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THE EFFECTS OF THE CHEMICAL STRUCTURE OF POLYURETHANE BINDERS ON THE MECHANICAL PROPERTIES OF ADHESIVELY BONDED POLYESTER NONWOVEN FABRICS

A Dissertation

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Degree

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Dong-Hwa Shin

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ABSTRACT

The purpose of this study was to synthesize totally amorphous polyurethanes with glass transition temperatures [T_g] below -50° C in order to achieve flexibility below the freezing temperature (0° C). This was used as binder for polyester nonwoven fabrics, and the effects of the chemical structures of the binder on the mechanical properties of the fabrics were investigated.

Based upon experimentation, the reactants selected in order to synthesize the 100% amorphous polyurethane binders were hexamethylene diisocyanated-extended polyproplene glycol with trimethylol propane [crosslinking agent] and stannous octoate [catalyst]. Methylene chloride was added to the reactants to lower the exothermic heat of reaction and to avoid a substantial increase in viscosity by the chain-extending reaction. Again, based upon experiments, the standard conditions of curing time (48 hours) and temperature (60° C) were determined to produce satisfactory polymer films.

For web formation and bonding, the fibers were carded to form a unidirectional web and spray bonded with five different degrees of crosslinked polyurethane binders and three different amounts of binder add-ons. Various techniques were utilized to characterize and examine the polyurethane films. The degree of crosslinking was

determined by the swelling technique, and differential scanning calorimetry monitored the T_g of the binders. Intrinsic viscosity and differential refractive index were measured for the polymer films to ensure the replication of polyurethane synthesis each time.

The mechanical performance of nonwoven fabrics was analyzed using the Instron tensile tester to investigate the stress-strain behavior of the final product. The relationship between the binder properties with the chemistry of polyurethane and the effects of binder add-ons were also investigated. In the lower binder add-on region, the density of crosslink in the binder played an important role for an increase in tensile strength; however, in the highly crosslinked binder region, it was observed that the effect of binder modulus on fabric modulus became smaller with increasing binder techniques. The optimum mechanical properties were obtained at the ratio of PPG to TMP of 0.7 to 0.3 with 50% binder add-on.

Unlike conventional latex binders, the advantage of this particular polyurethane indicated that the binder toughness did not affect the flexibility of the nonwoven fabrics, due to their 100% amorphous nature. Furthermore, this binder maintained flexibility in the extremely cold region because the T_g for the linear polyurethane was -58^{o} C; the T_g for the crosslinked polyurethane film was also

low, ranging from -49 to -52^{o} C. As a result of the chemical structure of this polyurethane, a large number of H-bonding provide inter- and/or intra-molecular forces that greatly enhance the adhesive and cohesive abilities of this binding polymer. The apparent disadvantage of the use of this polyurethane as a binder was its high viscosity, such that a solvent had to be employed to dilute the solution in order to effectively disperse the binder onto the fabric.

Future studies indicated by the above results should include the synthesis of aqueous polyurethanes, binder adhesion and cohesion investigations, and the development of new research areas in composites for polyurethanes.

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CHAPTER I

INTRODUCTION

Nonwoven fabrics, relative newcomers to the textile field, present great promise and challenge for the industry due to significant economic advantages and virtually endless specialized uses. The definition of nonwoven fabrics has long been an area of considerable debate and discussion. The following working definition was provided by Truelove (104):

> **Nonwovens are a manufactured sheet, web, or batt of directional- or random-oriented fibers, produced and bonded by mechanical, chemical, or physical means. The fibers may be of natural or man-made origin. They may be taple or continuous filaments or be formed in situ.**

Nonwoven fabrics are now used everywhere. The exact date that nonwovens were first produced is not well established, since the methods of producing them are so varied. Historically, the first nonwoven paper was made by Ts' ai Lun in AD 105 (110). This technique of fabric design has been with mankind for literally hundreds of years. However, recent usage of nonwoven materials has become quite diversified and much more extensively applied beyond the manufacture of paper (33). For example, on the farm, milk is processed through nonwoven filters; gardens exist based on a system of geotextile nonwoven fabric channels without the normal use of soil; aircraft fuel

tanks are made of three-dimensional nonwovens; hospitals operate more efficiently and economically using disposable biomedical items; domestically, baby diapers, sanitary napkins, wipes, and tea bags are widely used; protective clothing is employed for factory personnel using heat and/or chemically resistant nonwoven materials; insulating materials, floor and wall coverings, and even building foundations have been developed for construction purposes; the United States low-earth orbit shuttle is partially covered by heat-reflecting nonwoven tiles; the automotive industry has shown considerable interest in nonwovens, laminated and coated fabrics for automobile carpeting and mats, where they offer greater bulk/weight economically (80).

The rapidly increasing acceptance of nonwovens in a wide variety of end-use products is creating a demand for highly specialized technology and advanced raw materials (113). A report issued by Frost and Sullivan Inc. (29) concluded that the nonwoven fabric market in the U.S.A. would grow 60% in real terms during the period 1978-1988. Indeed, their estimate has proven to be even a bit conservative - the real growth approaches 85-95% (53).

Modern nonwoven fabrics are generally customized to perform a specific function. The large volume potentials for nonwovens are as reinforced films and composites that

could be used in aircraft, missiles, space craft, and satellites (88). Nonwoven fabrics are preferable for many purposes because they are quite adequate and less expensive in disposable uses, or in other situations, they are more durable and lighter (26).

The biggest problem in trying to use nonwovens in the apparel area is their papery appearance and lack of draping capacity (65). In fact, most apparel applications of textiles require fabric with low bending rigidity. Generally, the characteristics of the fabric must be chosen as a function of its use. The properties of both woven and nonwoven fabrics are determined by a complex interaction between fiber properties, structural geometry, and- particularly in the case of nonwovens-specific bonding properties (28). Woven fabrics can accomodate a wide variety of small deformations through yarn bending, angle of intersection, and tightness of weave, etc. In contrast, deformations in nonwoven fabrics are restricted because the whole structure is a cohesively bonded network (66). A problem with adhesive-bonded nonwovens is the usual positive correlation between the tensile strength and the stress modulus. The stronger the fabric, the stiffer it becomes. To overcome this, flexible soft binders are being developed (12). In fact, numerous studies have been conducted on adhesive-bonded nonwovens to investigate those

factors that influence strength and stiffness properties and to discern the working relationship between these two properties (8, 59).

Present Study

Nonwoven textile fabrics using staple fibers are normally made in two separate and distinct steps: a) web formation and b) bonding of the fibers. The web structure used in the present study is a unidirectional web. Polyester fibers of 1.5 denier with regular tenacity were chosen. This polyester fiber is highly crystalline and thermally/chemically resistant. It is also very versatile fiber which can be commercially engineered for many specific end uses. For web formation and bonding, the fibers were carded to form a web and spray-bonded with different degrees of crosslinked polyurethane binders.

The initial purpose of this study was to synthesize 100% amorphous polyurethane binders for nonwoven fabrics in order to achieve flexibility below the freezing temperature. In this regard, the selection of the proper monomers furnishes the important basis which creates a product for specific performance (112). Additional parameters [such as variations in molecular weight and/or degree of crosslinking] can then be used to further improve the performance of a particular combination of monomers.

If a softer type of product is desired, a binder with a relatively low glass transition temperature [T_g] should be selected. In the current research, polyurethane binders were produced from two difunctional prepolymers [polyoxypropylene glycol and hexamethylene diisocyanate], a multifunctional crosslinking agent [trimethylol propane], and a catalyst [T-9]. Operationally, the solvent [methylene chloride] was used to dilute the polymers to lower their viscosity. Then, using a spraying method, a series of polyurethane binders with different amounts of crosslinking agent compositions was applied to polyester webs. The various weight percentages of binders applied to the fabric provided the route by which to examine the relationship between fabric and binder strength. In addition, basic studies on the catalysis, kinetics, and mechanisms of polyurethane reactions leading to nonwoven binders, as well as studies of structure-property relationships were included to permit urethane polymers to be designed to meet desired end-use properties. However, the research empahsis was based largely on experimental and empirical.

The amount and distribution of binder throughout the fibrous webs are important variables affecting the resultant physical properties and quality of nonwoven fabrics (88). In this study, the stress-strain behavior of

the polyurethane binder [as applied to polyester nonwoven fabrics] were mechanically tested, and the results were analyzed and interpreted.

There are a number of additional factors which control the tensile and flexural of nonwoven fabrics. These include surface tension, viscosity, fiber-binder compatibility, etc. These were not addressed in the present study, but they were recognized as factors to be included in more should be fruitful areas of extensive investigation of future process-engineering studies.

Objectives of Present Study

The purpose of the present study was to investigate the effects of the chemical structure of the polyurethane [polyoxypropylene glycol/hexamethylene diisocyanate based] binders on the mechanical properties of polyester nonwoven fabrics. The study was divided expressly into three tasks:

1) Synthesize and characterize a series of 100% amorphous polyurethane binder. In order to formulate totally amorphous polymer binders, combinations of two monomers with a crosslinking agent and a catalyst were carefully selected. Both linear and crosslinked polyurethane films were made to examine the effects of their chemical structures on the binder properties. The degree of crosslinking were determined by the swelling

technique and differential scanning calorimetry [DSC] monitored the glass transition temperatures [T_g] of binders. Intrinsic viscosity and differential refractive index were measured for the polymer films to ensure the replication of polyurethane synthesis each time. Curing temperature and time were examined, as were binder spraying methods, to optimize processing parameters.

2) Analyze the mechanical performance of nonwoven fabrics using the Instron tensile tester to investigate the stress-strain behavior of the final product: such as tenacity, elastic modulus, percent elongation at T_{max}, tear strength, and energy-to-break.

3) Relate the binder characteristics to the nonwoven fabric mechanical properties. The relationship between the binder properties with the chemistry of polyurethane and the effects of binder add-ons were also studied.

CHAPTER II

REVIEW OF LITERATURE

Nonwovens

One of the unique and significant attributes of nonwovens is the almost unlimited variability of materials and methods for creating new and improved products specifically engineered to customers requirements. The wide variety and choice of fiber raw materials, the scope and versatility of different bonding techniques, the many options in finishing processes, and the opportunity for added value through new and sophisticated converting techniques have brought about new uses in areas previously closed to nonwovens.

The versatile and complex nature of the nonwovens industry is clearly shown in Figure 1 (32). There is a whole range of interesting areas for nonwovens. It is one of the most exciting and yet will be one of the most volatile segments of the textile industry in the years ahead (18).

History

The exact date when nonwovens were invented is difficult to establish because they evolved from so many different directions over time. Nonwoven-like materials existed in nature long before humans learned how to make

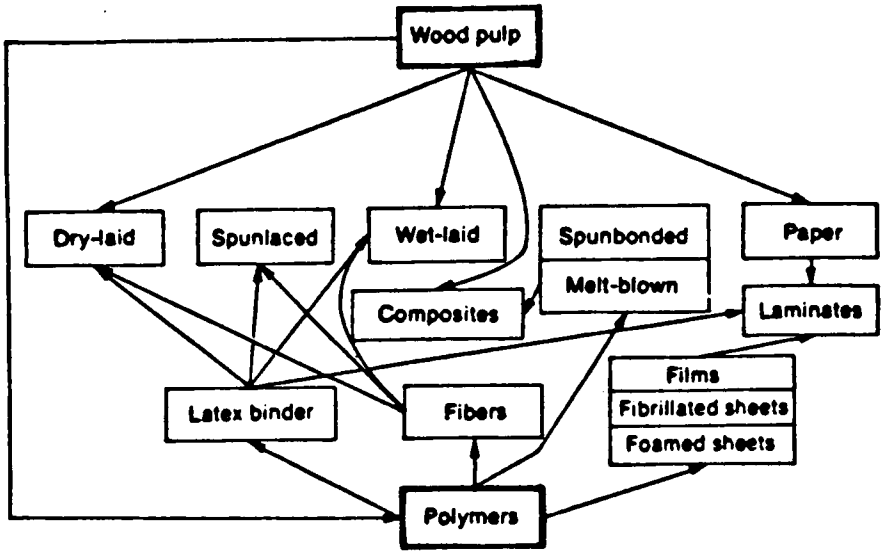


Figure 1. The Diverse and Interrelated Origins of the Nonwovens Industry as Related on a Flow Diagram.

them (111). These include the nests of many birds; the spun-bonded-like cacoon produced by the silkworm; and the paper-like hornet's nest.

Fibrous network structures were made from papyrus by the ancient Egyptians as early as 2400 B.C. (109). Ts'ai Lun made some papers using fiber from fish nets in A.D. 105. And paper-like cloths were being made from the inner bark of trees before recorded history.

The industrial process of paper making was first introduced in France by Henry and Searly Fourdrinier in 1803 (62). Bellford is credited with the invention of carded nonwovens in 1853 and was issued a British Patent. Tyas (105) claimed that the production of needle looms was established around 1870 by William Bywaters Ltd. Nottebohm (69) cited a German patent dated August 28, 1928, which claimed the production of a fleece in combination with a glued web to serve as shoe reinforcing materials. According to Batra (6), laboratory and pilot scale production of nonwovens started in the 1930's. Perhaps the first to make a material somewhat similar to a spunbonded nonwoven was Owens Corning Company, which produced glass insulation in 1937. Shearer and Millman (89) put the industrial production of bonded-fiber nonwoven fiber fabrics in commercial quantities around 1942.

The exact date when nonwovens were invented cannot be

determined. There is no doubt, however, about their recent rapid rise in utility over a broad range of applications.

Fibers for Nonwovens

One of the reasons nonwovens are unique is that various types of fibers are available for their construction. They can be natural or synthetic; they can vary in length from one mm to a continuous length; they can be straight or crimped; they can be unicomponent, bicomponent, or biconstituent; they can be low melting, high melting, or not melt at all. They can also be resistant or nonresistant to chemicals, temperature variations, abrasion, and ultraviolet light. They can be absorbent or repellent, weak or strong, stiff or flexible, elastic or nonelastic (111).

Natural Fibers: Cotton is used for products which need absorbency. Jute is commonly used as a backing for carpet and as insulation in automobiles. Wood pulp is used because of its low cost and absorbency. The inner portion of diapers and the absorbent layer from spunlaced operating-room gowns are made of wood pulp (33).

Man-made Fibers: Most nonwoven materials are constructed of man-made fibers. These fibers are moderate in cost, require no cleaning, and have uniform physical characteristics. They are also readily available in a

range of fiber types, diameters, staple lengths, crimp, and cross-sections.

Polyester is a principal fiber now being used. This fiber offers low cost, high strength, abrasion resistance, resilience, thermoplastic and hydrophobic properties, and retention of whiteness (34). Polyester is used in interfacing, window shades, diaper cover stock, and computer floppy disks. Rayon is valued for its absorbency and is used in liners, wipes, and surgical dressings (114). Polypropylene fiber is exceptionally low in cost, thermoplastic, hydrophobic, oleophilic, inert and soft, with high strength, abrasion resistance, and resilience (64). These characteristics have contributed to a rapid increase in the rate of consumption of this latter fiber. Typical end uses include diaper cover stock, geotextiles, filters, oil-spill scavenger devices, and indoor-outdoor carpets. Polyolefin is often used for mailing envelopes, work clothing, and house wrap. Tyvek® (DuPont) is becoming very important in the area of protective clothing as well as leisure apparel because of its liquid-repellent surface characteristics (51).

Many other man-made fibers are used in nonwoven constructions. Acrylic fibers are noted for their resistance to chemicals and ultraviolet light. Nylon fibers are tough, abrasion resistant, and resilient.

Nomex® nylon is noted for its high-temperature resistance and dimensional stability. Kevlar® aramid and carbon fibers are noted for their high-temperature resistance, superior specific strength, and specific modulus. Kynol® novoloid and polybenzimidazole [PBI] have good temperature resistance. Glass fibers have high strength, stiffness, inertness, and high-temperature resistance. Teflon® [polytetrafluoroethylene] is noted for its chemical resistance and water repellency. Vinyon® and some forms of nylon and polyester are valued for their ability to bond at low temperatures. In addition, there is an assortment of metallic and ceramic fibers that offer unusual properties for filters, composites, and other uses.

Most fibers are unicomponent. Some, however, are bicomponent of either a core-and-sheath or side-by-side configuration. Bicomponent fibers generally are used to achieve a high level of crimp or differing melting properties for the purpose of bonding. Biconstituent fibers are composed of two different materials dispersed throughout a single fiber. These are often used as super-absorbent fibers found in gas masks.

Fibers often contain additives such as delustrants, ultraviolet and high-temperature stabilizers, fire retardants, and pigments. Fibers also come in a variety of shapes. They can be round, triangular, square, dog-bone,

hollow, or irregularly shaped. The selection of fibers for the proper end product, staple length, denier, polymer type, cross-sectional type, crystallinity, and crimp should be considered in product design (1, 95).

Web Formation

A nonwoven product is created by assembling fibers into some type of web. The process used in the production of webs may affect the structure and the properties of nonwoven fabrics from the different geometrical arrangement of the fibers. There are four basic methods of web formation: 1) carding, 2) air-laying; 3) wet-laying; and 4) the spunbonded process (2).

Carding: The carding method of web production is based on the yarn-manufacturing process. In this case, the web of carded fibers is not condensed into a continuous strand of loose fibers. Instead, the full width of the fiber web is maintained.

A parallel-laid web is largely unidirectional, with the fibers oriented in the machine direction [MD]. As a result, the nonwoven is up to ten times stronger in the MD than it is in the cross-machine direction [CD]. Some cards used for production of parallel-laid webs are designed to randomize the fiber orientation and thus provide webs with equal MD and CD strengths. Parallel-laid nonwovens are

commonly used for diaper stock, shoeshine rags, wipes, and interfacing.

A carded web can also be cross-laid. Composite webs are produced by combining both parallel-laid and cross-laid webs. Carded nonwovens have a considerable range of end-use applications. They are used in geotextiles, liners, and slip covers for computer disks, apparel interfacing, indoor-outdoor carpeting, synthetic shoe leather, blankets, automotive sound and thermal insulation, papermaking felts, and numerous other products.

Air-laying: Webs can be made using fibers ranging in length from 1 mm to 75 mm. Long textile fibers must first be opened and disentangled to obtain good fiber dispersion and web uniformity. Short fibers, such as wood pulp, are obtained by processing roll pulp through defiberators. Manufactured fibers ranging in fineness from the subdenier to 300 denier per filament are used in air-laying. The fibers are oriented in the x, y, and z directions by air-laying. As a result, the web tends to be lofty and porous, with a low density. These properties make the web suitable for filters, fiberfill, padding, wipes, and other uses.

Wet-laying: This method is common for a papermaking process, as well as for nonwoven webs. When wet-laying, care must be exercised to protect entanglement of the long

fibers. This is accomplished by using smooth interior pipes with large-radius curves, positive-displacement pumps rather than centrifugal pumps, wire inclines of 10-35°, minimum agitation, and low consistancies.

Wet-laid nonwovens are used in automotive oil and air filters, milk filters, tea bags, roofing shingles, carbon and Kevlar® composites, electrical insulation, and other products.

Spunbonded Process: The spunbonded process is continuous, from the spinnerettes used for fiber formation to the finished, bonded, nonwoven fabric. The fibers are spun and then drawn or oriented, deposited uniformly on a moving screen, densified, and finally bonded by some suitable means. Most spunbondeds are melt-spun, thermally bonded polyester, polypropylene, and polyethylene.

Spunbonded nonwovens are noted for their low weight and high strength. End uses include geotextiles, fiber fabrics, protective clothing, primary backing for tufted carpet, wallpaper, house wrap, and other products.

The melt-blown process is a variation of the spunbonded process. In this technique, a high-velocity air jet from the spinnerette attenuates the fiber and blows random lengths of fibers against a forming drum or screen. The resulting mat is composed of ultra-fine fibers and has excellent filtration or insulation properties. The bonding

process has a significant potential because it can be used with several standard thermoplastic fiber-forming polymers, such as polystyrene, polycarbonates, silicones, and pitch (15, 35). Added to this, the viscosity of the melt, the velocity and temperature of the air, and the distance from the die to the collector can all be varied, as can the bonding process. End uses are filter media, insulation in outdoor apparel, wipes, etc.

Bonding Methods

Despite the importance of the bonding stage in the manufacture of nonwoven materials, the bonding process was given only minor consideration until the last ten years or so. Manufacturers now have a broad range of options that allow them to tailor webs with an almost infinite array of end-product properties.

The fibrous network within the nonwoven web must be bonded if adequate functional strength is to be achieved. The bonding methods of nonwovens have been variously categorized. Wagner (111) considers four methods used to bond nonwovens: inherent bonding, thermal bonding, mechanical bonding, and chemical bonding. Each of methods is discussed below.

Inherent Bonding: A nonwoven web is inherently bonded when it needs no further bonding after the web has been

formed. The best example is a highly linear extruded film that is broken down into an interconnected fibrous network by multiple penetration of pins and/or repetitive flexing.

Thermal Bonding: The thermal bonding process uses the thermoplastic properties of certain synthetic fibers to form a bond under controlled heating. The materials used in thermally bonded webs include blends of thermoplastic and nonthermoplastic fibers, unicomponent fibers with two different melting temperatures, and thermoplastic scrims and powders. Heat is provided by a variety of sources, including ovens, through dryers, dryer cans, smooth or patterned calender rolls, and ultrasonic methods (10). Thermal bonding is valued for its simplicity and is gaining wide acceptance. It offers several advantages over other bonding systems, including low energy requirements, high production speeds, and lower capital expenditure (63).

Mechanical Bonding: Web strength is derived from physical entanglement and the resultant interfiber friction. Physical entanglement is commonly obtained by either mechanical entanglement [needle] or fluid entanglement [water under pressure].

Needle punching relies on the use of barbed needles. Most needles are triangular, with three barbs on each edge of the triangle for a total of nine barbs. The needle-punch machine is equipped with up to six needle

boards, each having thousands of needles. These boards operate independently from one or both sides of the fabric. The needles come in many sizes. As the needles begin to penetrate the nonwoven, the barbs pick up individual fibers and push them into the fabric, where they become entangled with other fibers. Products manufactured with this method include papermaking felts, indoor-outdoor carpets, blankets, padding, filter fabrics, and synthetic leather. A new type of needle, the forked needle, has a V-shaped tip and is used to produce decorative patterns and velour effects (52).

Spunlaced process begins with a carded web that is carried by a belt under multiple water jets. The fine, high-pressure water jets cause the fibers to migrate, depending on the pattern in the carrier belt. The resultant fabric can have an overall smooth effect, a woven-fabric appearance, or numerous other patterns. The fabric derives its structural integrity from fiber entanglement. Spunlaced fabrics are used for disposable head-rest covers in trains and planes, medical gauze and dressings, dust cloths, wipes, and table linens (35).

Chemical Bonding: This type of bonding is accomplished by the use of solvents or binders.

Solvent bonding starts with the fiber's outer surface being softened. The fibers then bond together where they

come in contact with each other. The web is often compacted by calendering to further increase the degree of bonding. Solvent-bonded products include high-loft acrylic nonwovens that are bonded using sulfolane solvent, polyethylene Tyvek® spunbonded nonwovens that are bonded using freon®, and Cerex® nylon nonwovens that are bonded using acid.

Binders are adhesive-like materials that migrate by capillary attraction to crossover points between fibers. They vary considerably in cost, as well as their performance characteristics, and in their degree of softness, as expressed by their different glass transition temperatures [T_g]. Binders can vary in their degree of resistance to water and solvents. They are applied by spraying, saturation, coating, foam, or printing, depending on the product sought. The type of binder and the method of application considerably alters the degree of softness, stiffness, density, placement of binder, performance characteristics, and economics of a nonwoven.

End-Use Markets

Consumption of nonwovens disposables reached a milestone when it achieved the $1 billion mark for the first time in 1986; durable nonwovens also consumed about $800 million worth of roll stock in 1986 (52, 98). While

the diaper coverstock market is by far the largest end use for nonwovens, there are many smaller, and yet vital, segments in which nonwovens have become an integral part.

Filters: The availability of fibers and products and the commitment of the few large suppliers are the driving forces behind developments in the nonwovens filtration business. Nonwoven filter media are utilized primarily for 1) air/gas/dust filtration, such as for vacuum cleaners, baghouse filtration, face masks, and auto air filters; and 2) liquid filtration, such as for milk (dairy), tea bags, coffee filters, swimming pool filters, and micro-rated vessel bags.

Nonwoven Towels: The American affinity for throwing towels away after using them once or twice has spurred the household towels segment into a good market, e.g., household nonwoven towels, premoistened towelettes.

Automobile Market: The nonwovens in the automotive segment is at a crossroads in 1987, as all major car manufacturers are experimenting with nonwovens in upcoming models. Samples include automotive carpeting, headliners, trunks, door panels, passenger compartment floorcovering, and hoodliners.

Agricultural Applications: Even though this is an innovative end use, the amount of nonwovens being used for applications in the field of agriculture is relatively

small. Nevertheless, they are seen as heat shields, windbreaks, shading screens, protection against parasites, and seed substrates.

Geosynthetics: The term "geosynthetics" was adopted in 1987 because the breadth of the business is large and actually encompasses more than just geotextiles or geomembranes. Common uses incorporate asphalt overlays, soil stabilization, filtration, pond underliners, erosion control, and reinforcement (11, 93).

Medical Usage: One of the strengths of nonwovens in the medical area is the versatility and ability of the manufacturing processes to custom design fabrics for medical end uses. Examples here are OR gowns, masks, caps, packs, underpads, diapers, and sanitary napkins.

Others: The end uses of nonwovens are numerous. A few additional uses are nonwoven interlinings, floppy disk jackets, envelopes, battery separators, electrical insulation, air craft fuel tanks, protective clothings, and heat reflecting tiles for shuttles.

Future

There is no doubt that the future holds many opportunities in nonwovens because they offer an unusual variety of properties at a low unit cost. The future of nonwovens, however, lies in three major areas (44):

commodity nonwovens -- the characteristics of the commodity nonwovens are large volume, low cost, low technical assistance, and limited product design. Domestic disposable products and other highly competitive roll goods are examples. Component Nonwovens -- These have previously been called engineered structures, composites, laminates, or high-performance products. Component nonwovens will be considered with other nonwovens, knits, wovens, films, plastics, and a variety of other materials to achieve both additive and synergistic effects. Modified nonwovens -- These are substrates that have been changed by a finishing technique. The list of markets that use these component and modified nonwovens include: filtration, geotextiles, the transportation industry, electronic, apparel outwear, specialized wipes, and protective clothing.

Adhesively Bonded Nonwovens

Fiber networks in a web typically have low mechanical strength. This is partly due to the inhomogeneous structure of these networks, which results in a poorly developed stress-transfer mechanism between the fibers(79). However, the strength of the web fiber network can be improved substantially by application of synthetic, polymer-based binding materials. The actual increase in strength depends on the polymeric system used. This

strength increase is probably due to a better stress transfer throughout the fiber network (37). Functionally, the quality of the binder depends on the characteristics of the binder cohesion, binder and fiber adhesion, and binder distribution.

Binder Properties

In order to formulate an adequate binder which can generate the properties needed by the designated end-use, the selection of the proper monomers is critical and determines the product versus the target performance. Additional means, such as variations in molecular weight and/or degree of crosslinking, can then be incorporated to further improve the performance of a particular combination of monomers. It is also necessary to select the proper solvents and process design for application of the binder.

At the point of application, the adhesive must have the following properties (2): 1) specific adhesion to the adhered surface; 2) ability to wet the adhered surface; and 3) the requisite flow properties. Various types of nonwoven binder systems have been compared by Siegel (92) in terms of bonding speed, thermoplastic nature, pollution aspects, cost, and processing characteristics. The possible use of catalysts or crosslinking agents with binders and the provision of wettable, reactive surfaces

for the substrate treatment must also be considered. Croydon (17) outlined how to enhance the fabric characteristics, such as hydrophobicity, absorbency, and resilience, by a correct choice of binder. New binders are expected to produce major changes, not only in the primary properties of adhesively bonded webs, but in secondary characteristics, such as fire- and water-repellency and flushability for disposable uses.

New technology has been introduced for curing of nonwovens. Radiation curing (14) produced films of higher breaking elongation and provided superior web strength in uncompressed webs. For the long term, there will be more advanced technologies involving use of electron beams or lasers (113) for bonding, of lasers for creating multiple holes in polymer films to impart flexibility and porosity.

Monomer Composition: The first step in designing a nonwoven binder is selection of the proper combination of monomers. The monomers commonly employed in industry are listed in Table 1. The various considerations in the selection of the main monomers are discussed below.

Glass transition temperature - T_g - is one of the most critical properties of a polymer. For nonwoven binders, the T_g can vary from -60 ^{o}C (soft/tacky) to +50 ^{o}C (tough/leathery). The T_g of the homopolymers are listed in Table 2. Any copolymer T_g can be estimated by calculation

TABLE 1. Monomers Utilized as Binders in Nonwovens (68).

Acrylic	Vinyl	Other Monomers
Methyl Methacrylate	Vinyl Acetate	Styrene
Ethyl Acrylate	Vinyl Chloride	Ethylene
Isobutyl Acrylate		Butadiene
Butyl Acrylate		Itaconic Acid
Acrylonitrile		Propylene Glycol
Methacrylic Acid		Hexamethylene-Diisocyanate
Acrylamid		

TABLE 2. Glass Transition Temperatures (T_g) of Homopolymers (2, 112).

Homopolymer	T_g (^oC)
Acrylonitrile	135
Methyl Methacrylate	106
Styrene	100
Vinyl Chloride	91
Vinyl Acetate	29
Methyl Acrylate	9
Ethyl Acrylate	-22
n-Butyl Acrylate	-54
2-Ethyl-Hexyl Acrylate	-55
Butadiene	-70

$$1 / \text{Copolymer } T_g\ (^oK) = W_1 / T_{g_1}\ (^oK) + W_2 / T_{g_2}\ (^oK) + \ldots.$$

W = weight fraction

using the Fox equation (also given in Table 2). In general, the higher the value of the glass transition temperature, the harder will be the polymer binder and the stiffer and stronger the resultant nonwoven fabric.

According to the Fox equation, the addition of a high T_g monomer to a lower T_g monomer will lower the T_g of that copolymer. Binders are normally copolymers of different monomers and have intermediate properties. Polymers having the same T_g do not necessarily have the same properties, however, T_g is still a guide to produce desired properties of nonwovens. The first Kevlar/Neoprene inflated tube was evaluated on a Boeing 757 and failed on inflation at -40 ^{o}C due to brittleness of the coating at low temperature (88).

Solvent resistance is not only influenced by molecular weight of the binder polymer but also by the stereochemistry and the functional groups. Acrylonitrile [$-CH_2-\underset{CN}{CH}--$] is often used to improve the solvent resistance of the emulsion polymer. Solubility of polymers are determined by the solubility parameter of the solvent and in particular, the polymer-solvent interaction parameter (90).

Crosslinking can be achieved either by using a crosslinkable monomer during polymerization or by the addition of external crosslinking agents during formulations. The degree of crosslink can be controlled

and varied for the desired toughness of the end product. In general, the greater the crosslink density, the stronger the web. Crosslinking helps to improve laundering and dry cleaning characteristics of nonwovens.

Molecular weight of the polymer can be regulated using either a chain transfer agent, multifunctional monomers, or crosslinking agent depends on the type of polymerization. Variations in molecular weight affect the strength of the polymers and their filming tendencies. Optimum properties of the nonwoven are obtained with molecular weight controlled to achieve the best balance between the polymer strength and filming-forming characteristics.

Binder Cohesion

Several factors contributing to binder cohesion are: a) physical attractive forces [H-bonding] between polymer chains; b) chemical crosslinks; c) molecular immobility; and d) degree of film formation (120). Chemical crosslinks connect chains through covalent bonds, yielding a continuous three-dimensional network. It is used to enhance the mechanical integrity and chemical resistance of binders. Decreasing the flexibility of the polymer chain decreases chain mobility and enhances cohesion by preventing the slippage of polymer chains past each other. This is not particularly useful for binders of nonwovens,

because there is concomitant increase in stiffness. One additional factor is critical for developing good cohesive strength. The binder must be capable of film formation.

Fiber and Binder Adhesion

To obtain good adhesion between fiber and binder, it is necessary for the binder polymer to adequately wet the fiber (48, 87). Considering the substrate, synthetic fibers that have low surface energy, such as polyester, are much more difficult to wet than rayon, for example, which has a higher surface energy. Even if surface tension is optimized, wetting may be impaired by polymer rheology. If the viscosity of the polymer inhibits good flow, adequate contact cannot be made with the fiber.

Dilution can be employed to reduce polymer viscosity, and additional heating also will improve the flow of the polymer. Factors that impair film formation, such as crystallinity, high T_g, and high melt viscosity, will also hinder adhesion by reducing polymer flow. Premature crosslinking of the polymer can also reduce adhesion to the fibers for the same reasons. It is important that wetting be achieved prior to crosslinking. Once wetting is achieved, specific interactions between fiber and binder will yield a strong bond. There are several mechanisms by which adhesion can be achieved (77, 78). These will be

elaborated on below.

A. Adsorption and Wetting. It is generally necessary for the binder in its fluid form to wet the surface of the fibers. Thus, the surface energy of the fibers must be greater than the surface energy or surface tension of the polymer binder in order for effective wetting to occur.

B. Interdiffusion. An effective bond can be formed if the molecules of each phase diffuse into the surface layers of the other phase. Such interdiffusional processes will cause a localized molecular entanglement that will significantly contribute to interfacial adhesion.

C. Electrostatic Attraction. A difference in electrostatic charge between the fiber and the binder matrix at the interface can contribute significantly to the adhesion between them.

D. Chemical Covalent Bonding. It is obvious that direct chemical covalent bonding will greatly enhance interfacial adhesion. However, specific chemical functional groups are required at the fiber surface and in the binder matrix for such interactions to occur.

E. Chemical Secondary Bonding. Low energy intermolecular forces, such as those associated with

hydrogen bonds, dipolar interactions, dispersion forces, and van der Waals forces, undoubtedly play an important mechanistic role in the development of interfacial adhesion between fiber and matrix.

F. Mechanical Adhesion. Purely mechanical interlocking between the two phases can also contribute to adhesion.

In any given fiber-polymer system, all of the above adhesion mechanisms are probably operative to varying extents. In certain systems, one or another of the mechanisms may play a greater role, but the complexities of adhesion are best understood in terms of these fundamental mechanisms.

Binder Distribution

The web structure, binder polymer properties, and binder application method will all affect distribution of the binder (103). Some of the following factors may be helpful in understanding the distribution modes of binders on the web. Figure 2 displays a binder droplet in a dense web and in an open web (20). In the dense web, the probability of a droplet being in close proximity to fiber crosspoints is high. Capillary forces will draw the droplet into the crevice between fibers as shown. In contrast, it is lesslikely that the binder droplet in an

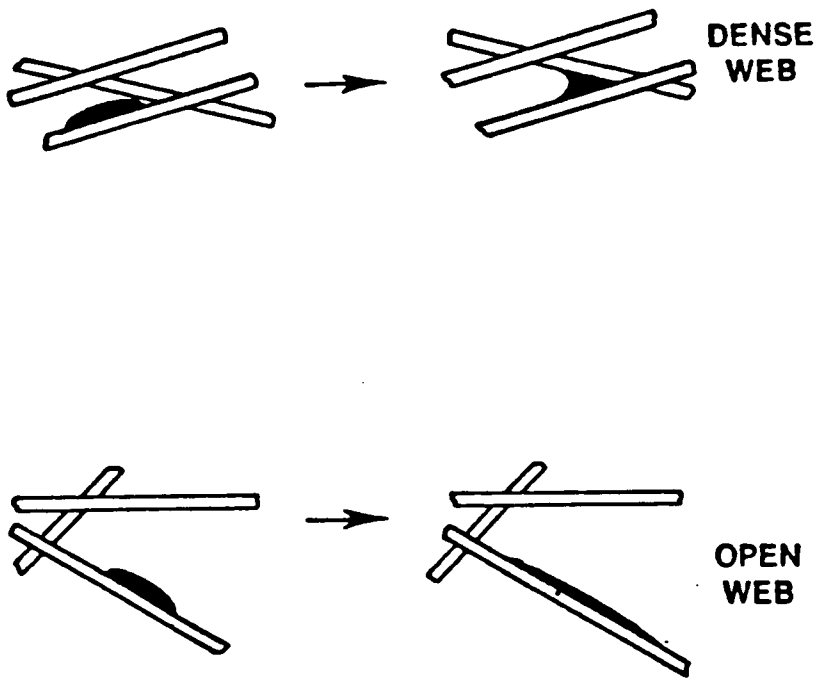


Figure 2. Influence of Capillary Forces on Binder Distribution.

open web will contact a fiber crosspoint. Even if the droplet wets and spreads over the fiber surface, it is unlikely that the liquid will make contact with a crosspoint before it is immobilized by the drying process. Should the liquid spread to the crosspoint, however, capillary forces will again draw it into the crevice.

Binder Application

Wood (119) has described the spray, saturation, and foam-bonding techniques used for binder application to nonwoven fabrics. The theoretical aspects of binder application are also discussed in terms of calculating the amount of binder required for a particular web and the impregnation capacity of binders.

Saturation: By means of immersion, saturation is achieved in its simplest form by using a traditional padding machine, or specially designed machines that impregnate between two screens or between a drum and a screen. Many lightweight web structures of under 50 g/m^2 are bonded by saturation achieved in the nip of squeeze rolls.

Spraying: The binder is introduced into or onto the textile structure by means of sprayers arranged over the moving web (119). Several procedures may be adopted during spray applications, as follows: a) individual layers from

web-forming can be spray-bonded and then laid upon each other to form a compound structure prior to drying; b) a single fibrous web structure can be sprayed; or c) binder may be applied by spraying individual fibers directly during web formation.

Foam Saturation: Processes for foam formation have been described by Knaus (56), for lightweight webs of 15-100 g/m^2 intended for interlinings. Advantages of this process are exact binder dosing, uniform binder distribution, and soft handle.

Mechanical Behavior

Numerous studies (12, 36) have been conducted on adhesively bonded nonwovens to determine the factors that influence strength and stiffness properties and the interrelationships between them.

Of major importance in the mechanical behavior of adhesively bonded nonwovens is the mode of breakdown under tensile stress. This is of interest within the context of the binder and fiber characteristics as these affect the rupture. Sauer and Stradling (83), using an Instron Tensile Tester, have measured the initial modulus and breaking loads of air-laid webs saturated with acrylic binders. In an unsaturated web, the applied stress is transmitted to the fibers through inter-fiber friction and entanglement, which is so weak that the load is largely

carried by fibers that are aligned parallel to the applied stress. The mechanical properties of webs are thus dependent upon angular orientation of the fibers. The binder strengthens the web by forming fiber-fiber bonds, which allow fibers to be loaded to a larger fraction of the breaking load (101). A theoretical model of tensile response incorporating binder deformation was reported by Hearle (39). A method was formulated to predict fabric stress in terms of applied strain and other fiber, binder, and fabric parameters by considering the geometrical deformation and energy changes of individual units under uniaxial strain (40). It was observed that the properties of fabric were greatly influenced by the fiber modulus and to only a limited extent by binder (41). Perner et al. (75) have discussed the influence of fiber crimp on fabric properties and suggested a theory explaining the relationships between fiber crimp and fabric properties (40). Allan (1) showed that replacing straight fibers by helically crimped fibers improves drapability by virtue of the lateral flexibility of the fiber segments between bond sites. Korchan (57) has concluded that crimp is a more important factor than staple length in determining fabric properties, although the two should be considered together. Schröder and Korchan (86) have shown that fabric strength increases with fiber length up to an optimum value. The optimum value depends more on fiber crimp than fiber

fineness. Krcma and Zastera (60) have described experiments that expanded on the structural mechanics of adhesively bonded nonwoven fabrics. The structure is characterized by the mean length of the free-fiber sections between crossover points, and results have been shown that this can be controlled by adjusting the wettability of fibers with binders. Olson and Freeston (71) have produced a theoretical model for the behavior of a three-dimensional fabric that has been analyzed for behavior of the fabric-to-fabric modulus over a variety of fiber distributions. Results indicate that out-of-plane fibers decrease the modulus ratio and increase fabric extensibility.

The overall mechanical properties of adhesively bonded nonwovens are influenced by the fiber types, web structures, binder properties, and bonding techniques (35).

Rupture Mechanism

The nature of failure, in particular the relationships to the tensile properties, has been discussed by a number of workers. Winchester and Whitwell (117) have defined three major types of response based on characteristic stress-strain curves and the corresponding types of breakage. Type I webs have few bonds, and the predominant effect on the binder is to increase the average effective fiber length. The bonds are isolated and primarily serve

to tie groups of fibers together in series. Type II webs contain a matrix with many fixed points. Failure in this system involves a combination of fiber and bond breakages. The excellent bonding in Type III webs results from a considerable spreading of the binder material. The nonwoven fabric approaches a sheet of film in which the base fibers are dispersed.

The three possible modes of fabric rupture which have been suggested by Tikhomirov (100): 1) fiber breakage; 2) cohesive failure in the adhesive binder; and 3) interfacial failure of adhesive bonds between adhesive and fiber surface -- if the fiber strength and the cohesion of the adhesive are higher than the adhesive forces. The mechanism(s) which is operative is obviously dependent upon the fiber properties, the binder properties, and the amount of binder present. Oszanlav (73) has developed a technique of tensile deformation of nonwoven fabrics using an extensometer stage in a scanning electron microscope. The result showed that the failure of all the nonwovens examined was invariably due to the breakdown of the binder component. The bond failure started at an early stage of the uniaxial deformation and increased progressively towards the fabric rupture point. The result (46) suggested that bonding in the materials tested was by breakdown in binder cohesion. Fredrick (27), however, indicated that fabric breakdown is the result of fiber

rupture.

It would appear from the literature that with adhesively bonded fabrics from dry-laid webs, the tensile strength depends upon the binder cohesion if the adhesion between fiber and binder is good. With wet-laid materials, which typically use low-strength fibers and a considerable amount of bonding, the tensile strength will depend upon the fibers rather than the strength of bonding.

Polyurethane

Polyurethanes are synthesized by addition polymerization, which was discovered by Bayer in 1937 (30). In this type of addition, two or more hydroxyl-group containing compounds react with di- or polyisocyanates.

$$HO - R - OH + O = C = N - R' - N = C = O$$

$$\left(R - O - \underset{\underset{O}{\|}}{C} - NH - R' - NH - \underset{\underset{O}{\|}}{C} - O \right)_n$$

This simple equation is an expression of the principle of the polyaddition reaction which leads to this exceptionally adaptable polymeric structure. As polyisocyanates, one- or multi-ring aromatic, ar-aliphatic, aliphatic, or cycloaliphatic compounds can be used. The versatility of compounds is even more extensive for the polyol reactant. From the two largest raw material areas, which are the polyester and polyester polyols, there are

innumerable compounds available with respect to functionality, chain length, and reactivity. The versatility of reactants permits the construction of a wide array of polymers suitable to some specific need. It is exactly because of this versatility that polyurethanes are called "tailor-made plastics" (70).

The reaction of diols with diisocyanates according to the equation above leads to linear polyurethanes. If there is a tri- or polyol or tri- or polyisocyanate present in the reaction, branching and crosslinking of the polymer chains will occur. The crosslink density of such a polymer depends on the amount of higher functional raw materials. This crosslinking contributes to the extension of the property spectrum of the final product.

Depending on their structure, polyurethanes produce a broad range of properties (31). Besides the primary structure [chemical composition, chain length, chain stiffness, degree of crosslinking, branching], the morphology of polyurethane is determined to a high degree by the possible interaction between the polymer chains [interchain forces].

Soft, elastomeric products are obtained by reaction of long chain, non-crystalline, unbranched, OH-functional polyethers with stoichiometric amounts of diisocyanates. The intermolecular forces are essentially those of the

polyether-segments. As a result, hardness and strength are comparatively low. The products exhibit rubber-like properties and are amorphous, as determined by X-ray diffraction analysis. With increasing chain stiffness, decreasing chain length, and increasing crosslink density, stiffer and lighter networks are formed. Therefore, harder and less elastomeric products are obtained.

The thermomechanical properties of linear segmented polyurethanes are substantially different from those of chemically crosslinked products (22). When mechanical forces are applied, changes in the orientation and mobility of structures within the hard-segment domains can occur. In this process, the initial hydrogen bonding is lost and new, energetically more favorable hydrogen bonding takes place (Fig. 3). The mobility depends to a large extent upon the chemical nature and chain length of the soft segment. In order to obtain good elastomeric properties, especially impact resistance, the soft segment should be amorphous and possess a sufficiently low glass transition temperature.

Polyurethanes are distinguished by their good adhesion to different substrates and by high flexibility, even at low temperatures. In addition, the thermoplasticity (85) and resistance of polyurethane to most solvents, a function of composition or degree of crosslinking, are additional

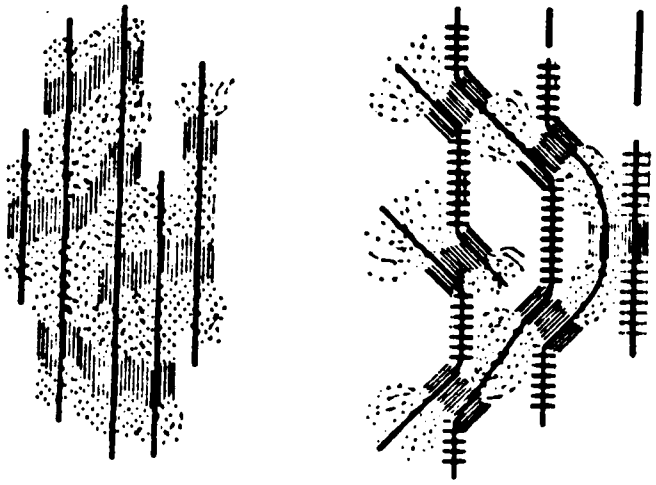


Figure 3. Changes in the Orientation of Structures with Applied Mechanical Forces. Left: As a Result of Stretching, a Portion of the Soft Segments are Stressed by Uncoiling and the Hard Segments are Oriented in the Stress Direction. Right: A Complete Reorientation after Stress and Thermofixation.

advantages compared to other polymers.

Polyurethanes [compared with SBR, acrylics, nitrocellulose, and PVC] have the following advantages: a) they can be applied from solution, dispersion, low-solvent or solvent-free high-solid systems, or as solid granulate or powder; b) adhesion resistance, tensile strength, and tear resistance are high compared to other polymers (84); c) softness or hardness can be obtained through variation of polymer structure without the use of plasticizers (99); and d) brittleness caused by exposure to light or longtime storage can be minimized. However, the polymers mentioned above are generally less expensive than polyurethanes. Therefore, polyurethanes are normally used if their particular properties are critically needed.

One of the most exciting areas of research and new applications for polyurethane is in the medical field (55). Segmented polyether-based polyurethanes are the most widely used blood contact materials because of their unique combination of physical properties, hydrolytic resistance, and thromboresistance. Biomedical uses include heart pacemaker connectors, haemodialysis components, blood contact tubing, blood bags, and gas therapy tubing. Artificial hearts have been fabricated from polyurethanes and considerable attention has recently been drawn to the development of the University of Utah's "Jarvik" artificial

heart.

The combination of polyurethane and textiles is distinguished by being comfortable to wear, rugged, and easy to care for. Some of the typical properties are: interesting leather-like surface; warm, comfortable touch; wash and cleaning stability; good adhesion between substrate and coating; high elongation and elasticity; good abrasion resistance; high flexibility at low temperatures; very good resistance to oils and solvents; and low specific weight.

Crosslink Network

Effective crosslinks may result from chemical bonds, entangled chains, looped chains, and interchain crystal formation. Chemical crosslinks usually occur as a result of exothermic reactions upon heating the polymer to some predetermined temperature. Looped and entangled chains follow from multiple crosslinking as a result of normal chain configuration. Interchain crystal formation is endothermic (67).

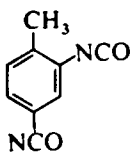
One can readily understand that the effective crosslinks are due to chemical bonds, but entangled and looped chains also contribute to the density of crosslinks. It is also possible that some bonds which are labile do not react because of steric effects in the crosslinking reaction.

Barrall suggested (5) that crosslink networks can be explained as shown in Figure 4. In **a**, all "effective" crosslinks are chemical bonds. In **b**, a percentage of the "effective" crosslinks are due to closely entangled chains. On swelling with a good solvent, these chains may become untangled and more independent. In case **c**, the chains are looped over and would, upon swelling or deswelling, yield an "effective" but not a chemical crosslink.

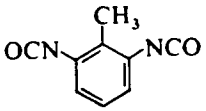
Raw Materials

Isocyanates: Isocyanates with two or several NCO groups in the molecule are needed for the formation of polyurethanes. Aromatic, as well as aliphatic and cycloaliphatic, isocyanates are suitable building blocks for polyurethane chemistry.

In terms of the world market, TDI [Toluene Diisocyanate] is still the largest diisocyanate on a worldwide basis. The most important product is TDI-80 consisting of 80% of the 2,4-isomer and 20% of the 2,6-isomer. This is the standard isocyanate for the manufacture of flexible polyurethane foam.



2,4-TDI



2,6-TDI

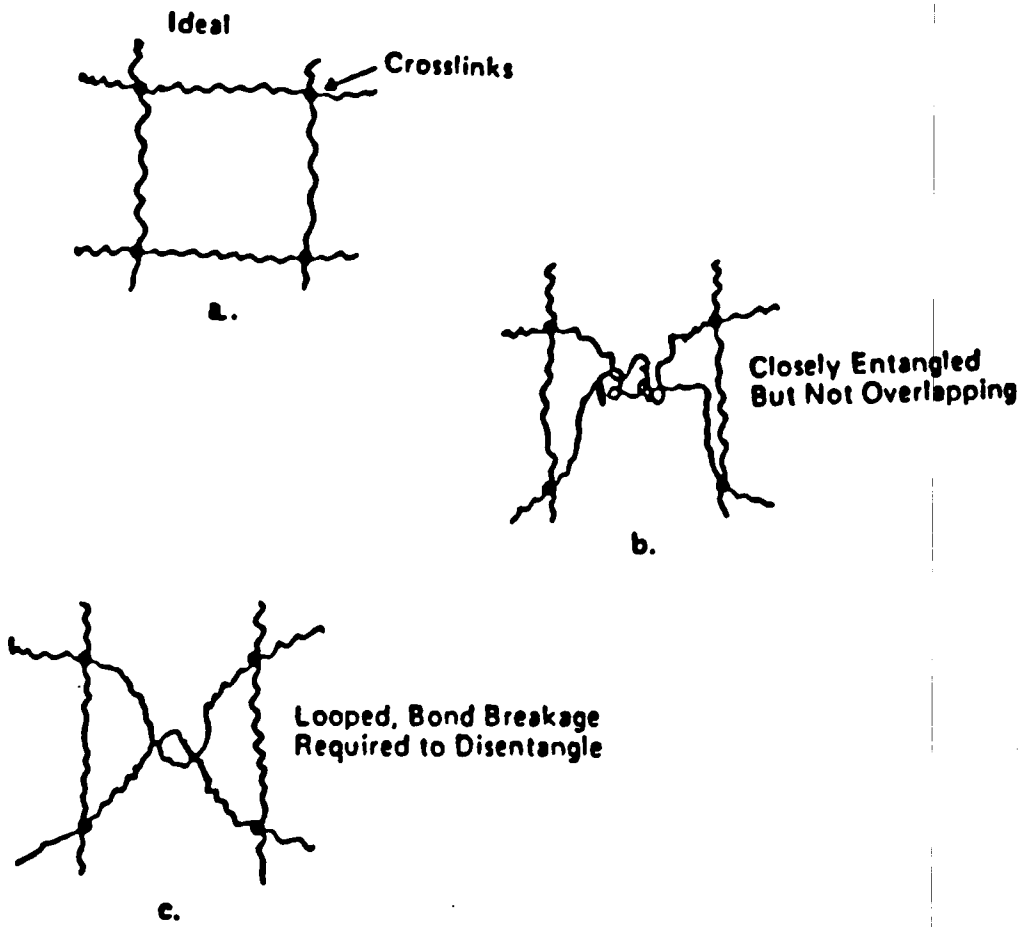
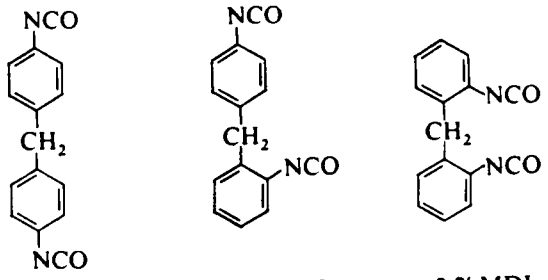


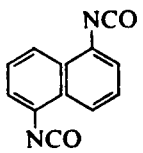
Figure 4. Models of Crosslink Networks.

MDI [Diamino-Diphenyl Methane Diisocyanate] is a mixture consisting of many chemical individuals. This class is frequently used in the manufacture of a high-performance polyurethane elastomers (100).



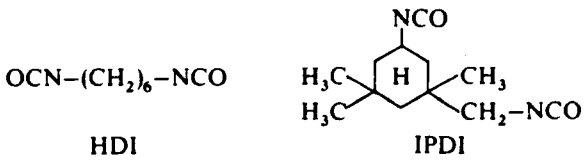
4,4'-MDI 2,4'-MDI 2,2'-MDI

NDI [Naphthalene-1,5-diisocyanate] is a specialty among the aromatic isocyanates. It is used in the manufacture of high-performance cast elastomers [Vulkollan®].



NDI

However, the most important basic products in the aliphatic and cycloaliphatic series are HDI [Hexamethylene Diisocyanate] and isophorone diisocyanate [IPDI]. These are mainly used for coatings.



Polyols: Besides the isocyanates, compounds with several hydroxyl functions in the molecule are the important components, especially the higher molecular weight hydroxyl terminated polyethers and polyesters,for the final formation of polyurethanes.

Polyethers are called polyetherpolyols or polyalkylene glycols. Typical difunctional starting alcohls are ethylene, polypropylene, tetramethylene, and butadiene glycols. For the trifunctional polyethers, glycerine and trimethyolpropane are the primary starters used. Higher branched polyaddition products are obtained through the use of oligofunctional starters such as pentaerythritol, sorbitol, mannitol, alkyl glucoside, or sucrose. Amines as starter components lead to the especially active basic aminopolyethers. Commercially, ethylenediamine, triethanolamine, and toluenediamine are being used (70).

Numerous product groups are available as starting materials for polyesters(55). Polyesters with lower molecular weights (well under 10,000) can be made from saturated aliphatic or aromatic dicarboxylic acids and

polyfunctional alcolods. Polycarbonates and polymers made from lactones also belong to this group. Saturated polyester resins are more highly branched and are based on aromatic dicarboxylic acids. These resins also can be reacted to polyurethanes through crosslinking with di- and polyisocyanates.

CHAPTER III

EXPERIMENTAL TECHNIQUES

The research performed in this study involved the synthesis of binders and the production of fibrous webs. The synthsis of the polyurethane was closely controlled; likewise, the final products were thoroughly evaluated with respect to their various mechanical properties. The principal binder was an amorphous polyurethane binder with a glass transition temperature [T_g] of -50°C or lower. In order to make a 100% amorphous polymer, polypropylene glycol and hexamethylene diisocyanate were used (96, 97). Trimethylol propane was also used as a crosslinking reagent. These adhesive binders were used with polyester fiber. This fiber was chosen because it can be obtained in a highly crystalline form, it is thermally/chemically resistant, and it is versatile in its usage as a textile fiber.

Starting Materials

Fibers

The fiber used for the experiments was KODEL® Type 411 polyester [Lot No. CK-1379] from Eastman Chemical Products, Inc. Following properties were reported by the company: 1.5 denier; 1.5 inch length; round cross-section; regular tenacity; 100% crystalline; and dull.

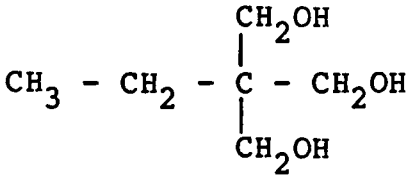
Chemicals

Various chemicals were used in the synthesis of the polyurethane binder. Their physical properties were obtained from the handbook of chemistry and physics (114). They included:

A. Polypropylene glycol [PPG] was NIAX Polyol 2025 from Union Carbide Corp. [Hdroxyl 55.6; water 0.02; acid 0.01]. The hydroxyl content corresponds to an average molecular weight of 2016, assuming all molecules were difunctional. The structure of this glycol is:

$$HO \left(CH - CH_2 - O \right)_n H$$
$$\quad\;\; | \quad\quad\quad\

C. Trimethylol Propane [TMP] was obtained from Matheson, Coleman, and Bell Inc.. It was ground and then stored in a desiccator at room temperature over P_2O_5. TMP is a crosslinking agent with the structure of:

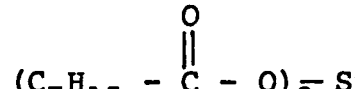


Mol. Wt. = 134.18

M.P. = 58°C

b.p. = 160°C

D. Stannous Octoate [T-9] was from M & T Chemicals and was used as a catalyst. Its structure is:



Mol. Wt. = 403.10 gm/mole

d = 1.31 (20°C)

One ml of T-9 was mixed into 10 ml of PPG as a stock catalyst solution and stored in the desiccator over P_2O_5.

E. Methylene Chloride was obtained from Fisher Chemicals and was 'analytical grade'.



M.W. = 84.94

d = 1.3266

b.p. = 40°C

F. Methanol was obtained from Fisher Chemicals and was 'spectra grade'.

CH_3OH

M.W. = 32.04

d = 0.7914

b.p. = 65.15^{o}C

Web Formation

The web formation consisted of Kodel 411 polyester fibers, supplied by Eastman Chemical Products, Inc., which were opened on a spiral opener specifically designed for small samples at the Starlab in Knoxville. Approximately 50 gm of the polyester fiber was placed in a stainless steel pan (5X20X55 cm^3), which was designed to fit between two control blocks. These control blocks function to determine the width of the lap and to prevent excess pulling of laps into the feed roll and the lickerin roll which parallels the fibers. The carding machine used was a John Hollingsworth Model which produced unidirectional, anisotropic webs. The opened fibers were put through the carding machine twice in order to obtain a uniform, high quality web.

Binder Preparation

The preparation of linear and crosslinked polyurethane

films was studied first in order to establish the correct synthesis technique and perfect the precision of polymerization with specific monomers.

Linear Polyurethane

A 10% molar excess of the diisocyanate [relative to polyol] was added to the polyol in the presence of a catalyst to produce a polyurethane film with acceptable thickness and uniformity. This procedure, reported by Smith (96, 97), was used for the preparation of polymer films in this study.

The experimental setup consisted of a three-necked flask equipped with a mechanical stirrer and a septum cover over one neck. A manometer and vacuum pump were connected in series to the third neck [Fig. 5]. The PPG, which was stored with molecular sieves [4Å], was weighed directly into the three-necked flask in order to prevent any weight loss during transfer. The PPG was degassed by heating at 85-90°C in an oil bath at a pressure of <5 mm Hg with constant stirring. The oil bath was removed, with the PPG taking about 30 minutes to cool down to 25°C. While stirring, the T-9 [catalyst; 0.2%, with respect to the reactants] was injected by syringe through the septum cover; after 5 minutes, the HMDI also was added by injection. This mixture was stirred an additional 5

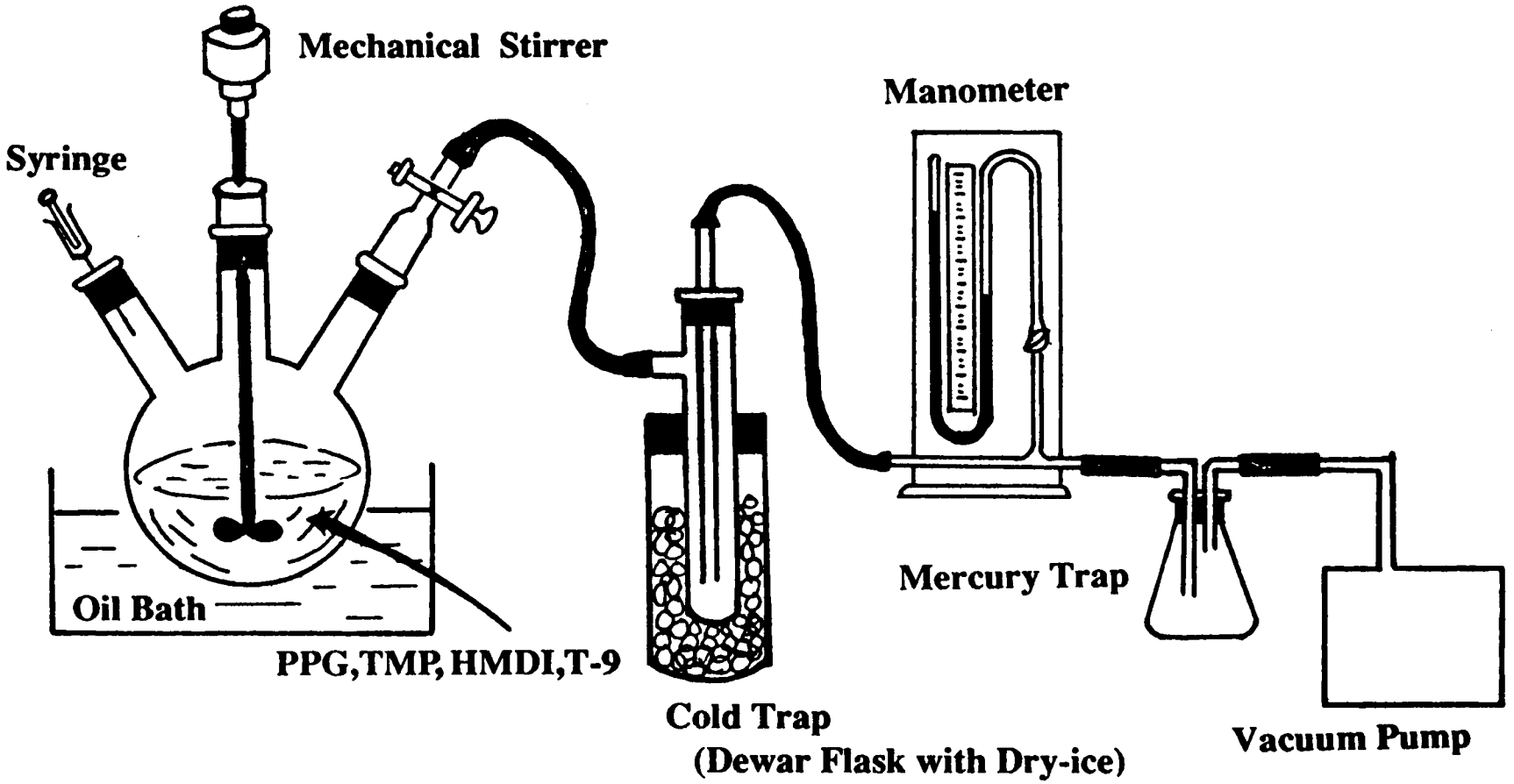


Figure 5. Arrangement of Experimental Apparatus for the Polymerization of Polyurethane.

minutes and then cast into a Teflon-coated tray [20X25 cm] to produce a layer about 0.125 cm thick. This tray was placed in a vacuum oven to cure at <5 mm Hg and 60°C for 48 hours. After preliminary investigation, the standard conditions of curing time and temperature were determined to produce satisfactory polymer films. This preparation yielded a transparent, amorphous polyurethane films.

Crosslinked Polyurethane

The procedure for the synthesis of the crosslinked polyurethane was essentially the same as used for the linear polyurethane, except for the addition of the crosslinking agent, TMP, with the PPG at the beginning of the synthesis. Crosslinked polyurethane films with different degrees of crosslinking were prepared by using different equivalent ratios of the trifunctional alcohol [TMP] with the difunctional alcohol [PPG] and HMDI. The ratios between PPG and TMP used in this study were: 0.9:0.1; 0.8:0.2; 0.7:0.3; 0.6:0.4; and 0.5:0.5.

With the synthesis of practical binders for fabrics, adjustments were made to increase the amount of polymerization catalyst [T-9] to a 2% level [0.2% was used for polyurethane films]. This compensated for the decrease in the rate of polymerization due to solvent effects. Methylene chloride was used to dilute the viscous polymer

mixture and thereby facilitate the control of the amount of binder actually added to the polyester web weight. The order of addition of reagents and solvents was important in preventing rapid polymerization due to high concentration of catalyst. The methylene chloride should be added after the degassing of the mixture of PPG and TMP; this is followed by the addition of the T-9 catalyst and HMDI to the flask using a syringe through the septum cover.

Application of Binders to Fibers

The binder is applied to the fiber webs as an aerosol mixture of polyurethane and solvent. In order to obtain optimum and uniform binder distribution on polyester nonwoven webs, a priliminary study was performed of the amount of solvent [methylene chloride] in which to dissolve the solid polyurethane. Although 2, 5, 7, 10, and 15 % by weight of polyurethane in methanol were utilized, only the 5% solution provided satisfactory and uniform "wetting" of the webs.

The polymer solution, well stirred, was added to a 100 ml jar to which was attached an airbrush with 10 lbs/in^2 nitrogen gas. The nozzle of the airbrush was held about 6 inches from the surface of the web and moved at a constant and steady rate parallel to the surface. In order to achieve uniform and sufficient adhesive bonding, the

polymer solution was applied to both sides of the webs. The amount of binder necessary to achieve 30, 40, and 50 weight percent binder to total web weight was calculated and thereby determined the amount of solution to be applied by spraying.

Measurement of Film Characteristics

Various techniques were used in order to examine the satisfactory polymerization of polyurethanes within the film samples. These are outlined below.

Differential Scanning Calorimetry [DSC]

The glass transition temperature of the linear and crosslinked polyurethane films were measured by Differential Scanning Calorimetry [DSC]. This was accomplished on a liquid nitrogen chamber attached to a DSC unit [Perkin-Elmer DSC-2B Model]. The instrument was calibrated in the -30^{o}C to 200^{o}C temperature range using indium and cyclohexane. DSC was operated at a heating rate of 20^{o}C/min for all measurements. Sample sizes were adjusted within 5-10 mg in order that a constant sensitivity could be employed. Also, the extent of crystallinity within the polymer film could be qualitatively determined by the nature of the DSC output. With this instrument, it can be seen that crystalline

polymers possess both a glass transition and a melting transition, whereas totally amorphous polymers have only a glass transition state.

Viscometry

The intrinsic viscosity of the polyurethane film was measured in order to check the consistency of linear polymerization within the film sample. Four different concentrations of solutions of the film were prepared in methanol [0.5, 1.0, 1.5, and 2.0 gm/dl]. The methanol was distilled and stored with 4Å molecular sieves before use. A No. 1 Ubbelohde Viscometer was used for these determinations. These measurements consisted of the flow time of a standard volume of solution through a capillary tube of fixed length, at 25°C in a constant temperature bath. From the folw time of solvent and polymer solutions, relative and specific viscosities were calculated. Intrinsic viscosity of the dilute polyurethane solution was determined by the extrapolation of relative and specific viscosities from the graph.

Differential Refractive Index

One of the best methods for verification of the precise polymerization of linear polymer films involves the consistent differences in refractive indices between dilute

polymer solutions and their solvent.

For this study, four different concentrations of polyurethane solutions were prepared with methanol, all below 0.01 gm/ml. These dilute solutions were permitted to stand for 24 hours in order to ensure the attainment of equilibrium [i.e. homogenization]. The refractive indices of the polymer solutions and solvent were measured using a Bruce-Phoenix Differential Refractometer. The principal source is a type AH-3 mercury lamp, operated by transformer [110 volt; 6 cycle] and equipped with mounted monochromic filters for isolating blue and green light of wavelengths 4358 Å and 5460 Å. The galvanometer readings were obtained for pure solvent and four solutions of different concentrations at angles of 0° [d_1] and 180° [d_2]. The differential refractive index [d n] of each dilute solution was calculated from the data.

Swelling Ratios

Swelling ratios and sol fractions [percent extractable] of the crosslinked polymers were determined in spectra-grade methylene chloride and methanol in order to examine the precision of the degress of crosslinking within the polymer films.

Small pieces of the crosslinked polyurethane were weighed [Wi] on a Mettler analytical balance and then

immersed in 10 ml of each solvent. The swollen pieces were removed, blotted dry with filter paper, and reweighed after 12, 24, 36, and 48 hours [Ws]. Evaporation of solvent during the weighing operation was minimized by saturating the balance atmosphere with solvent vapor. This was accomplished by placing a full petri dish of solvent beside the balance pan. Needless to say, the measurements were made accurately but with haste. The weights of the swollen polymer pieces were constant after 24 hours; thereafter, 24 hours was used for the swelling times. The solvent was removed by placing the swollen polymer pieces under vacuum [1-2 mm Hg] for 24 hours at 30^{o}C, and the samples were weighed again [Wf]. The swelling ratio was determined from the weight after the solvent was removed. The sol fraction also was calculated (76).

Mechanical Properties

Polyurethane Films

For these determinations, testing procedures as given in ASTM D 412-80 [Part 35] (4) were followed. The specimen size used was 3/8 in. [0.94 cm width] X 3/4 in.[1.88 cm gauze length]. The range of thickness was varied from 0.02 in.[0.05 cm] to 0.05 in. [0.125 cm]. The test piece was mounted on a paper frame, as illustrated in Figure 6.

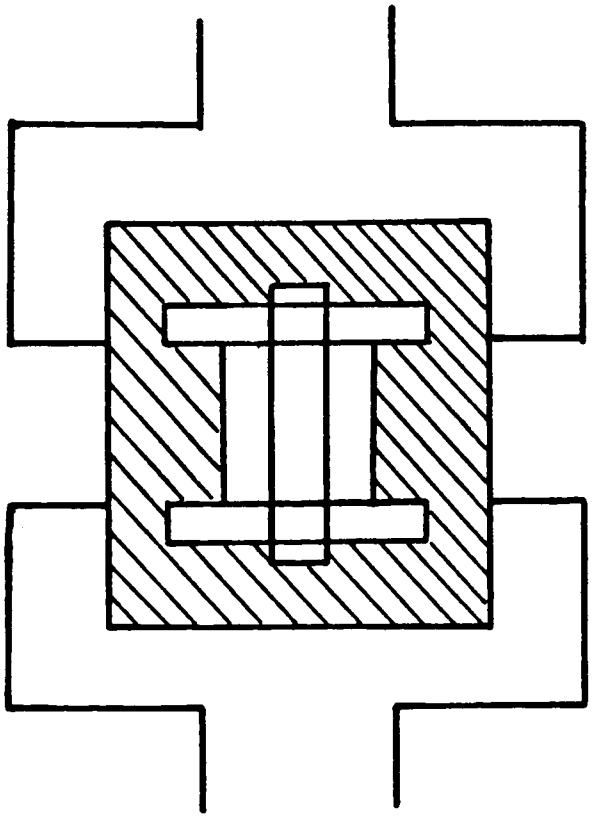


Figure 6. Cardboard Frame for Mounting Polyurethane Film Samples for the Instron. The Square in the Center Represents the Cardboard (5 cm X 5 cm); The Inner Square (2 cm X 2 cm) Represents a Hole Cut into the Cardboard. The Film Sample is Taped to the Cardboard.

Specimens were conditioned for 24 hours at 20°C and 65% RH. Care was taken to grip the specimen properly to avoid possible slippage. Before mounting on the Instron tensile tester, the specimen was attached to the cardboard frame by self-adhesive paper labels, as shown. Both sides of the paper frame were cut before the extension of the specimen. Four specimens were tested for each type of crosslinked polyurethane film. Test conditions of 5 in.[12.5 cm]/min cross-head speed and 5 in. [12.5 cm]/min chart speed at constant strain rates were selected for these determinations. From the stress-strain curve, the tensile strength, elastic modulus, and the percent elongation at break were determined according to the standard methods.

Nonwoven Fabrics

Mechanical properties of polyester webs that had been adhesively bonded with polyurethane binders were obtained on the Instron at constant strain rate, using the testing conditions as given in ASTM D 1117-80 (3). Since the polyester webs were processed by a dry-laid parallel technique, their mechanical properties in the cross-machine directions were observed, as well as their machine directions.

After the webs were cured in a vacuum oven at 60°C for 24 hours, they were conditioned for 48 hours at 20°C and 65% RH, prior to testing of their mechanical properties on

the Instron. Specimen sizes for the Instron were 1 in.X 4 in.[2.5X10 cm^2]. and the gauze length was 2 in. [5.0 cm]. The cross-head and chart speeds were both at 5 in.[12.5 cm] /min. Tenacity, percent elongation at T_{max}, elastic modulus, tear strength, and energy- to-break were determined for three different binder weights at five different levels of polyurethane crosslinking. Ten specimens for each type of crosslinked polyurethane binder were tested and averaged.

Electron Microscopy

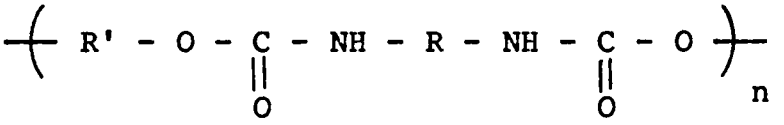
Uniform distribution of binders over fiber webs determine the quality of properties of nonwoven fabrics. It has been reported (96) already that PPG- and HMDI-based polyurethane is a highly viscous material. In order to directly observe the bonding nature, the surface of polyurethane adhesively bonded polyester nonwovens were examined and an image recorded with an ETEC Auto Scan Electron Microscope [SEM]. Specimens for the SEM examination were prepared by placing a piece of sample fabric on an aluminum SEM mount to which double-stick tape had been applied. In order to increase resolution and avoid charging of the sample in the SEM, all specimens were sputter-coated with gold/palladium with a Denton Vacuum DV-515 unit. Micrographs of sample surfaces were taken by Polaroid Camera attached to the SEM.

CHAPTER IV

RESULTS AND DISCUSSION

Synthesis of Polyurethane

Polyurethane can be formed by a variety of methods. The most widely employed synthetic method involves the reaction of di- or poly-functional hydroxyl compounds with di- or poly-functional isocyanates. The general structure of a linear polyurethane derived from a dihydroxy compound, HO-R'-OH, and a diisocyanate, O=C=N-R-N=C=O, can be represented by the general formula:

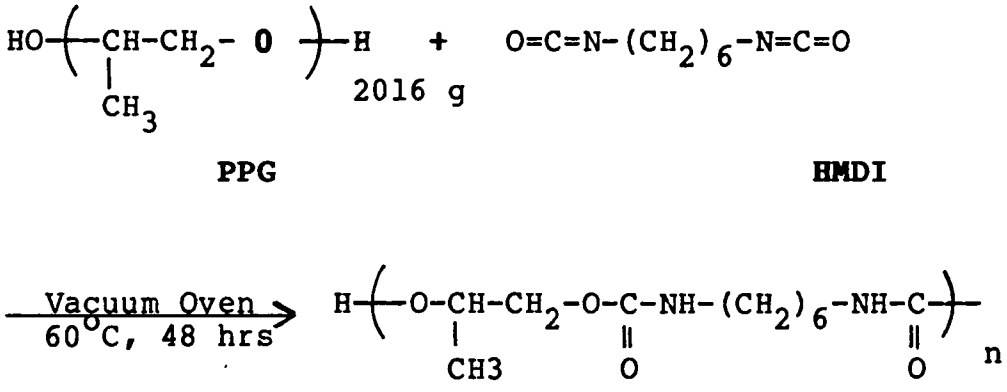


The functionality of the hydroxyl-containing component, as well as the isocyanate, can be increased to three or more to form branched or crosslinked polymers. The nature of R and R' may be changed significantly, such as in total molecular weight, linear versus branched, and aliphatic versus aromatic compounds. For these reasons, the polyurethanes are rather unique in that crosslinking, chain flexibility, and intermolucular forces can be varied widely and virtually independently (61). With these characteristics, it is not unexpected that the polyurethanes as a group include fibers, soft and hard elastomers, flexible and rigid foams, coatings for many

purposes, especially as binders for nonwovens, and highly crosslinked plastics.

Linear Polyurethane

The polyurethane films were prepared by a addition copolymerization of PPG with HMDI, as represented below:



PPG **HMDI**

Polyurethane

Polyurethane films were prepated by a one-step cast technique; all reactants were mixed together initially and then allowed to cure. Selected curing temperature [60° C] and time [48 hrs] provided transparent, amorphous polyurethane films. These films were used to investigate the applicability of synthesized polyurethane binders to the polyester nonwovens.

Crosslinked Polyurethane

A knowledge of the crosslinked structure entails an understanding of the network formation process. The formation of polyurethane networks is one of the more complicated cases (20) because: a) the relative reactivity

of functional groups need not be the same and may change during the reaction and b) some of the units may be short and form rigid sequences, essentially different from flexible sequences of bonds in the macrodiol. The formation of crosslinked polyurethane is depicted schematically in Figure 7.

Five different degrees of crosslinked polyurethane films were made by varying the equivalent ratios between PPG and TMP. Films were all transparent. The higher the crosslink density, the easier to peel off from the curing tray was observed.

Catalysis

Catalysis plays a vital role in the preparation of urethane polymers, because it not only affects the rates of the chemical reactions responsible for chain propagation, extension, and crosslinking but also affects the ultimate properties of the resulting polymers. Another important function of catalysts is to bring about completion of the reactions resulting in an adequate "cure" of the polymers.

Organometalic compounds [e.g., T-9] are extreamly effective catalysts for the isocyanate-hydroxyl reactions. It is reported (84) that T-9 increases the reaction rate of the polyurethane synthesis from 600 to 3500 times faster [depends on the concentration of catalysts in the

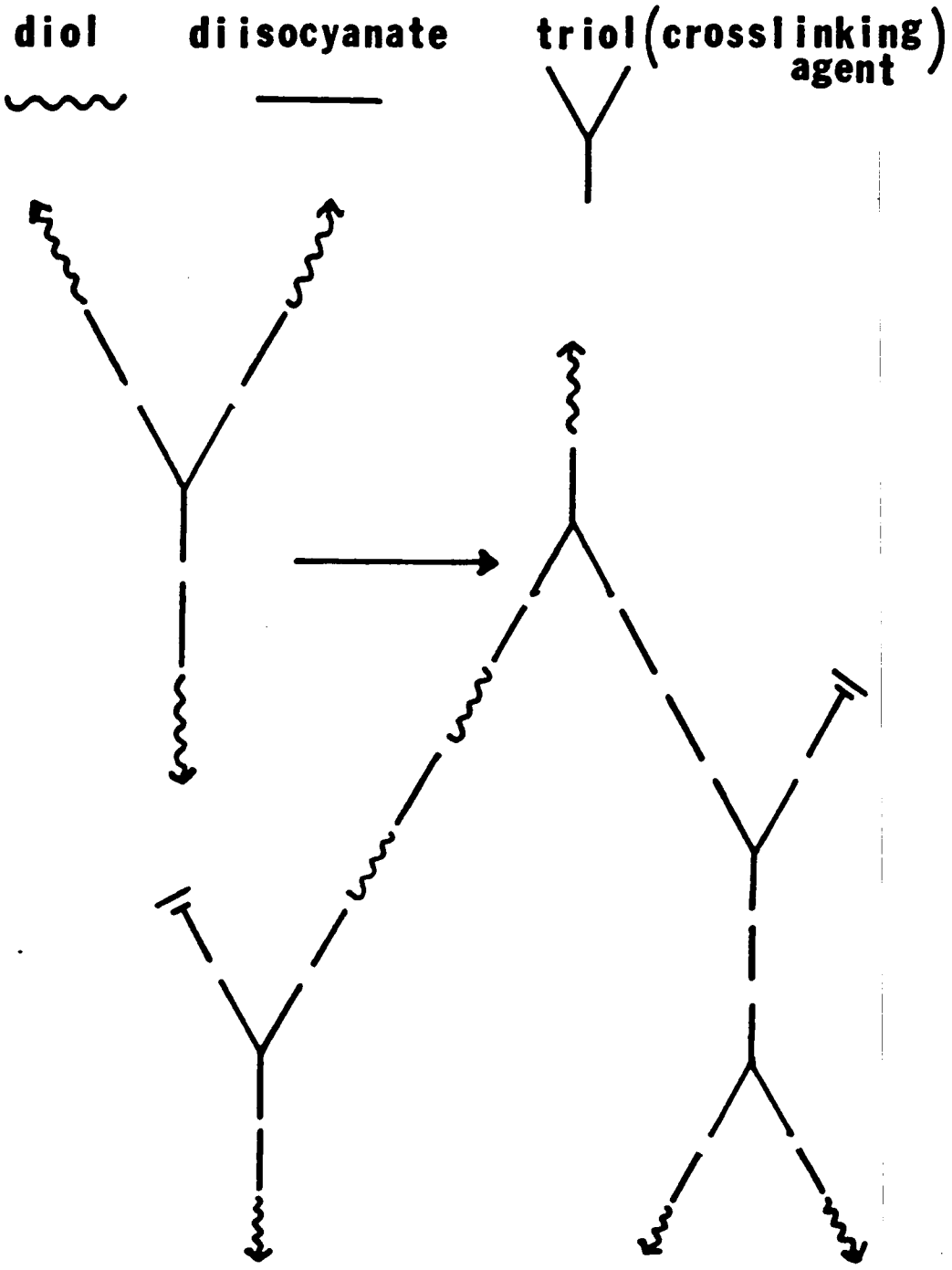


Figure 7. Schematic Representation of the Formation of Network Polyurethanes.

reactants] than that of the uncatalyzed. 0.2% of T-9 respect to the weight of reactants was used and it resulted an optimum curing time, temperature and desirable final products.

The polyurethane formation by organometallic compounds [e.g., stannous octoate; T-9] can be explained by taking into account the structure of the catalysts and the coordination vacancies (8, 118). The alcohol [diol] is non-activated, and the metal has at least two vacancies. The latter are occupied by the alcohol and the isocyanate, respectively, and the reaction takes place as depicted in Figure 8.

This mechanism implies metals characterized by at least partially or completely occupied d orbitals with an energy similar to one of the first unoccupied s or p levels [e.g., Sn^{+2}, Cu^{2+}].

Differential Scanning Calorimetry

Polymers are capable of undergoing a variety of phase transitions, either endothermically or exothermically. Highly crystallized materials may show a well-defined melt transition, but little with respect to a crystallization or glass transition. In contrast, amorphous materials give no response for a melt transition nor a crystallization transition, but they will show a pronounced glass

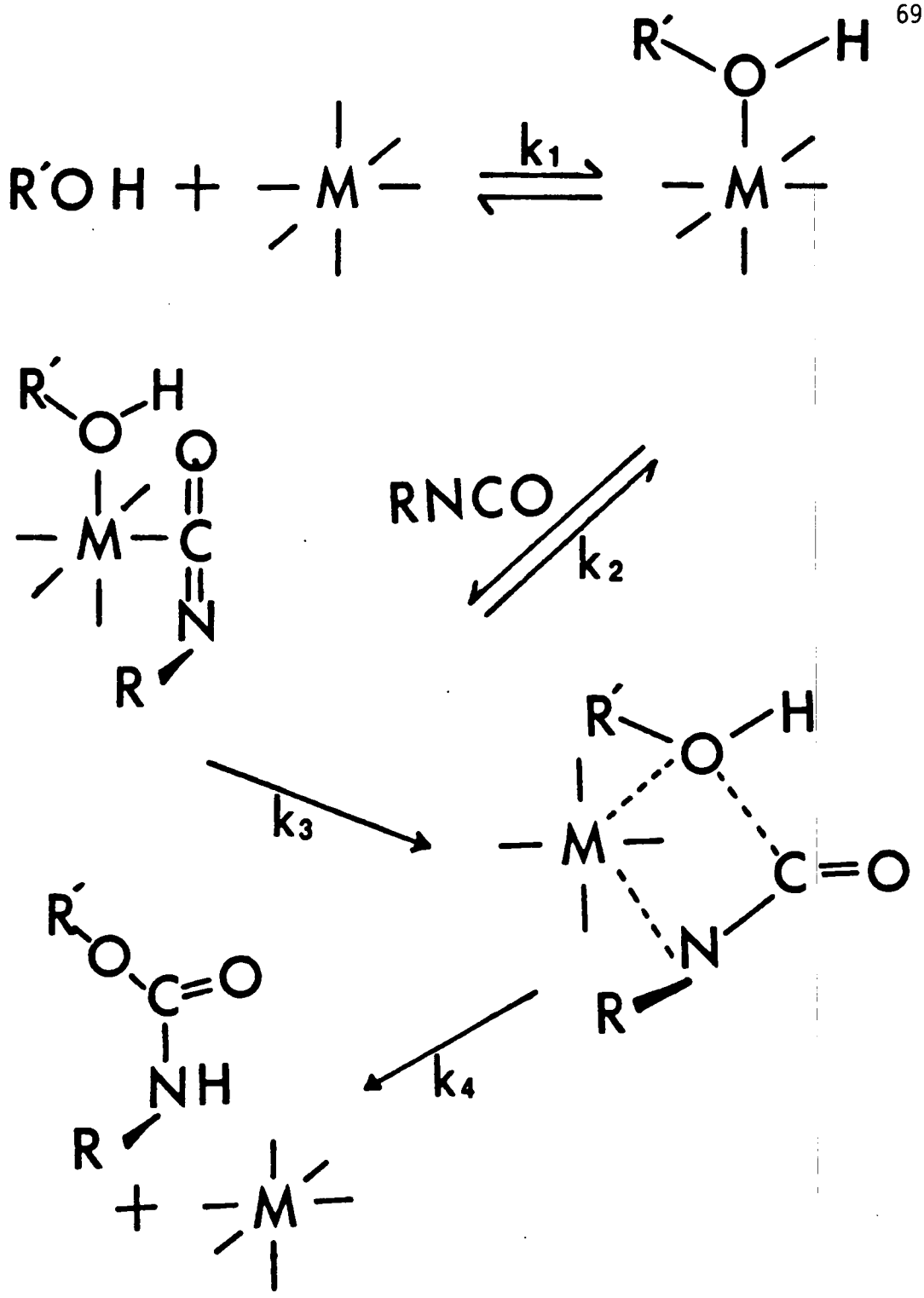


Figure 8. Proposed Mechanism for Urethane Formation Catalyzed by an Organo-metallic Compound.

transition [Fig. 9].

The temperature range utilized was from 210°K [-60°C] to 573°K [300°C]. The glass transition [T_g] was the only signal detected both from the linear and crosslinked polyurethane films. This is taken as evidence that 100% amorphous polyurethane was successfully synthesized from PPG and HMDI. The glass transition temperature for the linear polyurethane was -58°C, and that for the crosslinked polyurethane film ranged from -49 to -52°C. The degree of crosslinking did not significantly affect this transition. Five different amounts of crosslinked polyurethane were tested, but the total range of T_g was only 3°C. The increase in T_g with higher crosslinked polyurethane elastomers is probably due to increase in interchain forces; the cohesive energy density of the elastomers increases with the crosslink density. However, the small increase shown within the crosslinked polyurethanes are due to large portions of soft segments [PPG] in the polymer structrue.

Viscometry

Intrinsic viscosity [η] is defined as:

$$[\eta] = \left(\frac{\eta_{sp}}{c}\right)_{c=0} = \left(\frac{\ln \eta_r}{c}\right)_{c=0}$$

where η_r = relative viscosity; η_{sp} = specific viscosity;

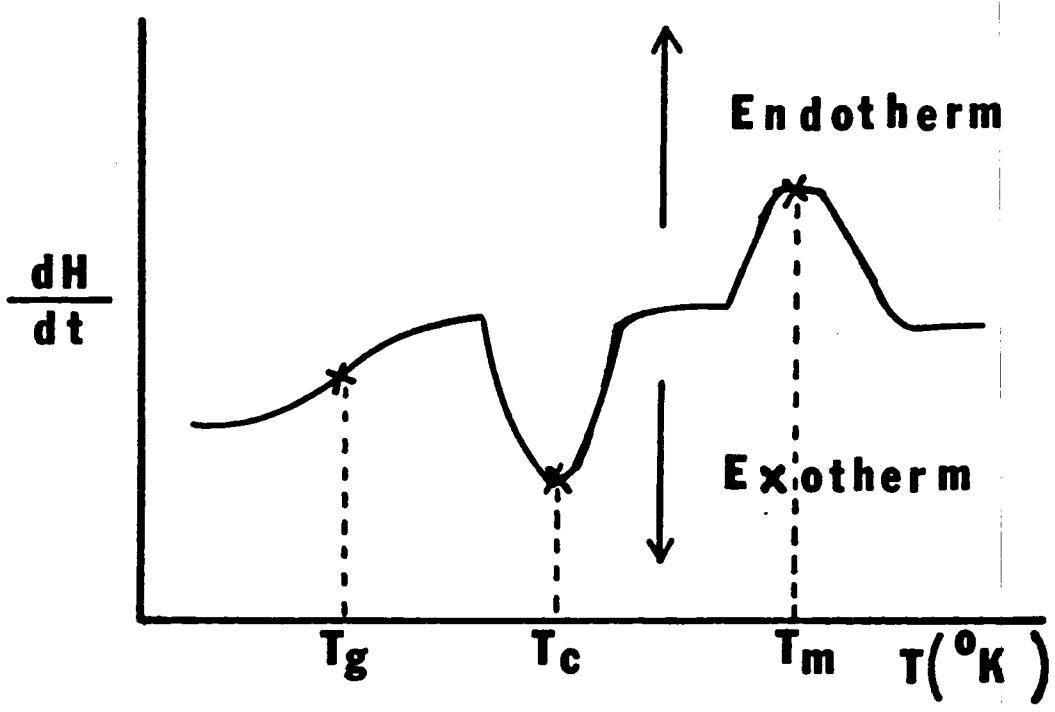


Figure 9. Differential Scanning Calorimetry (DSC) Output for the Polymeric Materials. T_g = Glass Transition Temperature; T_c = Maximum Crystallization of the Polymer Material; T_m = Melting Point.

c = concentration; $\eta_{sp} = \eta_r - 1$; $\eta_r = t/t_o$; t = flow time of solvent; t_o = flow time of solution. Table 3 presents the parameters used and the results of calculations using the above equation.

From the linear regression data, Figure 10, and Table 4:

$y = a + bx$ x = concentration

y = viscosity / c

The straight lines obtained in these extrapolations are not described by theory but have been empirically related by Huggins and Kraemer (47, 58),

Huggins $\eta_{sp}/c = [\eta] + k' [\eta^2] c$

Kraemer $\ln \eta_r/c = [\eta] - k'' [\eta^2] c$

where k' and k'' are the Huggins and Kraemer constants. If $k' - k'' \cong 0.5$, the solvent used for the polymer solution is considered as a "good solvent". As shown in Table 5, the difference between the constants [k' - k''] of 0.420 is close to 0.5. Therefore, this is evidence that methanol is a good solvent for the linear polyurethane.

Each of the synthesized linear polyurethane films was examined using the viscometry method (7). The intrinsic viscosity values were all 0.72-0.74, providing evidence for consistency in the synthesis technique and the identical nature of the products.

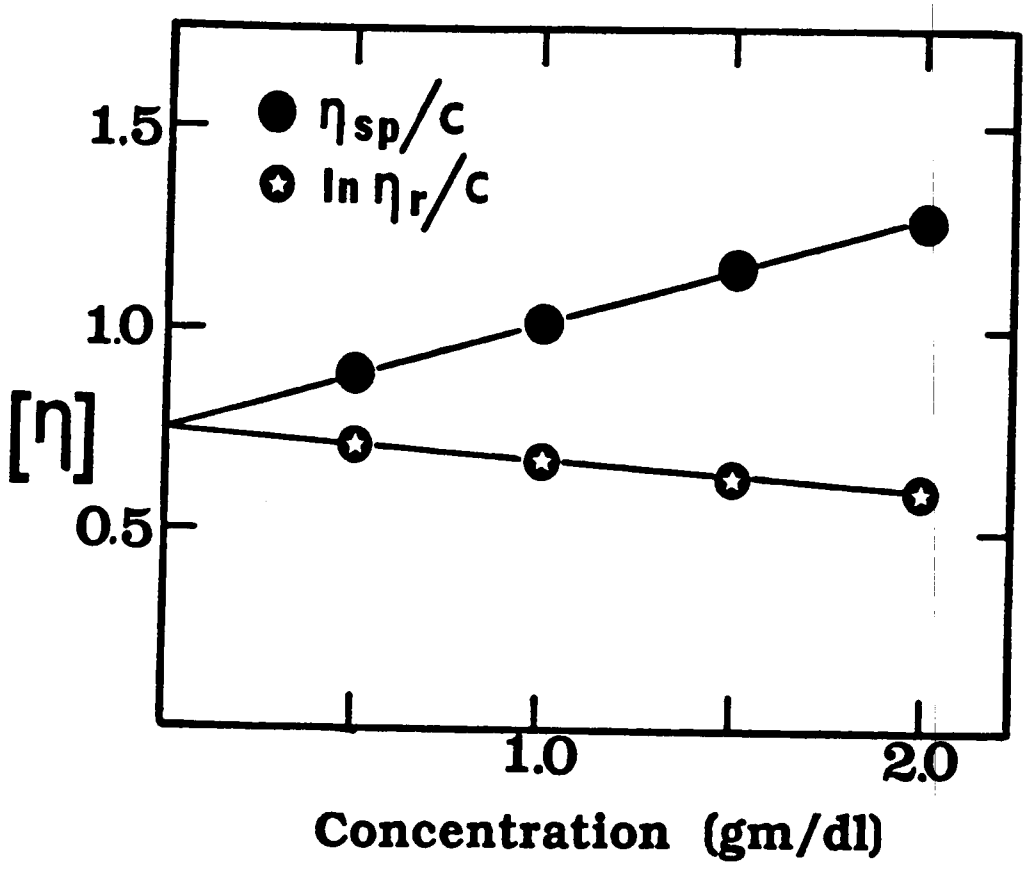


Figure 10. Intrinsic Viscosity of Linear Polyurethane Solution.

TABLE 3. Determined Viscosities for the Linear Polyurethane Films.

Soln.	Conc. (gm/dl)	Flow Time Sec.	η_r	η_{sp}	ln η_r/c	η_{sp}/c
MeOH		72.2				
#1	0.5	103.7	1.436	0.436	0.724	0.872
#2	1.0	144.6	2.003	1.003	0.695	1.003
#3	1.5	196.3	2.719	1.719	0.667	1.146
#4	2.0	263.9	3.655	2.655	0.648	1.328

Table 4. Viscosity and Slope Data From Figure 10.

	a (n)	b (slope)	R (correl. coeff.)
ln η_r/c	0.7475	-0.0512	0.9957
η_{sp}/c	0.7095	0.3022	0.9970

Table 5. Huggins (k') and Kraemer (k'') Constants for Polymer Solutions in the Present Study.

Soln. #	k'	k''
1	0.482	0.058
2	0.480	0.082
3	0.494	0.089
4	0.537	0.084
Avg ($\bar{x}$)	0.498	0.078

$k' - k'' = 0.498 - 0.078 = 0.420$

Table 6. Refractive Indices of Polyurethane Solutions.

Soln	Conc. (gm/ml)	d1		d2		Δ d		Δn(x10^{-4})	
		Gr	Bl	Gr	Bl	Gr	Bl	Gr	Bl
MeOH		5.45	5.39	5.18	5.16				
#1	1.0x10^{-3}	5.45	5.56	5.47	5.54	-0.45	-0.21	2.6	1.9
#2	2.5 "	5.13	5.22	5.31	5.40	-0.78	-0.41	4.1	3.7
#3	5.2 "	4.82	4.82	5.33	5.34	-1.22	-0.75	7.1	6.8
#4	7.8 "	4.76	4.78	5.75	5.77	-0.29	-1.22	11.1	11.1

Differential Refractive Index

The Brice-Phoenix Differential Refractometer is designed for the direct measurement of the differential refractive index [n] between a dilute solution and its solvent. In practice,

$$\Delta d = (d_1 - d_2)_{soln} - (d_1 - d_2)_{solvent}$$

where d_1 and d_2 are directly obtained from the galvanometer reading at the angles of 0° and 180°. These are related to the differential refractive index (n) by the relation

$$\Delta n = K \Delta d \qquad [K = 9.06 \times 10^{-4}]$$

where K is the instrumental calibration constant. Measurements of d_1 and d_2 were performed with both green light [5460 Å] and blue light [4358 Å], which were isolated from the mercury lamp. Measured values for the actual refractive indices are given in Table 6.

From the linear regression data and Figure 11:

		Correlation Coeff.
Green Light:	$\frac{dn}{dc} = 0.1389$	0.9940
Blue Light:	$\frac{dn}{dc} = 0.1378$	0.9980

The differential refractive indices with the green light and blue light are virtually identical. Therefore, this is confirmation that the samples were efficiently polymerized within the films.

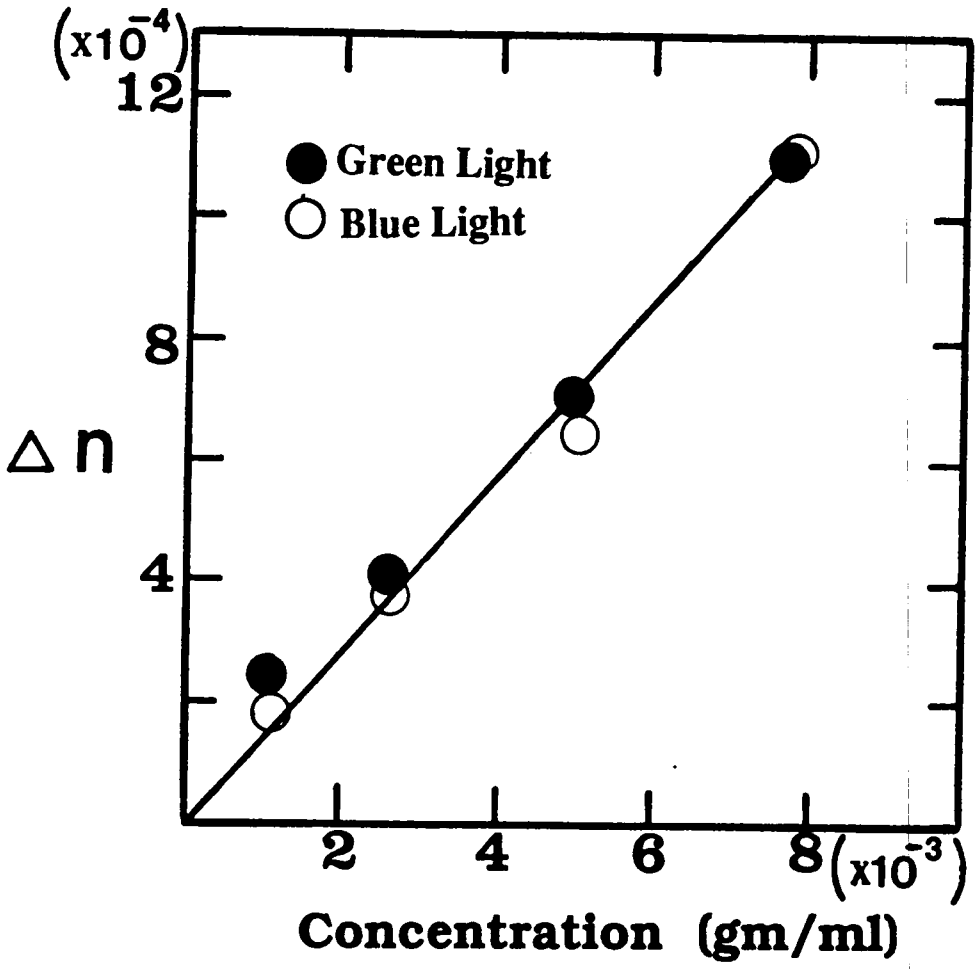


Figure 11. Differential Refractive Indices of Polyurethane Solutions at Green Light (5460 Å) and Blue Light (4358 Å).

Swelling

The phenomenon of swelling is characteristic of polymers possessing network structures (49). If the network structure is permanent in the sense that its essential skeletal structure is not disrupted by the action of the solvent, a state of equilibrium swelling can be attained. Swelling is accompanied by an increase in the entropy of mixing of the solvent with the polymer (76).

Equilibrium swelling of crosslinked polyurethane in methylene chloride and methanol was determined. Methanol was found to be a good solvent for the linear polyurethane by the viscometry method. However, for the crosslinked polyurethane, methylene chloride was determined to be a better solvent, as based on swelling ratio data [Table 7].

These were calculated from the following equations:

$$\text{Swelling Ratio} = (W_s / W_f) - 1$$

$$\text{Sol Fraction (\% extractable)} = (W_i - W_f) / W_i$$

W_i = initial sample weight

W_s = swollen sample weight

W_f = final sample weight

As shown in Table 7, PPG and TMP mole ratios of 0.9 : 0.1 and 0.8 : 0.2 were used to examine the swelling ratios in methylene chloride and methanol. Both of the crosslinked polyurethane films were swollen about six [6] times more in methylene chloride than in methanol. In order

Table 7. Swelling Ratios of Crosslinked Polyurethane in Methylene Chloride and Methanol.

PPG:TMP	Solvent	w_i	w_s	w_f	Sol Frac	Swelling Ratio
0.9:0.1	MeCl	0.2972	5.1548	0.2621	0.1181	18.67
	MeOH	0.2525	1.5265	0.2508	0.0067	5.09
0.8:0.2	MeCl	0.2512	2.9507	0.2400	0.0446	11.19
	MeOH	0.2223	0.7528	0.2152	0.1319	2.64
0.7:0.3	MeCl	0.0431	0.3112	0.0421	0.0232	6.15
0.6:0.4	MeCl	0.0157	0.1000	0.0154	0.0191	5.49

w_i = initial sample weight; w_s = swollen sample weight; w_f = final sample weight; **swelling ratio** = $(w_s / w_f) - 1$; **sol fraction** (% extractable) = $(w_i - w_f) / w_i$.

to dilute the viscous polyurethane binders for spraying on the polyester webs, methylene chloride was selected because of its compatibility with polyurethane. The higher the crosslinked polymer, the lower was the swelling ratio and sol fraction. This observation probably reflects the frozen molecular movement within the network structure.

Mechanical Properties

To facilitate the convenient understanding of the results, a code was developed for the different samples. The details of this code for the experiments are shown in Table 8.

Mechanical properties of adhesively bonded polyester nonwovens with various polyurethane binder concentrations and degree of crosslinking are shown in Table 9 for the machine direction [MD] webs. These data have been used to construct Figures 12-16, wherein the variation in the mechanical properties are graphically displayed. Because of the inherent differences in the nature of the webs, the mechanical properties of cross-machine directional [CD] webs were also examined. These data are presented in Table 10 and graphically displayed in Figures 17-21.

It is evident from Figure 12 that the modulus of nonwoven webs increases with increasing crosslinking density of the polyurethane binder. For the low levels of

Table 8. Explanation of Sample Codes.

TMP:PPG	Binder Add On	Machine Direction	Cross-Machine Direction
0.1 : 0.9	30%	P-1-a-M	P-1-a-C
	40	P-1-b-M	P-1-b-C
	50	P-1-c-M	P-1-c-C
0.2 : 0.8	30	P-2-a-M	P-2-a-C
	40	P-2-b-M	P-2-b-C
	50	P-2-c-M	P-2-c-C
0.3 : 0.7	30	P-3-a-M	P-3-a-C
	40	P-3-b-M	P-3-b-C
	50	P-3-c-M	P-3-c-C
0.4 : 0.6	30	P-4-a-M	P-4-a-C
	40	P-4-b-M	P-4-b-C
	50	P-4-c-M	P-4-c-C
0.5 : 0.5	30	P-5-a-M	P-5-a-C
	40	P-5-b-M	P-5-b-C
	50	P-5-c-M	P-5-c-C
Web		P-0-0-M	P-0-0-C

Fiber	Polyester	P
TMP : PPG	0.1 : 0.9	1
	0.2 : 0.8	2
	0.3 : 0.7	3
	0.4 : 0.6	4
	0.5 : 0.5	5
Binder Add On	30%	a
	40%	b
	50%	c
Carding Direction	Machine	M
	Cross-Machine	C

Table 9. Machine Directional Mechanical Properties of Adhesively Bonded Polyester Nonwovens with Various Polyurethane Binder Concentrations and Degrees of Crosslinking.

Sample Code	Tenacity #	% Elongation Tmax	Elastic Modulus	Tear Strength ($x10^{-2}$)	Energy to Break ($x10^{-2}$)
P-0-0-M	0.13	65.5%	0.21	3.83	4.79
P-1-a-M	0.13	65	0.25	4.42	5.52
P-1-b-M	0.16	63	0.28	5.24	6.56
P-1-c-M	0.18	62.5	0.34	6.09	7.61
P-2-a-M	0.17	63	0.34	4.83	6.04
P-2-b-M	0.25	62.5	0.53	7.08	8.86
P-2-c-M	0.30	62	0.59	8.73	10.91
P-3-a-M	0.26	63	0.52	6.42	8.02
P-3-b-M	0.30	62	0.58	8.32	10.40
P-3-c-M	0.33	61	0.63	9.71	12.13
P-4-a-M	0.27	62.5	0.53	7.98	9.98
P-4-b-M	0.33	61.5	0.60	9.22	11.52
P-4-c-M	0.43	61	0.67	10.28	12.85
P-5-a-M	0.29	62	0.56	9.00	11.25
P-5-b-M	0.35	61.5	0.60	9.79	12.24
P-5-c-M	0.47	61	0.79	10.93	13.66

Units for all properties, except Elongation, are mN/Tex.

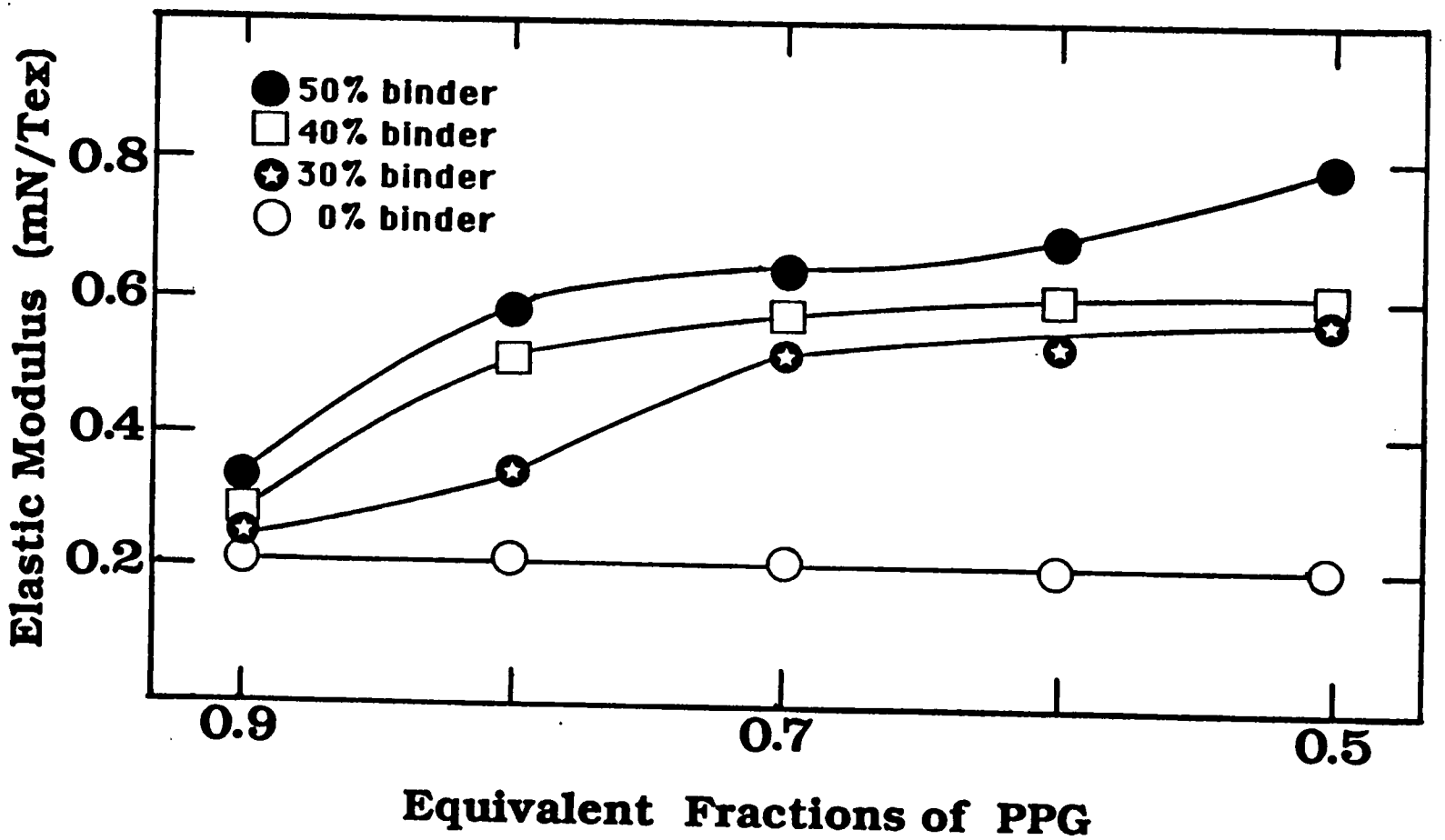


Figure 12. The Elastic Modulus of Machine Directional, Adhesively Bonded, Polyester Nonwovens as a Function of: 1) Different Crosslink Densities of Polyurethane Binder and 2) the Quantity of Applied Binder.

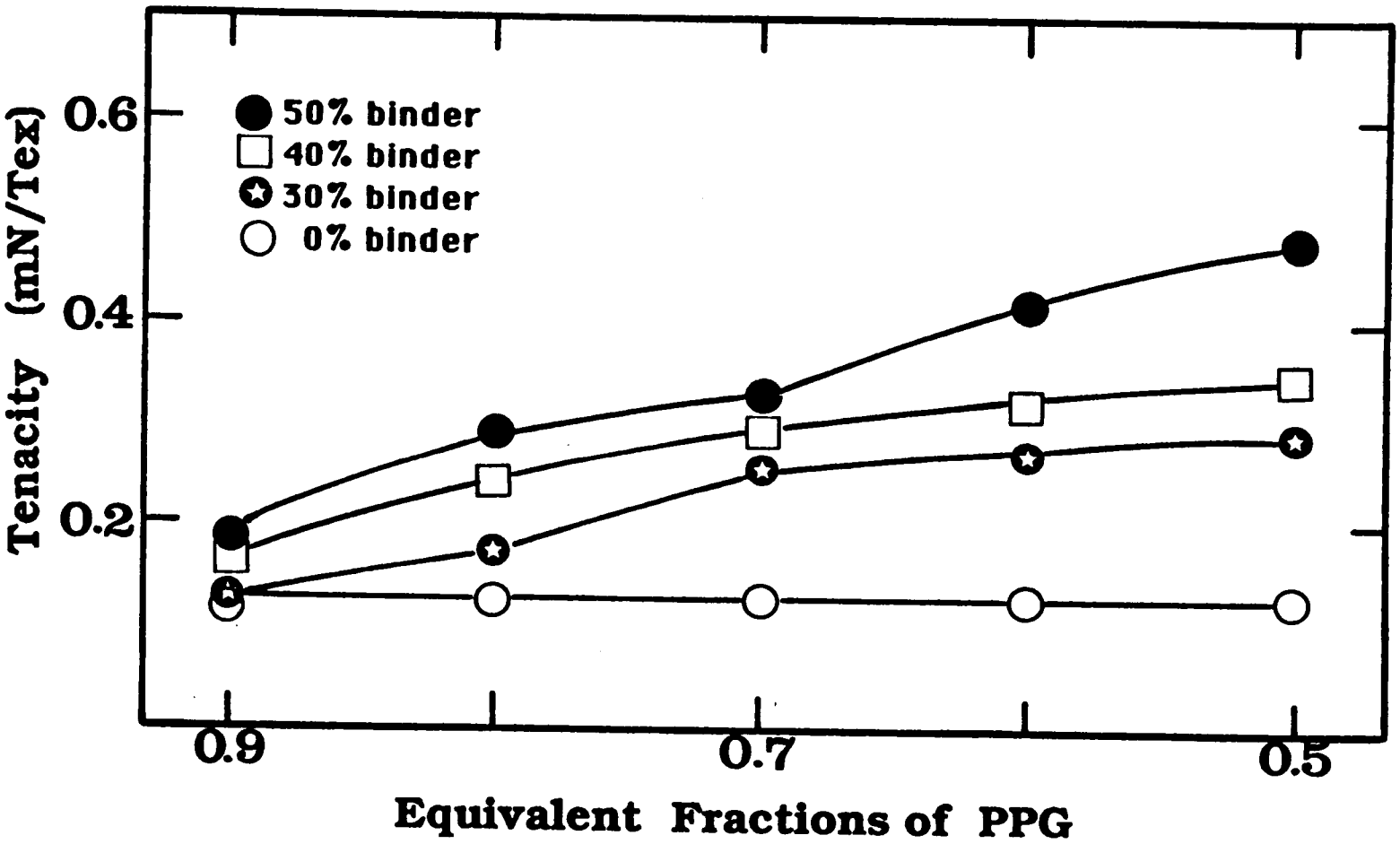


Figure 13. The Tenacity of Machine Directional, Adhesively Bonded, Polyester Nonwovens as a Function of: 1) Different Crosslink Densities of Polyurethane Binder and 2) the Quantity of Applied Binder.

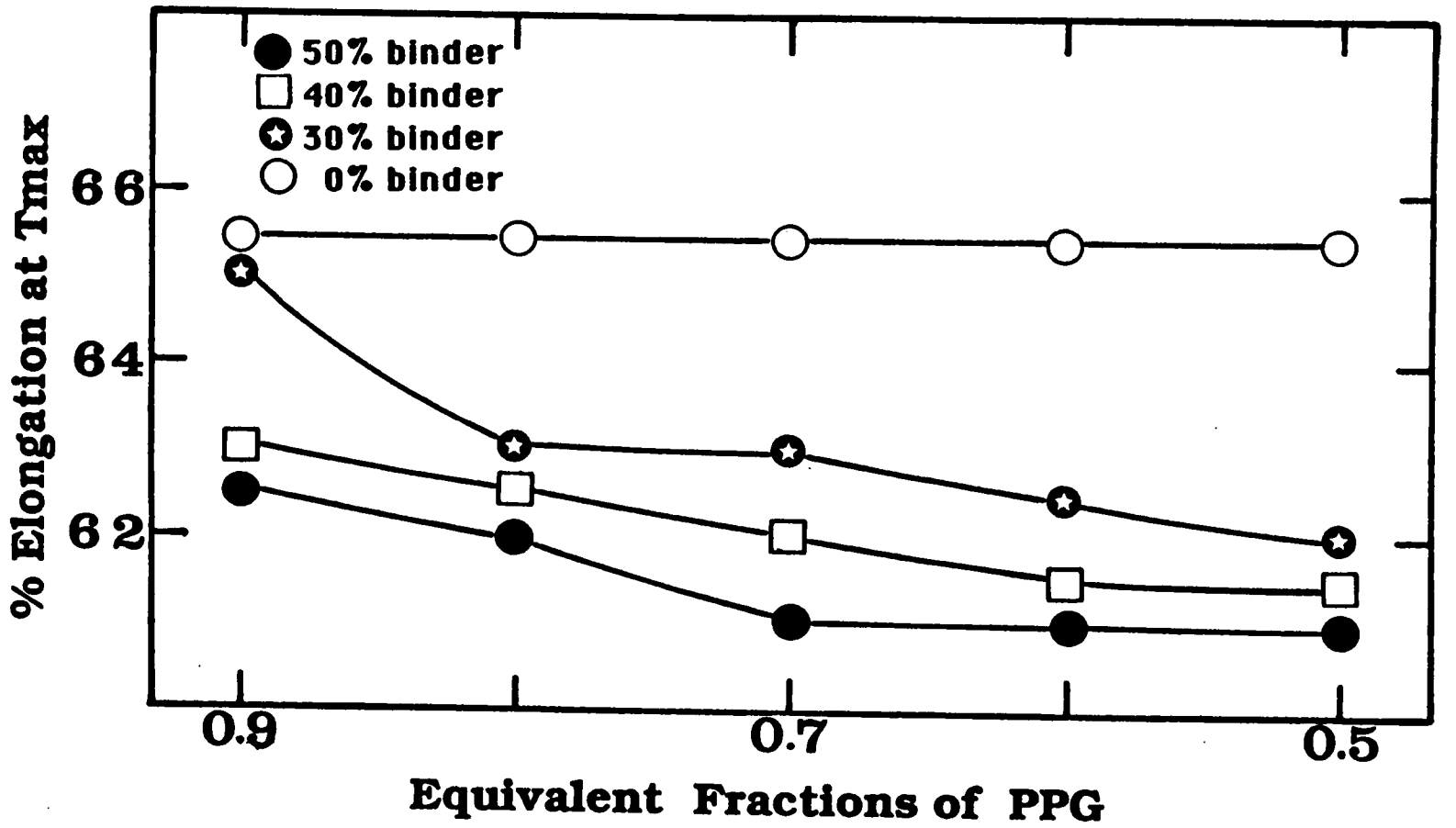


Figure 14. The % Elongation of Machine Directional, Adhesively Bonded, Polyester Nonwovens as a Function of: 1) Different Crosslink Densities of Polyurethane Binder and 2) the Quantity of Applied Binder.

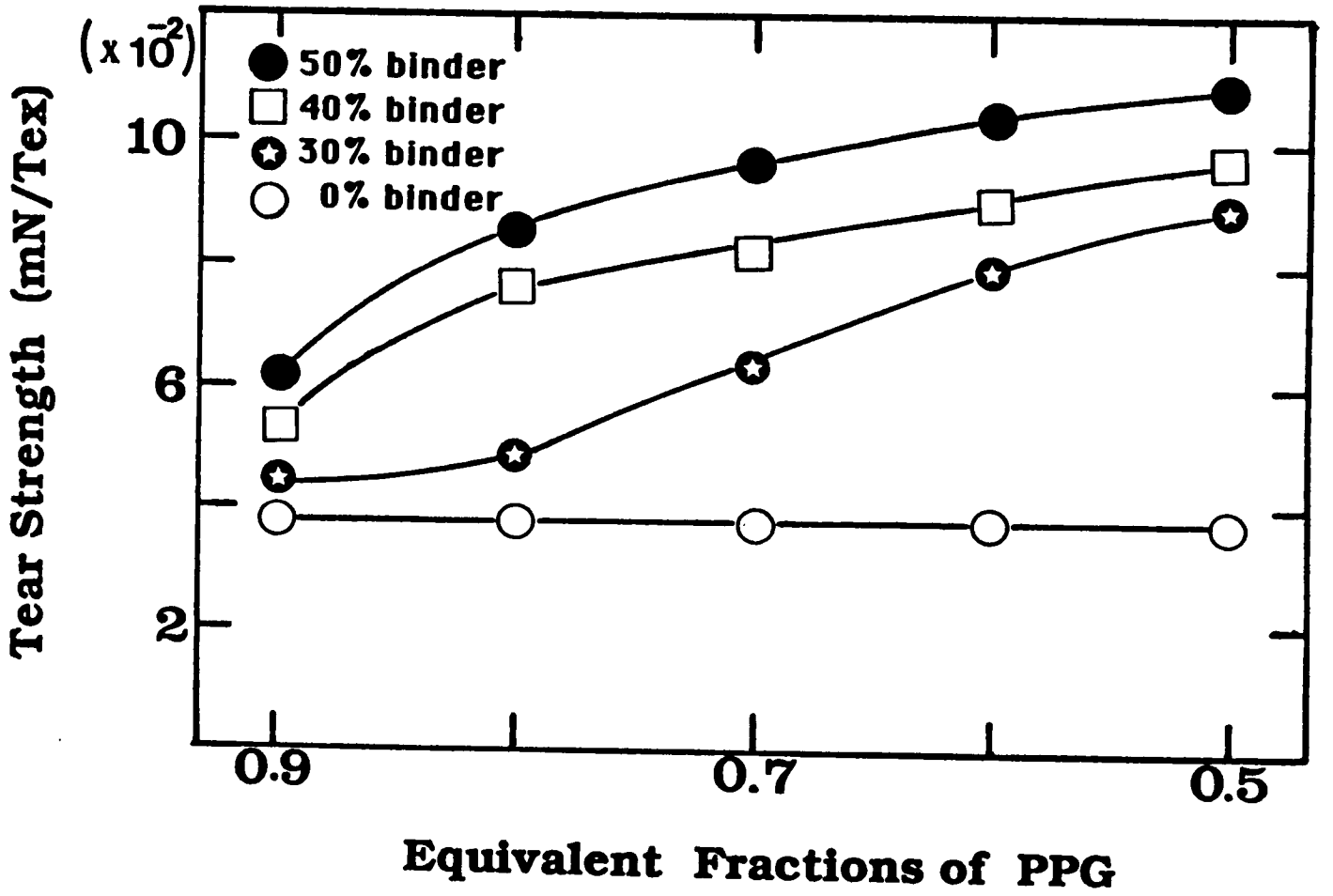


Figure 15. The Tear Strength of Machine Directional, Adhesively Bonded, Polyester Nonwovens as a Function of: 1) Different Crosslink Densities of Polyurethane Binder and 2) the Quantity of Applied Binder.

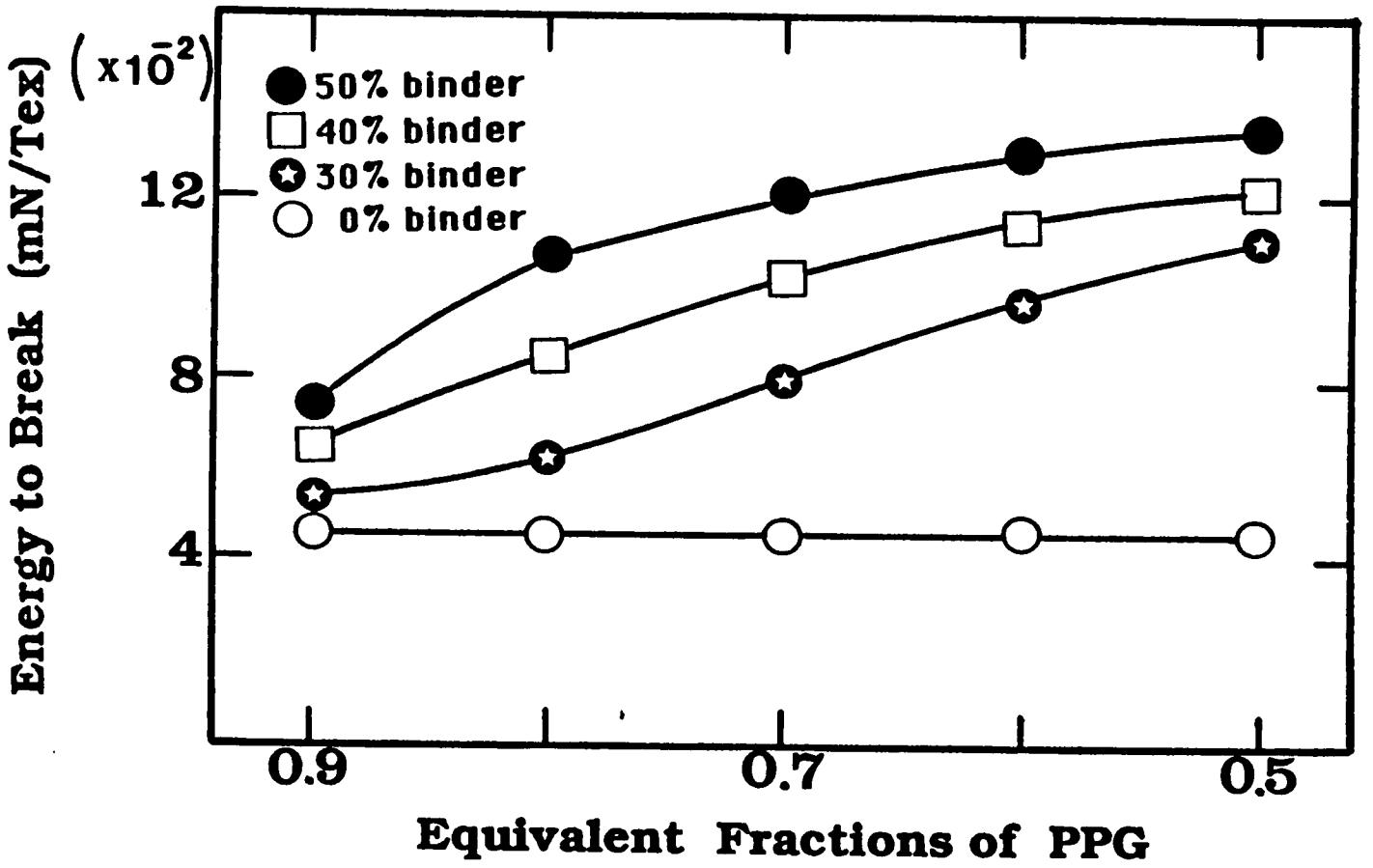


Figure 16. The Energy to Break of Machine Directional, Adhesively Bonded, Polyester Nonwovens as a Function of: 1) Different Crosslink Densities of Polyurethane Binder and 2) the Quantity of Applied Binder.

Table 10. Cross-Machine Directional Mechanical Properties of Adhesively Bonded Polyester Nonwovens with Various Polyurethane Binder Concentrations and Degrees of Crosslinking.

Sample Code	Tenacity #	% Elongation Tmax	Elastic Modulus	Tear Strength ($x10^{-2}$)	Energy to Break ($x10^{-2}$)
P-0-0-C	0.012	106%	0.021	0.50	0.63
P-1-a-C	0.018	107	0.042	1.18	1.48
P-1-b-C	0.018	103	0.047	1.64	2.05
P-1-c-C	0.020	103	0.050	2.16	2.70
P-2-a-C	0.019	101	0.045	1.55	1.94
P-2-b-C	0.020	99	0.051	1.95	2.44
P-2-c-C	0.030	95	0.070	2.49	3.11
P-3-a-C	0.019	100	0.046	1.62	2.02
P-3-b-C	0.021	95	0.054	2.00	2.50
P-3-c-C	0.031	93	0.070	2.67	3.34
P-4-a-C	0.019	100	0.050	1.70	2.11
P-4-b-C	0.022	94	0.060	2.19	2.73
P-4-c-C	0.031	92	0.071	2.75	3.44
P-5-a-C	0.022	100	0.051	1.75	2.19
P-5-b-C	0.023	93	0.063	2.29	2.86
P-5-c-C	0.033	87	0.075	2.81	3.52

Units for all properties, except Elongation, are mN/Tex.

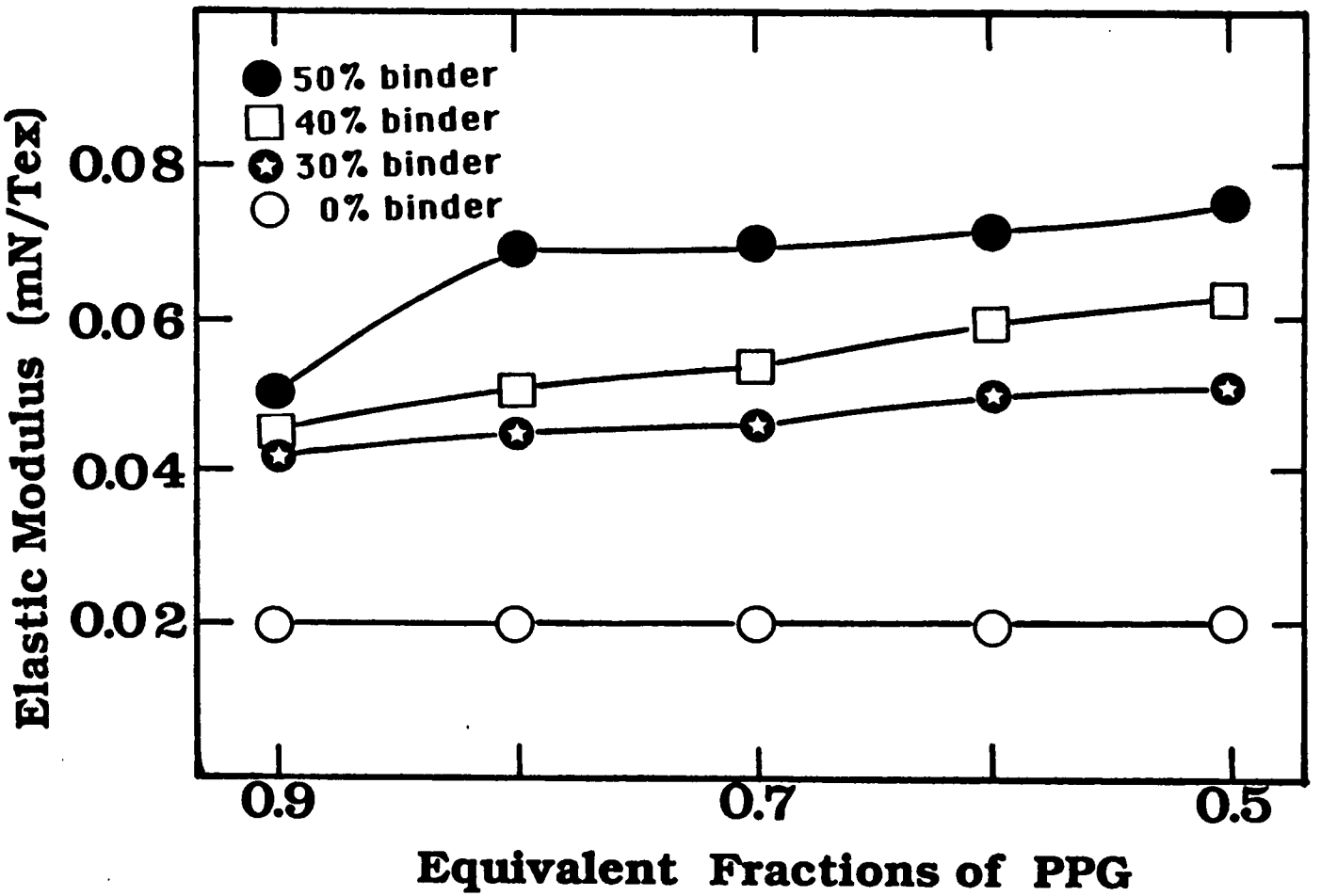


Figure 17. The Elastic Modulus of Cross-Machine Directional, Adhesively Bonded, Polyester Nonwovens as a Function of: 1) Different Crosslink Densities of Polyurethane Binder and 2) the Quantity of Applied Binder.

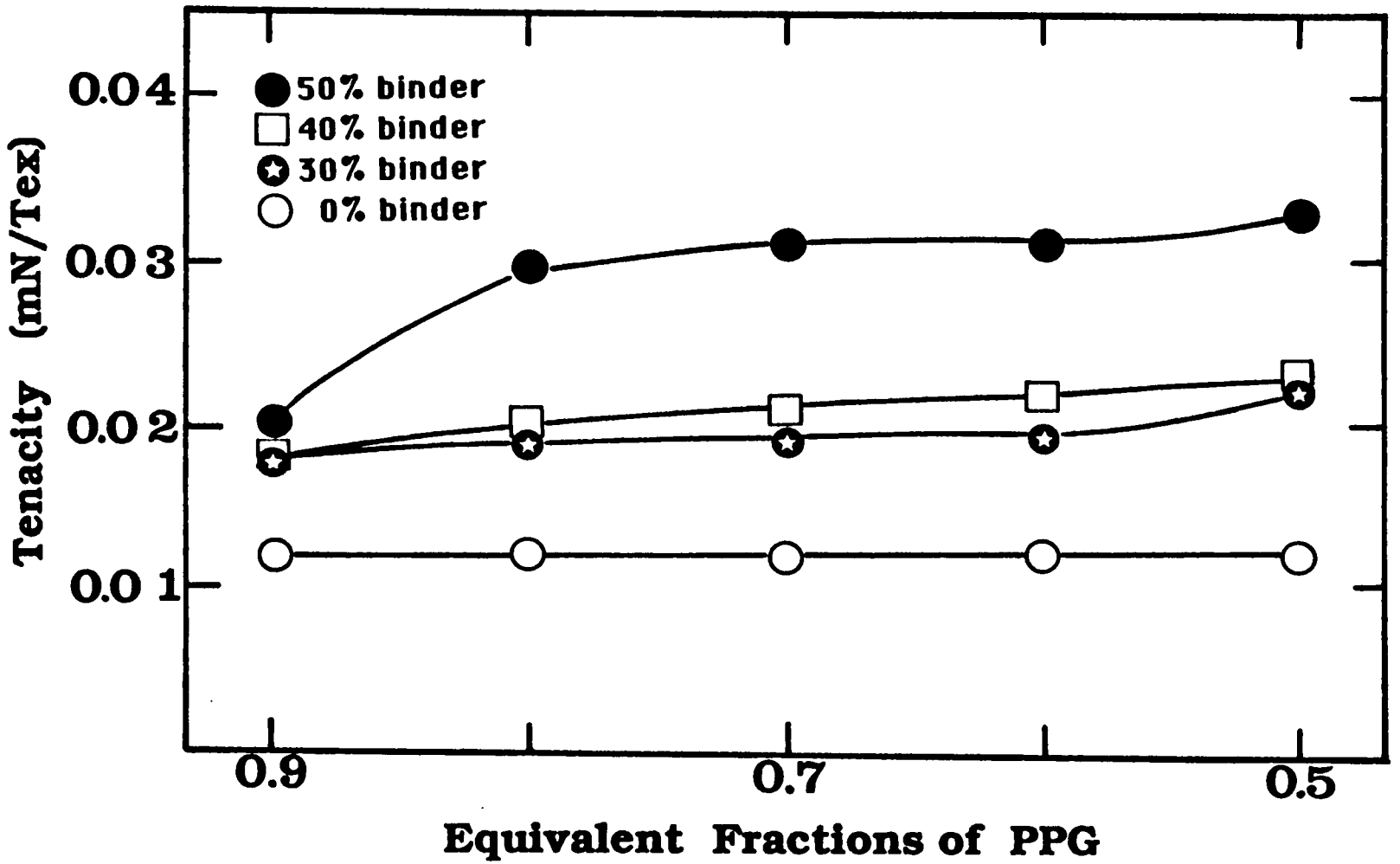


Figure 18. The Tenacity of Cross-Machine Directional, Adhesively Bonded, Polyester Nonwovens as a Function of: 1) Different Crosslink Densities of Polyurethane Binder and 2) the Quantity of Applied Binder.

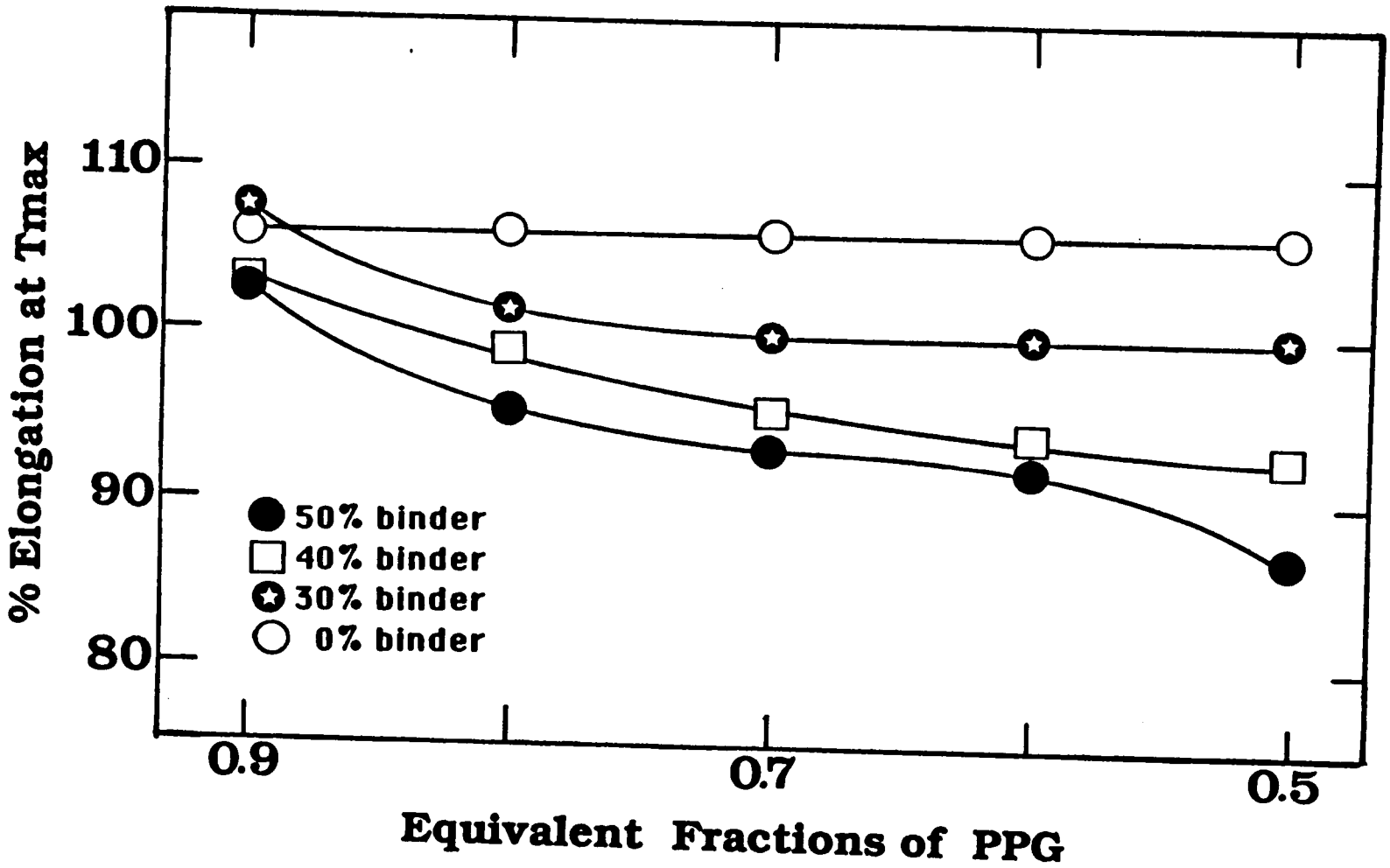


Figure 19. The % Elongation of Cross-Machine Directional, Adhesively Bonded, Polyester Nonwovens as a Function of: 1) Different Crosslink Densities of Polyurethane Binder and 2) the Quantity of Applied Binder.

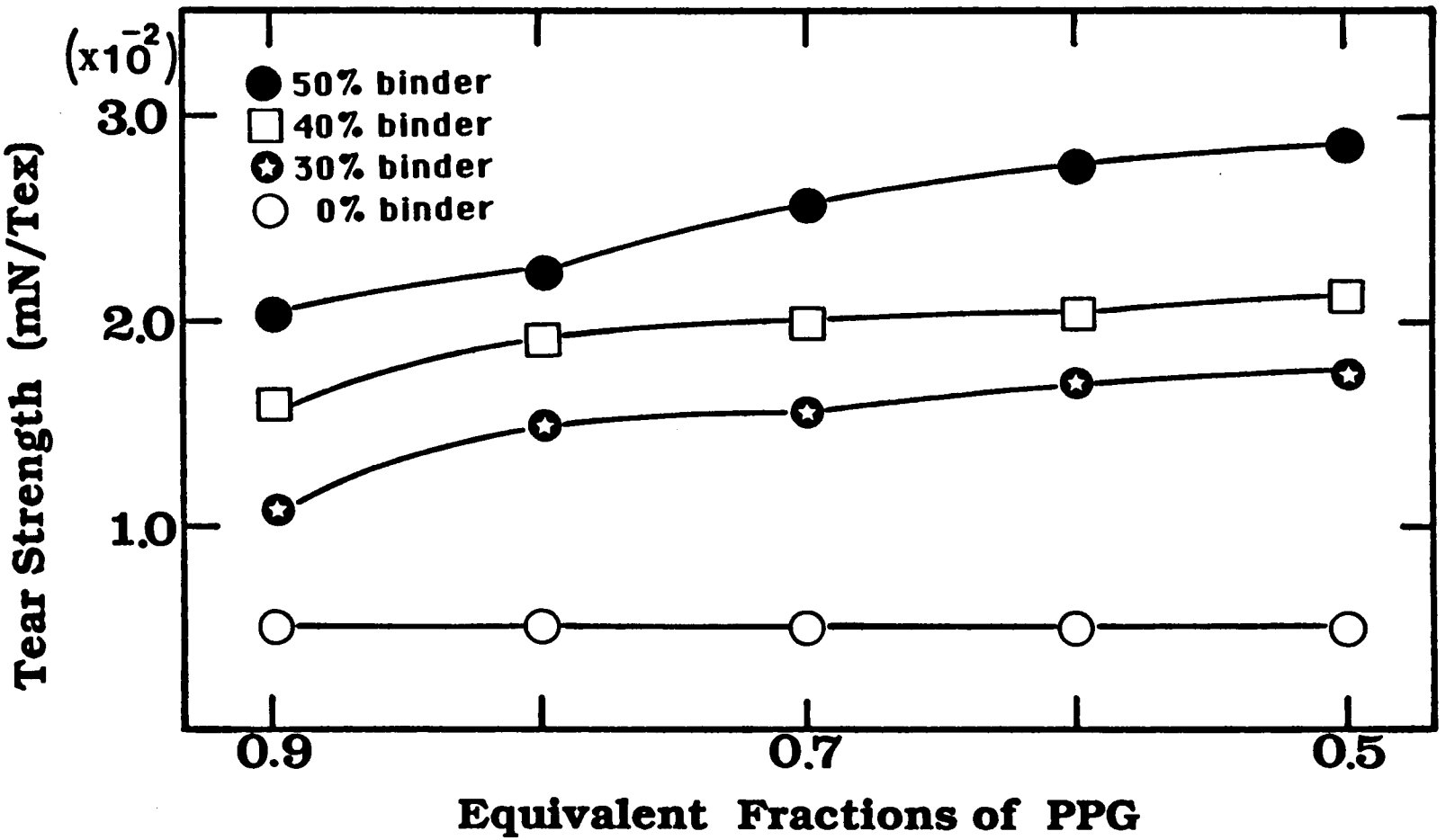


Figure 20. The Tear Strength of Cross-Machine Directional, Adhesively Bonded, Polyester Nonwovens as a Function of: 1) Different Crosslink Densities of Polyurethane Binder and 2) the Quantity of Applied Binder.

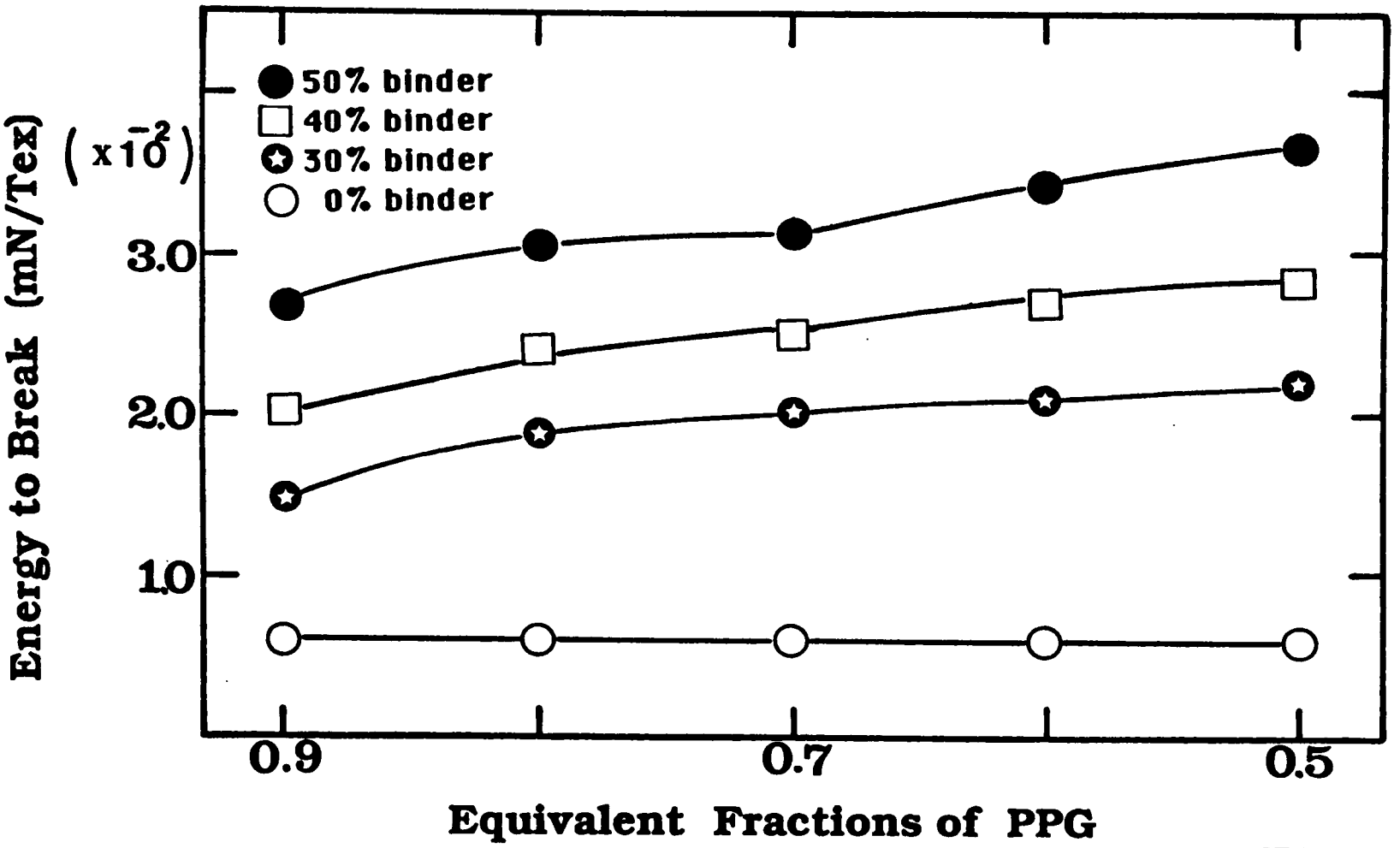


Figure 21. The Energy to Break of Cross-Machine Directional, Adhesively Bonded, Polyester Nonwovens as a Function of: 1) Different Crosslink Densities of Polyurethane Binder and 2) the Quantity of Applied Binder.

crosslinking studies, the level of increase is essentially similar at all three binder concentrations. At higher crosslinking densities, however, the modulus versus crosslinking curves reach a plateau at binder concentrations of 30% and 40%, but show an appreciable increase at 50% binder concentration on the nonwoven webs. This may be due to the interactive effect of binder concentrations rather than to the crosslinking density per se. A similar behavior was observed for a change in tenacities of the bonded webs versus crosslink density [Figure 13]. This is to be expected since no change exists in the extensibilities of the bonded webs with increasing crosslink density. The adhesive bonding does not change the molecular orientation in the binder film. With 30% binder add-on, the tear strength and energy-to-break of MD fabric [Figures 15 and 16] does not begin to show any appreciable change to degree of crosslink until about PPG : TMP = 0.5 : 0.5. This implies that the amount of crosslink density plays an important role in the mechanical properties of low-binder add-on fabric. With both 40% and 50% binder add-on, tear strength and energy-to-break increase gradually with an increase in crosslink density.

There is essentially no change in the elastic modulus or tensile strength of webs in CD with increasing crosslinking, as shown in Figures 17-19. Only at 50%

binder add on is there a slight increase in strength observed. This is probably due to a greater number of adhesive bonding points in the web. The elastic modulus of these samples was affected, not only by the percentage of binder add on, but also by the crosslink density of the binder [Figure 17]. This was not unexpected because the modulus is a measurement of stiffness, and it is obvious that a high degree of crosslinking gives the most immobility in the sample. Figure 19 shows that the % elongations are practically in the same range [90-110%] for all the samples, except those with 50% binder add on at a PPG : TMP ratio of 0.5 : 0.5. These results are to be expected due to the loose interfiber entanglement in CD. For both 30% and 40% binder add-on, the tear strength and energy-to-break of the CD fabric [Figures 20 and 21] increase gradually with an increase in crosslink density. The sharp increase of both properties is only seen in the 50% binder add-on for crosslink density values above PPG : TMP = 0.7 : 0.3. Since the polyester webs were processed by a "dry-laid parallel technique", their mechanical properties in the cross-machine direction were of lesser quality than those in the machine direction.

A major result of these experiments is the establishment of the relationship beween the amount of binder add-on with the degree of crosslinking as these determine the mechanical properties of the nonwovens.

Effects of Binder Properties

Recent work (120) in polymer adhesion has emphasized the importance of particular polymer properties upon the effectiveness of the binder. The most important of these properties are viscosity, surface tension, and T_g. These are the subject of the present study.

The kinetics of the wetting process are influenced by the viscosity of the binder in the fluid state. The desirable viscosity of the binder is achieved when the fluid can be spread out thinly and coated onto the fiber surfaces, by the process of spraying. Methylene chloride was used to dilute the polyurethane binder in order to obtain the various viscosities just prior to spraying. It should be mentioned that the total effective volume of fiber-polymer bond appears to be independent of the solvent used (24). That is, the solvent does not affect the mechanical properties of the binder or the nonwoven fabrics. The optimum condition for wetting and adhesion is the matching of the polarities of the two phases (50). The optimum wetting also commences when the situation is reached where spontaneous spreading occurs. It is suggested that both the interfacial properties and the cohesive strength of the polymer binder are important for the mechanical strength of the bonded network. The effect of surface treatment of the fibers or chemical modification

of the polymer binder are also important when an attempt is made to improve the joint strength.

Chemical compatibility between the fiber and binder is important in the formation of a proper bond. Matching of the solubility parameters of the adhesive and substrate will result in a high correlation with bond strength (24).

The flexibility of adhesively bonded nonwoven fabric is mostly dependent upon the glass transition temperature of the binder. The T_g of the polyurethane binder used here was approximately -50 ^{o}C, such that the fabric made from this binder was a rubbery state and slightly tacky at room temperature [25 ^{o}C]. The characteristics generated by the soft polyurethane binder in this study may be particularly useful for fabrics to be utilized by persons working at low temperatures, especially below 0 ^{o}C.

Large increases in the degree of crosslinking make amorphous polymers tougher and cause them to have higher modulus, fabric strength, and higher T_g, reduced elongation and swelling by solvents. The results show that the contribution of crosslink density on fabric properties is less than that of the binder concentration.

Nonwoven fabrics are composite of fiber and binder. The behavior of nonwovens varies with binders which have different mechanical properties due to their various polymer characteristics. Their viscoelastic behavior is

the most important property of polymers to nonwoven fabric properties. It performs like a perfectly elastic material at low temperatures. As the temperature increases, the polymer softens and the modulus decreases. However, for crosslinked polymers, the modulus decreases through the transition temperature and then stabilizes at a value in the rubber region as the temperature increases.

A number of investigations have been carried out to show the relations between binder films and bonded nonwoven fabrics. Michie (65) found a linear relation between the reciprocals of fabric and binder moduli, which led to the equation,

$$E_f = \frac{700\ E_b}{1 + 16\ E_b}$$

where E_f [g/Tex] is the fabric modulus and E_b is the binder modulus [g/Tex].

At low binder modulus, where 16 E_b is small compared to 1, fabric modulus becomes proportional to binder modulus. At high binder modulus, 16 E_b predominates in the denominator, and the fabric modulus then approaches a constant value.

The fabric modulus is overwhelmingly controlled by the binder modulus and binder content in the soft binder region. In the high binder modulus region, the effect of binder modulus on fabric modulus is getting smaller with

increasing binder stiffness, since the bond becomes so rigid by comparison with the fiber deformation. Hearle and Newton (36) also found that the fabric breaking strength and the binder content has a linear relationship.

Flory (24) has shown that tensile strength increases with increasing crosslink density, goes through a maximum, and then levels off. It was also indicated that the greater the crosslink density, the stronger the web. Increasing the binder content was found to increase the web strength by increasing the number and size of the web bonds.

The elongation of a nonwoven fabric depends upon the freedom of the fiber movement. Thus, the add-on and the flexibility of binder are two factors which influence the fabric elongation.

According to Kaeble (54), with a soft binder in the nonwovens, the rupture mechanism of the nonwoven fabric is most likely caused by binder failure. This occurs even at high binder content, due to the weak binder strength and low modulus. The rupture of a nonwoven bonded with a hard binder is caused by interfacial failure at lower binder content because of low peel strength and thin bonding. However, fiber failure occurs at high binder content due to the thick binder volume at fiber entanglements and high-bond strength.

Effects of Binder Concentration

The amount of binder applied, relative to the fabric weight, was 30, 40, and 50%, and produced distinct differences in the overall quality of the fabric. The performance of the nonwovens can be devided into low, medium, and high add-on and/or degree of crosslinking regions. Low binder content [i.e., 30%] exhibited the characteristics of poorly bonded webs reflected in low modulus, low tenacity, low tear strength, low energy-to-break, and high elongation. The bonds are generally small and unite two fibers together, thereby contributing little to the fabric strength except through fiber-to-fiber friction (60). When the degree of crosslink is very low, the binder strength is very weak that fiber orientation and fiber strength contribute to the strength of fabrics. Fabric strength and modulus increases very slowly as binder add-on increases in this region. Failure of the fabric is cause by fiber slippage and to a lesser extent, by bond breakage.

In the medium-binder add-on [i.e., 40% binder], both the modulus and strength of the fabric has increased sharply with increasing crosslink density. In this fabric, a matrix with many bonded points was formed. These bonded points unite the fibers into many sided irregular polygons. Failure occurs largely as a result of combination of fiber

and bond [including failures both in the binder and at the interface] breakage.

Fabric with higher binder add-on [i.e., 50%] showed high modulus, tenacity, tear strength, and energy-to-break and considerably reduced elongation in both CD and MD. In this add-on area, many fibers are locked together by strong bonds, and the bonded points connect fibers into a much less flexible structure. Elongation shows a distinct decrease since it now reflects only fiber elongation rather than extension of the matrix structure. Failure occurs almost entirely by fiber breakage originating at a weak point in the structure and propagating rapidly across the sample.

It is obvious from the above discussion that the amount of binder at bonding points depends upon the bonding conditions. Thus, the mechanism of fabric failure depends upon the binder concentration, the binder type, and bonding condition. Each of the figures [i.e., Figures 12-21] demonstrate that increases in binder concentration of a fabric increases tenacity, initial modulus, tear strength, and energy-to-break and decreases elongation.

Polyurethane Film

For the purpose of determining the effect of binder strength on the strength of nonwovens, binder films were

prepared and tensile properties were determined. Table 11 presents the mechanical properties of the polyurethane films. The relationships between these mechanical properties are shown graphically in Figures 22 and 23. The polymer binder should form a thin film and join adjacent fibers together and thereby improve the stress transfer characteristics of the fiber network. These films were very flexible and rubbery at room temperature [25 ^{o}C] and possessed high elongation, as well as relatively low tensile strength and modulus. The observed mechanical properties of the films are primarily due to the presence of a high fraction of the soft-chain segments, low T_g [-50 ^{o}C], and their amorphous nature. Increasing the amount of crosslinking agent, TMP, improved the mechanical properties of the films.

Tensile strength and elastic modulus increases significantly above the equivalent ratio of PPG : TMP of 0.7 : 0.3. The elongation at break of the films, however, decreases linearly with increased amount of TMP.

Dusek (21) reported that the sol-gel analysis would appear to be the best indicator in the investigation of the network. Swelling ratio decreases with the increase of crosslink density and elastic modulus, due to the immobilized molecular movement at high network structure [Figure 22].

Table 11. Mechanical Properties of Linear and Crosslinked Polyurethane Films.

TMP : PPG	Tensile Strength (lbs/in^2)	Elastic Modulus (lbs/in^2)	% Elongation at Break
0 : 1.0	9.27	5.53	293.40
0.1 : 0.9	92.02	28.88	577.25
0.2 : 0.8	97.54	30.97	522.20
0.3 : 0.7	101.31	34.17	463.33
0.4 : 0.6	122.15	49.68	402.70
0.5 : 0.5	135.61	65.99	357.50

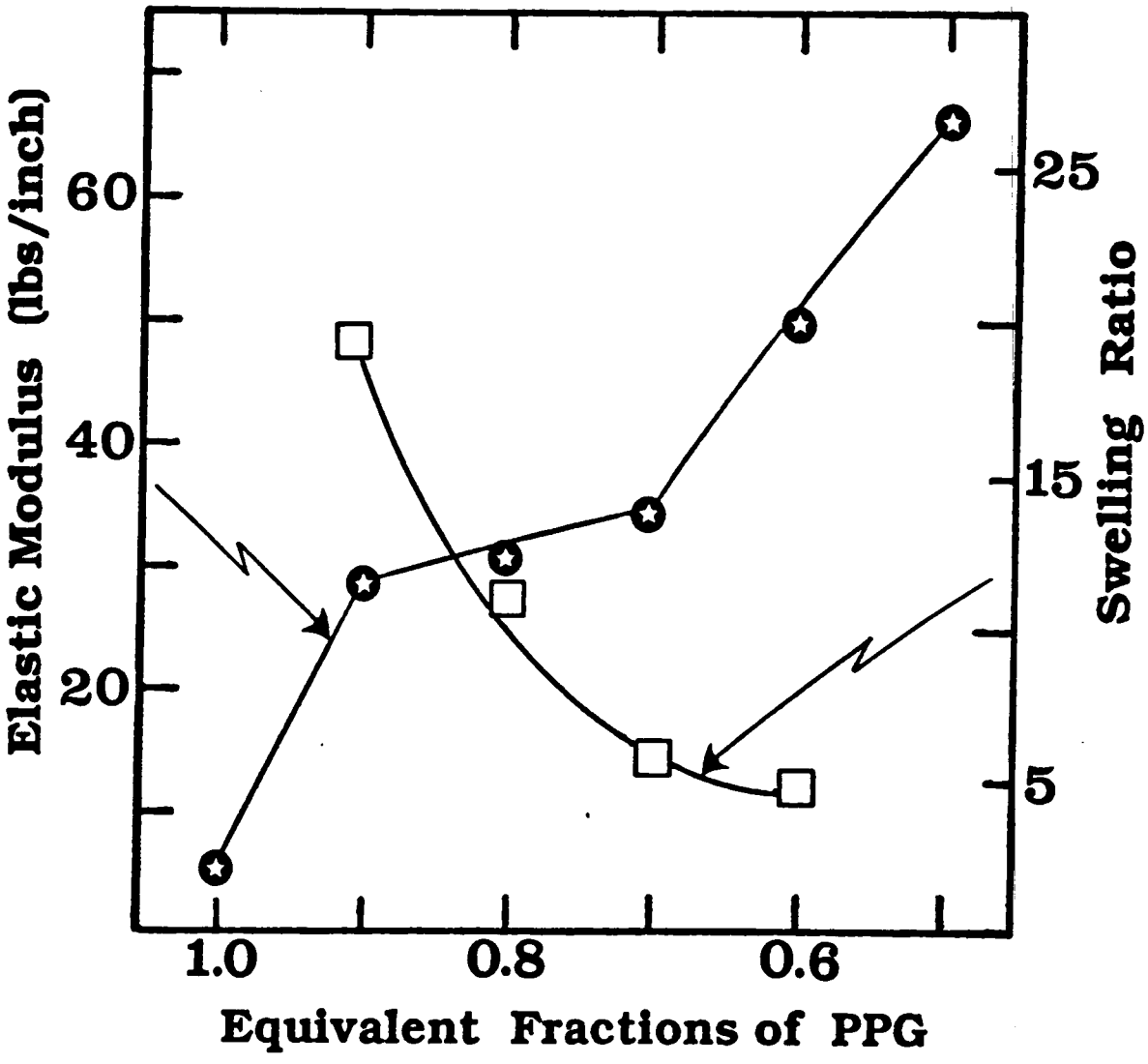


Figure 22 Comparison of Elastic Modulus and Swelling Ratio for Different Crosslink Densities of Polyurethane Film.

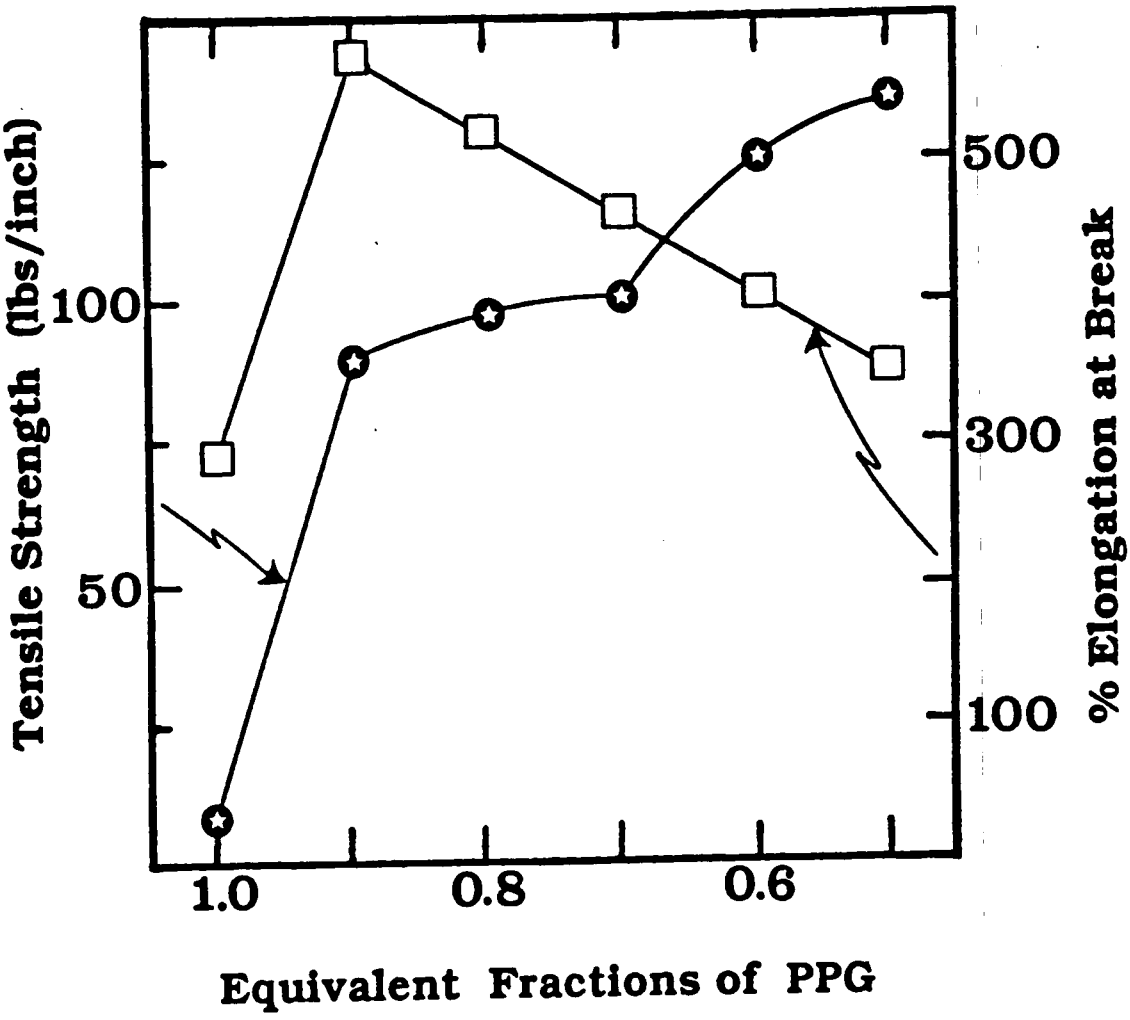


Figure 23. Comparison of Tear Strength and % Elongation for Different Crosslink Densities of Polyurethane Film.

Evaluation of mechanical properties of free films of binders do not appear directly related to the prediction of performance of adhesively bonded nonwoven fabrics. Even though the adhesively bonded nonwovens are made from nonwoven web and binder, the resultant fabric does not simply have additive values for its properties. This is obviously due to the complex nature of nonwoven fabrics. Final mechanical properties of nonwoven fabrics are influenced by fiber type, binder properties, fiber-binder adhesion, binder cohesion, bonding method, and other finishing methods.

SEM Examination

The scanning electron microscope [SEM] is an invaluable research tool for ascertaining the nature of the bonding, as well as the mechanism of fabric failure (16). Such features as fiber-to-fiber bonding, amount of loose material projecting from the surfaces, nature of laminations, and the degree of entanglement of the fibers can be assessed from the study of SEM photomicrographs (19).

Examination of the samples from this study showed that the fiber bonding is not uniform, and in many places, the fibers remain in the unbonded state. Both point and segment bonds are shown in Figure 24. The adhesive

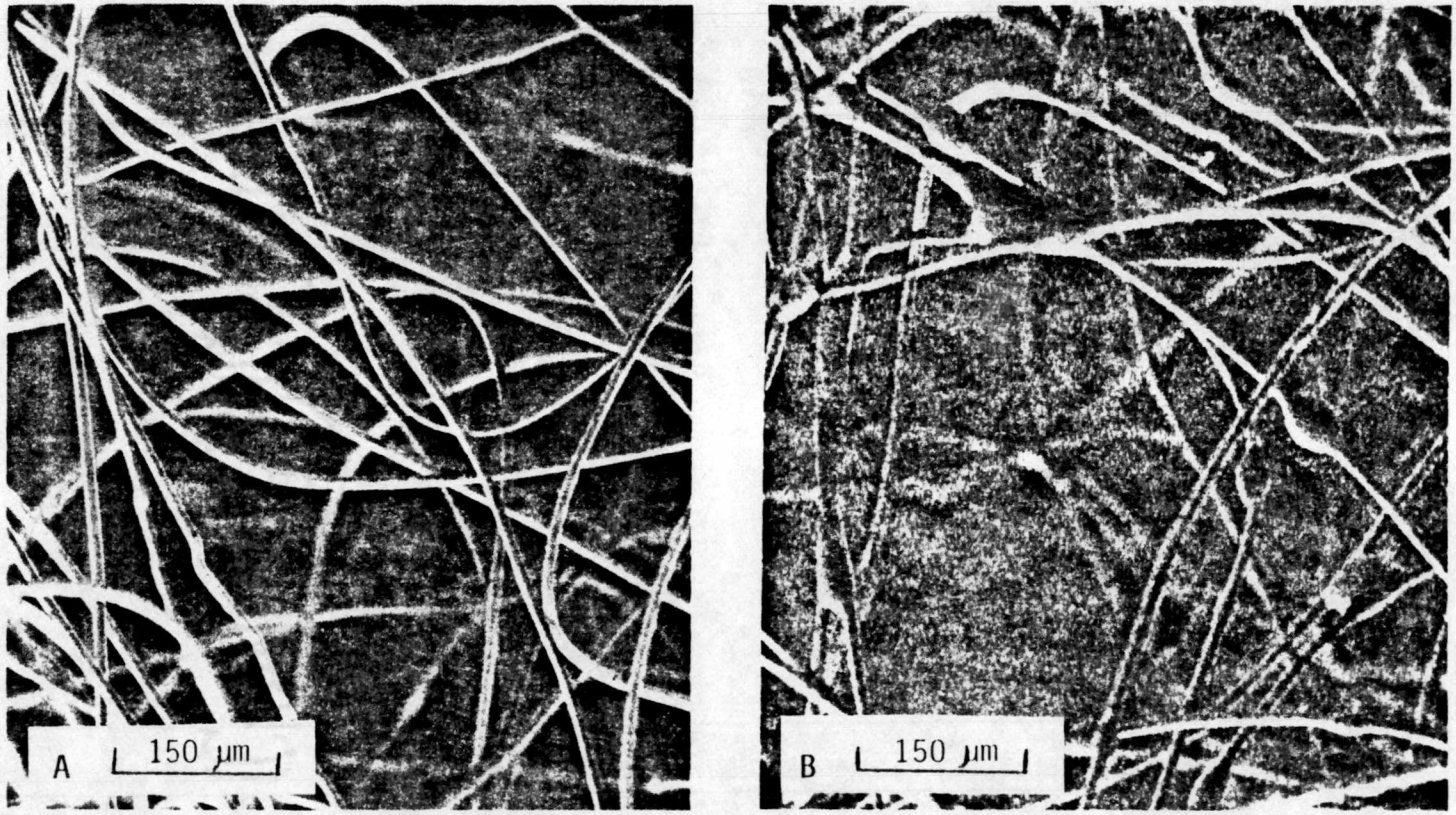


Figure 24. Scanning Electron Microscope (SEM) Photomicrographs of A) the Polyester Web and B) the Polyurethane-Bonded Nonwoven Fabric (30% Binder).

material is not uniformly distributed. There is a tendency for a polymer to deposit in the form of discrete particles, possibly due to the high surface tension of the polymer, in this case. One can also see that the bonds between base fibers are produced by flow of the polyurethane binder around the base fibers during the curing cycle in the vacuum oven. The binder polymer physically entraps the base fibers at points of entanglement and crossover. In the area of dense web, capillary forces drew the droplet into the crevice between fibers.

Polyurethane Composites

Composite structures are and will continue to be a key area in nonwoven laminating and coating. The reinforcement of rubber by fibers was pioneered by Dunlap in tires a century ago, but tires are just one of the family of flexible composites (42).

Commercially available polyurethane composite materials are introduced below. Shawmit [West Bridgewater, MA] now has the ability to bond two nonwovens with urethane film, providing a water barrier in incontinent sheets (80). Kenyon [Kenyon, RI] is noted for its K-Cote® polyurethane coatings for active sportswear, rainwear, and protective clothing. The Kenyon Company is applying polyurethanes to nonwoven substrates and is using nonwovens to make

composite coated fabrics containing two and three components [i.e., water repellent, flame retardant].

Portec Ltd. of Woburn, MA also announced a new polyurethane microporous fabric promising to find a strong market in the show and imitation leather field as a laminate to nonwoven support fabric (108). A treated nonwoven fabric [Burlington] for use in the manufacture of pneumatic tires or V-belts is formed by applying an isocycnates compound to a nonwoven fabric (107). Toray Industries Inc. (106) developed a moisture permeable waterproof coated fabric comprised of a basic fabric and a synthetic microporous layer consisting of polyurethane. The newly developed polyurethane-based melt-blown spunbonded fabric [Kanebo Synthetic Fibers, Ltd.] is claimed to possess softness and stretchability, in addition to the air permeability and easy-handle properties of other spunbondeds.

The above is not in any manner intended to be an inclusive discussion of polyurethane composites, but it should serve to give examples of the versatility of these types of materials.

CHAPTER V

CONCLUSIONS

Extensive research was performed on diisocyanated-extended polypropylene glycol to provide information about the characteristics of this polyurethane binder for nonwoven fabrics. The results and discussions presented above lead one logically to the following observations and conclusions:

1. Application of polyurethane binder [based on polypropylene glycol and hexamethylene diisocyanate] to light-weight polyester nonwovens is technically feasible. The properties of the resultant fabrics demonstrate the special performance of polyurethane binder at low glass-transition temperatures [e.g., $-50^{o}C$].

2. The preparation and characteristics of the binder was thoroughly investigated. In order to make totally amorphous polyurethane, polypropylene glycol [PPG] was selected, mainly because of it's large portion of soft segments [MW--2016 gm]; aliphatic hexamethylene diisocyanate [HMDI] also contributed flexibility to the polyurethane binder. The degree of crosslinking is an important parameter on the behavior of the binder. Crosslinking agent trimethyolpropane [TMP] proved particularly compatible with PPG, and a catalyst, stannous

octate [T-9] was utilized to optimize curing time and temperature. Two concentrations of T-9 [0.2% and 2.0%, resp.] were employed, with respect to the reactants used for binder films or binders applied to the nonwoven webs. Catalysts are added to the formulation to speed up the crosslinking reaction. The type and amount of catalyst materially affects the curing time, and therefore, the results can vary considerably. Methylene chloride was added to lower the exothermic heat of reaction and to avoid a substantial increase in viscosity by the chain extending reaction.

3. Different degrees of crosslinking of polyurethane were prepared through use of varying equivalent ratios of PPG and TMP. Ratios of PPG and TMP used in this study were: 0.9 : 0.1, 0.8 : 0.2, 0.7 : 0.3, 0.6 : 0.4, and 0.5 :0.5.

The mechanical properties of nonwovens were significantly affected by the degree of crosslinking in the polymer binder. However, the actual binder contents are even more important than the degree of crosslink in the binder. Tensile strength and modulus increase with increasing crosslink density to a maximum and then virtually cease to change (i.e., plateau).

In the lower degree of crosslinking region [PPG : TMP = 0.9 : 0.1, 0.8 : 0.2], the dominant effect on the fabric strength was the fiber type and its orientation, due to the

weak binder strength. There was no visible increase in strength and modulus with these configurations.

In the medium degree of crosslinking region [PPG : TMP = 0.7 : 0.3], noticeable changes in tensile strength and modulus were observed. This appears due to the effective optimum crosslink in the binder for the polyester nonwoven system utilized.

In the highly crosslinked binder region [PPG : TMP = 0.6 : 0.4, 0.5 : 0.5], it was observed that the effect of binder modulus on fabric modulus became smaller with increasing binder stiffness, probably because the bonds become so rigid by comparison with the fiber deformation. The increase in binder strength and toughness only has a small effect on overall fabric strength.

4. Polyurethane films were prepared by a one-step cast technique; all reactants are mixed together initially and then allowed to cure. Curing time and temperature were determined empirically. It took 48 hours / 60^{o}C to cure the polyurethane linear and crosslinked films. These curing time and temperature were obtained in laboratory ovens; commercial setups would obviously need to be investigated for the optimum conditions with their apparatus. Therefore, it is to be expected that the times and temperatures from this study may be significantly different from those commonly used in commercial

operations.

5. The results obtained from the testing methods for the linear and crosslinked polyurethane films were satisfactory. Viscometry and Differential Refractive Index generated consistent data for the linear polyurethane films. In order to examine the crosslink density, swelling ratio was calculated. The higher the crosslinked polymer, the lower was the swelling ratio and sol fraction were found. The T_g values for the linear and crosslinked polyurethane films were measured by Differential Scanning Calorimetry. This was accomplished on a liquid nitrogen chamber attached to a DSC unit due to the extreamly low T_gs of this perticular series of polyurethanes. The T_g for the linear polyurethabe was $-58^{o}C$, and that for the crosslinked polyurethane film ranged from -49 to $-52^{o}C$.

6. From the Scanning Electron Micrographs, it is apparent that the bonds between base fibers are produced by flow of the polyurethane binder in the low binder content nonwovens. With 50% binder add-on, there was a tendency for a polymer to deposit in the form of discrete particles. This is possibly due to the high surface tension of the polymer in this case.

7. The advantages of polyurethane-binder nonwoven fabrics for special situations are:

a) They can be used in arctic regions for work in low

freezing environments, even below -50°C. Because the glass transition temperature of this binder is below -50°C, it maintains flexibility in this extreme cold.

b) Since polyurethane binder is totally amorphous, nonwoven fabrics were flexible even using extreme degrees of crosslink density. One of the major problems with conventional latex binders is the increase of fabric stiffness with increases in binder toughness; this was not the situation with the polyurethane binders. The production of this important property for nonwovens would be a major achievement and an invaluable contribution.

c) As the chemical structure of polyurethane indicates, the amide bonds [-NH-C=O] structure provide a large number of H-bonding, inter- and/or intra-molecular, that greatly enhance the adhesive and cohesive abilities of this binding polymer.

8. As also determined from this study, the disadvantages of polyurethane binder nonwoven fabrics are:

a) The viscosity of polyurethane binders was sufficiently high such that a solvent [methylene chloride] had to be employed to dilute the binder for effective dispersment onto the fabric.

b) The glass-transition temperature of the polyurethane is -50°C. Therefore, the nonwoven fabrics at 25 °C displayed a slight degree of 'tackiness'. Special

care had to be taken in order to handle the sample fabrics for the mechanical test.

c) The market cost of polyurethane binder is slightly more expensive than other commercial binders. Therefore, it is cost-prohibitive only for selected applications.

9. Mechanical properties of adhesively bonded nonwovens were influenced by fiber type, binder properties, fiber-binder adhesion, binder cohesion, and bonding methods.

Future Recommendations

Polyurethanes are distinguished by their good adhesion to different substrates and high flexibility even at low temperatures. Specifically, the combination of polyurethane and textile is recognized as being comfortable to wear and easy to care for. Recently, their washability and cleaning stability, high elongation and elasticity, good abrasion resistancse, solvent resistance, and low specific weight have become attractive to the textile researchers.

Based upon the above-presented research, the following future research areas are recommended:

1. Synthesize aqueous polyurethanes with an amorphous nature and T_g of below the freezing temperature [0° C].

Even though waterborne polymers show poor wetting and/or adhesion with some substrates and their increased drying/curing times can contribute to slower line speeds, they are cost effective, and they minimize the use of and exposure to harzardous organic solvents.

2. Binder adhesion and cohesion studies are worthy of further investigation. The binder adhesion to the fibers plays an important role in determining the fabric strength. Adhesion can be increased without changing other structures in the nonwovens by exposure to ultraviolet radiation to produce surface oxidation. Fiber surface treatment will increase the adhesion of binders significantly. Binder adhesion with cohesion studies will better define the parameters necessary to produce even better nonwovens.

3. Scanning electron microscopy is a useful tool with which to investigate the rupture mechanism and initiating position of bond rupture. The nature of binder distribution can be observed to examine the factors influencing them.

4. Composites and laminating are and will continue to be a key area in nonwovens. These areas are not only inportant to textile industries but also automotives, construction business, and sports equipment etc.. In order to make good composite materials, a good resilient polymer with a high impact-resistant polyurethane is one of the best polymers.

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