INJECTION COMPRESSION MOLDING OF NON-LINEAR POSITIVE TEMPERATURE COEFFICIENT CIRCUIT PROTECTION DEVICES

By

Joseph T. Hardy

SUBMITTED TO THE DEPARTMENT OF MECHANICAL ENGINEERING IN
PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREES OF

BACHELOR OF SCIENCE IN MECHANICAL ENGINEERING

and

MASTER OF SCIENCE IN MECHANICAL ENGINEERING

at the`

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

FEBRUARY 2005

© 2005 Massachusetts Institute of Technology
All Rights Reserved

MASSACHUSETTS INSTITUTE
OF TECHNOLOGY
MAY 0 5 2005
LIBRARIES

Signature of Author: ______________________________
Joseph T Hardy
Department of Mechanical Engineering
January 15, 2005

Certified by: ______________________________
Jung-Hoon Chun
Professor of Mechanical Engineering
Thesis Supervisor

Accepted by: ______________________________
Lallit Anand
Professor of Mechanical Engineering
Chairman, Department Committee on Graduate Students

BARKER

INJECTION COMPRESSION MOLDING OF NON-LINEAR POSITIVE TEMPERATURE COEFFICIENT CIRCUIT PROTECTION DEVICES

by

Joseph T. Hardy

Submitted to the Department of Mechanical Engineering
on January 15, 2005 in partial fulfillment of the requirements for the Degree of
Master of Science in Mechanical Engineering

ABSTRACT

Polymeric self-resettable circuit protection devices have been manufactured for many years with an extrusion based process. These devices add negligible resistance to a circuit at normal power operating conditions but increases in resistance by several orders of magnitude at a pre-determined level of power in order to protect the circuit from over-current or over-voltage conditions. After the electrical surge stops, and power returns to a normal level, the resistance of the device drops, and the circuit may resume its normal operation. These devices are used in computers, cell-phones, and other consumer and industrial electronic devices where normal fuses are not convenient or practical.

The current manufacturing process extrudes long sheets of 2-mm thick polymer lined with 0.05-mm thick foil on both sides. This foil-polymer-foil structure, called plaque, is punched into 13 mm x 8 mm x 2 mm rectangles, called chips. The chips undergo heat treatment and radioactive cross-linking steps before wire leads are soldered onto them for easy electrical connection to either test or circuit boards. Though effective, this process produces more waste and remains less flexible than an injection-compression (IC) molding process. With this new process, devices are made individually in a multi-cavity mold, skipping the punching and soldering steps.

This thesis explores IC molding and its benefits and drawbacks for manufacturing circuit protection devices. IC molded devices were manufactured, tested, and compared to standard devices, produced by the extrusion process, in the areas of physical and electrical performance. Budget considerations prevented the study of individually IC molded devices and instead a 150 mm x 75 mm mold cavity was used to create an IC molded plaque from which chips could be punched and wire leads attached. In this way, any electrical variations across the IC molded plaque, produced by flow or thermal properties of the new process, could be studied with electrical tests, and physical variations across the IC molded plaque could be examined with a peel test. Cycle life data and data comparing device resistance to device temperature show that the new manufacturing process has potential to create equal or better performing devices than the existing extrusion process.

Thesis Supervisor: Dr. Jung-Hoon Chun
Title: Professor of Mechanical Engineering

Table of Contents

CHAPTER 1

INTRODUCTION

1.1 Discrete Manufacturing Processes

1.1.1 Injection Molding. Injection molding is a manufacturing process that allows plastic parts to be made quickly and cost effectively. Plastic pellets are fed from a hopper into a reciprocating screw. The purpose of the screw is to heat the pellets through shear and to homogenize the melted polymer before it is injected into the cavity. Fig. 1 shows the heating and homogenization of pellets. Heat is also added into the screw chamber from heaters that line the outside of the screw wall (Potsch et al., 1995).

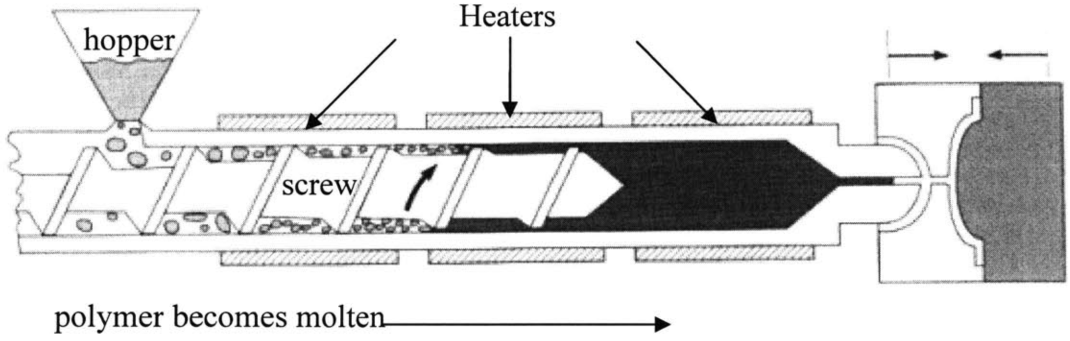

Figure 1 Injection molding screw unit with hopper and mold.

After the polymer travels the length of the screw it collects at the end of the chamber as molten polymer. The screw then pulls backwards allowing more molten polymer to fill the chamber. At this point, the screw acts as a positive displacement pump and moves forward, forcing the molten polymer through the nozzle and into the mold cavity.

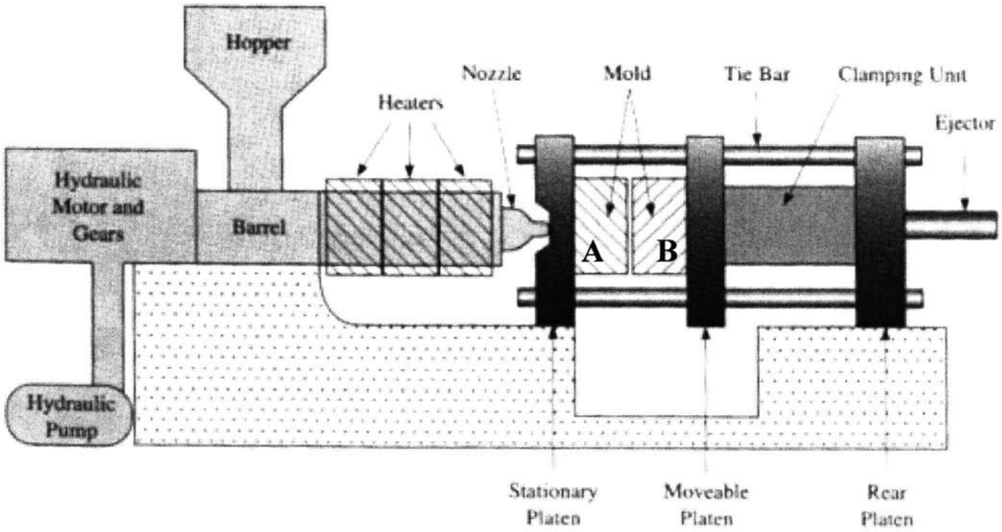

Figure 2 Basic injection molding machine layout.

The cavity is usually made of hardened steel for production runs or aluminum for prototyping runs, and has both a cavity side and a core side. The cavity side usually has an indentation and is concave, while the core side is a protrusion and is convex. For this thesis the core side will be called Side A and the cavity side will be called Side B as shown in Figs. 2 and 3. Side A is attached to the stationary platen, as shown in Fig. 2, and has a hole through which the polymer can enter during injection. Side B is attached to the moveable platen and moves open and closed during the injection molding process. It closes before injection and is held closed by a hydraulic clamp. During injection the pressure within the cavity reaches 7-14 x 10^6 N/m^2. The required clamp force is defined as the injection pressure times the projected cross-sectional area of the part (Potsch et al., 1995). After the part cools sufficiently, Side B of the mold moves back and the part is ejected by pins or a plate.

Water channels are often machined into the mold for active cooling. This allows the mold to stay relatively cool, and at a consistent temperature even after hundreds of molding repetitions. Keeping the mold at a low temperature allows the polymer to solidify rapidly and decreases the overall cycle time. In other cases, it is important for a mold to stay hot, allowing the viscosity of the polymer to stay low enough for consistent flow throughout the entire mold. Molds can be heated either by fluids, such as oil, or electric heaters. Some molds have both active heating and active cooling.

1.1.2 Injection Compression Molding. Injection-compression molding, IC molding, is a two step process. The plastic is melted in the same way as normal injection molding and is injected into a partially open cavity during the first step, as shown in Fig. 3. The shot size is created by the positive displacement of the screw, as with normal injection molding. In the second step, the hydraulic pump engages the moveable platen, as shown in Fig. 3, and moves Side B of the mold towards Side A, compressing the molten plastic into the shape of the cavity (Avery, 1998). The shot size determines the overall thickness of the part, and must be carefully controlled to ensure part-to-part consistency. After the polymer cools, the part is ejected by a set of pins or a plate, as with normal injection molding.

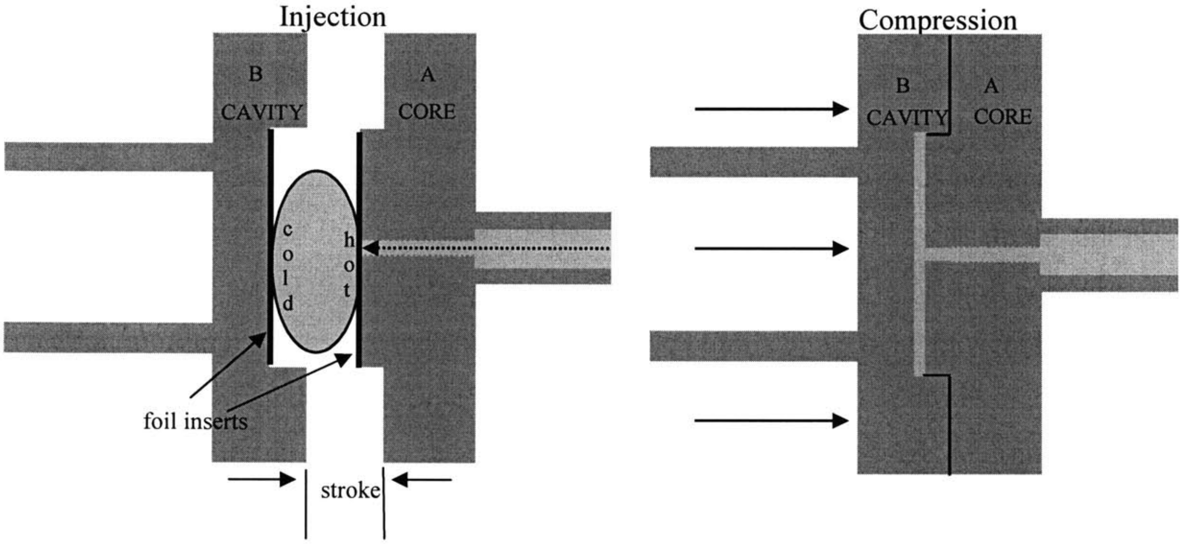

Figure 3 The two steps of IC molding: injection and compression.

IC molding adds a few notable parameters that are not available with normal injection molding: the stroke is the distance between Sides A and B when the molten plastic is shot into the open cavity, as shown in Fig. 3; the delay time is the time duration after the molten plastic has been injected before the mold begins to close; the speed at which Side B of the mold moves towards Side A, is the compression rate; the last new parameter is the pressure at which the compression takes place.

During normal injection molding the driving force of the screw forces the molten polymer to flow through small channels and into the mold cavity. The viscous flow of the polymer locks residual shear stresses into parts and rapid cooling creates thermal stresses. The effects of these combined residual stresses are most often made manifest in the physical deformation of parts after they are taken out of the mold. Thin-walled parts with large surface areas are most susceptible to these stresses and as a result, tend to bend and warp out of the intended shape most often (Avery, 1998). Supporting features are often designed into such thin-walled parts to prevent warping and give added rigidity.

During IC molding, the pressure that drives the polymer to fill the cavity does not come from the flow of the polymer, as with injection molding, but from the force of the closing cavity. For this reason, much of the residual stress that builds up during normal injection molding, does not exist in IC molding (Avergy, 1998). Less pressure is required because there are less viscous losses, and the thermal properties of the process allow the polymer to retain more heat before cooling. This minimizes part warpage, and helps to keep greater dimensional tolerance than standard injection molding.

IC molding is often used in cases where thin-walled parts must be made without ribs or supporting features, yet tolerance is very important. Two common uses of IC molding are for the manufacturing of compact discs, and lenses (Avery, 1998). Compact discs are very thin and have a large surface area, yet must maintain a high level of tolerance for optical alignment. Lenses, convex or concave, must also maintain their precise shape, or risk losing an intended magnification quality.

1.1.3 Insert-Molding. Sometimes it is desirable to manufacture a plastic part with metal inserts. Both normal injection molding and IC molding can accommodate for this added step with insert molding. Molds can be designed such that a metal part can be placed inside before molding, as shown in Fig. 4. Then, during molding, the polymer cools around the metal insert creating a finished polymer-metal object (Potsch et al., 1995). A common use of insert molding would be a plastic part with a threaded shaft insert. In this way, the part can be light, yet attached with the strength of a metal fastener.

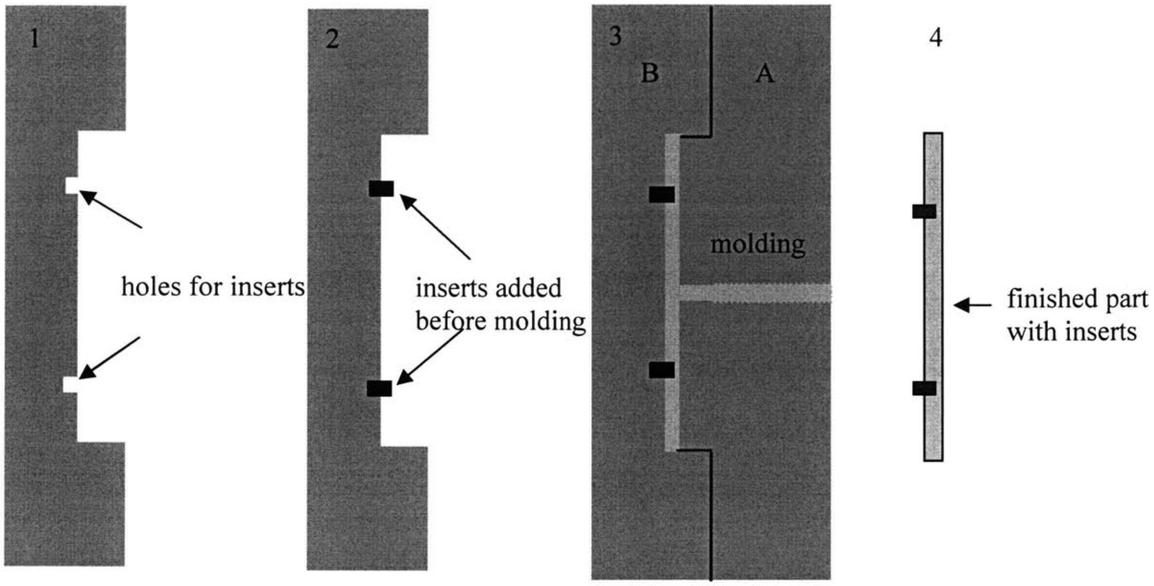

Figure 4 The insert-molding process: place inserts in mold, perform molding operation, remove part with inserts.

For this thesis, foil inserts were used with IC molding to create a large thin-walled part, called an IC molded plaque, or plaque, as shown in Fig. 3, from which devices could be made. The foil transmits current to the conductive polymer and adds physical strength to the structure. The adhesion between the polymer and foil is an important characteristic called the peel strength. It helps to determines how well electricity is conducted into the polymer and how strong the foil adheres to the polymer. This quality is examined in detail throughout Section 6.2: Peel Strength Analysis.

1.1.4 Processes Used for this Thesis. For this research a 150 mm x 75 mm cavity IC mold, as shown in Fig. 5, was used to create prototype devices for examination and analysis. The mold was set up such that polymer could be injected into the cavity and compressed to a final thickness between 5 mm and 0.25 mm depending on the amount of material in a single injection. The desired injection volume was varied on the digital display of the Battenfeld MB 1300 R2/ 250+250+50 LBK injection-compression molding machine by changing the positive displacement of the reciprocating screw before injection. The displacement of the screw was varied until the correct volume of conductive polymer was injected, and the desired plaque thickness was achieved. All

IC molded plaques were made at 2-mm thickness to match the thickness of existing devices. Foil inserts were added before each shot to provide the outside conductive layer that is needed for these circuit protection devices. The foil inserts were cut to a few millimeters less than the dimensions of the cavity. The foil was placed in the cavity side, Side A, and had to be taped onto the core side, Side B. Fig. 3 shows the location of the foil inserts during a normal IC molding operation. IC molding onto films or metal skins is commonly used by many automotive companies in Japan and North America to produce interior door panel components (Avergy, 1998).

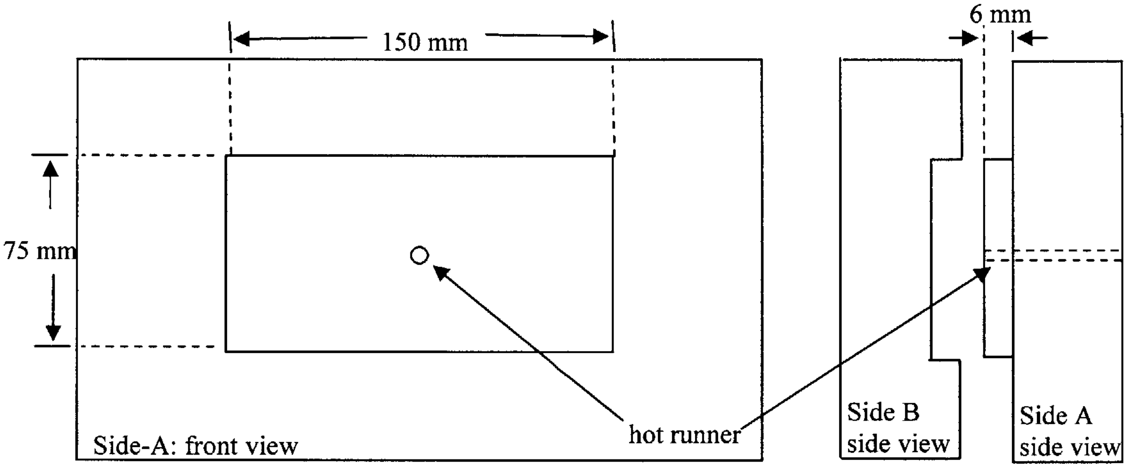

Figure 5 Side A of the mold, front view, and Side A and Side B, side-view.

The mold was initially heated by circulating fluid that passed through two channels behind the cavity on both Sides A and B. The fluid could not be heated to more than 110° C, and the mold surface never reached a temperature greater than 80° C. After much analysis, it was determined that the mold needed to be heated to a higher temperature, and so the fluid heating system was replaced by electrical heating.

Five ejector pins were located in Side B, as shown in Fig. 6, and could eject the IC molded plaque after each molding operation. In some instances, it was desirable to remove the plaque while the polymer was still very hot, and a pusher plate was inserted at the back of Side B, as shown in Fig. 6, to prevent part deformation that was caused by the ejector pins.

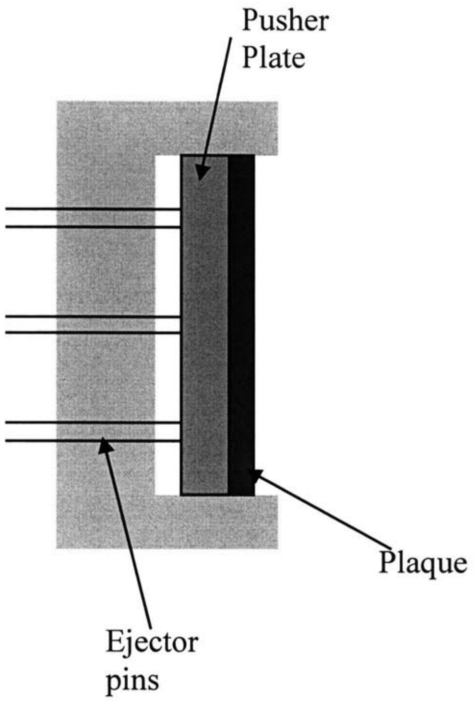

Figure 6 Side B of the IC mold with pusher plate and ejector pins.

The mold was created to accommodate a hot runner that was used throughout the research. The runner was usually heated to a temperature slightly greater than the final barrel temperature. The runner was placed in the middle of the mold on Side A as shown in Fig. 5. The hot runner allowed for quick cycle time during part production, because it was not necessary to remove the sprue.

1.2 Continuous Manufacturing Processes

1.2.1 Polymer Sheet Extrusion. Polymer sheet extrusion is a continuous process. The three basic steps are heating, extrusion, and cooling. In the heating phase, pellets are fed from the hopper into a reciprocating screw, much like injection molding, until the shear force and ceramic heaters melt the polymer to a molten phase. The polymer feeds down the screw until it becomes a homogenous molten flow. The molten flow is then fed through the die during the extrusion phase, and emerges as the shape of the die (Hensen, 1997). With sheet extrusion, the type used in the manufacturing of polymeric circuit protection devices, the die shape is usually in the form of a coat hanger (often called a "coat hanger" or "whale's-tale" die), and is placed 100 – 200 mm upstream from a set of rubber-coated heated rollers, as shown in Fig. 7. In this way, any thickness variations that exist in the polymer sheet after emersion from the die are quickly dispersed as the rubber rollers press the sheet. In the third phase of sheet extrusion, cooling, the polymer sheet is pulled through heated rollers where it achieves its final thickness, and is cooled with the ambient air, downstream from the rollers. The rollers are actively heated by oil that is circulated in and out during extrusion.

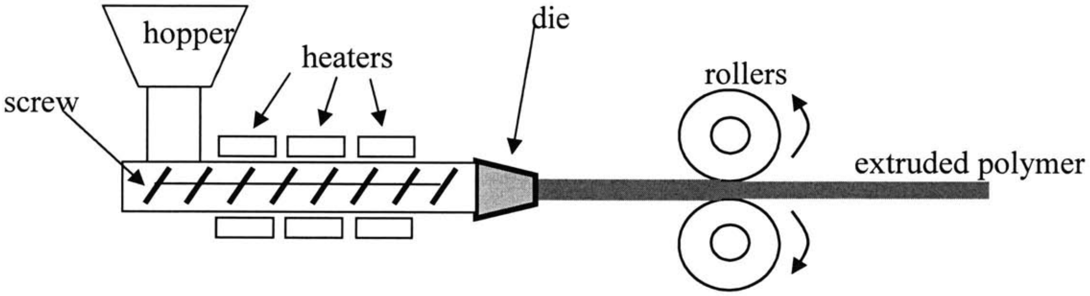

Figure 7 Sheet extrusion process.

1.2.2 Extruded Sheet Lamination. Metal foils can be added to the surface of the extruded polymer sheet with a continuous lamination process that is shown in Fig. 8. Foil is fed from rolls onto each side of the polymer sheet after the molten polymer flow emerges from the die (Hensen, 1997). A foil-polymer-foil multi-layer enters the rubberized rollers and leaves as a single structure. For the purposes of this thesis, foil is added to the existing polymer to create an electrode that will provide conductivity between the wire which is soldered onto the foil, and the conductive polymer. The foil-polymer-foil structure that emerges from the rollers is called an extruded plaque, or plaque.

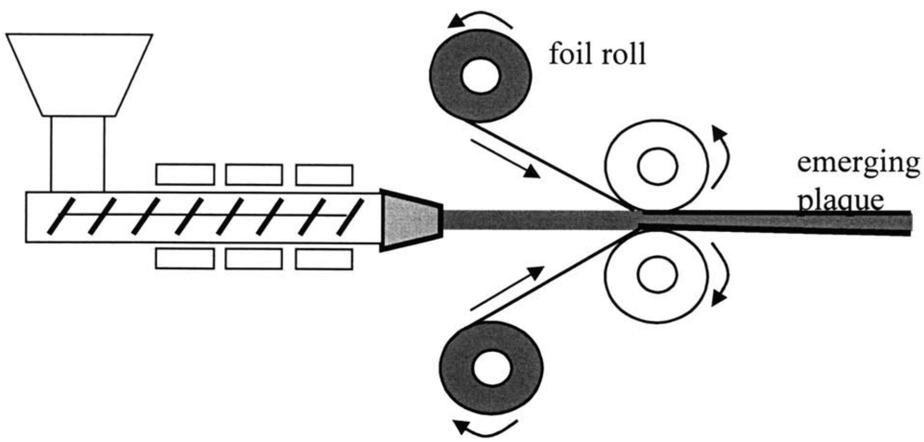

Figure 8 Polymer sheet lamination with foil rolls.

The adhesion between the polymer and foil is usually called the peel strength, and is examined through a peel test. This test consists primarily of peeling the foil from one side of the plaque at a constant rate. If the width of the peel specimen is known, and if the peel force is known, then the peel strength can be determined. Peel strength has units of force per length or N/cm. Section 6.2 examines peel strength behavior of both extruded and IC molded plaques.

CHAPTER 2

RE-SETTABLE FUSE TECHNOLOGY

2.1 Fuses

A fuse protects circuits by limiting the amount of electric current that can access the portion of the circuit that is downstream from the fuse. If the allowable current limit is reached, the fuse burns, protecting the circuit from a current that might hurt the electrical components downstream of the fuse. After an over-current event, fuses must be replaced in order for the circuit to become active again.

A fuse has many practical applications, but it does not seem particularly suited to some consumer electronics. For this reason, a self re-settable fuse is much more appropriate: one that will "trip" when current is high, and reset to its normal resistance during lower levels of current. In this way, consumer electronics can be protected from static shocks and power supply errors without the need for one-time-use fuses.

2.2 The Linear Positive Temperature Coefficient Effect

Conductive materials have a certain electric resistivity for a given temperature of the material. Temperature changes will result in a resistivity change. If the relationship between the temperature of the material and the resistivity is positive such that an increase in temperature causes an increase in resistance, than the medium is a positive temperature coefficient, PTC, material. If an increase in temperature causes a decrease in resistance, than the material is a negative temperature coefficient, NTC, material. Fig. 9 shows a graphical representation of this behavior. Most conductive metals have a linear positive temperature coefficient such that changes in the material temperature create a proportional change in resistance.

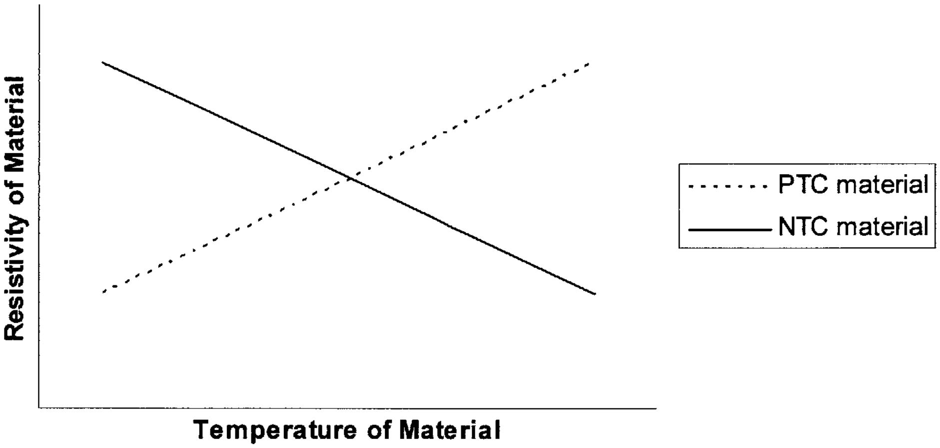

Figure 9 The temperature-resistivity behavior of linear PTC and NTC materials.

2.3 Conductive Polymers

Polymers have the capacity to conduct electricity when other elements are added within their polymeric matrix. A commonly added conductive element is carbon-black, but metal fibers and flakes have also been added to polymer matrices for effective electrical conduction (Sichel, 1982). Carbon-black is elemental carbon that is different from commercial carbons such as coke and charcoals by the fact that it is in particulate form (Cheremisinoff, 1987). A benefit to normal carbon-black over ferrous metal fillers, is that the resistivity of carbon-black does not degrade due to oxygen exposure. Some metals oxidize with time and change the resistance of the conductive polymer.

Carbon-black and the polymer base, high density polyethylene is most often used in this thesis, are mixed and homogenized to create even distribution of the carbon-black throughout the crystalline matrix. The carbon-black only resides in the amorphous portion of the semi-crystalline polymer after cooling. The carbon-black creates random conductive pathways across the polymer, giving it a conductive quality (Sichel, 1982). The resistivity of the polymer is inversely related to the number of these complete electrical paths that are formed during homogenization. If the homogenization is not complete, the carbon may not be used to its greatest efficiency, and the resistivity of the polymer may be higher than its optimum point.

A conductive polymer that has 30% carbon-black by weight will have a lower resistivity than a conductive polymer that has 20% carbon-black by weight, assuming equivalent mixing. A greater amount of carbon-black increases the statistical chances of more complete conductive paths throughout the polymer matrix. Therefore, a material with fewer paths will have greater resistivity.

2.4 The Non-Linear Positive Temperature Coefficient Effect

When conductive materials go through a phase change, the resistance-temperature behavior may go through a non-linear region. Conductive semi-crystalline polymers exhibit this non-linear effect in a temperature region that starts when the polymer first begins to lose its crystallinity at the lower melt temperature, Tlm in Fig. 10, about 30 degrees before the melt temperature, Tm. At Tlm the smallest crystals within the polymer begin to melt, and at Tm, the largest crystals can melt. The resistivity of the polymer no-longer increases linearly within Region 2, but at a new exponential rate as volume increases rapidly (Peacock, 2000).

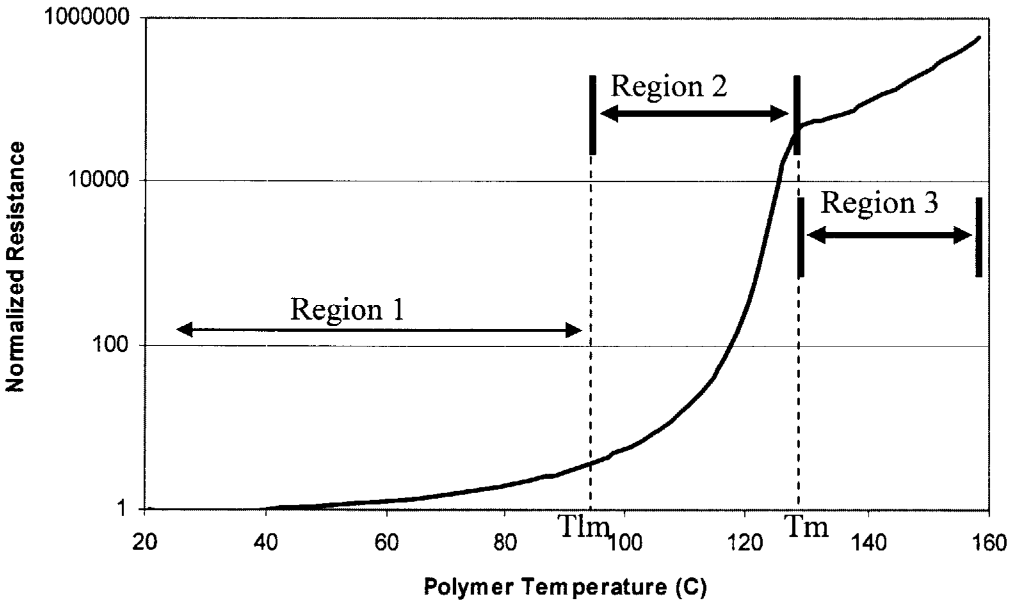

Figure 10 The three resistance-temperature regions of a typical non-linear PTC material across its range of operational temperatures.

Semi-crystalline polymers exhibit this non-linear region of resistance-temperature behavior most often. Amorphous polymers do not have a non-linear resistance-temperature region. The volume of a semi-crystalline polymer is made up primarily of polymer crystals, with a smaller percentage of amorphous regions. In temperatures well below the Tm or Tlm, the specific volume increases linearly with temperature. Once the polymer temperature reaches Tlm, 82 – 91° C for HDPE (Peacock, 2000), the smallest crystals begin to melt, and the specific volume of the polymer increases rapidly, at a greater-than-linear rate. As the temperature rises even closer to Tm, more and more of the bigger crystals melt, increasing the specific volume of the polymer even more. Once Tm is reached, all the crystals within the polymer have melted and the non-linear volumetric expansion ends, returning the polymer to its normal linear rate of volumetric expansion (Peacock, 2000).

In a conductive crystalline polymer, the resistance is closely related to the volumetric expansion that was described above. Low currents do not heat the polymer past the linear portion of the volumetric expansion, shown in Region 1 of Fig. 10. High currents will heat the conductive polymer rapidly until the specific volume begins to increases at a non-linear rate at Tlm. At this point, the conductive carbon-black pathways within the polymer begin to break exponentially as the specific volume increases rapidly due to melting crystals. The high percentage breaking of these conductive paths results in an exponential increase in the resistance because the current has fewer complete conductive pathways to travel across, as shown by Region 2. Once temperature of the conductive polymer reaches the melting temperature, Tm, all the crystals have melted and the resistance stops increasing at an exponential rate. This new linear resistance region is shown in Region 3.

Polymeric positive temperature coefficient (PPTC) devices use the non-linear resistance-temperature behavior of conductive polymers that is described above to protect circuits from dangerous current conditions. During normal operation, the resistance of a PPTC device is very low and allows low current to flow through easily. During a high-current event, the PPTC device protects the circuit by increasing from low resistance to high resistance (a typical increase of at least 4-6 orders of magnitude in resistance), effectively closing the circuit. Ohm's law, V = IR, shows that as the resistance of the PPTC device increases, the current through it decreases proportionally. After the over-current event, or trip event, the device cools and returns to its initial resistance, allowing low current to flow through the device once again.

2.5 Nodular Foil

One of the most important physical properties of a non-linear PPTC circuit protection device is the adhesion between the foil terminals and the polymeric base. This adhesion is achieved during the extrusion process when the hot polymer and foil are fed between hot rolls and pressed together. The foil surface that is pressed into the plastic has a rough microscopic structure that is known as a nodular structure.

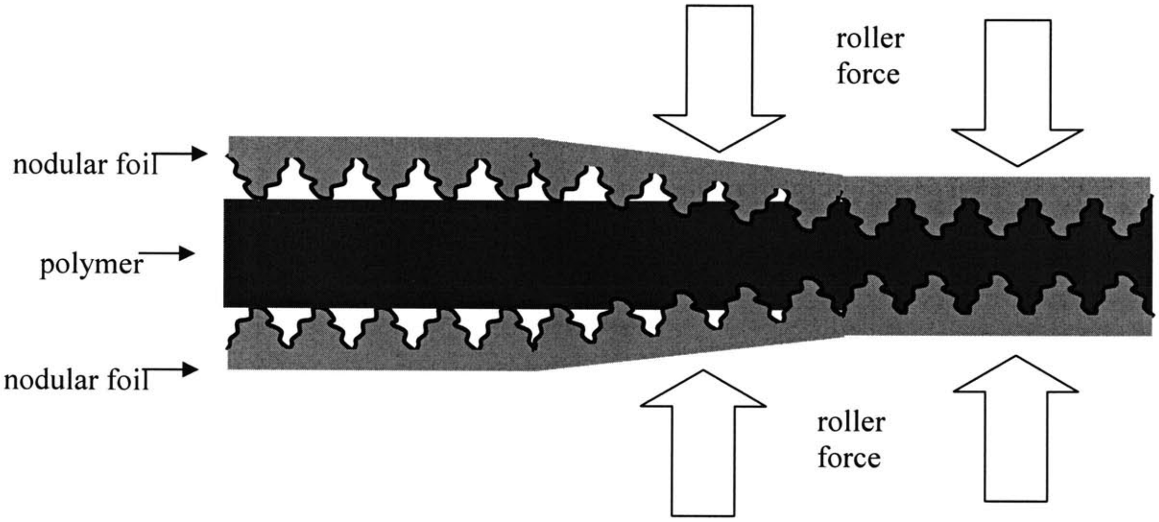

Figure 11 The nodular foil embedding itself into the hot polymer substrate during lamination.

As shown in Fig. 8, polymer is fed through rollers and between foil sheets. Fig. 11 shows how the nodular surface is pressed into the polymer by the roller force. Once the plaque, foil-polymer-foil structure, cools, there is a mechanical lock where the polymer has cooled around the nickel nodules. Fig. 12 is an SEM image of a nodular foil surface.

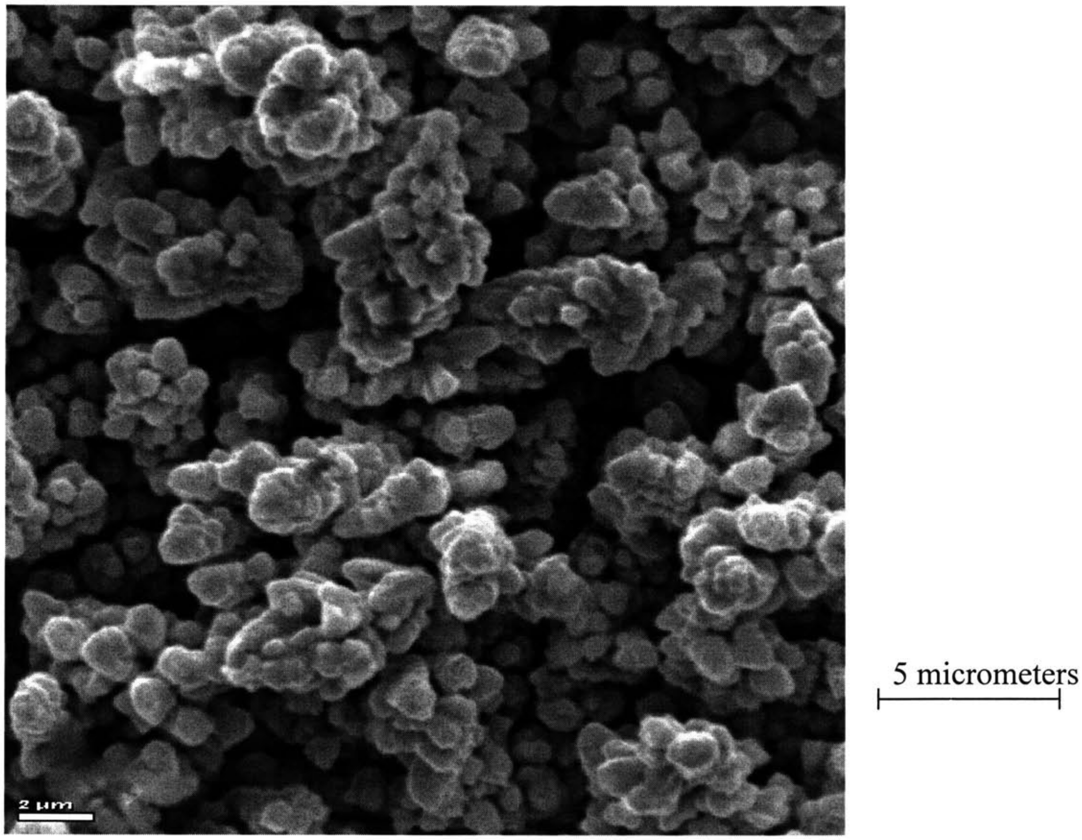

Figure 12 Scanning electron microscope image of a standard nodular surface magnified at 3000x.

For nodule growth, the foil is fed over rollers and through plating baths. The foil side that is against the rollers becomes very smooth, while the foil side that is in the bath becomes rough. By varying the current density between the cathode and anode, the nodules size can be controlled. If the nodules are too small, then the polymer cannot penetrate the nodular surface and the adhesion between the metal and polymer is weak. If the nodules are too large, the polymer may not penetrate far enough and air gaps might produce arching during electrical tests.

CHAPTER 3

PROBLEM STATEMENT AND MOTIVATION

3.1 Problem Statement

The objective of this research was to determine if an IC molding process could be used to manufacture non-linear PTC circuit protection devices. Past attempts at normal injection molding met with considerable challenges because of the inherent residual stresses that formed within the devices. For this thesis, an alternative to injection molding was attempted: injection-compression molding, see Section 1.1.2 for a description of this process.

3.2 Motivation: Limitations with the Extrusion-Based Manufacturing Method

As detailed in Section 4.1.1, non-linear PPTC circuit protection devices have been manufactured for many years through an extrusion-based process. This process allows the polymer to flow very evenly and gives the final plaque geometry a thickness variation of not more than 5%. In addition, the system allows the plaque to be formed with very low residual stresses by keeping the temperature constant during sheet formation. For HDPE based PPTC devices, the sheet is extruded at 200° C and pulled through rollers that are held at the same temperature. This allows for an even process in which the polymer can flow easily during sheet formation, and prevents residual stresses to form.

The extrusion process, though very effective for making these devices, has certain inherent manufacturing drawbacks. The most obvious drawback is the material that is wasted during the punching process. The plaque is punched into chips, leaving a shell of wasted foil and polymer. Additional waste is added to the process as each manufacturing run traditionally makes up to 10 meters of scrap plaque before the system reaches equilibrium. As the scrap plaque is being made, small chips are punched out and tested for resistivity. When equilibrium is reached, and the desired resistivity of the extruded polymer is obtained, then "good plaque" is kept for punching and assembly.

In some cases, there is an added redundancy to the normal manufacturing process that is detailed in Section 4.1. Most models of these circuit protection devices are fabricated with wire leads as shown in Fig. 14. In this case, it would be hard to get equal electrical performance from a contact directly between the polymer and the wire. Therefore, in the case of wire-leaded parts, the foil plays an important role of dispersing the current along the terminal before it enters the polymer matrix. In some designs however, the chip is not attached to wire leads, but to 0.4 mm thick rectangular brass terminals of the same geometry as the chip. These terminals provide added rigidity to the design and give an added thermal mass to the device that is important for specific proprietary reasons. In this "thick-terminal" design, the foil, which links the polymer to the brass, could potentially be eliminated. Elimination of the foil however can only take place if a strong adhesion can be obtained between the brass terminal and conductive polymer, and if electricity can flow equally well from brass to conductive polymer. Potentially, therefore, in some designs, the foil might be eliminated to reduce cost. For these designs, the extrusion process is wasteful both from the wasted plaque, and the unnecessary foil that can be eliminated with a polymer to brass terminal technology. This thesis does not provide an analysis of brass to polymer bonding, but an independent proprietary study confirmed that such bonding is possible to produce.

3.3 Alternative Manufacturing Method for Non-Linear PPTC Circuit Protection Devices

If foil is eliminated, and the plastic attached directly to the brass terminal, the circuit protection devices can no longer be produced by extrusion. Instead, they can be insert-injection-compression molded by the processes described in Sections 1.1.2 and 1.1.3. In this way, the terminals of the device act as inserts, and the polymer is shot between them for compression. Once the parts cool, a finished matrix of devices would emerge from the mold. These IC molded devices, unlike the plaque from the extrusion process, would not need to be soldered. Instead, after molding, they would be given a radioactive dose, as described in Section 4.1.4, for completion. This process therefore eliminates the need for foil, and skips the punching, soldering, and second heat treatment steps. Chapter 4 gives a detailed description of these steps.

CHAPTER 4

EXPERIMENTS

4.1 Sample Preparation

4.1.1 Fabrication of the Plaque. Plaque has been traditionally manufactured for many years with the extrusion process that is described in Sections 1.2.1 and 1.2.2. The research conducted for this thesis used IC molding, a process described in Sections 1.1.2 and 1.1.4 and shown in Fig. 3, to create plaque. By creating IC molded plaque, this thesis looks at the worst-case scenario of IC molding. Ideally, devices would be IC molded individually, so that they would not need to be cingulated or soldered after leaving the mold. Also, if devices are IC molded individually, the polymer travels a very small distance during compression. By creating IC molded plaque, or molded plaque, and punching chips from it, we can look at the worst case scenario of resistance variability, flow induced thickness variations, and physical properties.

4.1.2 Punching. The IC molded plaque, which is a sheet of foil coated polymer (see Section 1.1.4), must be punched into small chips after it has been fabricated. All the chips in this study were punched out of 2-mm thick plaque to a final geometry of 13 mm x 8 mm.

4.1.3 First Heat Treatment. During the sample preparation, the chips undergo two different heat treatment processes. The first heat treatment process brings the polymer above its melt temperature, Tm, as defined in Section 2.4, to relieve it of any residual stresses that were put into the polymer during plaque fabrication. The rate and time duration of this first heat treatment is proprietary. The most important quality of this first heat treatment is that the polymer is heated above the melt temperature for residual stress relief. The second heat treatment step is described in Section 4.1.6.

4.1.4 Cross-linking the Polymer with a Radioactive Dose. Polymers are made of many long molecular stings that are bonded with van der Walls forces, permanent dipoles, or hydrogen bonds. "Cross-linking creates points in this structure where portions of individual molecules are now rigidly fixed in position relative to each other" (Moore et al., 1984). The weaker bonds at these locations are replaced with much stronger covalent bonds due to the cross-linking. Normally, only thermoset polymers are cross-linked, but in some cases, thermoplastics, such as high density polyethylene, can also be cross-linked to give added rigidity at high temperatures (Moore et al., 1984).

All non-linear polymeric positive temperature coefficient circuit protection devices need to be cross-linked before they can undergo electrical stress. After the plaque has been made and the chips have been punched and heat-treated, the chips are put into a radioactive chamber. In this chamber a controlled electron-beam radioactive dose is administered that allows the polymer chains within the chips to cross-link with each other (Moore et al., 1984). Without cross-linking the devices will lose their initial physical geometry during their first trip event, making it difficult to achieve repeatable electrical performance for subsequent cycles of electrical stress. The radioactive dose frees hydrogen from the individual polymer molecules allowing carbon-carbon bonds to form between the old hydrogen bond sites. This bonding between polymer molecules prevents the molecules from sliding past each other when the temperature of the polymer increases past Tlm, as defined in Section 2.4 (Moore et al., 1984). Once there are random covenant bonds between the polymer molecules, caused by the radioactive dose, the devices can withstand multiple cycles of thermal stress (caused by high electrical power exposure) and maintain predictable electrical performance, as shown in Section 8.6.

The radioactive dose is administered in units of Mega-Rads. A Rad corresponds to the energy absorbed in a medium during radiation exposure, and is equal to 100 ergs/g. A small amount of radiation absorbed during exposure may not give the conductive polymer sufficient physical integrity during a thermal shock, while too much cross-linking can cause a conductive polymer to lose much of its non-linear resistivity increase that occurs during increased temperatures. This thesis does not conduct a study on radioactive doses and its effects on device performance. Instead, standard doses were given to IC molded devices that are currently used on similar geometry parts. All the devices examined in this study are 2-mm thick and made of a thermoplastic high density polyethylene (HDPE) with 35% to 38% carbon-black, by weight. A standard dose of 100 Mrads was administered to these devices which provided sufficient cross-linking for resettability, and adequate resistance-temperature performance.

4.1.5 Soldering and Coating. Once the chips have been heat-treated and cross linked, they are ready to receive wire-leads. The leads that were used for this experiment were 22 AWG Cu wire, plated with Sn. An Isopropyl alcohol based flux (Superior 45) was used to clean the wire leads and chips before soldering the leads onto the chips. The soldering was done by immersion of the leaded-chips into a bath of 245° C 60 wt.% Sn – 40 wt.% Pb solder.

After the chips receive their leads, the parts cool, and are then coated with an anti-arching agent. After coating, the parts are put into an oven at 150° C for one hour, to let the coating cure.

4.1.6 Second Heat Treatment. The last step for device preparation is temperature cycling. After the thermal history that comes with soldering and curing, the devices must be relieved of their thermal stresses. Temperature cycling lowers the device's resistance back to its post-radioactive dose level, and gives the device a final resistance that is recorded.

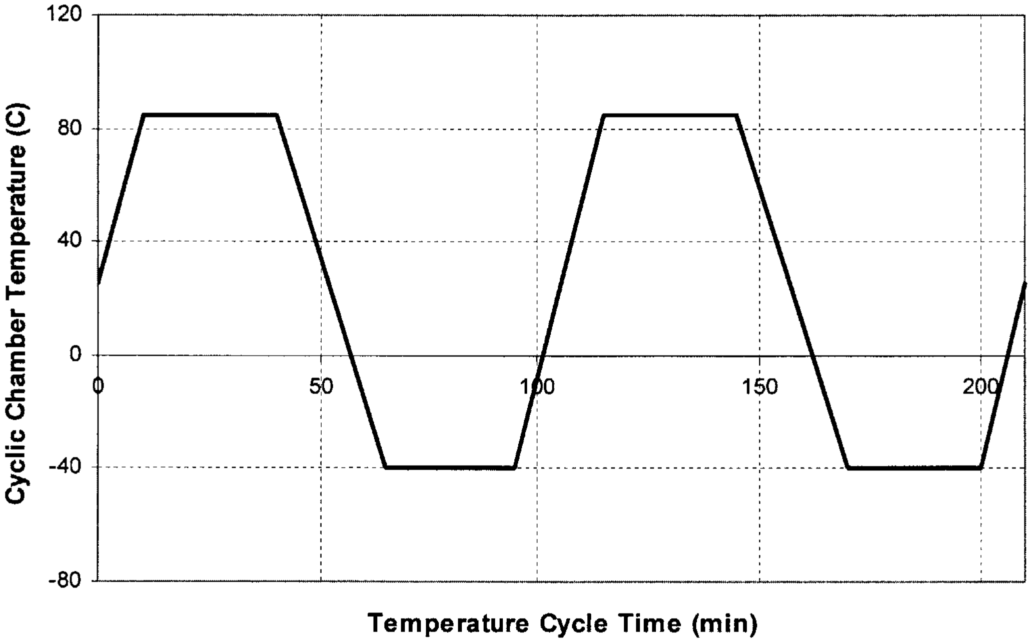

Figure 13 Two full temperature cycles.

One temperature cycle starts at 25° C, ambient temperature, rises to 80° C, cools down to -40° C and then raises back to 25° C. Fig. 13 shows two complete temperature cycles, but the parts used in this study all went through 12 temperature cycles. Each subsequent cycle lowers the resistance with diminishing returns. The first cycle lowers the resistance greatly, but the the 9th to 12th cycle lower the resistance an almost negligible amount. After temperature cycling is complete, the devices are ready for performance testing.

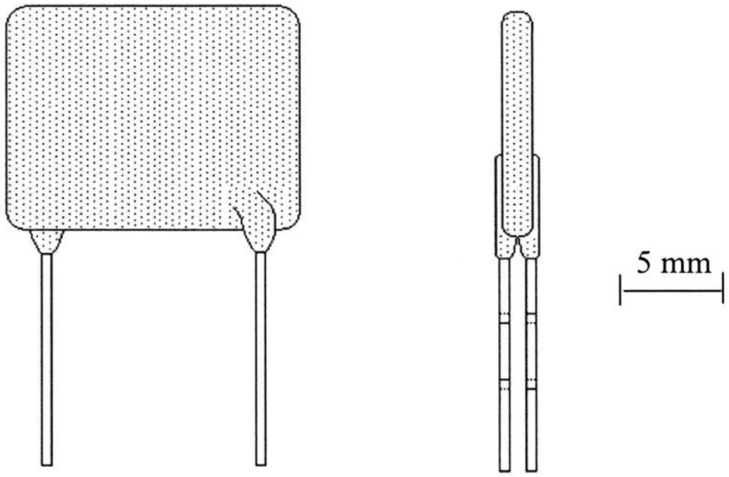

Figure 14   A normal circuit protection device after coating.

Fig. 14 shows what a normal device looks like after the steps described in Sections 4.1.1 to 4.1.6. The punched chip is housed in the large flat rectangular portion of the device. The long thin wire terminals are easy to mount on test boards or circuits boards. From this point on, a finished device will be called either a device or part.

4.2 Testing Procedures

4.2.1 Peel Test. The peel test is used to study the quality of the adhesion between the polymeric base of a PPTC device, and its outer foil layer, usually Ni. Peel strength, measured in force/length, is the measured unit during a peel test. If the peel strength is high, the Ni foil is known to have a good adhesion to the polymer, and devices are known to have the capability of standing up to large forces applied at its wire-leads. Devices with low peel strength may have small air gaps between the foil and polymer. These gaps may allow for arcing to occur during cyclic testing and cause failure within a device. Therefore, good adhesion is important for two reasons: to create a good conductive path between the foil and polymer, and to ensure physical integrity of the device.

In this research, the peel tests were conducted as follows. The plaque, molded or extruded, is cut into 12.5 mm wide strips. The foil on one side of the plaque is peeled up using a razor blade. This small amount of peeled foil is then fed through a pair of rollers and clamped by hydraulic jaws. The jaws, attached to a force measuring device, Instron 4501 machine, then pull the foil through the rollers, as shown in Fig 15. Computational software keeps track of the force required to pull the foil during the test, and then takes the average of that data, reporting the standard deviation and minimum and maximum values as well.

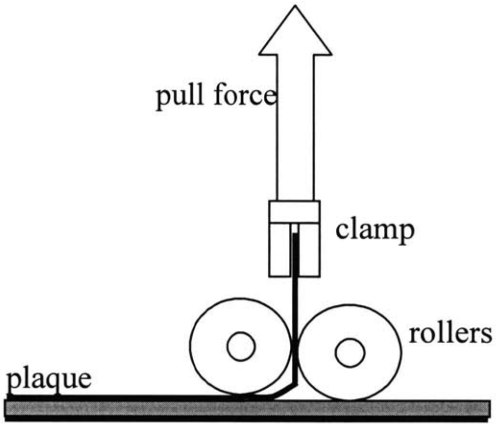

Figure 15 Test set-up for the peel test.

Peel strength analysis for this thesis will be analyzed more carefully in chapter 7. In particular, peel strength is a good indicator of whether or not the polymer is remaining hot enough during the injection-compression process.

4.2.2 The Resistance-Temperature Test. PPTC devices are categorized by their performance in different electrical tests. These tests measure inherent properties that come from the type of polymer base, the percent composition of carbon-black, and the geometry of the device. There are many standard tests that a new PPTC device design must pass before it can be put to use. For the purposes of this thesis, electrical performance will be mainly measured by the resistance-temperature (RT) test and various cycle life tests.

The RT test examines device temperature vs. device resistance. Devices are inserted on a test board and then into a temperature controlled chamber. The test board can read the devices' resistances during the test, while a chamber temperature gauge records the temperature. The devices are heated to a point above the melt, and then cooled back to room temperature. In this way, the non-linear positive temperature coefficient behavior of the devices, described in Section 2.4, can be examined very carefully from the RT test data.

Various test parameters can be varied to look at different polymer qualities. If the devices are to be heated and cooled once, then the operator enters "1 cycle." Devices are usually tested for either one or two cycles. Two cycles in the RT test can test the effectiveness of the radioactive dose that was administered to the devices. If the dose was adequate, than the polymer should be sufficiently cross-linked and display identical RT behavior during both cycles. If the dose is not sufficient, then the polymer within the device will melt during the first heat cycle and lose its physical integrity. Then, during the second cycle, a completely different resistance-temperature behavior will be observed.

The temperature to which the devices are heated is also varied. If the base polymer is high density polyethylene (HDPE), then the test chamber and devices will be heated to 160° C, but for some other polymers, the test chamber may be heated to as high as
200° C.

The heating is done in incremental steps. For regions below the non-linear portion of the RT relationship, Region 1 of Fig. 10, the device is heated quickly (usually in 5 degree increments). Once the device reaches its next temperature increment, the chamber remains at that temperature for one minute, before the resistance and temperature of the device is recorded. Then, throughout the non-linear region, the device is heated more slowly, in 2 degree increments, to get more readings. The typical heating profile for an HDPE polymer with 35 to 38% by weight carbon-black is:

1) 20-90° C 5 degrees per step. 1 minute soak time at each step.
2) 90-132° C 2 degrees per step. 1 minute soak time at each step.
3) 132-160° C 2 degrees per step. 1 minute soak time at each step.

In this way, the tester can control three different regions of the RT test: the region before the non-linear zone, the non-linear zone, and the region after the non-linear zone. The cooling rates are similar to the heating rates.

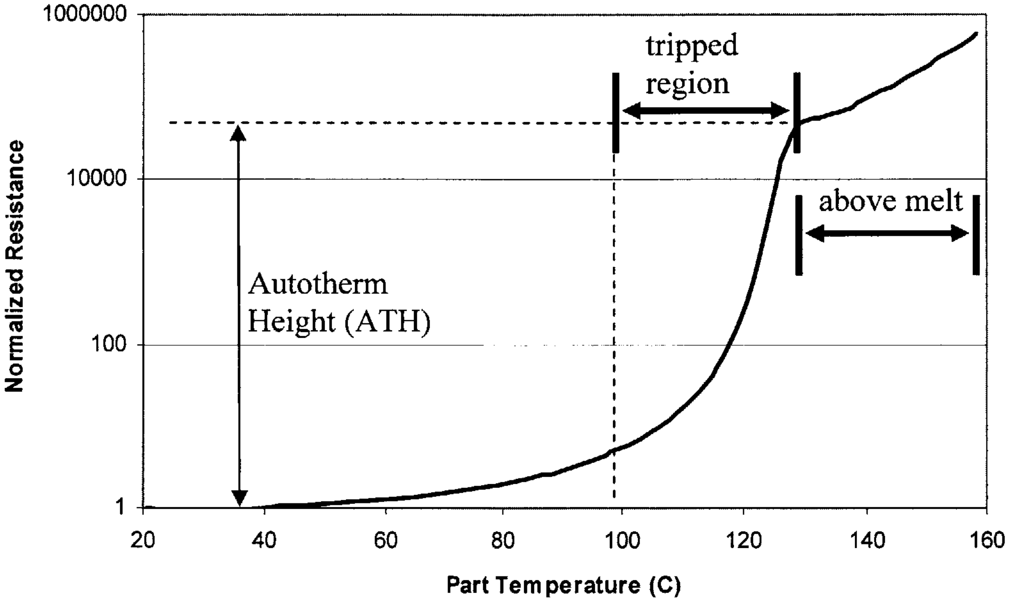

Figure 16 Normalized RT curve for a standard high voltage application PPTC device.

Fig. 16 shows the RT behavior for a standard PPTC device from 0 to160° C. The resistance starts very flat, and increases slowly with temperature. In this linear region, the resistance increases by 80% over roughly 80° C. So, for the linear region, the RT relationship is 1% increase in resistivity per 1 degree increase in temperature.

Then around 100° C, the device enters the non-linear region of PTC behavior, and the resistance increases 4 orders of magnitude above in 30° C. In this region, the polymer is expanding rapidly due to changes in crystallinity, as described in Section 2.4. The height of the non-linear increase plus the height of the initial linear region is called the autotherm height (ATH), and is measured in decades, or orders of magnitude, of resistance increase. For example, the ATH of Fig. 16 is approximately 4.5 decades of resistance increase. Finally at around 120° C, the material exits the non-linear region, and enters a new linear region of positive temperature coefficient, RT behavior.

4.2.3 Cycle Life Testing. In addition to RT testing, devices are also put through various cyclic tests where their electrical durability is tested. An important characteristic of these non-linear PPTC devices is that they will reset after a trip event. Resetting means that a device returns close to its initial resistance value after a trip event. This characteristic allows the devices to actively protect a circuit many times, incase that there are multiple power surges, static shocks, or other electrical anomalies. In some cases however, either because a device has been poorly constructed, electrically stressed too many times, or put under electrical conditions beyond its capacity, a device may "fail."

Cyclic testing has a few variables that are commonly varied to study different aspects of cyclic behavior. The amount of voltage and current delivered to the devices during each cycle is varied to study the effects of power on performance. Each time a device is cycled, it goes through the non-linear trip behavior discussed in Section 2.4. The device will start at an initial resistance Ro, jump to a higher resistance ,R2, during the power input portion of the cycle, and then return to a final resistance, Rf, that is close to Ro, at the end of the cycle. The time at which a device is left in the trip state during each cycle is also varied. Most often, cycles use 5 seconds of applied power, and then let the devices rest for 120 seconds before a new cycle of power. This allows the devices to cool to their initial temperature, making any new resistance measurements a function of the resistance change that comes from the cyclic history, and not from the temperature effects of the previous cycles.

Cyclic failure often occurs when the resistance of the device becomes higher than its initial level, Ri. After one cycle of electrical stress, a device will normally return to a new resistance, Rf, somewhere close to its Ri, with a small change, ΔR. The size of the ΔR depends greatly on the electrical conditions at which the device was tested, and the cycle number. For example, the device most commonly tested in this study was considered a "high-voltage" device. The device is expected to endure 100 cycles of 250-V 3-A power for 5 seconds during each cycle. This is just one of the several cyclic tests it must undergo. For the first few cycles, the resistance of a device will increase rapidly. As shown Fig. 17, the device goes from a normalized resistance of 1 to 1.6, in just 3 cycles. The polymer anneals during the initial cycles, finds a new stable resistance, and then slowly relaxes over subsequent cycles.

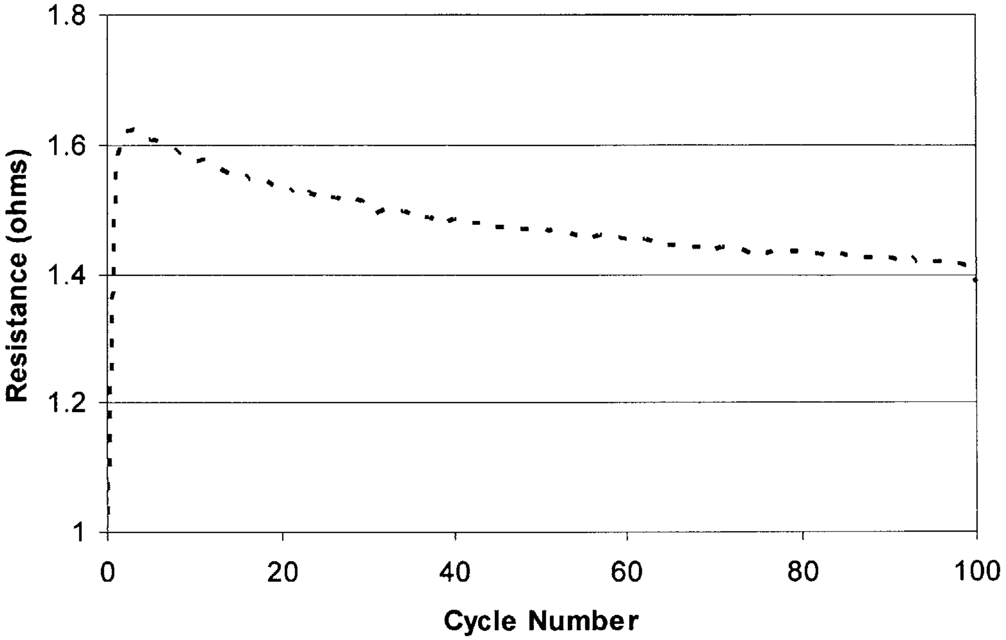

Figure 17 Normalized resistance (Rf/Ri) vs. cycle number for test parameters of 250-V, 3-A, 5-seconds power with 120-seconds rest between cycles.

For different conditions, the devices may not reach a peak resistance, as shown in Fig. 17, but instead, may continue to increase with each cycle. This usually happens with more aggressive power settings, and will cause the device to eventually fail. When a device increases in resistance, the joule heating becomes more substantial under high power conditions. If the device resistance becomes too high, failure becomes unavoidable for a subsequent cycle.

CHAPTER 5

TESTING OF PHYSICAL PROPERTIES

5.1 Bi-Refringence Stress Analysis with Acrylic Material

The conductive polymers that are used to create circuit protection devices, mostly high density polyethylene filled with carbon-black, are not transparent. For this reason, acrylic was initially used for its transparent quality and easy use in a birefringence stress analysis test. With conductive polymers, the only way to study residual stresses is through electrical performance. Acrylic, however, along with other transparent materials, can be put between two polarized sheets of plastic that are one-half wavelength out of phase with each other (Davis et al., 1982). The polarized light passes through the acrylic, and lines of equal stress appear to the naked eye within the polymer. This method of stress analysis is known as birefringence analysis.

5.1.1 Procedure. Acrylic pellets were put into the injection molding machine, and heated through the screw at 220° C. The polymer was then shot into the open mold, and compressed as described Section 1.1.2. There was no foil in the mold during the acrylic material runs. Injection compression molding parameters were varied to see what impact they would have on the amount of internal stresses within the polymer. This method of birefringence analysis was used to establish an initial understanding of parameters, and how they affect residual stresses within the polymer.

5.1.2 Experimental Results and Discussion. Each IC molded acrylic slab, plaque without foil, was visually inspected for residual stresses and photographed for recording purposes. It is difficult to view these pictures here, but the results pointed to a clear understanding of certain molding variables.

After looking at many different molded acrylic slabs with varied IC molding parameters, certain general conclusions could be made. First, a long delay time creates greater amounts of residual stress. Second, a slow compression speed also increases residual stress. Finally, if the stroke is too small, the IC process becomes very much like a normal injection molding process, and flow induced residual stresses form in this situation as well. See section 1.1.2 for a description of these IC molding variables.

Both long delay times and slow closing speeds add to the amount of time the polymer has to cool before the mold is completely closed. As the polymer cools, the viscosity increases, and it will be harder for the polymer to flow during compression. Therefore, it is important for the delay time to be very short, and the closing speed to be as quick as possible, in order to eliminate as much residual stress as possible. Also, it is important that the stroke be large enough that the process is IC molding-based, and not purely injection.

5.2 Peel Strength Test Procedure

The peel test, as described in Section 4.2.1 and shown in Fig. 15, was conducted on many IC molded plaques. Each IC molded plaque was cut into ten 12 mm strips. Each strip has foil on both sides as shown in Fig. 18, and can provide information about the flow and adhesion of the polymer at various locations within the plaque during molding.

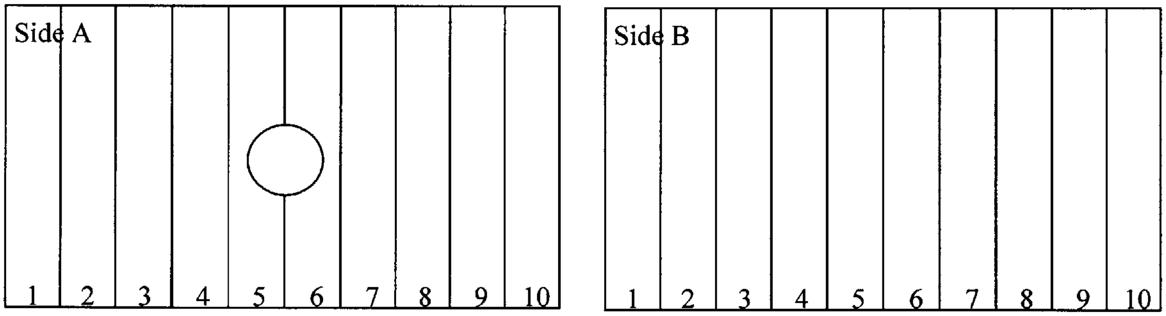

Figure 18 Cut pattern for IC molded plaque.

The strips are numbered from 1 to 10 starting at the left edge of Side A and ending at the opposite edge. Therefore, Strips 5 and 6 are the centermost strips, nearest to the sprue, and Strips 1 and 10 are the edge-most strips, where the compressed polymer traveled the furthest distance. Strips 5 and 6 on Side A are not used for peel strength data due to the entrance hole, as shown on Side A in Fig. 18. The polymer has to enter through this hole during injection. These center strips tend to rip during the peel test, and are therefore not used for data collection.

Plaque that is currently made for the production of conductive polymeric circuit protection devices has 0.05-mm thick foil on both sides. This foil can be used with ease during the extrusion process, but poses some difficulty for IC molding. The nodule size on 0.05-mm foil is very small and is difficult for the polymer to penetrate. If mold conditions are too cold, the peel strength between the 0.05-mm foil and the polymer will be too small for good adhesion. The rigidness of 0.1-mm foil provides a more rigid terminal, and larger nodules for better adhesion.

Normal extruded plaque that is made with 0.05-mm Ni foil and HDPE with 35.8% carbon-black, has an average peel strength of 9 N/cm and a standard deviation of 0.4 N/cm. The extrusion process allows the polymer to seep into the nodular structure while it is still in its molten phase. This gives the extruded plaque a very even peel strength along its entire surface.

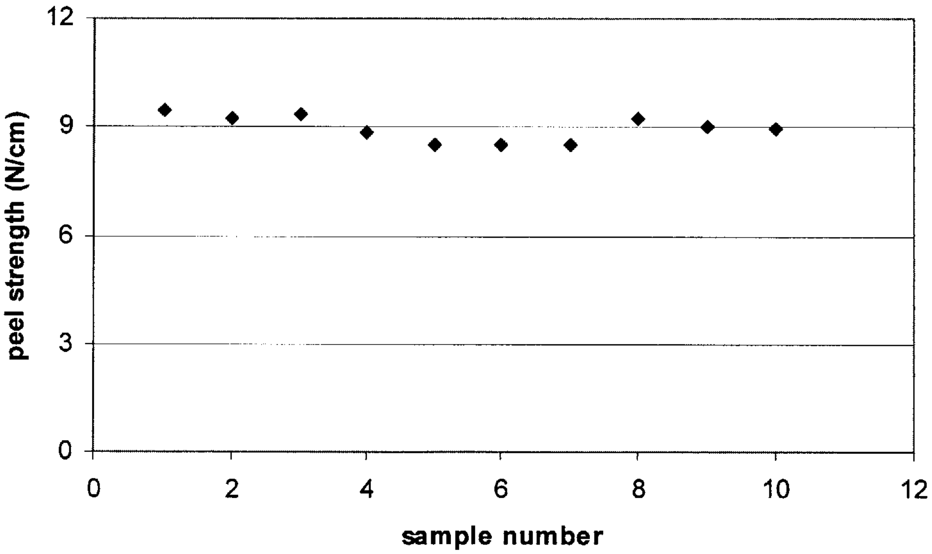

Figure 19 Peel strength values for ten samples taken from 2-mm thick extruded plaque.

Fig. 19 shows that normal extruded plaque has a very even peel strength. These values are taken from both sides of the plaque, and along the length of the plaque. Small variations are considered to be within the normal specifications of the devices, and do not effect the electrical conductivity of the nickel foil to the polymer, or the overall mechanical integrity of the devices.

5.3 Cooling Time Effects

5.3.1 Experimental Results. For the first many runs of IC molded plaque, 0.1-mm nickel foil was used. By using the thicker foil, it was easier to see how the polymer was behaving during the compression process. The thicker foil produces greater overall peel-strength values because of its larger nodule structure, and provides a broad range of values for a given plaque. Initially, before it was understood that the mold temperature must be much greater than 75° C, the thick foil helped to provide a greater understanding of how the polymer-foil interface acted during compression and cooling. Unless specified otherwise, 0.1-mm thick Ni foil was used for the experiments.

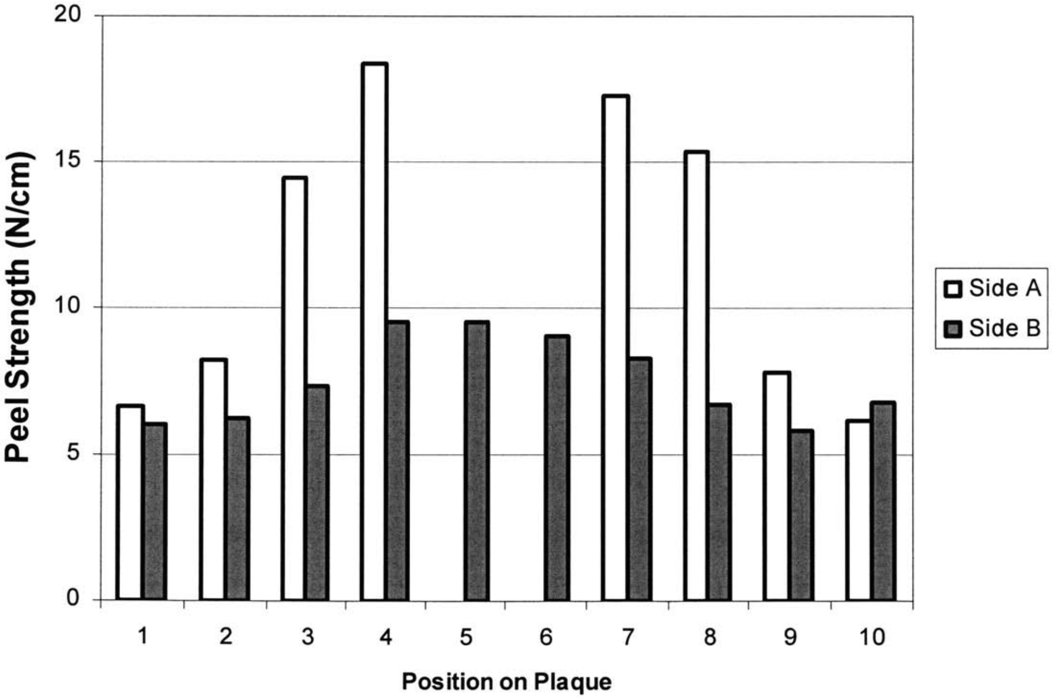

Figure 20 Peel strength data of IC molded plaque made in a 75° C mold.

The peel strength results from Fig. 20 show a distinct pattern that existed due to the temperature of the mold, 75° C. It is apparent that the peel strength, for both Side A and Side B, is greatest at the center of the plaque, Positions 5 and 6. Furthermore, the peel strength around the outside edges, Positions 1 and 10, is the lowest.

Another observation from Figs. 20 is that the peel strength is always greater on Side A of the plaque. The difference between sides ranges from 0.6 N/cm, at Positions 1 and 10, and 9 N/cm at Positions 4 and 7.

Fig. 21 compares the average peel strength of plaques with the amount of cooling time each plaque had in the mold. Each plaque has 8 peel values for Side A and 10 peel values for Side B. The values for each side were averaged so that the plaques could be compared. The peel strengths of Sides A and B were measured and charted against cooling time for comparison purposes. For this reason, at each cooling time, there are two values: Side A average peel strength and Side B average peel strength.

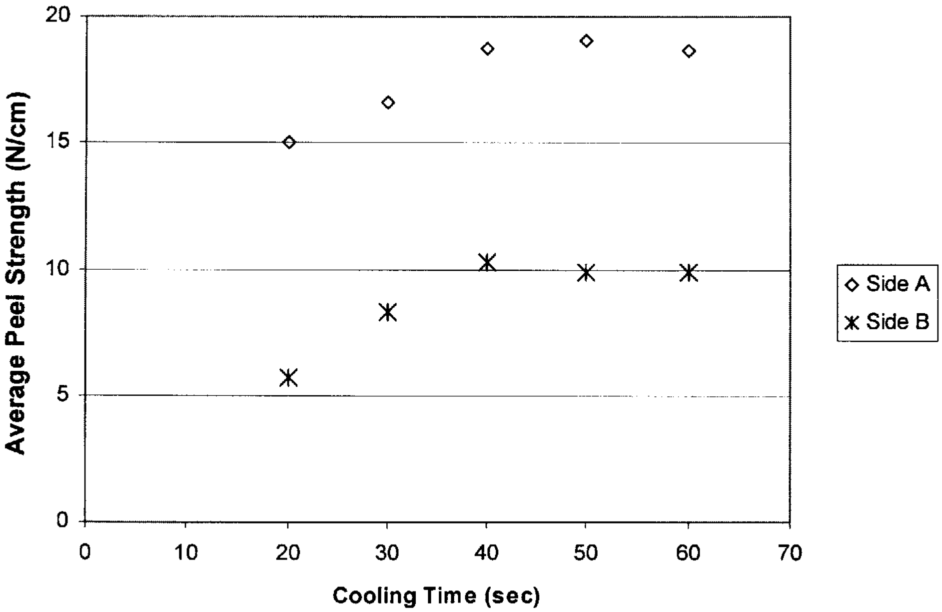

Figure 21 The average peel strength of plaque sides vs. the cooling time.

The average peel strength tends to increase with cooling time until 40 seconds is reached. At cooling time values of 40 seconds or greater, the peel strength tends to remain at the same level. Another observation is that both Sides A and B peel strength values increase at the same rate. Therefore, increasing the cooling time does not bring Sides A and B values of peel strength closer together when the mold temperature is 75°C.

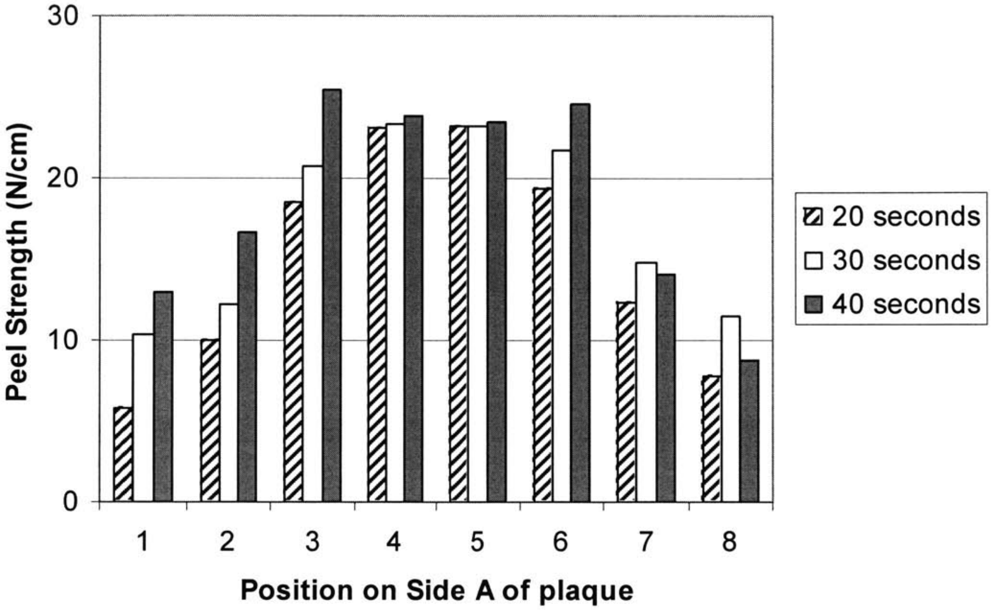

Figure 22 The peel strength values of side-A for a plaque that cooled for three different times within an 75° C mold.

Fig. 22 shows the peel strengths of three different plaques, each cooled for a different amount of time before removal from the mold. Positions 1 and 8 represent the outside edges of the plaque, while Positions 4 and 5 represent the middle of the plaque. As seen previously, the edges have a lower peel value due to the increasing viscosity of the polymer as it travels and cools. One new observation, however, is that a longer cooling time tends to increase the peel strength values more at the edges than in the center. Therefore, near the center of the plaque, Positions 4 and 5, the peel values increase only slightly with increasing cooling time, while beyond the center, Positions 1, 2, 3, 6, 7, and 8, the peel strength values increase significantly more with cooling time.

5.3.2 Discussion. The peel strength decreases with distance from the center of the plaque. Initially, the polymer is shot into the mold and sits as a thermal mass touching Side A and Side B. The heating fluid that flows through the mold is kept at 110° C, but the surface of the mold is usually around 75° C. For this reason, the polymer begins to cool rapidly as it stays in contact with Side B before compression. The last bit of polymer that enters the mold is the hottest during compression, as it has been exposed to the mold surface for the least amount of time. Fig. 23 schematically shows this phenomenon.

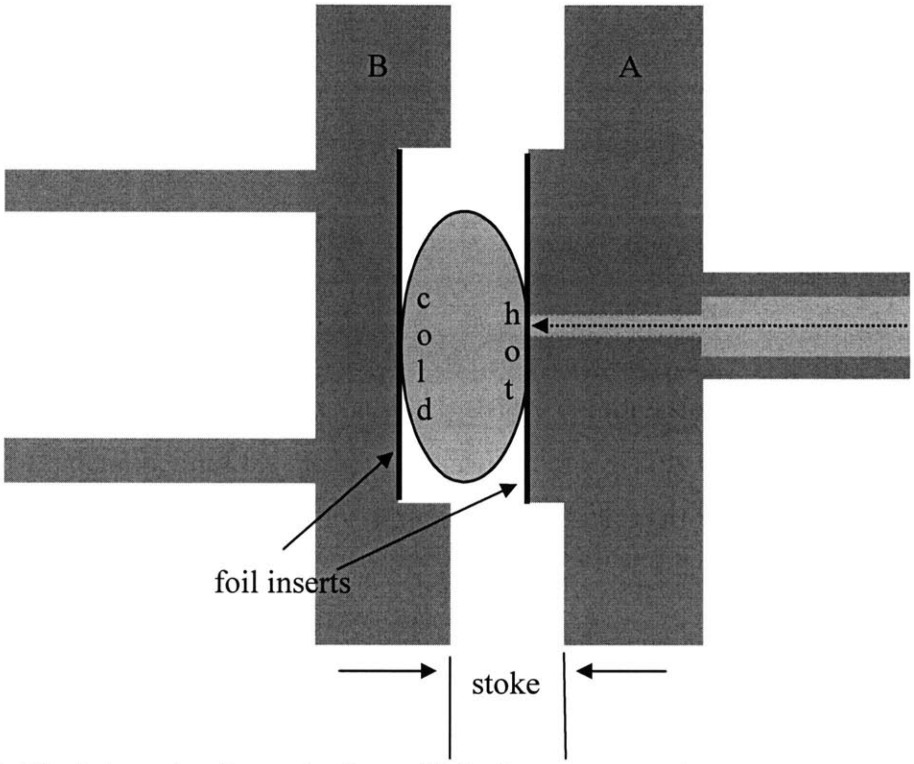

Figure 23 The injected polymer in the mold, before compression.

As the mold closes, the polymer spreads into the shape of the cavity, and begins to press against the nodular surface of the foil. The polymer closest to Side A is very hot and has sufficiently low viscosity to enters the nodular surface of the foil as it begins to be compressed. As the polymer on Side A moves further away from the center, it loses heat until it is no longer capable of entering the nodular structure. The polymer that starts closest to Side B of the mold is much cooler, has a very high viscosity, and can not seep into the nodular structure very well. For this 75° C mold, none of the polymer is able to penetrate the nodular structure on Side B. Once the injected volume of polymer has been fully compressed and cooled, there is a mechanical inter-connect between the polymer and the nodular surface where penetration of the nodules has occurred. During the peel test, the foil is pulled away from the polymer. If penetration has occurred, it will be reflected as high peel strength. For this reason, the foil nearest the center has a higher value of peel strength.

There is another indicator of nodular penetration other than peel strength. After the foil has been pulled away from the polymer during the peel test, visual inspection of the nodular surface can also reveal information about the molding process. If the nodular-side of the foil appears black, then it is clear that the polymer has entered the nodular structure. If the nodular side appears as it did before molding, a dull silvery color, then nodular penetration did not occur. For these tests, therefore, there was a strong correlation between the color of the nodular-side foil, and peel strength.

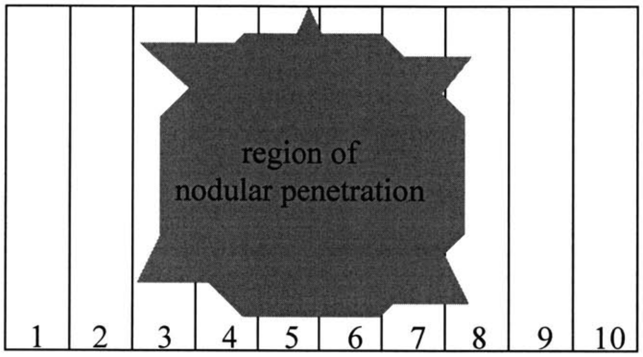

Figure 24 Representation of peeled foil samples, from the same plaque, laid next to each other after the peel test.

Fig. 24 is a schematic of how the nodular side of the foil looks after it has been peeled from Side A, when the mold temperature is 75° C. If the foil samples are assembled back together, as shown in Fig. 24, there is a clear region where the polymer had a low enough viscosity to penetrate the nodular structure. There is a clear transition between this low viscosity regime of penetration and the high viscosity region of less penetration. The nodular structure was either penetrated, or not penetrated. There were no grey areas.

In the region where penetration does not occur, the light areas in Fig. 24, peel strength can still attain fairly high numbers due to the many surface connections between the polymer and the foil. These connections, unlike the penetration region, are not permanent. During peel testing, the nodules in these regions disconnect completely from the polymer and do not cause polymeric fracture. In the region of penetration however, polymer has surrounded the nodular structure of the foil, and has to break from the main polymer structure during peel.

Increasing the cooling time gives the polymer within the mold more time to seep into the nodular structure, as shown in Fig. 21. When the cooling time is short, the viscous polymer, especially at the plaque edges, does not have the time to seep into the nodules completely. By increasing the cooling time, the polymer continues to seep into the nodules until it becomes too viscous for flow. Fig. 21 shows that after 40 seconds of cooling time, the polymer is no longer able to flow into the nodular structure any deeper.

Fig. 22 shows that the polymer in the middle of the plaque on Side A penetrates the nodules completely with very little cooling time, and achieves high peel strength values quickly. Increasing the cooling time, therefore, does not help these values because the polymer cannot penetrate any deeper within the nodular structure. The polymer along the edges is much more viscous, however, and can use the increased cooling time for greater penetration, causing increased peel strength at those locations.

5.4 Mold Temperature Effects

5.4.1 Experimental Results: After completing many runs and tests with plaque from the fluid heated mold, the peel strength results were still uneven. Changing various parameters such as stroke, compression rate, and delay time seemed to have little effect on the homogeneity of the foil/polymer adhesion across the plaque. The two main problems are summarized as: i) Side A tends to have higher peel strength than Side B, especially in the middle of the plaque, and ii) both sides have weaker peel strength as distance from the center of the plaque increases. In addition to the peel strength uniformity issue, Fig. 24 shows another problem, that the nodular penetration was not uniform across the plaque.

One of the few variables left to vary was the mold temperature. Until this point, the mold temperature had been constrained by a fluid heated mold that could only bring the mold temperature as high as 75° C. For this reason, the mold plumbing was reworked, to fit a series of cylindrical electric heaters that were placed throughout the mold for even heat distribution. The mold could now be heated throughout a much greater range of temperatures, from 20 to 300° C.

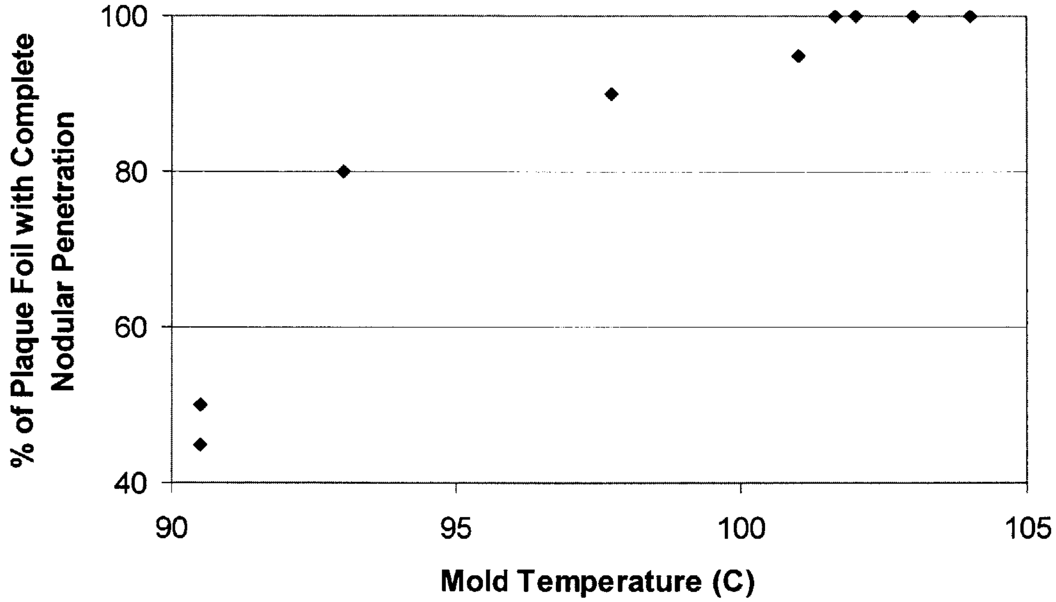

Figure 25 Effects of mold temperature on nodular penetration.

The results in Fig. 25 show that there is a significant improvement of nodular penetration when the mold is heated past 75° C. Recall that Fig. 24 shows the amount of nodular penetration on Side A of a plaque that was formed in a mold of 75° C. Side B had no penetration at all. Fig. 25 shows that at 90° C only 50 percent of the total plaque foil is being penetrated by the polymer. However, there is a significant increase in percent penetration as the mold temperature rises. When mold temperatures reach around 100° C, the foil is being penetrated at 100%.

Consistent nodular penetration shows that the polymer is retaining enough heat during the molding process to form a physically uniform plaque. It also means that peel strength values become more consistent across the molded plaque. Recall that in case of the 75° C mold, peel strength was low at the edges of the mold, and high in the middle where nodular penetration occurred, as shown in Fig. 20.

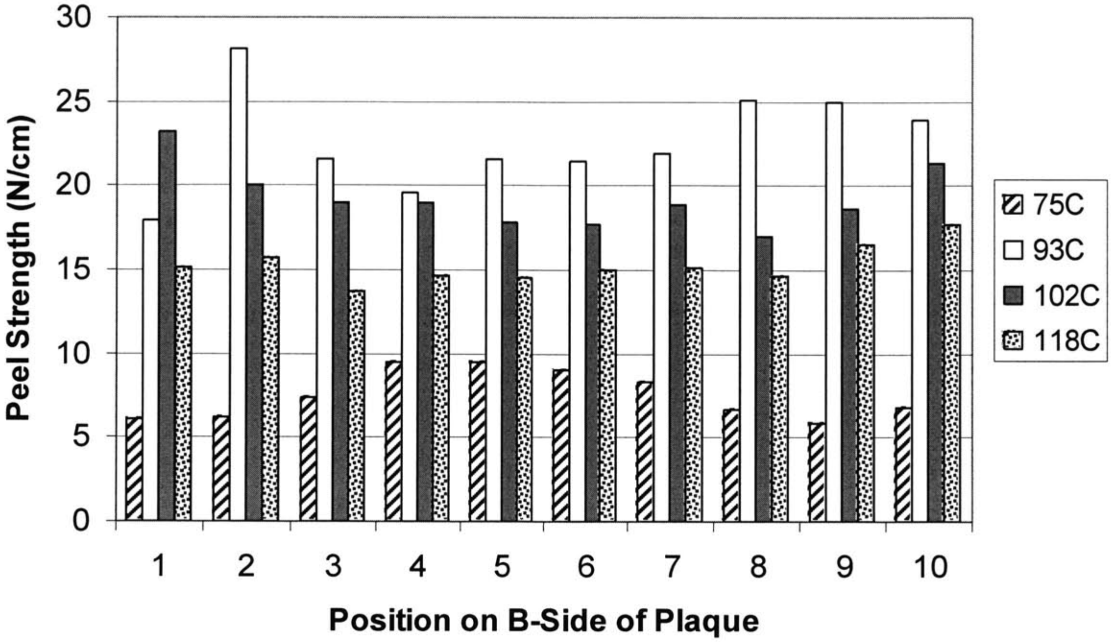

Figure 26 Side B peel strength values from plaques made at four different mold temperatures.

Fig. 26 shows the position on the plaque where the peel data was taken. Positions 1 and 10 are on the edges, and Positions 5 and 6 are in the middle, as described in Section 5.2. The data from four different plaques are shown. For each plaque, all molding variables are the same except for mold temperature, which is varied between 75° C and 118° C.

When the mold is heated at 75° C, the values of peel strength are high in the middle and low at the edges. There is a difference of 5 N/cm between the highest and lowest values of peel strength, and only the middle values attain sufficient peel strength values compared to those from the extruded parts in Fig. 19. The 93° C sample has much higher values than the 75° C sample, but still has values that vary as much as 10 N/cm. The 101° C sample is more consistent across the plaque, but has slightly higher values of peel at the edges, than in the middle. This sample's peel strength varies by 5.5 N/cm. The last sample, made at 118° C has the most consistent values of peel strength, varying no more than 4 N/cm in its peel strength values.

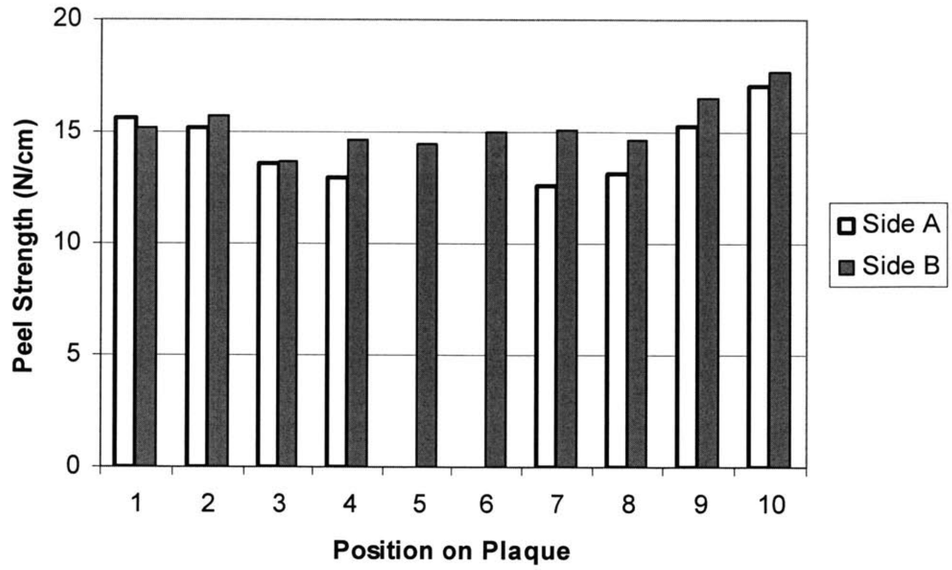

Figure 27 The peel strength data of a plaque that was formed in a mold at 118° C.

Fig. 27 shows that there is greater uniformity now between Side A and Side B for the hotter 118° C mold. In general, the peel strength is almost identical for a given location on the plaque, regardless of the side. There is a clear improvement in Fig. 27 over Fig. 20 in uniformity, both from side to side, and across the length of the plaque.

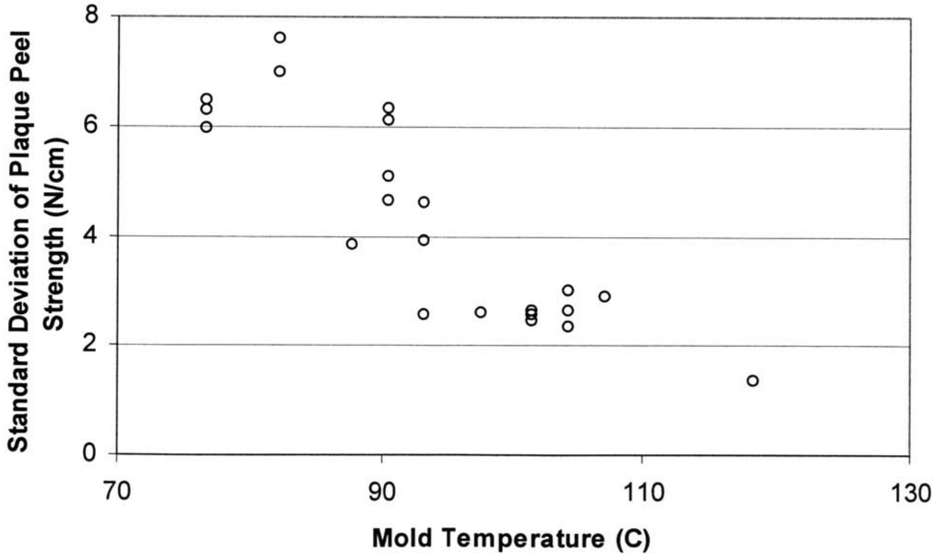

Figure 28 The standard deviation of peel strength from a plaque vs. mold temperature.

As mentioned previously, each plaque has 18 peel strength values associated with it, as shown in figure 18, 8 from Side A and 10 from Side B. Each plaque therefore has a standard deviation of its values that represents the amount the peel strength varies from the mean value of the entire plaque. Fig. 28 shows a clear inverse relationship between the standard deviation of peel strength values for a plaque and mold temperature.

5.4.2 Discussion. As the mold temperature increases, the polymer loses less heat during the compression phase of the molding process. For this reason, the viscosity of the polymer remains low with a hotter mold, and enables the polymer to flow more easily. At a mold temperature of around 100° C the polymer retains enough heat during the compression phase to penetrate the entire nodular foil surface, on both Sides A and B of the plaque, as shown in Fig 27.

Homogeneity of physical plaque properties does not exist until around 100° C. The foil can be peeled away at this point and an even black polymeric surface can be seen on the foil where the dull nodular surface used to exist. As discussed earlier, in Section 5.3.2, this black surface shows that the nodular penetration is sufficient to cause fracture during peel, leaving some of the polymer embedded within the nickel nodular structure of the foil.

Fig. 26 shows that as the mold temperature increases, the peel strength across the plaque become more consistent. For the 75° C mold, the viscosity increases substantially during the compression phase of molding, and the polymer can no longer penetrate the edges of the plaque. As evidence, the peel values are very low at the edges, and high in the middle. Also, penetration data was recorded for these samples, and the foil was still a dull silver at the edges. The 93° C case shows that the polymer is retaining enough heat for partial penetration of the nodular structure, even at the edges of the plaque, but there is still a great variation in peel strength values.

The 101° C sample from Fig. 26 has more consistent values of peel strength across the plaque, but shows a new trend. Instead of having its highest value of peel near the middle, the new trend shows that the peel strength peaks near the edges. A new phenomenon is occurring within the mold that is driven by the increased mold temperature. The polymer now flows very well during the molding process and viscosity remains low. When the polymer gets to the edges, the flow packs the material, and causes a slightly thicker plaque at the edges. The greater thickness and flow packing that occur at the edges of a 101° C mold temperature plaque, cause the peel strength to be greatest at the edges.

The last sample in Fig. 26 was made with a mold temperature of 118° C. For the first time with molded plaque, there is almost complete consistency in peel strength values across the plaque. There is still a small amount of evidence of flow packing from the slightly greater values on the right side (Position 10), but in general, it seems that the packing effects have almost completely disappeared. With the 101° C case, the viscosity increases enough during flow that the polymer cannot flow back towards the center of the plaque during the initial phase of cooling. With the 118° C case however, the polymer retains a low enough viscosity even after complete compression to flow back towards the center. This results in very consistent peel strength across the plaque.

One way to characterize the effects of increased mold temperature is to look at the standard deviation of peel strength values for a given plaque, as shown in Fig. 28. As the polymer retains more and more heat during the compression phase, it is able to penetrate the entire foil surface, and create more consistent peel values.

The final observation that can be made with Fig. 26 is that peel strength seems to decrease across the plaque with the highest mold temperatures. The 118 ° C data has a lower average peel strength of 15 N/cm compared to the 101° C case with an average of 18 N/cm. It would seem, therefore, that the 101° C case might be more favorable from a peel strength standpoint, however, current circuit protection devices rarely have peel strength greater than 9 N/cm. Fig. 19 shows the peel strength performance of standard extruded plaque. Notice that it has much lower values of peel strength. More important than high values of peel strength is consistency of peel performance along the plaque. Therefore, the 118° C case is more ideal due to its decreased variation.

This decrease in peel strength with higher temperature has two possible origins: viscous effects and polymer crystal size. When the mold temperature is at 101° C, the viscosity of the polymer is higher than the 118° C case. The polymer resists compression much more, and may cause itself to be pressed into the nodular structure even deeper. The polymer in the 118° C mold, however, resists compression much less due to its low viscosity, and may not seep into the nodular structure quite as deeply. This observation may seem to go against earlier observations about the 75° C fluid heated mold. In that case, the peel strengths were very small even with a polymer that resisted compression to a great degree. For the much cooler case of 75° C, the polymer resists compression, but has viscosity that is too high for any nodular penetration. Therefore, for the 75° C case, polymer resists compression, but cannot enter the nodular structure because of high viscosity; for the 101° C case, the polymer resists compression but can enter the nodular structure; and for the 118° C case, the polymer resists compression much less and fills the nodular structure less deeply than the 101° C case, but more consistently.

The crystalline effect comes from the cooling of the polymer. All samples mentioned in Section 5.4 have been cooled for 40 seconds before coming out of the mold. Plaques that are kept at different mold temperatures during the cooling phase will have different crystal growth. Also, the plaques will start cooling at a faster rate once they are taken out of the mold and exposed to ambient air temperatures (22° C). The plaque that is taken out at 118° C will lose heat more rapidly than the plaque that is taken out at 75° C. During this phase of cooling, crystal growth will also vary with cooling rate. In general, a slower cooling rate means larger crystal growth within the conductive polymer matrix. Since the peel strength for high temperature mold samples comes primarily from the polymer fracture mechanism, these varied crystal sizes might also be changing the peel strength values.

5.5 Foil Thickness Effects

5.5.1 Experimental Results. In order to compare the IC molding process with the extrusion process, 0.05-mm thick foil was used to create IC molded plaques. Now both the thickness of polymer, and thickness of foil is completely identical to standard extruded plaque.

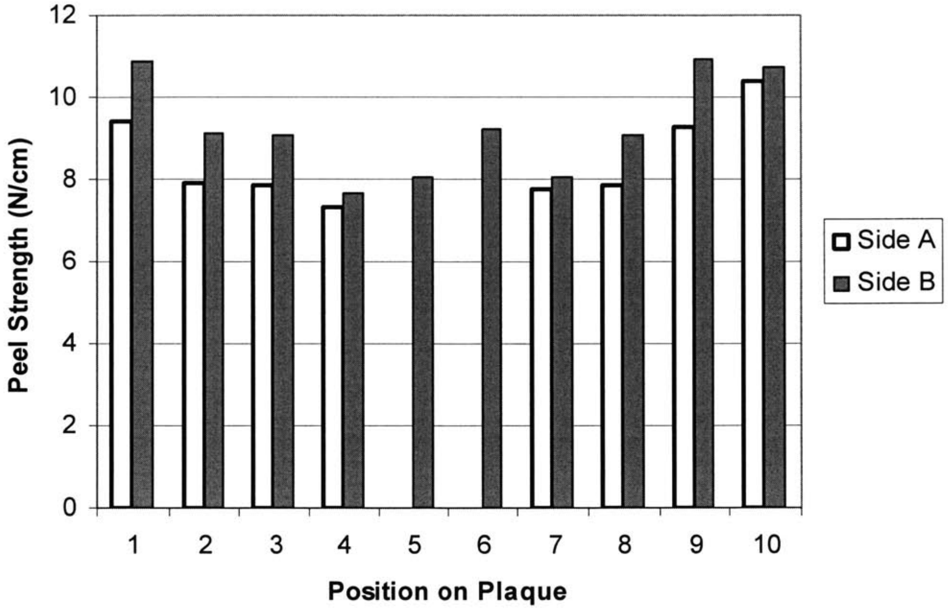

Figure 29 The peel strength from both sides of a thin-foil plaque that was made in a mold of 120° C.

Fig. 29 shows the peel strength of a thin-foil-plaque that was made in a mold at 120° C. The Side A to Side B comparison reveals that the penetration is almost equal from side to side. There is still a large amount flow packing that occurs at the edges, but the variance is only around 4 N/cm.

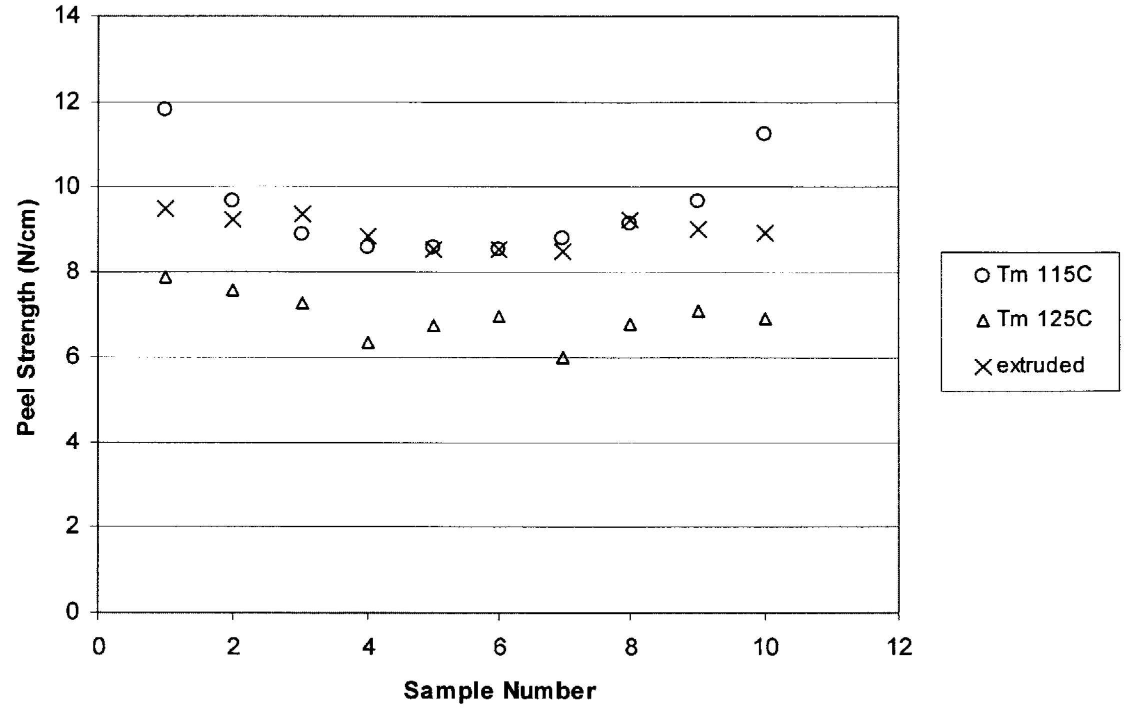

Figure 30 A comparison of peel strength values between two injection compression samples, Side B and one standard extruded sample.

Fig. 30 shows that the peel values for extruded and molded plaque are very similar, especially when the mold temperatures are around 115° C. Mold temperatures above 115° C drop the peel strength values below standard extruded plaque.

5.5.2 Discussion. The lessons that were learned from IC molding conductive polymer onto thick foil translated very well onto the thin foil counterpart. Fig. 29 shows that with thin foil we still get very good side-to-side uniformity of peel strength. Flow packing still exists at the edges with some temperatures. At 115° C and 120° C the peel strength still increases considerably at the edges, as seen in Figs. 29 and 30. At 125° C however, uniformity increases across the plaque, and the peel values vary much less, as seen in Fig. 31.

Fig. 31 shows that molded plaque can have very similar peel strength to extruded plaque, but that the edges will have packing effects. The results from the 115° C mold are almost identical to normal extruded plaque peel strength, but the packing effects exist at the edges. If the mold temperature is increased, uniformity is less of a problem, but now the peel values are a little lower than normal plaque.

Peel strength is used as an indicator of how well the polymer is flowing during compression. It is not the final variable in determining the over-all performance of a circuit protection device. Peel strength must be strong enough to create a strong connection and uniform enough to provide good electrical conductivity between the terminal and polymer.

The packing effects at the edges of a plaque will not be a problem once a multi-cavity mold is created for molding individual devices. The polymer will only be compressed a distance of 8 mm, half the device size, instead of 75 mm in the plaque cavity. The polymer will easily retain enough heat during the 8 mm of compression to allow the polymer to flow easily into the nodular structure and give the device an even peel strength across its surface.

Electrical performance tests are where devices ultimately prove their worth. If the peel strength is poor, arching may occur between the terminal and polymer, causing sparks and burning. It is also possible for a device with good peel strength to have other problems within the polymer itself: such as air pockets or insufficient cross-linking of the polymer chains. Therefore, while peel strength tells an important story about the development of IC molding as an alternative to extrusion, electrical performance will show how the devices behave under electrical stress.

CHAPTER 6

ELECTRICAL TEST RESULTS AND ANALYSIS

6.1 Chip Resistance vs. Position on Plaque

6.1.1 Procedure. In order to test the plaque for uniform resistivity, small chips were punched out of the plaques after molding, and before exposure to a radioactive dose. The chips are 8 mm x 13 mm, and 2 mm in thickness (the thickness of the plaque). This size was chosen to match the geometry of standard chips that are punched from 2-mm thick plaque. Chips were punched along the length of the plaque from edge to edge, in the same manner as peel strength strips were tested. Twelve chips were punched at equal intervals along the 150-mm dimension of the plaque.

6.1.2 Experimental Results and Discussion.

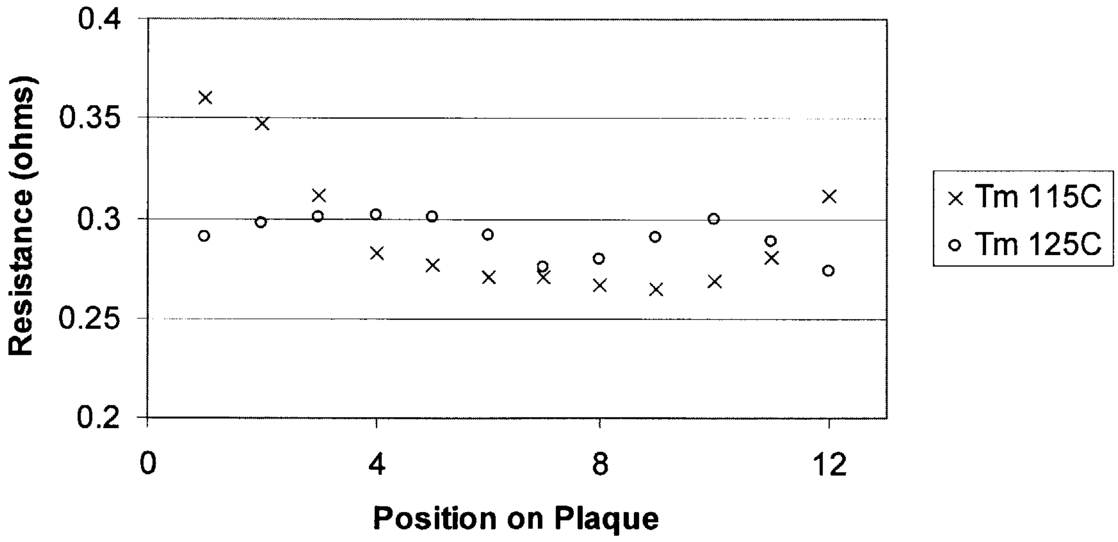

Figure 31 The resistance of punched chips from two plaques that were heated in molds of different temperatures.

Fig. 31 shows the resistance of chips that were punched from two different plaques. Positions 1 and 12 are at the edges of the plaque, and Positions 6 and 7 are in the middle. The plaques were made with molds of two different temperatures, 115° C and 125° C, while all other conditions were held constant. The resistance increases towards the edges and decreases in the middle of the 115° C plaque. The 125° C plaque has greater uniformity, but still has a low resistance in the middle.

Fig. 32 shows the thickness variation along the length of a plaque that was heated at 115° C on the left axis. There is clear evidence of packing at the edges as thickness increases at locations furthest from the center. The variation in thickness however is relatively small. The greatest thickness is almost 2.2 mm and the smallest is 2.0 mm. This is a variation of about 10%.

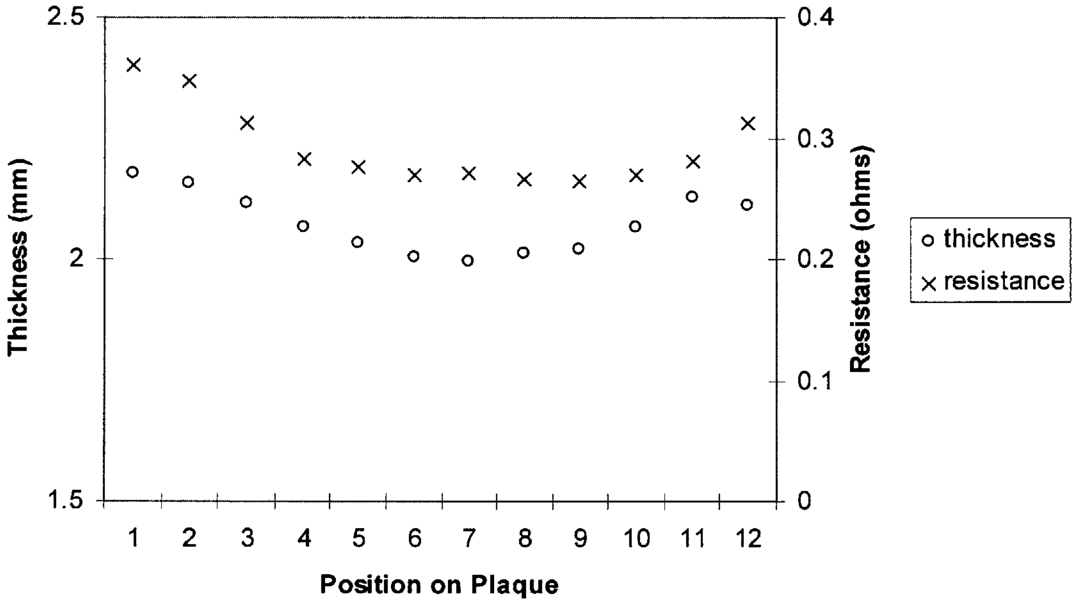

Figure 32 The thickness and resistance of chips taken from a plaque that was formed in a mold of 115° C.

The resistance variation across the same plaque however is much greater. The right axis of Fig. 32 shows that the resistance variation for the same 115° C plaque varies as much as 30%. The lowest resistance is 0.26 ohms and the greatest is 0.36 ohms. The resistance of a conductive material is given by the equation,

$$R = \frac{\rho L}{A} \tag{6.1.3}$$

where R is the resistance in ohms, ρ is the resistivity of the material in ohms/mm, L is the length of the conductive path (or thickness of the chip) in mm, and A is the area of the conductive path in mm^2. Eq. 6.1.3 shows that there is a linear relationship between resistance, R, and thickness, L. Therefore, a 10% variation in thickness cannot account for a 30% variation in resistance. The thickness plays a role in overall chip resistance, but only accounts for only one third of the resistance variation. Other causes must be considered to explain the remaining two-thirds of the resistance variation.

There are two other possible explanations for the increased resistance at the edges of the plaque: flow of the polymer components and conductive path orientation. During compression, the conductive polymer flows rapidly towards the edges of the plaque. The polymer is composed of 63% HDPE and 37% carbon-black, by weight. The carbon-black is mixed within the polymer matrix, as described in Section 2.3 of the background section. During the period of compression and flow, it is possible that the polyethylene matrix flows more rapidly than the carbon-black, causing the edges of the plaque to have a greater percentage of non-conductive polymer and a smaller percentage of conductive carbon-black. The resistance variation that is shown in Fig. 32 could therefore be a function of changing resistivity across the plaque, originating from a carbon-black density gradient that decreases with distance from the center of the plaque.

The second possible cause of increased resistance at the edges of the plaque is conductive path orientation. As the polymer flows towards the edges of the plaque, the polymer is flowing perpendicularly with the foil terminals. This sets up flow patterns and conductive paths that are perpendicular with the terminals. Therefore, the polymer that moves the shortest distance will have a random assortment of conductive paths while polymer towards the edges will have a greater proportion of paths that are perpendicular to the terminals, and less conductive across the plaque. Therefore, the resistance variation in Fig. 32 may be derived from a conductive path orientation gradient, with polymer at the edges having the least amount of complete paths across the plaque.

6.2 Resistance Jump from Radiation, Soldering, and Heat Treatment

6.2.1 Procedure. For further electrical testing to take place, the chips must be cross-linked, soldered with terminals, and undergo two heat treatments. The cross-linking ensures that the chips will maintain physical integrity during the melt phase of a trip event. Soldering wire leads onto the nickel-foil terminals gives a convenient electrical path for testing the chips, and the various heat treatments relieve any flow or thermal induced residual stresses. The purpose and process of each of these steps is detailed in Section 4.1. The resistance value of the chips directly after punching is called the out of plaque resistance (Ro). The resistance of the chips after the radioactive dose, soldering, and heat treatment processes is called the post-process resistance, Rpp. The three processes together prepare the chips for cycle life and resistance-temperature testing.

6.2.2 Experimental Results and Discussion. As a result of the three processing steps, the chips have an increased resistance, Rpp, compared to their Ro. The difference between the Ro and Rpp is called the resistance jump.

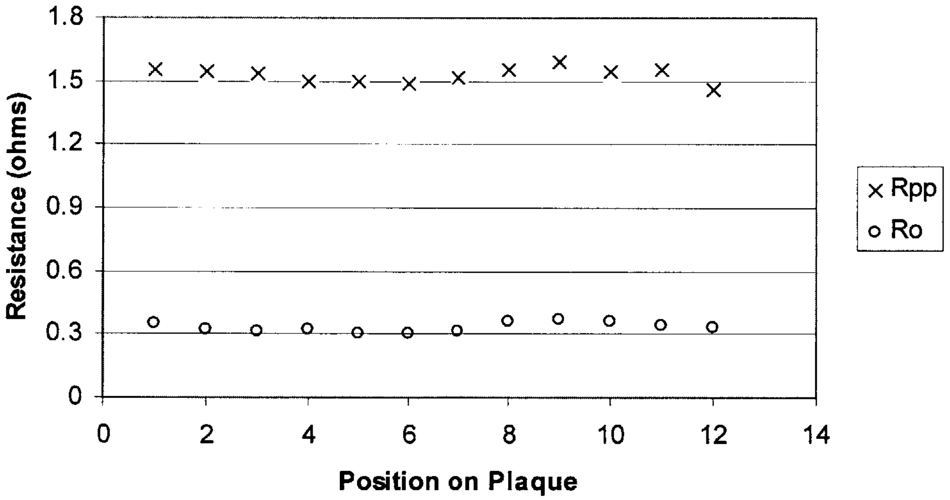

Figure 33 The Ro and Rpp of chips taken from the same plaque.

As shown in Fig. 33, there is a resistance jump of 1.2 ohms. The final resistance values are almost 5 times greater than the out-of-plaque values.

Before conductive polymer is cross-linked with a radioactive dose, the polymer crystals have well-defined boundaries. Between the crystals are spaces for the carbon-black to settle and form conductive paths. During the radioactive dose however the polymer chains are cross-linked, as described in Section 4.1.4, and the spaces between the crystals are infiltrated by polymer chains as well as carbon-black chains. This causes fewer complete electrical connections, and a higher overall resistance.

For chips that have been punched and not processed, the resistance varies by as much as 20%, but after cross-linking, soldering, and various heat treatments, the resistance varies by no more than 9%. Tests from this point on are performed on devices that have been put through the processing steps mentioned above.

6.3 Resistance-Temperature Test – Different Initial Resistances, Similar Autotherm Heights

6.3.1 Procedure. After chips have been put through the processing steps described in Section 6.2.2, they are ready for a resistance-temperature, RT, test. The wire leads of the devices are attached to a test board that can read their resistances. The test boards are then mounted in a chamber that can increase and decrease its ambient temperature. Normal RT test parameters can be found in the Section 4.2.2, along with a more in-depth description of the RT test.

6.3.2 Experimental Results and Discussion. The RT test examines the material characteristics of a conductive polymer. Residual stresses and lamination defects cannot be found using the RT test. Instead, it is primarily used to determine how much a device will increase in resistance during an over-current, or trip event.

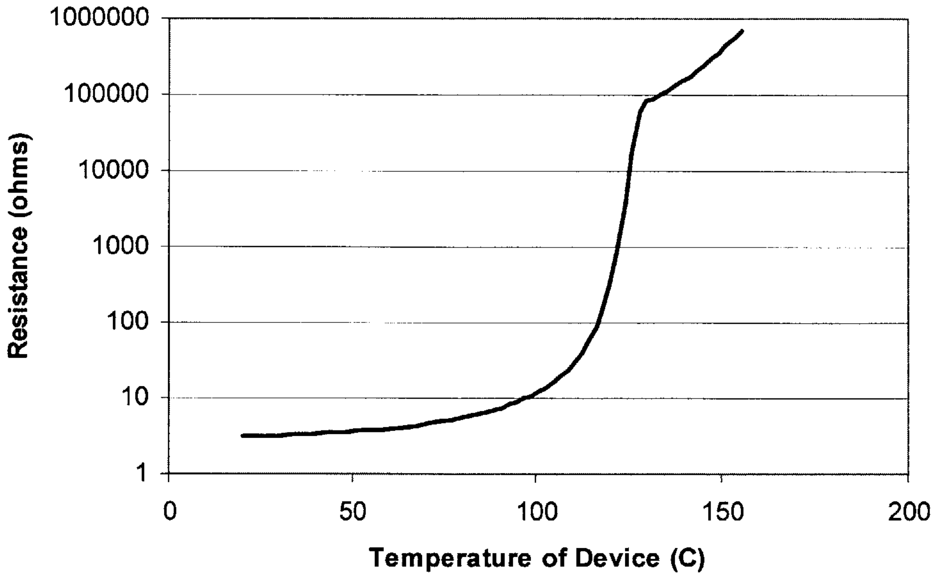

Figure 34 The RT curve for a standard extruded 38% carbon-black HDPE circuit protection device.

Fig. 34 shows the RT behavior of a circuit protection device that was produced by the extrusion process. The polymer used in the device was HDPE with 38% carbon-black by weight.

RT tests are normally performed in lots of 20 devices. The performance of a lot can be shown in two ways: i) average the resistances of all the devices in the lot at each temperature and use that data point for the resistance-temperature curve, or ii) find the device within the lot that represents the average data of the lot the best. Fig. 34 uses a single device's data as representative of a lot, as does the rest of the data in this section.

The initial resistance for RT and cycle life data is the same resistance as the post-process resistance, Rpp, described in Section 6.2.2. The term Rpp will not be used to represent the initial resistance. Instead, Ri, will be used in place of Rpp for the remaining sections.

Another important characteristic of an RT curve such as Fig. 34, is the height of the resistance jump from the initial resistance, Ri, to the resistance value at the end of the non-linear jump, around 130^{o} C. This jump is normally defined as the autotherm height, ATH. The autotherm height is the number of orders of magnitude, or decades, between the resistance of the device at 20^{o} C and the resistance of the device at 130^{o} C. For example, if the resistance of the device at 20° C is 2 ohms, and the resistance at 130° C is 2000 ohms, then the autotherm height is 3 decades. The initial resistance in Fig. 34 is 2.2 ohms, and the resistance at 130° C is 85732 ohms. The autotherm height, therefore, is 4.3 decades. Autotherm height is further discussed in Section 4.2.2.

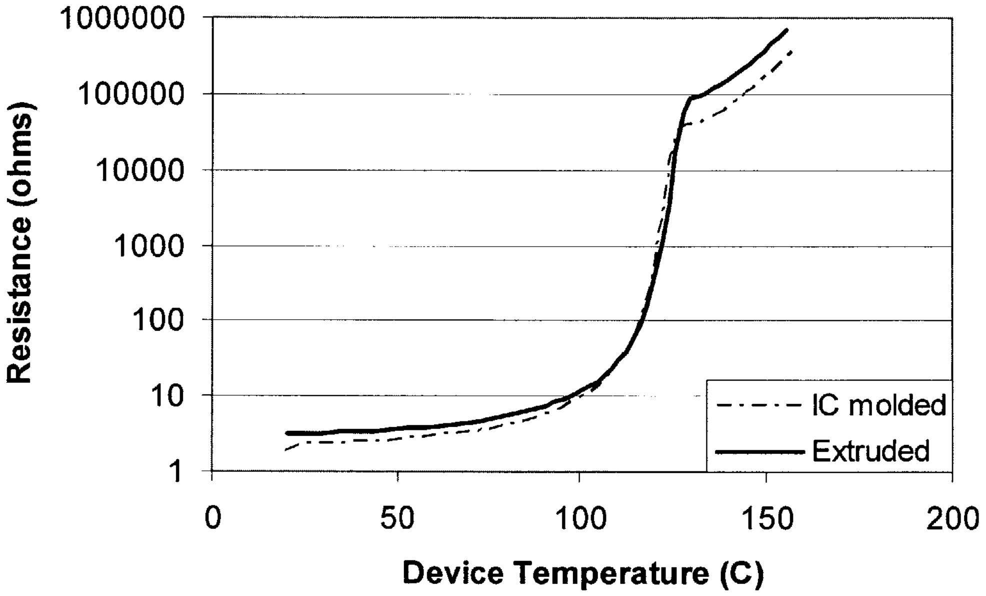

Figure 35 The RT behavior of extruded and IC molded devices.

The RT behavior of conductive polymers does not seem to change drastically when the IC molding process is used. Fig. 35 shows two sets of data: one is RT data from standard extruded plaque and the other is from IC molded plaque. The extruded plaque is composed of 38% carbon-black and the IC molded plaque is made of 37% carbon-black. With only a one percent difference in carbon loading, the curves should be nearly identical. It is clear that the initial resistance of the IC molded plaque is less than the extruded plaque, and that the final resistance is also lower. The IC molded plaque has an autotherm height of 4.39 decades, while the extruded plaque has an autotherm height of 4.47 decades.

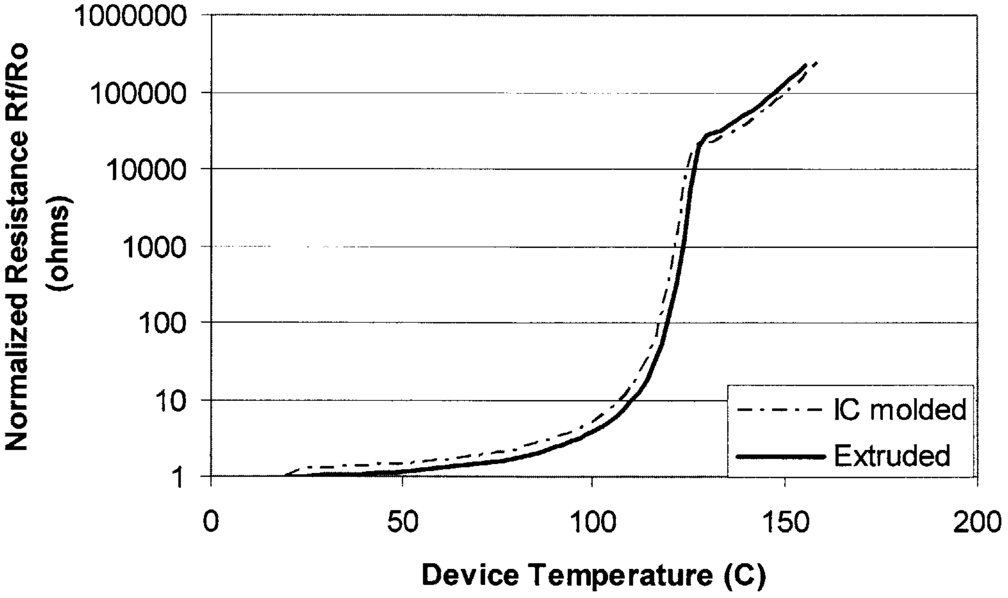

Figure 36 The normalized version of the resistance-temperature data from Fig. 37.

For normalization, all values of a devices resistance are divided by its initial resistance. This eliminates differences in initial resistance, and allows a pure comparison of autotherm height. Fig. 36 shows the normalized version of Fig. 35. Now, it is clear that both manufacturing processes have produced similar autotherm heights for the given conditions.

There is some evidence that the IC molding process uses the carbon-black more efficiently than the extruded process. One would expect that molded 37% carbon-black sample would have a greater resistivity than an extruded 38% carbon-black sample because there are less carbon chains for conductivity. The opposite occurred, however, and the molded sample has a lower initial resistance. The extruded device has an initial resistance of 2.3 ohms, and the IC molded device has a resistance of 1.7 ohms. This means that even though the IC molded sample has less carbon for conductive flow, it is still conducting electricity better than the 38% sample. Additionally, it is impressive that the IC molded sample has almost an identical autotherm height for a lower initial resistance.

6.4 Resistance-Temperature Test – Similar Initial Resistances, Different Resistance Jumps

In this section, the IC molded carbon-black level is decreased even further to 35.8% by weight of the polymer. This forces the initial resistance of the molded devices to increase, more closely imitating the initial resistivity of the extruded devices. If the initial observation of greater efficiency and utilization of the carbon-black continues, it would be expected that this lower value of carbon-black in the molded polymer should produce results that more closely mimic the extruded 38% carbon-black sample in Fig. 34.

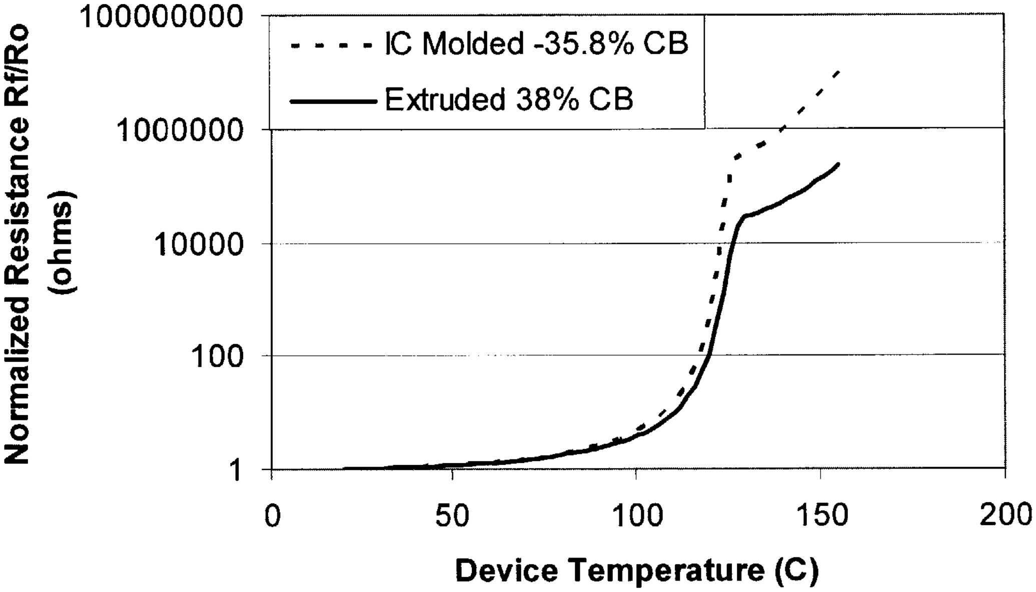

Figure 37 A comparison of RT performance between extruded 38% carbon-black devices and IC molded 35.8% carbon-black devices.

The average initial resistance of devices from the molded 35.8% carbon-black HDPE plaque was 2.46 ohms. As stated previously, the standard extruded parts have an initial resistance of 2.3 ohms. Therefore, in order to obtain similar initial resistances it was necessary to have 2.2% less carbon loading in the molded case. Fig. 37 shows the normalized resistance-temperature data for both molded 35.8% and extruded 38% devices, and it is clear that for similar initial resistances the molded sample is getting nearly one order of magnitude more autotherm height than the extruded sample. Since the initial resistances for these samples are very close, 2.46 ohms vs. 2.3 ohms, we can assume the autotherm height comparison from Fig. 37 is accurate, even though the data has been normalized. The molded autotherm height is 5.4 decades while the extruded sample has only 4.4 decades.

The results of Fig. 37 continue to give evidence that the IC molding process uses carbon-black more efficiently as a conductive medium within a polymer matrix. With 2.2% less carbon-black to conduct current, the IC molded plaque was able to hold an equivalent resistivity to the extruded plaque. In addition, by using less carbon-black to achieve the same initial resistance, the autotherm height increases substantially for the molded devices. Reduced carbon-black means that there are fewer electrical connections across the polymer to pull apart during the melt phase, causing a greater jump in resistance (autotherm height) across the non-linear region of the RT curve, Region 2 of Fig. 10.

The increased efficiency of the conductive element might be a function of the crystal growth within the polymer. Crystal growth occurs during the cooling phase of both manufacturing processes. In the case of extrusion, the polymer begins cooling after it is formed into a sheet, and is immediately exposed to the ambient temperature. Molding is much different however. The polymer, after compression, is forced to stay at a temperature that is much higher than ambient, until the polymer is rigid enough to leave the mold. During this cooling phase within the mold, the crystal growth may behave significantly different from that in the extrusion case.

6.5 Autotherm Height vs. Position on Plaque

As discussed in section 4.2.2, the autotherm height (ATH) of a non-linear positive temperature coefficient device is a property of the conductive polymer within the device. It is commonly known that autotherm height is related to initial resistance. For example, if two devices are made out of an identical conductive material, but one of them has a slightly higher resistance, it can be assumed that the higher resistance device has fewer complete electrical paths along the length of the polymer. During the non-linear portion of the RT curve, both devices lose many of their conductive paths as the base polymer expands but the higher resistance device ends up with many fewer conductive paths, causing a much greater final resistance, and greater autotherm height.

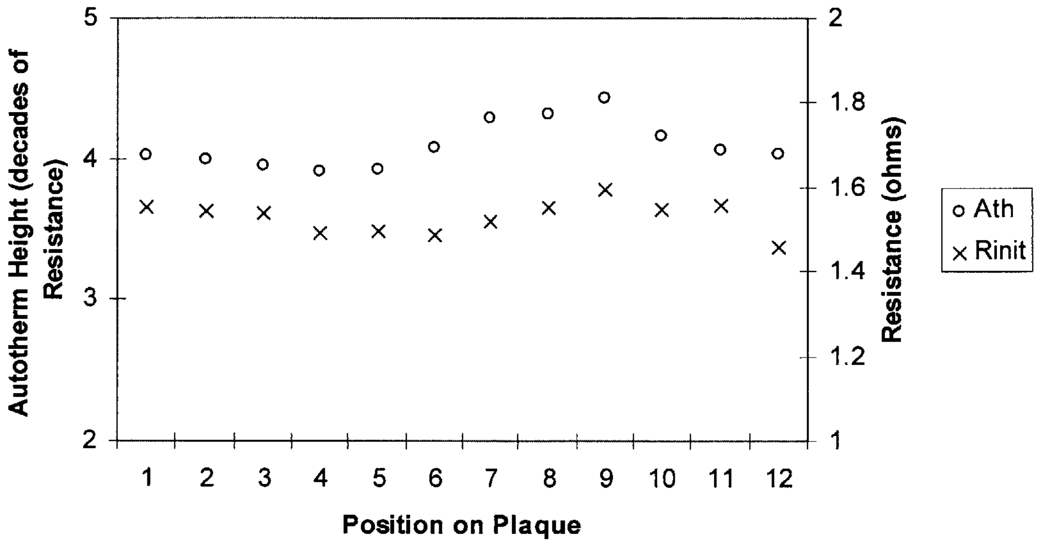

Figure 38 Resistance and autotherm height for devices taken from the same plaque.

Fig. 38 shows the position on the plaque from which the chips were taken. Positions 1 and 12 are edges, and Positions 5 and 6 are center. There is a clear direct relationship between the resistance and autotherm height. It is important therefore, to have very consistent resistances across a plaque in order to minimize the autotherm height differences.

Increased autotherm height is a generally desirable characteristic for circuit protection devices. A device that reaches a high resistance during trip will leak less current and keep the circuit protected. Equally important however is consistent autotherm height, to ensure that all devices have consistent trip performance. For this reason, consistent initial resistance is very important characteristic of plaque performance.

6.6 Cycle Life Behavior

6.6.1 Procedure. The types of devices that this IC molding process is trying to reproduce are known as "high-voltage" devices. The polymer composition and geometry of the device is designed to withstand large power surges. In cycle life tests the devices are tested at 250 V-3 A-100 Cycles, 600 V-2.2 A-100 Cycles, 600 V-7 A-10 Cycles, or 600 V-60 A-3 Cycles. Devices that undergo any one of these tests are considered sufficiently stressed that they do not undergo any other test. Each of these tests holds the device at the stated power level for 5 seconds, allows it to rest for 120 seconds between the power cycles in order to allow the device to cool to its ambient resistance before subjecting it to another power surge.

Cycle life testing measures a device's physical and electrical durability. If a device is poorly constructed and has a weak interface between the foil and polymer, arcing may occur early during cyclic testing and cause device failure. Cyclic testing is the most important indicator of device performance that is consider in this study.

6.6.2 600 V-2.2 A-100 Cycles. The IC molded devices easily passed the 250 V-3 A-100 Cycle test with 100% pass rate. Therefore, our analysis of cyclic performance begins with the 600 V-2.2 A test parameters.

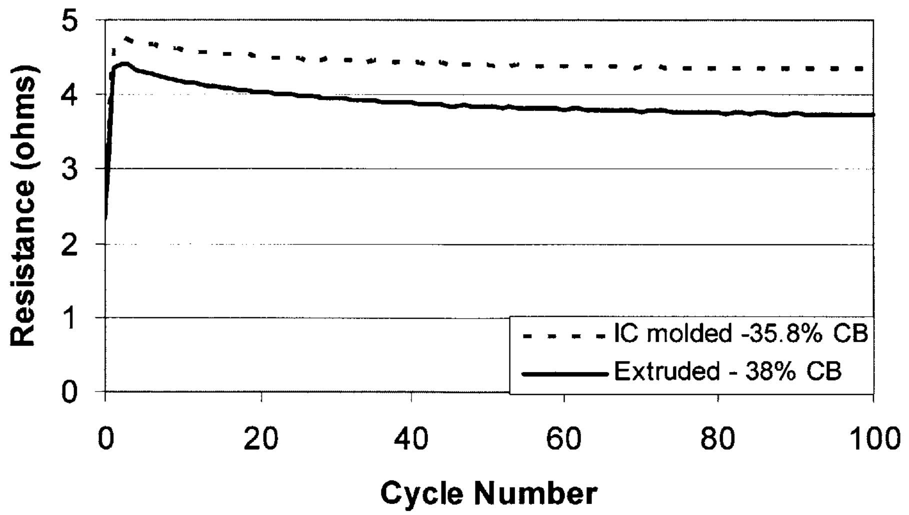

Figure 39 The cycle life performance of extruded 38% carbon-black devices and molded 35.8% carbon-black devices, tested under 600 V-2.2 A, 5 seconds on, 120 seconds off, conditions.

Fig. 39 shows the performance of a standard extruded device and molded devices during 600 V-2.2 A cycle life testing. The devices used in Fig. 39 were taken from the same lots as the device used for Fig. 37. This was done to provide consistent comparison between IC molded performance and extruded performance across the different types of testing.

The resistance behavior during 600 V-2.2 A cycle life testing is shown in Fig. 39. Before each additional power cycle, the testing machine measures the resistance of the devices. The resistance jumps significantly for the first two cycles, and then drops slowly during the additional 98 cycles that follow. The resistance is recorded for all 100 cycles, but the initial, 2nd cycle, 10th cycle, and 100th cycle resistances are used most often for comparison. The resistance at any particular cycle, Rf, divided by the initial resistance is known as the trip jump, TJ.

$$\mathbf{TJ = Rf/Ri} \qquad (6.6.5)$$

The 600V-2.2A cycle life data can therefore be summarized by the resistances and trip jumps, Eq. 6.6.5 of the 1st, 2nd,10th, and 100th cycle, Table 1 summarizes the trip jumps and resistances of Fig. 39.

Table 1 Comparison of resistances and trip jumps of extruded and molded devices.

	Extruded		IC Molded	
Cycle	Resistance (Ω)	Trip Jump	Resistance (Ω)	Trip Jump
0	2.3		2.5	
2	4.42	1.88	4.76	1.85
10	4.17	1.77	4.61	1.79
100	3.73	1.59	4.36	1.69

IC molding does not seem to change the long term 600 V-2.2 A cycle life performance substantially. As shown in Fig. 39 and Table 1, both types of devices jump similarly to start, and then gradually relax with subsequent cycles. The initial resistance for the IC molded device is 2.5 ohms, and for the extruded it is 2.3 ohms. This suggests that even though the molded device jumps higher, the two parts have similar trip jumps throughout their performance.

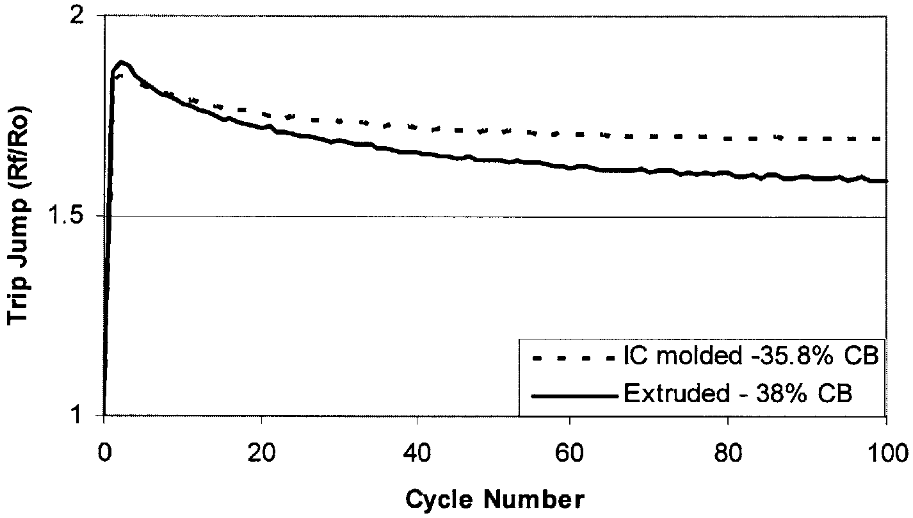

Figure 40 The trip jump history during 600 V-2.2 A cycle life for both extruded and IC molded devices.

Fig. 40 shows the trip jump behavior for both types of devices during the 100 cycles of testing. Both devices start at unity because Rf/Ri at the first cycle is dividing the initial resistance by itself. The beginning of cycle life is most similar with both reaching a maximum resistance quickly. Then, throughout the final 98 cycles, both parts lower in resistance with the extruded device reaching a lower final trip jump than the molded device.

The results that have been presented for the 600 V-2.2 A cycle life continue to show that the injection-compression molded devices have sufficient electrical performance potential. During testing, usually one IC molded device of 25 would fail.

The tendency for IC molded devices to relax at a slower rate, as shown in Fig. 40, does not implicate anything necessarily positive or negative. Unlike the increased autotherm height which has a distinct advantage, a greater long-term trip jump does not affect overall performance of the part. The circuit will have to carry a slightly higher load due to a greater long term trip jump, but this effect can be fixed by lowering the initial resistance of the device by increasing the carbon loading within the polymer.

6.6.3 600 V-7 A-10 Cycles. The IC molded devices had such a high success rate with the 600 V-2.2 A test that there were only small behavioral differences between the molded and extruded devices. In the case of the 600 V-7A test the devices fail much faster and more often, so we can examine failure more closely. This test also keeps the power on for 5 seconds each power cycle, and lets devices rest for 120 seconds between cycles.

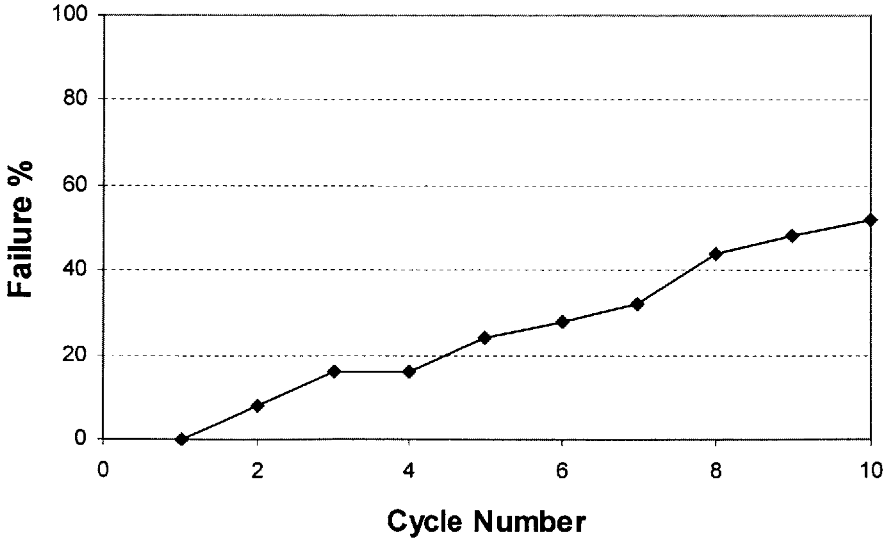

Figure 41 Failure Rate of molded 35.8% carbon-black devices in the 600V-7A test.

On average, as shown in Fig. 44, 5% of the devices fail with each additional cycle, with 50% failed at the end of the ten cycles. All the devices pass the first cycle, 92% pass the second cycle, and 84% pass the third cycle.

There is no readily available performance data for extruded devices at these parameters however the performance specification is that each device survives one cycle of 600V-7A power for 5 seconds without failing. Fig. 41 results show that we have satisfied this requirement, but only in the best case scenario. For safety-factor purposes, it is advantageous to have performance that consistently passes 2 to 3 times the number of cycles that a specification requires. For this reason, the 600V-7A cycle life of our IC molded devices should be characterized as good, but improvements should be made for greater assurance of proper performance.

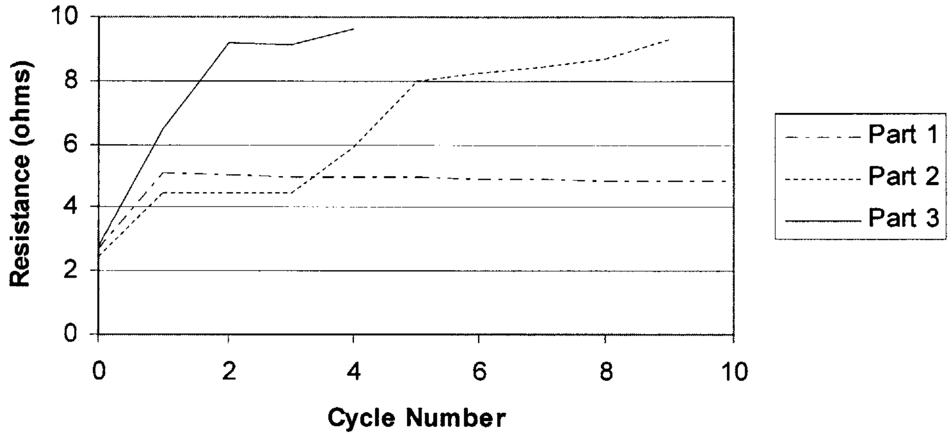

Figure 42 The resistance results of three different IC molded devices that underwent the 600V-7A test.

Half of the molded devices survived all 10 cycles of the 600V-7A test. These devices had a normal resistance jump after the first cycle, and then had a constant or slightly decreasing resistance throughout the remaining 10 cycles. Part 1 from Fig. 42 shows the resistance results of one of these parts. Some parts failed late in the test, like Part 2. The resistance jump is normal for Part 2, and it has normal behavior for a few cycles, but then the resistance jumps again until the part fails completely in the 10th cycle. Part 3 failed early and did not display any normal behavior. The resistance jumps very quickly until the part failed in cycle 5.

Abnormal resistance increases usually come from oxidation within the polymer. During a power surge, the device reaches a very high temperature due to joule heating, possibly causing a slight amount of internal burning. If burning (or oxidation) occurs within the polymer matrix, the subsequent resistance of the device will be higher, because there will be fewer conductive paths across the polymer. Any carbon-black that is within the oxidized polymer is no longer an active pathway. A higher resistance causes the part to heat up even more during the next cycle, which in turn causes more burning. This cycle continues until the temperature during a power surge is so great that the part burns completely.

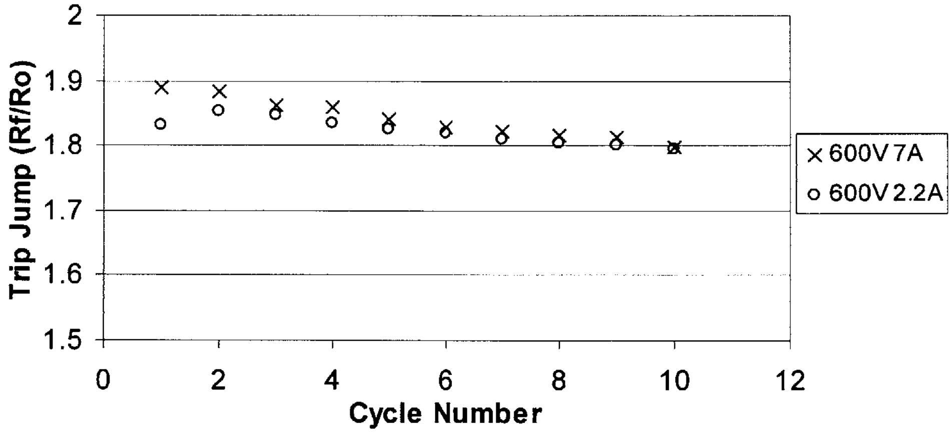

Figure 43 The 600V-7A and 600V-2.2A trip jump for molded 35.8% devices.

One last comparison is between the IC molded trip-jump data from the 600V-2.2A test with the same data from the 600V-7A test. Fig. 43 shows that the 7A test has a slightly higher trip jump initially, but that both tend to relax at the same rate for the first ten cycles. Keep in mind that the first ten cycles are much more aggressive for the 7A test, and that only half the parts survive. Even still, those parts that survive all ten cycles seem to have almost identical trip jump behavior to the 2.2A test.

6.6.4 600 V-60 A-2 Cycles. The most aggressive of the cyclic testing tests is the 600V-60A test. It would be very rare for a device to see this type of power surge in practical applications. Nevertheless, for high-voltage devices, the goal is that no more than 5% of the parts should fail during the first cycle of 600V-60A for five seconds.

The molded 35.8% carbon-black devices did not pass the 5% failure rate rule. Fifty of the molded 35.8% carbon-black devices were tested at the 600V-60A setting, and only 7 failed during the first cycle. This means that 86% of the devices passed, only 9% away from the goal of 95% survival.

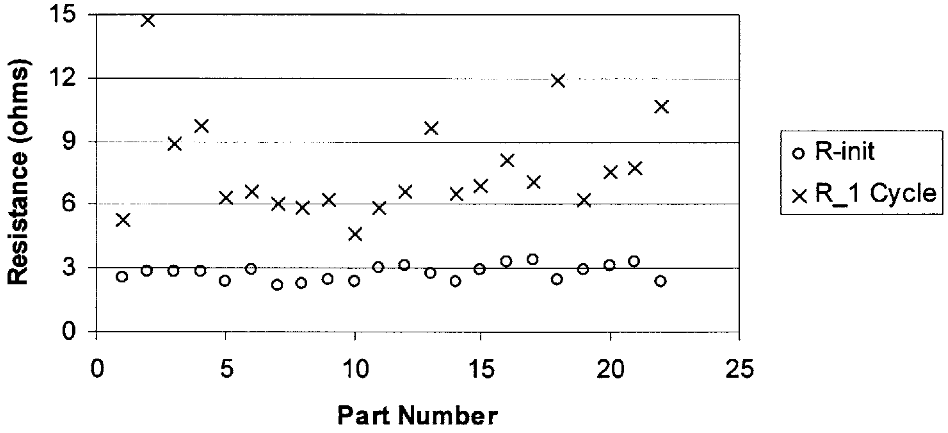

Figure 44 The initial and one cycle resistances of molded 35.8% carbon-black devices for the 600V-60A test.

The aggressive nature of the 600V-60A tests tends to affect parts after their first cycle, in random ways. Of the first 25 part lot, 22 passed the first cycle. The initial and post-one-cycle data of the surviving parts is compared in Fig. 44. Notice that the increase in resistance tends to hover around 6 ohms, but that some devices increase less, and some increase as much as 12 ohms. Unlike previous tests, substantial polymer oxidation may have occurred in this first cycle.

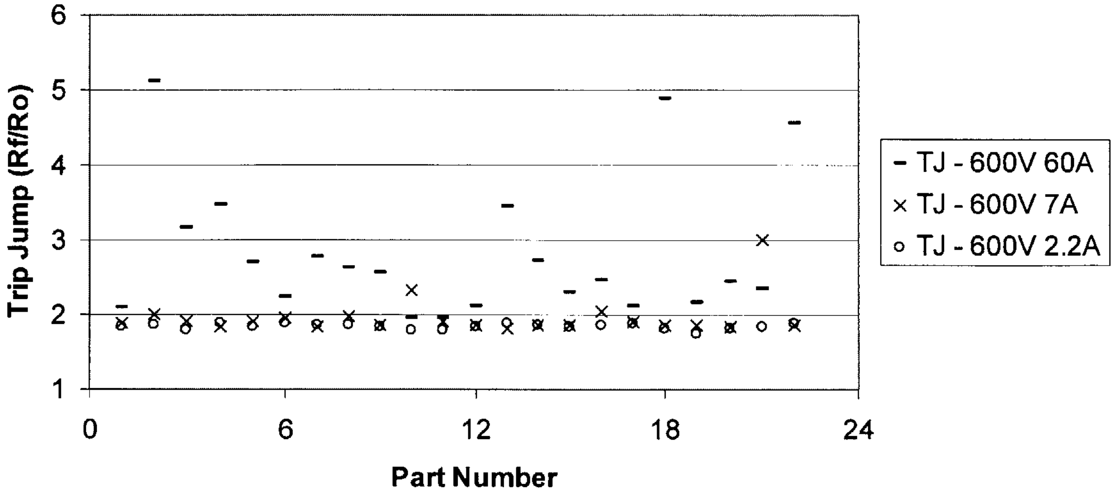

Figure 45 Comparison of the trip jump after one cycle of 600V and either 60A, 7A, or 2.2A for the molded 35.8% carbon-black devices.

The trip jumps were very consistence for many parts in the previous tests, but it did not hold to be as consistent for the 60A test. Fig. 45 shows the trip jump for 22 parts from each test after one cycle. The devices from each test were only used for that particular test, and not reused for other tests. It is clear that the average trip jump for both the 7A and 2.2A tests is around 1.8, but the trip jump for the 60A test is much more sporadic. The majority of the 60A parts have a trip jump magnitude between 2 and 3, but some go as high as 5. This shows that the first cycle of the lower amperage tests does not damage the polymer, while the 60A test oxidizes some of the polymer structure as early as the first cycle.

CHAPTER 7

CONCLUSTIONS

Polymeric non-linear positive temperature coefficient circuit protection devices work on the non-linear relationship between a devices resistance and temperature. The device is placed upstream of an electric circuit. For low ranges of electrical current, the polymer within the device has a low temperature and resistivity and allows current to pass through freely. If the electrical power level entering the circuit begins to surge, the temperature of the device will rise, causing the resistivity of the polymer within the device to increase rapidly, several orders of magnitude, blocking the high-current levels that are trying to enter the downstream portion of the circuit.

These polymeric circuit protection devices have been manufactured for many years by an extrusion-based process. Conductive polymer is extruded between hot rolls and laminated with 0.05-mm thick Ni foil on both sides to produce a nickel-polymer-nickel sheet, called plaque, with an overall thickness of 2-mm. 13 mm x 8 mm sized chips are punched from the plaque, leaving a shell of wasted plaque where chips were not punched. In addition, each extrusion run wastes many meters of plaque before achieving the targeted resistivity of polymer. Once the chips have been punched, they are heat treated for residual stress relief, given a radioactive dose for cross-linking, attached to wire-leads with solder, and then given one more final heat treatment.

This thesis studies the possibility of switching to a more efficient injection-compression (IC) molding based manufacturing method for polymeric circuit protection devices. Instead of making a large plaque and punching chips from it, this process would inject the conductive polymer between two metal terminals and compress them together at a high temperature. This process would create individual devices from the on-set, and eliminate the plaque phase, the punching and soldering, and the final heat treatment step.

For cost considerations, this thesis was not able to create a mold with multiple device-sized cavities. Instead a large cavity mold was fabricated that could create 150 mm x 75 mm x 2 mm IC molded plaques. These IC-molded plaques were then punched into chips and brought through the normal processing steps for device preparation.

Once fabricated, these IC-molded devices were put through the standard physical and electrical tests that extruded devices must undergo. The peel test, which examines the bond between the foil and polymer, gave very promising results. It showed that the IC molded plaques, when fabricated with mold temperatures around 115° C have very even peel strength in the middle regions, and slightly higher values at the edges. Since devices will ultimately be manufactured individually at a much smaller size, and not as plaques, these edge effects will be significantly reduced, and do not pose a foreseeable problem.

The first electrical test for the devices was the resistance-temperature (RT) test. This test looks at the relationship of the temperature and resistance of the conductive polymer within the device. If a device does not increase in resistance sufficiently with temperature, then it will not protect the downstream circuit in real applications. It was found in this study that IC molded devices increase in resistance equally to extruded devices for the given range of operational temperatures between 20° C and 160° C.

Cycle life tests expose the devices to a series of power surges that electrically stress the conductive polymer. Three cycle life power levels were examined: i) 600 Volt-2.2A for 100 Cycles, ii) 600 Volt-7A for 10 Cycles, and iii) 600 Volt-60 Amp for 1 Cycle. 95% of the IC molded devices passed the 600V-2.2 test for all 100 Cycles. 100% pass the first cycle of 600 V-7 A power, the industry standard, but could not provide the required safety factor with only 95% passing the second cycle. Finally, only 86% of the devices passed the one-cycle of 600 V-60 A power, with 95% being the stated performance goal. These cycle life performance discrepancies show that while the IC molded devices have not yet achieved equal cyclic performance to extruded devices, they show great potential for reaching the stated goals with future research.

This thesis has provided strong evidence that the IC molding-based process has potential to replace the standard extrusion process. This new process has both economic and waste incentives, and provides the potential for a faster cycle-time because of fewer processing steps. Further work should be done to improve the cycle life performance and promote a further understanding of the relationship between IC molding variables and electrical performance. In addition, a new multi-cavity mold should be fabricated that can accommodate the study of IC molded individual devices.

REFERENCES

Avery, J., 1998, *Injection Molding Alternatives, A Guide for Designers and Product Engineers*, Hanser Publishers, New York.

Cheremisinoff, N.P., 1987, *Polymer Mixing and Extrusion Technology*, Marcel Dekker, Inc., New York.

Davis, H.E., Troxell, G.E., and Hauck, F.W., 1982, *The Testing of engineering Materials*, McGraw-Hill Book Company, New York.

Hensen, F., 1997, *Plastics Extrusion Technology*, Hanser Publishers, New York.

Moore, G.R. and Kline, D.E., 1984, *Properties and Processing of Polymers for Engineers*, Prentice-Hall, Inc., Englewood Cliffs, NJ.

Peacock, A., 2000, *Handbook of Polyethylene, Structures, Properties, and Applications*, Marcel Dekker, Inc., New York.

Potsch, G. and Michaeli, W., 1995, *Injection Molding, an Introduction*, Hanser Publishers, New York.

Sichel, E.K., 1982, *Carbon-Black Polymer Composites*, Marcel Dekker, Inc., New York.