Weathering Studies of Epoxidized and Hydroxy-Fluoroester Pendent Guayule Rubber in Powder Coatings

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ABSTRACT: Although numerous coatings have been synthesized from guayule rubber derivatives, there have been no studies detailing the weatherability of such coatings. We report herein the results of accelerated weathering tests on powder coatings synthesized from epoxidized guayule rubber (EGR) and hydroxy-fluoroester pendent guayule rubber (FGR) derivatives. Our studies indicate that EGR and FGR powder coatings exposed to alternating cycles of fluorescent UVA light and water condensation for 400 h exhibit reduced yellowing and a high degree of gloss retention. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 493–497, 2004

Key words: epoxidized guayule rubber (EGR); hydroxy-fluoroester pendent guayule rubber (FGR); rubber, coatings; weatherability

INTRODUCTION

Guayule, *Parthenium argentatum gray*, a shrub that grows in semiarid regions of the southwest United States and northern Mexico, in guayule rubber derivative form has been used to synthesize numerous coatings.[1–9] During shrub processing, five major components are produced: high molecular weight guayule rubber, low molecular weight guayule rubber, organic soluble resins, water-soluble extracts, and bagasse.[11–14] In an effort to establish a domestic guayule industry and optimize potential revenue, it is important to make use of all its coproduct fractions.

Synthesis of epoxidized guayule rubber (EGR) was accomplished by epoxidation of the olefinic double bonds of guayule rubber using *m*-chloroperbenzoic acid (Fig. 1).[10] Hydroxy-fluoroester pendent guayule rubber (FGR) was synthesized from EGR by fluoro acid–catalyzed epoxide ring openings (Fig. 2).[10] These reactions were characterized by a significant increase in the glass-transition temperature (T_g), which rendered these rubber derivatives potentially attractive for use in surface coatings.[10]

EXPERIMENTAL

Materials

Bisphenol-A–based epoxy resins Epon 1001, Epon 1007 F, and Epon 2002 were obtained from Shell Chemical Company (Akron, OH). Carboxyl-functional polyester resin, Rucote 527, was obtained from Ruco Polymer Corp. Hydroxyl-functional polyester resin Albester 3020 and aliphatic polyisocyanate resin Alcure 4430 were obtained from McWhorter Technologies, Inc. Modarez MFP and Actiron CC-6 were obtained from Synthron, Inc., and benzoin was obtained from Generichem. Titanium dioxide, Ti-Pure R-960, and Sparmite barytes are products of E. I. Dupont de Nemours and Co. and Pfizer Inc., respectively. Methyl ethyl ketone (MEK) was obtained from Aldrich Chemical Co. (Milwaukee, WI). Bare steel panels, QD-36, obtained from the Q-Panel Company were wiped clean with MEK before use. All materials were used as received.

Procedure

The epoxy functionality of EGR was reacted with carboxyl functional polyester resin by modifications of a control formulation based on epoxy resins Epon 1001, Epon 2002, and polyester resin Rucote 527. The hydroxyl group accompanying the formation of the fluoroester group in FGR was a potential site for crosslinking with an isocyanate group. Hence, a suitable control formulation based on polyester resin Albester 3020 and isocyanate resin Alcure 4430 was also included in the study. The total binder amount was held constant to ensure that the pigment : binder ratio would be equal for all coatings.

Before processing, EGR and FGR were blended with the other resins in the formulation for proper mixing. The powder coatings were processed according to the standard practice of premixing, melt extrusion, grinding, and sieving. The ingredients were combined and
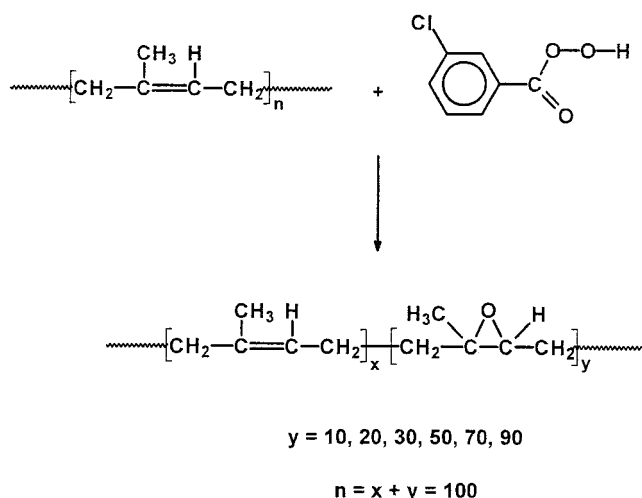
Figure 1 EGR synthesis.

processed in a Henschel FM-10 mixer at 2000 rpm for two stages of 60 s each. The mixture was melt extruded using a Werner and Pfleiderer ZSK 30 twin-screw extruder (Table I). Subsequently, the extrudate was ground in a micron powder system model SH Bantam mill equipped with liquid nitrogen cooling. The powders were sprayed onto mild steel panels with a Nordson Corona model NVC 4 spray system, and cured in a Despatch gas oven.

Characterization of cured coatings

The coated panels were tested according to ASTM protocols. Accelerated weathering was conducted according to ASTM D 4587-91 using a QUV fluorescent ultraviolet/condensation screening device having eight FS-40 fluorescent UVA lamps as its light source. The panels were exposed to alternating cycles of 4 h of fluorescent ultraviolet radiation at 60°C, followed by
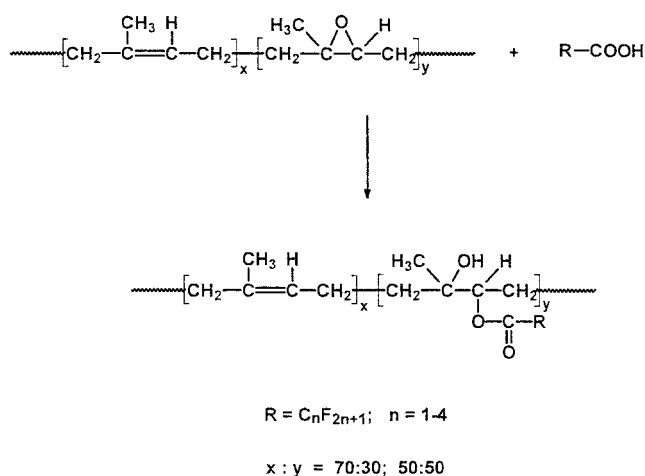

Figure 2 FGR synthesis.

TABLE I
Processing Parameters

Processing	EGR	FGR
	Extrusion	
Zone 1 temperature	90°C	90°C
Zone 2 temperature	110°C	110°C
Screw speed	101 rpm	100 rpm
Torque	30–55%	35–68%
	Chill rolls	
Roll speed	30 rpm	
Roll temperature	13°C	

4 h of condensation at 40°C. The extent of yellowing was measured with an ACS colorimeter. The gloss was determined on a Gardener statistical Novogloss instrument meeting ASTM D 523-89 standards.

RESULTS AND DISCUSSION

From a practical standpoint, the ability of an organic coating to withstand the natural degradative forces of sunlight and water is very important. Primarily, it is the behavior of the binder employed which decides the long-term performance of a coating. Numerous articles have been published regarding the natural weathering of coatings and its correlation to results predicted from accelerated weathering tests conducted in laboratories. However, no studies have been reported on the weathering performance of guayule derivatives based coatings. In this study, accelerated weathering test performance of two guayule rubber derivatives were evaluated.

Powder coatings with EGR (Table II) were formulated by replacing the total equivalents of the epoxy resins (Epon 1001 and Epon 2002) in the control formulation by EGR to the extent of 20 and 50%. Similarly, powder coatings with FGR (Table III) were formulated by replacing the hydroxyl equivalents of the polyester resin (Albester 3020) in the control formulation by those of FGR to the extent of 10 and 50%. Powder-coated panels were exposed to alternating fluorescent ultraviolet/condensation cycles for 400 h and checked every 100 h for their gloss readings and change in color.

EGR

Incorporation of EGR lowered the gloss of the control formulation in direct proportion to its percentage (Table IV). At the end of 400 h of accelerated weathering, it was observed that the control formulation had the lowest gloss retention of 51 versus 60% for 20% EGR (Experiment 1) and 62 for 50% EGR (Experiment 2). In fact, the 20% EGR (Experiment 1) had higher final

TABLE II
EGR-Based Powder Coatings

Ingredient	Equivalent weight	Control (g)	Experiment (g)	Experiment 2 (g)	Cure temperature
TiO$_2$	—	150.00	150.00	150.00	150°C for 30 min
Epon 1001	475	60.00	52.00	36.75	
Epon 2002	718	65.00	55.75	40.00	
EGR	242	—	5.75	16.25	
Rucote 527	650	140.00	151.50	172.00	
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	
Epon : EGR equivalents	—	—	80 : 20	50 : 50	

gloss than that of the control. Also, before exposure, the coatings formulated from EGR (Experiments 1 and 2) yellowed more than the control but after 400 h exposure, the control panel had the highest b value compared to Experiments 1 and 2 (Table V).

Color theory states that colored objects absorb different wavelengths of light, and the color reflected by objects is complementary to the wavelengths absorbed. The dark brown color of rubber is attributed to the presence of the carbon–carbon double bond (chromophores) and is further enhanced by methyl groups (auxochromes). Formation of EGR involves reduction in unsaturation of the rubber backbone; consequently, EGR is lighter in color (buff colored) and imparts a distinct yellowness to coatings.

When natural rubber is exposed to UV radiation, the bond between the methylene groups breaks generating free radicals (Fig. 3). These methylene radicals can recombine or join in the same or another polymer chain, giving rise to cyclopropane derivatives (Figs. 4 and 5).[15,16] The net result of such a recombination is the decrease in unsaturation of the final coating and consequent reduction in yellowness of the coatings.

Aromatic epoxy resins are known to undergo photodegradation on UV exposure,[15,16] with consequent radical formation, and this is the key step for main-chain scission and degradation (Fig. 6).

Hydrogen atoms around epoxy rings are quite labile, and their abstraction leads to either alcohol, ketone, or aldehyde moieties. The degradation of the main chain leads to the formation of keto and quinoid type structures, which in turn are responsible for yellowing.[15,16] Epoxy resins, therefore, exhibit poor exterior durability. The yellowing of the commercial epoxy resin dominates over the reduced yellowing of the EGR; hence the net result can only be seen as a lower b value for EGR-based coatings relative to the control after 400 h of UV exposure. The results of our accelerated weathering test suggest that EGR has better exterior durability than that of aromatic epoxy resins.

FGR

Incorporation of FGR also lowered the gloss of the control formulation in direct proportion to its percentage (Table VI). At the end of 400 h accelerated weathering, it was observed that coatings containing 10% FGR (Experiment 3) exhibited a gloss retention of 96% compared to 85% for the control and 73% for coatings containing 50% FGR (Experiment 4).

TABLE III
FGR-Based Powder Coatings

Ingredient	Equivalent weight	Control (g)	Experiment 3 (g)	Experiment 4 (g)	Cure temperature
TiO$_2$	—	150.00	150.00	150.00	170°C for 30 min
Albester 3020	492.50	172.25	158.00	96.95	
FGR	324.28	—	11.50	63.25	
Alcure 4430	266.00	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	
Polyester : FGR equivalents	—	—	90 : 10	50 : 50	

TABLE IV
Gloss Measurement on UV Exposure (400 h) for EGR Powder Coatings

Gloss (60°)	Control	Experiment 1 (80 : 20)	Experiment 2 (50 : 50)
Initial gloss	74.3	70.6	46.6
After 400 h	37.9	42.3	29.1

Figure 5 Cyclopropane derivative formation.

FGR is similar in color to EGR (i.e., buff colored), whereas the commercial polyester is water-white in color; hence FGR-based coatings are more yellow than the control. The color of the guayule rubber is further enhanced by the presence of pendent methyl, hydroxyl, and fluoroester groups (auxochromes).[15–28] Comparison of the $b*$ values at 0 h indicates that coatings containing FGR are considerably more yellow than the control (Table VII). However, after exposure, FGR-based coatings became less yellow (decreased in $b*$ value), whereas the control coatings became more yellow (increased in $b*$ value).

Aliphatic polyester and polyurethane coatings retain most of their initial color on exposure to accelerated weathering tests because they cannot form an adequately long sequence of conjugated double bonds to act as chromophores. Aliphatic polyester and polyurethane both undergo carbonyl radical formation, leading to either chain scission or crosslinking reactions (Fig. 7).[15,16] Aromatic polyurethanes, however, are isomerized to the enol form upon absorption of

TABLE V
Extent of Yellowing ($b*$ Values) for EGR Powder Coatings

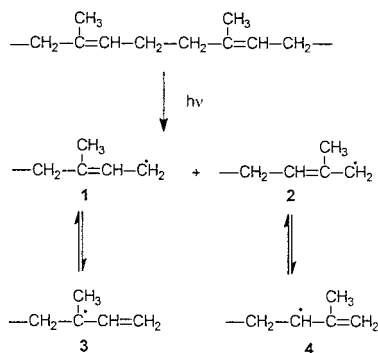|	Initial gloss	After 400 h
Control	0.97	6.13
Experiment 1 (80 : 20)	1.41	5.71
Experiment 2 (50 : 50)	2.89	5.84

Figure 3 Rubber (*cis*-polyisoprene) photodegradation.
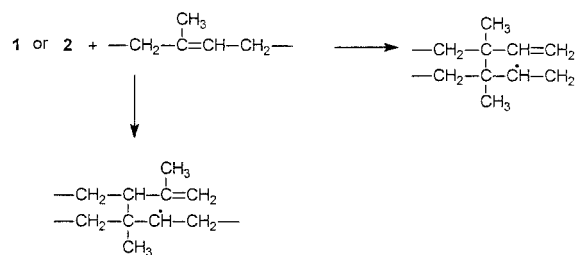
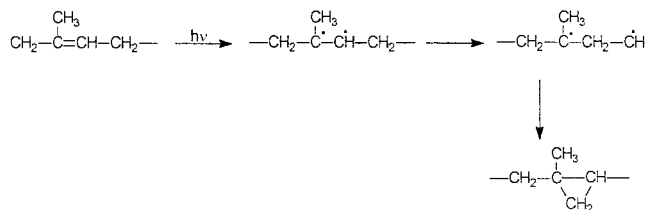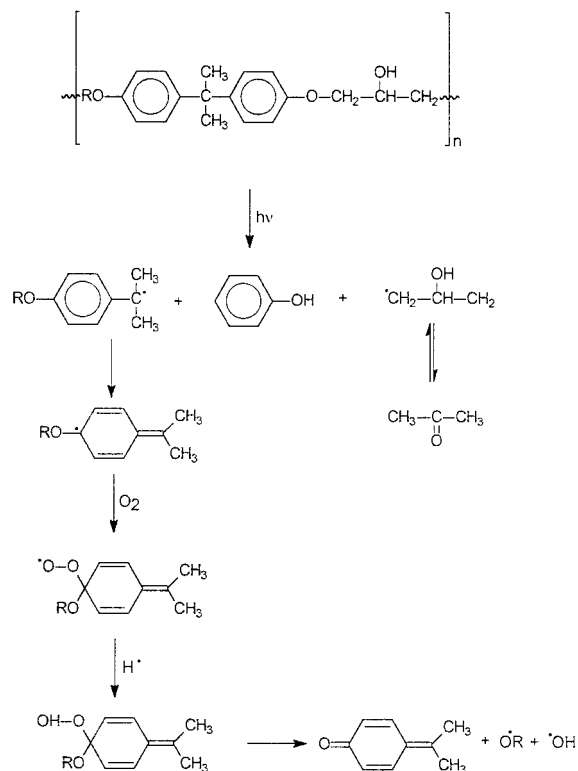**Figure 4** Recombination of radicals with polyisoprene.

Figure 6 Epoxy resin photodegradation.

TABLE VI
Gloss Measurement on UV Exposure (400 h) for FGR Powder Coatings

Gloss (60°)	Control	Experiment 3 (90 : 10)	Experiment 4 (50 : 50)
Initial gloss	68.8	66.2	48.9
After 400 h	58.6	63.7	35.9

TABLE VII
Extent of Yellowing (b^* Values) for FGR Powder Coatings

	Initial	After 400 h
Control	1.84	2.05
Experiment 3 (90 : 10)	5.96	4.11
Experiment 4 (50 : 50)	10.03	5.68

energy and, because this has more than three conjugated double bonds, it is colored. On the other hand, aliphatic polyurethane systems are isomerized only partly on energy exposure, and further color development is inhibited (Fig. 8).

The control polyurethane coating showed a marginal increase in b value, whereas the FGR-based coatings showed a decrease in their yellowness index. The reduction in yellowness is presumably attributable to the loss of unsaturation arising out of recombination of cleaved rubber backbone free radicals as explained earlier. FGR can therefore be said to exhibit good exterior durability.

CONCLUSIONS

The weathering durability of modified guayule rubber derivatives (EGR and FGR) was demonstrated. Incorporating EGR and FGR into powder coatings resulted in gloss reduction and a high degree of yellowness. Replacing commercial aromatic epoxy resins by EGR in powder coatings reduced the extent of yellowing and improved gloss retention upon exterior exposure. Similarly, replacing commercial hydroxy functional resin in powder coatings by FGR resulted in good gloss retention at the 10% level and reduced yellowing upon exterior exposure. Thus, EGR- and FGR-modified coatings displayed matte finishes and high gloss retention in accelerated weathering tests.
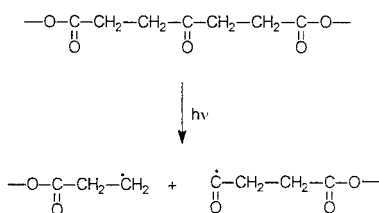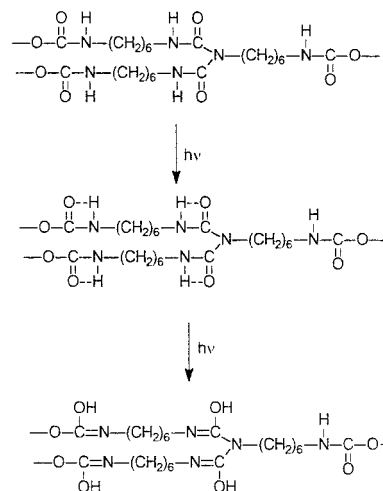

Figure 7 Polyester photodegradation.

Figure 8 Polyurethane photodegradation.

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