

# Chlorinated Poly(vinylidene Fluoride)

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## Synopsis

Chlorinated poly(vinylidene fluoride) (PVF<sub>2</sub>) was prepared by introducing chlorine gas into a CCl<sub>4</sub> suspension of PVF<sub>2</sub> at reflux temperature. Polymer crystallinity and softening point decrease, while solubility and adhesion increase with the degree of chlorination. In contrast to PVF<sub>2</sub>, the chlorinated polymer is soluble in low-boiling common organic solvents, such as acetone, methyl ethyl ketone, and 1,2-dimethoxyethane. Chlorinated PVF<sub>2</sub> is resistant to dehydrochlorination and is thermally more stable than PVF, chlorinated PVF, PVC, or chlorinated PVC. Chlorinated PVF<sub>2</sub> coatings on wood, prepared by solution casting at room temperature, show outstanding weathering resistance.

## INTRODUCTION

High molecular weight poly(vinylidene fluoride) (PVF<sub>2</sub>) has exceptionally good thermal stability, ultraviolet radiation resistance, chemical inertness, and flexibility.<sup>1</sup> These properties make the polymer an ideal candidate for many coating applications where extreme durability and high performance are required. Because the polymer is high melting and insoluble in common organic solvents, the preparation of coatings is often accomplished by applying a PVF<sub>2</sub> dispersion in a high temperature or latent solvent to the substrate and evaporating the solvent at 260°C.<sup>1</sup> Alternatively, finely dispersed PVF<sub>2</sub> can also be applied as a powder coating from a fluidized bed at 210–290°C.<sup>2</sup> If necessary, the poor adhesion of PVF<sub>2</sub> can be overcome by adding a polyacrylate to the fluoro-polymer–latent solvent dispersion.<sup>3</sup> However, none of the above coating techniques is applicable to heat-sensitive substrates, such as wood, cotton fabric, or plastics because of the high temperatures involved.

In order to improve upon the solubility of PVF<sub>2</sub>, Jackson and Stilmar prepared vinylidene fluoride–tetrafluoroethylene–vinylester terpolymers.<sup>4</sup> These materials were soluble in low-boiling ketone solvents and gave noncoalesced coatings upon evaporation of the solvent; to obtain a continuous, uniform surface, the coating had to be baked at 160–200°C.

Since in our earlier work we noticed that chlorination decreases the melting point and increases the solubility of the analogous poly(vinyl fluoride) (PVF),<sup>5</sup> we investigated the effect of chlorine substitution on the properties of PVF<sub>2</sub>. A brief description of the chlorination procedure has been reported in a patent.<sup>6</sup>

## EXPERIMENTAL

### Materials

The PVF<sub>2</sub> used in this study was obtained from the Borden Chemical Company, Monomer-Polymer Laboratories;  $\eta_{sp/c} = 1.72$  (*N,N*-dimethylacetamide, 110°C, 0.1 g/100 ml).

### Polymer Characterization

The degree of chlorination of PVF<sub>2</sub>, defined as the number of chlorine atoms in 100 monomer units, was determined from the chlorine analysis of the polymers. The following equation was used in the calculations:

$$\Phi = \frac{64.04 \%Cl}{35.5 - 0.345 \%Cl}$$

Reduced specific viscosities were measured in *N,N*-dimethylacetamide at 110°C and 0.1 g/100 ml polymer concentration.

Accelerated weathering tests were carried out in an Atlas twin-enclosed carbon arc Weather-O-Meter; cycle, 102 min; light, 18 min; light and water spray.

### Preparation of Chlorinated PVF<sub>2</sub>

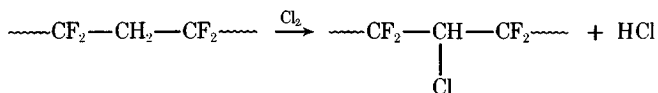
A typical polymer preparation was carried out as follows: A three-necked 500-ml flask equipped with stirrer, condenser, thermometer, and gas inlet tube was charged with 50 g PVF<sub>2</sub> and 150 ml CCl<sub>4</sub>. The dispersion was purged with nitrogen and heated to reflux. Chlorine gas was introduced at a rate of 170 ml/min while the flask was illuminated with a 275-W General Electric sunlamp at a distance of 5 cm. Chlorination was continued for 6 hr. At the end of this time, the flask was purged with nitrogen and the reaction product was poured into 1 liter methanol. The solid polymer was filtered, washed on the filter with methanol, and dried under vacuum at 70°C. The polymer yield was 54.30 g (Cl = 8.32%;  $\eta_{sp/c} = 1.55$  dl/g).

## RESULTS AND DISCUSSION

### Polymer Preparation

Chlorination experiments carried out under the reaction conditions described above are summarized in Table I and Figure 1.

The reaction involves the replacement of polymer hydrogen atoms by chlorine, and HCl is evolved:



The data show that initial rapid chlorination is followed by a slowing down of the reaction. After 6 hr, the degree of chlorination,  $\Phi$ , increases linearly with time. From solution viscosity data, it appears that the polymer does not degrade

TABLE I  
Chlorination of PVF<sub>2</sub><sup>a</sup>

Hours of chlorination	Cl, %	$\Phi^b$	$\eta_{sp}/c^c$
0	0	0	1.72
0.5	1.0	1.9	1.71
2	5.3	10.0	1.69
6	8.3	16.3	1.55
24	16.3	34.9	1.65
48	26.1	63.0	<sup>d</sup>

<sup>a</sup> 50 g PVF<sub>2</sub>, 150 ml CCl<sub>4</sub>, 76°C.

<sup>b</sup> Number of Cl atoms in 100 monomer units.

<sup>c</sup> *N,N*-Dimethylacetamide, 110°C, 0.1 g/100 ml.

<sup>d</sup> Incompletely soluble.

TABLE II  
Chlorination of PVF<sub>2</sub>, PVF, and PVC<sup>a</sup>

Polymer	Temperature, °C	Hours of chlorination	Cl, %	$\Phi^b$
PVF <sub>2</sub>	20–40	4	2.5	4.6
PVF <sub>2</sub>	76	6	12.2	25
PVF	20–50	4		59 <sup>c</sup>
PVF	76	1	16.3	25
PVC	20–40	4		59 <sup>c</sup>

<sup>a</sup> 10 g polymer, 150 ml of CCl<sub>4</sub>.

<sup>b</sup> Number of chlorine atoms in 100 monomer units.

<sup>c</sup> Data from Fig. 1 of ref. 5.

significantly during chlorination; but at very long reaction times crosslinking takes place.

The data presented in Table II compare qualitatively the rates of chlorination

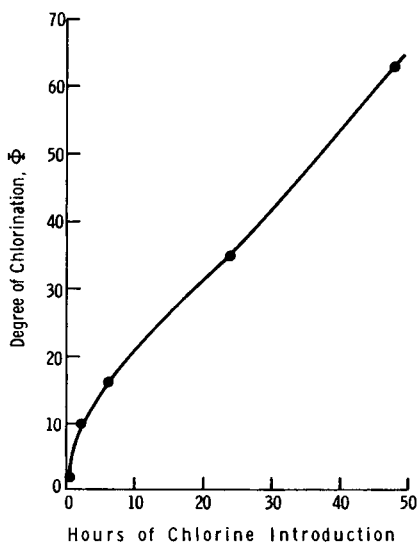


Fig. 1. Chlorination of PVF<sub>2</sub>.

of PVF<sub>2</sub>, PVF,<sup>5</sup> and PVC.<sup>5</sup> According to these results, PVF<sub>2</sub> reacts slower than either PVF or PVC. The lower reactivity of PVF<sub>2</sub> is due to the fact that it has fewer hydrogen atoms per monomer unit available for substitution and that the strongly electron-withdrawing CF<sub>2</sub> groups deactivate the methylene carbons toward electrophilic attack by the chlorine radical. The fact that PVF<sub>2</sub> reacts at all is somewhat surprising in view of the report that the analogous poly(vinylidene chloride) cannot be further chlorinated.<sup>7</sup>

## Polymer Properties

### *Solubility*

PVF<sub>2</sub> is soluble only in high-boiling polar solvents, such as *N,N*-dimethylacetamide, dimethyl sulfoxide, *N*-methylpyrrolidone,  $\gamma$ -butyrolactone, and cyclohexanone; it is insoluble in the low-boiling common organic solvents.<sup>8</sup> Chlorination increases the solubility and polymers containing more than 6 wt % chlorine are soluble in acetone, methyl ethyl ketone, and 1,2-dimethoxyethane (Table III). The increased solubility of chlorinated PVF<sub>2</sub> allows the preparation of 20 wt % solutions and the casting of films from the above solvents at room temperature.

### *Crystallinity*

Chlorination destroys the regularity of PVF<sub>2</sub> and, consequently, reduces crystallinity. As the degree of chlorination increases, the crystallinity of the polymers decreases. Polymers containing more than 8% chlorine appear to be amorphous. X-ray diffraction spectra of chlorinated PVF<sub>2</sub> are shown in Figure 2.

### *Softening Point*

Figure 3 shows the effect of chlorination on the softening point of PVF<sub>2</sub>. As expected, the softening point decreases with an increase in the chlorine content of the polymer because of reduced crystallinity. In this respect, PVF<sub>2</sub> behaves similarly to other crystalline polymers such as PVF<sup>5</sup> and polyethylene.<sup>9</sup>

TABLE III  
Some Properties of Chlorinated PVF<sub>2</sub>

Polymer		Solubility <sup>a</sup>	Adhesion to aluminum	Clarity % of haze <sup>d</sup>
Cl %	$\Phi$			
0	0	insoluble	poor <sup>b</sup>	75
1	1.9	insoluble	poor <sup>b</sup>	62
5.3	10.0	partially soluble	good <sup>c</sup>	48
8.3	16.3	soluble	good <sup>c</sup>	36
16.3	34.9	soluble	good <sup>c</sup>	34

<sup>a</sup> 0.1 g polymer, 1 ml acetone.

<sup>b</sup> Delaminates during molding.

<sup>c</sup> Passes cross-cut adhesive tape test.<sup>10</sup>

<sup>d</sup> 0.020-in.-thick sheet, ASTM D 1003-61.

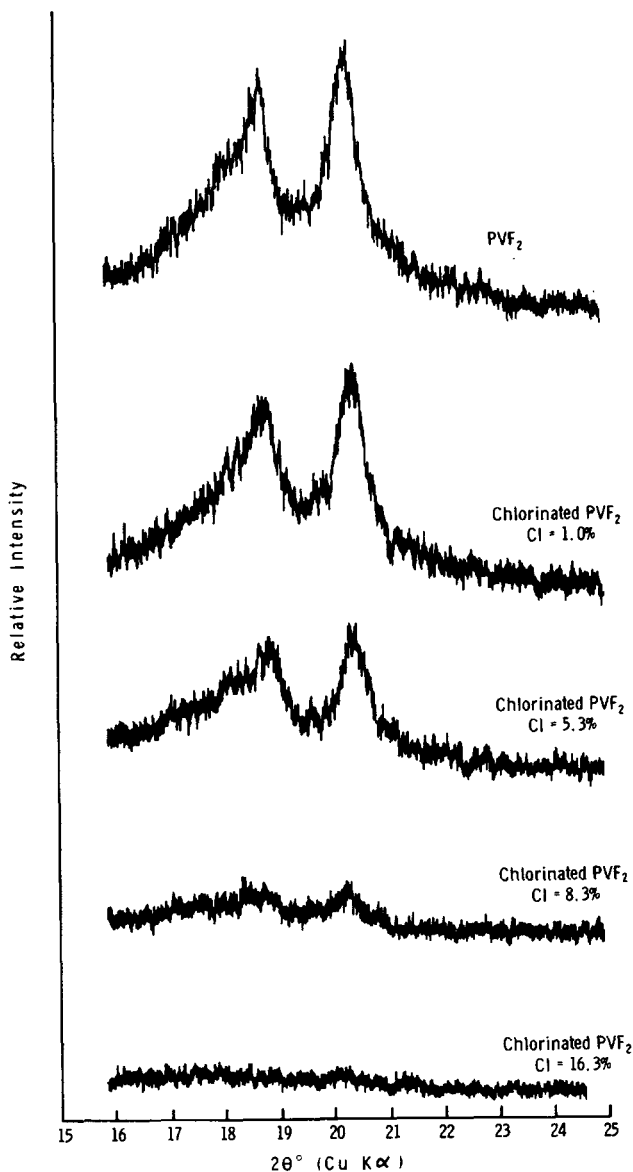


Fig. 2. X-ray diffraction spectra of PVF<sub>2</sub> and chlorinated PVF<sub>2</sub>.

### *Clarity of Molded Sheets*

Approximately 0.020-in.-thick sheets of chlorinated PVF<sub>2</sub> were compression molded at 188°C in a steel die and tested for clarity by ASTM D 1003-61. It was found that chlorinated PVF<sub>2</sub> is clearer than PVF<sub>2</sub>, and the clarity increases with the degree of chlorination. The increase in clarity is consistent with the reduced crystallinity of chlorinated PVF<sub>2</sub>. The results are summarized in Table III.

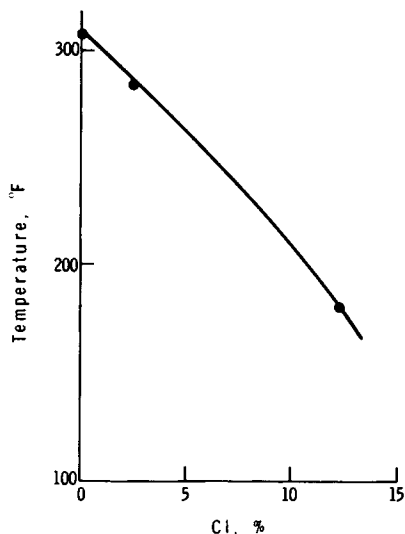


Fig. 3. Vicat softening point of chlorinated PVF<sub>2</sub>.

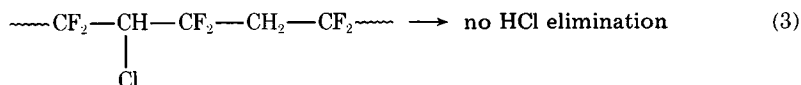
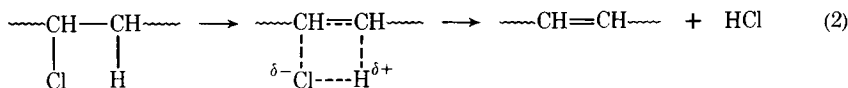
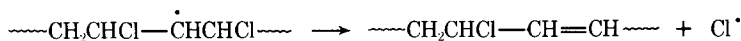
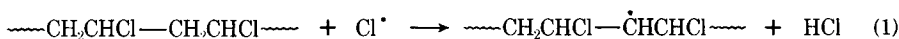
#### *Adhesion to Aluminum*

It was found that chlorinated PVF<sub>2</sub> shows better adhesion to aluminum than PVF<sub>2</sub>. This was demonstrated by placing the polymer between an aluminum plate and a steel plate and compression molding the assembly in a die at 188°C. The aluminum plate used in this operation was cleaned with acetone followed by boiling trichloroethylene and treated with a chromate etching solution; the steel plate was sprayed with a silicone mold release. After removal from the press, the chlorinated PVF<sub>2</sub> formed a uniform, strongly adhering film over the aluminum and could not be separated by either hand or by the cross-cut adhesive tape test.<sup>10</sup> PVF<sub>2</sub> molded under the same conditions shows no adherence to aluminum and separates easily when removed from the die. The results are summarized in Table III.

#### *Thermal Stability*

Compared to other polymers, many of the fluoropolymers, such as PVF<sub>2</sub>, poly(tetrafluoroethylene), and tetrafluoroethylene-hexafluoropropylene copolymer, are thermally very stable. The stability imparted by the fluorine substitution is believed to be caused by the high dissociation energy of the carbon-fluorine bond and by the high electronegativity of the fluorine atom which shields the carbon chains from attack.<sup>11</sup> On the other hand, most chlorine-containing polymers, such as PVC, poly(vinylidene chloride), etc., are relatively unstable and yield HCl upon degradation. The decomposition of PVC may occur either by a free radical,<sup>12</sup> [eq. (1)], or by an ionic<sup>13</sup> process [eq. (2)]. In both cases, the presence of hydrogen and chlorine atoms, situated on adjacent carbons, seems to be a prerequisite for facile HCl elimination. Since chlorinated PVF<sub>2</sub> does not satisfy this requirement, one would expect it to be resistant to dehydrochlori-

nation [eq. (3)]:



In agreement with this prediction, it was found that chlorinated PVF<sub>2</sub> sheets, compression molded at 188°C, do not discolor either during molding or when heated in air at 150°C for 18 hr. Under the same conditions, chlorinated PVF or chlorinated PVC dehydrohalogenate and discolor badly.

The exceptional thermal stability of chlorinated PVF<sub>2</sub> was also demonstrated by thermogravimetric analysis (Table IV). In these experiments, chlorinated PVF<sub>2</sub> appears to be only slightly less stable than PVF<sub>2</sub> and is far superior to PVF, chlorinated PVF, PVC, and chlorinated PVC. The slightly lower thermal stability of chlorinated PVF<sub>2</sub>, relative to PVF<sub>2</sub>, may be caused by small amounts of head-to-head units present in the starting PVF<sub>2</sub><sup>14</sup> giving rise to chlorinated

TABLE IV  
Thermogravimetric Analysis of Chlorinated PVF<sub>2</sub>, Chlorinated PVF, and Chlorinated PVC<sup>a</sup>

Polymer	Cl, %	Φ	Temperature at 10% wt loss, °C
PVF <sub>2</sub>	0	0	423
Chlorinated PVF <sub>2</sub>	1.0	1.9	421
Chlorinated PVF <sub>2</sub>	2.5	4.6	404
Chlorinated PVF <sub>2</sub>	5.3	10.0	407
Chlorinated PVF <sub>2</sub>	8.3	16.3	402
Chlorinated PVF <sub>2</sub>	12.2	25	393
Chlorinated PVF <sub>2</sub>	16.3	34.9	393
PVF <sup>b</sup>	0	0	333
Chlorinated PVF <sup>d</sup>	11.7	17	292
Chlorinated PVF <sup>d</sup>	38.9	81	298
PVC <sup>c</sup>	56.8	0	227
Chlorinated PVC <sup>d</sup>	57.6	3.2	228
Chlorinated PVC <sup>d</sup>	63.6	31.8	225

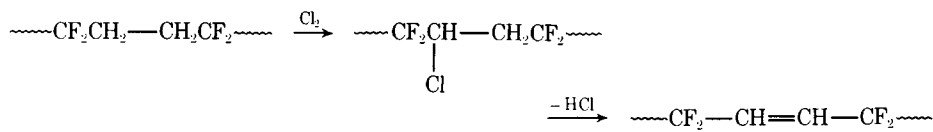
<sup>a</sup> He atmosphere, heating rate = 4.6°C/min.

<sup>b</sup> Dalvor 720, Diamond Alkali Company.

<sup>c</sup> Geon 103 EP, B. F. Goodrich Chemical Company.

<sup>d</sup> Polymer preparation described in ref. 5.

structures susceptible to dehydrochlorination:



### Weathering Resistance

The unique polymer structure, with its resistance to dehydrochlorination, also imparts excellent weathering resistance to coatings prepared from chlorinated PVF<sub>2</sub>. This was demonstrated both by outdoor weathering (Table V) and by accelerated weathering tests (Table VI). The chlorinated PVF<sub>2</sub> used in these experiments was cast onto wood panels from a 20% methyl ethyl ketone/acetone (4/1) solution, and the solvent was evaporated at room temperature. For comparison, coatings prepared from a commercial polyurethane varnish were also evaluated. In both weathering tests, the chlorinated PVF<sub>2</sub> coating remained unchanged and provided good protection to the wood surface against weathering.

TABLE V  
Outdoor Weathering of Polymer-Coated Wood Panels<sup>a</sup>

Wood	Polymer coating	Cl, %	Coating thickness 0.001 in.	Results
Redwood	chlorinated PVF <sub>2</sub>	8.3	1.3	coating unchanged
Redwood	chlorinated PVF <sub>2</sub>	16.3	1.3	coating unchanged
Redwood	Z-spar <sup>b</sup>	—	1.5	coating disappeared
Douglas fir plywood	chlorinated PVF <sub>2</sub>	8.3	1.3	coating unchanged, white spots
Douglas fir plywood	chlorinated PVF <sub>2</sub>	16.3	1.3	coating unchanged, white spots
Douglas fir plywood	Z-spar <sup>b</sup>	—	1.5	coating disappeared

<sup>a</sup> Florida, 45° south, three months.

<sup>b</sup> Brolite Z-spar V-274, polyurethane marine varnish with UV Shield, Andrew Brown Company, Los Angeles.

TABLE VI  
Accelerated Weathering of Polymer-Coated Wood Panels<sup>a</sup>

Wood	Polymer coating	Cl, %	Coating thickness 0.001 in.	Exposure time, hr	Results
Redwood	chlorinated PVF <sub>2</sub>	8.3	1.3	420	coating unchanged
Redwood	Z-spar <sup>b</sup>	—	1.5	420	coating disappeared
Douglas fir plywood	chlorinated PVF <sub>2</sub>	8.3	1.3	564	coating unchanged
Douglas fir plywood	Z-spar <sup>b</sup>	—	1.5	564	coating disappeared

<sup>a</sup> Atlas twin-enclosed carbon arc Weather-O-Meter.

<sup>b</sup> Brolite Z-spar V-274, polyurethane marine varnish with UV Shield, Andrew Brown Company, Los Angeles.



TABLE VII  
Mercury Lamp Exposure of Unsupported Polymer Films<sup>a</sup>

Film	Cl, %	Thickness 0.001 in.	Time to brittle failure, days
Chlorinated PVF <sub>2</sub>	16.3	0.5	63
Chlorinated PVF <sub>2</sub>	8.3	0.5	80
PVF <sup>b</sup>	—	0.6	41

<sup>a</sup> 450-W Hanovia medium-pressure quartz mercury vapor lamp.

<sup>b</sup> du Pont, Tedlar-20TR.

Under the same conditions, the polyurethane coating completely disintegrated, resulting in cracking and flaking of the wood surface.

The excellent ultraviolet radiation stability of unsupported chlorinated PVF<sub>2</sub> films was also confirmed in experiments using a mercury vapor lamp as the irradiation source. The data summarized in Table VII show that, based on the time required for embrittlement, chlorinated PVF<sub>2</sub> outperforms commercial PVF film, one of the premium ultraviolet radiation resistant polymers.

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