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EFFECT OF REPEATED MICROWAVE HEATING ON THE

IMPACT RESISTANCE OF A POLYPROPYLENE CONTAINER

presented by

Ubonrat Siripatrawan

has been accepted towards fulfillment of the requirements for

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# EFFECT OF REPEATED MICROWAVE HEATING ON THE IMPACT RESISTANCE

## OF A POLYPROPYLENE CONTAINER

By

Ubonrat Siripatrawan

### A THESIS

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

# MASTER OF SCIENCE

School of Packaging

#### ABSTRACT

### EFFECT OF REPEATED MICROWAVE HEATING ON THE IMPACT RESISTANCE OF A POLYPROPYLENE CONTAINER

By

Ubonrat Siripatrawan

The effect of microwave repeated heating on physical structure and property of a package material was studied by evaluating drop impact resistance and degree of crystallinity. Drop impact resistance of plastic syrup bottles was evaluated using the Bruceton Staircase free fall drop method. Drop impact orientation (flat bottom, bottom corners, and handle), fill level (full, <sup>1</sup>/<sub>4</sub>, <sup>1</sup>/<sub>2</sub>, and <sup>1</sup>/<sub>4</sub>), and temperature of package material ( $20 \pm 2 \circ C$ ,  $42.3 \pm 2.2 \circ C$ , and  $8.1 \pm 1.6 \circ C$ ) affected drop impact resistance of the bottles. Plastic OPP bottles filled with syrup at full, <sup>1</sup>/<sub>4</sub>, <sup>1</sup>/<sub>2</sub>, and <sup>1</sup>/<sub>4</sub> levels were heated in a microwave oven and subjected to 12 heating treatments. Unheated bottles filled with syrup at full, <sup>3</sup>/<sub>4</sub>, <sup>1</sup>/<sub>2</sub>, and <sup>1</sup>/<sub>4</sub> levels were used as control bottles. Drop impact resistance of unheated bottles and bottles subjected to microwave reheating was determined. Degree crystallinity associated with heat of fusion of the package material was evaluated using Modulated DSC. Degree crystallinity of the samples taken from unheated and microwave reheated bottles were compared. Decreased drop impact resistance and increased degree of crystallinity of the package material was observed after the bottles were repeatedly heated in the microwave oven.

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#### **CHAPTER 1**

#### **INTRODUCTION AND OBJECTIVES**

The motivation for the development of microwavable packaging materials has been influenced by need for convenience, aesthetics, and enhanced food quality. Classically, packaging technologists have been concerned with designing packages which: protect the quality attributes of foods, minimize the effects of physical abuse to the product during manufacture, storage and distribution, are relatively easy to manufacture, economical to the consumer and simple to open and use. The increased usage of microwave ovens has a direct effect on the design of the product and its heating performance in the microwave oven and highlights the importance of the relationship between food formulated for microwave heating and the appropriate packaging.

Generally, microwavable containers should allow heat penetration, tolerate rapid temperature change and preserve food quality (Rubbright, 1990). Moreover, the appropriate packaging material for use with a microwavable food should not heat excessively or prevent efficient microwave heating. The container must also be thermally compatible with the food, i.e. it should not melt, distort or be otherwise impinged by hot food, and it should provide shelf life properties commensurate with the food and its use. Microwave transparent materials, such as plastics and paperboard, microwave interactive materials, such as susceptors, and reflective materials, such as metals have been used for microwavable packaging. These materials provide both opportunities and problems for food manufacturers (Fisher, 1991). Polymeric packaging materials have been already well established in the microwave market and are now the most popular materials used for microwave packaging as a result of their microwave transparency, ease of processing and forming, consumer appeal, and safety (Sacharow and Schiffman, 1992).

To design and select a plastic material for use in a microwave oven and to avoid failure in the market place, product and package development must be thoroughly researched. The packaging technologist must first understand what role the package will have in relation to the heating phenomenon, such as the effect of microwave heating on structural properties, packaging performance, and the expected service life of the container in order to provide an appropriate container.

During microwave heating, the highest temperature will be found at or near the interface between food and the container. At the interface of food and container, the temperature of the container, if it is transparent to microwaves, will usually be a result of the food temperature and the cooling influence of the air on the outside of the container wall (Huang, 1987). When the food contains large amounts of fat, such as on the surface of soups, or in sauces and gravies, or a large amount of sugar, as on preserves and syrups, then the temperature may potentially become very high and may cause problems such as dimensional stability, discoloration, distortion, melting, and migration from plastic packaging (Katt, 1991).

There have been many studies concerning food/package interactions especially with respect to the migration of packaging components into foods due to heating at high

temperatures in the microwave oven. One such example is the migration of volatile compounds from a thermoformed microwavable container (made from polypropylene/Saran/polypropylene coextruded material) into food during microwave exposure (Dixon et al, 1988). Plasticizer has also been known to migrate from a laminated film incorporating susceptor material (Bishop and Dye, 1982). Odor pick-up and retention resulting in a change in the flavor of the food has been observed (Laperle, 1988).

However, there are other problematic areas that need special attention. One problem, known as "runaway heating" occurs in thermoplastics as they approach their heat distortion temperature, which is the temperature at which an arbitrary deformation occurs under arbitrary test conditions. This can cause melting or severe distortion of the container (Korshak, 1971). Another concern with plastic containers is change in physical property such as loss of desired packaging performance and discoloration of the container, after repeated heating in a microwave oven (Peason, 1995; Sacharow and Schiffmann, 1992). Therefore, performance testing of microwavable packaged products is necessary.

The mechanical properties, among all the properties of polymeric packaging materials, are often the most important because they influence virtually all service conditions and the majority of end-use applications (Shah, 1984). Mechanical properties of plastic materials may be affected by elevating temperature during microwave heating. There are many interesting correlations that can be made with effect of microwave heating on the quality of package container. Impact resistance is one of the most important mechanical properties of the plastic materials and an increase or decrease in impact resistance may be caused by microwave heating.

Physical testing of plastics can be classified as thermal, mechanical, dimensional, transmission, and electrical (Seymour and Carraher, 1984). In this study, attention was focused on the mechanical and thermal testing. The mechanical testing of plastic materials is usually carried out to determine their suitability for a particular application, to control functions, or to obtain a better understanding of their behavior under various conditions. Most mechanical tests are carried out on molded test pieces. However, there are some tests that can be performed on the finished containers and these will often give results more in keeping with the end-use performance. Drop impact resistance of a blow molded thermoplastic container (ASTM D2463) is one of the physical tests that can be used to simulate the actual impact conditions.

There is little information available in the literature which correlates change in physical properties of plastic containers with heating in a microwave oven. A few technical papers address the potential effect of microwave heating on the crystallinity of polymeric packaging materials. It is assumed that heating in a microwave at elevated temperatures may lead to a change in percent crystallinity of the packaging materials due to melting and recrystallization. Determining percent crystallinity is consequently important to evaluate its effect on packaging performance. The reason which necessitates such investigation is, in particular, the fact that the physical character of a polymer such as its tensile strength, and impact resistance depends substantially on the percent crystallinity of the polymer.

In this research, it was hypothesized that repeated heating of plastic containers by microwaves may affect the degree of crystallinity which may result in a change in the impact resistance of the package. Repeated microwave heating and free fall drop testing

of the containers were designed to simulate the actual use situation environment. The microwave heating parameters were studied under comparable conditions to determine changes in the container's crystallinity and performance. Drop impact resistance, was used to simulate actual impact conditions and was evaluated using the free fall drop test. Differential Scanning Calorimetry (DSC), a technique measuring heat flow into or out of a material as a function of time and temperature, was used to assess the heat flow associated with percent crystallinity of the material.

The consequences of this investigation might be expected to provide significant information about the capability and limitations of the packaging and the compatibility of package and product to repeated heating in the microwave. This information will potentially help packaging technologists prepare appropriate container specifications for microwave use, to develop more convenient and successful packages for microwave food products.

The purpose of this study was to determine if there were changes occurred in the structural and physical properties of packaging material due to repeated heating in the microwave and to identify and quantify these changes.

The specific objectives of this research were:

1. To evaluate drop impact resistance and failure of a container when subjected to sudden shock resulting from a free fall.

2. To compare the performance of a container to withstand the sudden shock resulting from a free fall after repeated heating in microwave oven.

3. To determine changes in degree of crystallinity of package material due to repeated microwave heating.

4. To study the effect of the change in percent crystallinity resulting from microwave heating on packaging performance.

#### CHAPTER 2

#### LITERATURE REVIEW

#### **Microwave Heating Characteristics**

Microwaves are a form of electromagnetic energy, and are similar to visible light, x-rays, radio wave and ultraviolet energy. Microwave generally include the frequency spectrum from 0.3 to 300 GHz (gigaherts) or wavelength of 1 mm to 1 m.(Sacharow and Schiffmann, 1992). All electromagnetic waves are composed of rapidly alternating electric and magnetic fields which oscillate at different rates. The energy frequency in industrial ovens commonly used in plant manufacturing operations operate at 915 MHz, while in domestic retail ovens they operate at 2450 MHz. This means that the electromagnetic field is alternating 2450 million times per second (Fisher, 1991).

Robertson (1992) described two main mechanisms by which microwaves produce heat in foods including dipole rotation and ionic polarization. Ionic polarization occurs when ions move in response to an electric field. Ions, due to their inherent electrical charge, are accelerated by the microwave field, leading to multiple collisions with nonionized molecules. Kinetic energy is given by the field to the ions, which collide with other ions, converting kinetic energy into heat. The more concentrated or the more dense the solution, the greater the frequency of collision, and the more kinetic energy that is

released. At microwave frequencies, numerous collisions occur, and much heat is generated. However, it is a less important mechanism than dipole rotation.

Microwave heating also results from interactions of the food constituents containing polar molecules (such as water) with an electromagnetic field. These molecules have a random orientation and orient themselves when applied with the rapidly changing alternating electrical field according to the polarity of the field. These interactions lead to instantaneous heat generation within the product due to molecular friction primarily by the agitation of weak hydrogen bonds associated with the dipole rotation of free water molecules and with the electrophoretic migration of free salts in an electrical field of rapidly changing polarity. These effects are predominantly related to the aqueous ionic constituents of food and their associated solid constituents. Such rotation of molecules leads to friction within the surrounding medium, and then generate heat (Singh and Heldman, 1993). Once the heat is generated it is then transferred to other points in the product by conduction and convection. The specific heat, thermal conductivity, density and viscosity all effect the rate of heat transfer (Fisher, 1991).

#### **Dielectric Properties**

The dielectric properties of a material are critical to microwave heating. The dielectric property of a material is the physical description of how well a material can potentially heat when it interacts with electromagnetic energy. The important electrical properties are the relative dielectric constant ( $\varepsilon$ '), and the relative dielectric loss ( $\varepsilon$ ''). The dielectric loss factor for the material, which represents the quantity to which an extremely applied electrical field will be converted to heat, is shown by the following equation:

 $\epsilon$ " =  $\epsilon' \tan \delta$ 

 $\varepsilon$ ' describes how much energy is reflected away from the product and how much energy is transmitted into the product.  $\varepsilon$ '' describes how lossy a product is or how well a material absorbs electrical energy and converts it into heat. tan  $\delta$  or loss tangent provides an indication of how easily the material can be penetrated by an electrical field and how well it dissipates electrical energy as heat (Engelder and Buffler, 1991).

If the lossiness of a product is large, it will effectively absorb energy passing through it and heat rapidly. If the lossiness is small, microwave radiation will pass right through the product without heating it. Most glass, plastic and paper packaging materials have low dielectric constants compared to food and are transparent to microwave energy. Many factors influence the dielectric properties of food. A few of these are; moisture content, temperature, salt content, physical state, and chemical composition (Fisher, 1991).

#### **Microwave Heating Characteristics of Foods**

Microwave heating characteristics of foods are related not only to their dielectric properties but also to electrical transmission properties related to dielectric heating processes and to thermal and transport properties that affect heat and mass transfer in both conventional and dielectric heating processes (Engelder and Buffler, 1991).

Microwave heating of foods involves two phenomena: coupling of energy by the product from an electromagnetic field and attenuation of absorption of the coupled energy within the product. These phenomena involve reflection and transmission of energy at product surfaces and alteration of energy within the product. This results in instantaneous

temperature increase within the product in contrast with conventional heating process that transfer energy from the surface with long thermal time constants and slow heat penetration.

Microwave heating occurs as a result of the interactions between microwave and a dielectric material. The relationship between microwave power absorbed by the material being heated and the conversion of the microwave energy to heat can be approximated with the following equation (Decareau, 1992, and Singh and Heldman, 1993):

$$P = \sigma E^2 (watt/cm^3)$$

where P = the power absorbed (watt/cm<sup>3</sup>)

 $\sigma$  = the equivalent dielectric conductivity

E = the electrical field strength (volts/cm)

The main difference between microwave heating and other heating methods is penetration depth. The penetration depth is the distance from the surface of a dielectric material to where the incident power is decreased to 37% (1/e) of the incident power at the surface. Microwaves penetrate deeply into food materials and are converted to heat as they penetrate (Decareau, 1992). The equation for converting dielectric property data into penetration depth is :

dp = 
$$1/(2\alpha)$$

where dp = penetration depth

 $\alpha$  = attenuation constant

=  $(2 \pi/\lambda) \{\epsilon'/2 [(1+\tan^2 \delta)^{1/2} - 1]\}^{1/2}$ 

#### **Factors Affecting Microwave Heating**

From the experiments conducted by Lau (1995) to determine the heating characteristics of food materials in a microwave oven, the conclusion drawn was that the temperature rise induced in a food and food packaging due to microwave heating depends on two main physical mechanisms; the interaction of the food package with the microwave field determines the power deposited and the increase of temperature throughout the food package in accordance to heat transfer mechanisms. He also observed that the power absorbed by a food load in a microwave oven depended on the dielectric properties of the food, the position of the food in the cavity, and the use of packaging materials.

Schiffmann (1990) pointed out a number of factors that affect microwave heating performance in microwave ovens:

- a) Oven parameters include output wattage, output frequency, presence or absence of a turnable and turntable materials of the, position of the food in the oven cavity, material construction of the floor, timebase for pulsed-power control, stability of input power, presence or absence of filament transformer, age and condition of the magnetron, and time delay of the magnetron, i.e., cold vs warmstart.
- b) Food parameters include nature of the food-single component vs. multicomponent, dielectric properties of the foods over the range of temperatures to be encountered, thermal properties of the food (thermal conductivity, heat transfer coefficient, specific heat, heat of fusion), evaporation, initial temperature of food, shape of the food and its components, and regularity of food shape.

c) Packaging including material of construction (plastics, glass, paperboard, and metal films, transparency or reflectively), size (length, width, and depth), shape (round, oval, rectangular, etc.),

The shape of food items is critical to microwave heating results. For many foods, it is the food container or dish that determines the food shape and therefore affects the heating performance. Varied different temperature profiles are found in round, oval, and rectangular containers. As the size of the container changes, so will the temperature profiles.

The sphere is the ideal shape as energy tends to be focused to give heating at or toward the center of the sphere. The cylinder is the next best shape in terms of heating performance. Round and oval are preferred over rectangular or square because rectangular and square shape will give edge and corner heating results which may at times be extreme. Food in the corners of a rectangular container will be overcooked before the remainder of the food is ready. Food products heat more uniformly if formed with round corners. Even when food product or package corners are unavoidable they should have generous radii to minimize the overheating effect (Sacharow and Schiffmann, 1992).

The bottom of the container should be bowed somewhat to make the food depth thinner in the center where it receives less microwave power, than along the edges, thereby contributing to more uniform heating. This also serves to elevate the food slightly thus reducing heat loss to the cooler oven floor.

The side wall of the container should have generous draft angles rather than be at 90 °C angle with the bottom commensurate with stacking. On the other hand, the wall

should not be so shallow that overheating of a thin food profile at the surface occurs (Ohlsson and Rissman, 1978).

The composition of the food material affects how it heats in the microwave field. The moisture content of food directly affects the amount of microwave power absorption. A higher amount of water in a food increases the dielectric loss factor. In the case of low moisture content, the influence of the specific heat (the amount of energy needed to heat 1.0 g of food to 1.0 °C) on the heating process is more pronounced than that of the dielectric loss factor. The specific heat determines how rapidly a given volume of food will heat once a given amount of power is deposited within it. The lower a food's specific heat capacity, the more quickly it will heat. Food or components with high fat and sugar and low water content have low specific heats. Therefore, due to their low specific heat, some foods with low moisture content also heat at acceptable rates in microwave oven (Singh and Heldman, 1993).

Oil has about one-half the specific heat of water, and can heat twice as fast for a given heat input. High-solid foods, such as jellies and preserves, have low specific heats and may not only heat fast but to very high temperatures (Fisher, 1992). This was also observed in the study by Katt (1991) that as the sugar concentration in the food system increased, the heating rate increased. Compared to a water control with a heating rate of  $1.10 \,^{\circ}$ F/second, the addition of 20 % fructose increased the heating rate to  $1.20 \,^{\circ}$ F/second, and at 50 % fructose the rate was  $2.10 \,^{\circ}$ F/second.

Thermal conductivity is a measurement of a material's ability to transfer heat in response to a temperature difference. Conduction heat transfer depends on temperature difference. Even in microwave cooking it plays an importance role in spite of the

penetrating nature of microwave energy. The power absorption characteristics of a food load changes significantly as its temperature rises due to the change in its dielectric properties. For food products with high conductivities, most of the power is deposited on the surface and at sharp corners. For food product with low conductivities, standing waves are set up within the load and the power is more evenly distributed (Lau, 1995).

#### **Microwave Packaging**

Generally, packaging requirements for all foods must perform certain functions. Chief among these are to protect and preserve the products contained, ensure the wholesomeness of the food, allow ease of manufacturing, and provide consumer usability. For packaging specific to microwavable foods, the three main applications are reheating, cooking, and defrosting. The packages for microwavable foods must also provide adequate venting, control the arcing within the package itself, allow for uniform reconstitution temperatures in both multiple and single component foods, protect the user from the potential hazards of heated products, such as discharge of viscous materials at their boiling point, provide for safe handling and opening when hot, prevent taste and odor from migrating out of the packaging material into the food, maintain structural integrity under varied thermal conditions, and achieve uniform heating to provide microbiologically safe food preparation (Rubbright, 1990; Fisher, 1997; Robertson, 1993).

Schiffmann and Sacharow (1992) defined the desired properties of packaging materials for microwave ovens, as the following; will not heat excessively, or prevent effective microwave heating, thermally compatible with the food-that is, should not melt,

distort or be otherwise affected by the hot food. Therefore, the selection of materials must be made after careful consumer use testing.

Microwave packaging can be classified as active, passive, and shielding according to their interaction with microwaves. Active packaging is packaging constructed of materials which respond to microwaves with the result that incident energy is converted into heat or is focused to increase its intensity in a predetermined region of the food. Active packaging may combine active and passive elements (Rubbright, 1990).

Passive packaging is packaging which does not modify the microwave energy field and does not become hot. Such materials are essentially transparent to microwave energy, including plastics, glass, and paper products. Passive packaging includes both rigid and flexible forms. Rigid packages dominate meals in compartmented trays and for larger serving sizes, individual lunch and vended items. Shielding packages include metallic structure that can reflect microwaves. Therefore, a product encased in a metallic structure would not exhibit any microwave heating, since no energy is able to penetrate the material to reach the product (Robertson, 1993).

Generally, packaging materials that are used in microwave ovens include plastic, paperboard, and glass. Plastics are well suited to microwave use and when properly selected can be used for shelf stable, refrigerated and frozen foods. They are divided into microwave only and dual-ovenable categories. Dual-ovenable containers are designed to withstand the rigors of both microwave and conventional ovens. Crystalline polyester and thermosets are good examples of dual-ovenables that are used in higher priced containers. The problem that the package developer and food technologist must face is to ensure that the microwavable package is not exposed to excessively high temperature. The selection

of materials must be made after careful consumer use testing as well as in-house test kitchen analysis (Sacharow and Schiffmann, 1993).

Paperboard is a popular microwave packaging material because of cost considerations. The properties of paperboard which make it attractive in microwave food use are its transparency to microwaves, ready availability in many forms, ease of application, mechanical strength and stiffness, printability and relative economy. However, the deficiencies of paperboard are its low resistance to moisture and grease, poor tearing resistance, low barrier to mass transfer of gasses, moisture and food components, and lack of resealability and shapeability.

For glass, the advantages of glass as packaging container include inertness, nonabsorbency, and a high degree of transparency to microwaves. Glass is a rigid structure and has no migration problems associated with food and beverage products. However, properties which mitigate against its use are its relatively high heat conductivity, high weight and brittleness. Another possible problem with glass is that the surface may become extremely hot and dangerous to handle. Also, the glass surface temperature may be deceptively low while the central volume of the contents may be boiling hot.

Another category is susceptors which originally were developed to overcome the problem of inability of products to brown and to assist in crisping microwavable pizza and popcorn. Susceptors are materials consisting of metallised structures applied to a heat resistant surface such as polyester film or kraft paaperboard. They absorb microwave power and convert it into heat. This heat is then transferred to product by conduction or radiation, creating localized areas of high temperature on the food surface which causes browning. However, the contact heating phenomenon found with susceptors for products

such as pizza and similar products makes somewhat different demands upon the susceptor. Another problem encountered with susceptors is irregularity of heating. Moisture condensation can also be a problem with susceptors. As the contact surface of the food becomes very hot, evaporation of water occurs which makes the susceptor a less effective microwave heater (Zucherman and Miltz, 1993; Sacharow and Schiffmann, 1993).

#### Plastic Packaging for microwave oven

Plastic materials that have been used in microwave ovens include : polyethylene, polypropylene (PP), acrylonitrile, butadiene styrene (ABS), polycarbonate, nylon, styrene acrylonitrile(SAN) and mixtures of styrene and acrylic sold under the trade name Dylark (Calto, 1978).

Polyolefins including polyethylene, polypropylene, polybutylene and copolymers of ethylene with propylene and other monomers have been developed in various forms and are used most commonly in microwavable containers. Polyolefins are generally remain tough at freezer temperatures, are translucent to opaque in thick sections and are available in an exceptionally broad range of grades with different specialized properties. Polypropylenes, gaining favor as trayware for microwave foods such as vegetables, can be filled with inorganic fillers such as calcium carbonate or talc to raise their useful temperature limits by increasing the stiffness of formed parts.

Polypropylene has been used as a replacement for glass in maple-syrup bottles because of the lower cost, contact clarity, and ability to withstand hot-filling of the syrup. Savings in shipping costs can also be a major consideration (Talvitie and Gaunt, 1982). Interest in PP has become even more intense recently, and has been quite favorable

compared to other commonly used plastics that can be steam sterilized (Szulczynski, 1978). Sweintekand and O'Donnell (1994) reported on a microwave ready syrup bottle. The polypropylene bottle features several advantages for microwavable packaging. Its shape allows it to fit inside microwave ovens. Bottle geometry can be created to assist in uniform heating of the syrup.

Polypropylene filled with up to 40% by weight of an inorganic compound such as calcium carbonate, is stiffer at temperatures reached by foods heated in microwave ovens; it is used to provide stable handling when removing heavier food loads from the oven. The appearance of containers made from filled resin is better than of unfilled PP and some observers say that they look better than unfilled CPET trays. Filled PP, used for frozen foods intended for microwaving, is not dual-ovenable and is not recommended for reuse.

Polyester (PET) includes a large class of thermoplastic materials extensively used in microwave packaging intended for single use, but also saved for reuse in the freezer. CPET, a crystallized form of PET, exhibits heat resistance to 445 °F and is currently the superior material for dual-ovenable plastic ware. PCTA, polycyclohexane terephthalateacid (modified) has a higher temperature range with approximately a 50 °F advantage over CPET. Mica-filled nylon is an alternative to CPET or thermoset polyester containers, which was the former preferred material for dual ovenable premium meals (Sacharow and Schiffmann, 1992).

High density polyethylene, though rigid, distorts at temperatures around  $170 \degree F$ and is brittle at low temperature. PP has a higher distortion temperature, around 230 °F, is not rigid and has a tendency to become brittle. ABS can tolerate temperatures in the 190 to 220 °F range depending on the grade. It is somewhat subject to damage by

abrasion. Polycarbonate has a distortion temperature near 250 °F and is extremely break resistant. Nylon is strong, but has a low tolerance to temperatures of 150 to 170 °F. SAN is strong, but limited to 190 °F. Styrene and acrylic mixtures, though tolerant to temperatures up to 230 °F, are relatively brittle (Decareau, 1992).

Styrenics are polymers or copolymers of styrene with other monomers and may be polymerized in the presence of toughening rubbers, forming materials such as styrenebutadiene. Styrenics are characterized by their ease of rapid forming into containers shaped by injection molding, blow molding and especially thermoforming. General purpose polystyrene (PS or GPPS) is a crystal clear plastic used extensively in food service for takeout containers and in some microwave applications where temperatures are limited approximately to 90-100 °C. Impact resistant grades, which contain the aforementioned rubbers, may be translucent or opaque and withstand heat to the same extent as GPPS. High heat resistant grades of PS are produced by copolymerizing styrene with alpha methyl styrene or other high temperature monomers. The polymer has high deflection temperatures up to the order of 120 °C (Decareau, 1992; Sacharow and Schiffmann, 1992).

Expanded polystyrene, although it has good food heat retention properties, has not been completely favorable for microwave oven usage. Although transparent to microwave energy it is not resistant to high temperatures attained by some food products (Decareau, 1992). Monte and Landau-West (1983) tested a wide variety of frozen foods heated in expanded polystyrene containers. The foods were heated to 180 °F and held at this temperature for 10 minutes. Any container leakage, major distortion or softening that might result in container failure resulted in a "not recommended" rating for that product.

Fatty foods (such as fried foods, gravies, certain cheese sauces, fatty meats and buttered foods) gave high failure rates. Foods with much gravy showed breakdown of the container at the gravy line.

Stehle (1979) compared the quality of polysulfone, a thermoset polyester, a thermoplastic polyester, and poly-4-methyl pentene-1 containers. A variety of food items were used to test the reaction to high fat temperatures, high sugar temperatures, and protein stain or residual. Bacon was used for high fat temperatures; peanut brittle for high sugar temperatures; beef patties and meat loaf for protein residual; and pork roast for high fat and protein residual. Appropriate utensils and accessories made from these plastics were used. The study concluded that cookware made from polysulfone and thermoset polyester can be used with any food and for all microwave cooking purposes. The cookware made from thermoplastic polyester and methyl pentene isomer warped or became distorted in some of the shapes tested.

#### **Mechanical Properties of Polymeric Packaging Materials**

The mechanical properties, among all the properties of plastic materials, are often the most important because virtually all service conditions and the majority of end-use applications involve some degree of mechanical loading. Material selection is quite often based on mechanical properties such as tensile strength, modulus, elongation, and impact strength. Numerous factors affect various mechanical properties of polymers, including molecular weight, processing, extent and distribution of crystallinity, composition of polymer and use temperature.

Crystallinity has a number of important effects upon the mechanical properties of a polymer. Yield stress and strength, and hardness increase with an increase in crystallinity as does elastic modulus and stiffness. Physical factor that increase crystallinity, such as slower cooling and annealing, also tend to increase the stiffness, hardness, and modulus of a polymeric material. Polymers with at least some degree of crystallinity are denser, stiffer, and stronger than amorphous polymers. However, the amorphous region contributes to the toughness and flexibility of polymers. Increasing the percentage of crystallinity decreases the impact strength and increases the probability of brittle failure. A reduction in the average molecular weight tends to reduce the impact strength and vice versa. (Seymour and Carraher, 1984).

Most linear polymers are hard brittle plastics at temperatures below their characteristic glass transition temperature (Tg), leathery and rubbery at temperatures just above the Tg, and viscous liquid at temperatures above the melting temperature (Tm). Some polymer, including networked, highly cross-linked, and highly crystalline polymers, are difficult to melt and often undergo solid phase thermal degradation before melting occurs (Seymour and Carraher, 1984).

The impact properties of the polymeric materials are directly related to the overall toughness of the material. Impact strength is the amount of energy which a plastic material can absorb before it breaks. The higher the impact strength of a material, the higher the toughness and vice versa. Impact resistance is the ability of a material to resist breaking under a shock loading or the ability to resist the fracture under stress applied at high speed. Factors affecting impact properties includes temperature, orientation, processing conditions, and degree of crystallinity.

Impact resistance is one of the most widely specified mechanical properties of polymeric materials. The impact resistance of plastic materials is strongly dependent upon temperature. At lower temperatures the impact strength is reduced drastically. The reduction in impact is even more dramatic near the glass transition temperature. Conversely, at higher test temperatures, the impact strength is significantly improved (Shah, 1984; Spath, 1957).

Processing conditions play a key role in determining the impact resistance of a material. Inadequate processing conditions can cause the material to lose its inherent toughness. High processing temperature can also cause thermal degradation and therefore, reduced impact strength. Improper processing conditions also create a weak weld line that reduces overall impact strength. Molecular orientation introduced into drawn films and fibers may give extra strength and toughness over the isotropic material. However, such directional orientation of polymer molecules can be very susceptible in a molded part since the impact stresses are usually multiaxial.

Impact resistance, or resistance of brittle fracture, is also a function of the molecular weight of a polymer. A reduction in the average molecular weight tends to reduce the impact strength and vice versa. Impact resistance of brittle polymer is increased by additional plasticizers. Thus, polyvinyl chloride (PVC), plasticized by relatively large amounts of dioethyl phthalate, is much less brittle than unplasticised rigid PVC (Seymour and Carraher, 1984).

The impact resistance of bottles can be improved by biaxial drawing which has contributed to the success that PET has experienced due to stretch blow molding. However, there are several processing techniques, such as extrusion blowing that cannot

create this orientation effect. Therefore, other approaches such as impact modifier must be provided to improve the property. Impact modifiers primarily used for packaging purpose especially for the production of sheets and bottles, improve the impact resistance of any type of plastic while maintaining transparency (Meyer and Leblanc, 1995)

Troy, Shortridge, and Fozey (1985) studied the impact modifier performance in 16 ounce PVC bottles using a drop impact resistance test. Impact modifier (methacrylatebutadiene-styrene) are added to PVC blow molding compounds. PVC bottles with impact modifier can resist the higher drop heights before failing than those of the bottles without impact modifier. This indicates that impact modifier can be used to overcome the brittle characteristics of unmodified PVC resins. Besides methacrylate-butadiene-styrene, chlorinated polyethylene, EVA, acrylic resin derivatives, and ABS are also used as an impact modifiers (Briston, 1994).

#### **Effect of Temperature on Mechanical Properties**

Polymers pass through different physical states according to their temperature; at low temperature, since the internal mobility of the macromolecules is "frozen", they solidify and present a glassy, amorphous appearance. As the contact temperature rises, the material passes through a phase of relaxation, characterized by an erratic behavior on the path of Young's modulus (the ratio of stress to corresponding strain below the proportional limit of a material, or a measure of material's stiffness) and other physical properties.

Generally, both crystalline and amorphous polymers are brittle at low temperature and both have relatively low impact strengths. As the temperature of a material decreases,

its ultimate strength and young's modulus increase; this applies to tension, compression, and bending. At the same time elongation (the increase in the length of a test specimen produced by a tensile load) decreases (Seymour and Carraher, 1984; Spath, 1957).

At low temperatures, the atoms vibrate with small amplitudes. With increasing temperature, the vibrations increase in magnitude and eventually become coordinated to the degree that translational chain motions are produced, which involve many chain atoms at elevated temperatures (Calister, 1994).

When a polymer is heated to a certain temperature, changes of a physical nature, can occur. These may consist of various transitions, which are accompanied by changes in the physical properties of the material (brittleness, elasticity, devitrification, softening, melting, etc.).

Kemp and Kennedy (1987) indicated that the effect of heat on polymers can manifest itself in 2 ways:

- a) the polymer softens or melts. The kinetic energy of the chains becomes large enough to overcome the intermolecular forces, and the plastic flows easily;
- b) the structure is degraded. Some macromolecular compounds undergo scission to lower molecular weight products or even to monomer without changing chemical composition-i.e. are depolymerized, others release low-molecular weight fragments with simultaneous change in chemical composition-i.e. are decomposed. Both processes are called degradation.

Korshak (1971) pointed out that polymers exposed to high temperature undergo chemical transformations of three main kinds: purely thermal conversions, which include thermal degradation and cross-linking of the polymer; oxidative degradation and cross-
linking; and hydrolytic degradation. The course of each of these reactions depends to a great extent on the structure of the polymer.

Degradation is a rupture of the macromolecular structure, which results in a progressive decrease in the molecular weight of the polymer, and hence in the deterioration of its mechanical properties. Cross-linking consists of the formation of bonds between the macromolecular chains, with consequent increase in the molecular weight of the polymer; this means that the physical and mechanical characteristics of the polymer and its heat resistance may improve to a certain extent as a result (Korshack, 1971).

Mechanical stress due to impact arises usually during distribution. Mechanical stress due to pressure changes within the package is normal during production processes involving heat treatments of foodstuffs. In these cases the stress results due to thermal expansion of the content. The volume increases due to heating of the contents from an initial temperature to the high temperature. If the free volume in the package is smaller than the volume increase of the incompressible aqueous phase, the inner pressure would cause rupture of the package or of the closure. The pressure is also affected by gaseous components of the product and by expansion of the package itself (Kemp and Kennedy, 1987).

#### Effect of Heat on Degree of Crystallinity

Polymer properties depend on the phase state (amorphous or crystalline) of the polymers as well as their molecular weight, and chemical composition. Polymers are closely packed, having conformation of the lowest possible energies. If at a certain

temperature the cohesion energy of the chain is larger than the kinetic energy, then conditions are suitable for parts of the macromolecule to exhibit close packaging and incorporation into a crystalline arrangement. When cohesive energy exceeds the kinetic energy of the chains, provided that there is not too large of a steric hindrance, crystallization take place (even in polymers which do not crystallize under normal condition) (Miller, 1966).

Crystallization is temperature dependent to a considerable extent. Primary crystallization comprises formation of the crystal nuclei and growth of the spherulites. The secondary crystallization has great practical importance. It is this latter stage which is responsible for the undesirable volume and other physical changes which take place usually after processing. Its course and extent are affected markedly by the thermal history of the polymer (Kemp and Kennedy, 1987).

Crystallites in polymers reinforce their structure and improve their mechanical properties and resistance to elevated temperatures. Therefore, an important consideration of the polymer change is the change in crystallinity of the polymer because crystallinity can play a significant role in the physical character of a polymer such as clarity, tensile strength, and impact strength (Seymour and Carraher, 1984).

Zucherman and Miltz (1993) studied the changes in degree of crystallinity of thinlayer susceptors during microwave heating. The structure used was a metallized polyethylene terephthalate film laminated to paperboard with a polyurethane-based adhesive. The sample was heated in a 700 watt microwave oven. The degree of crystallinity of the PET film before and after heating in the microwave was measured using DSC. The results showed that microwave heating affected the crystallinity of the

metallized PET. They concluded that the degree of crystallinity of the film was reduced during heating in the microwave oven caused by relaxation of the oriented PET film. In addition, differences in thermal diffusivity between aluminum and PET, resulting in differences in heating and expansion rates may have added to this effect.

Brennen (1978) investigated the effect of thermal conditioning on percent crystallinity of low density polyethylene film used for food storage. Specimens were analyzed without thermal conditioning and after having annealing at 100 °C for 12 hours. The results showed that the annealing increased percent crystallinity by boosting the high temperature crystallinity of the material.

In pharmaceutical packaging, various types of sterilization processes are employed. One of these is gamma irradiation. This process may not only sterilize, but may also affect material properties and thermal characteristics of the polymeric packaging material (Breakey and Cassel, 1979). This is in agreement with the study of Trice and Goolsby (1990). They determined the physical and thermal property changes of polypropylene packaging subjected to gamma irradiation using DSC. Results showed that the gammairradiated sample, when compared to the nonirradiated material, had melting point depression, and broadening of the endotherm with a much smaller peak amplitude in the isothermal crystallization region. This was due to crosslinking which occurred during the irradiation process.

Christie, Gregory, and Wood (1993) determined the effects of polypropylene crystallization on film forming by investigating the effects of operating parameters (quenching temperatures) on the finished product properties of a film grade PP homopolymer. This study showed correlations between operating parameters and

crystallinity in PP films. Processing conditions had a dramatic impact on final crystallinity and corresponding film properties. Increases in density because of aging due to secondary crystallization also affect final film properties. These results were supported by Shah (1984) who found that increases in percent crystallinity decreased the impact strength and increased the probability of brittle failure.

Nicastro, et al (1993) studied the effect of heat sealing on the seal strength and crystallinity of unoriented cast polypropylene film with thickness of 3 mil. PP samples were heat sealed at 135, 137.8, and 140.6 C, dwell time 0.5, 1, and 10 second, and pressure 3, 15, and 30 psi. The results indicated that sealing temperature had a significant effect on the increase in percent crystallinity of the film seal region, while heat sealing dwell time and pressure had little effect on the increase in crystallinity. This increase in crystallinity increased the seal strength due to the larger amount of interdiffusing polymer chain segments. In contrast, Selikhova (1989) observed that a greater crystallinity may actually increase the brittleness of the polymer in the seal region and cause the seal layer of film laminate to be more susceptible to delamination.

#### **Mechanical Testing for Polymeric Packaging Materials**

After being in use for a period of time, materials undergo many changes due to mechanical stress and various other influences such as humidity, temperature, radiation, and chemical radiation. The impact test, among other methods, can be used to investigate such changes. Impact tests can be divided into six major classes and subdivided into many different types having slight variation as follow: Pendulum impact tests, High rate tension

tests, Falling weight impact tests, Instrument impact tests, High rate impact tests, and miscellaneous tests (Shah, 1984).

Most physical test are carried out on a molded test piece or, in the case of permeability, on film or sheet. For the test that can be carried out on the finished container, impact tests on plastic bottles are useful when change in material and /or bottle design is contemplated. Performance tests will quickly show any fundamental weakness that may lead to leakage of the contents during distribution. Drop impact resistance evaluation of a blow molded thermoplastic container can be carried out using a standard test (ASTM-D 2463) which practically simulates end-use environmental conditions. It is also useful for comparing different materials as well as evaluating the influence of processing conditions on the impact properties of bottles (Briston, 1994; Shah, 1984).

#### **Drop Impact Test**

Drop impact resistance of blow molded thermoplastic containers can be determined by three conventional tests: the Static Drop Height, the Bruceton Staircase, and the Cumulative Drop methods. These standard test method are used to evaluate the effect of construction, materials and processing conditions on the impact resistance of blown containers (ASTM-D 2463, 1996).

In the Static drop height, the container is dropped from a fixed height and the percent failure report. For the Bruceton staircase methods, a set of containers are dropped from various heights. The drop height is raised or lowered depending on the result obtained from the previous test, if the previous test container did not fail, the next bottle will be tested at a higher height. If the previous container failed, the drop height of

the next bottle will be lowered. The mean failure height and standard deviation are then calculated from the data obtained. In the cumulative drop test, each of 20 bottles is subjected to successively higher drop heights until breakage occurs, and the number of broken bottles at each drop height is recorded (Briston, 1994).

Troy, Shortridge, and Fazey (1985) used the drop ten test protocol for testing PVC bottles in groups rather than one at a time to find drop heights that span the range from no breaks to all break and to reduce testing times to just slightly longer than those of the Bruceton test in which bottles are dropped individually. If more than half the bottles break, the drop height is lowered. Likewise, if breakage is very low the drop height is raised. They concluded that values derived from the Drop ten test are highly reproducible. In addition, this test generated more data, since results are based on a lot more bottles than used in the three most common tests (Bruceton, Static, and Cumulative tests).

Meyer and Labrant (1995) performed drop testing to determine the effect of an impact modifier on the performance of 750 ml. extrusion blown PETG containers with and without impact modifier by comparing the drop heights and the percent of failures at specific drop heights. The result showed that breakage levels of both unmodified and impact modified bottles increased with increasing drop heights. The impact modified bottles exhibited little breakage compared with unmodified bottles. Successive increases of impact modifier improved the bottle failure drop height.

Besides impact modification, test conditions such as impact angle, fill level and wall thickness can influence the results of a drop impact resistance. Bottles dropped onto a flat surface have higher drop height resistance than those dropped at an angle of 10

degrees because stress is concentrated in angle drops at a single point instead of being dispersed over the entire bottom of the bottle.

#### **Determination of Percent Crystallinity**

Measurements which can be related to the crystalline state of a polymer are : x-ray diffraction, density, nuclear magnetic resonance absorption, heat capacity, infrared absorption of low molecular weight compounds and deuterium exchange. Each of these measurements describes something about the polymer, not necessarily the percentage crystallinity, but something about the regularity of packing, the freedom of motion of the molecules or the extent of intermolecular hydrogen bonding of the polymer (Sperling, 1986; Miller, 1966).

Percent crystallinity can be determined by quantifying the heat associated with melting (fusion) of the polymer. Differential scanning calorimetry (DSC) is a thermal analysis technique to measure the temperatures and heat flows associated with transitions in materials as a function of time and temperature. Such measurements provide quantitative and qualitative information about physical and chemical changes that involve endothermic or exothermic processes, or changes in heat capacity. Percent crystallinity of polymer can be determined by quantifying the heat associated with melting endotherm (fusion) of the polymer by developing a ratio against the heat of fusion for a 100 % crystalline sample of the same material, or more commonly by rationing against a polymer of known crystallinity to obtain relative value (Thomas, 1995).

The conventional instrument used for making DSC measurements is the heat flux design shown in Figure 1. In this design, a metallic disks is the primary means of heat

transfer to and from the sample and reference. The sample, which is placed in a metal pan, and the reference (an empty pan) sit on raised platforms formed in the constantan disc. As heat is transferred through the disc, the differential heat flow to the sample and reference is measured by area thermocouples formed by the junction of the constantan disc and chromel wafers which cover the underside of the platforms (Anonymous, 1997).

Modulated DSC (MDSC) is a relatively new thermal analysis technique which provides the same information as conventional DSC, but in addition has the unique ability to measure heat capacity continuously (Mele et al, 1995).

The general equation which describes the resultant heat flow at any point in a DSC experiment is:

	aQ / at		Cpp+t(1,t)
where	dQ / dt	=	total heat flow
	Ср	=	heat capacity
	β	=	heating rate
	f (T, t)	=	heat flow from kinetic (absolute temperature
			and time dependent) process

C = 0 + QT + 0

DSC can measure only heat flow which is composed of two components. One component is a function of the sample's heat capacity and rate of temperature change, and the other is a function of absolute temperature and time (Thomas, 1995).

MDSC determines the total, as well as heat capacity (reversing) heat flow component and kinetic (nonreversing) component of total heat flow, to provide increased understanding of complex transitions in materials (Figure 2). MDSC is able to do this based on the two heating rates seen by the material; the average heating rate which

provides total heat flow information (dQ / dt) and the sinusoidal heating rate which provides heat capacity (reversing heat flow, Cp $\beta$ ). The kinetic (nonreversing) heat flow is determined as the arithmetic difference between the total heat flow and the heat capacity component: Nonreversing heat flow = Total heat flow - Reversing heat flow (Anonymous, 1997; Thomas, 1995).



Figure 1. Heat Flux DSC Schematic (Anonymous, 1997).



Figure 2. Nonreversible, Reversible, and Total Heat Flux Signal (Thomas, 1995).

#### **CHAPTER 3**

#### **MATERIALS AND METHOD**

#### 3.1 Samples

Plastic containers: 46 cases of the 24 ounce plastic bottles were provided by a product manufacturer. The containers were extrusion blowmolded from polypropylene into a squat jug shape. The dimensions of the bottle were; height 7 inches with an eclipse bottom and were pinched at 2 points of the bottle's handle. The bottles were filled commercially with sugar syrup and closed in the normal manner (Figure 3). All bottles were placed in an environmentally controlled room maintained at  $20 \pm 2$  °C, and  $50 \pm 5$  % relative humidity.

#### 3.2 Wall Thickness of Materials Used

Six bottles were selected randomly so that they were representative of the lots being tested. The thickness of the material was measured at flat bottom, body wall, right bottom corner, left bottom corner, and side seam of each bottle. The wall thickness measurement was carried out using a Magna-Mike instrument (Model 800, Parametics, MA) composing of a steel target ball, magnetic probe, and control unit. To measure the wall thickness, a 3/4 inch diameter target ball was dropped into the bottle and a magnetic

probe tip was applied to the outside of the bottle. The ball was attracted to the probe through the nonmagnetic plastic container, the container was moved over the tip of the probe to locate the points at which measurements were to be made. The field strength varies as the distance between the ball and the probe changes, which is converted with a thickness measurement.

#### 3.3 Determination of the Impact Orientation of the Bottles By Free Fall Drop Test

A drop test was designed to establish the critical impact orientation using a free fall drop. The hypothesis was that impact of a particular orientation(s) can lead to bottle breakage.

ASTM D-2463 (1997), Standard Test Method for Determining Drop Impact Resistance of Blow-molded Thermoplastic Containers, was used for this purpose. This standard consists of dropping containers filled with tap water. Since data developed with a water-filled container may not be representative of what might be expected with a product of high specific gravity, the containers filled with syrup as received, were used as test samples.

Lansmont Model PDT 56 E Drop Tester was used to simulate the free fall drop. This machine was used in compliance with ASTM D-2463 standard test method. It is equipped with a drop leaf pneumatic actuation system which prevents package rotation and assures reproducible results. The container was dropped on to a 46"x 36" x 0.5" steel plate mounted in concrete.

Prior to the test, 50 bottles filled with syrup to the full level, were conditioned for 24 hours at  $20 \pm 2$  °C and  $50 \pm 5$  % relative humidity to bring the bottles into equilibrium

with an average room conditions. For any one of the test orientations (including face, flat bottom, handle, right bottom corner, and left bottom corner), a set of 7-10 bottles was used. The bottles were then subjected to the free fall drop test using the Free Fall Drop Tester (Lansmont Model PDT-56E). Drop impact resistance was determined using the Bruceton Staircase or "Up and Down" method (ASTM standard D-2463, 1997). It consists of dropping a set of containers from various heights, the drop height being raised or lowered depending on the result of the previous test, that is, if the previous container failed, the drop height is lowered; if the previous container did not fail, the drop height is raised.

The drops were conducted on several package orientations: face, flat bottom, right bottom corner, left bottom corner, and handle (Figure 3), from a drop height of 24 inches at increments or decrements of 3 inches. A positioning jig was used to hold a test container at the desired orientation. A new container was used for each drop. Following each drop, the container was visually observed. When a container in a set failed, the following rule was applied, if the first container dropped did not fail, the second container was dropped from a height 3 inches higher. If the first container failed, drop the second container was dropped from a height 3 inches lower.

#### **Result Evaluation**

All specimens were examined for failure after dropping them at the particular height. A failure was defined as any fracture visible to the observer. Any mark of contained liquid on the exterior of the bottle emerging from any aperture other than the molded opening was also considered a failure. Bottles were squeezed gently after impact



Figure 3. Syrup Bottle: (1) left bottom corner, (2) right bottom corner, (3) handle, (4) flat bottom, (5) face.

to determine any pinhole type failure. Since not all bottles failed at the same drop height, a mean failure height and standard deviation were calculated from the data.

#### Statistical Analysis

Statistical analysis was conducted using a Completely Randomized Design with 5 impact orientations. SAS software version 6.12 (SAS Institute, Inc.) was used to run a one-way analysis of variance in association with Duncan's Multiple Range Test. The ANOVA and Duncan's Multiple Range Test were used to establish significant difference using p-value  $\leq 0.05$  (Steel, Torrie, and Dickey, 1997).

# 3.4 Determination of Drop Impact Resistance of the Bottles Filled with Syrup at Different Levels

The preliminary test established that impact orientations at the right bottom corner and handle had potential to cause failure of the container. An experiment was then designed to establish the failure drop height of bottles filled with syrup at full, <sup>3</sup>/<sub>4</sub>, half, and <sup>1</sup>/<sub>4</sub> levels. The bottles were dropped onto their right bottom corner and handle using the Bruceton Staircase free fall drop method (ASTM Standard-D2463, 1997). The first bottle was dropped from 21 inches onto its handle and from 36 inches onto its right bottom corner with increments or decrements of 3 inches, thereafter.

#### Statistical Analysis

Statistical analysis was conducted using a Completely Randomized Design of the 4 fill levels. SAS software version 6.12 (SAS Institute, Inc.) was used to run a one-way analysis of variance in association with Duncan's Multiple Range Test. The ANOVA and

Duncan's Multiple Range Test were used to establish significant difference using p-value  $\leq$  0.05 (Steel, Torrie, and Dickey, 1997).

### 3.5 Effect of Microwave Repeated Heating on the Drop Impact Resistance of the Bottles

It was hypothesized that repeated microwave heating of a plastic container may affect its mechanical properties such as drop impact resistance. Repeated microwave heating and free fall drops were conducted to simulate the actual situation likely to occur in end-use.

#### 3.5.1 Microwave exposure

Empty plastic syrup bottles were filled with sugar syrup at full,  $\frac{3}{4}$ ,  $\frac{1}{2}$ , and  $\frac{1}{4}$  levels, respectively. Heating time was varied (2.00, 1.45, 1.30 and 1.00 minutes, respectively) in proportion to the level of syrup. The heating times used, followed the directions indicated on the label to reach a specific end temperature. Each container was placed upright in the microwave oven (Gold Star: 2450 MHz, max. microwave output 800 W. with a cavity measuring 13  $\frac{1}{4}$ " x 8"x 14  $\frac{1}{2}$ ") at exactly the same location (center of the glass plate) for every run so as to maintain the same electric field. Each container was heated at the same starting temperature (20 °C) to reach the specific end temperature (58-60 °C) and then cooled to room temperature before the next reheating in the microwave oven.

A microwave heat treatment scheme (Figure 4) was developed to simulate the microwave heating directions as found on the product's label. For each experiment, one set of bottles (approximately 84 bottles, each bottle contains 710 ml sugar syrup) was subjected to 12

different microwave heating variables. Heating time was dependent on product fill level. The heating and reheating regime as described above is presented in more detail in Table 1.

#### 3.5.2 Temperature of the Sample After Reheating in Microwave Oven

Sixteen bottles (uniform initial temperature 20 °C) filled with syrup at full, <sup>3</sup>/<sub>4</sub>, <sup>1</sup>/<sub>2</sub>, and <sup>1</sup>/<sub>4</sub> levels were placed on a fixed location in the center of a household microwave oven (Gold Star, 2450 Hz, max. 800 W) operating at full power for 2.00, 1.45, 1.30, and 1.00 min., respectively. After heating in the microwave oven, the temperature in syrup and on the inside and outside bottle surfaces were measured using a pocket-probe digital thermocouple (Electronic Development Laboratories Inc., NY).

#### Statistical Analysis

A statistical analysis to determine combination effects of three different product areas and 4 fill levels on product and package material temperature was performed by Factorial Design. SAS software version 6.12 (SAS Institute, Inc.) was used to run a multiple analysis of variance. When the effect of product area and/or fill level was significant, statistical difference of means was performed using Duncan's Multiple Range Test using p-value  $\leq 0.05$  (Steel, Torrie, and Dickey, 1997). 42

### Figure 4. Flow Diagram of Microwave Heat Treatments

Step 1: Heat each bottle in the set (120 bottles, each bottle contains 710 ml. sugar syru	<b>p)</b>
for 2 min. and cool to room temperature ( $\sim 20$ °C)	
$\downarrow$ $\rightarrow$ take 10 bottles for drop testing	
Step 2: Heat each of 110 bottles for 2 min. and cool to room temperature (~20 °C)	
$\downarrow \qquad \rightarrow \text{ take 10 bottles for drop testing}$	
Step 3: Heat each of 100 bottles for 2 min. and cool to room temperature (~20 °C)	I.
$\downarrow$ $\rightarrow$ take 10 bottles for drop testing	
Step 4: Remove 177.5 ml. of syrup from each bottle to leave 532.5 ml (3/4 level) in th bottle	e
Heat each of 90 bottles for 1.75 min. and cool to room temperature (~20 °C)	
$\downarrow$ $\rightarrow$ take 10 bottles for drop testing	
Step 5: Heat each of 80 bottles for 1.75 min. and cool to room temperature (~20 °C	)
$\downarrow$ $\rightarrow$ take 10 bottles for drop testing	
Step 6: Heat each of 70 bottles for 1.75 min. and cool to room temperature (~20 °C	)
$\downarrow$ $\rightarrow$ take 10 bottles for drop testing	
Step 7: Remove 177.5 ml. of syrup from each bottle to leave 355 ml (1/2 level) in the bottle	;
Heat each of 60 bottles for 1.5 min. and cool to room temperature ( $\sim 20 \text{ °C}$ )	
$\downarrow \qquad \rightarrow take 10 bottles for drop testing$	
Step 8: Heat each of 50 bottles for 1.5 min. and cool to room temperature ( $\sim 20 \circ C$ )	)
$\downarrow$ $\rightarrow$ take 10 bottles for drop testing	
Step 9: Heat each of 40 bottles for 1.5 min. and cool to room temperature (~20 °C)	)
$\downarrow$ $\rightarrow$ take 10 bottles for drop testing	
Step 10: Remove 177.5 ml. of syrup from each bottle to leave 177.5 ml (1/4 level) in the bott Heat each of 30 bottles for 1 min. and cool to room temperature (~20 °C) ↓ → take 10 bottles for drop testing	le
Step 11: Heat each of 20 bottles for 1 min. and cool to room temperature (~20 $^{\circ}$ C)	ł
$\downarrow$ $\rightarrow$ take 10 bottles for drop testing	
Step 12: Heat each of 10 bottles for 1 min. and cool to room temperature (~20 °C)	)
$\downarrow$	

take 10 bottles for drop testing

Microwave heating treatment	Condition of Heating			
1	Full level heat for 2.00 min / cool, 1 time			
2	Full level heat for 2.00 min / cool , 2 times			
3	Full level heat for 2.00 min / cool, 3 times			
4	From treatment 3, remove syrup to 3/4 level in the bottle			
	heat for 1.45 min/ cool, 1 time			
5	From treatment 3, remove syrup to <sup>3</sup> / <sub>4</sub> level in the bottle			
	heat for 1.45 min/ cool, 2 times			
6	From treatment 3, remove syrup to <sup>3</sup> / <sub>4</sub> level in the bottle			
	heat for 1.45 min/ cool, 3 times			
7	From treatment 6, remove syrup to $\frac{1}{2}$ level in the bottle			
	heat for 1.30 min/ cool, 1 time			
8	From treatment 6, remove syrup to $\frac{1}{2}$ level in the bottle			
	heat for 1.30 min/ cool, 2 times			
9	From treatment 6, remove syrup to $\frac{1}{2}$ level in the bottle			
	heat for 1.30 min/ cool, 3 times			
10	From treatment 7, remove syrup to <sup>1</sup> / <sub>4</sub> level in the bottle			
	heat for 1.00 min/ cool, 1 time			
11	From treatment 7, remove syrup to <sup>1</sup> / <sub>4</sub> level in the bottle			
	heat for 1.00 min/ cool, 2 times			
12	From treatment 7, remove syrup to <sup>1</sup> / <sub>4</sub> level in the bottle			
	heat for 1.00 min/ cool, 3 times			

 Table 1. Microwave Heating Treatment

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#### 3.5.3 Drop Impact Resistance of Microwave Reheated Bottles

After heated in the microwave oven (Figure 4), the bottles were cooled to  $20 \pm 2 \circ C$  and conditioned for 24 hours at the testing room conditions to bring the bottles into equilibrium with average room conditions ( $20 \pm 2 \circ C$  and  $50 \pm 5 \%$  relative humidity). The bottles were then subjected to free fall drop testing using the Free Fall Drop Tester (Lansmont Model PDT-56E) to determine drop impact resistance using the Bruceton Staircase Method.

# 3.5.4 Effect of Microwave Reheating on the Drop Impact Resistance of the Bottles

Unheated bottles filled with syrup at full,  $\frac{3}{4}$ ,  $\frac{1}{2}$  and  $\frac{1}{4}$  levels were used as control bottles for comparison to microwave reheated bottles from treatments 1-3, 4-6, 7-9, and 10-12, respectively. For drop height evaluation, the Bruceton Staircase Method was used to determine effect of microwave heating on drop impact resistance. Before drop testing, all bottles were stored at  $20 \pm 2$  °C,  $50 \pm 5$  % relative humidity at least 24 hours.

#### Statistical Analysis

Statistical analysis was done using a Completely Randomized Design. SAS software version 6.12 (SAS Institute, Inc.) was used to run a one-way analysis of variance to assess the influence of repeated heating on the drop impact resistance of the bottles. When the effect of microwave heating was significant, statistical difference of means was performed using Duncan's Multiple Range Test using p-value  $\leq 0.05$ (Steel, Torrie, and Dickey, 1997).

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#### 3.6 Effect of Temperature on the Drop Impact Resistance of the Bottles

The effect of the package material temperature on the drop impact resistance was determined by comparing drop impact resistance of the bottle when dropped at room temperature  $(20 \pm 2 \,^{\circ}C)$ , at elevated temperature following heating in the microwave, and at low temperature after cooling in a refrigerator. After heating at full power in the microwave oven, all bottles were then immediately subjected to the free fall drop test to determine the drop impact resistance at handle and right bottom corner using the Bruceton Staircase Method.

After heating in the microwave oven, the bottles were refrigerated for 24 hours at a temperature of 5-9 °C. The bottles were then subjected to the free fall drop test to determine their drop impact resistance at right bottom corner and handle using Bruceton Staircase Method. This test was developed to identify influence of temperature on impact resistance. This test was also used simulate the actual product's end use requirement. <u>Statistical Analysis</u>

Statistical analysis was done using Factorial Design. Cochran's Test was used to determine significant influence of the three temperatures when data were qualitative. SAS software version 6.12 (SAS Institute, Inc.) was used to run a multiple analysis of variance to assess the influence of the effect of temperatures and repeated heating on the drop impact resistance of the bottles. Duncan's Multiple Range Test was then used to establish statistical difference of means using p-value  $\leq 0.05$  (Steel, Torrie, and Dickey, 1997).

### 3.7 Determination of the Change in Percent Crystallinity of the Packaging Material by Thermal Analysis

Heat of fusion which correlates to percent crystallinity of the container can be determined by Modulated Differential Scanning Calorimeter (TA Inst. 2200, TA Instruments Inc., DE). Heat of fusion of the bottle exposed to microwave heating was compared to that of the control (unheated) bottle to determine the effect of repeated heating on the percent crystallinity of the packaging material.

To measure percent crystallinity, two unheated bottles and two bottles which were subjected to microwaves were selected and 4 material specimens were cut from the bottom and upper part near the handle of each bottle and weighed in a tared aluminum pan, and then placed in the MDSC cell to measure the endothermic processes or changes in heat capacity. The temperature of the specimen was programmed through its melting point while recording the thermal curve of temperature and heat flow associated with transitions in the samples as a function of time and temperature.

Experimental conditions included:

Heating rate : 2.5 °C/ min

Reference: empty aluminum MDSC pan

Starting Temperature: -50 °C

Limit Temperature: 175 °C

Polymer crystallinity can be determined using Modulated DSC by quantifying the heat associated with fusion of the polymer. Heat of fusion was reported as relative % crystallinity by comparing unheated polymer against heated polymer to obtain relative values.

#### **CHAPTER 4**

#### **RESULTS AND DISCUSSIONS**

#### 4.1 Wall Thickness of the Bottles

The wall thickness of the bottles used were measured at different positions: body wall, bottom face, right bottom corner, left bottom corner, and side seam. The thickness of the bottle measurements (Table 2) represent 6 replications. Thickness varied at the different positions.

Area	Thickness (inch) <sup>a</sup>
Body wall	0.055 <u>+</u> 0.001
Bottom face	0.181 <u>+</u> 0.009
Right bottom corner	$0.106 \pm 0.006$
Left bottom corner	$0.188 \pm 0.008$
Side seam	$0.057 \pm 0.002$

#### Table 2. Wall Thickness of the Bottle Material.

<sup>a</sup> mean with standard deviation

#### 4.2 Determination of the Impact Orientation of the Bottle by Free Fall Drop Test

This experiment was performed in order to establish the particular orientation which was the most susceptible to breakage due to a free fall drop. Bottles filled with syrup were tested for fracture, leakage, or breakage by dropping them from various heights using the Bruceton Staircase Method. Since not all bottles failed at the same drop height, test results were statistically evaluated (Table 3). According to ASTM Standard Test Method for Drop Impact Resistance of Thermoplastic Containers (1996), drop height from a free fall drop provides a measure of the drop impact resistance of plastic bottles.

Results of the one-way analysis of variance (Table 4) for drop heights of the bottles dropped onto their handles, face, flat bottom, right bottom corner, and left bottom corner orientations showed that bottles dropped with different drop orientations exhibited significantly different drop impact resistance ( $p \le 0.05$ ).

Orientations	Drop Height <sup>(</sup>	
	(inch)	
Handle	$22.6 \pm 0.7^{a}$	
Right bottom corner	38.6 ± 1.3 <sup>b</sup>	
Left bottom corner	$43.8 \pm 0.7^{\circ}$	
Face	$48.0 \pm 1.5^{d}$	
Flat bottom	51.0 <u>+</u> 1.0 °	

 Table 3. Drop Height Failure of the Bottles at Various Orientations.

<sup>a-e</sup> means with same superscript alphabets are not significantly different  $(p \le 0.05)$ . comparison are made only within the same column.

<sup>f</sup> mean with standard deviation

# Table 4. Analysis of Variance of Drop Height of the Bottles at Various Orientations(at 20 °C).

Source of Variation	d.f.	Mean Square	F
Orientations	4	516.060	136.524*
Error	20	3.780	

\* denotes a statistically significant difference ( $p \le 0.05$ ).

Bottles falling onto their handles, right bottom corner, and left bottom corner were more susceptible than those falling onto their face or flat bottom. Drop impact resistance was low at the bottom corners because stress was concentrated at a single point (angle drop) instead of being dispersed over the entire bottom or surface of the bottle. The low drop impact resistance at the handle was in good agreement with that reported by Briston (1995) who stated that the weak positions on the bottles were generally at mold parting lines and pinch-off regions. Hence, bottles that were impacted on their handles corresponds to where the resin was pinched off. These bottles were prone to breakage.

It was also evident that the right bottom corner was less resistant to impact than that of the left bottom corner, even though these two positions cause local areas of stress concentration. One possibility is that the material was thinner at the right bottom corner (Table 2). As the thickness increases, the impact resistance increases, and the energy required to fracture the specimen also increases (Shah, 1984). It is also possible that being on the same side as where the handle was pinched off resulted in decreased impact resistance at the right bottom corner. The right bottom corner and handle were the weakest points and therefore, were use as targets for further experiment.

#### 4.3 Determination of Bottle Drop Impact Resistance

Generally, drop impact resistance is determined by dropping blow-molded containers filled with water. Data developed from water-filled containers may not be representative of a product having high specific gravity such as syrup. Thus, in this study, the bottles were filled with syrup which is the actual product contained. To establish a

correlation between breakage, drop height, and fill level and to simulate specific end-use, drop impact resistance of the bottles was determined at full, three quarters, half, and quarter fill levels of syrup. Product weight was proportional to fill levels (Table 5). The higher the fill level, the higher the weight.

Fill Level	Product Weight (g) <sup>a</sup>
Full	907.5 <u>+</u> 2.4
Three quarter	694.9 <u>+</u> 3.1
Half	<b>483</b> .9 <u>+</u> 2.9
Quarter	<b>271.4</b> <u>+</u> <b>2.0</b>
man with standard deviation	

Table 5. Weight of the Plastic Bottle Filled with Syrup at full, 34, 1/2, and 1/4 Levels.

\* mean with standard deviation

The weak points of the bottle had been established as right bottom corner and handle. Hence, this experiment was performed by dropping the bottles at these two points.

Tables 6 and 8 show drop impact resistance of bottles dropped at right bottom corners and handles, respectively. One-way analysis of variance of drop heights at the right bottom corner (Table 7) and on the handle (Table 9), found that fill level of the syrup significantly affected drop impact resistance of the bottles ( $p\leq0.05$ ). The influence of fill levels on drop impact resistance both at right bottom corner and handle found that the higher the fill level, the higher the weight of the sample, and , therefore, the lower the drop impact resistance (Figure 5).





Level of Syrup	Drop Heights		
	(inch)		
Full	39.0 <u>+</u> 2.1 <sup>a</sup>		
Three quarter	45.6 <u>+</u> 2.5 <sup>b</sup>		
Half	54.0 <u>+</u> 1.3 <sup>c</sup>		
Quarter	57.0 <u>+</u> 2.1 <sup>d</sup>		

Table 6. Drop Heights of the Bottles Filled with Syrup at full, <sup>3</sup>/<sub>4</sub>, <sup>1</sup>/<sub>2</sub>, and <sup>1</sup>/<sub>4</sub> Levels and Dropped at the Right Bottom Corner.

<sup>a, b, c, d</sup> means with superscript alphabets are not significantly different ( $p \le 0.05$ ). comparison are made only within the same column.

<sup>e</sup> mean with standard deviation

# Table 7. Analysis of Variance of Drop Height Failure of Bottles Filled with Syrup at full, 34, 1/2, and 1/4 Levels and Dropped at the Right Bottom Corner.

Source of Variation	d.f.	Mean Square	F
Level of Syrup	3	334.20	67.515*
Error	16	4.950	

\* denotes a statistically significant difference ( $p \le 0.05$ ).

# Table 8. Drop Height of the Bottles Filled with Syrup at full, <sup>3</sup>/<sub>4</sub>, <sup>1</sup>/<sub>2</sub>, and <sup>1</sup>/<sub>4</sub> Levels and Dropped onto their Handles.

Level of Syrup	Drop Heights	
	(inch)	
Full	22.8 <u>+</u> 1.5 <b>*</b>	
Three quarter	25.8 ± 1.5 <sup>b</sup>	
Half	33.8 <u>+</u> 1.3 °	
Quarter	$40.5 \pm 1.5^{d}$	

<sup>a, b, c, d</sup> means with superscript alphabets are not significantly different ( $p \le 0.05$ ). comparison are made only within the same column.

<sup>e</sup> mean with standard deviation

Source of Variation	d.f.	Mean Square	F
Level of Syrup	3	281.55	105.534*
Error	14	2.67	

 Table 9. Analysis of Variance of Drop Height Failure of Bottles Filled with Syrup at full, <sup>3</sup>/<sub>4</sub>, <sup>1</sup>/<sub>2</sub>, and <sup>1</sup>/<sub>4</sub> Levels and Dropped onto their Handles.

\* denotes a statistically significant difference ( $p \le 0.05$ ).

## 4.4 Effect of Microwave Repeated Heating on the Drop Impact Resistance of the Bottles

#### 4.4.1 Temperature of the Sample after Heating in Microwave Oven

Bottles filled to full, three quarter, half, and at the quarter level were heated in a microwave oven, at full power for 2.00, 1.45, 1.30 and 1.00 min, respectively (Figure 4), which simulated the directions for reheating indicated on the product label. During microwave heating, the closure allowed steam to escape, while causing a slight pressure within the package. The temperature of the syrup, and inside and outside surface of the bottles was measured at several positions using a pocket-probe digital thermocouple (Electronic Development Laboratories Inc. NY).

Heating time was increased with fill levels, in order to raise the food product to the specific end temperature (58-60 °C). The mean temperatures at each product package area resent 4 replications (Table 10). The temperatures measured at each product area were quite uniform (low standard deviation). Syrup, which is high in sugar and hence has low specific heat, heated quickly in the microwave. Buffler and Stanford (1991), reported that the lower a food's specific heat capacity, the more quickly it will heat. Furthermore, bottle geometry (squat shape with round corner) also promotes uniform heating of the

product since food products heat more uniformly in a microwave oven if packaged in a container with round corners. Keeping the closure on during heating also promotes more uniform temperature.

The effect of fill level and product area (syrup, inside, and outside bottle surface) on measured temperatures was examined. Using factorial analysis (Table 11), only the product area was significantly influenced by the temperature measured, whereas level of syrup and the interaction factors of product area and level of syrup were insignificant  $(p \le 0.05)$ . The effect of level of syrup on the temperature was the same for all product areas. Since only effect of product area was significant, the product area effect was the best estimate of the difference of the sample's temperature and is presented in Table 12.

Fill Level	Time	Product Area of Interest		
	(min.)	Syrup	Bottle (inside)	Bottle (outside)
Full	2.00	57.4 <u>+</u> 2.0	56.5 <u>+</u> 2.6	43.0 <u>+</u> 2.6
Three quarter	1.75	57.0 <u>+</u> 1.4	56.3 <u>+</u> 2.9	43.0 <u>+</u> 2.1
Half	1.50	58.8 <u>+</u> 2.2	56.0 <u>+</u> 1.8	44.5 <u>+</u> 1.3
Quarter	1.00	60.5 <u>+</u> 1.3	57.3 <u>+</u> 2.5	44.5 <u>+</u> 2.6

Table 10. Temperature (°C)<sup>a</sup> of Samples after Heating in Microwave Oven.

<sup>a</sup> mean with standard deviation

Main effect	d.f.	Mean Square	F
A: Product Area	2	1009.64	197.539*
B: Level of syrup	3	12.05	2.359
Interaction			
AxB	6	8.20	1.605
Residual Error	36		

 Table 11. Analysis of Variance of Temperatures of Samples after Heating in

 Microwave oven.

\*denotes a statistically significant difference ( $p \le 0.05$ ).

#### Table 12. Temperature of the Product and Package Wall.

Product Area	Temperature <sup>d</sup>	
	(°C)	
Syrup	58.2 <sup>a</sup>	
Inside wall	56.3 <sup>b</sup>	
Outside wall	43.8 °	

<sup>a, b, c</sup> means with superscript alphabets are not significantly different ( $p \le 0.05$ ). comparison are made only within the same column.

<sup>d</sup> mean with standard deviation

Temperature of the product (Table 12) from the highest to the lowest were as follows: syrup, inside bottle wall, and outside bottle wall. The temperature of the inside bottle surface was slightly lower than that of the syrup, but higher than that of the outside bottle surface. As the plastic bottle itself does not absorb microwave energy, rise in temperature depends on the presence of a microwave absorber (water, dipolar ion, etc.) in the contained food. At the interface of a food and plastic container which is reasonably transparent to microwaves, the temperature of the container will be a result of the food temperature (Sacharow and Schiffmann, 1992). Thermal conduction plays a part in any microwave heating process when a temperature gradient exits, i.e. high temperature region to the low temperature region (Hallstrom, Skjolderbrand, and Tragardh, 1988). Heat energy was transferred from the syrup (which had high energy density) to the bottle which had low energy density. The temperature of the inside wall (56.3 °C) was, therefore, somewhat close to that of the syrup (58.2 °C) than the outside surface.

Also, the surface of microwave cooked foods, or the outside of the container wall will be cooler than the inside because the surrounding air does not heat (Decareau, 1992). Heat was lost from the surface to the cool oven, which also reduced the surface temperature. Subsequently, temperature at the outside wall surface (43.8 °C) was lower than the syrup and inside wall (56.3 °C) of the bottle.

#### 4.4.2 Effect of Microwave Reheating on Drop Impact Resistance of the Bottles

This test was done to determine the influence of microwave reheating on the impact resistance of the bottles. A three steps approach was used. First, drop height of unheated bottles was measured using a free fall drop test. Second, another set of bottles was heated in the microwave oven, as described in Figure 4, and then were subjected to the free fall drop test. Before drop testing, all bottles were conditioned for 24 hours at room temperature ( $20 \pm 2 \circ C$ ,  $50 \pm 5 \%$  relative humidity). Third, drop heights of unheated and microwave reheated bottles were compared. The magnitude of change in drop heights of the bottles was used as an indicator of microwave heating influence on the drop impact resistance.

Drop heights of the bottles after reheating in the microwave oven as dropped onto their right bottom corner or handle are shown in Figure 6. Figure 6 shows that there was correlation between drop height and microwave heating treatments (right bottom corner,  $R^2 = 0.9232$ ; handle,  $R^2 = 0.8672$ ). Figure 6 also shows that the bottles dropped at right bottom corner exhibited lower drop heights than those dropped at the handle.

Unheated bottles filled at full, <sup>3</sup>/<sub>4</sub>, <sup>1</sup>/<sub>2</sub>, and <sup>1</sup>/<sub>4</sub> syrup levels were used as control bottles and compared to microwave reheated bottle, treatments 1-3, 4-6, 7-9, and 10-12, respectively. Comparisons of drop impact resistance between unheated and heated bottles when dropped at right bottom corner and handle are shown in Table 13 and 15, respectively. In Tables 14 and 16 are shown the results of one-way analysis of variance in association with Duncan's Multiple Range Test of effect of microwave reheating on drop impact resistance of the bottles dropped onto their right bottom corner and handles.

From one-way analysis of variance in association with Duncan's Multiple Range Test (Table 14 and 16), microwave heating was found to have significantly affected the drop impact resistance. A statistically significant difference in drop height was observed between unheated bottles (control) and the bottles reheated 9 times when dropped at right bottom corner (Figure 7), and for 7 times when dropped onto their handle (Figure 8). Further reheating caused the drop impact resistance to decrease considerably. There are actually two issues including practical and statistical significance to address with respect to the difference observed. Drop impact resistance of the microwave reheated bottles was statistically different from unheated bottles, however, the decrease in drop impact resistance was probably not large enough to be of practical importance for the actual enduse performance of the bottle.

Degree of crystallinity can have a number of important effects on the properties of a polymeric material (Seymour and Carraher, 1984). The decrease in drop impact resistance, after repeated heating in the microwave oven may result from changes in physical character of the polymer.

Kemp and Kennedy (1987) found that when a polymer was heated to a specific temperature, change in physical structure occured. Change in polymer structure may result from various molecular transitions, which can lead to change in the physical properties of the material such as brittleness.

Impact properties of polymers are often modified by adding an impact modifier or plasticizer (Meyer and Leblanc, 1995). Polymers modified with low molecular additives become hard and brittle with loss and/or change in properties due to loss of these additives by evaporation from the polymer surface, or through migration during contact with solvents, water, oil, etc., (Kemp and Kennedy, 1987). Therefore, it could be possible that repeated heating of the bottles in the microwave may induce the loss of additives or impact modifiers, causing the plastic to become brittle.

In this work, the effect of additive loss on impact resistance of the bottles was not studied.

Microwave Reheating Treatment <sup>8</sup>	Level of Syrup	Drop Height <sup>f</sup> (inch)
-	Full	$39.0 \pm 2.1^{a}$
1	Full	$38.4 \pm 1.2^{a}$
2	Full	$37.5 \pm 1.7^{a}$
3	Full	39.7 <u>+</u> 1.5 <sup>a</sup>
-	3/4	45.6 ± 2.5 <sup>b</sup>
4	3/4	42.7 <u>+</u> 1.5 <sup>b</sup>
5	3/4	43.8 <u>+</u> 1.5 <sup>b</sup>
6	3/4	44.4 <u>+</u> 2.5 <sup>b</sup>
-	1/2	54.0 <u>+</u> 1.3 <sup>d</sup>
7	1⁄2	$49.2 \pm 1.5^{cd}$
8	1/2	$49.8 \pm 1.5^{cd}$
9	1/2	48.7 <u>+</u> 1.5 <sup>°</sup>
-	1/4	$57.0 \pm 2.1^{\text{f}}$
10	1/4	54.0 <u>+</u> 1.9 °
11	1/4	54.0 <u>+</u> 1.7 <sup>e</sup>
12	1⁄4	$51.7 \pm 1.3^{de}$

 Table 13. Effect of Microwave Reheating on Drop Impact Resistance of the Bottles

 Dropped at the Right Bottom Corner.

<sup>a-e</sup> means with superscript alphabets are not significantly different ( $p \le 0.05$ ). comparisons are made only within the same column.

<sup>f</sup> mean with standard deviation

<sup>g</sup> refer to microwave heat scheme in Figure 4

#### Table 14. Analysis of Variance of Effect of Microwave Reheating on Drop Impact Resistance of the Bottles Dropped at the Right Bottom Corner.

Source of Variation	d.f.	Mean Square	F
Treatments	15	185.318	49.762*
Error	58	3.72	

\* denotes a statistically significant difference ( $p \le 0.05$ ).

Microwave Reheating Treatment <sup>8</sup>	Level of Syrup	Drop Height <sup>f</sup> (inch)
-	Full	$22.8 \pm 1.5^{ab}$
1	Full	$22.5 \pm 1.5^{a}$
2	Full	$22.2 \pm 1.5^{a}$
3	Full	$22.0 \pm 1.4^{a}$
-	3/4	$25.8 \pm 1.5^{\circ}$
4	3/4	$25.5 \pm 1.5^{bc}$
5	3/4	$26.3 \pm 2.5^{\circ}$
6	3/4	$26.3 \pm 1.3^{\circ}$
	1/2	33.7 ± 1.3°
7	1/2	$30.0 \pm 2.1^{d}$
8	1/2	$28.5 \pm 1.5^{cd}$
9	1⁄2	$28.0 \pm 1.4^{cd}$
-	1/4	$40.5 \pm 1.5^{\text{f}}$
10	1/4	36.7 <u>+</u> 1.3 <sup>e</sup>
11	1/4	36.8 <u>+</u> 2.5 <sup>e</sup>
12	1/4	$36.0 \pm 2.1^{e}$

 Table 15. Effect of Microwave Reheating on Drop Impact Resistance of the Bottles

 Dropped onto their Handles.

<sup>a-c</sup> means with superscript alphabets are not significantly different ( $p \le 0.05$ ). comparisons are made only within the same column.

<sup>f</sup> mean with standard deviation

<sup>g</sup> refer to microwave heat scheme in Figure 4

#### Table 16. Analysis of Variance of Effect of Microwave Reheating on Drop Impact Resistance of the Bottles Dropped onto their Handles.

Source of Variation	d.f.	Mean Square	F
Treatments	15	145.630	38.802*
Error	48	3.75	

\* denotes a statistically significant difference ( $p \le 0.05$ ).












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# 4.5 Effect of Temperature on the Impact Resistance of the Bottles

To investigate the effect of temperature on the bottle impact resistance, the drop height impact resistance of the bottles at room temperature ( $20 \pm 2 \circ C$ ), after heating in microwave oven ( $42.3 \pm 2.2 \circ C$ ), and at refrigeration ( $8.1 \pm 1.6 \circ C$ ) was compared.

#### 4.5.1 Drop Impact Resistance at Right Bottom Corner

Bottles from the microwave heat scheme (Figure 4) were kept in a refrigerator for 24 hr, before subjected to the drop test. The bottles were dropped immediately upon taking them from refrigeration. The measured temperature of outside surface of the bottle was at  $8.1 \pm 1.6$  °C. The results are shown in Table 17. At quarter and half-filled levels, the mean drop heights of the bottle was 20.2 and 17.5 inches, respectively. Bottles filled to the three quarter and full levels broke at 16 inches, which was the lowest height setting of the drop testing machine. It was possible that the bottles would actually break at less than 16 inches, therefore a drop height of 16 inches cannot be reported as the actual drop height.

Bottles from microwave heating treatment (Figure 4) were dropped immediately after heated in microwaves at the measured temperature of  $42.3 \pm 2.2$  °C (outside surface). For bottles that were dropped at right bottom corner, number of bottle failures was very small, even at the maximum drop height (66 inches) of the drop testing machine. Mean failure drop height could not be established. Therefore, the result was reported as nonfailure across all treatments.

Microwave Reheating Treatment <sup>b</sup>	Level of Syrup	Drop Height <sup>*</sup> (inch)
1	Full	≤16.0
2	Full	≤16.0
3	Full	≤16.0
4	3/4	≤16.0
5	3/4	≤16.0
6	3/4	≤16.0
7	1/2	16.8 <u>+</u> 1.5
8	1/2	17.5 <u>+</u> 1.7
9	1/2	17.5 <u>+</u> 1.7
10	1/4	20.2 <u>+</u> 1.6
11	1/4	19.8 ± 2.1
12	1/4	19.8 <u>+</u> 1.5

Table 17. Drop Height Failure of the Bottles Dropped at the Right Bottom Corner at 8 °C.

\* mean with standard deviation

<sup>b</sup> refer to microwave heat scheme in Figure 4

Since data from dropping the bottles at 8 °C (Table 17) and 42 °C were not quantitative, the results for bottles dropped onto their right bottom corner were transferred to two nominal possible outcomes as "failure" or "nonfailure". The statistical significance of effect of temperature of the bottles on the drop heights was determined using Cochran's test. Statistical comparison of drop impact resistance of the bottles at 20, 42, and 8 °C was tabulated in Appendix A. The analysis showed that temperatures of the bottles significantly influenced the drop impact resistance (p<0.05). 66

# 4.5.2 Drop Impact Resistance onto their Handles

For bottles dropped at the handle, it was found that they broke at 16 inches which was the lowest height of the machine. Since the bottles may actually break at less than 16 inches, the actual drop height could not be determined.

Drop height failure of drops at the handle at low temperature (8 °C) was not quantitative (Table 18). Therefore, only drop height data of the bottles at room temperature (20 °C), and after heating in the microwave (42 °C) were compared to determine the effect of temperature on drop impact resistance (Table 19).

Using factorial analysis, individual parameters (temperature and microwave reheating treatments) had a significant influence on the bottle's drop impact resistance (Table 20). Whereas, interaction factors of temperature and microwave heating were nonsignificant. Thus, it could be concluded that these factors acted independently of each other. Therefore, the results for the individual parameters of temperature and microwave heat treatments are shown in Table 21 and 22, respectively.

At a higher product temperature, the bottle had increased drop impact resistance. Lower product temperature decreased the drop impact resistance (Figure 9).

The impact resistance of the bottles was strongly dependent upon the product temperature. At low temperature, the impact resistance was reduced and all plastics tend to become rigid and brittle. Conversely, at higher test temperature, the impact resistance was improved (Calister, 1994).

Microwave	Level of Syrup	Drop Height*
Reheating		(inch)
<b>Treatment</b> <sup>b</sup>		
1	Full	≤16.0
2	Full	≤16.0
3	Full	≤16.0
4	3/4	≤16.0
5	3/4	≤16.0
6	3/4	≤16.0
7	1/2	≤16.0
8	1/2	≤16.0
9	1/2	≤16.0
10	1/4	≤16.0
11	1/4	≤16.0
12	1⁄4	≤16.0

 Table 18. Drop Height of Bottles Dropped onto their Handles at 8 °C.

<sup>a</sup> mean with standard deviation
 <sup>b</sup> refer to microwave heat scheme in Figure 4

Microwave Reheating Treatment <sup>b</sup>	Level of Syrup	Drop Height at 20 °C <sup>*</sup> (inch)	Drop Height at 42 °C <sup>*</sup> (inch)
1	Full	22.2 <u>+</u> 1.5	33.0 <u>+</u> 2.1
2	Full	22.5 <u>+</u> 1.5	33.0 <u>+</u> 1.9
3	Full	22.0 <u>+</u> 1.4	33.6 <u>+</u> 2.2
4	3/4	25.5 <u>+</u> 1.5	39.0 <u>+</u> 2.1
5	3/4	26.3 <u>+</u> 2.8	39.0 <u>+</u> 2.4
6	3/4	26.3 <u>+</u> 1.3	38.3 <u>+</u> 1.3
7	1/2	30.0 <u>+</u> 2.1	<b>42</b> .0 <u>+</u> 2.1
8	1/2	28.5 <u>+</u> 1.5	<b>42</b> .6 <u>+</u> 1.2
9	1/2	28.0 <u>+</u> 1.4	<b>42</b> .0 <u>+</u> 1.9
10	1⁄4	36.8 <u>+</u> 1.3	<b>45</b> .8 <u>+</u> 2.5
11	1⁄4	36.8 ± 2.5	46.5 <u>+</u> 1.5
12	1⁄4	36.0 <u>+</u> 2.1	46.2 <u>+</u> 1.5

Table 19. Comparison of Drop Height at 20 °C and 42 °C of the Reheated Bottles Dropped onto their Handles.

<sup>a</sup> mean with standard deviation
<sup>b</sup> refer to microwave heat scheme in Figure 4

Table 20.	Analysis of Variance of Drop Height at 20 °C and 42 °C of the Reheated
	Bottles Dropped onto their Handles.

Main effect	d.f.	Mean Square	F
A: Temperature	1	3294.24	754.135*
B: Microwave Reheating	11	219.71	50.298*
Interaction			
AxB	11	6.05	1.386
Residual Error	74	4.368	

\*denotes a statistically significant difference ( $p \le 0.05$ ).

Temperature	Drop Height (inch)		
20 °C	28.2 ª		
42 °C	40.1 <sup>b</sup>		

 Table 21. Effect of Temperature of the Product on Drop Impact Resistance.

<sup>a, b</sup> means with superscript alphabets are not significantly different ( $p \le 0.05$ ). comparison are made only within the same column.

Table 22. Effect of Microwave Reheating on the Drop Impact Resistance.

Level	Drop Height °
of Syrup	(inch)
Full	27.7 <b>*</b>
Full	27.6 *
Full	27.3 ª
3/4	32.2 <sup>b</sup>
3/4	32.6 <sup>b</sup>
3/4	32.2 <sup>b</sup>
1/2	35.6 °
1/2	35.5 °
1/2	35.0 °
1/4	41.2 <sup>d</sup>
1/4	41.6 <sup>d</sup>
1/4	41.1 <sup>d</sup>
	Level of Syrup Full Full <sup>3</sup> / <sub>4</sub> <sup>3</sup> / <sub>4</sub> <sup>3</sup> / <sub>4</sub> <sup>1</sup> / <sub>2</sub> <sup>1</sup> / <sub>4</sub> <sup>1</sup> / <sub>4</sub>

<sup>&</sup>lt;sup>a-d</sup> means with superscript alphabets are not significantly different ( $p \le 0.05$ ). comparisons are made only within the same column.

<sup>e</sup> mean with standard deviation <sup>f</sup> refer to microwave heat scheme in Figure 4





Generally, most polymers are hard and brittle at temperature below their Tg, change from leathery to rubbery increase as the temperature is increased above Tg. At low temperature (8 °C), the temperature of the PP bottle was close to its Tg ( -8 °C), therefore make the polymer more brittle than at 25 °C and 42 °C.

At low temperature, the internal mobility of the molecules of the polymer is less than at higher temperature. Additionally, at low temperature, the molecules of polymer are so sluggish that they cannot absorb and dissipate the energy of a sudden shock. As temperature rises, the material passes through a phase of relaxation, and the modulus is low (Shah, 1984; Sperling, 1986). Thus at lower temperature, the polymer is more susceptible to brittleness than at higher temperature.

# 4.6 The Change in Percent of Crystallinity of the Packaging Material

Crystallinity affects many important polymer physical properties, such as strength, stiffness, and brittleness. In this study an attempt was made to determine the effect of repeated microwave heating on the crystallinity changes in the polymeric packaging material. However, to understand the effect of repeated heating on drop impact resistance due to change in physical structure of the polymer required Modulated DSC evaluation of degree of crystallinity of the polymer.

It was hypothesized that after repeated heating in microwave oven, percent crystallinity of the bottle may increase which may result in change of the impact resistance of the plastic container. Crystallinity changes were investigated using Modulated DSC.

In Figures 10 and 11 (Appendix B), are shown thermal curves of the Modulated DSC heat capacity and nonreversing heat flow. Test specimens were taken from the

bottom and from the upper part of the bottle close to the handle of unheated bottles. In Figures 12 and 13 (Appendix B), thermal curves are shown of samples from the bottom and upper part of microwave repeatedly heated bottles (12 times). Furthermore, in Figure 14, it is shown that after reheating in the microwave, the polymer showed a higher heat of fusion than that of the unheated polymer.

This heat of fusion is reported as percent crystallinity by ratioing against the heat of fusion for a 100 % crystalline sample of the same material. The degree of crystallinities of the unheated and microwave reheated bottles were compared by using 209 J/g, the heat of fusion of theoretically 100 % crystalline polypropylene (Miller, 1966). The total heat of fusion associated with the thermal curves and percent crystallinity of the samples are summarized in Table 23. Degree of crystallinity of the bottle exposed to microwave repeated heating was approximately 2.7 % higher than that from the control bottle.

During heating in the microwave, the temperature of the bottle will increase via heat conduction from the product. A number of importance transitions occur in polypropylene at high temperatures. These may result from torsional and rotational motions in both amorphous and crystalline regions. These transitions can make polymers consist of unit configurations sufficiently alike to pack into a lattice (Symour and Carraher, 1984). Miller (1966), reported that thermal motion of a polymer increases with increasing temperature, and when cohesion energy exceeds the kinetic energy of the chains, crystallization may take place (even in polymers which do not crystallize under normal condition). Nicastro, et al (1993) reported that increased mobility in the amorphous segment and melting of the semi-crystalline region resulted in the formation of

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a more crystalline structure. These mechanisms may have caused crystalline inducement

of the sample after reheating in the microwave.

Sample	Melt Peak Temperature (°C)	Enthalpy (J/g)	Degree of Crystallinity (%) <sup>*</sup>
Unheated			
Upper part	153.16 <u>+</u> 0.44	93.9 <u>+</u> 0.2	45.0 <u>+</u> 0.1
Bottom	153.45 <u>+</u> 0.11	93.6 <u>+</u> 0.6	44.8 <u>+</u> 0.2
Heated	······································		
Upper part	153.19 <u>+</u> 0.40	98.8 <u>+</u> 0.3	<b>47</b> .3 <u>+</u> 0.1
Bottom	152.96 <u>+</u> 0.16	99.0 <u>+</u> 0.0	47.4 <u>+</u> 0.0

Table 23.	Total Heat of Fusion Associated with Degree of Crystallinity of	Unheated
	and Heated Bottles in Microwave.	

<sup>a</sup> % crystallinity based on the reported theoretical value of 272 J/g for 100 % crystalline polypropylene (Miller, 1966).

Christie, Gregory, and Wood (1993) showed that processing conditions have a dramatic impact on final crystallinity and corresponding polymer properties. In addition, Nicastro, et al (1993) provided an excellent example of change in crystallinity due to high temperature exposure. They found that high temperature achieved during heat sealing increased percent crystallinity of cast polypropylene film. This resulted in an increase in brittleness of the polymer. Additionally, Shah (1984) and Kail (1991) reported that increases in percent crystallinity decreased the impact strength and increased the probability of brittle failure.

The results from this study suggest that repeated microwave heating induced crystallinity formation, which may probably decreased the impact resistance of the polymer.

# **CHAPTER 5**

#### SUMMARY AND CONCLUSIONS

Drop height measurement using a free fall drop instrument and the Bruceton Staircase Method provided a measure of the drop impact resistance of plastic syrup bottles. Bottles dropped onto their handles or right bottom corner were more susceptible to breakage then when dropped onto a flat bottom or face drop because the stress was concentrated in bottom corner (angle drop) at a single point instead of being dispersed over the entire bottom or surface of the bottle. The low drop impact resistance at the handle resulted from the weak points on the bottles due to the presence of mold parting lines and pinch-off regions. Drop impact resistance of the bottles was determined at full, 3/4, 1/2, and 1/4 syrup levels to establish a correlation between breakage, drop height, and fill level. The higher the fill level, the higher the weight of the sample, and the lower the drop impact resistance.

Bottles filled at the, 3/4, 1/2, and 1/4 levels were heated in a microwave oven, at full power for 2.00, 1.45, 1.30 and 1.00 min, respectively. These times were used to simulate directions on the product label. Heating time was correlated to fill level in order to raise the food product to a specific temperature ( $60^{\circ}$ C). Temperature of the product

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and container surfaces were as follows: syrup (58.2 °C), inside bottle wall (56.3 °C), and outside bottle wall (42.3 °C). Since the plastic bottle does not absorb microwave energy, rise in material temperature depended on the presence of a microwave absorber (water, dipolar ion, etc.) in the contained food. The temperature of the container was, therefore, a result of heat transfer from the high temperature region (syrup) to the low temperature region (bottle's wall). Temperature at the outside of the container wall is cooler than at the inside surface because the surrounding air does not heat. Heat was lost from the surface to the oven which also reduced the surface temperature (Decareau, 1992).

Drop heights of unheated and microwave reheated bottles were compared. The magnitude of change in drop heights of the bottles was used as an indicator to determine microwave heating influence on the drop impact resistance. A significant difference in drop height was observed after the bottles experienced reheating for 9 times when dropped at the right bottom corner, and 7 times when dropped at the handle. Heating times greater than this caused the impact resistance to decrease considerably.

The impact resistance of the bottles was strongly dependent upon the temperature of the product. At higher test temperature, the impact resistance was significantly greater. Conversely, at lower temperature, the impact resistance was reduced drastically. This is most likely because the internal mobility of the polymer molecules of the polymer is less than at higher temperature and the polymer molecules are so sluggish that they cannot absorb and dissipate the energy of a sudden shock from free a fall drop (Shah, 1984; Sperling, 1986).

Thermal curves of (Modulated DSC) the heat capacity and nonreversing heat flow of test specimens taken from unheated bottles and repeatedly heated bottles were

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compared. Degree of crystallinity associated with heat of fusion of the specimens taken from the bottle exposed to microwave repeated heating was approximately 2 % higher than those from the unheated bottle, indicating that repeated heating in the microwave can induce crystallinity.

A possible mechanism for the inducement of crystallinity within the bottles is as follows; during repeated heating in the microwave oven, the temperature of the bottle is raised as well as the temperature of the product inside due to heat conduction, thus resulting in change of the physical structure. Thermal mobility of a polymer increases with increasing temperature. A number of important transitions occur in polypropylene at high temperature. These may result from torsional and rotational motions in both amorphous and crystalline regions. These transitions can make polymers consist of unit having configurations sufficiently alike to pack into a lattice and result in the formation of a more crystalline structure (Seymour and Carraher, 1984; Nicastro, et al, 1993).

Results suggest that repeated microwave heating induced crystallinity formation which may probably decrease the impact resistance of the syrup bottle.

# **CHAPTER 6**

#### RECOMMENDATIONS

The recommended further studies are as follow:

1. Change in mechanical properties of the package material due to microwave reheating can be determined by measuring dynamic mechanical behavior of the polymer using Dynamic Mechanical Analysis (DMA). DMA measures the change in the modulus (normalized stiffness) and damping (energy dissipation) of viscoelastic materials with temperature, as these materials are subjected to oscillatory stresses (forces) and resultant strains (displacements).

2. Determination of the effect of additive loss on impact resistance of the bottles since it could be possible that repeated heating of the bottle in the microwave may induce loss of additives or impact modifier, causing the plastic to become brittle.

The following recommendations are for achieving higher impact resistance and duration of protection of the product packaged.

1. Copolymerization of propylene with other olefins, such as ethylene can improve its impact resistance.

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2. Decrease percent crystallinity of the package material since high crystallinity makes polymers harder and more easily fractured. The brittleness depends on the percent crystallization.

3. Addition of additive such as impact modifier to improve impact resistance.

4. Avoid using this product at low temperatures, especially at a temperature close to its Tg since thermoplastics above their Tg are rubbery in nature, while below Tg they are hard and brittle.

5. Increase the thickness of the bottle at its weak point including handle and bottom corners.

6. Bottle design can also be made to minimize wall collapse by strengthening the container by changing its geometry.

**APPENDICES** 

#### **APPENDIX A**

# **Cochran's Test for Related Frequencies**

Statistical Comparison of Drop Impact Resistance of the Bottles Dropped at the Right Bottom Corner at 20, 42, and 8 °C ( $\alpha = 0.05$ ).

 $H_0: F_{20^{\circ}C} = F_{42^{\circ}C} = F_{8^{\circ}C}$ 

$H_1$	:	F	20°C	≠	F	42°C	≠	F <sub>8°C</sub>
-------	---	---	------	---	---	------	---	------------------

Treatment	20°C	42°C	8°C	Row Total (F <sub>r</sub> )
1	1	1	1	3
2	1	1	1	3
3	1	1	1	3
4	1	0	1	2
5	1	0	1	2
6	1	0	1	2
7	1	0	1	2
8	1	0	1	2
9	1	0	1	2
10	1	0	1	2
11	1	0	1	2
12	1	0	1	2
Column Total (F <sub>c</sub> )	12	3	12	27

1 = failure, 0 = nonfailure

$$\Sigma F_{c} = 27$$
  

$$\Sigma F_{c}^{2} = 297$$
  

$$\Sigma F_{r} = 27$$
  

$$\Sigma F_{r}^{2} = 63$$
  

$$\chi 2_{(a-1,\alpha)} = (a-1)[a(\Sigma F_{c}^{2}) - (\Sigma F_{c})^{2}] / (a \Sigma F_{r} - \Sigma F_{r}^{2})$$
  

$$\chi 2_{(a-1=2,\alpha=0.05)} = 18$$
  

$$\chi 2_{(a-1=2,\alpha=0.05)} = 18 > \chi 2_{(a-1,\alpha) Table} = 5.99$$
  

$$\chi 2_{(a-1=2,\alpha=0.05)} = 18 > \chi 2_{(a-1,\alpha) Table} = 5.99$$
  
Reject hypothesis that H<sub>0</sub> : F 20°C = F 42°C = F8°C

APPENDIX B







Figure 11. MDSC Analysis of Sample from the Upper Part close to Handle of Unheated Bottle.

**APPENDIX B** 



**APPENDIX B** 







**BIBLIOGRAPHY** 

# **BIBLIOGRAPHY**

- Anonymous, 1997. Modulated DSC<sup>™</sup> Compendium: Basic Theory and Experimental Consideration. Thermal Analysis Instruments Co., Delaware.
- ASTM Designation : D 2463-95. 1997. Standard test method for drop impact resistance of blow-molded thermoplastic containers. Annual book of ASTM standards volume 8.02, American Society for Testing and Materials.
- Brandrup, J. and Immergut, E.H. 1989. Polymer handbook 2<sup>nd</sup> Edition. John Wiley & Sons, Inc. New York.
- Breakey, D. W. and Cassel, R. B. 1979. Use of thermal analysis methods in foam research and development. Thermal Analysis Application Study No.29, The Perkin-Elmer Corporation, Connecticut.
- Brennan, W. P. 1978. Characterization and quality control of engineering thermoplastics. Perkin-Elmer Thermal Analysis Application Study No.22, The Perkin-Elmer Corporation, Connecticut.
- Briston, J. H. 1994. Rigid and semi-rigid plastic containers. John Wiley & Sons, Inc. New York.
- Buffler, C. R. and Stanford, M. A. 1991. Effects of dielectric and thermal properties on the microwave heating of foods. *Microwave World*. 12 (4) : 15-22.
- Calato, A. E. 1978. Microwave properties of materials for microwave cookery. Microwave Energy Appl. Newsl. 11 (6): 3-6, 13.
- Calister, W. D, Jr. 1994. Materials science and engineering. John Willey & Sons, Inc. New York.
- Christie, A. W., Wood, C. A., and Gregory, R. B. 1993. Polypropylene crystallization effects on film forming. Polymers, Laminations & Coatings Conference. 39-41.
- Engelder, D. S. and Buffler, C. R. 1991. Measuring dielectric properties of food products at microwave frequencies. *Microwave World*. 12 (2) : 6-15.

- 86
- Hallstrom, B., Skjoldebrand, C. and Tragardh, C. 1988. Heat transfer and food products. Elsevier Science Publishing Co., Inc. New York.
- Huang, H.F. 1987. New product concepts in microwavable food packaging. *Microwave world*.8(6): 5-7.
- Fisher, R. W. 1991. Interaction of packaging & foods to provide superior quality microwaveable food products. Session 5 : Design for Plastics Packaging. 8<sup>th</sup> Annual Food Plas Conference. March 5-7. Orlando Florida.
- Katt, J. L. 1991. The effect of starches and sugars on microwave cooking. Microwave world. 12(2):19-23.
- Korshak, V.V. 1971. The chemical structure and thermal characteristics of polymers. Israel program for scientific translations, Wiener Bindery Ltd., Jerusalem.
- Lau, R. 1995. Modeling and microwave heating characteristics of food and food packaging systems, using computer simulation. The 8<sup>th</sup> Microwave Association Conference, Packed, Wrapped and Microzapped. 14-15 Sep.
- Mele, B. V., et al. 1995. Modulated DSC evaluation of isothermal cure & vitrification for thermosetting systems. *Thermochimica Acta*, 268. 121-142.
- Meyer, J. P. and Leblanc, D. 1995. Polyethylen terephthalat schlagzah modifizieren. Kunststoffe. 85 (4): 452-456.
- Miller, M. L. 1966. The structure of polymers. Reinhold Publishing Corporation. New York.
- Monte, W. C. and Landau-West, D. 1983. Expanded polystyrene containers in microwave cookery. J. Am. Dietet. Assoc. 83 (3): 323-327.
- Nicastro, et al. 1993. Change in crystallinity during heat sealing of cast polypropylene film. *Plastic Film & Sheeting*. 9 (4): 159-167.
- Ohlsson, T. and Risman, P. O. 1978. Temperature distribution of microwave heatingspheres and cylinders. *Journal of Microwave Power*. 13 (4): 303-310.
- Peason, R. 1995. Plastics play vital role in the food revolution. *Packag. week*. 11(1): 30-32.
- Rubbright, H.A. 1990. Packaging for microwavable foods. Cereal foods world. 35(9): 927-930.

- Sacharow, S. and Schiffmann, R.F. 1992. Microwave packaging. Pira international, Leatherhead, England.
- Selikhova, V. I., et al. 1989. Effect of orientation and annealing on melting and recrystallization processes in polypropylene. *Polymer Science U.S.S.R.* 31(2):804-808.
- Shah, Vishu. 1984. Handbook of plastics testing technology. John Wiley & Sons, Inc. New York.
- Singh, R. H. and Heldman, D.R. 1993. Introduction to food engineering. Academic Press, Inc. New York.
- Spath, W. 1961. Impact testing of materials. Gordon and Breach Science Publisher. New York.
- Sperling, L. H. 1986. Introduction to Physical Polymer Science. John Wiley & Son, Inc. New York.
- Stehle, A. P. 1979. Packaging and utensil perspective : shape of things to come. Microwave Energy Appl. Newsl. 12(4) : 13-15.
- Steel, R. G.D., Torrie, J. H. and Dickey, D. A.1997. Principles and procedures of statistics: A biometrical approach. McGraw-Hill Inc. New York.
- Swientek, B. 1994. Formulating and packaging microwaveable foods. *Prepared Foods*. 6(4): 36-38.
- Szulczynski, J. Z. 1978. Polypropylene is wining the bottle battle. *Plastic Engineering*. 3(6): 47-49.
- Talvitie, J. P. and Gaunt N. M. 1982. Polyethylene for thin-wall packaging. Canadian Packaging. 2(8): 26-33.
- Thomas, L. E. 1995. Characterization of melting phenomena in linear low density polyethylene by Modulated DSC. TA. Instruments Publication No. TA 227.
- Trice, R. W. and Goolsby, R. D. 1990. Effects of irradiation on the mechanical properties of polyethylene sulfide sulfone film. *SAMPE Journal*. 26 (5) 26-28.
- Troy, E.J., Shortridge, T.J., and Fazey, A.C. 1985. A test plastic-bottle designers can count on. *Plastic Engineering*. 11(8): 33-36, 38.
- Zuckerman, H. and Miltz, J 1994. Changes in thin-layer susceptors during microwave heating. *Packaging Technology and Science*. 7(4): 21-26.