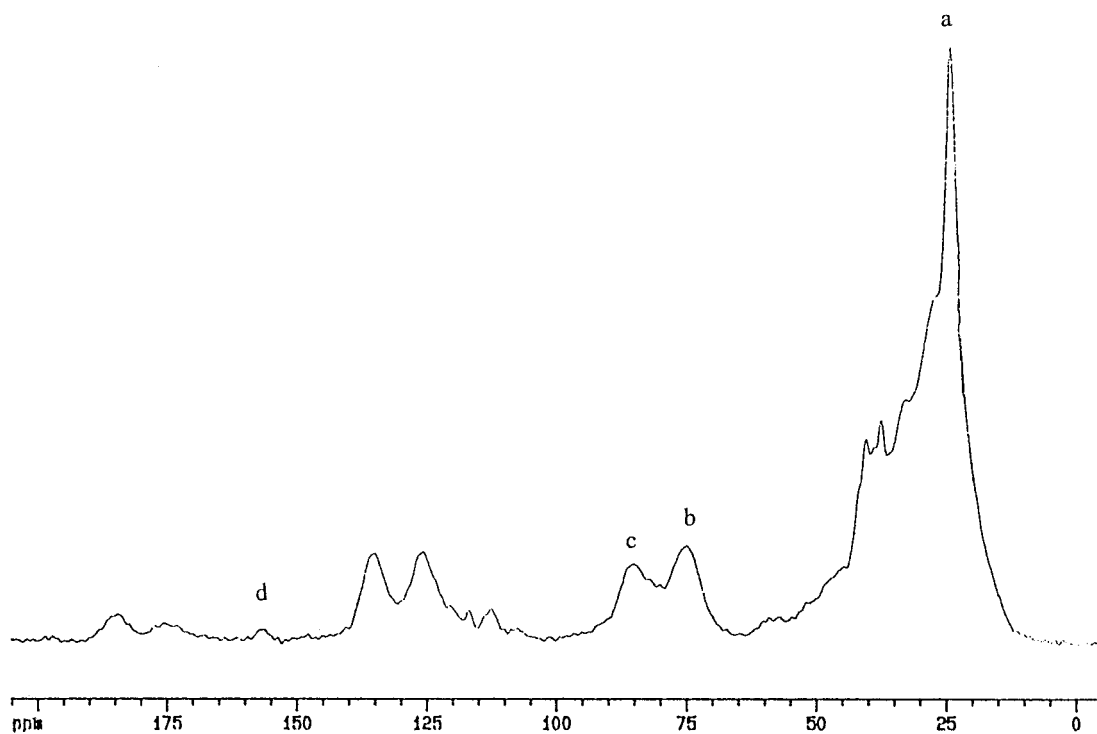
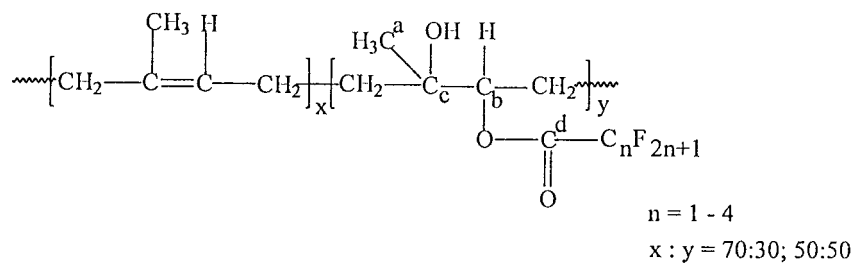


Figure 7 Solid-state ^{13}C -NMR spectrum of hydroxyfluoroester of secondary high molecular weight guayule rubber (FGR).

Table III Thermal Characteristics of PFGR Derivatives

Compound	Equiv. of Pentafluoropropionic Acid	Decomposition Temperature ($^{\circ}\text{C}$)	T_g ($^{\circ}\text{C}$)
39% EGR	—	384	-30.9
PFGR 3	0.25	418	4.0
PFGR 4	0.50	419	12.0
PFGR 5	1.00	417	25.0

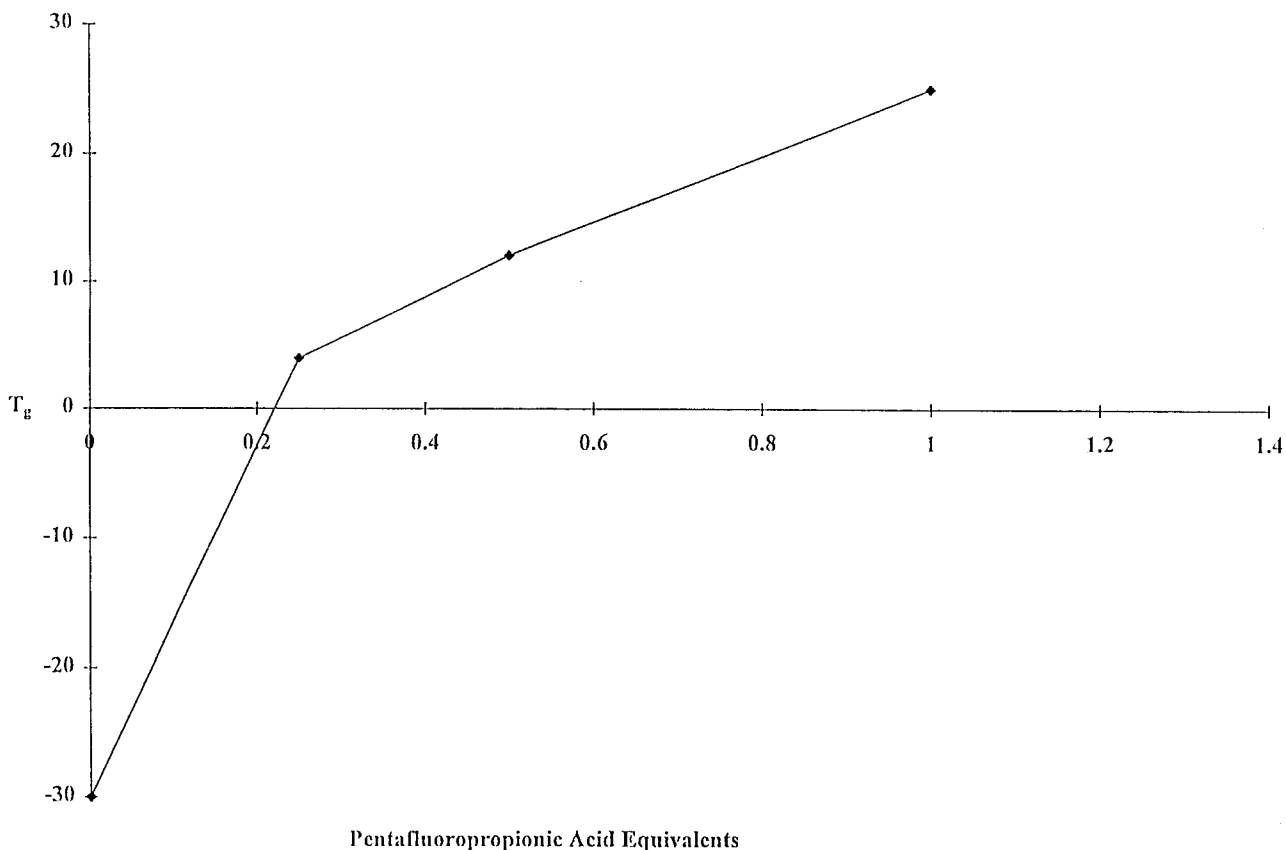


Figure 8 Graph depicting T_g enhancements at various pentafluoropropionic acid loadings (equivalents).

quently the fluoroester functionality (Figs. 10, 11).^{17,31} TGA studies confirmed that FGR polymers were more stable thermally than EGR and can be attributed to the incorporation of perfluoro chains; however, the thermal stability was not a function of the fluorinated acid chain length (Tables IV, V).

Table IV Thermal Properties of 30% EGR and Its Fluoro Derivatives

Compound	Decomposition Temperature (°C)	T_g (°C)
SHMWGR	380	-59.9
EGR 30%	384	-36.9
TFGR 1	412	18.0
PFGR 1	422	12.0
HFGR 1	422	5.0
NFGR 1	422	-2.0

Contact Angle Measurements

Equilibrium contact angle measurements were performed for SHMWGR, EGR, Teflon, the high T_g trifluoroester (TFGR 1), and the resulting polyurethane coating (PUFGR) and are included in Table VI).

Table V Thermal Properties of 50% EGR and Its Fluoro Derivatives

Compound	Decomposition Temperature (°C)	T_g (°C)
SHMWGR	380	-59.9
EGR 50%	394	-25.0
TFGR 2	431	45.0
PFGR 2	428	36.0
HFGR 2	422	30.0
NFGR 2	422	22.0

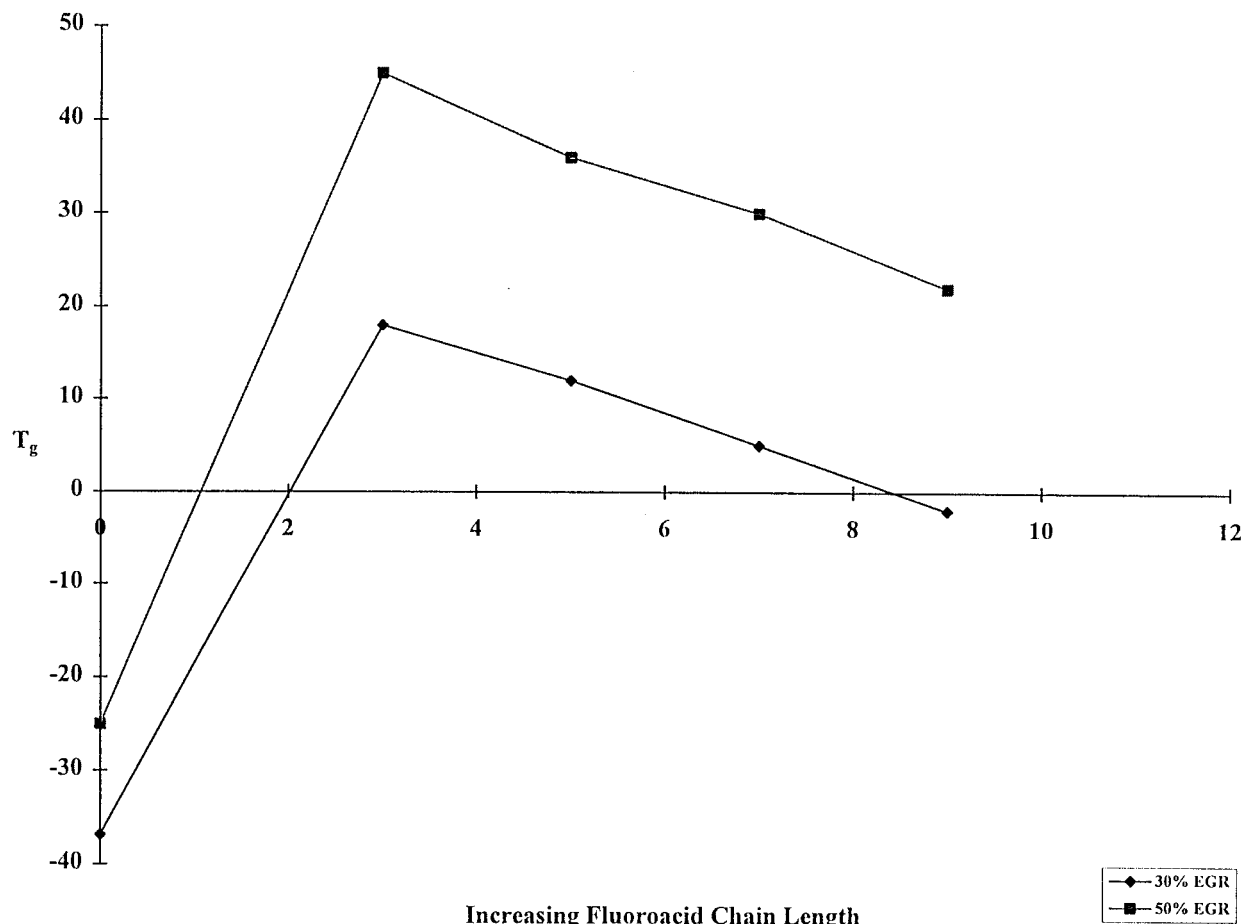


Figure 9 Graph depicting relationship of T_g with increasing fluoroacid chain length.

The lower contact angle of TFGR 1 is a likely result of fluorinated side chain rearrangement allowing water penetration to the polar hydroxyl and carboxyl groups. A similar phenomenon of contact angle reduction due to fluorinated block rearrangements was reported by Chapman et al.^{34,35} The contact angle of the PUFGR increased because the polar hydroxyl groups reacted with isocyanate, giving a nonpolar surface.

CONCLUSIONS

The formation and characterization of FGR polymers was accomplished via an acid catalyzed epoxide ring-opening reaction. The structures were confirmed by ^1H -, solid-state ^{13}C -, and ^{19}F -NMR; FTIR; and DSC analysis. The

FGR polymers possessed higher T_g s than SHMWGR. Further, it was shown that T_g elevation for the FGR polymers was proportional to the increased fluoroacid content. However, with increasing fluoroacid chain length, the T_g decreased, a likely consequence of increased chain length. The FGR polymers produced are thermally stable, soluble in organic solvents, and can be incorporated in a variety of coatings and adhesive formulations.

This work was supported by the Cooperative State Research, Education, and Extension Service, U.S. Department of Agriculture, under Cooperative Agreement 92-COOP-1-6921. A special thanks to Dr. Daniel Kugler and Mrs. Carmela Bailey for their support and encouragement. The authors also wish to acknowledge the assistance of Dr. Thomas Schuman and Mr. Sharathkumar Mendon.

Rate: 10.0 °C/min

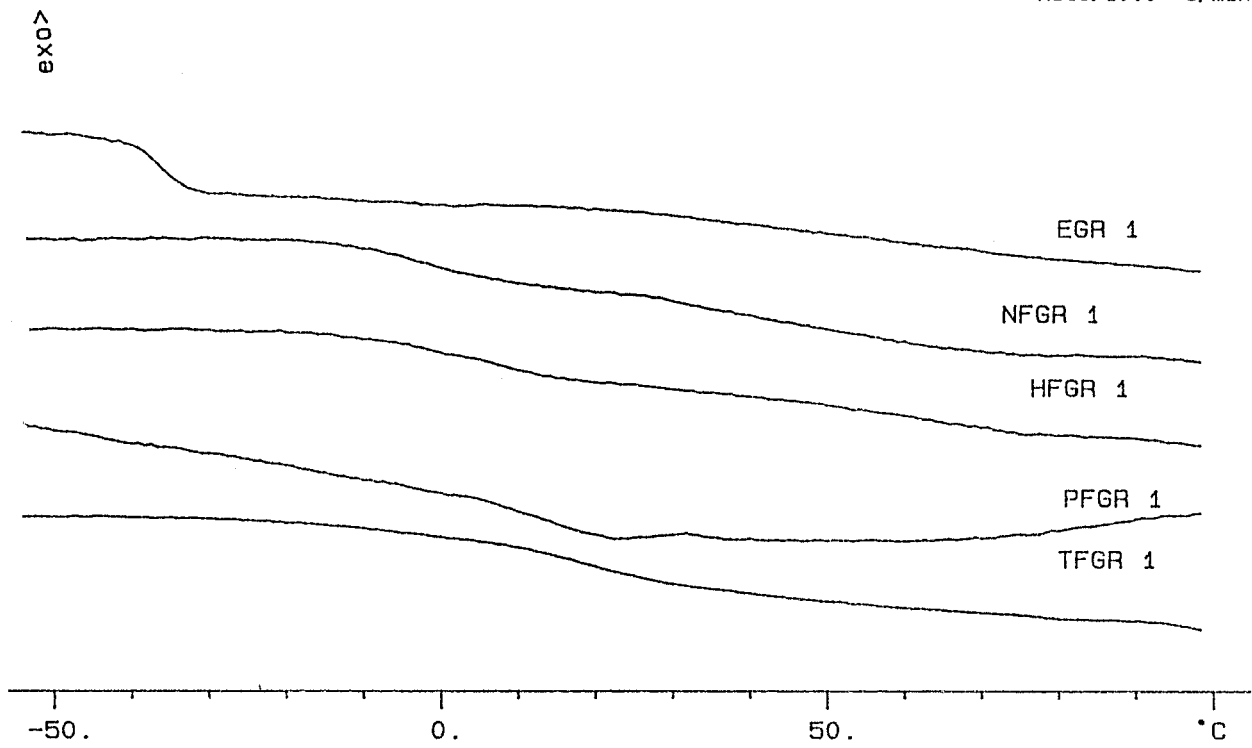


Figure 10 DSC thermogram of 30% epoxidized secondary high molecular weight guayule rubber (EGR) and its fluoro derivatives (FGR).

Rate: 10.0 °C/min

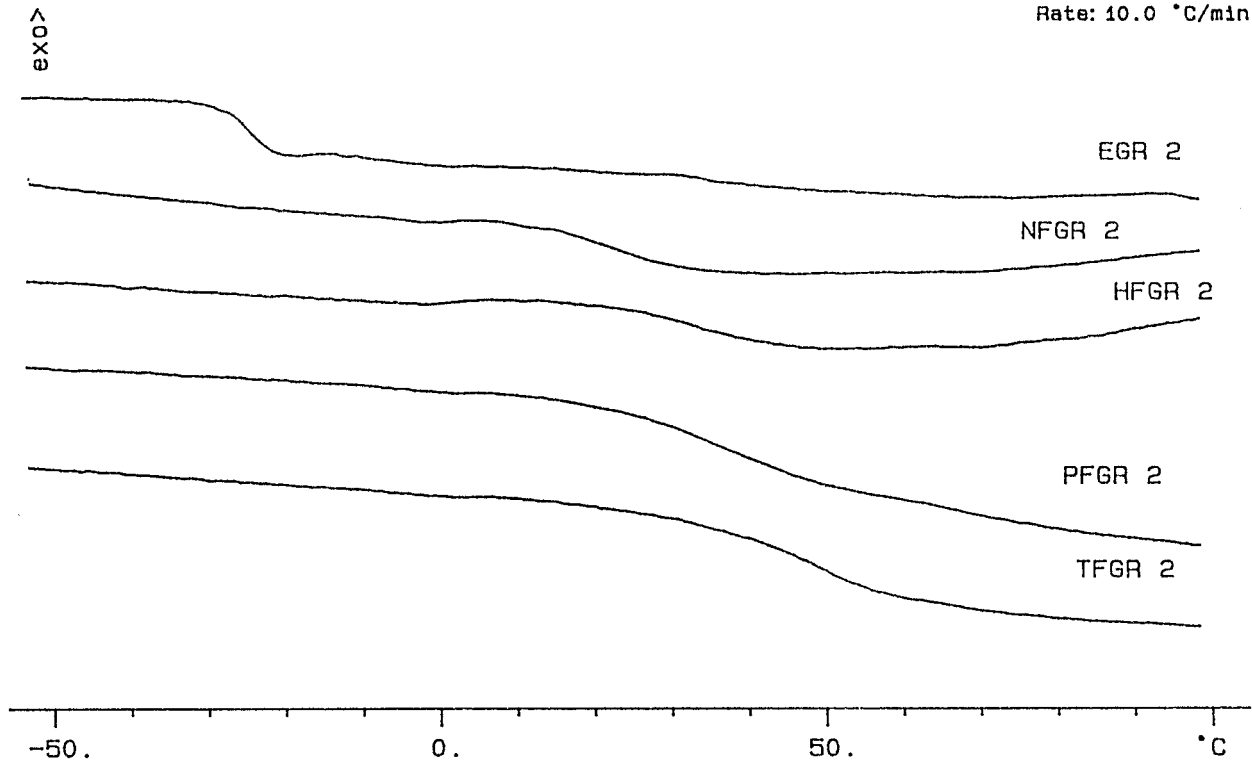


Figure 11 DSC thermogram of 50% epoxidized secondary high molecular weight guayule rubber (EGR) and its fluoro derivatives (FGR).

Table VI Contact Angle Measurements

Compound	Water Contact Angle (°)
SHMWGR	99.7 ± 0.5
EGR	93.8 ± 0.9
TFGR 1	87.6 ± 1.3
PUFGR	110.3 ± 1.7
Teflon	107.5 ± 3.6

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