Applications of Epoxidized and Hydroxy-Fluoroester Pendent Secondary High-Molecular-Weight Guayule Rubber in Coatings

SANDHYA GUPTA, SHARATHKUMAR K. MENDON, SHELBY F. THAMES

Department of Polymer Science, University of Southern Mississippi, Box 10037, Hattiesburg, Mississippi 39406

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ABSTRACT: The epoxidation of secondary high-molecular-weight guayule rubber to yield epoxidized guayule rubber (EGR) and the subsequent opening of the oxirane rings by fluoroacids to yield fluorinated guayule rubber (FGR) were reported in an earlier article.[1] The oxirane and hydroxyl groups that occur in EGR and FGR, respectively, enable these derivatives to be integrated into the binder system of coatings. The coating industry has long been interested in nontoxic multifunctional crosslinking agents that do not emit volatile organic compounds (VOCs). Ring-opening reactions of epoxides and reactions between hydroxyl and isocyanate groups are prime examples of crosslinking that do not emit VOCs. This study was conducted to ascertain the viability of guayule rubber derivatives that contain epoxide and hydroxyl groups as crosslinking agents in solvent-based coatings and powder coatings. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 1718–1724, 2001

Key words: secondary high-molecular-weight guayule rubber; epoxidized guayule rubber; guayule hydroxy-fluoroesters; epoxidized guayule rubber coatings; hydroxy-fluoroesters guayule coatings

INTRODUCTION

Guayule, *Parthenium argentatum gray,* is a shrub that grows in the semiarid regions of the southwest United States and northern Mexico. During shrub processing, five major components are produced: high-molecular-weight guayule rubber (HMWGR), low-molecular-weight guayule rubber, organic soluble resins, water soluble extracts, and bagasse.[2–5] In an effort to establish a domestic guayule industry and to optimize potential revenues, it is important to utilize all coproduct fractions of guayule.

During separation and isolation of HMWGR (molecular weight $> 10^6$ g/mol), secondary high-molecular-weight guayule rubber (SHMWGR; molecular weight 4×10^5 - 6×10^5 g/mol) is obtained as a precipitated coproduct. SHMWGR is readily soluble in several organic solvents, and synthetic modifications of the *cis*-1,4-polyisoprene repeat unit can be effected. For instance, epoxidized guayule rubber (EGR) was synthesized by the epoxidation of olefinic double bonds with *m*-chloroperbenzoic acid (Fig. 1).[1] The subsequent ring opening of the oxirane group yielded fluorinated guayule rubber (FGR) (Fig. 2). The reactions were characterized by a significant increase in glass-transition temperature (T_g), which contributed to their potential utility in surface coatings.

EXPERIMENTAL

Materials

EGR (equivalent weight = 242) and FGR (equivalent weight = 324.28) were synthesized as re-

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Correspondence to: S.F. Thames (shelby.f.thames@usm.edu).

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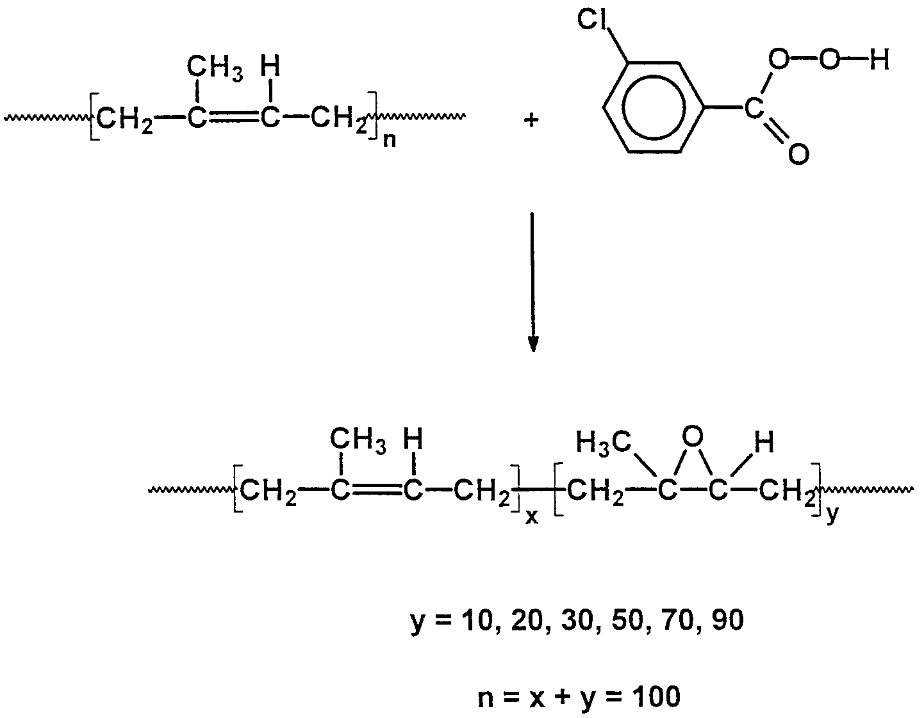

Figure 1 EGR synthesis.

ported in an earlier article.[1] Bisphenol-A-derived epoxy resins Epon 1001, Epon 1007F, and Epon 2002 were obtained from Shell Chemical Co. (Houston, TX). Hydroxyl functional polyester resins, 30-3002 and 57-5776 were obtained from McWhorter Technologies, Inc. (Carpentersville, IL),

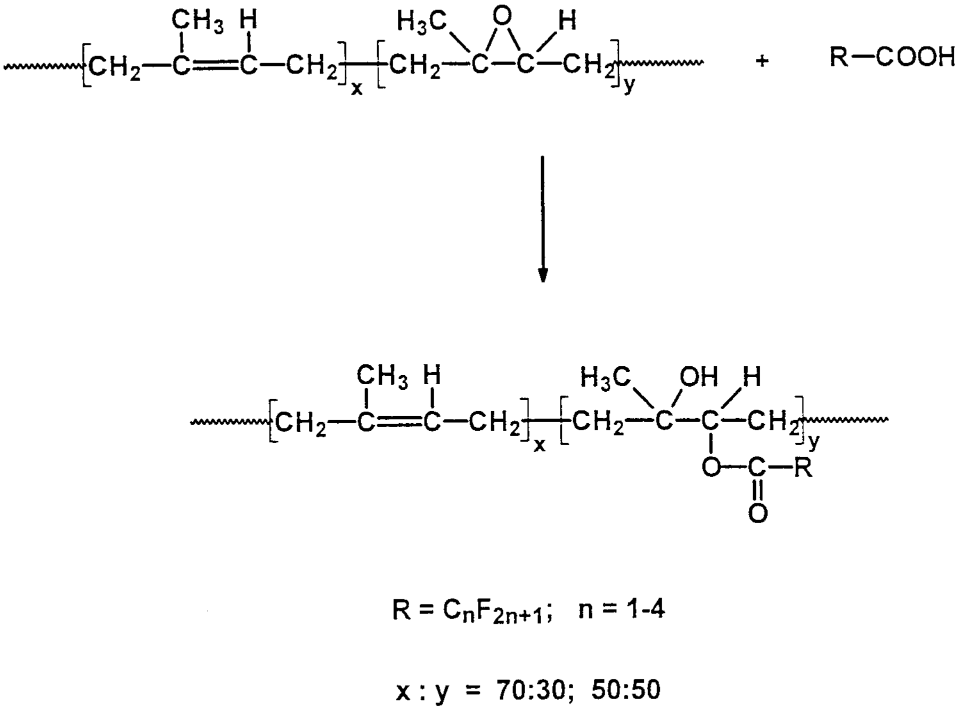

Figure 2 FGR synthesis.

Table I EGR Powder Coatings

Ingredient	Control	Epon : EGR (80 : 20)	Epon : EGR (50 : 50)
TiO_2	150.00	150.00	150.00
Epon 1001	60.00	52.00	36.75
Epon 2002	65.00	55.75	40.00
EGR	—	5.75	16.25
Rucote 527	140.00	151.50	172.00
Actiron CC-6	0.50	0.50	0.50
Benzoin	4.00	4.00	4.00
Modarez MFP	6.00	6.00	6.00
Total	500.00	500.00	500.00

Table II FGR Powder Coatings

Ingredient	Control	Epon : FGR (90 : 10)	Epon : FGR (50 : 50)
TiO_2	150.00	150.00	150.00
30-3002	172.25	158.00	96.95
FGR	—	11.50	63.25
24-2430	92.75	95.50	104.80
Barytes	74.50	74.50	74.50
Actiron CC-6	0.50	0.50	0.50
Benzoin	4.00	4.00	4.00
Modarez MFP	6.00	6.00	6.00
Total	500.00	500.00	500.00

and carboxyl functional polyester resin Rucote 527 was obtained from Ruco Polymer Corp. (Hicksville, NY) Aliphatic polyisocyanate resins 24-2430 and Desmodur N-3300 were procured from McWhorter Technologies and Bayer (Pittsburgh, PA), respectively. Phenolic resin Methylon 75-108 was obtained from Occidental Chemical Corporation (Dallas, TX). Modarex MFP and Actiron CC-6 were obtained from Synthron, Inc., and benzoin was procured from Generichem (Totowa, NJ). Titanium dioxide, Ti-Pure R-960, and Sparmite barytes were products of DuPont (Wilmington, DE) and Harcros Pigments (Fairview Heights, IL), respectively. Methyl ethyl ketone (MEK) and xylene were purchased from Aldrich Chemical Co. (Milwaukee, WI). Bare steel panels QD-36 were purchased from Q-Panel Co. (Cleveland, OH) and were wiped clean with MEK before use. All other materials were used as received.

PROCEDURE

Procedure

EGR and FGR were formulated into powder coatings and solvent-based coatings. Powder coatings with EGR were formulated with the epoxy resins Epon 1001 and Epon 2002 and the polyester resin Rucote 527 at two different Epon : EGR ratios, 80 : 20 and 50 : 50. Similarly, solvent-based coatings with EGR were formulated with the epoxy resin Epon 1007F and the phenolic resin Methylon 75-108 at two different Epon : EGR ratios, 80 : 20 and 50 : 50. The concomitant formation of a tertiary hydroxyl moiety during fluoroester production provided a potentially reactive site for crosslinking reactions with an isocyanate functionality. Powder coatings were formulated by the blending of FGR with polyester resin 30-3002 and polyisocyanate resin 24-2430 at polyester : FGR ratios of 90 : 10 and 50 : 50. Solvent-based coatings were formulated by the blending of FGR with polyester resin 57-5776 and polyisocyanate resin Desmodur N-3300 at polyester : FGR ratios of 90 : 10 and 50 : 50.

To ensure proper blending, the guayule derivatives were mixed in solution with the other resins present in each formulation. Powder coatings were processed according to the standard practice of premixing, melt extrusion, grinding, and sieving. The ingredients (see Tables I and II) were precisely weighed and added to a Henschel FM-10 mixer (Purnell, Intl., Houston, TX) and mixed at 2000 RPM for two 60-sec periods, followed by melt extrusion on a Werner and Pfleiderer (Ramsey, NJ) ZSK 30 twin screw extruder (see Table III). The chilled extrudate was ground in a micron powder system model SH Bantam mill (Hosokawa Micron Power Systems, Summit, NJ) equipped with a liquid nitrogen cooling jacket. The particle size was regulated by sifting through a 125-μ mesh on a Kem-U-Tech laboratory sifter

Table III Processing Parameters

	EGR Powder Coatings	FGR Powder Coatings
Extrusion		
Zone 1 temperature	90°C	91°C
Zone 2 temperature	110°C	110°C
Screw speed	101 rpm	100 rpm
Torque	55%	68%
Chill rolls		
Roll speed	30 rpm	30 rpm
Roll temperature	55°F	55°F

Table IV EGR Solvent-Based Coatings

Ingredients	Control	Epon : EGR (80 : 20)	Epon : EGR (50 : 50)
Epon 1007F	66.32	53.05	18.20
EGR	—	1.60	1.11
Methylon 75-108	12.18	12.18	12.18

(Kemtech, Inc., Bristol, PA). The powder coatings were sprayed onto mild steel panels with a Nordson Corona (Amherst, OH) model NVC 4 spray gun and cured in a Despatch gas oven (Despatch Industries, Minneapolis, MN). EGR and FGR powder-coated panels were cured for 30 min at 150 and 170°C, respectively.

For solvent-based coatings, the guayule derivatives were first dissolved in MEK to a solids level of 40%. The ingredients of the formulation (see Tables IV and V) were blended in a Lightnin mixer (General Signal, Dublin, Ireland) and applied to steel QD-36 panels at 6 mils wet-film thickness. EGR- and FGR-coated panels were cured in a vented oven at 190°C for 20 min and 150°C for 30 min, respectively.

Characterization of Cured Coatings

All coated panels were tested as per ASTM standards. Film thicknesses were measured by Gardco Minitest 4000 (Paul N. Gardner Co., Inc., Pompano Beach, FL). Adhesion was measured by the crosscut tape test as per ASTM D-3359, pencil hardness was measured according to ASTM D-3363, and flexibility was assessed by the conical mandrel test, which conformed to ASTM D-522. Impact resistance was determined according to ASTM D-2794, and solvent resistance was determined using MEK double rubs as per ASTM D-4752. Gloss measurements were recorded with a Gardner statistical Novogloss instrument (Paul N. Gardner Co., Inc., Pompano Beach, FL) meeting ASTM D-523-89 standards. The salt fog test for corrosion resistance was performed for 400 h as per ASTM B-117. Spot tests were conducted according to ASTM D-1308.

RESULTS AND DISCUSSION

EGR Formulations

Epoxy resins are characterized by high chemical resistance, excellent adhesion, low shrinkage, excellent toughness, and good flexibility. It was of interest, therefore, to determine the influence of EGR on epoxy coatings.

Tables VI and VII summarize the test results of the powder coatings and solvent-based coatings formulated with and without EGR. EGR imparted a distinct off-white color. Marked enhancements in impact resistance were noted on incorporation of EGR in powder coatings. The control formulation failed at 40 in.-lb for both direct and reverse impact resistance tests, whereas EGR-based formulations displayed impact resistance levels of 120/80 and 160/160 in.-lb at 20 and 50% levels, respectively. A moderate decline in solvent resistance was noted with powder coatings containing 50% EGR. Of particular interest was the influence of EGR on the surface characteristics and concurrent gloss reduction. Although the control coating was smooth and glossy, EGR-based coatings were textured and matt-like in appearance. EGR incorporation resulted in a gloss reduction of 17% at 20% concentration and 75% at 50% concentration in powder coatings. In solvent-based coatings, EGR inclusion resulted in a gloss reduction of 15% at 20% concentration and 82% at 50% concentration, but all other coating properties, notably solvent resistance and pencil hardness, remained unaffected by the inclusion of EGR. EGR, thus, demonstrated high matting efficiency in both solvent-based coatings and powder coatings.

FGR Coatings

Fluoropolymers are traditionally characterized by good resistance to heat, chemicals, and weathering; water and oil repellency; and low surface energy. Hence, FGR was formulated into both solvent-based coatings and powder coatings at 10 and 50% levels in an effort to determine its effect on coating properties.

Tables VIII and IX summarize the test results obtained from FGR-modified powder coatings and

Table V FGR Solvent-Based Coatings

Ingredients	Control	Epon : FGR (90 : 10)	Epon : FGR (50 : 50)
57-5776	16.70	15.00	8.30
FGR	—	1.70	8.45
Desmodur N-3300	8.45	8.45	8.45

Table VI EGR Powder Coating Test Results

	Control	Epon : EGR (80 : 20)	Epon : EGR (50 : 50)
Appearance	Smooth	Orange Peel	Textured
Dry film thickness (mils)	2.70	2.60	2.90
Impact resistance [direct/reverse (in.-lb)]	40/40	120/80	160/160
Adhesion	Passes	Passes	Passes
Flexibility (1/8 in.)	Passes	Passes	Passes
Gloss (60°)	78.6	74.6	45.1
Salt fog resistance	Passes	Passes	Passes
MEK double rubs	100+	100+	70+
24-h spot test			
Water	No effect	No effect	No effect
10% NaOH solution	No effect	No effect	No effect
20% H_2SO_4	No effect	No effect	No effect

solvent-based coatings. In powder coatings, FGR incorporation resulted in an 18% gloss reduction at 10% concentration and a 63% gloss reduction at 50% concentration. FGR incorporation in solvent-based coatings resulted in a gloss reduction of 15 and 22% at incorporation levels of 10 and 50%, respectively. All other coating properties were unaffected by incorporation of FGR. Coatings containing FGR also exhibited a distinct off-white color relative to the control. Similar to EGR, powder coatings containing FGR displayed orange peel at 10% concentration and a textured surface at 50% concentration. The low gloss in coatings containing guayule rubber derivatives was attributed to the microphase separation that arises out of incompatibility between the guayule-rubber-derived resin and the other resins employed in the coating.

Solvent-based low-gloss coatings have been traditionally formulated by raising the pigment concentration to a point where the roughness induced by the protruding pigment particles causes most of the incident light to be scattered in all directions rather than to be reflected sharply in one direction. However, high pigmentation levels usually have a negative effect on the mechanical properties of coatings. In this context, our novel guayule rubber derivatives have a significant role to play as they can greatly reduce the gloss of the binder system itself by functioning as a reactive matting agent. More importantly, gloss reduction occurs without any deleterious effect on the mechanical properties or the chemical resistance properties of the coating system. This enables low-gloss coatings to be formulated at lower pigmentation levels by a judicious blend of conventional matting agents and either EGR or FGR, depending on the binder system employed.

Powder coatings formulated with high pigmentation levels suffer from poor flow in addition to inadequate mechanical properties. Consequently, raising the pigmentation level is not a viable for-

Table VII EGR Solvent-Based Coating Test Results

	Control	Epon : EGR (80 : 20)	Epon : EGR (50 : 50)
Dry film thickness (mils)	1.45	1.30	1.20
Impact resistance [direct/reverse (in.-lb)]	160/160	160/160	160/160
Adhesion	Passes	Passes	Passes
Flexibility (1/8 in.)	Passes	Passes	Passes
Pencil hardness	6H	6	6H
Gloss (60°)	130.5	122.0	47.7
Salt fog resistance	Passes	Passes	Passes
MEK double rubs	100+	100+	100+
24-h spot test			
Water	No effect	No effect	No effect
10% NaOH solution	No effect	No effect	No effect
20% H_2SO_4	No effect	No effect	No effect

Table VIII FGR Powder Coating Test Results

	Control	Epon : FGR (90 : 10)	Epon : FGR (50 : 50)
Appearance	Smooth	Orange peel	Textured
Dry film thickness (mils)	1.80	1.94	1.90
Impact resistance [direct/reverse (in.-lb)]	120/40	120/40	120/40
Adhesion	Passes	Passes	Passes
Flexibility (1/8 in.)	Passes	Passes	Passes
Gloss (60°)	62.4	56.5	37.8
Salt fog resistance	Passes	Passes	Passes
MEK double rubs	100+	100+	100+
24-h spot test			
Water	No effect	No effect	No effect
10% NaOH solution	No effect	No effect	No effect
20% H_2SO_4	No effect	No effect	No effect

mulation option for low-gloss powder coatings. Adding incompatible waxes or plasticizers leads to smooth and color stable coatings, but the approach is limited by the wax's tendency to leach from the surface, an effect that limits the use of this procedure to light colors and limited gloss levels.[6] Many applications in the industrial and automotive accessories fields demand textured finishes because they hide imperfections in the substrate better than smooth coatings. Textured finishes can be obtained by the addition of up to 0.5% cellulose acetate butyrate, but problems of poor reproducibility and contamination of other batches limit the utility of this approach. Our results with EGR and FGR demonstrate that epoxy–polyester, polyester-triglycidyl isocyanurate (TGIC), and polyurethane powder coatings can now be formulated to have low-gloss textured surfaces without any concurrent loss of other coating properties. Thus, our novel guayule rubber derivatives herald a new class of reactive matting additives effective at low concentrations.

CONCLUSIONS

Modified guayule rubber derivatives were synthesized and formulated in novel solvent-based and powder coating formulations. It was noted that incorporation of EGR and FGR significantly lowered the gloss level of coatings. More importantly, such gloss reduction was obtained without any sacrifice in important coating properties, such as impact resistance and hardness. Thus, both guayule rubber derivatives show promise as reactive matting agents in coatings, especially in pow-

Table IX FGR Solvent-Based Coating Test Results

	Control	Epon : FGR (90 : 10)	Epon : FGR (50 : 50)
Dry film thickness (mils)	1.50	1.60	1.40
Impact resistance [Direct/reverse (in. lb)]	160/160	160/160	160/160
Adhesion	Passes	Passes	Passes
Flexibility (1/8 in.)	Passes	Passes	Passes
Pencil hardness	5H	6H	6H
Gloss (60°)	127.2	120.4	115.0
Salt fog resistance	Passes	Passes	Passes
MEK double rubs	100+	100+	100+
24-h spot test			
Water	No effect	No effect	No effect
10% NaOH solution	No effect	No effect	No effect
20% H_2SO_4	No effect	No effect	No effect

Differential scanning calorimetry studies of all resin blends containing EGR and FGR showed a single T_g, which indicated a complete reaction of the guayule rubber derivatives with the other resins. The T_g's of the various resin systems are given in Table X.

Table X T_g's of Resin Blends

Item	T_g (°C)
Epon 1001 + Epon 2002 + Rucote 527	45.2
Epon 1001 + Epon 2002 + Rucote 527 + EGR (Epon : EGR 80 : 20)	52.7
Epon 1001 + Epon 2002 + Rucote 527 + EGR (Epon : EGR 50 : 50)	58.9
Methylon 75-108 + Epon 1007F	108.8
Methylon 75-108 + Epon 1007F + EGR (Epon : EGR 80 : 20)	121.4
Methylon 75-108 + Epon 1007F + EGR (Epon : EGR 50 : 50)	131.4
30-3002 + 24-2430	63.7
30-3002 + 24-2430 + FGR (Epon : FGR 90 : 10)	62.2
30-3002 + 24-2430 + FGR (Epon : FGR 50 : 50)	64.4
57-5776 + Desmodur N-3300	40.2
57-5776 + Desmodur N-3300 + FGR (Epon : FGR 90 : 10)	46.3
57-5776 + Desmodur N-3300 + FGR (Epon : FGR 50 : 50)	47.6

der coatings where they provide a pleasing textured effect. Powder coatings formulated with the guayule rubber derivatives exhibited good shelf stability and showed no change in properties even a year after their manufacture.

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