

Modification of Poly(vinyl Chloride). XIX. Electroplating of Poly(vinyl Chloride)

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Synopsis

As a preliminary treatment in the PVC-electroplating procedure, treatment with dimethylformamide followed by sensitization leads to a finely roughened and a highly hydrophilic surface with reducing power. This is caused by the formation of an ionic complex compound between dimethylformamide and tin(II) chloride adsorbed in the PVC surface. A much more finely and deeply etched surface which exhibits higher adhesion through the mechanical interlocking effect is obtained with the PVC blends containing the plasticizer with a low value of interaction parameter and with a solubility parameter approximate to that of PVC. Adhesion of the metal layer to the PVC surface thus obtained is improved about 1.5 times by thermal aging at 120°C for 20 min.

INTRODUCTION

The preliminary treatment in the electroplating procedure of poly(vinyl chloride) (PVC) has been carried out in several ways, such as blending with Leostat¹ (Lion Oil and Fat Co.), vacuum metalizing of aluminum,² or etching the surface with a solution of sodium hydrosulfide in liquid ammonia.³ These methods, however, are of no practical use because of the poor adhesion of the metal layer to the PVC surface.

Chemical etching by chromic acid is ineffective in increasing the hydrophilic property (wettability) of the surface of PVC. However, immersing PVC in a good solvent such as dimethylformamide (DMF) or pyridine and then washing in tap water result in a finely roughened and hydrophilic surface. In addition, the former solvent is known to form an ionic complex compound with alkyl chlorides⁴ or tin(II) chloride.⁵ Consequently, immersion of PVC in DMF as preliminary treatment in the PVC-electroplating procedure could have characteristic effects upon the wettability of the surface as well as the sensitization with tin(II) chloride.

In this paper, some conditions, the mechanism of DMF treatment, and some properties of the electroplated PVC will be described, based on the results of the measurement of critical surface tension, peel adhesion, and micrograph study.

EXPERIMENTAL

Materials

The PVC homopolymers used were 103 EP-8 and 101 EP (Japanese Zeon Co.) having degrees of polymerization of 800 and 1450, respectively. Plasticizers were obtained commercially. DMF was purified by vacuum distillation at 80°C/20 mm Hg, and other solvents, by normal distillation.

PVC Molding

PVC and the plasticizers shown in Table III were blended in a two-roll mill with heating at 160°C for 10 min. The blended sheet was about 0.5 mm thick. The sheets were compression molded under a specified stress of 70 kg/cm² at 170°C for 10 min, then cooled to 40°C within 15 min in cold press under a specified stress of 25 kg/cm². The size of the sample thus obtained was 2 × 40 × 50 mm.

Critical Surface Tension

The samples were prepared for measurement by washing for 10 min in tap water containing an anionic surface-active agent, and then rinsing with distilled water. After the washings, the samples were dried for 30 min in dry hot air (40°–50°C) and cooled in a desiccator for at least 24 hr. The contact angle between the samples and aqueous ethanol was measured at 25°C with a contact-angle goniometer (Erma Model G-I). The readings were taken within 30 sec on drop formation. The drop volumes were 0.001 ml. Solutions used for measurement were mixtures of water and ethanol having various surface tension value (21.4–72.1 dynes/cm). Critical surface tension (γ_c) of the sample was determined according to Zisman's method.⁶

Electroplating Procedure

Solvent Treatment. The samples were immersed in the operating bath containing the indicated solvent, then taken out, washed in tap water or ethanol, and rinsed thoroughly with distilled water. Immersing and washing conditions are shown in Table I. Typical conditions for DMF treatment are 3 min at 30°C for immersion and 30 min for washing.

Sensitizing. The treated samples were immersed in a sensitizer solution at 30°C for 30 min and washed in tap water for 30 min, then rinsed with distilled water. The formulation of the solution was: SnCl₂·2H₂O, 24 g/l; HCl (37%), 20 ml/l.

Activation. The sensitized samples were immersed in 2% aqueous solution of silver nitrate at 30°C for 15 min to deposit silver metal, washed in tap water for 30 min, and then rinsed with distilled water.

Electroless Plating. The electroless plating bath (No. 100) of the Okuno Seiyaku Co. was used to deposit a conductive layer of copper on the activated surface. The bath was operated at 30°C with a plating time of about 60 min.

TABLE I
Effect of Solvent Treatment on PVC Surface Properties

| Condition of solvent treatment | | | Condition of washing | | | γ_e , dynes/cm | | | SnCl ₂ absorbed (U) ^b , Sn mg/cm ² | |
|--|-----------|-----------|----------------------|-----------|-----------|-------------------------|----------------|-------------------|---|---------------|
| Solvent | Temp., °C | Time, min | Washings | Temp., °C | Time, min | Sample no. ^a | None (control) | Solvent treatment | | Sensitization |
| Dimethylformamide | 30 | 3 | tap water | 20 | 30 | I | 25.8 | 28.9 | 33.8 | 0.8 |
| | | | | | | II | 27.7 | 34.7 | 29.2 | 0.6 |
| | | | | | | III | 24.2 | 33.9 | 71.8 | 1.0 |
| | | | | | | IV | 38.1 | 45.2 | 56.7 | 0.5 |
| Cyclohexanone | 50 | 10 | ethanol tap water | 20 | 60 | I | 25.8 | 25.9 | 25.8 | 0.9 |
| | | | | | | II | 27.7 | 27.4 | 24.2 | 0.5 |
| | | | | | | III | 24.2 | 33.8 | 34.4 | 1.0 |
| Tetrahydrofuran | 30 | 5 | ethanol tap water | 20 | 60 | I | 25.8 | 37.7 | 37.0 | 0.6 |
| | | | | | | II | 27.7 | 39.9 | 37.7 | 0.6 |
| | | | | | | III | 24.2 | 35.1 | 35.8 | 1.2 |
| Morpholine | 50 | 10 | tap water | 20 | 60 | I | 25.8 | 33.0 | 33.2 | 0.6 |
| | | | | | | II | 27.7 | 36.1 | 36.5 | 0.7 |
| | | | | | | III | 24.2 | 36.3 | 63.5 | 1.9 |
| Pyridine | 50 | 10 | ethanol tap water | 20 | 1440 | I | 25.8 | 33.1 | 36.8 | 1.0 |
| | | | | | | II | 27.7 | 43.1 | 41.6 | 0.7 |
| | | | | | | III | 24.2 | 39.1 | 63.8 | 2.1 |
| Control (scrubbed with abrasive paper No. 6/0) | 50 | 10 | ethanol tap water | 20 | 30 | I | 25.8 | 29.9 | 28.6 | 0.5 |
| | | | | | | II | 27.7 | 29.9 | 25.9 | 0.5 |
| | | | | | | III | 24.2 | 28.4 | 28.0 | 1.0 |

^a I: PVC blend with 5 phr commercial polymeric plasticizer; II: PVC blend with 2 phr tribasic lead carbonate; III: PVC blend with 20 phr dibutyl phthalate, IV: control (PVC: Geon 101 EP).

^b Refers to symbol used in Figure 2.

Copper Electroplating. After electroless plating, the samples were metal coated using a standard electroplating bath consisting of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 210 g/l.; H_2SO_4 (98%), 55 g/l.; brightener 3 ml/l. The samples were first "struck" in this bath for 5 min at 0.05 amp/cm², then plated for 55 min at 0.1 amp/cm². For adhesion studies, a 2-mil-thick layer of copper was plated.

Jacket Peel Adhesion Test

After a 24-hr relaxation period, adhesion of the metal layer to the PVC was determined by measuring the force needed to pull a 10-mm-wide strip of metal from the plated surface. The test was carried out on a recording Autograph P-100 at 20 mm/min jaw rate separation, with the peeling strip nominally vertical to the sample surface.

Aging and Thermal-Cycle Test

The results of aging and the thermal-cycle test are discussed below under "peel adhesion." The plated samples treated under the following conditions: The samples were aged in a desiccator at room temperature or in the oven at 80°–120°C for the indicated time. The thermal-cycle test was carried out on the conditions as follows: The samples were maintained at 80°C for 30 min; allowed to remain at room temperature for 10 min; maintained at -40°C for 30 min; allowed to remain at room temperature for 10 min. This cycle was repeated four times.

Analysis and Measurement

The surface layer absorbing tin(II) chloride at sensitization was scratched and the scratched powder was fused by the alkali chlorate fusion method. The fusion mixture was dissolved in 5% hydrochloric acid, and the amount of tin(II) chloride in the solution, after reducing by metallic antimony, was determined by iodometry.

The composition of the powdered compound of DMF and tin(II) chloride absorbed on the PVC surface was determined by infrared spectroscopy.

The micrographs of the PVC surface after solvent treatment were taken with a scanning electron microscope (Hitachi HSM-2).

RESULTS AND DISCUSSION

Effect of Solvent Treatment with DMF

Upon solvent treatment of PVC, the appearance of the surface is observed to be roughened; the wettability, γ_c , increases slightly, as shown in Table I and in Figures 3a, b, and c. Similar effects are observed on the PVC surface by scrubbing mechanically with an abrasive paper.

On the other hand, γ_c is not always observed to increase with increasing amount of tin(II) chloride absorbed upon sensitization. However, with

DMF or pyridine treatment, γ_c increases remarkably with increase in the amount of tin(II) chloride absorbed.

Such a result suggests that DMF absorbed on the PVC surface interacts strongly with PVC as well as with diffusing tin(II) chloride and increases the wettability of the surface.

Formation of Complex between DMF and Tin(II) Chloride

DMF absorbed on the PVC surface by DMF treatment is not completely removed by washing for 5–60 min, and increases the wettability of the surface (Table II).

The presence of DMF on the washed surface is confirmed by detecting the ν C=O absorption band near 1660 cm^{-1} , as shown in infrared spectra (Figure 1, curve A). Such a strong interaction of DMF with PVC seems to result from weak ionic bonding such as $[\text{HCON}(\text{CH}_3)_2\text{R}]^+\text{Cl}^-$ between DMF and PVC.⁴ The γ_c of the DMF-treated surface increases much more by sensitizing with tin(II) chloride, and the increased γ_c is not decreased by washing in tap water for 60 min (Table II). On the other hand, the ν C=O absorption band is observed to shift in the low-frequency region of 1640 cm^{-1} with adsorbed tin(II) chloride, and a similar tendency is also observed on the isolated ionic complex compound⁵ between DMF and tin(II) chloride:

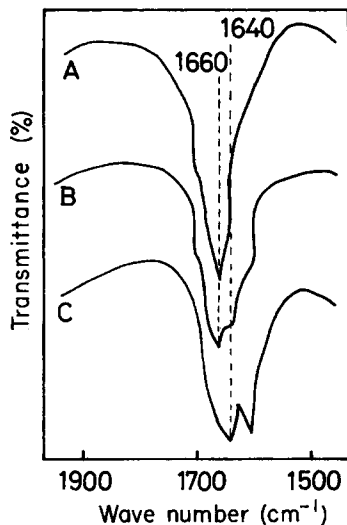
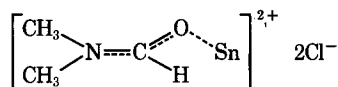


Fig. 1. IR spectra of the DMF-treated PVC and the complex compound: (A) DMF-treated PVC; (B) sensitized (A); (C) complex compound between DMF and tin(II) chloride.

TABLE II
Effect of DMF Treatment, Sensitization, and Washing

| Sample no. ^a | DMF treatment time/ γ_c ratio ^b | | | | | Washing time/ γ_c ratio ^c | | | | | Washing time/ γ_c ratio ^d | | |
|-------------------------|---|-------|-------|-------|------|---|--------|--------|--------|-------|---|--------|--|
| | 1 min | 3 min | 6 min | 9 min | 27.6 | 5 min | 15 min | 30 min | 60 min | 5 min | 30 min | 60 min | |
| I | 27.8 | 28.9 | 27.1 | 27.6 | 27.6 | 28.3 | 28.7 | 28.9 | 28.7 | 39.1 | 38.8 | 38.3 | |
| II | 33.8 | 34.7 | 32.4 | 32.5 | 32.5 | 32.2 | 34.2 | 34.7 | 34.5 | 29.9 | 29.2 | 29.8 | |
| III | 34.0 | 37.4 | 34.2 | 34.1 | 34.1 | 36.9 | 37.2 | 37.4 | 37.5 | 71.7 | 71.8 | 72.0 | |

^a Samples I, II, and III same as in Table I.

^b γ_c determined for samples washed in tap water at 20°–26°C for 30 min.

^c γ_c determined for DMF-treated samples at 30°C for 3 min, and then washed in tap water for the indicated time.

^d γ_c determined for samples sensitized at 50°C for 30 min, and then washed in tap water at 20°–26°C for the indicated time. Sensitization was preceded by DMF treatment for 3 min at 30°C, followed by washing in tap water at 20°–26°C for 30 min.

TABLE III
Effect of Plasticizer on γ_c and Adhesion

| Name | Plasticizer | | μ^a | SP ^b | γ_c ,° dynes/cm | | | Peel adhesion, ^d kg/cm |
|---------------------|-------------|--|---------|-----------------|------------------------|---------------|---------------|--------------------------------------|
| | phr | | | | Control | DMF treatment | Sensitization | |
| Dimethyl phthalate | 10 | | 0.50 | 10.3 | 27.9 | 37.3 | >72.1 | 0.8 (0.9) |
| Diethyl phthalate | 10 | | 0.43 | 9.9 | 27.2 | 37.7 | >>72.1 | 0.6 (0.7) |
| Dibutyl phthalate | 10 | | 0.15 | 9.4 | 24.2 | 33.9 | 71.8 | 0.9 (1.3) |
| Dibutyl phthalate | 20 | | 0.15 | 9.4 | 24.1 | 34.1 | 72.0 | 0.9 (1.3) |
| Dioctyl phthalate | 10 | | 2.52 | 8.9 | 21.0 | 32.2 | 48.4 | 0.3 (0.6) |
| Dilauryl phthalate | 10 | | 2.96 | 7.8 | 27.6 | 30.1 | 33.4 | 0.4 |
| Tricresyl phosphate | 10 | | 2.29 | 9.7 | 28.4 | 34.6 | >72.1 | 0.6 (0.6) |
| Tricresyl phosphate | 20 | | 2.29 | 9.7 | 29.1 | 39.0 | >72.1 | 0.7 (0.8) |
| Dimethyl sebacate | 10 | | 0.36 | 9.1 | 28.3 | 38.1 | 72.1 | 0.3 |
| Diethyl sebacate | 10 | | 0.27 | 8.9 | 30.6 | 33.6 | >72.1 | 0.3 |
| Dibutyl sebacate | 10 | | 0.28 | 8.7 | 29.4 | 32.6 | >>72.1 | 0.6 (0.6) |
| Dioctyl sebacate | 10 | | 2.63 | 8.5 | 29.9 | 32.2 | >72.1 | 0.3 (0.4) |
| None (control) | — | | — | — | 38.1 | 45.2 | 56.7 | 0.3 |

^a Interaction parameter, calculated using the Flory-Rehner equation on crosslinked PVC ($\nu_e = 4.09 \times 10^4$) swelling in plasticizer at 50°C.

^b Solubility parameter, calculated from Small's equation.

^c Critical surface tension value (wettability).

^d Figures in parentheses are peel adhesion values after aging at 120°C for 10 min.

On the basis of these data, it seems reasonable to assume that the DMF absorbed on the PVC surface leads to formation of a complex compound with tin(II) chloride diffusing into the surface at the sensitization process, and the ionic complex compound serves to increase the wettability and reduce the silver ion diffusing during the following activation process.

Effects on Wettability and Peel Adhesion

Effect of Plasticizer. Although both PVC and plasticizer are etched out during the surface treatment, their weight ratio and the appearance of the resulting surface seem to be influenced by the compatibility of plasticizer with PVC. As shown in Figure 2, wettability γ_c is much more influenced by the kind of plasticizer than the amount of tin(II) chloride absorbed on the PVC surface during the sensitization process.

These effects are clearly shown by the results in Table III. In addition, the plasticizers which serve to increase γ_c always cause higher adhesion, except in the case of the sebacate plasticizers. Such plasticizers, in general, are unique in their low value of interaction parameter (μ) and with solubility parameters (SP) approximately that of PVC, i.e., 9.6. It is concluded, therefore, that one of the important factors to give higher adhesion is to use the PVC blends with a plasticizer which has a strong interaction and good compatibility with PVC. With the sebacate plasticizers, however, a high γ_c is accompanied by low adhesion, which suggests the role of a more complicated factor, such as plasticizer efficiency, than solubility and interaction parameters.

Micrographs of the PVC surface after DMF treatment, show that the most finely and deeply etched surfaces are seen on the PVC blends with the good plasticizers, e.g., dibutyl phthalate (Fig. 3a).

On the basis of these results, the high adhesion appears to be related to these finely etched surfaces which promote a mechanical interlocking effect and exhibit high wettability and reducing power through formation of the ionic complex described above.

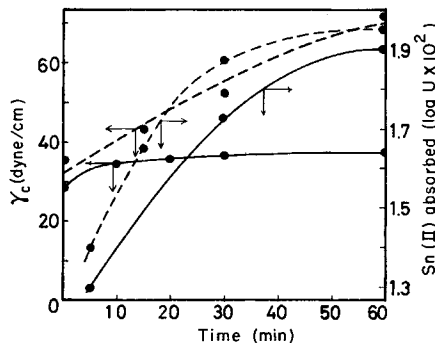


Fig. 2. Effect of time of sensitization on γ_c and the amount of tin(II) chloride absorbed: (—) I; (---) III. Symbols I, III, and U refer to Table I.

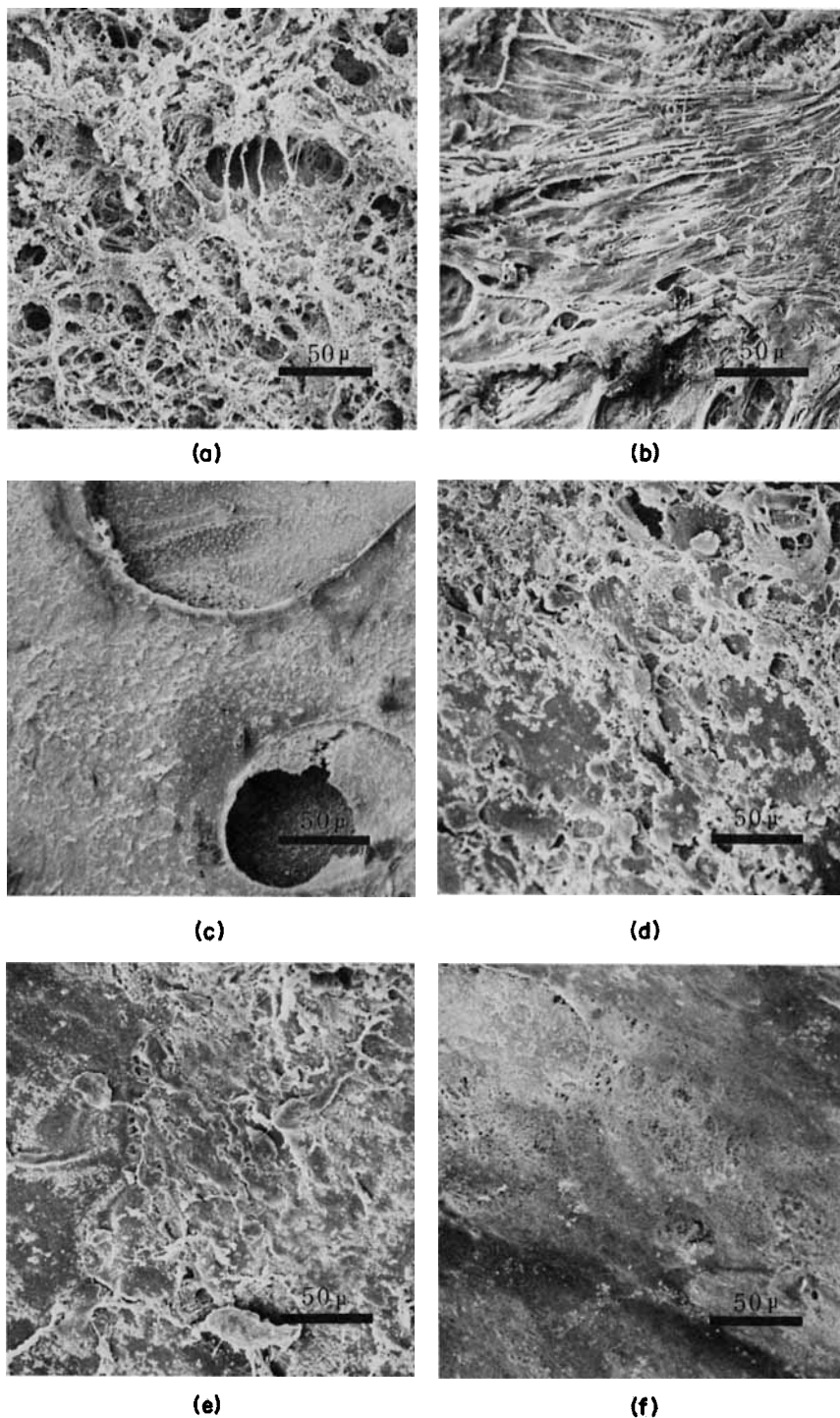


Fig. 3. Micrographs of PVC surface-treated with solvent: (a) DMF-treated III; (b) pyridine-treated III; (c) THF-treated III; (d) DMF-treated IV; (e) DMF-treated PVC blends with 20 phr of dimethyl phthalate; (f) DMF-treated PVC blends with 20 phr of dilauryl phthalate. Symbols I, III, and IV refer to Table I.

TABLE IV
Effect of Preparative Conditions of Sample

| Blending condition ^a | | | Peel adhesion, kg/cm | Molding condition ^b | | | Peel adhesion, kg/cm |
|---------------------------------|-----------|------------------------------------|----------------------|--------------------------------|-----------|------------------------------------|----------------------|
| Temp., °C | Time, min | γ_c , ^c dynes/cm | | Temp., °C | Time, min | γ_c , ^c dynes/cm | |
| 135 | 10 | >72.1 | 0.6-0.7 | 150 | 10 | 37.3-68.9 | 0.3-0.5 |
| 160 | 5 | 67.5 | 0.3-0.5 | 170 | 5 | 55.7 | 0.4-0.5 |
| 160 | 10 | >72.1 | 0.7-1.2 | 170 | 10 | >72.1 | 0.7-1.2 |
| 160 | 20 | 71.9 | 0.6-0.8 | 170 | 20 | 48.5-67.5 | 0.5-0.9 |
| 200 | 10 | >72.1 | 0.5-0.8 | 185 | 10 | 48.7-71.9 | 0.2-0.8 |

^a Samples ($\overline{D.P.} = 1450$, with 20 phr of dioctyl sebacate) were compression molded at 170°C for 10 min, and then cooled at "normal cooling" rate (see Table V).

^b Similar samples as under (a) were blended at 160°C for 10 min.

^c Determined for the samples sensitized under the preferred conditions described in the experimental section.

TABLE V
Effect of Cooling Rate and Degree of Polymerization

| Molding Temp., ^a °C | γ_c , ^b dynes/cm | | Peel adhesion, kg/cm | |
|--------------------------------|------------------------------------|--------------------------------|----------------------|----------------------------|
| | D.P. = 800 | D.P. = 1450 | D.P. = 800 | D.P. = 1450 |
| 150 | 46.1 | 63.4-72.1 | 0.1-0.2 | 0.3-0.4 |
| 170 | >72.1 | >72.1 (38.1-70.3) ^c | 0.3-0.6 | 0.5-0.9 (0.1) ^c |
| 185 | — | >72.1 | — | 0.3-0.5 |

^a All samples except (c) were blended with 20 phr tricresyl phosphate at 160°C for 10 min, and compression molded for 10 min at indicated temperature, then cooled to 40°C under pressure within 15 min (normal cool).

^b Refers to Table IV.

^c Similar samples as under (a) were compression molded at 170°C for 10 min, then cooled to room temperature under pressure overnight (slow cool).

TABLE VI
Effect of Aging and Thermal-Cycle Test^a

| Test | Peel adhesion, kg/cm |
|---------------------------------|----------------------|
| Aging test, ^b days | |
| 1 | 0.6-0.7 |
| 5 | 0.5-0.7 |
| 8 | 0.8-0.9 |
| 30 | 0.7-1.0 |
| Thermal-cycle test ^c | 0.6 |

^a Sample PVC ($\overline{D.P.} = 1450$) with 20 phr of dibutyl phthalate was used.

^b Aging was carried out at room temperature.

^c For thermal-cycle test, refer to experimental section.

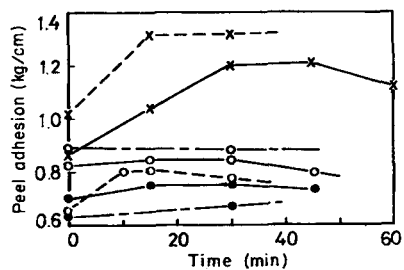
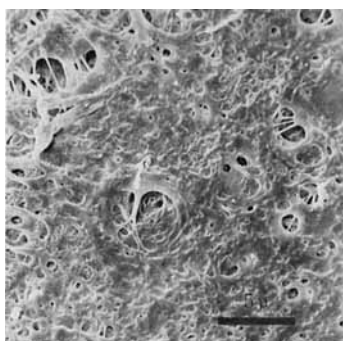
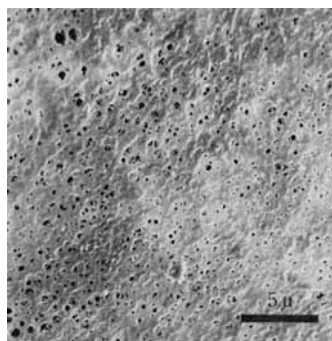


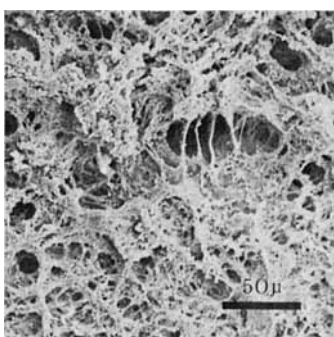
Fig. 4. Relationships between stock temperature, time, and peel adhesion: (O) I; (●) II; (X) III; (---) 80°C; (—) 100°C; (- - -) 120°C. Symbols I, II, and III refer to Table I.



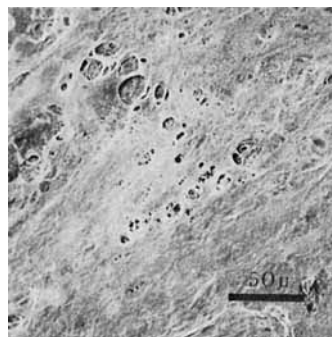
(a)



(b)



(c)



(d)

Fig. 5. Micrographs of PVC surface treated with DMF: (a) and (c) I and III before aging, respectively; (b) and (d) I and III after aging at 100°C for 20 min, respectively. Symbols I and III refer to Table I. (a) and (b) scale bar = 5 μ ; (c) and (d) scale bar = 50 μ .

Conditions of Compression Molding. The temperature of blending hardly affects the adhesion at the optimum molding condition of 170°C for 10 min. The temperature of molding, however, greatly affects γ_c and adhesion, even at optimum blending condition of 160°C for 10 min. As shown in Table IV, the optimum condition for the compression molding is assumed to be 170°C for 10 min under the specified stress of 70 kg/cm². A higher temperature causes locally poor γ_c and adhesion.

The cooling rate of the sample after molding also affects γ_c as well as adhesion. Table V illustrates that "normal cool" gives superior result over "slow cool."

Table V also illustrates that higher adhesion is observed with PVC having a higher degree of polymerization (1450).

Aging, Stock Temperature, and Thermal-Cycle Test. As shown in Table VI and Figure 4, adhesion of the metal layer slightly increases by about a factor of 1.5 when the electroplated samples are aged several weeks at room temperature or 30 min at 100°–120°C, respectively.

As shown in Figure 5, the roughened surface is observed to be flattened when the stock temperature is increased from 100° to 120°C. The increase in adhesion, therefore, seems to be produced by interlocking the metal deposit in the etched porous surface more tightly through flattening of the etched surface upon heating. Furthermore, as shown in Table VI, the electroplated PVC thus obtained shows excellent resistance to the thermal-cycle test, which is a measure of durability.

From these results, a preliminary treatment with DMF in the PVC-electroplating procedure has been found to play a predominant role in producing bright finishes with excellent adhesion of the metal layer.

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Received February 14, 1972

Revised May 4, 1972