5-2009

THE EFFECT OF BOND STRENGTH OF FLEXIBLE LAMINATES ON PUNCTURE RESISTANCE

Rijosh Cheruvathur

Clemson University, rijoshj@clemson.edu

THE EFFECT OF BOND STRENGTH OF FLEXIBLE
LAMINATES ON PUNCTURE RESISTANCE

A Thesis
Presented to
the Graduate School of
Clemson University

In Partial Fulfillment
of the Requirements for the Degree
Master of Science
Packaging Science

by
Rijosh John Cheruvathur
May 2009

Accepted by:
Dr. Duncan O. Darby, Committee Chair
Dr. Kay Cooksey
Dr. Roger L. Kaas
Dr. Patrick D. Gerard

ABSTRACT

This work was aimed at understanding whether the bond strength of laminates will affect the puncture resistance of the laminate. Even though a strongly bonded adhesive layer in between two webs will considerably improve the mechanical properties of the laminate compared to that of the individual materials, there is a general belief in the packaging industry that having a lower bond strength helps to improve the bending or, in other words, the flexibility of the laminate thereby increases the tear and puncture resistance.

Laminations of aluminum foil and polyethylene terephthalate (PET) were used as a model system to determine the validity of this industry paradigm. The variables used in this study were adhesive coating weight, adhesive system and additives used to control bond strength. The weight of coating was controlled to around 1.5 pounds per ream using different Meyer rods. Two popular polyurethane based adhesive systems, Tycel from Liofol® and Adcote® from Rohm and Haas were used with talc and microcrystalline polypropylene wax as additives. The additive loading was adjusted at 5%, 10%, 15% and 20% with respect to the total percent solids in the pure adhesive mixture. The cured, off-machine and time based values for adhesive bond strength and puncture resistance were measured. Two probes, ASTM probe and a hemispherical probe were used to measure the puncture resistance of the laminates from both PET and Foil sides. The off-machine bond strength for both the adhesive systems using talc and PP wax shows a gradual decrease in values. The cured laminates underwent material failure at low percentage loading of the additive up to 10 % as the cured bond strength values were higher than the

strength of PET film. Above 10% additive loading, the bond strength values showed a quadratic decrease similar to off-machine bond strength values. However, the puncture strength of cured laminates did not show any corresponding change for different percent loading of additives. The ASTM probe gave higher puncture values than the hemispherical probe. The puncture strength showed a gradual increase over a time period of 4 to 4.5 hours. The trend is initially linear changing to a quadratic mode at longer time periods. It was also noted that the mode of puncture changed from multiple substrate failure with delamination to a single substrate failure with no appreciable delamination as curing time approached 4.5 hours showing that most of the curing process takes place in the initial 4 hours after lamination.

DEDICATION

I would like to dedicate this manuscript to my loving mom, Mrs. Lucy John. It is due to her constant love and motivation that I am standing where I am right now and no words can describe my gratitude towards her. Mom, your calming words and prayers helped me stay sane through all the difficulties and hardships of graduate studies.

ACKNOWLEDGEMENTS

TABLE OF CONTENTS

Table of Contents (Continued)

LIST OF FIGURES

List of Figures (continued)

LIST OF TABLES

LIST OF CHARTS

List of Charts (continued)

List of Charts (continued)

List of Charts (continued)

List of Charts (continued)

List of Charts (Continued)

CHAPTER ONE

1.   INTRODUCTION

Packaging has been in use since humankind started making use of leaves and other natural materials to store, transport and preserve food. Some of the early man-made materials used for packaging included pottery, wood, woven containers, glass, metal, paper and paperboard. After World War II, synthetic plastics, which were then a new material, began to be used widely in the area of packaging. One of the early plastics to be used in packaging, polyethylene, still remains the leading packaging plastic due to its low price and desirable properties.

Due to the continued advancements in the manufacturing and use of plastics, market penetration in the field of packaging increased rapidly during and after the 1970's. The primary driving force was the low density offered by polymeric materials as compared to conventional materials like glass and metal. Easy manufacturing of plastic materials also aided for the increased use of these materials. Some inherent properties of plastics, such as low melting points, made them suitable for fabrication methods like thermoforming, blow molding, casting and so on. All of these factors combined to make packaging the largest single market for plastics.

Table 1.1 shows a list of the most popular plastic resins by their sales volume in the plastics industry for the year 2007, published on www.societyplasticsindustry.org. Figure 1.1 shows the distribution of use of plastics in different market areas published by the American Plastics Council [1]. The chart clearly shows that packaging is the industry

sector where plastics are most widely used with a 34 percent market share followed by Consumer and Institutional sector with 22 percent share. Even though these values are for the American market, it can be related to current global trends.

Resins Comprising Market Distribution	
Low Density Polyethylene (LDPE)	Styrene Butadiene Latexes (SBL)
Linear Low Density Polyethylene (LLDPE)	Thermoplastic Polyester
High Density Polyethylene (HDPE)	Nylon (PA)
Polypropylene (PP)	Polyvinyl Chloride (PVC)
Polystyrene (PS)	Polyurethanes
Epoxy	

Table 1.1: List of Plastics in packaging [Source: Major market volumes are derived from plastic resin sales and captive use data as compiled by Veris Consulting, LLC, and reported by ACC's Plastic Industry Producers' Statistics Group, includes ACC estimates (www.americanplasticscouncil.org)].
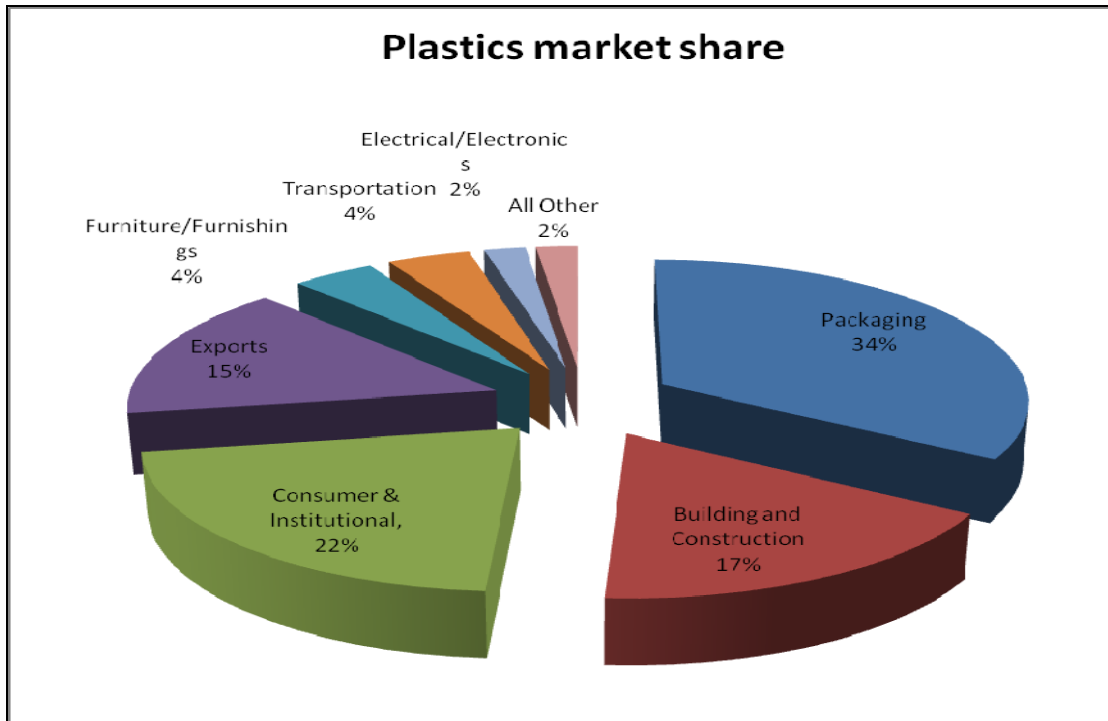
Figure1.1: Plastics market share [Source: American Plastics Council 2007 www.americanplasticscouncil.org)]

As the demand for plastic materials in packaging increased, so did the desired requirements. In many cases, these cannot be met by any single material. One way to address this issue is to combine two or more materials together to act as one- providing benefits of all the materials. One of the main methods of doing this is called lamination.

Laminations are used throughout the flexible packaging industry to create packages that have desired characteristics that one material alone cannot provide. Adhesive lamination involves combining two or more substrates together with the help of adhesives, thermal energy and pressure. The adhesives are generally polymers that begin with a lower molecular weight and crosslink upon cure. Adhesives can be solvent-free, water-based or

organic solvent-based depending on the chemistry. Energy required for laminating two substrates is usually supplied as heat energy, both in the laminating nip and in a hot room for curing at elevated temperature. In the case of room temperature curing, heat is provided solely at the laminating nip rolls and in the oven for drying off solvents.

In most cases it is difficult for the average consumer to distinguish between the multiple layers of a lamination. The adhesives used in lamination are often carried and applied to the web (primary substrate) in a low viscosity solvent like water or organic solvents like ethyl acetate. The percent solid is a measure of the amount of solids in the adhesive mixture. The solids are what create adhesion. The solvent should be removed to allow the adhesive to work.

There are two methods of water-based and solvent-based lamination- wet lamination and dry lamination. In wet lamination, one of the substrates being laminated must be porous enough to let the solvent evaporate through it. The second method of lamination is dry lamination where the adhesive is applied and the web must be dried before being laminated to a second web.

Most adhesives come in two parts, often labeled as adhesive and as curing agent. They react when mixed together forming interlocking polymer chains. So when the adhesive goes into a laminate structure, the chemical groups on the chain can adhere onto the substrate providing a strong adhesion. The reaction begins immediately, but takes approximately ten days to reach a 90% completion, thus being "cured".

Surprisingly little research has been done in trying to find a predictable method to control the strength of the adhesive bond. While having two webs with a strong adhesive bond improves the tear and puncture resistance over a single web, having lower bond strength is rumored throughout the flexible packaging industry to improve these properties since both the webs would be able to bend and slide past each other rather than just acting as one. It is believed in the industry that lower bond strength will improve the puncture resistance of a laminate. However no work has been reported on this general belief. The purpose of this research is to control the adhesive bond strength in a flexible laminate and to check the effects on puncture resistance. Two adhesive systems were used for this study and two additives, talc and polypropylene wax, were introduced into the adhesive system in an effort to bring down the bond strength values. The bond strength and puncture testing were carried out on samples before, after and during cure.

CHAPTER TWO

2.   LITERATURE REVIEW

2.1   Introduction

The basic functions of a package are to protect, contain, carry and dispense a product. Over time the demands on packaging increase. Now, a package carries the extra burden to motivate, promote, glamorize, and sometimes to build up or even disguise the contents [1]. According to an industry expert, flexible packaging can be defined as "Packaging that can be wadded up and thrown away" [6]. Current packaging technology can be described as a combination of art, science and engineering, drawing from Packaging Science, Material Science, Physics, Mathematics, Electronic, Mechanical and Chemical Engineering along with Graphic Design, Logistics and so on. Some of the common packaging types include bottles, cans, shrink/ stretch wraps, overwraps, bags, pouches, flexible lidding/ forming webs, bands and labels.

2.2   Materials

Materials used in packaging can broadly be classified into rigid/ semi-rigid and flexible.

Rigid/ semi-rigid materials- Glass, metal, Paperboard

Flexible materials- Paper, Plastics, Foils

 Some of the widely used materials in packaging include paper & paperboard, flexible packaging, metal cans and drums, rigid plastic packaging and glass containers. Paper and paperboard are still among the most economical materials, whereas metals provide a high

degree of strength, rigidity and barrier properties. Glass has excellent barrier properties and gives the product an expensive look, but has a major disadvantage in the transportation due to breakage [1].

2.2.1 Glass

Glass can be defined as an inorganic material melted at high temperatures and cooled quickly so that it solidifies in a vitreous or non crystalline condition [2]. It is essentially a super cooled liquid. Glass shows no sharp melting point, but gradually softens with heat and solidifies on cooling. All commercial grades of glass are based on silica. Silica is high purity sand and can be represented by the general chemical formula, SiO_x. The most common glass used in packaging is soda-lime glass which is made up of sodium and calcium compounds with silica. Transition metal compounds are added to impart color to glass. The major disadvantages of glass include its weight and breakability [2].

Glass is inert to most chemicals and is tasteless and odorless. So it is an ideal material to store reactive chemicals, foods sensitive to volatiles loss and also for carbonated beverages. Glass is also stable at high temperatures making it suitable for hot filling and retortable products. Retorting is the process of subjecting the packaged product to high temperatures and pressure in order to kill all the micro-organisms [2].

2.2.2 Metals

Metal cans comprise 60% of all rigid containers used in the United States for food beverages and beer [4]. Mainly two metals, aluminum and steel, are used in the packaging industry. Aluminum cans dominate the soft drink and beer packaging segment

while steel cans dominate in the food industry. Aluminum and steel show good ductility and strength properties and hence can be used in very thin structures. An additional benefit of aluminum is its relatively light weight compared to other metals and its easy recyclability. According to some industry experts, steel is advantageous due to its easy recyclability also [4].

2.2.3   Paper and Paperboard

Paper can be defined as a matted or felted sheet usually composed of plant fiber [2]. Modern paper is almost exclusively made from cellulose fiber from wood. Paper can be characterized according to its weight, thickness, brightness, fiber content, moisture content and viscoelasticity. Paperboard is the term used for heavier paper usually weighing more than 250 grams per square meter. The quality of paper depends on the fiber source, method used to extract the fibers from wood, treatments on the finished paper and also on the machinery used for production [2].

The longer the fiber, the better will be the tensile, fold, tear and puncture strength properties. However shorter fibers will give a smooth surface texture and a more consistent density across the width of the sheet [1][2].

2.2.4   Foils

Foils can be defined as a very thin sheet of metals like Tin, steel and Aluminum. Tin and steel foils are not used to any significant extent in packaging. The word foil thus generally refers to aluminum foil. In thickness, foils used in packaging can range from 26 gauge to around 700 gauge (6.5 µm to around 180 µm). Aluminum foil appears in a wide

8

variety of packages. It provides excellent barrier to light, oxygen and other gases. Foil also prevents flavor loss. Foil can also be used to increase the aesthetic appeal of the package. It has excellent heat conductivity, which is useful in heat sealing applications. The main disadvantages of using aluminum foil are public perception that it is not microwavable and the concern for the formation of pinholes. The formation of pinholes will act against the moisture barrier and other barrier properties offered by the material. Multiple layers of foil can be combined together so that there will be no continuous hole. Also, the moisture barrier can also be ensured by coating foil with a plastic or laminating it to a plastic [4].

2.2.5 Plastic films

Flexible packaging is perceived well by the consumers as it takes up less space in waste disposal and landfills, provides source reduction and possesses the required functional properties required by some packaged products. These factors make it the fastest growing area in packaging [1].

Films can be defined as thin sheets of plastic. The classification between film and sheet is made based on its thickness which relates to its flexibility. If thickness of the material is less than 0.003 inches, it is called a film and materials with thickness values greater than 0.010 inches are considered sheet [5]. A plastic is often used as a generic term for a polymer, which can be defined as a very big molecule with molecular weight in the range of thousands to several thousands of grams made up of regular repeating units. Polymers can be classified as crystalline, semi-crystalline or amorphous depending on the order of

alignment or orientation of the molecular chains. In crystalline polymers, the molecular chains are arranged in an orderly fashion. In amorphous polymers, the chains are not aligned or can be said to be randomly oriented. In semi-crystalline polymers, there will be both crystalline and amorphous regions. The same terminology applies in films too. Plastic materials can be used in a variety of forms like bottles, cups, bags or pouches. Bags and pouches are made from plastic films.

Films can be produced either by flat die extrusion, calendering, solution casting or by blown-film extrusion depending on the resin characteristics and the desired film properties. Extrusion is the process of melting the polymer resin pellets into a molten liquid, called extrudate and squeezing the extrudate through an opening called a die. The energy required to melt the resin comes mainly from the frictional forces inside the screw of the extruder.

In flat die extrusion or casting, the molten polymer coming out of the extruder, called extrudate is rapidly cooled to obtain a highly amorphous film with a highly random orientation with very good optical properties. Orientation along both machine (along the length of the film) and cross direction (along the width of the film) can be enhanced by varying the take up speed or by using a tentering frame. A tentering frame attaches itself to the edge of the film after it is extruded and moves apart in the machine direction thereby stretching the film and increases the crystallinity of the film.

In calendaring, the molten plastic is passed through a set of nip rollers and a series of heated rollers. Calendered films will have very good dimensional stability and better

gauge control. In the blown film process, the molten polymer is extruded through a circular ring die through which air can be blown in. A steady air pressure is maintained within the hot extrudate from the die exit till the collapsing tower. The film is blown in all directions while still molten, thereby achieving some limited orientation. The slow cooling in blown film will enable the film to achieve a considerable level of crystallinity and orientation in blown film compared to cast film [1]. Solution casting involves dissolving the resin in a suitable solvent and allowing the solution to dry out over a flat surface thereby removing all the solvent particles resulting in a film.

When two or more films are combined, the resulting structure is called a composite structure. If the composite structure is made by the application of heat and/ or adhesive it is called a laminate. Another way to achieve this is by extruding multiple layers together, resulting in a co-extruded structure [1]. Some widely used films include polyethylene, polypropylene, ethylene copolymers, polyvinyl chloride, polyester, polystyrene, polyamide (Nylon), cellophane, ionomer and polycarbonate.

2.2.5.1 Polyethylene

Polyethylene is the least expensive material available in packaging. It can vary in densities from 0.890 to 0.960 and can be classified as Low Density Polyethylene (LDPE), Linear Low Density Polyethylene (LLDPE) and High Density Polyethylene (HDPE). LDPE film has good moisture barrier properties and is odorless and tasteless when processed correctly, but its barrier to essential oils and flavor is only fair. The surface of LDPE film is non-polar and has to be subjected to surface treatments to make it

susceptible to inks coatings and adhesives [1]. Different methods of surface treatments are discussed later in this chapter. LDPE can be used for packaging fresh produce or in meat packaging, where a high oxygen transmission rate is desired. It can be combined with other films to increase the barrier properties thereby making it useful for other packaging applications. HDPE has a higher moisture barrier, better chemical resistance and enhanced strength. It is the stiffest and least clear in the PE family of films. HDPE is mainly used in packaging milk, breakfast cereal bags, crackers and other snack foods [1].

2.2.5.2 Polypropylene (PP)

Polypropylene is widely used in the field of packaging, both in amorphous (castPP) and oriented (OPP) forms.   PP has higher temperature resistance and also better water vapor barrier properties compared to PE. OPP can either be made by blown film (double bubble) process or by orienting the film on a tenter frame both giving similar physical properties like clarity, high tensile strength, better barrier properties, high tensile strength and adequate impact strength. PP becomes brittle at freezing temperatures, but orientation is proven to reduce this drawback [1]. PP also has a narrow heat seal range and hence close control of temperature is important on a packaging line. The film must be surface treated for oxidizing the surface to achieve printability and application of adhesives. Coefficient of friction can be lowered by the addition of slip additives. Heat seal range, slip and sparkle can be improved by coating the film with acrylic and other coatings. OPP can be metalized to improve the appearance and a thicker layer of metal will remarkably improve the barrier to moisture, light and gases [1]. Metallization is the process of

coating the surface of the film with a thin layer of metal. This process is done under vacuum.

2.2.5.3 Ethylene Copolymers

Ethylene acrylic acid (EAA) and ethylene methacrylic acid (EMAA) are used as sealant layer in composite structures to increase strength and sealability. Sealing is achieved when a thermoplastic material is heated above a certain temperature where the molecular chains flow and entangles. The seal is achieved when the material is cooled to room temperature. The temperature at which the molecular chains undergo this long range segmental motion is termed glass transition temperature, Tg. The heat seal range is always above the Tg of the polymer. Another copolymer, Ethylene vinyl alcohol (EVOH) can be used as a coextrusion or inside coatings to make a multilayer structure with improved barrier properties to moisture and gases. Ethylene vinyl acetate (EVA) is used in combination with other plastics to improve film-to-film adherence and heat sealability [1].

2.2.5.4 Polyvinyl Chloride (PVC)

PVC is widely used in the sheet form for thermoformed packages. Thermoforming involves heating the polymer above its Tg and forming it over a mold with application of air or vacuum. PVC is inherently a rigid plastic, but can be made into a soft pliable material in the flexible film form with the addition of certain chemicals called plasticizers. PVC is tough, resistant to oils and greases and has adequate barrier properties which make it ideal for packaging meat, poultry, fish and produce both as rigid

tray and low shrink films [1]. It is also widely used in pharmaceutical field to form blister packages.

2.2.5.5 Polyester (PET)

PET is a high performance film made from the reaction between terephthalic acid and ethylene glycol. This reaction is called a condensation reaction since the by-product is water. PET is a linear thermoplastic material. Although it is costly, it shows exceptional tensile strength, good impact strength, toughness, stiffness, dimensional stability, chemical resistance, clarity and some barrier properties. Orientation of the film can be done either by blown-bubble or tenter frame process thereby enhancing all of its properties [1, 4].

Heat treatments can be done on PET to improve the heat resistance. Heat resistance can be further increased by adding some nucleating agents to achieve a higher level of crystallinity.

2.3 Rationale for multilayer flexible packaging

Packaging materials can broadly be classified into monolayered materials and multilayered materials. Monolayered materials include films, foils and paper. Multilayers include coated substrates, coextrusions and laminates. The material for a particular product is chosen from a variety of conventional and new materials. When no single material can provide all the desired properties necessary to contain and protect a product, it is often important to incorporate a multilayer package. Disadvantages or shortcomings of one material can be overcome by the presence of the other material. Each layer in a

14

multilayer structure can provide one or more packaging functions. Some of the major functions include providing strength, printability, barrier and heat sealability [6].

There are several methods to produce a multilayer packaging material [1]. These methods can broadly be classified into co-extrusion, coatings and lamination. These are widely used processes in the flexible packaging industry. The decision whether to coat, laminate or co-extrude is made after considering factors like forms of coating and laminating materials, thickness requirements of the layers, formability of the structure- both before and after combining, specific property requirements like barrier to moisture and gases, sealing capability requirements and printing requirements [4]. For example, paper can be turned into a gas and moisture resistant material by laminating or coating with plastic films while retaining its stiffness and printability. Combinations of material can also provide an economical advantage compared to using monolayered structures [4].

Multilayered structures can be represented either graphically or verbally. In graphical representation, each line stands for a layer whereas in verbal, each layer is separated with a forward slash- the slash standing for the interface. A structure can also be defined in three levels- class, generic and specific [6].

Class: Film/Adhesive/Foil/Adhesive/Film

Generic: 48 PET/PU Adhesive/35Foil/PU Adhesive/3milLLDPE

Specific: 48 gauge LBT/2# Adcote 548/35gauge 1145-0 foil/2#Adcote 548/3 mil LL800 film

2.4   Multilayer Types

2.4.1   Co-extrusion

Blown-film and cast film extrusion dies can be designed to be fed from more than one extruder, thus producing a co-extrusion with multiple layers. One advantage of coextrusion is making possible the sandwiching of recycled material in between virgin polymer layers which can be of ecological and economical significance [2].

Coextrusion is usually cheaper compared to laminating since all the layers are joined together in a single step. The number of layers can range from 5 up to 10 or more depending on the design and function of the package. Each type of polymer is extruded from a separate extruder and the extrudates can be split further in the die to achieve the desired number of layers. The molten polymers are kept separate and are typically brought in contact in a feed block or just before the die exit. Blown films, cast films and extrusion coatings can be made through coextrusion. Either a feed block die or a multi-manifold die can be used. While extruding materials which do not stick to each other, (like HDPE and Nylon) thermoplastic adhesives called tie layers are often used as the intermediate layer [5].

Figure 2.1 shows a schematic of a coextrusion set up using three different extruders and a multi-manifold die. The extrudate is quenched on to a chilled steel roll and wound on a

winder.
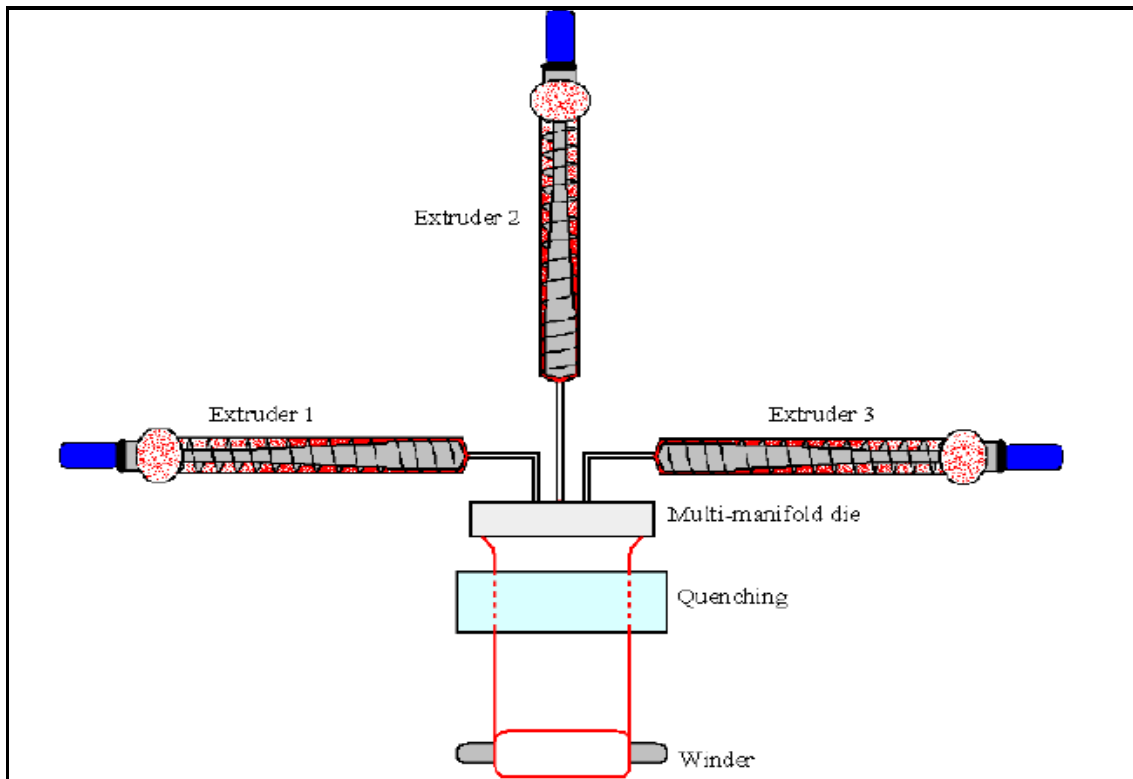
Figure 2.1: Schematic for Coextrusion (Source: Darby PKGSC 430)

2.4.2   Coatings

Coating can be defined as the process of applying one or more layers of a fluid or melt to another material thereby enhancing the performance of the coated material [4]. It is a common method to enhance the properties of a single packaging material. It can be applied to protect a film surface, to improve barrier properties or to offer heat sealability. Other benefits of coating range from providing waterproofing, dying and preservative functions or a combination of roles. In the past, wax was coated onto cereal boxes to preserve crispness. Coatings are preferred over lamination when the thickness

requirements are less than 0.3 mils due to the problems associated with the handling of such thin films [4]. With advancements in science and chemistry, newer chemicals became available as coating materials to improve a wide range of properties such as barrier to moisture and gases, resistance to oils and greases and heat sealability [1].

The amount of coating on surfaces can be stated in terms of coating weight. It is generally expressed in mass per unit area; for example pounds per square inch or grams per square meter according to English system and pounds per ream or pounds per 1000 square inches (MSI) in the U.S system. Coating can also be stated in terms of thickness on substrates with sufficient surface smoothness.

Depending on the form of coating material, the coating process can be classified as water soluble coating, organic soluble coating, emulsion coating, hot melt coating, extrusion coating and metal deposition. Water soluble coatings include coating of starches onto paperboard, ethyl cellulose to plastics and so on. Organic soluble resins like PVDC, nitrocellulose etc. can be applied to plastic films and papers. Polyolefins are extrusion coated onto paper, films and foils to increase its strength and toughness [4].

In cases where the coating is applied as a liquid, one of the most important properties in achieving an efficient coating is the viscosity of the coating liquid. Depending on the viscosity, coatings can be applied using a variety of coaters such as gravure, forward roll, reverse roll, Meyer rod, knife , air knife, extrusion and so on [1]. Two of the most common systems, gravure and extrusion coaters are shown in figure 2.2 and 2.3

respectively.
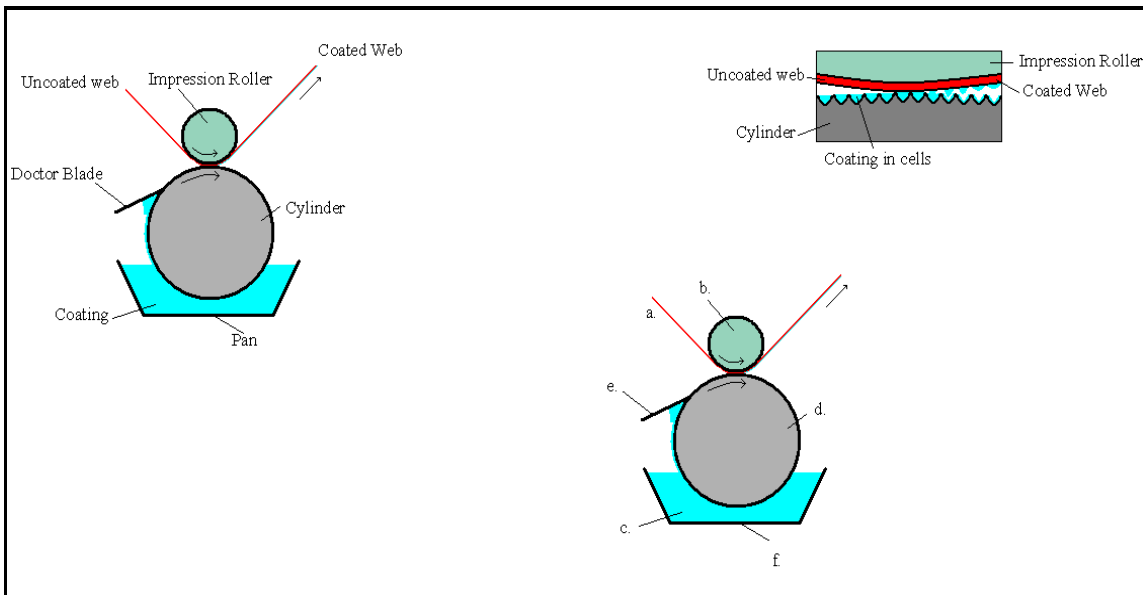
Figure 2.2: Gravure coater (Source: Darby, PKGSC 430)
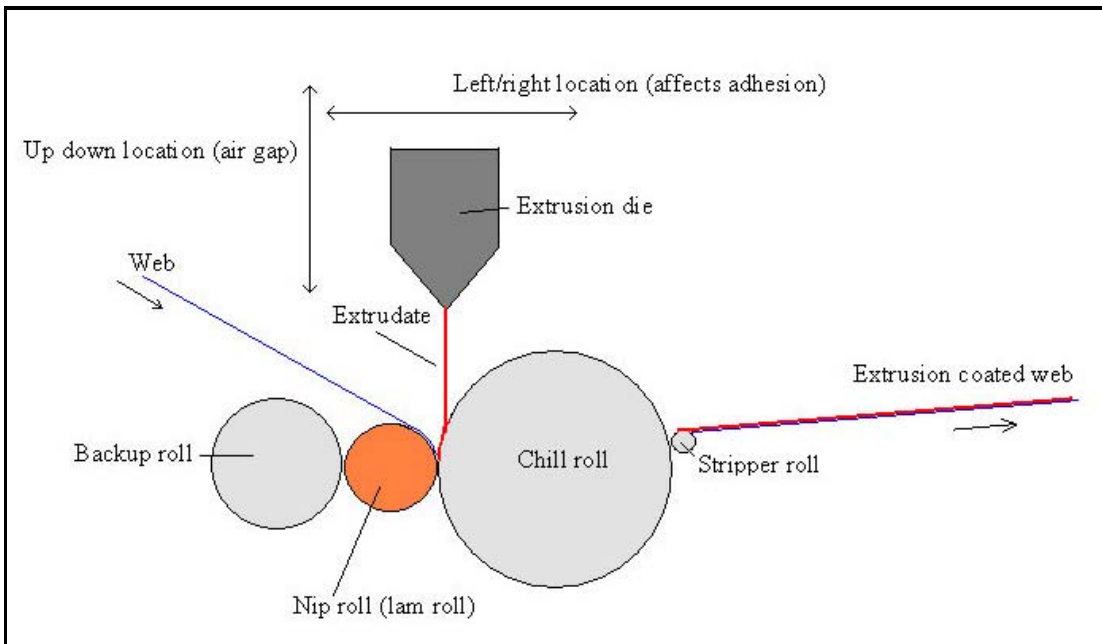
Figure 2.3: Extrusion coater (Source: Darby PKGSC 430)

2.4.3   Adhesion and Adhesives

Adhesion is the process by which two separate bodies (adherends or substrates) are held together, often by using a third material (called an adhesive) by intermolecular forces. The adhesive action can be achieved by heating the substrates and pressing them together as in heat sealing of thermoplastic materials [5].

An adhesive can be defined as a material than can hold two materials together by means of chemical bonds, intermolecular forces, including Van der Waals forces and hydrogen bonding or by physical entanglements [5]. Bond separation in adhesives can occur at different places across the cross section of a composite structure. Adhesive bonds act at the substrate-adhesive interface and cohesive bonds act within the adhesive holding it together. The strength of the entire structure will depend on both these forces [5].

The adhesive bond strength is affected by surface tension, solubility parameter and viscosity. These factors should be assessed in order to match up a particular adhesive to a set of substrates. In order to achieve good wettability, the critical surface tension of the substrate should be greater than the surface tension of the adhesive. The surface tension of the substrate can be increased by surface treatment techniques like corona discharge and plasma treatment or by applying a primer. The viscosity of the adhesive also plays a critical role in making good adhesive bonds. A low viscosity aids in spreading out the adhesive on the substrate evenly. Viscosity decreases with temperature and increases with molecular weight. Moreover, the solubility parameter of both the adherends and the adhesive should be similar for achieving desirable adhesive bond strength [5].

20

Cohesive bond strength relates to the strength within the adhesive and is attributed to the physical state and chemical nature of the adhesive material. Since performance of the adhesive depends on the adhesive bond strength, an adhesive system should preferably have an adhesive bond strength that exceeds or is equal to its cohesive bond strength. A higher molecular weight increases cohesive bond strength while decreasing the wettability. Hence a balance between these factors is necessary in obtaining a desired level of overall bond strength [5].

Adhesives can broadly be classified into natural and synthetic adhesives. They can also be differentiated by solvents used (organic solvent based or water based), applied temperature (hot melt) or whether the adhesive is reactive or not. Solvent based adhesives consist of a base polymer dissolved in an organic solvent with some additional ingredients. The strength of the adhesive is achieved as the solvent evaporates and the polymer chains in the adhesive crosslink together to act as a strong network. They are very common in the industry, but the main problem is with removing the solvent vapors due to the restrictions on emissions. Water based adhesives use water as the solvent. Hot melt adhesives are essentially molten polymers and achieve desired strength as it cools down and solidifies. They do not react chemically or emit harmful solvents. Examples are EVA, PE and atactic PP adhesives. Reactive adhesives are composed of low molecular weight polymers which on application will begin to polymerize, eventually achieving the desired bond strength values. Examples are polyurethanes and cyanoacrylate adhesives. These are versatile and can be used on a variety of substrates [5].

2.4.4 Surface treatments

In order to make the adhesives, coatings and inks stick onto or 'wet' the surface of the film, surface treatment may often be necessary. Wettability is achieved when the critical surface tension of the substrate surface is greater than the surface tension of the wetting liquid [1, 2]. Surface tension can be defined as the tendency of a liquid to decrease its surface area. Surface treatment increases the surface tension of the substrate. Surface treatments include flame treatment, plasma discharge, corona discharge and application of chemicals known as primers. Corona treatment is done at atmospheric pressure in air. A high voltage current is applied close to the surface of the substrate thereby oxidizing the surface [6]. If this is carried out in an inert gas atmosphere under vacuum, the process is called plasma treatment.

2.4.5 Lamination

Lamination can be defined as the process of bonding together two or more materials- usually films and foils. These materials are referred to as webs in a lamination line. A web of material can be defined as a long continuous material. Through lamination, it is possible to marry together the benefits of these webs and negate their drawbacks. The bonding is achieved by heating and drying the adhesive layer and with the application of pressure [4].

Bonding between the web and the adhesive is achieved either by chemical means with adhesives and curing agents or by using temperature alone. The mode of bonding can be chemical, mechanical or a combination of both.

2.4.5.1 Thermal lamination

In thermal lamination, a thermoplastic adhesive such as EVA, is first applied on to one of the webs and dried. Coating is not required if the material itself is thermoplastic. The webs are then heated and passed through two rollers pressing against each other called the lamination nip. The pressure at the lamination nip will give enough force to assure intimate contact required for bonding [4].

The temperature and other conditions for thermal lamination are governed by the composition and thermal properties of the webs to be joined and that of the adhesive. Plastic films and aluminum foil can be joined with heat seal coated film, paper or cellophane using this method [4].

2.4.5.2 Hot melt lamination

In hot melt lamination, the adhesive used is either molten wax or polymeric blends with wax. Molten adhesive is applied to one of the webs and then both the webs are passed through the lamination nip. The waxes provide some level of barrier to gases and moisture, but not to the extent of polyolefin adhesives. This method of lamination is usually used to join paper and glassine rather than plastics [4].

2.4.5.3 Extrusion lamination

This method of lamination uses a web of extruded polymer as the adhesive and the heat source. It is generally more economical than adhesive lamination. The system works well for porous substrates and for systems where the extrudate and laminated web are compatible. Only few of the polymers are compatible with each other and this limits the

usage of this method of lamination for many combinations. Nevertheless, extrusion lamination is commonly used throughout the converting industry.

Figure 2.4 shows the schematic representation of an extrusion lamination line. The steel roll in the lamination nip is large and is cooled to remove the heat from the extrudate after the materials have bonded.
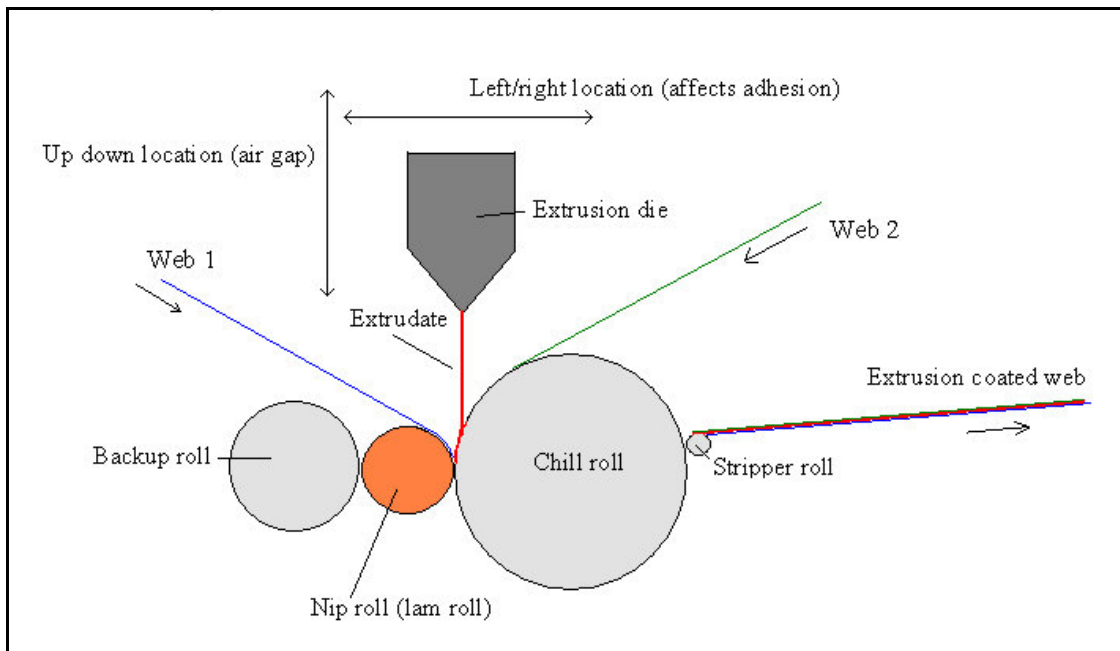
Figure 2.4: Extrusion Lamination (Source: Darby, PKGSC 430)

2.4.5.4 Wet bond and dry bond lamination

This classification in lamination is based on whether the applied adhesive is wet or dry at the time of joining both the webs involved. Commercial drying methods include convection drying, hot air impingement, infrared, conduction heating and radio frequency heating. In convection drying, the web is passed through a heated tunnel through which

heated air is passed either in same direction as the web or in the opposite direction. In impingement drying, the hot air is forced on to the web surface, enabling faster and more efficient drying. Infrared heating makes use of an infrared source to heat up the web and air is passed over the web to remove the volatiles. Conduction drying employs a heated surface onto which the web is brought in contact [4].

In wet bond lamination, one web must be porous enough to allow the evaporation and escape of the solvent from the adhesive. Thus, one web always features paper, paperboard or non-woven fibers and the other web is foil or any plastic film. The adhesive is applied onto the non porous web and combined with the porous web. This solvent can be an organic solvent or water and is allowed to evaporate through the porous web while passing through a drying tunnel [3][4].

Figure 2.5 shows a schematic of the wet bond lamination process. It can be seen that the primary substrate is coated with the adhesive and then the secondary substrate is brought in contact before passing the structure through the drying tunnel. The lamination nip follows after the drying tunnel.
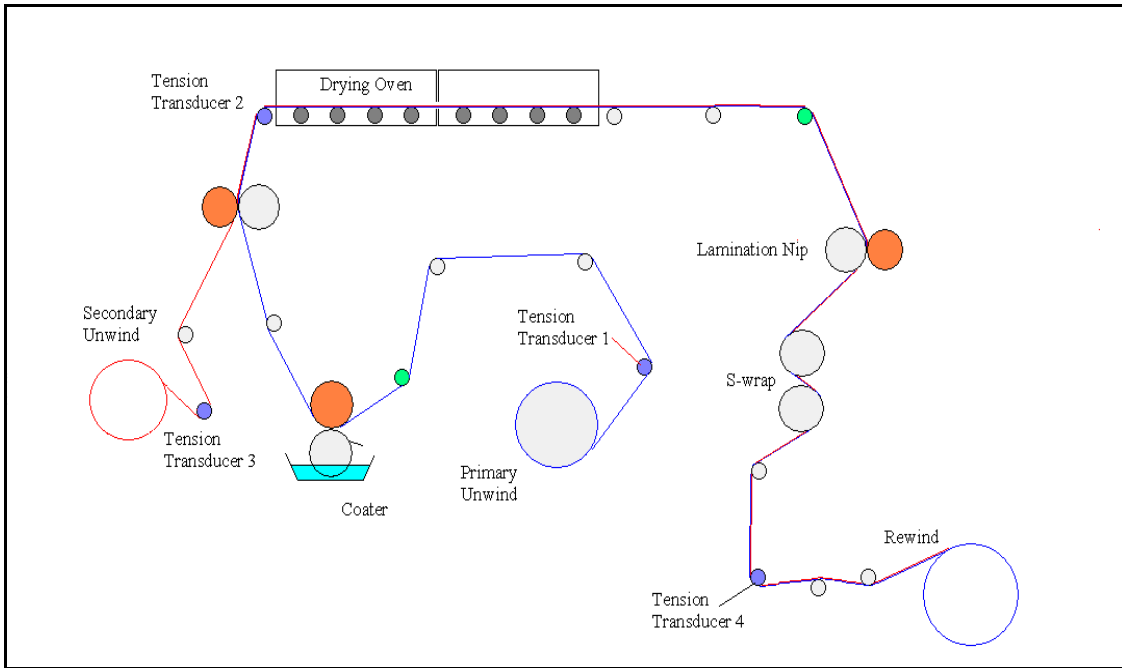
Figure 2.5: Wet bond laminator (Source: Darby, PKGSC 430)

In dry bond lamination, the solvent is dried before the webs are brought together. The adhesive is applied on to the primary web using any of the coating methods and the solvent is dried by passing the substrate through a drying tunnel. This is then brought in contact with the secondary web at the laminating nip and the structure is rewound and stored for curing of the adhesive. The curing process starts as soon as the adhesive is applied and can take up to 10 days for complete cure [3] [4].

Figure 2.6 shows the schematic for a dry bond lamination. Here, the primary substrate is coated with the adhesive and is dried by passing through a drying tunnel. The secondary substrate is brought in contact with the dried adhesive at the lamination nip and is rewound.

26
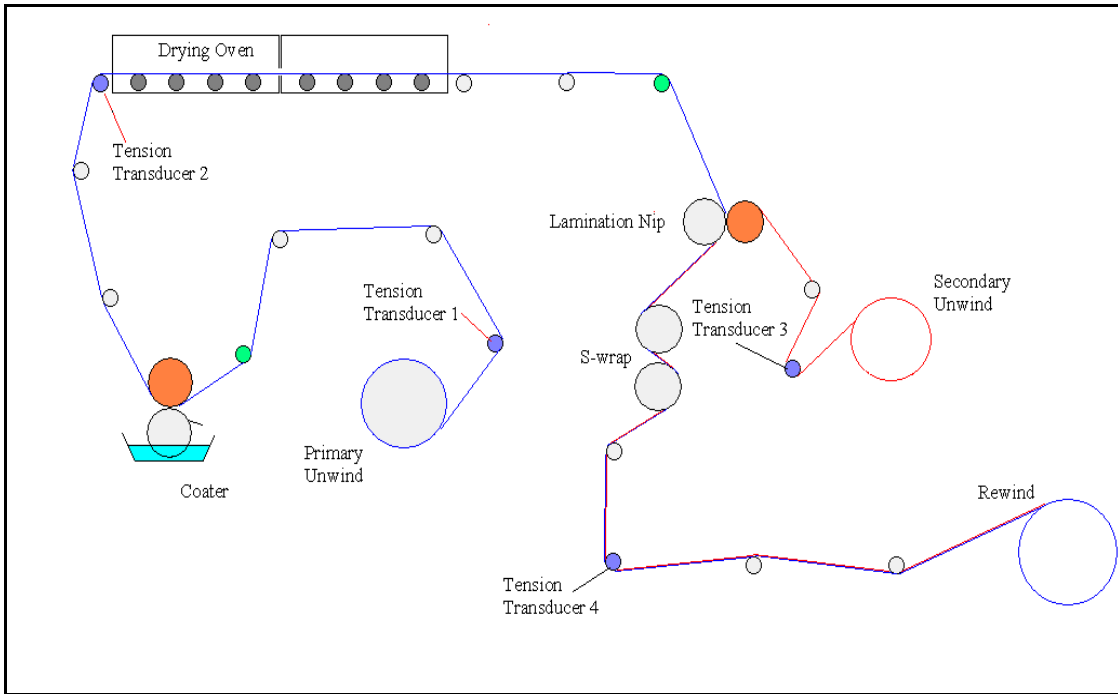
Figure 2.6: Dry bond laminator (Source: Darby, PKGSC 430)

2.4.5.5 Solventless lamination

Solventless or 100% solids lamination is the fastest growing adhesive laminating technique in the converting industry. This method of lamination does not use solvents and hence need not answer the issues of solvent handling or volatile organic compounds (VOCs) recovery. It is thus considered to be eco-friendly. Solventless lamination uses a reactive adhesive system. Additionally it offers lower capital cost and lower operating costs than solvent-based or water-based lamination. It can either be a single component or a two component system. The adhesive action is achieved when the components react and polymerize.

Figure 2.7 shows a schematic for solventless lamination. The adhesive is typically applied using three to five rollers. These rollers usually alternate between rubber and steel.
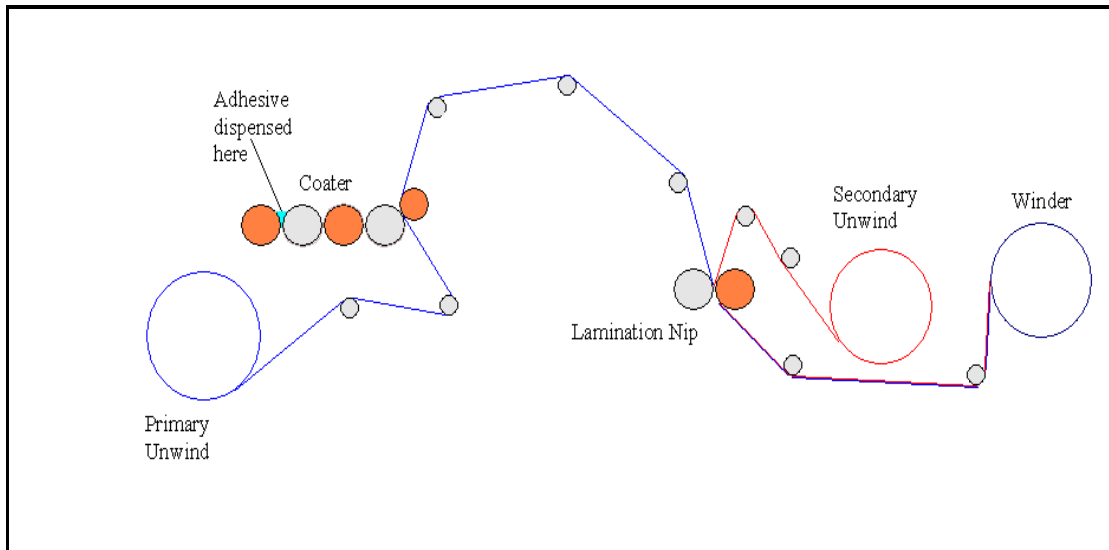
Figure 2.7: Solventless laminator (Source: Darby PKGSC 430)

2.5   Laminate Properties

2.5.1   Bond Strength

Bond strength is one of the main properties of a laminate structure. When the bond strength is measured right after the substrates are brought together, it is referred to as the off-machine bond strength, green strength or green tack. Bond strength after curing the adhesive completely is called cured strength. Bond strength can be measured on a Universal Testing Machine like Instron or SATEC using a proper load cell. Depending on the strength of the adhesive and adherend, there can be three modes of failure: Adhesive bond failure, cohesive bond failure and material destruction (Figure 2.8). Adhesive bond

failure happens at the adhesive-adherend interface when the adhesive bond strength is lower than the cohesive bond strength. In this mode of failure, the adhesive layer separates off and remains with one of the substrates. Cohesive bond failure happens when cohesive bond strength is lower than the adhesive bond strength. The adhesive layer splits in the middle and stays with both the substrates. The third type of bond failure is material destruction and occurs when the substrate strength is lower than both adhesive and cohesive bond strengths. In practice, one or more of these failure modes may occur in bond strength testing.
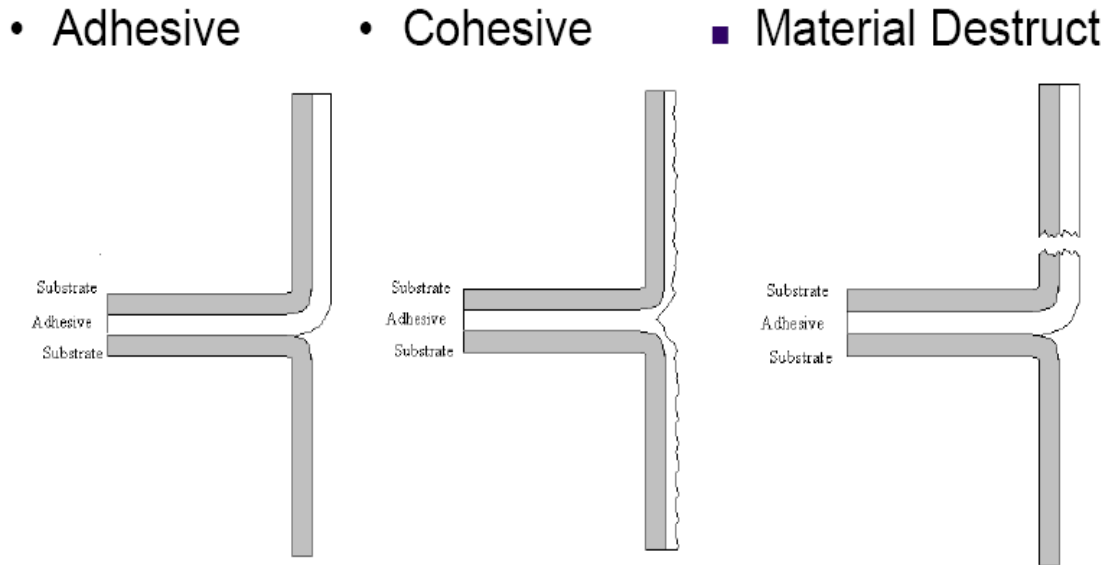
Figure 2.8: Bond failure mechanisms (Source: Darby, PKGSC 430)

2.5.2 Puncture Resistance

A high value for puncture resistance is important in flexible packaging. Puncture can be caused due to abrasion of the outer surface of the package during filling and forming operations or while shipping. It can also be caused by sharp objects like staple pins, nails, sharp corners or even the product itself. One instance where puncture can be caused by the product can be in packaging bone-in-meat packages.

Puncture resistance is basically a material property and it can be increased by using relatively tougher and stronger plastic films like nylon and polyester. A material is said to be "strong" if it has a high tensile strength and is said to be "tough" if the area under the stress- strain curve is large. However, the puncture mechanism in composite structures

can be quite complex. The weakest layer in the structure such as foil or paper can often decide the puncture mechanism [10].

Puncture resistance can be measured using a Universal Testing Machine like Instron® or SATEC® with appropriate puncture probe, load cell and data capture software. American Standards for Testing and Materials, ASTM specifies the testing procedure for puncture resistance in ASTM F 1306. This method is further explained in the following chapter. The selection of probe design can play a crucial role in the values obtained. The probe could be sharp, flat, beveled or with spherical tip design. It should be carefully selected to relate to the potential cause of damage [10].

2.6   <u>Relevant work</u>

There has been only a handful of research articles published in the field of Puncture testing of flexible laminates. One of the earliest reported works is by S. R Agarwal (1973). In this work, maximum force and energy required to puncture were measured on a variety of laminates and mono layered materials. The variation with respect to rate of puncture and the side from which puncture is tested were also studied and compared in this work. The maximum force required to puncture the laminates increased with the rate of testing up to 5 cm per minute, but further increase showed a decrease in values. It was also reported that the puncture resistance was dependent on the testing side [7].

In a later work, Agarwal et al (1974) reported the probe design greatly affects the puncture properties of a flexible laminate and asserted the need to standardize the

puncture testing method [8]. In this work, a flat ended cylindrical probe with 2mm diameter and a needle probe were used to puncture the laminates.

In a more recent work, Lange et al (2002) reported that the probe selection played an important role in deciding the puncture mechanism. According to this article, DIN and ASTM probes proved to develop premature cracks in the puncture area leading to erroneous results whereas a hemispherical probe with a rounded tip with 0.5mm radius gave the most reproducible results [10]. The rate of testing was also found to influence the results obtained. A testing rate of 1-1000mm per minute was found to be satisfactory. The specimen size or area of testing was not found to be a factor in deciding the puncture properties and it was observed that the puncture values were directly proportional to the test area.

The work done by Ian Wood (2005) titled "Manipulating the adhesive bond strength in flexible laminates" can be considered as the base work for this study. In his work, Wood observed coating weight to be the most promising variable in controlling the bond strength values in a flexible laminate with aluminum foil and PET. He also reported that when talc is used as an additive at 5, 10, 15 and 20 % loadings, it did not play any role in deciding cured bond strength. Temperature was found to be the least effective in controlling the adhesive bond strength values [13].

CHAPTER THREE

3.   MATERIALS AND METHODS

This section covers the materials and equipment used to conduct this research followed by the methods and procedures.

The materials are listed below in table 3.1

Substrates	1 mil Aluminum Foil 1145 alloy (Primary Substrate)
	Polyethylene Terephthalate (PET) film Hostaphan$^®$ 2600N from Mitsubishi
Adhesive Systems	Tycel$^®$ 7966/ 7287 from Liofol
	Adcote$^®$ 555/536B from Rohm and Haas
Additives	Talc from J.T. Baker CAS # 14807-96-6
	Polypropylene wax (PP wax)

Table 3.1: List of Materials

3.1 Materials

The substrates used for this work included 1 mil Aluminum foil supplied by All- Foils in Cleveland, OH as the primary substrate and Mitsubishi Hostaphan® 2600N polyester as the secondary substrate. This film is chemically primed on one surface enabling wetting with adhesive, coatings etc. It also has good slip and dimensional stability.

The basic properties of Hostaphan® 2600N film is given in table 3.2 below

Tensile Strength	32,000 psi
Tear Strength	20 g/ mil
Modulus	600,000 psi
Coefficient of friction	Static- 0.40 Kinetic- 0.37
Thickness	48ga

Table 3.2: Properties of Hostaphan® 2600N (Source: Product brochure www.m-petfilm.com)

3.2 Preparation of the Adhesive Mixture

Adhesive mixtures were prepared followed by application of the adhesive on to the primary substrate and making the laminate. Two adhesive systems, Tycel 7966/ 7287 from Liofol and Adcote 555/536B from Rohm and Haas were used. These adhesives can also be termed as "workhorse" adhesives since they are widely used in the industry. The adhesives were mixed according to the formulas provided in the product data sheets by the manufacturers. Both of the adhesives selected for this study were two part adhesive systems, consisting of a resin and a curing agent. Both these components are supplied in liquid form.

Talc and Polypropylene wax were used as additives and were introduced into the adhesive system to control the adhesive bond strength values. Talc was selected as it is an inorganic material and is used in the industry as an additive to reduce material costs. It can also interfere with the adhesive bonding mechanism by attaching itself to the polymer chains in the adhesive system. Polypropylene wax is a low molecular weight polymer and is an organic material, unlike talc. Untreated polypropylene is not compatible with polyurethane adhesives or PET. Hence by introducing PP wax into the adhesive system, the adhesive bond strength could be decreased.

Talc was purchased from J.T Baker (CAS # 14807-96-6). PP wax was purchased from Trauffer, a chemical manufacturer from Switzerland. PP wax and talc were added to the adhesive system at 5%, 10%, 15% and 20% of the total percent solids of the adhesive by weight. The product details of talc and PP was is given in table 3.3 below

Talc		PP wax	
Synonyms	Talc, Agalite, Snowgoose, Talcum	Synonyms	PP5 Microwax, Microcrystalline wax
Chemical formula	$H_2O.3Si.3/4Mg$	Chemical formula	$-CH_2-CH-CH_3$
Molecular weight	96.33	Molecular weight	Not available
Ingredients	Talc-99% Silica-up to 1%	Particle size	Not available

Table 3.3: Properties of Additives (Source: Product Information sheets)

Using a Dial O Gram 1600g Triple Beam Balance, the resin was first weighed into a container. This was then mixed with a weighed quantity of ethyl acetate (solvent). In the last step, the curing agent was added into this mixture under constant stirring. The initial

percent solids were around 75 and were brought down to 30 to 35% in order to make an efficient coating. These low percent solids were utilized to improve the ease of handling of the adhesive by lowering the viscosity. This aided in the wetting of the adhesive on the substrate surface and also in the spreading out of the adhesive making an even coating.

A quick and easy way to estimate the percent solids in an adhesive mixture is by using a Zahn 2 cup. A Zahn 2 cup is a cylindrical cup with a precisely drilled hole in the bottom. The time taken for the liquid to efflux out of the hole will give an idea about the viscosity and percent solids of the adhesive mixture. The percent solids in each adhesive mixture were further confirmed by measuring the wet and dried weights and calculating total solid percents for each mixture.

$$\text{Total percent solids} = (\text{dry weight}/\text{wet weight}) \times 100$$

The values for total percent solids are given in table 3.4 in the following page.

Adhesive	Additive and % loading	Percent Solids	Zahn 2 cup viscosity (seconds)
Adcote 555/ 536B	Pure Adhesive	33.51	17.64
	5% Talc	31.03	17.77
	10% Talc	34.60	18.16
	15% Talc	35.97	18.40
	20% Talc	36.49	19.09
	5% PP wax	34.95	17.99
	10% PP wax	35.40	18.55
	15% PP wax	36.23	18.88
	20% PP wax	36.86	19.70
Tycel 7966/ 7287	Pure Adhesive	32.54	17.50
	5% Talc	32.62	17.53
	10% Talc	34.69	17.76
	15% Talc	32.33	17.93
	20% Talc	36.02	18.09
	5% PP wax	33.21	17.91
	10% PP wax	34.60	18.25
	15% PP wax	33.75	18.73
	20% PP wax	34.28	19.43

Table 3.4: Percent solids and Zahn 2 cup efflux time results

After mixing, the adhesives were placed on a Corning PC-351 hotplate/ stirrer (stirring only) to keep the adhesive mixture consistent. The beaker was securely sealed to prevent any evaporation of the solvent which would cause an increase in the percent solids. The time delay between preparation and application of the adhesive was kept to a minimum

because the polymerization cross linking reaction takes place as soon as the curing agent is mixed with the resin.

3.3   Coating and Drying

Coating weight was controlled using Meyer Rods. Meyer Rods are wire wound metal rods designed to regulate the amount of adhesive applied. As the diameter of the wire increases, the gap between successive windings on the rod increases. These open spaces will perform both metering and application of the adhesive on to the substrate.
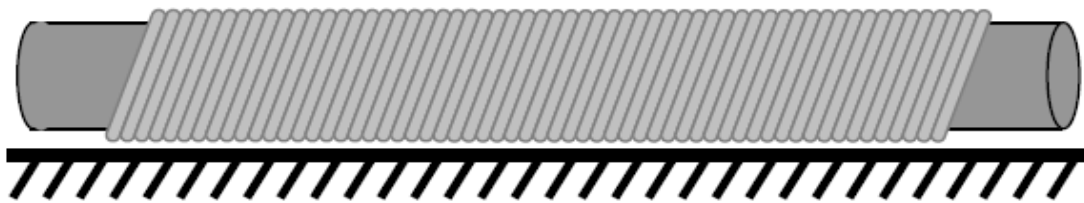
Figure 3.1: Meyer rod

The viscosity of the adhesive is dependent on the percent solids or in other words, the polymer chains and their molecular weight in the adhesive mixture. The percent solids and thus the viscosity of the adhesive mixture should be low enough to enable it to spread out across the surface of the substrate resulting in an even coating. It is thus important to control the percent solids in the adhesive mixture to around 30 to 35 percent. If the viscosity is too high, the adhesive will not spread out as desired.

The Meyer rods were mounted on a CSD Laboratory Drawdown Machine Model II (figure 3.2) from Consler Scientific. This drawdown machine has a steel shoe on to which the Meyer Rod is mounted and applies a constant weight on the substrate. This constant weight avoids the chance of variability in the coating weight from the operator applying different weights for different drawdowns. The adhesive was applied to aluminum foil using a "scoopula" in front of the rod. The rod was pulled manually, thus applying an even coating over the foil.

Figure 3.2: Drawdown machine CSD-II

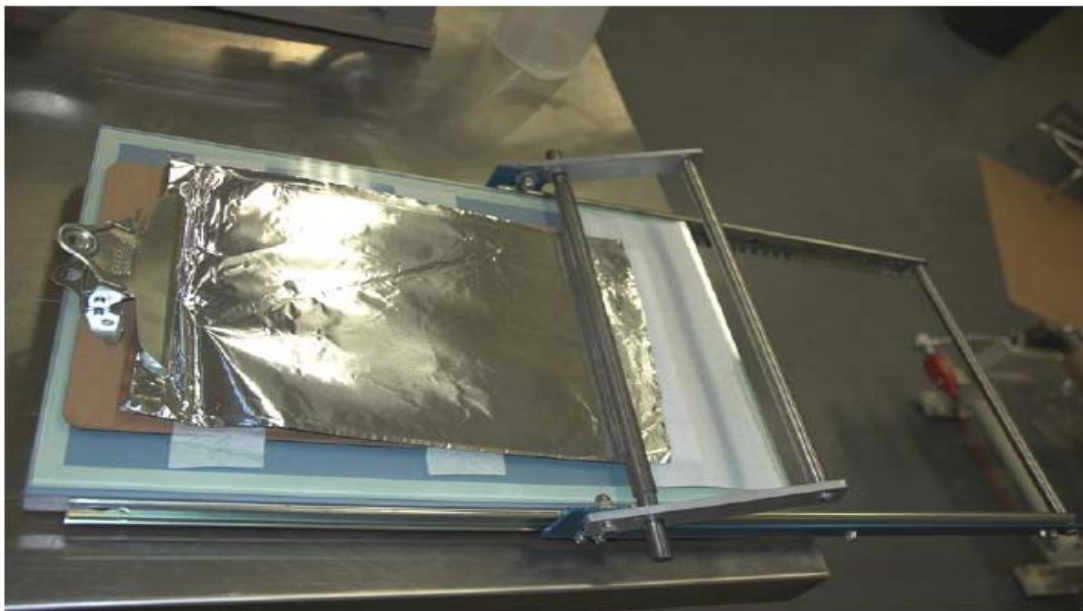After coating, the foil was placed in a BlueM Electric Company constant temperature cabinet at 70ºC for 30 seconds to dry. Samples were cut from the foil using a template to check for the adhesive coating weight. The adhesive coating weight is the weight of adhesive applied on to the substrate and is expressed in pounds per ream (lb/ream or

#/ream). It can be referred to as the coating weight or adhesive weight. The template dimensions were designed to make the conversion from grams to pounds per ream easy. The square sample cut using the template was first weighed using an analytical balance made by Denver Instruments. The adhesive was then wiped off using ethyl acetate. The sample was weighed again to obtain the coating weight.

3.4   Lamination and Curing

The treated side of the PET film was placed on the coated side of the foil and enclosed in between two sheets of release paper. This was then placed in a manila folder for support before passing through a Jackson Hirsch Card Guard Model 7200 Laminator. The temperature of the laminator was set at a constant value of 170º F. The variability in temperature control was checked and found to be +/- 10º F. In order to monitor the temperature of lamination, Cole Parmer irreversible temperature sensing strips were placed in between the foil and the PET sheets while passed through the laminator.

Control of the adhesive weight was accomplished by varying the size of the Meyer Rod used. An initial study where different Meyer rods numbered from 1 through 20 were used to coat the Aluminum foil. The coating weights were measured and it was noted that #6 rod gave a coating weight of 1.5 pounds per ream which can be considered as the industry standard in adhesive weight. Meyer rod #3 and #12 were also selected as these rods gave a coating weight around 1 pound per ream and above 2 pounds per ream respectively. The temperature at the interface between the adherends was measured by running Cole Parmer Irreversible Temperature Indicators through the laminator. The

indicators were placed in between the PET and the foil to get the actual temperature at the adhesive/ substrate interface.

3.5   Bond Strength and Puncture Testing

The Bond Strength of the laminate was measured using the procedure ASTM F 904-98 (2003)- Comparison of Bond Strength or Ply Adhesion of Similar Laminates Made from Flexible Materials. When the substrates are brought in contact with each other, a one inch wide strip of release paper was inserted so that an area of no bond could be achieved. This part of the laminate was placed in the grips while testing for bond strength. Each sample was placed in between the rubber padded grips of the SATEC T10000 testing machine. The pressure on the grips was controlled pneumatically so as to prevent any slippage. The strength of the adhesive bond was tested immediately after the lamination and after 10 days allowing complete cure of the laminate. Figure 3.3 below shows the testing assembly.
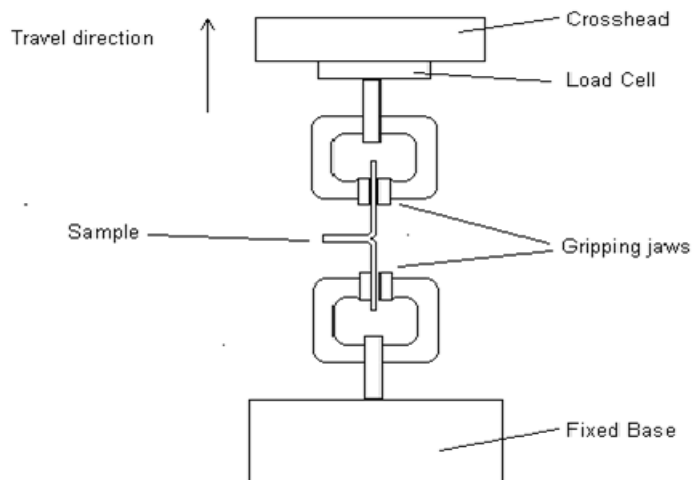

Figure 3.3: Schematic for Bond Strength testing (Source: Darby, PKGSC 430)

41

The SATEC machine was equipped with a 500 pound load cell. It was made sure that the bond strength fell within 20 to 80 percent of the full scale limit of the load cell. Bluehill™ (version 2) software was used to capture the data points and to analyze the results. The specimens were conditioned at 23+/- 2º C and 50+/- 5% RH. One inch wide samples were mounted with each substrate in opposite grips. The grips were pulled apart at a constant rate of 28cm/minute. The program was set to take data points 200 times every second and to report the maximum load and the average load to break.

The puncture resistance was measured using method ASTM F 1306- 90 (2002) Slow Rate Penetration Resistance of Flexible Barrier Films and Laminates. This test was done in a compressive mode on the SATEC T 10000 under standard conditions of temperature and humidity 23ºC and 55% RH. At least 5 samples were tested and the cross head speed was set at 25mm/minute.
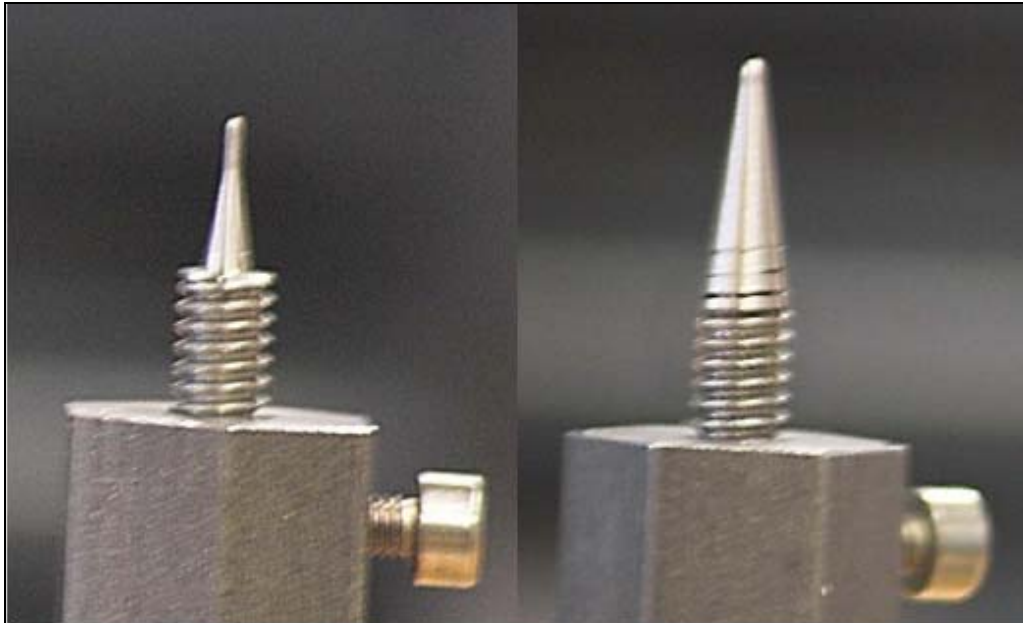
Figure 3.4: Hemispherical probe and ASTM Probe

The laminate sample was secured in the clamping mechanism shown in Figure 3.6. The rubber O-rings attached to the edge of the specimen holder prevented any slippage during the testing procedure. The samples were punctured from both sides- foil and PET to understand whether the testing side has any effect on the puncture properties. Two probes were used to puncture the samples, in order to compare the values and to determine how much of a role the probe design has on the puncture resistance values. One of the probes used was the ASTM specified probe and the second one was a probe with a hemispherical tip. Figure 3.4 shows the hemispherical and the ASTM probe respectively. The hemispherical probe was designed from Lange's work on puncture strength of different laminates [10]. The engineering drawings for these probes are given in figure 3.5 in the following page.
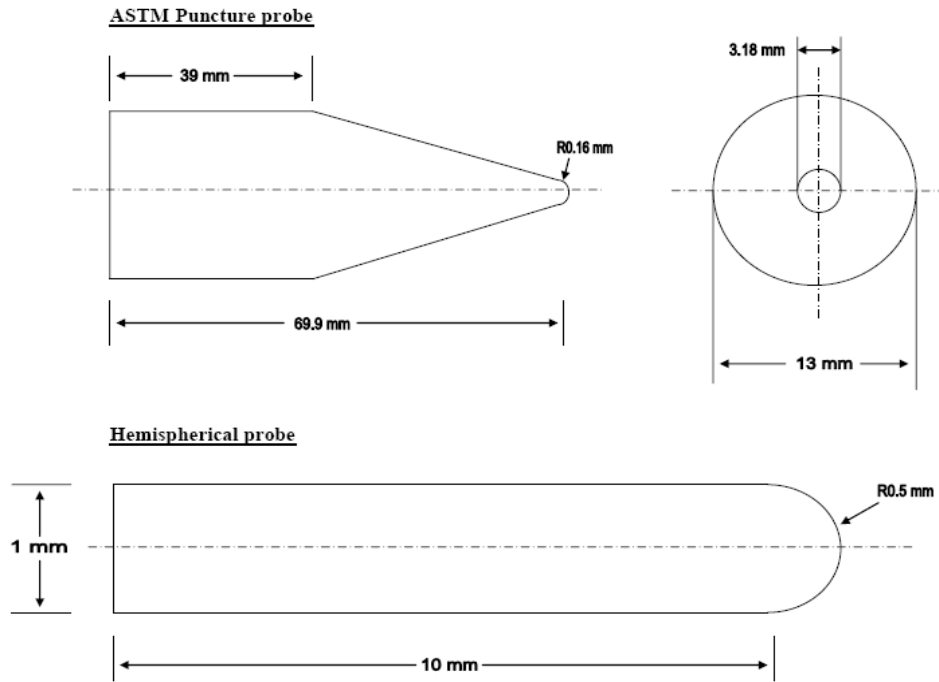
Figure 3.5: Engineering drawing of ASTM and hemispherical probes

The ASTM probe has a rounded tip of radius 0.16mm with a tapered stem. The hemispherical probe has a radius of 0.5mm at the tip and has a straight stem of diameter 1mm.

A puncture probe test speed of 25 mm per minute was used for all samples. A five pound load cell was used for this study. It was made sure that the load range to break was between 20 to 80% of the load cell capacity. The peak load and energy to break were noted.
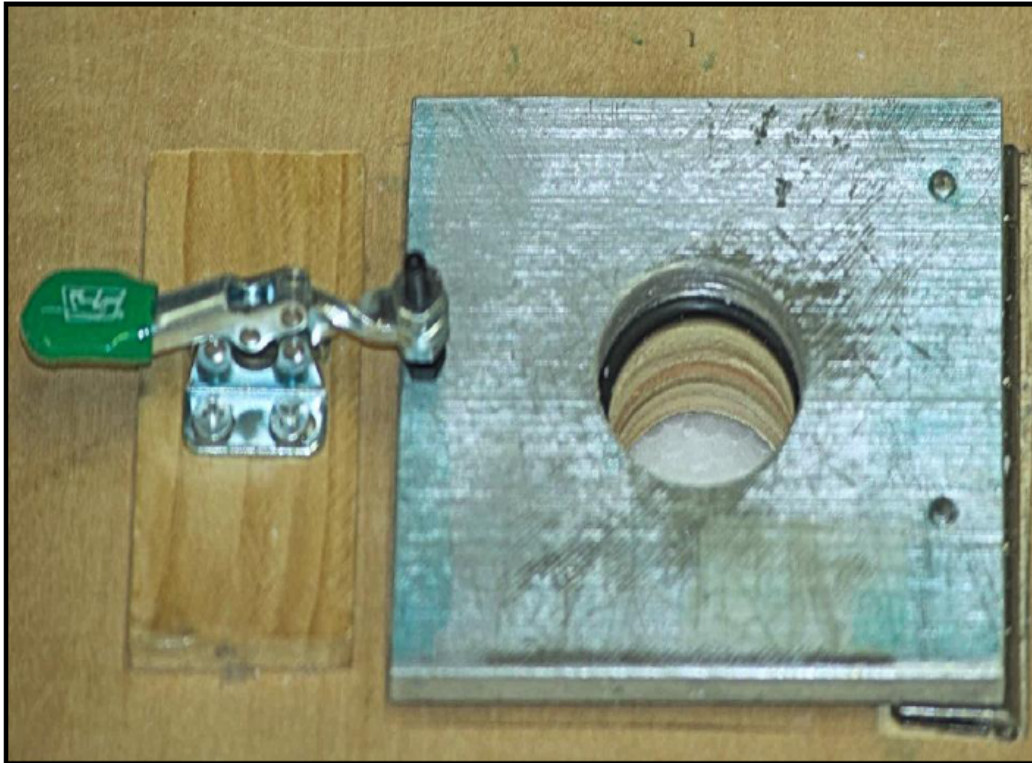
Figure 3.6: Specimen holder for puncture testing

3.6   Data Analysis

The bond strength and puncture resistance results were analyzed using SAS, a statistical data analysis software. The off-machine and cured bond strength data were analyzed to check if the interaction of the variables like additive type, percentage loading of the additive, adhesive type and coating weight had a significant effect on the bond strength values. Regression analyses were done on these results to see if the change in values followed any trend, whether quadratic or linear, with respect to the percentage loading of the additive.

The puncture data of the cured laminate were analyzed to check if there was any significant effect based on the variables mentioned above and also for regression. The regression analysis was done on time-based puncture results to check if the values showed a corresponding change with change in time of cure. In this case, all the samples were made using Tycel with 20% loading of talc and hence variability due to change in additive and adhesive was not of concern.

CHAPTER FOUR

4.   RESULTS AND DISCUSSION

4.1   Adhesive Coating Weight

The primary substrate, aluminum foil, was coated with the adhesive mixtures using different Meyer rods numbered 3, 6 and 12. Both the adhesives, Tycel™ and Adcote™, were loaded with talc and polypropylene wax at 0%, 5% 10%, 15% and 20% of total solids by weight. The coating weight was measured on three samples each and the average values were determined. The data is shown in Table 4.1 through Table 4.4

	Adcote with 0% PP wax	Adcote with 5% PP wax	Adcote with 10% PP wax	Adcote with 15% PP wax	Adcote with 20% PP wax
Meyer Rod 3	1.32	1.1	1.11	1.37	0.82
Meyer Rod 6	1.72	1.43	1.52	1.62	1.48
Meyer Rod 12	2.87	1.68	1.7	2.12	1.68

Table 4.1: Coating weight results for Adcote with Polypropylene wax

	Adcote with 0% Talc	Adcote with 5% Talc	Adcote with 10% Talc	Adcote with 15% Talc	Adcote with 20% Talc
Meyer Rod 3	1.32	0.86	0.67	0.65	0.7
Meyer Rod 6	1.72	1.3	1.15	1.05	1.25
Meyer Rod 12	2.87	2.45	2.67	2.6	2.8

Table 4.2: Coating weight results for Adcote with Talc

	Tycel with 0% PP wax	Tycel with 5% PP wax	Tycel with 10% PP wax	Tycel with 15% PP wax	Tycel with 20% PP wax
Meyer Rod 3	1.13	0.88	1.05	1.02	1.38
Meyer Rod 6	1.78	1.23	2	2.3	2.64
Meyer Rod 12	2.08	3.02	3.78	4.21	4.6

Table 4.3: Coating weight results for Tycel with Polypropylene wax

	Tycel with 0% Talc	Tycel with 5% Talc	Tycel with 10% Talc	Tycel with 15% Talc	Tycel with 20% Talc
Meyer Rod 3	1.13	1.2	0.65	0.73	0.58
Meyer Rod 6	1.78	1.77	1.25	1.48	1.38
Meyer Rod 12	2.08	3.01	2.63	3.61	3.65

Table 4.4: Coating weight results for Adcote with Polypropylene wax

It can be seen from the data that the coating weight increased from Meyer rod #3 through #12. As expected, a thicker coating of adhesive is applied onto the substrate when a Meyer rod with higher number is used. The purpose of applying variable coating weight was to see if the bond strength and puncture strength are affected as the adhesive coating weight is increased.

The increase in coating weight with increasing percentage loading of the additive was not consistent. The coating weight is governed by a combination of various factors. These include density, viscosity, flow etc. of the adhesive mixture. The Meyer rod actually controls only the volume of coating. The density of the adhesive mixture is dependent on the individual densities of the additives as well as the resin and the curing agent. So if the

additive density is too high or too low compared to the density of pure adhesive components, the coating weight will increase with increasing percentage loading of the additive. The reverse is true if the density of the additive is very small compared to that of the pure adhesive. A higher density of the adhesive mixture will also increase its viscosity. This affects the flow properties of the adhesive and it will be difficult to get an even coating on the surface of the substrate.

The bond strength and puncture resistance values for off machine, cured and the time based study are discussed in the following sections of this chapter.

4.2 Bond Strength

The off-machine or "green" bond strengths were measured immediately after both substrates were brought in contact with each other and laminated together. The laminated structures were stored for 10 days at room temperature and relative humidity (75ºF and 50 +/- 5% RH) to achieve complete cure. Bond strengths were measured on these cured samples. The results are shown from Chart 4.1 through Chart 4.8. The terms MR and PP wax in the chart, stand for Meyer rod and polypropylene wax respectively.
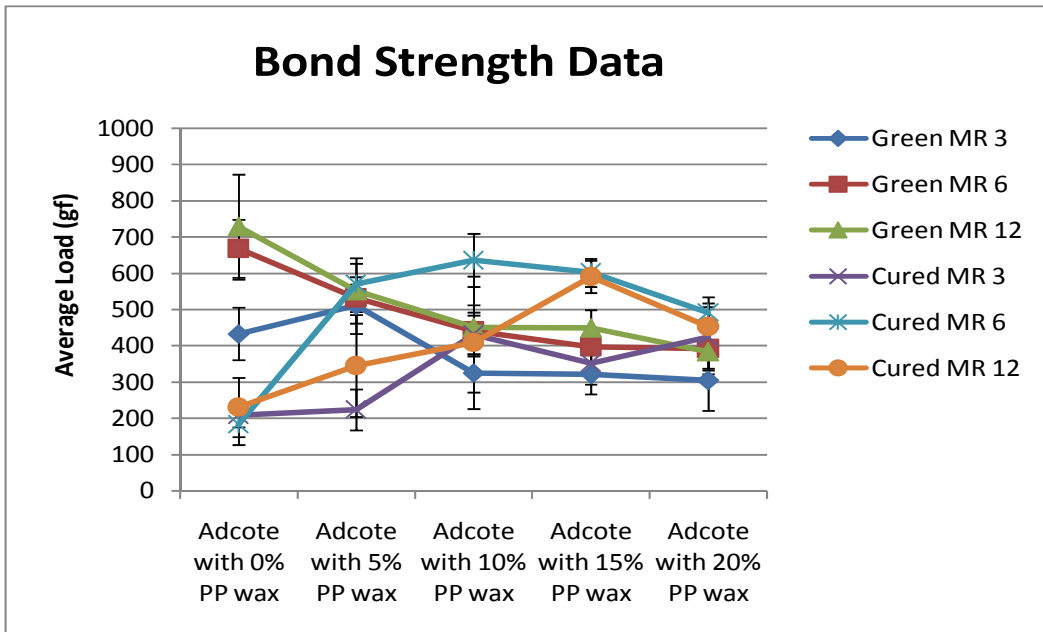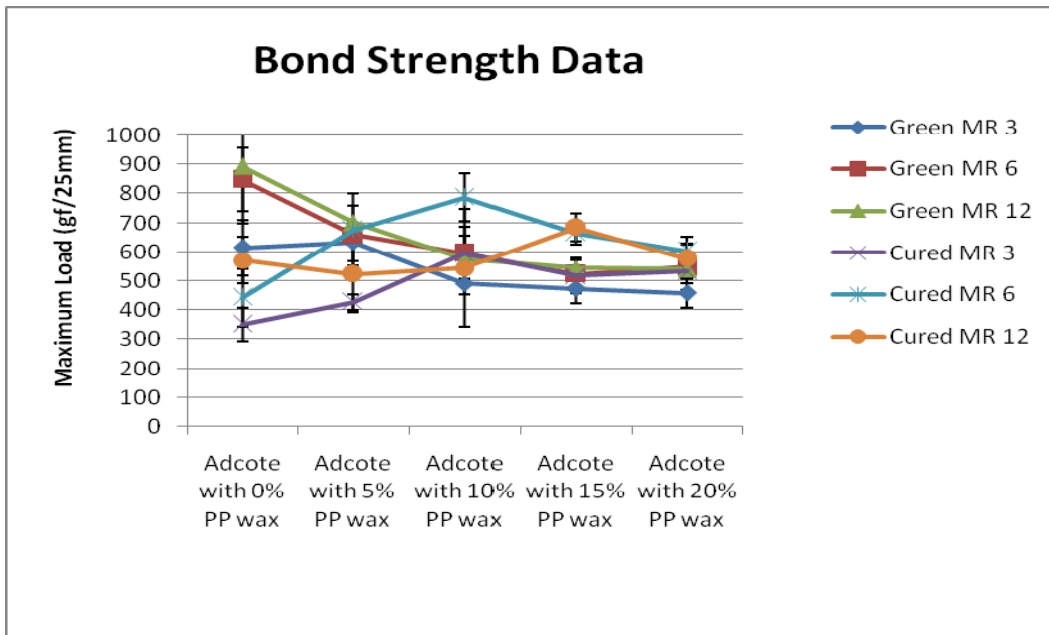
Chart 4.1: Average load (g$_f$) of Adcote Vs % PP wax
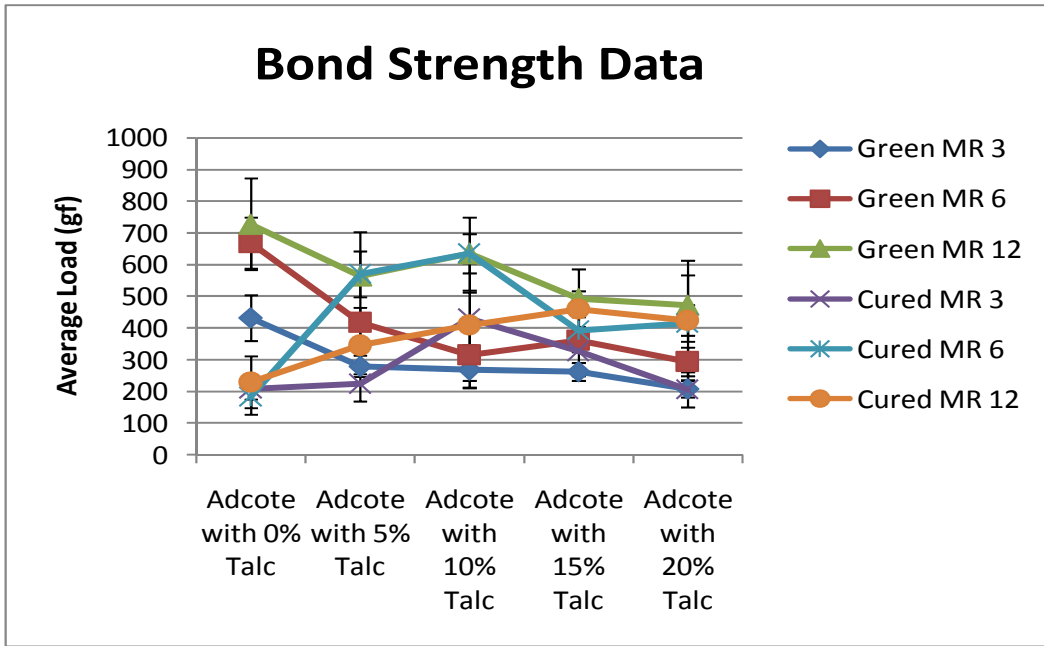

Chart 4.2: Maximum load (g$_f$ /25mm) of Adcote Vs % PP wax

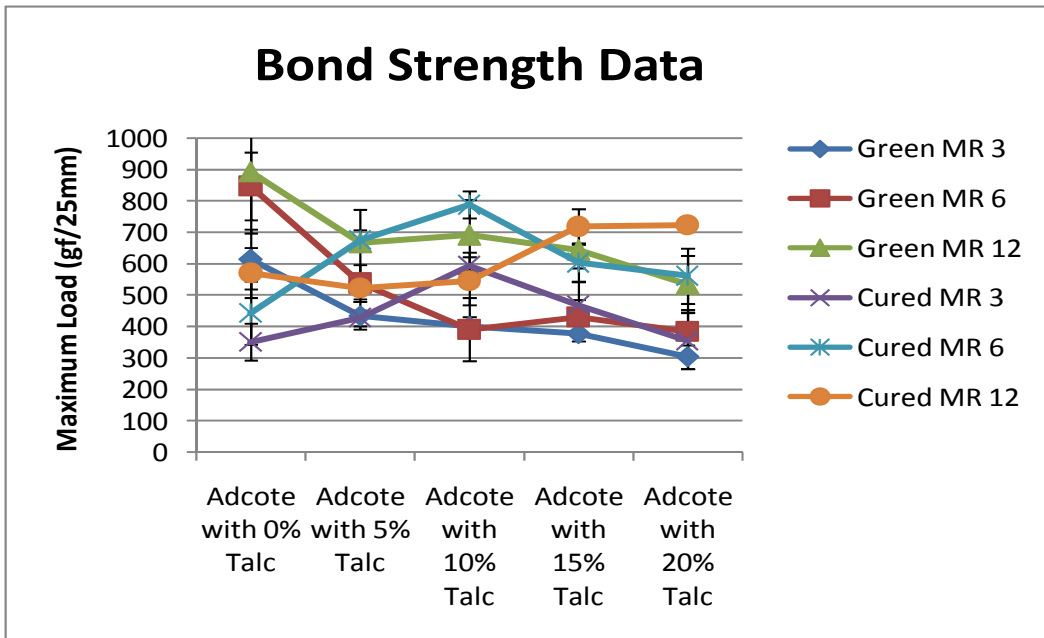**Chart 4.3: Average load (g$_f$) of Adcote Vs % Talc**

Chart 4.4: Maximum load (g$_f$ /mm) of Adcote Vs % Talc
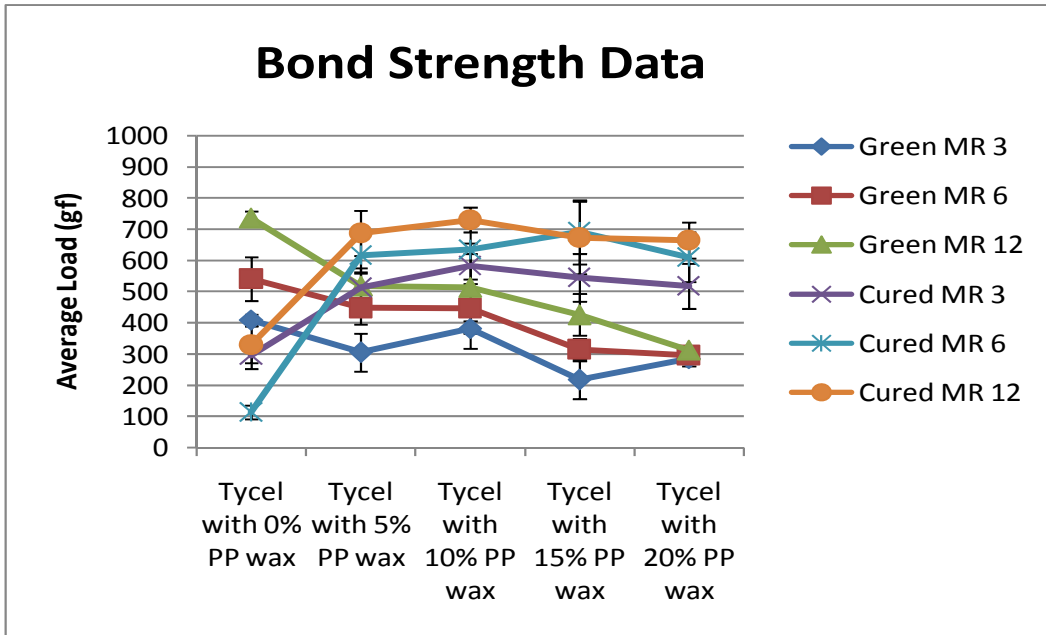
Chart 4.5: Average Load (g$_f$) of Tycel Vs % PP wax
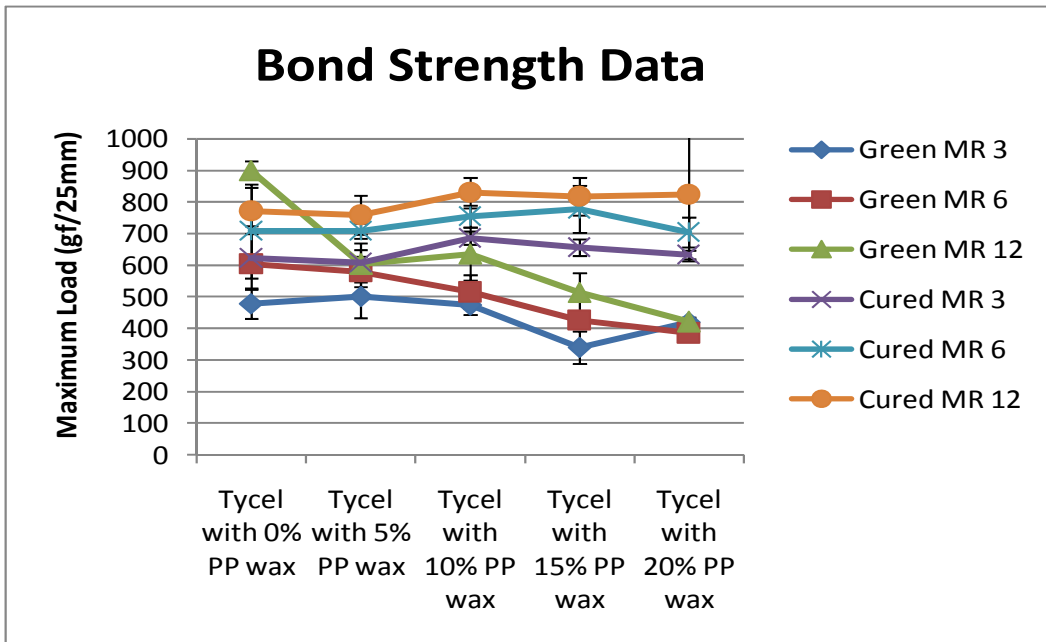

Chart 4.6: Maximum Load (g$_f$ /25mm) of Tycel Vs % PP wax
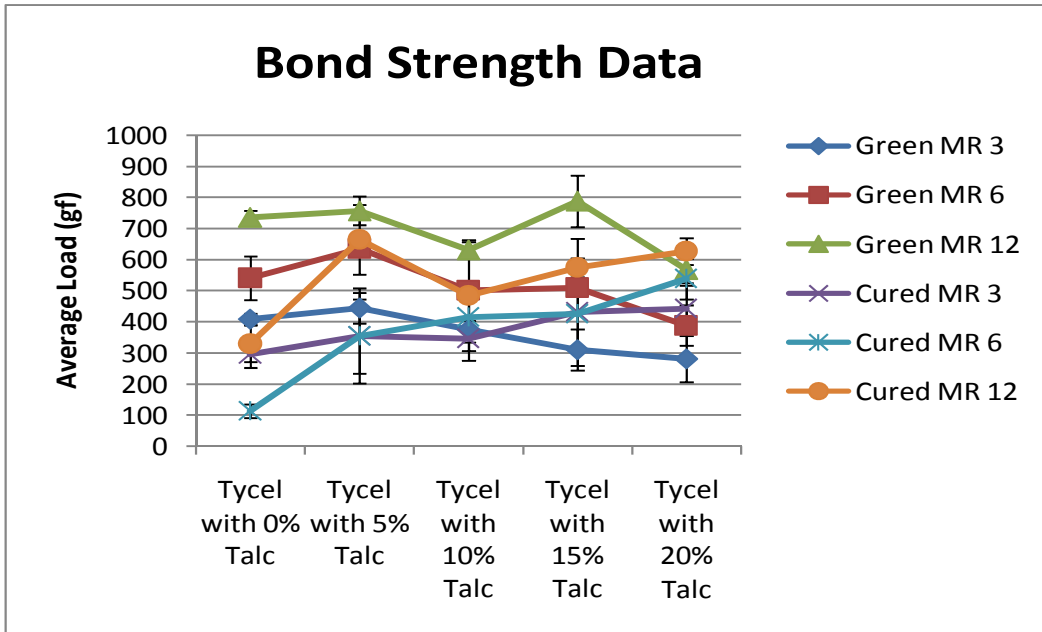
Chart 4.7: Average Load (g_f) of Tycel Vs % Talc
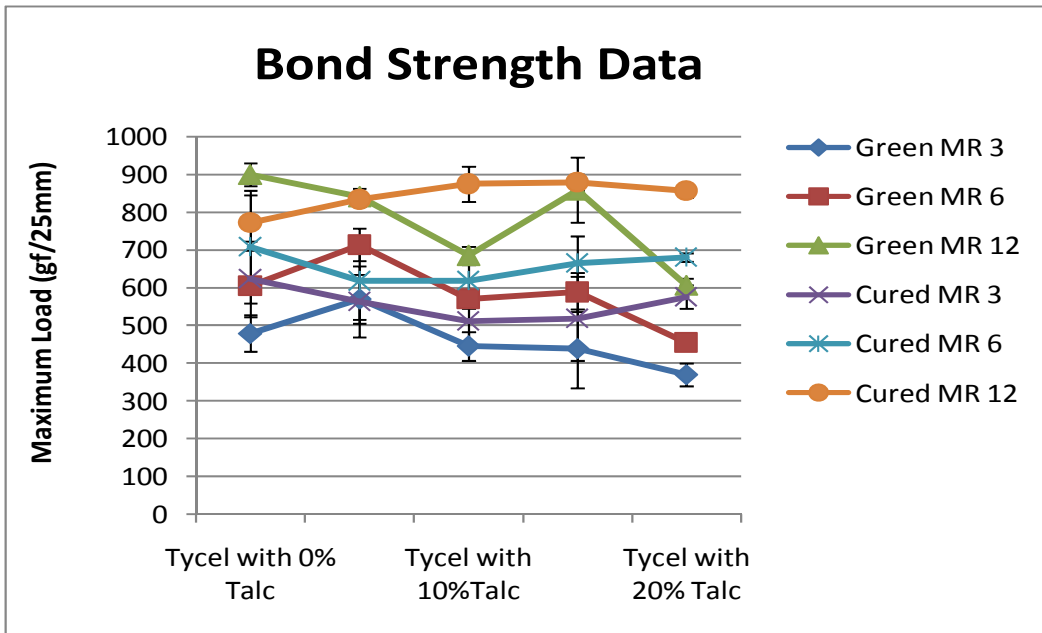

Chart 4.8: Maximum Load (g_f /25mm) of Tycel Vs % Talc

From the data for bond strength values, it can be seen that in most cases for the off-machine bond strength, the increasing Meyer rod number, thus increasing coating weight, gave increasing values. But the trend is erratic and statistic analyses were used to make sure if there is any significant effect on bond strength due to any of the variables like coating weight, percent additive, type of additive and adhesive. For cured bond strengths, the pattern is even more complex. The main problem associated with testing for cured bond strengths was material destruction. The PET film tore off before the adhesive failed. This was predominant with low percentage loading of the additives. With increasing percentage of additive, for both Talc and PP wax, there was no material destruction and the mode of failure was cohesive. This means the cohesive bond strength of the adhesive was lower than the material strength as well as the adhesive bond strength causing the structure to fail within the adhesive layer.

Regression models of first and second order (linear and quadratic) were fitted with the bond strength curves using SAS™ program. The coefficients of the regression equation and the R-square values are obtained and are reported. The maximum value of R-square is 100 which correspond to a perfect fit. The term 'p' stands for percent loading of the additive. By plugging in values for p in the regression equation, we can obtain the expected value for the bond strength. The results are given in Appendix A through C. Appendix A shows the regression results for green bond strength with respect to the percentage loading of additives for different coating weights and adhesive system. Both average and maximum load curves for off-machine bond strength showed a decent fit (R-square value 0.50 or more) with a quadratic regression model. For cured bond strengths,

regression analyses were done avoiding all the samples which showed material break. The results for cured bond strength are given in Appendix B (with material break) and in Appendix C (without material break). The quadratic increase in values with increasing percentage of additives is absent while samples which gave a cohesive failure were analyzed. In this case, for average load, the R-square values were small to confirm any effect in the percentage loading of the additive. The quadratic term did not improve the R-square value. However, for Tycel, high R-square values were obtained with a quadratic model for maximum load and it can be said that for Tycel, the maximum load decreases quadratically with increasing percentage loading of the additive. The type of additive used, whether talc or PP wax was not found to affect the bond strength values at these high loading percentages.

Variables	Affects Off-machine Bond Strength	Afects Cure Bond Strength
Additive Type	No	No
Additive Percentage	Yes	No
Adhesive Type	No	No
Adhesive weight	No	No

Table 4.5: Regression Analysis Summary on Bond Strength

Table 4.5 gives a summary on the regression results for the effect of all the variables on the off-machine and cured bond strength values.

4.3   Puncture Strength

The puncture results are presented in Plot 4.9 through 4.40. The comparisons were made between probe design, direction of testing-as to which side makes contact with the probe first. The hemispherical probe gave values (charts 4.25 to 4.40) lower than those obtained (charts 4.9 to 4.24) with the ASTM probe due to the difference in the probe design. The energy at break values showed a greater dependence on the probe design compared to the load. In most cases, the energy at break values were found to be up to 50% lower for hemispherical probe compared to ASTM probe. However, the hemispherical probe values showed a very narrow spread in values with a small standard deviation. The load to break values showed a 20 to 25% decrease in values between ASTM and hemispherical probes. The hemispherical probe has a rounded tip of radius 0.5mm with a straight stem, whereas the ASTM probe has a rounded tip of radius 0.16mm with tapered stem. The tapered portion of the probe comes in contact with the material during penetration thereby increasing the area of impact considerably. The tip diameter is also larger in the case of ASTM probe.

The direction of testing also was found to affect the puncture values to a great extent. When the laminates were punctured from the PET side, the energy to break and load at break values were found to be lower than those achieved while the samples were punctured from the foil side using ASTM probe. The differences in values were not significant for the hemispherical probe depending on the direction of testing due to its smaller impact area and design features.

Regression analyses were done on the puncture data to statistically determine if any trend in change of values can be established. The results are provided in Appendix D through Appendix K. Both linear and quadratic regression models gave considerably low R-square values for load to break as well as energy to break. This proves a lack of change in puncture values with increasing percentage loading of the additive. The addition of a quadratic term into the linear regression model did not improve the R-square values. This gives enough evidence to confirm that the puncture strength is not dependent on any of the variables used for this study.
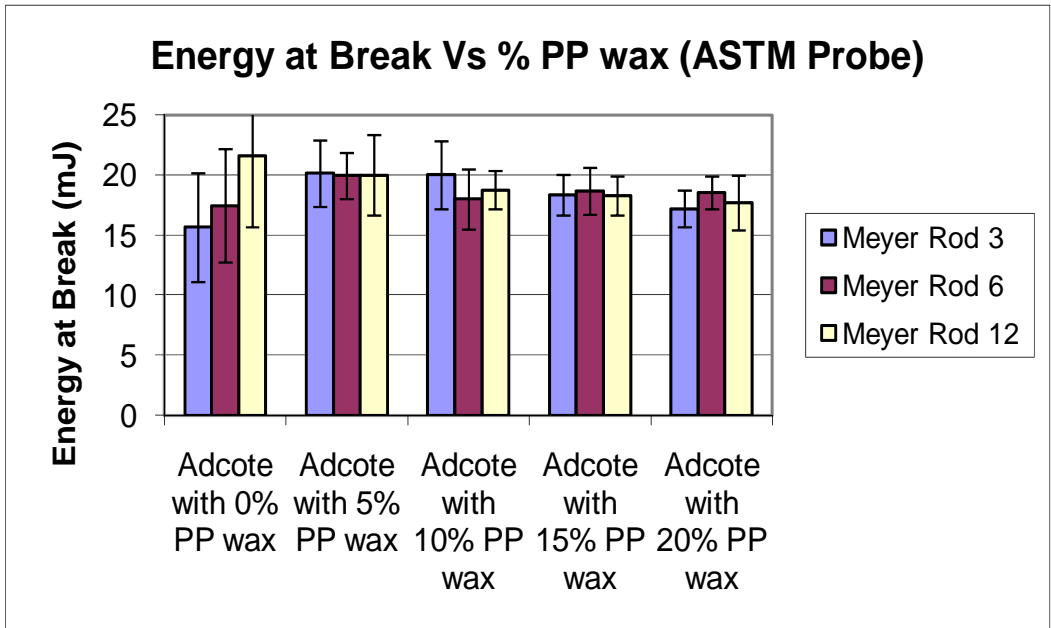
Energy at Break Vs % PP wax (ASTM Probe)

Chart 4.9: Puncture Strength- Energy Vs percent loading with Polypropylene wax- Foil side up ASTM probe

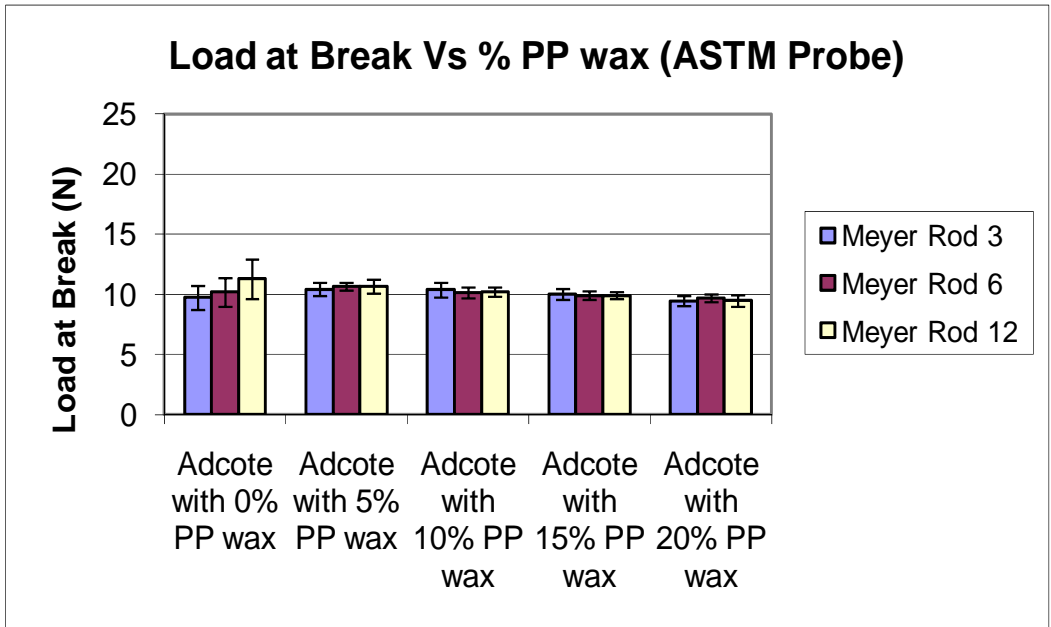**Load at Break Vs % PP wax (ASTM Probe)**

Chart 4.10: Puncture Strength- Load Vs percent loading of Polypropylene wax- Foil side up (ASTM probe)

Chart 4.11: Puncture Strength- Energy Vs percent loading of Talc- Foil side up (ASTM probe)

Chart 4.12: Puncture Strength- Load Vs percent loading of Talc- Foil up (ASTM probe)

Chart 4.13: Puncture Strength- Energy Vs percent loading of PP wax- Foil up (ASTM probe)

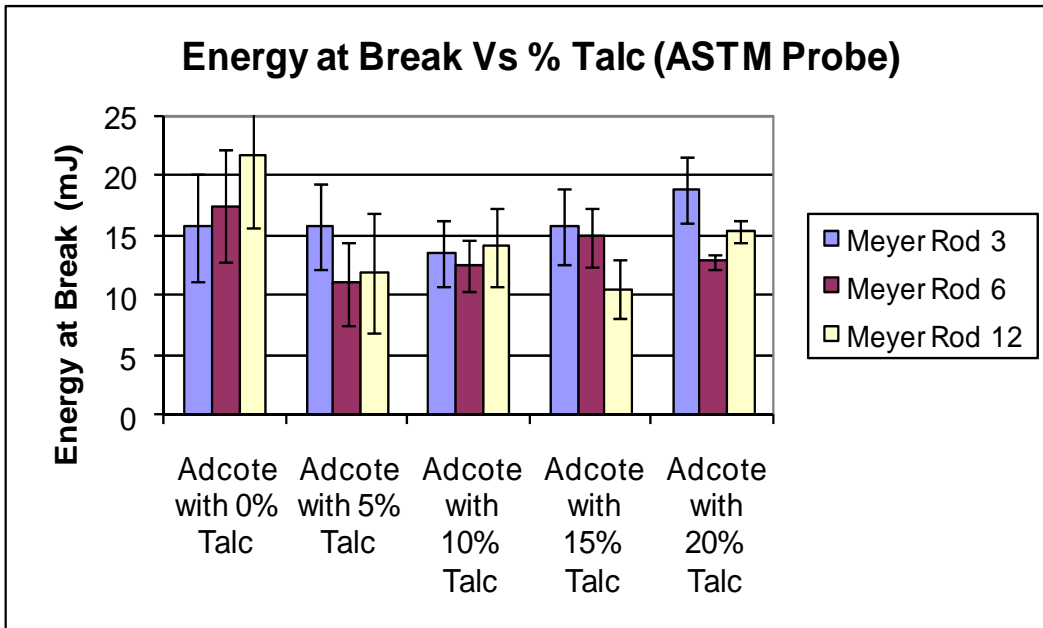**Chart 4.14: Puncture Strength- Load Vs percent loading of PP wax- Foil up (ASTM probe)**

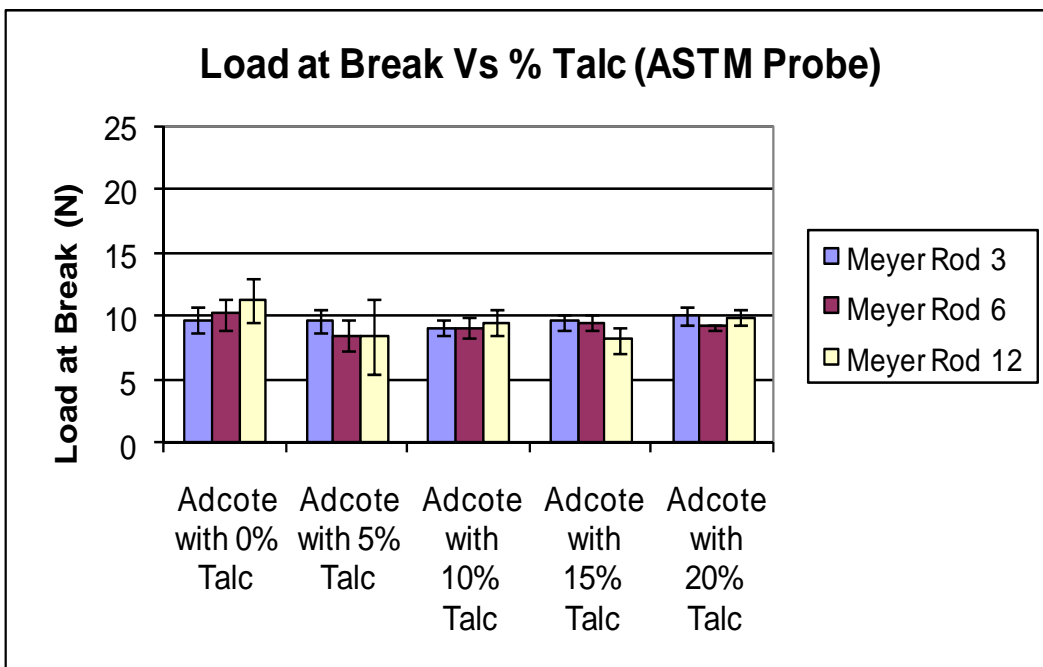**Chart 4.15: Puncture Strength- Energy Vs percent loading of Talc- Foil up (ASTM probe)**

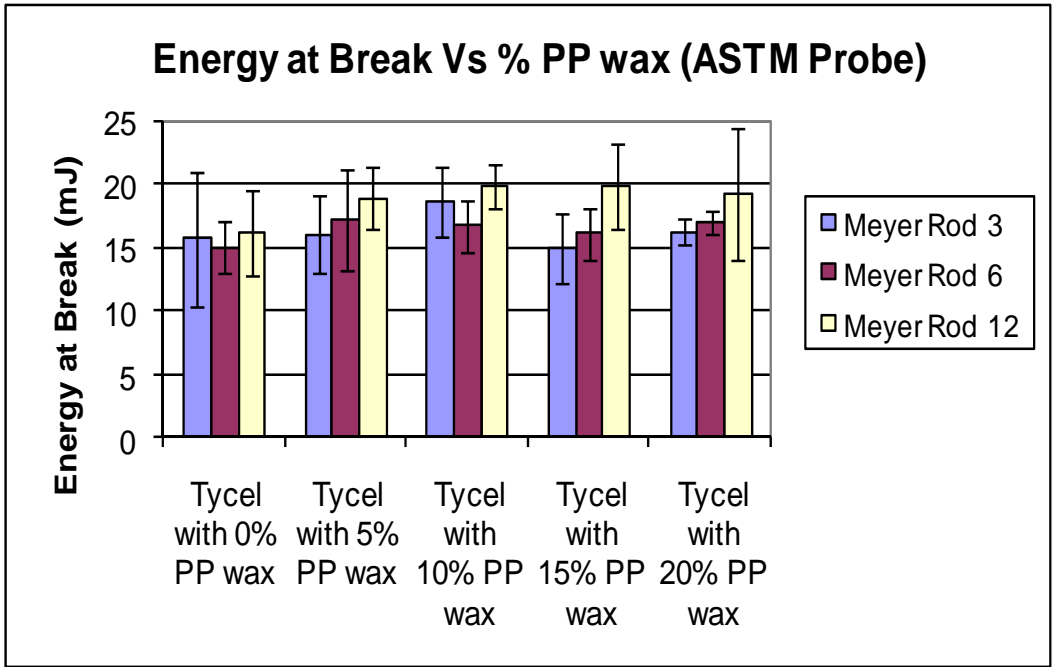**Chart 4.16: Puncture Strength- Load Vs percent loading of Talc- Foil up (ASTM probe)**

Chart 4.17: Puncture Strength- Energy Vs percent loading of PP wax- PET up (ASTM probe)
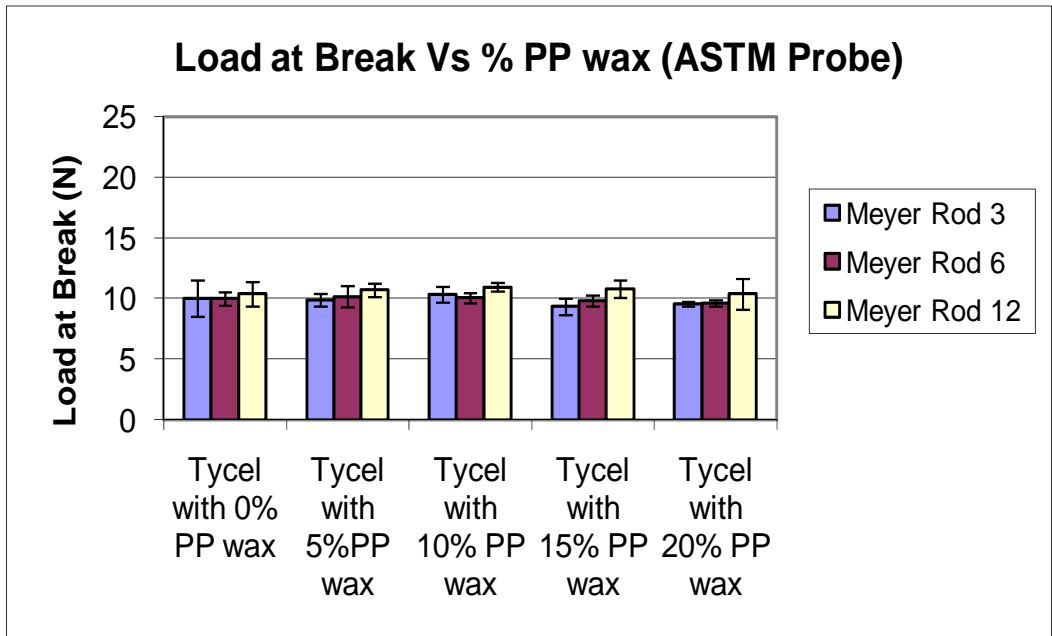

Chart 4.18: Puncture Strength- Load Vs percent loading of PP wax- PET up (ASTM probe)

Chart 4.19: Puncture Strength- Energy Vs percent loading of Talc- PET up (ASTM probe)

Chart 4.20: Puncture Strength- Load Vs percent loading of Talc- PET side up (ASTM probe)

Chart 4.21: Puncture Strength- Energy Vs percent loading of PP wax- PET up (ASTM probe)

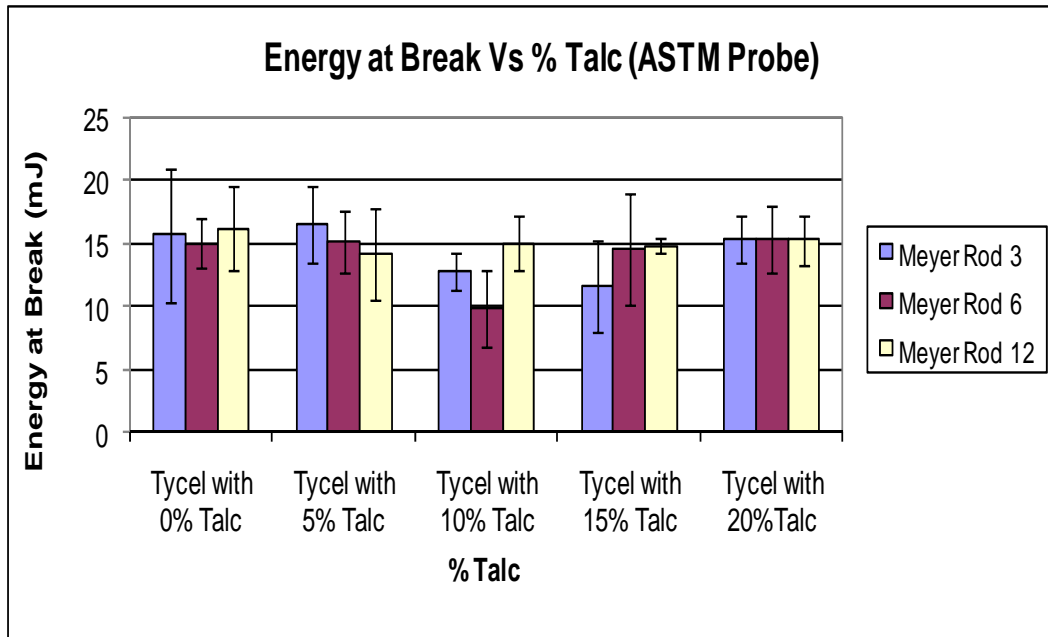Chart 4.22: Puncture Strength- Load Vs percent loading of PP wax- PET up (ASTM probe)

64

Chart 4.23: Puncture Strength- Energy Vs percent loading of Talc- PET up (ASTM probe)
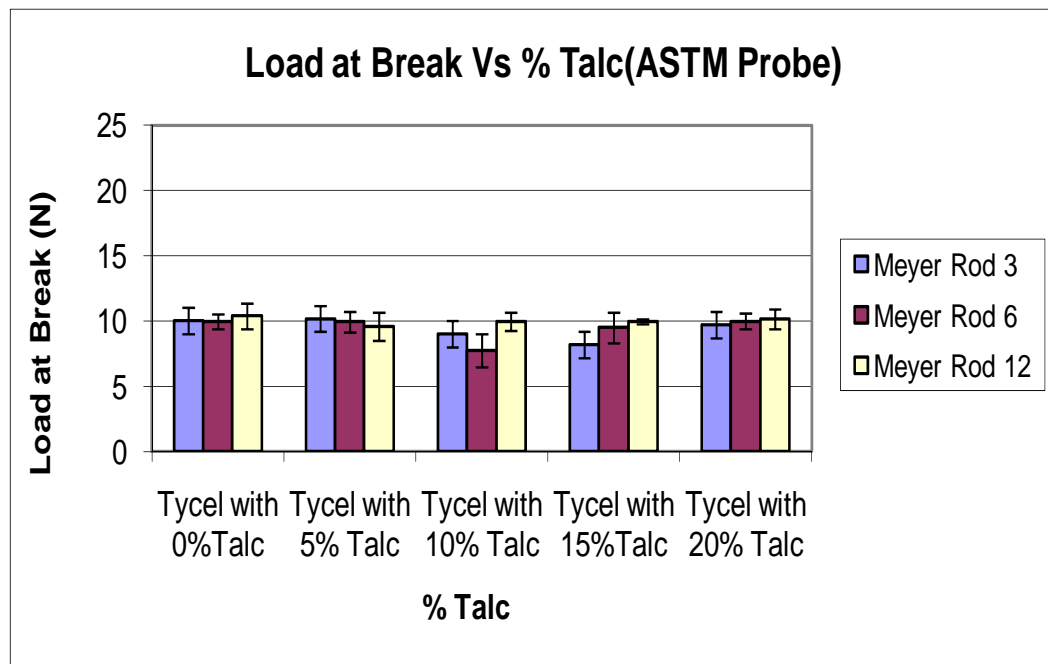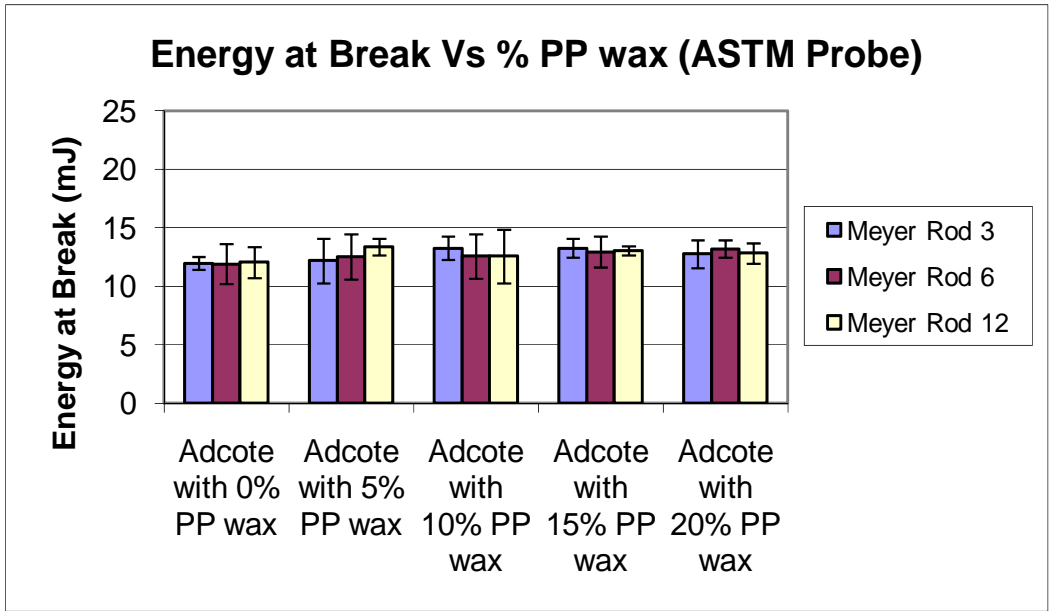

Chart 4.24: Puncture Strength- Load Vs percent loading of Talc- PET up (ASTM probe)

Chart 4.25: Puncture Strength Energy Vs percent loading of PP wax Foil up Hemispherical probe

Chart 4.26: Puncture Strength- Load Vs percent loading of PP wax-Foil up (Hemispherical probe)

Chart 4.27: Puncture Strength- Energy Vs percent loading of Talc- Foil up (Hemispherical probe)

Chart 4.28: Puncture Strength- Load Vs percent loading of Talc- Foil up (Hemispherical probe)

Chart 4.29: Puncture Strength- Energy Vs percent loading of PP wax- Foil up (Hemispherical probe)
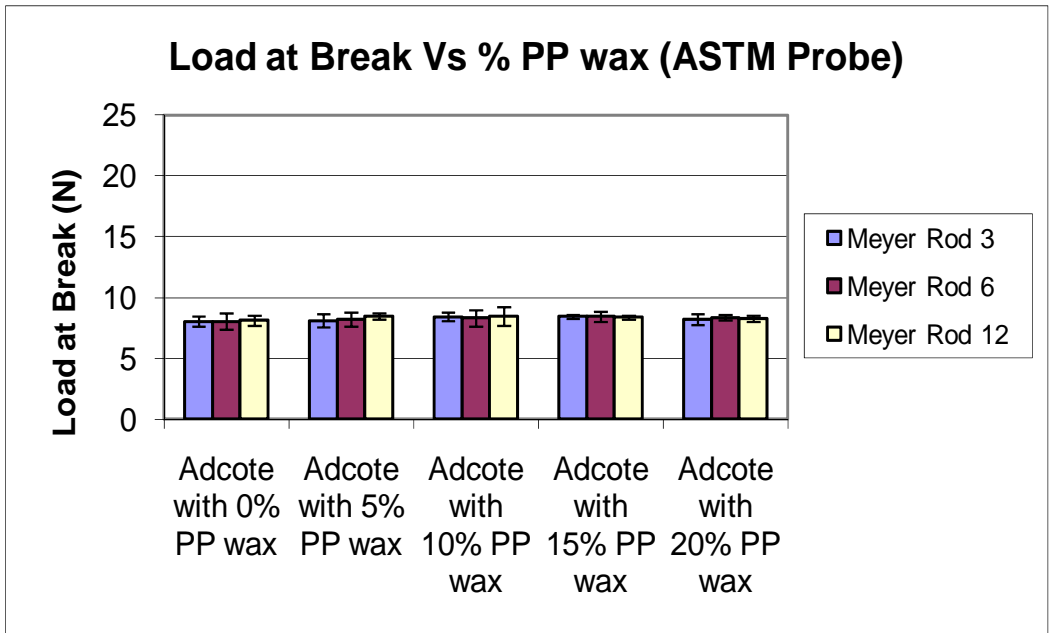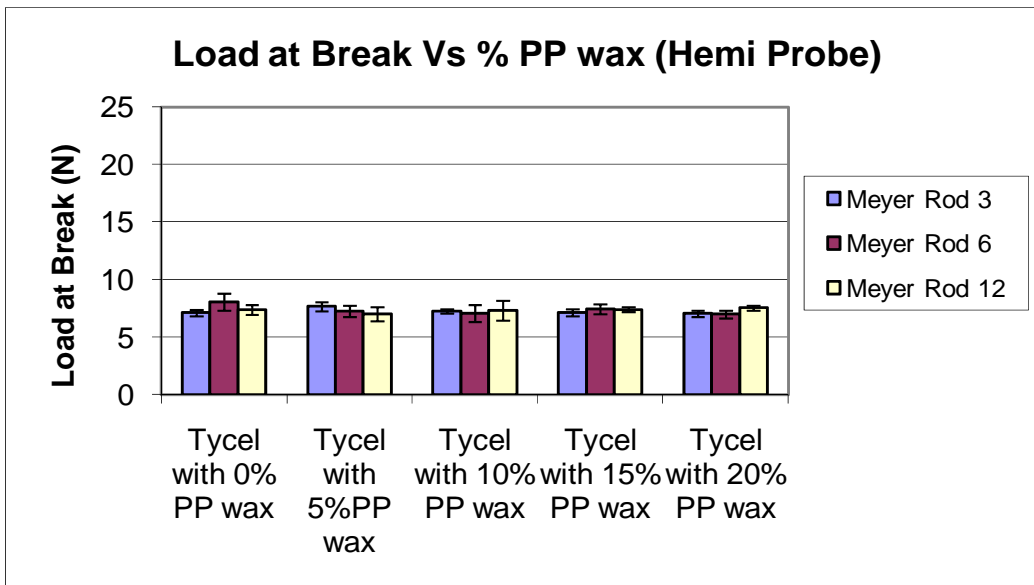

Chart 4.30: Puncture Strength- Load Vs percent loading of PP wax- Foil up (Hemispherical probe)
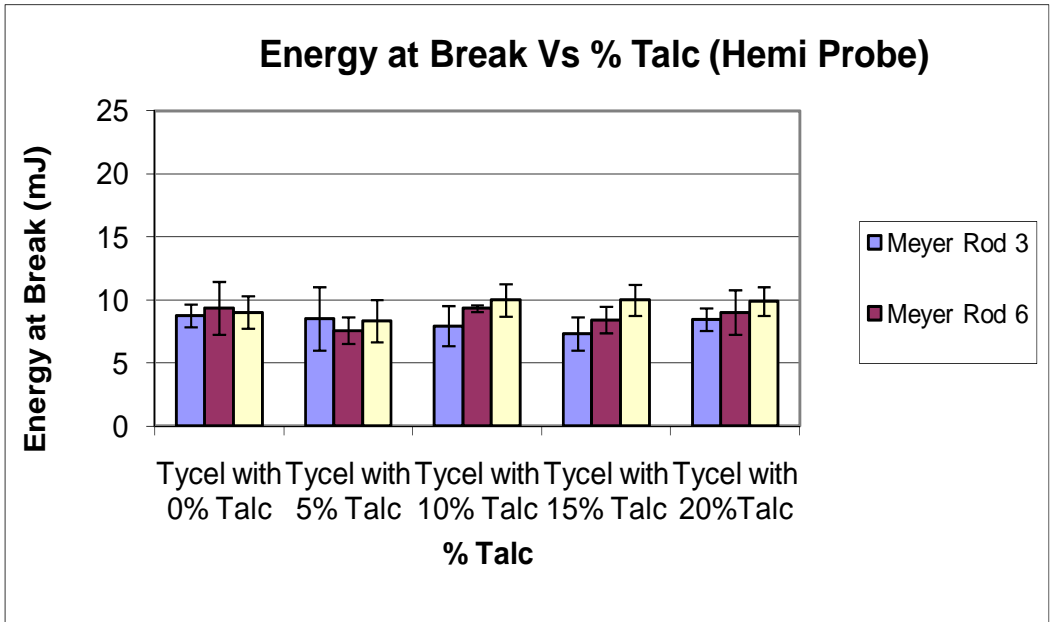
Chart 4.31: Puncture Strength- Energy Vs percent loading of Talc- Foil up (Hemispherical probe)
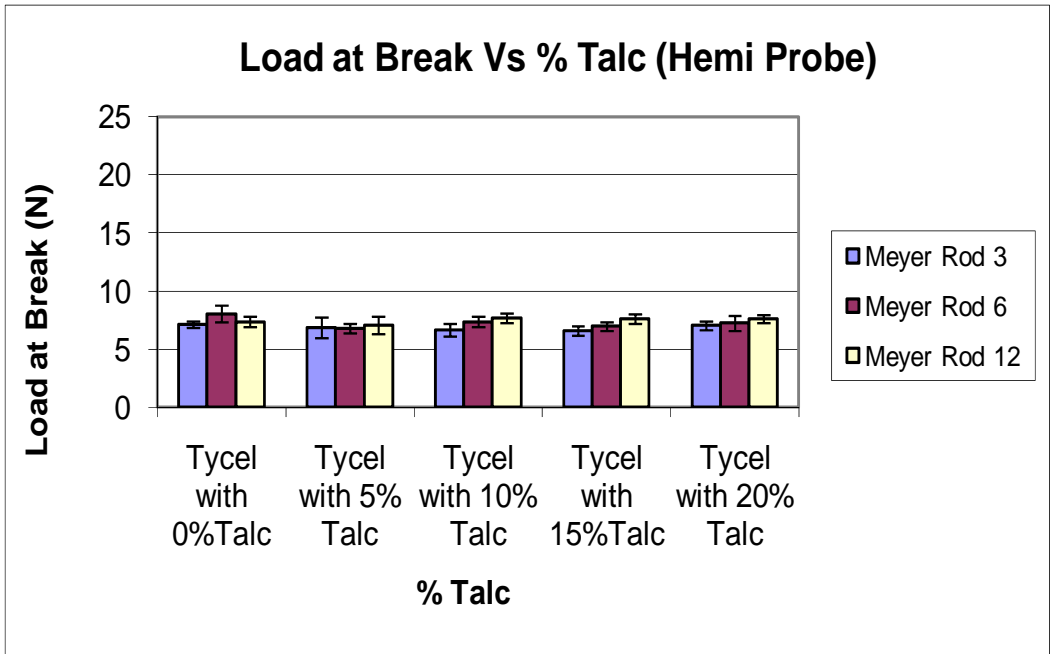
Chart 4.32: Puncture Strength- Load Vs percent loading of Talc- Foil up (Hemispherical probe)
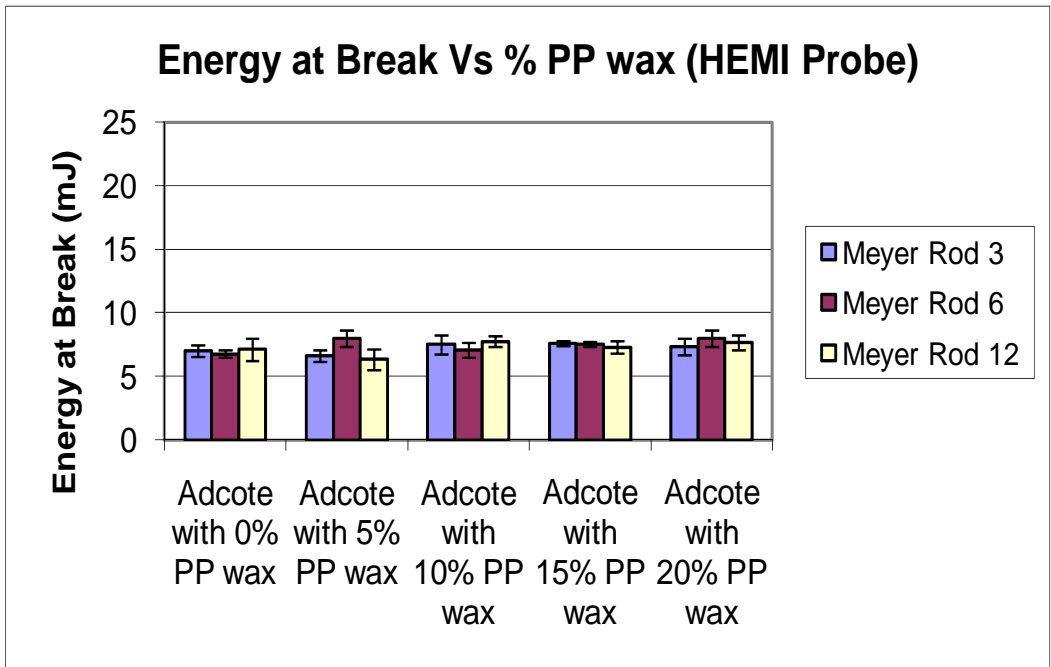
Chart 4.33: Puncture Strength- Energy Vs percent loading of PP wax- PET up (Hemispherical probe)
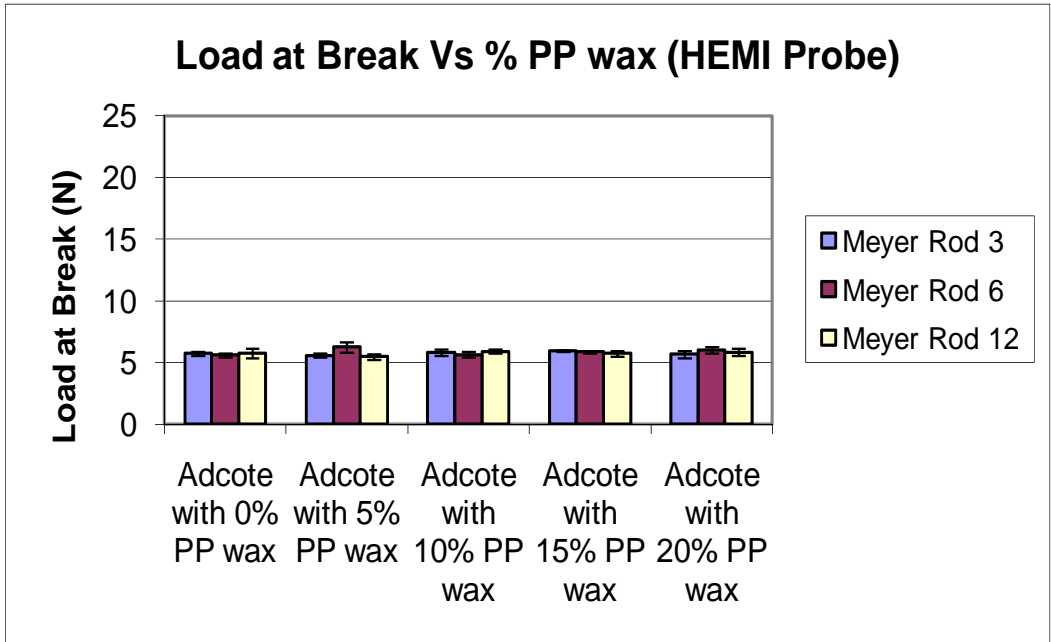
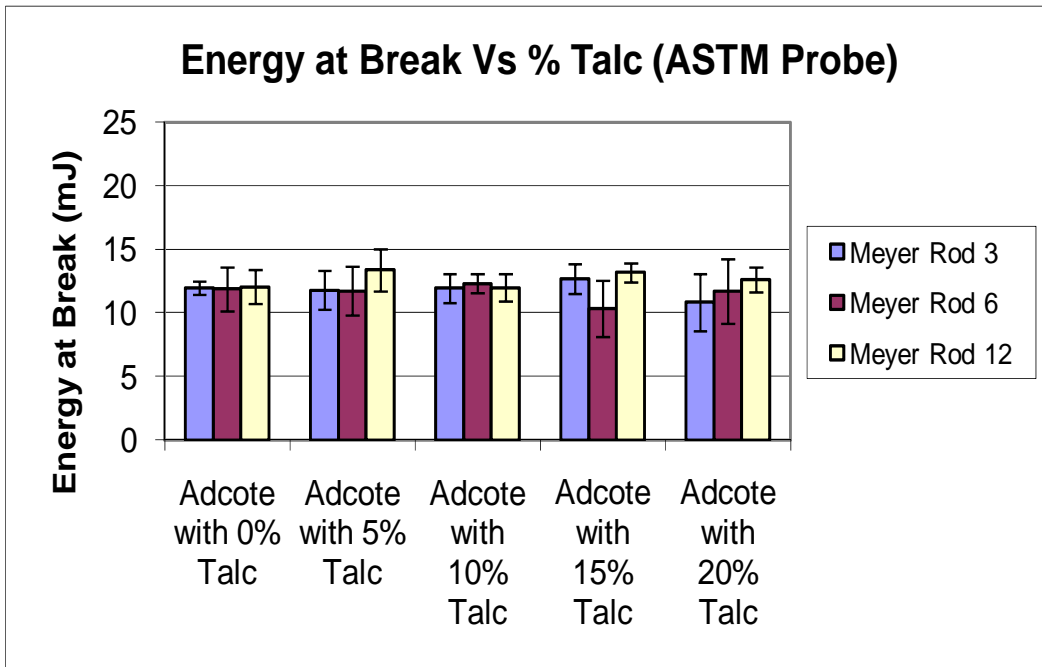**Chart 4.34: Puncture Strength- Load Vs percent loading of PP wax- PET up (Hemispherical probe)**
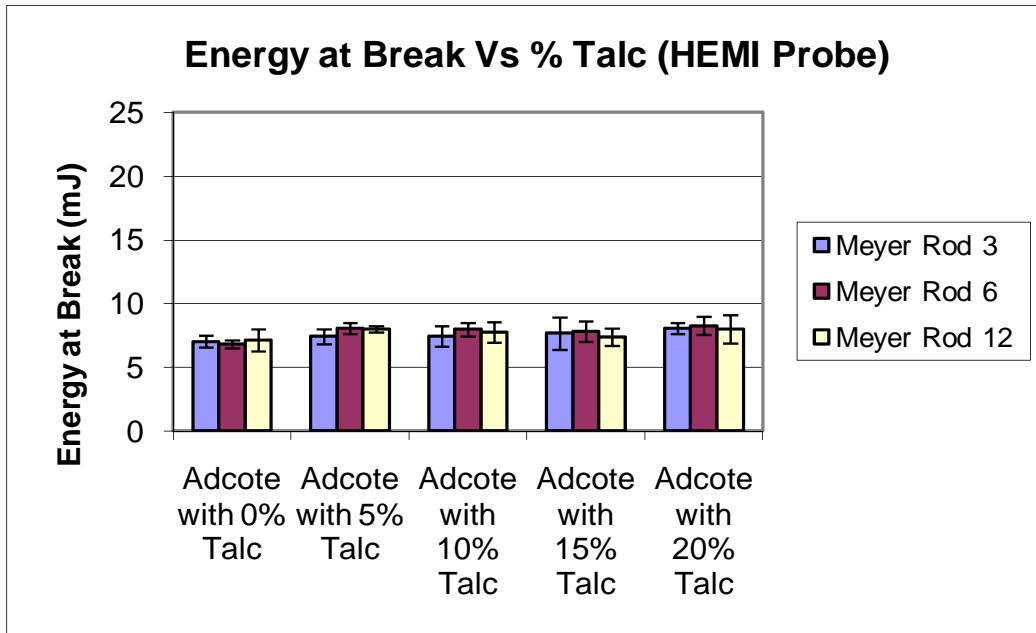
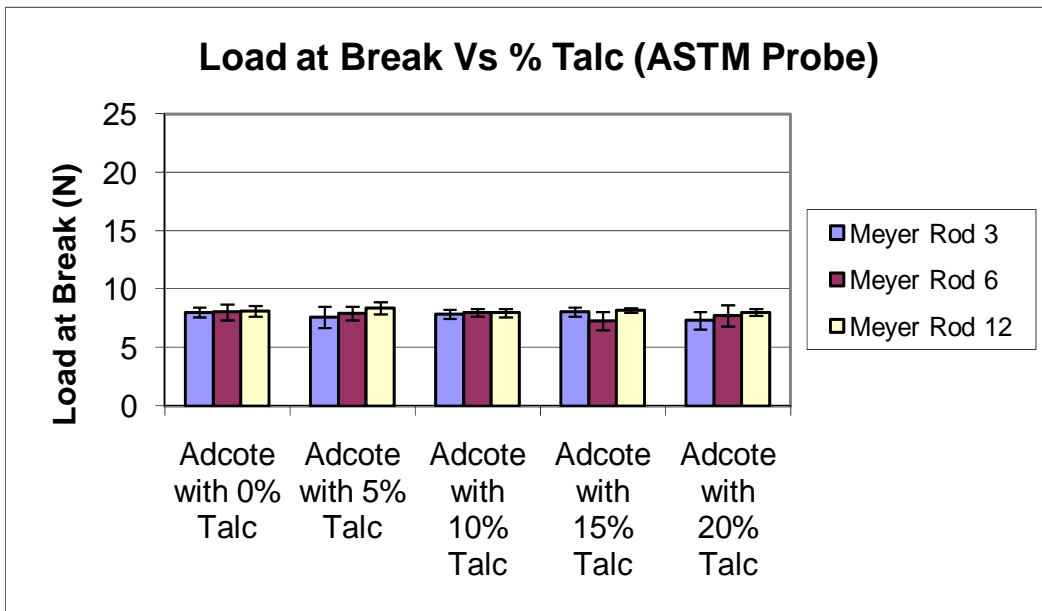**Chart 4.35: Puncture Strength- Energy Vs percent loading of Talc- PET up (Hemispherical probe)**
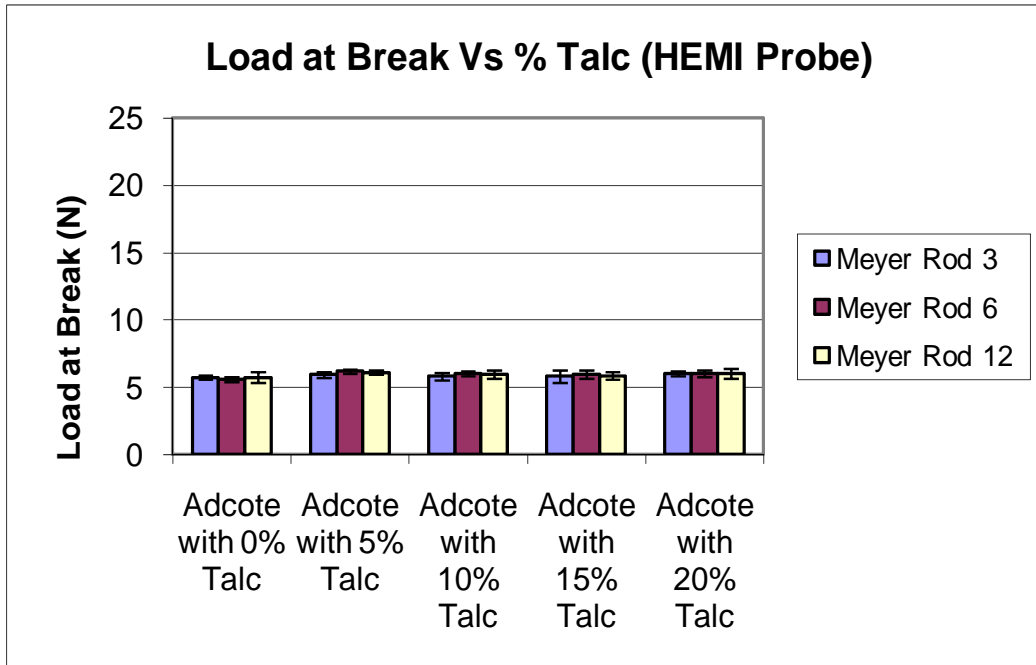
Chart 4.36: Puncture Strength- Load Vs percent loading of Talc- PET up (Hemispherical probe)
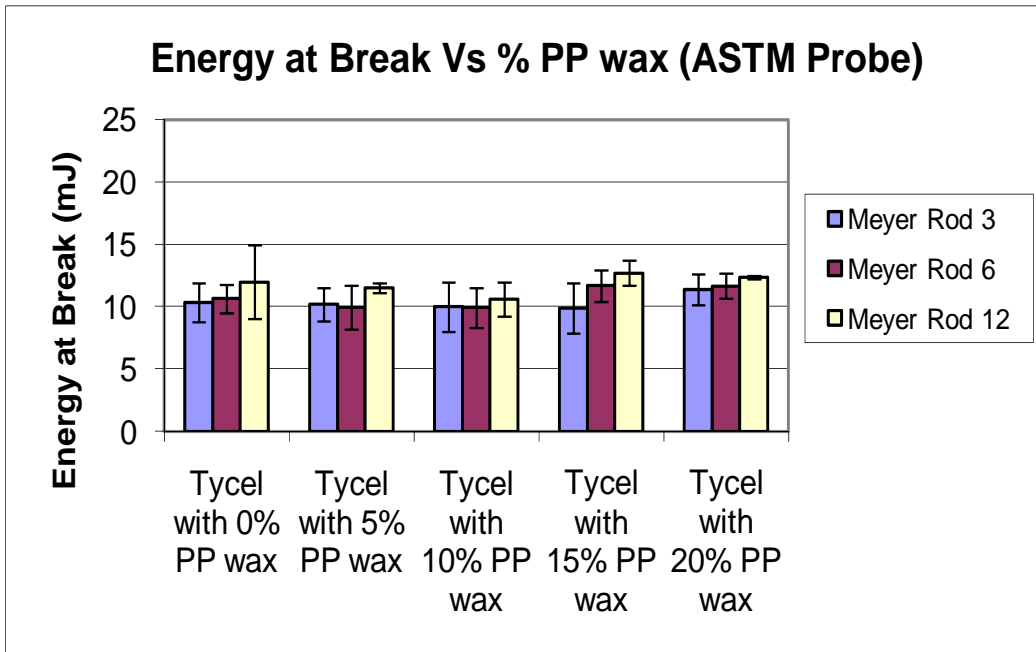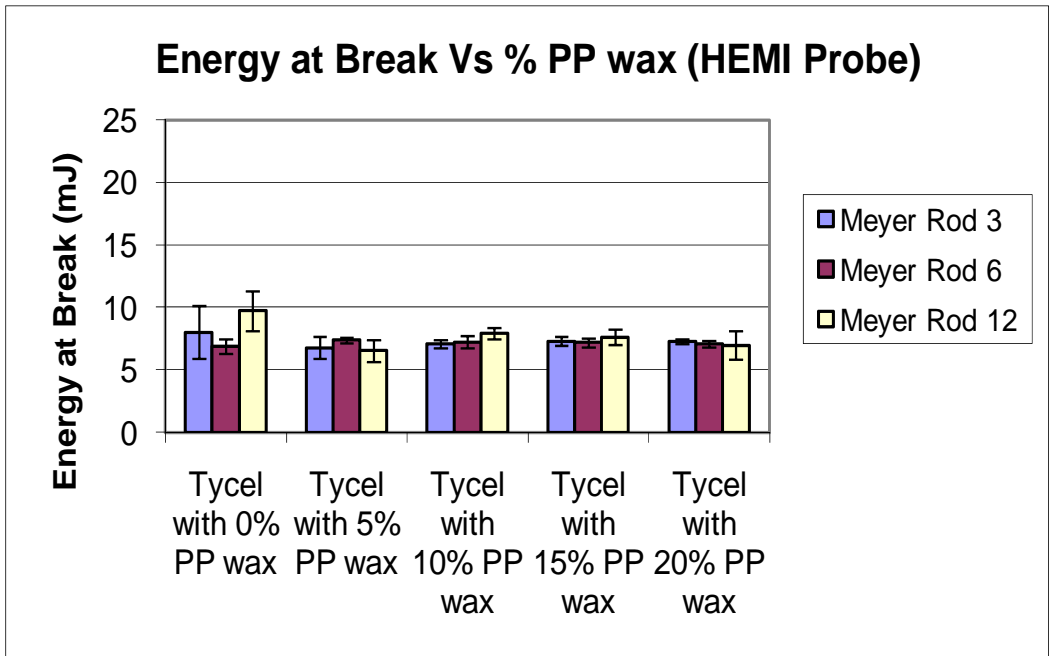
Chart 4.37: Puncture Strength- Energy Vs percent loading of PP wax- PET up (Hemispherical probe)
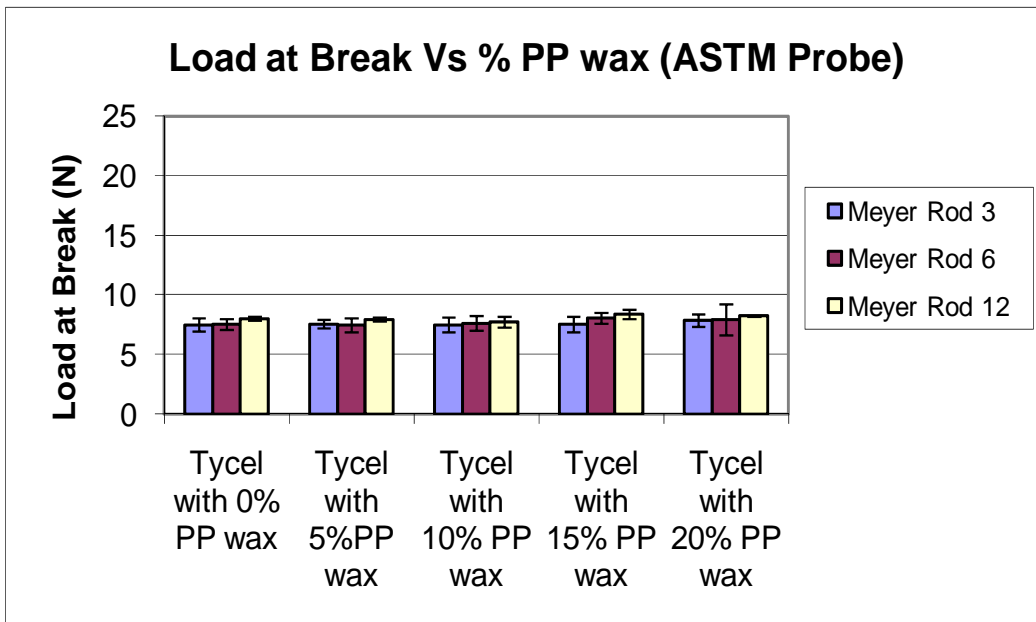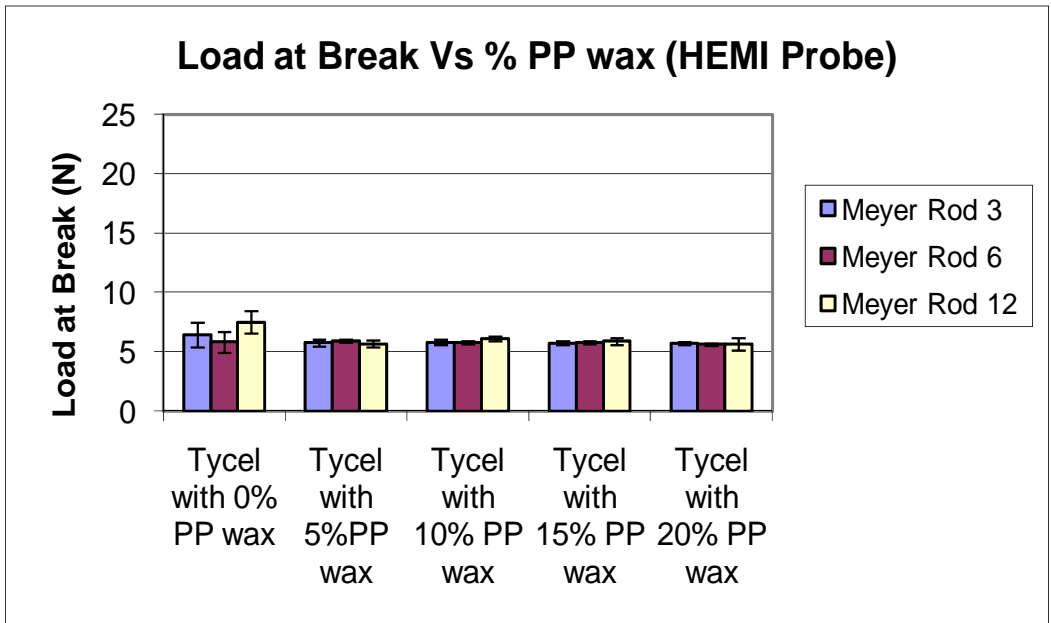

Chart 4.38: Puncture Strength- Load Vs percent loading of PP wax- PET up (Hemispherical probe)
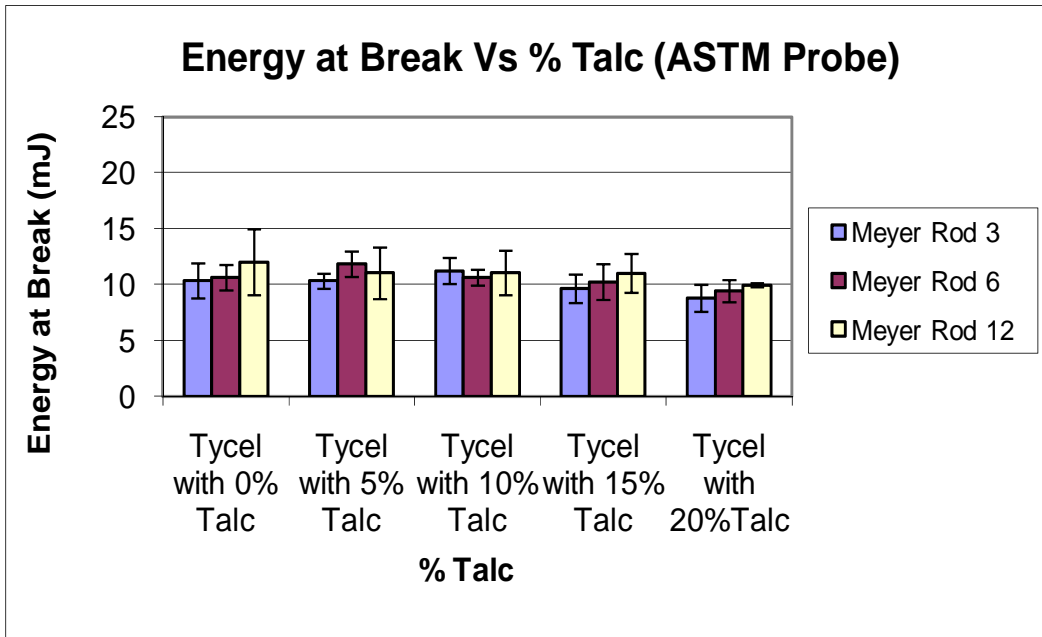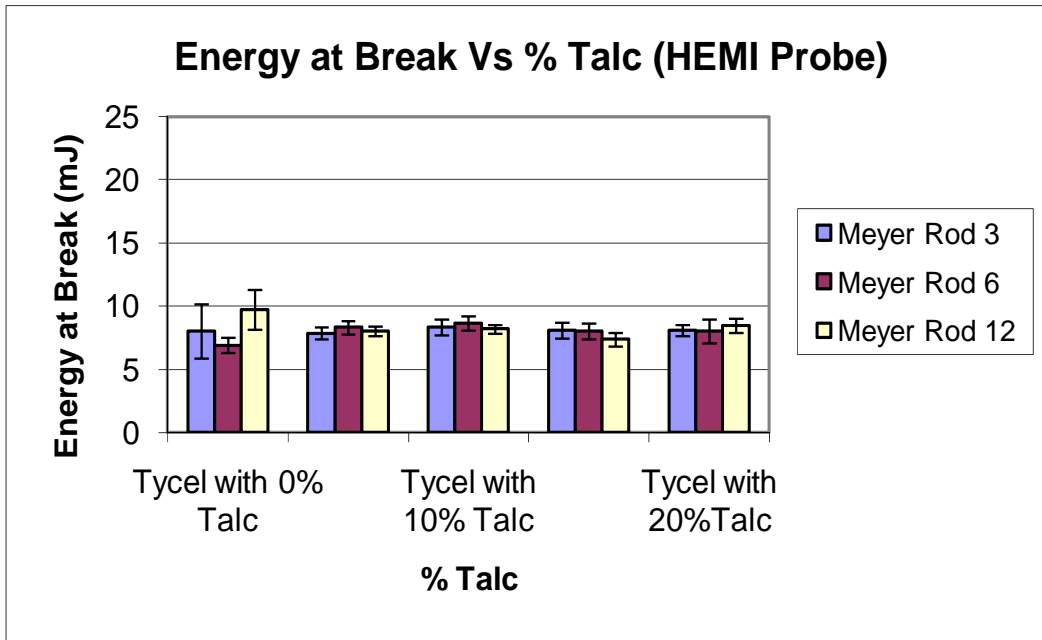
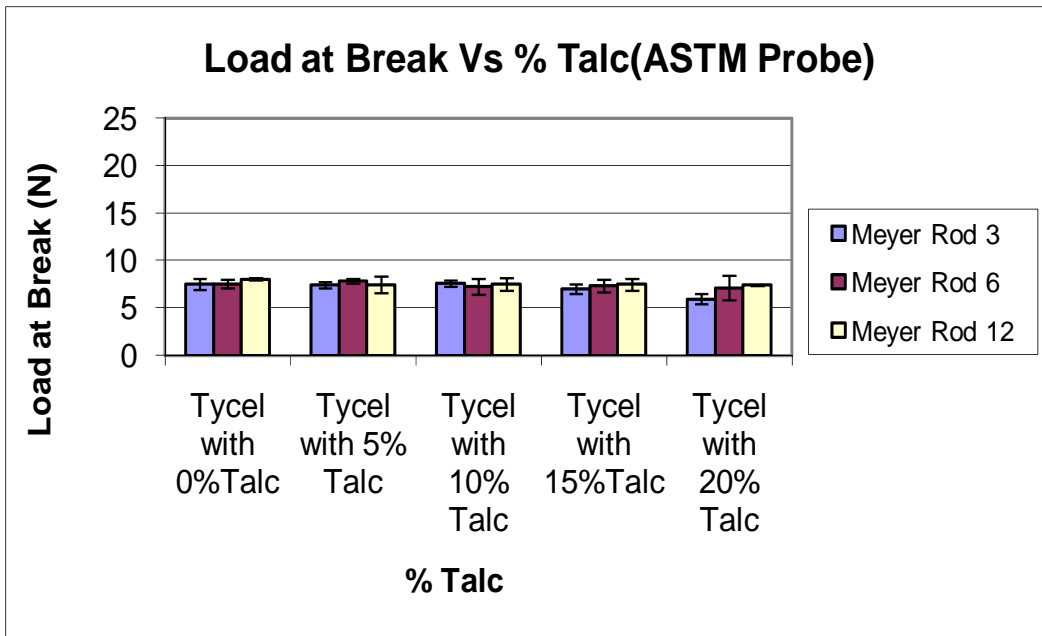**Chart 4.39: Puncture Strength- Energy Vs percent loading of Talc- PET up (Hemispherical probe)**

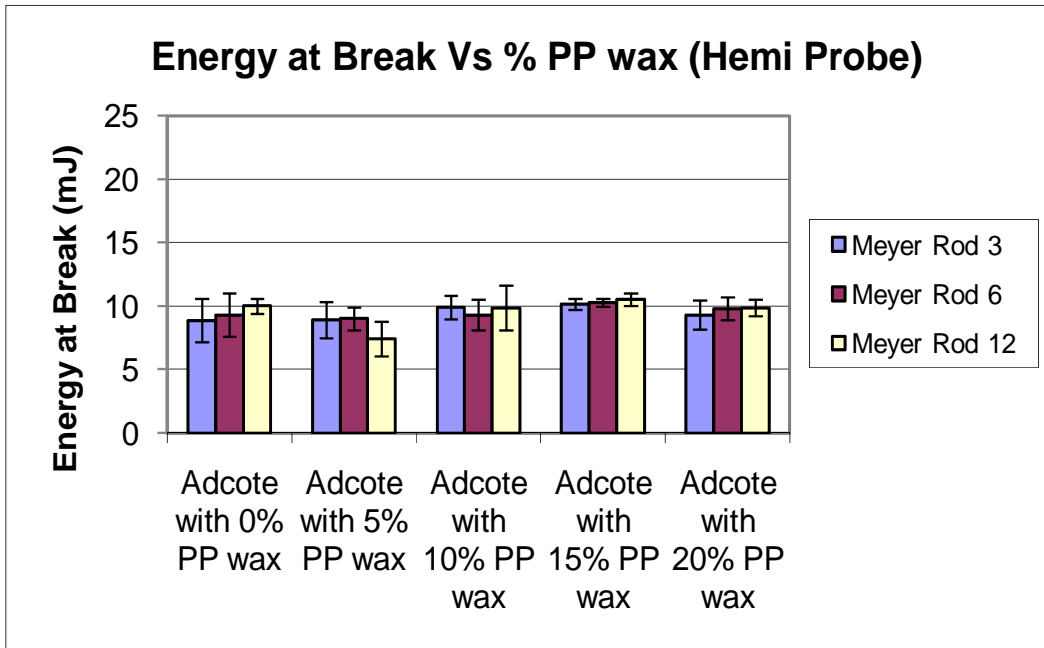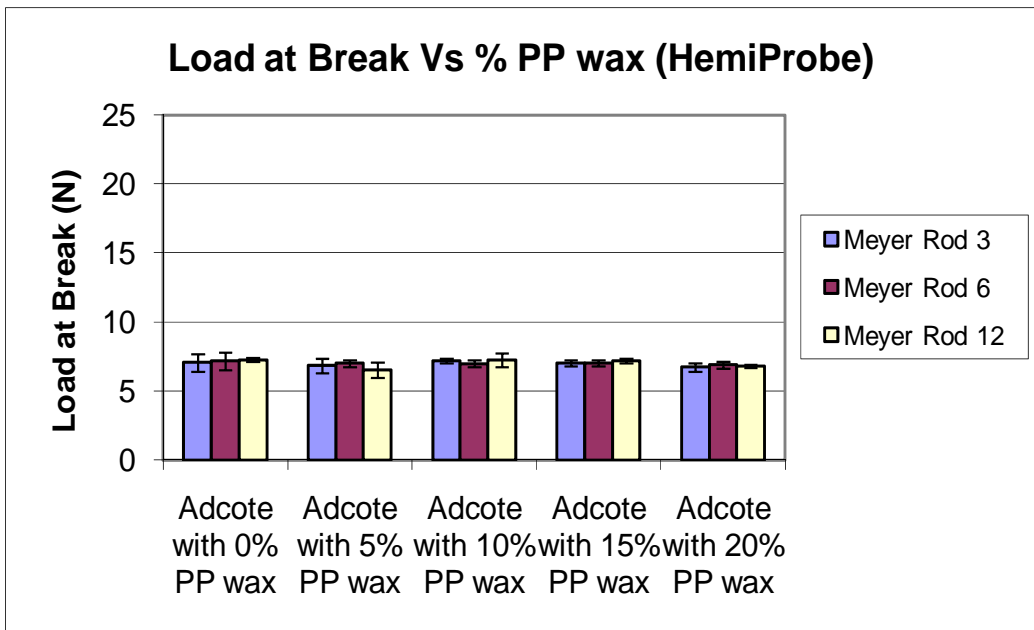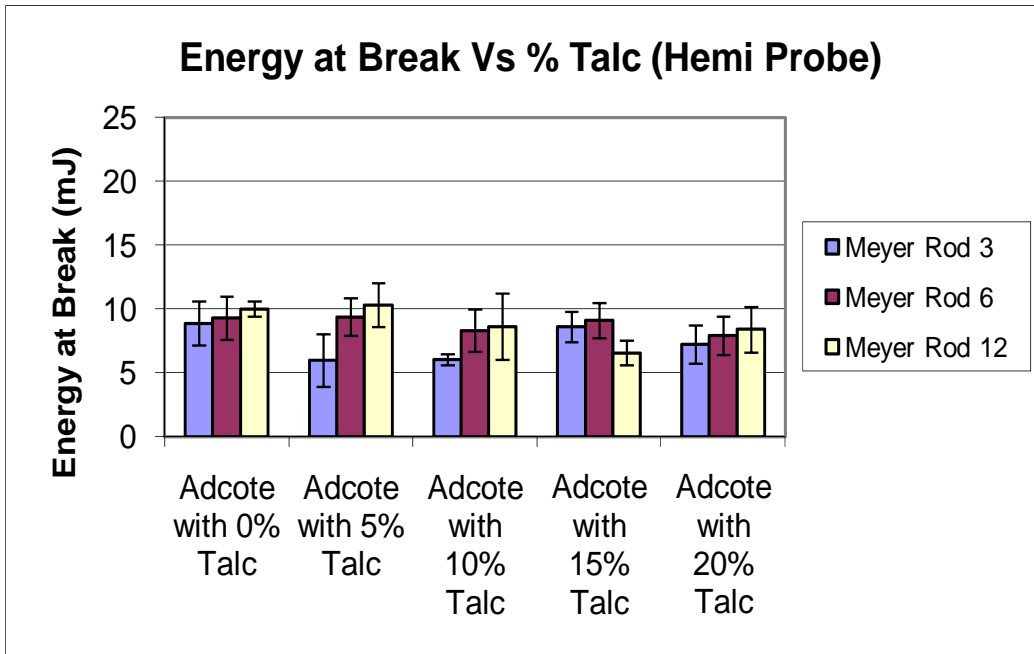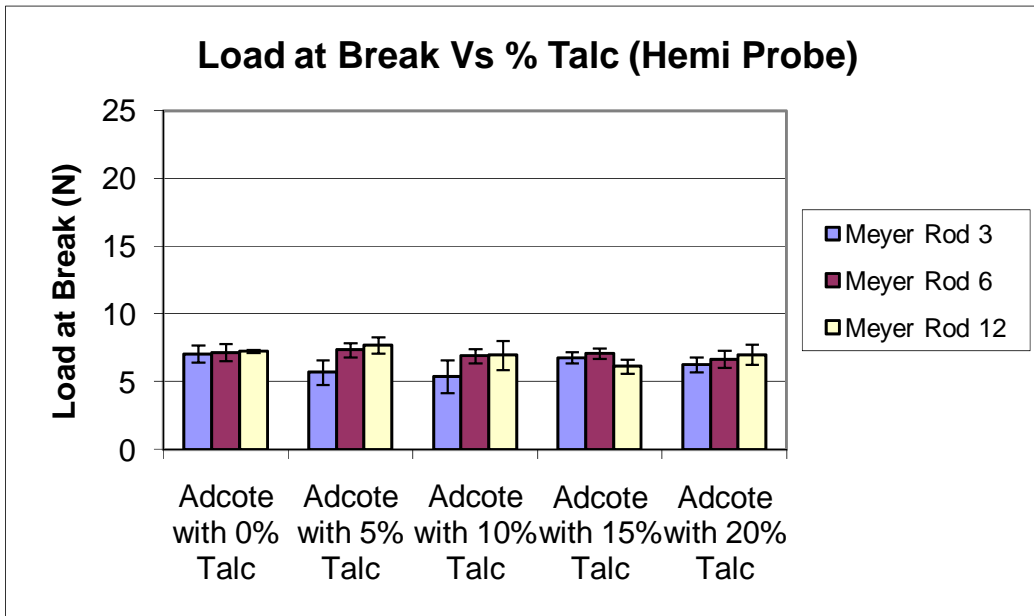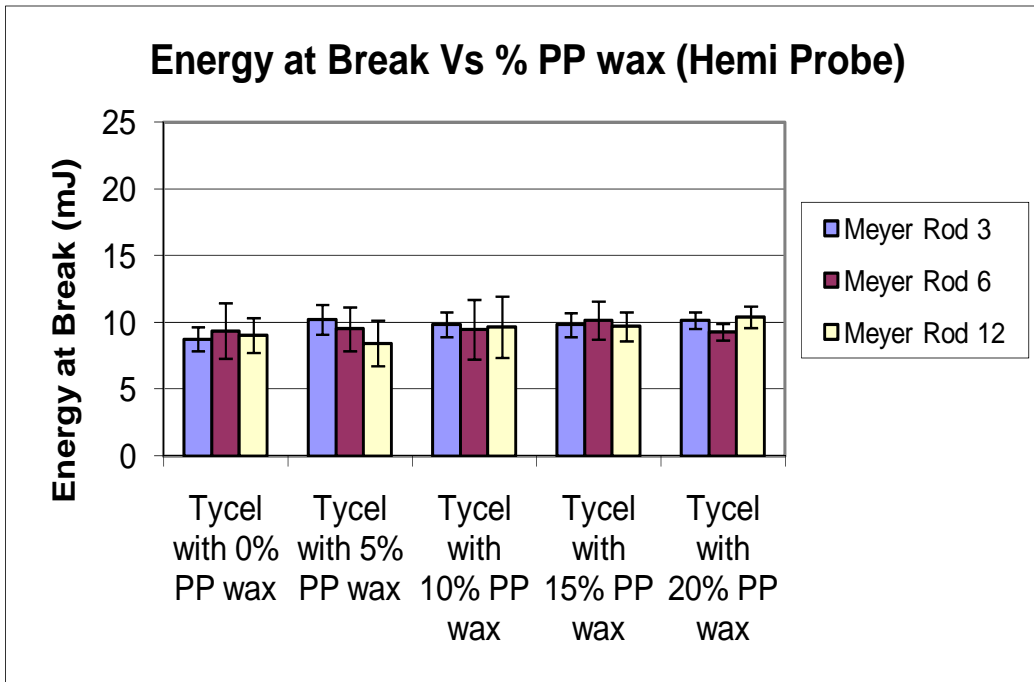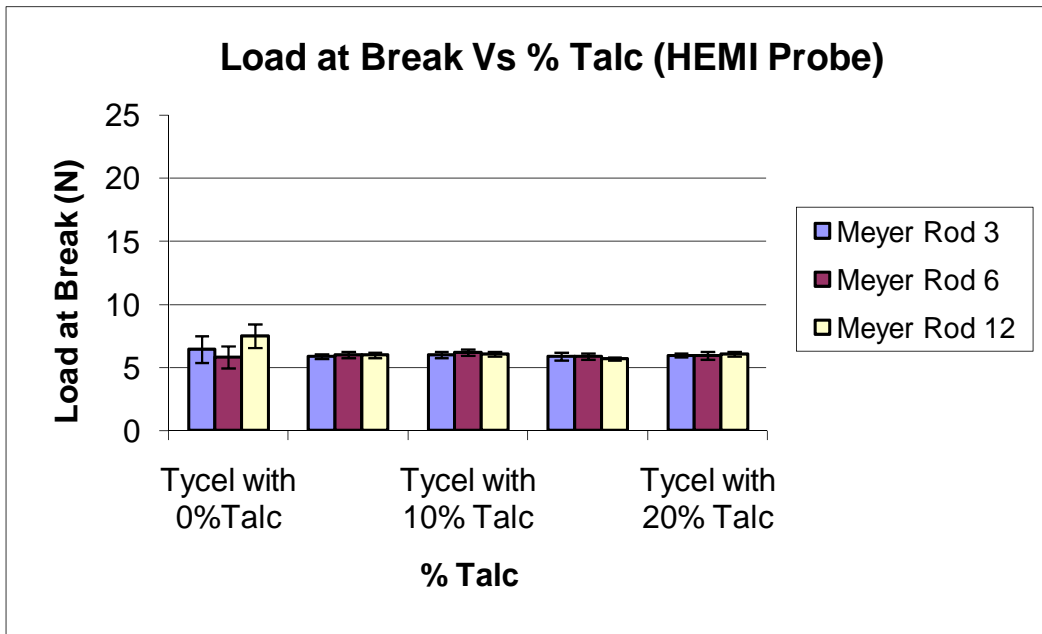**Chart 4.40: Puncture Strength- Load Vs percent loading of Talc- PET up (Hemispherical probe)**

4.4   Time based study

The bond strength and puncture resistance were measured at regular intervals after lamination to determine the effect of the level of cure on these properties. For this study, Tycel™ was used as the adhesive with 20 percent loading of talc as the additive. Tycel™ and talc were selected because during the initial study, this combination resulted in bonds free from material breakage and the bond strength values were found to decrease quadratically with increasing percentage loading of the additive. All the failures using this blend were cohesive and smooth without any zippering action.

The results were analyzed to obtain a time dependent curve for both bond strength and puncture resistance. In bond strength testing, both average load and maximum load were reported and analyzed. Both the ASTM and the hemispherical probes were used to puncture the samples from both the foil side and the PET side. In puncture, both energy to break and load to break were reported and analyzed. The values were compared against each other.

Chart 4.41 shows the average bond strength and chart 4.42 shows the maximum bond strength for Meyer rods #3, #6 and #12 respectively. Samples were tested each hour and for all the rods, the values increased with time. Most of the change occurred between hours 1 to 5. The increase in bond strength was more pronounced with Meyer rod #12.
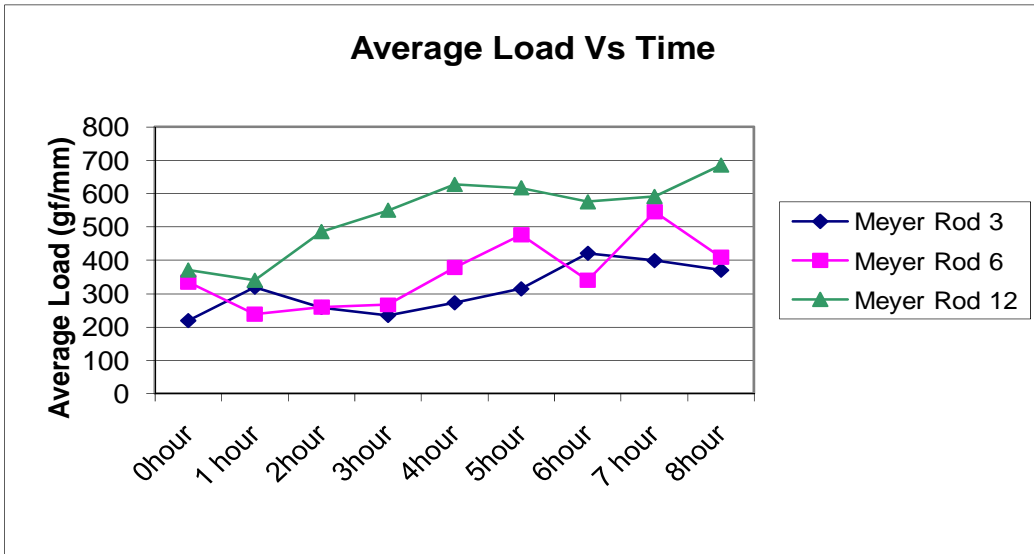
Chart 4.41: Bond Strength- Average Load for Tycel with 20% Talc Vs Time
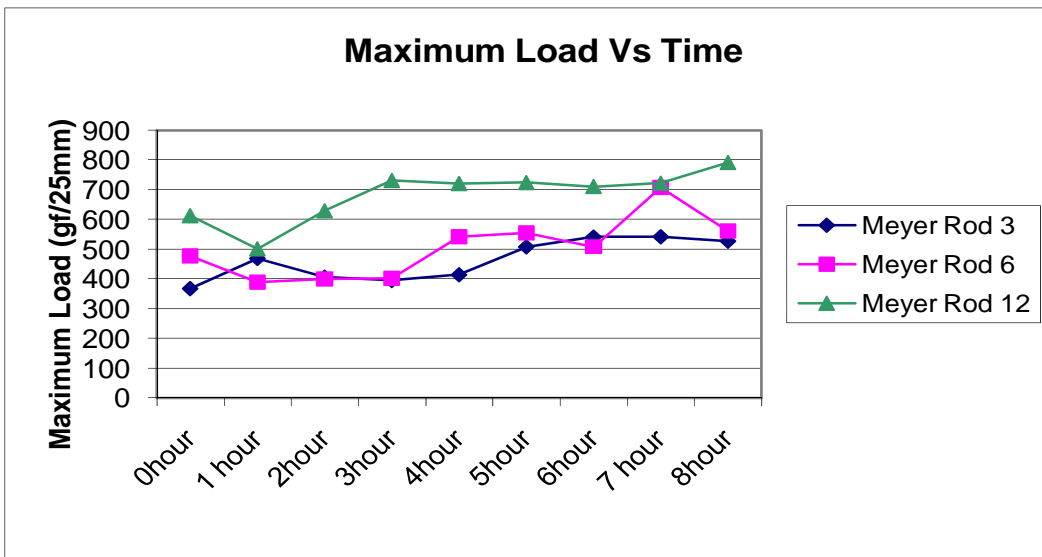
Chart 4.42: Bond Strength- Maximum Load for Tycel with 20% Talc Vs Time

75

The puncture results are presented through charts 4.43 through chart 4.50. The results show that, for both the ASTM and the hemispherical probes, there is a marked difference in values depending on the side from which puncture was made. When puncture is made from the foil side, the values increased slightly with increasing time. The regression analysis (Appendix L and M) results gave a decent fit with linear model. This proves that the puncture values do change by a narrow value as the bond strength increases with cure time. When puncture was achieved from the PET side, the values stayed pretty constant over time and these results are confirmed with the regression analyses. PET was a very strong material and when puncture was made from that side, the only material which came into play was PET. So when the PET failed, the entire structure failed. When puncture was made from the foil side, the foil developed cracks, initiating the puncture mechanism and eventually punctured through the structure.
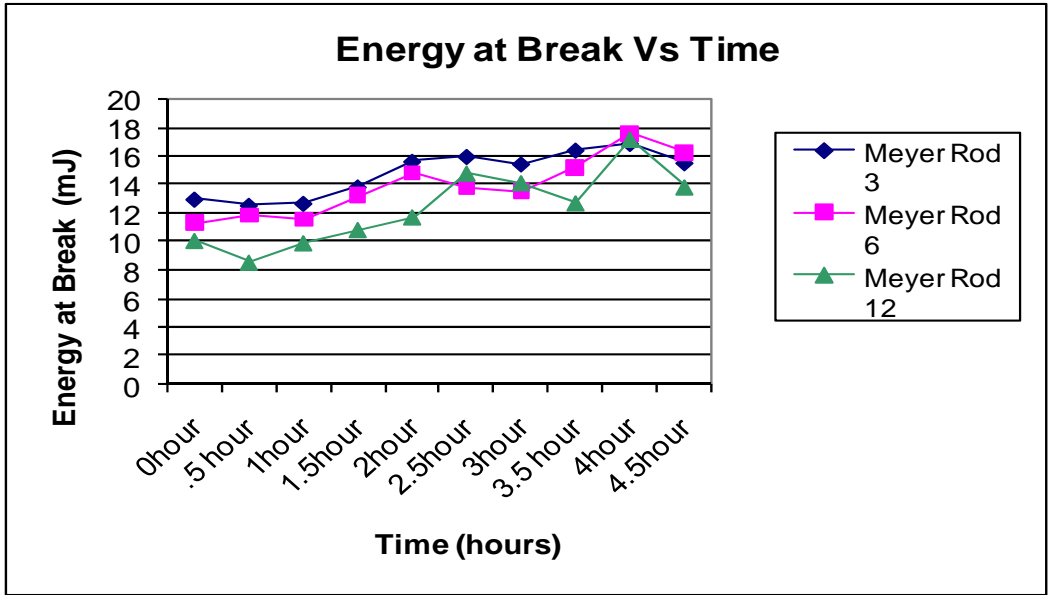
Chart 4.43: Puncture Strength- Energy at Break for Tycel with 20% Talc using ASTM probe-Foil side up
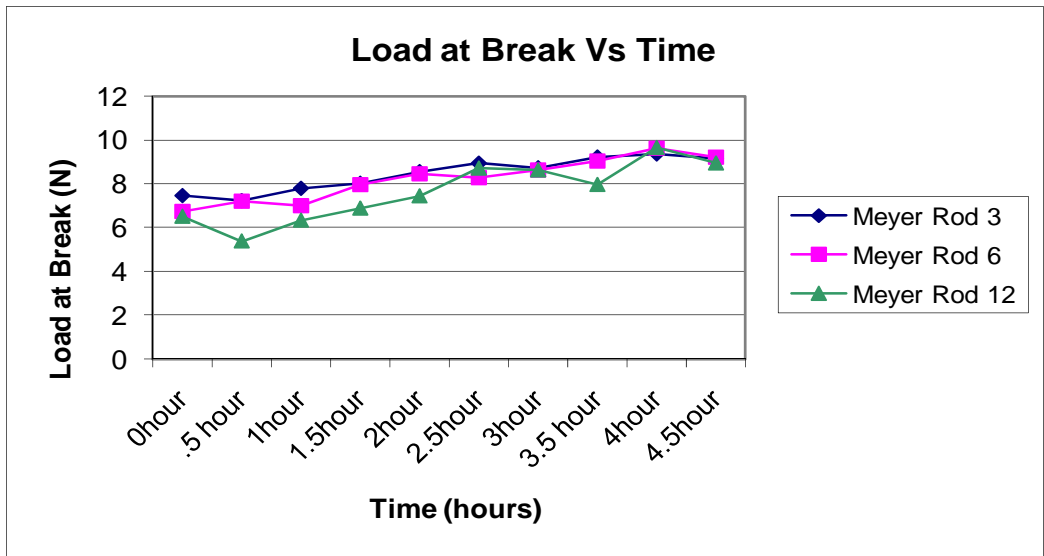
Chart 4.44: Puncture Strength- Load at Break for Tycel with 20% Talc using ASTM probe-Foil side up
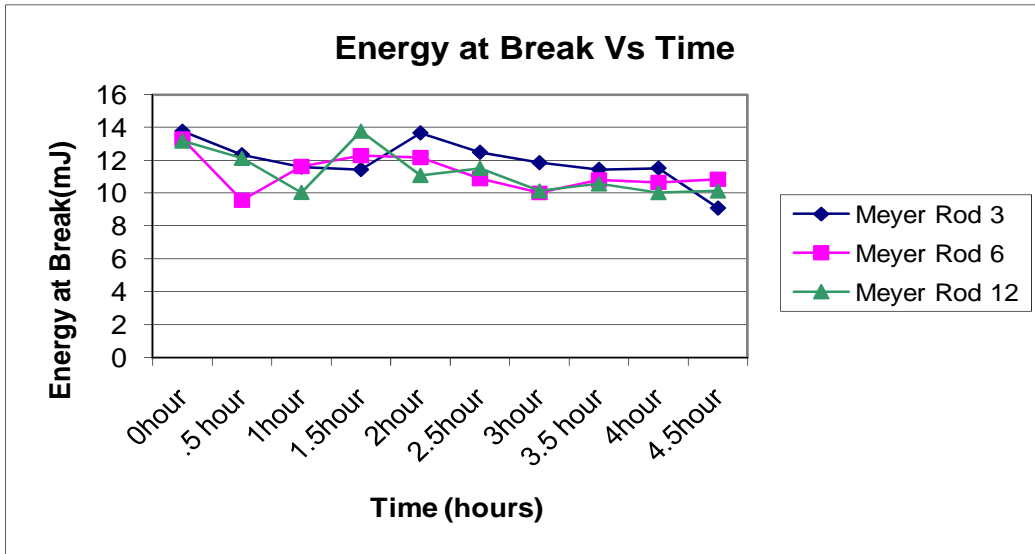
Chart 4.45: Puncture Strength- Energy at Break for Tycel with 20% Talc using ASTM probe-PET side up
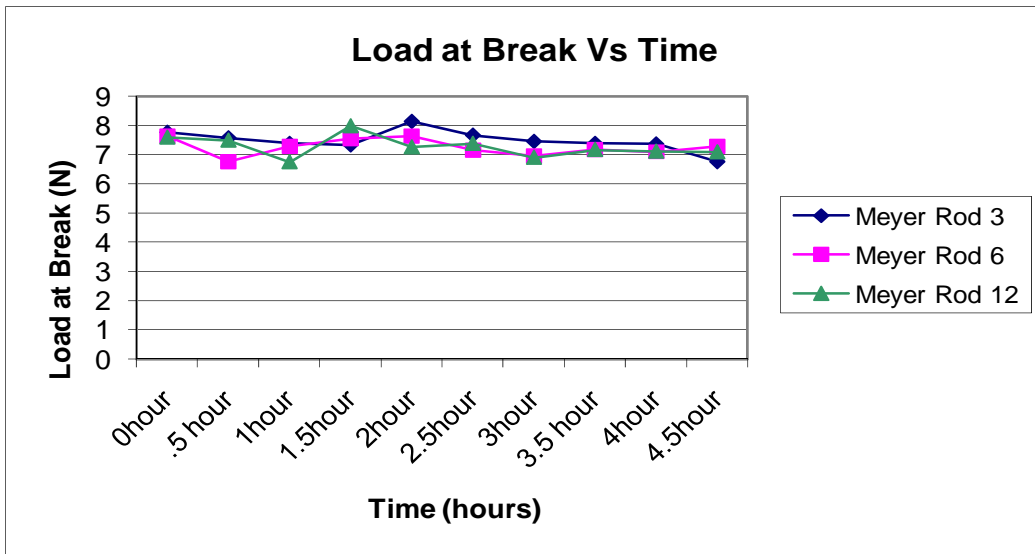
Chart 4.46: Puncture Strength- Load at Break for Tycel with 20% Talc using ASTM probe-PET side up
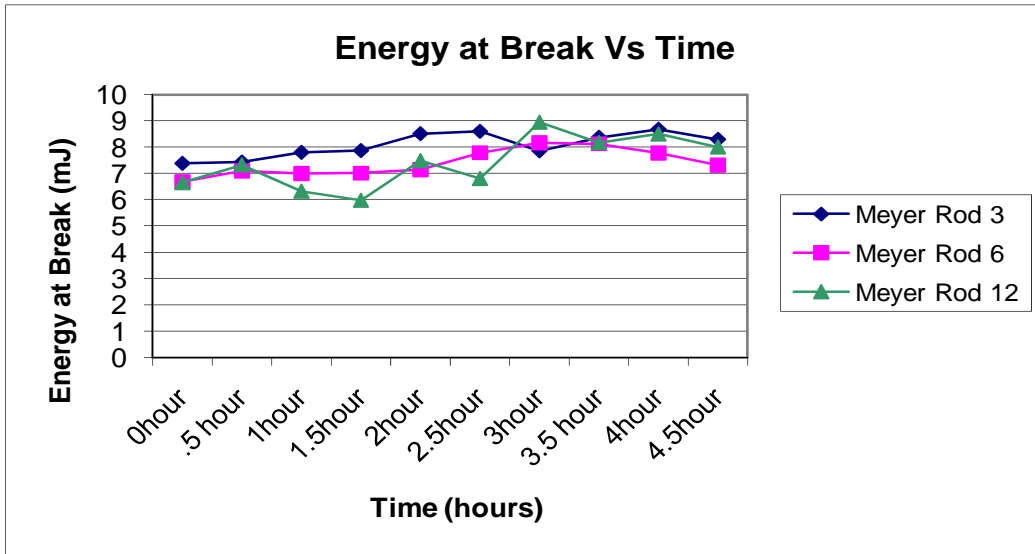
Chart 4.47: Puncture Strength- Energy at Break for Tycel with 20% Talc using hemi probe-Foil side up
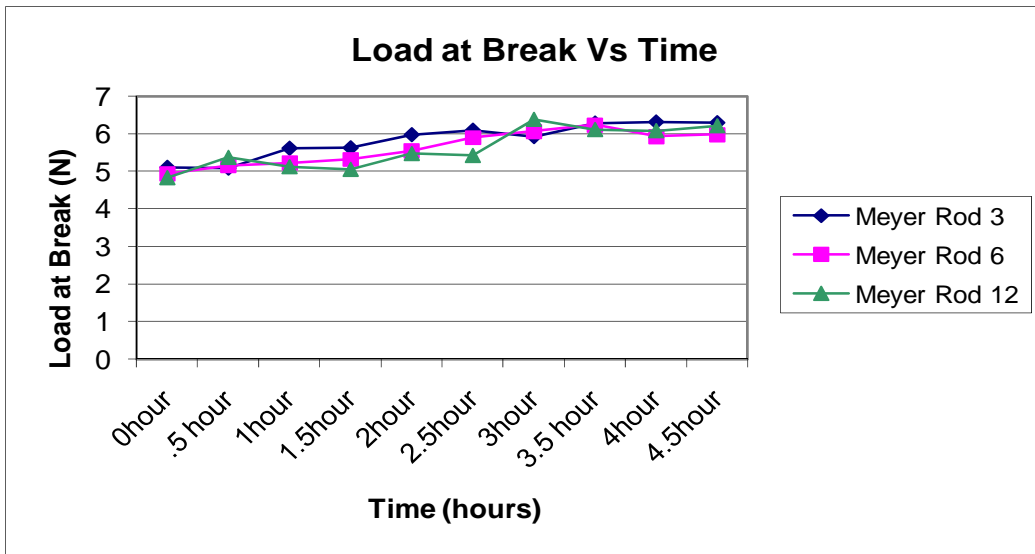
Chart 4.48: Puncture Strength- Load at Break for Tycel with 20% Talc using hemi probe-Foil side up
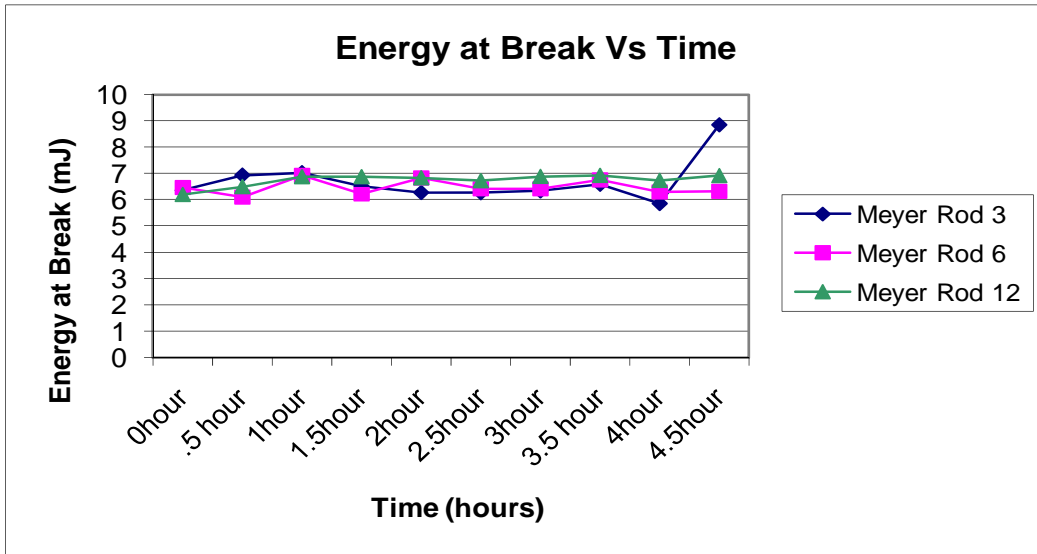
Chart 4.49: Puncture Strength- Energy at Break for Tycel with 20% Talc using hemi probe-PET side up
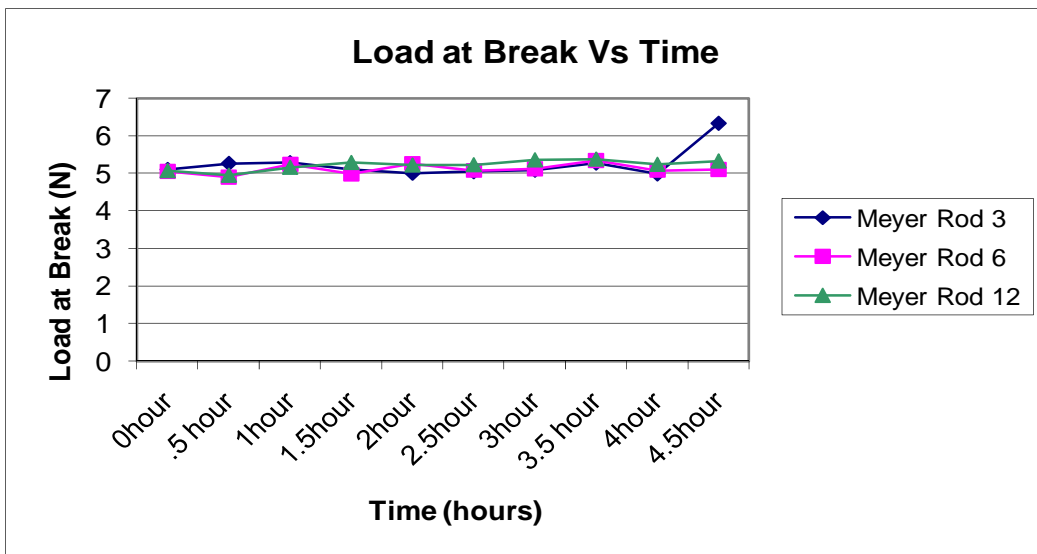
Chart 4.50: Puncture Strength- Load at Break for Tycel with 20% Talc using hemi probe-PET side up

Figure 4.1 and 4.2 shows the delamination that occurred in the laminates as they were punctured using ASTM probe from foil side and from PET side. The extent of delamination was found to decrease over time as the adhesive is cured. It was also noted that when the curing time reached 4-4.5 hours, the delamination disappeared and the puncture was found to happen as a single failure rather than multiple structure failures.

It is difficult to see the delamination area in the pictures below due to reflection from the laminate. However in figure 4.1, the cloudy area near the center of the third sample from left to right in the bottom row (Meyer rod 12- 2 hours), represents the area of delamination.
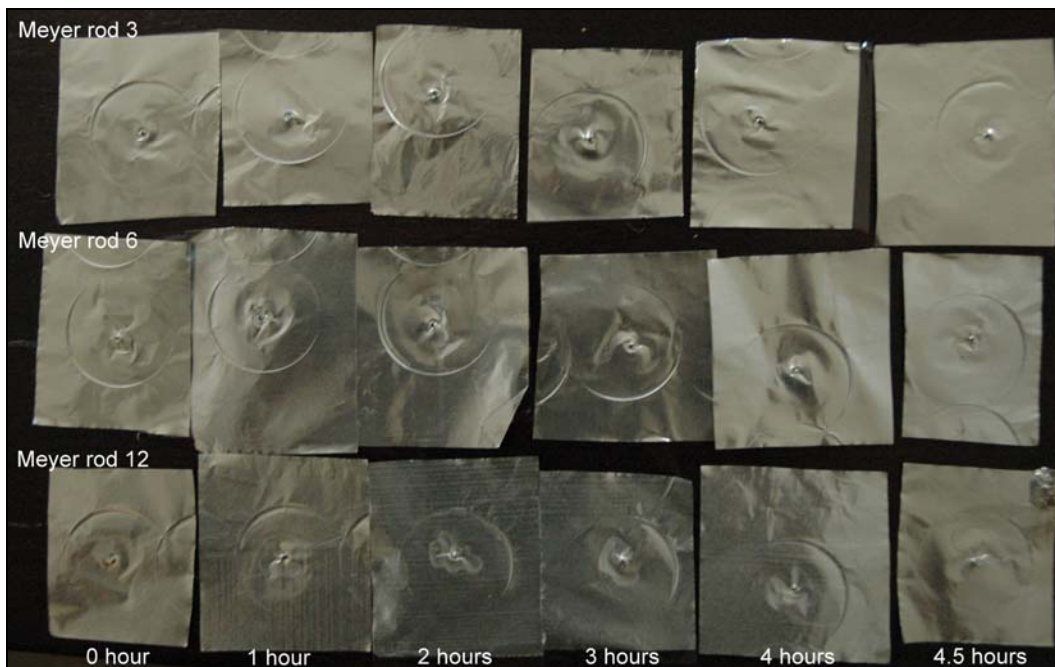
Figure 4.1: Delamination over time using ASTM probe from foil side

Figure 4.2: Delamination over time using ASTM probe from PET side

The puncture profiles of cured laminate laminate with no adhesive and that of pure materials, PET and foil is presented in figure 4.3. The x- axis represents the deformation or probe penetration distance and y- axis represents the load at break.

The laminate with no adhesive gave two distinct material failures. The PET and foil were held together with the help of shampoo as it offered to represent a "zero bond" laminate in a meaningful manner. The completely cured laminate gave a smooth curve showing only one material failure. It can also be seen that the puncture strength of foil is very low compared to that of PET. The effect of probe design, ASTM compared to hemispherical probe, can also be understood from the difference in values obtained for both the materials. In foil, the differences in values are not as significant as in PET.
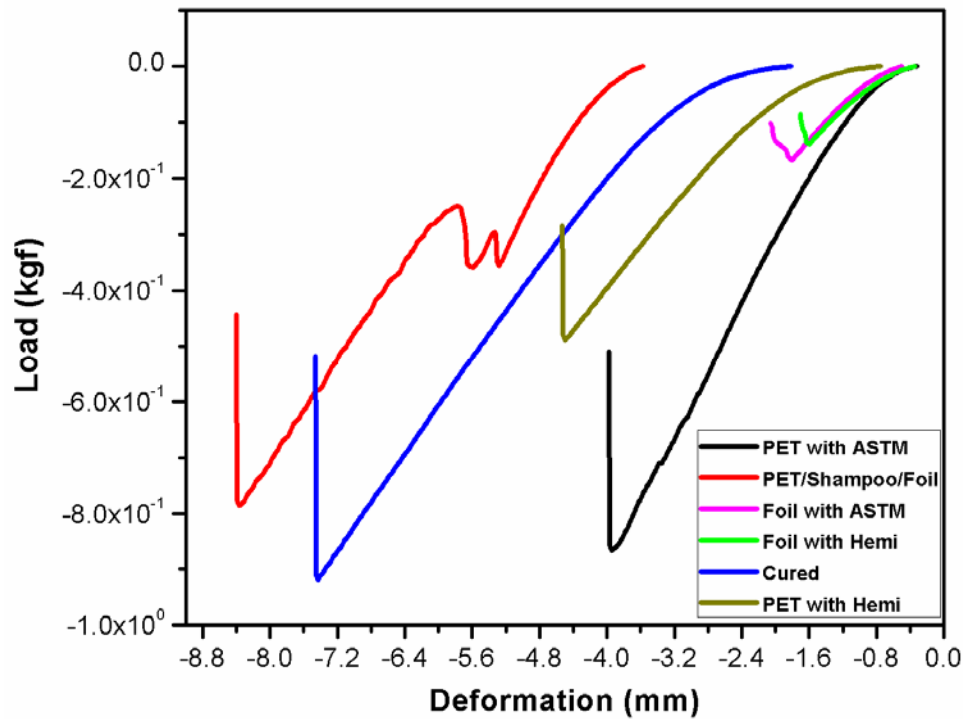
Figure 4.3: Puncture profiles

Figure 4.4 shows the change in mode of failure from multiple structure failures to single structure failure with increase in curing time. In the plot, individual curves represent the puncture profiles of samples over time. The time increases from left to right. It can be clearly seen that the material failure changes from a two stage failure to a single substrate failure as time approaches 4 to 4.5 hours.
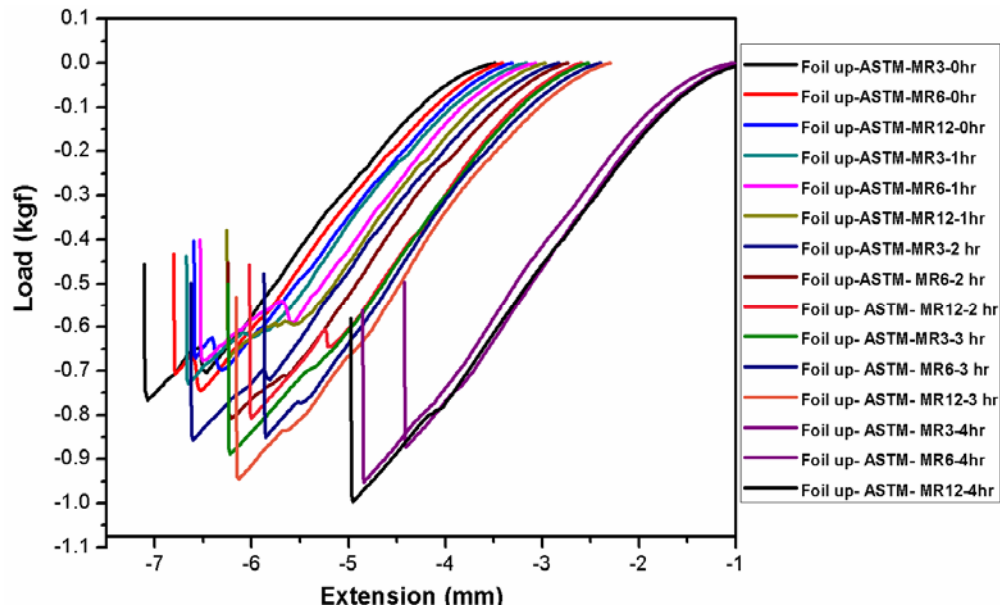
Figure 4.4: Puncture profile over curing time

This leads to the conclusion that, when some critical bond strength is obtained, the structure tends to behave as a single material and puncture resistance is no longer affected by bond strength. This finding is further confirmed by the initial puncture resistance results with cured samples. The puncture profiles show that all the cured samples failed in a single step rather than multiple structure failure. The amount of additive, type of additive, adhesive weight or coating weight all exhibited no effect on the puncture values or the mode of failure. The side from which puncture was made played a major role in deciding the puncture strength, along with the probe design.

Hence, while designing a structure for good puncture resistance it is important to consider the shape of the puncturing product and to design for puncture considering the side from which the puncture is expected.

4.5   Bond Strength Vs Puncture over Time

The average loads over time were plotted against puncture energy and puncture load in the odd numbered charts from 4.51 through 4.61. The maximum bond strength values over time were plotted against the puncture values in the even numbered charts from 4.52 through 4.62.

The puncture values were expected to decrease as the bond strength values increased as the adhesive is cured according to the hypothesis that lower bond strength will increase the puncture properties of the laminate. However, from the data it can be seen that bond strength values did not have an effect on the puncture resistance for most of the laminate samples. The regression analysis results between bond strength and puncture strength are given in Appendix N through Appendix Q. These results also confirm no change in puncture strength with a change in bond strength with very low R-square values except for Meyer rod 12 data. In Meyer rod 12 data (chart 4.59 and 4.60), it was observed that the puncture values actually showed an increasing trend with increasing bond strength for average and maximum load using ASTM probe tested from the foil side. This change in values did not happen when tested from the PET side. This helps to further confirm that the testing direction plays a key role in deciding the puncture strength and is not dependent on the adhesive coating weight.

The puncture values for hemispherical probe were always found to be lower than those values observed using ASTM probe design. The same observation was made while

85

testing the puncture properties for completely cured samples. A summary of results on

the puncture resistance is given in Table 4.6

Variables	Affects Puncture Resistance
Additive Type	No
Additive Percentage	No
Direction of Testing	Yes
Probe Design	Yes
Adhesive Type	No
Adhesive weight	No

Table 4.6: Summary on regression analysis of Puncture Resistance
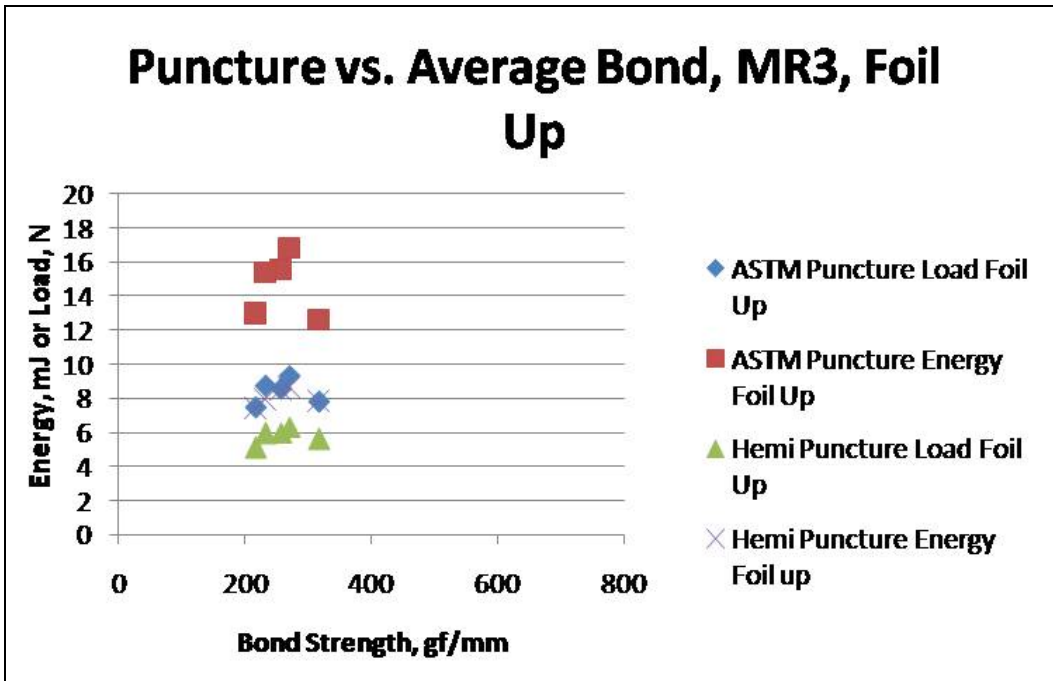
Chart 4.51: Puncture Vs Average Bond Strength- Meyer rod 3-Foil Up
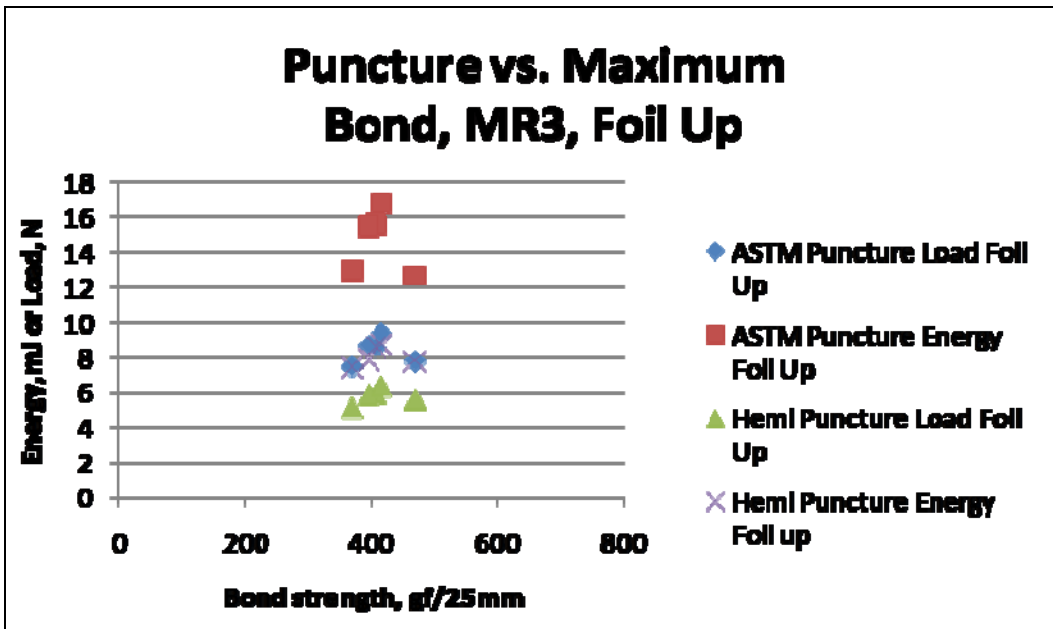
Chart 4.52: Puncture Vs Maximum Bond Strength- Meyer rod 3-Foil Up

87
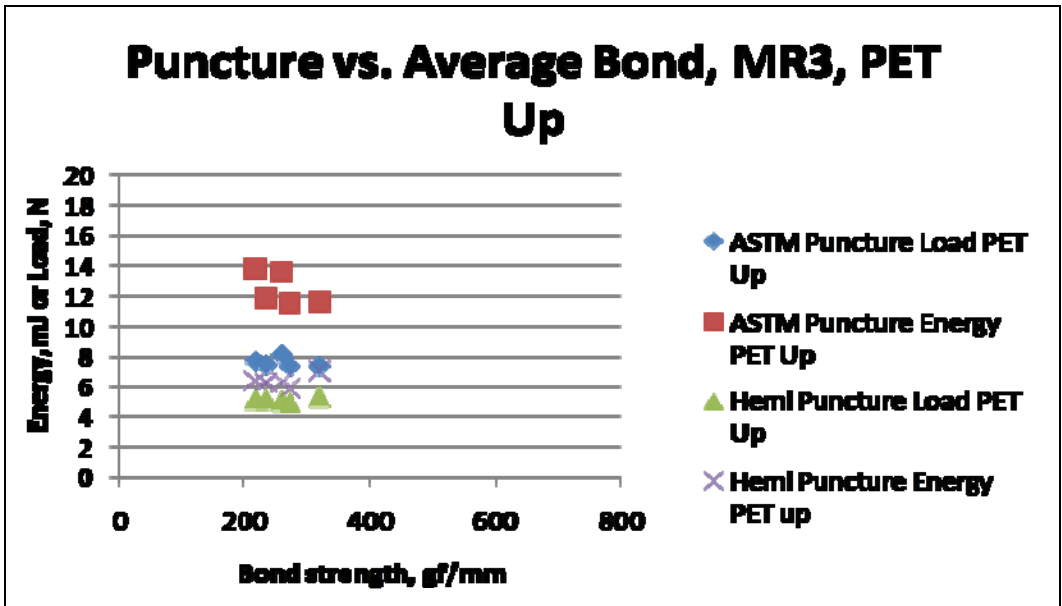
Chart 4.53: Puncture Vs Average Bond Strength- Meyer rod 3-PET Up
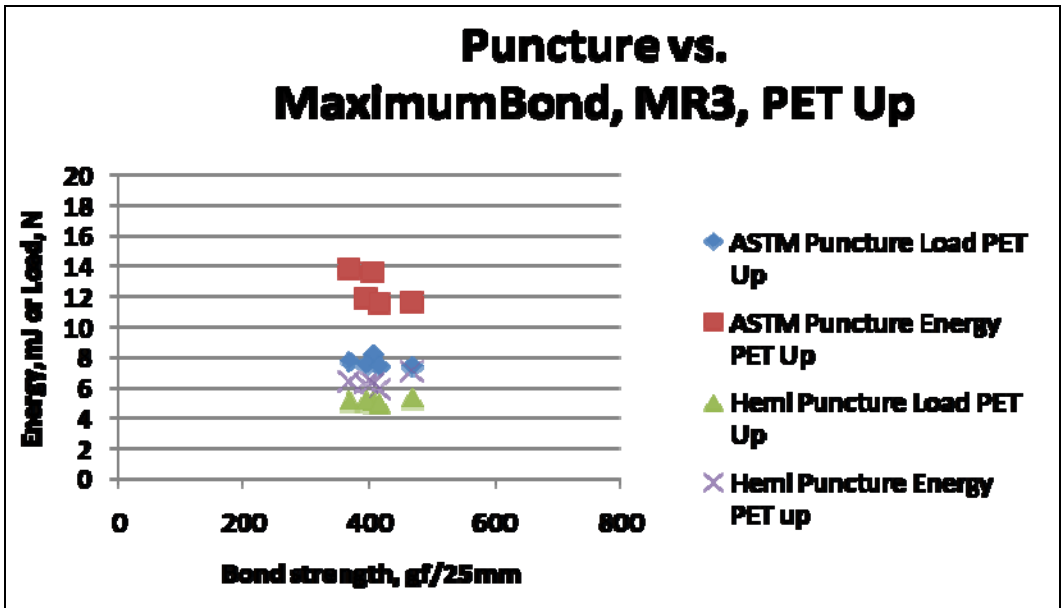
Chart 4.54: Puncture Vs Maximum Bond Strength- Meyer rod 3-PET Up
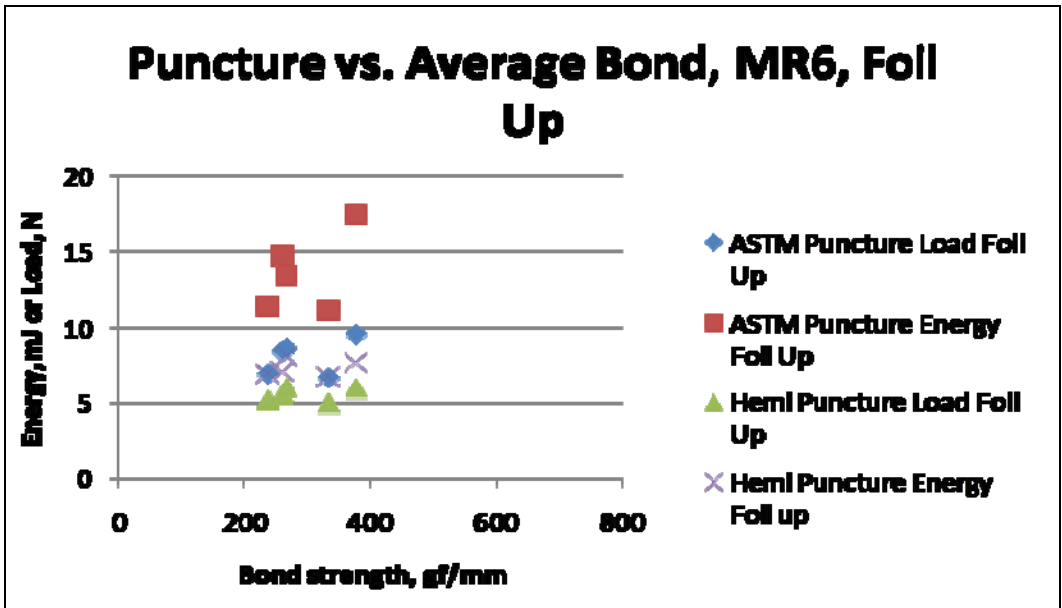
Chart 4.55: Puncture Vs Average Bond Strength- Meyer rod 6-Foil Up
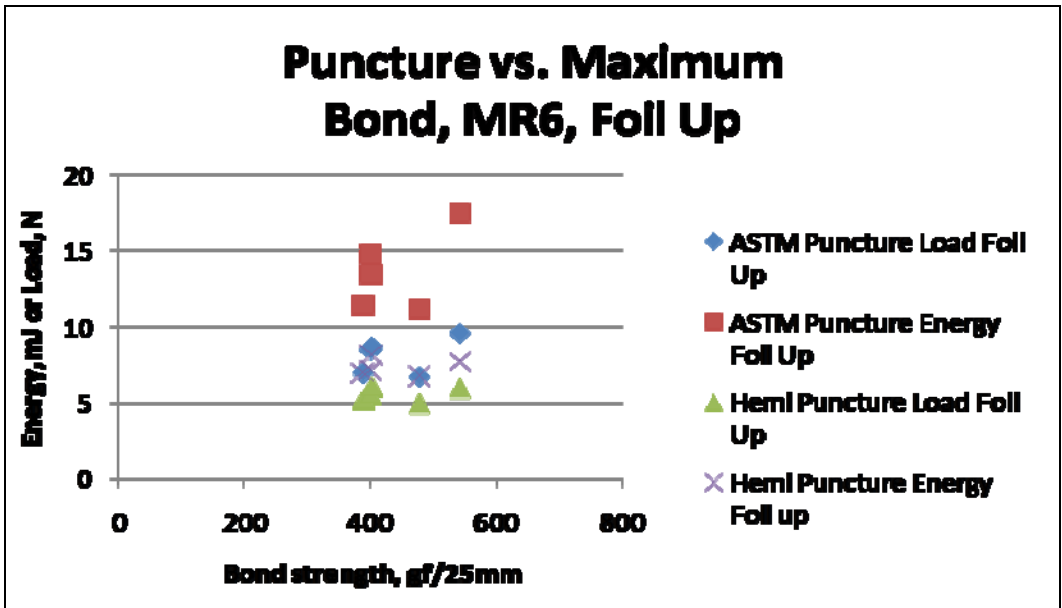
Chart 4.56: Puncture Vs Maximum Bond Strength- Meyer rod 6-Foil Up
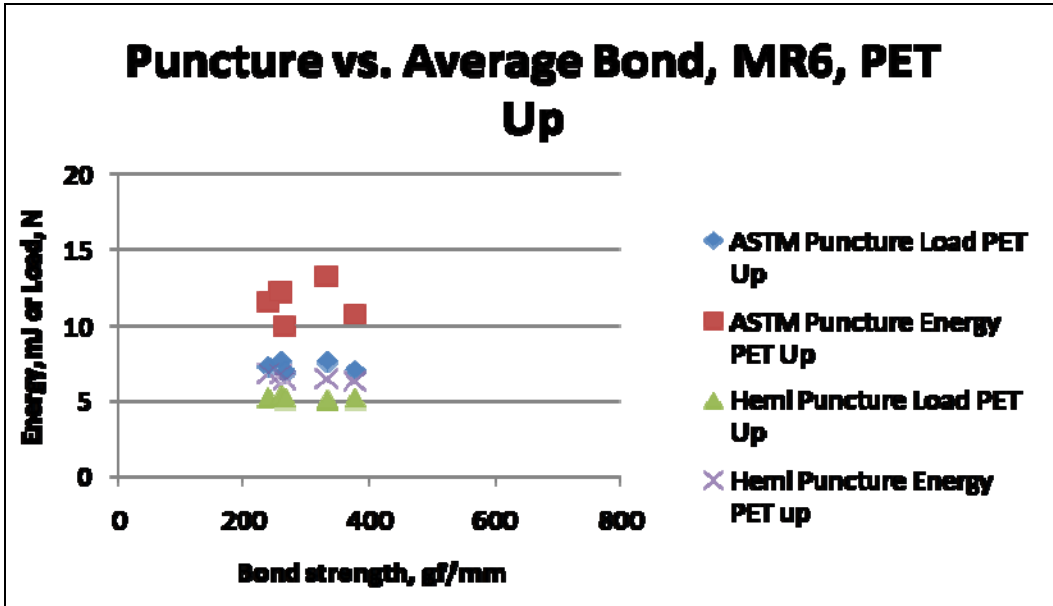
Chart 4.57: Puncture Vs Average Bond Strength- Meyer rod 6-PET Up
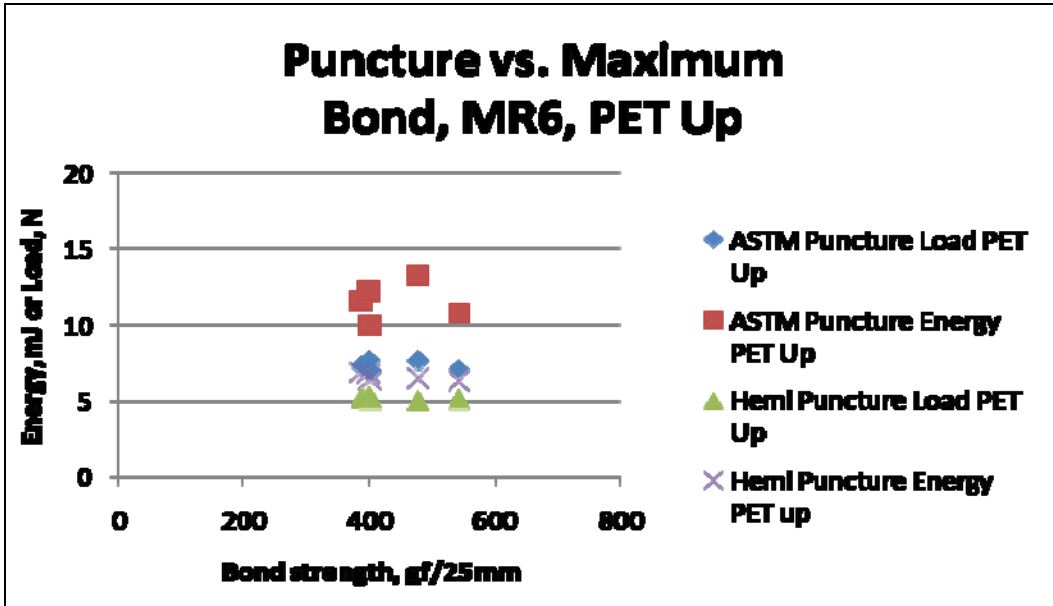
Chart 4.58: Puncture Vs Maximum Bond Strength- Meyer rod 6-PET Up
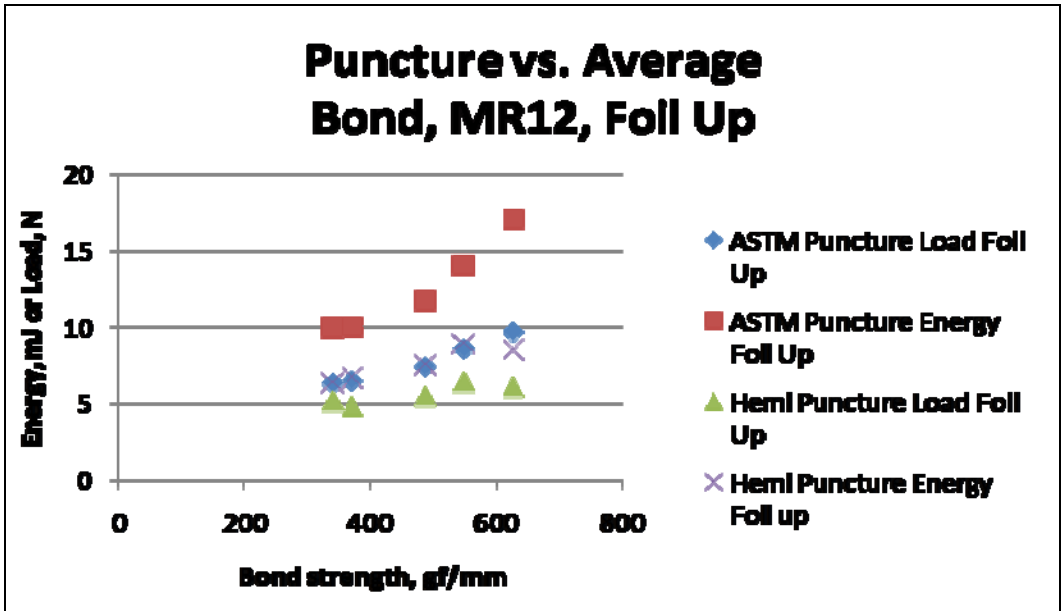
Chart 5.59: Puncture Vs Average Bond Strength- Meyer rod 12-Foil Up
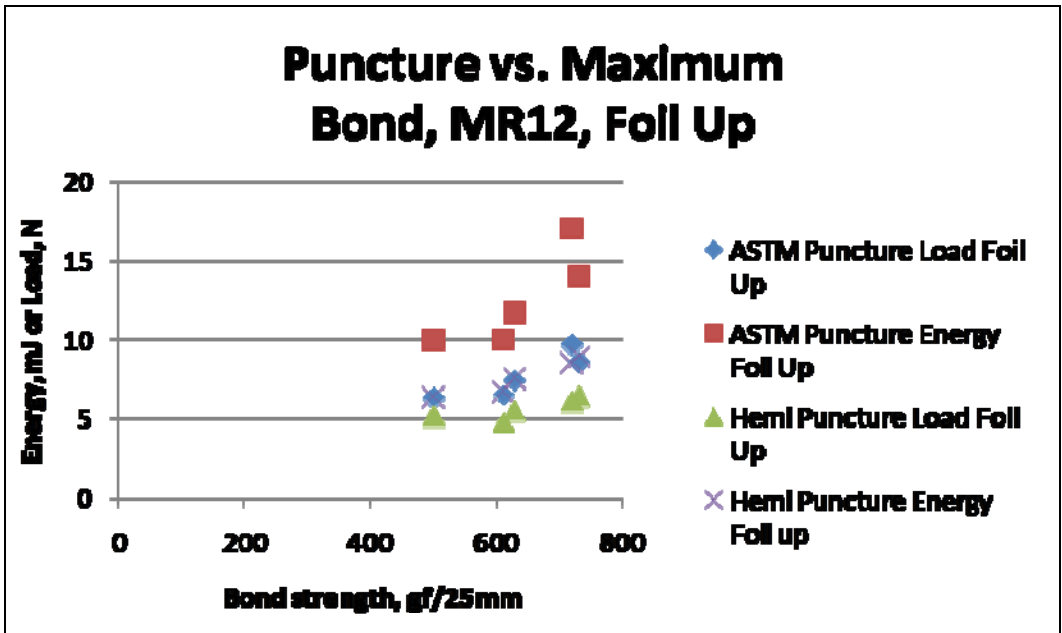
Chart 4.60: Puncture Vs Maximum Bond Strength- Meyer rod 12-Foil Up
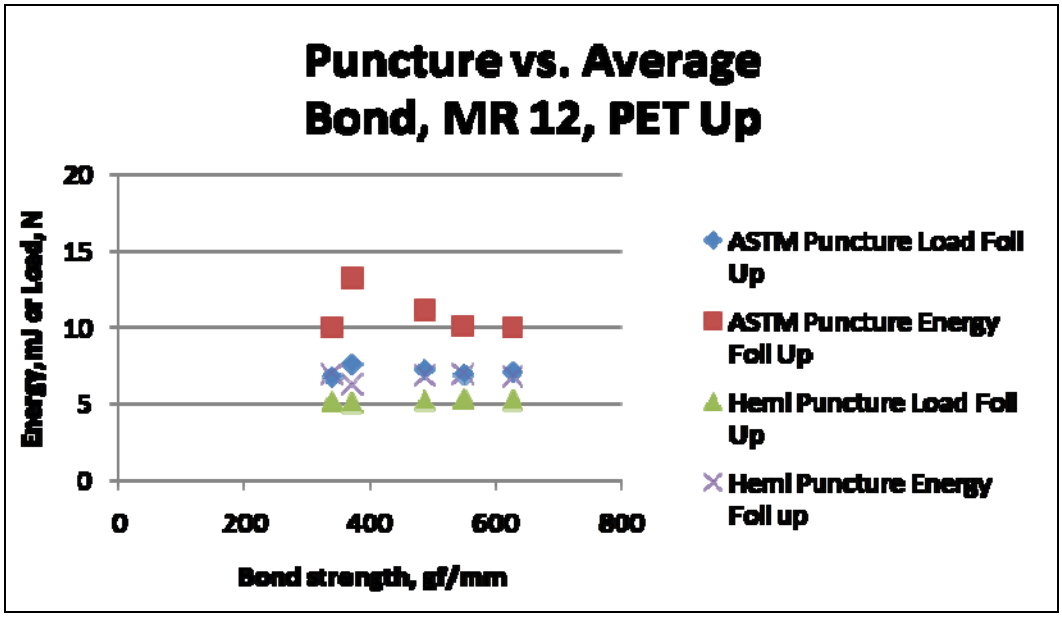
Chart 4.61: Puncture Vs Average Bond Strength- Meyer rod 12-PET Up
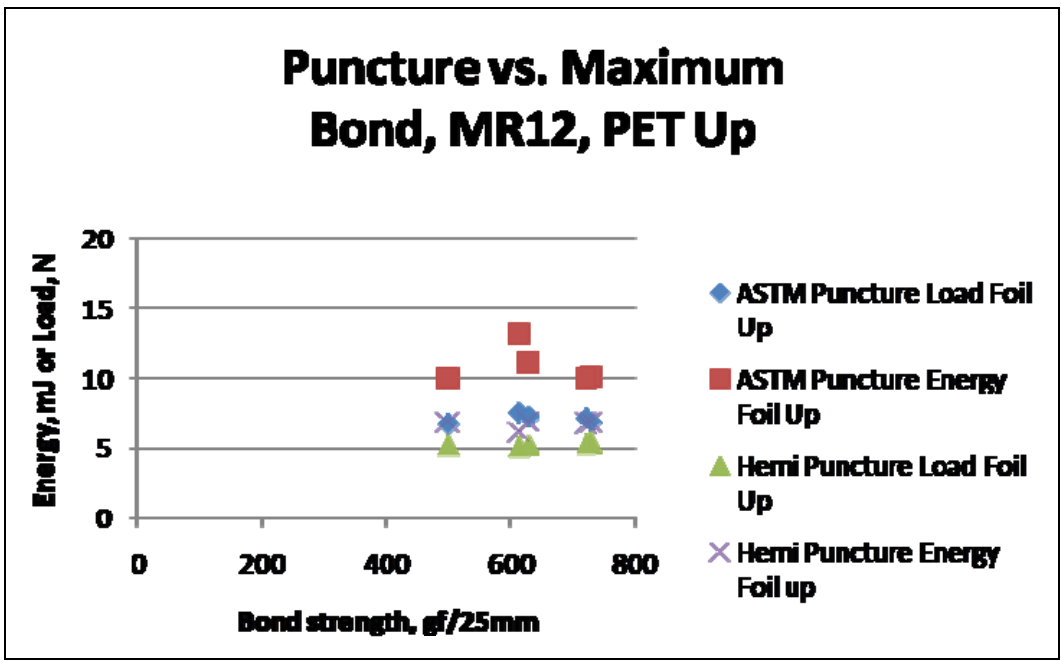
Chart 4.62: Puncture Vs Maximum Bond Strength- Meyer rod 12-PET Up

CHAPTER FIVE

5.   CONCLUSIONS AND RECOMMENDATIONS

The first part of this research was aimed to determine if the use of talc and polypropylene wax at different percent loadings as additives to polyurethane adhesives would control the bond strength in a flexible laminate. The second part of the objective was to assess how much of an effect does the bond strength play in deciding the puncture strength of the laminate.

The off-machine bond strengths show a gradual decrease in bond strength values as the loading percentage of the additive increases. However, this decrease in values is not observed in cured bond strengths which really define the performance of the laminate. In the cured bond strength results, the values are offset due to a change in the bond failure mechanism. At lower percent loadings of the additive, 0% to 5%, the failure mechanism is dominated by material break rather than at the adhesive-material interface. The bond strength values for these samples were found to be much lower than that of off-machine bond strength values. This tendency is not observed at higher percent loading of the additive. This happens because when the additive concentration in the adhesive mixture is lower than a certain level, ~5%, the adhesive bond strength is higher than the material strength. It was also observed that the break always happened in the PET layer. The cured bond strengths were found to increase quadratically reaching a maximum value around 10 to 15 percent loading of the additive and then decrease or level off due to the low bond strength values due to material destruction. These data points were avoided for data

93

analysis to get a clear idea of how the percentage loading of additives is affecting the bond strength values. The results avoiding data points which showed material break did not provide an increasing or decreasing trend to the values. The puncture resistance results showed no corresponding change in values with respect to the additive loading. It was also observed that with this set of tests, the puncture values depended mainly on two factors, the test direction and the probe design. The strongest material in the laminate, PET, was found to determine the puncture strength. The ASTM probe, which has a considerably larger area of contact with the laminate sample, was found to give higher puncture strength values compared to the hemispherical probe.

So, in order to further confirm that the bond strength value does not have a substantial effect on the puncture resistance of a foil/adhesive/PET flexible laminate, bond strengths were measured on samples as they are cured at regular intervals. The bond strength values were found to increase over time. The puncture values on these samples also showed no change with respect to the bond strength values. But, as the adhesive layer is getting cured, the mode of puncture changes, from two separate failures to a single material failure. This proves that, as the adhesive is cured, the laminate begins to act as a single material. This further confirms the findings in the first set of testing that the puncture resistance depends on the material properties of the components and the position of these materials in the structure, such as which layer is on the inside and which layer is on the outside. It can also be concluded that since the probe design affects the puncture results, careful selection of the probe is important. The probe design, in general

applications, should be selected depending on the size and geometry of the potential puncturing element.

Both foil and PET are brittle materials. So, as future work, it will be interesting to combine materials that are different, such as foil and polyethylene or PET and polyethylene. Furthermore, other properties of a flexible laminate like tear strength, impact strength, flexural strength etc. at different bond strengths should also be studied. A thorough exploration can be done in understanding the contribution of each component towards puncture resistance and the mechanism of puncture in a multi-component flexible structure.

In this work, bond strength values below 200 grams were not achieved. It will also be interesting to see what happens to puncture and other properties in the bond strength range between 0 and 200 grams.

APPENDICES

<center>APPENDIX A</center>

Regression results for Green Bond Strength

	Average Load		Maximum load	
	Regression equation	R-square	Regression equation	R-square
Adcote with Talc- MR 3	$412.6-21p+.59p^2$	66.09	$593.2-26.2p+.63p^2$	76.57
Adcote with Talc- MR 6	$646.1-45.6p+1.47p^2$	78.81	$826.5-61.4p+2.04p^2$	80.78
Adcote with Talc MR 12	$707.2-17.9p+.31p^2$	34.91	$858.7-26.8p+6p^2$	45.45
Adcote with PP wax- MR 3	$467.3-8.6p-.02p^2$	38.85	$636.5-12.7p+.16p^2$	51.71
Adcote with PP wax- MR 6	$668.7-32.2p+.94p^2$	80.13	$840.5-38.5p+1.19p^2$	74.49
Adcote with PP wax- MR 12	$717.52-34.6p+.95p^2$	68.25	$889.6-44.1p+1.34p^2$	70.67
Tycel with Talc- MR 3	$283.4+24.8p-1.34p^2$	46.1	$505.2+.16p-.23p^2$	18.63
Tycel with Talc- MR 6	$313.9+46.3p-2.46p^2$	67.48	$520+29.1p-1.67p^2$	60.23
Tycel with Talc- MR 12	$510.1+49.3p-2.49p^2$	58.03	$592.8+40.4p-1.85p^2$	45.63
Tycel with PP wax- MR 3	$256.7+16.4p-.97p^2$	35.6	$487.4+3.7p-.72p^2$	74.46
Tycel with PP wax- MR 6	$345.3+20.5p-1.24p^2$	50.45	$505.02+12.3p-1.05p^2$	77.9
Tycel with PP wax- MR 12	$497.6+10.2p-.96p^2$	64.22	$562.41+19.13p-1.43p^2$	76.07

<center>97</center>

Regression results for Cured Bond Strength with material failure

	Average load		Maximum load	
	Regression equation	**R-square**	**Regression equation**	**R-square**
Adcote with Talc-MR 3	$194.5+20.6p-.96p^2$	31.47	$340.1+26.4p-1.26p^2$	45.83
Adcote with Talc-MR 6	$217.8+36.12p-1.37p^2$	64.73	$445.7+32.4p-1.35p^2$	52.64
Adcote with Talc MR 12	$232.5+40.7p-1.56p^2$	34.27	$613.5+32.6p-1.44p^2$	42.45
Adcote with PP wax- MR 3	$191.2+21p-.49p^2$	55.04	$341.8+29.9p-1.04p^2$	63.77
Adcote with PP wax- MR 6	$231.3+70.6p-2.93p^2$	86.04	$455.1+53.2p-2.35p^2$	62.49
Adcote with PP wax- MR 12	$230.6+32.7p-.98p^2$	43.76	$545+3.49p-.002p^2$	4.17
Tycel with Talc-MR 3	$356.11+7.4p-.57p^2$	11.58	$624.4-12.2p+.13p^2$	44.53
Tycel with Talc-MR 6	$339.2+14.7p-.75p^2$	12.34	$675.8+2.9p-.63p^2$	36.89
Tycel with Talc-MR 12	$379.8+38.6p-1.74p^2$	27.54	$752.5+31.9p-1.81p^2$	72.91
Tycel with PP wax-MR 3	$362.1+34.7p-1.38p^2$	62.69	$609.9+8.5p-.35p^2$	9.89
Tycel with PP wax-MR 6	$375.5+48.1p-1.83p^2$	69.27	$694.1+11.1p-.49p^2$	8.39
Tycel with PP wax-MR 12	$367.1+60.7p-2.38p^2$	72.52	$761.4+5.7p-.12p^2$	5.35

Regression results for Cured Bond Strength without material failure

	Average load		Maximum load	
	Regression equation	**R-square**	**Regression equation**	**R-square**
Adcote with Talc-MR 3	526.82-15.35p	50.47	653.58-14.27p	38.00
Adcote with Talc-MR 6	552.33-7.87p	26.73	730.12-8.46p	23.04
Adcote with Talc MR 12	955.77-26.58p	46.74	912.94-9.45p	67.21
Adcote with PP wax- MR 3	215.50+11.21p	51.64	639.25-6.06p	17.20
Adcote with PP wax- MR 6	769.28-13.18p	50.70	961.4-18.43p	64.47
Adcote with PP wax- MR 12	1001.09-27.4p	70.51	1007.57-21.57p	58.84
Tycel with Talc-MR 3	499.34-8.28p	29.72	$519.74+10.35p-.74p^2$	42.61
Tycel with Talc-MR 6	489.80-5.92p	16.42	$469.51+42.15p-2.14p^2$	63.52
Tycel with Talc-MR 12	671.81-9.85p	17.79	$601.64+58.20p-2.79p^2$	88.21
Tycel with PP wax-MR 3	430.82+7.18p	27.25	$507.87+26.22p-1.01p^2$	36.25
Tycel with PP wax-MR 6	466.83+11.55p	36.92	$584.9+30.12p-1.20p^2$	31.24
Tycel with PP wax-MR 12	486.03+13.11p	33.70	$679.57+19.97p-.65p^2$	5.93

APPENDIX D

Puncture regression results- Hemispherical probe (PET side up) Quadratic Model

	Energy (mJ)		Load (N)	
	Regression equation	R-square	Regression equation	R-square
Adcote with Talc- MR 3	$7.09-.03p+.0006p^2$	17.73	$5.78+.003p+.0003p^2$	4.68
Adcote with Talc- MR 6	$6.99+.15p-.005p^2$	35.53	$5.69+.07p-.003p^2$	28.43
Adcote with Talc MR 12	$7.37+.04p-.001p^2$	2.65	$5.81+.03p-.001p^2$	4.27
Adcote with PP wax- MR 3	$6.83+.06p-.002p^2$	15.58	$5.64+.03p-.001p^2$	6.89
Adcote with PP wax- MR 6	$7.07+.05p-.0005p^2$	17.8	$5.76+.02p-.0006p^2$	3.43
Adcote with PP wax- MR 12	$6.9+.01p+.001p^2$	15	$5.65+.002p+.0004p^2$	6.58
Tycel with Talc- MR 3	$7.96+.03p-.001p^2$	.45	$6.4-.08p+.003p^2$	14.30
Tycel with Talc- MR 6	$7.05+.26p-.01p^2$	39.83	$6.2-.02p+.0005p^2$	5.33
Tycel with Talc- MR 12	$9.66-.33p+.01p^2$	45.00	$7.02-.19p+.007p^2$	51.55
Tycel with PP wax- MR 3	$7.83-.16p+.007p^2$	9.56	$6.37-.1p+.004p^2$	22.40
Tycel with PP wax- MR 6	$6.97+.07p-.003p^2$	10.89	$6.22-.06p+.001p^2$	23.13
Tycel with PP wax- MR 12	$9.14-.28p+.01p^2$	27.81	$6.88-.15p+.005p^2$	37.26

Puncture regression results- Hemispherical probe (PET side up) Linear Model

	Energy (mJ)		Load (N)	
	Regression equation	**R-square**	**Regression equation**	**R-square**
Adcote with Talc- MR 3	7.06+.05p	17.63	5.77+.008p	4.53
Adcote with Talc- MR 6	7.24+.05p	27.45	5.83+.01p	10.81
Adcote with Talc MR 12	7.42+.02p	2.42	5.86+.006p	1.98
Adcote with PP wax- MR 3	6.91+.03p	14.30	5.70+.004p	2.04
Adcote with PP wax- MR 6	7.09+.04p	17.71	5.79+.008p	2.94
Adcote with PP wax- MR 12	6.83+.04p	14.43	5.63+.01p	6.24
Tycel with Talc- MR 3	8.01+.007p	0.27	6.25-.02p	8.29
Tycel with Talc- MR 6	7.59+.04p	11.31	6.17-.01p	5.12
Tycel with Talc- MR 12	9.00-.06p	18.49	6.66-.05p	28.62
Tycel with PP wax- MR 3	7.49-.02p	1.71	6.19-.03p	14.39
Tycel with PP wax- MR 6	7.13+.003p	0.29	6.15-.03p	21.07
Tycel with PP wax- MR 12	8.65-.09p	19.53	6.64-.05p	29.01

Puncture regression results-Hemispherical probe (Foil side up) Quadratic Model

	Energy (mJ)		Load (N)	
	Regression equation	**R-square**	**Regression equation**	**R-square**
Adcote with Talc- MR 3	$8.28 - .33p + .02p^2$	13.75	$6.81 - .2p + .01p^2$	18.55
Adcote with Talc- MR 6	$9.33 - .03p - .002p^2$	8.84	$7.2 + .007p - .002p^2$	11.52
Adcote with Talc MR 12	$10.56 - .29p + .008p^2$	26.60	$7.55 - .09p + .002p^2$	15.32
Adcote with PP wax- MR 3	$8.65 + .19p - .007p^2$	12.59	$6.98 + .03p - .002p^2$	9.16
Adcote with PP wax- MR 6	$9.16 + .02p + .001p^2$	8.53	$7.13 - .01p + .0002p^2$	4.58
Adcote with PP wax- MR 12	$9.27 - .06p + .006p^2$	10.28	$7.06 - .003p - .0001p^2$	0.74
Tycel with Talc- MR 3	$8.93 - .19p + .008p^2$	7.60	$7.17 - .1p + .005p^2$	13.78
Tycel with Talc- MR 6	$15.39 - 1.19p + .05p^2$	63.56	$11.39 - .77p + .03p^2$	76.68
Tycel with Talc- MR 12	$8.7 + .1p - .001p^2$	12.45	$7.25 + .02p - .00009p^2$	8.61
Tycel with PP wax- MR 3	$9 + .16p - .005p^2$	18.02	$7.24 + .04p - .003p^2$	18.37
Tycel with PP wax- MR 6	$15.69 - 1.03p + .04p^2$	62.46	$11.47 - .73p + .03p^2$	79.13
Tycel with PP wax- MR 12	$8.84 + .0003p + .004p^2$	15.05	$7.29 - .03p + .002p^2$	7.18

APPENDIX G

Puncture regression results- Hemispherical probe (Foil side up) Linear Model

	Energy (mJ)		Load (N)	
	Regression equation	R-square	Regression equation	R-square
Adcote with Talc- MR 3	7.49-.01p	0.29	6.33-.01p	0.58
Adcote with Talc- MR 6	9.42-.06p	8.58	7.28-.02p	10.02
Adcote with Talc MR 12	10.18-.14p	24.13	7.43-.04p	13.85
Adcote with PP wax- MR 3	9.01+.04p	6.36	7.09-.11p	4.18
Adcote with PP wax- MR 6	9.10+.04p	8.34	7.12-.01p	4.51
Adcote with PP wax- MR 12	8.98+.06p	7.52	7.06-.01p	0.72
Tycel with Talc- MR 3	8.56-.04p	3.02	6.94-.01p	1.49
Tycel with Talc- MR 6	13.13-.29p	33.99	9.94-.19p	41.47
Tycel with Talc- MR 12	8.77+.07p	12.26	7.25+.02p	8.61
Tycel with PP wax- MR 3	9.27+.05p	12.54	7.38-.01p	7.81
Tycel with PP wax- MR 6	13.80-.28p	38.19	10.14-.2p	48.77
Tycel with PP wax- MR 12	8.64+.08p	13.85	7.18+.01p	4.23

Puncture regression results- ASTM probe (PET side up) Quadratic Model

	Energy (mJ)		Load (N)	
	Regression equation	R-square	Regression equation	R-square
Adcote with Talc- MR 3	$11.74+.13p-.008p^2$	6.92	$7.88+.02p-.002p^2$	7.16
Adcote with Talc- MR 6	$12.03-.07p+.002p^2$	1.93	$8.10-.05p+.09p^2$	7.59
Adcote with Talc MR 12	$12.30+.08p-.003p^2$	2.38	$8.18+.005p-.0006p^2$	2.63
Adcote with PP wax- MR 3	$11.80+.19p-.007p^2$	16.19	$7.98+.06p-.003p^2$	12.80
Adcote with PP wax- MR 6	$11.96+.09p-.001p^2$	8.33	$8.03+.04p-.001p^2$	7.41
Adcote with PP wax- MR 12	$12.28+.13p-.005p^2$	4.81	$8.17+.06p-.003p^2$	7.64
Tycel with Talc- MR 3	$10.29+.12p-.008p^2$	15.26	$7.49-.001p^2$	14.08
Tycel with Talc- MR 6	$10.85+.15p-.013p^2p^2$	42.41	$7.53+.08p-.008p^2$	42.07
Tycel with Talc- MR 12	$18.88-1.3p+.05p^2$	67.65	$16.50-1.57p+.06p^2$	27.27
Tycel with PP wax- MR 3	$10.32-.01p-.001p^2$	4.04	$7.46+.04p-.003p^2$	9.24
Tycel with PP wax- MR 6	$10.22+.11p-.008p^2$	7.32	$7.29+.17p-.011p^2$	36.38
Tycel with PP wax- MR 12	$18.8-1.2p+.04p^2$	67.07	$16.48-1.45p+.05p^2$	25.33

APPENDIX I

Puncture regression results- ASTM probe (PET side up) Linear Model

	Energy (mJ)		Load (N)	
	Regression equation	R-square	Regression equation	R-square
Adcote with Talc- MR 3	12.12-.03p	1.76	7.98-.02p	5.22
Adcote with Talc- MR 6	11.95-.04p	1.82	8.04-.02p	7.11
Adcote with Talc MR 12	12.47+.02p	1.12	8.21-.007p	2.12
Adcote with PP wax- MR 3	12.16+.05p	10.01	8.10+.01p	5.86
Adcote with PP wax- MR 6	12.03+.06p	8.21	8.09+.02p	6.31
Adcote with PP wax- MR 12	12.53+.02p	1.90	8.30+.004p	0.54
Tycel with Talc- MR 3	10.70-.05p	7.76	7.55-.02p	12.95
Tycel with Talc- MR 6	11.50-.11p	27.89	7.92-.07p	30.60
Tycel with Talc- MR 12	16.62-.4p	46.95	13.62-.41p	16.15
Tycel with PP wax- MR 3	10.39-.04p	3.89	7.6-.02p	4.68
Tycel with PP wax- MR 6	10.60-.04p	3.25	7.85-.05p	13.79
Tycel with PP wax- MR 12	16.74-.38p	47.30	13.87-.40p	15.96

APPENDIX J

Puncture regression results- ASTM probe (Foil side up) Quadratic Model

	Energy (mJ)		Load (N)	
	Regression equation	**R-square**	**Regression equation**	**R-square**
Adcote with Talc- MR 3	$16.54+.07p-.0008p^2$	1.23	$9.86+.007p-.001p^2$	0.80
Adcote with Talc- MR 6	$16.79-.19p+.008p^2$	0.80	$10.02-.56p+.002p^2$	3.39
Adcote with Talc MR 12	$18.89-.59p+.02p^2$	6.24	$10.44-.16p+.006p^2$	5.28
Adcote with PP wax- MR 3	$16.18+.76p-.04p^2$	25.06	$9.81+.14p-.008p^2$	28.10
Adcote with PP wax- MR 6	$17.98+.17p-.008p^2$	1.73	$10.32+.02p-.003p^2$	18.32
Adcote with PP wax- MR 12	$19.32+.04p-.007p^2$	4.88	$10.62-.008p-.003p^2$	24.38
Tycel with Talc- MR 3	$16.55-.23p+.008p^2$	2.38	$10.35-.13p+.004p^2$	7.38
Tycel with Talc- MR 6	$15.87-.29p+.015p^2$	3.73	$10.24-.15p+.007p^2$	7.60
Tycel with Talc- MR 12	$16.02+.17p-.006 p^2$	1.41	$10.26+.019p-.0008p^2$	0.16
Tycel with PP wax- MR 3	$15.64+.26p-.013 p^2$	2.86	$10.02+.012p-.002p^2$	7.50
Tycel with PP wax- MR 6	$15.43+.21p-.007 p^2$	5.36	$10.02+.03p-.002p^2$	11.64
Tycel with PP wax- MR 12	$16.31+.57p-.02 p^2$	16.27	$10.36+.11p-.005p^2$	8.37

APPENDIX K

Puncture regression results- ASTM probe (Foil side up) Linear Model

	Energy (mJ)		Load (N)	
	Regression equation	R-square	Regression equation	R-square
Adcote with Talc- MR 3	16.60+.06p	1.22	9.92-.009p	0.64
Adcote with Talc- MR 6	16.22-.02p	0.12	9.91-.02p	2.92
Adcote with Talc MR 12	17.18-.08p	1.55	10.02-.03p	2.52
Adcote with PP wax- MR 3	18.02+.03p	0.33	10.21-.02p	4.41
Adcote with PP wax- MR 6	18.35+.02p	0.26	10.47-.04p	14.66
Adcote with PP wax- MR 12	19.65-.09p	4.09	10.75-.06p	22.87
Tycel with Talc- MR 3	15.99-.06p	1.52	10.05-.04p	5.33
Tycel with Talc- MR 6	14.81+.03p	0.49	9.76-.01p	0.46
Tycel with Talc- MR 12	16.43+.05p	0.99	10.32-.001p	0.01
Tycel with PP wax- MR 3	16.28+.002p	0.00	10.13-.03p	6.41
Tycel with PP wax- MR 6	15.80+.06p	3.50	10.14-.02p	8.02
Tycel with PP wax- MR 12	17.39+.14p	8.80	10.63+.001p	0.02

APPENDIX L

Puncture regression results- Time based Tycel with 20% Talc-Foil side up

	Quadratic model		Linear model	
	Regression equation	R-square	Regression equation	R-square
ASTM probe- MR 3	$12.03+1.86t-.21t^2$	30.28	$12.65+.93t$	28.09
ASTM probe - MR 6	$11.14+1.07t+.04t^2$	38.83	$11.02+1.25t$	38.76
ASTM probe MR 12	$8.65+2.05t-.13t^2$	36.54	$9.05+1.45t$	36.07
Hemi probe- MR 3	$7.28+.62t-.08t^2$	29.89	$7.54+.24t$	25.10
Hemi probe - MR 6	$6.55+.70t-.10t^2$	24.50	$6.86+.25t$	19.19
Hemi probe - MR 12	$6.53+.25t+.05t^2$	28.53	$6.39+.46t$	28.07

APPENDIX M

Puncture regression results- Time based-Tycel with 20% Talc PET side up

	Quadratic model		Linear model	
	Regression equation	**R-square**	**Regression equation**	**R-square**
ASTM probe- MR 3	$12.65+.28t-.19t^2$	26.41	$13.23-.58t$	22.54
ASTM probe - MR 6	$12.13-.57t+.05t^2$	10.56	$11.96-.33t$	10.11
ASTM probe MR 12	$12.67-.71t+.02t^2$	19.28	$12.60-.60t$	19.23
Hemi probe- MR 3	$7.04-.81t+.21t^2$	22.31	$6.41+.14t$	4.78
Hemi probe - MR 6	$6.35+.19t-.04t^2$	3.36	$6.49-.009t$	0.09
Hemi probe - MR 12	$6.33+.38t-.06t^2$	12.02	$6.52+.10t$	7.36

Puncture (load at break) Vs Bond regression results- Time based Foil side up

	Average Load		Maximum Load	
	Regression equation	**R-square**	**Regression equation**	**R-square**
ASTM probe- MR 3	238.93+2.55load	0.25	402.88+.98load	0.04
ASTM probe - MR 6	143.30+18.75load	14.94	266.11+21.79load	15.87
ASTM probe MR 12	-170.58+83.72load	97.21	187.80+58.49load	77.91
Hemi probe- MR 3	273.64+47.13load	8.43	284.92+21.78load	7.05
Hemi probe - MR 6	226.03+12.47load	1.03	362.54+14.41load	1.08
Hemi probe - MR 12	-438.71+163.85load	77.92	-24.26+118.91load	67.38

Puncture (energy at break) Vs Bond regression results- Time based Foil side up

	Average Load		Maximum Load	
	Regression equation	**R-square**	**Regression equation**	**R-square**
ASTM probe- MR 3	307.68-3.23energy	2.28	469.51-3.98energy	3.74
ASTM probe - MR 6	132.51+11.89energy	27.69	249.95+14.07energy	30.56
ASTM probe MR 12	-4.86+38.25energy	93.39	314.27+25.87energy	70.15
Hemi probe- MR 3	91.41+20.98energy	8.61	293.66+14.59energy	4.5
Hemi probe - MR 6	231.44+8.66energy	0.80	374.41+9.24energy	0.72
Hemi probe - MR 12	-269.58+98.17energy	86.08	50.46+77.58energy	88.26

APPENDIX P

Puncture (load at break) Vs Bond regression results- Time based PET side up

	Average Load		Maximum Load	
	Regression equation	**R-square**	**Regression equation**	**R-square**
ASTM probe- MR 3	606.33-45.37load	14.82	777.20-48load	17.94
ASTM probe - MR 6	373.11-10.65load	0.31	586.23-19.65load	0.84
ASTM probe MR 12	735.37-36.57load	0.99	365.98+38.30load	1.78
Hemi probe- MR 3	-634.95+175.61load	28.91	-573.21+193.07load	37.78
Hemi probe - MR 6	2813.97-488.72load	63.33	3119.05-519.35load	56.40
Hemi probe - MR 12	-3775.29+815.78load	52.55	-2423.29+587.73load	44.78

APPENDIX Q

Puncture (energy at break) Vs Bond regression results- Time based PET side up

	Average Load		Maximum Load	
	Regression equation	**R-square**	**Regression equation**	**R-square**
ASTM probe- MR 3	510.97-20.09energy	34.58	669.82-20.74energy	39.83
ASTM probe - MR 6	274.9+1.75energy	0.15	438.22+.36energy	0.00
ASTM probe MR 12	936.08-42.39energy	22.63	766.12-11.7energy	2.83
Hemi probe- MR 3	-48.92+48.51energy	27.53	65.62+54.20energy	37.15
Hemi probe - MR 6	1400.48-168.09energy	63.93	1617-178.63energy	56.93
Hemi probe - MR 12	-514.99+147.7energy	12.43	487.13+22.63energy	0.48

REFERENCES

[1]   Handbook of Package Engineering, Third Edition by Joseph F. Hanlon, Robert J. Kelsey, Halley F. Forcinio; CRC Press 1998

[2]   Fundamentals of Packaging Technology, Second Edition by Walter Soroka; Institute of Packaging Professionals 1999

[3]   Converting for Flexible Packaging by Adolph Miller; Technomic Publishing Company Inc. 1994

[4]   Plastics in Food Packaging- Properties, Design and Fabrication by William E. Brown; Marcel Dekker Inc. 1992

[5]   Plastics Packaging- Properties, Processing, Applications and Regulations 2nd Edition by Susan E. M. Selke, John D. Culter, Ruben J. Hernandez; Hanser 2004

[6]   Converting in Packaging (PKGSC 430) class notes: Dr. Darby

[7]   Puncture resistance of flexible materials: S. R. Agarwal. Technical Engineering- Methods, Research, Testing; June 1973

[8]   Puncture resistance of flexible by S. R. Agarwal, U. S. Kumta. Technical Engineering- Methods, Research, Testing; October 1974

[9]   Pinhole resistance of flexibles- Part 1: New methods measure puncture, flexing and abrasion in films and laminates by K.H. Hu and J. B. Breyer; Technical Engineering- Methods, Research, Testing; December 1971

[10]   Understanding puncture resistance and perforation behavior of packaging laminates by Jakob Lange, Haroun Mokdad and Yves Wyser; Journal of Plastic film and Sheeting, Vol. 18- October 2002

[11]   ASTM F 1306-90 (Reapproved 2002): Standard Test Method for Slow Rate Penetration Resistance of Flexible Barrier Films and Laminates

[12]   ASTM F 904-98: Standard Test Method for Bond Strength of Flexible Barrier Materials

[13]   Manipulating adhesive bond strength in flexible laminates by Ian Wood