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Flexible packaging Permeability document: The Applications of DATA-CURVE-FITTING for Flexible Packaging Permeability Tests

Abstract: With regards to the industries of food, pharmaceutics, cosmetic, most of daily chemical and part of other industry productions, high barrier packaging materials are remarkably effective in prolonging the shelf life and improving the preservation quality of packaging contents. However, the barrier property of such materials can be changed with the influence of environment factors, particularly, in the regard of temperature. Meanwhile, because differences exist in molecule arrangement in polymer for various kinds of materials, the regularities of change in barrier property with respect to temperature fluctuation varies for different materials. Thus, we should test and analyze the temperature influence on each kind of material independently. Even though we know the regularities of some materials that barrier property links with the temperature, it is still undoable in getting the permeability parameters for one kind of material by taking the data of other similar kinds of materials at specifically temperature for reference. Furthermore, permeability tests can be easily operated at routine temperature directly (e.g.: 10~50℃), whereas it tends to be very difficult and costly to run such tests at non-routine temperature (e.g.: refrigeration temperature, high temperature for sterilization, etc.). Carrying out permeability tests at non-routine temperature needs the equipments with superexcellent temperature resistance, such as good heat resistance or cold resistance, as well as that operator needs to actualize the ideal test environment at such temperature. Mistakes can be often made in packaging materials chosen caused by taking the barrier property of materials at routine temperature into account only. At the same time, severe pecuniary loss will be followed these kinds of mistakes as well. In this way, barrier property of materials at non-routine temperature becomes very useful in the field of practical application. The DATA-CURVE-FITTING methodology could be the way out to such puzzle of matching up the best use of barrier materials with packaging at different temperature, especially the non-routine ones. Based on film permeation theory applied broad, the DATA-CURVE-FITTING methodology can be used to obtain the permeability parameters of barrier materials at non-routine temperature easily and economically by analyzing the permeability data got in tests operated at routine temperature based on such method and the model of film permeation theory without actualizing the appointed test environment of non-routine temperature costly. This DATA-CURVE-FITTING methodology for permeability test has been proven to be highly scientific and objective through observations on a large number of actual testing data.

Key Words: DATA-CURVE-FITTING, permeability, packaging materials, non-routine temperature, flexible packaging

As we all know, for foods, pharmaceuticals, and cosmetics, oxygen and water vapor are major factors causing deterioration and invalidation. That is why barrier property is the key indexes in evaluating packaging materials. However, barrier property of materials is closely related to temperature fluctuation, which influences barrier property of materials obviously. Therefore it is required to test the barrier property of materials at the actual application temperature before designing packaging. However, some actual application temperature of the

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materials, such as refrigeration temperature and sterilization temperature are beyond the scope of routine laboratory testing temperature or the testing equipment's normal working temperature. For laboratory tests, we take routine application temperature as non-routine temperature.

In fact, there are many difficulties to test the barrier property of materials directly at non-routine temperature, such as high cost, low efficiency, inconvenient operation, and so on. Thus, Labthink developed the DCFP technique to resolve these testing difficulties. You can get the barrier property of materials at non-routine temperature easily, conveniently and economically.

1. THE INFLUENCE OF TEMPERATURE FLUCTUATION ON BARRIER PROPERTY

1.1 THE REASON FOR INFLUENCE

Temperature rise will affect both films and permeable gases. For films, when temperature rises, polymer cohesion becomes lower, which leads the free volume of polymer to increase, and reduces obstacles effectively for permeable gas molecules that are inside polymer and in diffusion process, which accelerates diffusion speed in the end. As to permeable gases, temperature rise will result in the increase of gas molecule energy, which makes gas diffusion in polymer more easily. Thus, with the increase of temperature, gas transmission becomes more faster, and the barrier property of packaging materials becomes lower. The relationships of permeability coefficient, diffusion coefficient, solubility coefficient of inorganic gases with temperature are all conform to Arrhenius equation:

$$P = P_0 e^{-E_P/RT} \qquad (1)$$

$$D = D_0 e^{-E_D/RT} \qquad (2)$$

$$S = S_0 e^{-\Delta H/RT} \qquad (3)$$

Where: P, D, S——permeability coefficient, diffusion coefficient and solubility coefficient

P_0, D_0, S_0——the respective pre-exponential term

E_P, E_D, ΔH——activation energy of permeation, activation energy of diffusion, and sorption enthalpy

R——gas constant, 8.31441J/mol·K

T——temperature in degree Kelvin

From the Arrhenius equation, we can see that temperature fluctuation could affect P, D, S, and influence the barrier property of materials. Whereas, barrier property change caused by temperature fluctuation in various kinds of materials are different.

1.2 INFLUENCE DEGREE

To test the influence degree on barrier property caused by temperature fluctuation, we have launched a set of gas permeability tests from 0℃ to 70℃ used Labthink differential pressure method gas permeability tester. The tested specimens include Polycarbonate (PC) film (125um), Polyethylene terephthalate (PET) film (25um), Polypropylene (PP) film (200um), Polyvinyl Dichloride (PVDC) film (30um) and aluminum (AL) film (100um). Please see Figure 1 for the data.

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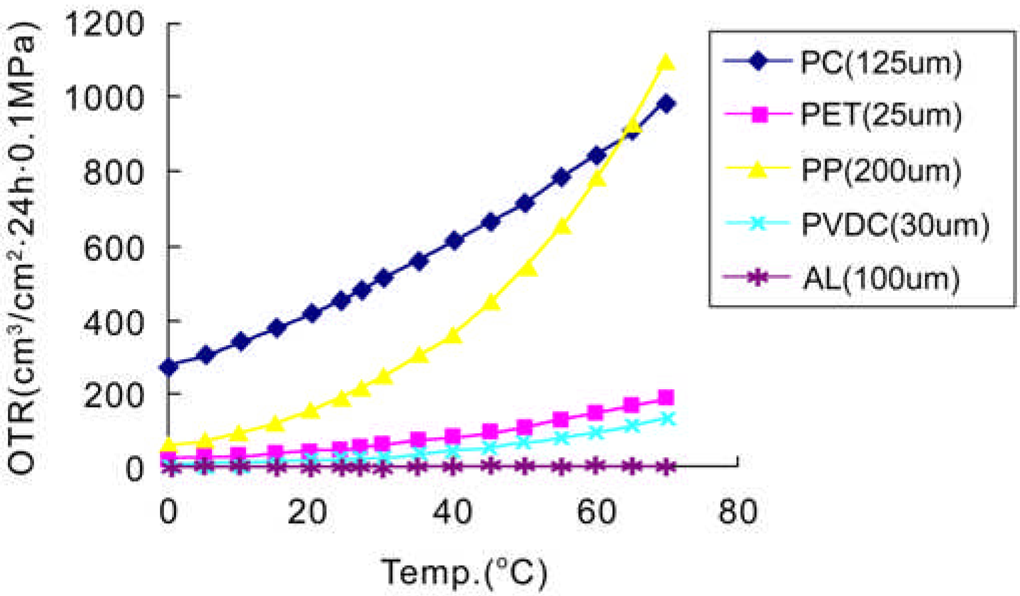

Figure 1. Temperature Influence on Barrier Property of Materials

According to Figure 1, temperature has an obvious effect on gas transmission rate of all specimens except aluminum film, but the influence degree is not the same. For PET film, we take a comparison of 30℃ and 40℃, oxygen transmission rate (OTR) at 40℃ increases 38% than 30℃. For PC film, the increment is 20%. For PP film, it is 46%. And for PVDC film, it is 56%. With the temperature increasing, OTR will continue to increase with accelerated trend.

1.3 The Loss Caused By Temperature Fluctuation

Actually, it is a hard task to ensure the application temperature of products is the same as measuring temperature of packaging materials. Since temperature fluctuation leads the change of barrier property of materials, the packaging perhaps unable to reach expected shelf life and preservation quality. At the same time, the improper selection of barrier packaging materials will place a big financial burden on enterprises. And the failure of packaging design and product invalid not only impacts the product itself, but also the reputation of enterprises.

2. BEST METHOD TO GET BARRIER PROPERTY AT NON-ROUTINE TEMPERATURE

2.1 DATA CURVE FITTING IN PERMEATION

It is very difficult to get barrier property of materials at all application temperature. First, test precision is low and test error is unavoidable. Second, the manufacturing process of testing instrument is complex and testing cost is high. Third, test efficiency is low and operation is inconvenient. Fortunately, Data Curve Fitting in Permeation (DCFP) can overcome the mentioned difficulties excellently. In brief, DCFP is one of the mathematical explorations of permeability analysis techniques, it is based on theoretical basis of Fick's law, Henry's law and Arrhenius equation. With DCFP technique, we can obtain gas transmission rate, permeability coefficient, diffusion coefficient and solubility coefficient at non-routine temperature, using permeability data at routine temperature. It does not need special equipment in the application of DCFP, but only a little time to finish.

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2.2 APPLICABLE TESTS

DCFP is convenient to use. Large numbers of test data based on actual tests prove that DCFP has better application effect and higher fitting precision. For the reason of space limit, here only takes the applicable test of PET film (20um), PP film (200um), and PVDC film (30um) for example, and other materials will not be elaborated. The adoptive instrument is VAC-V1 differential pressure method gas permeability tester. Conventional test range of this instrument is 0.1~100000 $cm^3/m^2 \cdot 24h \cdot 0.1MPa$. Its vacuum resolution is up to 0.1Pa, and the vacuum in test chamber can be assured below 20Pa. Temperature control range is between room temperature and 50℃, with a precision of ±0.2℃. Constitution of testing instrument is shown in Figure 2. It consists of Labthink VAC-V1differential pressure method gas permeability tester, data processing system, vacuum pump with a capacity of 0.1Pa and oxygen gas.

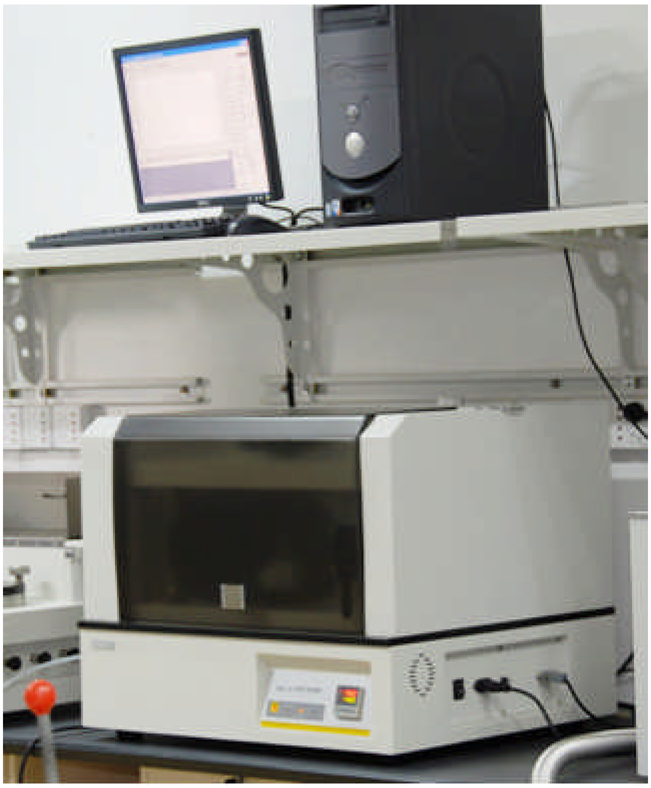

Figure 2. VAC-V1 Differential Pressure Method Gas Permeability Tester

With temperature controlling function of the instrument, oxygen permeability tests at 23℃, 25℃, 30℃, 33℃, 35℃ and 37℃ are performed for more than five times respectively. Then OTR and permeability coefficient (P) at these temperature are employed in DCFP technique. In the mean time, OTR and P at other temperature (such as 40℃, 43℃, 45℃, etc.) are tested to compare with the fitting data (data from DCFP). Please see Figure 3 and Table 1 for the data.

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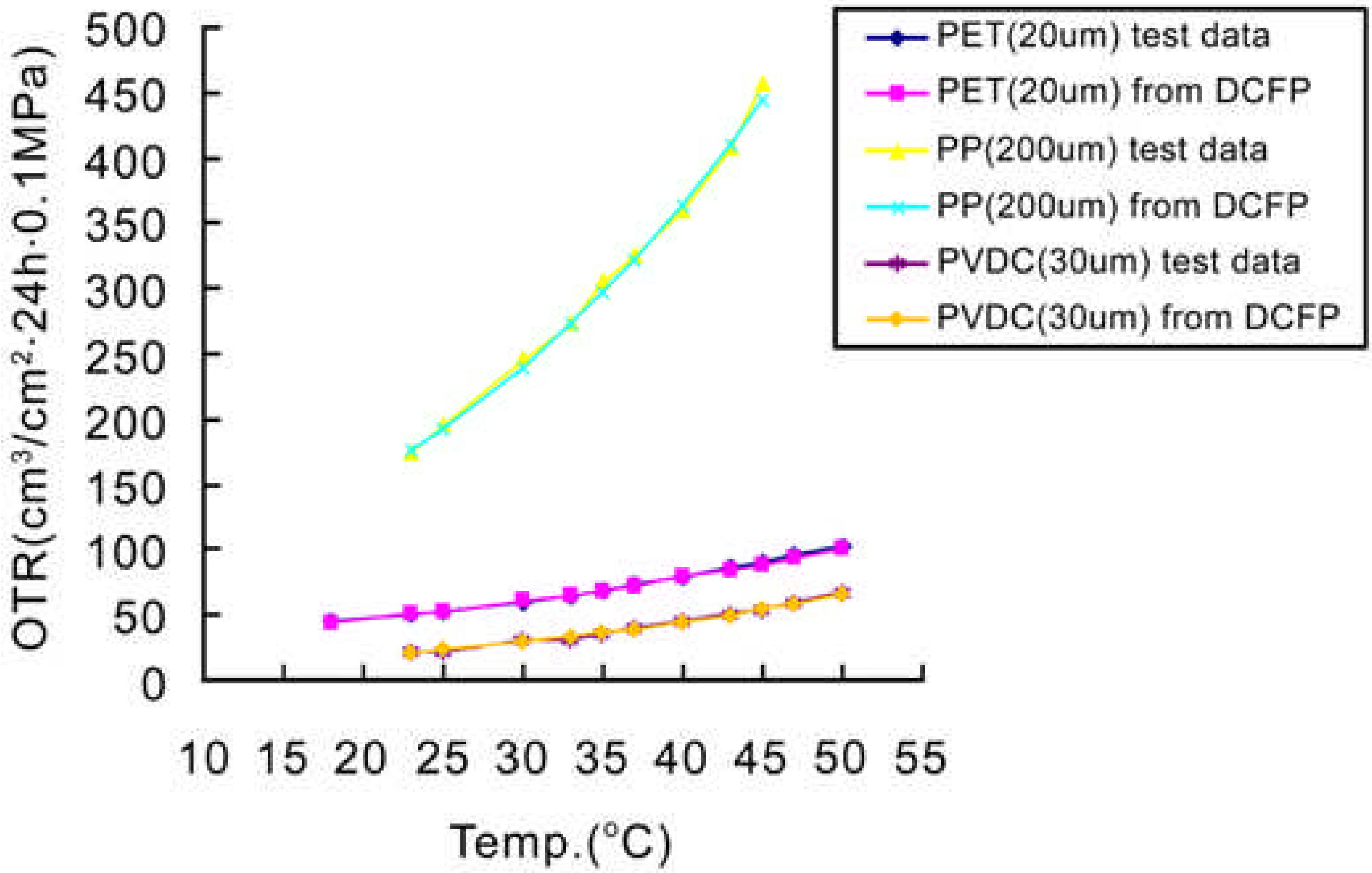

Figure 3. Diagram of Test Data and Fitting Data

Table1. List of Test Data and Fitting Data of PET Film

Test Temp.℃	OTR[1] (Mean)	P[2] (Mean) E-12	Fitting OTR[1]	Fitting P[2] E-12	Error
18	45.579	1.388	43.383	1.321	-4.83%
23	50.839	1.548	50.038	1.524	-1.55%
25	52.666	1.604	52.906	1.611	0.44%
30	59.369	1.808	60.621	1.846	2.10%
33	65.443	1.993	65.64	1.999	0.30%
35	68.884	2.098	69.156	2.106	0.38%
37	74.080	2.256	72.81	2.218	-1.68%
40	78.493	2.390	78.56	2.393	0.13%
43	86.194	2.625	84.643	2.578	-1.79%
45	89.987	2.741	88.887	2.707	-1.24%

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47	95.632	2.912	93.288	2.841	-2.44%
50	102.181	3.112	100.188	3.052	-1.93%

Note: 1. The unit of OTR is cm^3/m^2·24h·0.1MPa.

2. The unit of P is cm^3·cm/cm^2·s·cmHg.

The lines in Figure 3 are made up of OTR at different temperature for films like PET film, PP film, and PVDC film. There are two lines for each film; one consists of the data tested at actual temperature, and the other from DCFP. The colors of lines for real tests are oxford blue, yellow and purple correspondingly with PET film, PP film and PVDC film. While the colors of lines for DCFP are lilac, sky blue and brown. From Figure 3, it is easy to find out that two corresponding lines of each film lap over each other perfectly.

DCFP provides an effective way to get barrier property of packaging materials at non-routine temperature, such as temperature over 100℃ and below 0℃. Figure 4 is the OTR curve of PET film (20um) from -173℃ to 177℃, the inclusive data of it are from DCFP.

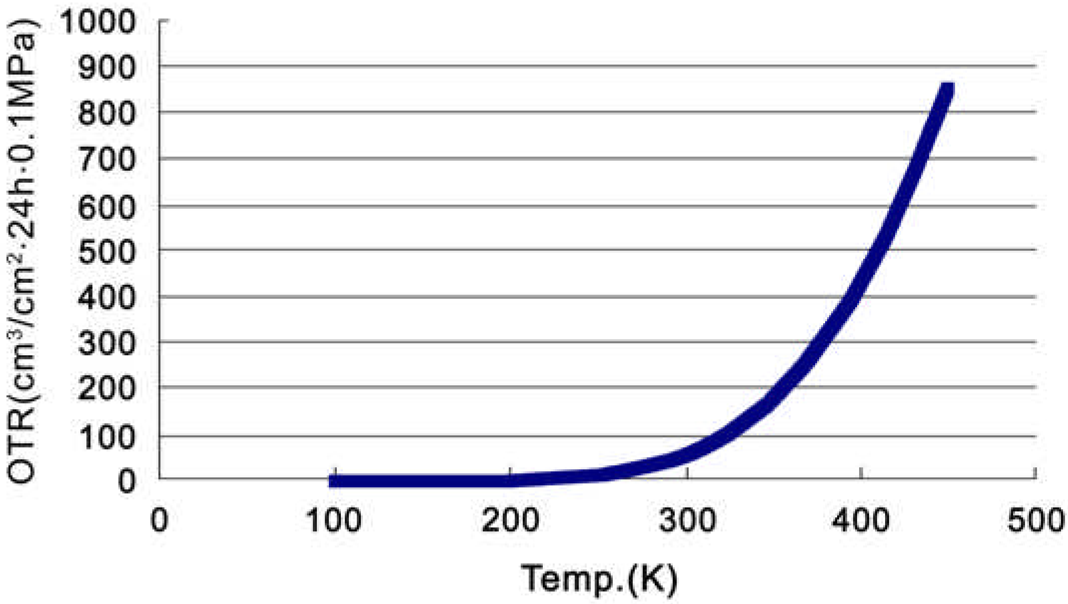

Figure 4. OTR Curve of PET film (20um) at Non-routine Temperature

DCFP provides an effective way to adjust material thickness to the most economic state on the premise of ensuring barrier property of materials. Moreover, DCFP possesses the following advantages in application and popularization. First, precision of results is high. Second, cost is low. Third, it is convenient and easy to use.

3. Application of DCFP in China

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The influence of temperature on barrier property of material is very significant. And the effect on each kind of material varies with each other. Thus, the materials could be better used for packaging only when their temperature characteristics are obtained. With DCFP technique, permeability parameters in non-routine conditions can be obtained accurately, easily, conveniently and economically. The application of DCFP not only reduces the difficulty greatly, which will be met in obtaining permeability parameters at actual application temperature, but also avoids the loss effectively, which is caused by difference between application and measuring temperature.

Now, Labthink has established database of permeability parameters for different materials at a very wide temperature scope from -100℃ to +100℃. The database includes the permeability parameters of PC film, PET film, PP film, PE film, and so on. Based on its advantage in application, DCFP technique wins general popularity in China. DCFP technique has been already listed as one of the China national research items in 2007, and will expand in the whole packaging industry after completing in 2008.