



CARILON Polymer Barrier Properties

L. E. Gerlowski, J. R. Kastelic

Technical Progress Report WRC 291-87
Project No. 62182

1788967 #11

SHELL DEVELOPMENT CO.
RECEIVED
X 6 '88
WHR 221
TOP
Refer to Technical Files For Complete Distribution

CONFIDENTIAL



Shell Development Company
DIVISION OF SHELL OIL COMPANY

Westhollow Research Center
Houston, Texas

This document is the property of Shell Development Company. Possession or access should be limited to those employees of Shell Oil Company, its divisions and subsidiaries. Distribution or disclosure in whole or in part to any individual not an employee of Shell Oil Company, its divisions and subsidiaries requires written authorization of Shell Development Company. Unauthorized disclosure may be against the business interests of Shell Oil Company, its divisions and subsidiaries. Distribution, reproduction, sale, copying and disposal must be in accordance with guidelines for "Confidential" information.

Exportation of this document is subject to license under the Export Administration Act of 1969.

CARILON Polymer Barrier Properties

Technical Progress Report **WRC 291-87**

Project No. 62182

PRINTED: January 1988

AUTHORS: L. E. Gerlowski, J. R. Kastelic

REVIEWER: R. N. French

APPROVAL: M. T. Fleischer

REFERENCE: Based on work through August 1987

SHARED

Under the Research Agreement between SIRM and Shell Oil Company dated January 1, 1960, as amended.



TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	iv
SUMMARY	1
OVERVIEW	1
PERMEATION MEASUREMENTS	2
PHYSICAL PROPERTY CORRELATIONS	3
PLACEMENT IN MARKET PLACE	6
ALTERATIONS	7
Annealing.....	7
Hydrogenation.....	9
Fluorination.....	10
Blending.....	10
Fillers.....	10
FUTURE	11
REFERENCES	12

LIST OF TABLES

- TABLE I Permeability Values of Neat Carilon Polymers
- TABLE II Water Transport Parameters
- TABLE III Water Vapor Transmission Rates
- TABLE IV Gas Transport Properties of Carbon Dioxide in Several Polymers
- TABLE V Container Comparison
- TABLE VI Annealing Effects on Carilon Polymers
- TABLE VII Effects of Fluorination on Carilon Barrier Properties
- TABLE VIII EVAL/Carilon Blends

LIST OF FIGURES

- Figure 1 Carbon dioxide diffusion coefficient correlation with specific free volume.
- Figure 2 Carilon polymer oxygen permeability dependence on crystallinity.
- Figure 3 Dependence of Carilon (055/037) permeability on temperature 5°C to 80°C.
- Figure 4 Water vapor transmission rate (WVTR): Dependence of WVTR on temperature.
- Figure 5 Dependence of oxygen permeability on Carilon Polymers molecular weight (as measured by lvn).
- Figure 6 Dependence of carbon dioxide permeability on Carilon Polymers molecular weight (as measured by lvn).
- Figure 7 Oxygen permeability of Carilon/EVAL blends.
- Figure 8 Carbon dioxide permeability of Carilon/EVAL blends.
- Figure 9 SEM of high aspect ratio mica filled Carilon a. injection molded sample, b. injection molded sample which was subsequently forged to provide orientation.

ABSTRACT

Initially, measurements made at Westhollow of representative Carilon moldings indicated that the neat polymer fits in the realm of thermoplastic materials such as polyethylene terephthalate and polyvinyl chloride. These measurements have been confirmed at outside laboratories. Alterations in processing methods have been made to reduce the gas permeability by controlling the morphology of the semi-crystalline polymer. Continuing developments involve either annealing of the polymer films near the melt temperature for short periods of time or controlled cooling from the melt. Both procedures have reduced the permeation of oxygen and carbon dioxide through Carilon E to levels near Saran and Borex (two commercially available barrier polymers). This reduction in permeability correlates well with independent measurements of crystallinity. The values of gas permeability provide Carilon E the capability of existing as a monolithic barrier container for dry foods. The water vapor transmission rate is currently too high to allow use as a universal monolithic barrier container. Future work will involve methods to reduce the water vapor transmission rate to a point where Carilon polymers can be both a gas and water or flavor vapor barrier.

Technical Progress Report WRC 291-87

CARILON Polymer Barrier Properties

by

L. E. Gerlowski, J. R. Kastelic

SUMMARY

Recent developments in the understanding of transport of gases through Carilon polymers have allowed us to reduce the permeability to levels of barrier polymers. These developments are based on morphology controlled crystallization to increase the barrier properties. Slow cooling from the melt under a positive pressure and annealing of formed films for a short time near the melt point both result in an increase in crystalline levels. The lowest oxygen permeabilities for Carilon E and EP (m.p. 218°C) are 0.77 and 1.4 cc(STP)-mil/100sqin-d-atm at 30°C, respectively. In these same units and conditions, Saran has an oxygen permeability of 0.5, Barex of 1.0 and EVAL of 0.05. The permeation measurements, correlations to establish consistency of transport properties, alterations used to produce lower permeabilities, placement in the market place, and the goals of the future work are discussed in this report. Currently, the lowest reproducible value for oxygen permeability through Carilon E is 0.8 cc(STP)-mil/100sqin-d-atm at 30°C. For Carilon EP (218°C m.p.) the lowest reproducible value for oxygen permeability is 1.4 cc(STP)-mil/100sqin-d-atm at 30°C. The lowest water vapor permeation values for the Carilon E and Carilon EP (218°C m.p.), are 3.2 and 3.0 gm-mil/100sqin-d at 100°F and 90 RH, respectively. Saran, Barex and polyethylene terephthalate have oxygen permeabilities of 0.5, 1.8 and 8.5 cc(STP)-mil/100sqin-d-atm at 30°C. Saran and polypropylene (the two best commercial water vapor barriers) have water vapor permeabilities of 0.2 and 0.53 gm-mil/100sqin-d at 100°F and 90 RH.

p3 says 0.05 - which is correct?

OVERVIEW

Polymers used in food packaging must be able to provide a barrier to oxygen, carbon dioxide, flavor ingredients, water, etc. from transporting into or out of the packaged food. This requirement on permeation is in

addition to providing the structural support necessary to hold the food inside the container. Currently, most high barrier plastic packages consist of coextruded layers of polypropylene, tie layers and ethylene vinyl alcohol (EVAL). The polypropylene provides structural support and prohibits water vapor transport. The EVAL layer prohibits gas transport through the container wall. The premise of using Carilon Polymers in plastic packaging is to provide the same product as the coextruded container but as a monolayer container.

Gas transport properties for the neat Carilon E and EP (mp 218°C) polymers have been established for oxygen, carbon dioxide, and water vapor. The majority of these measurements have been made on compression molded films to represent a formed container. Similar permeation values to the compression molded samples have been measured on extruded, injection molded and solution cast Carilon-EP (mp 218°C). The most reproducible means to manufacture the Carilon-E films has been with solution casting and heat treatment below the melt temperature. These permeation measurements have been correlated with amorphous density, crystalline level, and temperature. No correlation has been found with limiting viscosity number (lvn). The strongest correlation and most promising means to increase gas barrier properties was found with degree of crystallinity. By increasing the level of crystallinity with thermal annealing, a reduction in permeation properties to barrier levels has been attained. Alterations to the base polymer including chemical (hydrogenation, surface fluorination), physical (annealing) and blending with other polymers have been attempted with some success to reduce the gas permeation.

PERMEATION MEASUREMENTS

The transport properties of oxygen, carbon dioxide, and water vapor have been established to determine where Carilon polymers fit in the realm of plastic packaging polymers. These measurements have been made primarily at WRC with the newly acquired MOCON equipment. Additional measurements have been made with a high pressure, high temperature diffusion cell (also at WRC) and at external laboratories at University of Texas at

Austin (D. R. Paul), Rutgers University (S. M. Gilbert), and several water transport measurements made at KSLA.

The majority of measurements have been made on compression molded films from powder or nibs. To make these films, the polymer was heated 20°C above its melt point and cooled after molding out of the press. This operation was done to represent a standard melt processed sample. Film samples produced in this manner are referred to as neat polymers. Neat films which were produced with this technique were measured for gas permeability and are summarized in Tables I-III. As these measurements show, values of normally produced Carilon E and Carilon EP (m.p. 218°C) have oxygen permeability values of 4.23 and 3.58 cc(STP)-mil/100sqin-d-atm at 30°C, carbon dioxide permeability values of 21.7 and 27.4 cc(STP)-mil/100sqin-d-atm at 30°C, and water vapor permeation values of 12.1 and 4.4 gm-mil/100sqin-d at 100°F and 90% RH, respectively. These values indicate that the terpolymer barrier properties are better than the copolymer; however these values are of unstabilized copolymer. One would expect the copolymer to have better barrier properties than the terpolymer. These permeation values were measured at the given temperatures to compare with other commercially available products. At 30°C, Saran has an oxygen permeability of 0.5 and EVAL 0.05 cc(STP)-mil/100sqin-d-atm. At 100°F and 90% RH, Saran has a water vapor permeability of 0.05 and polypropylene of 0.53 gm-mil/100sqin-d. These commercially available polymers represent the competition for Carilon polymers.

PHYSICAL PROPERTY CORRELATIONS

Correlations of gas transport properties with other physical properties have been made to insure that Carilon polymers exhibit the expected trends. These correlations include transport property dependence on amorphous density, dependence on crystallinity, dependence on temperature, and dependence on lvn.

The transport of gases through semi-crystalline polymers occurs through the amorphous domain of the polymer structure. The crystalline region is considered to act as a non-permeable dispersed phase. Lee (1) has shown that a correlation exists between the diffusion coefficient of a gas

through the polymer and the specific free volume (SFV) of the polymer. The specific free volume is the difference between the amorphous density of a polymer and the volume at 0°K. Allen (2) has recently established a means to estimate the amorphous density of Carilon polymers. Van Krevelen (3) has provided correlations based on structure of the polymer to theoretically calculate the amorphous density. Calculations with Van Krevelen's method are in good agreement with Allen's measurements (2). To determine crystalline levels, Allen has also established ideal heat of fusion to be 54.5 cal/gm for Carilon E and 56.9 cal/gm for Carilon EP (218 - 224°C mp)(4). With these ideal values, measurements from DSC can be used to estimate the degree of crystallinity for a given sample. Thus, with these values for Carilon polymers we can estimate the specific free volume of the polymer. The diffusion coefficient has been measured from time lag measurements of carbon dioxide transport through several Carilon polymer films (5). The diffusion coefficient is dependent on the degree of crystallinity by (6):

$$D = D_{am} (1 - X)^2 \quad (1)$$

where D is the measured diffusion coefficient, D_{am} is the amorphous phase diffusion coefficient, and X is the degree of crystallinity. Once the diffusion coefficient in the semi-crystalline polymer and the degree of crystallinity are known, the amorphous diffusion coefficient can be calculated. Figure 1 contains this correlation for several well characterized polymers and Carilon E. Table IV contains the transport parameters of diffusion coefficient (D), sorption coefficient (S), and permeability coefficient (P). The sorption coefficient (S) represents the level of dissolved gas at equilibrium. The three transport parameters are related by (6):

$$P = D S \quad (2)$$

As Table ^{IV} _V indicates, the level of sorption coefficient is high relative to other polymers. This evaluation indicates that ways to decrease the

on this point, }
now
crystalline
the
EVOH
polymers }

Why? what does
this imply or
mean?

permeation of gases can be best achieved through 1. decreases in sorption coefficient or 2. increases in crystallinity.

Within a polymer family, equation 1 indicates that permeation through highly crystallizable polymers should be somewhat dependent on processing conditions. Processing parameters such as annealing and controlled cooling can result in higher levels of crystallinity and formation of higher aspect ratio crystal domains (crystal domains with high length to diameter ratios) (7). Higher levels of crystallinity result in a higher volume of non-transporting medium. Higher aspect ratio crystals result in crystal domains which increase the tortuous path of diffusion through the polymer. Figure 2 contains a correlation of permeability of oxygen with degree of crystallinity for various Carilon polymers. The solid line in Figure 2 is from the equation:

$$P = P_{am} (1 - X)^2 \quad (3)$$

where P_{am} (the amorphous permeability) has been calculated from each permeation measurement and independently determined crystalline level of that sample. The dashed lines in this figure represent plus and minus one standard deviation from this curve. Several samples of Carilon E and Carilon EP have been annealed to increase the crystalline level (see alterations section). These samples are included in this Figure to indicate ultimate properties achievable with this technique.

Transport of gases through polymers is usually highly temperature dependent as are most molecular transport processes. Most polymers follow an Arrhenius relationship of permeation with temperature. The activation energy is usually in the 7 - 15 cal/mole range (4). The dependence of permeability of Carilon EP (055/037 mp 217°C) compression molded samples over a temperature range of 5°C to 80°C is shown in Figure 3. The activation energy associated with this plot is 12.7 kcal/mole, in the expected range. * Some polymers show a change in slope of this curve at the glass transition temperature which is predicted from free volume arguments. Figure 3 shows no break in the curve over this temperature range indicating

* on this point, review Am. Can. paper reference
water in EVOH - may be something

no glass transition temperature. Figure 4 contains similar curves for water transport through Carilon polymers and several other polymers.

The dependence of permeation on molecular weight has been examined. No correlation was found between permeability values and measurements of lvn. Graphs of oxygen and carbon dioxide permeability of Carilon polymers versus lvn are shown in Figures 5 and 6, respectively. The lack of dependence is expected since most samples are not that low in molecular weight to show an effect. *(lower molecular weight might produce greater crystallinity)*

PLACEMENT IN MARKET PLACE

The ultimate question for barrier food packaging is how does Carilon as a monolayer container compare with current commercial products for high barrier food packaging. This question was posed to our barrier packaging subsidiary Rampart. Rampart produces a 4 oz container used to package apple sauce which is made of a coextruded structure of polypropylene, regrind, tie layer, EVAL, tie layer, regrind, and polypropylene. This structure is coextruded in a sheet of 70 to 100 mils thickness with approximately 10% of the thickness EVAL. This sheet is thermoformed and cut into the 4 oz containers with wall thickness ranging from 20 to 40 mils. They subsequently label the container and send it out to be filled and an aluminum lid is welded to the top. The barrier requirements that are set for the container are 4 - 8 cc(STP)/container-year for oxygen and 3 gm/container-year for water vapor permeation. A similar requirement of not more than 1% loss of water over a year for a packaged product has been established in the literature (8).

These requirements placed on a similar monolayer package made from Carilon with current and expected permeability values are shown in Table V. In this table we compare required amount of Carilon polymer necessary to meet the oxygen or water vapor transmission requirements. The required amount is expressed as the necessary wall thickness. Future reductions in oxygen permeability will result in linear reductions in required wall thickness. As this table shows, the Carilon-E polymer with an oxygen barrier of 1.0 will require a wall thickness of 20-40 mils, similar to the commercial competition. However, the water vapor transmission needs to be

reduced an order of magnitude in order to meet the requirement for water vapor transmission.

ALTERATIONS

Several chemical and physical treatments are being investigated as a means to improve the barrier properties of Carilon polymers. Five alterations are currently being investigated; annealing, hydrogenation, fluorination, alloy/blending, and fillers. Of these, annealing appears to be the most promising currently for gas transport reduction, and fluorination appears to be the most promising for reducing the water vapor transmission. Of course these treatments each impose some additional process cost, but annealing and/or controlled cooling rate should not be prohibitive.

Does annealing most change D.S.?

Annealing following forming has shown the most promise for increasing the barrier properties of Carilon polymers. Treating solution cast samples and melt processed samples near or slightly above the melt temperature has resulted in reduction in gas permeation. This reduction in gas permeation correlates through the expected dependence on increases in crystallinity due to the annealing (Figure 2). Annealing of semi-crystalline polymers is known to perfect crystalline structure (6,7). In the vicinity of the melt point, crystallites do not melt completely and may act as nucleation sites for more complete crystal growth upon cooling. The nucleation sites are speculated to cause the observed increase in overall crystallinity of thermally treated samples. A variety of thermal treatment protocols were explored and are described in Table V along with the resulting measured permeability and first heat of fusion from a DSC scan. Three thermal treatments have been used (i) forging - pressing of films at high pressure but below the melt temperature; (ii) compression molding - pressing the film, powder, or nibs at high pressures above the melt temperature; and (iii) annealing - heating the film at temperatures near the melt temperature without the imposition of pressure. All thermal treatments cause controlled melting and re-crystallization. These treatments are believed to be the most likely possible pathways to high levels of crystallinity. Forging near melting imposes the additional conditions of mechanical deformation by forcing the polymer to flow in the

solid state. A positive benefit which can result from forging is the generation of stress induced crystallization. Compression molding cycles were designed to explore primarily the influence of cooling rate and isothermal annealing alone or in combination with controlled (time-temperature) partial melting. In these thermal treating experiments, when possible one batch each of Carilon E (056/001) and Carilon EP (86/005 m.p. 318°C) were used to minimize batch to batch variability. General observations from this study include:

- I. There appears to be an optimum compression molding temperature 15°C above the resin melting point (indicated by DSC). Temperatures 5 - 10°C above or below this optimum yield measurably lower gas permeabilities.
- II. A moderate cooling rate from the melt appears to be optimum. Very slow cooling rates are not beneficial to gas barrier properties possibly due to additional degradation which can result from holding the polymer at high temperatures for long times. Additional degradation can consequently lower the over all crystallinity and effect barrier properties. Extremely rapid quenching is detrimental to barrier properties, most likely due to formation of much smaller crystallites and a lower total crystallinity.
- III. Low levels of solid state orientation induced by forging to not appear to improve barrier properties of extruded sheet, mica filled molded plaques or 4% EVAL-F filled extruded sheet. This lack of orientation effect on barrier is independent of the cooling rate used. Forged samples become markedly more transparent, as do oriented solid phase pressure formed cups and biaxially drawn films. This increase in transparency likely indicates a reduction in average crystallite size and this could counteract the effect increased crystallinity has on barrier properties.

- IV. Compression molding of previously melt processed preforms (such as extruded sheet or molded plaques) generally gives better barrier values than that achieved by compression molding neat resin.
- V. Finally, post annealing can improve barrier performance but the temperature should be close to melting (within 10°C of T_m).

We should also note that some of the increases in crystallinity that we see could be a result of oxidative chain scission. Chain scission in the amorphous phase could result in a more crystallizable region and thus in an increased crystallinity (as has been speculated by D.H. Handlin). A lower ductile polymer is an undesirable consequence of such chain scission and has been observed to some extent in Carilon specimens. These decreases in ductility could also result from increased crystallinity from annealing. Hence, there will be some trade off between physical properties and increases in barrier properties through annealing, and an even higher trade off if a high degree of oxidative chain scission does occur. Also, slight changes in the beta relaxation temperature (near room temperature) might be induced by some of the annealing protocols. These shifts in beta relaxation could also lead to decreases in ductility. This shift should not markedly influence barrier properties since no discontinuous change in amorphous density occurs at secondary transitions.

Table V will be completed and further investigated to examine the ultimate in barrier properties for Carilon polymers. Efforts will be made to assess possible oxidative molecular weight changes and relaxations shifts which can arise during thermal processing.

Hydrogenation has been proposed as a means to produce a more polyvinyl alcohol like structure with very strong hydrogen bonding between alcohol and ketone groups. By hydrogenation to different levels it is hoped that a range of barrier polymers can be produced with a range of processing and barrier properties, much like the currently available range of EVAL polymers. Carilon has been successfully hydrogenated in solution over a

sodium borohydride catalyst. The resulting polymer has 100% alcohol nature in its functional groups. However, the polymer shows a very low degree of crystallinity. Attempts are currently being made at producing a film from the hydrogenated polymer which can be tested for barrier measurements.

Fluorination has been proposed as a means to reduce barrier properties of Carilon polymers based on work performed by D. R. Paul (9). These investigators showed a 50X reduction in oxygen permeation through fluorinated polyethylene. A similar technique is used in producing polyethylene gasoline tanks for automobiles. In this case, the transport of gasoline vapors is greatly reduced by the presence of fluorine gas in the blow molding operation to manufacture the tank. In both of these instances, the alteration to the polymer is believed to be on the surface. Long time fluorinated Carilon polymers show no reduction in gas permeation, but a 10 X reduction in water vapor transmission (Table VI). Short time fluorinated samples will be investigated to examine the commercial practicality of such a process to reduce WVTR in Carilon polymers.

Blending with other polymers with a high level of chain functional density has been proposed as a means of increasing the amorphous density of the polymer and thus reducing the permeability. Several blends have been tried with EVAL with limited success (the reduction in permeability appears to follow the standard rule of mixing, thus indicating no benefits to increases in amorphous density - Figures 7-8, Table VII). Several other polymers are being investigated which have a high density of functionalized groups along the backbone.

Fillers with platelet shape have been claimed to reduce the permeability of various polymers. Unless the aspect ratio is high, only rule of mixing reduction in permeabilities have been found with fillers. High aspect ratio mica blended in with Carilon at 15% mica showed a reduction in permeability which slightly exceed the rules of mixing (Table VII). The improvement is dependent upon the alignment of the platelet filler with the plane of the film. This alignment was generally the case for the injection molded Carilon samples (Figure 9-a), and absolutely the case for the subsequently forged material (Figure 9-b). General alignment in the

injected samples was surprisingly high, with only two narrow regions of "scrambled" alignment between aligned walls and core.

FUTURE

Work to reduce the permeability of oxygen and water vapor through Carilon polymers will continue. Improvements through further optimization of morphological structure, increased stabilization, induced crystal nucleation, and increased amorphous density will be sought. Further work to improve moisture vapor transmission involving surface treatment and coatings will be pursued. Given the same manning plan as 1987, by the end of 1987 we hope to substantiate an oxygen barrier level of 0.75 and 1.5 cc(STP)-mil/100sqin-d-atm for Carilon E and EP, respectively. These values would place Carilon E in the realm of monolithic oxygen barrier properties. By the end of 1988 we hope to substantiate barrier levels of 0.5 and 1.0 cc(STP)-mil/100sqin-d-atm resulting from addition of low levels of blend components which substantially increase the amorphous density. It should be noted that these values will represent ultimate property values of these polymers. For the water vapor permeability, we are currently at a level of 5 to 12 gm-mil/100sqin-d. Our effort will be concentrated at reducing this value by a factor of 2. [The water vapor permeation is substantially high because of the high equilibrium water level of the polymer.] Due to the inherent nature of the Carilon polymers, this problem of high water vapor transmission will not be easily overcome.

Is there a way to make the polymer hydrophobic? Fillers

REFERENCES

1. Lee, W. M., Selection of Barrier Materials from Molecular Structure, Polym. Eng. and Sci., 20 (1), 65 (1980).
2. Allen, R. C. and P. C. Wang, WRC MRS, Oct., 1986.
3. Van Krevelin, D. W., Properties of Polymers. Their Estimation and Correlation with Chemical Structure. Elsevier Scientific Press, Amsterdam, 1976.
4. Allen, R. C., Carilon Polymer R&D Notes, Feb., 1987.
5. Koplos, G. J., and L. E. Gerlowski, A Device To Measure Transport Properties of Gases Through Polymer Films, WRC TPR #73-87.
6. Crank, J. and G. S. Park, Diffusion in Polymers, Academic Press, NY, 1968.
7. Tadmor, Z. and C. G. Gogas, Principles of Polymer Processing, Wiley Interscience, NY, 1979.
8. Salame, M. and S. Steingiser, Barrier Polymers, Polym.-Plast. Technol. Eng., 8(2), 155-175 (1977).
9. Kiplinger, C. L., D. F. Persico, R. J. Lagow, and D. R. Paul, Gas transport in partially fluorinated low-density polyethylene, J. Appl. Polym. Sci., 31, 2617-2626 (1986).

TABLE I PERMEABILITY VALUES OF NEAT CARILON POLYMERS

Batch	t ¹ (mils)	O ₂ ²	CO ₂ ²	H ₂ O ³	Hfus(1) ⁴	Crystal ⁵
Carilon-EP Polymers						
054/014 std ⁶	11.0	2.64	15.4	7.9	20.3	0.356
055/020 std	9.2	3.22	16.6	6.9	22.9	0.402
055/020 std	11.4	3.65	18.7	16.6	22.9	0.402
055/021 std	7.8	3.77	26.4	--	22.4	0.393
055/022 std	11.8	4.95	23.0	17.6	19.0	0.333
055/022 std	10.1	3.30	23.1	--	19.0	0.333
055/037 std	5.6	2.69	20.1	12.2	32.8	0.575
055/037 std	12.7	4.57	27.3	--	19.1	0.335
055/037 std	11.7	3.39	24.8	--	19.1	0.335
055/038 std	0.8	8.52	69.9	--	19.5	0.342
055/038 std	0.9	5.97	48.3	--	19.2	0.337
055/038 std	0.9	7.29	57.0	--	18.0	0.316
055/038 std	0.8	8.80	65.6	--	18.6	0.326

Carilon-E Polymers

054/012 std	9.3	4.65	29.6	6.7	18.3	0.333
054/012 std	9.3	5.30	21.0	3.5	18.3	0.333
054/012 std	8.0	4.32	38.4	3.5	18.3	0.333
054/004 std	7.7	3.23	22.3	3.7	--	--
054/010 std	11.1	3.66	25.6	4.5	27.7	0.504

-
1. t = film thickness
 2. units = cc(STP)-mil/100sqin-d-atm at 30C.
 3. units = gm-mil/100sqin-d at 90%RH and 100 F.
 4. first heat of fusion from DSC heat trace, units = cal/gm.
 5. fraction crystalline calculated from Hfus(1)
 6. std = standard compression molding protocol where the polymer is heated 30 - 40 C above its melt temperature and cooled rapidly by removing from mold when solidified and placed between aluminum plates

Measurements made outside of WRC

Laboratory	Polymer	Temp (C)	PO2	PCO2	WVTR
University of Texas - (D.R. Paul)	012 (-EP)	35	8.62 +/-0.12	76.9 +/-11.6	--
WRC	"	30	5.3	22.6	3.5
Rutgers University (Gilbert)	025 (-EP)	23	1.8	16.0	0.11
	037 (-EP)	23	1.6	7.44	--
MOCON	-E	23	0.35	9.0	6.3
	-EP	23	0.32	12.4	5.3

units for permeation are same as on previous page

Temp (C) is the temperature of the measurement, most WRC measurements are made at 30 C to represent a realistic package life temperature.

WVTR = water vapor transmission rate

These measurements, when corrected for temperature, indicate good agreement between WRC, U. Texas, and Rutgers for oxygen and carbon dioxide permeability. The water vapor measurements show good agreement with Mocon and WRC measurements.

Table II Water Transport Parameters

Polymer	P (gm-mil/100sqin-d)	D(cm ² /s X 10 ⁸)	S(kg/m ³)
Carilon E (054/005)	24.5 6.61*	4.8	27.9
Carilon EP (055/022) 4.7% P	4.59 4.65*	0.75	27.9
Carilon EP (055/012) 8.5% P	4.72 5.11*	0.92	23.4
Carilon EP (055/023) 10.5% P	3.73	0.79	21.5
PVC	1.0	2.13	1.8
Saran		0.38	
Polyvinyl-alcohol	87	1.0	36.0
Polypropylene	0.317	23.3	0.062

* WRC measurement, all other Carilon measurements from KSLA, all other polymer data from Sweeting.

TABLE III Water Vapor Transmission Rates

A. Comparison with Manufacturer Data (90% RH and 100 F)

Film	WRC	Reported Value	Source
EVAL-XL	1.46	1.52	Kurray
EVAL-E	0.545	0.4 - 1.4	"
EVAL-F	1.97	0.95 - 3.8	"
Saran-HB	0.0503	0.05	Dow
Polypropylene	0.53	0.53	Sweeting
Mylar (PET)	1.49	1.5	NBS

B. Carilon Data (90% RH and Given Temperature)

Sample	LVN* thickness	15 C	20 C	25 C	30 C	35 C	40 C
Terpolymers							
5% C3 055/014	1.9 10.9	2.14	3.28	5.23	7.69	11.0	18.3
8.9% C3							
055/012	1.37 8.8	2.07	3.30	5.42	8.10	12.0	17.5
055/012	1.37 8.8	2.38	3.88	6.23	9.44	13.8	20.0
055/031	1.30 8.8	2.77	5.32	7.29	10.3	--	15.7
055/031	1.30 6.2	1.65	3.74	5.89	8.40	--	13.6
Copolymers							
055/010	2.2 10.3	2.53	3.97	6.15	8.67	12.3	17.1
055/010	2.2 10.3	3.28	5.18	8.04	11.4	16.0	22.1
054/005	3.3 12.5	5.48	8.65	13.4	19.5	27.2	38.8
055/004	1.0 7.8	2.49	3.72	5.49	7.44	10.5	14.2
055/004	1.0 7.8	2.37	3.63	5.22	7.59	9.77	13.1

all permeability values in units of gm-mil/100sqin-d

* limiting viscosity number

TABLE IV GAS TRANSPORT PROPERTIES OF CARBON DIOXIDE IN SEVERAL POLYMERS

POLYMER	D	Calculated from S (D,P)	P	D/S
Carilon-EP batch 055/037	0.64	0.037 ^①	39.4	17.3
literature values from Lee(1)				
Saran	3.02	0.0004	1.91	7550,
EVAL	0.42	0.0001	0.05	4200
Polyethylene terephthalate	15.1	0.0026	64.6	5810.
Polyvinyl chloride	2.09	0.0043	15.1	486.

note: values not corrected for crystallinity

units at 25 C

D - 10^{-9} cm²/s

S - cm³(STP)/cm³ - cm Hg

P - cm³ (STP)-mil / 100 sqin-d-atm

NOTE: The diffusion coefficient (D) and permeability coefficient (P) are the measured values, the sorption coefficient (S) is calculated from these.

- ① what rationale do we have for a 10x to 100x higher S when compared to these other polymers?
- Surface degradation, (zero crystallinity?)
 - Surface crosslinked (" " ?)
 - Degradation products at surface which enhance sorption?
- What can reasonably be hypothesized, then measured or confirmed?

TABLE V Container Comparison

Requirement	WRC equivalent for 4 oz container 20 mil wall thick	Req'd Carilon wall thickness	P req'd for 20-40 mil wall
----- WVTR (@4 gm-mil/100 sq in-d) -----			
< 1% moisture loss per year (Salame)	0.185 $\frac{\text{gm-mil}}{100\text{sqin-d}}$	430 mil	0.37 $\frac{\text{gm-mil}}{100\text{sqin-d}}$
0.003 $\frac{\text{gm}}{\text{container}}$ (Rampart)	0.171	470	0.34
----- Oxygen (@1.0 cc(STP)-mil/100 sq in-d-atm) -----			
0.004 - 0.008 cc(STP)/con- tainer (Rampart)	0.23 - 0.46	43 - 21	0.46- 0.92

0.004 - 0.008
cc(STP)/con-
tainer
(Rampart)

*Per day
converts back
to P. 3 comment
and question.*

Table VI Annealing Effects on Carilon Polymers

Controlled Cooling Experiments

Carilon-EP

Polymer	Cooling ¹ Protocol	t(mils)	O ₂ ²	CO ₂ ²	H ₂ O ³	Hfus(1) ⁴	Crystal
022	Al plate quench	10.5	7.25	49.1	--	19.0	0.333
022	ice	10.7	6.00	42.9	10.9	19.4	0.340
022	ice	11.8	5.31	37.2	17.9	17.6	0.309
022	slow	10.4	3.43	28.9	6.9	21.4	0.375
022	slow	10.5	3.57	26.7	--	21.0	0.368
022	teflon insulated	9.8	1.86	16.7	--	22.0	0.386

Controlled Morphology Experiments

Polymer	Treatment Protocol ¹	O ₂ ²	CO ₂ ²	WVTR ³	H(1) ⁴
Carilon-EP					
86/005 (mp 218°C)	F 205° C, AC	-	29.3	--	19.0
extruded sheet	F 205° C, O/NC	-	48.0	--	19.0
vacuum oven dried nibs					
	CM 250° C, QC	2.47	--	9.11	--
	CM 250° C, QC, FA at 207° C 30 sec, AC	2.76	--	11.6	--
	CM 250° C, QC, FA at 207° C 30 sec, O/NC	5.46	--	13.3	--
	CM 225° C, A/WC	2.42	17.3	10.1	--
	CM 230° C, A/WC	1.41	9.6	6.01	--
	CM 240° C, A/WC	2.43	17.3	8.05	--
	CM 230° C, AC	1.78	8.4	6.8	23.1

Table VI (continued)

Polymer	Treatment Protocol ¹	O ₂ ²	CO ₂ ²	WVTR ³	H(1) ⁴
	CM 230° C, O/NC	2.24	11.4	6.0	--
	CM 220° C, AC	4.95	--	14.3	--
	CM 250° C, QC	5.18	35.7	9.1	--
	CM 250° C, A/WC	2.63 3.33	17.6 22.1	8.5 10.3	22.4 22.6
	CM 250° C, AW/C to 200° C, hold 5 min, RC	4.37	30.7	10.4	--
	CM 250° C, AW/C to 175° C, hold 5 min, RC	5.51	39.3	10.0	--
	CM 250° C, A/WC to 220° C, hold 5 min, O/NC	2.68	--	8.28	--
Carilon-E 056/001 (mp 256° C)	SC	20.1	8.0	--	36.0
	SC, A at 200° C for 20 s	4.5	12.1	--	36.0
	SC, A at 245° C for 20 s	0.81	7.7	--	39.0
	CM from powder 270° C, A/W C	1.92 1.78	16.7 17.2	-- --	
	CM injection molded plaque at 265° C 1 min	0.77	--	4.16	34.0
Miscellaneous					
Carilon-EO	CM 240° C, RC	10.7	--	17.1	--
87/001 + 5% EVAL-F extruded	F 205° C, AC		35.4		
87/001 + 30% mica	F 205° C, AC		29.1		
	F 205° C, O/NC		55.4		

Table VI (continued)

¹Definitions

F = Forged = A formed plaque is heated to a given temperature under high pressure in compression molding press

FA = Flash annealed = Plaque heated quickly for 1 min in a compression molding press

CM = Compression molded = Formed from powder or nibs in press at high pressure (for Carilon-E, formed under vacuum to attempt to reduce degradation)

SC = Solution cast = cast from solvent/non-solvent solution

A = Annealed = placed in oven to given temperature (not pressure formed), cooled at 10°C/min

AC = Air cool = cooled press with flowing air as cooling medium cooling rate = 4°C/min

A/WC = Air/water cool = cooled press with flowing air and water as cooling media, cooling rate = 9°C/min

O/NC = Overnight cool = no cooling medium. plaque left in press overnight, cooling rate = 1°C/min

QC = Quench cool = plaque taken out of press at T_m and placed between aluminum plates, cooling rate = ^m30-40°C/min

RC = Restrained Quench = plaque taken out of press at T_m and placed between insulating medium

^{2,3,4} UNITS: O₂ = cc(STP)-mil/100sqin-d-atm

CO₂ = " "

Hfus(1) = Heat of fusion on first DSC scan = cal/gm

Table VII Effect of Fluorination on CARILON Barrier Properties

Samples treated various times at room temperature in 1% F1 + 99%N₂

<u>Fluor.</u> <u>Time</u>	<u>Sample</u> <u>Number</u>	<u>O₂</u>		<u>CO₂</u>		<u>H₂O</u>	
		<u>Before...After</u>	<u>Before...After</u>	<u>Before...After</u>	<u>Before...After</u>	<u>Before...After</u>	<u>Before...After</u>
10 hr	125-1B	3.65	5.6	18.7	41.6	20.0	1.29
24 hr	125-3A	4.72	1.15	22.9	44.3	17.1	1.36
36 hr	PK-2TER	2.7	-	20.2	-	13.6	0.94
48 hr	X	13.7	6.14	-	58.6	-	1.76

OXYGEN AND CARBON DIOXIDE BARRIER UNITS: cc·mil/100sqin·day·atm, 30°C

WATER VAPOR TRANSMISSION RATE UNIT: gm·mil/100sqin·day, 100°F, 90% R.H.

Table VIII EVAL/Carilon Blends

wt% EVAL	wt% Irganox	PO2	PCO2	WVTR
0	0	7.22 +/-0.67	15.9	15.2 +/-2.6
0	0.5	7.22 +/-0.12	15.7 +/-1.4	13.9 +/-1.4
1.0 (predicted)	0.5	11.1 +/-3.0 (7.1)	15.3 +/-3.8 (14.4)	--
5.0 (predicted)	0.5	7.49 (6.5)	14.5 (14.3)	--
10.0 (predicted)	0.5	4.8 (5.8)	-- (12.8)	--
20.0 (predicted)	0.5	3.33 (4.6)	8.91 (10.1)	17.5
15.0 (MICA) (predicted)	0.5	3.24 (5.2)	8.58 (11.4)	13.1

 predicted values are calculated from 0% values and assuming volume fraction rule - $P = P(0) \cdot (1 - x)^2$ where x is volume fraction blended component to which the transporting gas is relatively impervious

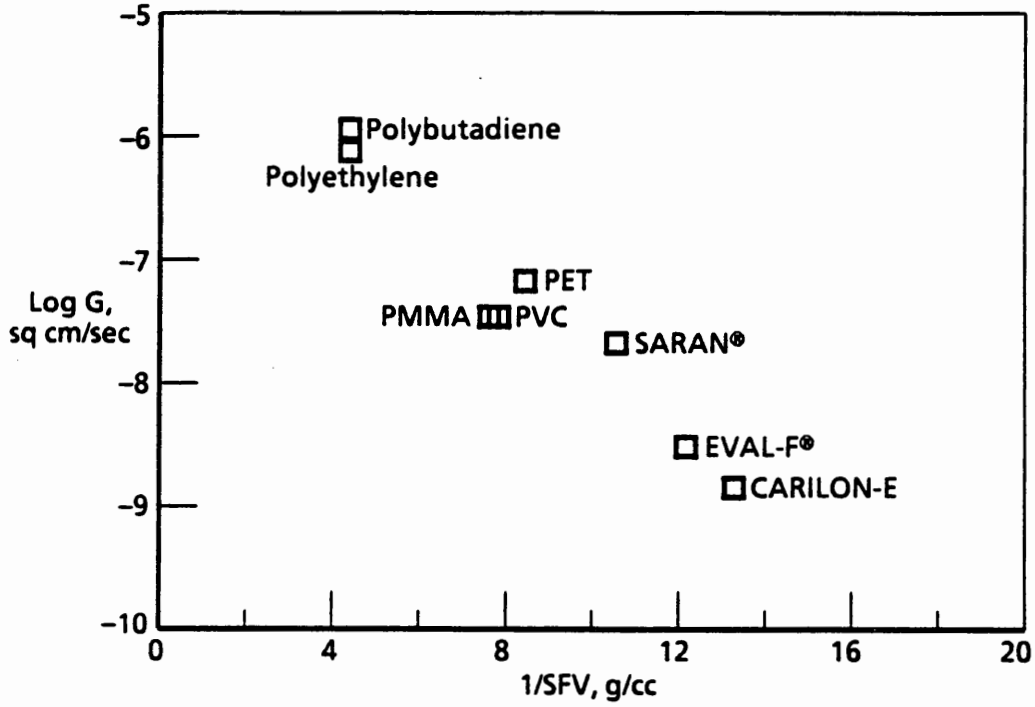


Figure 1. Carbon Dioxide Diffusion Coefficient Correlation with Specific Free Volume

011325-1

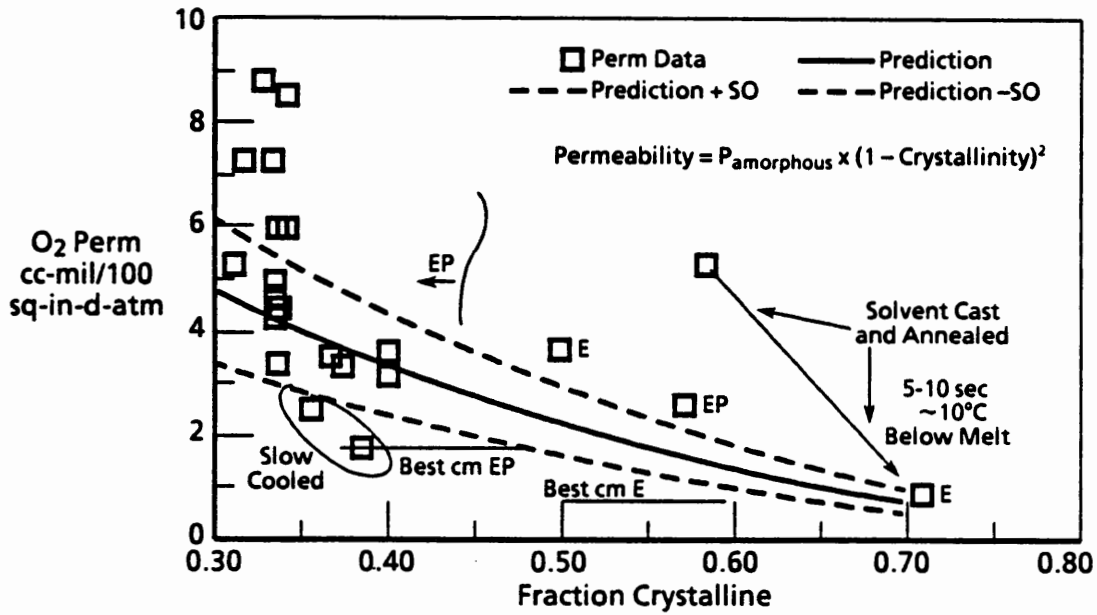


Figure 2. CARILON Polymer Oxygen Permeability Dependence on Crystallinity

011325-2

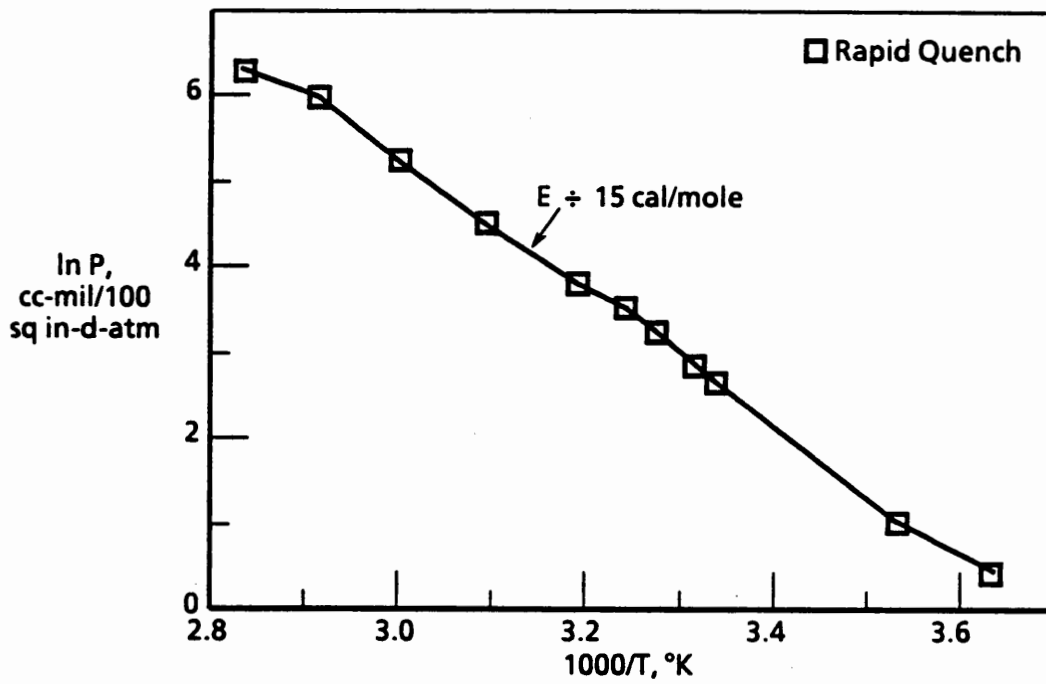


Figure 3. Dependence of CARILON (055/037) Permeability on Temperature 5°C to 80°C

gas: CO₂?

011325-3

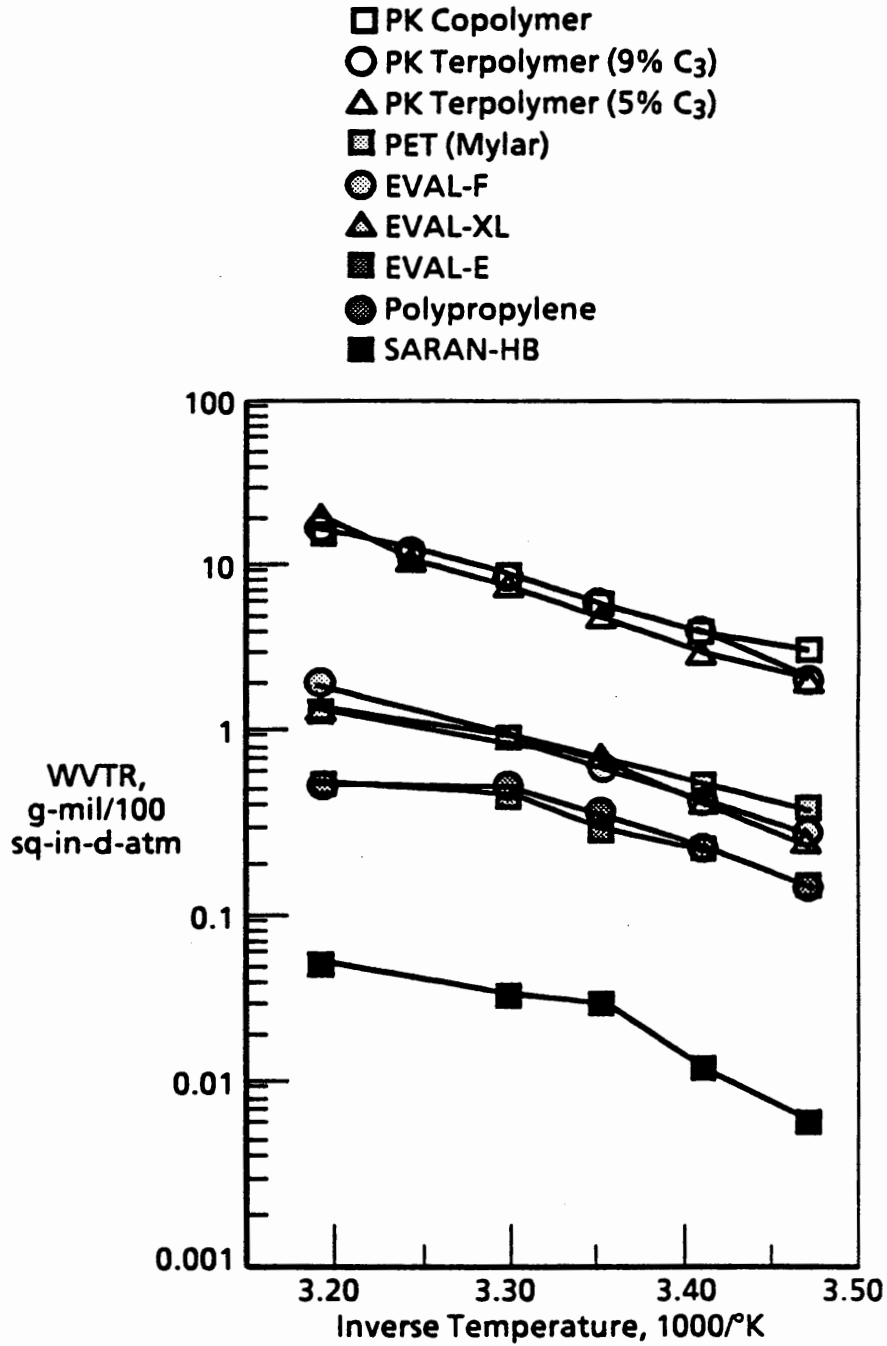


Figure 4. Water Vapor Transmission Rate (WVTR):
Dependence of WVTR on Temperature

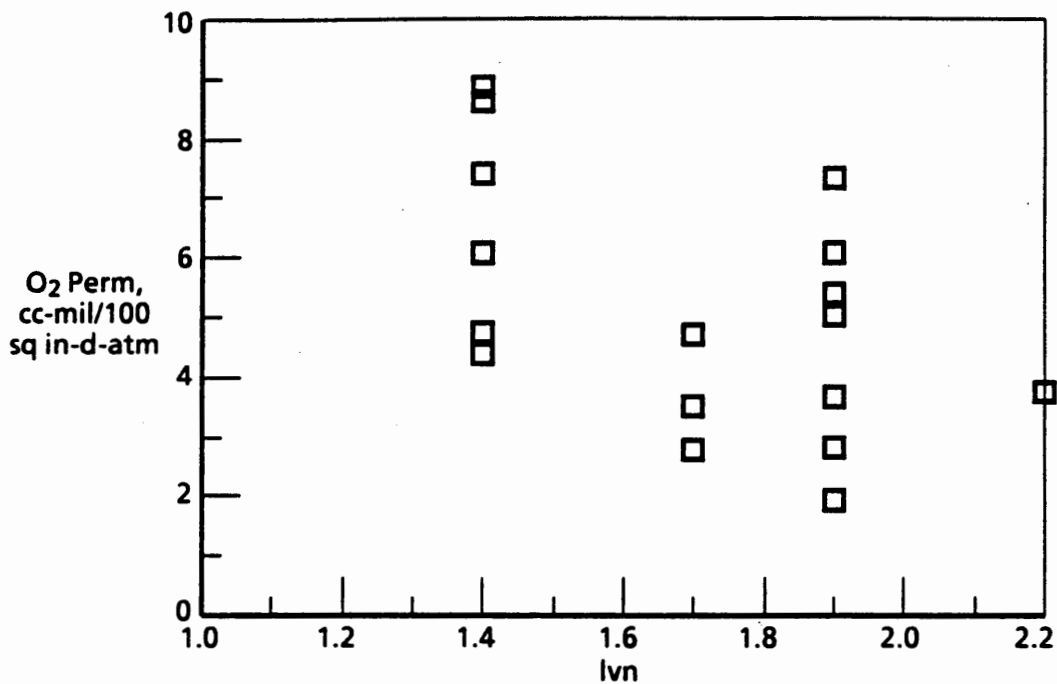


Figure 5. Dependence of Oxygen Permeability on CARILON Polymers Molecular Weight (as Measured by lv_n)

011325-5

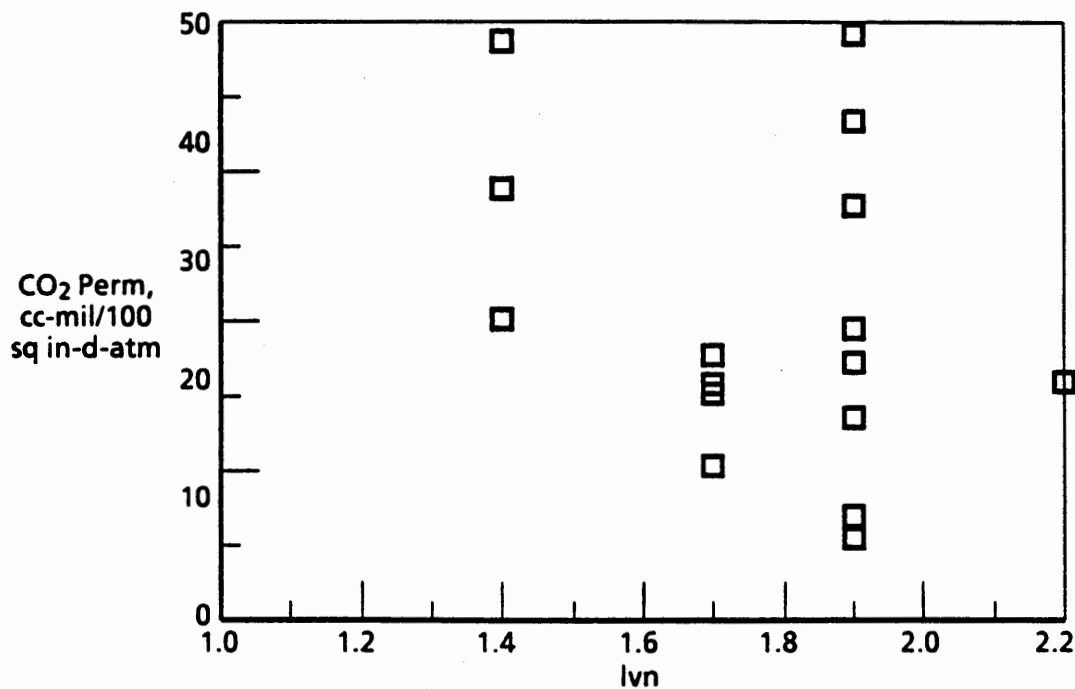


Figure 6. Dependence of Carbon Dioxide Permeability on CARILON Polymers Molecular Weight (As Measured by lv_n)

011325-6

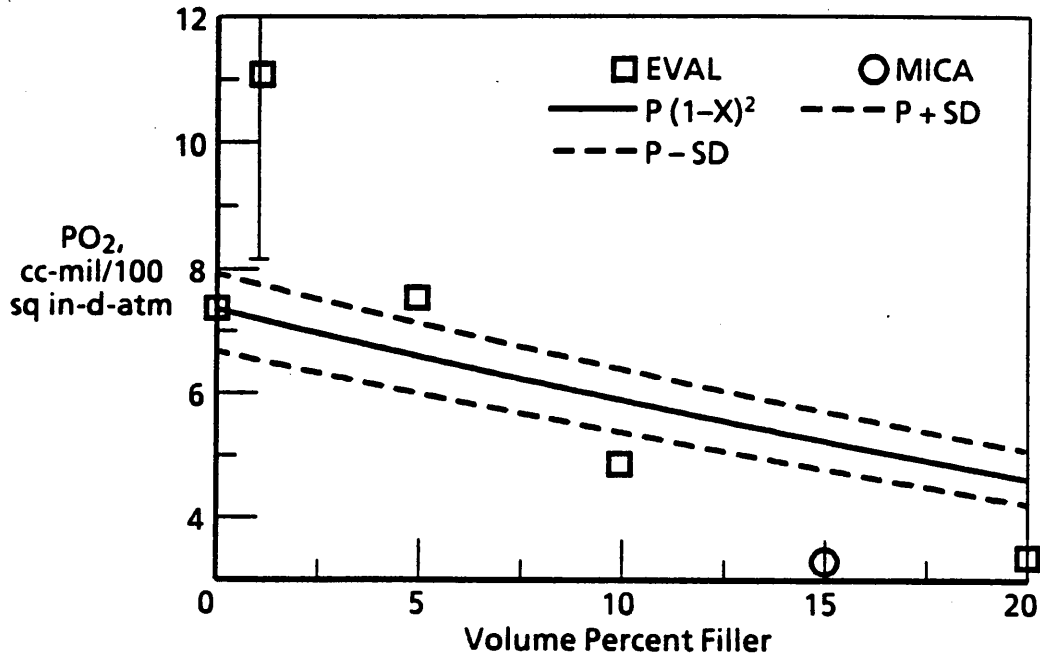


Figure 7. Oxygen Permeability of CARILON/EVAL Blends

011325-7

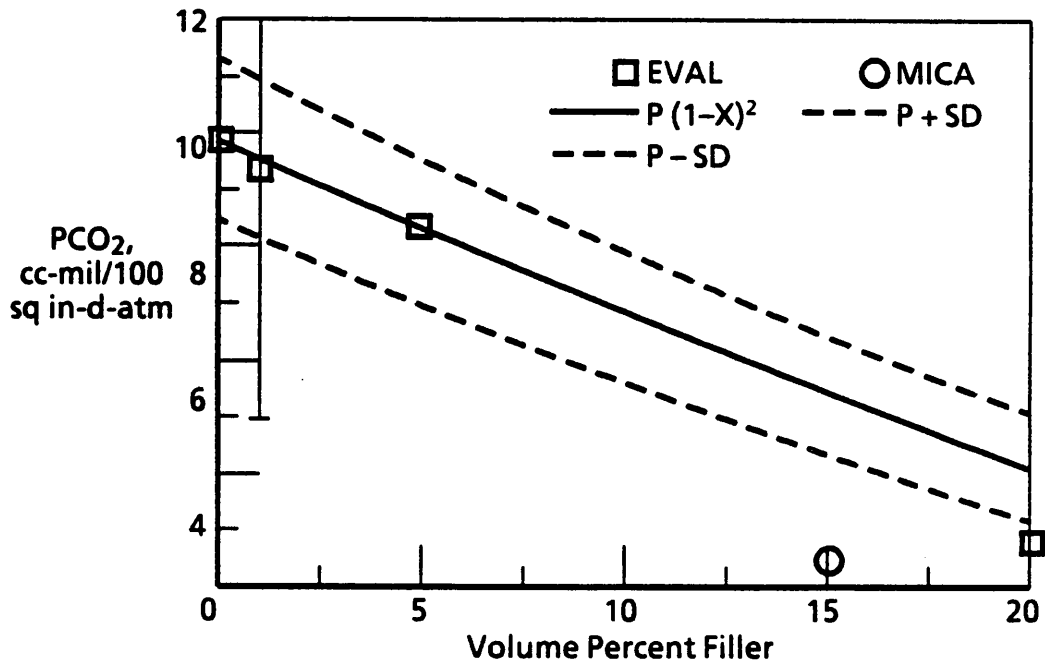
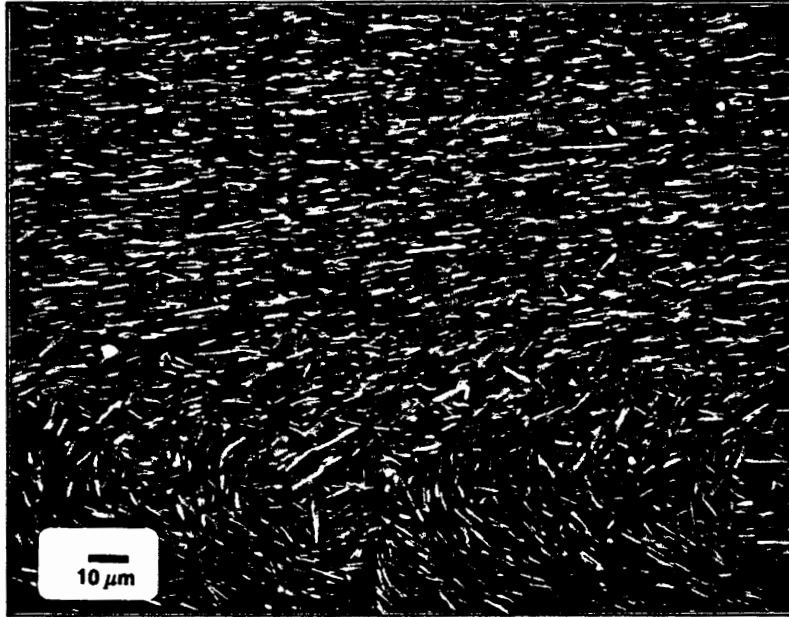
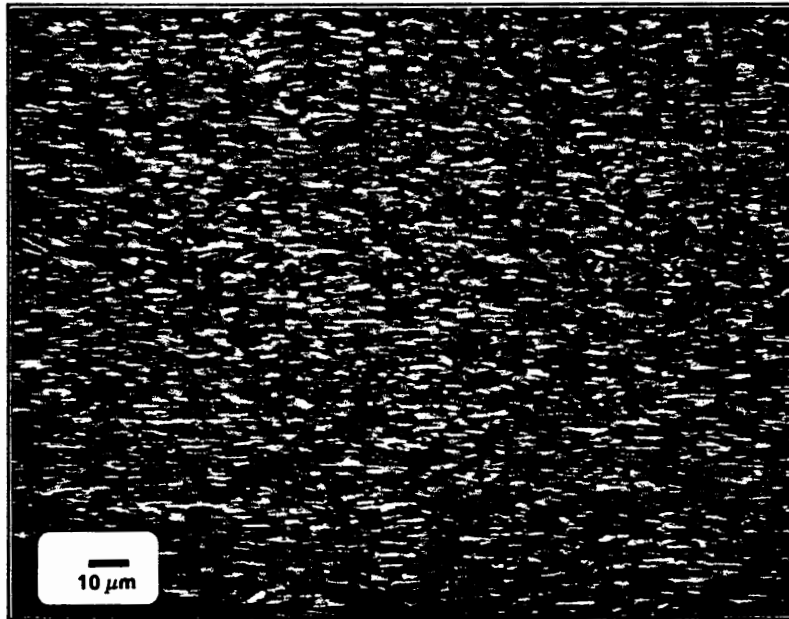


Figure 8. Carbon Dioxide Permeability of CARILON/EVAL Blends

011325-8



a. Injection Molded Sample



b. Injection Molded Sample Which Was
Subsequently Forged to Provide Orientation

Figure 9. SEM of High Aspect Ratio Mica Filled CARILON

DISTRIBUTION

Shell Development Company

2 - Bellaire Research Center

Shell Oil Company

1 - Legal - Patents and Licensing
1 - HS & E - Administrative Services
9 - P&AS - Office Operations - Information and Library Services

Shell Chemical Company

1 - Polymers & Catalysts
1 - Polymers & Catalysts - Plastics

