Flex-Resistant Permeable PVC Films

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Synopsis

Microporous poly(vinyl chloride) films with flex resistance in excess of 400,000 flexes at 20°C and 65% R.H. and in excess of 30,000 flexes at −15°C, and water vapor permeability in excess of 250 g/m^2 24 hr have been prepared from controlled expansion and curing of plastisols, which contain a poly-(vinyl chloride) (PVC) resin with a K value of 75 or more and a plasticizer with a solubilizing power not greater than that of dioctyl phthalate. Controlled curing produces uniformity in the morphology of the cell walls while maintaining sufficiently high melt viscosity to retain the open structure of the porous material.

INTRODUCTION

Leather-like materials of a composite structure which are useful as shoe upper materials or upholstery materials should be permeable to water vapor and have a high flex resistance. For these purposes, one component of the composite, the base material, is normally coated with a microporous film. The commonly used microporous films have been made of polyurethane and they can sustain 400,000 Bally flexes at 20°C and 65% R.H. or more and 30,000 Bally flexes or more at −15°C, and they have water vapor permeabilities in excess of 250 g/m^2 24 hr. Such levels of performance are generally considered to be acceptable for materials used as shoe upper materials. In the past, microporous poly(vinyl chloride) (PVC) films with water vapor permeabilities in excess of 250 g/m^2 24 hr have never approached the high values of flex resistance necessary in shoe upper materials and have, therefore, been deemed unacceptable for such application.[1] Nevertheless, the high cost of polyurethane relative to PVC has stimulated sustained efforts to adapt PVC to such end use applications.

In the course of an extensive study of a new leather-like material consisting of a gelatin-bonded synthetic labeled Nathetic,[2] we have explored systematically the correlation between the thermal treatment and mechanical properties of microporous PVC films over a wider range of temperatures and curing times than are normally considered practicable. This paper reports our finding that, under certain conditions, microporous PVC films can be thermally treated to meet the requirements for flex resistance and water vapor permeability while maintaining high levels of performance in application as shoe upper materials with respect to adhesion, heat resistance, scuff resistance, etc. Microporous PVC films so treated are hereinafter called "hyper-PVC films." [3]

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EXPERIMENTAL

Plastisol Preparation. The plastisols were prepared by standard techniques[4] using commercially available materials listed in Table I.

Water Vapor Permeability. Water vapor permeability was measured according to DIN 53333, the "cup" method.

Flex Resistance. Flex resistance was measured according to IUP/20[5] on a Bally flexometer. Microporous PVC films, 0.5-mm thick, were laminated onto a 1-mm-thick nonwoven substrate. Flex resistance is reported as the number of flexes the sample can withstand until the PVC film cracks and the substrate can be seen through the crack by visual inspection.

Tear Strength. Tear strength was measured according to DIN 53329 on an Instron machine.

Energy at Break. Energy at break of 0.5-mm-thick microporous PVC films was determined from the area under the stress–strain curve obtained according to DIN 53328.

Melt Viscosity. The Brabender Plastograph was used as a temperature-scanning rheometer to study the melt viscosity of PVC plastisols.[6–8] The rate of heating was 3°C/min, and the sample materials were worked at 20 rpm. The sample plastisols did not contain blowing agent or cell regulator.

TABLE I
Materials Used for Preparation of Plastisols for Microporous PVC Films

Chemical name	Trade name	Manufacturer
PVC		
Poly(vinyl chloride)	Vestolit E 8001	Hüls SWH
Plasticizers		
Dioctyl phthalate	Palatinol AH	BASF
Dinonyl phthalate	Bisoflex DNP	BP Chemicals
Ester of phthalic acid and C_9–C_{11}		
alcohols	Palatinol 911	BASF
Butyl benzyl phthalates	Santicizer 160	Monsanto
Ester of polyethylene glycol and		
diethyl hexoic acid	Flexol 4GO	Union Carbide
Epoxidized soy bean oil	Reoplast 39	Ciba-Geigy
Viscosity-Depressing Agents		
Ester of fatty acids and polyglycols	Deplastol	Henkel & Cie. GmbH
Blowing Agents		
Diphenylsulfone-3,3'-disulfohy-		
drazide	Porofor D33	Bayer
Azodicarbonamide	Genitron AC	Fisons Industrial Chemicals
Fillers		
Chalk	Krita CFF "Sjöhästen"	Kritbolaget, Sweden
Titanium oxide	(titanium oxide)	Kronos Titan, Norway
Stabilizers		
Barium–cadmium compound	Ferro 2020-NL	Ferro, Holland
Cell Regulators		
65% Emulsion of long-chain		
hydrocarbons in water	Luvostab 10	Lehmann-Voss, West-Germany

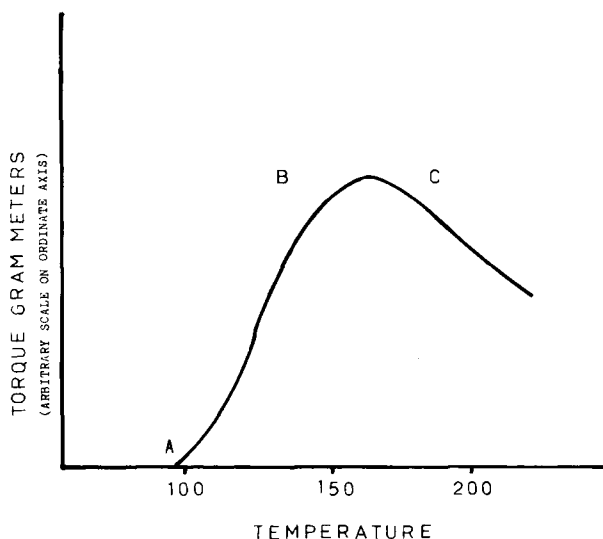TORQUE GRAM METERS (ARBITRARY SCALE ON ORDINATE AXIS)

TEMPERATURE

Fig. 1. Brabender torque–temperature diagram for plastisol composition 3 in Table II.

K Values. The K values of Vestolit E 8001 and E 7001 were determined according to DIN 53726, from the relative viscosity of solutions of 0.005 g PVC/ml in cyclohexane. The K values for the two resins were 78 ± 1 and 68 ± 1, respectively, two units lower than those reported by the manufacturer, Hüls.

RESULTS AND DISCUSSION

Preparations of Microporous Films

We summarize briefly the film preparations by making reference to the Brabender diagram shown in Figure 1. The viscosity of the PVC plastisol, measured

TABLE II
Examples of Plastisol Composition Which, When Properly Cured, Lead
to "Hyper-PVC Films"[a]

Ingredients Example	Plastisol composition, phi						
	1	2	3	4	5	6	7
Vestolit E 8001 PVC with K value 75[b]	100	100	100	100	100	100	100
Dioctyl phthalate	76				38		
Dinonyl phthalate		76				76	
Esters of phthalic acid and C_7–C_{11} alcohols			76	38	56		76
Epoxidized soya bean oil	3–4	3–4	3–4	3–4	3–4	3–4	3–4
Deplastol	2	2	2	2	2	5	2
Porofor D33	2.5–3	2.5–3	2.5–3	2.5–3	2.5–3	2.5–3	2.5–3
Luvostab 10	7–0	7–9	7–9	7–9	7–9	7–9	7–9
Chalk						40	
Barium–cadmium complexes							1.5
Pigment	2–10	2–10	2–10	2–10	2–10	2–10	2–10

[a] Blowing time, 60 sec; blowing temperature, 170° C; curing time, 180 sec; curing temperature, 185° C.
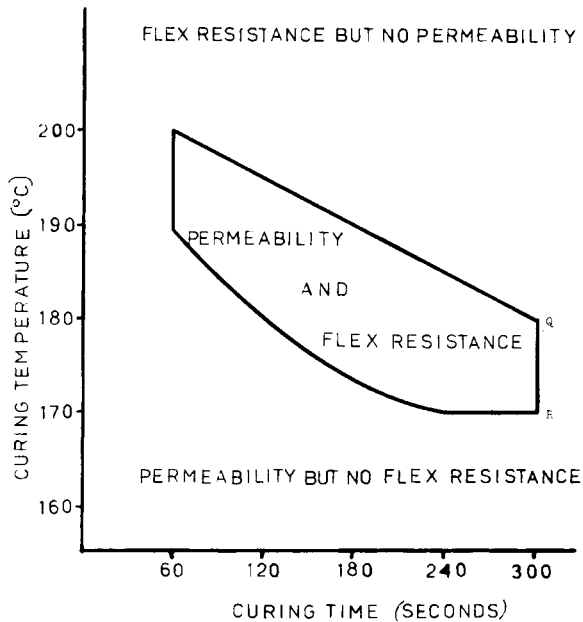
Fig. 2. Domain of curing conditions which lead to "hyper-PVC films."

as a torque on the Brabender plastograph, varies with temperature at a constant rate of heating, shown here for 3°C/min. The plastisols for making PVC films contain the resin with a plastisol, a stabilizer, a blowing agent, and a filler.

To develop trends, we discuss the curve in Figure 1 in three regions. Region AB: The resin particles absorb the plasticizer, and the viscosity increases as a result of the decreasing lubricating effect of the plasticizer. Region BC: The resin particles have absorbed most of the plasticizer and begin to fuse into a homogeneous system; the plastograph reading becomes indicative of the melt viscosity of the plasticizer PVC. Region C: The resin particles have fused together, and the melt viscosity decreases with temperature in a manner typical of homogeneous polymer systems.

In order to obtain "hyper-PVC films," certain limitations must be imposed on the plastisol formulation. Moreover, a uniform pore structure is a necessary prerequisite for hyper-PVC formation. Large fluctuations in pore sizes in the film impedes the attainment of high flex resistance, because large cells can initiate rapid local damage.

The "hyper-PVC films" were derived from a plastisol containing a paste making PVC resin with a molecular weight corresponding to a K value not less than 75. The plastisol also contained 60–90 phr plasticizer of a solubilizing power not greater than that of dioctyl phthalate and a blowing agent with a decomposition range of 100–150°C. The process of producing "hyper-PVC films" consists of two steps, viz., a blowing step and a curing step.

In the blowing step, the plastisol was heated in an oven of 165–170°C for 1 min. Below 165°C, the decomposition rate of the blowing agent is too slow for practical purposes; the dwelling time in the oven increases with decreasing temperature. Above 170°, the decomposition rate is too fast and will result in an uneven pore
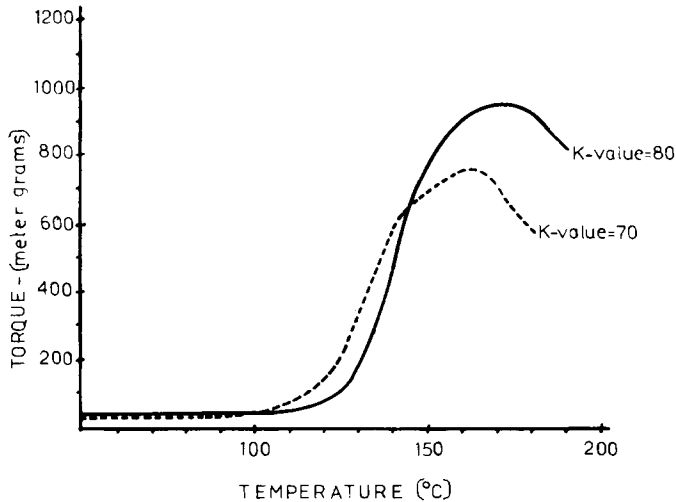
Fig. 3. Effect of molecular weight of PVC resin or melt viscosity of PVC plastisol.

structure. The expanding gas can burst the cell walls to form an interconnecting porous structure, while the melt viscosity is high enough to maintain this structure during the time of treatment. We found that such conditions prevailed if the blowing step is performed somewhat to the left of, but close to, the point B in Figure 1.

Curing of Microporous PVC Film

The curing step following the blowing step can either be performed consecutively in one properly programmed temperature cycle, or curing can be imposed on expanded PVC films after storage.

In the present context, the curing time is defined as the residence time of an expanded PVC film on a suitable support in an oven preheated to a given curing temperature. After completion of the curing cycle, the film on its support is removed from the oven. No dependence of the hyper-PVC properties on the mode of cooling to room temperature was found.

The properties of the final product depend much more sensitively on the curing conditions than on the conditions during the blowing step. In particular, the plastisol composition must be chosen such that the open cell structure does not collapse during curing, while at the same time the melt viscosity is sufficiently low to permit fusion of the plastisol in the cell walls into a homogeneous structure during the curing time. That is, the plastisol viscosity to the right of point C on Figure 1 may not exceed or fall below a narrow critical range during the curing step. This circumstance restricts in a characteristic way the applicable plastisol composition.

For the plastisol compositions studied, and shown in Table II, we found ideal curing conditions to fall into the domain bounded by OPQR on the time–temperature curing diagram given in Figure 2. These boundaries are chosen to embrace "hyper-PVC film" with acceptable flex resistance and water vapor permeability.
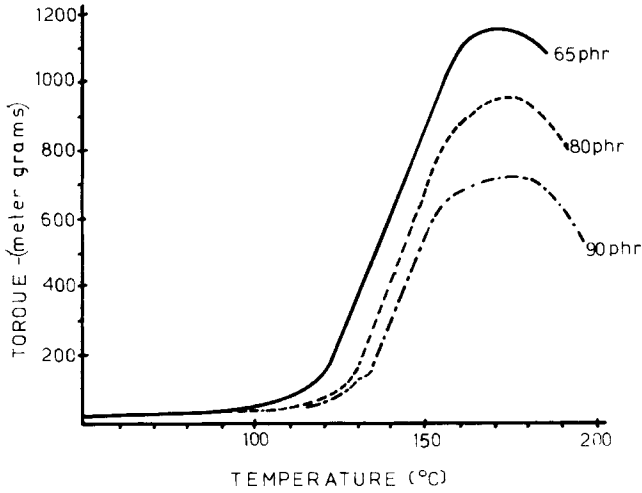
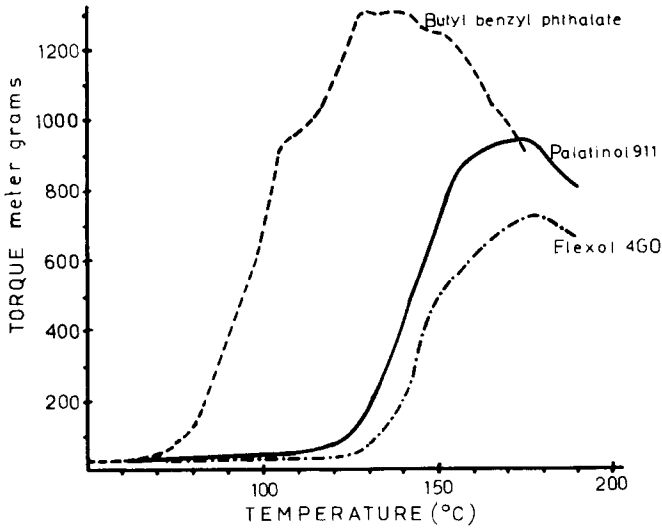Fig. 4. Effect of plasticizer concentration on melt viscosity of PVC plastisol.

Fig. 5. Effect of solubilizing power of plasticizer on melt viscosity of PVC plastisol.

"Hyper-PVC films" can be prepared if the molecular weight of the PVC resin and the content of plasticizer in the plastisol meet the requirements stated in the previous section. On the one hand, the molecular weight of the PVC resin must not fall below a value corresponding to a K value of 75. Already at a K value equal to 70, as Figure 3 illustrates, the melt viscosity beyond point C in Figure 1 is reduced drastically such that "hyper-PVC" cannot be formed by curing. On the other hand, a series of commercial plasticizers can be used for the preparation of "hyper-PVC" providing the plasticizer concentration is controlled within narrowly defined limits, as Figure 4 demonstrates for the plasticizer Palatinol 911. The melt viscosity becomes too high at 65 phr, whereas at 90 phr it becomes too low and leads to rapid collapse of the cell structure during curing. Optimal results with this plasticizer are obtained when the concentration falls in the range of 70–80 phr.

TABLE III

Properties of PVC Film Examples Made of Composition and Under Blowing and Curing Conditions Listed in Table I

Property	Example 1	2	3	4	5	6	7
Flex resistance 20°C, 65% relative humidity	1,500,000	1,500,000	1,500,000	700,000	450,000	450,000	1,000,000
Flex resistance −15°C	50,000	100,000	100,000	50,000	60,000	40,000	80,000
Water vapor permeability in g/m² for 24 hr	320	360	300	360	390	360	350

The actual concentration to be chosen within limits of tolerance depends on the plasticizer used, because the melt viscosity during curing depends on the solubility of the resin in the plasticizer at a given temperature. Figure 5 demonstrates that the melt viscosity depends strongly on the solubilizing power of the plasticizer, and we found that the cell structure remains stable during curing only if the solubilizing power of the plasticizer does not exceed that of dioctyl phthalate.

Fillers, of course, always increase the melt viscosity, but we found that they can always be incorporated in the plastisol in amounts up to 40 phr and in judiciously chosen combinations with plasticizer to maintain the proper melt viscosity during curing.

"Hyper-PVC Films"

The films prepared as described in the last two sections have an open, permeable cell structure in a homogeneous single-phase matrix and reach flex resistance in excess of 400,000 Bally flexes at 20°C and in excess of 30,000 Bally flexes at −15°C, with a water vapor permeability in excess of 250 g/m² 24 hr. Table III summarizes the results of seven examples with compositions given in

TABLE IV

Composition of Two Examples Which Do Not Meet the Criteria for "Hyper-PVC Film"

Composition A[a]	phr	Composition B[10][b]	phr
Vestolit E 7001, $K < 75$	100	Vestolit E 8001, $K \geqslant 75$	100
Dinonyl phthalate	76	Butyl benzyl phthalate	45
Reoplast 39	3.5	Dialphanol phthalate	7
Deplastol	2	Azodicarbonamid	1
Porofor D 33	2.5	Ba−Cd−Zn stabilizer	1
Luvostab 10	8	Epoxy plasticizer	5
Pigment	5	Ammonium bicarbonate	1.6
		Water	1.5
		Emulsifier	1

[a] Blowing time, 60 sec; blowing temperature, 170°C; curing conditions, 1: 120 sec, 175°C; 2: 180 sec, 185°C.

[b] Blowing time, 75 sec; blowing temperature, 165°C; curing time, 75 sec; curing temperature, 180°C. Blowing agent decomposes at > 150°C and the solubilizing power of the plasticizer combination is larger than that of dioctyl phthalate.

TABLE V

Properties of Examples of Conventional PVC Films Made of Composition and Under Conditions Listed in Table III[a]

Property	A1	A2	B
Flex resistance 20°C at 65% relative humidity	142,000	450,000	70,000
Flex resistance −15°C	14,000	50,000	50
Water vapor permeability in g/m² for 24 hr	270	25	360

[a] A1, A2, and B do not meet the degree of both flex resistance and water vapor permeability set for the "hyper-PVC film."

Table II. In all cases, they were cured under conditions such that they fell within the curing domain shown in Figure 2.

By contrast, the compositions listed in Table IV could not be cured to obtain "hyper-PVC" properties because their specifications do not meet the limits set forth in earlier sections. Composition A, which contains a PVC resin with a K value of 70, fails to give "hyper-PVC" properties when cured inside or outside

TABLE VI

Properties of PVC Film Examples Made of Composition and Under
Blowing Conditions Listed in Table II:3[a]

	1	2	3		
Property	90 sec,[b] 170°C[c]	120 sec 200°C	240 sec, 170°C	180 sec, 185°C	90 sec, 185°C
Flex resistance 20°C at 65% relative humidity	150,000	1,500,000	500,000	1,500,000	400,000
Flex resistance −15°C	10,000	75,000	45,000	100,000	50,000
Water vapor permeability in g/m² for 24 hr	250	25	350	360	400

[a] With (1) curing conditions below the domain marked in Figure 2 and (2) curing conditions above this domain, compared with films (3) prepared under the curing conditions inside the domain marked in Figure 2.

[b] Curing time.

[c] Curing temperature.

TABLE VII

Energy at Break and Tear Strength of Films Made of Composition 3 in Table V as a
Function of Curing Conditions at Three Plasticizer Concentrations

Curing temp., °C	Curing time, sec	Energy at break, arbitrary units	Tear strength, kp/min
(a) 65 phr Plasticizer			
170	120	85	0.75
	240	208	1.52
180	120	148	1.17
	240	253	1.98
190	120	249	1.80
	240	364	2.34
(b) 83 phr Plasticizer			
170	120	51	0.72
	240	138	1.07
180	120	167	1.16
	240	255	1.68
190	120	242	1.41
	240	303	1.72
(c) 95 phr Plasticizer			
170	120	65	0.40
	240	134	0.82
180	120	146	0.81
	240	146	1.04
190	120	146	0.96
	240	138	1.14

the curing domain in Figure 2, as demonstrated by examples A1 and A2 in Table V. Composition B, which contains a plasticizer with a solubilizing power greater than that of dioctyl phthalate and a blowing agent, azodicarbonamide, which decomposes above 150°C, also fails to give "hyper-PVC" properties when cured inside the curing domain in Figure 2, as is demonstrated by example B in Table V.

As a further illustration, we have cured composition 3 given in Table II under conditions which fall inside and outside the curing domain shown in Figure 2. Indeed, example 1, cured below these conditions, has unacceptably low flex resistance, and example 2, cured above the proper domain, has unacceptably low water vapor permeability, as is demonstrated in Table VI.

The effect of curing conditions on energy at break and tear strength of microporous PVC films made from composition 3, Table II, is demonstrated in Table VII for three different plasticizer concentrations. In all cases, the energy at break and the tear strength are increased by a factor of at least 2 when the curing conditions are intensified from 2 min at 170°C to 2 min at 190°C. For the same increase in curing conditions, the flex resistance of films with 83 phr plasticizer increases from 150,000 to 800,000 Bally flexes.

The curing domain shown in Figure 2 corresponds to a subtle balance between sufficient fusion of cell walls to obtain mechanical properties while maintaining sufficiently high viscosity to retain the open structure of the porous material. It is well known, of course, that a monotonic dependence exists between curing and morphology in PVC films.[9] We have studied the structure of PVC and "hyper-PVC films" by electron microscopy and found, in general, the trends to be expected in the structures so resolved. Clearly, the performance in flex testing is a very sensitive function of the details of the microstructure and their dependence on curing conditions. In particular, one can expect that when curing has produced uniformity in the morphology of the cell walls to a sufficient degree, the flex resistance rises to above acceptable limits to make "hyper-PVC" an attractive candidate for the finish of leather-like materials.

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