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CARILON® Thermoplastic Polymer Food Packaging Analysis

Evaluation of Barrier Properties of Recent Polymers and Formed Containers

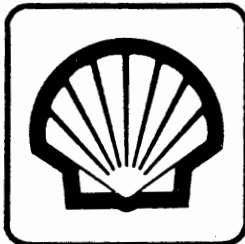
L. E. Gerlowski, J. R. Kastelic

Technical Progress Report WRC 265-89
Project No. 62182

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CARILON® Thermoplastic Polymer Food Packaging Analysis

Evaluation of Barrier Properties of Recent Polymers and Formed Containers

Technical Progress Report **WRC 265-89**

Project No. 62182
CARILON Thermoplastic Polymer Venture Support

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

REVIEWERS: A. J. Lesser, W. H. Korcz

APPROVAL: M. A. Matovich

PARTICIPANTS: P. A. Kinneberg, N. E. Peck, C. E. Wilson, R. J. Knabe

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ABSTRACT

Current analysis indicates CARILON® Thermoplastic Polymers have adequate oxygen barrier and high temperature resistance for use in retort food packaging. However, the water vapor transport is too high to meet weight loss requirements of packaged food without the assistance of an additional processing step (coating, etc.). The benefits and limitations of this polymer are discussed in this report. Specific issues addressed include: apparent improvements in barrier properties coinciding with improved stability Moerdijk Demonstration Unit (MDU) polymer, effect of container forming on barrier properties, use of coatings, organoleptic analysis, and barrier analyses of various lid sealing techniques. From these measurements, several conclusions are important; the improved stability of later MDU polymers results in more perfect crystal formation and enhanced barrier properties; the best container manufacturing process is one which provides orientation in the solid state (SPPF) for barrier properties; and current metal to plastic jar lidding technologies do not provide adequate barrier for use in retort food packaging.

Technical Progress Report WRC 265-89**CARILON® Thermoplastic Polymer Food Packaging Analysis
Evaluation of Barrier Properties of Recent
Polymers and Formed Containers***by***L. E. Gerlowski, J. R. Kastelic****SUMMARY AND CONCLUSIONS**

We have continued to study the barrier properties of CARILON® Thermoplastic Polymers. It is apparent that the best manufacturing process for barrier is one which provides orientation in the solid state (e.g., SPPF). A second observation from this work is improvements to stability of the polymers have resulted in enhanced barrier properties. With these two barrier enhancements over previous work, the oxygen barrier is more than adequate for small retortable containers. However, the water barrier improvements are not adequate to meet the requirements for shelf life.

From a barrier viewpoint, two deficiencies remain with our CARILON containers. The water barrier inadequacies are best met with a PVDC coating or polypropylene co-extrusion. The other deficiency is commercial lidding technologies do not supply adequate barrier for these all plastic containers. We have had limited success with metal caps on extrusion blow molded jars and heat sealable metal foil laminates. The majority of lidding barrier success has been realized with polymer to polymer welding. Better solutions to these two deficiencies will be the focus of the 1990 program.

INTRODUCTION

We have recently formed CARILON Thermoplastic Polymer into containers by several methods. These methods include sheet extrusion, injection molding (IM), extrusion blow molding (EBM), and solid phase pressure forming (SPPF). The containers were all made from improved melt stability polymer from the Moerdijk Demonstration Unit (MDU). The visual appearance of the formed containers is similar to polypropylene (PP) in the same configuration. We have analyzed these containers for oxygen and water barrier properties.

We have observed that, along with improvements in melt stability, improvements in oxygen and water barrier properties have been attained.

Using the obvious solution to overcome water transport deficiencies of the CARILON polymer, containers were coated with PVDC based coatings. In addition, other experimental approaches such as blending, surface alteration, etc. have been screened as a means to reduce water transport. These coated and treated containers were analyzed for barrier performance. The coated containers meet the stringent barrier requirements for baby food and are to be used in test packs with various food companies.

Past work had been aimed at evaluating and improving the barrier properties of the CARILON polymer (1). Now that we feel comfortable that adequate oxygen barrier can be achieved with the current polymer, work has now expanded to consider the barrier-adequacy of the total container. In addition to the polymer itself having appropriate barrier properties, the lidding system must also have adequate barrier. This requirement is extremely important for plastic containers. In the current glass and metal markets, the container is essentially impermeable to gases. The food packers use various sealing systems, all of which exhibit gas transport through the seal area. In addition to barrier performance, the sealing system must also be able to survive a food sterilization step (hot fill, retort, etc.). Proper seals are difficult to attain for plastic containers. This is evidenced by the lack of an all plastic retortable container in today's market. The only retortable plastic containers in commercial use today have either a double seamed metal end or a specialized metal foil composite heat seal end. For the CARILON polymer containers, several sealing methods have been analyzed including metal laminate heat sealing, polymer to polymer welding, and conventional gasketed metal lids. In order to provide such a system for test packs, the barrier properties and retort performance have been evaluated to insure the total package is adequate.

POLYMER IMPROVEMENTS

We had previously shown oxygen barrier to be dependent on the crystalline level of the polymer (1). More recently, we have observed an

improvement in oxygen barrier coinciding with improvements in polymer stability. We have also seen that the water barrier limits the use of the polymer in a monolithic structure. Along these lines, several methods have been analyzed to improve the water barrier properties. In this section of the report, an analysis of these improved polymer properties is presented. Then, the mechanism of water transport through CARILON is discussed. The objective of this work is to develop a strategy to reduce water vapor transport rate (WVTR). With this fundamental knowledge, results of two alternative methods are presented to reduce the water transport (blending and surface alterations). This section of the report is aimed at the base polymer properties, hence, the final section discusses results of scalping measurements performed at National Food Laboratories (NFL) in Dublin, California.

Oxygen and Water Barrier

Process improvements at the MDU reactor have led to cleaner polymers as experience with the polymerization process has progressed. These cleaner polymers are evident in whiter pellets and improved melt stability. The conventional wisdom is that the polymer from the MDU now has many less molecular defects than earlier batches. Speculation on defect types includes crosslinks, gels, cyclized chains and many other molecular level details. Changes at the molecular level are difficult to analyze since we generally measure bulk properties (DSC stability, tensile properties, etc.). Permeation of gases, however, is a molecular process and can be affected by such changes.

The permeation of gases through semi-crystalline polymers occurs by sorption into the polymer surface and diffusion through the amorphous region. The permeability of a gas through a homogeneously dispersed crystalline polymer can be described by:

$$P = D_a * S_a * (1 - X)^2 \quad (1)$$

where D_a is the diffusion coefficient of the gas in the amorphous region, S_a is the sorption coefficient of the gas in the amorphous region, X is the crystalline volume fraction and P is the overall permeation coefficient. CARILON polymers have been shown to follow this relationship for oxygen and carbon dioxide (1).

As the polymer processing has improved, we have also noticed a significant reduction in oxygen permeability values (Table I, Figure 1). For an explanation of this observation, we look at the contributions from each the amorphous and crystalline phases. First, the diffusion through the amorphous phase is a function of the specific free volume (2,3). The specific free volume can be related linearly to the amorphous density (4). Density gradient column measurements do not show drastic increases in amorphous density for CARILON ter-polymers with similar melting points to three decimal places (Table II). From this result, we infer that even though the defects exist in the amorphous regions, the concentrations of these defects are so small that they are not measurable with this technique. We surmise that the specific free volume and hence amorphous diffusion are not significantly affected by the polymer improvements.

This turns attention to the crystalline regions. These same polymer batches do not show drastic increases in crystallinity that would explain reduced oxygen permeability by equation (1) (Table I). It is more likely that the types of crystals formed in a more perfect polymer could reduce the gas permeability. In other polyolefins (polyethylene), research has shown that decreases in defects increase the aspect ratio of the crystalline spherulites (5). Since the crystalline spherulites are impermeable to gases, increased aspect ratio results in a longer diffusion path and equation (1) no longer holds. The relationship of aspect ratio to permeability has been quantified (6) and shows that the permeability can be reduced by an order of magnitude by the proper concentration and aspect ratio of impermeable species. Based on these inferences, recent attention (1989) to explain improvements in gas permeability has focused on crystalline features.

Two methods are available to estimate the effect of spherulite dimensions in semi-crystalline polymers. Scanning electron microscopy (SEM) has been used for this measurement for several years. D. L. Handlin has

shown that imperfections in CARILON polymer backbone reduces the spherulites from long thin needle like crystals (which would have lower permeability) to dispersed small spheres (which would have higher permeability) (7). The second method is based on the DSC heating curve. As the crystals become more perfect, they generally form more distinct and sharpened melting peaks. As more and more defects occur, the peak becomes broadened by lower melting constituents. Figure 2 compares several melting peaks from the latest improved quality polymer batches and previous polymer batches. As these DSC curves show, the overall volume percent crystallinity is about the same. However, the curve of 88/047 shows a much narrower peak indicating a narrower distribution of crystallite size. From the electron micrographs, these crystallites are represented by the long, narrow type needed to reduce permeability. As we would expect from these observations, this polymer has improved oxygen barrier properties. Hence, the increase we see in oxygen barrier correlates with the general impression that the process is providing a cleaner, more defect free polymer.

Water Sorption Characteristics

The primary deficiency of CARILON polymer used in a barrier container is its water barrier. To be considered a barrier to water, a container must limit water loss to less than 3% of the food weight over the shelf-life of the package. This requirement is based on Federal guidelines for 'truth in labeling'. Also, when most foods lose three to five percent weight, the consistency and flavor changes can be detected in the taste. In most commercial packaging sizes (4-12 oz.), CARILON polymer packages will not meet this requirement.

To provide insight in how to overcome this deficiency, a study has been made to determine the water transport properties of CARILON polymers. In particular, the sorption properties of the polymer are extremely high. To address this problem, we first measured the sorption characteristics. Two food packaging grade ter-polymers (89/007 and 89/021) and one co-polymer (88/034) were chosen. Pellets were exposed to various humidities in a constant humidity chamber to determine the sorption curve. The sorption

curve is the weight uptake in the polymer as a function of water activity is shown in Figure 3. Water transmission values were also measured on films and containers made from these polymers, and are included in Table III.

The water sorption characteristics of the CARILON polymers are highly non-linear. This relationship suggests that simple Henry's law relationships are not followed. Other polymers which behave in this manner are nylons, alcohol copolymers, etc. (8). This behavior is typically labeled Type II or anomalous. The sigmoid behavior of the water sorption curve implies that at high water activities, the sorption is the dominant mechanism in the transport equation. When this is the case, the water essentially moves through the polymer as a uniform front. The front velocity progresses at a rate proportional to time (8).

With this understanding of the water transport mechanism in CARILON polymers, we can more intelligently address the question of how to reduce water transport in the polymer. Ideally, we would like to keep the exposure of the polymer to low water activity environments. This can be most easily accomplished by keeping the polymer surface (food surface) from direct contact with the water. Thus a functional barrier which lowers the water activity at the polymer surface would best resolve this deficiency. Also, surface alterations which provide a non-wettable surface could also help reduce water transport. In essence, some of the benefits of CARILON polymer which make it attractive for decoration and painting are limiting its use in water transport.

Blending (LCP, PP)

For CARILON polymers, the property which needs the most improvement is reduction of water vapor transport. Ideally, we would like to find a blend additive which behaves synergistically, and dramatically reduces water transport at a low volume percent. While, at the same time does not compromise the otherwise outstanding property set found in CARILON polymers.

Polymer blending affords a means by which an improvement to a particular property can be achieved. Physical properties of a blend are generally determined by the level of interaction between the blend components

(or lack thereof). Blends are sought that maximize a key property improvement while minimizing significant compromise to all other desirable properties. This can sometimes be successfully accomplished when a small amount of polymer 'A' manifests itself in a blend in an unusual and synergistic manner. For example, polymer 'A' might exist as a skin when a sheet is extruded or a part is formed (skin concentration effect). An other example would be for polymer 'A' to form a platelet structure within a large continuous polymer 'B' matrix. An example of the latter structure is the DuPont SELAR® technology where polyethylene and amorphous nylon are blended in a manner favorable to formation of a nylon platelet phase and a polyethylene continuous phase.

Two polymers were blended at low levels with CARILON polymer for water barrier improvement: a liquid crystal polymer (LCP) and polypropylene (PP). Both of these polymers have excellent water transport barrier properties. We had envisioned these polymers to form platelets during the container manufacturing step and thus reduce water transport.

Liquid crystal polymers (LCP's) blend very well with CARILON. In particular, VECTRA R A900 was chosen based on some previous blend work which indicated compatibility (9). We were able to show a 3X reduction in water vapor transport in compression molded plaques at 20% LCP (Figure 4). Morphological analysis (Figure 5) indicates that most of this reduction was due to increased tortuosity. Similar samples were also produced by sheet extrusion and injection molding. The extrusion resulted in long thin strands of LCP in the CARILON polymer and not much reduction in water transport rate. Molded specimens had somewhat more bi-directional orientation from the injection molding operation and resulted in a more plate like dispersion. The injection molded samples had a somewhat reduced water transport rate. Compression molding, which produced the most plate-like particles resulted in the greatest reduction in permeability. The morphologies as a result of the process are shown in Figure 5 and water transport comparisons are included in Table IV.

In essence, the reduction seen in water transport from LCP blending is physical in nature. The LCP appears to act as an inert member and transport is entirely in the CARILON phase. It appears that adequate water

vapor transmission rates could be achieved with either higher LCP loading or improved processing, however, neither are practical at this time. The economics at a greater than 20% LCP loading are not attractive, and processing the LCP dispersion to form platelets of higher aspect ratio is not easily controlled.

A second system was also considered. Polypropylene (6.7 wt%) with a compatiblizer (3.3 wt% ADMER - a functionalized polypropylene product made by Mitsui) was dry blended with CARILON polymer (90 wt%) and extruded into sheet. Unlike the LCP, the dispersed polypropylene resulted in spherical shapes in the extruded sheet and a thin layer of PP on the outer surfaces. The spherical dispersion was advantageous in the forming process. At CARILON polymer thermoforming temperatures, polypropylene is in its melt state and conforms readily to the surrounding matrix. Thus, thin platelets of polypropylene in CARILON polymer can be formed by elongating and thinning the spheres. This blend, much like the LCP, can then prohibit water transport by both the more tortuous-path mechanism and the thin-outer-layer mechanism. The diffusion path through the mixture will depend on how well the polypropylene can be dispersed in the CARILON polymer. In this case, an extruder with a barrier screw with a MADDOX mixing tip was used to gain as much physical dispersion as possible. This resulted in the morphology shown in Figure 6 and permeability reduction of 64%, to 1.8 gm-mil/100 in²-d (Table IV). This result is indeed promising, although we need to be able to reach an overall WVTR of just below 1.0 gm-mil/100m²-d. Improvements to this approach necessitate better control of the dispersion of polypropylene in the CARILON polymer. To meet this goal, a better understanding of the compatiblizer needs to be established, and work will be aimed at meeting this goal.

Halogenation

As a means to reduce transport of water through CARILON polymers, chemical surface alterations have been considered. In following with the recommendation to limit the activity of water into the polymer, chemical alterations have been tried which reduce the hydrophilic nature of the

polymer surface. The first choice for reduction of water transport by chemical surface alteration is halogenation. This mechanism has been utilized commercially in fluorination of polyethylene (PE) gasoline tanks and soft drink syrup concentrate containers. PE is known to readily absorb many of the hydrocarbons which make-up gasoline. A short exposure to fluorine gas during the blow molding process greatly reduces the transport. Thus, we are considering chlorination and fluorination along the lines of vinylidene chloride and fluoride polymers, respectively. These two polymers have very low surface free energies and are not readily wet by water. Similar work by Barrie (9-a) on epoxies has shown significant water reductions from epoxy fluorination.

Halogenation of ketones is a well documented, fast reaction (10). Mechanisms have been presented and accepted which, in the presence of acid, consist of enolization and halogenation at the alpha position to the ketone group. These reaction schemes have been well formulated on small molecules, but very little information is available on polymers. Since CARILON polymers are the first alternating polyketone olefin co-polymer reaching commercialization, such experiments will be breaking new ground.

We have previously shown that gas phase fluorination treatment can reduce the water vapor transmission rate through polyketones by an order of magnitude which would meet the requirements for food packaging (11). Gas phase fluorination, however, is not the most desired processing operation for safety considerations. For this reason, we have recently attempted solution fluorination and chlorination of CARILON polymers. In each case, we have used an acid solution with an appropriate reducing agent (cuprous fluoride and chloride). Several reaction parameters were investigated (time and temperature). The results and effect on permeability to water are shown in Table V. As these tables indicate, even at short times we are seeing some level of halogenation. However, in solution, it appears that the reaction is not approaching an appropriate level to reduce water transport (via XPS). At longer reaction times, we see an increase in surface chloride concentration, but we also see a more degraded polymer due to the high temperature acid environment. This degraded polymer results in an increase in WVTR. Solution fluorination did not provide a measurable surface alternation, or

permeability alteration. Gas phase alterations were much more promising. As exposure time to Cl_2 increased, a corresponding WVTR reduction was found (up to 23%). Although this is not at the required level of long time fluorination reduction (10X reduction), alternate reaction conditions (increased pressure, temperature) may allow for improved properties. Although solution surface alterations are interesting, a stronger reacting system must be developed (either in solution or gas phase) to provide a higher degree of the desired chemical surface alteration.

Organoleptics

Measurements of flavor scalping compounds by CARILON polymer containers has recently been conducted at National Food Laboratories. Scalping refers to the ability of a polymer to extract flavor components or other food constituents from the food into the polymer. The other half of the organoleptic equation, migration, is the transport of substances from the polymer into the food. Only scalping was addressed in this study, and migration inferences have been obtained from test pack information.

The measurements made by National Food Laboratories (NFL) consisted of exposing CARILON polymer swatches to known concentrations of a food simulant dissolved in water. These samples were prepared in closed containers and sterilized (to simulate retort) and stored. Controls of polypropylene were also run side by side with the CARILON polymer samples. The simulants and results are summarized in Table VI. The entire report from NFL is included in Appendix I. As these results indicate, CARILON polymer scalping characteristics are as good as or better than polypropylene. This is consistent with test pack results that indicated no significant off taste from CARILON polymer stored with food in glass containers.

CONTAINER MANUFACTURE

We have found the barrier properties of the container to be dependent on the processing technique used to form the containers. In particular, orientation or additional heat treatment processes which can

increase crystallinity or crystal growth improve oxygen barrier properties significantly. Along these lines, we have considered several container manufacturing processes to form containers. Extrusion blow molding provides the least crystal enhancements while solid phase pressure forming appears to enhance barrier properties significantly.

Extrusion Blow Molding (EBM)

The EBM process consists of extruding a tubular profile directly into an open clam shell type mold. The mold is closed and the tube is clamped at the bottom. Air is then blown into the melted tube to form the polymer into the shape of the mold. The entire forming process typically takes place in the melt state. Several test containers were made with the extrusion blow molding (EBM) process. One was an eight ounce peanut butter shaped jar and the others were 4 and 5 ounce baby food shaped jars. Each jar had a continuous thread neck finish.

These containers were measured for oxygen and water barrier properties. The results are shown in Figures 7, 8 and 9. The polymer batches used to make these containers were 88/047 and 89/021, each made specifically for food packaging evaluations. The polymer batches to be used in food packaging currently contain a three part stabilizer system which should meet FDA type guidelines (AO 1330, IRGANOX 1056, and GMS). The level of crystallinity attained with this process was only 33-35%. At this level of crystallinity, a typical oxygen barrier of 1.1 cc-mil/100 sq-in-d-atm was attained. Based on these measurements, a nominal 30 mil container wall would be necessary to provide adequate oxygen shelf life over one year in a four ounce container.

The water transport properties obtained from this process were also quite high. These values are also included in Figures 7, 8 and 9. At these water transport levels, a coating or other barrier is needed to meet the requirements of not more than three percent weight loss over the container shelf life.

Solid Phase Pressure Forming (SPPF)

The test pack containers from 1988 were formed with the solid phase pressure forming process (SPPF). This process was shown to result in a boost in crystallinity and barrier. The increase in barrier properties was beyond that expected from just the crystallinity level improvement. In addition, a certain degree of clarity is added to the package. With the solid state orientation, much like other polyolefins, the container can be made to have contact clarity.

The oxygen barrier analysis of several of these containers is included in Figure 10. With the SPPF process, an oxygen barrier of 0.4 cc-mil/100 sq-in-d-atm can be achieved. The crystallinity of the clear side wall of these containers is 50.4%. Even at this high crystalline level, the oxygen barrier is better than that predicted by equation 1. This improvement may be due to amorphous phase densification, or optimal shape of the crystallite phase. Density measurements do not indicate amorphous phase densification to occur. Examination of the DSC heating curve shows a very narrow peak, indicating an improved effectiveness crystalline phase (much like the improved base polymer arguments). The required nominal wall thickness for this a four ounce baby food container from this technique would be in the 10 mil range to meet oxygen barrier requirements.

The water barrier properties of the SPPF containers are also shown in Figure 10. This measurement indicates that additional benefits are seen in water transport over the extrusion blow molding process. Although, the reduction that must be achieved for 3 percent weight loss over one year shelf life is still not obtained.

Annealing

To improve the crystalline levels in the EBM containers, several were annealed based on earlier findings of post annealing improving oxygen barrier properties (1). A first set was annealed ten to fifteen degrees centigrade below the melting point. A second set was annealed at the temperature of crystalline initiation (172 C) taken from the cooling DSC

curve (Figure 11). These containers were annealed 3 minutes in an air oven to represent a commercial type process. The analysis of these containers are shown in Figure 12. Those annealed at the higher temperature resulted in worse oxygen and water barrier properties than the non-annealed. We feel that this is a result of oxidative degradation of the polymer at these conditions. However, in the lower temperature annealing experiments, the resulting containers showed significant improvements in crystallinity and oxygen barrier. The annealing, especially at the crystalline initiation point appears to improve crystalline level and type. This improvement in crystallinity results in subsequent improvements in barrier properties (e.g., for peanut butter jar the wall thickness could need to be 20 mils versus an annealed 30 mils).

Processing Analysis

These experiments and measurements have shown the method used to manufacture the containers can significantly effect the barrier properties. Figure 12-a shows the effect of crystallinity on oxygen permeability. This relationship has been previously documented (1) and is included with the latest container measurements. As we can see, the newer EBM containers reside within the lower permeability regions of these measurements. The SPPF containers are significantly improved in oxygen barrier over the previous measurements with earlier MDU polymer. This data, thus, indicates the chronological improvement to the polymer with fewer defects, resulting in improvements to oxygen permeability.

Since the container is to be designed basis an oxygen barrier requirement, this result has a direct effect on the amount polymer needed in a container and hence economics. The lower the oxygen permeability of a given container, the thinner the wall necessary to provide adequate oxygen barrier for a given container. The results obtained from this study are summarized in Table VII as to the effect of processing technique for a four ounce baby food container. Wall thicknesses are based on the oxygen barrier properties measured which satisfy a 4 ppm oxygen gain over a one year shelf life. As these values show, the SPPF process provides the best container in

a single operation. EBM and subsequent annealing also provide a boost in barrier properties to an attractive level.

COATING DEVELOPMENTS

Thermoset

The test pack performed at Heinz in 1988 utilized a thermoset water barrier on the package interior. Although no significant problems were found with this system, little work has progressed beyond that point. The thermoset system was made by PPG Industries and is a test polymer made especially for our needs. Since then, PPG has been working on PVDC systems to provide better barrier properties.

Polyvinylidene chlorides (PVDC)

PVDC coating systems have been used effectively by the film industry. Both solvent based and latex based systems are available. With the growing concerns in air and water pollution, latex based systems are gaining in popularity. There are several disadvantages to using PVDC coatings in rigid container systems. The first is adhesion, most rigid containers are made from hydrophobic polyolefins that are not easily wet by the latex or adhered to by the PVDC. The second is the heat and ultra violet stability of the PVDC. At temperatures of moderate food sterilization most PVDC polymers yellow slightly. At retort type conditions, the yellowing becomes darker brown. To alleviate these problems we have been working with PPG Industries on PVDC based coatings for CARILON polymers.

ICI Industries makes a commercial grade PVDC latex for polyethylene terephthalate (PET) beer bottles in Europe (VICLAN 834). CARILON polymers appear to have similar surface properties to PET. Since this PVDC system was developed to adhere to PET, we have had success with adhesion to CARILON polymers. However, in addition to the PVDC yellowing at retort conditions, we have found that it emits small quantities of acid. This acid environment, at high temperature, also results in yellowing the CARILON polymer (12). Be

that as it may, we have applied this latex to CARILON polymer EBM containers successfully with the Nordson Impact Spray system. The resulting containers pass oxygen and water transport requirements before and following retorting, even though they yellow. The results of these measurements can be found in Table VIII and Figure 13.

PPG Industries is working with us in developing a non-yellowing PVDC system which adheres to the CARILON polymer. Their system, for the present time, is solvent based. However, they feel in the long run they can produce a latex based system. The PPG coated systems analyzed are also included in Figure 13 and TABLE VIII. As these values show, the coating can meet requirements with significant decreases in yellowing over the ICI coating. However, the success rate of adhesion following retort is significantly less than the ICI systems (50% versus 99%). PPG is currently working on solving this problem.

To be used as a water barrier coating, PVDC provides an additional benefit in reducing the oxygen permeability of the container also. This reduction can allow for thin walling of the container to even less than the required 20 mils of a single mono-layer container. At a given oxygen transport requirement of 4 ppm per year, the reduction in wall thickness afforded by the PVDC coating is shown in Figure 14. As this figure indicates, by increasing the coating thickness from 0.4 mils to 0.5 mils, the CARILON wall thickness can be reduced by half.

LIDDING ANALYSIS

The lidding system used in plastic containers is quite important. Many lids used in glass or metal containers rely on a gasketed sealing area. The gasket is typically a rubbery polymer which has a high permeability. The sealing area can be quite small, and thus can allow for a rather large amount of oxygen transport over the shelf life of the container. For example, the oxygen barrier of several commercial lids on glass containers have been measured and are summarized in Table IX.

Lids can be of several types, e.g., continuous thread (CT), push-on, twist-off (PT) or double seamed (DS). A CT is a lugged metal lid

which turns on continuous threads on the glass container to form a seal between the glass lip and rubber gasketed metal. A PT is a lugged metal lid which is forced over non-continuous threads on the glass container. The PT lid forms a seal on the glass lip and along the threaded area of the glass container. In addition, CT and PT rely on a vacuum inside the container to provide most of the bearing pressure on the gasket. A third metal lid is the conventional double seamed (DS) lid that is gasketed along the seaming surfaces. This is the sealing system used by the metal canning industry for decades. We simulated the vacuum in the gas barrier measurements by imposing an external force on the center of the lid to match the deformation seen in commercial packages. We measured barrier properties of these lids on impermeable containers.

The lid with the most amount of gasket material has the best barrier properties (PT). The lid with the least amount of gasket material has the worst barrier properties (CT). The manufacturer of the CT lids also provided us with a lid with improved barrier gasket material. This version (CT-II) did have improved barrier properties over the original lid, but not to the desired level. The projected oxygen transmission over one year's shelf life of these lids is high for what we expected to find. The best possible lidding candidate is the PT lid, which allows about 3 ppm oxygen gain over a one year shelf life with an impermeable container (e.g., glass). Oxygen sensitive baby foods have a requirement of 5 ppm oxygen gain over one year. For a permeable container (e.g, CARILON) this would easily lead to total oxygen levels over a year in excess of the 5 ppm requirement.

In addition to inadequacies in barrier, the retort performance of these metal-lidded CARILON polymer containers was not adequate from a sealing point of view. The 5 oz baby food jar was analyzed for retort performance with a continuous thread metal lid. Following retort, the success rate of lid seals was much less than 10%. Measurements of the neck area before and after retort, with and without the lid, show the neck dimension changes drastically following retort (Figure 15). This dimensional change of 30 mils from the radius is apparently enough to loosen the lids from the container. Attempts were made to anneal the containers with metal supports in the flange area to increase modulus and disallow polymer movement via 'memory'. Various

annealing conditions were attempted with limited success in reducing dimensional changes following retort (Figure 15). Based on the dimensional change and barrier limitations of this lidding technique, a test pack with this lidding system was cancelled.

In search of a better sealing system, polymer to polymer welding was viewed as a solution. In particular, spin welding (SW) (13,14) has been utilized to weld 6-25 mil CARILON polymer films to the 5 oz baby food jars. We have measured adequate permeation of containers lidded with this technique to allow for less than 5 ppm oxygen gain and less than 3% weight loss over a one year shelf life for the 5 oz coated baby food jar. An oxygen transmission comparison of these containers is shown in Figure 16 breaking down the transmission through the container body and lid seal. Also shown is the same container with the standard CT gasketed material for comparison. As we can see, the CT lid accounts for much of the oxygen and water transmission. With a CARILON polymer inner-seal, most of this transmission through the lid can be reduced. However, the SW process needs to be optimized before this technique could be used in a test pack. Problems with excessive flash generation and polymer crumbs resulting in the food are currently limiting the use of this technology.

CONCLUSIONS AND RECOMMENDATIONS

From these analyses, it is apparent that the best manufacturing process is one which provides orientation in the solid state (SPPF) for barrier properties. The improved stability of the polymer results in more perfect crystal formation and enhanced barrier properties. And, the water barrier of the CARILON polymers is not sufficient alone, but needs an additional coating or treatment to meet the requirements of the food packaging industry.

From the observations of water transport, an inner-liner/coating system could provide a significant short term solution. Ideally, the inner-liner should be an FDA direct food contact retort approved water barrier. The most obvious material which meets this requirement currently is polypropylene (PP). A coextrusion of thick CARILON polymer and thin

polypropylene will be used to form sheet, from which containers can be solid phase pressure formed. This will take advantage of the improved oxygen barrier of CARILON polymers from the SPPF process. This recommendations will be pursued in 1990 as a means to produce test pack and test market containers.

A commercial lidding system which has adequate barrier properties is also essential to success. Currently, double seamed metal ends are used on commercially retorted plastic containers. Also, heat seal membrane lids sealed to PP are becoming popular. With the inner-liner system, polypropylene will be the inner surface as well as the sealing surface. Thus, commercially available heat seal materials for polypropylene may be applicable here. These two systems, in conjunction with the inner-liner system, will be evaluated in 1990.

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TABLE I. CARILON® BARRIER PROPERTY IMPROVEMENTS

<u>YEAR</u>	<u>BATCH</u>	<u>CRYSTALLINITY (%)</u>	<u>PO₂*</u>	<u>AMORPHOUS PO₂* AT 25°C</u>	<u>AMORPHOUS WVTR AT 100°F</u>
85	014	0.36	2.6	4.5	19.1
	020	0.40	3.4	6.7	19.4
	021	0.39	3.8	7.3	
	022	0.34	6.0	9.9	25.2
	022	0.33	3.7	6.0	
	037	0.34	4.0	6.5	
	038	0.33	0.85	1.4	
86	005	0.33	5.8	9.6	--
	005	0.41	5.2	3.7	19.7
86	001(E)	0.39	0.8	1.6	--
88	047	0.35	1.9	4.5	14.2
	047 (Annealed)	0.38	0.3	0.8	10.7
TEST PACK					
88	004	0.42	0.8	2.4	--
	047	--			
89	007	0.37	0.5	1.3	
89	021	0.35	1.9	4.5	
89	021(SPPF)	0.40	0.37	1.0	

* cc (STP)-mil/100 in²-d-atm @ 25°F

** gm-mil/100 in²-d

TABLE II. PHYSICAL PROPERTY COMPARISON OF OLD AND NEW CARILON®
POLYMERS

PROPERTY	BATCH (YEAR/NUMBER)		
	<u>86/007</u>	<u>88/004</u>	<u>89/007</u>
Oxygen Permeability (cc (STP)-mil (100 in ² -d-atm)		0.8	0.5
Melt Point (C)		228	217
Crystallinity	31.6%	41.7%	37.0%
density (gm/cc)	1.2374	1.23__	1.2361

(86/007 information taken from R.C. Allen, WRC TPR 145-87)

TABLE III. WATER SORPTION AND PERMEABILITY PROPERTIES OF CARILON®
THERMOPLASTIC POLYMER

<u>POLYMER BATCH</u>	<u>CRYSTALLINITY (%)</u>	<u>WVTR</u> [*]	<u>MAXIMUM SORPTION (wt%)</u>
89/007 ^{**}	0.36	20.0	1.48
89/021 ^{**}	0.41	20.0	1.60
88/034 ^{***}	0.48	18.3	2.10

* gm-mol/100 in²-d @ 100% RH, 100°F

** ter-polymer (approx. 5% C₃)

*** co-polymer

TABLE IV. EFFECT OF PROCESSING ON WATER VAPOR TRANSMISSION RATE OF VECTRA® 9000 LCP AND CARILON® THERMOPLASTIC POLYMER BLENDS

PROCESS	% LCP	WVTR ($\frac{\text{gm-mil}}{100 \text{ sqin-d}}$)*
COMPRESSION MOLDING	0	11
	5	8.5
	20	3.5
INJECTION MOLDING	0	10
	10	8
EXTRUSION	0	10
	10	10
EXTRUSION/ THERMOFORM	% PP	
	0	5.5
	10	1.9

* Room temperature, 55% relative humidity

TABLE V. ATTEMPTS TO SOLUTION HALOGENATE CARILON®
THERMOPLASTIC POLYMER SURFACE

<u>REDUCING AGENT</u>	<u>REACTION TIME</u>	<u>TEMPERATURE</u>	<u>Cl/F SURFACE CONTENT⁺</u>	<u>WVTR gm-mil/100sqin-d</u>
None				12.7 [*]
Cuprous Chloride, HCl	1 min	50°C	1%	12.2 [*]
	10	50°C	3%	12.3 [*]
	29 hr	50°C	3%	12.8
Gas Chlorine	0 min	RT	-	20.0 ^{**}
	2.5 min	RT	9%	18.5 ^{**}
	5 min	RT	18%	17.0 ^{**}
	10 min	RT	12%	15.4
Cuprous Fluoride Water	5 min	50°C	<1%	12 [*]
Gas Fluorine	1 d	RT	10	1.0 [*]

(RT = room temperature)

+ as determined by XPS

* 90% Relative Humidity, 100°F

** 100% Relative Humidity, 100°F

Table VI PERCENTAGE OF FOOD SIMULATING COMPOUND "SCALPED"

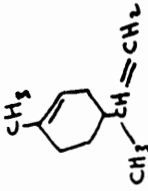
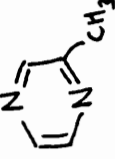

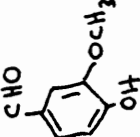

COMPOUND	STRUCTURE	FOUND IN	NUMBER OF DAYS STORED AT 90°F	FOOD SIMULATING SOLVENT	CARILON™ THERMOPLASTIC POLYMER		POLYPROPYLENE	
					AMBIENT FILL	RETORT	AMBIENT FILL	RETORT
D-LIMONENE		CITRUS	30	WATER ACID	50	-	100	-
ALLYLISOCYANATE	$\text{CH}_2 = \text{CHCH}_2\text{NCS}$	MUSTARD, CAULIFLOWER, CABBAGE, BRUSSELS SPROUTS	1	WATER ACID	5	-	15	-
2-METHYLPIRAZINE		COCOA, BARLEY, BEEF, CHICKEN BROTH, PORK TURKEY, CHEESES, NUTS, POTATOES	30 120 30 120	WATER WATER ACID WATER ACID	1 - 1 -	1 15 4 25	3 - 2 -	1 20 2 40
2,4-DIMETHYLTHIAZOLE		COCOA, BEEF BROTH, NUTS	30 30 120	WATER ACID ACID	5 10 -	1 1 100	1 5 -	1 1 100
VANILLIN		VANILLA	30 120 30 120	WATER WATER ACID WATER ACID	5 - 10 -	2 25 2 25	2 - 4 -	2 2 2 35
ISOAMYL ACETATE		BANANA OIL	30 60 30 60	WATER WATER ACID WATER ACID	5 - 25 -	1 5 1 -	20 - 30 -	30 25 25 -

TABLE VII. DEPENDENCE OF CARILON® THERMOPLASTIC POLYMER BARRIER PROPERTIES ON MANUFACTURING TECHNIQUE

<u>MANUFACTURE METHOD</u>	<u>MELT POINT (CENTIGRADE)</u>	<u>CRYSTALLINITY %</u>	<u>OXYGEN PERM (cc-mil/100sqin-d-atm)</u>	<u>REQ'D WALL THICKNESS MILS</u>
Extrusion	220	35	1.1	35.0
SPPF	220	41	0.75	21.0
	220	40	0.5	14.0
	227	-	0.7	20.0
EBM	217	36.5	1.1	35
*EBM "Anneal"	217		0.3	10
Increase MP EBM	255	~60	0.5	16

* (annealed 3 min at 172°C, temp. determined from crystallization temperature from DSC trace of nibs)

SPPF = Solid Phase Pressure Form

EBM = Extrusion Blow Mold

Anneal => re-heat formed containers to induce additional crystals to form

Slow Cool => form in heated mold to allow for longer crystal growth period

Increase MP => moving toward copolymer

TABLE VIII. WATER BARRIER COATING/CONTAINER

<u>COATING</u>	<u>THICKNESS (Mils)</u>	<u>WATER WEIGHT LOSS (% YEAR)</u>		<u>YELLOWING</u>
		<u>BEFORE RETORT</u>	<u>AFTER RETORT</u>	
EBM 5 oz. Jars:				
None	--	7.1	9.2	--
ICI PVDC	0.8	1.6	2.0	Slight to Dark
PPG PVDC	0.8	1.0	1.6	Very Slight
SPPF 4 oz Cups:				
PP Inner- Liner	2.5	<0.1	<0.1	None
<hr/>				
Requirement		3.0	3.0	None

Note: ICI PVDC yellowing is slight at 220-230°F retort,
dark at 240-250°F

TABLE IX. OXYGEN BARRIER LIDDING ANALYSIS
LID ON GLASS JAR (SIMULATE COMMERCIAL PACKAGE)

<u>Lid</u>	<u>CC</u> <u>PKG-D</u>	<u>PPM</u> <u>YEAR</u>
Metal CT - I	0.0035	11.2
Metal CT - II	0.0026	8.3
Metal PT (Baby Jar)	0.0010	3.2
Double Seam [*]	0.0073	20.0

Note:

Metal CT - II is 'improved barrier' gasket over CT - I from manufacturer
PPM per year for 4 oz baby food package

* Double seam was performed on non-optimized system

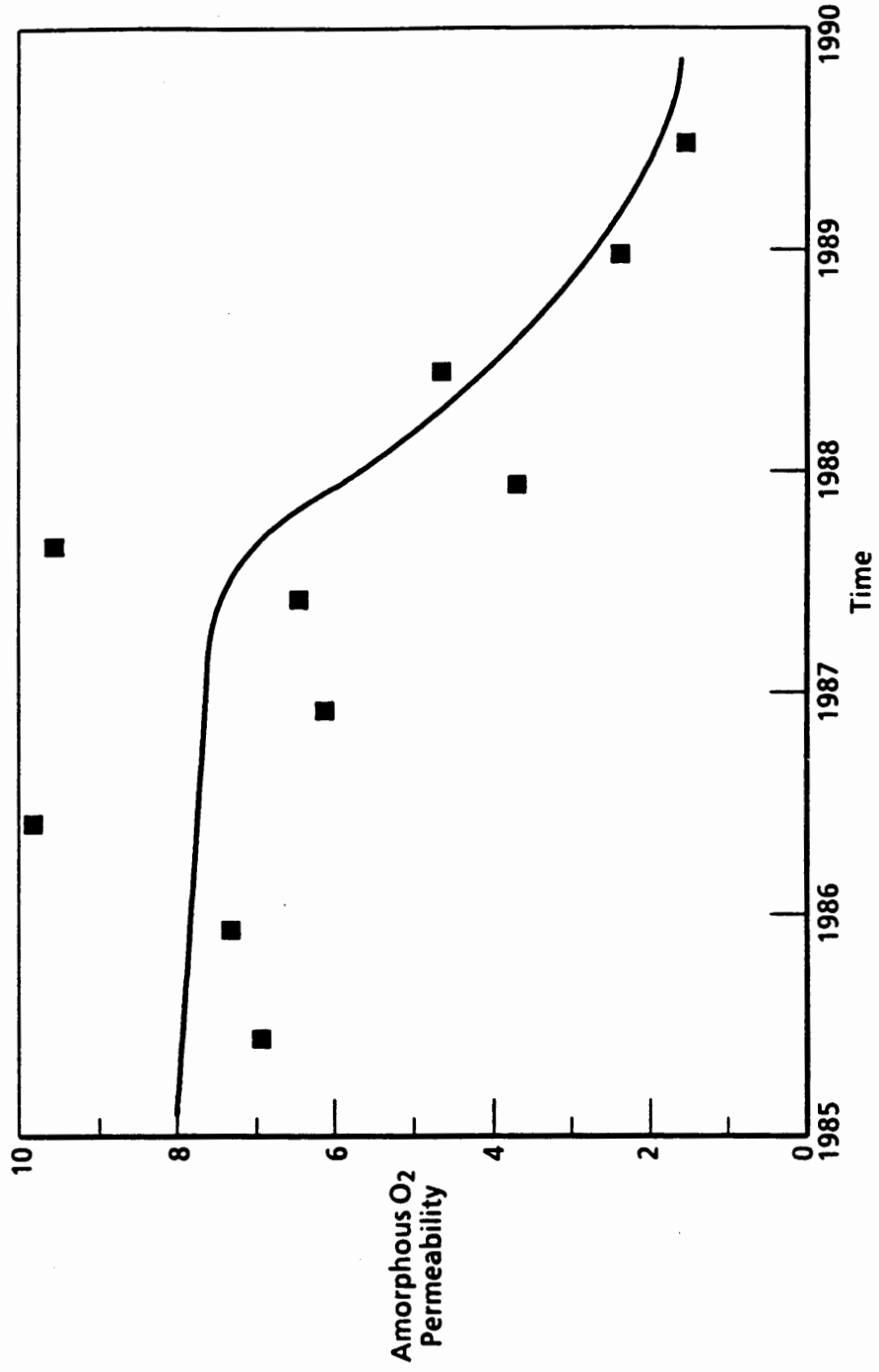


Figure 1. Oxygen Permeability Improvement

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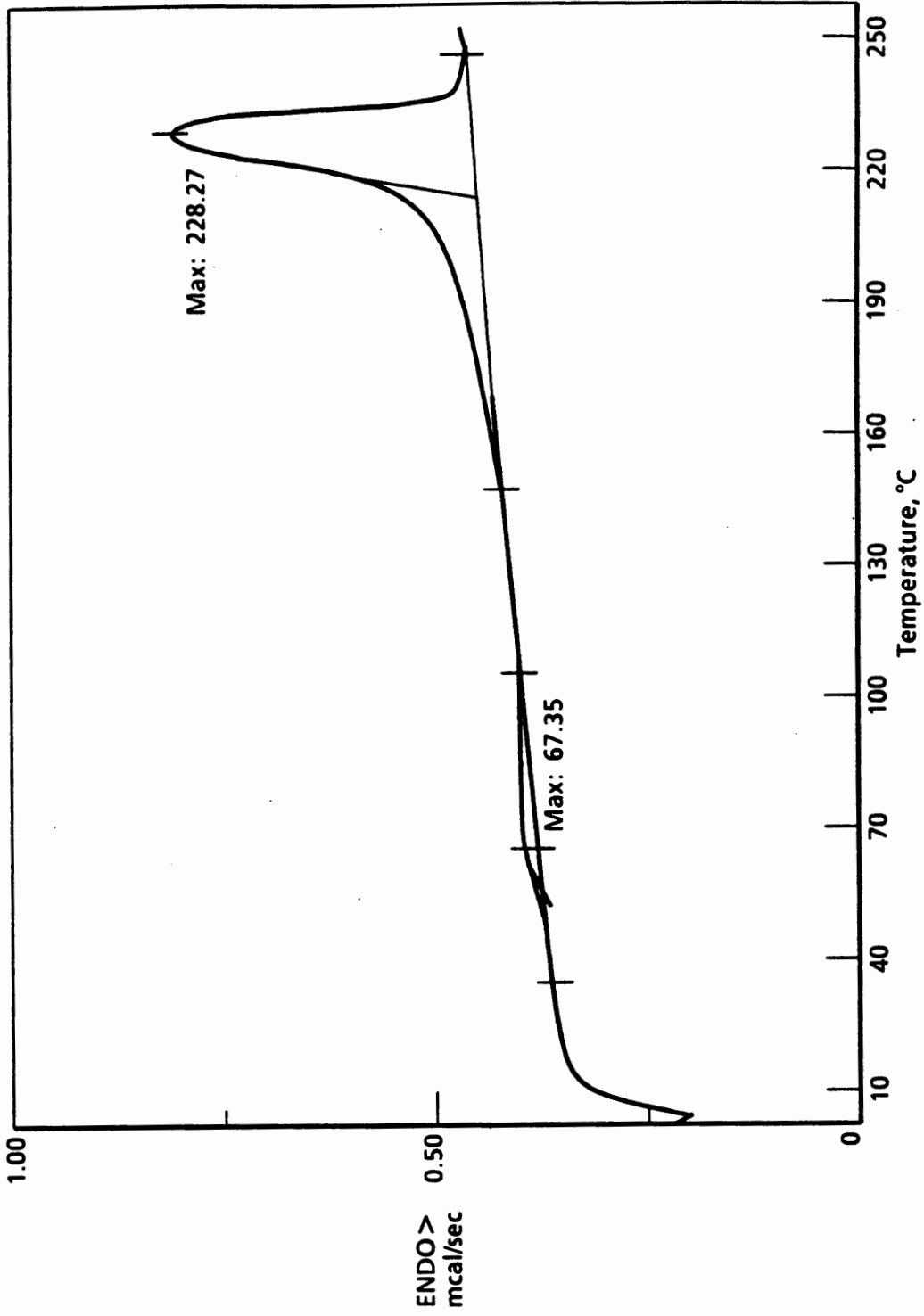


Figure 2a. "Older" Polymer (85/022) Which Has an Oxygen Permeability of 3.7

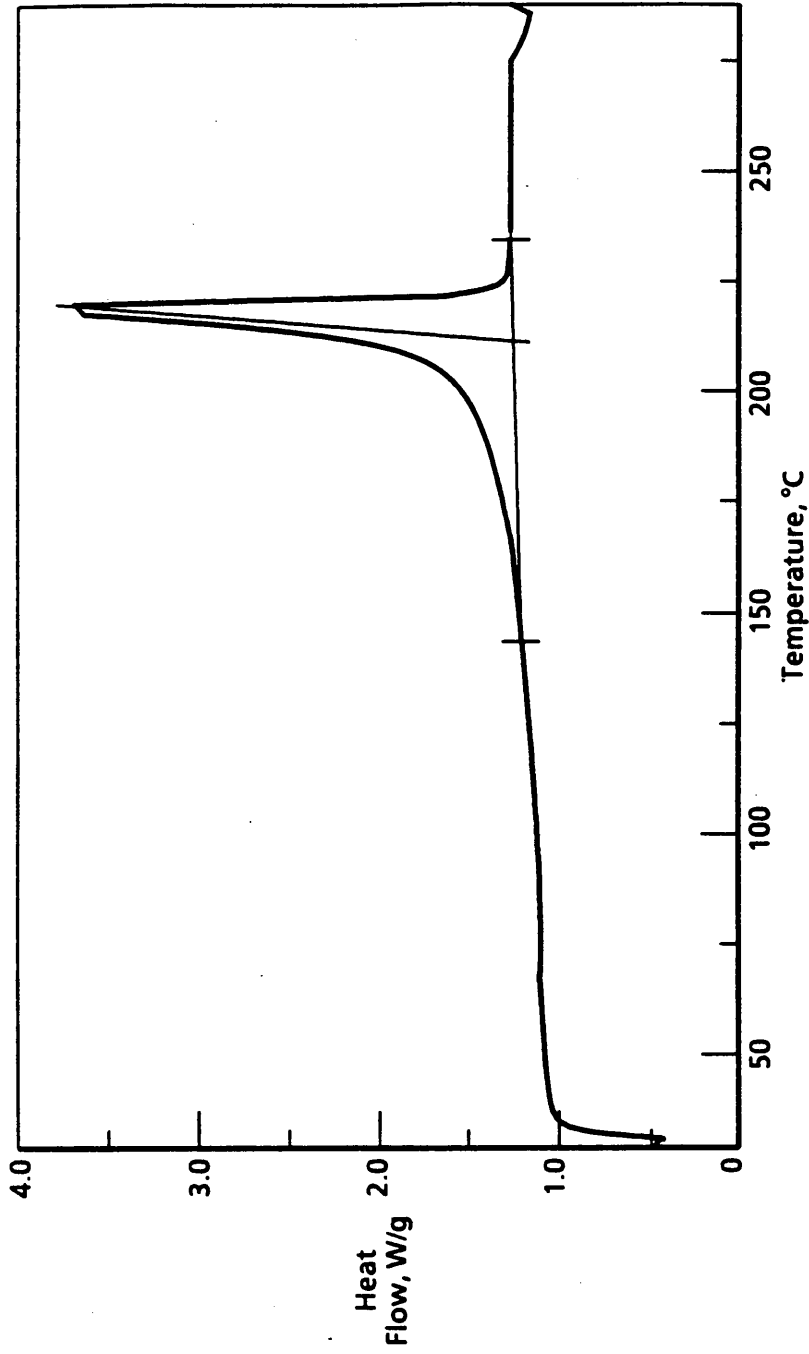


Figure 2b. "More Stable" Polymer (88/047) Which Has an Oxygen Permeability of 1.9
Note similar crystalline level to Figure 2a, but a much narrower distribution

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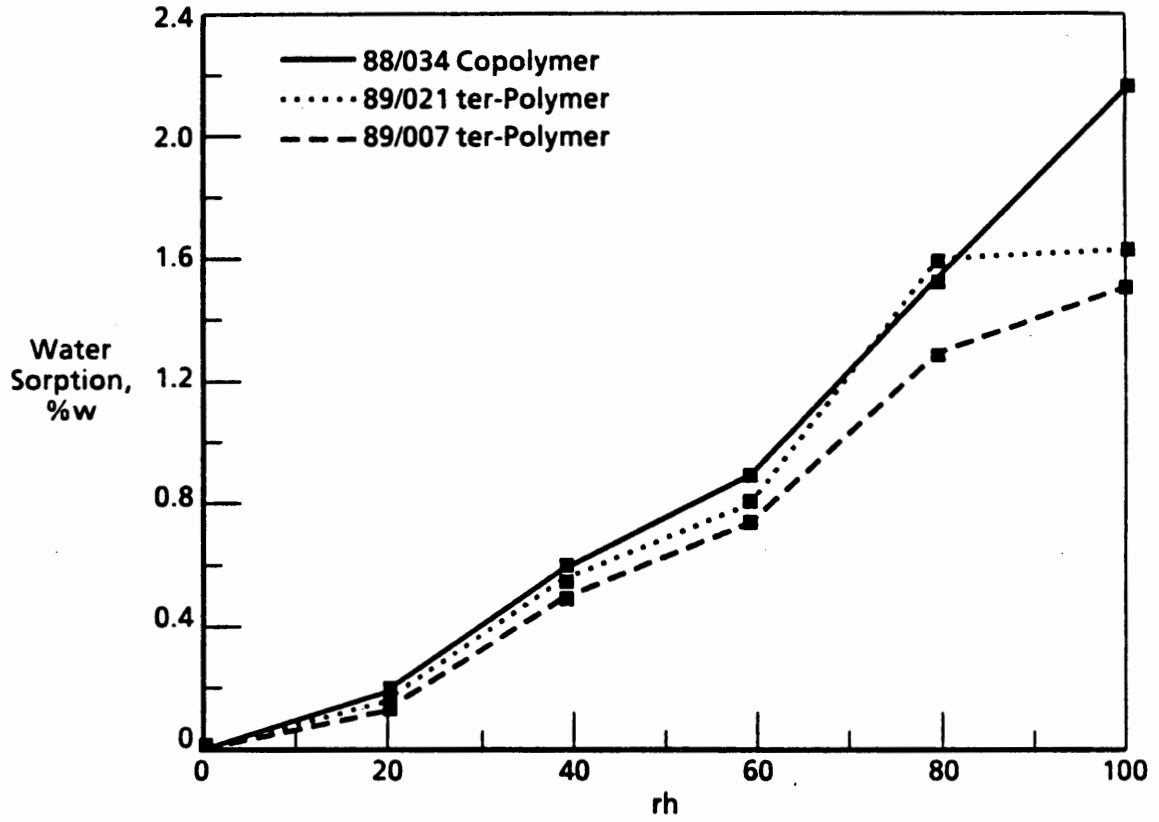


Figure 3. Water Sorption Curve of CARILON® Thermoplastic Polymers

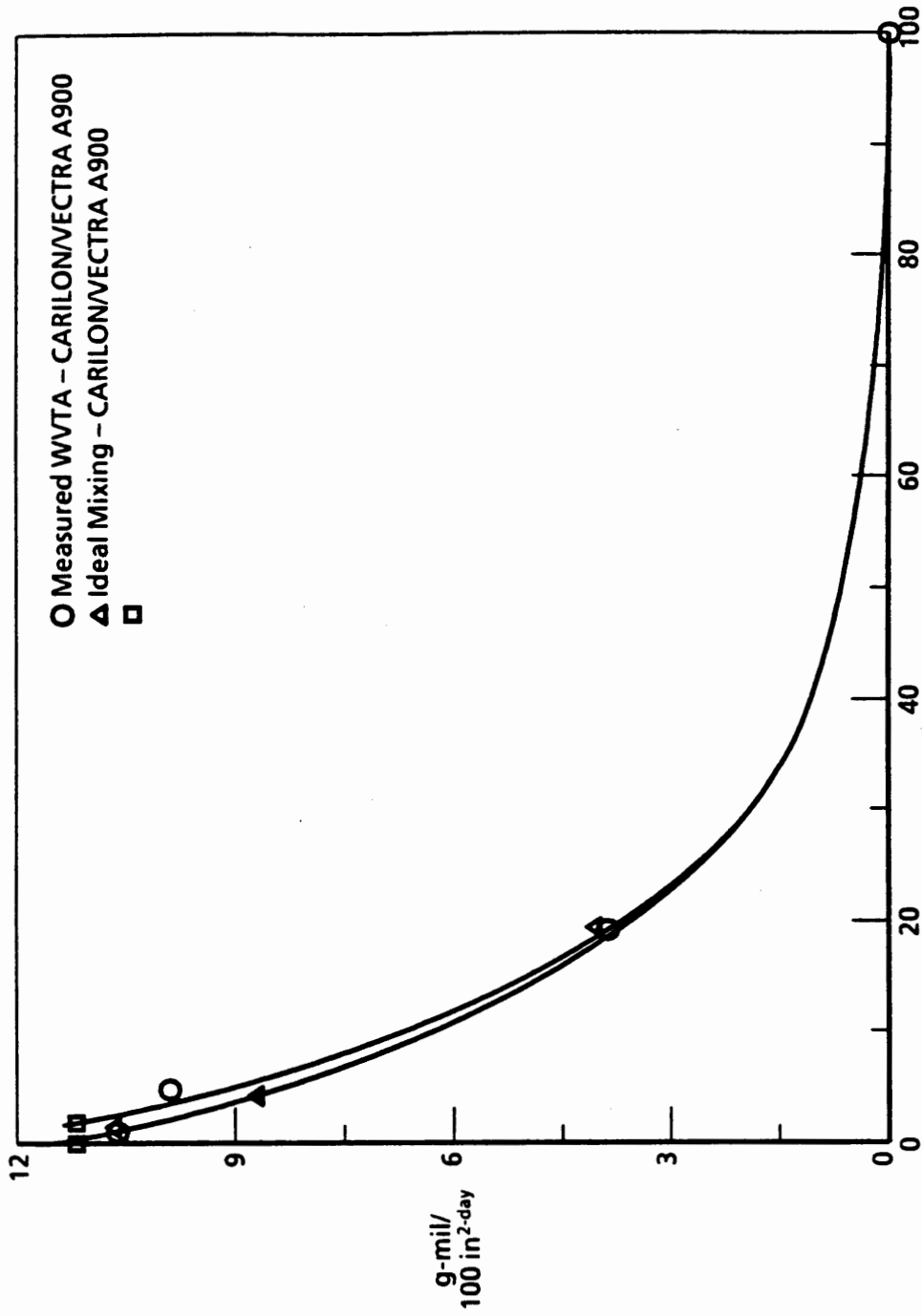


Figure 4. WVTA vs. Percent Additive for CARILON® Thermoplastic Polymer 88/008 Blended with VECTRA A900®

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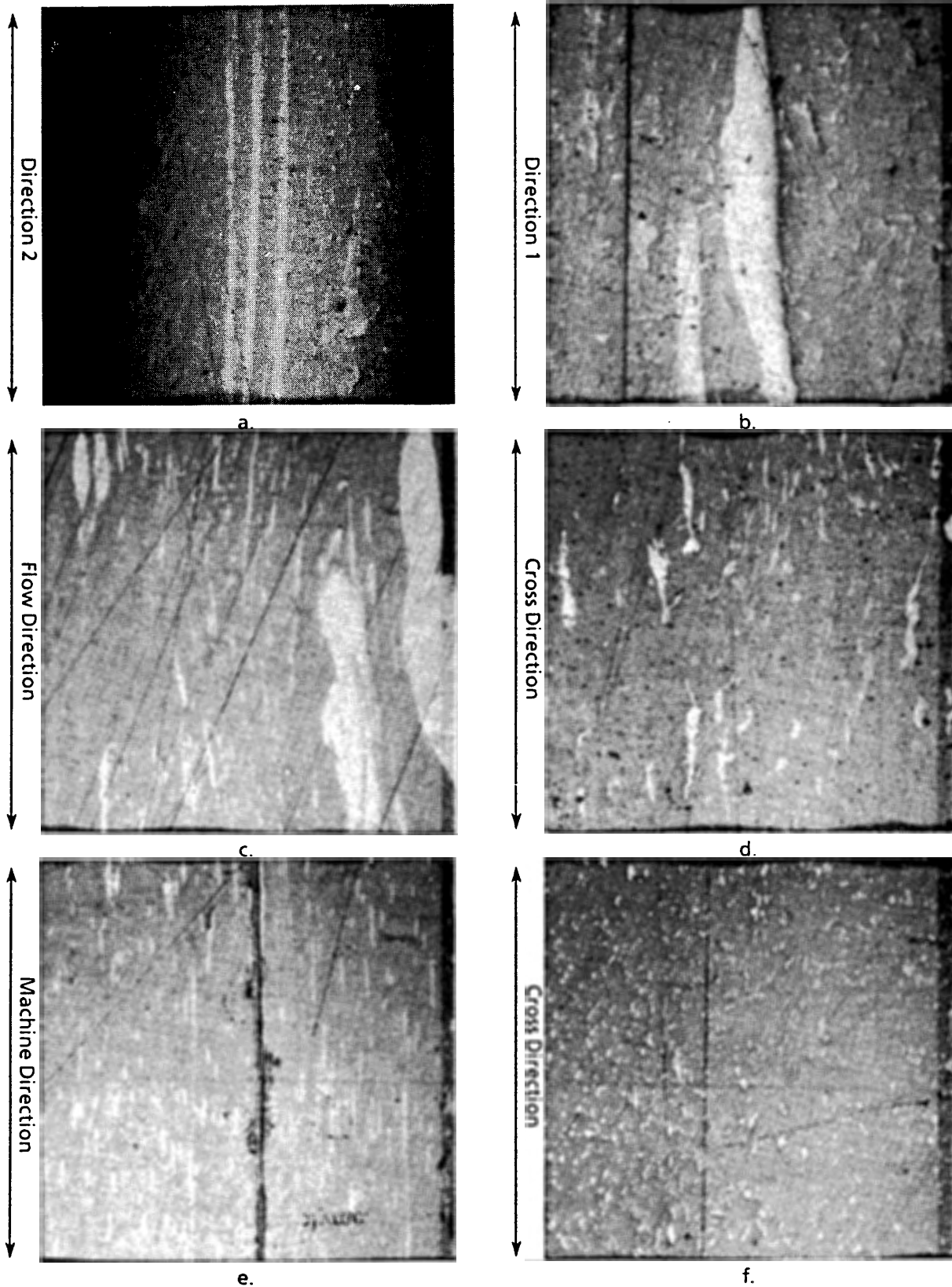
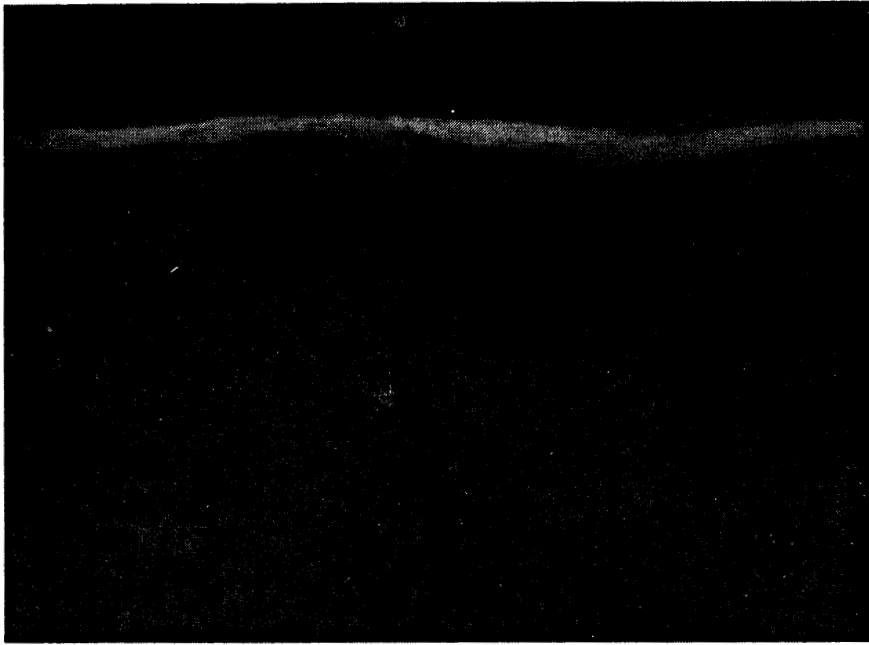
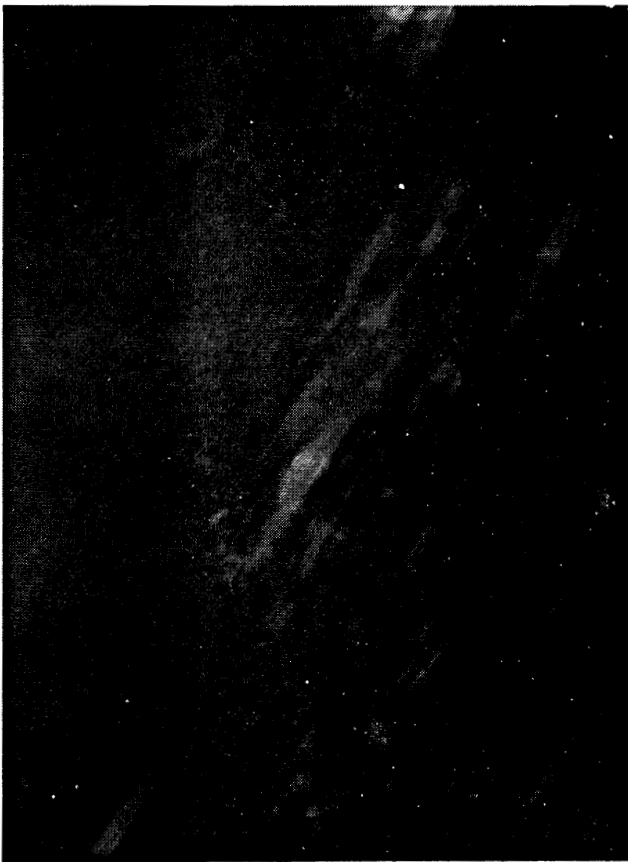


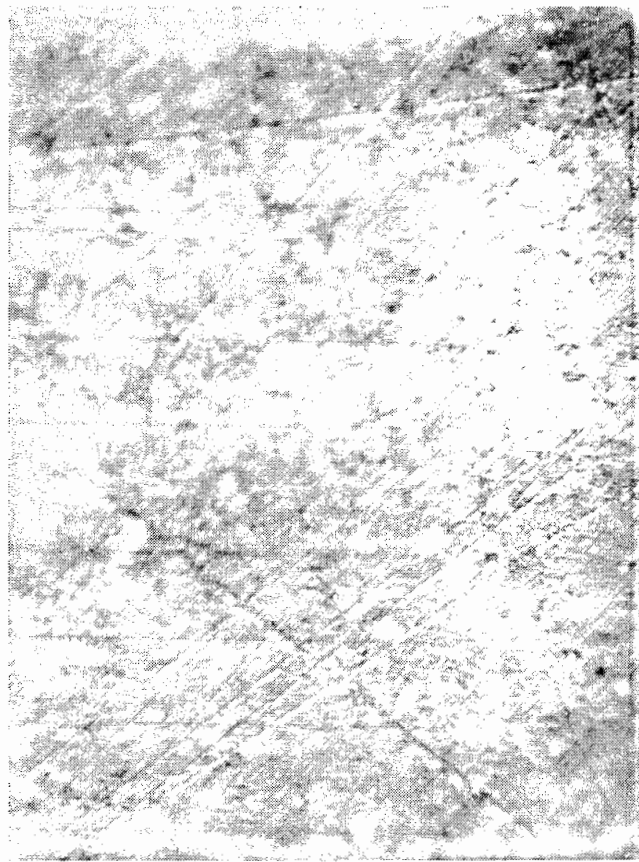
Figure 5. Micrographs of VECTRA 9000/CARILON® Thermoplastic Blends
Effects of various processing techniques. Light areas are LCP, dark areas are CARILON polymer matrix. 5a and b show platelet formation of LCP in compression molding and 5c and d show bar like formation at LCP in injection molding with larger aspect on the flow direction (c) and shorter aspect in the cross direction (d); and 5e and f show needle like formation at LCP in short extension with very long aspect in the flow direction (e) and circles in the cross direction (f).



a. Thin Layer of PP Along Sheet Edges



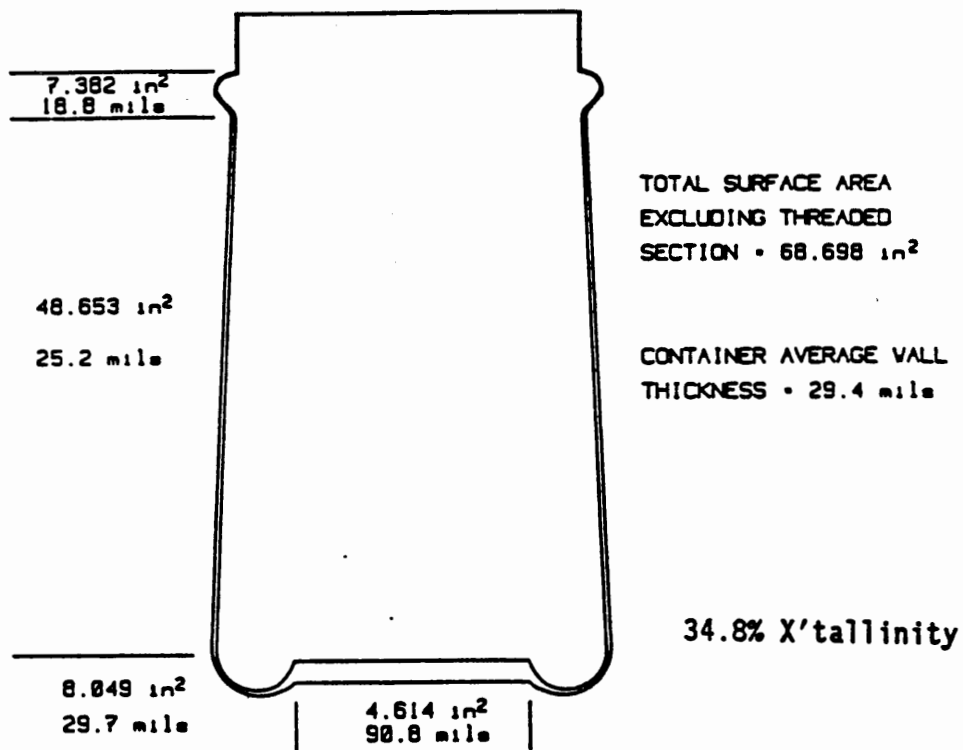
b. PP Platelets (Light Areas)
Dispersed in SPPF Container



c. Spherical Dispersion of PP in Sheet

Figure 6. Polypropylene ADMER (10%) Blended with CARILON® Thermoplastic Polymer in Extruder
Micrographs of Sheet 1 SPPF'ed Cup Cross Section

Polymer Batch: 88/047
Melt Point: 217°C
Ivn:

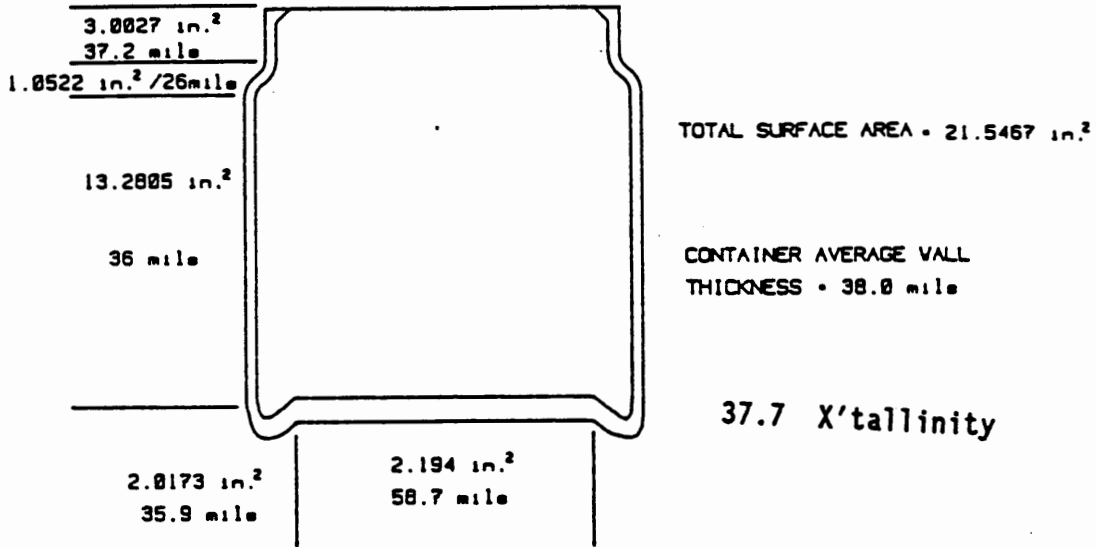


Oxygen	cc O ₂ (STP)/ Container/Day	cc (STP)-mil 100 sqin-d-atm	ppm/Year 4 oz Container
Container	0.0090	1.9	14
Side Wall	0.0071	1.5	11

Water	g H ₂ O/ Container/Day	g-mil 100 sqin-d	% Loss/Year 4 oz Container
Container	0.14	6.0	16.4

Figure 7. Peanut Butter Jar Barrier Analysis

Polymer Batch: 88/042
Melt Point: 220°C
Ivn:



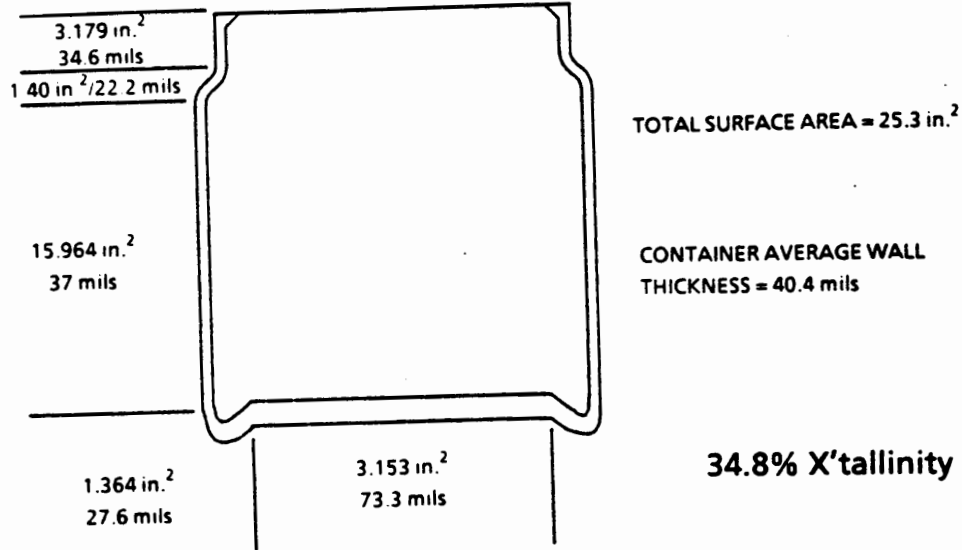
RFS

Oxygen	cc O ₂ (STP)/ Container/Day	cc (STP)-mil 100 sqin-d-atm	ppm/Year 4 oz Container
Container	0.0046	0.81	6

Water	g H ₂ O/ Container/Day	g-mil 100 sqin-d	% Loss/Year 4 oz Container
Container	0.021	3.7	10.1

Figure 8. 4 oz Baby Food Container

Polymer Batch: 89/021
Melt Point: 220°C
Ivn:



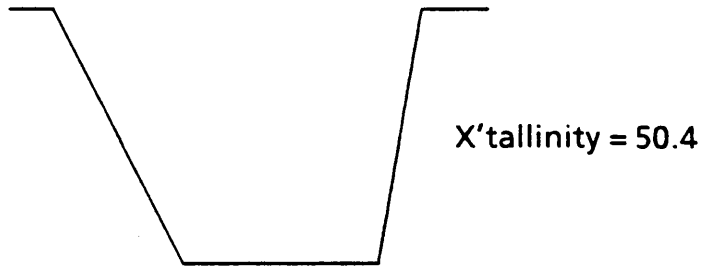
RFS

Oxygen	Retort	cc O ₂ (STP)/ Container/Day	cc (STP)-mil 100 sqin-d-atm	ppm/Year 4 oz Container
Container	N Y	0.0046	1.9	2.9
PVDC Coated ICI	Y	0.00055	X	2.1

Water	Retort	g H ₂ O/ Container/Day	g-mil 100 sqin-d	% Loss/Year 4 oz Container
Container	N Y	0.026 0.033	4.1 5.3	6.5 8.1
PVDC Coated ICI	Y	0.08	X	2.0
PPG	N	0.04	X	1.0
	Y	0.06	X	1.7

Figure 9. 5 oz Baby Food Container

Polymer Batch: 89/021
Melt Point: 220°C
Ivn:



Average Wall Thickness = 13.5 mils
Container Surface Area = 14.0 sq in

Oxygen	cc O ₂ (STP)/ Container/Day	cc (STP)-mil 100 sqin-d-atm	ppm/Year 4 oz Container
Container 89/021	0.00081	0.37	3.2
89/046	0.0008	0.35	3.1

Water	g H ₂ O/ Container/Day	g-mil 100 sqin-d	% Loss/Year 4 oz Container
Container	0.045	5.48	16.0

Figure 10. 4.5 oz SPPF Cup Analysis

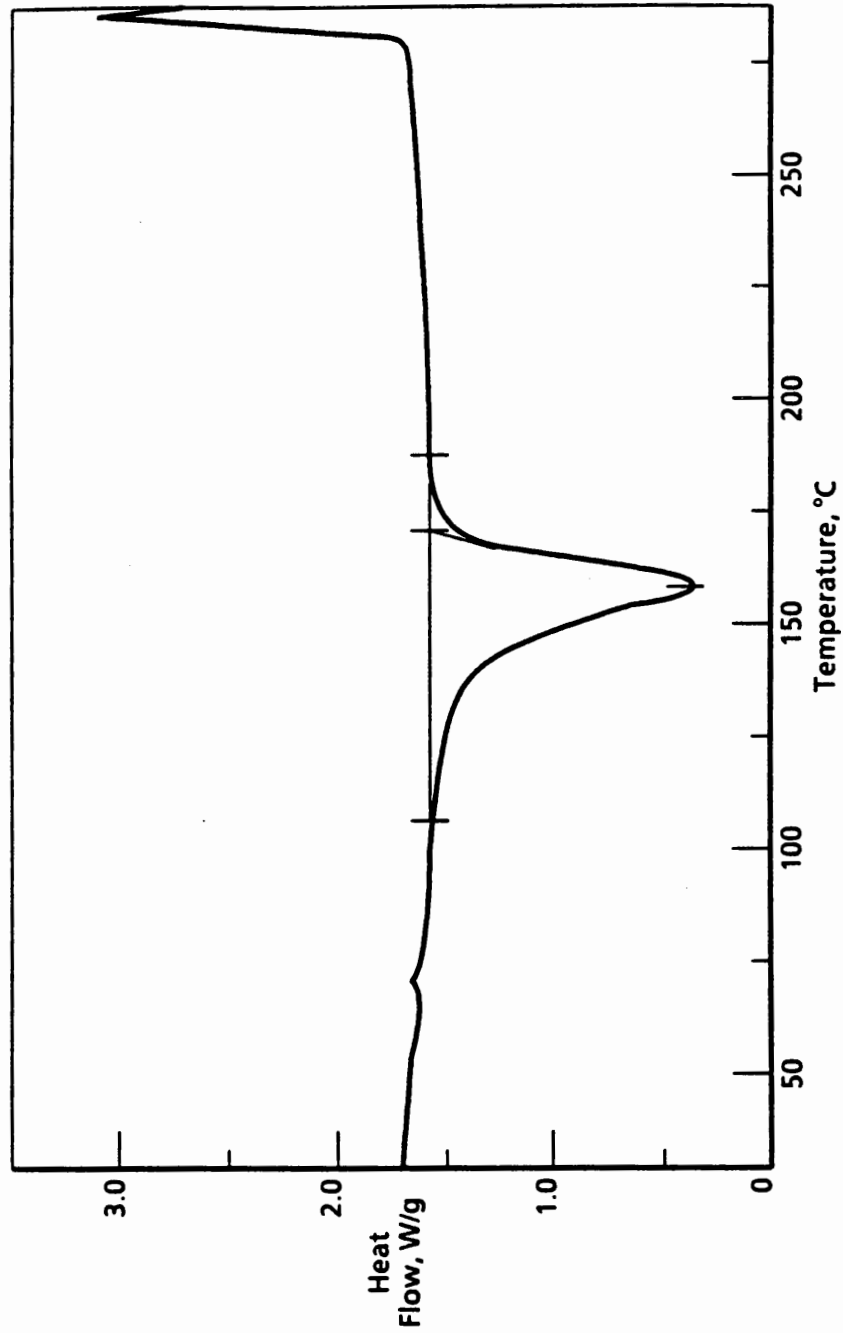
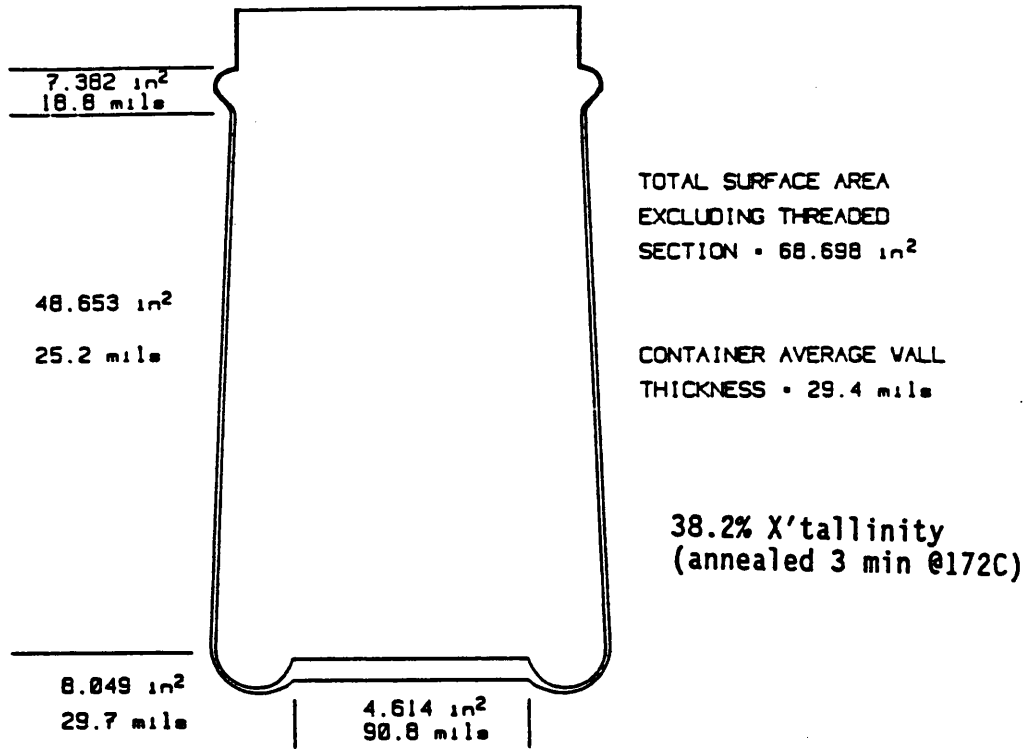


Figure 11. DSC Cooling Curve of EBM Material
for Annealing Temperature Determination

014086-10

Polymer Batch: 88/047
Melt Point: 217°C
Ivn:



Oxygen	cc O ₂ (STP)/ Container/Day	cc (STP)-mil 100 sqin-d-atm	ppm/Year 4 oz Container
Container Annealed at 210°C	0.140	6.1	45
Container Annealed at 172°C	0.0070	0.3	2.3

Water	g H ₂ O/ Container/Day	g-mil 100 sqin-d	% Loss/Year 4 oz Container
Container Annealed at 210°C	0.096	4.1	4.1

Figure 12. Annealed Peanut butter Jar Barrier Analysis

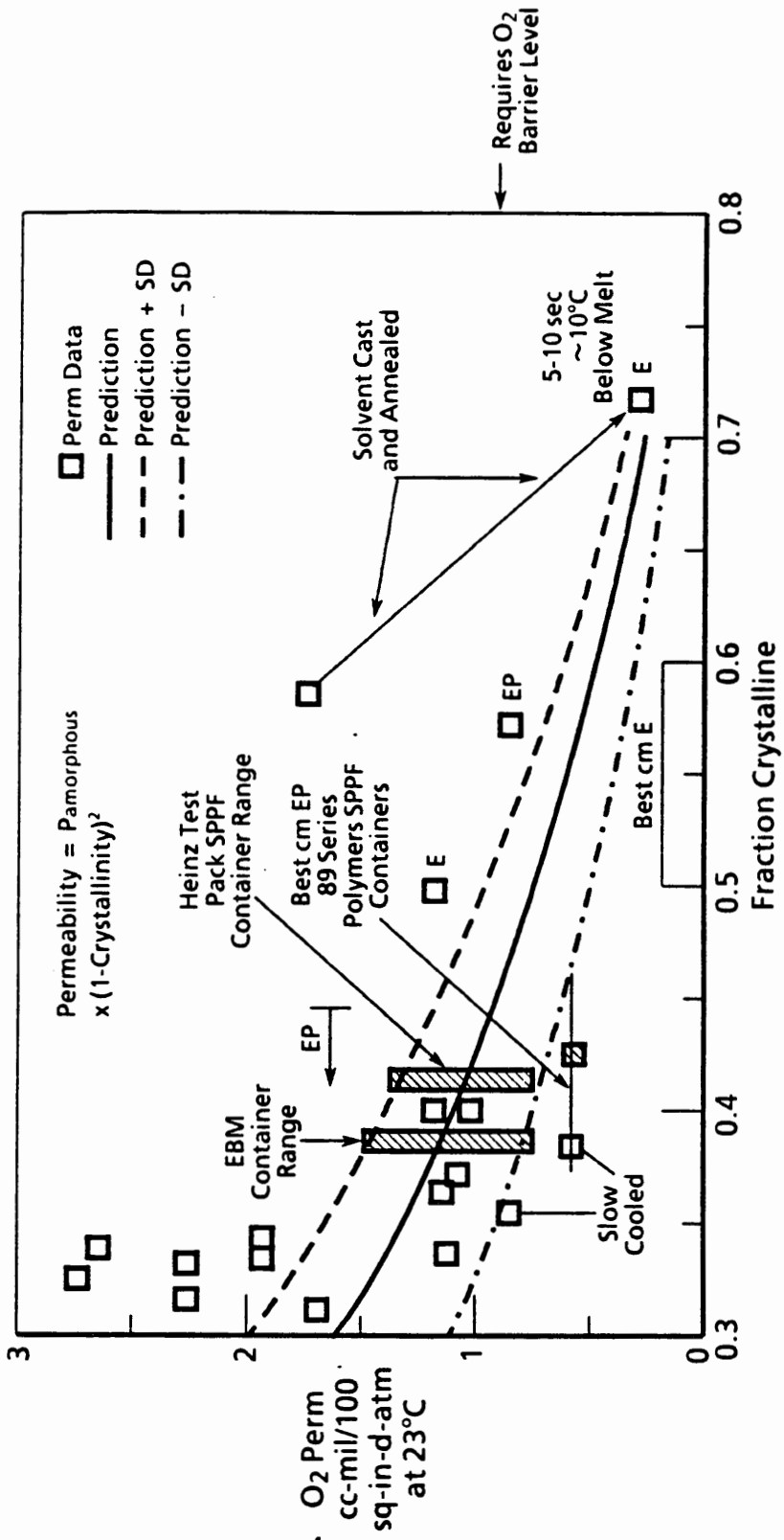
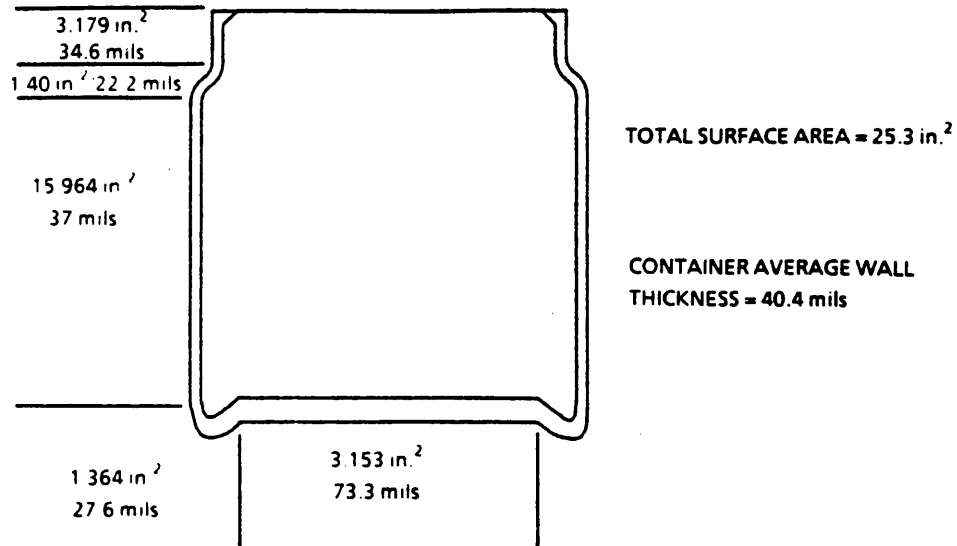


Figure 12a. Oxygen Permeability Dependence on Crystallinity

014086-12

Polymer Batch: 89/021
Melt Point: 220°C
Ivn:



Oxygen	Retort	cc O ₂ (STP)/ Container/Day	ppm/Year 4 oz Container
CT-Metal	Y	0.005	19.0
SW - 6 mil	Y	0.0026	9.9
SW - 6 mil + CT-Metal	Y	0.0017	6.5
SW - 25 mil	N	0.00075	2.7
ICI PVDC Coated	Y	0.0009	2.8
SW - 25 mil	N	0.00095	3.0

Water	Retort	g H ₂ O/ Container/Day	% Loss/Year 4 oz Container
CT-Metal	Y	0.044	10.7
SW - 6 mil	Y	0.095	23.1
SW - 6 mil + CT-Metal	Y	0.044	10.7
SW - 25 mil	Y	0.006	1.9

Figure 13. 5 oz Baby Food Container Lid System Analysis

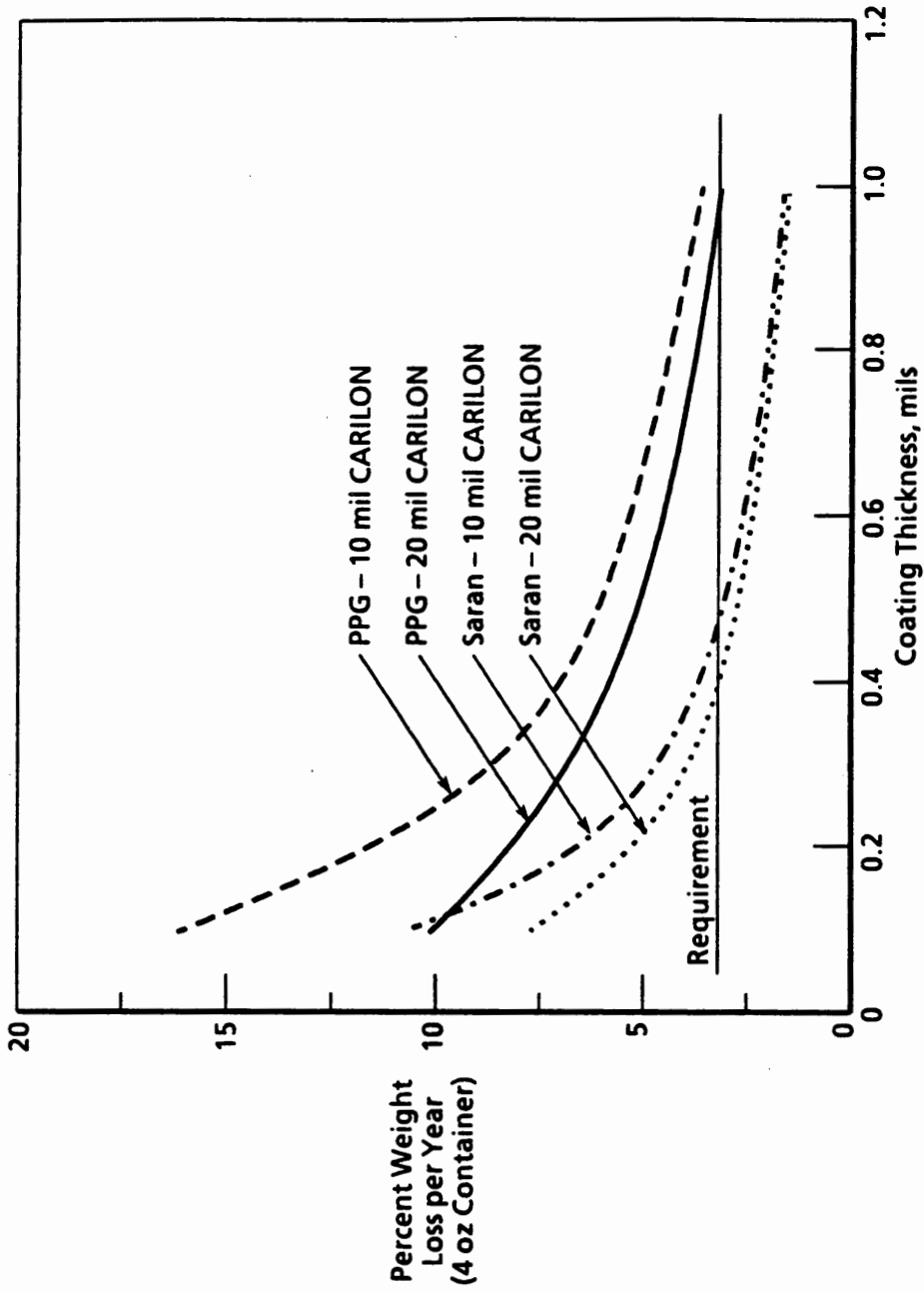


Figure 14. Coating Effectiveness - Water Weight Loss CARILON™ Thermoplastic Polymer Containers

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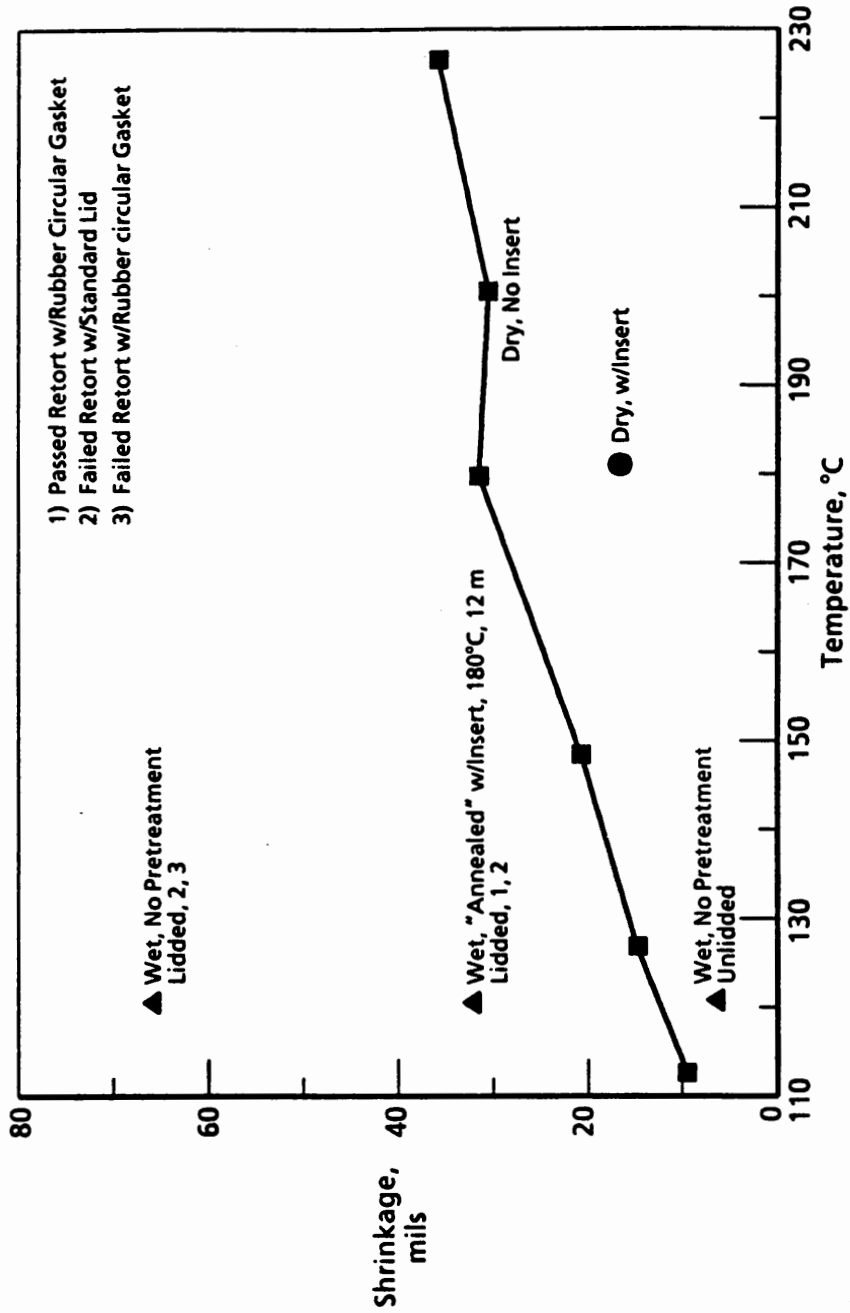


Figure 15. Neck Thread (Radius) Dimensional Analysis

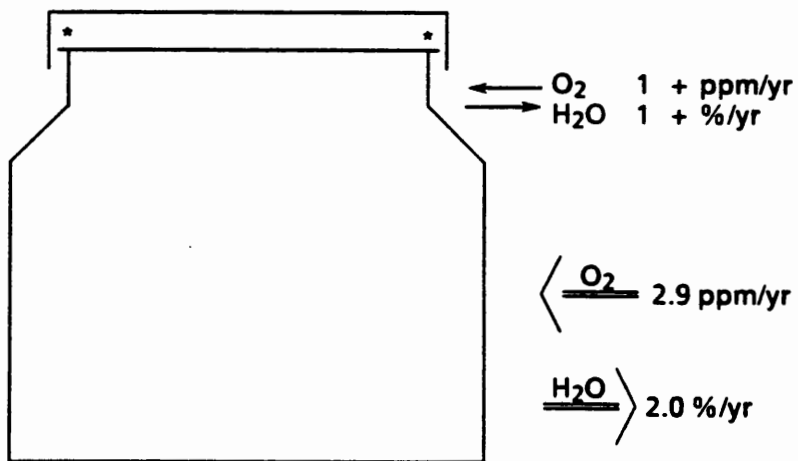
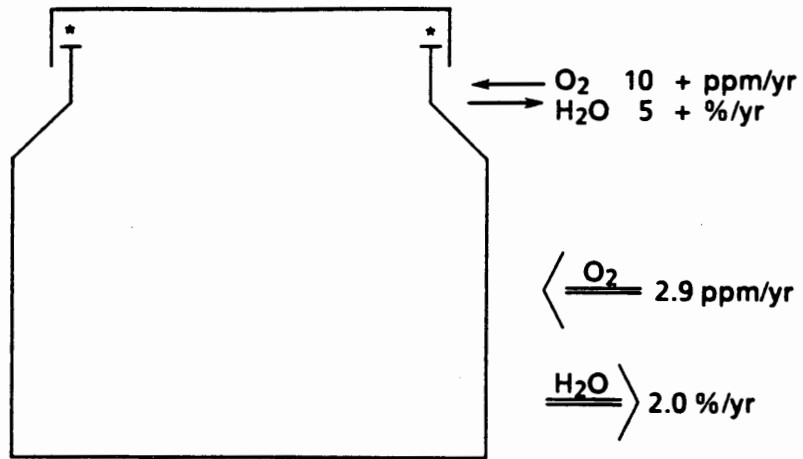


Figure 16. Summary of Transmission Through Potential Test Pack Containers and Lid System

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