Synthesis and Evaluation Properties of Waterborne Epoxy-ester Resins

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Introduction

Due to the imposition of increasing legislative restrictions on the emission of volatile organic compounds to the atmosphere, water-borne paints are finding more and more importance for coating applications and industry. Eco-friendly paints are emulsion paints, powders, UV curable paints, and water-borne paints using water dispersed resin or water soluble resin.
Epoxy resins have been used various fields which are heavy duty coatings, floor coatings and waterproof coatings, and anti-corrosion paints. However, to synthesize waterborne type of epoxy resins are very difficult because they have high functionality which result in gel formation during the water dispersion or water soluble stage. Those kinds of problems can be solved an esterification between epoxy resin and monobasic fatty acids to form epoxy esters to reduce their functionality and graft polymerization on the fatty acid long chain with acrylic monomers[1, 2].
One of the major objectives is to synthesize self-emulsifying epoxy ester resin which is water dispersion epoxy ester resin without emulsifiers and to investigate step reactions. Acrylic acid has been used to graft polymerization on epoxy ester resin of the alkyd long chain by thermal initiator and to make more carboxylic groups which can be dispersed in water. Self-emulsifying epoxy ester resins without emulsifiers can be improved water resistance and they have been studied to develop eco-friendly anti-corrosion paints are applicable for various interior parts of ships.

Experimental

Materials

Epoxy resin(YD-011, Kukdo Chemical) and Dehydrated Castor Oil Fatty acid (DCOFA, Japan Oil Ind. Co.) were industrial grade. Butyl cellosolve acetate (B-Cell) was used for synthesizing for Epoxy ester resin. Acrylic acid (AA, Junsei Chemical), Methyl Metacrylate (MMA, Junsei Chemical), and Styrene (SM, Junsei Chemical) were extra pure grade and were used for graft polymerization of epoxy ester resin. Initiator was tert-butyl peroxide (98%, Sigma Aldrich) and triethylamine (TEA, Samchun Pure Chemical) for neutralizing agent was dried over 4 A° molecular sieve before us e. Emulsifier was extra pure grade and used for emulsifying epoxy ester resin.
TiO_2 (Ti-pure, Dupont) and dispersion agent (BYK), defoamer (BYK), wetting agent (BYK) were industrial grade.

Synthesis process

Formulations for the epoxy ester resins are given in Table 1 and formulations for self-emulsifying epoxy ester resins are Table 2. A 500 ml round bottom, a four-necked separable flask with a mechanical stirrer, a thermometer, and a condenser with drying tube and N_2 inlet was used as reactor. The reaction was carried out in a constant temperature heating mantle. Firstly, Epoxy resin, DCOFA and B-Cell were charged into the 4-neck flask respectively, and stirred at 200 °C for about 4h and the reaction monitored by acid value and collection of condensation water. Solvent-borne epoxy ester resin has been synthesized. To synthesizing of self-emulsifying waterborne resin (WBEA-1), acrylic monomers with initiators were dropped on solvent-borne epoxy ester resin and reacted for about 4h at 140 °C. Before adding a

neutralizing agent (TEA) reaction temperature was cooled at 80 ˚C and then added a TEA and stirred for the next 1h. After that distilled water was added and stirred for 1h while maintaining the temperature at 55˚C [2, 3].
WBEA-2 has been made with emulsifiers and added water by high speed stirrer on the epoxy ester resin [4].

Fourier Transform Infrared (FT-IR) spectroscopy
The IR spectra are recorded using a JASCO FT/IR-6100 (Japan) equipped with a Miracle accessory, an attenuated total reflectance (ATR). FT-IR has been monitored of synthesizing between epoxy ester resin and acrylic monomers and to verifying -COOH groups.

Paint development
Formulations for eco-friendly paints using WBEA-1 and WBEA-2 are EWBP-1 and EWBP-2 which were given Table 3.

Coating and drying process
Self-emulsifying epoxy ester resins and emulsifying epoxy ester resin were applied on the glass plates using an application at 100㎛ thickness and then dried for 120 min at a room temperature.

Peel strength
The adhesion property of dried coatings was measured by hydraulic adhesion tester (model : F108-2B, Elcometer) according to ASTM D 4541.

Water Resistance (Water proof property)
Water resistance property of dried coating was measured by immersion test method according to ISO 2812-1 at 23 ± 1℃ and 50 ± 2% R.H.

Anti-corrosion
Anti-corrosion property of dried coating was measured by salt spray test of 5% NaCl according to KS D 9502 and test time was 300h. Evaluation of anti-corrosion was appearance test of dried coating.

Weathering
Weathering property of dried coating was measured by Xenon arc test method according to ISO 4892-2 and test time was 300 h. Operation condition of Xenon arch were that BPT (Black panel temperature) was (65 ± 3)℃and relative humidity was (50 ± 5) %. Evaluations of weathering were color difference and gloss retention.

Results and Discussion

Fourier Transform Infrared (FT-IR) spectroscopy
Figure 1. shows that scheme of self-emulsifying epoxy ester resin including 1st step and 2nd step.
Figure 2. shows that FT-IR spectra were used to controlling the process of reaction. Synthesis was controlled by monitoring the appearance and strength of characteristic peaks of -COOH groups of C=O (1700 ~ 1730 cm^{-1}). Solvent-borne epoxy ester resin had little -COOH groups and -COOH groups had been increased by graft polymerization between solvent-borne epoxy ester resin of fatty acid chains and acrylic monomers. Acrylic acids and fatty acid of long chains made -COOH groups during the graft polymerization.

Peel strength
Table 4. shows that adhesion properties of eco-friendly paint using self-emulsifying epoxy ester resin (EWBP-1) and. forced emulsifying epoxy ester resin (EWBP-2). Adhesion properties had almost same because epoxy ester resin had strong adhesion property on steel substrate and acrylic monomers had not effected on improving adhesion properties.

Water Resistance (Water proof property)
Table 4. shows that water resistance of eco-friendly paint using self-emulsifying epoxy ester resin (EWBP-1) and. forced emulsifying epoxy ester resin (EWBP-2). EWBP-1 had no blistering, but EWBP-2 had blistering on dried film after 30 days. Because emulsifier had been reduced water resistance property and was a weaken point of dried film, but EWBP-1 had good water resistance because of no emulsifiers in the resins.

Anti-corrosion
Table 5. shows that anti-corrosion of eco-friendly paint using self-emulsifying epoxy ester resin (EWBP-1) and forced emulsifying epoxy ester resin (EWBP-2). EWBP-1 had good anti-corrosion property, but EWBP-2 was poor. Because EWBP-2 had emulsifier which had been reduced water resistance and was a weaken point of dried film.

Weathering
Table 5. shows that weathering of eco-friendly paint using self-emulsifying epoxy ester resin (EWBP-1) and forced emulsifying epoxy ester resin (EWBP-2). Color difference of EWBP-1 was 3.5, but EWBP-2 was 5.3. EWBP-1 had lower color difference than EWBP-2. Because EWBP-1 had acrylic chain which had good weathering than epoxy ester resins.

Conclusions

Self-emulsifying epoxy ester resins (WBEA-1) were synthesized between solvent-borne epoxy ester resin and acrylic monomers by graft polymerization and then water dispersion without any emulsifier. Synthesis process was 2 steps and process was optimized.
Graft polymerization by acrylic monomers had been increased -COOH groups which can be dispersed in water without any emulsifiers and we had been verified characteristic peaks of -COOH groups of C=O (1700 ~ 1730 cm^{-1}) by FT-IR .
Eco-friendly paints using WBEA-1 and WBEA-2 are EWBP-1 and EWBP-2. EWBP-1 had good water resistance and anti-corrosion compared to EWBP-2 because EWBP-1 had no emulsifiers which were weaken points of dried coatings.
Peel Strength has almost same those of resins because of epoxy resin has strong adhesion properties. Color difference of EWBP-1 had lower color difference than EWBP-2, because EWBP-1 had acrylic chain which had good weathering than epoxy ester resins.

Acknowledgements

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Table 1. Formulations for the synthesis of epoxy ester resin (units : equivalent ratio).

Sample	Epoxy (YD-011)	DCOFA	Acid value
Epoxy ester resin	0.5	0.5	21

Table 2. Formulations for the synthesis of self-emulsifying epoxy ester resin (units : mole ratio)

Sample	Acrylic monomers		Neutralizing agent TEA[c]	Theoretical T_g
	MMA[a]	AA[b]		
WBEA-1	2.37	0.24	0.35	101.3
WBEA-2	Forced emulsifying resin with emulsifiers			

[a] methyl methacrylate, [b] acrylic acid, [c] triethyl amine

Table 3. Formulations for eco-friendly paints

	Materials	EWBP-1	EWBP-2
Mill Base	WBEA-1	250	-
	WBEA-2	-	250
	TiO2	230	230
	Inhibitor	100	100
	Water	50	50
Let Down	Additives	8	8
	WBEA-1	250	-
	WBEA-2	-	250
	Additives	5	5
	Water	127	127
	Total	1,000	1,000

Table 4. Physical properties of EWBP-1 and EWBP-2 coatings.

Sample	Peel strength (N/mm^2)	Water resistance (after 30 days)
EWBP-1	6.2	No blistering
EWBP-2	5.9	Blistering

Table 5. Environmental properties of EWBP-1 and EWBP-2 coatings.

Sample	Anti-corrosion (300 h)	Color difference
EWBP-1	Good	3.5
EWBP-2	Medium	5.3

Figure 1. Scheme of self-emulsifying epoxy ester resin.

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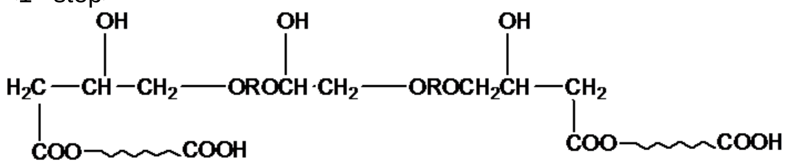

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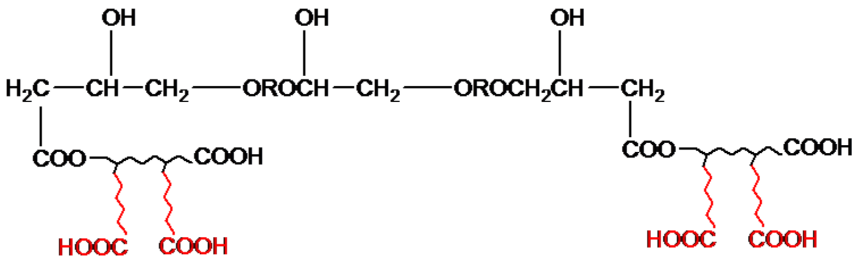

Figure 2. FT-IR chart of self-emulsifying epoxy ester resin during synthesis.