Cationic UV-Cured Coatings Containing Epoxidized Soybean Oil Initiated by New Onium Salts Containing Tetrakis(pentafluorophenyl)gallate Anion

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Different formulations containing epoxidized soybean oil (ESO) and a commercial cycloaliphatic epoxy resin (UVR6110) were cured by onium tetrakis(pentafluorophenyl)gallate (Gallate) on steel panels. The resulting coatings were clear and their mechanical properties were tested by the Sward hardness test, cross-hatch tape adhesion test and MEK double rub test. The new initiators have the advantage of good solubility, high reactivity, and the production of colorless coatings. The best formulations obtained contain 50% ESO, 50% UVR6110, and 0.5% silwet if sulfonium gallate is used as initiator, and 60% ESO, 40% UVR6110, and 0.5% silwet if iodonium gallate is the initiator.

INTRODUCTION

About eight percent of all industrial materials cured by photochemical routes are cured via cationic polymerization. Cationic polymerization has certain advantages over radical polymerization processes. There is lower shrinkage, the processes are less sensitive to oxygen, the coatings have better flexibility, and the systems release fewer volatile organic compounds (VOC). Cycloaliphatic epoxide resins are widely used in the UV-initiated cationic cure industry because they offer high reactivity and the coatings have good scratch and abrasion resistance, excellent adhesion to metal, as well as good hardness.[2] The major products are used as varnishes for metal cans, inks for metal, paper and plastics, coatings for plastics, sealants and potting materials (electronics market), and as exterior coatings used on food packaging materials. The growth of UV-initiated cationic cure has been mainly limited by the range of the applicable chemistries, and by the costs of the raw material for formulations.

Soybean oil is one of the most readily available and least expensive vegetable oils in the world today. For many years, soybean oil and its derivatives have been major ingredients in commercial alkyd resins. Since epoxidized soybean oil (ESO) can be cationically polymerized by the epoxy crosslinking reaction,[3] it can be used to replace some of the cycloaliphatic epoxy resins in various formulations to lower the cost.[4-6] For example, a novel application under prototype development uses ESO as part of an epoxy formulation as a roof sealant coating. The coating is applied and cured within minutes by sunlight. The coating is filled with white pigment in order to provide a white surface that helps to reflect sunlight aiding in keeping the roof and building cooler. One of the limitations of this, however, is the solubility of initiators in the nonpolar ESO.

Diaryliodonium and triarylsulfonium salts are two common cationic initiators used in the UV-cure industry. Upon irradiation, these salts generate strong Brönsted acids that can initiate the cationic polymerization of epoxides and vinyl ethers. The solubility of these salts in formulations depends on the structure of the cation and the anion. Recently, we have synthesized a new anion, tetrakis(pentafluorophenyl)gallate, and paired it with various cations.[7] Salts containing this anion were found to have both good solubility and reactivity in nonpolar resins. In this paper, we report the cationic UV-cure of formulations containing ESO with two new photoinitiators.

EXPERIMENTAL

Materials

Fully epoxidized soybean oil, Vikoflex 7170, was supplied by Elf Atochem. Cycloaliphatic epoxy resin Cyracure UVR 6110 and polyol Tone 0301 (Polyol) were supplied by Union Carbide. Silicone surfactant Silwet L-7602 was

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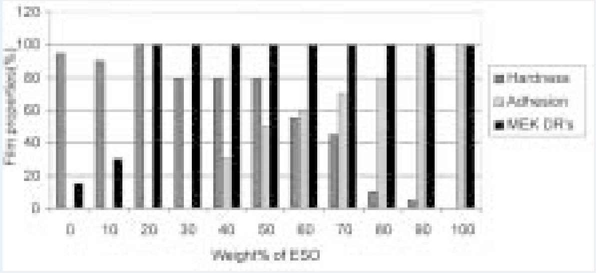

Figure 1—Properties of cured coatings containing different amounts of ESO using SGa as initiator.

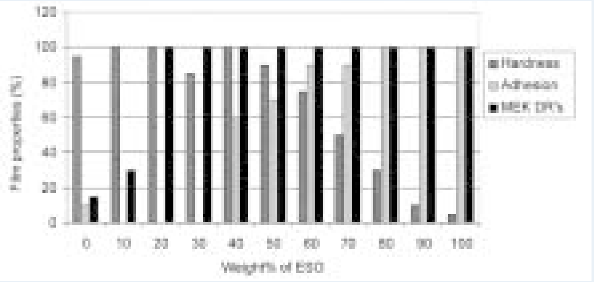

Figure 2—Properties of cured coatings containing different amounts of ESO using IGa as initiator.

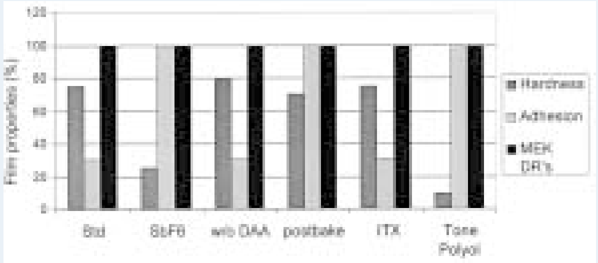

Figure 3—Properties of cured coatings initiated by sulfonium salt.

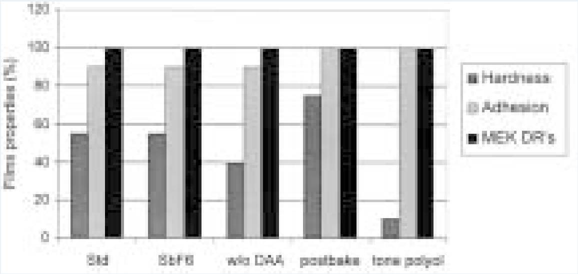

Figure 4—Mechanical properties of cured coatings initiated by iodonium salts.

obtained from OSi Specialties. From Aldrich, 4-hydroxy-4-methylpentan-2-one (DAA) was obtained. UVI 6974 (10% diphenyl-4-thiophenoxyphenylsulfonium hexafluoroantimoniate and 90% bis[4-(diphenylsulfonio)sulfide bishexafluoroantimoniate in propylene carbonate) was supplied by Union Carbide. Octoxyphenylphenyl iodonium hexafluoroantimoniate was supplied from GE Silicones. Octoxyphenylphenyl iodonium tetrakis(pentafluorophenyl)gallate (IGa) was synthesized as reported before.[6]

Synthesis of Diphenyl-4-thiophenoxyphenylsulfonium (10%) and Bis(4-(diphenylsulfonio)sulfide (90%) Tetrakis(pentafluorophenyl)gallate (SGa)

Distillation under reduced pressure was employed to remove the propylene carbonate solvent present in the commercial UVI 6974. Then, equivalent moles of UVI 6974 without solvent and LiGa(C$_6$F$_5$)$_4$ were mixed in dichloromethane. After filtration followed by passing the residue through a short silica column, a sticky liquid was obtained with yield of 85%. After standing for several days this sticky liquid solidified into a white waxy solid. The product was characterized by ^{1}H NMR and ^{19}F NMR. ^{1}H NMR (CDCl$_3$) δ 7.3-7.5 ppm (aromatic Hs). ^{19}F NMR (CDCl$_3$) δ-132.8 (sm, 2F), -162.8 (m, 1F), -166.7 (sm, 2F).

General Procedure for Coatings

A thin layer of formulation was applied to steel panels (S-36 obtained from Q-Panel) using a drawdown bar #5. The liquid coating was then cured by exposure to a Fusion UV system F300 with an H bulb. (I = 300 Watts/in^2). Belt speeds were varied from 10 to 160 fpm. The dosages ranged from 2500 to 144 mJ/cm^2, respectively.

Testing Methods

The through-cure was tested by the thumb-twist test. Cured film properties were determined after 24 hr of postcure at room temperature unless otherwise mentioned. The Sward hardness test (using the Gardner/Sward Hardness Rocker Mode1#GS1, meets and exceeds ASTM D2134), cross-hatch tape adhesion test (ASTM D3359)

Table 1—Conversion of Film Property Values to Index Values

Index Value (%)	Sward Hardness	Adhesion	MEK DRs[a]
0	0	0	0
10	2	1B	1-50
20	4		
30	6	2B	>50
40	8		
50	10		
60	12	3B	>100
70	14		
80	16		
90	18	4B	>180
100	20	5B	>200

(a) Methylethylketone double rub, evaluation for solvent resistance (ASTM D5402).

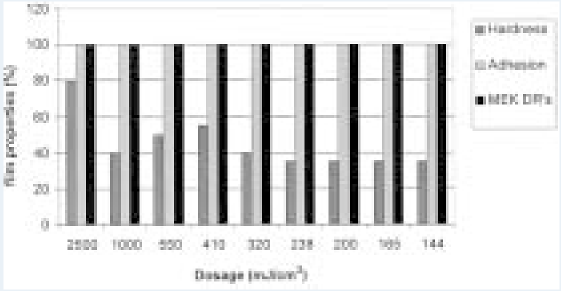

Figure 5—Mechanical properties of coatings cured by SGa at different speed.

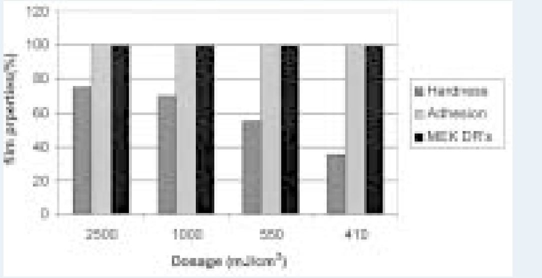

Figure 6—Mechanical properties of coatings cured by IGa at different speeds.

and solvent resistance (ASTM D 5402) were carried out for each formulation. Dry film thickness was measured by a Mikrotest magnetic coating thickness gauge and was around 25 microns.

For graphing convenience, index values from 0 to 100% were used to evaluate the properties of the cured films (*Table* 1).

RESULTS AND DISCUSSION

Dependence on Formulation

Formulations containing different percentages of ESO were prepared (*Tables* 2 and 3) to test the effects on coating properties. In the case of UVI 6974, the formulation turned cloudy when the percentage of ESO was more than 50% by weight because of the poor solubility of the initiator. All other formulations remained clear providing more chances to investigate coatings containing higher weight percents of ESO. All coatings were cured at 10 fpm.

The properties of the cured coatings are shown in *Figures* 1 and 2. ESO can be as high as 80% by weight without decreasing the chemical resistance (MEK DR > 200). Adhesion and hardness are properties that conflict with one another. With the increase of ESO in the formulations, adhesion increases. However, the hardness decreases dramatically, possibly because the hydroxy group contained in ESO serves as a chain transfer reagent. After balancing the two properties, hardness and adhesion, we determined that formulations containing 50% ESO (in the case of SGa) and 60% ESO (in the case of IGa) were the best compromise.

Optimizing the Curing Conditions

With the ratio of the two resins fixed, other conditions were changed to test their effect on the coating properties. The formulations used to optimize the curing conditions are in *Tables* 4 and 5. In the first tests, the new initiators were compared with their SbF_6 counterpart (S12 and I12). Secondly, the role of diluent DAA was evaluated. Thirdly, the effect of postbake on coating properties was studied. Then, polymerizations were carried out using ITX as sensitizer. Finally, polyol Tone 0301 was added to replace 30% UVR 6110. All the coatings were cured at 10 fpm. The properties of the dry coatings are shown in *Figures* 3 and 4.

SGa and IGa have much better solubility in formulations than $SSbF_6$ and ISbF6. They still dissolve in the formulations even without the diluent DAA doing any damage to the coating properties. SSbF6 and ISbF6 only dissolve in formulations in the presence of diluent. Under similar conditions, coatings cured by SGa have better

Table 2—Formulations with Different Ratio of ESO to Cycloaliphatic Epoxide Resin UVR 6110

	ES0	ES1	ES2	ES3	ES4	**ES5**	ES6	ES7	ES8	ES9	ES10
ESO (g)	0	0.18	0.36	0.54	0.72	**0.90**	1.08	1.26	1.44	1.62	1.80
UVR(g)	1.8	1.62	1.44	1.26	1.08	**0.90**	0.72	0.54	0.36	0.18	0
Init[a] (g)	0.2	0.2	0.2	0.2	0.2	**0.2**	0.2	0.2	0.2	0.2	0.2
Silwet (g)	0.01	0.01	0.01	0.01	0.01	**0.01**	0.01	0.01	0.01	0.01	0.01

(a) Init is the 30% solution of SGa in DAA so the percentage of pure SGa in formulation is 3%.

Table 3—Formulations with Different Ratio of ESO to Cycloaliphatic Epoxide Resin UVR6110

	EI0	EI1	EI2	EI3	EI4	EI5	**EI6**	EI7	EI8	EI9	EI10
ESO (g)	0	0.18	0.36	0.54	0.72	0.90	**1.08**	1.26	1.44	1.62	1.80
UVR(g)	1.8	1.62	1.44	1.26	1.08	0.90	**0.72**	0.54	0.36	0.18	0
Init[a] (g)	0.2	0.2	0.2	0.2	0.2	0.2	**0.2**	0.2	0.2	0.2	0.2
Silwet (g)	0.01	0.01	0.01	0.01	0.01	0.01	**0.01**	0.01	0.01	0.01	0.01

(a) Init is the 35% solution of IGa in DAA so the percentage of pure IGa in formulation is 3.5%.

Table 4—Formulations Containing S with Fixed 1:1 Ratio of ESO to Cycloaliphatic Epoxide Resin UVR6110

	S11	S12	S13	**S14**	S15	S16
Initiator	3%SGa	2% SSbF_6 [a]	3% SGa	**3% SGa**	3% SGa	3% SGa
DAA	7%	8%	None	**7%**	7%	7%
Postbake	No	No	No	**@120°C for 10 min**	No	No
ITX	None	None	None	**None**	1%	None
Tone 0301	None	None	None	**None**	None	Replace 30% UVR6110

(a) SSbF_6 is the pure UVI6974 without propylene carbonate.

Table 5—Formulations with Fixed 40:60 Ratio of ESO to Cycloaliphatic Epoxide Resin UVR6110

	I11	I12	I13	**I14**	I15
Initiator	3.5%IGa	2% ISbF_6 [a]	3.5% IGa	**3.5% IGa**	3.5% IGa
DAA	6.5%	8%	None	**7%**	7%
Postbake	No	No	No	**@120°C for 10 min**	No
Tone 0301	None	None	None	**None**	Replace 30% UVR6110

(a) ISbF_6 is octoxyphenyl phenyl iodonium hexafluoroantimoniate.

hardness but poorer adhesion than those cured by SSbF6. In the case of the iodonium salt, little difference was detected. DAA was insignificant in the case of coatings cured by SGa. However, coating hardness increased when IGa was used as the initiator. This can be explained because iodonium salts are better oxidants than sulfonium salts. Thus, in the presence of iodonium salts, radical promoted cationic polymerization occurs. DAA not only functions as a diluent but also as a hydrogen donor. Adding ITX to the formulation does not change the coating properties, but the coatings are yellow with the color likely caused by the sensitizer. Polyol was used in the cationic UV-cured formulations as a chain transfer reagent. Its function is to increase the smoothness of coating surfaces by increasing the curing of the deeper layer. We found that although adding Tone 0301 yields excellent adhesion, it destroys the hardness of the coatings. Among these formulations, postbaking the cured panel gave the best results. Since postbaking can relieve internal stress produced during the polymerization and complete the polymerization via thermal processes, it can also increase the adhesion and hardness at the same time.

Dependence on Cure Speed

Different belt speeds were evaluated in order to find the highest curing speeds (*Figures* 5 and 6). All the coatings were postbaked at 120°C for 10 min. In the case of SGa, the curing speed can be as fast as 160 fpm. IGa is not as reactive as SGa because iodonium salts absorb more of the UV light at the curing surface than sulfonium salts, which slows down the curing of the molecules underneath. The highest curing speed obtained in the case of IGa is 54 fpm. It was also found that at the highest curing speeds, there was no difference in the coatings after postbaking. When the belt speed increased, the polymerization rate decreased, and the internal stress decreased. This is the same reason why we employed postbaking.

CONCLUSION

IGa and SGa have excellent solubility and reactivity in ESO. When these new photoinitiators are used, up to 50-60% ESO can be added to formulations without damaging the mechanical properties of the cured coatings. The resulting coatings are colorless due to the high purity of the initiators. Curing speed can be as fast as 160 fpm (144mJ/cm^2) with SGa. Either postbaking at 120°C for 10 min or curing at high speed can increase the adhesion and hardness of the coatings.

ACKNOWLEGMENT

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