

Cationic Ultraviolet Curable Coatings from Castor Oil

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ABSTRACT: Coatings formulated from castor oil glycidyl ether (COGE), epoxy resin UVR 6100, and photoinitiator UVI 6990 produced smooth coatings with excellent gloss and good flexibility, adhesion, gloss retention, and water resistance. Formulations containing up to 50% COGE afforded promising coating performance attributes. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 8–13, 2000

Key words: castor oil; glycidyl ether; epoxides; UV cure; coatings

INTRODUCTION

Technical innovations continue to drive UV-curable coatings markets toward more industrial applications. However, progress to date has been limited as a result of a restricted supply of raw materials.^{1,2} Considerable research efforts were focused on the use of vegetable oil and their derivatives for UV-curable coatings.^{3–6} As a vegetable oil, castor oil represents a promising raw material based on its low toxicity and availability as a renewable agricultural resource. Modification of castor oil, containing about 90% hydroxyl-containing fatty esters, with glycidyl ether functionality⁷ has provided a promising product for cationic UV-curable coatings applications.

EXPERIMENTAL

Materials

UVR 6100 cycloaliphatic epoxide, and UVI 6990 mixed triarylsulfonium hexafluorophosphate

salts supplied by Union Carbide Chemicals and Plastics Company, and COGE purchased from Aldrich Chemical were used as received. COGE used was pale yellow in color with a Gardner Max. of 8, had a viscosity of 476 cPs at 25°C, and possessed an epoxide equivalent weight of 540 (Fig. 1). Fourier Transform Infrared and Nuclear Magnetic Resonance spectra of COGE showed the presence of some hydroxyl groups, indicating that other components are also present apart from the major triepoxide functional compound.

Coating Formulations

Cationic UV-curable coatings were formulated from COGE, UVR 6100, and UVI 6990 (Table I). COGE and UVR 6100 combined at 0 : 100, 10 : 90, 20 : 80, 30 : 70, 40 : 60, 50 : 50, and 60 : 40 (w/w) ratios on a Vortex Shaker for 15 min were subsequently mixed with UVI 6990 and blended on the Vortex Shaker for 30 min.

UV Curing

Ten samples prepared via application of 76 μm (3 mil) wet film onto cold-rolled bare steel Q-panels were cured twice at a belt speed of 60 rpm using a DRS-120 Fusion System D mercury lamp with an output power level of 600 Watts/inch. For comparison, five samples were further heat treated in a forced air oven at 150°C for 30 min.

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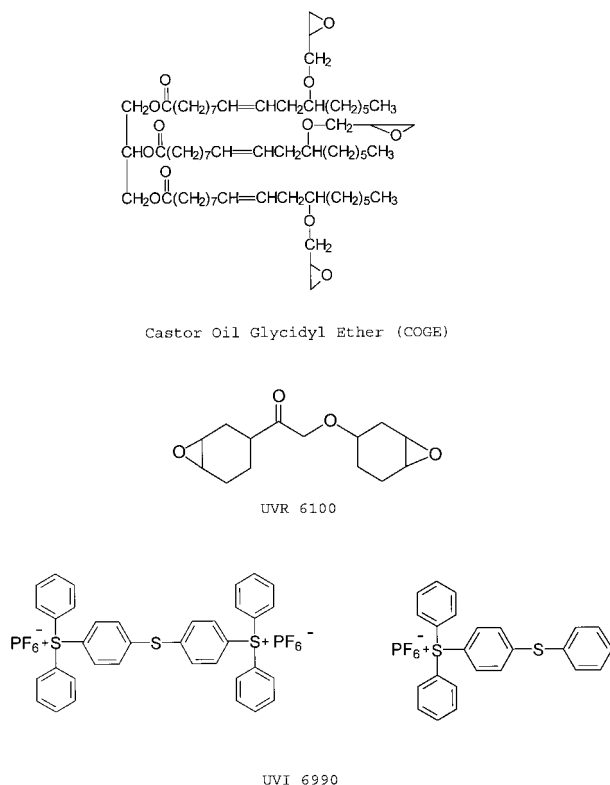


Figure 1 Major components of materials used.

Differential Scanning Calorimetric (DSC) Analysis

To provide thermal data for assessing the degree of cure (D), coating aliquots encapsulated in 40- μ L aluminum DSC pans were analyzed immediately after radiation on a Mettler DSC 30 from 30 to 275°C at a heating rate of 10°C/min holding at 275°C for 30 min under N_2 . Residual heat, ΔH_n , from DSC thermograms⁸ and the total heat of reaction, ΔH_0 ,⁹ obtained after heat cure were used in the following equation to calculate D :^{9–11}

$$D = 100 \times \left(1 - \frac{\Delta H_n}{\Delta H_0} \right)$$

Glass transition temperatures obtained on the UV-cured films (T_{gp} , 20 days after cure), postheat

treated films (T_{gt}), and heat-cured films (T_{gh}) via DSC at a heating rate of 5°C/min under N_2 are given in Figure 2.⁸

Characterization of Coating Film Properties

Coating films prepared via application of 101.3 μ m (4 mil) wet film by a draw bar onto flat polypropylene sheets were UV cured three times at a belt speed of 60 rpm using a DRS-120 Fusion System D mercury lamp. Cured films were stored at room temperature for 20 days and were then evaluated for tensile strength, modulus, and elongation at break on a MTS 810 Mechanical Tester with specimens of 100 \times 10 mm size. A minimum of five specimens were tested for each sample at a crosshead speed of 2.5 cm/min.

Characterization of Coating Properties

Dry film thickness was measured with a Gardco Minitest Microprocessor Coating Thickness Gauge. Pencil hardness was determined according to ASTM D 3363. Adhesion was evaluated by the crosshatch tape test (ASTM D 3359). Impact resistance was measured with a BYK-Gardner Heavy Duty Impact Tester Model IG-1120, with 1.8 kg (4 lb) mass and 1.27 cm (0.5 in) diameter round-nose punch (ASTM D 2794). Yellowness index measurements were recorded with an Applied Color System CS-5 Chroma-Sensor. UV resistance was determined by exposing the films in an Atlas Ultraviolet Condensation Screening Device equipped with F40 UVB lamps. Specular gloss was measured with a Gardco Statistical Novogloss glossometer as specified by ASTM D 523.

RESULTS AND DISCUSSION

Coating Formulations

Virtually 100% solids formulations of epoxy resins (COGE and UVR 6100) and a photoinitiator salt (UVR 6990) provided suitable fluid cationic UV-curable coatings (Table I). COGE and UVR

Table I Formulations of COGE UV Curable Coatings^a

	COGE0	COGE1	COGE2	COGE3	COGE4	COGE5	COGE6
COGE, g	0	10	20	30	40	50	60
UVR 6100, g	100	90	80	70	60	50	40

^a All formulations contain 4 g of UVI 6990 initiator.

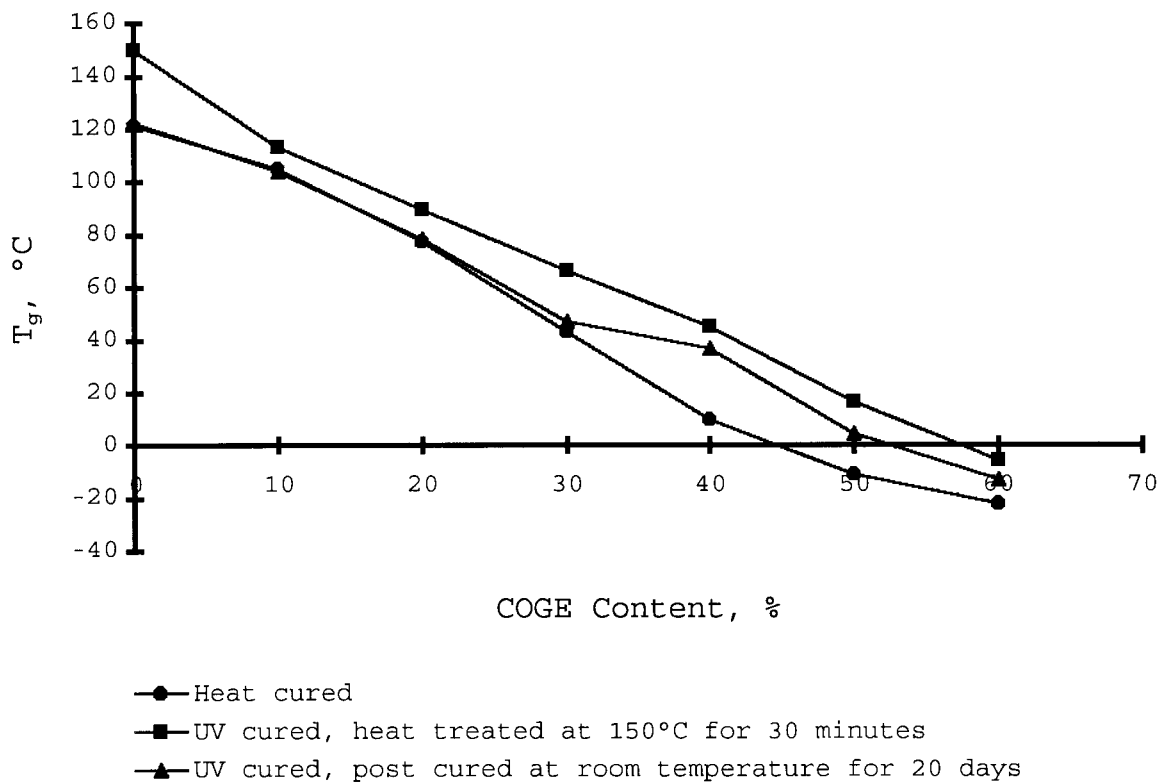


Figure 2 DSC thermograms— T_g versus COGE content.

6100 were compatible at all concentrations. However, upon addition of the photoinitiator, formulations with 70, 80, 90, and 100% COGE formed hazy formulations due to precipitation of the photoinitiator. For this reason, formulations with greater than 60% COGE could not be evaluated.

Curing of Coatings

D , ΔH_n , and ΔH_0 values obtained by DSC analysis are tabulated in Table II. ΔH_0 decreased with COGE content in the coating due to a higher epoxide equivalent weight (540 g/mol) than UVR 6100 (136 g/mol).¹² The D -value increased from 81.5% for the control sample COGE0 with 0%

COGE to 98.7% for the COGE6 sample with 60% COGE content.

Because cationic curing processes are insensitive to atmospheric oxygen, the curing reaction may continue even in the absence of UV light.⁸ Continuation of postcure at room temperature resulted in an increase in D -value vs. postcure time (Table II). The D -value of samples COGE0 and COGE1 increased from 81.5 to 95.7% and 88.8 to 98.1%, respectively, 20 days after the UV treatment.

Postcure effects on cationic cured coatings may also be enhanced by thermal treatment.¹³ Glass transition temperatures increased in the order of

Table II ΔH_n , ΔH_0 , and D Values by DSC Analysis

	COGE0	COGE1	COGE2	COGE3	COGE4	COGE5	COGE6
ΔH_n , J/g	100.1	53.2	38.3	12.8	11.87	7.8	3.7
ΔH_0 , J/g	541.1	474.6	420.5	359.0	320.9	313.5	284.5
D , %	81.5	88.8	90.9	96.4	96.3	97.5	98.7
D_{20} , %	95.7	98.1	98.2	98.2	98.4	99.4	99.2

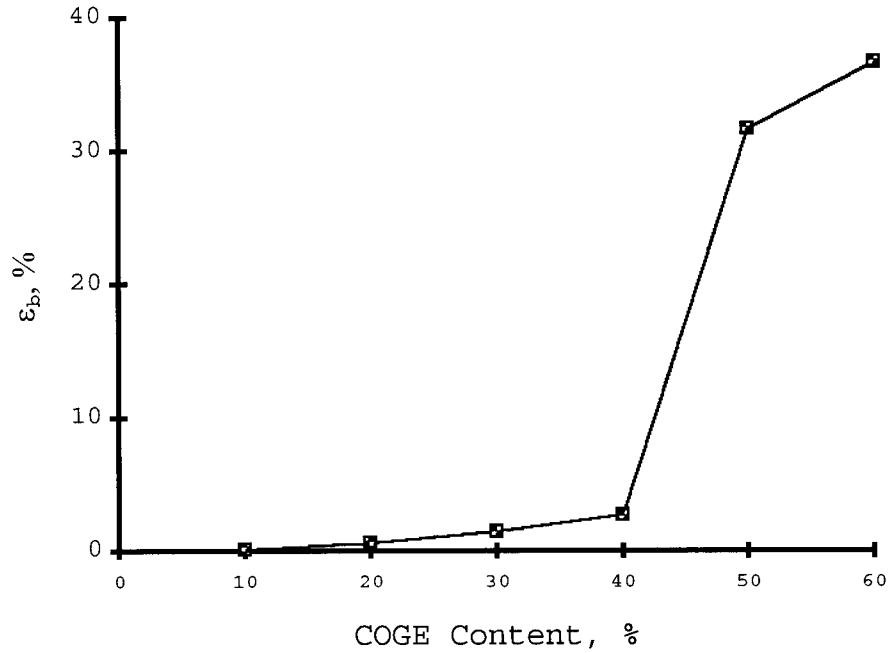


Figure 3 Elongation at break versus COGE content.

heat-cured films [T_{gh}] \leq 20-day room temperature postcure films [T_{gp}] < postheat-treated films [T_{gt}]. Therefore, heat treatment shortened the postcure process as evidenced by higher glass transition temperatures (Fig. 2).

Physical Properties of Coating Films

Modulus (E), break stress (σ_b), and elongation at break (ϵ_b) properties are graphed in Figs. 3–5. The 100% UVR 6100 sample COGE0 was too rigid

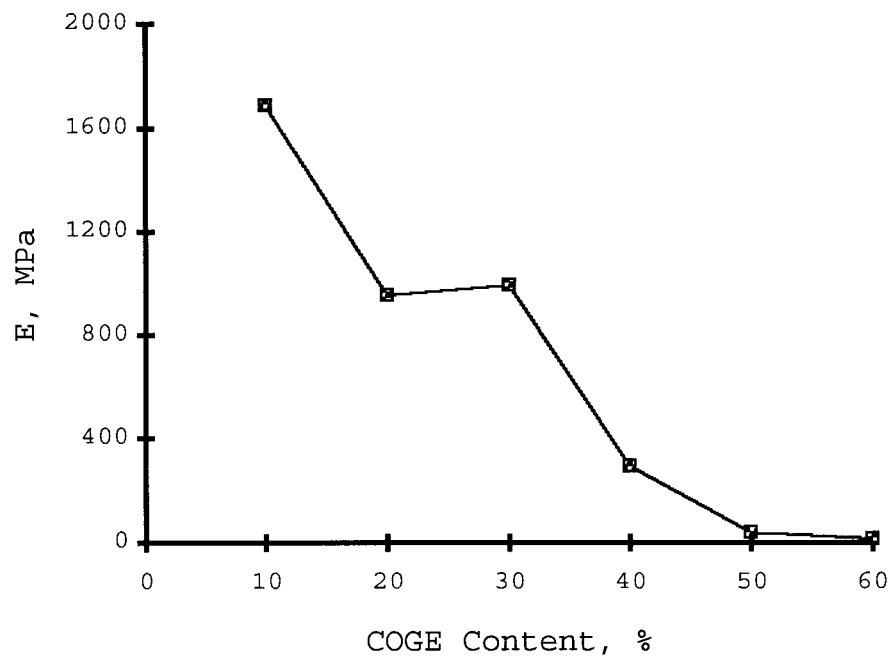


Figure 4 Modulus versus COGE content.

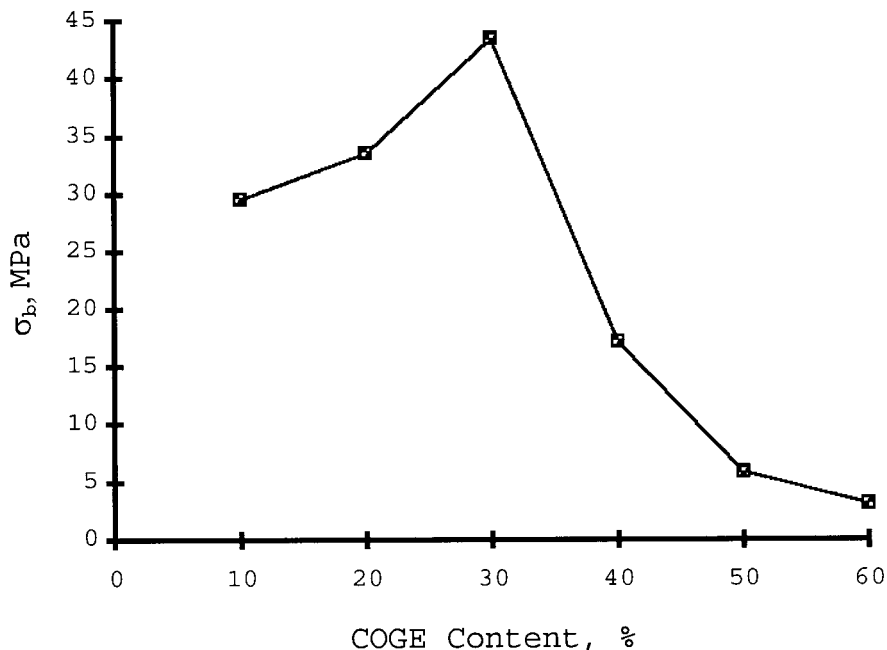


Figure 5 Break stress versus COGE content.

and fragile for evaluation with the tensile test. Incorporation of COGE in various concentrations generated more flexible films. The elongation at break increased sharply at 40% COGE content (Fig. 3), and the modulus decreased sharply at 30% COGE content (Fig. 4). The highest value for break stress reached 43.5 MPa at 30% COGE concentration and then declined (Fig. 5). Therefore, cured films containing 30–40% COGE concentration transformed from a plastic to a rubbery material (Fig. 6).

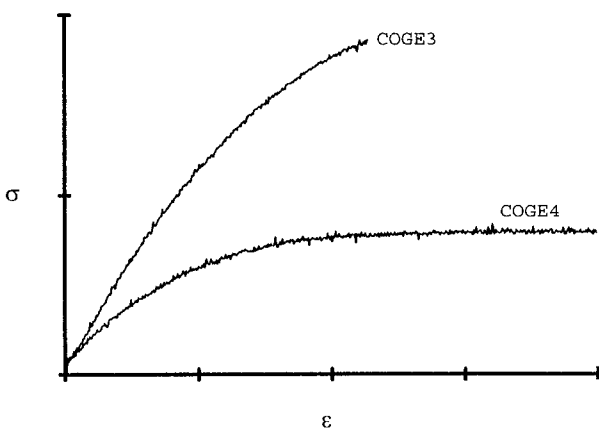


Figure 6 Stress-strain curves of COGE3 and COGE4.

Coatings Properties

COGE-derived coating had a slight tinge of yellow color, and there was no appreciable change in color after postcure. Formulations incorporating COGE resulted in improved adhesion to cold-rolled bare steel substrates (Table III). For instance, coatings with 30% or higher COGE content provided better adhesion (5B, 100%) than those with lower or no COGE content (4B, 80%). Pencil hardness of the films decreased from 9H to HB when COGE content was increased from 0 to 60%.

Coating films incorporating COGE displayed a smooth surface with excellent gloss and improved gloss retention over a range of COGE concentrations. For example, the gloss retention for 10% COGE was 68.1 vs. 7.6% for no COGE (Table III). After the dramatic improvement at 10% COGE, the gloss retention decreased from 68.1 to 39.1% over the range of 10 to 50% COGE content. At 60% COGE, the gloss retention dropped to 10.9%. COGE also reduced UV stability as evidenced by higher yellowness indexes of COGE coatings after 100 h of UV/condensation exposure at 60°C. Coatings containing no COGE also exhibited shrinkage from faster surface cure.¹²

Direct and reverse impact tests revealed enhanced flexibility for COGE cationic-curable coatings. COGE3 coating withstood 120 in-lbs direct

Table III Properties of COGE UV-Cured Coatings

	COGE0	COGE1	COGE2	COGE3	COGE4	COGE5	COGE6
Thickness, mil	0.62	0.93	0.77	0.70	0.84	0.69	0.58
Adhesion	4B	4B	4B	5B	5B	5B	5B
Gauge pencil hardness	9H	7H	5H	4H	3H	2H	HB
Gloss, 60°C	86	103	122	119	120	109	109
Gloss retention, %	7.6	68.1	56.9	54.2	43.8	39.1	10.9
Yellowness index	1.95	1.90	2.16	3.40	3.29	4.96	6.14
Yellowness index	9.90	14.73	15.74	17.23	30.58	37.73	36.55
Direct impact, in-lb	0	20	20	120	160	160	160
Reverse impact, in-lb	0	0	4	80	160	160	160
Conical bend	Fail	Fail	Fail	Pass	Pass	Pass	Pass
Scribe corrosion, mm	2	0.5	0.5	0.5	1	1	2.5
Salt fog test, surface blisters	No. 8, dense	No. 8, few	No. 8, few	No. 8, medium	No. 8, medium dense	No. 8, dense	No. 8, dense

impact and 80 in-lbs reverse impact, while the control coating COGE0 had approximately 0 in-lbs impact resistance. Moreover, flexibility increased with higher COGE content. COGE4 coating withstood 160 in-lbs of both forward and reverse impact.

COGE resulted in improved water resistance at the 10–40% levels in salt fog spray test results. Coatings with 10 and 20% COGE content showed less scribe corrosion (0.5 mm) and fewer surface blisters (No. 8, few) than the control (2 mm, No. 8, dense). However, when the COGE content was increased to over 40%, more surface blistering was observed.

CONCLUSIONS

Cationic UV-curable coatings were developed containing up to 60% castor oil glycidyl ether (COGE) concentrations. The D-value increased with higher COGE concentrations. UV-cured coatings continued to postcure in dark, room temperature conditions. Heat treatment of coatings exposed to UV enhanced the postcuring and increased glass transition temperatures. COGE-containing coatings produced smooth films with better gloss, gloss retention, and flexibility than the control coating, which was formulated from the commercially available epoxy resin, UVR 6100. Moreover, coatings with 10–40% COGE concentrations were superior in water resistance.

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