Studies on the Influence of Monomers on the Performance Properties of Epoxy Acrylate Resin

AMRITA SHARMA*, DEVENDRA AGARWAL and JAGABIR SINGH[#]

Department of Oil & Paint Technology,
Harcourt Butler Technological Institute, Kanpur 208002, UP, India

[#]Jubilant Organosys Ltd. Plot 1A, Sector 16, Noida – 201301

sharma_amrita@rediffmail.com; Fax No. +915122501541

Received 3 December 2007; Accepted 1 January 2008

Abstract: Twelve blend samples were prepared by physical mixing of epoxy acrylate resins with various monomers *viz.* ethoxylated phenol monoacrylate (EOPA), tripropylene glycol diacrylate (TPGDA) and trimethylol propane tri acrylate(TMPTA), having weight ratio of epoxy acrylate resin and monomers are 50:50, 60:40, 70:30, 80:20. These samples were cured under UV radiation using 5% photo initiator by weight. These blends were evaluated for mechanical, chemical & thermal properties. It was found that the sample having mono & tri functional monomers shows better properties than the samples having di functional monomer.

Keywords: Epoxy acrylate, UV radiation, Monomers, Performance properties, Chemical resistance.

Introduction

Photo-initiated curing reactions are powerful processes to quickly create highly cross-linked polymer networks by supplying an appropriate form of energy, generally ultraviolet (UV) light, to a thermosetting material like epoxy, unsaturated polyester, acrylic resins *etc.*, containing photo initiating species¹⁻⁵

In recent years, epoxy acrylate prepolymer suitable for use in ultraviolet (UV) curing systems, command the largest use in the market and are typically used in applications ranging from paper and card over-print varnishes, wood coatings, screen and lithographic inks and solder resist inks for printed circuit boards⁶⁻⁹. Other areas such as vacuum metallizing base coatings, adhesive laminates, release coatings and video disc coatings are also becoming more important¹⁰. Epoxy acrylates are noted for adhesive properties, flexibility, non-yellowing, hardness, and chemical resistance¹¹⁻¹³. The epoxy backbone promotes tough-ness and flexibility to cured films whilst the carbon-carbon and ether bonds of the same improve the chemical resistance. The epoxy acrylate resins have the merits of: (a) high reactivity (b) possibility of structural variation in backbone (*e.g.* bisphenol A or epoxy novolacs)¹⁴⁻¹⁶ which provides good coating properties after curing and (c) excellent adhesion performance (due to

the presence of pendant hydroxyl groups). However, the UV cured films based on epoxy diacrylate as oligomer are very brittle and the relative elongation at break is very low¹⁷⁻¹⁹. The epoxy acrylate resin can further be cross linked with different functionality monomers to change or modify its performance. These acrylic monomers are the essential part of every UV/EB formulation. Nevertheless, there are only a few studies published explaining the underlying logic of explaining the use of acrylic monomers. In the past experimental works, trimethylolpropane triacrylate (TMPTA) has been used by various researchers^{20, 21}.

Therefore, for the first time we tried to prepare a blend by physical mixing of epoxy acrylate resin with mono, di & tri functional monomers and studied the effect by using different concentration of these monomers.

Experimental

Materials

Epoxy resin (M/s Parik Resin), acrylic acid (M/s E. Merck), triethylamine (M/s E. Merck), ethoxylated phenol monoacrylate (M/s Cognis), tripropylene glycol diacrylate (M/s Cognis), trimethylol propane triacrylate ((M/s Cognis), Darocure 1173 (M/S Ciba Specialty Chemical), Ethyl alcohol (Ranbaxy Laboratories Ltd.), NaOH (M/s E. Merck), H₂SO₄ (M/s S. D. Fine Chemicals) were used during the investigation.

Preparation of epoxy acrylate resin

A general purpose, bisphenol a based epoxy resin (EEW: 180), acrylic acid and triethyl amine were used for the synthesis of epoxy acrylate resin. The epoxy acrylate resin was synthesized by reacting epoxy resin and acrylic acid in 1:1 mole ratio. Tri ethylamine was used as a catalyst. The acid value of prepared resin was 3.0 mg KOH/gm solid as shown in Scheme 1.

Scheme 1

Preparation of blends of epoxy acrylate & monomers

Epoxy acrylate resin was physically mixed with different monomers of different concentration with an interval of 10 wt. %. All the samples were designated as shown in Table 1.

Curing of blend samples

The blend samples with 5 wt. % photo initiator [Darocure 1173] were cured in a UV Oven at a speed of 10 meter per minute in atmospheric air with 80 watts /cm mercury vapor bulb.

Table 1. Sample designation of various blend samples

S. No.	Epoxy Acrylate, Wt. %	EOPA, Wt. %	TPGDA, Wt. %	TMPTA, Wt. %	Sample Designation ^a
1	50	50	0	0	R ₁ M ₁
2	60	40	0	0	R ₁ M ₂
3	70	30	0	0	R ₁ M ₃
4	80	20	0	0	R ₁ M ₄
5	50	0	50	0	R ₁ D ₁
6	60	0	40	0	R ₁ D ₂
7	70	0	30	0	R ₁ D ₃
8	80	0	20	0	R ₁ D ₄
9	50	0	0	50	R ₁ T ₁
10	60	0	0	40	R ₁ T ₂
11	70	0	0	30	R ₁ T ₃
12	80	0	0	20	R ₁ T ₄

^aR : Epoxy Acrylate, M : EOPA, D : TPGDA, T : TMPTA

Preparation of panels

The blend samples were applied on sand blasted steel panels of size 150 × 100 × 1.25 mm with a bar applicator (M/s Sheen Instruments Ltd., U.K.). A dry film thickness of about 10-15 μ was maintained on all the panels. The films were cured as per the cure schedule discussed earlier.

Mechanical properties

Adhesion

The adhesion properties of the cured films were evaluated by cross - cut adhesion test method. In this test, parallel cut were made on the coating in two directions to form a series of small squares, originally one hundred of them, 1.25 mm in size. An adhesive tape was applied to the cross cuts, the tape was rolled at the place to assure good adhesion, and then removed with a force perpendicular to the coated substrate. The number of squares removed, gave the numerical value of its adhesiveness.

Impact resistance of cured film

The impact resistance of the cured film samples was evaluated by dropping a hemi-spherical shaped 2-Lb weight from different heights, ranging from 25 to 15 inches (DEF1053 specification). The tests were carried out on the uncoated side of the panels facing the falling weight.

Pencil hardness

As per the specification in ASTM D3363, pencil hardness of the cured films was determined by using a calibrated set of drawing leads ranging from 6B, the softest, to 6H, the hardest. The first pencil that scratches out the coating from the substrate was reported as the coating's hardness.

Chemical properties

The panels were also examined for a visual change in the film by conducting spot test with different chemicals like H₂SO₄ (10% Sol.), NaOH (10% Sol.) & Toluene *etc.* for 24h at ambient temperature.

Thermal Properties

The thermal stability of the blend samples was determined by comparing the onset degradation temperature (up to 5% wt. loss) of the cured samples with Thermogravimetric analyzer (TGA) of Universal V3.9A TA instrument, at a heating rate of 20°C/min. in nitrogen atmosphere from 50 to 600°C.

Results and Discussions

Adhesion, Impact resistance & Pencil hardness of cured film of blend samples

Table 2 shows the surface properties of the cured film of different blends samples. The table indicates that except R₁D₁, R₁D₂, R₁D₃, and R₁D₄, all the blend samples pass through adhesion test. The blend samples with EOPA & TMPTA shows improved adhesion & pencil hardness which is due to the very bulky side group present in EOPA, directly linked to the polymeric network, limiting the freedom of movement of this network. Whereas in TMPTA, the polarity of the linkage group gives more degree of dipolar interaction which leads to better mechanical properties. The TPGDA shows inferior mechanical properties except impact resistance as compared to EOPA & TMPTA. This is due to the higher freedom of movement around the linkage, enabling the stretch with the polarity, giving dipolar interaction which is responsible for mechanical properties.

Table 2. The surface properties of the cured film of different blends samples.

Sample code	Mechanical properties of paint films		
	Adhesion*	Impact resistance, inches	Pencil hardness
R ₁ M ₁	2	25	3H
R ₁ M ₂	2	25	4H
R ₁ M ₃	1	25	5H
R ₁ M ₄	1	20	5H
R ₁ D ₁	5	25	HB
R ₁ D ₂	4	25	H
R ₁ D ₃	3	25	H
R ₁ D ₄	3	25	2H
R ₁ T ₁	2	10	5H
R ₁ T ₂	2	15	5H
R ₁ T ₃	1	15	5H
R ₁ T ₄	1	15	5H

*1 = No removal of paint film; 2 = 5-20% removal of paint film; 3 = 20-50% removal of paint film; 4 = 50-80% removal of paint 5 = 80-100% removal of paint film

Comparative acid, alkali & solvent resistance of epoxy acrylate modified with different monomers & their different concentrations cured under UV – Radiation

Table 3 shows the comparative acid, alkali & solvent resistance of cured film blends. A quick perusal of Table 3 signifies that the coating film prepared with TMPTA offered maximum resistance towards acid, alkali & solvent, as compared to the film of other monomers. This behavior is due to the high reactivity of TMPTA, which results in a more complex structure, resulting better resistance as compared to other samples.

Thermal properties

The system was evaluated for thermal stability in nitrogen atmosphere by thermogravimetric analysis. The thermogravimetric (TG) traces were obtained for samples R₁M₁, R₁D₁ & R₁T₁ which are shown in Figures 2, 3 & 4 respectively. The experimental data obtained at initial (T_i),

peak (T_p) and final (T_f) decomposition temperature as well as char residue at 445°C derived from the traces are given in Table 4. Figures 2, 3 & 4 clearly indicate that both R_1M_1 & R_1D_1 samples show two step mass loss in TG traces while the R_1T_1 sample show single step mass loss. The improved resistance to thermo-oxidative degradation may possibly be due to the high cross link density of R_1T_1 blend sample. The char yield was also higher in sample R_1T_1 than other samples. This is due to the limited cross linking in other samples.

Figure 1. Acid value *versus* reaction time

Figure 2. TGA traces of epoxy acrylate with EOPA (sample R1M1)

Figure 3. TGA traces of epoxy acrylate with TPGDA (sample R₁ D₁)

Figure 4. TGA traces of epoxy acrylate with TMPTA (sample R₁ T₁)

Table 3. The comparative acid, alkali & solvent resistance of cured film blends

Sample code	Chemical properties of paint films		
	H ₂ SO ₄ ,	NaOH	Toluene
R ₁ M ₁	Fail	Fail	Pass
R ₁ M ₂	Pass	Pass	Pass
R ₁ M ₃	Pass	Pass	Pass
R ₁ M ₄	Pass	Pass	Pass
R ₁ D ₁	Pass	Pass	Fail
R ₁ D ₂	Pass	Pass	Fail
R ₁ D ₃	Pass	Pass	Pass
R ₁ D ₄	Pass	Pass	Pass
R ₁ T ₁	Pass	Pass	Pass
R ₁ T ₂	Pass	Pass	Pass
R ₁ T ₃	Pass	Pass	Pass
R ₁ T ₄	Pass	Pass	Pass

Table 4. Thermal behavior of isothermally cured blends of Epoxy acrylate resin / monomers (heating rate 20°C/min.)

Code	I Stage				II Stage				Char yield
	T ₀ °C	T _p °C	T _F °C	Mass loss, %	T ₀ °C	T _p °C	T _F °C	Mass loss, %	
R ₁ M ₁	260	351.1	370	27.4	375	423	445	82.2	11.46
R ₁ D ₁	145	350	380	37.3	385	435	445	69.4	17.29
R ₁ T ₁	190	422	445	58.3					39.58

Conclusion

From the preceding results & discussions it can be concluded that the films of blend sample containing EOPA & TMPTA shows better adhesion, hardness, chemical resistance & thermal resistance properties as compared to TPGDA. Epoxy acrylate resin containing EOPA & TMPTA can be used in harsh environment such as automobiles and it is also suitable for metal coating at ambient temperature. As Epoxy acrylate resin containing TPGDA has high impact resistance so it can be used as an oligomer in UV-cured coatings for plastic instead of flexible urethane acrylate.

References

1. Shi W, Ranby B, *J Appl Polym Sci*, 1994, **51**, 1129–1139.
2. Dakin VI, *J Appl Polym Sci*, 1996, **59**, 1355–1363.
3. Andrzejewska E and Andrzejewska M, *J Polym Sci Pol Chem*, 1998, **36**, 665–673.
4. Bajpai M, Shukla V and Kumar A, *Prog Org Coat*, 2002, **44**, 271–278.
5. Abadie MJM, Xiong Y and Boey FYC, *Eur Polym J*, 2003, **39**, 1243–1247.
6. Holman R and Oldring P, UV and EB curing formulation for printing inks, coatings and paints. SITA Technology, 1988.
7. (a) Hourston DJ and Zia Y, *J Appl Polym Sci* 1984, **29**, 629; (b) Elsabee M Z, Dror M, Berry G C, *J Appl Polym Sci*, 1983, **28**, 2151.
8. Elsabee M Z, Dror M, Berry G C, *J Appl Polym Sci*, 1983, **28**, 2151.

9. Cassidy EF, Xiao HX, Frisch KC and Frisch HL, *J Polym Sci: Polym Chem Ed* 1984, **22**, 2667.
10. Costanza J, Silveri A, Vana J. Federation of Societies of Coatings Technology, 1986.
11. Roey C, Photopolymerisation of surface coatings. New York: Wiley, 1982.
12. Ketley DA and Toao H J, *J Radiation Curing*, 1979, April 22.
13. Perkins CW. *J Radiation Curing* 1981; January 16.
14. Opera S, Vlad S, Stanciu A, and Macoveanu M, *Eur. Polym. J.* 2003, **36**, 373.
15. Bajpai M, Shukla V, and Kumar A, *Prog. Org. Coat.* 2002, **44**, 271.
16. Chattopadhyay D K, Panda S S, Raju K V S N, *Prog. Org. Coat*, 2005, **54** (1), 10.
17. Idriss Ali K M, Mubarak A K, Mokhlesur R and Mahmuda G, *J. Appl. Polym. Sci.* 1997, **66**, 1997-2004.
18. Kim.B K and Paik S H, *J. Appl. Polym. Sci. Part A: Polym Chem.* 1999, **37**, 2703.
19. Rayss J, Podksciely W M and Wodomski, J, *J. Appl. Polym. Sci.*, 1993, **49**, 835.
20. Khan Mubarak A, Tasneen S S, Habib M Ahsan and Rahman M Mizanur, *Polymer Radiation Engineering*, 2004, **43**, 301-308.
21. Chattopadhyay D K, Siva Sankar Panda and Raju KVS N, *Progress in organic coating*, 2005, **54**, 10-19.