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A Study of Heat-Seal Strength in the Presence of Edible Oil Surface Contamination of Ethylene–Methacrylic Acid Copolymer Films

by

David H. Britt

A Thesis

Submitted to the

Department of Packaging Science

College of Applied Science and Technology

in partial fulfillment of the requirements

for the degree of

MASTER OF SCIENCE

Rochester Institute of Technology

1998

Department of Packaging Science
College of Applied Science and Technology
Rochester Institute of Technology
Rochester, New York

Certificate of Approval

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M.S. DEGREE THESIS

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December 2, 1998

A Study of Heat-Seal Strength in the
Presence of Edible Oil Surface Contamination of
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December 2, 1998

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by

David H. Britt

ABSTRACT

Packages made from flexible film often use a heat-sealing process to ensure closure. The process involves joining two surfaces of film with heat and pressure across a period of time. Heat-seal problems arise when another substance partially obstructs the film-to-film contact. This substance acts as a surface contaminant. In packaging operations, the product being packaged is often the source of contamination in the sealing process.

Testing heat-seal strength is a primary method for evaluating seal performance of flexible film. Test procedures require contaminant-free film samples to maintain accuracy and precision in results. This study altered the test method to explore the effects of contaminated samples. It was necessary to develop a contamination technique. The new technique applies an equal distribution of contamination for each sample.

This study's hypothesis is that a non-contaminated seal will be stronger than a contaminated seal. The findings supported that contamination could block film-to-film contact preventing a continuous seal, resulting in seal strengths less than a non-contaminated seal test. Results from two types of film and different seal temperatures supported the findings.

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1 INTRODUCTION

1.1 Statement of the Problem

An occurrence with flexible packaging films is an inability to heat seal properly in the presence of surface contamination. An open or weak seal can be a result of the improperly formed heat seal. Essential to study a defective seal is an understanding of the mechanisms that create a properly-formed heat seal. A properly-formed seal is created with thermoplastic films under specific conditions. The following are generally recognized as the three most critical conditions: an elevated temperature of the sealing surfaces, pressure that pushes the surfaces together, and a designated time of exposure.

When these conditions exist in correct balance, polymeric chains are able to flow across the sealing interface and mix with the adjacent surface. Provided that the conditions remain constant, mixing will continue until the interface is indistinguishable. The heat seal is complete after the conditions have subsided, and the chains once again resist flow. Diffusion is the process that describes the heat seal or process of polymer chains flowing together on the microscopic level. Blocking or impeding diffusion of the chains can occur by a contaminant trapped at the interface between the surfaces.

At the macroscopic level, non-contaminated seals reach their full strength potential when diffusion is not impeded. Contaminated seals have some of the diffusion partially blocked causing weakened seals. The ultimate seal strength or amount of diffusion is inversely proportional to the amount of diffusion blocking. In cases of extreme contamination, diffusion can not occur and no seal will be formed.

1.2 Scope and Aim of the Study

This study evaluated surface contamination effect on the heat seal performance of a thermoplastic film. Contamination is a substance that makes another substance impure by mixing. Various substances can contaminate a heat seal. Contaminant substances

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that tend to cause sever sealing problems have similar properties. These properties are the ability to wet-out and adhere to the surface of common thermoplastic films. An example of a contaminant substance with these properties is an edible cooking oil, such as peanut oil. Oil will readily distribute across a surface and is difficult to remove. This study used peanut oil as the surface contaminant. The control used to contrast the data is a non-contaminated surface. It is beyond the scope of this paper to examine the effects of different types of contaminants, or to determine the severity of one type versus another.

The sealing surface used in flexible packaging films is typically a group of thermoplastics called polyethylene and polyethylene copolymers. Polyethylene and its copolymers are a large group of thermoplastic compounds that have common chemistry. Polyethylene is a polymer made from ethylene monomers containing a carbon-carbon double bond. The polymer structure is formed when the monomer double bonds are broken, and monomers join to a long chain of carbon atoms with hydrogen atoms. Copolymers of ethylene have additional and dissimilar monomer types incorporated into the polymer chain. Dissimilar monomer is added during the polymerization process, thus incorporating it into the polymer chain. In the case of ethylene methacrylic acid copolymer, methacrylic acid and ethylene are copolymerizised to produce the copolymer. Adding methacrylic acid changes the characteristics, including the improvement of the heat-seal performance of the polymer. Increasing the amount of methacrylic acid will increase the heat-seal performance. This improved performance prompted the use of ethylene methacrylic acid copolymer as the film type of the study. This study evaluated two different types of ethylene methacrylic acid copolymer: 9% methacrylic acid, and 12% methacrylic acid. This study evaluated only ethylene methacrylic acid copolymer film. No speculations were made through comparisons with other film types.

Film type and seal conditions are common variables for heat-seal studies. Numerous studies suggest that the seal conditions are interdependent, and all affect seal strength. The interrelationship of time, temperature, and pressure makes it impossible to

form a seal, if one of these three conditions is omitted or at an improper level. However, complex study of each condition is not always needed to differentiate the performance of film samples. In this study the variation of heat seal temperature was used to gain the depth for evaluating the seal performance and the effects of contamination. The scope of this study did not look into the effects of seal time or pressure.

1.3 Hypothesis

This study has one main research hypothesis. The object is not to prove the hypothesis correct beyond reasonable doubt. The object is to state that the probability statistically supports the hypothesis with significant confidence, and to gain better insight to this area of work. The method used to support the hypothesis will be to reject the reverse conditions, or null hypotheses. By rejecting the null hypothesis the testing will provide evidence supporting the hypothesis.

The main research hypothesis is that non-contaminated seals are stronger than contaminated seals. The null hypothesis is that contaminated seals are equal to or greater than the strength of the non-contaminated seals. This hypothesis was analyzed by a series of paired-difference t-tests. The t-tests were used to indicate the significance of the results.

The data gathered to study the main hypothesis was also used to explore other findings. These findings were designed to explore the differences: between non-contaminated heat-seals made from 12% methacrylic acid and 9% methacrylic acid film, between contaminated heat-seals made from 12% methacrylic acid and 9% methacrylic acid film, and between the heat-seal performance of 12% methacrylic acid and 9% methacrylic acid film. Heat-seal performance evaluated each film and the effect of the contamination on seal strength. These findings were analyzed by a similar series of paired-difference t-tests used to analyze the main hypothesis.

1.4 The Importance of the Study

Peanut oil is packaged in flexible pouches in many countries. In these packaging operations the oil that is being packaged causes the seal contamination. A typical packaging machine where this operation could occur is called a vertical-form-fill-seal (VFFS) machine. Oil is introduced in the filling stage of the packaging machine and the final seal is made through the product.

Product contamination of seals frequently occurs accidentally. In packaging of peanut oil, product contamination of the seal is done by design. Typical of most VFFS, the film forms a tube that is heat-sealed on the bottom. The machine overfills the pouch with oil, and a seal is made through the product. This method of sealing is used to reduce or eliminate the headspace that contains oxygen. Oxygen contributes to rancidity that leads to a reduction of shelf life. Peanut oil will benefit from this method of sealing when packaged in a flexible pouch, provided that the seals maintain integrity.

1.5 Summary

In summary, this a study of thermoplastic heat-seal performance that have been affected by surface contamination. Contamination and film type were two factors examined to determine their effect on heat-seal performance. Peanut oil, an edible cooking oil, was used to contaminate heat-seal surfaces of ethylene methacrylic acid copolymer film samples. The main hypothesis studied the comparison between contaminated and non-contaminated heat-seal film samples. Temperature, a condition of heat-seal creation, was varied to gain depth in the results. Time and pressure of the sealing conditions were held constant. The variations of factors and conditions allowed for investigation into other findings. Examined was the difference between methacrylic acid levels of the film samples. These different acid levels revealed an effect in performance between the two polymers. The factors and conditions of the study resulted in the collected heat-seal strength data, which speculates on the heat-seal integrity in a packaging application.

2 LITERATURE SEARCH

2.1 Mechanisms of Adhesion

The basic goal of this study is to evaluate a condition of the adhesion between polymer surfaces. Characteristics of an adhesive are a function of the type or mechanisms of adhesion, and the conditions that form the adhesion. Nature of a condition can be tested by varying the condition. Insight into the nature of the condition can be uncovered through analysis of the results. The mechanism behind the condition needs to be understood for the analysis. The mechanisms of adhesion are a complex and in-depth field of study. The mechanisms that cause adhesion can be grouped into three main theories. C. Heilter has listed the three main groups, and briefly describes each:

> "The theories postulated for adhesion can be classified broadly as (1) mechanical, (2) diffusion, and (3) chemical or molecular.
> The mechanical theory of adhesion ascribes the formation of a joint to flow of the adhesive into pores in the substrate, so that after solidification the adhesive is, so to speak, hooked into place...
> The diffusion theory of adhesion may be regarded as the application of the mechanical theory on a molecular scale... The theory considers the work required to produce and fill the voids at the molecular level. It employs the concepts of the flexibility of molecular chains in polymers, and the mobility of chain segments...
> The chemical or molecular theory of adhesion ascribes the forces at an interface or within a solid entirely to either long or short range molecular interactions." [Heitler, 1969]

Heitler's list includes the diffusion theory of adhesion. This theory is most relevant to this study. The diffusion theory is the most widely accepted mechanism of adhesion for heat sealing polymers. The theory was written by S. S. Voyutskii. Heitler describes Voyutskii's theory as a mechanical theory on a molecular scale. Voyutskii's theory states that polymer chains move across a surface into holes between the molecules on the other side. The chains will entangle producing adhesion between the surfaces.

W. C. Wake explains the entanglement by comparing viscosity of liquids with diffusion of polymers. Solubility is the ability of a liquid molecule to freely flow. A liquid molecule is able to move around the other molecules and through the holes created between other molecules. The theory of diffusion is similar and occurs when a molecule at the end of a polymer chain end moves through a hole of a polymer matrix. The difference between solubility and diffusion is that once the chain is through the hole, the chain becomes entangled in the matrix.

> "In the case of viscosity of a liquid the theory of rate processes postulates the movement of a molecule into a hole existing momentarily in the continuum, energy being required to form or enlarge the hole and move the molecule or segment of a molecule into it."
> "Diffusion of a small molecule through a liquid similarly involves utilization of holes existing in the liquid and implies solubility. Where the molecules are very small, solubility is high because holes existing due to the natural packing of the molecules of the liquid and their thermal motion can easily accommodate them." [Wake, 1968]

2.2 Conditions of Adhesion

It is generally accepted that three main conditions temperature, pressure, and time affect the process of diffusion. Temperature affects the movement of polymer chains, and movement is more complex than described in Wake's example. Motions of polymers gain their complexity through size and branching of the chains. S. L. Rosen describes the motions of polymer chains. Diffusion occurs when the molecular motions reach a sufficient level that allows entanglement of the chains. Molecular motion is a result of energy, often in the form of heat. Elevated temperatures increase molecule motion and the rate of diffusion. Rosen describes in detail the molecular motions of polymer chains as they relate to the energy needed to initiate the movement. The categories are listed in decreasing activation energy or temperature.

> "...the various molecular motions occurring in an amorphous polymer mass may be broken into four categories:
> 1. Translational motion of entire molecules, which permits flow;

2. Cooperative wriggling and jumping of segments of molecules approximately 40 to 50 carbon atoms in length, permitting flexing and uncoiling;
3. Motions of a few atoms along the main chain (five or six, or so) or of side groups on the main chains.
4. Vibrations of atoms about equilibrium positions, as occurring crystal lattices, except that the atomic centers are not in a regular arrangement in an amorphous polymer." [Rosen, 1971]

The translational motion of entire molecules, or polymer flow allows molecules to move and fill the holes in an adjacent polymer. Another important condition of diffusion is the contact needed between the two polymer surfaces. Pressure is needed to ensure contact between polymer surfaces. Voyutskii stresses the good contact or coalescence needed for adhesion to occur.

"The term autohesion, or self-adhesion, refers to the ability of two contiguous surfaces of the same material to form a strong bond which prevents their separation at the place of contact...
...to obtain high autohesion values it is necessary that the cohesive strength of a material be sufficiently high and that a fairly good coalescence of both surfaces of the material take place at contact." [Voyutskii, 1963]

The final condition of diffusion is time. Paraphrasing Voyutskii's work, Wake uses time as an example to defend the diffusion theory as the primary means of adhesion between polymers over the absorptive or chemical theory.

"...One of the principal arguments in favor of the diffusion theory is the growth of bond strength with time when two surfaces are brought together. Voyutskii argues that if an absorptive mechanism were involved when two surfaces are brought together, complete elimination of the inter should immediately lead to maximum bond strength is exponential, a fact explicable in terms of diffusion theory." [Wake, 1968]

H. W. Theller describes in detail the heat sealing process on a molecular level. He attributes heat-sealing forces to polymeric diffusion. Theller points out the importance of secondary chemical bonds in the heat-sealing process. A polymer is made

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up of a matrix of entangled polymer chains that are held together by secondary chemical

bonds. These same forces will hold the polymer chains together, after diffusion has

entangled the chains of two surfaces.

"...The term autohesion, or self-adhesion, refers to the ability of two surfaces of the same material in contact with each other to form a strong bond.

As the interface temperature of the two layers of material being heatsealed is increased from ambient, seals of significant strength begin to appear considerably below the melting point depends on the type of polymer..."

"...From the first appearance of measurable seal strength to a temperature almost to the melting point, bonds are formed that, when tested, fail at the interface -- they peel apart. A peel seal is not necessarily a weak seal. Peel strengths range form just above zero up to the strength of a fused seal.

The ultimate force that holds heatseals together is the same force that binds the chain molecules in the polymer structure itself: secondary valence forces. For these forces to come into play in the heatsealing process, enough movement and deformation of the polymer chains must take place for the molecules in the two surfaces to move into intimate contact with each other. The atomic groups on chains in the adjacent surface must move to within about 5 Angstrom units of each other -- a primary prerequisite for secondary bonds to form. The bonds form instantaneously if the molecules have sufficient energy and the proximity condition is met.

On a molecular scale the smooth surfaces of heatseal layers are of course not smooth, but very rough. Most polymers used in heatseal layers have a high amorphous content by design, and can be expected to have surfaces exhibiting clumps of tangled disordered chains and chain ends. The surface molecular order should nevertheless be somewhat greater than that of the bulk structure, due to the tendency of chains to lie parallel to the interface.

The first thing that must take place in the heatsealing process is to flatten the webs to bring the two surface into molecular contact over as high a percentage of the total area as possible..."

"...Increasing vigor of microbrownian movement with temperature, and the consequent increased depth of the zone of intermingling could explain the rapid increase of seal strength in the middle part of the curve of Fig A (Fig. A, refers to a typical heat seal curve -- peel strength vs. seal temperature; where the strength starts at zero, increases with temperature, then levels off). Heatseals in this portion of the curve are still peel seals. Inspection of the sealed surfaces after peeling reveals that much of the area appears to retain its shiny appearance, but with many rough spots where significant diffusion and sealing took place -- the areas of molecular contact of the original surfaces." [Theller, 1988]

2.3 Surface Contamination and Boundary Lubrication

Theller explains the importance of intimate contact between sealing surfaces. He refers to the polymer surface roughness that prevents total contact prior to total diffusion. Polymer surfaces soften during heat sealing, and the percentage of contact between surfaces increases until the original interface disappears. In order to eliminate the original interface the polymer surfaces need to displace air and contaminants. When enough contaminant is present between sealing surfaces it interferes with the adhesion between polymers.

Any foreign substance between the sealing polymers could be considered a contaminant. The chemical nature of the contaminant could increase its potential to cause problems with adhesion. Oils are often used as contaminants to prevent or decrease adhesion. Frictional adhesion between metal-to-metal contact is often not desired, and oil is used because of its unique characteristics. R. T. Davies describes oil's propensity to align and form a thin film between surfaces. He also illustrates the effect of the oil lubrication on adhesion. His work is based on frictional forces of metal to metal, but the basic formula used relates to all forms of adhesion and surfaces. Davies's fundamental premise is that oil will form a layer between surfaces preventing adhesion. Sealing polymeric materials through oil must also follow the basic theories of adhesion. Polymer surfaces add a complexity to the equation, because of their softness and surface movement. In summary, the sealing area is decreased by contamination, and this contamination will decrease the overall strength of the seal.

"In order to visualize boundary lubrication it is best to consider the extreme case where lubrication is achieved by a unimolecular film of a polar long chain compound, olec acid, for example. Here the lubricant orients itself on the surfaces by attachment via the polar ends while the carbon chains stand vertically, analogous to the pile on a carpet..."

"...it may be shown that the basic adhesion theory equation:

$$F = A \times S$$

Where; F = Force,
A = Area of junctions,

S = Shear strength, can now be rewritten in the following form:

$$F = (\Theta \times A \times \Sigma m) + [(1-\Theta) \times A \times \Sigma e]$$

Where; A = total contact Area

Θ = Fraction of A which is metal to metal contact

$(1-\Theta)$ = Fraction of A which is lubrication contact

Σm = Shear strength of metal junctions, and

Σe = Shear strength of lubrication" [Davies, 1968]

2.4 Oil

Triglycerides are the building blocks of edible oils. A triglyceride molecule is composed of one glycerol molecule attached to three fatty acid molecules. Fatty acids are straight carbon chain structures that have polar and non-polar ends. The carbon chains differ slightly. Differences in fatty acids can be broken down into three major types; saturated (palmitic and stearic), mono-unsaturated (oleic), and poly-unsaturated (linoleic). [Vaisey-Genser and Eskin, 1987]

The polar end of a fatty acid molecule will align itself on a polar surface. Bonding between the polar ends of adjacent fatty acids allows the molecules to join forming clusters. The results of the clustering gives oil its lubricant properties.

3 MATERIALS AND METHODS

3.11 Materials, Resin Synthesis

The DuPont Company manufactured both acid copolymer resins used in this study. Amounts of ethylene, methacrylic acid, catalyst, and processing conditions dictate the final molecular structure and chemical nature of the resin. Commonalties in production and general characteristics between the two resins are many. The resins compositions are similar and contain the same type of molecules. However, they differ in the amount of comonomer that is polymerized along with the ethylene majority molecule. Specifically the comomer was methacrylic acid (MAA). One resin contains 9% MAA and the other 12% MAA.

Ethylene methacrylic acid polymer is produced by an addition copolymerization reaction. Addition polymerization forces a monomer's double bonds to open, with help from a catalyst, so that it can bond with other monomers. Copolymerization adds a second monomer into the reaction. The process that creates EMAA is called a random copolymerization. The random copolymerization process creates large molecules of branched carbon chains with methacrylic acid molecules randomly incorporated into the chains. The manufacturing process introduces ethylene gas and methacrylic acid to be copolymerized in a high-pressure reactor to produce ethylene methacrylic acid (EMAA) resin. The high-pressure polymerization occurs under extreme conditions; pressures range from 10,000 to 30,000 psi, and temperatures increase to around 204°C or 400°F. [Schwartz, 1982] Ziegler-Natta catalyst, metal alkyls, and metal halides are introduced to catalyze the reaction. Figure 3.1 demonstrates the chemical formula for producing ethylene methacrylic acid.

Figure 3.1: Copolymerization of Ethylene Methacrylic Acid

Ethylene	+	Methacrylic Acid	=	Ethylene Methacrylic Acid
$(CH2=CH2)N$	+	$CH3CH=COOH$	=	$-(CH2)N(CH3)CCOOH(CH2)N-$
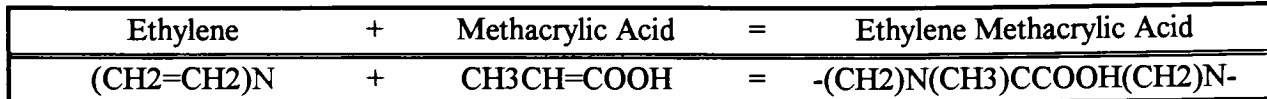
[Hoh, 1993]

3.12 Materials, Resin Classification

There are many characteristics that define EMAA as a polymer resin. This section will cover some of the characteristics that classify EMAA as an unique polymer, different from other polymers. The first separation is based on the ability of a polymer to flow. A45ll polymers are divided into two groups based on their ability to flow: thermosets and thermoplastics. Both are able to flow and solidify, but thermosets crosslink, allowing for only one solidification. Thermoplastics can flow again after solidification, and are able to repeat the flow and solidify process multiple times. EMAA resin is a thermoplastic. The thermoplastic ability allows EMAA resin to be formed into pellets; the pellets formed into film, and finally the film heat-sealed forming a package. Each step requires the ability to flow and solidify.

The thermoplastic ability is gained through the resin's structure and molecular composition. Average molecular weight, molecular weight distribution, amount of branching, and interchain secondary forces are all characteristics that define a resin's structure and molecular composition. A resin's structure and molecular composition also affect other characteristics besides ability to flow, such as toughness, melt point, and stiffness. This combination of characteristics separates this resin from other polymers.

When processing a polymer each chain of the resin may have a different length or weight. A measure of these characteristics provides the average molecular weight and molecular weight distribution. Both of these characteristics greatly affect a resin's properties. Properties affected by the average molecular weight and molecular weight distribution that are pertinent to this study include; melt point, softening point melt, melt

viscosity flow, and stiffness. Typically as a resin's molecular weight is lowered it becomes easier to melt, has a higher flow, and is softer. The opposite is true when a resin's molecular weight is raised, they become more rigid and have higher melt points. EMAA resin is considered to have a broad molecular weight distribution, and to have relatively low average molecular weight with molecular weights greater than 50,000. [Schwartz, 1982]

The amount of branching assists in forming the final properties of a resin. Highly-branched polymer chains are common among most high-pressure ethylene and ethylene copolymer resins. The intense high-pressure condition promotes branching, or molecules with side chains. Branching prevents the chain from packing tightly. A resultant resin density is inversely proportional to the amount of branching. This property allows branched homopolymer polyethylene to be categorized by its density. Density of the homopolymer correlates directly with the properties. Low-density homopolymers are typically desired for heat-seal applications because lower densities require low temperatures to heat-seal.

However, this correlation to density is not true for copolymers. Branching and the amount of copolymer contained in the resin affect copolymer resin's density. Increasing the MAA content increases the density of EMAA copolymer. The ability to heat seal at low temperatures with EMAA increases as the MAA content increases and branching increases. Figure 3.2 is a representation of an EMAA chain. The illustration has straight long lines that represent the carbon chain, and small side groups represent the MAA molecules are attached to the chain.

Figure 3.2: Chain Structure for Ethylene Methacrylic Acid

Ethylene Methacrylic Acid

MAA
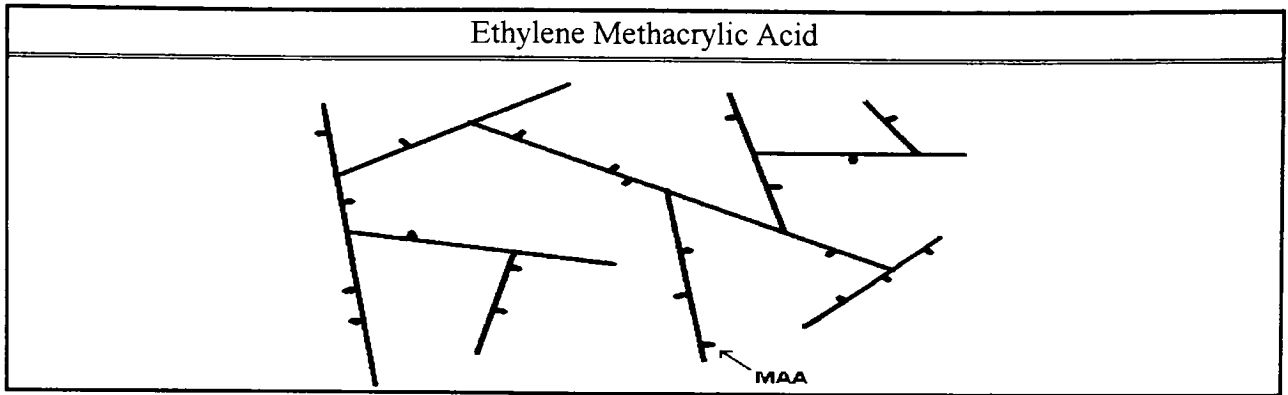
[Hoh, 1993]

Figure 3.3 illustrates the chemical structure of ethylene methacrylic acid and the two main interchain forces. This specific chemical structure and interchain forces set the unique characteristics of EMAA versus homopolymer and other copolymer. Low-density polyethylene (LDPE) homopolymer can be similar to EMAA in chain length and branching, but the MAA groups greatly affect the properties. MAA groups have two main effects upon the EMAA characteristics, the disruption of crystalline regions, and Hydrogen bonding.

Figure 3.3: Chemical Structure of Ethylene Methacrylic Acid
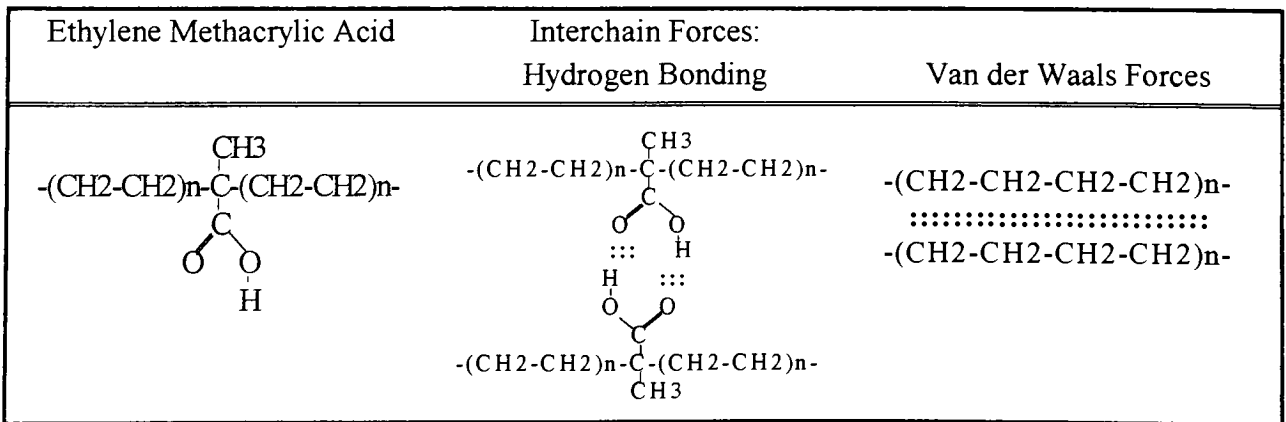
[Hoh, 1993]

Both homopolymers and copolymers have regions of crystallinity formed after a melt phase, and during solidification when two carbon chains can form weak bonds if in close alignment. The force of attraction is called Van der Waals Forces. Crystalline regions form when large sections of the polymer structure become bonded. The MAA groups interfere physically with the carbon chain's tendency to align side by side and form crystalline structures. In comparison LDPE does not contain these side groups and crystallinity will propagate more readily.

The other benefit of the MAA groups is the ability to hydrogen bond to other MAA groups. These hydrogen bonds are very strong, and hold chains in fixed positions. The hydrogen bonding that occurs between chains is random. This random bonding interferes with forming an orderly crystalline structure by locking the carbon chains into position. The overall effect of hydrogen bonding will be to disrupt large regions of crystallization in the polymer.

Despite the many factors that hinder a polyethylene or an ethylene copolymer's ability to form crystalline regions, a large percentage of the polymer will be crystalline. Homopolymer polyethylene can have crystallinity from 65% to 95% of its structure. [Schwartz, 1982] The percentage of crystallinity will determine many properties of the polymer, including its sealing temperature. These regions inhibit the ability to flow readily. A greater temperature is required to melt the crystalline regions than the amorphous regions. Amorphous regions lack the order of the crystalline regions. Adding MAA will decrease crystallinity and lower the sealing temperature.

The MAA also adds polarity to the resin. The oxygen atoms at the end of the MAA groups have a strong negative charge. Hydrogen at the end of the MAA groups has a strong positive charge. Hydrogen bonding is a result of the attraction between the positive and negative ends. Thus, strong adhesion will occur with polar substrates. This attraction between molecules is not limited to EMAA groups. EMAA groups will attract other types of polar molecules. This polarity will increase the resin compatibility to polar substances.

3.13 Materials, 9% & 12% EMAA Resin Characterization

In this section the properties that separate the two test EMAA samples will be characterized. The characterization of the two ethylene methacrylic acid resins used in this study was accomplished through several standard tests. The first test performed was to confirm the copolymer or MAA amount in the test resins. The result show that the levels of MAA were at expected levels. Testing continued with melt flow index, density, melt and freeze peaks. Table 3.1 contains the test data.

Table 3.1: Characterization of Ethylene Methacrylic Acid Resin

Test	Method	9% EMAA	12% EMAA
Percent Copolymer	DuPont	9 %	12 %
Melt Index	ASTM D-1238	1.1 g/10 min	1.2 g/10 min
Melt Peak	DSC	97.5 °C	96.5 °C
Freeze Peak	DSC	84.5 °C	82.2 °C
Density	ASTM D-792	0.94 g/cc	0.95 g/cc

[de Garavilla, 1991]

Melt Index, or MI, tests a resin's ability to flow at elevated temperatures. A higher melt index would indicate a resin that has a greater flow. Melt Index is often used when comparing various polymers because it correlates to density, average molecular weight, and crystallinity. Melt index is a simple and common test used for determining the amount of polymer that will flow through a specific diameter orifice under a given load, across a specific period of time, when exposed to a given temperature.

The resins in this study have a similar MI, the difference occurring in the amount of MAA. The 12% EMAA has slightly greater molecular weight and less crystallinity, resulting in a higher MI. The higher concentration of acid does not allow for the molecules to pack as tightly and they will flow more readily. The 12% EMAA requires less energy to achieve the same state of melt as the 9% EMAA. The data showed a

slightly greater weight collected for the 12% EMAA resin. This was expected because of the lower crystallinity levels in the 12% resin when compared to 9% MAA.

This difference in crystallinity also affected the melt peak and freeze peaks in a similar manor. The point at which the resin melted and solidified was slightly lower for the 12% MAA resin. This was expected because more energy is required to melt the crystalline regions than the amorphous regions. The total energy required will be less if there are fewer crystalline regions, equating with lower melt temperature.

Resin density results were also as expected. Data showed that the 12% MAA resin had slightly greater density than the 9% MAA resin. The percentage of MAA in a resin is measured by weight. An increase in the percentage of MAA adds weight to the polymer chains but little to its bulk. The greater weight chains are more dense.

3.14 Materials, Film Processing

Table 3.2: Processing Conditions of Ethylene Methacrylic Acid Film

Condition	Type
Machine Type	Blown Film
Extruder Type	2 inch Welex® Extruder
Screw Type	Single Flight with Mixing head
Screw Length to Diameter Ratio	30:1
Die Diameter	8 inch
Die Gap	20 mils
Blow Up Ratio	2.25:1
Film Thickness	2 mils

[de Garavilla, 1991]

The previous Table 3.2 summarized the processing conditions that produced the films for these study. The DuPont Company manufactured both acid copolymer films. These conditions were used for both resin types to produce blown films of 2-mil thickness.

3.15 Materials, Film Characterization

Several tests were used to characterize both acid copolymer films used in the study. Table 3.3 summarizes the results of the film characterization. The characterization is based on physical tests that determine the film's reaction to stress and strain. The results of the tests reflect the difference in molecular composition. Both films absorb initial stress energy by stretching their molecular chains. Each film withstands the elongation until the films pass their yield point. Prior to the yield point the film would return to its original condition. Past the yield point stress energy permanently changes the molecular orientation within the structure, and deforms the sample. The 12% EMAA film can handle higher total stress or ultimate tensile, yet has a lower yield point. Stress-Strain testing allows for a secant modulus results that indicates that the 12% EMAA is stiffer.

Table 3.3: Characterization of Ethylene Methacrylic Acid Film (2 mil)

Test	Method	9% EMAA	12% EMAA
Ultimate Tensile	ASTM D-882	3250 psi*	4400 psi*
Yield Strength	ASTM D-882	3200 psi*	3050 psi*
Elongation	ASTM D-882	475%*	525%*
Secent Modulus	ASTM D-882	19.9 Kpsi*	25.3 Kpsi*
Elmendorf Tear	ASTM D-1922	115 gram/mil	96 gram/mil
Spencer Impact	ASTM D-3420	4.58	5.45

* Average of machine and transverse direction   [de Garavilla, 1991]

3.16 Materials, Contaminant Type

Oils are used for two main purposes, cooking and lubrication. Peanut oil is just one of many edible oils derived from plants. Other oils include soy-bean, palm, cotton, and sunflower. Oil is also processed from animals and fish. Oils are similar in that they are all polar compounds. All oils are composed of fatty acids, which are hydrocarbon chains with a polar group at one end. Fatty acids differ with length and type of

hydrocarbon chains and type of polar group. One oil may contain several types of fatty acids.

A commercially available peanut oil was used as the contaminant in this study. Ingredients contained one hundred percent peanut oil. Peanut oil contains the following percentages of fatty acids; 46% oleic, 29% linoleic, 13% palmitic and stearic, and 12% other monounsaturated fatty acids. [Vaisey-Genser and Eskin, 1987]

3.21 Methods, Test Design and Analysis Techniques

A paired-difference t-test was used to analyze the data. The measurement of the control group or non-contaminated samples was compared to the test group or contaminated samples. The intent was to determine if the data reflected a significant difference and to support the main research hypothesis. A research hypothesis was formed, which stated the expectation to be tested. An opposite hypothesis, the null hypothesis, was derived from the research hypothesis. It is the null hypothesis that will be tested. The null hypothesis will be either rejected or accepted by the test data. If accepted, the data would suggest that the research hypothesis is incorrect. If the null hypothesis were rejected, the data would therefore support the research hypothesis. It is beyond the scope of this study to prove that the research hypothesis is correct; one individual test is unlikely to be conclusive.

3.22 Methods, Sample Conditioning and Preparation

Care was taken in environmental conditioning of the film samples, both prior to and after the seals were created. Conditioning is necessary to insure equilibrated states for all samples. The film had a two-week conditioning period at 72°F and 70% RH before it was coated with contaminant and sealed. After coating, within two hours, all samples were sealed. The sealed samples were held forty hours in a constant atmosphere prior to opening the seals. Forty hours will allow the seals to reach their full potential.

Special care was taken in sample preparation. This study called for a deviation from the sample preparation of standard heat-seal procedures. The procedure states that samples must be free of wrinkles, dust, and other contamination. The deviation will purposely add a known amount of contaminant to determine its effects on different sealing surfaces.

Equal amounts of edible oil, specifically peanut oil, were applied by common coating techniques. The "draw down" uses of a rod tightly wound with wire to meter the liquid contaminant. This technique provides an equal distribution of liquid per application. The technique works by administering the liquid to the top of the film, and uses the rod as a squeegee. The rod allows only a metered amount of liquid to remain on the film. The amount remaining is determined by the gaps between the diameter of the peaks. By changing the gauge of the wire various gap sizes can be obtained. This study used only one size rod. Amounts of contaminant or coating weight were measured, results in chapter 4.

3.23 Methods, Heat-Seal Testing

Heat-seal testing procedures used in this study were taken from DuPont test procedures that are in accordance to ASTM F88-85, Standard Test Method for Seal Strength of Flexible Barrier Materials. The test was designed to measure the strength of both polyethylene and polyethylene copolymer seals. The DuPont test includes procedures for creating the seal that ASTM F88-85 does not cover.

The method used was designed to be a measurement of seal strength for flexible materials. While many factors are involved with heat-seal testing, not all can be tested simultaneously. For example, the procedure does not measure seal constancy or continuity. These factors are important but are not revealed by this test. Seal strength measurements gathered through this method would show the force needed to open a seal. The test data from this method will produce only one indication to the overall package integrity.

A set of the DuPont procedures is located in the Appendix. These procedures have been determined to have 90% reproducibility. [DuPont, 1960] The data was measured in peak seal strength, and recorded in grams per inch. Compliance to procedures was followed except for modifications made to meet necessary testing objectives, such as sample preparation.

A change in the heat seal device was another modification. A Sentinel heat sealer was used instead of a J&A Keller Precision heat-sealer. DuPont standards for sealing polyethylene and polyethylene copolymers with the Sentinel recommend a pressure of 40 psi, 1 second dwell, and a varied temperature range. [DuPont, 1960] Another minor change was the switch from cellophane to a polyester film release sheet.

4 DATA AND RESULTS

4.1 Sample Identification

Designations were used in order to simplify tables. Each film specimen heat-sealed in this study was given a designation. The designation was based on the sample type. Every sample differed by means of methacrylic acid content of the film and the presence of surface contamination. The designation per sample type is given in Table 4.1

Table 4.1: Sample Key

Film Sample Type	% Acid	Surface Oil	Designation
Ethylene Methacrylic Acid Copolymer	9%	NO	9NC
Ethylene Methacrylic Acid Copolymer	9%	YES	9C
Ethylene Methacrylic Acid Copolymer	12%	NO	12NC
Ethylene Methacrylic Acid Copolymer	12%	YES	12C

4.2 Contaminant Coating Weights

A draw-down technique created the samples and individual heat seal specimens were cut from these samples. The testing used two samples sheets per type. In addition to supplying the specimens for the heat seal testing the sample sheets were used to test coating weight of contaminant on the sample. This testing was done to ensure similar contamination levels between sample types. The test recorded a specimen of a known area; the specimen was then cleaned and weighed again to determine the weight of the film. The difference between coated film and cleaned film represented the coating weight. Data located below on Table 4.2. The average coating weights of the two samples were equal with slight result differences between sheets. These results yielded an equal base from which to compare the contaminated samples to each other and against the control samples. A coating of 0.015 grams per inch would be considered a relatively

thin coating. During heat seal testing the actual coating between the heat seal surfaces is doubled because the sample is folded.

Table 4.2: Contamination Coating Weights

Contaminated Sample	Coated Film (Grams/3 inch^2)	Uncoated Film (Grams/3 inch^2)	Coating Weight (Grams/3 inch^2)	(Grams/inch^2)
9C sheet #1	0.648	0.548	0.10	0.01
9C sheet #2	0.824	0.625	0.20	0.02
Average Coating				0.015
12C sheet #1	0.725	0.623	0.10	0.01
12C sheet #2	0.767	0.566	0.20	0.02
Average Coating				0.015

4.3 Heat-Seal Data

The next table, 4.3, lists the experimental specimen data from the heat seal testing. A set of three specimens composes a sample type. Each set of specimens was prepared under identical conditions. Results were derived from averaging specimen data to derive an average strength-per-sample type for a specific temperature. The experiment was designed to produce these averages for further statistical analysis.

Each specimen was heat-sealed then tested for the strength of that seal. The strength was measured in grams per inch. The temperatures denoted in the table below are bar temperature settings at the time of the heat seal. A few minutes elapsed between specimens to make certain that the bar temperature equilibrated for each seal.

In Table 4.3 identification of the individual specimens are designated by the specimen designation numbers of 1, 2, or 3, following the sample designation. The table also uses the letters "AVG" to represent the result of an average of specimens.

Table 4.3: Heat-Seal Measurements - Complete Data

Sample Designation (Sample: Specimen Number)	Heat Seal Strength (gram/inch) per Temperature				
	100°C	112°C	125°C	137°C	150°C
9NC:1	580	3100	3275	3300	3475
9NC:2	840	2700	3450	3200	3300
9NC:3	780	2850	3350	3375	3375
9NC:AVG	733	2883	3358	3292	3383
9C:1	0	740	2525	2500	3100
9C:2	0	510	3600	2575	2975
9C:3	0	780	2400	2625	2950
9C:AVG	0	677	2508	2567	3008
12NC:1	1350	3100	3625	3475	3475
12NC:2	1100	3000	3500	3500	3450
12NC:3	1300	3375	3500	3375	3500
12NC:AVG	1250	3158	3542	3450	3475
12C:1	0	1100	2950	3050	3150
12C:2	0	1250	2775	3300	3050
12C:3	0	960	2850	3200	3200
12C:AVG	0	1103	2858	3183	3133

4.4 Statistical Value Identification

Several equations are used in determining the results. Designations are assigned to values to simplify the equations of the statistical analysis. The following table, 4.4, lists the designations. The designations represent values derived from the data, equations where data generated the end result, or values from constants obtained through statistical tables. All the values are statistical terms used to compute a result in order to determine the validity of the hypothesis testing.

Table 4.4: Value Key

Value	Notes	Designation
Average		AVG
Population Mean		μ
Sample Mean of Difference		χ
Standard Deviation of Difference		σ
Sample Size		η
Degrees of Freedom		η-1
Hypothesized Difference		δ
Computed τ Value	$\tau = (\chi-\delta)/(\sigma/\sqrt{\eta})$	τ
Probability	95% Probability	ρ
Critical τ Value	Determined from Statistical t table	τ^*

4.5 Statistical Analysis

The next five tables, 4.5 - 4.9, analyze the heat seal data from Table 4.3. Each table compares sample types that represent a particular variable to be analyzed and evaluated. The main hypothesis or variable compared the seal strengths between contaminated and non-contaminated samples. Two similar film types were tested to assist in supporting the results, Tables 4.5 and 4.6. Comparisons were made between the different film samples for both contaminated and non-contaminated states, Tables 4.7 and 4.8. Historical testing indicates that, in the non-contaminated state, one film sample would perform better as a heat sealant. Table 4.7 supports the historical testing with its conclusions. The final comparison, Table 4.9, attempts to determine whether one film sample is better than the other as related to sealing through the contamination.

The tables of analysis for each state followed a similar rationale for examination. All of the tables start with research and null hypothesis, followed by seal data, t-test computations, and end with results of the null hypothesis. The difference-paired t-test computes a t-value from the seal data. Testing parameters allow a critical t-value to be derived from a t-distribution critical-value table. Both computed and critical t-values are compared to accept or reject the null hypothesis.

The first two tables, 4.5 and 4.6, analyze the main research hypothesis, comparing the control sample to the contaminated samples. In both samples, 9% EMAA film and 12% EMAA film, the null hypothesis is rejected where the data supports the hypothesis. The results show that the seal strength of the control groups is greater than of the contaminated groups. In each case the trend of the control sample's strength is roughly 900 grams per inch greater than the contaminated samples. The results are significant, showing that there is a low probability that the results were attributable to chance. Concurring results between the film types also decreased the likelihood that chance entered into the results.

The next two tables, 4.7 and 4.8, analyze the differences between the film type under contaminated and non-contaminated states. Supplementary hypotheses were developed to examine the data. The hypothesis states that 12% EMAA film will have greater seal strength than 9% EMAA film whether contaminated or non-contaminated samples are compared. Both null hypotheses are rejected by the data, supporting the hypotheses. The results show that the 12% EMAA seal strength is greater than the 9% EMAA in either state. Trends average roughly 275 grams per inch greater, favoring the 12% EMAA. The results are significant with a low probability of error.

A supplementary hypothesis was formed to analyze the data between the film types under both contaminated and non-contaminated states. The results of this concurrent analysis of both main variables in the study are located on Table 4.9. This supplementary hypothesis states that 12% EMAA film will perform better than 9% EMAA film when sealed through contamination. The null hypothesis is the reverse conditions that state 9% EMAA film will perform equal to or better than 12% EMAA film when sealed through contamination. The results show that the null hypothesis is rejected, and therefore, the hypothesis is supported. The 12% EMAA film has a smaller difference between sealing through contamination and sealing clean film, thus is better at sealing under these conditions. 12% EMAA film trends averaged 7% greater sealing

performance than the 9% EMAA. Significant results are obtained from the data with a 95% probability.

Table 4.5: Statistical Analysis of 9% EMAA Film
Paired Difference τ-test of Contaminated and Non-Contaminated Seals

Research Hypothesis:

H: $\mu(9NC) > \mu(9C)$

H: $\mu(9NC) - \mu(9C) > 0$

Null Hypothesis:

H*: $\mu(9NC) \leq \mu(9C)$

H*: $\mu(9NC) - \mu(9C) \leq 0$

Heat-Seal Strength Data	Strength per Temperature				
Series Designation	100`	112`	125`	137`	150`
AVG-9NC	733	2883	3358	3292	3383
AVG-9C	0	677	2508	2567	3008
Difference	733	2207	850	725	375

Mean of Difference	χ	=	978
Standard Deviation of Difference	σ	=	709
Sample Size	η	=	5
Degrees of Freedom	$\eta-1$	=	4
Hypothesized Difference	δ	>	0
Computed τ Value, $\tau = (\chi-\delta)/(\sigma/\sqrt{\eta})$	τ	=	3.082
Probability	ρ	=	0.05
Critical τ Value	$\tau*$	=	2.132

Results: Reject Null Hypothesis, if $\tau > \tau*$	YES	3.082	>	2.132
Accept Null Hypothesis, if $\tau \leq \tau*$	NO	3.082	≤	2.132

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Table 4.6: Statistical Analysis of 12% EMAA Film
Paired Difference τ-test of Contaminated and Non-Contaminated Seals

Research Hypothesis:

    H: $\mu(12NC) > \mu(12C)$

    H: $\mu(12NC) - \mu(12C) > 0$

Null Hypothesis:

    H*: $\mu(12NC) \leq \mu(12C)$

    H*: $\mu(12NC) - \mu(12C) \leq 0$

Heat-Seal Strength Data		Strength per Temperature				
Series Designation		100`	112`	125`	137`	150`
AVG-12NC		1250	3158	3542	3450	3475
AVG-12C		0	1103	2858	3183	3133
Difference		1250	2055	683	267	342

Mean of Difference	χ	=	919
Standard Deviation of Difference	σ	=	744
Sample Size	η	=	5
Degrees of Freedom	η-1	=	4
Hypothesized Difference	δ	>	0
Computed τ Value, $\tau = (\chi-\delta)/(\sigma/\sqrt{\eta})$	τ	=	2.763
Probability	ρ	=	0.05
Critical τ Value	τ*	=	2.132

Results: Reject Null Hypothesis, if $\tau > \tau$*	YES	2.763	>	2.132
Accept Null Hypothesis, if $\tau \leq \tau$*	NO	2.763	$\leq$	2.132

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Table 4.7: Statistical Analysis of Non-Contaminated Film
Paired Difference τ-test of 12% EMAA and 9% EMAA Seals

Research Hypothesis:

    H: $\mu(12NC) > \mu(9NC)$

    H: $\mu(12NC) - \mu(9NC) > 0$

Null Hypothesis:

    H*: $\mu(12NC) \leq \mu(9NC)$

    H*: $\mu(12NC) - \mu(9NC) \leq 0$

Heat-Seal Strength Data	Strength per Temperature				
Series Designation	100`	112`	125`	137`	150`
AVG-12NC	1250	3158	3542	3450	3475
AVG-9NC	733	2883	3358	3292	3383
Difference	517	275	183	158	92

Mean of Difference	χ	=	245
Standard Deviation of Difference	σ	=	165
Sample Size	η	=	5
Degrees of Freedom	η-1	=	4
Hypothesized Difference	δ	>	0
Computed τ Value, $\tau = (\chi-\delta)/(\sigma/\sqrt{\eta})$	τ	=	3.311
Probability	ρ	=	0.05
Critical τ Value	τ*	=	2.132

Results: Reject Null Hypothesis, if $\tau > \tau$*	YES	3.311	>	2.132
Accept Null Hypothesis, if $\tau \leq \tau$*	NO	3.311	≤	2.132

Table 4.8: Statistical Analysis of Contaminated Film
Paired Difference τ-test of 12% EMAA and 9% EMAA Seals

Research Hypothesis:

    H: $\mu(12C) > \mu(9C)$

    H: $\mu(12C) - \mu(9C) > 0$

Null Hypothesis:

    H*: $\mu(12C) \leq \mu(9C)$

    H*: $\mu(12C) - \mu(9C) \leq 0$

Heat-Seal Strength Data		Strength per Temperature				
Series Designation		100`	112`	125`	137`	150`
AVG-12C		0	1103	2858	3183	3133
AVG-9C		0	677	2508	2567	3008
Difference		0	427	350	617	125

Mean of Difference	χ	=	304
Standard Deviation of Difference	σ	=	245
Sample Size	η	=	5
Degrees of Freedom	$\eta-1$	=	4
Hypothesized Difference	δ	>	0
Computed τ Value, $\tau = (\chi-\delta)/(\sigma/\sqrt{\eta})$	τ	=	2.776
Probability	ρ	=	0.05
Critical τ Value	τ*	=	2.132

Results: Reject Null Hypothesis, if $\tau > \tau$*	YES	2.776	>	2.132
Accept Null Hypothesis, if $\tau \leq \tau$*	NO	2.776	≤	2.132

Table 4.9: Statistical Analysis of 12% EMAA and 9% EMAA Film
Paired Difference τ-test of Contaminated and Non-Contaminated Seals

Research Hypothesis:

H: [μ(12C) - μ(12NC)] > [μ(9C)-μ(9NC)]

H: [μ(12C) - μ(12NC)] - [μ(9C)-μ(9NC)] > 0

Null Hypothesis:

H*: [μ(12C) - μ(12NC)] ≤ [μ(9C)-μ(9NC)]

H*: [μ(12C) - μ(12NC)] - [μ(9C)-μ(9NC)] ≤ 0

Heat-Seal Strength Data	Strength per Temperature				
Series Designation	100`	112`	125`	137`	150`
AVG-9NC	733	2883	3358	3292	3383
AVG-9C	0	677	2508	2567	3008
Percent Difference	0%	23%	75%	78%	89%
Heat-Seal Strength Data	Strength per Temperature				
Series Designation	100`	112`	125`	137`	150`
AVG-12NC	1250	3158	3542	3450	3475
AVG-12C	0	1103	2858	3183	3133
Percent of Difference	0%	35%	81%	92%	90%
Heat-Seal Strength Data	Strength per Temperature				
Series Designation	100`	112`	125`	137`	150`
% Difference - 12NC/12C	0%	35%	81%	92%	90%
% Difference - 9NC/9C	0%	23%	75%	78%	89%
Difference	0%	11%	6%	14%	1%

Mean of Difference	χ	=	0.07
Standard Deviation of Difference	σ	=	0.06
Sample Size	η	=	5
Degrees of Freedom	η-1	=	4
Hypothesized Difference	δ	>	0
Computed τ Value, $\tau = (\chi-\delta)/(\sigma/\sqrt{\eta})$	τ	=	2.370
Probability	ρ	=	0.05
Critical τ Value	τ*	=	2.132

Results: Reject Null Hypothesis, if τ > τ*	YES	2.370	>	2.132
Accept Null Hypothesis, if τ ≤ τ*	NO	2.370	≤	2.132

5 DISCUSSION

5.1 Discussion of Results

The previous chapter presented the data and discussed the results without speculation. This chapter will draw from earlier chapters to speculate on the causes for the results. Combining this study's results with other researcher's work uncovered in Chapter 2 improves support for the hypothesis. Each variable of the study is included in the following section, and examined to gain a better understanding of its effect.

5.2 Effect of Oil

Tables 4.5 and 4.6 are similar in design. The intent was to determine the validity of the main hypothesis, whether or not seal contamination affects seal strength. In Chapter 2 the equation for the basic adhesion theory was quoted as the force between surfaces equals the contact area multiplied by strength. Theoretically, to reach the total potential strength a system must have a one-hundred-percent contact. It is difficult for flexible films to achieve high coalescence with or without contamination. Film must overcome surface roughness, softness, and stiffness properties.

During the heat sealing process the film will soften until the surfaces are in a melt phase. Once melted the polymer will be able to gain better coalescence, aided by the heat sealing pressure. The molten polymer must then work at dispersing and encapsulating any remaining entrapped air. When this entrapped air is replaced by contaminant, the work needed to disperse and encapsulate increases. In the case of an oil contaminant the work is radically increased for several reasons. One reason is that oil is a liquid and much more dense than air. Before air is entrapped most of it is easily evacuated by the initial pressure of the heat-seal process. Greater forces are needed to evacuate the higher density oil; subsequently, more oil will remain entrapped.

Another reason for increased problems with oil is that oil has a better affinity to the polymer than to the surrounding air. This affinity is because oil is composed of carbon chains similar to that of the polymer. The problem this causes is two-fold. The greater affinity allows for a thin oil residue to remain between the surfaces after the pressure of the heat seal. Heat-seal diffusion is affected by the affinity between the mixing of shorter oil carbon chains hindering the long chain entanglement that determines the ultimate strength of the heat-seal bond.

An additional difference between air and oil is the effect it has on the heat or energy required to form the seal. The conductivity of oil will allow it to absorb more energy than air, energy that would otherwise be used in diffusion. This would explain the seemingly greater effect of contamination at lower temperatures where there is less energy. Paradoxically, less energy creates a stronger seal.

Chart 5.1 shows the data on a curve, plotted temperature versus strength. Non-contaminated samples reveal an expected heat-seal curve and strength increasing with temperature to a plateau region. The contaminated samples indicate a depressed curve. At lower temperatures there is a vast difference between the control samples and the contaminated samples. When the curve plateaus the difference becomes less pronounced. The plateaus result from sufficient temperature to encapsulate the oil. It does not reach the potential set by the control sample because the voids formed by pockets of oil remain in the seal inferface.

Considering that the individual analysis of Tables 4.5 and 4.6 were not comparing different films, the contamination effect could be examined with minimal variations. In each case the contaminant decreased contact area that directly affected the total strength.

5.3 Effect of Film Type

Analysis between film types is represented in Tables 4.7 and 4.8. Data of the two films were compared to each other in both control and contaminated states. These tests were not intended to validate the main hypothesis directly. Alternate hypotheses were

conceived to explore the effects of seal-through contamination by varying film type. The data from these tests were derived from the data collected from the main hypothesis.

Table 4.7 compares 9% EMAA to 12% EMAA in a control state; in other words a typical heat seal. The point of this test and comparison was to confirm the expected results stated in Chapter 3. Chapter 3 discussed the similarities and differences between the resin and film types used in this study. Historical data and properties indicate that 12% EMAA seal performance is superior to the 9% EMAA. These findings were supported by the test data. Heat-seal curves of the control samples are similar, Chart 5.1. In the plateau section of the heat-seal curve, the two curves are of comparable strength. However, the resin characteristics that separate the films are more pronounced at lower temperatures. The greater strength results at lower bar temperatures are accounted for by the melt point and other physical properties of the 12% EMAA that are more suited to heat sealing than are the characteristics of the 9% EMAA.

In Table 4.8, 9% EMAA was again compared to 12% EMAA. This test analyzed the films in the contaminated state. The purpose was not to actually compare the films but to determine if the same properties held true as in the previous test. Example, if two samples were tested, compared, and the results showed one sample had tested better, then theoretically, adding a new variable to both should not affect the results' magnitude, if it could be proven that the variable had a similar effect on two samples. Table 4.8's results indicate that this logic applied to this study. The new variable, contamination of the seal interface did not change expectations that the 12% EMAA had a higher seal strength than the 9% EMAA.

5.4 Performance of Film Type

It appears that contamination affects seal strength, wherein 12% EMAA has stronger seals than 9% EMAA, and 12% EMAA is stronger regardless of contamination. Comparing the 'Mean of Difference' of Table 4.7 and 4.8 gives evidence that the contamination variable affects the film types in different capacities. These tests do not

answer whether the 12% EMAA actually performs better at sealing through contamination than 9% EMAA. The 12% EMAA seems to be less affected by the contamination variable because of a greater difference concerning the contamination results. This comparison does not suggest whether the greater difference is statistically significant.

A new analysis of the data is needed to support an alternative hypothesis, that 12% EMAA is less affected by the contamination variable. Table 4.9 determines this by analyzing the difference between non-contaminated and contaminated results of the different film types. In order to determine whether 12% EMAA is better at sealing through contamination than 9% EMAA, the difference between the non-contaminated and contaminated state of 12% EMAA must be smaller than that of the 9% EMAA. It was determined that statistically 12% EMAA was superior.

Table 4.9 determined that 12% EMAA actually performed better sealing through contamination than 9% EMAA. In theory the same amount of contaminant would cover an equal area on similar surfaces and would have a similar decreasing effect on seal strengths. However, this analysis indicates that the properties that separate the film types, as distinct heat sealants, also affect their ability to seal through contamination. These film properties, both chemical and physical, are statistically important in determining the end result. In other words, these film properties do not have linear effect when contamination is included as a variable in testing seal strength.

Chart 5.1: Heat-Seal Curves for Ethylene Methacrylic Acid Film
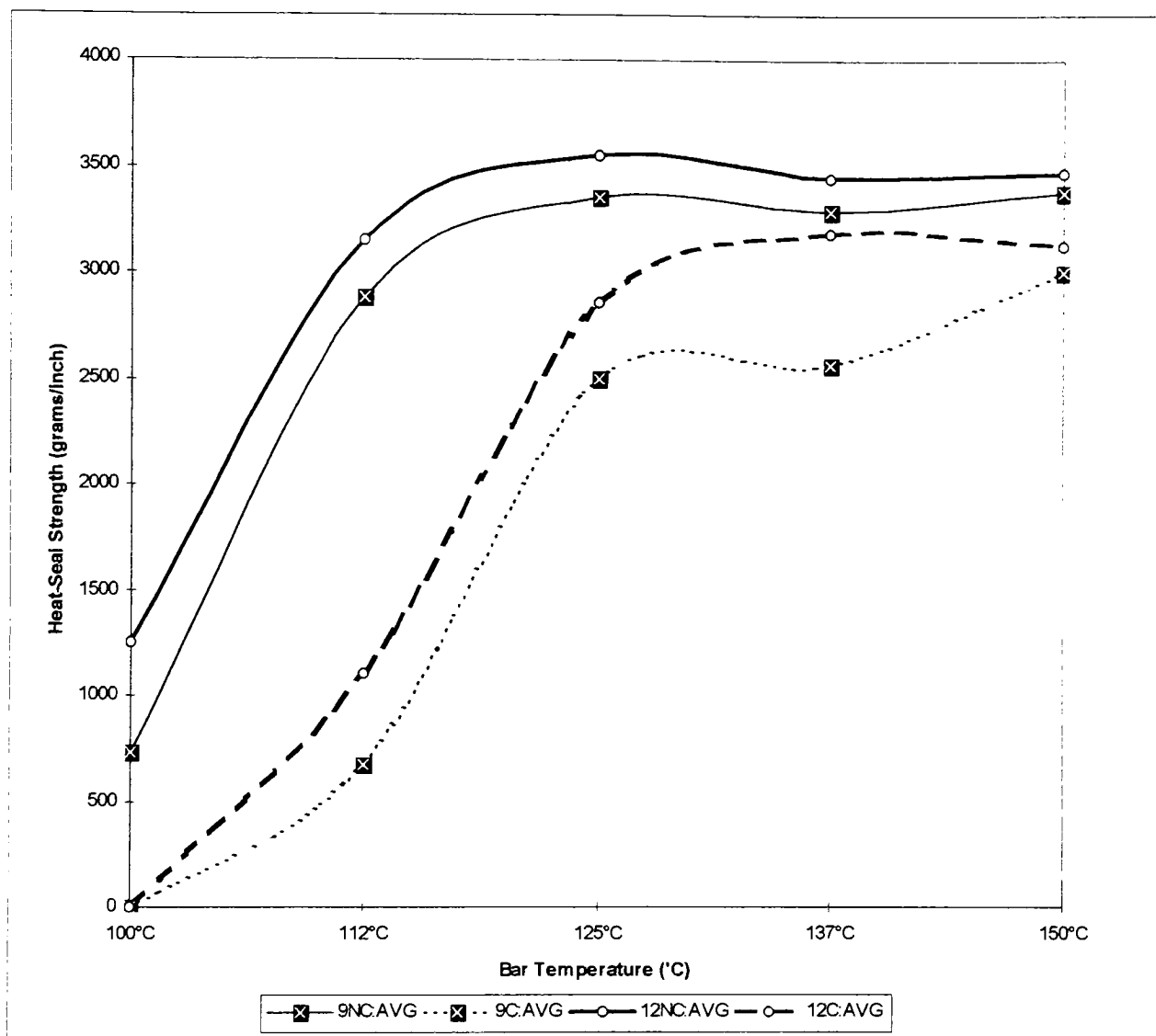
6 SUMMARY & CONCLUSION

6.1 Results

A study was conducted on the heat-seal performance of ethylene - acid copolymer films, exploring the effects of surface contamination. Evaluations between contaminated samples and control samples examined contamination's effects on seal strength. The two similar films used in the study added depth to the testing. Two film types allowed for more than one comparison between control and contaminate groups. Analysis of between-the-film types was also investigated. This analysis permitted correlations between the films, regarding seal through contamination seal performance.

This study has again supported a known fact that 12% EMAA films have a lower seal initiation temperature than 9% EMAA films and as a result will form stronger seals at lower temperatures. The hypothesis was supported. Both EMAA films were adversely affected when contamination was introduced into the seal interface. The statistical findings went further to suggest that 12% EMAA film performed better than 9% EMAA film. In other words, the 12% EMAA film was not as adversely affected by the contamination as the 9% EMAA film.

6.2 Contaminant Application

In addition to the results a goal of this study was to develop a method or technique of applying a contaminant to the samples. Contaminate coating weight was not considered a variable to be studied. However, inaccurate application techniques could lead to deviation of the results. It is important in any study to duplicate testing parameters as closely as possible. A technique was developed and utilized in this study. The method of metering a liquid contaminant permitted an equal distribution of the contaminant across the specimen, and between samples.

6.3 Further Research

The importance of this study is recognized by those who have studied heat sealing, or understand the problems that contamination can cause in the packaging industry. It is recommended that further testing be completed in the field of seal-through contamination. Other tests might include hot tack testing, varying contaminate coating weights, using dissimilar polymers, or different contaminants. It is also recommended that application techniques should be standardized to ensure quality of the results.

APPENDIX: Heat-Seal Procedure

Spruance Polyethylene Film Plant Operating Instruction: <u>No. P-6003-A</u>

Subject: <u>Heat Seal Measurement</u>

Originally Effective: <u>May 9, 1960</u>

I. Purpose

It is the purpose of this instruction to describe the standard procedure for measuring the strength of Polyethylene Heat Seals.

II. Applicability

This method is applicable to extruded Polyethylene Films to 0.004" thickness.

III. Safety Considerations

Care should be taken to prevent finger burns from the heat sealing bar.

IV Interference

A. The heat seal strength of the film is dependent on the temperature, dwell time, and sealing pressure. Any variation of any one of these variables will give inaccurate results.

B. Do not exert any stress on the film specimen during the sealing or until the seal has cooled

C. The sealer bar must be kept clean.

V. Apparatus

A. J & A Keller Precision Heat Sealer*   *(Appendages onto this instruction have added the Sentinel Heat Sealer)

B. Release sheets of 300 PD Cellophane*   *(Appendages onto this instruction have added the use of PET Film)

C. Modified Suter Single Strand Strength Tester*   Separation rate is 20"/min. Two clamps form the jaws, the lower being rigidly mounted and the upper free to pivot. *(Appendages onto this instruction have added the Instron Tester)

D. Sample Cutter, 1" wide.

VI. Principle

Polyethylene film is sealed together at standard conditions between the hot metal heater and the silicone pad of the heat sealer. The heat seal strength is the force (in Grams / Inch) required to pull the seal apart.

VII. Procedure
      A. Set the sealer to the following conditions:
            1. Dwell Time - 1 sec *(revised)
            2. Pressure - 40 psi *(revised)
            3. Temperature - 140 +/- 2 ~C *(Unless heat seal curve is desired)
      B. Select a sample of film free of wrinkles, dust and other contaminations.
      C. Cut samples approximately 4" wide and 6" long.
      D. Sandwich the sample with sealant side together between two layers of release sheet. Turn the sealer "ON" and insert the sample sandwich between the jaws of the sealer so that the seal will be about 1/2" from the end of the sample. The seal will be made MD of the film.
      E. Trip the foot pedal to activate the jaws of the sealer. Do not exert any tension on the film during the sealing operation.
      F. Remove the sample, allow sufficient time for the seal to cool to room temperature* and remove the release sheets. *(ASTM 88F-85, at least 40 hours in 73.4~F / 50% RH)
      G. Repeat steps C. through F per temperature setting.
      H. From each sample cut 3 - 1" wide specimens per temperature setting.
      I. Clamp the loose ends of the specimen into the Suter Tester and allow the lower clamp to fall.
      J. On the appropriate scale of the tester read the force (in Grams / Inch) required to cause the seal to fail.
      K. Report the heat seal value of each specimen and the average of the three.
      L. On questionable heat seal values run a check form the original sample or request re-sample.

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