# Adhesive Properties onto Galvanized Steel Plates of Grafted Poly(vinylidene fluoride) Powders with Phosphonated Acrylates

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ABSTRACT: Hydrophilic fluoropolymers were obtained by grafting phosphonated monomers onto activated poly(vinylidene fluoride) (PVDF). By using an ozonization technique, dialkylperoxide and hydroperoxide groups were formed onto PVDF which may be decomposed thermally in a subsequent step to initiate graft copolymerization. By using an iodometric titration technique, the effect of ozone oxidation time and temperature on the concentration of peroxides was studied. However, degradation was observed by viscosimetry and FTIR for the hardest ozonization conditions. An effect of the grafting conditions (monomer concentration and monomer end groups) on the degree of grafting was determined and diester-acrylated phosphonate is grafted at a higher rate than are the homologous acid derivatives. Adhesion of the graft copolymers applied to galvanized steel substrates was studied. The experiments clearly show stronger adhesive properties of PVDF coatings containing phosphonic acid functions than those of the ones containing carboxylic acid functions. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 611–620, 1999

**Key words:** ozonization; graft copolymerization; phosphonic acid; steel substrates; poly(vinylidene fluoride); adhesion

# **INTRODUCTION**

One of the dominant themes in research on corrosion protective coatings is the maintenance of adhesion under environmental exposure. This main parameter generally depends on the chemistry of both the substrate and the coating.<sup>1</sup> Defects of organic coatings related to metal corrosion are always preceded by a significant reduction of adhesion as a consequence of water penetrating the coating/metal interface. Accordingly, it is im-

portant to use organic coating systems which present barrier properties and resist the interfacial action of water. In this article, poly(vinylidene fluoride) (PVDF) is used as an adhesive coating to protect galvanized steel plates from corrosion. Fluoropolymers are known for their barrier properties, their thermal and chemical resistance, in addition to their good weatherability. However, their hydrophobic surface properties are inconvenient to promote adhesion on surface steel substrates which are usually polar and hydrophilic.

Surface functionalization of a polymer is a convenient and effective process to improve its hydrophilicity. Graft copolymerization appears to be one of the most versatile techniques to provide

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appropriate functional groups to allow further modification and functionalization of the polymer.

Among the techniques including photo-,<sup>2</sup> radiation- (gamma rays,<sup>3-5</sup> electron beams<sup>6-8</sup>), and plasma-initiated<sup>9</sup> grafting, ozonization may be used. According to the literature, the treatment of a polymer by ozone yields to the formation of peroxides such as dialkylperoxides and hydroperoxides which are able to initiate radical polymerization.<sup>10-14</sup> No studies have been carried out for the hydrophilization of polymer substrates by means of ozone-induced grafting using phosphonated acrylates (dialkylphosphonate and phosphonic acid derivatives) as hydrophilic monomers.

In this article, we describe the activation by ozone of PVDF and the grafting of phosphonated acrylates. Finally, adhesive properties of the graft copolymers are evaluated.

### **EXPERIMENTAL**

#### **Materials**

Powdered PVDF Kynar 1000 LD was kindly supplied by Atochem (Serquigny, France). Galvanized steel plates (Zn 86 g/m<sup>2</sup>, Cr < 15 mg/m<sup>2</sup>) supplied by Cockerill Sambre (Liege, Belgium) were washed with diethyl oxide in an ultrasonic sound tray to remove grease and oil traces. Phosphonated acrylate monomers such as dimethyl(2-acryloxyethyl)phosphonate (DAP) and its phosphonic acids derivatives (DAP monoacid and DAP diacid) were obtained using a simple synthetic method starting from commercial compounds.<sup>15–18</sup> Acrylic acid (AAc) monomer stabilized with 0.02% hydroquinone monomethylether was used as obtained. All other chemicals were reagent grade and were used without further purification.

## **Ozone Treatment**

Ozone was evolved using a silent discharge through an oxygen current (Trailigaz Minibloc 76 Model). Powdered PVDF was activated through the ozone current  $(24 \text{ g/m}^3)$ . Exposure times and temperatures were varied from 6 to 24 h and from 30 to 60°C. The ozone-treated PVDF was stored at 4°C and then subjected to the determination of peroxide concentration, chain degradation, and graft polymerization.

#### **Determination of Peroxide Concentration**

The determination of dialkylperoxide and hydroperoxide groups onto PVDF was performed according to Wagner et al.'s method.<sup>19</sup> The ozonetreated PVDF (1.0 g) was immersed in decalin (30 mL) to swell. Sodium iodide, 10 mL, in an isopropyl alcohol solution (20 g/L) and 2 mL of acetic acid were added. Then, the solution was kept at 110°C for 10 min under argon bubbling. After cooling at room temperature, deionized water (10 mL) was added and the solution was titrated with N/100 sodium thiosulfate.

The content of peroxides (dialkylperoxide and hydroperoxide) was calculated from the amount of isolated  $I_2$  as follows<sup>15</sup>:

$$ROOH\,+\,2I^-\,+\,2H^+ \rightarrow ROH\,+\,H_2O\,+\,I_2$$

 $ROOR' + 2I^- + 2H^+ \rightarrow ROH + R'OH + I_2$ 

 $I_2 + I^- \leftrightarrows I_3^-$  Yellow coloration

$$I_3^- + 2 S_2 O_3^{2-} \rightarrow 3 I^- + S_4 O_6^{2-}$$

Peroxide concentration

$$= \frac{N_{\text{S}_2\text{O}_3^{2^-}} \times V_{\text{S}_2\text{O}_3^{2^-}}}{2 \times m_{\text{polymer}}} (\text{in mol/g})$$

with  $N_{S_2O_3}^{2-}$  the sodium thiosulfate normality,  $V_{S_2O_3}^{2-}$  the equilibrium sodium thiosulfate volume (L), and  $m_{\text{polymer}}$  the polymer weight titrated (g).

## **Determination of Degradation**

Simultaneously to the formation of peroxides, the ozonization of PVDF led to chain scission, which could be evaluated by a viscosimetric method in a dimethylformamide solution (5 g/L) at 25°C. Measurements were obtained with a capillar viscosimeter of a 0.58-mm diameter VCD AMTEC type. PVDF degradation could also be observed by infrared spectroscopy. Spectra were recorded on a Fourier transform spectrometer (Nicolet 510P Co.) from films obtained under pressure (170°C, 200 bars).

## Synthesis of Phosphonated Acrylate Monomers

Monomers of the following structures were synthesized using a relatively simple synthetic method:

$$DAP = DAP(1)$$

DAP monoacid = MDAP 28% (1)

+44% (2) +28% (3)

DAP diacid = DDAP 
$$(3)$$

DAP (1) was obtained by an esterification reaction between acryloyl chloride (1.58 mol) and dimethyl(2-hydroxyethyl)phosphonate (1.32 mol) in a dichloromethane solution (1300 mL) and in the presence of triethylamine (1.32 mol). 2,6-Di-*tert*butyl-4-methyl phenol (Ionol) was added to the mixture as a polymerization inhibitor. A white precipitate of  $Et_3N \cdot HCl$  was formed and filtered. Then, the resulting solution was evaporated and the monomer was distilled under a vacuum (85°C,  $2.10^{-3}$  mbar).<sup>16</sup>

The synthesis of phosphonic acid monomer derivatives (DAP monoacid and DAP diacid) was performed in two steps, that is, silylation of a dimethylphosphonate function by  $BrSi(CH_3)_3$  and then hydrolysis with an excess of methyl alcohol.<sup>15,17,18</sup> By using an equivalent amount of brominated silane and DAP (1), a mixture of three functional phosphonated groups was obtained (DAP monoacid MDAP). The relative contents of 1, 2, and 3 were determined by <sup>31</sup>P-NMR. More details will be given in a further publication.

However, with an excess of  $BrSi(CH_3)_3$  (1/2.1), dimethylphosphonate was converted quantitatively to phosphonic diacid (DAP diacid **3**). In any case, the reaction was performed under nitrogen bubbling at room temperature.  $BrSi(CH_3)_3$  was added dropwise to the stirred solution of DAP (0.1 mol) in 60 mL of dichloromethane  $CH_2Cl_2$ . After 2 h, the solvent was evaporated. Then, an excess of methyl alcohol (20 mL) was added and the solution was stirred for 2 h. The solvent was removed under a vacuum and monomers (MDAP and DDAP) were obtained as colorless liquids.

#### DAP

Yield 70%; <sup>1</sup>H-NMR (CDCl<sub>3</sub>,  $\delta$  ppm): 6.4–5.7 ppm (m, 3H, CH<sub>2</sub>=CH—), 4.2 (t<sub>d</sub>, 2H, —O—CH<sub>2</sub>—), 3.7 (d, 6H, —O—CH<sub>3</sub>, J = 11.2 Hz), 2.0 (t<sub>d</sub>, 2H, —P—CH<sub>2</sub>—); <sup>31</sup>P-NMR (DMSO-d<sub>6</sub>): single peak at 30 ppm corresponding to dimethylphosphonate function —P(O)(OMe)<sub>2</sub>; %P<sub>found</sub> 14.8 (%P<sub>theoretical</sub> 14.9%).

#### MDAP (DAP Monoacid)

#### DDAP (DAP Diacid)

Yield 100%; <sup>1</sup>H-NMR (CD<sub>3</sub>OCD<sub>3</sub>,  $\delta$  ppm): 10.8 (H acid), 6.4–5.7 ppm (m, 3H, CH<sub>2</sub>=CH—), 4.2 (t<sub>d</sub>, 2H, —O—CH<sub>2</sub>—), 2.1 (t<sub>d</sub>, 2H, —P—CH<sub>2</sub>—); <sup>31</sup>P-NMR (DMSO-*d*<sub>6</sub>): single peak at 21 ppm corresponding to phosphonic diacid function —P(O)(OH)<sub>2</sub>; %P<sub>found</sub> 17.5 (%P<sub>theoretical</sub> 17.3%).

# Graft Polymerization<sup>20-23</sup>

Powdered-oxidized PVDF was grafted with phosphonated acrylate monomers and AAc by the two following methods:

#### Method 1: Solution Polymerization

Ozone-oxidized PVDF (30 g) was accurately weighed out and placed in a glassy reactor with acrylate monomers (15 g) and dimethylformamide (200 mL). The reactor was then filled with nitrogen and placed in an oil bath controlled at 90°C for 24 h. The polymer was precipitated into ethyl alcohol to remove the homopolymers formed during grafting and then dried under reduced pressure for 48 h at 60°C.

According to Gineste's works,<sup>23</sup> ozone-oxidized PVDF (5.0 g) was placed in a test tube with AAc (1.5 g),  $CuSO_4$  as a homopolymerization inhibitor (0.1 mg), and deionized water (10 mL). After nitrogen bubbling, the test tube was placed into a water bath controlled at 60°C for 12 h. Then, the polymer was washed thoroughly with deionized water and soaked for 6 h in the same medium to extract the residual AAc and poly(acrylic acid) (PAAc). The powdered graft copolymer was subsequently washed with ethyl alcohol and dried under a vacuum to a constant mass.

#### Method 2: Bulk Polymerization (Brabender)

Oxidized PVDF (30.0 g) was mixed homogeneously with the different liquid monomers synthesized (15.0 g). Then, the mixture was placed into a mixing cell (Brabender Rheomix model) at 130°C with a rotating rate of 64 rd/min and polymerized in an air atmosphere for the prescribed time. The graft copolymer was dissolved in dimethylformamide and the homopolymer was removed by precipitation in ethyl alcohol. The polymer was filtered and dried under a vacuum for 48 h at  $60^{\circ}$ C.

### Determination of Grafting Degree (GD)

The GD was defined as the weight ratio of grafted monomer units to the graft copolymer. In the case of grafted phosphonated acrylate units, GD was determined from both elemental analysis and thermal gravimetric analysis (TGA). Thermal analyses were performed on a TA Instruments TGA51 apparatus (under nitrogen with a heating rate of 10°C/min).

#### **Elemental Analysis**

GD was calculated from the phosphorus content of the grafted PVDF ( $\ensuremath{\%P_{found}}\xspace$ ) as follows:

$$\text{GD} (\%) = \frac{\% P_{\text{found}}}{\% P_{\text{monomer}}} \times 100$$

where  $\%P_{\rm monomer}$  represents the phosphorus content in each monomer used.

# TGA

The GD was calculated from the percentage weight loss of grafted monomer units which have a different degradation temperature from the PVDF main chain. The amount of AAc grafted was determined by conductimetric titration<sup>15</sup>: A graft copolymer (PVDF-g-PAAc) was dissolved into dimethylformamide and titrated with a KOH/EtOH solution (N/100). The GD was calculated as follows:

$$\mathrm{GD}~(\%) = \frac{ \begin{matrix} C_{\mathrm{OH}^-}~(\mathrm{mol/L}) \\ \times ~V_{\mathrm{eq}}~(\mathrm{L}) \times M_{\mathrm{AAc}}~(\mathrm{g/mol}) \\ \hline 1000 \times m_{\mathrm{sample}}~(\mathrm{g}) \\ \end{matrix} \times 100$$

where  $C_{\rm OH^-}$ ,  $V_{\rm eq}$ ,  $M_{\rm AAc}$ , and  $m_{\rm sample}$  represent the KOH/EtOH solution concentration, the volume at equilibrium, the molecular weight of AAc (72 g/mol), and the weight of the graft copolymer titrated, respectively.

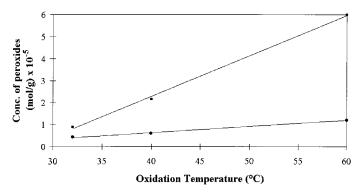
#### **Adhesive Measurements**

Graft copolymers were dissolved in a dimethylformamide/N-methylpyrrolidone solution (70/30 by weight) at 50°C. The obtained solutions of a 20 g/L copolymer concentration were deposited onto galvanized steel plates using a BarCoater (120  $\mu$ m Braive Instruments) and heated at 190°C to remove the solvents. The thickness of the films obtained was about 20–25  $\mu$ m. Coated steel plates were left at room temperature for 24 h and adhesive properties in dry and wet states were evaluated by the following methods:

# **Dry Adhesion**

*Crosscut Testing (ISO 2409 or NF T 30-038).* This test consisted of crosscutting the coating with a multiple knife and applying Scotch tape and then peeling it. Pieces of the coating were removed and the residual adhesive areas were quoted from zero to five. Zero notation corresponds to a perfect adhesive coating, whereas five means no residual adhesive areas.

Conical Mandrel Bend Testing (NF T 30-078). The coated steel plates were bent with a different curve radius along them. Coating failure was ob-



**Figure 1** Relationship between oxidation temperature and concentration of peroxides in PVDF oxidized with ozone for  $(\bullet)$  6 h and  $(\blacksquare)$  24 h.

Ozoi	ne Oxidation	$\begin{array}{c} \text{Concentration} \\ \text{of Peroxides} \\ (\times \ 10^{-5} \ \text{mol/g}) \end{array}$	
Time (h)	Temperature (°C)		
_	_	$0.05^{\mathrm{a}}$	
6	32	0.42	
24	32	0.90	
6	40	0.60	
24	40	2.10	
6	60	1.20	
24	60	6.00	

Table IConcentration of Peroxides Formed onPVDF at Various Ozone-Oxidation Times andTemperatures

<sup>a</sup> Virgin PVDF.

served and evaluated by the parameter T which must range from zero to three in the case of a PVDF coating. T is defined as follows:

#### $T = k \times \text{length of coating failure}$

k depends on both the curve radius and the coating thickness.

## Wet Adhesion

Water Immersion. The plates were immersed in water at 40°C for 24 h. Then, they were dried for 1 h and the adhesive properties were evaluated from the crosscut testing.

*Boiling Water Testing.* The plates were put into boiling water for 30 min, dried for 1 h, and then submitted to the crosscut testing.

# **RESULTS AND DISCUSSION**

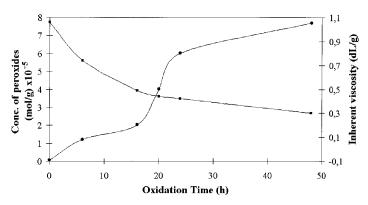
#### **PVDF** Oxidation Intensity

Ozone oxidation of powdered PVDF was carried out at various times and temperatures. Figure 1 shows the relationship between peroxide concentration and temperature for PVDF oxidized for 6 and 24 h. It is observed that the concentration of peroxides increases linearly with temperature and the longer the time the higher the concentration (Table I). The temperature of 60°C seems to be an efficient oxidation temperature. Figure 2 shows the dependence of peroxide concentration on the oxidation time for PVDF ozonized at 60°C. The concentration increases rapidly with time and finally levels off. This oxidation threshold can be explained by a loss of accessible ozone sites and also by a decomposition of peroxides and mainly hydroperoxides at high temperatures. This behavior was also observed in earlier studies on the PVDF ozone-oxidized at 60°C for 16 h.13 The authors demonstrated that only 10% of the titrated peroxides exhibited a hydroperoxide form. Similar results were also obtained on polyethylene powders ozonized at high temperatures.<sup>24,25</sup>

## **Degree of Degradation**

Table II shows a relationship between the inherent viscosity (and, consequently, the molecular weight) of PVDF and the ozone-oxidation time. As the ozone oxidation proceeds, the inherent viscosity decreases, indicating that the polymer chains were broken.

The curve in Figure 2 seems to reach a limit value which may be explained by the loss of sites enabling chain scission. According to the earlier



**Figure 2** Relationship between oxidation time and both  $(\bullet)$  concentration of peroxides and  $(\blacksquare)$  inherent viscosity of PVDF oxidized with ozone at 60°C.

Ozone-Oxidation Time at 60°C (h)	Inherent Viscosity $\eta_{inh}$ (dL/g)
Virgin PVDF	1.06
6	0.74
16	0.49
20	0.44
24	0.42
48	0.30

Table IIRelationship Between the InherentViscosity of Oxidized PVDF and theOzone-Oxidation Time

results, hydroperoxides were probably at the origin of this feature.

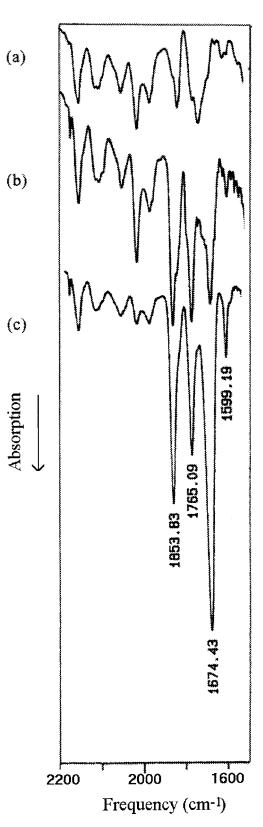
A compromise can be obtained between the oxidation intensity and the loss of molecular weight. The best conditions are 60°C for 20 h, corresponding to the coordinates of the curves' intersection point in Figure 2.

The degradation of PVDF can also be observed by infrared spectroscopy. IR spectra (Fig. 3) suggest the formation of acid fluoride end groups ( $\nu_{\rm C=O} = 1854 {\rm ~cm^{-1}}$ ) probably induced by a  $\beta$ -scission mechanism revealing a main-chain C—C breaking. These groups may subsequently be hydrolyzed to a carboxylic acid function in the presence of moisture during storage. The wavelength number may be shifted to 1750 cm<sup>-1</sup>.<sup>26</sup>

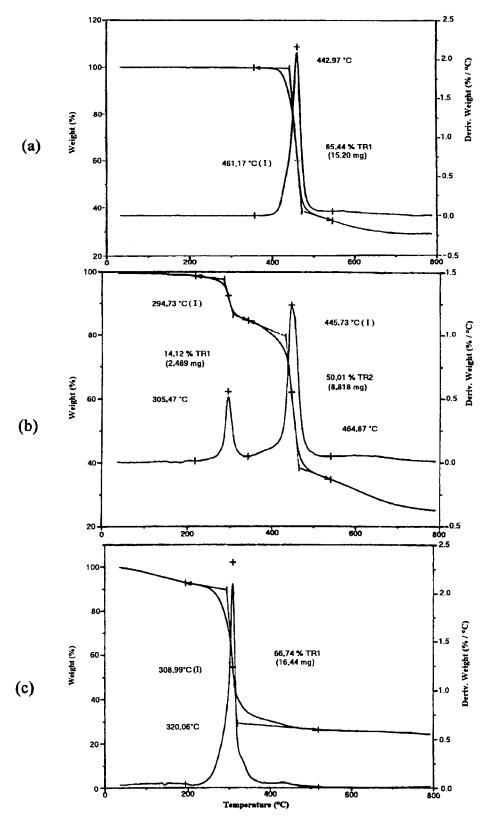
Besides, unsaturated functions such as —CH= CF— ( $\nu_{C=C} = 1674 \text{ cm}^{-1}$ ) and carbonyl groups such as —CF<sub>2</sub>—C(O)—CF<sub>2</sub>— ( $\nu_{C=O} = 1763 \text{ cm}^{-1}$ ) were formed onto ozonized PVDF, revealing a C—H bond scission. However, in all cases, the higher time and temperature, the greater the intensity of the absorption peak [Fig. 3(b,c)]. The formation of these degradation side products may be from the thermal decomposition of hydroperoxides formed onto PVDF during the ozone treatment.

### Effect of Polymerization Conditions on GD

The GD previously defined was calculated for the phosphonated monomers by both elemental analysis and TGA. Figure 4 shows TGA thermograms of (a) virgin PVDF, (b) PVDF grafted with DAP, and (c) DAP homopolymer abbreviated as PDAP. The overlapping of the three TGA thermograms shows that the degradation temperature of DAP-grafted units occurs at a lower value (close to 300°C) than that of PVDF units (around 450°C). The same results were obtained for PVDF grafted



**Figure 3** IR spectra of (a) virgin PVDF and PVDF ozonized at 60°C for (b) 6 h and for (c) 24 h.



**Figure 4** TGA thermograms of (a) virgin PVDF, (b) PVDF grafted with DAP, and (c) homopolymer PDAP.

	Graft Copolymerization		GD (%)	
No.	$\frac{Monomer/PVDF}{(GD_{theoretical})}$	Time (min)	Elemental Analysis	TGA
	DAP			
1	0.5/1 (33%)	60	15.3	16.4
2	0.5/1 (33%)	60	13.6	13.2
3	0.5/1 (33%)	90	15.7	15.2
4	0.5/1 (33%)	$24~\mathrm{h^a}$	14.6	14.1
	DAP monoacid			
5	0.05/1 (4.8%)	10	1.1	Not detected
6	0.1/1 (9%)	10	2.5	4.9
7	0.5/1 (33%)	10	25.8	26.5
8	0.5/1 (33%)	10	25.7	25.4
9	0.5/1 (33%)	90	26.9	27.6
10	0.5/1 (33%)	90	27.5	29.4
	DAP diacid			
11	0.5/1 (33%)	60	3.8	Not detected
12	0.5/1 (33%)	60	2.2	Not detected
13	AAc (23%)	$12 \ \mathrm{h^a}$	8% by conductimetric titration	Not performed

Table III Values of GD for the Different Graft Copolymers Synthesized

<sup>a</sup> Solution polymerization.

with phosphonic acid derivative monomers (MDAP and DDAP). Thus, the percentage weight loss observed at lower degradation temperatures give directly GD values.

Table III shows GD values when poly(vinylidene fluoride) oxidized with ozone for 24 h at 60°C was graft-copolymerized with DAP, DAP monoacid, and DAP diacid. Graftings were carried out at various monomer/PVDF weight ratios and different polymerization times. Both solution and bulk polymerizations were investigated.

The results obtained for DAP grafting (1-4)show no dependence of the GD on the polymerization time. A limiting value of around 15% was reached whatever the polymerization method used. Grafting of DAP monoacid (5-10) yields higher GD values than those of DAP-grafted PVDF. At a constant polymerization time, GD values increase with the monomer/PVDF weight ratio. These results suggest a better surrounding by the monomer of active sites produced thermally from peroxides, increasing the chance to initiate polymerization. GD values around 25% obtained for a 10- and 90-min polymerization times (7-10) indicate a rapid decomposition of peroxides at 130°C in the oxidized polymer (method 2) and, consequently, a high initiation rate. However, monomer diffusion appears to be a limiting kinetic factor in the polymerization propagation stage. Whatever the polymerization time, the GD has a limit value. This can also depend on the monomer tendency to react in radical polymerization. This could explain the weakest GD values obtained for DAP-grafted PVDF compared to DAP monoacid-grafted PVDF.

In any case, the results show a good reproducibility for bulk polymerization, and the GD values calculated from TGA and elemental analysis are similar. Therefore, TGA seems to be a good analytical technique to determine rapidly the GD.

Finally, DAP diacid grafting onto PVDF (11– 12) shows weak values of the GD even for a 60min polymerization time. Such an observation may be explained by taking into account the polycondensation of the functional group — $P(O)(OH)_2$ which leads to an increase of the monomer viscosity. The chance of monomer diffusion to the active sites formed onto PVDF was then reduced. So, to obtain high GD values, we suggest to graft DAP (diester phosphonate) first and then to modify the graft copolymers by a halogen silane agent.

#### Adhesive Properties

All the previous copolymers synthesized were coated onto steel plates and their adhesive prop-

Sample	Crosscut Testing (Cotation/5)	Conical Mandrel Bend Testing T Value	Water Immersion Testing (Cotation/5)	Boiling Water Testing (Cotation/5)
Virgin PVDF	5	>3	5	5
Ozone-oxidized PVDF	1–2	>3	5	5
PVDF paint without primer	5	>3	5	5
PVDF paint + primer	0	0	0	0
DAP-grafted PVDF 1-4	1 - 2	>3	1–2	5
MDAP-grafted PVDF 5–10	0	0	0	0
DDAP-grafted PVDF 11 and 12	0	>3	0	0

Table IVResults of Adhesion Tests of Grafted PVDF Coatings in Comparison with a PVDF PaintReference Coated With or Without Adhesion Primer

0, very good adhesive properties; 5, poor adhesive properties.

erties were investigated. A commercially available PVDF paint system, coated onto an anticorrosion-treated substrate, serves as a reference; in some cases, a universal primer was used to improve the coating adhesion. For each monomer family, adhesive results are represented by one mean value (Table IV).

The crosscut testing results show an improvement in the adhesive properties for the ozoneoxidized PVDF and all the graft copolymers synthesized, comparatively to the virgin PVDF and the PVDF paint coated without an adhesion primer (column 2). This fact may be easily explained by the hydrophilic functional groups introduced in PVDF.

The carbonyl group content in the ozone-oxidized PVDF sample is too low to give high adhesive coatings. The same remark can be made for DAP-grafted PVDF samples.

The best results were obtained when PVDF was graft-copolymerized with DAP monoacid and DAP diacid monomers. The highest polarity of acid groups compared to ester groups yields good adhesive properties. This fact was confirmed by the PAAc-grafted PVDF sample (Table V).

According to the literature, polar forces may be at the origin of the firm bonding observed at galvanized steel surfaces. But these molecular inter-

Table VComparison of Dry Adhesion of PAAc-<br/>Grafted PVDF and MDAP-Grafted PVDF

Copolymer	GD (%)	Crosscut Testing (Cotation/5)
PAAc-grafted PVDF MDAP-grafted PVDF	$8.0 \\ 2.5$	0-10

actions are also especially sensitive and attractive to water molecules.

As adhesion in the wet state is more important for corrosion protection, water immersion and boiling water testings were performed (columns 4 and 5). The results show an efficiency of the phosphonic acid groups in the adhesive bond to metal compared to the dialkylphosphonate group and the carboxylic acid group (Table VI). Therefore, phosphonic acid groups seem to present a high resistance to water disbondment.

# CONCLUSIONS

Grafting of phosphonated acrylates onto PVDF powders was studied using an ozone treatment to oxidize the polymer surface. Based on the above investigations, it can be concluded that

- 1. The concentration of peroxides created onto the oxidized PVDF increases with the ozone-oxidation time and temperature. In parallel, chain scission occurs and causes decrease of the molecular weight.
- 2. Grafting of acrylic monomer with dialkylphosphonate and phosphonic acid end groups enhances both the hydrophilicity and adhesive properties of PVDF applied on galvanized steel plates.
- 3. Adhesive bonds formed by phosphonic acid groups seem to be stronger and more resistant to dry and wet adhesions compared to dialkylphosphonate and carboxylic acid groups already known for their adhesive properties.<sup>5,6</sup>
- 4. Graft copolymers containing phosphonic

	GD	Water Immersion Testing	Boiling Water Testing
Copolymer	(%)	(Cotation/5)	(Cotation/5)
PAAc-grafted PVDF	8.0	5	5
DAP-grafted PVDF	15.3	1–2	5
MDAP-grafted PVDF	2.5	0	0

Table VIComparison of Wet Adhesion of PAAc-, DAP-, and MDAP-GraftedPVDF

acid functions applied onto washed galvanized steel plates exhibit the same adhesive properties as those of a PVDF paint coated with an adhesion primer applied onto a cleaned and anticorrosion-treated galvanized steel plates.

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