PREPARATIONS AND APPLICATIONS IN UV CURING COATINGS OF EPOXY ACRYLATES CONTAINING CARBOXYL

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ABSTRACT

This paper introduces preparations of epoxy acrylates containing carboxyl through the reactions of Epoxy acrylates with butanedioic anhydride, pentanedioic anhydride, cis-butenedioic anhydride, phthalic anhydride, tetrabromophthalic anhydride and Δ^4-tetrahydrophthalic anhydride. These epoxy acrylates containing carboxyl have been applied to UV-curing coatings and their effects on properties of UV-curing coatings have been studied.

Key words: Epoxy Acrylates Containing carboxyl, Preparation and Application.

INTRODUCTION

Bisphenol A epoxy acrylates are extensively used in UV curing wood coatings, plastic coatings, metal coatings and paper coatings[1][2][3][4]. But there are some intrinsic imperfections at the properties of bisphenol A epoxy acrylates, such as yellowing, bad flexibility and bad adhesion to plastic. In this paper, bisphenol A epoxy acrylates have been modified with butanedioic anhydride, pentanedioic anhydride, cis-butenedioic anhydride, phthalic anhydride, pentanedioic anhydride, tetrabromophthalic anhydride and Δ^4-tetrahydrophthalic anhydride. These anhydride modified bisphenol A epoxy acrylates have been used in UV curing coatings and have significantly improved the properties of the UV curing coatings such as hardness, abrasion performance and adhesion to plastic and metal.

EXPERIMENTAL

1. Materials

Bisphend A epoxy resin (Epikote 828) was procured from Shell. Irgacure 651 procured from Ciba was used as the photoinitiator. Acrylic acid, butanedioic anhydride(BDA), pentanedioic anhydride (PDA), cis-butenedioic anhydride (cis-BDA), phthalic anhydride (PA), tetrabromophthalic anhydride (TBPA), Δ^4-tetrahydro phthalic anhydride (THPA) were procured on the market. TPGDA and TMPTA procured from Ucb were used as the monomers.

2. Preparation of Epoxy Acrylates Containing Carboxyl.

Epikote 828 (0.1mol), acrylic acid(0.2mol), inhibitor (moderate) were added into a three-necked flask equipped with an agitator. Agitator was started and triethylamine was added in. Then, the mixture was heated to 90℃~100℃ and reacted for an hour at the temperature. Then the mixture was continuely heated to about 115℃ and reacted at the temperature for 5 hours. Then BDA(0.03mol) was added in and the mixture reacted continuely for 2 hours at the temperature of 115℃. The acid value of the product was 55~60 mgKOH/g.

3. UV Curing Coating Formulation for Testing Purposes.

Formulations for testing purposes were prepared with fixed amounts of the oligomer at 50%, the photoinitiator at 5%, the TMPTA at 20% and the TPGDA at 25% (see table I).

Table I UV Curing Coating Formulation for Testing Purposes

Materials	Oligomer	TMPTA	TPGDA	Irgacure 651
Parts by weight	50	20	25	5

4. Test Methods

A tinplate (5×8cm) was coated with the formulated solution and cured passing under a UV lamp (254nm, 3kw) at the band speed of 3m/min. The cured film was used to determine its hardness with the help of pencil hardness tester. A circular glass plate (10cm in diameter) was coated with these formulations and then cured under the same UV lamp. The cured film was used to determine its abrassion performance with the help of Taber abrassion tester from Ericsson according to GB/T 15102-94.

Similarly a PVC substrate sheet and a steel substrate sheet (5×8cm) were coated with these formulations and then cured under the same UV lamp, The cured films were respectively used to determine their adhesion to PVC and metal according to GB/T 9286-88.

RESULTS AND DISCUSSION

1. Film Hardness

Seven different formulations were prepared according to table I with seven oligomers such as Epikote828 epoxy acrylate (EA), BDA modified Epikote 828 epoxy acrylate (BDAMEA), PDA modified Epikote828 epoxy aerylate (PDAMEA), cis-BDA modified Epikote828 epoxy acrylate (cis-BDAMEA), PA modified Epikote828 acrylate (PAMEA), TBPA modified Epikote828 epoxy acrylate (TBPAMEA) and THPA modified Epikote828 epoxy acrylate(THPAMEA). The hardness of the cured films of the formulations determined by the pencil method is shown in table II.

Table II Pencil Hardness of the Cured Films

Oligomers	EA	BDAMEA	PDAMEA	cis-BDAMEA	PAMEA	TBPAMEA	THPAMEA
Pencil Hardness	3H	3H	3H	4H	4H	4H	4H

We can see from table II that the cured films composed of cis-BDAMEA, PAMEA, TBPAMEA and THPAMEA have shown higher peneil hardness (PH) than that of the cured films composed of EA, BDAMEA and PDAMEA. The cis-BDAMEA has additive middle bond groups which can easily provide more crosslinking networks with the monomers, yielding higher PH than that of EA. PAMEA has also shown higher PH than that of EA, because of the PAMEA molecule containing rigid ring structure. Similar observations have also been noticed with TBPAMEA and THPAMEA.

2. Abrassion Performance

Abrassion Performance (AP) of the cured films of all the EA, BDAMEA, PDAMEA, cis-BDAMEA, PAMEA, TBPAMEA and THPAMEA are shown in table III.

Table III Abrassion performance of the cured films

Oligomer	EA	BDAMEA	PDAMEA	cis-BDAMEA	PAMEA	TBPAMEA	THPAMEA
AP(mg/1000r.g)	8.4	7.5	7.6	6.8	6.8	6.8	6.8

From table III, we can see that the order of the PA of various cured films from high to low is as follows:

THPAMEA ≈ TBPAMEA ≈ PAMEA ≈ cis-BDAMEA>PDAMEA ≈ BDAMEA>EA.

BDAMEA has shown higher AP than has EA because the BDAMEA molecules contain additive carboxyls which can form hydrogen bonds each other. PDAMEA has shown the same AP as that of BDAMEA because the molecule structure of PDAMEA is similar to that of BDAMEA. Among the PAMEA and BDAMEA, the PAMEA shows higher AP than that of BDAMEA because of the rigid ring structure of PAMEA. Similar observations have also been noticed with TBPAMEA and THPAMEA.

3. Adhesion to PVC

The anhydride modified bisphenol A epoxy acrylates such as BDAMEA, PDAMEA, cis-BDAMEA, PAMEA, TBPAMEA and

THPAMEA have shown better adhesion to PVC than that of the non-modified bispheol A epoxy acrylate such as EA(see figure 1)

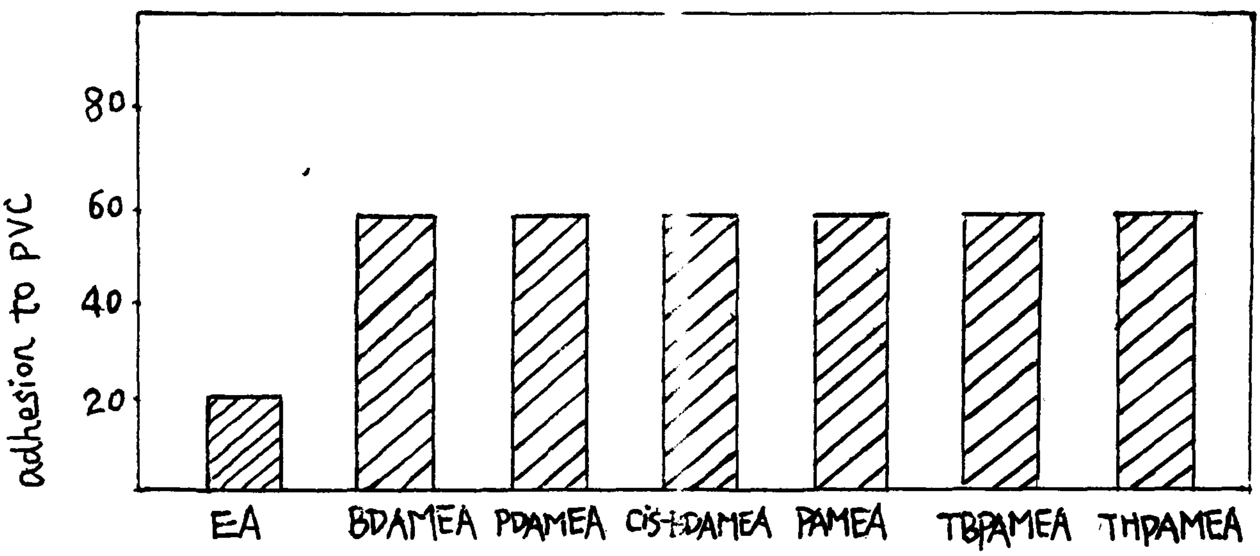

Figure 1 Adhesion to PVC of the cured films.

The acidity of the anhydride modified bisphenol A epoxy acrylates have erosion effect on the surface of PVC, resultig the better adhesion to PVC of the cured films of the anhydride modified bisphenol A epoxy acrylates than that of the non-modified bisphenol A epoxy acrylate.

4. Adhesion to Metal

The results of adhesion to metal of the cured films of various oligomers are similar to that of adhesion to PVC. The surface of metal has always adsorbed a layer of water in enviroment and the carboxyls of the anhydride modified bisphenol A epoxy acrylates such as BDAMEA etc. can form hydrogen bonds with the water adsorbed on the surface of metal while the formulation solution of BDAMEA is coated on the surface of metal and cured under UV lamp, yielding better adhesion to metal than that of EA. Similar observations have also been noticed with PDAMEA, cis-BDAMEA, PAMEA, TBPAMEA and THPAMEA.

CONCLUSION

Bisphenol A epoxy acrylates modified with anhydride had shown higher abrassion performance and better adhesion to PVC and metal than that of non-modified bisphenol A epoxy acrylate when they were applied in UV-curing formulations.

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