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# The Properties of Polyvinyl Fluoride Film*

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High molecular weight polyvinyl fluoride (PVF) prepared by the methods of Kalb et al.[1] has been fabricated into thin transparent films of excellent toughness, high tensile strength and flexibility, and high resistance to outdoor weathering.[2] This paper will present information on the optical, physical, chemical (hydrolytic), and electric properties of thin PVF films in the range of thickness from 0.0005 to 0.004 in. The effect of biaxial orientation on the physical properties is examined also.

## MATERIALS

The investigation of the effects of various physical and chemical treatments on the properties of PVF was carried out on three commercial grades of films: Teslar 20, a transparent film, highly oriented biaxially; Teslar 40, a transparent film, less oriented biaxially; and Teslar 20 (or 40) P, a colored film. (Teslar PVF Film is the registered trade name for polyvinyl fluoride film available from E. I. du Pont de Nemours and Co., Inc., Film Department, Wilmington, Delaware.) The transparent forms have a density of 1.38 g./cc. In the following discussion whenever polyvinyl fluoride is used without differentiation as to film type, it should be understood that the property being discussed is the same for all film types.

## OPTICAL PROPERTIES

Polyvinyl fluoride is transparent to both visible and ultraviolet radiation, as shown in Figure 1. The transmission data shown here were obtained on films immersed in mineral oil to reduce scattering loss at film surfaces. PVF absorbs strongly in the infrared region, particularly in the wave-length region of 7 to 13 microns (Fig. 2).

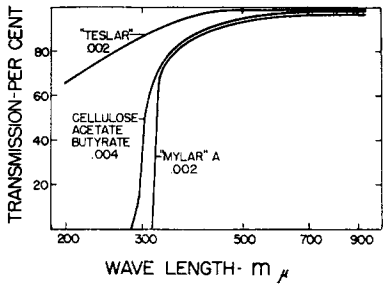


Fig. 1. Visible and ultraviolet light transmission of films.

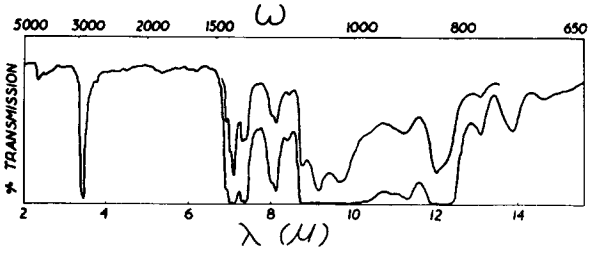


Fig. 2. Infrared spectrum of polyvinyl fluoride.

PVF films are moderately crystalline,[3] as shown by the x-ray diffraction patterns in Figure 3. The crystalline melting point is approximately 200°C. The film has an average refractive index of 1.45, but three optical axes can be distinguished in oriented films with refractive indexes ranging from a low of 1.444 in the thickness direction to a high of 1.464 in the plane of the film.

## PHYSICAL PROPERTIES

In order to provide the proper perspective for the following discussion of the effect of variables on PVF film properties, it should be helpful to consider first how some of its properties compare generally with those of other films. In Tables I and II, we compare the highly oriented Teslar 20 to three other commercially available, widely known

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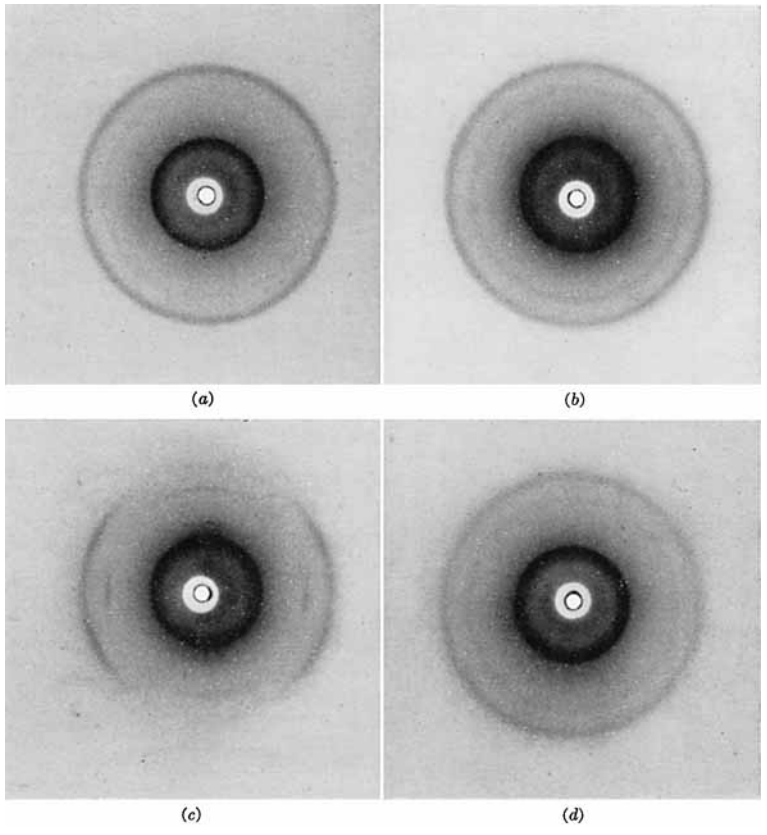



Fig. 3. X-ray diffraction diagrams showing orientation of PVF film: x-ray beam perpendicular to film surface (*a*) Teslar 20 and (*b*) Teslar 40; x-ray beam parallel to film surface (*c*) Teslar 20 and (*d*) Teslar 40.

films. Teslar 20 combines outstanding resistance to flexural fatigue with the tensile, tear, and impact properties of other typical strong, unplasticized organic films. This value of 230,000 flexes at room temperature is equivalent to the performance of low density polyethylene. The flex life of 200-gauge Teslar 20 decreases only slowly with temperature, being about 100,000 flexes at −17°C. (0°F.). The

TABLE I
Film Strength Properties (25°C.)

| | Teslar Type 20 | Mylar A[a] | Cellulose acetate butyrate | Polyvinyl chloride |
|---|---|---|---|---|
| Thickness, mils | 2.0 | 2.0 | 4.5 | 2.0 |
| Tensile strength, psi | 16,000 | 24,000 | 3,600 | 7,200 |
| Tensile modulus, psi | 260,000 | 550,000 | 120,000 | 360,000 |
| Tensile elongation, % | 135 | 140 | 95 | 110 |
| Impact strength, kg. cm./mil | 5.7 | 5.8 | 2.3 | 0.3 |
| Mullen burst strength, psi/mil | 40 | 52 | 10 | 13 |
| Tear strength, g./mil | 18 | 33 | 14 | 20 |
| Flex life, cycles | 230,000 | 5,000 | 80 | 120 |

[a] Mylar is the registered trademark for polyester film available from E. I. du Pont de Nemours & Co., Inc.

TABLE II
General Film Properties

| | Teslar Type 20 | Mylar A | Cellulose acetate butyrate | Polyvinyl chloride |
|---|---|---|---|---|
| Thickness, mils | 2.0 | 2.0 | 4.5 | 2.0 |
| Density, g./cc. | 1.38 | 1.38 | | 1.36 |
| Zero strength temp., °C. | >300 | 250 | 150 | 150 |
| Cold crack temp., °C. | <−180 | <−180 | | |
| Shrinkage at 130°C., % | 3 | 1 | — | — |
| Permeability, g./100 m.²/hr./mil | | | | |
| $H_2O$ at 40°C. | 190 | 130 | 11,000 | 130 |
| $O_2$ at 25°C. | 0.3 | 0.3 | — | — |
| $N_2$ at 25°C. | 0.02 | 0.04 | — | — |
| $CO_2$ at 25°C. | 1.3 | 1.8 | — | — |

brittleness temperature for 200-gauge, clear or pigmented, type 20 film is below −130°C. (but above −196°C.), and its zero strength temperature is 300°C. It is quite inert. It is insoluble in all nondegrading solvents below 150°C. and has fairly low permeability to gases and water vapor.

## WEATHERING RESISTANCE

Polyvinyl fluoride is resistant to oxidation, hydrolysis, depolymerization, and other degradation reactions. This inertness is especially noticeable in its resistance to weathering. An early experimental film, exposed in Florida facing south at an angle of 45° to the horizontal, retained more than half of its original elongation at the end of 10 years.[1] Another experimental film has been outdoors for 16 years and is still clear and tough. Transparent PVF films of the types discussed in this paper have been exposed in Florida for up to four years and their changes in properties followed. Simultaneously, severely accelerated weathering tests have been developed. It has been determined empirically for these films that the logarithm of the film tensile elongation at break decreases approximately linearly with time in the accelerated weathering test. This relation has been shown to hold over the entire range from initial film elongations of 100–300% down to film brittleness at 0–5% elongation.

It has also been found that this same relation applies to the decrease in film elongation during outdoor exposure. In Figure 4, the solid line represents typical data obtained thus far from Florida weathering of the types of PVF films discussed in this paper. The dashed extrapolation assumes the straight line relation will continue to hold as in accelerated tests. It can be seen then, that a typical PVF film having an initial extensibility of 140% should take 7–8 years to drop to 10% elongation and better than 10 years to reduce the residual elongation to 5% or less. Other experimental PVF films have been made which are still more resistant to weathering.

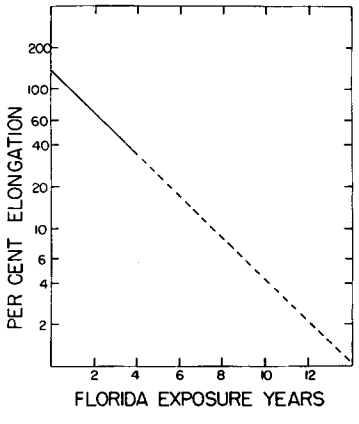



Fig. 4. Weathering of transparent polyvinyl fluoride films.

Florida weathering is more severe than in more northerly areas. Correlations between rates of weathering in various areas of the country are not well developed. Comparative weathering tests to develop these correlations are underway in our laboratory and others.

## ABRASION RESISTANCE

The inertness of PVF film outdoors is also reflected in the relative constancy of other properties. Data indicating its resistance to abrasion, erosion, and crazing are given in Table III. The abrasion data were determined by ASTM Test D658-44 and are given as the times required to wear through the films expressed in minutes per mil of film thickness. The decrease in abrasion resistance due to weathering is no more than 20%. By comparison,

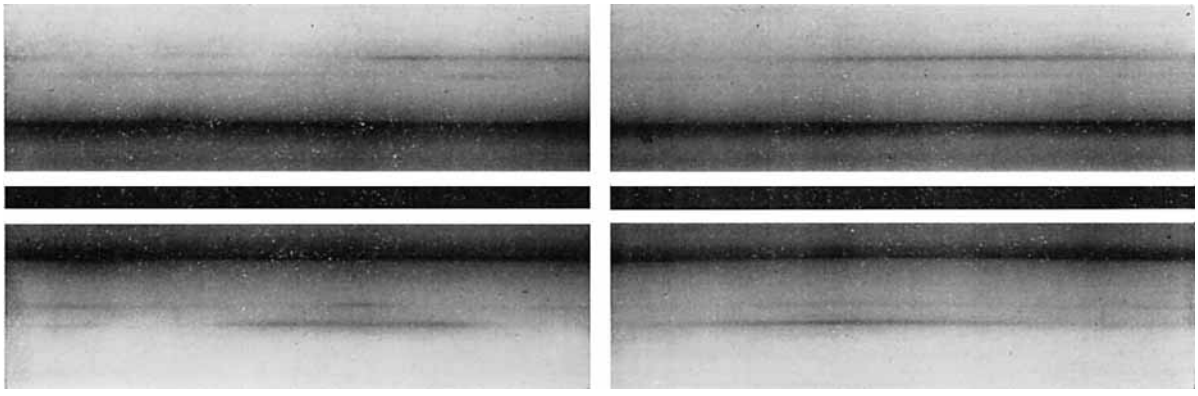
TABLE III
Effect of Weathering on PVF Films

| Film | Exposure | Thickness, in. | Abrasion resistance, min./mil film thickness | | Retention of gloss (20°), % |
|---|---|---|---|---|---|
| | | | Initial | Aged | |
| Unoriented PVF | — | 0.0042 | 4.8 | 4.1 | 74 |
| | 4 yr. in Florida | 0.0037 | 4.6 | 4.2 | — |
| Oriented PVF | — | 0.0015 | 3.4 | 3.0 | 75 |
| | 2 yr. in Florida | 0.0016 | 2.9 | 2.2 | 80 |

the abrasion values obtained for typical paints, varnishes and enamels in this test are of the order of ½–1 min./mil. Loss of gloss was measured by ASTM Test D523-53T. The high degree of gloss retained by these films after aging indicates how little surface crazing and erosion occurred.

## EFFECT OF BIAXIAL ORIENTATION

As was mentioned earlier, two of the types of PVF film differ primarily in the extent to which they are oriented in the plane of the film. The type of orientation and its degree may be deduced



(a) (b)

Fig. 5. Weissenberg x-ray diffraction diagrams showing orientation of PVF: (*a*) Teslar 20; (*b*) Teslar 40.

from x-ray diffraction evidence. In Figure 3*a* and 3*b* we show patterns for Teslar 20 and Teslar 40 (high and low orientation) obtained by passing the x-ray beam through the film normal to the film surface. These patterns indicate the crystalline nature of PVF and show that the crystalline regions are essentially randomly arranged around the thickness axis. In Figures 3*c* and 3*d* we show patterns obtained by passing the x-ray beam through the edge of the film parallel to its surface. These patterns clearly show that the crystalline regions in Teslar 20 are strongly oriented with respect to the plane of the film and are much more random in Teslar 40. This difference between the two films is also demonstrated by the Weissenberg x-ray diffraction patterns shown in Figure 5. Further evidence of greater orientation for Teslar 20 is found in refractive index data: for Teslar 20 the birefringence is 0.0186, whereas for Teslar 40 it is only 0.006.

TABLE IV
PVF Film Strength Properties at 25°C.: Effect of Orientation

| | Teslar type 20 (2 mils) | Teslar type 40 (2 mils) |
|---|---|---|
| Tensile strength, psi | 16,000 | 8,000 |
| Tensile modulus, psi | 260,000 | 260,000 |
| Tensile elongation, % | 135 | 250 |
| Impact strength, kg. cm./mil | 5.7 | 2 |
| Mullen burst strength, psi/mil | 40 | 15 |
| Tear strength, g./mil | 18 | 180 |
| Flex life, cycles | 230,000 | 10,000 |
| Shrinkage, %, at 130°C. | 3 | — |
| 150°C. | 6 | — |
| 170°C. | 21 | 1 |
| 180°C. | 30 | 2 |
| 190°C. | 40 | 20 |

The meaning of this difference in film orientation in terms of film properties is illustrated in Table IV. It may be noted that the highly oriented film is outstanding with respect to tensile, impact, and burst strengths and in flex life. The less oriented film is outstanding with respect to elongation, tear strength, and lack of shrinkage at high temperatures.

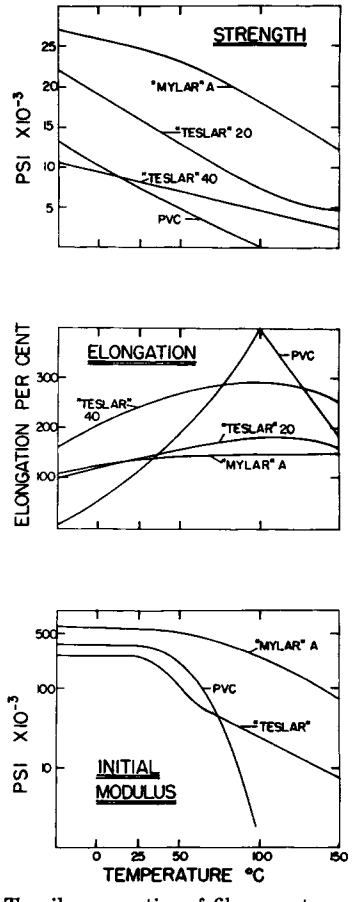



Fig. 6. Tensile properties of films vs. temperature.

### TEMPERATURE DEPENDENCE OF PROPERTIES

The temperature dependence of the tensile properties of PVF films (measured at 100% elongation per minute on an Instron tester) is shown in Figure 6. The relatively low dependence of PVF tensile properties on temperature is primarily a result of its crystalline nature and the high melting point (200°C.) of the crystals. The temperature dependence of the tensile strength and elongation is about the same for the highly oriented film as for oriented film. This characteristic is even better illustrated by elongation. After 500–1000 hr. at 150°C. the two PVF films are essentially indistinguishable with respect to extensibility and also with respect to impact strength. The near equivalence of the properties of oriented and unoriented films after heat aging suggests a possible change in structure of one or both. No such structural modification has been detected by x-ray diffraction techniques employed to date in this study.

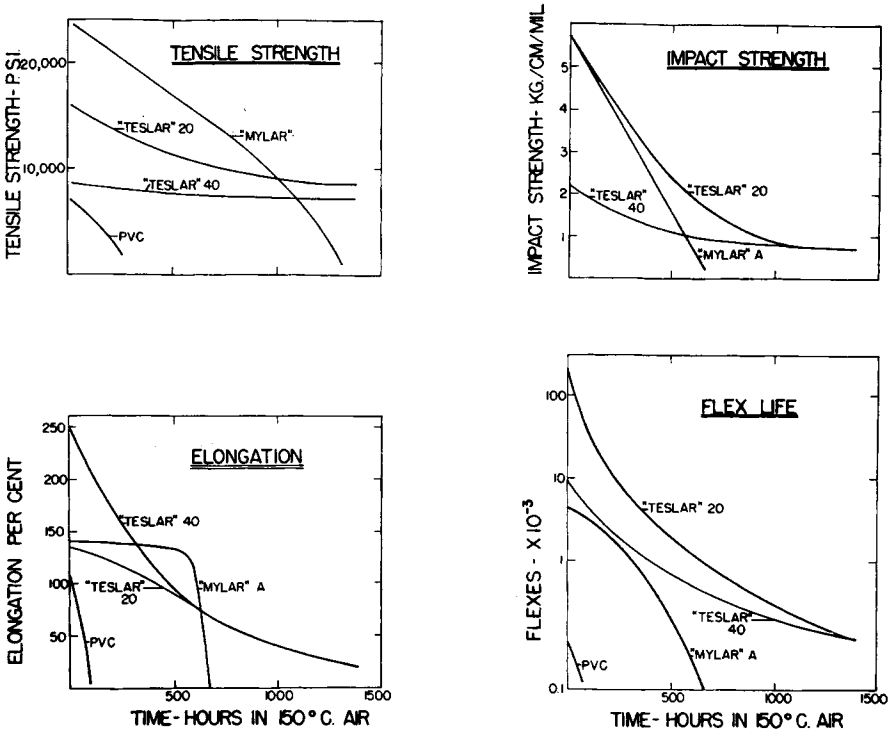



Fig. 7. Variation of film properties due to heat aging.

the lesser oriented one. High extensibility at elevated temperatures results in good thermoforming characteristics for Teslar 40. The stiffness of the two PVF films (as indicated by the initial tensile modulus) is essentially the same at all temperatures.

The stability of the physical structure of PVF films and their general resistance to oxidative and hydrolytic attack is brought out by following film property changes during high temperature wet and dry aging. Figure 7 shows the effect of heating films in air in the dark at 150°C. for up to 1500 hr. PVF films discolor under this treatment but retain a considerable strength and flexibility. Note that, as aging progresses, the tensile strength of the more oriented PVF film approaches that of the lesser

### RESISTANCE TO HYDROLYSIS

Figure 8 illustrates the relatively small effect on PVF film properties produced by aging in steam. Although only the performance of highly oriented film is shown, the low orientation film behaves similarly. Tensile strength and stiffness are not measurably altered after 1500 hr. Changes in extensibility and impact strength are slight. Flex life is halved, but remains at the high level of over 100,000 cycles to failure.

Clearly, polyvinyl fluoride is highly resistant to hydrolysis. Its general chemical inertness is illustrated additionally by the data collected in Table V. After soaking 7 days at 60°C. in 10% aqueous solutions of HCl and NaOH, films were

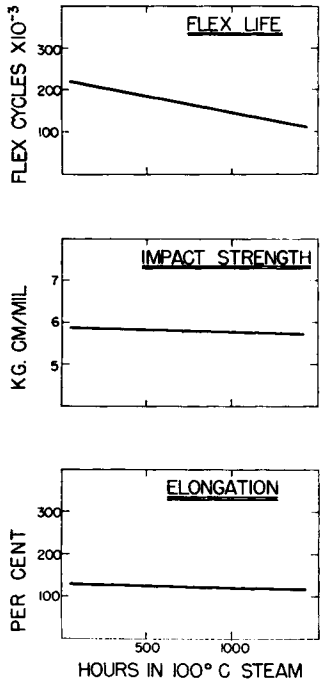



Fig. 8. Variation in PVF film properties due to steam aging.

washed, dried, and tested for changes in tensile and impact properties. No changes could be detected. As reported earlier,[2] there is no appreciable effect when PVF is boiled 2 hr. in 10% HCl, 10% NaOH, $CCl_4$, benzene, acetone, or methyl ethyl ketone.

TABLE V
Chemical Resistance of Films

| Conditions of immersion (7 days) | Property changes in films | | | |
|---|---|---|---|---|
| | Tesla 20 Tesla 40 | Mylar A | Cellulose acetate butyrate | Polyvinyl chloride |
| 10% HCl, 60°C. | No change in tensile properties or impact strength | No change in tensile properties or impact strength | Brittle | 90% loss of original elongation |
| 10% NaOH, 60°C. | No change in tensile properties or impact strength | Dissolves | Brittle | 80% loss of original elongation |

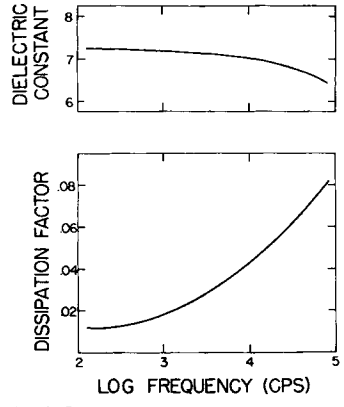



Fig. 9. Polyvinyl fluoride film electrical properties vs. frequency at 25°C.

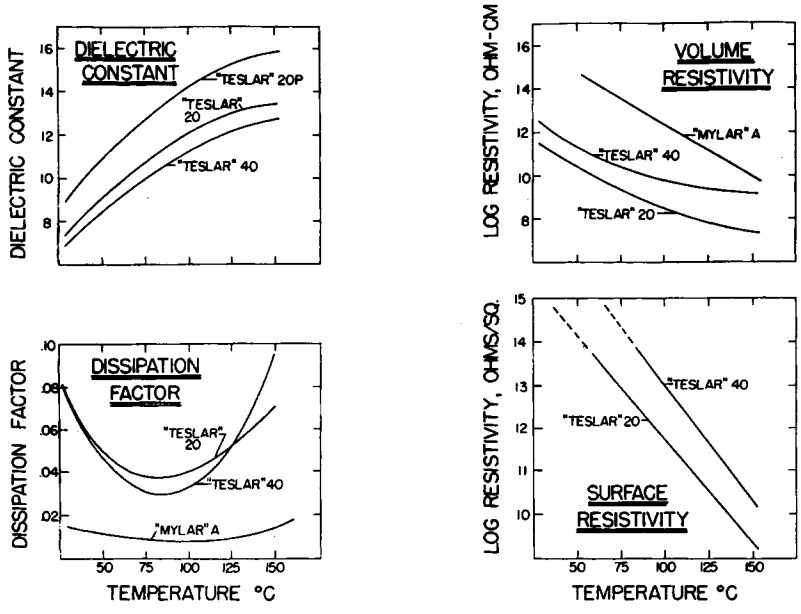



Fig. 10. Film electrical properties vs. temperature at $10^5$ cycles/sec.

### ELECTRICAL PROPERTIES

Maintenance of strength at elevated temperatures and general nonreactivity suggests a variety of applications for PVF film including electrical uses. Figures 9–11 show electrical properties and their variation with film and test variables. Figure 9 shows the general level of dielectric constant and dissipation factor vs. frequency at room temperature. Dielectric constant, which is high at room temperature, increases sharply with increasing temperature (Fig. 10). Note that the pigmented film (type 20P) has a significantly higher dielectric constant than the transparent films.

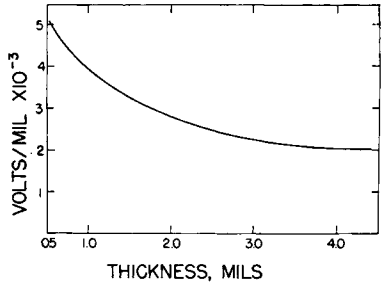



Fig. 11. PVF film dielectric strength at 25°C.

Dissipation factor goes through a pronounced minimum at about 80°C. when determined at $10^5$ cycles/sec. Colored film dissipation factors are essentially the same as those of the transparent film. Teslar 20P has essentially the same volume resistivity as Teslar 20 and essentially the same surface resistivity as Teslar 40.

The dielectric strength of PVF film varies with film thickness, as shown in Figure 11 and ranges from 2000 to 5000 volts/mil. It is essentially the same for transparent and colored varieties.

The authors gratefully acknowledge the assistance of Mr. E. J. McMahon who obtained the electrical data reported here.

## References

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## Synopsis

Polyvinyl fluoride can be made into clear and pigmented films in thickness ranging from 0.0005 to 0.004 in. and in both biaxially oriented and essentially unoriented forms. These films are extremely long-lived outdoors and are strong, tough, flexible, and inert. Useful lives of 10 years and more in Florida exposure have been demonstrated, and it has been shown that there is a linear relation between exposure time and the logarithm of film extensibility in both natural and accelerated weathering. Biaxial orientation of PVF film results in high tensile and impact strength and great resistance to flexural fatigue. Lesser degrees of orientation result in higher tear strength, greater extensibility at higher temperatures, and decreased shrinkage at high temperatures. Both oriented and unoriented films retain a large proportion of their strength properties after 1500 hr. in steam or in 150°C. dry heat. Both are highly resistant to nonoxidizing acids, bases, and solvents. PVF films have high dielectric constants, good dielectric strength, and intermediate electrical resistivity and dissipation factor.

## Résumé

On peut faire des films clairs et pigmentés de fluorure de polyvinyle d'épaisseurs variant de 0,0005 à 0,004 pouce; ils sont orientés soit biaxialement soit essentiellement non orientés. Ces films sont extremêment résistants aux traitements extérieurs et sont forts, durs, flexibles et inertes. Des durées d'emploi de 10 ans et plus, lors de leur exposition en Floride ont été démonstrées; il y a une relation linéaire entre le temps d'exposition et le logarithme de l'extensibilité du film dans une exposition aux intempéries soit naturelles soit accélérées. L'orientation biaxiale de films de PVF accroît la force à la traction et la force d'impact; en outre, elle confère une grande résistance à la fatigue par flexion. Des degrés moindres d'orientation entrainent une plus grande force au déchirement, une plus grande extensibilité à des températures plus élevées et une diminution du rétrécissement aux températures élevées. Les films orientés et non orientés gardent une grande partie de leurs propriétés de résistance après 1500 heures dans la vapeur ou chauffés a sec a 150°C. Les deux sont tres résistants aux acides non-oxydants, bases et solvants. Les films de PVF ont des constantes diélectriques élevées, une bonne résistance diélectrique, une resistivité électrique moyenne et un facteur de dissipation moyen.

## Zusammenfassung

Polyvinylfluorid kann zu klaren und pigmentierten Filmen mit Dicken von 0,0005 bis 0,004″ verarbeitet werden und zwar sowohl in biaxial orientierter als auch im wesentlichen unorientierter Form. Die Filme haben im Freien eine extrem lange Lebensdauer und sind fest, zäh, biegsam und inert. Gebrauchslebensdauern von 10 und mehr Jahren wurden bei Bewitterung in Florida erhalten und es wurde geziegt, dass eine lineare Beziehung zwischen Einwirkungsdauer und dem Logarithmus der Filmdehnbarkeit bei natürlicher und beschleunigter Bewitterung besteht. Biaxiale Orientierung von PVF-Filmen führt zu hoher Zug- und Schlagfestigkeit und grossem Widenstand gegen Biegungsermüdung. Ein geringerer Orientierungsgrad liefert eine höhere Reissgestigkeit, grössere Dehnbarkeit bei höheren Temperaturen und herabgesetzte Schrumpfung bei höheren Temperaturen. Sowohl orientierte als auch unorientierte Filme behalten einen grossen Teil ihrer Festigkeitseigenschaften nach 1500 Stunden in Dampf oder bei 150°C trockener Hitze bei. Beide sind sehr beständig gegen nicht-oxydierende Säuren, Basen und Lösungsmittel. PVF-Filme besitzen eine hohe Dielektrizitätskonstante, gute dielektrische Festigkeit, mittleren elektrischen Widerstand und Verlustfaktor.

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