

Comparative Studies on the Permeability to Water and to Water Vapor of Plastic Materials by the Hygrophotographic Technique*

JOSEPH SIVADJIAN and DAVID RIBEIRO,
Institut Pasteur, Paris, France

Synopsis

The permeability of a great number of plastic materials to water and water vapor at the normal temperature was studied, as well as the variation of this permeability for each increase of 10°C. of the temperature up to 95°C., by means of the hygrophotographic recording technique. It was concluded that for plastic materials which are sufficiently permeable to water, such as polyethylene, polypropylene, and Tedlar, this permeability at normal temperature is slightly higher than their permeability to water vapor at the same temperature. However, the difference of the two values diminishes as the temperature is increased, becoming practically equal at extreme temperatures of 85 and 95°C. The permeability of PVF (Teslar and Tedlar) to water at normal temperature and atmospheric pressure is higher than that of the corresponding chloride derivative PVC and of polypropylene in vacuum. For the polyfluoride derivatives, such as Kel-F, which are extremely resistant to the passage of moisture, the permeability to water and to water vapor for the same temperature remains constant for the entire range temperatures studied (25–95°C.). The permeability of PVC tubes to water at normal temperature was also studied; it was shown that for tubes which are supple and lose their shapes under the action of the vacuum, it is preferable to use hygrophotographic films, but for tubes which are perfectly rigid and capable of supporting the vacuum, the permeability to water may very easily be studied by putting in pieces of hygrophotographic plates.

A previous paper¹ described in detail the hygrophotographic technique and its application to the study of the permeability of plastic materials to water and to steam.

In this paper the results obtained from the study of the permeability of plastic films in a limited temperature range of 25–65°C. were also given.

We have continued this research, extending it to other plastic materials recently introduced on the market or still in the experimental stage. The first part of the present work is devoted to the study of the permeability to water of these new plastic materials between 25 and 65°C. Then, in the second part, we have widened our investigation still more and made a

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comparative study of the permeability of these same plastics to water as well as to water vapor, in a wide range of temperatures varying from 25 to 95°C.

While in our earlier work, the tests on permeability at the normal temperature of 25°C. were carried out in liquid water, the tests at elevated temperature took place only in an atmosphere saturated by steam. We have admitted however, perhaps without valid reason, that on contact with hot water, the properties of the plastic materials may have undergone profound modifications, and that the results obtained under these conditions could be without any relation to the normal properties of the film studied.

However, the introduction on the market of plastic materials of completely new compositions endowed with a very great resistance to water, brought us to believe that it was, henceforth, possible to enlarge the field of our investigations by pushing our studies as far as the maximum temperature of 95°C. that water permits us to obtain and also to make a comparative study by measuring separately the permeability of our plastic materials to water in the liquid state as well as to water in the form of steam.

To our knowledge, this was the first time that, thanks to the hygrophotographic technique, such a program of studies was made possible.

The experiments at normal temperature were carried out by immersing a part of our materials into liquid water contained in a desiccator and placing the other part on a support placed above, in an atmosphere saturated with steam which covers the liquid.

For higher temperatures, we were obliged to operate separately for the water and the vapor heated at the same temperature, for the vapor is never at the same temperature as the liquid which it covers.

EXPERIMENTAL

Preparation of Plastic Bags

We have studied in particular the permeability of halogenated plastic materials, especially monochlorinated and mono and polyfluorinated plastic polymers and the change of the permeability as a function of rising temperature. We have also worked with polyethylenic and polypropylenic films called Manolene and Profax.

The Teslar or Tedlar film is a monofluorinated polyvinyl derivative corresponding to PVC, but while, in spite of certain difficulties due to the decomposition of PVC on contact with flame, we have been able to prepare bags capable of supporting a vacuum,¹ it was impossible for us to obtain a vacuum in the Teslar and Tedlar (PVF) bags, which contract and shrink as soon as they are heated to their melting point on a surface of a certain extent.

For our studies, we had at our disposal two different kinds of Saran films of entirely different properties. The first sample had a certain rigidity. With this sample, we were able to make bags by heating with a



Fig. 1. Kel-F film, $66\ \mu$ thick, showing the formation of multiple creases in parallel lines under the action of the heat.

pressing-iron and to create a vacuum by the usual process, but as the Saran sample we obtained later, was extremely supple, it was impossible for us to work in the vacuum. The experiments were therefore carried out at atmospheric pressure just as for the Teslar and the Tedlar films.

The Kel-F films (polychlorotrifluorinated ethylene) can be sealed very easily by means of a very highly heated iron with which a suitable pressure is exerted on a film folded in two and placed between two sheets of Teflon TFE (polytetrafluoroethylene). The Kel-F bags can then be sealed by the flame of a Bunsen burner after creation of a vacuum.

During our tests with the Teflon TFE, we noticed in fact, that any plastic film can be sealed very easily by simply heating with a pressing iron held at a suitable temperature for the film, on placing them previously between two sheets of Teflon TFE. In this way no adhesion is produced, neither with the pressing iron nor with the protecting sheet of Teflon. We therefore abandoned the use of plates or sheets of aluminum or copper, described in our first paper.¹ The metallic sheets have the inconvenience of often sticking to plastics.

We have studied the permeability of different samples of Kel-F received from the Minnesota Mining and Manufacturing Co. or prepared by the W. S. Shamban Co., Culver City, California, from the commercial (Minnesota Mining and Manufacturing Co.) resin. Kel-F 81 film is a homo-

polymer of chlorotrifluoroethylene and Kel-F 82 film is a copolymer of chlorotrifluoroethylene and vanillydene fluoride.

These films present no difficulty and can be successfully worked; the manufacturing of bags being carried out by soldering with a pressing iron for sealing, and for a vacuum being created by use of a flame in front of a hypodermic needle with which the air is withdrawn.

The Kel-F 66 μ film (Shamban), when heated at 95°C., undergoes a dilatation and afterwards a sudden contraction when taken out of hot water, as we detected the immediate formation of multiple creases in parallel lines (Fig. 1).

On the other hand, the preparation of bags with the Teflon TFE films gave us much difficulty. It is impossible to obtain the fusion of these films by heating with a flame or with a pressing iron.

With the advice of the manufacturers of these films, we were able to obtain a solder suitable to the Teflon TFE films by inserting a frame of Teflon FEP between the two sheets to be soldered and heating them together for a sufficiently long time at 700–750°F. by means of a pressing-iron heated to the maximum.

Preparation of Plates

The technique of preparation and calibration of the plates was described in detail in the previous paper.¹

We have noticed that when we heated our plates wrapped in films at temperatures of 85 and 95°C., these plates underwent a certain browning recognizable on the examination of the side of the support, which, in its normal state, should be a light yellow.

The browning of the plates during heating highly diminishes their transparency and makes the results of the measurements no longer acceptable. We carried out many tests to find out the reasons for the partial opacification of hygrophotographic plates at high temperatures. The unblackened 9 × 12 cm. hygrophotographic plates were divided into four parts: the first was wrapped in 200 μ Manolene, the second in 143 μ Kel-F; these two samples were then heated in water at 80°C. The third piece of plate was stored in a box without any treatment, and the fourth piece was heated in a dry oven without a plastic sheet at the same temperature. After 20 min. of heating, we reassembled the different pieces and have photographed them by the contact process, noticing no change due to the action of the heat.

We then blackened two plates, numbered 1 and 2, which we have divided into six parts each. Next, we have wrapped two pieces of plate 1 in a Manolene 100 μ bag. In a second bag, we placed two pieces of plate 2, without having submitted them to drying in a desiccator over P₂O₅ and then heated them in water at 85°C. After a 1/2 hr. of heating, we photographed them. They were normally discolored without having undergone opacification. We have put the remainder of these two plates in the desiccator over P₂O₅, and, 6 hr. later, we once again took two pieces of

each of the two plates, wrapped them in two Manolene 100 μ bags, then heated as before in water at 85°C. for $\frac{1}{2}$ hr. On photographing them, we saw that plate 2 had undergone a marked opacification, while plate 1 remained in a normal state.

The last pieces of these plates were stored again in the desiccator for eight days, and were then treated as previously. This time, the two plates had undergone an opacification more marked than the previous time. Opacification is also notable some times after 12 hr. of storage and of dehydration over P_2O_5 . In conclusion, it seems to us, therefore, that this opacification by heating at a high temperature is due to prolonged storage of the plates over P_2O_5 and to the extreme and prolonged dehydration which is the result.

The duration of the dehydration of the plates and their stay within the desiccator over P_2O_5 must, therefore, not be more than 2 hr.

RESULTS

Results on the comparative action of temperature on the permeability to water and water vapor of various plastic films are summarized in Table I.

DISCUSSION OF RESULTS

In our first paper,¹ we showed that for commercial Saran film between normal temperature (25°C.) and 45°C., the permeability constant P is increased twofold for every 10°C. rise in temperature and consequently Van't Hoff-Arrhenius's law is verified, but between 45 and 65°C., this increase is greatly speeded up, and as a result, deviates considerably from the law.

Sarge,² who studied the permeability variation of Saran film between 25 and 49°C., concluded, agreeing with us, that the permeability is doubled for every 10°C. rise in temperature.

On the other hand, according to Doty et al.,³ who worked between temperatures of 25 and 38°C., the effect of temperature on the permeability constant ranges from no effect at all for polystyrene to a doubling of P per 5°C. increase for polyvinylidene chloride.

The increase in permeability of Mylar films as a function of the temperature, although not quite conforming with the law of Van't Hoff-Arrhenius, nevertheless is fairly regular over the entire temperature range (25–65°C.) at which we worked in our first series of experiments.

What surprised us, in the case of Teslar, was the relatively high permeability of these films composed of fluorocarbon resin.

Table II gives several comparative values of the respective permeabilities P at normal temperature. It shows that the Teslar PVF films at normal atmospheric pressure had a much higher permeability than the PVC films under vacuum.

Our studies on polyethylene films (Manolene) showed that the permeability of thick films was much higher than that of thinner films, and we had

TABLE II

Film	Film thickness, μ	P , $\mu\text{g.}/\text{mm.}/\text{mm.}^2/\text{hr.}$ $\times 10^{-3}$
PVC (Lucolene)	30	3.66
	70	7.78
Teslar	26	13.50
	75	20.20

attributed this increase of the permeability of thick films to the physical conditions prevailing during their manufacture process.

Therefore, in our previous work, we pointed out that this result is due to the structure of these films conditioned by their methods of obtention. Obtaining these very thin films imposes, during the calendaring or the extrusion blowing, conditions which lead to molecular orientations which are the more marked the thinner the films.

Then we noted that, as we concluded in the case of polyethylene films (Manolene), the permeability constants of Mylar (polyethylene terephthalate) films, 31 and 60 μ , measured at normal temperature, are almost identical (12.0 and 15.7), while for thick film (151 μ), this constant differs greatly from the preceding value, becoming 21.9.

These results are confirmed by Ito⁴ who states that in the case of polymer film to which the vapor has affinity, the permeability coefficient P increases with increasing thickness of the films. In the process of permeation, one side of the film is wet and the other dry. The proportion of the former increases with increasing film thickness. This is the most probable cause for the increase of P with the increase in the film thickness.

Generally speaking, the comparative study of the permeability to water on the one hand and to water vapor on the other, for the same given temperature, showed that this permeability is slightly higher in the case of water than in the case of water vapor at low temperatures for relatively permeable plastic materials, such as Tedlar or Profax. At high temperatures (85 and 95°C.), the permeabilities become practically equal. In all cases, the permeability of polypropylene (Profax) is clearly weaker than that of Tedlar.

In the case of FEP, of which the permeability to water is also a little higher than the permeability to steam, the deviation of the two values remains apparently the same for all temperatures, while it is accentuated for Saran. However, the Saran film used in the present study was very different from the sample previously used.

For plastic materials very slightly permeable to water, such as Kel-F, no difference was verified, the permeability to water being the same as the permeability to water vapor for all the temperatures studied.

As for Kel-F, we have studied several samples, Kel-F films (Shamban Co.) 55 and 143 μ thick and Kel-F 81 and 82. Unfortunately, the samples of Kel-F 81 and 82 at our disposal were not sufficient to enable us to carry out a complete study.

In spite of the incomplete character of our studies of Kel-F 81 and 82, the comparison of the results obtained with the three types of Kel-F permitted us to conclude that their permeability, at normal temperature, is about the same for water and for water vapor.

Kel-F was also studied by Myers et al.⁵ According to these authors, Kel-F films (plasticized homopolymers) provide exceptional gas and water vapor resistance.

Konovalov⁶ studied the permeability at elevated temperature of films of polyethylene, of polytrifluorochloroethylene (Kel-F), of polytetrafluoroethylene (Teflon TFE), of polyvinylchloride (PVC), of polyvinylidenechloride (Saran), and of polyamides 0.035–0.055 mm. thick, by measuring the loss of weight of permeability cells, of which one of the surfaces had been formed by the plastic sheet to be studied. He noted in this way the weakest permeabilities for Kel-F, Teflon, and Saran.

Water Permeability of PVC Tubes

We have also studied the permeability to water of tubes made of plastic materials (PVC).

For example, we introduced into the interior of a piece of tube 10–15 cm. long, two pieces of hygrophotographic plates, exactly as in the case of plastic sheets, that is to say, their sensitive surface on the outside. We closed the two extremities of the tubes with rubber stoppers, one being pierced in the middle with a hole, through which we have introduced a glass tube and, after having made a vacuum in the interior, we sealed the glass tube and coated the two extremities with a mixture of melted paraffin and wax, termed cytoparaffin, including their stoppers in order to ensure the water-tightness. Afterward, the tube was immersed in water while another tube prepared in the same manner was kept in a desiccator over P_2O_5 .

The tubes were crushed and flattened under the action of the vacuum. After the first tube was kept in the water for six days, we removed the plates on the seventh day as those in the control tube stored dry, and then photographed them. It can clearly be seen that the tube kept in the water permitted a certain amount of moisture to pass through, causing discoloration of the plates. In a second series of experiments, we replaced new hygrophotographic plates in our two tubes and, after having rendered them water-tight, we immersed them in water as well as another new tube of a larger diameter.

The plates inside the tube placed twice in the water showed much greater discoloration (Fig. 2 left) than those in the control tube kept dry the first time (Fig. 2, right). This, however, is to be expected because the moisture is retained in the walls of the tube having already been once immersed in the water.

According to this analysis, it can be seen that the tube which was twice immersed in water let pass the second time $0.086 \mu\text{g. water/mm.}^2/\text{hr.}$ while the control tube showed a permeability rate of $0.067 \mu\text{g./mm.}^2/\text{hr.}$

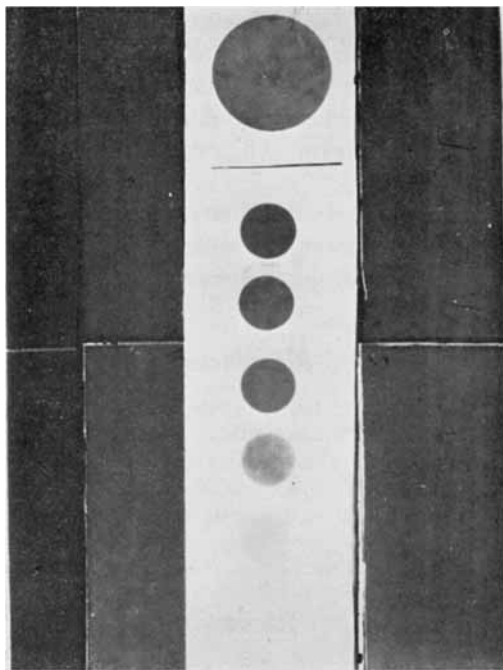


Fig. 2. Hygrophotographic recording of the permeability of PVC pipes to water. The plates inside the tube placed twice in the water showed greater discoloration (left) than those in the tube kept dry the first time (right).

We find a value almost identical ($0.062 \mu\text{g.}$) for the permeability of the larger tube.

To prevent the crushing of the tubes, we also carried out tests in which the thin hygrophotographic films were rolled up in the interior, the sensitive side turned to the internal surface of the tubes. The experiments were carried out under atmospheric pressure, and when we had stoppered the two ends of the tube with rubber stoppers, we waterproofed them by dipping both corked-up ends in cytoparaffin. Then we immersed a tube treated in this way in water and kept it in the dark, while we placed an identical tube in a desiccator over P_2O_5 , and also put it in a dark place. After a few days, we measured the discoloration of the films. We noticed that the film taken from the tube immersed in water is very much discolored, and that the check film is also somewhat discolored. This was perhaps due to the dampness of the air which remained in the tube as well as to the dampness of the film itself, being composed of a layer of gelatin and of a cellulosic support which is also hygroscopic. To determine the exact quantity of water vapor absorbed through the walls of the tube, the degree of discoloration of the check film must be deducted from that of the film taken from the tube which was immersed in water.

The permeability of the PVC tube, measured by the foregoing method, i.e., by the difference of discoloration obtained in a desiccator and in

water is $0.0081 \mu\text{g./mm.}^2/\text{hr.}$ for a tube 2.5 mm. thick which had stayed for 188 hr. in water. The permeability constant P , is therefore $0.018 \mu\text{g./mm./mm.}^2/\text{hr.}$ For another piece of tube which had been in water for 12 days (262 hr.), we found a permeability of $0.0175 \mu\text{g./mm.}^2/\text{hr.}$, which gives, in terms of unit thickness, a permeability constant of $0.040 \mu\text{g./mm./mm.}^2/\text{hr.}$

If these values are compared with those established working in a vacuum, we can conclude that the amount of water which permeates through the walls of a PVC tube, at atmospheric pressure, is one-fourth that amount absorbed in vacuum.

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Résumé

Les auteurs ont étudié la perméabilité d'un grand nombre de matières plastiques vis-à-vis de l'eau et de la vapeur d'eau à la température normale, ainsi que la variation de cette perméabilité pour chaque augmentation de 10° de la température jusqu'à 95°C . Cette étude a été faite au moyen de la technique de l'enregistrement hygrographique de l'humidité. Les auteurs ont pu conclure que pour les matières plastiques qui sont suffisamment perméables à l'eau, comme les polyéthylènes, les polypropylènes et le Tedlar, cette perméabilité à la température normale est légèrement plus élevée que leur perméabilité vis-à-vis de la vapeur d'eau à la même température. Cependant, la différence des deux valeurs diminue au fur et à mesure que la température augmente et elles deviennent pratiquement égales aux températures extrêmes de 85° et de 95°C . La perméabilité du PVF (Tedlar et Teslar) à l'eau à la température et à la pression atmosphérique normales est plus élevée que celle du dérivé chloré correspondant, le PVC et du polypropylène dans le vide. Dans le cas des dérivés polyfluorés, comme les Kel-F, qui sont très résistants au passage de l'humidité, la perméabilité à l'eau et à la vapeur d'eau pour une même température donnée reste constamment la même pour toute la zone des températures que nous avons étudiées, de 25° jusqu'à 95°C . Les auteurs ont étudié également la perméabilité de tubes de PVC à l'eau à la température normale et montré que, lorsque ces tubes sont flexibles et déformables sous l'action du vide, il est préférable d'étudier leur perméabilité à l'eau au moyen de films hygrographiques; mais que, lorsque les tubes sont parfaitement rigides et capables de supporter le vide, leur perméabilité à l'eau peut être très facilement étudiée en y introduisant des fragments de plaques hygrographiques.

Zusammenfassung

Die Autoren haben die Wasser- und Dampfdurchlässigkeit einer grossen Zahl von Kunststoffen bei normaler Temperatur und die Abhängigkeit dieser Durchlässigkeit von der Temperatur in Intervallen von 10° bis zu einer Temperatur von 95°C untersucht. Die Untersuchung wurde mit Hilfe des hygrographischen Verfahrens durchgeführt. Die Autoren fanden, dass für Kunststoffe, die für Wasser genügend durchlässig sind, wie Polyäthylen und Polypropylen, die Wasserdurchlässigkeit bei Normaltemperatur

etwas höher ist als die Durchlässigkeit für Wasserdampf. Die Differenz zwischen den beiden Werten nimmt jedoch mit steigender Temperatur ab und bei extremen Temperaturen von 85–95° werden die beiden Werte praktisch gleich. Die Wasserdurchlässigkeit von PVF (Teslar oder Tedlar) bei normalem Druck und normaler Temperatur ist höher als die der entsprechenden Chlorverbindung PVC und Polypropylen in Vakuum. Für die Polyfluorverbindungen, wie das Kel-F, die äusserst undurchlässig für Feuchtigkeit sind, ist die Durchlässigkeit für Wasser und Wasserdampf bei der gleichen Temperatur im untersuchten Bereich von 25–95°C stets gleich gross. Die Autoren untersuchten auch die Wasserdurchlässigkeit von PVC-Röhren bei Normaltemperatur. Wenn diese Rohre weich und durch Vakuumeinwirkung verformbar sind, ist es vorzuziehen ihre Wasserdurchlässigkeit mit Hilfe von hygrophotographischen Filmen festzustellen. Sind die Rohre jedoch völlig starr, so kann ihre Wasserdurchlässigkeit leicht untersucht werden, indem Stücke hygrophotographischer Platten in sie eingebracht werden.

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