

# UV RADIATION ENERGY CONSUMPTION IN CURING PROCESS OF EPOXIDIZED SUNFLOWER OIL- NANOCOMPOSITE COATINGS

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## ABSTRACT

Epoxidized sunflower oil (ESO) can be cured with ultraviolet radiation using either cationic or hybrid initiation. The organoclay was prepared by cationic exchange process, in which sodium ions were replaced by alkyl ammonium ions. Organoclay was incorporated into epoxidized sunflower oil UV-curable systems. The effects of diluents and types of photo initiators were studied. It was found that the formulations with hybrid photoinitiator required energy in curing process less than those with cationic photoinitiator. Moreover, the formulations without diluent can be cured with lower radiation energy than those with diluent. The X-ray diffraction patterns of organoclay-incorporated UV-curable film showed exfoliated structure of organoclay in the UV-curable coating film.

## 1. INTRODUCTION

Nanocomposite polymers have increased attention over the last decade because of their distinct characteristics, in particular superior mechanical and barrier properties, as well as improved thermal stability and fire retardancy (1,2). Organoclay-based nanocomposites are often made of linear polymers such as polyolefins (3,4), polystyrene (5,6), polyurethanes (7), which are completely soluble in the organic solvents.

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 preparation of composite polymers (8,9). This UV-radiation curing technology has become attractive especially in paint, ink, and coating industries due to its very low consumption of energy and its minor emission of volatile organic compounds. By adjustment of the light intensity, ultrafast curing can be carried out at the desired rate at ambient temperature (10).

**KEYWORDS :** Epoxidized sunflower oil, UV curable coatings, nanocomposite coatings

In recent years, there has been a growing trend in using vegetable oils as renewable resources especially in oleochemical productions. Several derivatives of vegetable oils are used as polymerizable monomers in radiation curable system due to their environmental friendly character and low cost when compared to 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 (11,12). Epoxidized vegetable oils, for examples epoxidized palm oil and epoxidized soybean oil were utilized in UV-curable coating systems (13,14). Vernonia oil, natural oil containing epoxide groups, was utilized as a polymerizable monomer in cationic UV-cured coatings (15). Due to abundance of sunflower oil in Thailand, the objective of this work is to study feasibility of using epoxidized sunflower oil as a UV-curable monomer in coating formulations without additional diluents. The nanocomposite polymeric coating films of epoxidized sunflower oil with incorporation of organoclay were prepared and their energy consumption in curing process were investigated.

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## 2. EXPERIMENTAL

Sunflower oil was epoxidized using the method reported by French et.al. (16) Organoclay was modified montmorillonite prepared by cationic exchange process as described previously (17).

### *Effect of diluent and photoinitiator types in drying of ESO-UV curable nanocomposite films*

Organoclay was incorporated into clear UV-curable coating formulations using epoxidized sunflower oil as a monomer. Epoxidized sunflower oil / Organoclay nanocomposites with different contents of the organically modified clays (0.5-1.5% by weight) were prepared by mixing with a high speed disperser at a speed of 700 rpm for 30 min. The coatings with film thickness of 60 microns was coated on tin plates and cured in UV chamber. The energy of UV radiation used to obtain a completely dried film was recorded. Coating formulations used in this study are shown in Table 1.

Table1. Coating formulations used in study.

Formulations	ESO <sup>1</sup> (g)	TMPTA <sup>2</sup> (g)	Organoclay <sup>3</sup> (g)	Cationic PI <sup>4</sup> (g)	Radical PI <sup>5</sup> (g)	Photosensitizer <sup>6</sup> (g)	Wetting agent <sup>7</sup> (g)
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

1= Epoxidized sunflower oil, 2 = Trimethylolpropane triacrylate, Cognis Thai Ltd., 3 = Modified montmorillonite with C18, 4 = Irgacure 250, Ciba Specialty Chemicals (Thailand) Limited, 5 = Darocure 1173, Ciba Specialty Chemicals (Thailand) Limited, 6 = ITX, Ciba Specialty Chemicals (Thailand) Limited, 7 = Perenol F-40, Cognis Thai Ltd.

## 3. RESULTS AND DISCUSSION

Coating formulations with different levels of organoclay, using cationic photoinitiator, was coated on tin plates and cured under UV-radiation. The energy used to obtain dried coating films was monitored and compared with the formulation using hybrid photoinitiator (combination of radical and cationic photoinitiators). The results of UV-radiation energy used in curing the coated films are shown in Figure1.

The coating formulations using hybrid photoinitiator showed lower UV-radiation energy consumption in curing process than those using cationic photoinitiator. This can be explained that radical photoinitiator in the hybrid system acted as synergist to help initiating the polymerization process of ESO UV-curable system. In addition, the more organoclay content incorporated in the formulation, the higher the UV-radiation consumption in curing process.

Diluent is one of the basic compositions used in UV-curable formulations. Most diluents used in UV-curable formulations are active diluents. Active diluents are used not only to adjust the viscosity of the formulations for applications but also to take part in UV-curing process. Trimethylol propane triacrylate (TMPTA) was used as an active diluent in this study. Hybrid photoinitiator was utilized in all coating formulations. ESO/organoclay UV-curable coating formulations were prepared with and without addition of diluent (F1-F4 versus F5-F8) as shown in Table1. Coating formulations were coated on tin plates and cured under UV-radiation. The results of UV-radiation energy consumption to obtain dried coating films were monitored and shown in Figure 2.

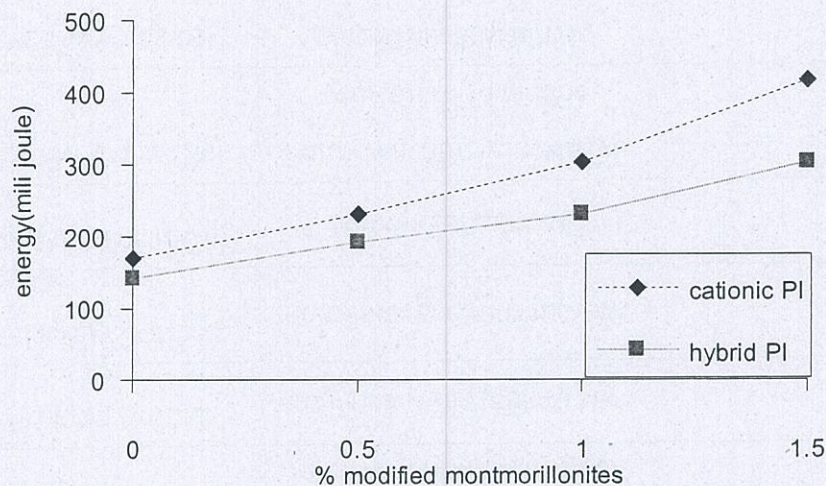


Figure1. UV-radiation energy consumption of ESO/organoclay curable formulations with different types of photoinitiators as a function of organoclay contents

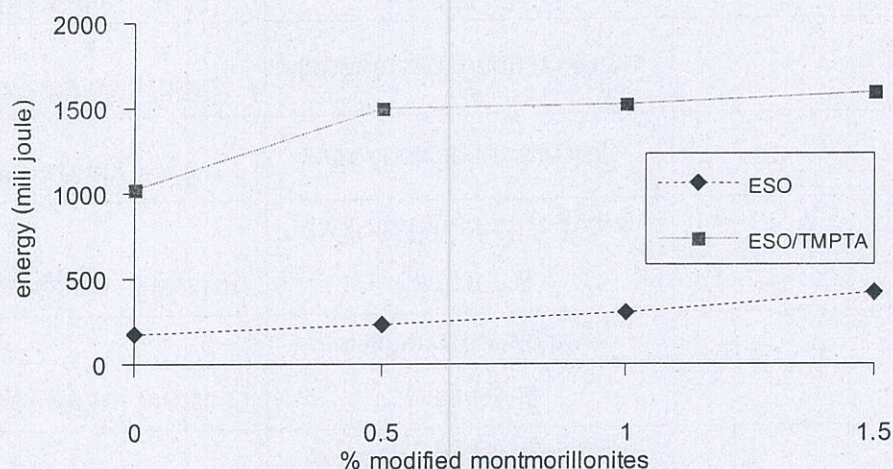


Figure2. UV-radiation energy consumption of ESO/organoclay curable formulations with and without active diluent as a function of organoclay contents

The results showed that incorporation of active diluent into ESO/organoclay curing system rendered significantly higher UV-radiation energy consumption in curing process. The UV-radiation energy used to obtain dried films dramatically increased as organoclay was incorporated. The higher the levels of organoclay in the formulations imparted slightly higher level of UV-radiation energy consumption in curing process.

Coating formulations without active diluent utilized lower UV-radiation energy to obtain dried films. The incorporation of organoclay did not impart significant increase in higher energy consumption as shown in formulations with active diluent. Moreover, the higher levels of organoclay in the formulation provided slight increase in UV-radiation consumption.

Dried UV-curable film with organoclay incorporation was investigated using X-ray diffraction measurement to obtain the characteristic of organoclay dispersed in dried film. The results of XRD profiles of organically modified clay (organoclay) and UV-curable film with incorporation of organoclay are shown in Figure 3.

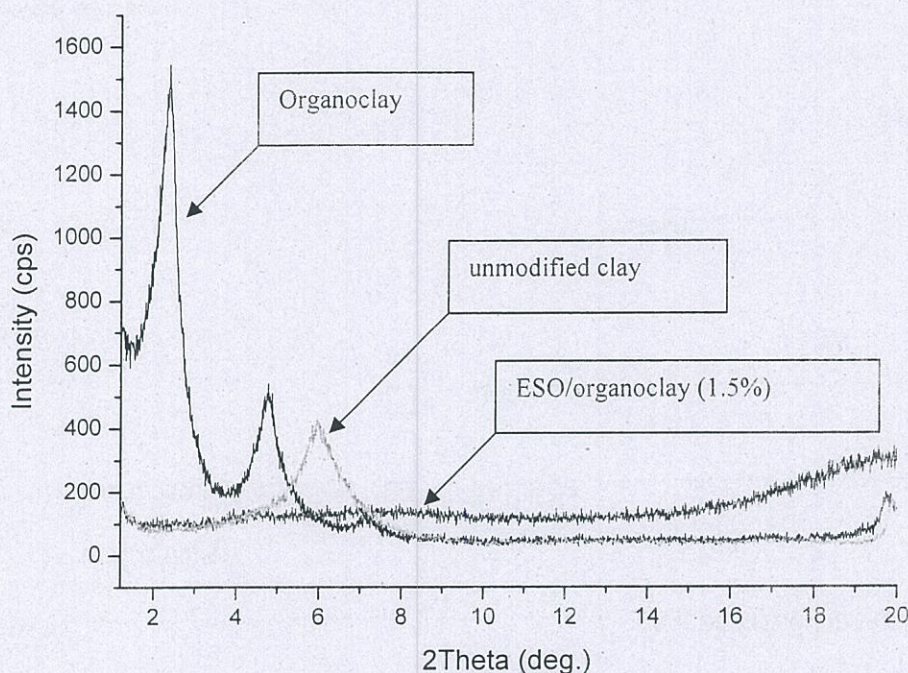


Figure 3. XRD profiles of epoxidized sunflower oil UV curable films with and without incorporation of organoclay.

The XRD profile of organoclay showed the  $2\theta$  peak at  $2.37^\circ$  and gave d-spacing value of  $37.25 \text{ \AA}$ . This mean organoclay has intercalated characteristic relate to unmodified clay that normally give d-spacing of  $14.89 \text{ \AA}$ . The XRD profile of organoclay incorporated with ESO as polymerized monomer did not show the  $2\theta$  peak at  $2.37^\circ$  which was found in XRD profile of organoclay. This can be explained that ESO, a polymerized monomer in ESO-organoclay UV-curable coating formulation, entered between galleries of intercalated platelets of organoclay and forced them apart so they no longer interact with each other. This condition is modeled as exfoliated character. As a result, ESO-organoclay UV curable coating has exfoliation structure of filler which the coating film can be considered as a nanocomposite film.

#### 4. CONCLUSIONS

Epoxidized sunflower oil (ESO) can be cured with ultraviolet radiation using either cationic or hybrid initiation. However, ESO-Organoclay UV-curable systems using hybrid photoinitiators showed lower UV-radiation energy consumption in curing process than those using cationic photoinitiator. The higher levels of organoclay incorporated in the formulations showed slight increase in UV-radiation energy consumption in curing process in both cationic and hybrid photoinitiator systems. In addition, it was found that the formulations using hybrid photoinitiator without diluents can be cured with lower radiation energy than those with diluent. The higher organoclay contents in the formulations did not cause significant change in energy consumption in both with and without diluent systems. The X-ray diffraction pattern of ESO-organoclay UV-curable film showed exfoliated structure of organoclay in the UV-curable coating film.

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