

Ultraviolet-Curable Epoxidized Sunflower Oil/Organoclay Nanocomposite Coatings

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ABSTRACT: Hybrid nanocomposite coating films, prepared by the incorporation of epoxidized sunflower oil into organoclay, can be cured by ultraviolet radiation with either cationic or hybrid initiation. The organoclay used in this study was prepared by a cationic exchange process in which sodium ions were replaced by alkyl ammonium ions. The effects of types of photoinitiators on energy consumption in the curing process were studied. Formulations with a hybrid photoinitiator required less energy in the curing process than those with a cationic photoinitiator. Moreover, the physical properties of dried films were

examined as a function of the organoclay incorporation, and it was found that the hardness of the films increased as the amount of organoclay in the formulation increased. The X-ray diffraction patterns of an ultraviolet-curable organoclay-incorporated film showed an exfoliated structure of the organoclay in the ultraviolet-curable coating film. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 2164–2167, 2008

Key words: coatings; nanocomposites; organoclay; radiation

INTRODUCTION

Ultraviolet (UV)-radiation curing is one of the most effective processes for rapidly transforming a liquid coating film into a solid film. This well-proven technology offers a number of advantages making it suitable for the preparation of composite polymers.^{1,2} UV-radiation curing technology has become attractive especially in the paint, ink, and coating industries because of its very low consumption of energy and its minor emission of volatile organic compounds. Through the adjustment of the light intensity, ultrafast curing can be carried out at the desired rate at the ambient temperature.³

In recent years, there has been a growing trend of using vegetable oils as renewable resources, especially in oleochemical production. Several derivatives of vegetable oils are used as polymerizable monomers in radiation-curable systems because of their environmentally friendly character and low cost in comparison with products from petroleum. Moreover, the long fatty acid chains of vegetable oils impart desirable flexibility and toughness to some brittle resin systems such as epoxy, urethane, and polyester resins.^{4,5} Epoxidized vegetable oils, such as

epoxidized palm oil and epoxidized soybean oil, have been used in UV-curable coating systems.^{6,7} Vernonia oil, a natural oil containing epoxide groups, has been used as a polymerizable monomer in cationic UV-cured coatings.⁸

Nanocomposite polymers have attracted increased attention over the last decade because of their distinct characteristics, including superior mechanical and barrier properties and improved thermal stability and fire retardancy.^{9,10} Organoclay-based nanocomposites are often made of linear polymers such as polyolefins,^{11,12} polystyrene,^{13,14} and polyurethanes,¹⁵ which are completely soluble in organic solvents.

Because of an abundance of sunflower oil in Thailand, the objective of this work was to study the feasibility of using epoxidized sunflower oil (ESO) as a UV-curable monomer in coating formulations without additional diluents. Nanocomposite polymeric coating films of ESO with the incorporation of organoclay were prepared, and their energy consumption in the curing process was investigated.

EXPERIMENTAL

Sunflower oil was epoxidized with the method reported by French et al.¹⁶ The organoclay was modified montmorillonite (Mo-MMT) prepared by a cationic exchange process as follows. Octadecyl amine (1.08 g) was mixed with 1 mL of concentrated HCl and 15 mL of water and heated at 80°C for a

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TABLE I
Coating Formulations

Formulation	ESO (g)	TMPTA (g) ^a	Organoclay (g) ^b	Cationic photoinitiator (g) ^c	Radical photoinitiator (g) ^d	Photosensitizer (g) ^e	Wetting agent (g) ^f
F1	91.30	—	—	2.70	5.00	0.5	0.5
F2	90.80	—	0.50	2.70	5.00	0.5	0.5
F3	90.30	—	1.00	2.70	5.00	0.5	0.5
F4	89.80	—	1.50	2.70	5.00	0.5	0.5
F5	45.65	45.65	—	2.70	5.00	0.5	0.5
F6	45.40	45.40	0.50	2.70	5.00	0.5	0.5
F7	45.15	45.15	1.00	2.70	5.00	0.5	0.5
F8	44.90	44.90	1.50	2.70	5.00	0.5	0.5
F9	96.30	—	—	2.70	—	0.5	0.5
F10	95.80	—	0.50	2.70	—	0.5	0.5
F11	95.30	—	1.00	2.70	—	0.5	0.5
F12	94.80	—	1.50	2.70	—	0.5	0.5

^a Trimethylolpropane triacrylate from Cognis Thai, Ltd. (Bangkok, Thailand).

^b Mo-MMT with C18.

^c Irgacure 250 from Ciba Specialty Chemicals (Thailand), Ltd. (Bangkok, Thailand).

^d Darocure 1173 from Ciba Specialty Chemicals (Thailand), Ltd. (Bangkok, Thailand).

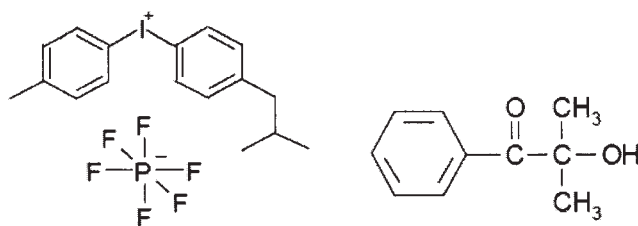
^e ITX from Ciba Specialty Chemicals (Thailand), Ltd. (Bangkok, Thailand).

^f Perenol F-40 from Cognis (Thailand), Ltd. (Bangkok, Thailand).

few minutes, and then it was mixed with 100 mL of a sodium montmorillonite dispersion (2.5 g of sodium montmorillonite dispersed in 100 mL of water at 80°C). The mixture was stirred vigorously for half an hour. The white precipitate thus formed was filtered and washed repeatedly to make it free of chloride ions. The precipitate was subsequently dried in air and then in an oven at about 50°C for 4 h. Mo-MMT was then ground into fine powder, and an octadecyl ammonium organophilic compound (i.e., organoclay) was obtained.¹⁷

Effects of photoinitiator types on the drying of UV-curable ESO nanocomposite films

Clear UV-curable coating formulations were prepared as shown in Table I. Organoclay (0.5–1.5 wt %) was incorporated into clear UV-curable coating formulations with a high-speed disperser at a speed of 700 rpm for 30 min. Trimethylolpropane triacrylate was used as an active diluent in this study. Irgacure 250 and Darocur 1173 were used as cationic and radical photoinitiators in this study, respec-



Irgacure 250

Darocur 1173

Figure 1 Chemical structures of the photoinitiators.

tively. The structures of both photoinitiators are shown in Figure 1.

The coating, with a film thickness of 60 μm, was coated onto tin plates and cured in a UV chamber. The energy of UV radiation used to obtain a completely dried film was recorded.

Physical property testing and characterization of UV-curable coating films

The physical properties of dried UV-cured coating films, including the hardness (ASTM D 2240)¹⁸ and impact strength (ASTM D 5628),¹⁹ were tested. The physical properties of dried films incorporated with organoclay were examined with respect to those without organoclay. The X-ray diffraction (XRD) intensities of dry films incorporated with organoclay were recorded with a Rigaku Rint 2000 DMAX diffractometer using monochromatic Cu Kα radiation.

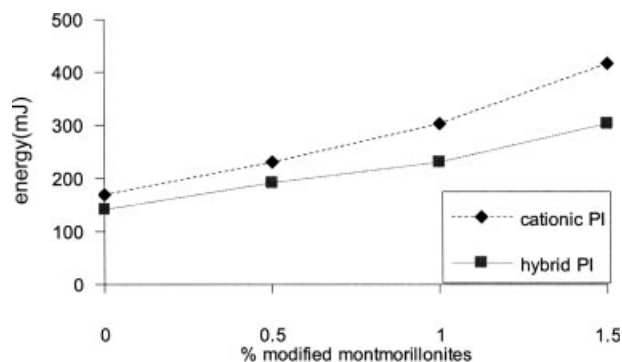


Figure 2 UV-radiation energy consumption of UV-curable ESO/organoclay formulations with different types of photoinitiators (PIs) as a function of the organoclay content.

TABLE II
Physical Property Testing Results for UV-Curable ESO/Organoclay Films with a Hybrid Photoinitiator

Physical property	F1 (ESO)	F2 (ESO/Mo-MMT 0.5%)	F3 (ESO/Mo-MMT 1%)	F4 (ESO/Mo-MMT 1.5%)
Impact strength:				
backward/forward (inch-lbs)	140/140	160/160	160/160	160/160
Hardness (g)	100	200	300	350
Flexibility (mm)	3	3	3	3
Adhesion (crosscut)	5B	5B	5B	5B
Gloss (at 60°)	80.5	78.2	77.5	76.4

RESULTS AND DISCUSSION

Coating formulations with different levels of organoclay, using a cationic photoinitiator, were coated onto tin plates and cured under UV radiation. The energy used to obtain dried coating films was monitored and compared with that of films made with a hybrid photoinitiator (a combination of radical and cationic photoinitiators). The results for the UV-radiation energy used in curing the coated films are shown in Figure 2.

The coating formulations using a hybrid photoinitiator showed lower UV-radiation energy consumption in the curing process than those using a cationic photoinitiator. This can be explained as follows. The radical photoinitiator in the hybrid system acted as a synergist, initiating the polymerization process of the UV-curable ESO system; that is, the radical photoinitiator initiated polymerization through the remaining unsaturated part of the fatty acid of ESO, whereas the cationic photoinitiator initiated through the epoxy group of ESO.

Physical properties of UV-curable coating films

The physical properties of coating films, such as the hardness, impact strength, flexibility, adhesion, and gloss, were tested according to the American Society for Testing and Materials. The results of physical property testing are shown in Tables II and III.

The physical testing results in Table II showed that the UV-curable coating formulations incorporated with organoclay and using a hybrid photoinitiator provided greater impact strength and hardness than those without organoclay. This can be explained as follows. The intercalation structure of

the organoclay was changed to an exfoliation structure by the diffusion of ESO molecules into the interlayer spacing of the intercalation structure of the organoclay. The change in the organoclay structure enhanced the hardness and impact strength of the cured films. The structural changes of the organoclay were characterized with XRD, as shown in Figure 3.

The physical testing results showed that the UV-curable coating formulations incorporated with organoclay and using a hybrid photoinitiator provided greater impact strength and hardness than those without organoclay. This can be explained as follows. The intercalation structure of the organoclay was changed to an exfoliation structure by the diffusion of ESO molecules into the interlayer spacing of the intercalation structure of the organoclay. The change of the organoclay structure enhanced the hardness and impact strength of the cured films.

Organoclay structure changes of UV-curable coating films

Dried UV-curable films with organoclay incorporation were investigated with XRD measurements to obtain the characteristics of the organoclay dispersed in dried films. The results of XRD profiles of the organically modified clay (organoclay) and UV-curable films with the incorporation of the organoclay are shown in Figure 3.

The XRD profile of the organoclay showed a 2 θ peak at 2.37° and gave a *d*-spacing value of 37.25 Å. This mean organoclay had intercalated characteristics related to the unmodified clay, which normally gave a *d*-spacing of 14.89 Å. The XRD profile of the organoclay incorporated with ESO as a polymerized monomer did not show the 2 θ peak at 2.37° that was

TABLE III
Physical Property Testing Results for UV-Curable ESO/Organoclay Films with a Cationic Photoinitiator

Physical property	F9 (ESO)	F10 (ESO/Mo-MMT 0.5%)	F11 (ESO/Mo-MMT 1%)	F12 (ESO/Mo-MMT 1.5%)
Impact strength:				
backward/forward (inch-lbs)	140/140	160/160	160/160	160/160
Hardness (g)	100	200	300	350
Flexibility (mm)	3	3	3	3
Adhesion (crosscut)	5B	5B	5B	5B
Gloss (at 60°)	81.2	79.5	77.8	74.1

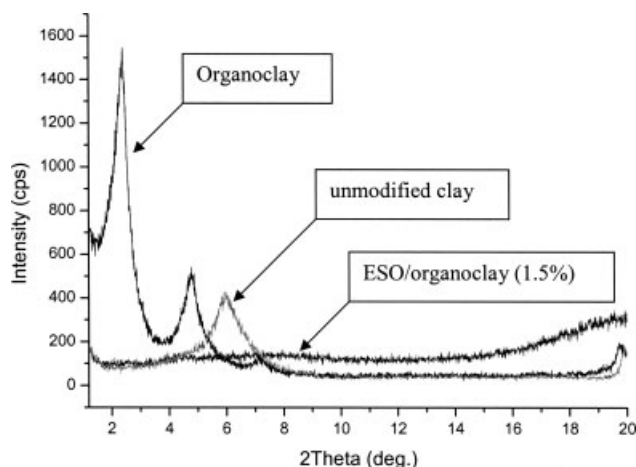


Figure 3 XRD profiles of UV-curable ESO films with and without the incorporation of the organoclay.

found in the XRD profile of the organoclay. This can be explained as follows. ESO, a polymerized monomer in the UV-curable ESO/organoclay coating formulation, entered between galleries of intercalated platelets of the organoclay and forced them apart so that they no longer interacted with one another. This condition was modeled as exfoliation. As a result, the UV-curable ESO/organoclay coating had the exfoliation structure of the filler, and the coating film could be considered a nanocomposite film.

CONCLUSIONS

ESO can be cured by UV radiation with either cationic or hybrid initiation. However, UV-curable ESO/organoclay systems using hybrid photoinitiators showed lower UV-radiation energy consumption in the curing process than those using a cationic photoinitiator. The higher levels of organoclay incorporated into the formulations led to a slight increase in UV-radiation energy consumption in the curing process with both cationic and hybrid photoinitiator systems. In addition, the formulations using a hybrid photoinitiator without diluents could be cured with less radiation energy than those with a

diluent. The higher organoclay contents in the formulations did not cause significant changes in energy consumption in the systems with and without diluents. The X-ray diffraction pattern of a UV-curable ESO/organoclay film showed an exfoliated structure of the organoclay in the UV-curable coating film.

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