PROCEEDINGS

OF

EUROPAK '85

First Ryder European

Conference on Plastics

And Packaging

Presented on September 17-18, 1985

RC, ltd

EUROPAK '85

FIRST RYDER EUROPEAN CONFERENCE ON PLASTICS AND PACKAGING

PROGRAM

September 16th (Monday)

2.00 – 5.00 p.m. Registration in Hotel foyer

September 17th (Tuesday)

8.00 – 10.00 a.m. Registration in the foyer

QUEENS HALL

9.30 – 10.00 a.m.	*Coffee and Biscuits – Lakeside Pavillion*
10.00 a.m.	**Conference Introduction** Leonard B. Ryder, *President, Ryder Associates Inc. (U.S.A.)*
10.10 a.m.	**"Shelf Life Prediction of High Barrier PET/EVAL Multilayer Bottles for Soft Drinks, Wine and Beer"** K. Ikari, T. Sato, T. Negi, *Kuraray Company (Japan)*
10.50 a.m.	**"Oriented EVOH Film: Properties, Applications, and Implications"** George O. Shroeder, *George O. Shroeder Associates (U.S.A.)*
11.30 a.m.	**"Unique Process for Laminar Barrier Containers"** S. C. Swallert, *Du Pont de Nemours International S.A. (Switzerland)*
12.30 p.m.	*Group Luncheon – Lakeside Pavilion*
1.55 p.m.	**Opening Remarks**
2.00 p.m.	**"Permeation Studies on Barrier Containers"** S. Marcus, *Dow Chemical Co., (U.S.A.)*
2.40 p.m.	**"Retorted EVOH Multi-Layer Cans With Excellent Oxygen Barrier Properties"** James A. Wachtel, *American Can Co. (U.S.A.)*
3.20 p.m.	*Coffee and Biscuits – Lakeside Pavillion*
3.50 p.m.	**"Stretch-Blown PVC Bottles With PVDC Barrier Coating Improvements"** P. Grange, *B.A.P., Solvay & CIE (Belgium and France)*
4.30 p.m.	**"Coating as Cost Effective and Quality Alternative to High Barrier Plastics"** Gordon Dodson, *Nordson Corporation (U.S.A.)*
5.10 p.m.	**"High Barrier and Other Multilayer Packaging Structures"** J. Rochefort, *ONO SA (France)*
6.00 p.m.	*Cocktails and Drinks – Lakeside Pavilion*
7.00 – 8.30 p.m.	*Dinner – Lakeside Pavilion*
9.00 – 10.30 p.m.	*Hospitality Reception – [illegible] Room*

September 18 (Wednesday)

Moderator: Leonard B. Ryder

9.30 a.m.	*Coffee and Biscuits – Earls Room*
9.55 a.m.	**Opening remarks**
10.00 a.m.	**"High Tech Extrusion Equipment for High Barrier Sheeting"** Frank Nissel, *Welex Inc. (U.S.A.)*
10.40 a.m.	**"In Line Thermoforming of Special Performance Plastics Packaging"** A. Stadler, *Ballaplast Maschinenbau GmbH (Fed. Rep. of Germany)*
11.20 a.m.	*Coffee and Biscuits – Earls Room*
12.00 p.m.	**"Implications of PET Packaging Revolution in North America"** Peter Weggeman, *Fairfield Associates (U.S.A.)*
12.50 p.m.	*Group Luncheon – Palace Suite, Earls Room*
1.55 p.m.	**Opening Remarks**
2.00 p.m.	**"Husky/Sidel: New Integrated Approach to Oriented Containers"** R. Schad, *Husky Injection Moulding Systems (Canada)*
2.40 p.m.	**"Recycling – a Challenge, Not a Threat"** T. Planke, *A/S Tomra Systems (Norway)*
3.20 p.m.	*Coffee and Biscuits – Earls Room*
3.50 p.m.	**"RHB-2000: A Universal Quick-Change Machine for Oriented Containers"** S. Belcher, *Cincinnati Milacron (U.S.A.)*
4.30 p.m.	**"Comparative Economics of High Barrier Plastics Containers"** R. H. Foster, *Eval Company of America (U.S.A.)*
5.10 p.m.	**Closing Remarks**
5.25 p.m.	**END OF CONFERENCE**

TABLE OF CONTENTS

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SHELF-LIFE PREDICTION OF HIGH-BARRIER PET/EVAL MULTILAYER BOTTLES FOR SOFT DRINKS, WINE AND BEER

by

DR. K. IKARI
MANAGER R&D - EVAL DIVISION

TOSHIAKI SATO
ASSISTANT SENIOR RESEARCHER

TAICHI NEGI
ASSISTANT SENIOR RESEARCHER

KURARAY COMPANY, LTD.

For Presentation at

EUROPAK '85

First Ryder European Conference

on

Plastics and Packaging

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KYOICHIRO IKARI

Joined Kuraray Company, Ltd. after graduation of applied Chemistry Dept. of Tokyo Institute of Technology, Japan in 1957. Currently General Manager of EVAL Research and Development Division in OSAKA Head Office. Previously, belonged to R&D Division of Kurashiki Laboratory and engaged EVAL and PVA application, processing and their physical chemistry.

TOSHIAKI SATO

Joined Kuraray Co., Ltd. after obtaining a Master's Degree in Chemical Technology at Osaka University, Japan in 1975; currently Assistant Senior Researcher of Polymer Processing R&D Laboratories and working on barrier materials.

Previously engaged in R&D of isopurene for synthetic rubber, new flavors and perfumes, etc. Currently working and living with his family (wife, daughter and two sons) in Kurashiki, a city located to the west of Osaka.

TAICHI NEGI

Joined Kuraray Co., Ltd. after obtaining a Master's Degree in Department of Chemistry, faculty of Science at Osaka University, Japan in 1972. Currently Assistant Senior Researcher of Polymer Processing R&D Laboratory, working on barrier materials and thermoforming property.

Previously engaged in manufacture of EVAL polymer and production of EVAL films. Currently working and living with his family (wife and a son) in Kurashiki a city located to the west of Osaka.

Introduction

Nowadays, PET mono-layer bottles are used worldwide for carbonated beverages (soft drinks, draft beer), because of the usefulness of the excellent pressure-durability and clarity of PET resins.

However, in line with the increasing use of PET mono-layer bottles, the CO_2 gas barrier property and oxygen gas barrier property of these bottles have been found to be insufficient for this market by users. 2ℓ PET mono-layer bottles have a shelf-life of about 15 to 16 weeks, which means that soft drinks in such bottles, if kept at room temperature and 65% R.H., would lose 15% or more of their CO_2 gas (about 4 volumes of CO_2) in this period of time. Small-capacity PET mono-layer bottles (0.5ℓ or less) have a shelf-life of 8 weeks or less; it is generally held that PET mono-layer bottles cannot be optimumly used for carbonated drinks.

As a promising field of application for PET mono-layer bottles, the preservation of wine and beer has been drawing attention. The taste of wine and beer is changed by oxygen, so their containers in particular are required to have an excellent oxygen gas barrier property.[1)] PET mono-layer bottles cannot satisfactorily be used for this market. The currently available bottles are PET mono-layer bottles coated with poly (vinylidenchloride) (PVDC) for improved oxygen gas barrier property; data on their gas permeability are also available.[2)] Even these improved containers feature a short shelf-life, and there is a strong demand to double it.

Thus, EVAL®, featuring the most superb properties as a barrier resin, besides being easy to mold, has recently been drawing a lot of attention from two different points of view: CO_2 gas barrier and oxygen gas barrier. An increasing number of reports on the manufacture of high-barrier PET/EVAL bottles by joining PET and EVAL resins have been issued worldwide.

Various bottle manufacturing methods thus far developed include PET/EVAL co-extrusion sheet thermo-forming, PET/EVAL co-extrusion pipe blowing, PET/EVAL co-injection preform blowing, PET/EVAL blend injection blowing, and EVAL coating, among others.

In this report we should like to discuss the EVAL gas barrier properties needed for commercially designing PET/EVAL high-barrier bottles and some examples of application of high-barrier PET/EVAL bottles.

Note: EVAL is the registered trademark of Kuraray Co., Ltd. for ethylene-vinyl alcohol copolymer.

[I] EVAL's gas barrier property (CO_2 gas, O_2 gas)
[II] Shelf-life simulation
- Application to soft drinks and beer (CO_2 gas)
- Application to wine and beer (O_2 gas)

[I] EVAL's gas barrier property

Experiment

The PET resins employed in this test were commercial PET and modified PET, which were used in combination with ethylene vinyl alcohol (EVOH). The EVOH used was EVAL-E and EVAL-F, both made by Kuraray.

The CO_2 gas permeability coefficients were measured with a Permatran C-IV carbon dioxide permeability instrument, while an Oxtran 10/50 oxygen permeability instrument was used for measuring the O_2 gas permeability coefficients.
Both instruments are made by Modern Controls, Inc.Moisture level was adjusted for both the carrier gas and the test gas during the test process.

By using a special attachment, it was possible to measure in the bottle; the gas permeation rate under stable condition was measured and evaluated in the bottle and film.

Results and Discussion

Gas permeation of plastic bottles includes sorption of gas into plastic bottles, diffusion of the solved gas into the bottle outer wall and desorption of gas from the bottle outer wall. This means: P (gas permeability coefficient) = S (gas solubility coefficient) x D (gas diffusion coefficient).

1) Gas barrier property of EVAL and PET (Po_2, Pco_2)

EVAL has much better gas barrier property than PET:

1) Po_2: 1/20 - 1/40 times
2) Pco_2: 1/20 times

2) Effects of solubility of O_2 and CO_2 gas (So_2, Sco_2)

The solubility ratio of plastics (PET or EVAL):

EVAL or PET: Sco_2/So_2 = 50 - 100

As shown here, Sco_2 and So_2 differ greatly, i.e. CO_2 is far more soluble into plastic resin than O_2 (for PET in particular). For CO_2 permeation, the solubility factor into plastic resin should be taken into account.

Poly- mer	R.H.of Polymer	CO_2			O_2		
		$P\times10^{12}$	$D\times10^{10}$	$S\times10^{2}$	$P\times10^{12}$	$D\times10^{10}$	$S\times10^{2}$
PET	any	14.2	4.14	3.43	1.83	50.8	0.036
EVAL-F	0 (%)	0.017	0.030	0.56	0.004	0.25	0.015
	65	0.033	0.052	0.63	0.012	-	-
	93	0.385	0.323	1.19	0.091	4.33	0.021
EVAL-E	0	0.094	0.118	0.80	0.031	1.19	0.026
	65	0.120	0.143	0.84	0.046	-	-
	93	0.580	0.518	1.12	0.213	7.11	0.030

Units ; P = (cc at STP)·cm/ cm^2·sec·cmHg
D = cm^2/sec S = cc/cc·cmHg

Table I Permeability Coefficients of PET, EVAL at 20℃

3) Effects of temperature

The temperature dependence of Po_2 and Pco_2 in EVAL is slightly higher than in PET but is almost the same as in PVDC Latex. (Figs. 1, 2)

When the temperature becomes 20°C higher than room temperature, the Sco_2 of PET resins becomes 1/2, while Dco_2 is increased 3 times, bringing Pco_2 to 1.5 times.

In a similar way, the Sco_2 of EVAL resins becomes 1/3, while Dco_2 is increased 12 times, bringing Pco_2 to 4 times.

This shows that EVAL has greater temperature dependence than PET; however, as shown below, EVAL's gas barrier property is clearly far superior within the normal application temperature range.

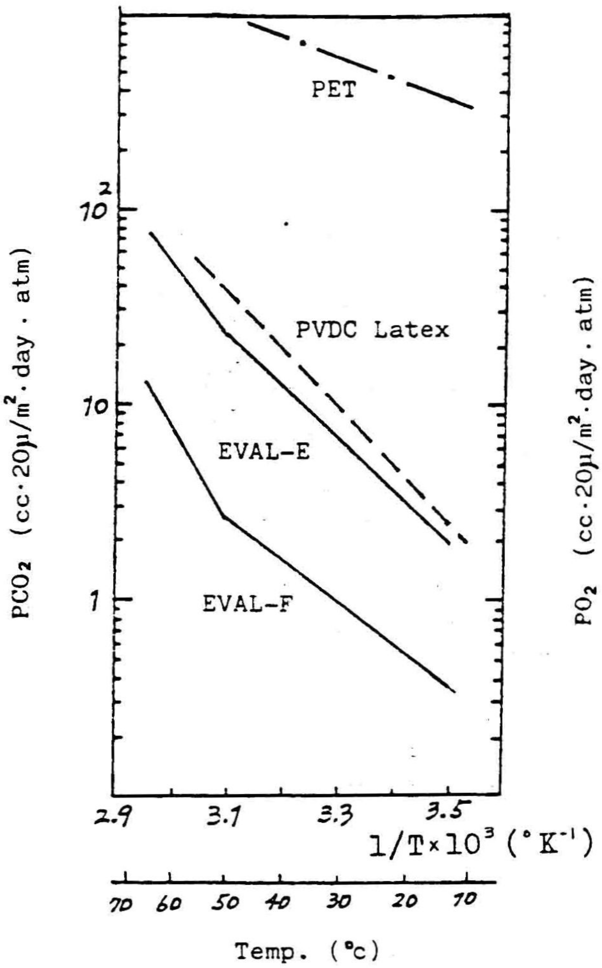

Fig. 1 Temperature Dependence of PCO_2 at 0% R.H.

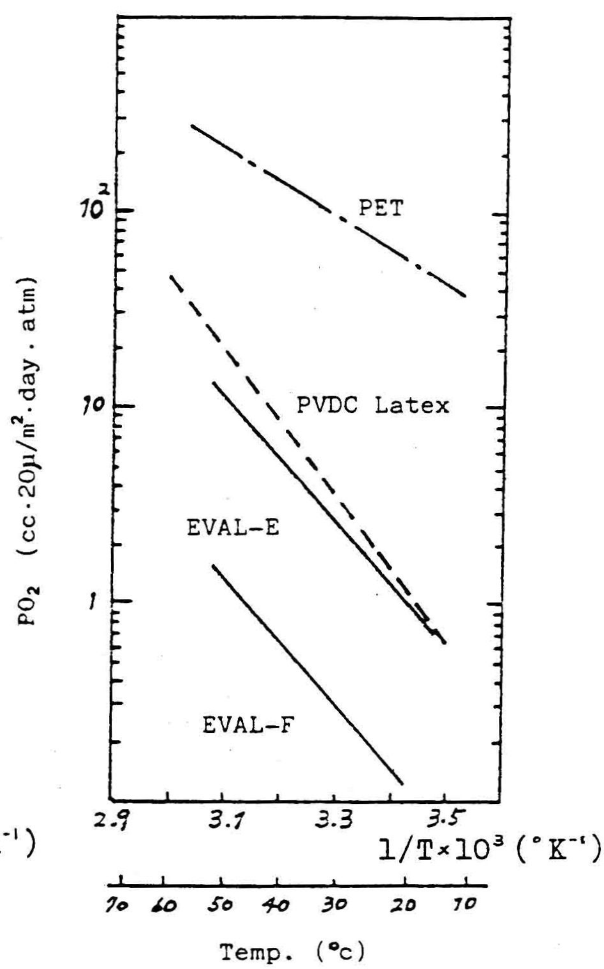

Fig. 2 Temperature Dependence of PO_2 at 0% R.H.

4) Effects of relative humidity.

EVAL resin is a hydrophilic polymer; the moisture level in EVAL varies depending on the external relative humidity. (Figs. 3, 4) The gas permeability coefficient of EVAL varies depending on the moisture level,[3] so it is affected by relative humidity.

EVAL's moisture content remains almost stable in the normal storage temperature range of 10 - 50°C, as long as the relative humidity is constant; this suggests that relative humidity dependence gradient remains hardly unchanged at the storage temperature of 10 - 50°C.

EVAL resins show larger gas permeability coefficients than Saran at a relative humidity of 95% or more but since the range of normal storage humidity is 80% or less, it already possesses a practically effective gas barrier property. The P_{CO_2} and P_{O_2} of EVAL resin are 1/2 of those of Saran at 20°C 80%R.H. (Figs. 3, 4)

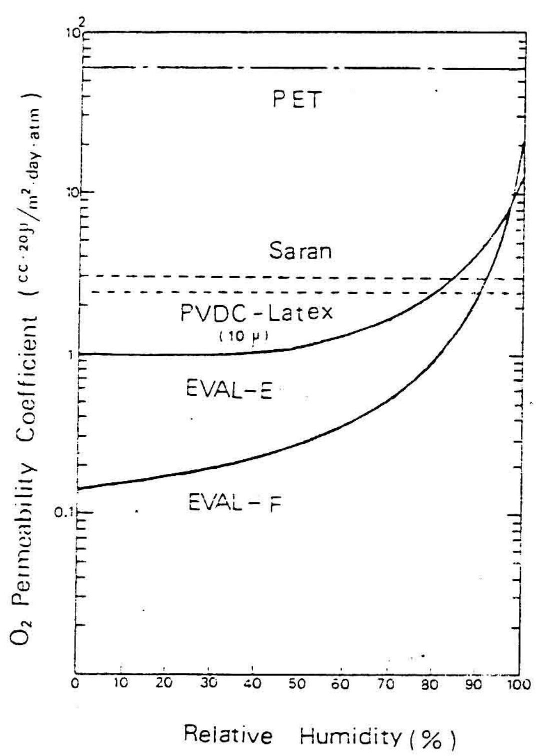

Fig 3 Humidity Dependence of P_{O_2} (20°C)

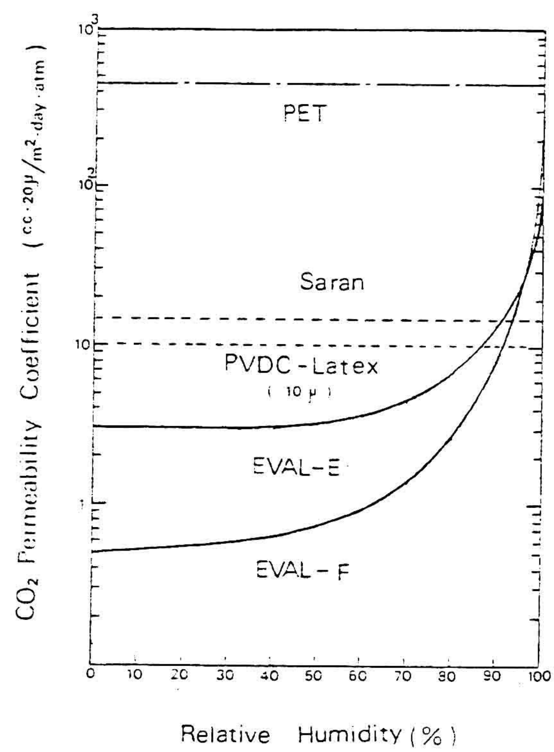

Fig 4 Humidity Dependence of P_{CO_2} (20°C)

5) Effects of crystallinity

EVAL resin is a crystalline polymer; when the crystallinity varies, the gas permeability coefficient also changes. EVAL's crystallinity can be obtained by measuring its density.

EVAL's crystallinity is related to moulding conditions; as the crystallinity increases, the gas permeability decreases, with the effects of crystallinity especially conspicuous under high humidity. (Fig. 5)

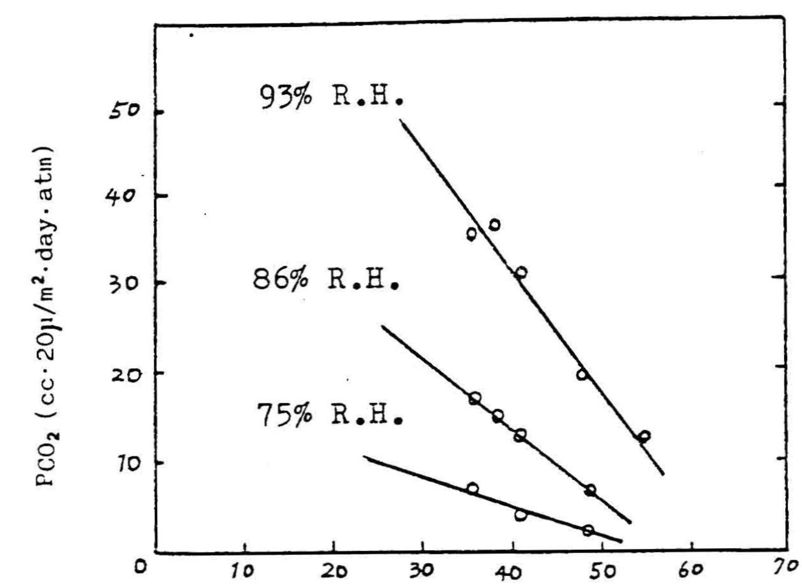

Fig. 5 Crystallinity Dependence of EVAL-F PCO_2 at 20°C

6) Summary

The following items should be taken into account when using the gas barrier property of EVAL resin for PET/EVAL multilayer bottles. (Table II)

(a) As the storage temperature increases, both PET and EVAL show greater gas permeability coefficients, but the gas permeability coefficient of EVAL is still lower than that of PET.

(b) As storage humidity increases, gas permeability increases for EVAL. An improved gas barrier property might be expected by reducing the relative humidity of the EVAL layer (putting the EVAL layer more towards the bottle outer wall).

(c) By increasing crystallinity, EVAL's gas barrier property can be used more effectively. For this purpose, selecting the bottle blow temperature or applying heat treatment to blown bottles may prove effective; attention should also be paid to molding conditions and molding processes.

Action	PET	EVAL	Comparison
Temperature ↑	↑	↑	EVAL ≒ PET
Humidity ↑	No change	↑	EVAL only
Crystallinity ↑	↓	↓	EVAL > PET
Multilayer Construction	No change	Outer EVAL↓	EVAL only

Humidity ⇒ Position of EVAL ⇒ Die design, Delamination

Crystallinity ⇒ Bottle making condition ⇒ Blow temperature, Heat treatment

Table II Permeability Coefficient Behavier

[II] Shelf-life Simulation

The authors have clarified several methods for designing containers for soft drinks, beer and wine, based on the detailed permeation data shown in [I] above.

The effects on shelf life of EVAL layer thickness, EVAL layer position, container size, etc., have been studied and their roles clarified. At the same time, shelf life was computed for prototype containers under various storage conditions from the standpoint of CO_2 gas retention and O_2 gas barrier property.

Simulation Method

Step I: Barrier property requirements

1. CO_2: when carbonated to 4.0 vol. of CO_2 - not more than 15% loss

2. O_2: not more than 5 ppm gain per bottle

Step II: Bottle design (Table III)

Cylinder shaped with the same surface area as commercial PET mono-layer bottles.

Step III: Computing the relative humidity of EVAL layer at storage temperature & storage humidity (Fig. 6)

Computing the water vapor pressure of the EVAL layer by equation (1) in Figure 6 and converting into relative humidity.

Step IV: Find P, D & S values of EVAL and PET

These may be read from the graphs (like Figs. 1 -4) of temperature dependence and humidity dependence for EVAL and PET.

Step V: Computer simulation (Fig. 7)

The simulation program was prepared by following Henrry's law for gas solubility and Fick's law for gas diffusion. Divide the PET layer and EVAL layer into M number of segments by a thickness of ℓ and compute the permeation rate at all segments by the passage of time T. At this stage, the actual CO_2 gas permeability may be approximated by subtracting the volume of gas reduced either by solving or permeation from the inner CO_2 gas volume.