

Acrylate-Vinylidene Chloride Copolymers Derived from Corresponding Water-Borne Latexes: Influence of Acrylate Units on their Potential as Heavy-Duty Anticorrosive Coating Materials

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ABSTRACT: A series of aqueous latexes with solid contents of 56%–59% were synthesized by binary emulsion copolymerization of vinylidene chloride (VDC) with an acrylate, namely methyl acrylate (MA), ethyl acrylate (EA), butyl acrylate (BA), hexyl acrylate (HA), or 2-ethylhexyl acrylate (EHA). Differential scanning calorimetry (DSC) and Fourier-transform infrared (FTIR) spectroscopy showed that the acrylate units with short ester side-chains, such as MA and EA, made the copolymers hard and the crystallization tendency of their PVDC segments was reduced. Hydrophobic acrylates with relatively long ester groups, such as HA and EHA, gave flexible copolymers, and favored the crystallization of their PVDC segments. BA endowed the copolymers with medium flexibility and crystallization tendency. As coating materials, the copolymers bearing MA and EA adhered poorly to the tinplate before or after 100 hr of salt-spray corrosion, whereas those bearing BA, HA, or EHA showed good adhesion to tinplate when they had little or no crystallinity. After 100 hr of salt-spray corrosion, only BA–VDC80, containing 80% VDC, retained both excellent adhesion to metal and excellent barrier performance. Further study demonstrated that BA–VDC80 could protect tinplate from rusting for at least 250 hr under harsh salt-spray corrosion. Scanning electron microscopy, FTIR-attenuated total reflectance spectroscopy and DSC were used to evaluate the corroded BA–VDC80 film. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40192.

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INTRODUCTION

In high-humidity or underwater environments, heavy-duty anti-corrosive coating materials are required for metal protection.¹ Normally, these heavy-duty anticorrosive coating materials need at least two characteristics. One is good barrier properties against corrosive substances.^{2,3} The other is tight adhesion to metal substrates,^{4–6} because sufficient adhesion can protect the substrate more effectively, especially under humid conditions, where water can make the adhesion lose efficacy. Furthermore, occasional scratches and abrasions on the coating are normally unavoidable, and tight adhesion can prevent or retard the coating from peeling off the metal surface.

Water-borne coating materials have attracted great interest in both academic and industrial research because of the increasing requirements for environmental protection.^{7–14} However, water-based coating materials usually exhibit poorer protection performances than their corresponding solvent-based ones.¹⁵ Tech-

nological advances have produced water-borne epoxy resins with high performances, comparable to those of their solvent-borne counterparts.¹⁶

Aqueous latexes of poly(vinylidene chloride) (PVDC) or its copolymers can be synthesized by emulsion polymerization,^{17–20} and they are much cheaper than other water-borne coating materials applicable in heavy-duty anticorrosion, such as epoxide resins. PVDC films have excellent barrier properties,^{20–23} better than those of nylon, ethylene vinyl alcohol, poly(ethylene terephthalate), and low-density polyethylene.²³ However, its adhesion to metal is very poor. Moreover, PVDC is unstable and poor in film formation.²⁴ PVDC itself, therefore, cannot act as a heavy-duty anticorrosive coating material. To date, studies of copolymer latexes of vinylidene chloride (VDC) with (meth)acrylate, acrylonitrile, or vinyl chloride have focused on improving film formation and the stability of the formed film.^{25,26} Their target applications are as coatings for paper, fibers, or packaging.^{27–31} Certain patents^{32,33} have claimed that the

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cheaper and environmentally benign acrylate–VDC copolymer latexes could be used as coating materials to protect metals; however, how the type and content of the acrylate units influenced the performance of the formed films were never addressed. In this study, with heavy-duty anticorrosion applications as the target, a series of acrylate–VDC copolymer latexes were prepared and used as coatings for tinplate. Their protection abilities were tested in high-humidity environments with salt. The influences of the content and type of acrylate unit in the copolymers on their protective performances were systematically studied.

EXPERIMENTAL

Materials

VDC was purchased from Tianjin Daguchem and distilled at 35°C before use. Methyl acrylate (MA, 98%), ethyl acrylate (EA, 98%), butyl acrylate (BA, 98%), ammonium persulfate (AR), sodium metabisulfite (AR), and ferrous sulfate (AR) were purchased from the Tianjin Kewei Chemical Company and used directly. Hexyl acrylate (HA, 95%) and 2-ethylhexyl acrylate (EHA, 98%) were purchased from Alfa Aesar and used directly. Acrylic acid (99.5%) was purchased from the Damao Chemical Reagent Factory and used directly. Commercially available emulsifiers, SGN-20 and SGN-30, a mixture of anionic and non-ionic surfactants, were purchased from the Tianjin Hezhongtai Company. BYK-348, used as an additive, was purchased from Altana.

Preparation of Latex by Emulsion Polymerization

A total of 86.7 g of a mixture of VDC, acrylate, and acrylic acid (3.3%) was added to 50 g of aqueous SGN-20 (3%) in a 250 mL round-bottomed flask under vigorous stirring at 5°C to form an emulsion. The mixture was stirred for 1 hr in a closed system sealed with a glass stopper in order to prevent VDC from volatilizing. The polymerization was performed in a 250 mL four-necked flask equipped with a Teflon mechanical stirrer, a constant-pressure dropping funnel, a reflux condenser, and a thermometer, under a nitrogen atmosphere. Aqueous SGN-30 (15.4%; 11 g) was first added, and then half of an initiating system composed of 3.3 g of aqueous $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (9.1%), 3.3 g of aqueous $\text{Na}_2\text{S}_2\text{O}_5$ (9.1%), and 1.0 g of aqueous $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (0.23%) was introduced. The prepared emulsion solution was then added dropwise to the reactor at a constant rate for 2.5 hr at 30°C. After introduction of all the emulsion solution, polymerization was performed at 30°C for 4 hr. The other half of the initiating system was then added and polymerization was carried out at 40°C for 2 hr to complete the reaction. The solid content of the mixture was determined according to ASTM D1489.³⁴ Without filtration the emulsions were directly taken for the characterizations.

Preparation of Coating Film

BYK-348 (about 1%) was added to the latex solution under vigorous stirring for 30 min to improve substrate wetting. After filtering with a 0.125 mm fiber mesh, the mixture was centrifuged at 3000 rpm for 10 min to remove bubbles. A wet film of the latex, of thickness 500 μm , was cast on a glass panel using a mold. A wet film of the latex, of thickness 150 μm , was cast with a mold on a tinplate sheet abraded with 240-grit silicon

carbide paper in order to eliminate mechanical interlocking effects. The periphery of the tinplate was also coated with latex. Because of the different minimum film formation temperatures of these latexes, the coating films were placed in an oven at 60°C for 0.5 hr, and then dried at room temperature for 48 hr. The films were put into the oven at 60°C for 4 hr before determination of their properties. Dry-coated films of thickness $150 \pm 5 \mu\text{m}$ were made on glass panels, and of thickness $50 \pm 2 \mu\text{m}$ on tinplate sheets.

Characterization

The apparent viscosity was measured at room temperature using a rotary viscometer (NDJ-79). The latex particle diameter was measured using a Malvern Mastersizer 2000. Gel permeation chromatography (GPC) of the samples was carried out using a Viscotek GPC270 system. Freshly distilled tetrahydrofuran was filtered through membrane with an average pore size of 0.22 μm and used as an eluent at 30°C. The flow rate was set to be 1.0 mL min^{-1} . ^1H NMR spectra were recorded on Bruker AVANCE III 400M spectrometer operated at 400 MHz. The chemical shifts are given in parts per million (ppm). Fourier-transform infrared attenuated total reflectance spectroscopy (FTIR-ATR; Shimadzu FTIR-8400S, Japan) was used to examine the dry films. Scanning electron microscopy (SEM; Philips XL-30) was used to observe the film/tinplate interface. Differential scanning calorimetry (DSC) measurements were carried out using a PerkinElmer DSC8000 in the temperature range -40°C to 180°C at a heating rate of $20^\circ\text{C}/\text{min}$. The glass-transition temperature (T_g) was determined as the median of the glass-transition range of the second heating process. The oxygen gas transmission rates (OGTRs) of the films were measured at room temperature and 23% relative humidity, using a Systech Illinois Model 8001. The water vapor transmission rates (WVTRs) of the films were measured at 37.8°C and 90% relative humidity, using a Systech Illinois Model 7002. The experiments lasted for 24 hr. The films were cut into 33×33 mm specimens before use. Anticorrosion measurements were performed on the coating films in a salt-spray testing chamber (Q-FOG Cyclic Corrosion Tester) with 5% aqueous NaCl at 35°C , according to ASTM B117-07.³⁵ The adhesion strength of the coating to the tinplate was measured using the cross-hatch tape test, according to ASTM D3359-08.³⁶ The coating adhered to the tinplate in 1 cm^2 zone was cut into 100 grids. A 3M Tape (width 25 mm) was adhered to the grids, and then removed for observation of the damaged grids in each sample. The adhesion strength was divided into six grades, that is, 5B, 4B, 3B, 2B, 1B, and 0, representing peeling areas of 0, 5%, 5%–15%, 15%–35%, 35%–65%, and $>65\%$, respectively.³⁶

RESULTS AND DISCUSSION

Properties of Latexes

Binary emulsion copolymerization of the acrylate and VDC was used for preparing the acrylate–VDC latexes. In order to study the influences of the content and type of acrylate unit in the copolymers on their protective performances for metals, different acrylates, namely MA, EA, BA, HA, and EHA, were each copolymerized with VDC. The polymerization yields in all cases were more than 96%, and the solid contents were in the range 56%–59% (Table S1, Supporting Information). Except in the

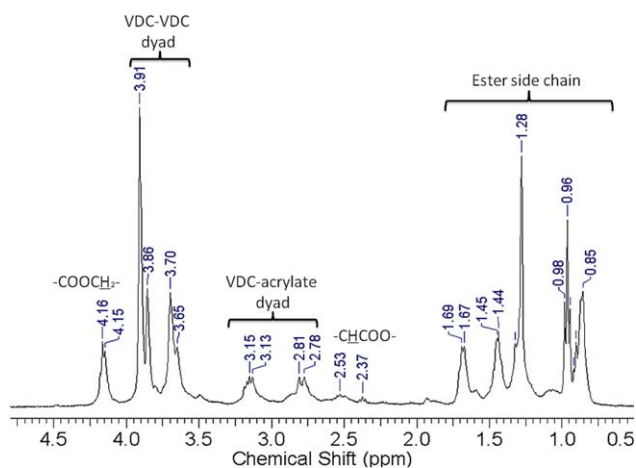


Figure 1. Typical ^1H NMR spectrum of acrylate-VDC copolymer (EHA-VDC70 copolymer as the representative). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

case of the MA-VDC latex, the latexes with VDC contents of 90% (abbreviated as acrylate-VDC90) were unstable and coagulated during storage. Even for the MA-VDC latexes, raising the VDC content above 90% led to instability. The polymerization conditions adopted were therefore such that the VDC content was normally controlled to be <90%. Although the latex solutions had solid contents higher than 56%, they were not viscous (<30 mPa s; Table S1, Supporting Information). Moreover, the average diameters of the latex particles in all the products were in the range 104–130 nm, similar to those reported by Kodani.²⁵ GPC characterization showed that the molecular weights of all the samples were more than 10^5 (Table S1, Supporting Information).

^1H NMR was attempted to characterize the obtained acrylate-VDC copolymers. The solubility of these copolymers, especially the copolymers with higher VDC content, was poor in the normal deuterated solvents, such as CDCl_3 , d_6 -DMSO, d_6 -acetone, and d_4 -methanol. Thus, it was difficult to characterize all the samples by NMR, and only the representative copolymers that had certain solubility in CDCl_3 were characterized by ^1H NMR (Figure 1). The signals from both VDC and acrylate units exist in the spectrum. Besides the big quantity of VDC-VDC dyad (3.5–3.9 ppm), VDC-acrylate dyad (2.7–3.3 ppm) can also be seen clearly,³⁷ verifying that the acrylate-VDC copolymers are successfully prepared.

Properties of Coating Materials

The copolymers were examined using DSC, from which T_g and the melting temperature could be obtained (Figure S1 and Table S2, Supporting Information). A glass transition was observed for all the samples, whereas obvious melting peaks were seen only for certain copolymers with high VDC contents, such as BA-VDC90, HA-VDC90, and EHA-VDC90. Figure 2 shows that the copolymers with acrylate units with shorter ester side-chains usually have higher T_g s. When the VDC content is in the range 65%–90%, reducing the VDC content leads to increased T_g values for MA-VDC and EA-VDC, but T_g decreases for HA-VDC and EHA-VDC. For BA-VDC, a maximum T_g

appears at ca. 70% VDC content. The variations in T_g are similar to those reported by Penzel,²⁰ Kodani,²⁵ and Powell.³⁸ When the VDC contents in the copolymers are the same, the T_g values of the copolymers are in the ordering of MA-VDC > EA-VDC > BA-VDC > HA-VDC \geq EHA-VDC. It was known that the acrylate units in the copolymer chains affected the T_g from two aspects. One is the polar interactions between VDC and acrylic ester units, which lead to the stiffening of the polymer chains and thus to an increase in T_g .³⁹ The other is the plasticizing effect that results in the decrease of T_g .⁴⁰ Among these five acrylate monomers, the longer the hydrophobic ester side-chain, the stronger is the plasticizing effect. Since the ester side-chain of MA unit is very short, its plasticizing effect is very weak. The polar interactions between these MA units and VDC segments are therefore dominant, resulting in an increase of T_g of the copolymers. Furthermore, more MA units also imply more polar interaction sites among the polymer chains, which lead to the T_g increase on increasing the MA content. Increasing the length of the ester side-chain of the acrylate will enhance the plasticizing effect; therefore, the copolymers with longer side-chained acrylate units have lower T_g when the VDC content in the copolymer is the same. Moreover, in the copolymers with long ester side-chained acrylate units, such as HA and EHA, the plasticizing effect surpasses the polar interaction force, thus, resulting in the T_g decrease on increasing the acrylate content. The competing of plasticizing effect and polar interaction in the BA-VDC copolymers leads to the appearance of a maximum T_g at certain BA content.

FTIR is a sensitive method for detecting crystallization in acrylate-VDC copolymers.^{20,25,26} In the FTIR of pure PVDC, two absorption bands at ca. 1048 and 1075 cm^{-1} are thought to be related to crystalline and amorphous PVDC segments, respectively.²⁴ Figure 3 shows typical FTIR-ATR spectra of BA-VDC copolymers. The copolymers with VDC contents of 90%–80% have a doublet peak at around 1042 and 1067 cm^{-1} . Compared with pure PVDC, the wavenumbers of this doublet peak in BA-VDC copolymers shift a little, which can be attributed to the change in the circumstance molecular interaction. It can therefore be concluded that BA-VDC copolymers with VDC contents $\geq 80\%$ are semicrystalline. As the VDC content decreases,

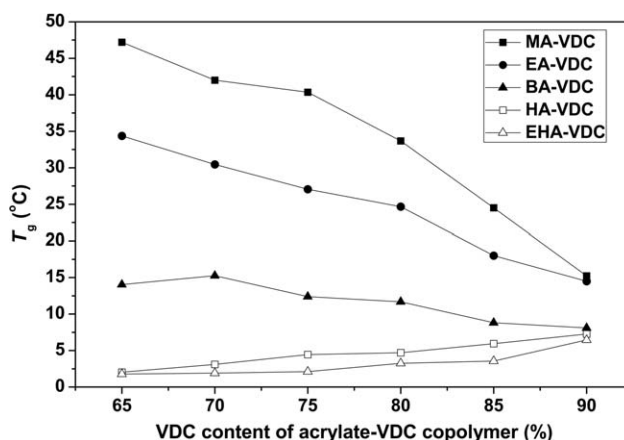


Figure 2. Relationship between compositions of acrylate-VDC copolymers and their T_g values.

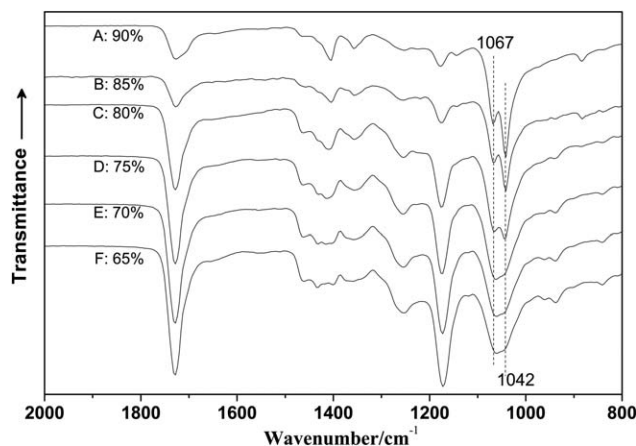


Figure 3. FTIR spectra of BA-VDC films with VDC contents of (A) 90%, (B) 85%, (C) 80%, (D) 75%, (E) 70%, and (F) 65%.

the intensity of the peak at 1042 cm^{-1} decreases, indicating a reduction in crystallinity. When the VDC content is lowered to 75% or less, the doublet peak is replaced by a single peak at 1067 cm^{-1} , indicating that the copolymers become amorphous. A similar phenomenon can also be seen for other acrylate-VDC copolymers (Figure S2, Supporting Information). The difference among these copolymers is the lowest amount of the VDC moiety required for crystallization. Copolymers with acrylate units bearing shorter ester side-chains need higher VDC contents to become semicrystalline. The lowest VDC contents of the semicrystalline copolymers are around 90%, 85%, 80%, 75%, and 75% for MA-VDC, EA-VDC, BA-VDC, HA-VDC, and EHA-VDC, respectively. It can therefore be deduced that acrylate units with long hydrophobic ester side-chains are more favorable for crystallization of PVDC segments due to their good plasticizing effect.

Anticorrosive Performances of Coating Materials

The potential application of these water-borne acrylate-VDC latexes as heavy-duty anticorrosive coating materials was tested. We evaluated the anticorrosive performance from two aspects. One was the adhesion of the acrylate-VDC coating to the metal before and after being incubated in a salt-spray testing chamber. The other was the barrier properties of the coating, determined from the corrosion of the metal surface after incubation for a certain time in a salt-spray testing chamber.

Tinplate coated with a dry film of thickness $50\text{ }\mu\text{m}$ was used for the anticorrosion tests. The adhesion of the coating to the tinplate was measured using the cross-hatch tape test, according to ASTM D3359-08.³⁶ The higher the adhesion grade, the stronger is the adhesion between the metal and the coating materials. Figure 4 shows the initial adhesion of these acrylate-VDC coatings to tinplate. All the MA-VDC coatings have nearly no adhesion to tinplate. The adhesion of the EA-VDC coatings to tinplate increases with decreasing of VDC content, and the highest grade, 5B, is only achieved by EA-VDC65. In contrast, the BA-VDC, HA-VDC, and EHA-VDC coatings have excellent

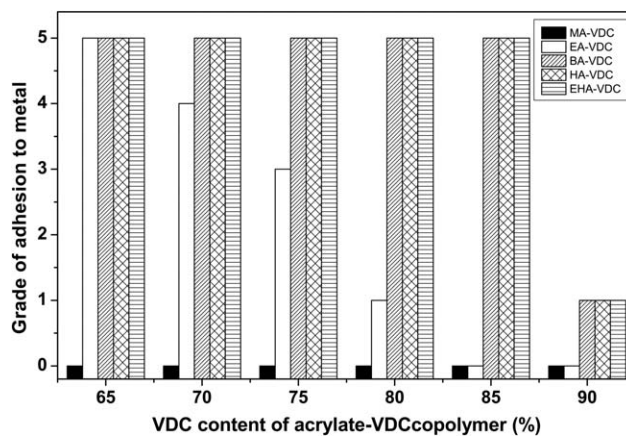


Figure 4. Initial adhesion of acrylate-VDC coatings to tinplate.

adhesion to tinplate when the VDC content is within the wide range 65%–85%.

After being corroded by salt-spray according to ASTM B117-07 for 100 hr,³⁵ the adhesion of these acrylate-VDC coatings to tinplate was measured again (Figure 5). Similar to the MA-VDC coatings, all the EA-VDC coatings adhere poorly to tinplate. The HA-VDC and EHA-VDC coatings can only maintain their good adhesion when the copolymers have a relatively low VDC content (65%–75%). Compared with the other coatings, the BA-VDC coatings maintain good adhesion over a wider range of VDC contents. At a VDC content of 85%, its adhesion grade decreases from 5B to 3B, unlike the others, whose adhesion grades fall to 0. In the VDC content range 65%–80%, the adhesion grades of the BA-VDC coatings are still the highest, grade 5B. It can therefore be concluded that the incorporation of acrylate units bearing a relatively long and hydrophobic ester side-chain into the PVDC main chains can effectively enhance the adhesion of coatings to metal when the content of acrylate units reaches a certain extent. Moreover, the intermediate BA unit is more efficient than the other acrylates, bearing longer or shorter side-chains, in increasing the adhesion of coatings to metal. Why do the different acrylate units endow the acrylate-VDC coating films so different adhesion property? This is

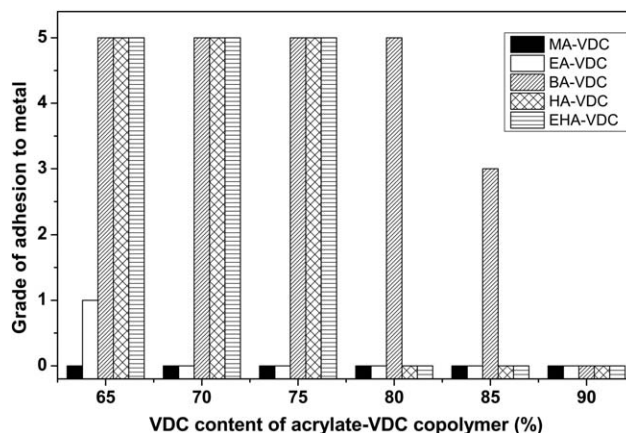


Figure 5. Adhesion of acrylate-VDC coatings to tinplate after being corroded in salt-spray chamber for 100 hr.

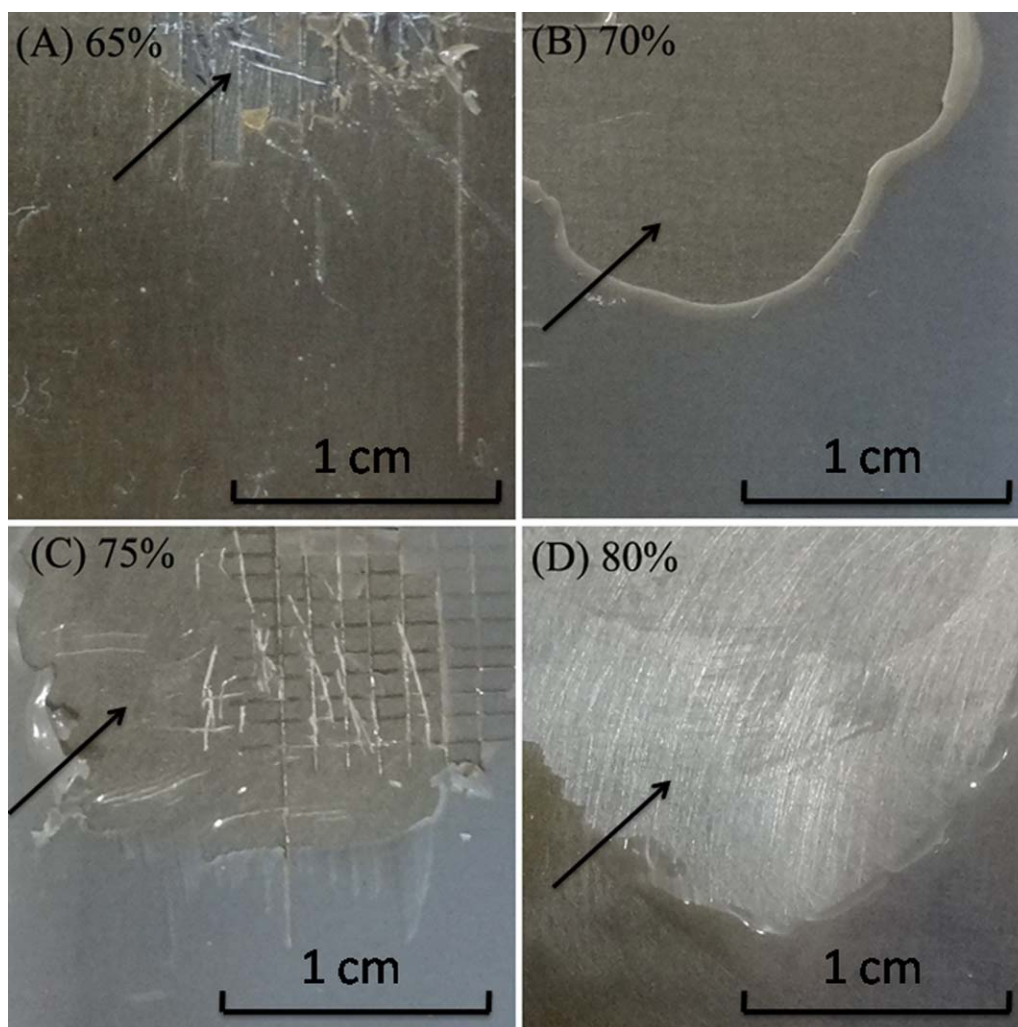


Figure 6. Typical photographs of tinplate surfaces protected by BA-VDC coatings with excellent adhesion after corrosion in salt-spray chamber for 100 hr; VDC contents of the copolymer are (A) 65%, (B) 70%, (C) 75%, and (D) 80% (the zones indicated by the arrows are the tinplate surfaces where the BA-VDC coating materials were peeled off after the corrosion tests). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

tentatively discussed as follows: it is known that the adhesion of PVDC film to metals is very poor.²³ The introduction of the ester units into the coating films helps to their interaction with the metal surface through the weak chelating of ester groups with metals. Moreover, in all these acrylate-VDC copolymers there exist ca. 3.3% carboxylic acid groups. Without this small amount of carboxylic acid groups, all the acrylate-VDC coating films show poor adhesion to metal. Therefore, it can be deduced that these carboxylic acid groups are mainly responsible for the good adhesion. For the effective interaction between the coating films and metal, it is important for these carboxylic acid and ester groups to segregate efficiently into the interface between coating film and metal. However, two factors disfavor their efficient segregation. One is the strong polar interactions among polymer chains, which usually lead to the higher T_g . The other is the crystallization of the PVDC segments, which result in the physical crosslinking of polymer chains and thus restrict the motions of the functional groups. The higher the degree of crystallization, the less the motions of the functional

groups. As for MA-VDC and EA-VDC copolymers, their poor adhesion to tinplate can be attributed to their stronger polar interactions among polymer chains, which stiffen the polymer chains, and restrict the segregations of the carboxylic acid and ester groups. With respect to the BA-VDC, HA-VDC, and EHA-VDC copolymers, the acrylate units with longer hydrophobic side-chains have good plasticizing effect, favoring the segregation of carboxylic acid and ester groups into the interface. Among the BA-VDC, HA-VDC, and EHA-VDC copolymers the polar interactions are also weak. Therefore, such copolymers with little or no crystallinity show better adhesion to tinplate.

The coatings with excellent adhesion to tinplate after 100 hr of salt-spray corrosion were partially peeled off from the tinplate surface. Typical photographs of tinplate surfaces protected by BA-VDC coatings with 65%–80% VDC are shown in Figure 6. Unlike the tinplate covered with BA-VDC80, the tinplates covered with BA-VDC65, BA-VDC70, and BA-VDC75 lose their metallic luster after 100 hr of salt-spray corrosion. The tinplates

Table I. OGTRs and WVTRs of Acrylate–VDC Coatings with Excellent Adhesion to Tinplate

Entry	Acrylate–VDC coating	OGTR (mL/m ² /day)	WVTR (g/m ² /day)
1	BA–VDC80	24.2	2.66
2	BA–VDC75	50.0	4.61
3	BA–VDC70	66.2	8.42
4	BA–VDC65	112	12.1
5	HA–VDC75	59.1	6.28
6	EHA–VDC75	65.2	4.20

covered with HA–VDC and EHA–VDC with 65%–75% VDC are not glossy either. Among these acrylate–VDC coatings, only BA–VDC80, therefore, possesses the potential to be used in heavy-duty anticorrosive applications, because of its excellent adhesion to metal and excellent barrier performance.

Why do these coatings with good adhesion to metal have such different protection capacities? This can be attributed to their different barrier properties against O₂ and water vapor (Table I). In the case of the BA–VDC coatings, the higher the VDC content in the copolymer, the better is the coating's barrier properties against O₂ and water. This can be ascribed to the excellent barrier properties of PVDC.²³ Therefore, because of the assurance of good adhesion to metal, coatings with higher VDC contents are preferred. At the same VDC content, the BA–VDC coating has a better O₂ barrier capacity than the HA–VDC and EHA–VDC coatings. This can be explained as follows: compared with the BA–VDC coatings, the HA–VDC and EHA–VDC coatings are more flexible. It is easier for more flexible coatings to form dynamic cavities that permit the passage of O₂. Unlike the order of the O₂ barrier capacities, the order of the water barrier capacities is EHA–VDC > BA–VDC > HA–VDC. This can be tentatively explained as follows. EHA–VDC is more flexible than BA–VDC, and this means that water molecules can pass through EHA–VDC faster than through BA–VDC. However, EHA–VDC is more hydrophobic than BA–VDC, which makes it more difficult for the polar water mole-

cules to pass through the EHA–VDC coating. The balance between these two opposing factors results in the order of the water barrier capacities being EHA–VDC > BA–VDC > HA–VDC.

The above results and discussion show that the content of acrylate units in the copolymers should be modulated in opposite ways to satisfy the requirements of adhesion and barrier performance, respectively. To satisfy both requirements simultaneously, the content of acrylate in the copolymer should be limited to a narrow range. This is why BA–VDC80 exhibits the best overall performance among these acrylate–VDC copolymers.

The anticorrosive performance of BA–VDC80, the best anticorrosive material among these acrylate–VDC coatings, was further studied. Figure 7 shows photographs of tinplate surfaces protected by BA–VDC80 coatings after different exposure times to salt-spray corrosion. The tinplate still keeps its metallic luster after 170 hr, and the adhesion to metal is still excellent, that is, grade 5B. After 250 hr of salt-spray corrosion, the tinplate loses its metallic luster, but it is not rusty. It should be mentioned here that even though the tinplate loses its metallic luster, the adhesion of the BA–VDC80 coating to the tinplate is still the best grade, 5B.

SEM was used to visualize the interface of the BA–VDC80 coating and tinplate before and after corroding in salt-spray for 250 hr (Figure 8). The interface can always be seen clearly before and after corrosion. In the interface zone, there are not only polymer joints, but also crevices. Before and after corrosion, the crevices do not change pronouncedly and the polymer joints can be clearly seen. This explains why the adhesion of the BA–VDC80 coating to tinplate is still very good after 250 hr of corrosion.

The thermal properties of the corroded BA–VDC80 film were analyzed using DSC (Figure 9). Compared with the one before corrosion, the DSC diagrams measured after corrosion for 170 and 250 hr do not show any obvious differences, and the *T_g* values are still around 11°C. This implies that the BA–VDC80 film is relatively stable under harsh salt-spray corrosion.

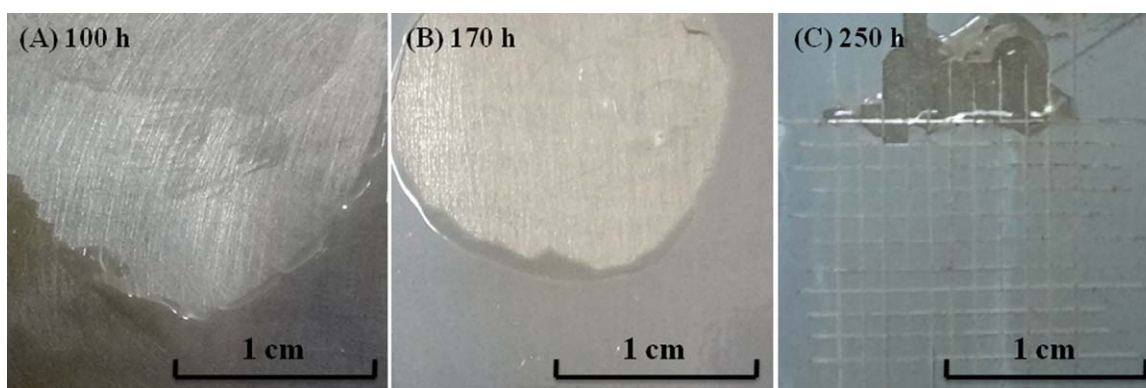


Figure 7. Typical photographs of tinplate surfaces protected by BA–VDC80 coating after corrosion in salt-spray chamber for (A) 100, (B) 170, and (C) 250 hr. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

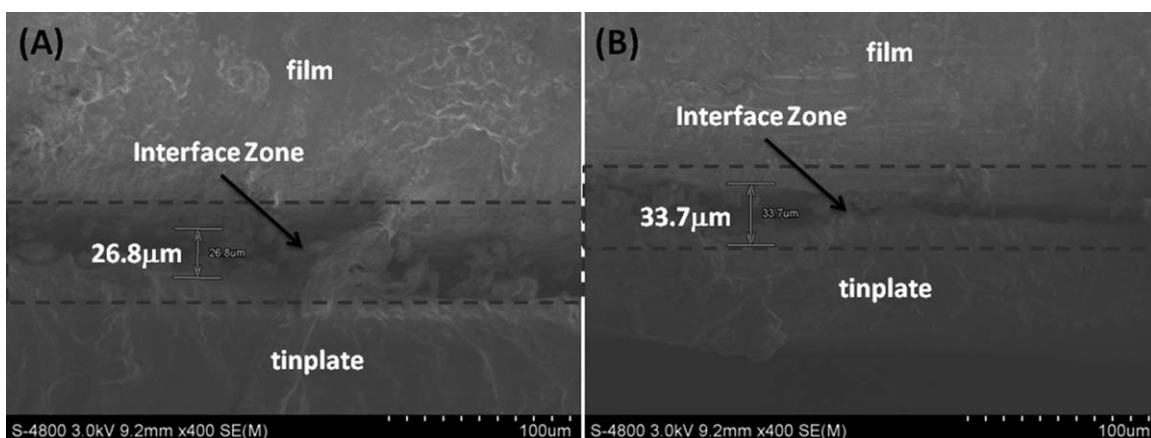


Figure 8. SEM images of lateral view of contact interface of BA-VDC80 coating film and tinplate surface (A) before and (B) after corrosion in salt-spray chamber for 250 hr.

FTIR-ATR was used to monitor the changes in the air- and tinplate-sides of the BA-VDC80 film during corrosion (Figure 10). We mainly compared the changes in the peaks at around 1720 cm^{-1} (ester carbonyl), 1640 cm^{-1} (COO^- carbonyl), and 1062 and 1040 cm^{-1} (crystallinity of PVDC segments). After 170 hr of corrosion, these typical peaks from the air-side surface of the film are almost unchanged, whereas the signal intensity at around 1640 cm^{-1} from the metal-side surface of the film increases a little. This means that after 170 hr of corrosion, the BA-VDC80 coating is still stable, but with a little metal-catalyzed hydrolysis of the metal-side surface. After 250 hr of corrosion, hydrolysis of both sides of the film becomes obvious, and the hydrolysis of the metal-side is more serious. Moreover, the peak at around 1042 cm^{-1} becomes stronger, whereas the one at around 1066 cm^{-1} becomes weaker, which indicates that the crystallinity of the coating becomes higher after 250 hr of corrosion.

CONCLUSIONS

A series of environmentally benign aqueous latexes of acrylate-VDC copolymers with VDC content in the range of 65%–90%

were synthesized by binary emulsion copolymerization. The properties of these latex solutions were (1) 56%–59% solid contents, (2) viscosity $<30\text{ mPa s}$, and (3) average latex particle diameters in the range 104–130 nm. Under the polymerization

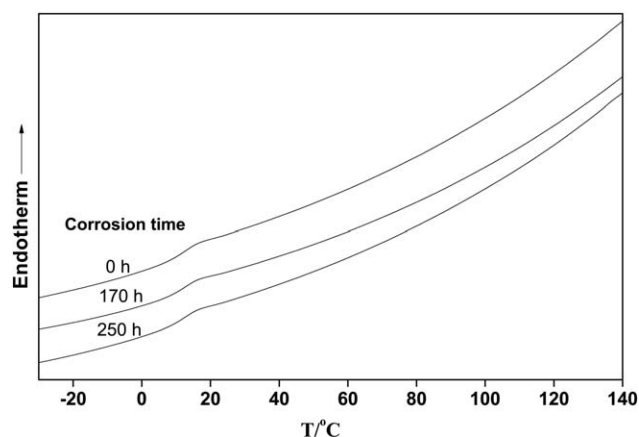


Figure 9. DSC diagrams of BA-VDC80 coating film before and after corrosion in salt-spray chamber for different times (second heating run).

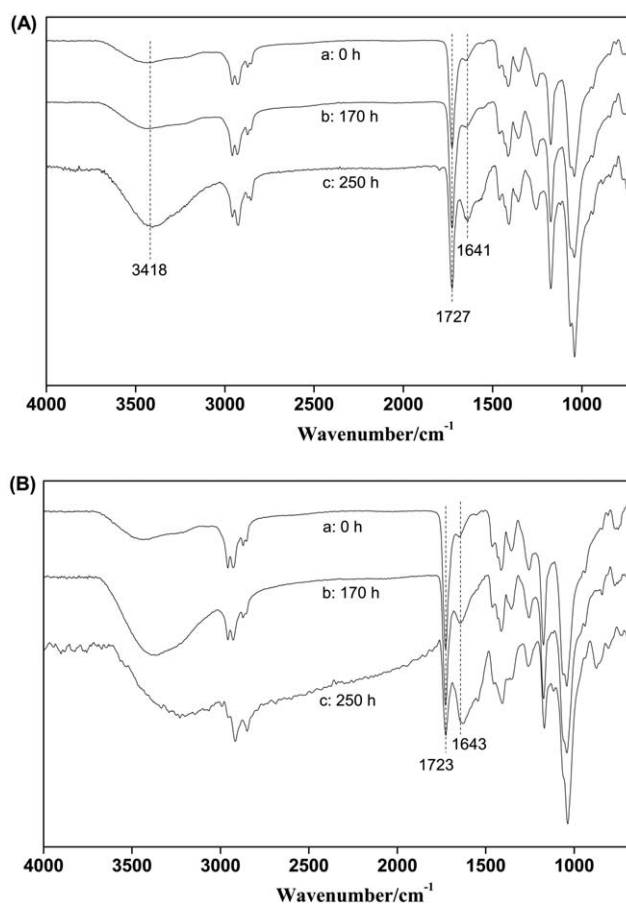


Figure 10. FTIR-ATR spectra of BA-VDC80 coating film before and after corrosion in salt-spray chamber for different times: (A) air side and (B) tinplate side.

conditions adopted here, the VDC content was usually controlled to <90% to obtain stable latexes.

With the same VDC contents, the acrylate-VDC copolymers bearing shorter ester side-chains had higher T_g , and the ordering was MA-VDC > EA-VDC > BA-VDC > HA-VDC \geq EHA-VDC. The acrylate units with longer ester side-chains favored the crystallization of PVDC segments of the acrylate-VDC copolymers. The lowest VDC contents of the semicrystalline copolymers are around 90%, 85%, 80%, 75%, and 75% for MA-VDC, EA-VDC, BA-VDC, HA-VDC, and EHA-VDC, respectively.

MA-VDC and EA-VDC coatings films without crystallinity, but with a T_g higher than room temperature had poor adhesion to tinplate before or after 100 hr salt-spray corrosion, whereas BA-VDC, HA-VDC, and EHA-VDC with little or no crystallinity and a T_g lower than room temperature had good adhesion to tinplate before and after 100 hr salt-spray corrosion. Among these acrylate-VDC copolymers with good adhesion to tinplate, BA-VDC80 that had more VDC segments and crystallinity exhibited better barrier performance after 100 hr salt-spray corrosion. The BA-VDC80 coating protected tinplate from loss of metallic luster for at least 170 hr. Although the tinplate lost its metallic luster after 250 hr of harsh corrosion, the surface of the tinplate was not rusty and the adhesion of the BA-VDC80 coating to the tinplate was still excellent. The thermal properties of the BA-VDC80 coating did not change obviously after 250 hr of corrosion, but hydrolysis of both sides of the film were obvious, and the crystallinity of the coating became higher. Among these acrylate-VDC coatings, BA-VDC80 exhibited the best potential for use in heavy-duty anticorrosive applications, because it has both excellent adhesions to metal and excellent barrier performance.

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