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James K. Cage[1]

Introduction to Food Packaging

REFERENCE: Cage, J. K., **"Introduction to Food Packaging,"** *Food Packaging Technology, ASTM STP 1113,* D. Henyon, Ed., American Society for Testing and Materials, Philadelphia, 1991, pp. 3–12.

ABSTRACT: The basic principles of packaging to preserve, merchandise, protect, market, and distribute are applied very effectively in the food industry. More recently, food packages have been developed which offer tamper-evident or tamper-resistant features, allow for product preparation, and provide dispensing features and many conveniences such as single serving portions. Often the food product and its package are developed to be an integrated unit such as an aerosol product.

Technological breakthroughs in metals, glass, paperboard, composites, and most especially plastics have provided a multitude of opportunities for improved food packaging. The plastics segment of the packaging industry has shown the most rapid growth for many reasons. Some of the most important are: some plastics can be used in microwave ovens; plastics have a wide range of physical and barrier properties; and plastics offer design capabilities and features not available with other packaging materials.

However, ecological and environmental concerns are growing rapidly, along with federal, state, and local regulations and laws which will have an effect on the whole packaging industry. Further, the demographic changes related to the increased percentage of older consumers will also have significant effects on food packaging in the future.

KEY WORDS: food packaging

The food industry with its numerous and varied products utilizes all the basic principles of packaging, which are to preserve, merchandise, protect, market, and distribute a product. In the beginning the goal was to provide a means of preserving seasonal food products. As our farm-oriented society became more urbanized, it became necessary to move or distribute food products from where they were grown to where they were used, and the package had to offer protection during this process. The distribution process lengthened the time it took to get the product to the consumers and thus increased the shelf life required for the food product. The packaging and mechanization that naturally followed make it possible for a very small segment ($\approx$4%) of the U.S. population to produce enough food to feed the entire country and to have a surplus to export to other countries as well.

As food products were distributed, they required identification and labeling. Also, the design, shape, and form of the package gained in importance. Even the color of the package became associated with certain products. The use of packaging to provide information to the consumer has placed packaging in the role of a "silent salesman," a function made necessary and of critical importance to self-service merchandising. The package communicates with the consumer on a conscious and subconscious level, through the use of materials, shapes, colors, printed words, pictures, etc. The package thus serves as the last link in the sales-communication chain, telling the consumer what the product is, how to use it, and many other pertinent facts.

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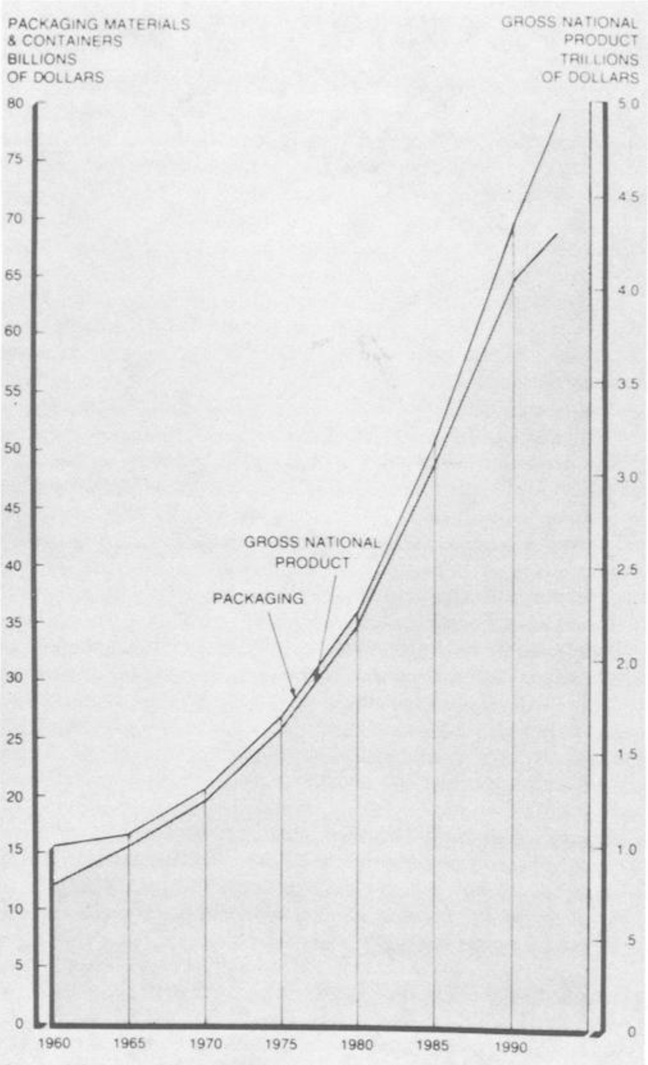
Packaging offers the food industry a marketing tool that is most useful in the growth and promotion of sales. In principle, the product and its package are an integrated unit. The properties of one determine the properties of the other. A moisture and/or oxygen-sensitive food product requires a package with adequate barrier properties. A high-acid, hot-filled food product requires a sanitary can with the proper lining material. Product development and package development should be conducted simultaneously and interactively. This could even include the changing or reformulation of a food product in order to make it easier or more economical to package. It is increasingly important for a company to plan carefully and be market smart about matching up a product with a package attractive to consumers.

The importance of this principle can be further supported by a familiar example: the retort pouch, which is a flexible packaging material made into a pouch and which can be thermally sterilized like a metal can. The retort pouch has failed as a commercial retail food package in the U.S., even though it has a long and successful history in other countries. Unlike those other countries, however, the U.S. has well-entrenched can making, glass making, and refrigerated distribution channels. The promoters of the retort pouch failed to see that the benefits the package provided were not highly prized in this society. Their focus was far too much on the package, not enough on the product.

The increase of the food industry to meet the population growth of the country was naturally followed by an expansion in the field of packaging. Of course, the packaging requirements for drugs, pharmaceuticals, hardware, personal care items, etc., also increased rapidly. The growth rate of packaging closely followed the growth of the Gross National Product over the past 30 years (Fig. 1). In fact, at year end, one of the leading national business magazines, *Forbes,* in the 9 Jan 1989 issue; treated packaging as an industry unto itself. Packaging was included when it reported trends and forecasts for major industries such as food, pharmaceuticals, electronics, steel, and other industrial segments. Previously, packaging was a manufacturing function which supplied many varied materials such as glass, paperboard, metal containers, plastic bottles, flexible films, and laminations. Except for a few major companies, packaging was segmented into the glass industry, paper industry, plastics industry, etc. Through acquisitions and growth, many glass companies now supply plastic containers and metal cans as well. The can companies now make plastic containers, trays, and jars, too. Paper companies have flexible packaging divisions. Thus, a packaging industry was born.

Initially, all the packaging materials were made from wood or wood derivatives (paper, folding cartons, and corrugated shipping cases), glass, and metals such as steel and aluminum. Increasingly, packages were made from two or more of these basic materials to obtain the optimum functional properties and economics. Even those materials that were used alone, like glass, which is made into bottles and jars, and steel, which is made into sanitary cans, were improved in shape, form, lining materials, and functional properties. Aluminum has become a very successful packaging material used for beverage cans and foil laminations. Technological breakthroughs in metals, glass, paperboard, composites, laminations, and especially plastics are providing a multitude of opportunities for improved food packaging (Figs. 2, 3). The major catalyst for packaging advancements has been the plastic materials rapidly being developed. The plastics segment of the packaging industry has shown the most rapid growth for many reasons (Fig. 4). Some of the most important are: (1) plastics have a wide range of physical and barrier properties; (2) plastics offer design capabilities and features not available with other packaging materials; and, more recently, (3) some plastics can be used in microwave ovens. Plastics can also be used in combination with coextrusions, which offer economic advantages (Fig. 5).

The opportunities for food packaging today are astronomical. The development of containers and packages is rapid and diverse to allow the food industry to meet the marketing



Source: U.S. Department of Commerce and Bureau of Economic Analysis

FIG. 1—*GNP and the growth of packaging.*

demands of its consumers. One major food company, the Campbell Soup Company, uses steel cans, aluminum cans, glass jars, as well as bottles, aseptic cartons, PET (polyethylene terephthalate) bottles, dual-ovenable CPET (crystallized polyethylene terephthalate) trays, microwaveable polypropylene trays and bowls, paperboard and fiber trays—just to name a few. The company seems determined to give its consumers the packaging options they want, and their wants are many and varied.

In today's intensely competitive food marketplace, a successful food package must function in a way that enhances convenience of use for the consumer. The challenge for food

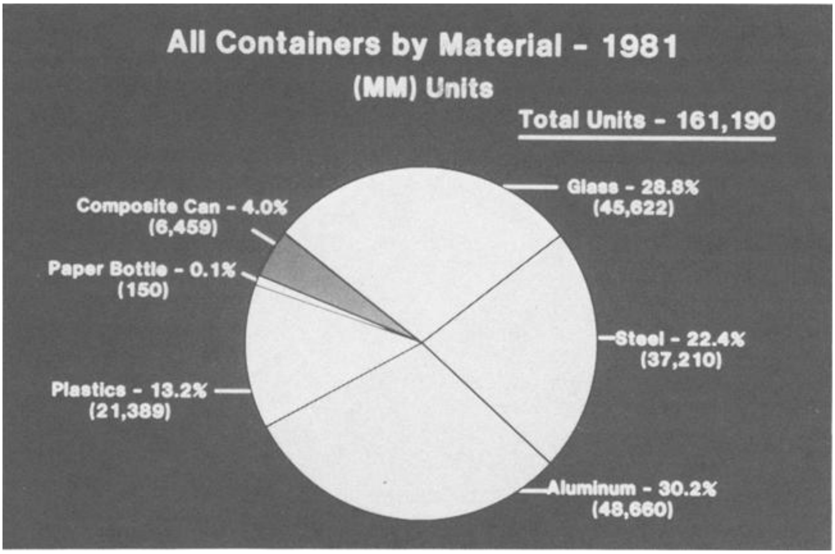


FIG. 2—*All containers by material, 1981 (mm units).*

processors and packaging suppliers is to find ways to adapt established convenience features to various types of packages. Thus, consumer convenient packaging seems to be one of the major marketing considerations in today's food packaging industry. One of the most significant developments over the past few years has been the squeezable plastic bottle for tomato ketchup. This plastic ketchup bottle requires very good barrier properties, specifically against oxygen permeation, and the ability to be hot-filled. This was not possible until coextruded plastic bottles containing a layer of a high barrier material, EVOH (ethylene vinyl alcohol),

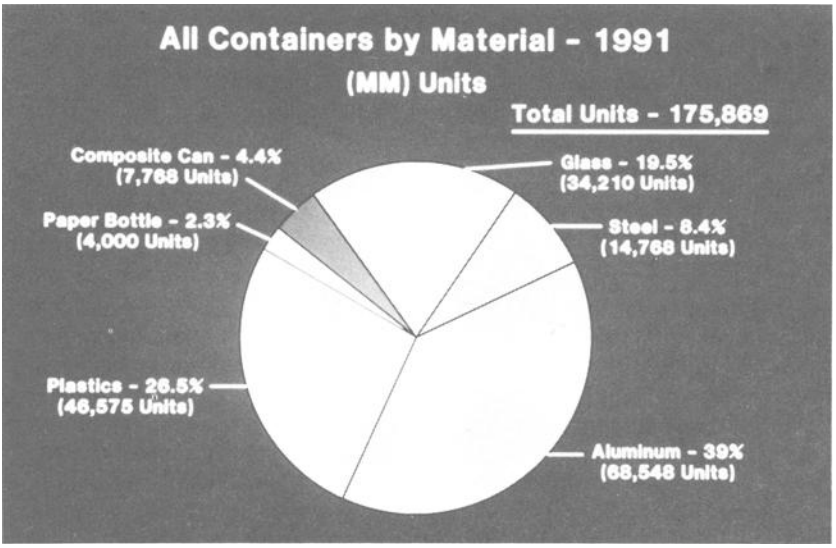


FIG. 3—*All containers by material, 1991 (mm units).*

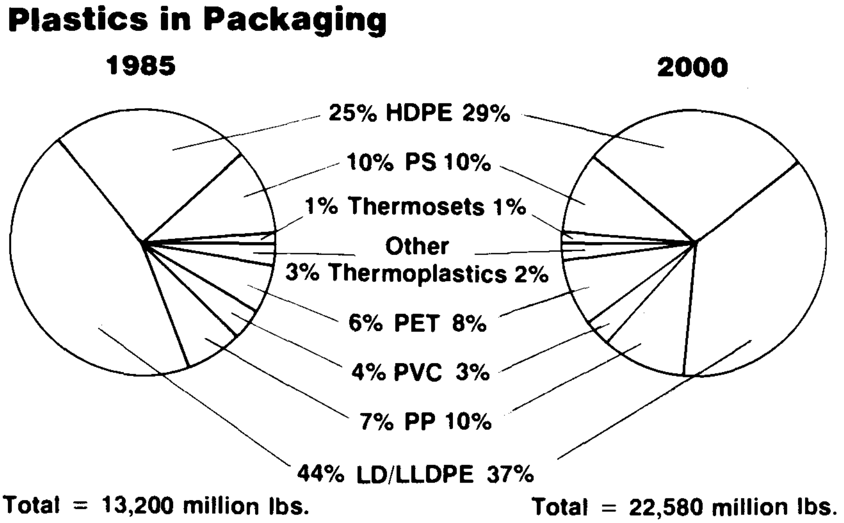


FIG. 4—*Plastics in packaging.*

could be commercially produced. The other coextruded layers had to be able to withstand the temperatures of hot-filling. Of course, this squeezable bottle had to have a dispensing closure to make it complete. The whole package system ended up costing more than the former glass bottle and metal closure, but the convenience of a squeezable ketchup bottle was a big marketing advantage.

Another convenience feature, recloseability, is now finding its way beyond traditional rigid containers such as metal coffee cans with plastic overcaps and into the flexible pouch/bag

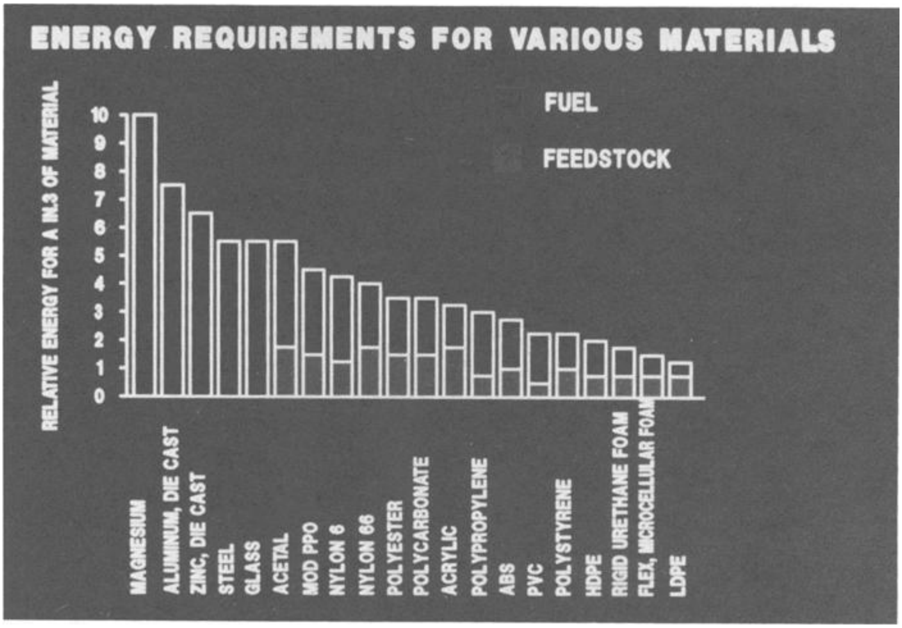


FIG. 5—*Energy requirements for various materials.*

type package. The development of "zipper pouches" and on-line application systems has provided a recloseable feature for such products as cereals, lunch meats, snack items, candies, cheeses, dry pastas, rice, and many other items.

Consumer research shows that single-serving portion packaging is much more important to consumers than it was a few years ago. Associated with portion packaging is the convenience feature of portability so that food products can be taken to school or to work and may even be microwaved in the package. The portable portion package must provide adequate protection during storing and handling, along with a convenient shape and light weight.

The use of microwave ovens for food preparation at home has led to many packaging developments. The dual ovenable CPET tray is widely used, and microwave-only, coextruded barrier polypropylene trays are used for both shelf stable and frozen foods. There are also paperboard combinations formed into tray-like cartons and more expensive plastic trays for the higher quality microwaveable food products.

Without doubt one of the most successful microwaveable products developed has been the microwave popcorn bag. It provides a high quality product in its own package for serving and in a short preparation time. The adaptation of an SOS (self-opening standup) bag to protect the product during shipping and merchandising and to withstand the preparation process in a microwave oven was a technological breakthrough. The current bags are improved by use of susceptor pads to increase the pop volume of the popcorn.

Demographic changes are a major driving force behind many recent developments in food packaging. More working mothers require the convenience of quick and easy-to-prepare foods. Singles and retired seniors like the single-serving, portion-controlled portable foods and recloseable features. Older seniors need easy-to-open-and-prepare food products. Many of these trends will continue as the population of the country grows older (Fig. 6).

Product/package safety is a major concern today even though the number of tampering complaints officially reported to the FDA has decreased over the last two years. As expected, young parents consider child-resistant and tamper-evident features to be very important. Other consumers, older ones in particular, find child-resistant and tamper-evident packaging to be effectively adult resistant, too. Efforts continue to develop more effective and economical tamper-evident features. But the recent Chilean grape incident clearly shows that not all tampering problems can be solved with packaging.

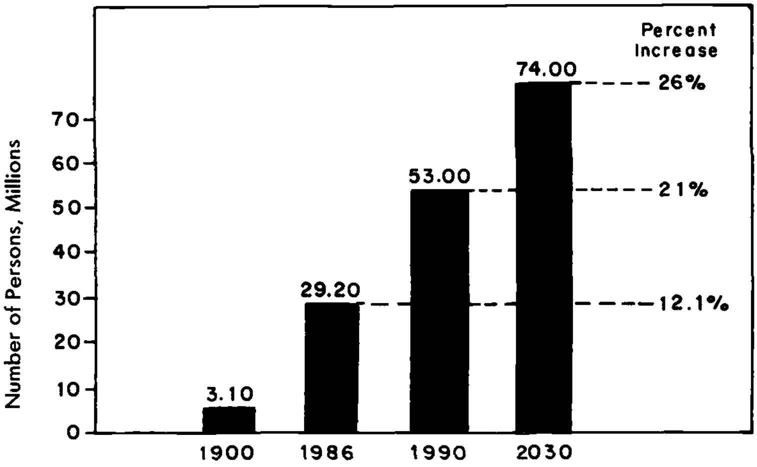


FIG. 6—*Number of persons 55+: 1900–2030.*

Packaging can aid in product safety in other unique ways. This may not be food packaging, but it's closely related. Self-treatment has complicated the problem of safe disposal of medical wastes. Diabetics alone discard an estimated one billion disposable syringes each year. One of the major syringe producers, Becton-Dickinson, has started sending thousands of letters and "Safe-Clips" storage tubes to diabetics on the East Coast. Safe-Clips are storage tubes with a 2000-needle capacity that enable the patients to clip off the hypodermic needle and dispose of it safely.

Another unique package is now available for the handling and storage of police evidence. The tube, called Safevidence, is made of a strong puncture-resistant plastic to safely contain syringes, especially in drug-related cases.

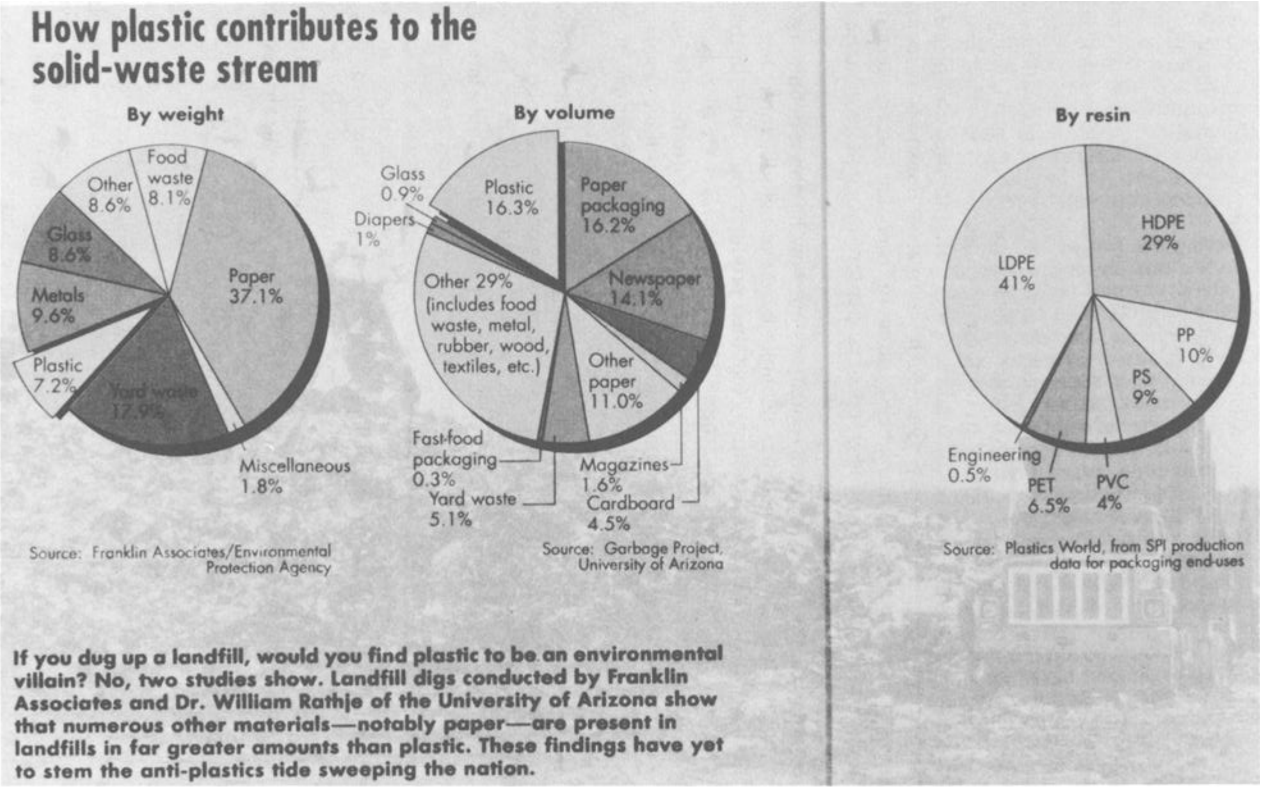
Consumers rely on the package label to not only supply product identification and the manufacturer's name and address, but much other information. A list of ingredients and preparation steps are considered important. In response to consumers' increased interest in health and nutrition, a growing number of food companies are moving to implement full nutritional labeling for their products. One such company, Sunshine Biscuit, Inc., announced intentions to have nutritional labeling on all of its cookie and cracker products by the end of 1989. The labels will include grams of fat per serving, cholesterol content, and other important nutritional information.

Some recent state and federal laws and regulations are now having a definite effect on package labeling. In the state of California, alcoholic beverage manufacturers are already required by Proposition 65 to inform consumers that their products could cause birth defects and now may have to include a cancer warning. Alcoholic beverages are already listed as reproductive toxins because they are associated with fetal alcohol syndrome. The state Scientific Advisory Committee now believes that at a very high level of alcoholic beverage consumption there is an increased risk for certain cancers. This is only one example of the role package labeling will play in the future.

Some of the convenience features, such as single-serving portions, portability, recloseability, and tamper evidence, are in direct conflict with the growing problem of solid waste management. Package design and choice of materials are now strongly influenced by the solid waste crisis. Environmental concerns could well become the packaging quality most selected by consumers in the 1990s. Even now, growing numbers of consumers are willing to pay more for more-recyclable products.

The most obvious focus is to redesign and use less packaging materials. But source reduction alone will not solve the solid waste problem. Before real progress can be made, several questions need to be clarified. Should some resins and additives be avoided because of increasing use of incineration? Should multilayer packages be avoided because they could interfere with recycling efforts? Can designers count on enough postconsumer waste collection to warrant the use of multilayer nonfood packages with recycle layers? Will container lightweighting accomplish enough source reduction or will extensive redesign be required?

Most of these serious questions involve plastics, which are really a very small portion of municipal solid waste (Fig. 7). Since plastics are basically newer packaging materials, less work has been done to recycle them. Currently, only 1% of plastics are recycled versus aluminum's 54%, papers' 30%, and glass' 25%. However, major efforts are underway by plastics companies and users to develop means of source reduction and recycling. The PET beverage bottles and the HDPE (high density polyethylene) milk containers are the two main areas for current work. This work is being done under the threat of legislation from cities, counties, states, and the federal government. Many trade associations are also cooperating in this effort. The Society of Plastics Industry (SPI) is requesting each state legislature to pass a coding law to identify all plastic packaging materials in a uniform manner (Fig. 8). The coding system developed by the SPI will facilitate recycling of plastics by identifying the resins used



Source: Franklin Associates/Environmental Protection Agency

Source: Garbage Project, University of Arizona

Source: Plastics World, from SPI production data for packaging end-uses

If you dug up a landfill, would you find plastic to be an environmental villain? No, two studies show. Landfill digs conducted by Franklin Associates and Dr. William Rathje of the University of Arizona show that numerous other materials—notably paper—are present in landfills in far greater amounts than plastic. These findings have yet to stem the anti-plastics tide sweeping the nation.

FIG. 7—*How plastic contributes to the solid-waste stream.*

VOLUNTARY GUIDELINES
PLASTIC BOTTLE MATERIAL CODE SYSTEM—
MOLD MODIFICATION DRAWINGS

FIG. 8—*Society for Plastics Industry plastic coding system.*

to make the containers. So far, 18 states have passed laws with legislation pending in 5 other states.

Besides source reduction and recycling, there are the other two means of disposing of solid waste, land fills and incineration. The areas remaining for landfills are becoming acutely scarce and expensive, and the potential cause of ecological problems (Fig. 9). Incineration is widely used in many parts of Europe (40% in West Germany, 50 to 75% in Sweden and Switzerland). In Japan, 55% of its sold waste is incinerated. All four methods will have to be considered to resolve the solid waste problem in this country. Thus, it appears that in the future, package design will be shaped by solid waste considerations.

A discussion on food packaging would not be complete without relating a role it can play in the Third World. Packaging can play a most important role in improving food distribution with the objectives of reducing waste and thus increasing food availability. The food spoilage rate in this country is the lowest in the world, about one third the level in the USSR and most developing nations. This will mean the utilization of more sophisticated packaging materials than the multiple Kraft paper and burlap bags currently being used. It is estimated that the amount of food that proper packaging would save from spoilage alone could increase significantly the ultimate yields of many existing harvests in these needy countries. It has been reported by agricultural experts that 50% of mainland China's food volume is lost to spoilage, rodents, and insects. China has invested heavily for the past several years in plastics packaging materials and converting plants. However, much of this improved packaging is now used for exported food products, and its broader internal use will take several more years.

Another benefit due to improved food packaging will be a reduction in food costs as a part

Current Disposal Practices..

	Incineration	Land Fill	Recycle
Japan	55%	20%	25%
United States	less than 10%	80+%	less than 10%
Switzerland	75%	20%	Low
West Germany	34%	60%	Low
Sweden	50%	50%	Low
United Kingdom	Low	75+%	Low

FIG. 9—*Current disposal practices.*

of disposable income. In this country, food costs are under 15% of disposable income, compared to 16% in Japan and Western Europe and much higher rates in the developing nations. The challenge for food packaging in this area is great, but the potential benefits are worthy of the effort.

The packaging industry has a wide host of opportunities before it; there are real challenges in the years ahead. As never before, the packaging users and the packaging suppliers must be partners in new package development. This is particularly true in the food and beverage business, which is strongly influenced and driven by packaging. The consumer demands for convenience food packaging will have to be reconciled with serious ecological considerations. The safety considerations of tamper-evident and child-resistant features will have to be balanced with the concerns and problems they cause senior citizens in our aging population. Last but not least, packaging must play a stronger and larger role in the preservation, protection, and distribution of food in the third world and the developing nations. This is a reversion back to the basic principles of packaging in the food industry.

Kenneth S. Marsh,[1] *Thomas Ambrosio,*[2] *and Dana Morton Guazzo*[3]

The Determination of Moisture Stability of a Dynamic System Under Different Environmental Conditions

REFERENCE: Marsh, K. S., Ambrosio, T., and Guazzo, D. M., "**The Determination of Moisture Stability of a Dynamic System Under Different Environmental Conditions,**" *Food Packaging Technology, ASTM STP 1113,* D. Henyon, Ed., American Society for Testing and Materials, Philadelphia, 1991, pp. 13–17.

ABSTRACT: Effervescent tablets defy standard analysis for moisture sensitivity. High humidity conditions cause effervescence with corresponding changes in the tablet composition. However, the time necessary to perform traditional shelf life testing on a product which requires a two-year shelf life was considered too lengthy. An accelerated testing protocol was therefore desirable.

Novel analytical techniques were developed to determine the product's response to humidity changes. Computer modeling was then employed to define product response to two isothermal storage conditions and three dynamic distribution environments in a nonfoil blister package. The results predicted that the two-year shelf life would be achieved.

The product's two-year shelf life was established in three months of research time. The product, Fibre Trim effervescent tablets, became the first effervescent tablet to be introduced in a nonfoil package worldwide.

The computer estimates have since been confirmed with storage studies.

KEY WORDS: computer modeling, modeling, isotherm, accelerated testing, moisture, distribution, effervescent, shelf life

Food and pharmaceutical companies are increasingly caught in the dilemma of rapidly moving new products into the marketplace while ensuring product shelf life through appropriate packaging. The typical result, overpackaging to meet time constraints, is bought at a substantial cost to the company.

This article demonstrates how one company confirmed a product's two-year shelf life in three months of research time, allowing for early product introduction with the most reasonable packaging cost. Computer modeling techniques were employed in the effort. However, the product, Fibre Trim, is an effervescent tablet and defied standard analysis. Novel analytical procedures were developed and used for both product information and computer input.

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Experimental

Computer estimation of shelf life has been used for moisture-sensitive products. The moisture isotherm serves as the translation between moisture influx into a hermetically sealed packaging system and the effects of this moisture on the product. An independent (usually organoleptic for foods) means is used to identify a moisture level above which the product is deemed unacceptable. Computer modeling can then be used to estimate the time necessary for the moisture level inside the package to rise from a production moisture level to a critical level under a given set of environmental conditions.

A typical isotherm determination requires that samples of the product be equilibrated with various relative humidities. Effervescent tablets would equilibrate with low relative humidity environments, but would begin to effervesce in the higher humidity chambers. A dynamic metaisotherm was designed to provide the required data for analysis. The term *metaisotherm* is used to signify the nonequilibrium departure from standard isotherms.

The elucidation of a critical moisture level is essential for the modeling of shelf life. This was accomplished by developing a dynamic study in which a product was stored at high humidity and evaluated over time. Sample net weights were determined periodically, with *equilibrium* defined as less than 1 mg difference between successive weighings. The initiation of effervescence, as defined by the onset of weight loss, was chosen as the demonstrable end point. The results of the first study showed changes in product quality which were too fast to pinpoint a reliable end point. The procedure was repeated at a lower humidity and yielded better results.

The product isotherms were run for 25 and 35°C. The product characteristic of effervescence precluded the use of standard equilibrium studies. Product was stored over various saturated salt solutions, and weight gain/loss was monitored with time. A multiple sample put-up was used. Each sample was checked only once. The multiplicity allowed sampling at frequent intervals, while assuring that each sample tested remained undisturbed in the chamber as long as possible. Again, weight loss with increased moisture adsorption was used as the indicator for effervescence. The value of moisture prior to effervescence was taken as the best available point for the moisture isotherm at the designated relative humidity. The shape of the isotherm was evaluated, with increased weight given to points below the critical moisture point. This was done to compensate for peak values that were measured after the occurrence of some weight loss. In other words, the data were evaluated on the basis of actual data, compensation for effervescent products, and knowledge of product isotherms with the intention of using the best predictor of product quality.

The packaging system was characterized in two steps. First, statistical analysis was performed on the formed blisters to establish the variability in the domes and walls of the blister cells. Second, transmission data for water vapor traversing representative blisters was obtained with Mocon instrumentation. (Blister packages were chosen as a cost-effective and appearance-improving alternative to foil packaging, which prior to this product were used on all effervescent tablets worldwide.)

Results

The isotherm data were obtained in terms of weight change. For isotherm purposes, the moisture content is required. This was calculated on a dry basis for each of the samples. The maximum weight gain value was used for each relative humidity which resulted in effervescence. The data are presented in Fig. 1.

The initial moisture was obtained by drying samples at 70°C for 4 h.

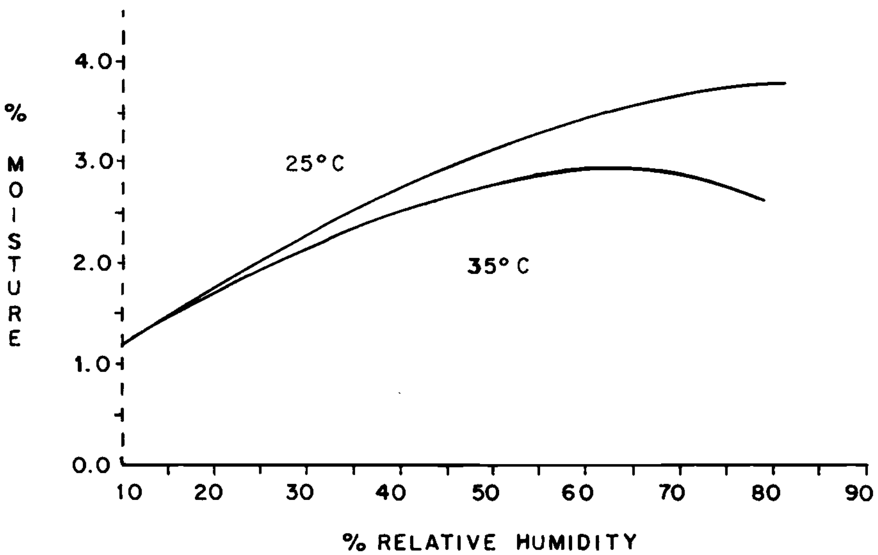

FIG. 1—*Metaisotherms for Fibre Trim tablets.*

The critical moisture content was taken as the lowest relative humidity that resulted in effervescence. For 25°C, this is 52% RH; at 35°C, the value is 42% RH.

The modeling of shelf life was performed via computer. The software is proprietary to Kenneth S. Marsh & Associates, Ltd. and calculates the length of time necessary for moisture content inside the product to increase from the measured initial content to the critical content as influenced by the packaging system and by environmental factors. The packaging system consists of the area of the package, the volume of the package, the permeability characteristics of the blister, and the net weight of the product. The program accounts for the change in the driving force of moisture across the package as moisture traverses the packaging film.

The packaging material used was polyvinylidene chloride-coated polyethylene/polyvinylchloride. Two isothermal storage conditions and three changing conditions were used. The isothermal conditions were 25°C/85% RH and 35°C/85% RH. The changing conditions were taken as those representing three environments in the United States: hot/humid climate, "average" condition, and a cold/humid climate. The data were obtained through the U.S. Weather Bureau [*3*] and represented a 30-year average for each month. The product changes were evaluated following exposure to these climates sequentially starting from each month. In other words, the shelf life is evaluated for product arriving in each environment in January, February, etc. Differences in shelf life reflect the exposure of the various conditions at different times in the product life cycle.

The results appear in Table 1. The dramatic differences between the evaluations using the 25°C isotherm and the 35°C isotherm are influenced by the onset of effervescence at lower relative humidity in the 35°C environment. The temperature influence itself would show a lesser effect. The reversibility or nonreversibility of the changing critical moisture is not discernible with the present data. Further research is necessary to determine if fluctuations of humidity and temperature could produce a reversible pumping action which will enhance the shelf life performance.

TABLE 1—*Shelf life of fibre trim tablets (computer simulations).*

Isothermal	Shelf Life, days
25°C/85% RH	645
35°C/85% RH	113

The distribution modeling was performed using environmental conditions representative of the three climactic regions. The distribution models were performed with estimates of actual moisture content in the region of commencement of effervescence, defined by either the 25°C or the 35°C isotherm. The 25°C isotherm will more accurately represent reality except in very abusive conditions. The 35°C isotherm is worse than anticipated for even the hot/humid conditions. The work of Fusari et al. [*1*] and Hostetler et al. [*2*] supports the fact that the 25°C isotherm is more representative in cases of noncontrolled warehouse storage.

Climactic Exposure Using 25°C (77°F) Isotherm

	Shelf Life, days		
Starting Month	Hot/Humid	Average	Cold/Humid
January	1367	3812	4413
February	1353	3800	4396
March	1339	3781	4381
April	1339	3762	4365
May	1353	3748	4371
June	1397	3739	4419
July	1432	3740	4439
August	1424	3769	4435
September	1419	3777	4444
October	1413	3790	4442
November	1402	3792	4436
December	1386	3806	4427

Climactic Exposure Using 35°C (95°F) Isotherm

	Shelf Life, days		
Starting Month	Hot/Humid	Average	Cold/Humid
January	370	929	1013
February	374	907	993
March	377	887	976
April	384	868	965
May	381	852	967
June	377	843	1001
July	374	860	1038
August	372	899	1058
September	369	952	1063
October	367	974	1060
November	365	965	1048
December	367	950	1031

Discussion and Conclusion

The shelf life of Fibre Trim tablets was determined using product attributes which were ascertained by nonconventional procedures. The nature of the effervescent tablet and the need for rapid results precluded the use of standard equilibrium studies to determine moisture adsorption. A dynamic procedure was used in which product changes were monitored as adsorption proceeded. The results allowed for the enclosed determinations, but hold more variability than customary with true equilibrium studies.

The moisture level which promoted weight loss from effervescence was chosen as the critical moisture level. This point contained variability, and judgment was used to pick the best level.

The above-stated variability led to dramatic differences of distribution life when 25 and 35°C isotherms were employed in the determination. Comparison with climactic data indicates that the 25°C data would be closer to reality. Hot/humid conditions would exceed 25°C in summer months, and shelf lives would be expected to be shorter than predicted solely from use of the 25°C data. However, this prediction relies on environmental storage for outdoor city conditions. The shelf life would be considerably enhanced because of air-conditioned distribution and retail storage, which would attenuate environmental abuse.

Shelf life calculations by extending the slope of the permeation steady state will not match the determinations performed in the computer predictions. The steady-state analysis assumes constant permeation and moisture transfer. Although constant permeation is realized, the actual moisture transfer is reduced as the pressure differential drops across the package. The computer analysis incorporates this.

Storage studies provided an independent indicator for product changes with time under actual storage conditions. Packaged tablets were stored under all the relative humidity conditions that were used to derive the moisture isotherm. This provided storage data for a wide spectrum of environmental conditions.

The 25°C data appear to be a good predictor of shelf life and agreed well with storage studies run concurrently with this work. The agreement with predictive and laboratory studies for intermediate storage times provided confidence in acceptance of the extended storage time predictions. The package performance data, when applied to representative locals within the United States, supports a shelf life of two years for domestic distribution.

The above analysis supplied confirmation of a two-year shelf life in three months of research time. Subsequent laboratory studies of longer duration verified the original projections of shelf life.

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Effect of Sorption of Organic Volatiles on the Mechanical Properties of Sealant Films

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ABSTRACT: The influence of sorption of organic volatiles on the mechanical properties of polymeric sealant films was investigated. Three sealant films were used, a commercial low-density polyethylene, and two developmental films, an ethylene vinyl alcohol copolymer of high ethylene content and a copolyester. Samples of the films were immersed in three different juices (orange juice, apple juice, and tomato juice) for up to 24 days at 22°C. Periodically, film samples were removed from the different juices and the stress-strain properties, heat seal strengths, and impact resistance of the test materials determined as a function of sorbed organic volatile levels or storage time. Statistically significant differences were found in the mechanical properties of the films as a function of sorbant level and storage time. The amount of change varied and was dependent on the film-juice system and the mechanical property evaluated.

KEY WORDS: sealant films, mechanical properties, volatile flavors—apple juice, tomato juice, orange juice, d-limonene, polymers

Plastic materials are being used widely to contain a variety of food products and beverages. Many of these foods contain aromatic organic volatiles which have affinity for plastic packaging materials [*1*]. For many food products, the sorption of organic volatiles (scalping) by the packaging material can lead to reduced product quality because flavor compounds often are present in foods at concentration levels well below the sorptive capacity of the packaging materials [*2*].

Marshall et al. [*3*] reported that orange juice developed a flat taste which was perceived as unfresh due to sorption of volatiles by the contacting polymer. Better than 60% of the d-limonene in an orange juice sample was sorbed by a low-density polyethylene (LDPE), while 40% was sorbed by an ionomer. Mannheim et al. [*4*], Durr and Schobinger [*5*], and Imai et al. [*6*] also have reported that plastic packaging materials sorbed d-limonene from orange juice. DeLassus et al. [*7*] found low-density polyethylene to be a poor barrier to aroma compounds in apple juice. Dry ethylene vinyl alcohol copolymer and a vinylidene chloride copolymer were good barriers to trans-2-hexenal, an important flavor compound in apple juice.

While sorption of product flavor constituents by the packaging material may reduce product quality, scalping may also lead to changes in the mechanical properties of the contacting

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polymer. For example, sorption of d-limonene by a LDPE and two ionomer films resulted in changes in the films' mechanical properties, including stress-strain, heat seal strength, and impact resistance [*8*]. Significant changes in tensile strength and in percent elongation were observed when various essence of oils (orange, lemon, eucalyptus, and peppermint) were placed in contact with LDPE and ethylene vinyl acetate copolymer [*9*].

Thus, it is important to characterize the influence of sorption on the mechanical properties of polymers as a function of the concentration of the sorbant and/or storage time. The major objective of this research was, therefore, to determine changes in the mechanical properties of three sealant polymers placed into contact with orange juice, apple juice, and tomato juice. Mechanical properties such as seal strength, modulus of elasticity, tensile strength, and impact resistance are material characteristics which influence a package's ability to resist dynamic and static forces. During distribution a product will be subjected to these forces as it is handled repeatedly, warehoused, and transported. Sorption of product flavor components by the material in contact with the product could result in loss of package structure and integrity.

Materials and Methods

Materials—Juice Products

The orange juice, apple juice, and tomato juice used in this study were 100% pure, from concentrate obtained from local sources. An antioxidant mix, Sustane W and Sustane 20 (BHA, BHT, TBHQ, and PG, 0.02% w/w total, UOP, Inc.) and the antibacterial agent sodium azide (Sigma Chemical Co., 0.02% w/w) were added to the different juices at the initiation of the immersion studies to prevent oxidative and microbial changes [*8*].

Probe Compounds

D-limonene, a principle component in the flavor profile of citrus products (97%, Aldrich Chemical Co., Inc., Milwaukee, WI) was used as the probe compound in orange juice because of its prominence in the flavor profile, ease of analysis, and because it is readily absorbed by polyolefins.

Determination of Flavor Probe Compounds in Juice and Films

To determine the d-limonene concentration in the orange juice and film extracts, the gas chromatographic (GC) technique of Imai et al. [*6*] was used. D-limonene was extracted from the films by immersion in ethyl acetate.

Plastic Films

Three plastic films were used in this study, Alathon 1645—a commercial LDPE, ethylene vinyl alcohol copolymer of high ethylene content, <25 mol% vinyl alcohol (EVOH), and a copolyester (Co-Pet). The PET was copolymerized to make it sealable. Both EVOH and Co-Pet films were developmental structures designed to provide sealant properties. The thickness of each was 41.9, 21.1, and 67.3 μm, respectively. The films were provided by the E. I. DuPont deNemours Co. (Wilmington, DE).

Mechanical Properties of Plastic Films

Stress-Strain and Heat Seal Strength

The mechanical properties of the respective film samples (roll stock, conditioned at 22°C, 50% RH) were determined prior to immersion and served as controls. Test film samples were immersed in juice containing the antioxidant blend and the mechanical properties determined as a function of sorbant concentration in the film at storage time. For stress-strain analysis, the films were immersed in the juices for a predetermined number of days, up to 24. In a series of preliminary studies, it was found that sorption of volatiles by sample films was essentially complete by Day 24. Thus, this time period was chosen as the end point to evaluate mechanical properties. The juice volume-to-film area ratio ranged from 1.01 to 1.06 m^3/m^2 for the different juice film samples, which is approximately the same surface-to-volume ratio in a 250-mL Brik pack carton. Following removal of the films from the juice, the samples were rinsed with distilled water for 1 min prior to measurement of mechanical properties. Stress-strain properties (tensile strength, modulus of elasticity, and percent elongation at break) were determined in accordance with ASTM Test Methods for Tensile Properties of Thin Plastic Sheeting (D 882-83), using an Instron Universal Testing Instrument, (Model TTC Instron Corporation, Canton, MA). The tensile strength of the material was calculated as the maximum stress observed on a sample during elongation of the material. Modulus of elasticity was calculated by drawing a tangent to the initial linear portion of the stress-strain curve, selecting a point on this tangent and dividing the tensile stress by the corresponding strain. Percent elongation at break was determined by dividing the elongation at the moment of rupture of the sample by the initial length of the sample and multiplying by 100. For all stress-strain measurements, 20 control samples (nonimmersed) were tested in both the machine direction (MD) and cross machine direction (CD). For the immersed samples, ten specimens were tested in the machine and cross machine directions for each time period (1, 3, 6, 14 and 24 days).

To determine the effect of sorption on heat seal strength, samples were prepared by taking an MD sample, cutting it crosswise, and heat sealing the two halves together using an impulse heat sealer (Sentinel Heat Sealer, Packaging Industries, Inc., Hyannis, MA). Sealing conditions for the nonimmersed samples were optimized to achieve maximum seal strength. Heat seal strength was calculated as the maximum stress a heat-bonded sample could withstand under an applied load.

Impact Resistance

Sample specimens of each film were immersed in the different juices for 24 days. A volume-to-film area ratio of 1.06 m^3/m^2 was utilized. Impact resistance was determined in accordance with the ASTM Test Method for Impact Resistance of Polyethylene Film by the Free-Falling Dart Method (D 1709-85). Since the control films broke at the standard drop height of 0.66 m, the drop height was reduced to 0.33 m. Measurement of the impact resistance of the control films was replicated three times.

Results and Discussion

Mechanical Property Values of the Control Test Films

Length, width, and thickness of the sample strips were compared prior to and following immersion in the different juice products. There was essentially no change in these dimensions for any of the test materials.

Mechanical property values for the control films (nonimmersed) are presented in Table 1.

TABLE 1—*Initial mechanical property values (nonimmersed) of the test films stored at 22°C.*

Mechanical Property	Alathon		EVOH		Co-Pet	
	MD	CD	MD	CD	MD	CD
Tensile strength, MPa	17.0 ± 1.70	15.9 ± 0.90	34.5 ± 2.8	28.5 ± 2.50	45.3 ± 3.80	38.3 ± 6.80
Modulus of elasticity, MPa	86.0 ± 9.0	93.0 ± 10.0	178.0 ± 24.0	164.0 ± 16.0	1290.0 ± 189.0	1250.0 ± 102
Elongation at break, %	398 ± 48.0	507 ± 50.0	455 ± 35.5	492 ± 41.8	4.00 ± 0.31	3.01 ± 0.0
Heat seal strength, N/m	516.7 ± 41.3	...	457.1 ± 56.2	...	1402.9 ± 179.6	...
Impact resistance, g	109.5	...	65.6	...	45.2	...

Stress-strain properties (tensile strength, modulus of elasticity, elongation at break) were determined in MD and CD orientation. The Co-Pet film had the highest tensile strength and modulus of elasticity and the lowest percent elongation at break. This material was, therefore, relatively stiff as compared to the other films. Both the Alathon (LDPE) and EVOH had similar elongation and modulus characteristics, which was attributed to the high proportion of ethylene in the EVOH. Co-Pet also had the highest heat seal strength, while Alathon and EVOH had similar values. The impact resistance of Co-Pet was the lowest, which would be expected given the relative stiffness of the film. The impact resistance of EVOH was about half that of Alathon. This was assumed to be due to the difference in film thickness, since the gauge of the Alathon was twice that of the EVOH film. Standard deviations ranged from a low of 5.7% [Alathon, tensile strength (CD)] to a high of 18.6% (Co-Pet, elongation at break, CD). In general, for the respective mechanical properties, the developmental films (particularly Co-Pet) exhibited higher standard deviations.

Immersion of Test Films in Orange Juice

The influence of d-limonene sorption on modulus of elasticity, percent elongation at break, tensile strength, and heat seal strength was determined for the three test films at several d-limonene concentrations. The influence of limonene sorption on impact resistance was measured at one concentration.

The effect of d-limonene sorption on mechanical properties was statistically evaluated by one-way analysis of variance [*10*]. Results were compared as a function of concentration of d-limonene in the three test films.

Stress-Strain Properties

Statistical evaluation of stress-strain properties is shown in Table 2. The influence of sorption of d-limonene on the tensile strength of the sample films is shown in Table 3. Statistical evaluation (Table 2) showed that sorption of d-limonene did not significantly affect the tensile strength of the three test films.

Modulus of elasticity values for the three test films as a function of d-limonene concentration are presented in Table 4. Statistical evaluation (Table 2) of the data showed that limonene sorption significantly affected the modulus of elasticity for the EVOH film in both machine and cross machine directions. As shown, the modulus for EVOH decreased as the

TABLE 2—*Statistical evaluation of the influence of sorption of d-limonene on the mechanical properties of the test films.*

	Alathon		EVOH		Co-Pet	
Mechanical Property	MD	CD	MD	CD	MD	CD
Modulus of elasticity	NS	97[a]	97	97	NS	97
Tensile strength	NS	NS	NS	NS	NS	NS
Seal strength	97	. . .[b]	97	. . .[b]	97	. . .[b]
Elongation at break	NS	NS	NS	NS	NS	NS

NOTE: NS = No significant difference at 97% confidence level.
[a] Significant difference at 97% confidence intervals.
[b] No data.

TABLE 3—*Relative percent change in tensile strength of the test films immersed in orange juice at 22°C.*

d-Limonene Concentration in Test Film, mg/g	Alathon, % change		EVOH, % change		Co-Pet, % change	
	MD	CD	MD	CD	MD	CD
0.00	100	100				
0.14	94	94				
0.28	108	90				
0.47	102	81				
1.46	103	100				
3.05	106	93				
0.00			100	100		
2.04			81	89		
2.41			94	100		
2.63			96	103		
4.31			91	88		
6.19			91	89		
0.000					100	100
0.003					105	111
0.008					104	107
0.013					101	106
0.019					106	109

TABLE 4—*Relative percent change in the modulus of elasticity of the test films immersed in orange juice at 22°C.*

d-Limonene Concentration in Test Film, mg/g	Alathon, % change		EVOH, % change		Co-Pet, % change	
	MD	CD	MD	CD	MD	CD
0.00	100	100				
0.28	89	98				
0.47	100	108				
1.46	101	103				
3.05	89	79				
5.20	94	...				
0.00			100	100		
2.04			92	72		
2.63			89	75		
4.31			69	70		
6.19			76	67		
9.26			52	...		
0.000					100	100
0.008					120	113
0.013					102	96
0.019					118	117
0.025					110	99

concentration of d-limonene sorbed increased. However, limonene sorption did not significantly affect the MD modulus for LDPE.

The relative changes in elongation at break for the respective test films are summarized in Table 5. Sorption of d-limonene did not significantly affect elongation at break for the three test films (Table 2).

Heat Seal Strength

The heat seal strength of the respective test films as a function of sorbed limonene levels are summarized in Table 6. Significant differences were observed for the films at the 97% confidence level (Table 2). As the amount of limonene sorbed increased, heat seal strength decreased.

Impact Resistance

The relative change in the impact failure weight of the sample films (immersed in the orange juice for 24 days) is shown in Table 7. The impact failure weight of the EVOH film increased as a result of sorption of aroma compounds (48%). The impact resistance of the LDPE film decreased (8%), which was in agreement with Hiroze et al. [*8*].

Immersion of Test Films into Apple Juice

Immersion of the film samples into apple juice usually resulted in change in mechanical properties within the first day of immersion (if change occurred) with little additional change

TABLE 5—*Relative percent change in elongation at break of the test films immersed in orange juice at 22°C.*

d-Limonene Concentration in Test Film, mg/g	Alathon, % change		EVOH, % change		Co-Pet, % change	
	MD	CD	MD	CD	MD	CD
0.00	100	100				
0.14	88	93				
0.28	121	82				
0.47	110	67				
1.46	106	91				
3.05	116	78				
5.20	109	...				
0.00			100	100		
2.04			92	93		
2.41			94	78		
2.63			96	102		
4.31			83	85		
6.19			88	86		
9.26			82	...		
0.000					100	100
0.003					107	102
0.008					106	106
0.013					115	119
0.019					105	107
0.025					106	113

TABLE 6—*Relative percent change in the heat seal strength of test films immersed in orange juice at 22°C.*

d-Limonene Concentration in Test Film, mg/g	Alathon, % change		EVOH, % change		Co-Pet, % change	
	MD	CD	MD	CD	MD	CD
0.00	100					
0.14	88					
0.28	81					
0.47	85					
1.46	81					
3.05	86					
0.00			100			
2.04			94			
2.41			88			
2.63			93			
4.31			88			
6.20			98			
0.000					100	
0.003					82	
0.008					70	
0.013					70	
0.019					83	
0.025					70	

subsequent to that. To determine significance of change in mechanical properties as a result of juice contact with the film, statistical analysis was performed using a contrast of means test [*10*]. The means of the data for each mechanical test performed on the immersed film samples (at the preselected storage intervals of 1, 3, 6, 14, and 24 days) were compared as a group to the initial values obtained for the films prior to immersion in the juice product.

TABLE 7—*Relative percent change in impact resistance of the test films immersed in apple juice, tomato juice, and orange juice at 22°C.*

Storage Time, days	Alathon, % change	EVOH	Co-Pet
	APPLE JUICE		
Initial	100	100	100
Final (24 days)	102	162	93
	TOMATO JUICE		
Initial	100	100	100
Final (24 days)	...	185	95
	ORANGE JUICE		
Initial	100	100	100
Final concentration[a]	92	148	115

[a] At d-limonene concentrations of 5.2, 9.3, and 0.03 mg/g film, respectively.

TABLE 8—*Relative percent change in tensile strength of the test films immersed in apple and tomato juice and stored at 22°C.*

	Alathon, % change		EVOH, % change		Co-Pet, % change	
Storage Time, days	MD	CD	MD	CD	MD	CD
			APPLE JUICE			
Initial	100	100	100	100	100	100
1	100	87	94	90	113	61
3	93	86	92	91	103	74
6	102	90	88	91	104	72
14	98	81	97	97	98	73
24	94	82	92	90	101	73
			TOMATO JUICE			
Initial	100	100	100	100	100	100
1	117	83	100	101	89	82
3	116	84	98	88	87	79
6	118	102	89	99	76	73
14	112	100	...	112	79	71
24	106	97	94	104	79	72

This analysis was used rather than a day-to-day comparison of means because of the greater degrees of freedom associated with the test. Some deviation in the values occurred after one day, but they were generally small and not significant in variation.

Stress-Strain Properties

The tensile strength of the test films was determined after immersion into apple juice, and the results are shown in Table 8. Statistically, there was no change in tensile strength for the MD Alathon, while the tensile strength (Table 9) decreased in the cross direction by an average of 15% (Days 1–24).

TABLE 9—*Statistical evaluation of the influence of immersion of the test films into apple juice and tomato juice at 22°C.*

	Alathon		EVOH		Co-Pet	
Mechanical Property	MD	CD	MD	CD	MD	CD
			APPLE JUICE			
Tensile strength	NS*	99.9[c]	90.0[a]	95.0[b]	NS	99.9
Modulus of elasticity	99.9	99.9	90.0	95.0	95.0	NS
Elongation at break	90.0	99.9	90.0	99.9	99.9	99.9
Seal strength	NS	...[d]	NS	...[d]	NS	...[d]
			TOMATO JUICE			
Tensile strength	99.9	NS	NS	95.0	99.9	99.9
Modulus of elasticity	99.9	99.9	95.0	99.9	99.9	99.9
Elongation at break	NS	NS	99.9	NS	99.9	99.9
Seal strength	NS	...[d]	99.9	NS	99.9	99.9

*NS No significant difference.

[a] Statistically significant difference (90% CL).

[b] Statistically significant difference (95% CL).

[c] Statistically significant difference (99.9% CL).

[d] No data.

The tensile strength of EVOH decreased significantly in both directions (8%). The decrease occurred within one day of immersion with little change thereafter. The tensile strength of Co-Pet also decreased in the CD (29%) with little change in the MD.

Modulus of elasticity results for all three films are summarized in Table 10. For Alathon, the modulus of elasticity decreased in both the machine and cross directions (Table 9), 34 and 33%, respectively (Days 1–24 average), following contact with apple juice. For EVOH, the modulus decreased an average of 13% in each direction. The average MD Co-Pet sample was also 15% lower than the control. There was no statistical difference in the CD sample (Table 9).

For the Alathon film samples, statistically significant changes (Table 9) in elongation at break were observed for samples tested in both the MD and CD following immersion in the apple juice (Table 11). An average decrease in elongation at break of 27% in the cross direction (Days 1–24) was observed after juice contact. An average decrease of 13% was found in the machine direction. Significant decreases (Table 9) were obtained for EVOH samples in both MD and CD, with an average decrease (1–24 days) of 19%.

Statistically significant decreases were also found in both the machine and cross direction for Co-Pet samples (Table 9). Average decreases (Days 1–24) of 17% (MD) and 40% (CD) were calculated.

Heat Seal Strength

Little evidence was found to support change in seal strength (Table 9) for the films immersed in apple juice (Table 12). Significant differences in seal strength were not obtained for any of the film-juice samples.

Impact Resistance

Results of the impact testing are shown in Table 7. The impact resistance of the Alathon and Co-Pet films was minimally affected, while the impact resistance of EVOH increased

TABLE 10—*Relative percent change in modulus of elasticity of the test films immersed in apple juice and tomato juice at 22°C.*

	Alathon, % change		EVOH, % change		Co-Pet, % change	
Storage Time, days	MD	CD	MD	CD	MD	CD
			APPLE JUICE			
Initial	100	100	100	100	100	100
1	60	59	75	75	88	92
3	59	59	89	74	91	96
6	57	68	90	98	84	85
14	74	78	82	89	80	83
24	77	69	95	86	79	84
			TOMATO JUICE			
Initial	100	100	100	100	100	100
1	126	153	93	94	112	106
3	136	123	88	105	104	105
6	119	114	89	99	97	97
14	103	107	116	163	104	97
24	98	105	141	161	108	94

TABLE 11—*Relative percent change in elongation at break of the test films immersed in apple juice and tomato juice and stored at 22°C.*

	Alathon, % change		EVOH, % change		Co-Pet, % change	
Storage Time, days	MD	CD	MD	CD	MD	CD
			Apple Juice			
Initial	100	100	100	100	100	100
1	88	69	83	84	81	62
3	86	84	85	80	78	55
6	88	83	76	84	87	59
14	83	64	82	79	85	63
24	90	67	78	79	86	61
			Tomato Juice			
Initial	100	100	100	100	100	100
1	114	71	101	90	99	92
3	146	93	106	83	99	91
6	121	93	85	80	99	91
14	112	83	...	104	95	87
24	106	77	98	99	92	91

substantially as a result of immersion in apple juice. This may have been due to plasticization of the film structure by sorbed penetrants.

Immersion of Test Films in Tomato Juice

To determine if the mechanical properties of the films changed due to immersion in tomato juice, the same statistical procedure used for apple juice was employed to evaluate the data. The means of the data for each mechanical test performed on the immersed film samples were compared as a group to the initial values obtained prior to immersion using a contrast of means method [*10*].

Stress-Strain Properties

The tensile strength of the films was determined following immersion, and the results are shown in Table 8. Statistically, the Alathon film showed no change in the CD (Table 9), while the MD tensile strength increased by 14% (average—Days 1–24). The tensile strength

TABLE 12—*Relative percent change in the heat seal strength of the test films immersed in apple juice and tomato juice at 22°C.*

Storage Time, days	Apple Juice			Tomato Juice		
	Alathon	EVOH, % change	Co-Pet	Alathon	EVOH, % change	Co-Pet
Initial	100	100	100	100	100	100
1	82	102	95	97	96	85
3	89	107	103	90	92	87
6	86	103	98	85	93	85
14	81	112	104	90	93	90
24	89	94	95	84	91	88

of EVOH film did not change significantly, while for Co-Pet, values were 18 and 25% lower for the MD and CD samples, respectively, as compared to the controls.

Modulus of elasticity values for the three test films are presented in Table 10. Statistically significant increases were observed (Table 9) for the respective film samples. Alathon MD and CD samples increased 16 and 20%, respectively, while EVOH increased an average (1–24 days) of 24% following immersion in the tomato juice.

Elongation at break results for the test films are summarized in Table 11. Both Alathon samples showed statistically significant changes, with the MD sample increasing by 20% and the CD sample experiencing a 17% decrease. The EVOH CD sample and the Co-Pet CD sample decreased 9 and 10%, respectively.

Heat Seal Strength

Heat seal values for the films immersed in tomato juice are presented in Table 12. Of the three test films, only Co-Pet showed a statistically significant change, which represented a 13% decrease (Table 9) from the control.

Impact Resistance

The impact resistance (initial and final) of the films is summarized in Table 7. The impact resistance of EVOH showed a marked increase following immersion, while that of Co-Pet appeared to be little affected.

Comparison of Effects of Immersion in Juices on the Mechanical Properties of Films

The results reported herein vary considerably from one film-juice system to another with respect to the specific mechanical property evaluated. These differences may be due in part to the variability observed for the mechanical property values of the control films (Table 1). Also, differences in juice composition may have influenced the results. For example, the volatile flavor composition of orange juice is made up primarily of d-limonene [*5*]. This compound is an aggressive terpene of known affinity for aliphatic polymers [*3–5*]. The volatile flavor composition of apple juice is made up of a mixture of aldehydes, alcohols, and esters [*7*] of varying polarities. No one component predominates, as is the case with orange juice. The aroma quality of tomato products has been related to the concentration of n-hexanal, trans-2-hexenal, cis-3-hexen-1-ol, and 2-isobutylthiazole [*11*].

Thus, each of the juices contain a series of volatile flavors which vary both in composition and concentration, which would be expected to be sorbed by the respective film samples at varying rates and levels. This, in turn, could influence the mechanical properties of the polymeric films. Mechanical properties of all three test films changed as a result of immersion into the different juices. No clear relationship was established with respect to film polarity and/or crystallinity. The mechanical properties of the films appeared to change more significantly in the apple and tomato juices than in the orange juice.

Conclusions

Three polymeric films were immersed in three juices to determine the effect of sorption of volatile flavor components on the mechanical properties of the films. Several material tests were chosen based on their relationship to package performance. Heat seal strength is important to maintain the integrity of the seal, while change in impact resistance and stress-strain properties can lead to loss of the physical structure of the package. To determine the value of these tests in relationship to package integrity, further research is required to develop a correlation with package damage due to static and dynamic forces in transportation, handling, and warehousing.

The volatile constituents of the juices were different as was the structure of the films. Significant changes in film mechanical properties were recorded for each of the film-juice systems. If change in the mechanical property occurred, it generally was observed within one day of immersion. However, no generalization can be applied to the different film-juice systems and associated changes in mechanical properties. The specific reason(s) as to why sorption or immersion impacted a specific property of one of the test films and not another is not fully understood. It is clear, however, that sorption can cause changes in the mechanical properties of polymeric films and should be considered when selecting a material for a given application.

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Eric B. Schaper[1]

High Barrier Plastics Packaging and Ethylene Vinyl Alcohol Resins (a Marriage)

REFERENCE: Schaper, E. B., "**High Barrier Plastics Packaging and Ethylene Vinyl Alcohol Resins (a Marriage),**" *Food Packaging Technology, ASTM STP 1113,* D. Henyon, Ed., American Society for Testing and Materials, Philadelphia, 1991, pp. 31–36.

ABSTRACT: In 1983, with the introduction of the first multilayer high barrier plastic bottle in the United States, a revolution was started in the food packaging industry. This revolution has gained momentum over the last five years so that today almost any type of food product is a candidate for packaging in a high barrier plastic container. Food products are not the only candidates, however; many nonfood products such as chemicals, health care products, electronic parts, etc. are taking advantage of the excellent cost/performance properties of high barrier plastics packaging. One of the primary reasons for the acceptance and functionality of this type of packaging is ethylene vinyl alcohol copolymer (EVOH) resins.

This paper will review multilayer plastics packaging applications, their markets and economics from 1983 to the present, and why EVOH resins play a very important role in the "packaging revolution."

KEY WORDS: packaging, high barrier plastics, ethylene vinyl alcohol resins

In 1983, with the introduction of the first multilayer high barrier plastic bottle, a revolution was started in the food packaging industry. This revolution has gained momentum over the last five years so that today almost any type of food product is a candidate for packaging in a high barrier plastic container. Food products are not the only candidates, however. Many nonfood products such as chemicals, health care products, electronic parts, etc. are taking advantage of the excellent cost/performance properties of high barrier plastics packaging. One of the primary reasons for the acceptance and functionality of this type of packaging is ethylene vinyl alcohol copolymer (EVOH) resins.

This paper will review multilayer plastics packaging applications from 1983 to the present and why EVOH resins play a very important role in the "packaging revolution."

Ethylene Vinyl Alcohol Copolymers (EVOH)

As the name implies, EVOH resins are copolymers of ethylene and vinyl alcohol. EVOH resins are produced by copolymerizing ethylene and vinyl acetate and then hydrolyzing the vinyl acetate to vinyl alcohol. The resulting polymer offers superior barrier properties to gases, solvents, odors, and aromas together with excellent processability. Table 1 indicates the barrier properties provided by EVOH resins.

Table 2 lists common converting operations for typical EVOH copolymer resins.

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TABLE 1—*Oxygen barrier properties of EVOH.*

Ethylene, mol %	Oxygen Permeability at 20°C 65% RH	85% RH
27	0.010	0.061
32	0.020	0.076
38	0.035	0.112
44	0.076	0.168
48	0.163	0.310

NOTE: Permeability units = c^3 mil/100 $in.^2$ day atm.

FDA Status:

EVAL(R) resins and films except L101 and F104 comply with the Federal Food, Drug and Cosmetic Act, 21CFR, Section 177.1360(a)(3) and may be used for direct food contact for all foods, except beverages containing more than 8% alcohol, under conditions of use B through H (21CFR, Sec. 176.170, Table 2) provided maximum thickness is 7 mil (0.007 in.).

EVAL(R) resin grades L101 and F104 may be used for all foods, except beverages containing more than 8% alcohol, under conditions of use B through H, provided there is a minimum 1-mil (0.001-in.) functional barrier between the EVOH layer and the food product.

It is this combination of properties that has made EVOH resins the barrier resin of choice for multilayer plastics packaging.

How has the development of EVOH resins affected the packaging of the foods we consume and the products we buy? To understand this, a review of the trends occurring in packaging over the last decade might be beneficial.

TABLE 2—*EVOH applications.*

Ethylene Content, mol %	Application
27	Melt phase thermoforming Film
32	Coextrusion blow molding Melt phase thermoforming Coextrusion coating Blown film Cast film
38	Solid and melt phase thermoforming Cast film Blown film Coextrusion coating
44	Solid and melt phase thermoforming Cast film Blown film Coextrusion coating Coextrusion blow molding
48	Cast film Specialty

High Barrier Plastics Packaging

High barrier packaging protects products from:

1. Ingress of oxygen.
2. Loss of carbonation.
3. Loss or gain of moisture.
4. Contamination.
5. Permeation of solvents, odors, and flavors.
6. Absorption of flavor constituents by the package.

Until the early 1970s, the only packaging materials that would provide this type of protection were:

1. Glass.
2. Metal.
3. Polyvinylidene chloride (PVDC).

In 1973, EVAL(R) EVOH resins were commercialized in Japan by Kuraray Company, Ltd. Multilayer packaging structures containing EVOH resins quickly demonstrated their ability to provide high barrier protection for a variety of products.

By the mid 1970s, EVOH resins had been introduced to the United States. Companies such as American National Can and Cryovac began producing high barrier flexible films for the packaging of meat and cheese products.

For the next eight years, the only commercial use for EVOH resins in the United States was flexible plastic packaging.

1983: The Year the Plastics Packaging Revolution Began

In late 1983, the first multilayer high barrier plastic bottle was introduced by American National Can. The bottle, called the "gamma" bottle, had a structure consisting of:

PP-Regrind-Tie-EVOH-Tie-PP

and was used to package Wishbone Bar-B-Que sauce.

This was quickly followed by another 28-oz "gamma" bottle for Heinz ketchup. Both of these products were filled at a temperature of 900°C, and the plastic containers demonstrated both the ability to withstand these temperatures and to provide a shelf life in excess of one year.

The packaging revolution had begun!!

1984: The Year of the Large Bottle

Ten more multilayer plastic packages were introduced during the year. Included were three of the largest bottles yet:

1. 64-oz Heinz ketchup.
2. 32-oz Hunt's ketchup.
3. 46-oz Campbell's V-8 juice.

A unique flexible packaging application was also introduced. This was a high barrier pouch used to contain the banana puree in a Betty Crocker's Muffin Mix kit.

1985: Plastics Break the Retort Barrier

During 1985, 37 new high barrier packages entered the marketplace. Included were 30 bottles of:

PP-Regrind-Tie-EVOH-Tie-PP

construction produced by four different suppliers:

1. American National Can.
2. Ball Plastics.
3. Continental Can.
4. Owens Illinois.

Packaged in these bottles were such diverse products as:

1. Aloe Vera nectar.
2. Jam and jelly.
3. Bar-B-Que sauce.
4. Ketchup.
5. Salad dressing.
6. Picante sauce.

1985 also saw two firsts:

1. *Single serve thermoformed container.* This 4-oz container for Mott's applesauce was produced by both Rampart Packaging and Ball Plastics. With the introduction of this container and subsequently other brands of applesauce in similar containers, the annual growth rate of applesauce consumed went from 0 to 8%.

2. *Single serve retort processed container.* This was probably the most significant development since the inception of high barrier plastics packaging. Until now, all of the products in high barrier plastic containers were packaged under "hot fill or ambient fill" conditions. The introduction of the "omni" container by American National Can proved the feasibility of plastics in general and EVOH in particular for containers that must withstand processing temperatures of 2750°F (1510°C) for 30 to 45 min. This container was used to introduce Hormel's new product line of single serve entrees. The container became the prototype for the next generation of plastic containers.

By the end of 1985, it was becoming quite evident that a new trend in food packaging was developing. The consumer was exhibiting a willingness to pay a premium for the convenience offered by plastic containers. Convenience such as:

1. Squeezability.
2. Shelf stable.
3. Single serve size.
4. Shatterproof.
5. Microwavability.
6. Self-contained serving medium.

were mentioned in many consumer surveys.

1986: The Year of the Lunch Bucket

As the convenience trend continued, 66 packages were introduced in 1986. Again, bottles led the way with 41 introductions including several nonfood products which required a resistance to solvent permeation. Twelve formed containers offering single serve convenience and microwavability were also introduced. These introductions included what is probably one of the most successful food product lines introduced during this decade.

This was the lunch bucket line of single serve entrees by Dial Corporation. This line includes 15 products ranging from meat products to soup. They were packaged in an 8-oz, bowl-shaped container from DRG Packaging and retort processed. The "bowl" shape has now replaced the traditional "can" shape as the preferred package configuration.

1986 also saw several firsts. These included:

1. High barrier tubes for packaging skin car products, hand cleaners, etc.
2. Plastic container for canned hams replacing the metal can.
3. The use of a high barrier multilayer film to retain flavor in cereal.
4. The first high barrier bottle introductions in Canada by Onex Packaging and Plax, Inc.

1987: The Year of the "Juice"

As the revolution grows, so do the number of new package introductions. A total of 94, including 54 bottles and 10 formed containers, were introduced during 1987. Included in these introductions were four more "retort" packages, the first medical application, and a series of bottles for infant juice. Both a 4-oz and a 25-oz bottle containing various juices were introduced by Gerber Products.

The most notable introductions in 1987 have to be the new concepts of packaging various juice products. Traditionally, citrus juices have been packaged in "gable top" paperboard containers using a structure of

LDPE-Paperboard-Tie-Foil-Tie-LDPE

or in monolayer polyethylene bottles. The problem with this type of structure is that the polyolefin interlayer will selectively absorb flavor constituents from the juice. This in turn shortens the shelf life of the juice package even under refrigerated conditions.

International Paper Company was the first supplier to introduce a new "gable top" paperboard container for packaging citrus juices. They replaced the traditional poly-paper-foil-poly structure with the following:

LDPE-Paperboard-Tie-EVOH-Tie-EVOH

which is produced by coextrusion coating. This structure provided not only a barrier to oxygen, but also prevented flavor "scalping" by having an EVOH layer in contact with the product.

This introduction was followed later in the year by a Tropicana bottle for freshly squeezed orange juice. This bottle also uses the concept of an EVOH layer in direct contact with the product to prevent "scalping."

1988: The Revolution Continues

As the trend towards more and more convenience-oriented packaging continues, so does the plastics packaging revolution.

TABLE 3—*Package introductions (EVOH).*

Year	Bottles	Formed	Flexible	Coex Coating	Tubes	Total
1983	2	...	1	...	...	3
1984	6	...	4	...	...	10
1985	30	5	2	...	...	37
1986	41	12	9	...	4	66
1987	54	10	3	20	7	94
1988 (thru June)	60	32	17	8	3	...
Total	165	44	27	23	11	270

Through the first six months of 1988, 60 new packages have been introduced. Included are:

1. Six new "retort" applications for single serve, microwavable entrees.
2. Flexible packages to protect the flavor of buttered popcorn.
3. A flexible package for instant coffee.
4. Six new applesauce products in formed containers.

Summary

To summarize what has happened in the plastics packaging area during a short five-year time span, one needs only to look at the data in Table 3.

Of the 270 high barrier package introductions, 92% are still in the marketplace. The common thread in all these introductions is the use of ethylene vinyl alcohol copolymers as the high barrier resin chosen to protect the packaged product. High barrier plastics packaging has proven to be an effective alternative to traditional forms of packaging.

LeRoy Pike[1]

Current Practices in the Measurement of Oxygen Transmission Rates of Packaging Films Under Humid Conditions

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REFERENCE: Pike, L., **"Current Practices in the Measurement of Oxygen Transmission Rates of Packaging Films Under Humid Conditions,"** *Food Packaging Technology, ASTM STP 1113,* D. Henyon, Ed., American Society for Testing and Materials, Philadelphia, 1991, pp. 37–45.

ABSTRACT: The techniques being used to measure the oxygen transmission rates of packaging films under humid conditions are briefly described and their advantages and disadvantages discussed. The techniques consist of various methods of humidifying the gas streams used in the standard methods for dry gas transmission rate measurements and the controlled humidity "sandwich" method. The new modern controls "H-System," which was designed especially for this purpose, is also described.

One must choose from the available techniques and equipment based upon the needs and funds available. Only very limited data are available for comparison of the techniques, so accurate statements about precision still cannot be made.

KEY WORDS: packaging films, oxygen transmission rates, humid conditions, methods of measurement

The standard test methods for determining gas permeability [*1–2*] specify the use of dry gases. However, packaging films are almost always used in environments containing water vapor. Often food-packaging materials are exposed to relative humidities of 50% and above. The use of highly water sensitive materials, such as the ethylene vinyl alcohol copolymers, during the last several years has forced both producers and users of packaging materials to devise and apply methods for measuring gas transmission rates, particularly that of oxygen, through packaging materials under humid conditions. However, to this author's knowledge, there are still no standard or official methods available for this purpose. This is largely a result of extremely poor between-laboratory precision when attempts have been made to collect data to support approval of methods for this purpose.

The poor precision is now known to result from the large effect of humidity on the transmission rate of ethylene vinyl alcohols used in the studies and the difficulty in generating and maintaining known humidities. However, it is believed that many laboratories have developed methods that provide satisfactory within-laboratory precision. This paper covers some of the procedures currently being used and discusses their advantages and disadvantages.

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Procedures Being Used for Measurement of Oxygen Transmission Rates Under Humid Conditions

ASTM Standard D 1434 [1] *with Humidified Gas Streams*

This standard contains two procedures, manometric and volumetric, and is one of the older techniques still in use. It was originally published by ASTM in 1956 and specifies the use of dry gases; however, some laboratories have used humidified gases with these procedures. This approach will often alert one to a highly water-sensitive material; however, it is fraught with many problems and uncertainties. A brief discussion of the techniques will reveal some of the problems. Very briefly, the manometric method involves measuring the rate of decay of a vacuum on the downstream side of a test film. Figure 1 is a simplistic diagram of a manometric cell. Obviously, if the partial pressure of water vapor is not the same on both sides of the film, water vapor as well as the gas being measured will also move through the film and affect the rate of decay of the vacuum. The pressure indicators normally used do not resolve the molecules generating the pressure, and it is almost impossible to maintain the same partial pressure of water vapor on the two sides of the test film. The resulting error depends upon the water vapor transmission rate (WVTR) of the film and how near the two partial pressures of water vapor can be maintained at the same level. Generating and maintaining constant levels of water vapor in gas streams turns out to be extremely difficult. The level of water vapor is highly dependent on the temperature and the pressure. Water vapor also tends to absorb and desorb on surfaces at unexpected times, causing erratic changes in level.

The volumetric method involves measuring change in volume at constant pressure on the downstream side of a test film. Changes in water vapor content of the downstream gas volume obviously affects its magnitude. All the problems cited under the manometric technique also contribute to errors when using the volumetric technique.

In short, neither of these techniques can distinguish between water vapor and test gas in the downstream side, and the water vapor level cannot be controlled in all cases and corrected for with the equipment commonly used.

ASTM Standard D 3985 [2] *with A Gas Stream Humidifier*

This standard covers the measurement of oxygen transmission rates of films using a coulometric detector. Modern Controls' (MOCON) "Ox-Trans" are the commercially available equipment for this technique, and they are used by most packaging film producers and users

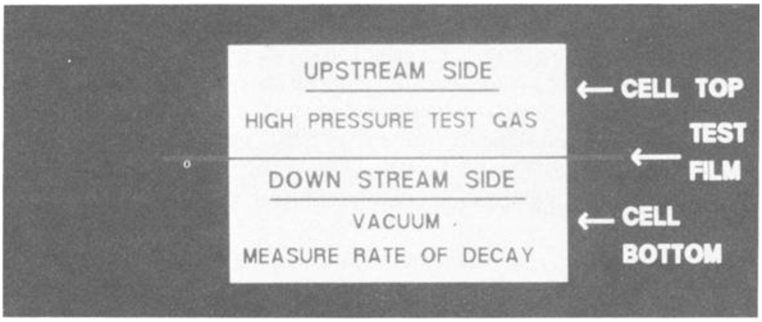

FIG. 1—*Simplistic diagram of manometric or dow cell.*

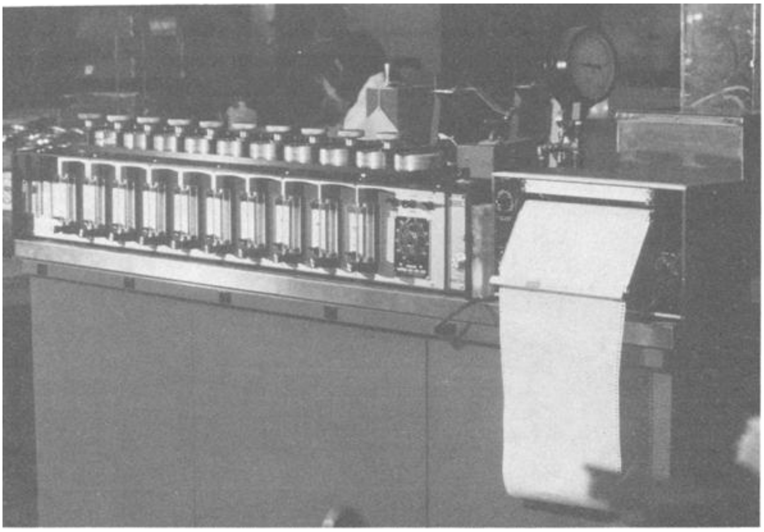

FIG. 2—*An Ox-Tran 10/50 with strip chart recorder.*

today. Figure 2 is a picture of an Ox-Tran 10/50 with strip chart recorder. A major advantage of this equipment is that the detector, a fuel cell, does not respond to most impurities, including water vapor, encountered during the measurement of oxygen transmission rates, but this prevents its use for gases other than oxygen. Once again the standard, D 3985, specifies the use of dry gases. This was included because during the interlaboratory testing of the technique satisfactory between-laboratory precision could not be obtained when humid gas streams were used. It is now known that this was largely the result of the difficulty in obtaining and maintaining the same humidities in the gas streams in different laboratories. Placing water in the bubblers on the Ox-Trans only assures one of some humidity in the gas streams. It may be anywhere between 40 and 90% relative humidity depending upon the temperature, the gas flow rates, the height of water in the bubblers, the degree of equilibration of the catalyst and surfaces, etc. Also, minor changes in the above conditions cause changes in the humidity levels in the transmission cells. The use of salt solutions in the bubblers to control humidity usually transfers enough salt spray to the catalyst beds used in the carrier gas stream ahead of the Ox-Tran transmission cells to poison them. This results in interference from residual oxygen in the carrier gas stream.

As a result, Ray Dorschner of American Can constructed a gas stream humidifier satisfactory for use with the Ox-Trans [*3*]. Figure 3 is a photo of similar equipment. The humidifier operates in the following way. Both gas streams, carrier and test gas, are split into two streams each. One stream of each gas flows through a water absorption column where it is humidified. Then the humidified and dry streams are combined in the correct ratio to provide the desired humidity as read from digital humidity indicators. Mass flow controllers are used to provide constant operation once correct settings have been accomplished. The unit also has provision for measuring the humidity of the gases as they exit out of the transmission cell.

This unit functions, but it suffers from the same things: temperature and pressure changes, adsorption-desorption problems, etc., cited above plus drifting of the humidity sensors. The author was forced to place coils for constant temperature liquid around the absorption columns as shown in Fig. 4 to maintain the temperature constant enough to prevent a sine wave output due to humidity variations with small changes in laboratory temperature.

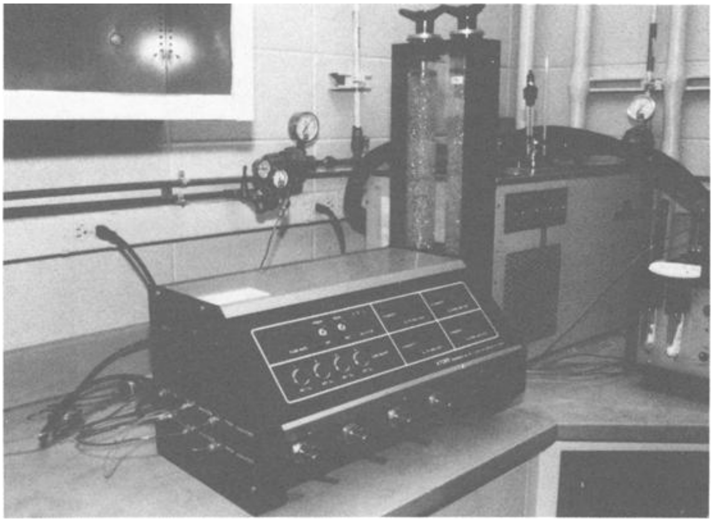

FIG. 3—*A gas stream humidifier.*

Drifting of the humidity sensors was overcome by using a Vaisala HM31 hand-held humidity and temperature indicator plus a glass cell for its sensor plugged onto the outlets from the transmission cells. Figure 5 is a picture of this equipment. The glass cell for the sensor is hard to see. Calibration of this unit can be easily checked over salt solutions at any time. This modified unit operates well up to relative humidities between 85 and 90%. Above

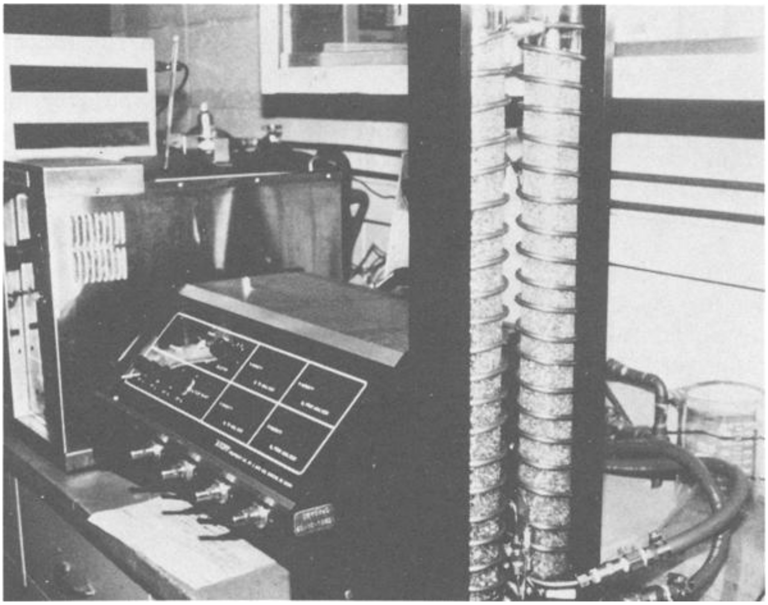

FIG. 4—*Copper tubing wrapped around the absorption columns of a humidifier for temperature control.*

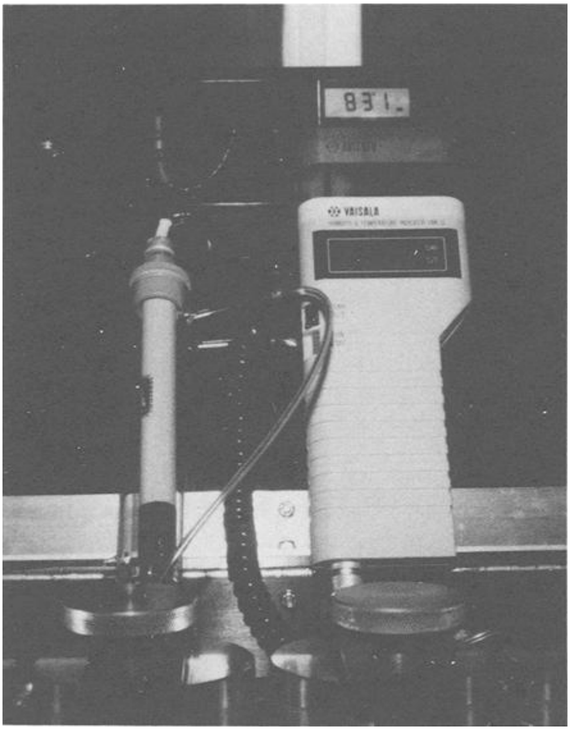

FIG. 5—*Vaisala humidity indicator with cell for sensor.*

this range, small decreases in laboratory temperature cause condensation in the gas lines. Another problem is that the catalyst for removal of residual oxygen in the carrier stream must be placed ahead of the absorption column. This requires extremely leakproof fittings and connections beyond the catalyst. Equilibration of the systems requires long periods of time. Large changes in humidity of a humidifier feeding a ten-station Ox-Tran sometimes requires days to equilibrate and maintain constant conditions in all cells.

The Sandwich Method [4]

This method is said to have been suggested by someone at an ASTM meeting, but it was developed by Rex Wood of Modern Controls. It consists, as diagrammed in Fig. 6, of placing wet filter paper on both sides of a sample to be measured and adding a thin layer of polyethylene film about 0.5 mils thick to both sides to reduce the rate of evaporation of the water. Then the entire "sandwich" is placed in an Ox-Tran and measured like any other sample.

This method has been used for some time in the author's laboratory. A long time, up to 24 h and more, may be required to degas the sandwich and obtain a stable baseline. Then, up to several weeks may be required to obtain steady-state rates depending upon the nature of the water-sensitive layer or layers and the protective layers of the sample being measured.

The use of salt solutions to obtain relative humidities below 100% are included in the method. Screens may be used to prevent direct contact of the wet filter papers with the samples, but limited data are available that indicate no difference in results from contact with

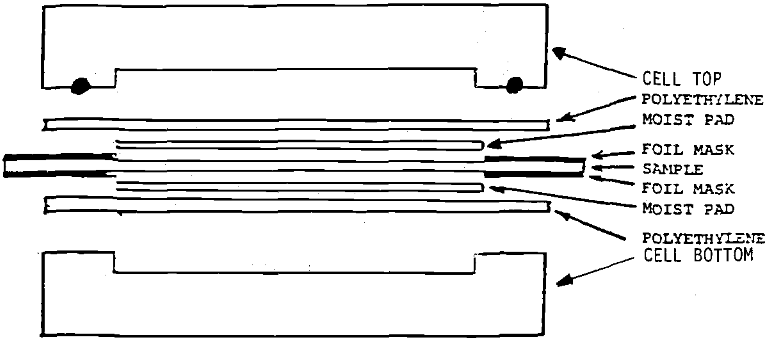

FIG. 6—*Diagram of sandwich used for humid measurements.*

the wet papers and no contact. The publication also contains equations for correcting for the effect of the thin polyethylene layers on the transmission rate of the sample. However, this effect is nil if one is measuring very low transmitting samples with respect to the polyethylene cover layers. Data provided by MOCON from the sandwich method are in Fig. 7.

The major advantage of the sandwich method is that cost is very low assuming that Ox-Trans are already available. Development of the technique requires some time and effort, particularly with the use of salt solutions, which tend to migrate into the sealing area and cause difficulty in sealing.

Data in the author's laboratory and that obtained by Kollen and Gray [5] indicate that the sandwich method and the humidified gas stream approach yield the same rates when care is exercised to be sure the humidities are really the same.

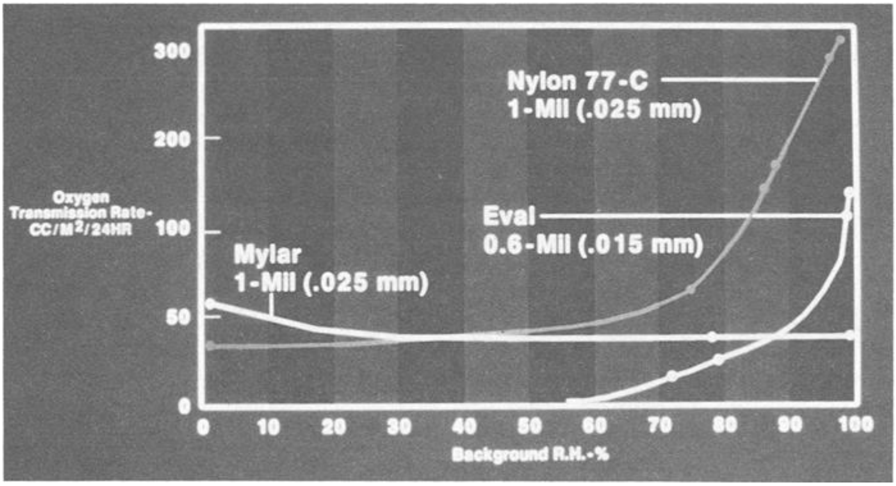

FIG. 7—*The effect of background relative humidity on the oxygen permeability of three water-sensitive films as measured with an Ox-Tran 10/50 using the sandwich method. All tests were conducted at 24 degrees C using 100% oxygen at 740 mm Hg atmospheric pressure.*

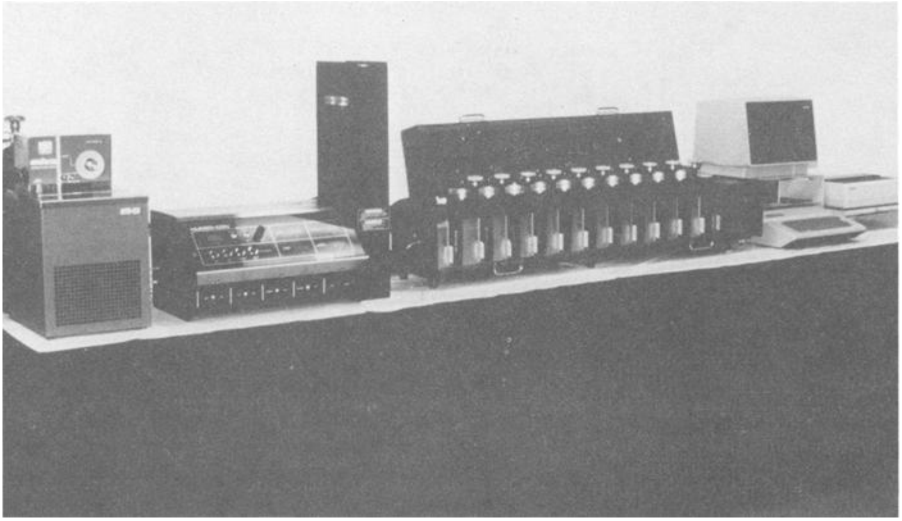

FIG. 8—*The H-system.*

The MoCon "H-System" [6]

Figure 8 is a photo of the "H-System," which is a well-designed combination of all the necessary units into a single system controlled appropriately for the purpose of measuring oxygen transmission rates of packaging films under humid conditions. It consists of a circulating bath for temperature control, a humidity generator, ten film test cells with gas distribution system and sensor, a computer for control and data acquisition, and a printer (as diagrammed in Fig. 9). The water bubblers and transmission cells are maintained at a slightly lower temperature than the rest of the system to prevent problems from condensation. Mass flow controllers are used to set and maintain appropriate gas flow rates. Platinum catalysts are used to remove traces of oxygen from the carrier gas stream. Heated lines are used to carry the humidified gases to the transmission cells. Cell No. 3 contains relative humidity probes in both the top and bottom half. Therefore, this is the state of the art equipment for making the measurement, and some eight or ten companies have purchased these new systems. The disadvantages are the limited experience with this equipment and the cost. Figure 10 contains data using the H-System to study ethylene-vinyl alcohol (EVOH).

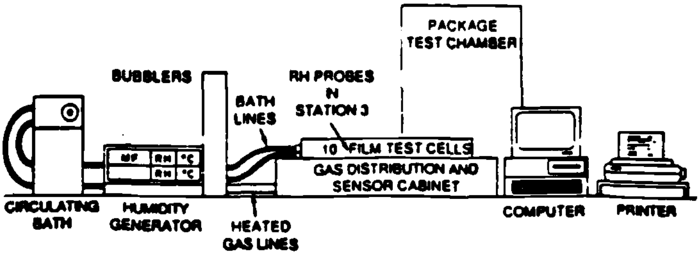

FIG. 9—*H-system block diagram.*

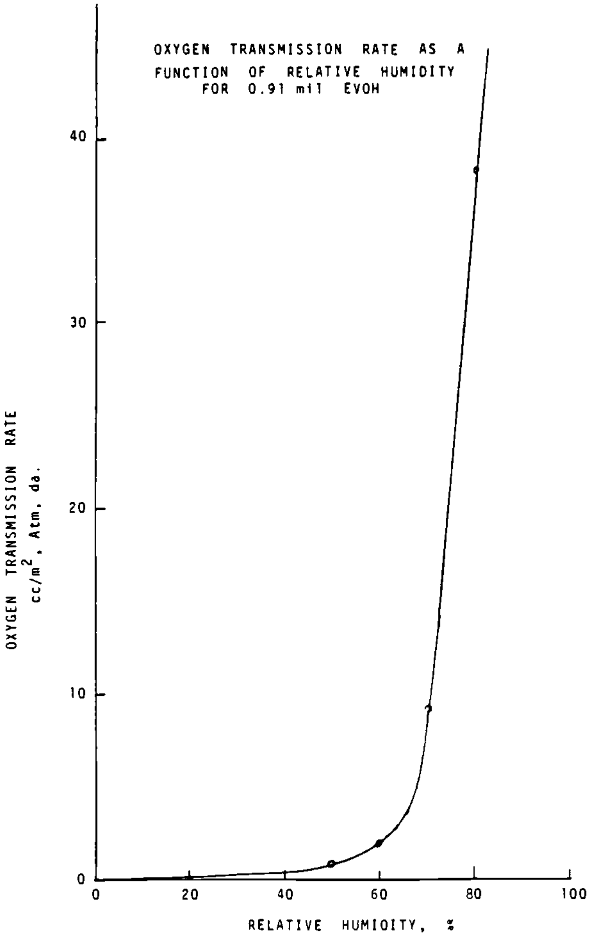

FIG. 10—*Oxygen transmission rate as a function of relative humidity for 0.91 mil EVOH.*

Conclusions

There is an obvious need for interlaboratory studies to develop reliable methods for measuring gas transmission rates under humid conditions suitable for industrywide use. This is a grand opportunity for ASTM.

Until reliable methodology is developed and validated, individual laboratories are forced to develop methods for internal use that will meet their needs. Where funds are available, the H-System is obviously the most sophisticated equipment available. Otherwise, the "Sandwich Technique" can provide reliable data in many situations. Satisfactory use of a gas stream humidifier requires extensive knowledge and constant care and attention. Humidifying the gas streams feeding volumetric and manometric cells is fraught with so many problems that this approach is discouraged.

Wide variation in results from different laboratories should be expected until validated methods are developed.

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Steven W. Gyeszly[1]

Total System Approach to Predict Shelf Life of Packaged Food Products

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REFERENCE: Gyeszly, S. W., "**Total System Approach to Predict Shelf Life of Packaged Food Products,**" *Food Packaging Technology, ASTM STP 1113,* D. Henyon, Ed., American Society for Testing and Materials, Philadelphia, 1991, pp. 46–50.

ABSTRACT: A total system approach should be used to simulate the shelf life of packaged food products. The main advantage of modelling the product-packaging-distribution system is in helping to make proper decisions during product and packaging development.

KEY WORDS: food, packaging, shelf life, model, system

The purpose of this article is to comment on modelling the shelf life of packaged food products from a total system point of view. The following information is restricted to cases where packaging controls or influences the shelf life of the food product. Oxygen and water vapor permeabilities of packages for moisture and oxygen-sensitive products is an appropriate example.

Shelf life is defined by the "Glossary of Packaging Terms" [*1*] as "the length of time that a container, or a material in a container, will remain in a saleable or acceptable condition under specified conditions of storage." Therefore, we must differentiate between shelf life of the product and package shelf life. The package shelf life must be at least equal to the required shelf life of the product. This is one reason why the shelf life of the package must be considered in modelling the shelf life of packaged food products.

The shelf life depends to a great extent on the distribution environment. The same or similar products with different distributions have different optimal shelf lives based on total cost and benefits. Thus, the distribution environment should be understood.

Requirements

Determination of the exact requirements is the first and most critical step of packaging development. The effectiveness and success of all the following steps of the development and the total project depend on the quality of the prepared requirements definition. Often the requirements are decided arbitrarily without actual data. Shelf life requirements of food products is a good example.

Marketing desires long shelf life. For a given product and distribution, however, longer shelf life generally represents higher packaging cost. Therefore, during the requirements definition phase of packaging system development, the expected relationship between required shelf life and the packaging cost should be estimated. Modelling the food product-packaging-distribution system is a useful tool for this task.

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Shortening the required shelf life for packaged food products is an economical necessity and has been the tendency in the last decade. Designing a product or package for the worst possible case may be necessary for some products but cannot be justified for most food products. Summing of the longest expected time for each segment of the distribution to determine the required shelf life gives good assurance but results in high cost. Application of statistics and probability to calculating the required shelf life is more reasonable where no health hazard exists with an expired product.

In preparation of the requirements definition, extra care should be taken against conflicting requirements that cannot be met. As an oversimplified example, if visual inspection of the product by the customer and flexible packaging are requirements for a moisture or oxygen-sensitive product for a given distribution, then the shelf life has certain limitations because the container should be plastic. If the conflict is not recognized and solved early on by changing the requirements, then resources and time are wasted because the development cannot produce acceptable results.

Separation of necessary and desirable requirements during the preparation of the requirements definition is a must. The packaging development is not finished until all necessary requirements are satisfied. The desirable requirements represent marketing or other advantages, but the product is acceptable without satisfying them. Therefore, the development can be completed without meeting desirable requirements. Longer shelf life is always desirable, but often there is no real justification for the extra expense. The required shelf life must be based on actual data about the product, market, and available packaging technology. The decision on the required shelf life of a packaged food product must be a team effort with active participation of senior management, marketing, product research and development, manufacturing, distribution, and packaging functions. The shelf life requirement should be a document describing the expected distribution environment and the products, and all of the assumptions made during decision making should be recorded. Thus, if conditions change, modification of requirements can be accomplished easily.

Accelerated Shelf-Life Testing

A common method in shelf-life prediction or packaging design is using data generated under accelerated storage conditions. The shorter testing time and lower expense make this method apparently advantageous. Theoretical and experimental studies [*2–4*] demonstrate, however, that the shelf-life prediction under actual storage conditions cannot be based on data generated under accelerated storage conditions. The shelf-life ratio at constant room temperature and under accelerated conditions is not the same for different products in different packages, especially for continuously fluctuating and unknown distribution environments.

Shelf-life prediction from accelerated data usually underestimates the actual shelf life, making the packaging unnecessarily expensive. Testing the packaged food products under the actual distribution environment is the best way to determine the shelf life, but it is time consuming and expensive.

The other method, gaining increased acceptance, is prediction of shelf life by modelling the permeability of the packages, the sensitivity of the product, and the distribution environment. Because of time and resource restrictions or limited understanding of the interrelationship of components, only a segment of the total system is usually modelled. The rest of the system is assumed to be constant or simply ignored.

A comprehensive shelf-life model must include the three main contributors and their interrelationship:

1. The product (initial and acceptable conditions, sensitivity, and other properties).
2. The package (permeability of the material and its temperature dependence, dimensions, mechanical properties).
3. Distribution (temperature, relative humidity, mechanical environment, time).

Product

Understanding the product is critical. Oxygen or moisture sensitivity is meaningless unless the degree of the sensitivity and the conditions are clearly defined. There is no justification for savings by not testing the sensitivity of the product because over- or underpackaging due to lack of experimental data costs more.

The shelf life of a product for a given distribution environment and packaging system depends on the difference between initial condition (quality) of the product and the limit of acceptable quality. Increase of the difference between the acceptable quality and the initial quality extends the shelf life or for the same shelf life lowers the package barrier requirement. In the case of long distribution time, the initial quality of the product can be designed so that the time function of the quality follows the time function of the probability of consumption.

Each of these factors and their components represents a cost. The goal of the development is to find the optimal combination resulting in minimum cost. The most common practice is having a product and a given distribution and the package designed for the required shelf life. Consequently, a limited number of options are available. If the initial quality or the distribution environment can be changed more economically than using a more protective product, then those options should be pursued.

Packaging System

Packaging should be treated as a system consisting of the package system (primary, secondary, tertiary packages), packaging operation, and packaging equipment. Even in cases when the shelf life of the product is apparently controlled by the permeability of the package system only, the packaging operation and equipment can have a significant effect on the shelf life. The initial condition in the headspace of the primary packages is controlled, and the properties of the packaging materials are influenced by the packaging operation and equipment. Therefore, it is advisable to conduct shelf-life testing with packages produced on the packaging line instead of using laboratory-made samples.

Each component of the package system (primary, secondary, and tertiary packages) should be taken into account simultaneously in shelf-life studies because all contribute to the interaction between the product and distribution environment. There are many ways to measure the permeability of different components through plastics. More sophisticated and expensive instruments and techniques yield more accurate data. More accurate permeability data, however, does not necessarily mean more accurate shelf-life prediction.

Permeability measurements are usually done on laboratory samples without subjecting them to the mechanical distribution environment, which can significantly increase permeability. In some cases, an apparently poorer barrier is more desirable because of its superior mechanical properties; the permeability does not increase significantly during distribution.

Formation of pinholes is also a concern. There are a few explanations, but a study is necessary to predict the probability of formation of pinholes in flexible plastic packages during distribution. Since the movement of molecules through the pinhole is flow instead of permeation, the mechanism and dependence on the environment is different. In extreme situations, the permeability becomes insignificant compared to the mass transfer through the pinholes.

Distribution

A major problem in total system modelling of shelf life of packaged products is the lack of data on distribution environments. Even when the product is not sensitive to the mechanical environment, only to moisture loss or gain, or oxidation or flavor loss, information about the mechanical distribution environment in addition to temperature and humidity data is necessary. The barrier properties can decrease because of interaction between packaging materials and the mechanical environment.

Estimation of the distribution environment based on statistics and probability is necessary if actual data is not available or cannot be generated economically. Based on the probability of temperature (related to the duration), the probability of shelf life for a given product-package combination can be estimated.

The main advantage of modelling the system for shelf-life prediction is in helping to make technical and business decisions by providing opportunity to evaluate options. Verification of the results of the modelling by actual jesting is crucial because of the number of assumptions. Error analysis to predict the validity of the model is mandatory. A computer saves time but cannot replace understanding of the problem from a system point of view.

Packaging professionals must work closely with product scientists and manufacturing and distribution people to collect the necessary information for modelling. The barrier properties of packaging materials is only one of the considerations in selection of a package and cannot be separated from other critical functions of packaging.

When a material is replaced, it is commonly required that the new material have exactly the same or better properties in all categories at less cost. Acceptable alternatives are discarded because the new material does not have identical properties with the old. A solution is identification of the required critical performances and performance specification instead of property specification.

Another example for the total system approach to shelf-life modelling is palletized, refrigerated, or frozen products. If products on the pallet are subjected to room or even higher temperatures for a given time period, some of them can reach temperatures that make the product unacceptable. Packaging has limited control over distribution for complete elimination of this situation; therefore, modelling is appropriate to predict the probability of a product reaching unacceptable quality in a given container. This information is also useful in designing packages.

The combination of the temperature and the time of the exposure determine the quality of temperature sensitive products. On a pallet, packages at the eight corners of the load are more subjected to the higher temperature. Modelling the heat transfer through the pallet load under surrounding temperature can help in deciding which is more advantageous—utilization of the pallet load as a heat sink or an open pallet pattern where the packages can cool down faster once replaced in the low-temperature environment. Also, the modelling can justify using dummy packages at the corner. The extra cost, including lower space utilization, can be compensated for with a higher degree of quality assurance or savings in the individual packages. Lower heat transfer of the packaging materials keeps the product longer at a lower temperature but takes longer to cool it down from a higher temperature. Modelling can find the optimal solution.

Conclusion

The appropriate modelling of the shelf-life of an environmentally sensitive packaged food product is a total system approach. Modelling the product, the packaging system, and the environment enables identification of the optimal solution, which could change the product or the distribution. The initial investment to generate the necessary data for the modelling of the total system saves more money in the long run. The system model is a decision-making tool, but the verification of the results is a must. The modelling cannot be developed without serious effort and participation of several functions of the corporation. Packaging organization can start and lead the activities, but without full commitment from the total corporation, shelf-life modelling cannot be successful. The purpose of the modelling is to develop an understanding of the problem; it should not be viewed as an intellectual, computer exercise without practical value.

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Time-Temperature Indicators as Food Quality Monitors[3]

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ABSTRACT: This paper summarizes the benefits that can be obtained by the use of time-temperature indicators (TTI) as monitors of quality in the food distribution chain and the requirements for their successful application. Modeling of the TTI response characteristics based on kinetic principles and the Arrhenius equation allows the estimation of the quality level of the food from the response of the attached TTI. The factors that define the reliability of the TTI under variable temperature exposure are analyzed.

KEY WORDS: food shelf life, time-temperature indicators, kinetics, storage, open dating, food quality

Food quality is a dynamic state continuously changing to lower values (except for the cases of maturation and aging). Regardless of the process used, quality cannot be fixed to a constant value. What the food processor aims for are control and optimization of the initial post-process quality and control and minimization of the subsequent quality loss rates.

The food product development scientist has to achieve a delicate balance and design a safe product of superior organoleptic quality (and perhaps nutritional value) after processing that will reach the consumer's table as close to that post-process state as possible. The scientist has to achieve this by inhibiting some quality loss reactions and reducing the rate of others, using the minimum extent of processing possible, no or very few essential additives, and the most functional and cost-effective packaging. Besides quality considerations, he also has to satisfy the marketing requirements of a "high quality," "fresh," and "natural" image, attractive presentation, and competitive cost. Successful fulfillment of these goals requires intensely optimized and efficient production steps following (and often improving on) current guidelines on good manufacturing practices (GMP) and vigorous quality control of the process and product according to the principles of the hazard analysis critical control points (HACCP) approach.

Ideally this quality control would extend to the point of consumption. However, general control by the manufacturer, once the product gets into the distribution network, usually is minimal and in the best case (for the few companies that have their own distribution system) ceases at the local distribution center level. During the storage and transportation distribution phases, temperature conditions are less than ideal, and too often temperature abuses occur. Reaction rates related to quality loss characteristics are strongly temperature dependent even when the other factors are controlled and maintained at desirable levels.

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The accelerated quality losses due to the higher temperature exposures can result in recognizably unacceptable products before and at the retail level. This leads to significant direct waste. It is very difficult to obtain an accurate estimate of what this waste amounts to. The food industry has been very reluctant to disclose quantitative information on spoilage losses, let alone finance-relevant studies to determine those losses. A major report was published by the National Science Foundation in 1979 under the title "Food Losses and Wastes in the Domestic Food Chain of the United States" [*1*]. This is the most comprehensive up-to-date effort to compile such data. From this report, estimated losses during distribution for four food categories are listed in Table 1.

The percentages listed in this table refer to losses occurring from the time a product leaves its major processor or producer until it enters the supermarket. Substantial losses can happen subsequently. Quality changes in a product often are not detected until the protective packaging is removed prior to consumption. In many cases these changes do not endanger health, but do cause varying degrees of consumer dissatisfaction. Lower product quality affects consumers, who do not receive full value for their food dollar. The costs to the food industry, in addition to the direct costs of waste and returns, include the expenses in quality control, pinpointing, and handling the detected quality problems. Another very important factor is loss of sales due to consumer discontent. Even if the quality defects are due to poor handling in the distribution chain or at the retail level, factors out of the food manufacturer's control, the responsibility both legally and in the eyes of the public lies with the manufacturer.

The task of solving the aforementioned problems of waste during distribution and of guaranteeing that consumers receive a high quality product has been a primary concern of both industry and government. A system in use that aims in assuring the consumer of a high-quality product at the time of consumption is date labeling or *open dating.* This system has resulted from increased consumer awareness and the voluntary support of supermarkets. The consumer has come to feel that the "younger" the food, i.e., the less time it has spent on its way from the producer or processor to the retail market, the higher its quality. Open dating can signify the time since production or a time past which the product should not be sold or consumed. In Table 2 different alternative types of open dating in use are summarized [*2*].

Since each type of open dating has disadvantages, it was proposed that a combination of two dates as well as information on home storage conditions would be the most appropriate. For example, a "best if used within _____ days of date" stamped on the package gives the food retailers a "sell by" date (the date stamped) and a date for the consumer's guidance [*2*].

Despite the usefulness of the open dating system as an inventory control method and as a guideline to the consumers on the expected shelf life of the products, it has an important inherent weakness. It refers to only one parameter of quality loss, time. The rate of quality loss and hence the shelf life of foods, especially that of minimally processed refrigerated ones, is strongly dependent on environmental factors, most importantly temperature. Thus, any date labeling would correspond to actual shelf life only for a single set of conditions. It has been made clear that during distribution and up to the consumption point this is far from

TABLE 1—*Food losses during distribution (Source: NSF, 1979).*

Food Type	Percent Loss
Frozen foods	1.0–2.9
Dairy products	0.7–3.5
Fresh beef	4.8
Fresh produce	9.1–16.6

TABLE 2—*Types of alternative open dating.*

Types of Dating	Advantages	Disadvantages
Pack date	Easy to define Useful for stock rotation	No indication of shelf life
Sell by or *pull* date	Gives last date product can be on grocer's shelf Easily enforced Good for regulatory purposes	No indication of allowable home storage for high quality
Use by date	Straight forward Easily understood	No direct information for stock rotation. Falsely implies that after the date, food inedible or unsafe
Best if used by date or *freeze by* date	High quality date but indicates that after date food is still usable	Difficult to decide upon, regulate

true. This makes the task of deciding the "shelf life" of a product and assigning an appropriate open date a difficult task. Two alternative approaches are usually taken by food scientists.

The first involves the use of previous experience (including any available studies of the distribution system and consumer complaint records), possibly in conjunction with mathematical and statistical models, to decide on a most probable average temperature as reference. The second approach is based on the same kind of information, but a temperature corresponding to a worst case scenario is used. The first approach includes a calculated risk that the product may reach the consumer past its acceptable quality in cases of temperature abuses. This can have a serious negative effect on the manufacturer's image. In a U.S. Food and Drug Administration (FDA) survey of 1374 food shoppers, 34% found that some food spoiled or grew stale before they thought it should [*3*]. The second, conservative approach, on the other hand, leads to a significant waste of perfectly good products, since a large portion of the products will not be subjected to the assumed abusive temperature conditions.

Thus, for open dating to be useful, it has to be put in the proper perspective and be used judiciously. Consumers should not regard it as a definite indication of freshness or an absolute guarantee of shelf life but as a date that shows a reasonable estimate of the high-quality lifetime of the product assuming it was and will continue to be handled properly until the time of consumption. Open dating should not be used as a safeguard that allows distribution, retail personnel, and consumers to improperly handle a product. Combination dating types with proper handling instructions could educate them on their responsibility for proper storage.

It is obvious that even an appropriate combination of open dating falls short of giving any information on the actual distribution conditions and thus the real quality state of individual products. Ideally, what would be needed is a cost-effective way to individually monitor the temperature conditions of products throughout distribution in order to indicate remaining shelf life. Such a system could lead to effective quality control of the distribution, optimized stock rotation, reduction of waste, and some meaningful information on product "freshness," much sought by the consumer. Time-temperature indicators (TTI) are a potential answer to this problem.

Generally a TTI can be defined as a simple, inexpensive device that can show an easily measurable, time-temperature dependent change that reflects the full or partial temperature history of a (food) product to which it is attached.

TTI operation is based on mechanical, chemical, enzymatic, or microbiological systems that change irreversibly from the time of their activation. The rate of change is temperature dependent, increasing at higher temperatures in a manner similar to most physicochemical reactions. The change is usually expressed as a visible response in the form of a mechanical deformation, color development, or color movement. The visible reading thus obtained gives some information on the time-temperature conditions that have preceded it. The extent to which this information reflects a real time-temperature history depends on the type of indicator and the physicochemical principles on which its function is based. Indicators can thus be classified according to their functionality and the kind of information they convey. Different classifications and terminology have been proposed.

We propose the use of a three-category classification:

1. *Critical Temperature Indicators (CTI).* CTI show exposure above (or below) a reference temperature. They involve a time element (usually short; a few minutes up to a few hours) but are not intended to show history of exposure above the critical temperature. They merely indicate that the product was exposed to an undesirable temperature for a time sufficient to cause a change critical to the safety or quality of the product. They can serve as appropriate warnings in cases where physicochemical or biological reactions show a discontinuous change in rate. Good examples of such cases are the irreversible textural deterioration that happens when phase changes occur (e.g., upon defrosting of frozen products or freezing of fresh or chilled products). Denaturation of an important protein above the critical temperature or growth of a pathogenic microorganism are other important cases were a CTI would be useful. The "critical temperature" term is preferred rather than the used alternatives "defrost," which is too limiting, and "abuse," which might be misleading as oftentimes undesirable changes warranting a warning can happen at temperatures that are presumed within the acceptable range of normal storage for the product in question, and not as extreme or abusive as the term implies.
2. *Critical Temperature/Time Integrators (CTTI).* CTTI show a response that reflects the cumulative time-temperature exposure above a reference critical temperature. Their response can be translated into an equivalent exposure time at the critical temperature. They are useful in indicating breakdowns in the distribution chain and for products in which reactions important to quality or safety are initiated or occur at measurable rates above a critical temperature. Examples of such reactions are microbial growth or enzymatic activity that are inhibited below the critical temperature. CTTI combinations can give a discretized approximation of real time-temperature history.
3. *Time-Temperature Integrators or Indicators (TTI).* TTI give a continuous, temperature-dependent response throughout the product's history. They integrate, in a single measurement, the full time-temperature history and can be used to indicate an "effective" temperature during distribution and possibly be correlated to continuous, temperature-dependent quality loss reactions in foods. An alternative name used for TTI is time-temperature monitors (TTM).

A different method of classification, sometimes used, is based on the principle of the indicators' operation. Thus, they can be categorized as mechanical, chemical, enzymatic, microbiological, polymer, electrochemical, diffusion based, etc.

Potential Applications of TTI

The ability of TTI to function as cumulative recorders of temperature history from their activation time to the time each response measurement is taken make them useful for two types of applications. TTI can be used to monitor the temperature histories of food products during distribution up to the time they are displayed at the supermarket. By being attached to individual cases or pallets they can give a measure of the preceding temperature conditions at each receiving point. These points would serve as information gathering and decision-making centers. The decision part would involve actions such as "ship first" and "reject" and maybe immediate investigation and reporting when a serious breakdown in the distribution chain is indicated. The information gathered from all stations could be used for overall monitoring of the distribution system, thus allowing for recognition and possible correction of the more problematic links. Additionally, it would allow targeting of responsibility and guarantee the producer and distributor that they deliver a properly handled product to the retailer, thus eliminating the possibility of unsubstantiated rejection claims by the latter. The presence of the TTI itself would probably improve handling, serving as an incentive and reminder to the distribution employees throughout the chain of the importance of proper temperature storage.

The second type of TTI applications involves their use as quality monitors. With quality loss being a function of temperature history and with TTI giving a measure of that history, their response can presumably be correlated to the quality level of the food. If that can be achieved, TTI can be used in either (or both) of two ways. The first would be as an inventory management and stock rotation tool at the retail level. The approach used presently is the first in, first out (FIFO) system according to which products received first and/or with the closest expiration date on the label are displayed and sold first. This approach aims in establishing a "steady state," with all products being sold at the same quality level. The assumption is that all products have gone through uniform handling; thus quality is basically a function of time. The use of the indicators can help establish a system that does not depend on this unrealistic assumption. The objective will again be the reaching of a "steady state" situation with the least remaining shelf life products being sold first. This approach could be coded LSFO (least shelf-life first out). The LSFO system could theoretically reduce rejected products and minimize consumer dissatisfaction. Secondly, TTI attached on individually packaged products can serve as dynamic or active shelf life labeling instead of (or in conjunction with) open date labeling. The TTI would assure the consumers that the products were properly handled with respect to the time-temperature history and would indicate remaining shelf life. Of course the indicator would tell nothing about loss of package integrity.

Existing applications are few but important in that they demonstrate the TTI potential as well as highlight the areas of existing problems that need to be solved for wider application or other types of applications to be successful.

Correlation of TTI to Food Quality

Although the force behind the development of TTI has been the realization of the strong dependence of food quality on storage temperature, the extrapolation from TTI response to a value relating to food quality is not straightforward. The initial approach was to assume an overall temperature-dependence curve (or zone enclosed between two such curves) for the self life (end-point approach) of a general class of foods, e.g., frozen foods, and aim for an indicator that has a similar temperature-dependence curve for the time to reach a specific point of its scale [*4*]. Thus, a one-to-one relation between the end of shelf life and a TTI response at any temperature is established. It was soon realized that such a generalization was insufficient as even foods of the same type differed significantly in their quality loss behavior and temperature dependence, e.g., frozen foods show a Q_{10} range of 2 to 17 [*5*]. The Q_{10} is defined as the increase in the rate of loss of shelf life for a 10°C higher storage temperature. Thus a product with a Q_{10} of 2 would lose shelf life twice as fast at 30 than at 20°C.

The rule was then adopted that the temperature behavior of the TTI should match that of the particular food to be monitored [*6, 7*]. This approach essentially required an infinite number of TTI models, which, even if theoretically possible, was not practically sound. Besides temperature dependence, another point that was generally neglected was the fact that for a continuous scale, proportional correlation between TTI response and quality level of the food, the response versus time and quality versus time function should be of the same form (e.g., both linear). That was rarely considered.

The difficulty in relating food quality to TTI response led to a number of experimental studies that aimed to establish correlations between the response of specific TTI and quality characteristics of specific products. The approach used involved side-by-side storage of indicators attached to the tested foods at different temperatures, plotting the response of the TTI versus time and the values of selected quality parameters of the foods versus time, and testing the statistical significance of the TTI response correlation to the quality parameters. Studies of that type were done by Singh and coworkers at the University of California, Davis for the U.S. Army Natick Laboratory for several frozen foods [*8*] and for nonfrozen perishables [*9*]. A number of articles were based on these studies [*10–12*]. Extensive sensory analysis in addition to chemical or instrumental measurements of quality parameters of foods stored at different temperatures with TTI attached were conducted.

Although this type of study offers useful information, it also has some important drawbacks. Since they did not involve any modeling of the TTI response as a function of time and temperature, they are applicable only for the specific foods tested and for the conditions used. Extrapolation to other similar foods or quality loss reactions is not possible. Even use of the correlation equations for the same foods at other temperatures or for fluctuating conditions is not accurate. As discussed by Wells and Singh [*13*], using the correlation equations derived at certain constant temperatures to predict changes for a variable temperature profile gave relatively poor results.

Despite the potential of TTI to substantially contribute in improved food distribution, reduce food waste, and benefit the consumer with more meaningful shelf life labeling ultimately leading to higher food quality at the time of consumption, their commercial application has thus far been very limited. There are a number of reasons for this. Although the need for better temperature control of distributed food products has been understood, food producers have been reluctant to adopt the idea of TTI. The main reasons are: cost, reliability, and applicability. The cost is volume dependent, and since most indicators currently have not gone into mass production due to low demand, the cost remains high, ranging from 5 to 50 cents per unit. Nevertheless, even at these prices, if the other questions are resolved, the cost-benefit analysis could very well be in favor of the indicators.

The reliability question has its roots in the earlier history of indicators. It is based partly on exaggerated claims by manufacturers of some early models and partly on lack of sufficient data, both from the food industry and from the suppliers. As previously discussed, most evaluation studies left a lot of questions unanswered. Furthermore, early attempts in using TTI as quality monitors were not well designed and thus were unsuccessful due to poor understanding of the concepts involved. This resulted in TTI being considered unreliable. Discussions in the 1970s by a group of food scientists convened by the NSF [*1*] and by the FDA with consumers [*3*] led to the idea that the government should make use of the tags on any product with an open date mandatory. This was before the underlying concepts of TTI kinetics were understood or their reliability demonstrated and may have resulted in resistance in TTI use by the food industry since they were not proven.

The most serious problem, however, has been the question of applicability. Both suppliers and relevant publications have done a poor job in explaining how the TTI response can be used as a quality measure. Since the initial idea of TTI behavior exactly mimicking food quality deterioration behavior proved impractical in most cases, a meaningful, general scheme of correlating TTI response and quality had to be established. Often the use of the wrong type of indicator or misinterpretation of the response of a TTI as it pertains to the quality of a certain food has been attributed to unreliability of the indicator when it actually was an incorrect use of the TTI concept.

Studies conducted in the University of Minnesota by Taoukis and Labuza used chemical kinetic principles to develop a systematic approach that allows the correlation of the response of a certain type TTI to the change in quality and the remaining shelf life of a food product that has undergone any (constant or variable) temperature exposure. TTI based on different operation principles were modeled to allow integration of these TTI to the developed application scheme [14]. The reliability of the TTI in predicting quality loss of foods under variable temperature conditions was also assessed [15]. The general approach and the conducted studies are summarized in this paper.

Mathematical Analysis

Quality loss of a food is evaluated by the measurement of one or more characteristic indices that can be physical, chemical, microbiological, or sensory. The change with time of a quality parameter, A, of a food can be usually expressed [16] as

$$\frac{-d[A]}{dt} = k[A]^n = k_A \exp(-E_A/RT)[A]^n \tag{1}$$

where n is the apparent reaction order, and k is the reaction rate constant. The rate constant is an exponential function of inverse absolute temperature, T, given by the shown Arrhenius expression, where k_A is a constant, E_A is the activation energy of the reaction that controls quality loss, and R is the universal gas constant. For constant temperature, the rate equation can be solved to a simple linear expression of time

$$f(A) = kt \tag{2}$$

where $f(A)$ is the quality function of the food. The form of the quality function of the food depends on the reaction order, e.g., for $n = 1, f(A) = \ln(A_0/A)$, where A_0 is the value of the quality index at time 0.

In Table 3 typical activation energies for important deterioration reactions in foods as calculated by Labuza [16] are shown. The activation energy, E_A is found from the slope (E_A = slope*R) of a plot of the natural logarithm of the reaction rate (shelf life) versus the reciprocal of the absolute temperature. Chemical reactions usually fall within 40 to 150 kJ/mol, whereas microbial growth and destruction have higher E_A values.

TABLE 3—*Typical* E_A *values (kJ/mol) for food quality losses* [16].

Diffusion controlled	0–60	Nonenzymic browning	100–180
Enzymic	40–60	Microbial growth	60–200
Hydrolysis	50–60	Spore destruction	250–350
Lipid oxidation	80–100	Vegetative cell destruction	200–600
Nutrient loss	20–120	Protein denaturation	300–500

By integrating Eq 2, the change of the quality function during a nonisothermal temperature exposure, $T(t)$, can be calculated

$$f(A)_t = \int_0^t k\,dt = k_A \int_0^t \exp\left[\frac{-E_A}{RT(t)}\right] dt \tag{3}$$

If the effective temperature, T_{eff}, is the constant temperature that causes the same quality change as exposure to $T(t)$, the variable temperature distribution, $f(A)_t$ can be expressed as

$$f(A)_t = k_A \exp\left(-E_A/RT_{eff}\right)t \tag{4}$$

If the response X of the TTI can be mathematically modeled by a response function $F(X)$ such that $F(X) = kt$, with k an Arrhenius function of T, then the effective temperature concept can also be used for the TTI. For an indicator exposed to the same temperature distribution, $T(t)$, as the food product, the response function can be expressed by Eqs 3 and 4 in the form

$$F(X)_t = \int_0^t k\,dt = k_I \int_0^t \exp\left[\frac{-E_{AI}}{RT(t)}\right] dt \tag{5}$$

$$F(X)_t = k_I \exp\left(-E_{AI}/RT_{eff}\right)t \tag{6}$$

where k_I and E_{AI} are the Arrhenius parameters of the indicator. The application scheme shown in Fig. 1 can be used to calculate the value of the quality index A, at any time, t, from the response X of the indicator, at that time. From the measured value X of the TTI at time t, the value of the response function is calculated, from which by solving Eq 6, T_{eff} is derived. The quality function $f(A)$ is then calculated from Eq 4 using the T_{eff} and the known quality loss parameters of the food. The value of the quality index A_t that gives the extent of the quality deterioration of the food is thus derived.

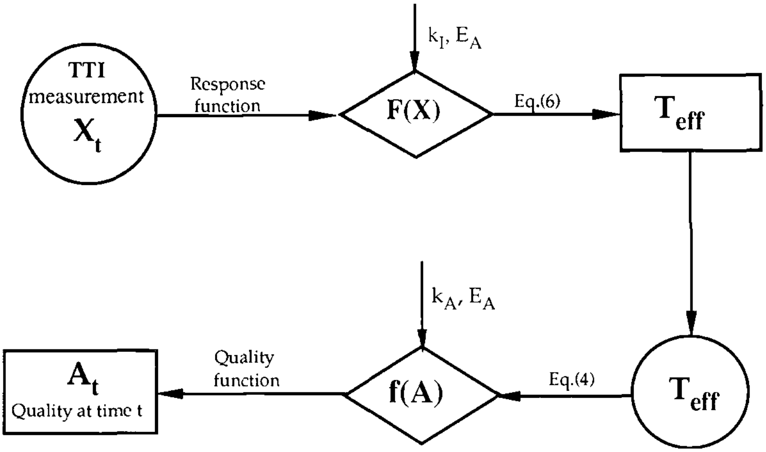

FIG. 1—*Schematic representation of the procedure for applying TTI as food quality monitors.*

Experimental Determination of TTI Response

To find the form of $F(X)$ function and calculate the k_I and E_A parameters of the time-temperature indicators, experiments under isothermal conditions were conducted. The TTI were stored at six constant temperatures ranging from 4 to 30°C in controlled (to within ±0.05°) temperature environmental chambers. Ten to twelve samples from each TTI type were stored at each temperature. TTI that were designed for use on refrigerated products were used, showing a useful response period of one to five weeks at 4°C. The three types of TTI used in the study are described below.

TTI Type I is the 3M Monitor Mark [*17*]. The measurable response, X (mm), is the advance of the diffusion front of a dyed fatty acid ester through a porous wick. Before activation the dye ester is separated from the wick by a barrier film so that no diffusion occurs. If the barrier is pulled off, diffusion progresses if the temperature is above the melting point of the ester. A prototype model with a −9°C melting point (model 4P) was used.

TTI Type II is the I-Point time-temperature monitor. Its operation principle is a color change caused by a pH decrease due to a controlled enzymatic hydrolysis of a lipid substrate [*18*]. At activation, the barrier that separates the lipase and the lipid substrate compartments is broken and the color change starts. Colors 0 (Green), 1 (Yellow), 2 (Orange), 3 (Red) visually compared to a printed reference color around the visible color window are used as a measure of change. The tag starts out green and turns to a dark red-brown color at the end. Instead of a visual measure, we measured the color of the window instrumentally with a Gardner XL-23 color meter. The tag was placed under a black blank card with a window cut out to expose only the reaction window to the detector of the color meter. The standard Hunter Lab values are directly given by the instrument where a is the green-to-red color dimension. Since the tag color went from green to red, only the a scale was used, which showed a value of 0 at the beginning (green) and went to a maximum value of 40 (red) when all the reaction possible occurred. A normalized response, X, ranging from 0 to 1 was used, where $X = a/40$. Commercial TTI models 4007, 4014, and 4021 were used in the experiments.

TTI Type III is the Lifelines Freshness Monitor®. The solid state polymerization of a thinly coated colorless diacetylenic monomer that changes to a highly colored polymer is measured as a relative reflectance change with a laser optic wand [*19*]. The data, X = % Reflectance, are stored in a handheld device. The indicator has two bar codes, one for identification of the product and the other for identification of the model of indicator. Before use, the indicators, active from the time of production, have to be stored in the freezer, where change is minimal. Commercial models 68 and 41 were tested.

From the conducted experiments a response function was defined and kinetic parameters were derived for each type of TTI. In Fig. 2 the obtained response of TTI Type I is shown as a representative example of the experimental results. The response X (mm) is plotted with time at four different storage temperatures. An $F(X) = X^2$ versus time plot at the same temperatures shows a good linear behavior, conforming to the $F(X) = kt$ equation. To determine the extent to which the temperature dependence of the response rate constants follows the Arrhenius equation, k is plotted versus the inverse of absolute temperature in a semilog plot (Fig. 3). The obtained results show a very satisfactory linear fit ($R^2 = 0.991$) and verify the assumption of Arrhenius behavior and allows the calculation of the kinetic parameters. Similarly, a well-defined $F(X)$ was determined and a good Arrhenius behavior was obtained for the other two types of TTI.

Table 4 summarizes the kinetic characteristics of the three types of TTI. It can be noted that the E_A values of the three indicators cover the range of the most important deteriorative reactions in foods.

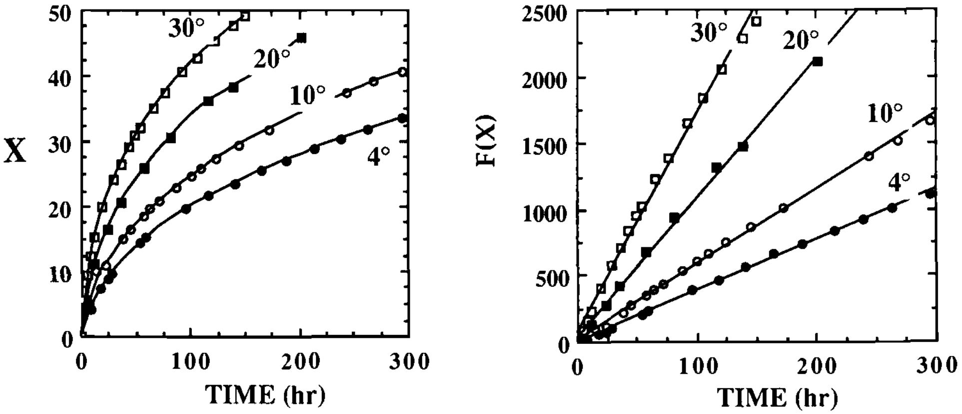

Figure 2—(a) *Plot of the response* X *(mm) versus time for TTI Type I for four constant temperatures;* (b) *Plot of the response function* F(X) = X^2 *versus time for TTI Type I for four constant temperatures. Points are average values of the response of multiple samples.*

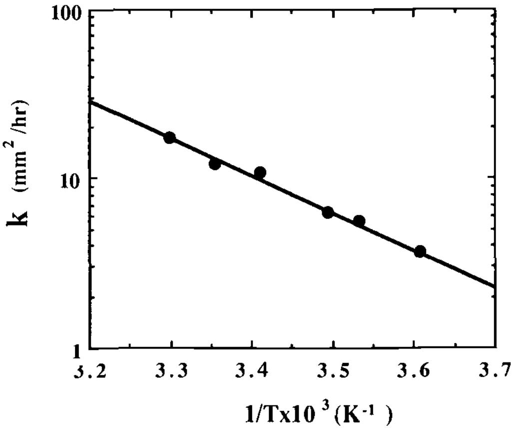

FIG. 3—*Response rate constants of TTI Type I plotted versus 1/T in a semilog scale (Arrhenius plot).*

TABLE 4—*Kinetic parameters for the three types of TTI.*

Type	Model	$F(X)$	E_A (kJ/mol)	k_I
I	4P	X^2	41.1	5.64×10^{-2} m²/s
II	4021	$[\ln(1/1 - X)]^{1/2}$	141	1.86×10^{20} s^{-1}
II	4007	$[\ln(1/1 - X)]^{1/2}$	137	7.28×10^{19} s^{-1}
III	41	$\ln(X/X_0)$	85.8	7.14×10^{9} s^{-1}
III	68	$\ln(X/X_0)$	82.4	2.62×10^{9} s^{-1}

Reliability of TTI Response

The applicability of the developed models assumes that the response of the TTI under variable temperature conditions can be predicted from the response at the isothermal conditions and is independent of the particular temperature profile. This fundamental assumption was systematically tested by nonisothermal experiments of two designs. The first study was designed to measure the so-called "history effect." Ten to twelve samples of each TTI type were stored in a controlled temperature chamber at a constant high temperature in the 20 to 30°C range for a period of time corresponding to one third of the total available TTI scale. They were then transferred to a constant low temperature of 4°C, and the rate of response at that temperature was measured and compared to that predicted from Arrhenius kinetics. The second design involved storage of twelve TTI of each type at a controlled variable sinusoidal temperature varying from 2 to 18°C every 4 h. A customized, computerized temperature controller was used to generate the desirable temperature distributions. The change in each TTI was statistically compared to that predicted from Arrhenius kinetics.

The described "history effect" experiments explore the occurrence of irreversible changes, when subjected to high storage temperatures, that will affect the rate of change at refrigerated temperatures, to an extent different than the Arrhenius relation would predict. Results from the "history effect" experiments for TTI Type I and a TTI Type II are shown in Fig. 4, where $F(X)$ is plotted versus time. For TTI Type I after exposure at 30°C for 22 h, the response at the low temperature (4°C) was not significantly different at the 95% level from the predicted. Thus, no "history effect" was shown. The same was shown for TTI Type III.

For TTI Type II (Fig. 4*b*), after exposure at high temperature the observed response of ten samples (points) at the low temperature was significantly different at the 95% confidence level from that predicted from the Arrhenius relation (solid line). The rate of change was faster than expected. The same positive history effect was observed in experiments with other models of the same series of TTI Type II. This is a negative factor as far as the accuracy of the predictions of the kinetic models is concerned. However, the occurrence of the "history effect" has been shown for deteriorative reactions in foods, e.g., in lipid oxidation [*20*] and loss of thiamin in dry foods [*21*]. Exposure to high temperatures might also accelerate microbial growth at low temperatures in foods [*22*]. In such foods, use of indicators that show a similar "history effect" might actually be beneficial.

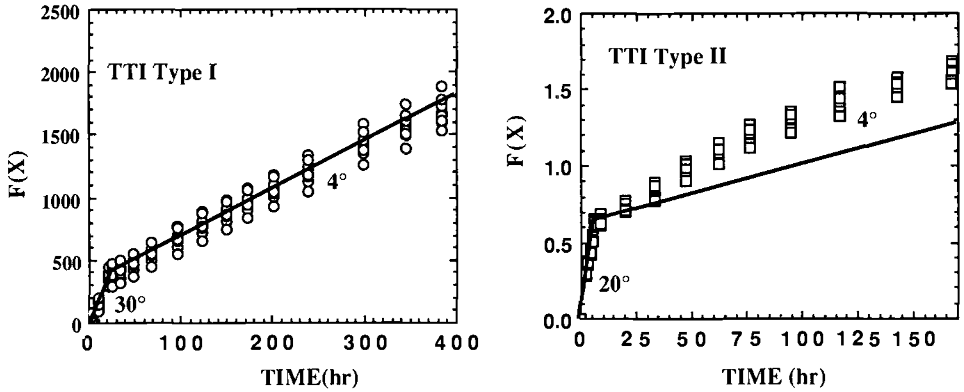

FIG. 4—*History effect study:* (a) *TTI Type I: Initial storage at 30°C followed by storage at 4°C.;* (b) *TTI Type II: Initial storage at 20°C followed by storage at 4°C. Points are observed response for twelve samples and the solid lines is the predicted response at the respective temperatures.*

For the variable temperature study the predicted and observed responses were not significantly different for all the tested TTI types. In this case of the variable sinusoidal temperature, which is representative of a more gradual and less abusive fluctuation, the "history effect" did not affect the response, probably being within the experimental variability.

With the described experiments it was established that all TTI types can be mathematically modeled, and their response under constant or variable temperature exposure follows an Arrhenius behavior (with the notable exception of TTI Type II after substantial exposure at high storage temperatures). If the kinetic parameters of the TTI and the food to be monitored by it are known, one can estimate the food quality level A at any time during the distribution from the TTI response by using the proposed application scheme. An important consideration then is the error involved in the estimation of A. This error can be due to a number of factors which collectively reflect to the accuracy with which the TTI response is translated to the actual exposure T_{eff} of the food.

There are three sources of error on the estimated T_{eff}:

1. The variation of $F(X)$ between tags under the same conditions of time and temperature. This variation can be minimized by good control of the manufacturing parameters of the TTI. It can be expressed by an average coefficient of variation of $F(X)$ under a number of different testing conditions.
2. The uncertainty in the Arrhenius equation that models the temperature behavior of the tag and allows the estimation of the T_{eff} from $F(X)$. This can be statistically expressed by the confidence limits (e.g, at the 95% level) of the values of the E_A and k_I parameters obtained by the linear regression fit of the Arrhenius plot.
3. The third error in T_{eff} involves an important underlying assumption of the application scheme—that the effective temperature of the food is equal to the effective temperature of the TTI for a given temperature distribution. This is true only when the activation energies of the food and the TTI are equal. Computer calculations with a number of assumed variable temperatures showed that if the activation energies of the food and the TTI differ by less than 10 kcal/mol, that is $|E_{A\text{TTI}} - E_{A\text{food}}| < 42$ kJ/mol, then the two T_{eff} differ in general by less than 1°C. The maximum error in T_{eff} is obtained in cases of abrupt stepwise changes between two temperature extremes. In this case the error in T_{eff} can be as high as 1.5°C as seen in Fig. 5 for a temperature changing between 2 and 18°C, where the error in the esti-

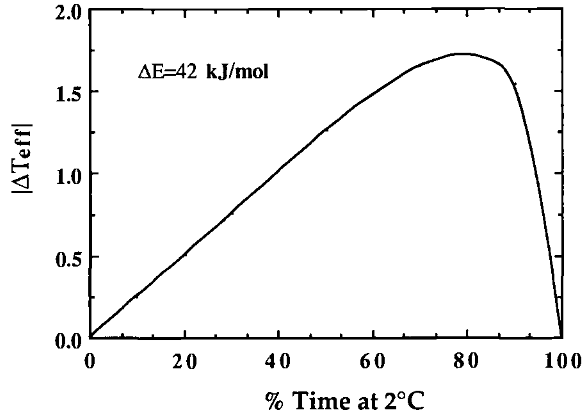

FIG. 5—ΔT_{eff} *caused by a 10 kcal/mol difference in the activation energies of the food and the TTI for different stepwise temperature profiles between 2 and 18°C.*

mated T_{eff} caused by a difference of 42 kJ/mol in the activation energies of the TTI and the food is plotted versus the % time of storage at the low temperature of 2°C.

The error due to the E_A difference, in contrast to the previous two, is systematic and not random. Thus, if the activation energy of the TTI is larger than the one of the quality loss reaction of the food, the T_{eff} of the TTI will be larger than the actual T_{eff} for the food. An appropriate correction factor could then be introduced. Such a factor could be based on simulations of a large number of actual distribution exposures and is under development.

In general the TTI manufacturer can express the reliability of a tag by giving the expected error in T_{eff} estimation. A ΔT_{eff} of 1°C is a reasonable target. Such an error in T_{eff} was calculated to cause an error of 7 to 19% in the estimated $f(A)$ for foods with activation energies of 40 to 125 kJ/mol, respectively.

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Flavor and Aroma Permeability in Plastics

REFERENCE: DeLassus, P. T. and Strandburg, G., "**Flavor and Aroma Permeability in Plastics,**" *Food Packaging Technology, ASTM STP 1113,* D. Henyon, Ed., American Society for Testing and Materials, Philadelphia, 1991, pp. 64–73.

ABSTRACT: Plastics have evolved into sophisticated food packages. This evolution requires flavor management from the package. Flavor loss can occur from a variety of mechanisms. Of particular interest are flavor losses that result from interactions of flavor molecules with the package. This paper presents the permeability, *P*, and the component parts, the diffusion coefficient, *D*, and the solubility coefficient, *S*, for selected flavor molecules. Use of these parameters to estimate flavor loss is included. The effects of temperature, humidity, concentration of the flavor, combination of flavors, size of the flavor molecule, and type of flavor molecule on the diffusion and solubility coefficients are discussed.

KEY WORDS: permeability, solubility, coefficient, diffusion, sorption, temperature, flavor, humidity, concentration, size

Flavor management for food products is important because people want food that tastes good. In addition to safety and nutrition, people expect food to retain the original flavors and to be free of alien flavors. In this paper, "flavor" is used in a broad nontechnical way that includes several human responses to both chemical and physical stimuli.

The retention of original flavors includes both chemical and physical considerations. Chemical reactions can remove original flavors from the food. Typical reactions include oxidation, hydrolysis, and decomposition. The reaction products, regardless of intrinsic flavor properties, are commonly viewed negatively. The reaction products represent excursions from expectations. Important physical processes can affect flavor retention when plastic packaging is used. Sorption of flavors *into* the plastic and subsequent diffusion *through* the plastic can remove flavor from a food product. In some cases, the removal could occur broadly across all the flavor components of the food product. This would lead to flavor diminution. In other cases, and perhaps worse, the removal could occur selectively. This would lead to an imbalance of the flavor while possibly retaining the flavor intensity. A weak "good" flavor is more likely to be acceptable than a strong "off" flavor.

This paper will review those physical interactions between food and plastic packaging that can lead to loss of flavor. Much of the information has been published in more detail. The reader is directed to the references for clarification. The data and methodology are applicable to flavor ingress also. Chemical reactions will not be treated.

Permeation

The permeation of a small molecule species (hereafter, the permeant) in a polymer is a multistep process. The permeant must collide with the polymer and adsorb to the surface.

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Then the permeant must dissolve into the polymer. In a series of random "hops," the permeant, on average, will move from the place where the concentration of its own kind is high to a place where the concentration is low. For an original flavor molecule, this means net motion from the inside surface of the package to the outside surface. At the outside surface, the permeant must come out of solution, desorb from the surface, and escape into the environment. In many situations, flavor molecules can move relatively freely in the food and in the environment. Typically, the surface properties of the polymer are not sufficiently different from the bulk properties to make an important difference. This means that the steps of solution and diffusion are dominant. Hence, the permeability, P, as shown in Eq 1 is an important property of the polymer.

$$P = D \times S \tag{1}$$

where

D = the diffusion coefficient, and
S = the solubility coefficient.

The permeability is a measure of the overall migration rate of a permeant through a polymer film. Equation 2 is an adaptation of Fick's first law of mass transport to a package.

$$\frac{\Delta M_x}{\Delta t} = \frac{PA \, \Delta p_x}{L} \tag{2}$$

where $\Delta M_x/\Delta t$ = the quantity of material x that crosses a film of area A and thickness L per unit time when the pressure difference of material x between the two sides of the film is Δp_x.

What is currently known as Fick's first law was expanded from the original expression [1] by Wroblewski [2] assuming that Henry's law was obeyed for the sorption of the penetrant. Equation 2 simply restates Wroblewski's result in parameters that are familiar in packaging. This equation applies to steady state only. It does not apply to the transient period that precedes steady state when the first permeant molecules are still working their way through the polymer.

The diffusion coefficient is a kinetic term that describes how fast a permeant molecule moves in a polymer host. It is also a measure of how much time is required to reach steady state after an initial challenge. The diffusion coefficient is determined by the size of the permeant and the size and frequency of fluctuations in the openings between polymer molecules. The diffusion coefficient is a combination of geometry and thermal effects. Large permeants, tight polymers, and low temperatures lead to low diffusion coefficients.

The solubility coefficient is a thermodynamic term that describes how many permeant molecules move in a polymer host. It is determined by all the usual parameters of solutions including temperature, chemical activities, and intermolecular interactions plus the state of the polymer relative to its glass transition temperature.

Experimental Considerations

Simple permeability data are inadequate for modelling the interactions of flavor molecules with plastic packaging. This is a consequence of the large solubility coefficients and the small diffusion coefficients. At ambient temperatures, the time to reach a steady-state permeation condition can range from a few minutes for a thin polyolefin film to many months for a barrier film. In many cases, the steady state is not reached during the storage time of the food in the package. Yet the solubility coefficients are so large for flavors in polymers that important depletion can occur before steady state is reached. Important quantities of flavor may never permeate through the film to the external environment; however, with a knowledge of the diffusion coefficient and the solubility coefficient, an estimate of flavor loss by sorption can be made.

Published reviews describe several methods to calculate P, D, and S in a single experiment [*3,4*]. The experimental technique and instrumentation for the data in this review have been described previously [*5,6*]. Briefly, the experimental procedure includes preparing a dilute solution of flavor(s) in nitrogen. This solution is introduced to the "upstream" side of the experimental film at $t = 0$. On the "downstream" side of the film, clean nitrogen gas sweeps past the film to a mass spectrometer. The mass spectrometer has been precalibrated and set to monitor the experimental flavor(s) continuously. Low concentrations of flavor compounds are used, always less than 10% of the saturation vapor pressure, typically about 100 ppm (mol/mol in N_2). This avoids the complications of concentration-dependent permeation that will be discussed later.

The permeability can be calculated from Eq 2 using the steady-state data. The diffusion coefficient can be calculated with Eq 3 where $t_{1/2}$ is the time to achieve a transport rate ($\Delta M_x/\Delta t$) that is half of the steady-state rate [*7*].

$$D = L^2/7.2t_{1/2} \tag{3}$$

Finally, the solubility coefficient can be calculated using Eq 1. These calculations ignore crystallinity in the film; hence, they yield "effective" values of P, D, and S.

The diffusion coefficient can be used to estimate the penetration depth (L^*) of a permeant in a polymer film [*8*]. Equation 4 shows this relationship where t is the time from initial challenge.

$$L^* \simeq 2(Dt)^{1/2} \tag{4}$$

Equation 4 starts with Eq 3 and assumes that the time to reach steady state is about $1.8t_{1/2}$. Both Eqs 3 and 4 apply for a diffusion coefficient that is not altered by the permeant concentration. The penetration depth can be used to estimate the quantity of permeant that has been absorbed (Q). Equation 5 shows this relationship where A is the package area and p_x is the pressure of the flavor permeant in the food.

$$Q = 0.5SAL^*p_x \tag{5}$$

Equation 5 applies to a linear concentration gradient in the polymer film where the equilibrium concentration at the surface is Sp_x and the concentration at the penetration front is zero. The average concentration would be $0.5Sp_x$. The volume of penetration is AL^*. Equation 5 expresses the fact that the amount absorbed is the product of the average concentration and the penetration volume.

The pressure of the flavor permeant can be a vapor phase pressure or the equivalent Henry's law pressure of the flavor dissolved in the food.

For those cases that *do* reach steady state during the storage time (for times sufficient to make $L^* = L$ using Eq 3), knowledge of P is required to consider losses to the environment in addition to losses by sorption in the package wall.

Test Parameters

Experiments have been conducted to study several interesting packaging variables, namely, temperature, humidity, concentration of the flavor, combination of flavors, size of flavor, and type of flavor. Usually several film types were tested, and *P*, *D*, and *S* were determined. Some of these experiments are reviewed here.

Temperature

Figure 1 shows how the permeability, diffusion coefficient, and the solubility coefficient vary with temperature for ethyl hexanoate at 12 Pa partial pressure in a vinylidene chloride copolymer film. The permeability increases with increasing temperature. Although in theory it is possible for the permeability to decrease with increasing temperature, the authors have never observed such a case. The diffusion coefficient increases with increasing temperature. This effect is universal. At higher temperatures the permeant and the polymer are more active. This means that "hopping" by the permeant in the polymer will be more frequent. The solubility coefficient decreases with increasing temperature. Another way to say this is that the heat of solution is negative. The heat of solution is the sum of the heat of condensation and the heat of mixing. Although the heat of mixing may be either positive or negative, it has a small magnitude. The heat of condensation is always negative and usually has a large magnitude for large molecules. Hence, the heat of solution for flavors in polymers is negative. This appears to be a general rule with flavors in polymers.

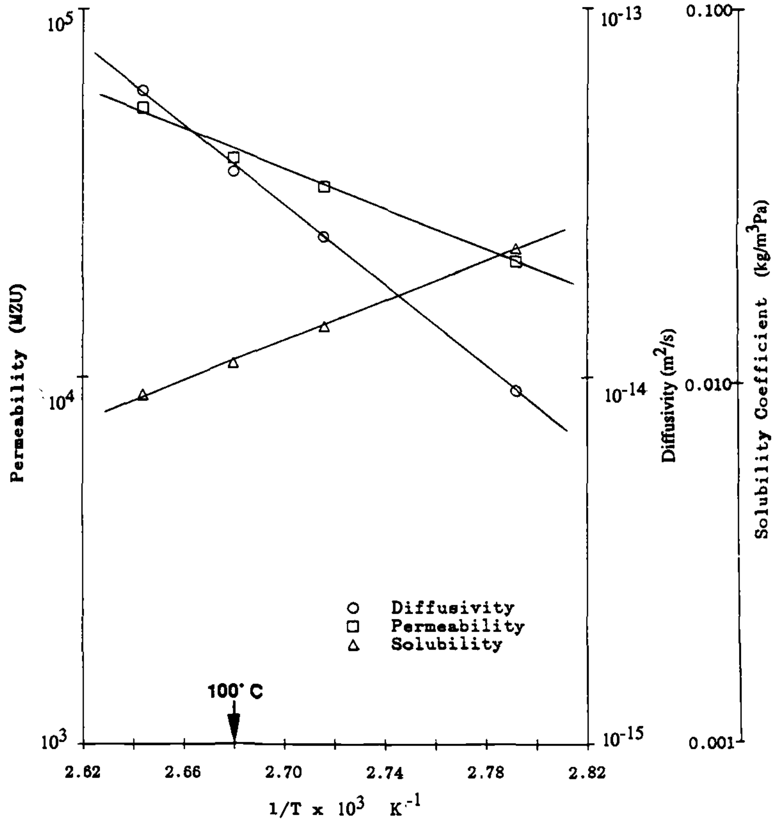

FIG. 1—*Permeability, diffusivity, and solubility coefficients of ethylhexanoate in a vinylidene chloride copolymer.*

Since *P*, *D*, and *S* change with the temperature, it is important to use data at the correct temperature when considering the suitability of a package for an application. Furthermore, there is a trap in accelerated testing based upon increased temperature. Increasing the temperature increases *D*, which speeds the test toward conclusion. However, a decreasing solubility coefficient might decrease the potential loss. A false sense of security or risk might result.

Humidity and Plasticizers

Plasticizers often increase the permeabilities of permeants in polymers by increasing the diffusion coefficient. Some polymers absorb enough water from the local environment that a plasticizing effect results. The effects of plasticizers and humidity on the permeability of oxygen in two good barrier polymers—vinylidene chloride copolymers and hydrolyzed ethylene-vinyl acetate copolymers (EVOH)—are well known [*9,10*]. The effects of plasticizers and humidity on the permeability of flavors has been determined recently.

Table 1 shows the permeability of some flavor and solvent molecules in a vinylidene chloride copolymer film both with and without plasticizer [*11*]. The permeabilities have been extrapolated from higher temperature experiments because, even with plasticizer, the vinylidene chloride film is a good barrier with a low diffusion coefficient for flavors. The higher temperature experiments shortened the experimental time and increased the transport rate above the detection limit of the instrument.

The plasticizer causes a large increase in the permeability of these permeants. For the same films the oxygen permeability would increase by a factor of 10 [*9*].

The effect of humidity on the permeability of d-limonene at about 14 Pa partial pressure in an EVOH film has been studied [*12*]. The EVOH was a blend of copolymers having 44 mol% and 32 mol% ethylene. Figure 2 shows the permeability in the film. The experiments with the dry EVOH were done quite warm because the dry film is a very good flavor barrier. An extrapolation to cooler temperatures is suggested in the figure. Below the glass transition temperature, the permeability would be between the extreme limits that are shown with the dashed lines. In a second set of experiments, water vapor at 100% RH was mixed with the d-limonene test vapor. The downstream side of the film was kept dry. The permeability increased greatly. When the temperatures of the dry experiments were used, the transport rate swamped the mass spectrometer detector. Hence, a cooler temperature was used. The results at the cooler temperatures were about 1000 times higher than the extrapolated dry data. The diffusion coefficients and the solubility coefficients were determined also. The sol-

TABLE 1—*Effect of plasticizer on the permeability of flavors and solvents in a vinylidene chloride copolymer film at 25°C.*

Permeant	Permeability, MZU	
	Without Plasticizer	With Plasticizer[1]
d-Limonene	180	8800
Benzaldehyde	4200	27000
Styrene	160	30000
Heptane	800	3200

NOTE: 1 MZU = 10^{-20} kg·m/m^2·s·Pa.

[1] About 6 phr (parts per hundred resin) total of epoxidized soybean oil and acetyl tributyl citrate.

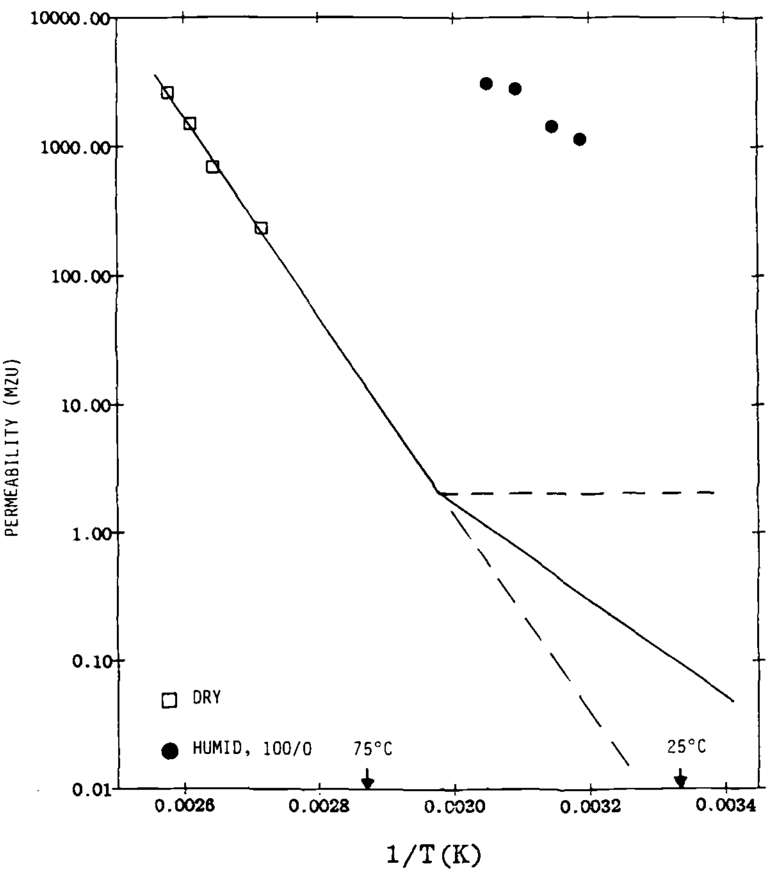

FIG. 2—*Permeability of d-limonene in EVOH 44/32 film.*

ubility coefficients were not affected by the humidity. The diffusion coefficients were about 1000 times higher with humidity. Water acts as a strong plasticizer in this system.

Similar experiments were performed with a vinylidene chloride copolymer film. The humidity did not affect the permeability.

Concentration

The concentration (or partial pressure) of flavor in equilibrium with a plastic can affect the permeability of the flavor. The solubility coefficients for flavors in plastics are high. Hence, when a large concentration of flavor exists in a food, the plastic could sorb enough flavor to be plasticized. The plasticizing effect could increase the permeability.

Permeation experiments have been done with different concentrations of flavor permeant. One source reports that no concentration effect was observed for the permeation of trans-2-hexenal, as apple aroma, in low density polyethylene [5]. Table 2 shows the results with the permeant concentration expressed in ppm (moles of permeant per mole of nitrogen carrier gas) and the partial pressure of the permeant.

On the other hand, Giacin and Hernandez report a strong effect of permeant concentra-

TABLE 2—*Permeability of trans-2-hexenal in low density polyethylene at 28°C.*

Permeant Concentration, ppm	Permeant Concentration, Pa	Permeability, MZU
72	7.2	1.17×10^6
144	14.4	1.16×10^6
216	21.6	1.53×10^6
288	28.8	1.18×10^6

NOTE: 1 MZU = 10^{-20} kg·m/m^2·s·Pa.

tion [*13*]. Zobel presents data that resolves the apparent contradiction [*14*]. He studied d-limonene permeation in polypropylene at 25°C. He found that, at permeant pressures less than about 10% of the saturated vapor pressure, the permeability was not affected. However, at permeant pressures above about 15 to 20% of the saturation vapor pressure, he found that the permeability increased sharply with increasing permeant pressure. Landois-Garza and Hotchkiss found that the permeability of ethyl propionate through dry polyvinyl alcohol was independent of concentration below about 30% of the saturation vapor pressure [*15*]. Above this concentration the permeability rose sharply. The data in Table 2 cover the range of 2 to 10% of the saturated vapor pressure of d-limonene. Giacin's studies were at higher concentrations. All the data are consistent when there is no plasticizing effect at low permeant pressures and a strong plasticizing effect at larger permeant pressures.

To model the permeation performance of a flavor in a plastic package, the concentration (or equivalent Henry's law pressure) of the flavor must be considered. When the flavor is in the food at very low concentrations, a simple situation probably exists. However, when a flavor is present closer to its saturation limit, a more complicated situation exists that requires specific data.

Competition

Foods typically have many flavor compounds that comprise the total flavor profile. If the components compete for solutions sites in a polymer or in some way facilitate solubility, the permeation could be affected. Table 3 shows the results of a study of apple flavors in low density polyethylene [5]. Four experiments are represented. First, three single permeant experiments were done at 144 ppm. Then a fourth composite experiment was done in which all three components, each at 144 ppm, were tested. The mass spectrometer detector was programmed to monitor each component separately. The permeabilities of two components rose slightly. The permeability of one component dropped slightly. In the composite experiment, the total concentration of permeants was 432 ppm. There *might* have been a slight

TABLE 3—*Multiple component permeation in low density polyethylene at 28°C and 144 ppm.*

Component	Permeability Alone, MZU	Permeability Together, MZU
Trans-2-hexenal	1.2×10^6	1.9×10^6
Hexanal	1.8×10^5	3.4×10^5
Ethyl-2-methylbutyrate	2.5×10^5	1.8×10^5

plasticizing effect. However, as a whole, no large effect was observed because of the combination of flavors. Other similar experiments confirm this. It appears that single component data may be used to model multiple component permeation of flavors.

Size of Flavor/Type of Flavor

Larger flavor molecules diffuse more slowly in a polymer than smaller flavors molecules. Larger molecules must wait for larger openings to occur in the polymer matrix before hopping. Figure 3 shows the diffusion coefficient for two families of permeant at 10 to 18 Pa partial pressure in a vinylidene chloride copolymer film. For both the linear esters and the *n*-alkanes, the diffusion coefficient decreases smoothly as the size of the permeant increases. When the oxygen in the ester backbone is counted as a carbon and the pendent oxygen is ignored, the diffusion coefficients for the two families fall on the same curve. For linear mol-

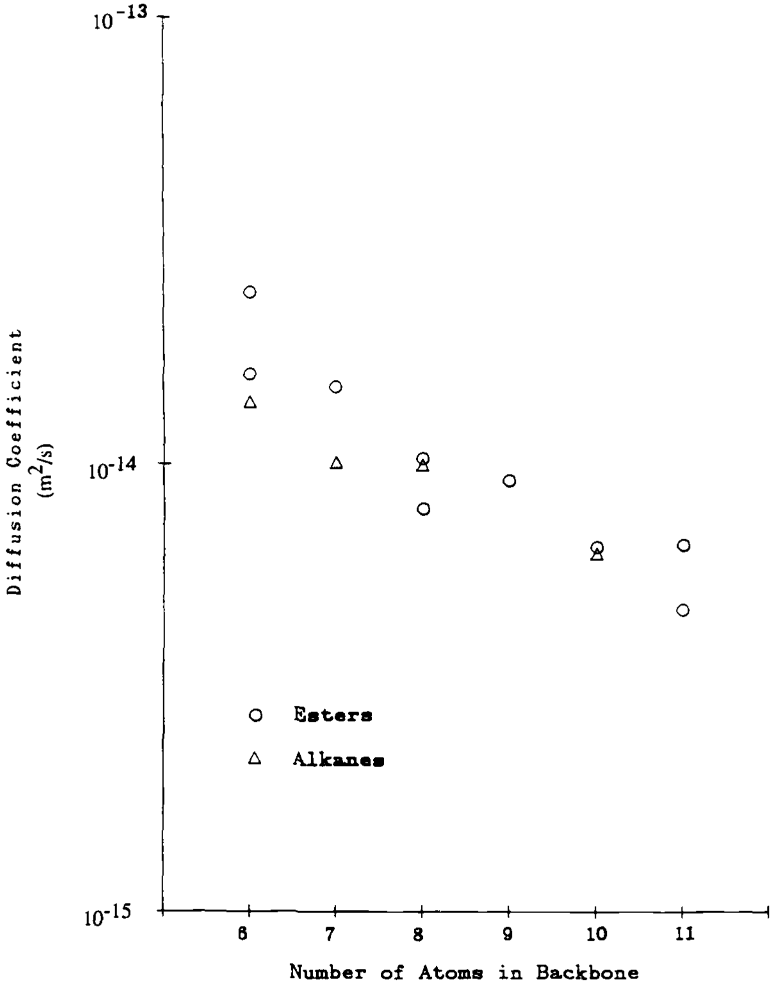

FIG. 3—*Diffusion coefficient at 85°C of esters and alkanes in vinylidene chloride copolymer.*

ecules, the diffusion coefficient changes slowly as the permeant changes size. For more spherical molecules, the diffusion coefficient is expected to change more rapidly [*16*].

The solubility coefficient has been observed to be strongly related to the boiling point within a family of permeants. Figure 4 complements Fig. 3. Figure 4 shows the solubility coefficients for linear esters and *n*-alkanes in a vinylidene chloride copolymer film. There is a strong correlation with the boiling point within a family. As the boiling point increases, the solubility coefficient increases. The act of solubilization from the vapor phase into a polymer may be analyzed as condensation followed by mixing. Within a family of permeants, the heats of condensation vary more than the heats of mixing, hence the solubility coefficients follow the boiling points closely. However, from family to family, the heats of mixing can vary greatly. Hence, there can be a large difference between families. The polar esters have a more favorable heat of mixing in this polar polymer. The nonpolar alkanes are much less soluble in this polar polymer. For very large esters and alkanes the difference between the families should become very small as the ester functionality is diluted and the ester becomes more alkane-like. The data in Fig. 4 anticipate this since the curves seem to converge at a larger size.

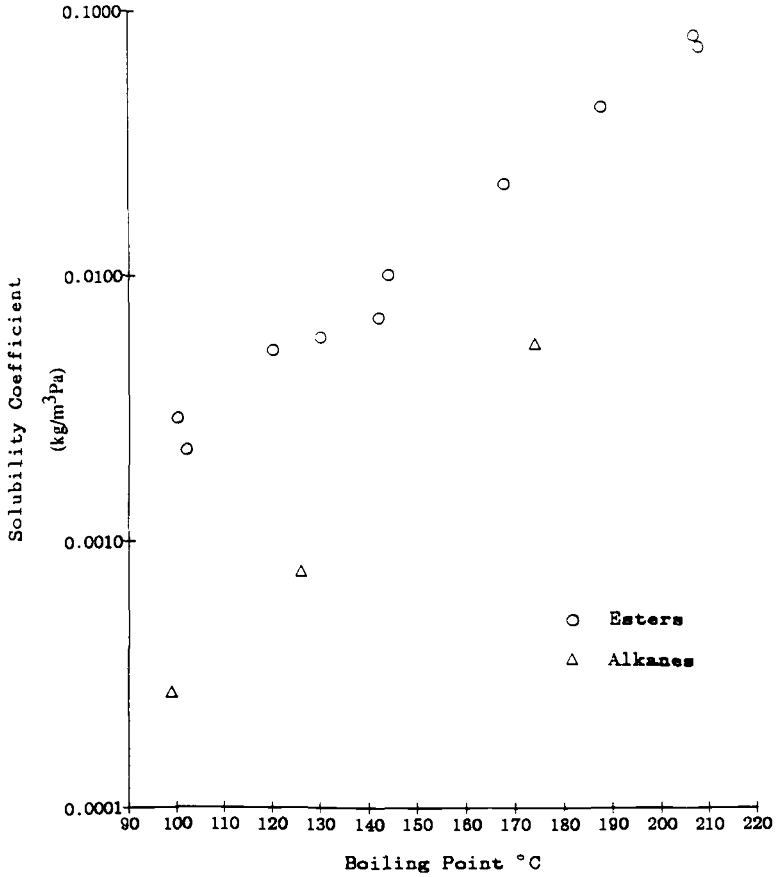

FIG. 4—*Solubility coefficient at 85°C versus boiling point of esters and alkanes in a vinylidene chloride copolymer.*

Predicting the diffusion coefficient in a given polymer now requires only a few data for molecules of various sizes. Predicting the solubility coefficient is a little more difficult since it requires some data from the same chemical family.

The permeability may increase or decrease with increasing size of permeant. When the solubility coefficient varies more rapidly than the diffusion coefficient, as it does in these two examples, the permeability increases with increasing permeant size.

Summary

The permeation of flavors in polymers is a function of several important variables. However, each variable contributes to the whole in a simple way. Experimental data may be applied successfully only if the important variables of temperature, humidity, and concentration are included.

Experimental data are sparse now. However, with an improved understanding, predictions will soon be possible to estimate permeation attributes. That understanding will be couched in the fundamental parts of the permeability, namely the diffusion coefficient and the solubility coefficient.

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Packaging for the 90's: Convenience Versus Shelf Stability or Seal Peelability Versus Seal Durability

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ABSTRACT: As the popularity of shelf-stable convenience foods increases, there is an emerging need to develop reliable, polymer-based food packages with peelable, heat-sealed lids for foods packaged under hot-fill, aseptic, or retort processes. For these products, seal integrity and package durability are critical to product safety and consumer acceptance. These concerns, in conjunction with the need to provide the convenience of peelable lids, give rise to the challenge of evaluating various aspects of package performance influencing seal integrity, durability, and peelability. Proper evaluation of these parameters requires testing techniques that yield data that are indicative of the attribute under consideration. The results of these tests, along with some fundamental understanding of mechanical and chemical properties of the materials being used, are key factors for measuring the performance of the package "system." Today, there are a variety of proprietary procedures for evaluating critical aspects of package performance. The plethora of test methods needs to coalesce into a set of standardized procedures that can be used to provide meaningful product performance data communicated in a common language that can be utilized and understood by all of the diverse groups involved in taking a packaging "system" from a concept to the grocery shelf. This need is critical in markets where issues such as consumer safety and liability risks are major factors influencing packaging acceptance.

This presentation provides a detailed review of techniques and equipment developed for easy-to-use, reproducible, standardized procedures to evaluate the performance of polymer-based food packages. It also discusses test results and their relationship to package performance. The discussion will focus on test methods, including equipment and instrumentation, applicable to:

1. Container seal integrity.
2. Lid peelability.
3. Container abuse resistance.

Normalized test data are used to supplement the discussion of the procedures utilized. The impact of fundamental specimen properties, instrument response limitations, and other factors influencing the results will also be reviewed.

KEY WORDS: sealability, peelability, heat seal, opening force, peel force, abuse resistance, burst resistance, product resistance

A wide variety of test methods are used to evaluate and predict food package performance. Indeed, the meaningfulness and validity of test procedure responses are critical as they should imply not only package characteristics which bear on peelability or other convenience ori-

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ented attributes, but also consumer safety. A failed seal is a major package defect which usually results in product spoilage. However, in the case of low-acid food products such a failure can lead to microbiological contamination and hence the possibility of the consumer's contraction of associated diseases (e.g., botulism). This event is potentially disastrous for the consumer and food packer alike.

Bearing these thoughts in mind, the authors will identify critical variables encountered in the testing of shelf-stable heat-sealed food packages and demonstrate how those variables impact on test results. Additionally, the responses measured in package evaluations will be related to package performance in terms of seal integrity, peelability, and durability/abuse resistance.

The processing which a seal must undergo is determined by the type of product being packaged. Hot filling is used to package high-acid foods such as applesauce. In this process the container is filled with a product at a temperature typically between 70 and 95°C, then sealed. The heat of the product upon introduction into the container is sufficient to kill agents which may cause spoilage of such a product, such as mold or yeast. Low-acid food products, on the other hand, require more stringent sterilization methods such as retorting or aseptic processing. Aseptic filling processes involve individual sterilization of the container, lid, and product, followed by filling and sealing the container in a sterile environment. The sterilization techniques may include exposing the lidding and container to antiseptic agents followed by drying at high temperatures. Finally, for products requiring retort processing, the container is filled and sealed and then sterilized by heating the package for a time sufficient to effectively kill off biological contaminants (e.g., 120°C for 1 h). These processes may include exposure of the seal to elevated temperatures following sealing. Additionally, the seal may be required to support stresses arising from pressure fluctuations outside the container (in the case of retort processing) or pressure buildup inside the container (in the case of hot-fill processing).

Obviously, the development of new package systems is a critical, complex process which includes extensive evaluations from package component qualification through commercialization. As a whole, testing of the package attempts to characterize the sealability/peelability, processibility, and durability (including both abuse and product resistance) of the package. Each test is aimed at quantifying particular performance characteristics of the package or its components. Major points of concern are that test results truly relate the characteristic under test and that a meaningful criterion against which the result can be judged exists.

Evaluation of Sealability and Peelability

Typically, container materials are determined by cost and barrier requirements. The evaluation of a lidding material's seal performance, when mated with a preselected container material or heat-seal substrate, is of primary concern. This evaluation is the preliminary step by which candidates for sealing layers are screened.

Basic Evaluation of Peelability

The objective of a seal layer's evaluation is to establish its range of sealability and level of peelability. The first step in such an evaluation is to seal "coupons" of the lidding to the heat-seal substrate. The coupons are subsequently cut into strips of a standard width of 1 in. as final preparation for heat-seal bond measurement, then peeled. This procedure is referred to as the flat strip heat-seal test.

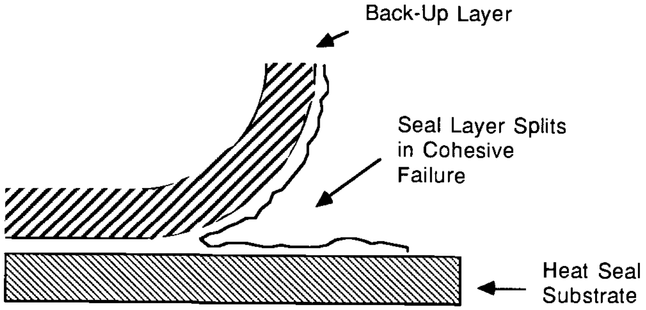
The sealing layer must be coated or laminated onto a backup layer (e.g., aluminum foil) for this evaluation. The seal and peel characteristics of the layer under examination will be influenced by the backup layer's thermal characteristics. For that reason, the structure of the backup layer used in screenings should be as similar as possible to that which will be used in commercial applications. Additionally, screenings of seal layers should be performed at heat-seal conditions which simulate those which the material will be exposed to in commercial use.

Critical Responses of the Flat Strip Heat-Seal Test

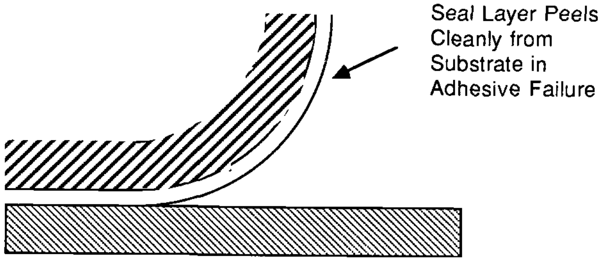
The critical responses recorded during heat-seal bond measurements are the bond strength and the mode of failure observed during peel. The two basic modes of failure that can be observed are "cohesive" and "adhesive" (Fig. 1). Unfortunately, evaluation of failure mode is inherently subjective, and accurate observation often requires an understanding of the mechanical character of the materials under test in addition to a trained eye.

Material-Test Parameter Interactions in the Flat Strip Heat-Seal Test

Critical parameters of the heat-seal bond test are the peel geometry (the angle relative to the plane of the heat-seal substrate at which the specimen is peeled from the heat-seal substrate), peel rate, and specimen temperature for a given type of lidding. These three param-



Strength of Heat Seal Layer is Weak Binding Force in Cohesive Failure



Adhesion Between Heat Seal Layer and Substrate is Weak Binding Force in Adhesive Failure

FIG. 1—*Illustration of cohesive and adhesive modes of separation.*

eters, acting simultaneously, set the distribution of energy expelled between bond rupture and viscous and elastic deformation of the specimen. The relative impacts of these three parameters on the peel are dependent on the mechanical properties and relative layer thicknesses of the specimen under test. The effect of peel rate is partially a function of the mechanical properties of the specimen, but also has an influence which is independent of material properties. For example, if one desires to force a fluid through an orifice at some increased flow rate, then the pressure drop across that orifice must be increased. In the same way, the force required to separate a bond at a higher peel rate must increase with increasing peel rate. In both cases the energy spent is completely dissipated.

The peel angle influences the radius of curvature of the specimen at the peel line (location where the seal layer separates from the substrate). For example, in Fig. 4, the peel angle imposed on the specimen is 90°, and if the specimen was pulled from the substrate in a pure shear mode (pulled to the left) the peel angle would be 0°. The peel angle of 90° will induce some radius of curvature of the lidding specimen at the peel line. If that peel angle was increased (i.e., the direction of the force applied to the specimen was greater than 90°), then the radius of curvature would decrease. The point at which the measured heat-seal bond becomes affected by the peel angle is, to a large degree, dependent on the structure of the specimen under test (i.e., the magnitude of the effect of peel angle on the radius of curvature of the specimen at the peel line depends on the rigidity of the seal and backup layers of the specimen).

Peel rate and angle can be set reproducibly with the use of a suitable tension testing machine and accompanying fixtures. Several methods have been accepted by ASTM for the measurement of adhesion between two flexible substrates [ASTM Test Method for Peel or Stripping Strength of Adhesive Bonds (D 903-49); ASTM Test Method for Peel Resistance of Adhesives (T-Peel Test) (D 1876-72)] as well as between one flexible layer and one rigid substrate [ASTM Method for Climbing Drum Peel Test for Adhesives (D 1781-76); ASTM Test Method for Floating Roller Peel Resistance of Adhesives (D 3167-76); ASTM D 1876-72). Additionally, a fixture has been developed at Alcoa Laboratories which is successfully used for measurement of the bond between one flexible substrate and semirigid substrate (Fig. 2). This fixture imposes a 90° peel angle on the specimen for the entire measurement cycle.

The effect of temperature on bond measurement may not ordinarily be considered critical as such measurements are generally carried out at room temperature, which is nominally stable. Indeed, for some combinations of seal layer and heat-seal substrate, the sensitivity of the heat-seal bond to typical fluctuations in room temperature can be considered negligible (Fig. 3). In the case of many flexible packaging materials, where the active sealing components of the materials are polymeric, the transitions in mechanical properties of those sealing components from rubber-like to fluid-like occur gradually over wide temperature ranges. Hence, the adhesion between layers can decrease dramatically, albeit gradually, as temperature increases.

It has been demonstrated at Alcoa Laboratories that reliable measurement of elevated temperature heat-seal bonds can be performed using an Instron tensile tester which has been fitted with an Instron Model 3111 temperature chamber. This equipment was used to generate the data presented in Fig. 3. Studies have revealed that for test temperatures of up to 150°C a 5-min temperature stabilization time (time required for specimen to come to temperature following installation in chamber) permits the specimen temperature to equilibrate. Heat-seal strengths can be measured at 180 or 90° peel angles, using the appropriate fixtures. The information generated with this method is critical to the qualification of seal layers for high-temperature applications.

ASTM Test Method for Effect of Moisture and Temperature on Adhesive Bonds (D 1151-

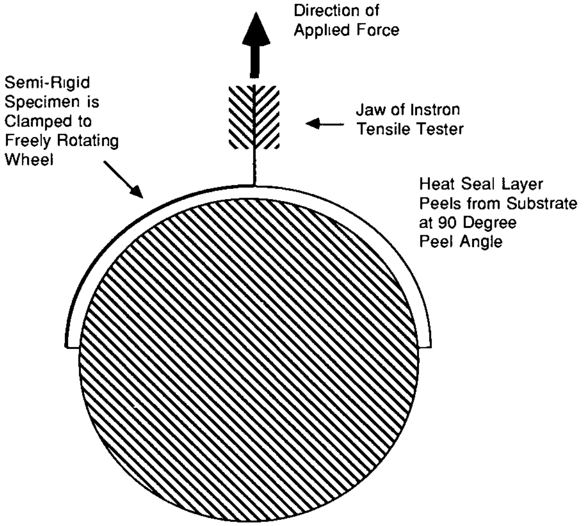


FIG. 2—*Illustration of fixture used for peeling heat-seal bond specimens at a constant 90° peel angle.*

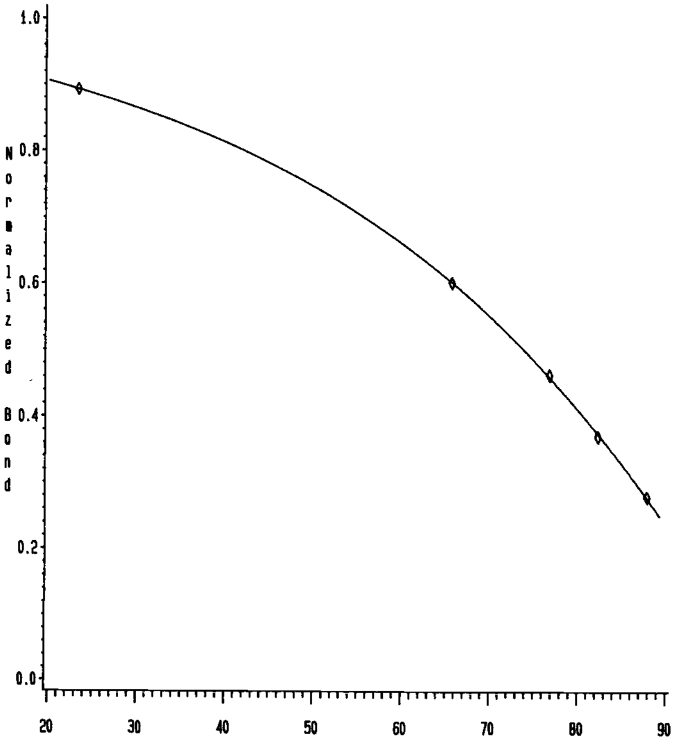


FIG. 3—*Effect of temperature on heat-seal bond.*

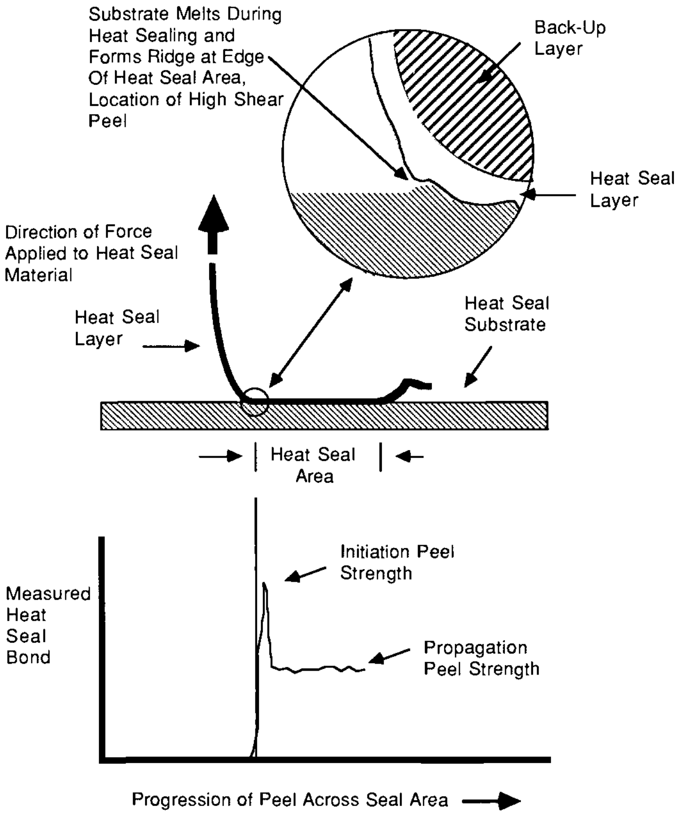


FIG. 4—*Effect of edges of heat-seal area on the measured heat-seal bond strength.*

84) addresses testing the effect of moisture and temperature on adhesive bonds. The procedure described above conforms with most guidelines in this standard. Preconditioning, which is discussed in the ASTM standard, is achieved by keeping all samples in a controlled temperature/humidity room. Humidity in the test chamber is not controlled.

The question of which part of the bond test data to use often arises as there may be a large degree of variation within a single measurement. Spikes in the heat-seal bond measurement may be observed at the beginning and end of the peel of strip-type specimens (Fig. 4). The nomenclature commonly used to denote these spikes is "initiation peel." The relatively smooth region between the points of initiation peel is commonly known as "propagation peel." As shown in Fig. 4, at peel initiation points the heat-seal substrate can be sufficiently deformed in the heat-seal process such that the effective peel angle in that area of the specimen causes a large degree of the bond separation to occur in shear mode, rather than the tensile peel mode. Crack propagation phenomena also bear on the difference between initiation and propagation peel. Therefore, the propagation peel data can be used to more clearly quantify the adhesion between two heat-sealed layers than the initiation peel because it is not confounded with effects generated at the edge of the heat-seal area. Indeed, the propagation peel mode is more representative of the peel mode induced when opening heat-sealed containers.

Seal Processibility and Product Resistance

After determining a lidding material's sealability and peelability to a specified substrate, the integrity of the seal under the pertinent processing conditions should be determined. Specifically, the ability to maintain seal integrity following exposure to elevated temperatures (associated with the food at fill and/or postfill sterilization conditions) and the food product must be quantified.

Temperature Considerations

Hot product fill and/or high temperature sterilization lower the seal strength of the polymers sealed to one another (as discussed above). Seal performance under such conditions can be inferred from the results of elevâted temperature bond measurement (as discussed above).

Product Resistance Considerations

Testing of seal resistance to a given product requires the measurement of seal strengths before and throughout a specified period of product exposure.

Since most products will be stored at room temperature, this is the preferred condition of storage. However, when time constraints do not permit long-term aging tests, "accelerated aging" at elevated temperatures may be required. In such a test, it is important to not use a temperature which is below the softening temperature of the sealant or the heat-seal substrate or a temperature which might cause unrealistic effects. A suggested temperature is 38°C, but correlations between elevated temperature and room temperature aging must be established.

Heat-seal/product interactions can be evaluated using flat strip heat-seal, pouch, or sealed container type specimens. Obviously, performing such tests with sealed containers affords the most comprehensive evaluation. Testing with flat strip heat-seal specimens exclusively relates information regarding the heat seal/product interactions, whereas evaluations with filled and sealed pouches relate the lidding material's product and seal resistance. In all cases, specimens not exposed to the packaged product should be tested as control samples [as suggested in ASTM Test Method for Heat and Moisture Resistance of Wood-Adhesive Joints (D 4502)]. Initial exposure times should include one hour, one day, one week, and four weeks. Related ASTM standards include ASTM Test Method for Resistance of Adhesive Bonds to Chemical Reagents (D 896-84) and ASTM Recommended Practice for Determining Durability of Adhesive Joints Stressed in Peel (D 2918-71). Because minor changes in food composition can result in substantial changes in aggressiveness, the specific product to be packaged is recommended for testing. Additionally, actual product/package processing conditions should be reproduced as closely as possible.

Evaluation of Container Seal Integrity and Durability

There are several characteristics of a container seal which reflect its integrity and durability: opening force, burst resistance, leakage, and abuse resistance. These characteristics are inherently complex ones which depend on a host of factors which are specific to end applications. Such factors include container size and shape, container flange dimensions and shape, container processing, and food product type. As with the testing of container components, the effects of testing practices and test parameters on results must be taken into account in the interpretation of test data.

Container Opening Force

The characteristic most easily related to "fundamental" testing of package components is the container opening force. The required container opening force is a feature of the package that is, to a large degree, specified by the market place. For example, consumers prefer container opening forces in the range of 3 to 5 lbf. However, for low-acid products, such as meats, packers may opt for seal layer/container combinations with higher heat-seal bonds for added assurance of seal durability.

The opening force is defined as the maximum force required to peel the lid from the container flange. This maximum or peak occurs where the width of the seal under peel is at its maximum width (Fig. 5). It should be noted that as the container peel is advanced beyond the location just described, the force required to remove the lid decreases dramatically (typically by a factor of 2 to 4). This level is defined as the container peel force. While the peel

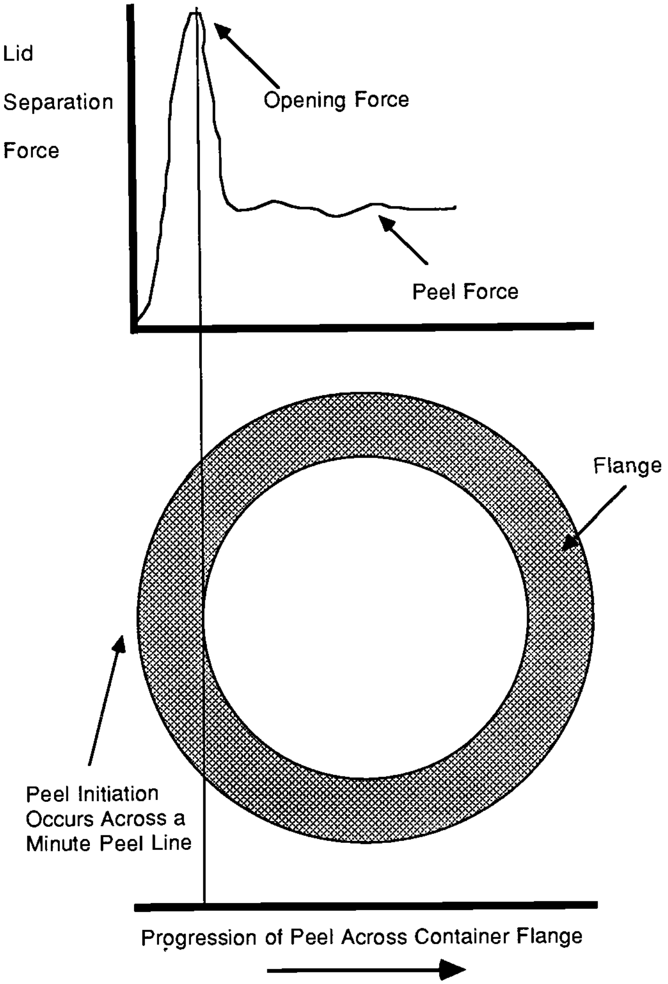


FIG. 5—*Illustration of the peel location-lid separation force relationship.*

force is representative of what an end customer will see, it is not as critical as the opening force from the consumer's standpoint and does not exhibit a direct correlation to the heat-seal bond strength as does the container opening force. This lack of correlation is related to the influences of combined tensile and shear peel experienced during the peel and is beyond the scope of this discussion.

All factors which bear on the flat strip heat-seal bond test results (discussed above) bear on the opening force measurement as well as container flange dimensions and seal geometry. Among those factors is the initiation peel strength of the seal layer. However, in the case of container opening, the initial separation of the seal layer from the container flange occurs across a minute peel line, as opposed to a peel line 1-in. wide in the case of flat strip peel tests, and its effect is diminished accordingly. Control of the peel angle during container opening is accomplished by using the fixture shown in Fig. 6. The fixture is compatible with an Instron tensile tester and provides a reproducible test condition.

Burst Resistance

Burst resistance, or burst pressure, is defined as the internal container pressure (over ambient) required to cause failure of the container seal and is generally considered as an indication

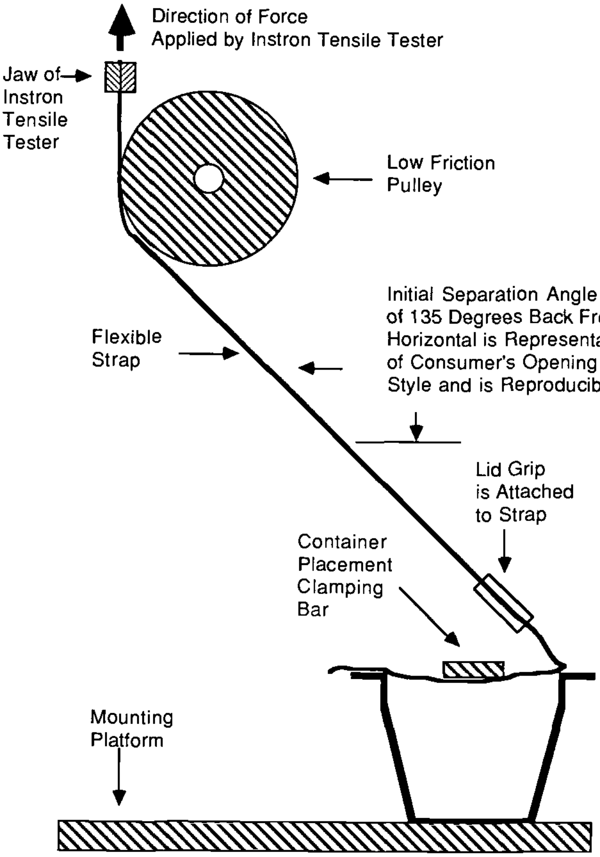


FIG. 6—*Illustration of Instron compatible peel test fixture.*

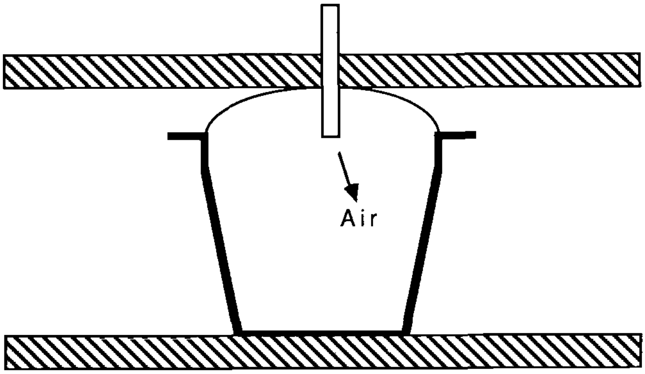


FIG. 7—*Burst test with lid restraint and (positive) internal pressurization.*

of seal "robustness" (i.e., abuse resistance). Burst resistance is of particular interest in situations where stress, due to pressure differentials across the container lid (which may be encountered in retort and hot-fill processing), must be supported by the container seal. However, it is a complex measurement from the standpoint of variables which can bear on results.

There are basically two test parameters which are predetermined: container pressurization rate and restraint height. The pressurization rate is simply defined as the rate at which the internal pressure of the container under test is increased. The restraint height is defined as the free distance above the container flange through which the lid is allowed to expand.

The introduction of restraint height into the burst test relates to the retort process. Containers are packed into "cars" in some brands of retort equipment. These cars, which are in turn loaded into the retort chamber, may hold containers at vertical spacings which would restrict the expansion of the container lids should the retort pressurization system fail. Lid restraint was thus introduced into the test to simulate this effect.

Several burst test methods have been encountered (Figs. 7, 8, and 9) which incorporate various methods of pressurization. Experience has shown that the methods illustrated in Figs. 7 and 9 offer more consistent pressurization than the method illustrated in Fig. 8. The vacuum test (Fig. 9) utilizes external vacuum to generate a pressure differential. The expansion of the lid may or may not be restrained. In some applications, lid expansion is unrestrained but is measured. In that case, if any decrease in lid expansion is observed during the test a

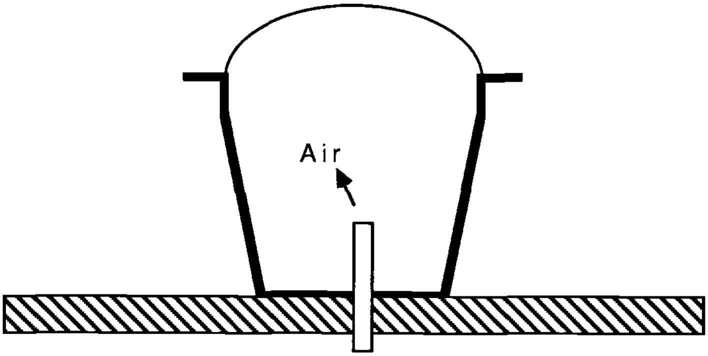


FIG. 8—*Burst test with puncture of container wall and no lid restraint.*

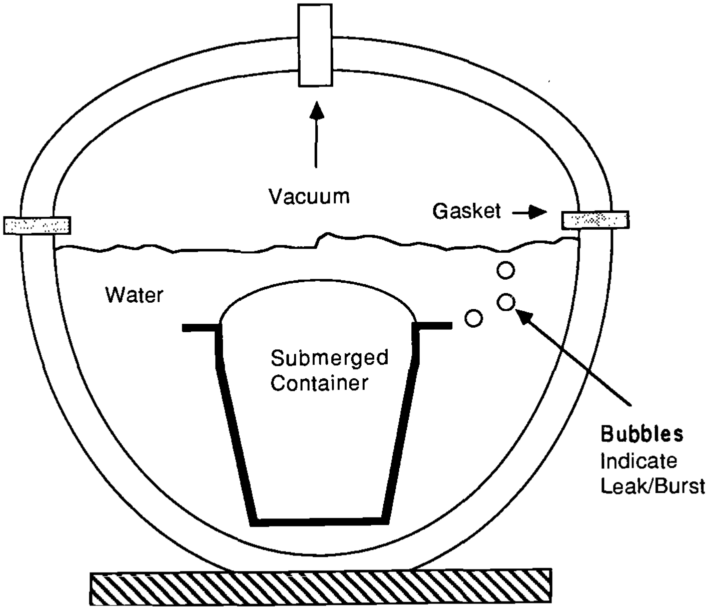


FIG. 9—*Burst test with application of partial vacuum to entire container (bell jar test).*

decrease of internal pressure differential due to a leak is the cause, and the pressure at which the leak appeared is recorded as the burst pressure.

The sensitivity of burst test results, using the test method illustrated in Fig. 7, to restraint height and pressurization rate has been examined. A "2 by 2 factorial with center-point" type designed experiment which covered the high and low practical limits of restraint height and pressurization rate was used to perform this evaluation. The experiment revealed that restraint height has a significant influence on the burst test result, while the pressurization rate and the pressurization rate-restraint height interaction are statistically insignificant, over the experimental region examined. The response surface illustrating the dependent-independent variable relationship is shown in Fig. 10. The deviation between measured and predicted values of burst pressure is shown in Fig. 11. The predicted values used for this comparison were derived from the statistical analysis.

Correlation Between Container Test Method Results

Container test results are of greatest value if they can be used to infer several characteristics regarding a container's peelability or durability. Bearing this in mind, the correlations between container opening and peel forces and burst pressures (measured from commercially sealed containers) were analyzed. The containers were sealed over the entire seal range (from undersealed to oversealed). The results of the analyses revealed that the correlation between either opening force (Fig. 12) or peel force (Fig. 13) and burst pressure had approximately the same precision.

The data and accompanying analyses indicate that although peel force is not related to the adhesion of a seal layer to a container, it is relatively sensitive to both opening force (a measure of peelability) and burst pressure (a measure of abuse resistance). However, the opening force also shows correlation, at a statistically significant level, to the burst pressure and

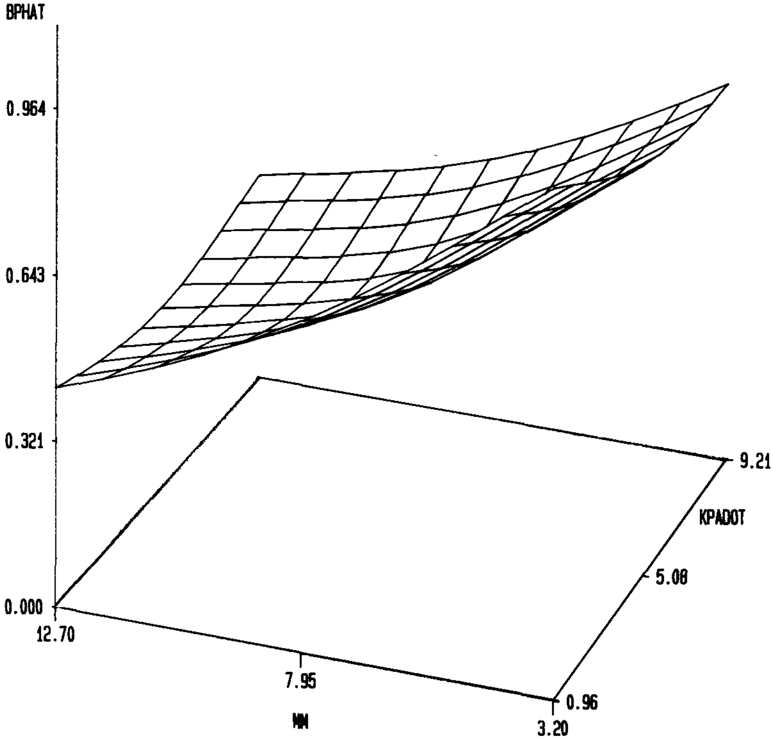


FIG. 10—*Predicted response of burst pressure to restraint height and pressurization rate.*

reflects the seal layer-container heat-seal bond. Figure 15 presents a graphical translation of these interrelations. The latter attribute of opening force is of particular value as it may possibly be used to check the operation of sealing equipment or even consistency of sealing materials. Figures 12, 13, and 14 illustrate individual data points, best fit line, and 95% confidence intervals about those fits.

Container Seal Leak Testing

Container seal integrity is probably the most critical package attribute the packer must provide from the standpoint of consumer safety. Several types of bench top seal integrity or seal leak testers are commercially available. The same technologies that some of these bench top testers employ has or is being incorporated into on-line testing units which are intended to provide 100% package inspection. Some test methods are theoretically capable of detecting leaks or holes in the package as a whole as opposed to detecting leaks in the seal alone.

All the leak test methods described below involve the application of a "positive" or "negative" external pressure to some portion of or the entire container. The simplest of these test methods is described in ASTM Test Method for Leaks in Heat-Sealed Flexible Packages (D 3078-84) (refer to Fig. 9) and relies on the experimenter's observation of air bubbles leaking from a sealed container submerged under water and exposed to negative pressure. A primary limitation of this and other methods which impose a negative pressure on the subject container or seal is that seal leaks, especially smaller leaks not easily found by visual inspection of a container seal, are prone to being plugged by the product inside the container.

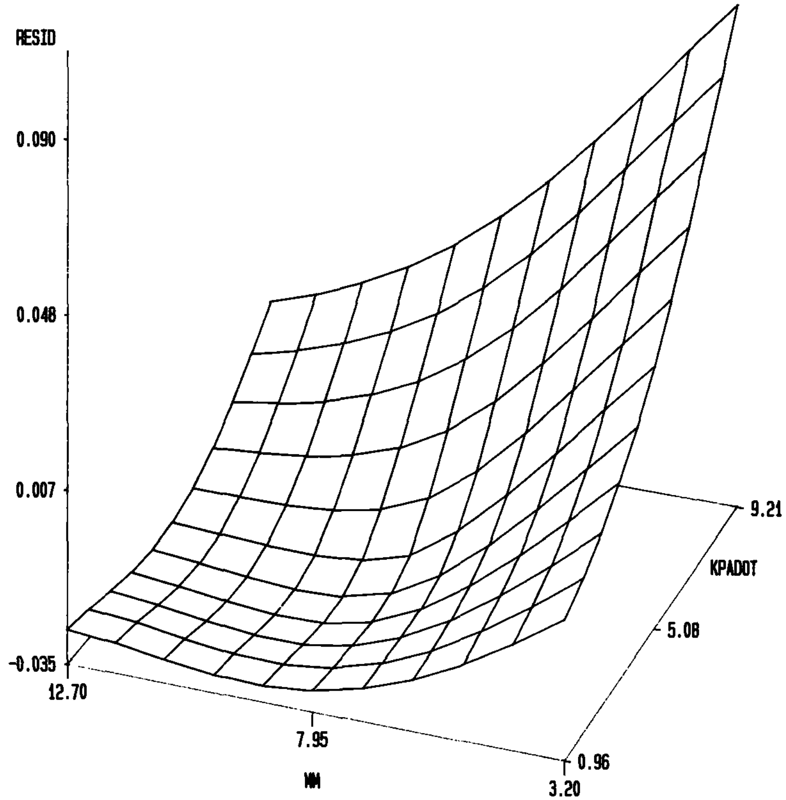


FIG. 11—*Residual error of empirical burst pressure relationship.*

Other leak test methods employ high air pressure directed at the container seal. If a seal leak is present, air passes through the seal leak and begins to "inflate" the container, thus raising the lid. If such deflection of the lid is detected, the container fails the leak test. Two variations of this test method are commercially available, with the basic difference lying in the method of confinement of applied air pressure. The method which is most effective (Fig. 16), at least theoretically, forms a seal pressurization chamber by supporting the underside of the container flange with a gasket and "blowing" the overhanging lidding up against a restraint plate forming the second gasket. Hence, no external force is applied to the container seal. However, another method uses gaskets clamped against the bottom and top of the container flange, thereby exerting a clamping force on the container's seal. The fault of this method is that leaks otherwise detectable can be effectively closed by this clamping action.

Container Abuse Testing

The general objective of container abuse testing is to evaluate the container seal's ability to maintain integrity through package processing and shipping. ASTM Method for Drop Test for Loaded Boxes (D 775-80) and ASTM Test Method for Mechanical-Shock Fragility of Products, Using Shock Machines (D 3332-88) can be used to evaluate this facet of seal performance. Several test methods recommended by the United States Department of Agriculture[2] (USDA) treat container drop, shipping, and vibration-type abuse resistance. Additionally, test methods recommended by the USDA include procedures for container preparation which may enhance the resolution of the tests (e.g., dyeing of test container's contents for visual identification of ruptured seals). It is advisable to incorporate burst testing into the evaluation of container seal durability at intermediate stages of the abuse testing. The continuous response of the burst test will provide benchmarks throughout the testing program, potentially indicating partial damage (as opposed to a ruptured seal) to the container at various stages of abuse testing. Such a method would necessitate beginning the test with a number of containers which would permit burst testing of a statistically valid number of specimens at each intermediate step, as well as the final stage of the abuse test.

Additionally, it is reasonable to apply these tests to heat-sealed containers in general, regardless of size or content, as the tests are pertinent to the condition which most or all containers will experience in shipping and handling. However, the acceptable failure rates or performance levels of containers holding various products may vary in relationship to the food packer's liability risk associated with specific products.

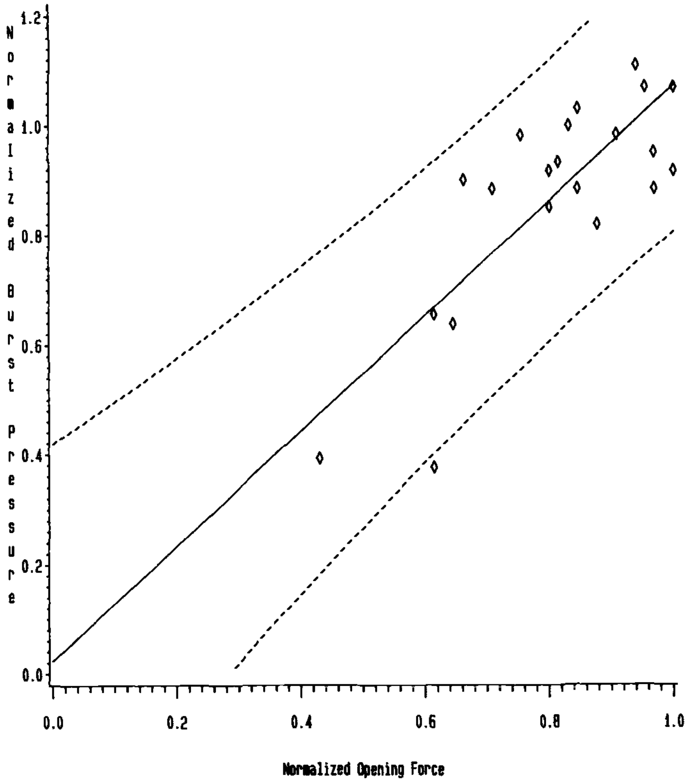


FIG. 12—*Comparison of correlations between container test methods (burst pressure versus opening force).*

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[2] United States Department of Agriculture, Processed Products Inspection Division, "Test Cycles for Small Size Semi-Rigid Containers," 1982.

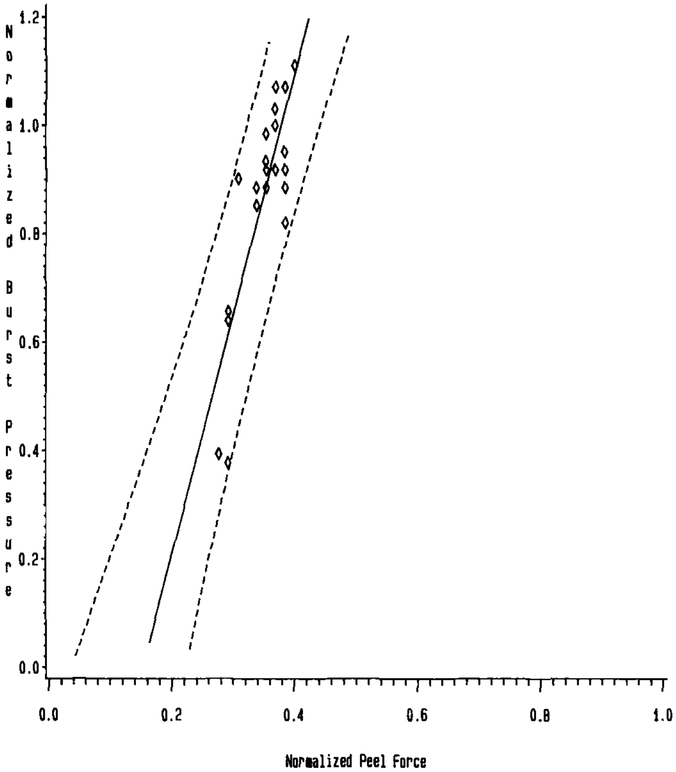

FIG. 13—*Comparison of correlations between container test methods (burst pressure versus peel force).*

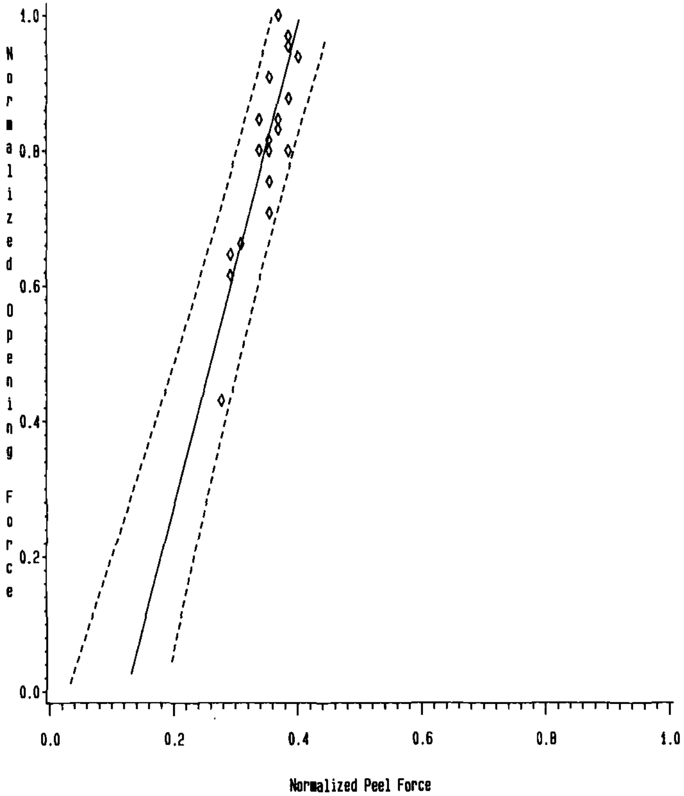

FIG. 14—*Comparison of correlations between container test methods (opening force versus peel force).*

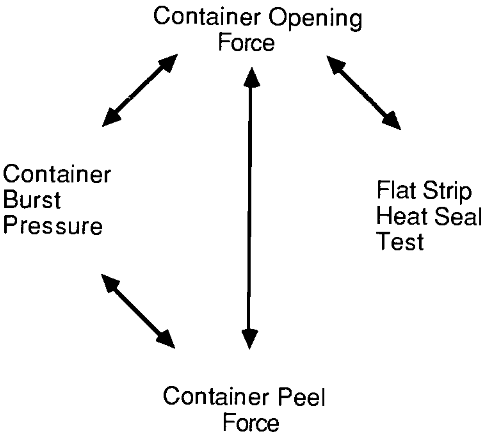

FIG. 15—*Interrelationships between measurement results.*

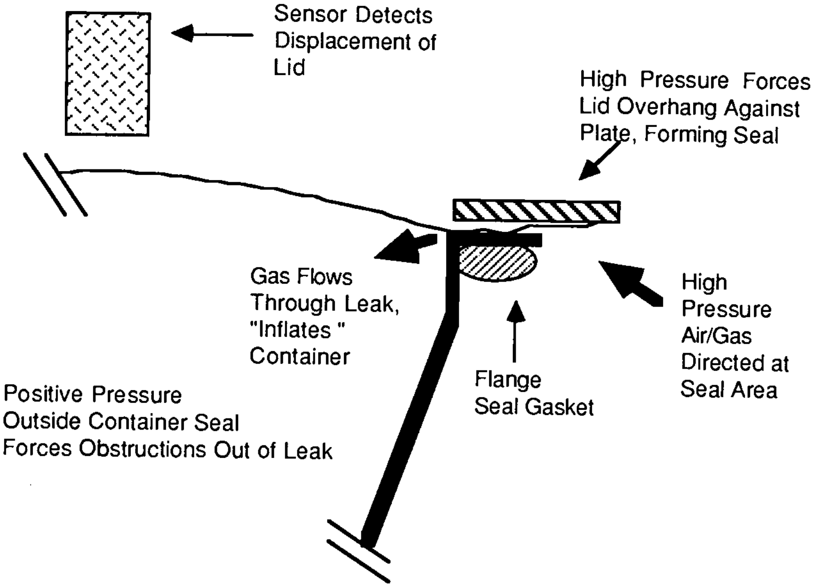

FIG. 16—*Leak detection by pressurization of container seal area, measurement of lid displacement.*

Conclusions

Even though reproducible measurement conditions can be imposed on specimens under test, results must be reviewed critically to confirm the validity of those results. For instance, should the seal layer delaminate from a laminated lidding material, the delamination will have a significant influence on the measured "apparent" bond strength. Such an event is quite critical from the standpoint of result validity but cannot be resolved in the output of the tensile testing instrument. For this reason it is very important to establish, as part of test methods, the recording of observations concerning test results which cannot be related solely by instrumentation. Examples of such pertinent information are modes of failure during peel, the cleanliness of peel (e.g., the observation of "stringing" of the seal layer). Such information is critical to the understanding of package performance. To reiterate, numbers alone do not paint a complete picture.

A thorough understanding of the interactions between specimen material properties and test conditions is often required to accurately evaluate the causes of seemingly anomalous test results. Determinations based on misunderstanding can result in discounting valid information, or perhaps more seriously, accepting or misinterpreting results which do not reflect the characteristics of a specimen under examination.

Another critical point is that those (i.e., technicians) performing measurements should understand and account for the effects of test parameters on results. The appreciation of these interactions is the primary motivation for the establishment of standardized test procedures. However, in this era of heat-sealable/peelable closures new and nonstandardized tests are being used for the evaluation of food packages and their components. In many cases individuals performing tests cannot be expected to fully understand the interactions of test parameters and packaging components. The factors contributing to those interactions relate to complex mechanical properties (including time and temperature dependence) of polymeric materials as well as the interactions between those material properties and mechanics of the test apparatus. In many cases, these interactions can only be deduced through the application of advanced experimental methods and detailed knowledge of material science and mechanics.

Furthermore, the need for criteria by which to judge test results is as pressing as the need for test methods. In the case of peelability, acceptable ranges of container opening force are basically market driven, making the criteria for related test results rather clear. In the case of burst pressure, it is commonly held that "more is better," but a precise value of burst pressure required to insure a container's processibility or abuse resistance is not currently in hand. Such criteria can be developed based on correlations with seal integrity failure rates and other results which are indicative of end performance requirements.

Satisfying the needs mentioned above will require significant amounts of time and commitment. However, the need for standardized test procedures in an industry which is following a trend leading to more critical performance requirements is a current one. A reasonable solution is for representatives of appropriate segments of the industry to collaborate and arrive at a basic set of standardized tests and pass/fail criteria that can be used to judge the performance of semirigid food containers which employ heat sealable/peelable closures, and provide for revisions to those methods as limitations of applicability become understood.

Overview

Food safety is a top issue today. Consumers are informed daily of the link between diet and health along with reports of potential food risks, such as microbial contamination, chemical adulteration, nutritional hazards, and illegal food additives. Another potential danger is that of the food package itself. What is the safety provided by the package and its interaction with the food it contains?

During the past ten years, a virtual explosion of new food product introduction has been witnessed, demonstrating a six-fold growth from 1980 to 1990. The industry has become technically more complex as new ingredients, additives, and processing techniques are introduced. The revolutions in food packaging and marketing are posing new challenges to food safety assurance.

Consumers have come to expect more of government regulators and the food industry and are asking pertinent questions related to the safety of the food supply. With regard to food packaging, questions are asked such as: How much product protection do packages supply? Do they help to preserve the nutritional worth of the food supply? Does packaging act as a source of food-related health risks by directly or indirectly contributing substances to products such as toxins or chemicals? Does packaging extend or shorten the shelf life of products? How are food packages developed, and what is the criteria for the packaging material selection?

These and other questions are being asked by the members of the F-2 Committee on Flexible Barrier Materials. The symposium on Food Packaging Technology from which this volume was taken was organized to provide a forum for the discussion of the research and test methods currently in use by members of the food and packaging industries along with academic interest. The nine papers presented at the symposium review emerging technologies in the food packaging industry. The topics include extended shelf life of food products through the use of computer modeling, time-temperature indicators, and a total system approach based on the dynamics of the food-packaging and distribution systems. Emerging markets for shelf stability versus convenience in packaging, material test method development, and new applications for high barrier plastics packaging are also discussed.

The paper by *Cage* provides a comprehensive overview of the basic principles of food packaging development, from conception to distribution; technological breakthroughs and ecological and environmental concerns are discussed.

Marsh, Ambrosio, and *Guazzo* demonstrate how one company confirmed a product's two-year shelf life in three months of research time, allowing for early product introduction with the most reasonable packaging cost. Computer modeling techniques were employed, and novel analytical procedures were developed and used for both product information and computer input.

Harte et al. evaluate the change in mechanical properties of polymers due to sorption of flavor compounds. Flavor component scalping by polymeric films is an important factor in the quality of flavored products, and the selection of appropriate packaging materials is aided by knowing the mechanical response of polymer sealant film in contact with aroma/flavor components. Sorption of three plastic films that are potential candidates as food contact material are investigated.

The use of ethylene vinyl alcohol copolymer (EVOH) resins in high-barrier plastics packaging is discussed by *Schaper.* The types of processing used with EVOH resins and how the use of these resins compare with alternative forms of packaging are reviewed, along with new and existing resin properties and applications.

Techniques used to measure the oxygen transmission rates of packaging films under humid conditions are described by *Pike.* Various methods of humidifying gas streams used in the standard methods for dry gas transmission rate measurements and the controlled humidity "sandwich" method are given. The new Modern Controls' "H-System," designed specifically for this purpose, is also described, along with advantages and disadvantages of each method.

Gyeszly contends that shelf life modeling must be based on the entire food packaging and distribution systems for selecting optimum packaging. A total system approach to modeling shelf life of packaged food products is described. Discussion of the major parameters of the shelf life simulation model includes recommendations for developing product and distribution-specific models. Development of appropriate shelf life simulation models is analyzed mainly from a packaging point of view with consideration of cost.

The paper by *Taoukis, Labuza,* and *Francis* addresses the reliability of time-temperature indicators (TTI) as food quality monitors under nonisothermal conditions. This study develops an application scheme based on the kinetic parameters of the TTI as well as the food distribution chain which allows for a direct correlation of the TTI response to the food's loss in quality. This is shown to be reliable under variable temperature conditions and should be of benefit to the packaged food industry, especially for refrigerated extended shelf life. Three major types of commercial TTI's were studied, a diffusion-based tag, an enzyme-based tag, and a polymerization-based tag.

Flavor management for food products is important because consumers want food that tastes good, in addition to safety and nutrition. *DeLassus* and *Strandburg* use "flavor" in a broad nontechnical way that includes several human responses to both chemical and physical stimuli. Results from a new experimental technique are used to illustrate the important variables for permeation of flavors and aroma in polymer films. The permeability is separated into its component parts, namely the diffusion and solubility coefficients. A review of physical interactions between food and plastic packaging that can lead to loss of flavor is given.

Matty, Stevenson, and *Stanton* provide a detailed review of techniques and equipment developed for easy-to-use, reproducible, standardized procedures to evaluate the performance of polymer-based food packages. The paper discusses test results and their relationship to package performance, with a focus on test methods, including equipment and instrumentation, applicable to container seal integrity, lid peelability, and container abuse resistance. The impact of fundamental specimen properties, instrument response limitations, and other factors influencing results is also reviewed.

This volume covers a wide range of topics in the area of food packaging, with applications and test methods that may be useful in all packaging disciplines. It was not intended to be totally comprehensive and the areas discussed are clearly not complete, but should provide the reader the kind of considerations necessary when developing packages for food.

The papers presented here have been successful both in illustrating various problems and in presenting potential solutions. This book should be useful to those in the food industry who develop, design, and test food and food packages. Hopefully, it will serve to stimulate all groups involved to work closely together to provide a safe food supply.

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