Application of Waterbased UV-Curable Dispersions to Plastic Coatings

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Introduction

UV-curable coatings have been applied to plastics mainly in mobile phone, customer electronics and automotive industry. High durability of UV-coatings against scratching is suitable for protecting a surface of thermoplastics. Typically, solvent-based UV coatings have been applied to it because of formulation flexibility and high performances.

UV topcoats are applied with dry film thickness of 10-20μm by spraying in those plastic applications. The adjustment of conventional spray-coatings to a workable viscosity is taken by diluting with a large quantity of organic solvents. Increasing awareness of environmental issues and implementation of legislation to reduce the emission of volatile organic solvents(VOC) have driven to develop waterborne systems.

The requirements for conventional plastic-topcoats include high gloss, high film hardness, high scratch resistance, moisture resistance, adhesion on a various type of basecoats or plastics directly. Aqueous types are also required to satisfy these demands not only reduce the emission of VOC. Therefore, formulating waterborne UV-coatings based on the advanced solventborne formulations is a possible approach to meet those high requirements.

One of the popular formulation of solventbased UV-topcoat is mixture of multi-functional acrylate monomers/oligomers and acrylic polymers. High-functional acrylates form a high crosslinking film and perform high scratch resistance. Acrylic resins have effect to improve adhesion to substrates and prevent a crack development by UV-radiation of cured films. Converting the formulation from solvent system to waterborne system can be accomplished by incorporating acrylic aqueous dispersions with acrylates. Performances of the UV-curable aqueous dispersions obtained by using this method are described in this paper.

Properties of waterbased acrylates/acrylic polymer dispersions

UV-curable acrylates/acrylic polymer dispersions have advantages as follows:

- Conventional acrylate monomers and oligomers can be used in waterbased formulation by dispersing with acrylic polymer.
- The similar formulations with industrial used solventborne UV-coatings can be achieved in waterbased UV-coatings.

The acrylic resins are available by copolymerization of methacrylate and acrylate monomers which contain carboxylic functional groups in amphiphilic glycol ether solvent. Compositions of the acrylic resins were optimized for polarity, molecular weight and quantity of functionality in the way that the stable dispersions were obtained. The acrylic resins are neutralized by tertiary amine or ammonia water before diluting by ion-exchanged water. UV acrylates are composed of multifunctional monomers and high functional urethane acrylates. A variety of acrylates can be used in combination depending on the applications and formulator requirement.

Preparation of UV-curable acrylates/acrylic polymer dispersions

The series of waterborne UV-curable dispersions(dispersion A-C) were prepared to evaluate the properties in plastic applications. They are composed of the same acrylic resin and the mixture of dipentaerythritol penta(hexa)acrylate(DPHA: Lumicure® DPA-620, TOA-DIC Zhangjiagang Chemical) and hexa-functional urethanacrylate. Contents of DPHA are 70, 60 and 50wt% in nonvolatile content of dispersion A, B and C, respectively. The samples have different double bond concentrations by varying the content of acrylic resins with that of DPHA . All of the dispersions are diluted by ion-exchange water and contain 5% lower of VOC.

Table 1. Properties of waterbased UV-curable acrylates/acrylic polymer dispersions

	solid content wt%	viscosity mPas(25°C)	pH	average particle size m	DPHA in solid wt%
Dispersion A	39	70	8.5	0.29	70
Dispersion B	39	340	7.5	0.28	60
Dispersion C	38	3090	7.5	0.29	50

Table 1 shows the properties of acrylates/acrylic polymer dispersions. Viscosity of the dispersion rises as reducing the content of DPHA. In other words, the content of acrylic polymer affects the viscosity. Some fractions of the acrylic resins are soluble in water not only dispersible and probably make strong

hydrogen-bond interaction in aqueous medium.

The dispersions have a milky white appearance. The particle size of the dispersions was measured by using laser light scattering method. All of the dispersions showed unimodal particle size distribution as seen in Figure 1 and had similar average particle size.

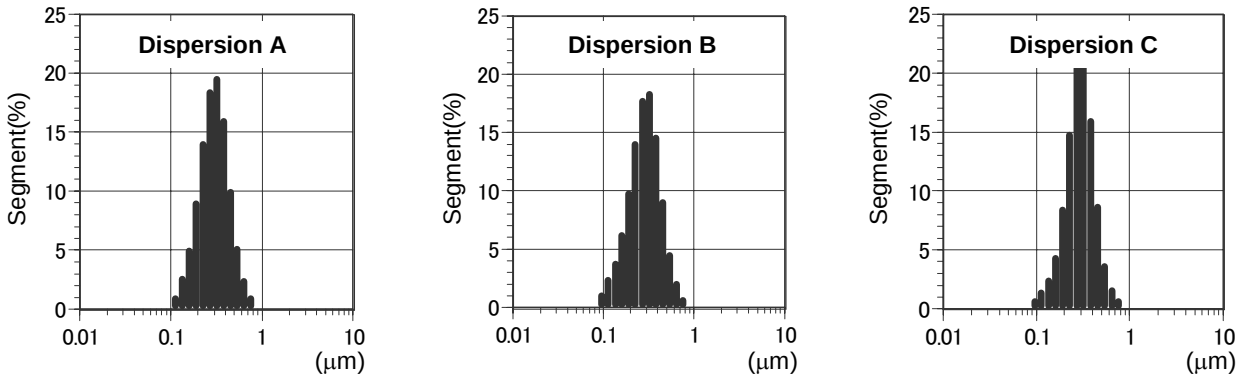

Figure 1. Particle size distribution pattern of the acrylates/acrylic polymer dispersions.

Mechanical properties

Figure 2 shows the results of the characterization of the dispersions by dynamical mechanical analysis (DMA). The test samples were prepared by blending 5phr of Irgacure® 500(Ciba Specialty Chemicals) as a photo initiator . The cured films with the thickness of approximately 100μm were obtained by applying a UV dose of 800mJ/cm^2 after flashing-off of water and solvents. The films have a broad tan δ peak in a range of 85 to 93^{o}C. It indicates the content of DPHA has almost no significant effect to glass transition temperature(Tg) of the films. However, the difference was found in the tensile storage modulus(E'). Dispersion A which has the highest content of DPHA had the highest E' in high temperature region. This behavior is due to the high crosslinking density of the film which contain large quantity of DPHA .

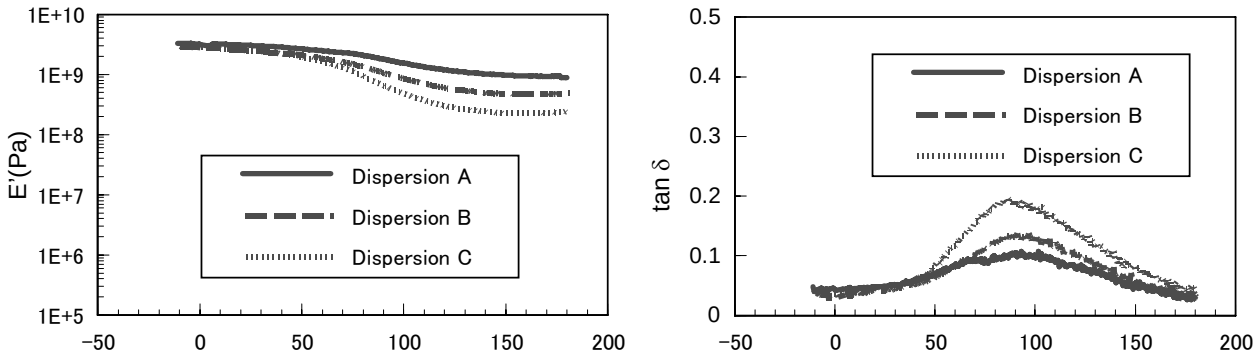

Figure 2. Temperature dependence of tensile storage modulus and tangent δ of the UV-cured films.

Film properties

The film properties of waterbased UV-curable dispersions were compared with commercial solventborne UV coatings which composed of DPHA and Unidic® C7-164(Dainippon Ink and Chemicals): commercially available UV-curable composition.

Evaluated formulations of UV-curable coatings(formulation A-C) were made by mixing each of dispersion(dispersion A-C, respectively) with 5phr of Irgacure® 500. The solventbased coating was prepared by blending 3phr of Irgacure® 184(Ciba Specialty Chemicals). All samples contained 0.8phr of BYK®-333(BYK-chemie) as a leveling agent. These coatings were applied to plastics and basecoats by drawing it down using a wire wound bar to achieve a dry film thickness of 10-15μm then flashed for 5 minutes at 70°C. the coatings were cured by passing them under a high-pressure mercury lamp and applied a UV dose of 800 mJ/cm^2.

Dry film properties were evaluated on following conditions.

- 20° and 60° angle gloss: on metallic acrylic polymer basecoat.
- Cross-cut adhesion test: on PC, ABS, and metallic basecoat; 5 = excellent, 0 = all film removed
- Scratch resistance: steel-wool abrasion test; #0000 steel-wool; 414g/cm^2 load; measured the haze value change with hazemeter after 50 double rub; smaller the haze value change indicates better scratch resistance.
- Pencil hardness: on PC, ABS, and PMMA
- Humidity resistance: 120hours of exposure at 65°C and 98% humidity; 5 = no appearance change, 0 = blistering and whitening on entire surface

Table 2. Film properties of the waterbased formulations.

		Formulation A	Formulation B	Formulation C	Solvent type
Gloss 20°	ABS	91	93	92	92
	metallic	98	100	102	100
Gloss 60°	ABS	95	95	94	95
	metallic	115	117	118	112
Cross-cut adhesion	PC	5	5	5	5
	ABS	5	5	5	5
	metallic	5	5	5	5
Scratch resistance	PMMA	0.9	1.3	2.4	4.6
Pencil hardness	PC	F	F	F	F
	ABS	HB	HB	HB	HB
	PMMA	4H	4H	4H	4H
Humidity resistance	ABS	5	5	5	5

All of the waterbased formulations formed high-performance films comparable to solventbased formulation as seen in Table 2. Discussing of the waterborne dispersions the difference of scratch resistance was observed. The result of abrasion test on formulation A which has the largest content of DPHA exhibited the smallest change of haze value. This indicates that the cross linking density affects the scratch resistance of the film.

Storage stability

Waterborne coatings often have a problem on storage stability in industrial applications. The same applies to the acrylates/acrylic dispersions. In many cases a poor storage stability of waterborne system is attributed to the hydrolysis of ester bonds. Severe hydrolysis results in the phase separation under storage or degradation of the film performances. The degree of hydrolysis can be measured by checking acid number change because acids are generated by hydrolytic reaction of the ester bonds. The acid numbers rise as the ester bonds are broken. Figure 3 shows the hydrolytic stability test results that compared acrylates/acrylic polymer dispersion to the acrylic-only dispersion for 10 days at 60^{o}C. This indicates that the hydrolysis mainly occurred on the ester bonds of the acrylates which are formed by condensation of polyvalent alcohol with acrylic acid.

Figure 4 shows the result of storage stability test of dispersions which were made at a pH range from 7.1 to 8.9 based on the composition of dispersion B. This result indicates hydrolytic stability of the dispersions can be improved by making it with lower initial pH. Figure 5 shows the humidity resistance of the dispersions aged for 1 month at 40^{o}C in various initial pH. These results indicate that the hydrolysis degrades the performance of cured films and causes blister on the surface. However, there were no appearance changes for the dispersions made in initial pH up to 7.3.

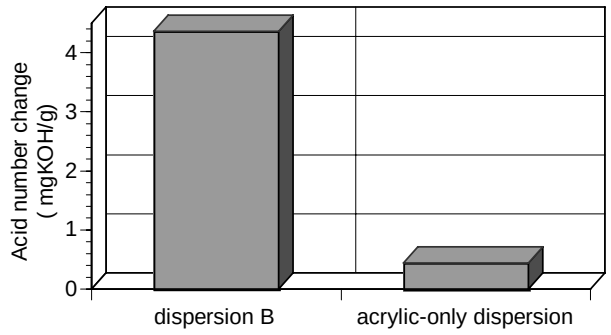

Figure 3. The pH dependence of hydrolysis compared dispersion B with acrylic-only dispersion after aging for 10 days in accelerated temperature of 60^{o}C.

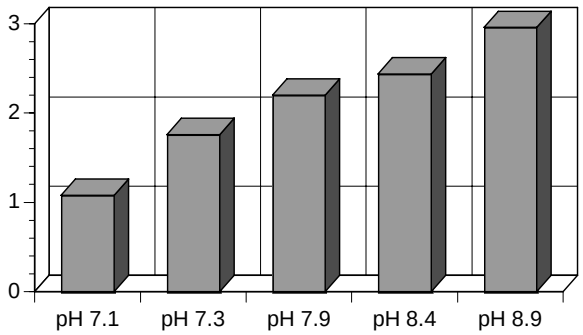

Figure 4. The comparison of hydrolytic stability of the dispersion B prepared in various initial pH after aging for 1 month at 40^{o}C.

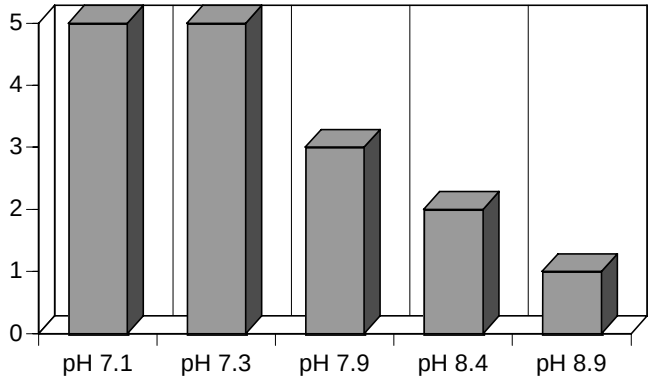

Figure 5. The humidity resistance of formulation B prepared in various initial pH after aging for 1 month at 40°C.

Conclusions

Waterbased UV-curable dispersions based on acrylates/acrylic polymer system were prepared and characterized the properties in terms of industrial applications. The dispersions have a possibility to be substituted for typical solvent-based plastic coatings because of extremely low emission of VOC and their high film performances. In addition, formulation flexibility of this UV-curable aqueous dispersion expand the possibility to apply waterbased UV coatings to other markets.