FLUOROPOLYMER DISPERSIONS FOR ULTRA-WEATHERABLE COATINGS

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ABSTRACT

Fluoro-olefin vinyl ether (FEVE) copolymers are well known as ultra-weatherable resins for the coatings industry. Due to increasing environmental regulation of solvents, traditional solvent based resins have been supplemented by the development of water based FEVE emulsions. However, the performance of coatings based on these emulsions is lower than that of coatings from solvent based resin. Recently, a class of FEVE water dispersions have been developed which offer excellent performance, equivalent of that obtained from solvent-borne FEVE resins. To make the dispersions, equimolar amounts of chlorotrifluoroethylene and a variety of functionalized vinyl ethers were polymerized. A portion of the hydroxy functional vinyl ether groups were denatured to form carboxylic acid groups, which were neutralized with an amine. The resulting polymeric carboxylate was dispersed in water. Lastly, solvent was evaporated, yielding an FEVE dispersion containing no solvents or emulsifiers. Stable dispersions were synthesized by adjusting parameters such as acid values and molecular weight. The resulting water dispersions were then crosslinked with water dispersible isocyanates. Pigmented coatings based on these dispersions had weatherability, durability, gloss, and water resistance comparable to solvent-based fluorourethane coatings. This paper will discuss the preparation of FEVE resin dispersions and properties of the resulting fluorourethane coatings along with a comparison of their properties with those obtained from conventional solvent-based FEVE resins and FEVE aqueous emulsions.

Introduction

Fluoropolymers are distinguished particularly by their high thermal, chemical and weather resistance, excellent surface properties (especially oil and water repellency) and optical properties (low refractive index). Accordingly, fluoropolymers are indispensable materials in a wide variety of industries.

Since fluoropolymers came on the market in 1930s, they have been applied as coating materials in order to achieve those characteristics mentioned above on the surfaces of various substrates. Typical examples include coatings made from aqueous dispersions polytetrafluoroethylene(PTFE), tetrafluoroethylene/hexafluoroethylene copolymers (FEP), and tetrafluoroethylene/perfluoroalkyl vinyl ether copolymers (PFA) for non-stick and anti-corrosion applications. However, those fluoropolymers are not necessarily suitable for use as coating materials due to their poor solubility in conventional organic solvents, the requirement of baking temperatures greater than 200□ and weak adhesion to substrates [1].

Among the well-known fluoropolymers, only polyvinylidene fluoride (PVdF) has been used for coatings as an organic dispersion, mainly for architectural applications due to its outstanding weatherability [2].

A unique solvent soluble fluoroolefinvinyl ether copolymer (abbreviated as FEVE copolymer, with the trade name “LUMIFLON”) was developed in 1982 by Asahi Glass. This copolymer consists of alternating sequences of fluoroolefin and several specific vinyl ether units (Fig.1), and is completely amorphous. This alternating sequence is responsible for extremely high weather resistance of the resultant paint finishes. Combinations of several kinds of vinyl ether comonomers provide the polymer with other useful physical properties, such as solubility in organic solvents, pigment compatibility , crosslinking sites and impart good adhesion, hardness and flexibility to the coating. The major reason for the use of FEVE copolymers as raw materials for coatings is their excellent weather resistance. The hydroxyl group in the FEVE polymer functions as the crosslinking site with blocked isocyanates or melamine resins for heat cured coatings, and with aliphatic polyisocyanates for on-site coatings [3].

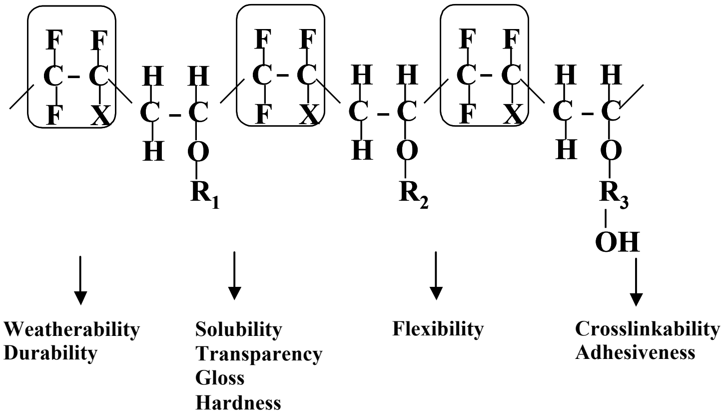


Figure 1. Polymer structure of FEVE copolymer

The first water-borne FEVE copolymers were aqueous emulsions prepared by emulsion polymerization. Vinyl ether monomers with polyoxyethylene (EO) unit were used as intramolecular emulsifiers to obtain stable emulsions and to maintain the alternating FEVE polymer sequence. The resulting emulsions have high molecular weight and toughness, so they can be used in one component systems. The resins can also be used in two component coatings by introducing more hydroxy functional vinyl ether monomer. . However, coating properties of FEVE emulsions are generally inferior to those of solvent types of FEVE copolymers. It is believed that emulsifier remaining in the polymer, and the high molecular weight of the FEVE polymer are the causes of these deficiencies. Adjustments in molecular weight and reducing the amount of added emulsifier were investigated, but they caused a reduction in overall coating performance.

In an attempt to improve the performance of water-based FEVE resins, dispersion of solvent-type FEVE resins were developed. Fluorourethane coatings made from these dispersions offered performance equivalent of that obtained from solvent-borne FEVE resins.

The sections below will discuss the preparation of FEVE resin dispersions. Properties of fluorourethane coatings prepared from these dispersions will be discussed, and compared to those of conventional solvent-based coatings and aqueous emulsion of FEVE resins.

Experimental

Solvent Polymerization (A). Solvent, several types of vinyl ethers, and potassium carbonate were placed in a stainless steel autoclave. After addition of the requisite amount of fluoroethylene monomer to the vessel, the reactor was heated to 65º C□ Then, the initiator was added. After stirring at 65° C at a pressure of 0.62Mpa for 8 hours, the reaction was terminated by the addition of hydroquinone. One of the vinyl ether monomers used was hydroxy functional, in order to introduce crosslinking sites. The resultant polymer contained approximately 50 mol% fluoroethylene units, and about 50mol% vinyl ether units.

Emulsion Polymerization (B). De-ionized water, emulsifiers, macromonomers, vinyl ethers, potassium carbonate were placed in a stainless steel autoclave. Next the requisite amount of fluoroethylene was introduced into the vessel, and the mixture stirred at 50ºC. and 0.35Mpa for 20 hours. The resultant polymer contained about 50 mol% of fluoroethylene units and almost 50mol% of vinyl ether units. A portion of the vinyl ether units contained polyoxyethylene units prepared by the reaction of a hydroxy functional vinyl ether (VE) unit and ethylene oxide (Hereafter this macromonomer is abbreviated as EOVE) [4]. Hydroxy functional vinyl ether units were also copolymerized. The ideal structure of FEVE emulsion is shown in Fig.2.

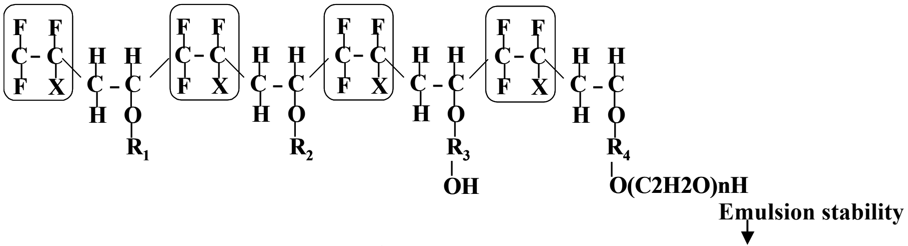
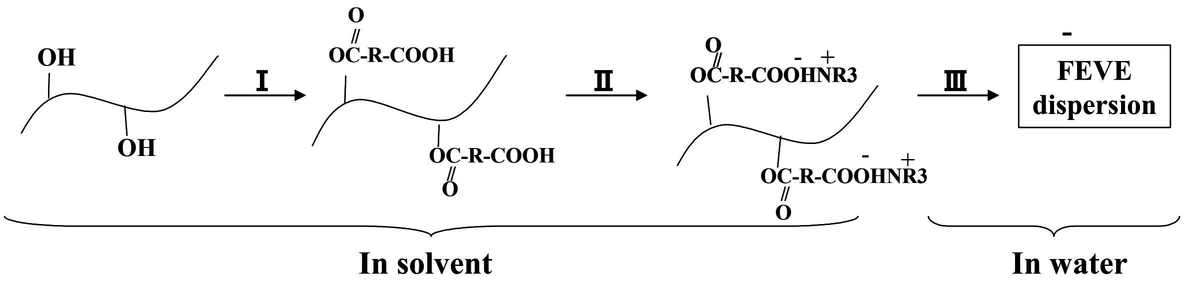


Figure 2. Polymer structure of FEVE emulsion

Preparation of FEVE Dispersion.. The process for preparing the FEVE dispersion is shown in Fig.3. The solvent based resin was dissolved in a hydrophilic solvent. A portion of the hydroxy functional vinyl ether groups of the FEVE copolymer were denatured to form carboxylic acid groups using an acid anhydride, followed by neutralization with an amine. The resulting polymeric carboxylate was dispersed in de-ionized water. Lastly, solvent was evaporated, yielding an FEVE dispersion containing no solvents or emulsifiers. This water dispersion could be crosslinked with water dispersible isocyanate. FEVE polymers of various molecular weights, acid numbers, and hydroxyl numbers were prepared.



□ : acid modification
□ : neutralization,
□ : dispersing in water & solvent evaporation

Figure 3. Process for Preparing FEVE Dispersion

Preparation of Coatings and Test Panels. Coatings were prepared from a solvent-based FEVE resin, a water emulsion FEVE resin, and the new dispersion type FEVE resin. For the solvent based resin,, the millbase was prepared by grinding TiO2 (trade name: Ti-Pure R-960) in a blend of solvent and FEVE copolymer until the pigment particle size was less than 5 µm. The millbase was diluted, then mixed with the isocyanate hardener (trade name: Desmodur N3300). The PVC of the resulting paint was 20%. A chromate treated steel panel was coated with this paint, and allowed to cure for 14 days at room temperature.

For FEVE emulsions and the dispersion, the millbase was prepared by dispersing TiO2 pigment (trade name: Ti-Pure R-706) in water along with a dispersant and a defoamer. The millbase was blended with additional polymer. A coalescer and leveling agent were added. Both single and two component coatings were prepared using FEVE water emulsions. In the case of the two component emulsion and dispersion, a water dispersible isocyanate hardener (trade name: Bayhydur 3100) was used. Chromate treated steel panels were coated with these formulated paints, and allowed to cure for 14 days at room temperature.

Results and Discussion

Physical Properties of FEVE Dispersions. Table 1 shows physical properties of several dispersions, compared to those of conventional FEVE emulsions E1 (one pack) and E2 (two pack). FEVE dispersions with various molecular weights, OH values and acid values were tested. In addition, dispersions with wide rage of particle diameters from 100 to 200nm .

Table 1. Characteristics of FEVE Dispersions and Emulsions

	Dispersions				Emulsions	
	D1	D2	D3	D4	E1	E2
Appearance	Milky White Liquid					
Ionic Characteristic	Anionic					
Non-volatile (wt%)	40	40	40	40	50	50
Molecular weight (Mn)	7000	7000	7000	15000	>50000	>50000
OH value (mg KOH/g-polymer)	85	85	85	35	10	55
Acid value (mg KOH/g-polymer)	5	15	25	10	0	0
MFT (□)	27	27	27	33	31	55
Particle diameter (nm)	180	130	100	100	140	140

For practical use, storage stability of resins is important. Table 2 shows the results of an accelerated high temperature storage stability test. Test results clarified that acid value is the most important variable related to storage stability of FEVE dispersions. Dispersion D1 with an acid value of 5 mgKOH/g-polymer coagulated after storage at 50ºC. for 4 weeks. On the other hand, dispersion D3 with a high acid value saw an increase in its molecular weight distribution. FEVE polymers with acid values ranging from 10 to 15 mgKOH/g-polymer had sufficient storage stability.

Table 2. Storage Stability of FEVE Dispersions and Emulsions.

	Acid value (mg KOH/g-polymer)	**Mw/Mn**	
		Init.	**After 4 weeks @ 50ºC.**
D1	5	2.3	Coagulation
D2	15	2.3	2.5
D3	25	2.3	3.5
D4	10	2.5	2.6
E1	0	3	3.2
E2	0	3	3.2

Dispersion Performance in 2-component Coatings. Table 3 shows the solvent resistance of crosslinked film based on dispersion D2 which was cured by a water dispersible isocyanate at ambient temperature for two weeks at various NCO indexes. When the NCO index was higher than 0.6, a sufficiently crosslinked film was obtained, as shown by the excellent solvent resistance of the coating. Table 4 shows physical properties of the crosslinked FEVE dispersion compared to two component coatings from emulsion and solvent types of FEVE copolymers. The FEVE dispersion coating gave film properties comparable to the solvent based FEVE coating, and it was superior to the two component FEVE emulsion based coating.

Table 3. Solvent Resistance of Crosslinked Film.

NCO Index	**Solvent resistance Xylene rubbing (100 times)**
1	Excellent
0.6	Excellent
0.3	Fair
0	poor

Table 4. Film properties of Two Component FEVE Coatings.

		FEVE Dispersion (OHV:85)	**FEVE solvent-borne (OHV:52)**	**FEVE emulsion (OHV:55)**	
Curing agent (NCO/OH=1)		Water dispersible polyisocyanate	HDI based polyisocyanate	Water dispersible polyisocyanate	None
Gloss 60 °	ISO 2813	88	90	78	78
Pendulum hardness	ASTM D 4366	79	80	75	19
Dupont impact	ASTM D 2794 (D=0.5”)	>1.0 m	>1.0 m	1.0 m	0.3m
Cross Cut Adhesion	ASTM D 3359	5B	5B	5B	0B
Water resistance*	ISO 2812 40° C24 h	4B	5B	3B	0B

*Cross cut adhesion test was done after soaking in hot water for 24h.

Fig.4 below shows the results of the QUV exposure test. Gloss retention of the dispersion film was greater than 90% after 5000h exposure, comparable to results obtained with the solvent based resin. On the other hand, degradation of the two component emulsion film started at 1000h .

Fig.5 shows the scanning electron micrographs of films based on an FEVE dispersion and an emulsion. As shown in those photographs, the FEVE dispersion provided a uniform film with no surface defects. In contrast, the emulsion based coating shows a number of surface defects which are believed to cause the differences in film performance, seen in properties such as gloss and water resistance.

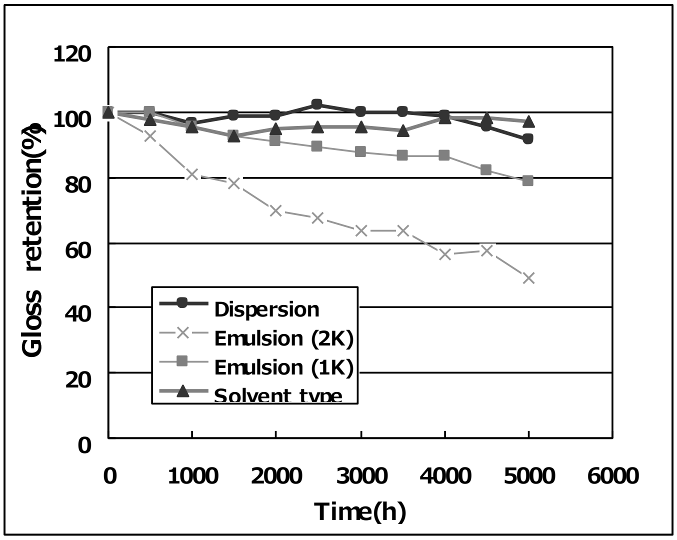


Figure 4. Accelerated weathering test result (QUV)

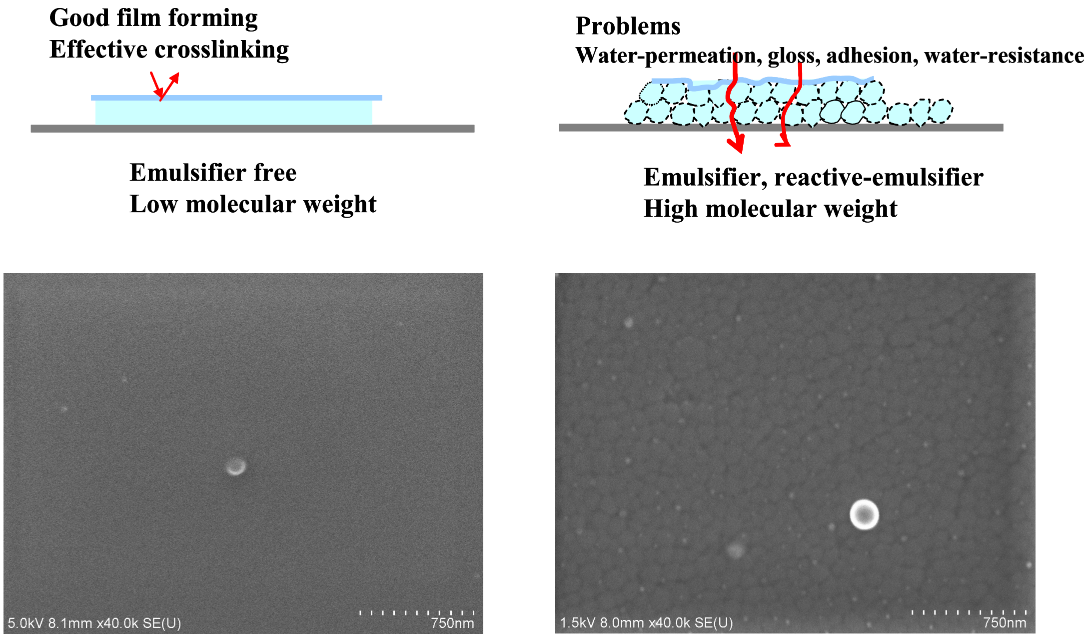


Figure 5. Scanning electron micrografs of film of FEVE dispersion and emulsion

Applications. Coating systems based on the crosslinkable FEVE dispersions with blocked and non-blocked water dispersible isocyanates give excellent film performances, such as weatherability, mechanical properties, and solvent resistance. The dispersions have properties nearly equal to those of solvent-borne FEVE resins. Coatings made from FEVE dispersions can be used in architectural , industrial maintenance, automotive, and aerospace coatings. They can be used in coil coatings, usually processed at high temperatures using blocked isocyanates, and in ambient cure coatings.

Conclusions

Stable FEVE dispersions were obtained by adjusting acid values. An FEVE dispersion with a high OH value was able to react with water dispersible isocyanate yielding coatings with good film performance. Pigmented coatings based on the FEVE dispersions offered excellent weatherability, high gloss, and excellent water resistance, properties equivalent to those from solvent-based FEVE coatings.

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