

Thermal Behavior of Nanoclay Reinforced Ultraviolet Curable Epoxy Acrylate

B. Shirkavand Hadavand*, F. Najafi†

Department of Resin and Additives, Institute for Color Science and Technology, Tehran, Iran

(Received 10 June 2013; published online 02 September 2013)

This study related to preparation of UV curable epoxy nanoclay nanocomposite and investigation on mechanical and thermal properties of their thin films. For achieving this UV-curable epoxy dimethacrylate was synthesized by epoxy resin (EPIKOTE 828), methacrylic acid, triphenylphosphine (PPh₃) as catalyst and para-methoxy phenol (PMP) as inhibitor at 80 °C for 2 hours (yield 99%). Formulation of UV curable resin was achieved by 5% w/w benzophenone and N, N dimethylaminoethyl methacrylate. The resin was reinforced by using 1-5% w/w modified nanoclay in total formulation. Synthesized resin was characterized by FTIR spectroscopy and thermal behaviors of nanocomposites were evaluated by TGA and DSC analysis.

Keywords: Nanoclay, Epoxy acrylate, Thermal behavior, UV cure.

PACS number: 82.35.Np

1. INTRODUCTION

UV-curable coating applications have gained wide interests, due to their advantages such as lower energy consumption, less environmental pollution, lower process costs, high chemical stability and very rapid curing even at ambient temperatures [1–3]. UV-curable coatings are continually being developed by many leading suppliers in an effort to reduce any detrimental effects to the environment and to meet high standards required by industry [4].

The bisphenol-A type epoxy diacrylates are a class of the most important and extensively used acrylate resins in UV-curing systems due to their high reactivity, low price and superior properties after UV-cured, for instance, high stiffness and strength, excellent solvent resistance, and so on [5]. Epoxy acrylate resin is popular due to its rapid cure, solvent-free characteristics, application versatility, low energy requirements, and low temperature operation [6–8]. However, it is so combustible that its application is narrowed. A number of methods have been used to improve the thermal properties of epoxy acrylate [9–12].

Nanotechnology provides improvements in the properties of epoxy adhesives. The enhanced mechanical and thermal properties of nanoclay/polymer nanocomposites with a relatively light weight compared with conventional polymer-based composites have attracted the focus of researchers in the last decade. Small amount of nanoclays, typically in the range of 3–5 wt % [13, 14] is enough for the enormous improvements in the mechanical and thermal properties of the nanocomposites. Investigations on the product developments of the nanoclay polymer nanocomposites have began explosively in major manufacturing industries in the world [15–17].

In this study, UV curable film with various percentage of nano clay were prepared and polymerized by UV irradiation. Their curing behaviors were characterized using DSC and FTIR spectroscopy.

2. EXPERIMENTAL

2.1 Materials

Epoxy resin (Epikote 828) procured from Momentive Company and methacrylic acid, triphenylphosphine (PPh₃), para-methoxy phenol (PMP), benzophenone and Triethanolamine procured from Merck Company. trimethylol propane triacrylate (TMPTA) procured from Aldrich Company. Nanoclay procured from Southern Clay Products, Inc. The properties of nanoclay are shown in Table 1. All chemicals were used without any purification.

Table 1 – Nanoclay properties.

Treatment	Organic modifier*	Modifier concentration	Moisture (%)
Cloisite® 15A	2M2HT	125 meq/100g clay	< 2%

* Where HT is Hydrogenated Tallow (~65% C18; ~30% C16; ~5% C14)

2.2 Synthesis of epoxy acrylate oligomer

The polymerization was performed in a round-bottom flask equipped with a mechanical stirrer, a thermometer, and a reflux condenser under nitrogen atmosphere. The epoxy acrylate oligomer was synthesized by the reaction of epoxy resin (1 mol) and methacrylic acid (2 mol), 1% by weight triphenylphosphine (PPh₃) as catalyst and 0.2% by weight para-methoxy phenol (PMP) as inhibitor. The reaction was performed at 80°C under a dry nitrogen atmosphere for 2 h (Fig. 1).

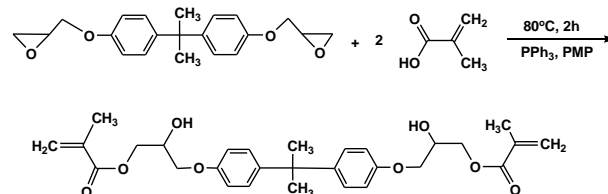


Fig. 1 – Preparation of UV curable epoxy-acrylate resin.

* shirkavand@icrc.ac.ir

† najafi@icrc.ac.ir

2.3 Preparation of UV-curable coating

Formulations of UV-curable coating consisting of oligomer, monomer, photoinitiator and nanoclay were prepared (Table 2). In each formulation the chemicals were mixed in a round-bottom tube equipped with a homogenizer, a thermometer, and a condenser under nitrogen atmosphere at room temperature for 1.5 h. For further characterization of the coatings, the UV-cured films, with the thickness of about 90 μ , were prepared by coating the formulated mixtures on a metal and glass sheet and irradiating under ultraviolet light source.

2.4 Characterization

FT-IR spectra were recorded on FT-IR spectrometer, Perkin Elmer Spectra 1, in the region of 450-4000- cm^{-1} . Differential scanning calorimetry (DSC), Perkin

Elmer Pyris Diamond 7, were performed under nitrogen atmosphere at a heating rate of 10 $^{\circ}\text{C}/\text{min}$ from room temperature to 400 $^{\circ}\text{C}$. Thermal gravimetric analysis was carried out at a heating rate of 10 $^{\circ}\text{C}/\text{min}$ from 30 to 450 $^{\circ}\text{C}$ under nitrogen atmosphere..

Table 2 - Formulation used to prepare UV-cured coating.

Component	Blank	parts by weight		
		1% w/w	3% w/w	5% w/w
Oligomer (Epoxy acrylate)	70	70	70	70
Monomer (TMPTA)	20	20	20	20
Photoinitiator (Benzophenone)	5	5	5	5
Co-initiator (Triethanolamine)	5	5	5	5
Additive (Nanoclay)	0	1	3	5

3. RESULTS AND DISCUSSION

The epoxy acrylate oligomer obtained was characterized by FT-IR. Figure 2 shows the FT-IR spectrum of the epoxy acrylate oligomer. The absorption bands at 1727 and 828 cm^{-1} relate to $\text{C}=\text{O}$ stretching and $\text{C}=\text{C}$ twisting of acrylate indicate the structure of synthesized oligomer.

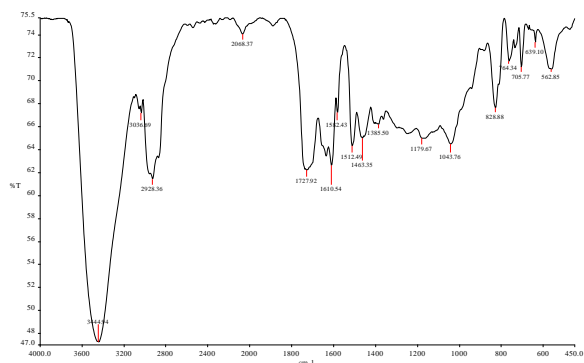


Fig. 2 – FT-IR spectra of synthesized epoxy acrylate oligomer.

In Figure 3 the curing of epoxy acrylate oligomer was shown in different curing times (7-400 seconds). As shown in this Figure the $\text{C}=\text{C}$ stretching vibration of methacrylate in 1635 cm^{-1} and CH_2 asymmetric bending of methacrylate in 1420 cm^{-1} are disappearing that means the UV curing process are done.

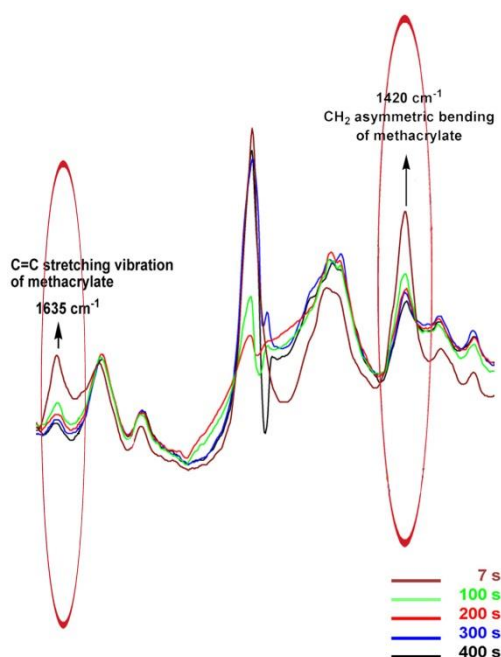


Fig. 3 – FT-IR spectra of curing epoxy acrylate oligomer in 7-400 seconds.

3.1 Thermal properties

The change in the heat capacity and the glass transition temperatures (T_g) were measured using the DSC technique for epoxy acrylate with and without nanoclay addition. In Figure 4 representative DSC curves of pure epoxy acrylate and 1 and 3 wt% filled nanoclay after the crosslinking process are represented.

The thermal stability of the crosslinked polymer plays an important role and is greatly influenced by the structure, chemical composition, kind and concentration of remaining polar groups, molecular chain rigidity and other chemical structural factors [18, 19]. The first stage of decomposition located between 100 and 200 $^{\circ}\text{C}$, was due to the trapped volatile materials were released.

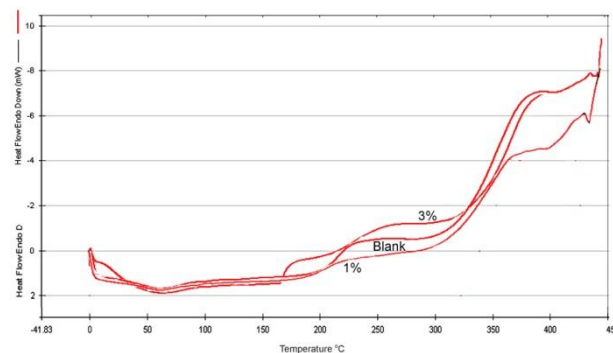


Fig. 4 – DSC thermogram of UV cured coating based on epoxy acrylate and nanoclay.

The main decomposition of the crosslinked polymer takes place in the second stage of degradation, at about the temperature 320 $^{\circ}\text{C}$. The third stage of de-

composition was due to the decomposition of aromatic structure at the temperatures higher than 470 °C. The temperatures above 450°C indicated the complete decrosslinking and thermal degradation of the cured films (Figure 5).

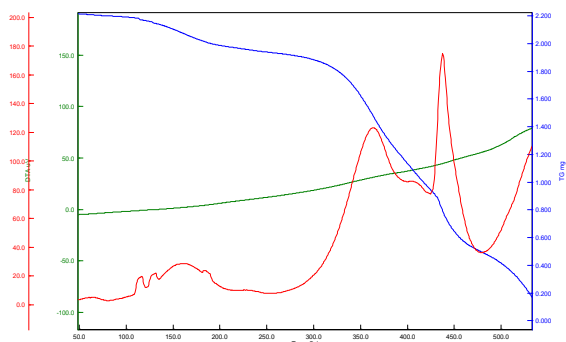


Fig. 5 – TGA and DTG thermogram of UV cured coating based on epoxy acrylate and nanoclay.

3.2 Morphology

In Figure 6, SEM image of fractured samples 2 w/w% nanoclay dispersing by homogenizer and cured by ultraviolet irradiation is shown. It is obvious that nanoclay were dispersed in a good form.

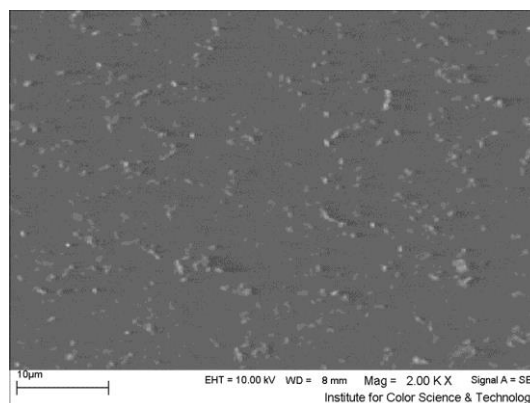


Fig. 6 – dispersion status of 2% wt. nano clay in polymeric matrix.

4. CONCLUSIONS

The epoxy acrylate oligomer was synthesized successfully and FTIR spectra indicated the structure of the resin. Then, the nanocomposite were prepared with epoxy acrylate resin and different percentage of nanoclay and dispersed by homogenizer. The SEM image indicates acceptable dispersion of nanoclay in polymeric matrix. The thermal stability of the epoxy acrylate resin increases with the higher content of nanoclay. This type of UV cured coatings may be recommended for their applications where thermal stability is the main concern.

REFERENCES

1. T. Y. Inan, E. Ekinici, A. Kuyulu, A. Gungor, *Polym. Bull.*, **47**, 437 (2002).
2. S. P. Pappas, *UV Curing: Science and Technology*, (Technology Marketing Corporation, Stanford, USA, 1978).
3. N. A. Kayaman, R. Demirci, M. C. akır, A. Gungor, *Radiat. Phys. Chem.*, **73**, 254 (2000).
4. *UV-Curable Coatings—Generic Testing and Quality Assurance Protocol*, Prepared by National Defense Center for Environmental Excellence (NDCEE), (Operated by Concurrent Technologies Corporation March 24, 1998).
5. J. B. Donnet, *Compos. Sci. Tech.*, **63**, 1085 (2003).
6. J. H. Lee, R. K. Prud Homme, I. A. Aksay, *J. Mater. Res.*, **16**, 3536 (2001).
7. A. Fieberg, O. Reis, *Prog. Org. Coat.*, 2002, **45**, 239.
8. F. M. Uhl, S. P. Davuluri, S. C. Wong, D. C. Webster, *Polymer*, **45**, 6175 (2004).
9. S. Y. Lu, I. Hamerton, *Prog. Polym. Sci.*, **27**, 1661 (2002).
10. H. B. Chen, Y. Zhang, L. Chen, Z. B. Shao, Y. Liu, Y. Z. Wang, *Indust. Eng. Chem. Res.*, **49**, 7052 (2010).
11. X. L. Chen, Y. Hu, C. M. Jiao, L. Song, *Polym. Degrad. Stabil.*, **92**, 1141 (2007).
12. X. L. Chen, Y. Hu, L. Song, W. Y. Xing, *Polym. Adv. Tech.*, **19**, 393 (2008).
13. Y. Ke, C. Long, Z. Qi, *J. Appl. Polym. Sci.*, **71**, 1139 (1999).
14. M. Song, D. J. Hourston, K. J. Yao, J. K. H. Tay, M. A. Ansarifar, *J. Appl. Polym. Sci.*, **90**, 3239 (2003).
15. C. Chen, D. Curliss, *Nanotechnology*, **14**, 643 (2003).
16. E. Sancaktar, J. Kuznicki, *Inte. J. Adhesion and Adhesives*, **31**, 286 (2011).
17. A. Jumahat, C. Soutis, J. Mahmud, N. Ahmad, *Procedia Engineering*, **41**, 1607 (2012).
18. D. K. Chattopadhyay, D. B. Rohini Kumar, B. Sreedhar, K.V.S.N. Raju, *J. Appl. Polym. Sci.*, **91**, 27 (2004).
19. D. Rosu, C. N. Cascavaf, C. Ciobanu, L. Rosu, *J. Anal. Appl. Pyrolysis*, **72**, 191 (2004).