

UV Radiation Energy Consumption in Curing Process of Epoxidized Sunflower Oil-Organoclay Hybrid Coatings

Nantana JIRATUMNUKUL^{1*} and Ravivan INTARAT¹

¹Department of Materials Science, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand

Received Aug. 25, 2006

Accepted Oct. 12, 2006

Abstract

Epoxidized sunflower oil (ESO) can be cured with ultraviolet radiation using either cationic or hybrid initiation. The organoclay was prepared by the 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 a hybrid photoinitiator required less energy in the curing process than those with a cationic photoinitiator. Moreover, the formulations without diluent can be cured with lower radiation energy than those with diluent.

Key words : Epoxidized sunflower oil, UV curable coatings

Introduction

Nanocomposite polymers have gained 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 the preparation of composite polymers.^(8,9) This UV-radiation curing technology has become attractive especially in the 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⁾

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 a radiation curable

system due to their environmentally 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 example 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 the abundance of sunflower oil in Thailand, the objective of this work is to study the 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 the incorporation of organoclay were prepared and their energy consumption in the curing process were investigated.

Experimental

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

*Corresponding author. Tel: +66-2218-5551 Fax: +66-2218-5561 e-mail:jnantana@sc.chula.ac.th

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 a film thickness of 60 microns was coated on tin plates and cured in a 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 ¹ (g)	TMPTA ² (g)	Organoclay ³ (g)	Cationic PI ⁴ (g)	Radical PI ⁵ (g)	Photosen- sitizer ⁶ (g)	Wettig agent ⁷ (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.

Results and Discussion

Coating formulations with different levels of organoclay, using a 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 a hybrid photoinitiator (combination of radical and cationic photoinitiators). The results of UV-radiation energy used in curing the coated films are shown in Figure 1.

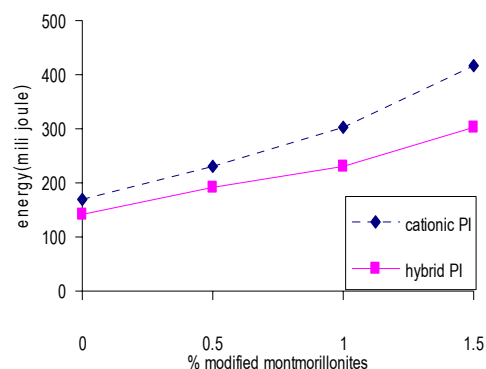


Figure1. UV-radiation energy consumption of ESO/ Organoclay curable formulations with different types of photoinitiators as a function of organoclay contents

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 due to that a radical photoinitiator in the hybrid system acted as a synergist to help the initiation of the polymerization process of the ESO UV-curable system. In that a radical photoinitiator will initiate polymerization through the remaining unsaturated part of the fatty acid in the ESO, while the cationic photoinitiator will initiate through the epoxy group of the ESO. In addition, the more organoclay content incorporated in the formulation, the higher the UV-radiation consumption in the curing process. This can be explained that the more organoclay was incorporated, the greater the possibility of the UV radiation being obstructed to provide complete polymerization. Therefore, there was a greater radiation energy required when a higher content of organoclay was incorporated.

*UV Radiation Energy Consumption in Curing Process of Epoxidized Sunflower
Oil-Organoclay Hybrid Coatings*

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 the UV-curing process. Trimethylol propane triacrylate (TMPTA) was used as an active diluent in this study. A hybrid photoinitiator was utilized in all coating formulations. ESO/organoclay UV-curable coating formulations were prepared with and without the addition of diluent (F1-F4 versus F5-F8) as shown in Table 1. 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.

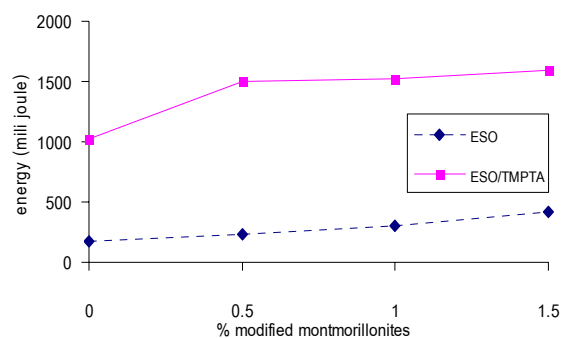


Figure 2. UV-radiation energy consumption of ESO/organoclay curable formulations with and without active diluent as a function of organoclay contents

The results showed that the incorporation of active diluent into the ESO/organoclay curing system rendered significantly higher UV-radiation energy consumption in the 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 a slightly higher level of UV-radiation energy consumption in the curing process.

Coating formulations without active diluent utilized lower UV-radiation energy to obtain dried films. This can be explained that the hybrid photoinitiator, used in the coating formulation with ESO, will help polymerization through epoxy groups as well as the remaining unsaturated part of fatty acid in ESO. The Addition of TMPTA increased the total amount of

unsaturated parts in the coating formulation while the performance of hybrid photoinitiator was the same. Therefore, the rate of curing of coating incorporated with TMPTA was lower or it required higher energy to achieve the same drying quality as coating without TMPTA. The incorporation of organoclay did not impart a significant increase in higher energy consumption as shown in formulations with active diluent. Moreover, the higher levels of organoclay in the formulation provided a slight increase in UV-radiation consumption.

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 the curing process than those using a cationic photoinitiator. The higher levels of organoclay incorporated in the formulations showed a slight increase in UV-radiation energy consumption in the curing process in both cationic and a 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 a significant change in energy consumption in both with and without diluent systems.

Acknowledgements

The authors wish to thank Cognis Thai Ltd., Ciba Specialty Chemicals (Thailand) Limited and Siam Nippon Co., Ltd. for contribution of diluent, photoinitiators and bentonite clay, respectively. In addition, we wish to thank the Department of Materials Science, Faculty of Science, Chulalongkorn University for financial and instrument supports for this study.

References

- Alexandre, M. and Dubois, P. 2000. Polymer-layered Silicate Nanocomposites : Preparation, Properties and uses of a new class of material. *Mater. Sci. Eng.* **28** : 1-6.

2. Vaia, R. A. and Giannelis, E.P.1997. Lattice model of Polymer melt intercalation in organically-modified layered silicates. *Macromolecules*. **30** : 7990.
3. Zhang, Q., Fu, Q., Jaing, L. and Lei, Y. 2000. Preparation and properties of polypropylene/montmorillonite layered nanocomposites. *Polym. Int.* **49** : 1561.
4. Kato, M., Usuki, A., and Okada, A. 1997. Synthesis of polypropylene oligomer-clay intercalation compounds. *J. Appl. Polym. Sci.* **66** : 1781.
5. Akelah, A. and Moet, A.1996. *J. Mater Sci.* **31** : 1064.
6. Doh, J. G. and Cho, I. 1998. Synthesis and properties of polystyrene-organoammoniummontmorillonite hybrid. *Polym. Bull.* **41** : 511.
7. Wang, Z. and Pinnavaia, T.J. 1998. Nanolayer reinforcement of elastomeric polyurethane. *Chem. Mater.* **10** : 3769.
8. Decker, C. 1996. Photoinitiated crosslinking polymerisation . *Prog. Polym. Sci.* **21** : 593.
9. Decker, C. 2002. Kinetic Study and New applications of UV radiation curing. *Macromol. Rapid. Commun.* **23** : 1067.
10. Technical Information, 2004. *UV curing, Technical principle and mechanism.* Ciba Specialty Chemicals
11. Crivello, V.J. and Ghoshai, R. 1994. UV-curable coating. *US Patent 5318808*, June.
12. Treybig, D. S., Wang, D. S. Sheih, P. S. and Ho, L. A. 1992. Advanced epoxy compositions, curable compositions and cured products. *US Patent 5151485*, Sept.
13. Wan Rosli, W.D., Kumar, R.N., Mek Zah, S. and Hilmi Mohd, M. 2003. UV radiation curing of epoxidized palm oil-cycloaliphatic diepoxide system induced by cationic photoinitiators for surface coatings. *Eur. Polym. J.* **39** : 593-600.
14. Raghavachar, R., Sarnecki, G., Baghdachi, J. and Massingill, J. 2000. Cationic, thermally cured coatings using epoxidized soybean oil. *J. Coat. Tech.* **72** : 125.
15. Thames, S.F. and Yu, H.1999. Cationic UV-cured coatings of epoxide-containing vegetable oils. *Surf. Coat. Tech.* **115** : 208.
16. Jourdan-Laforte, Eric 1980. *US Patent 4215058*, Dec.
17. Jiratumnukul, N., Pruthipaitoon, S. and Pitsaroup, T. 2006. Nanocomposite alkyd coatings. *J. Appl. Polym. Sci.* **102** : 2639.

*UV Radiation Energy Consumption in Curing Process of Epoxidized Sunflower
Oil-Organoclay Hybrid Coatings*