MODELING OF SOLUBILITY PARAMETERS AND PERMEATION DATA OF
ORGANIC SOLVENTS IN BUTYL GLOVES

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MODELING OF SOLUBILITY PARAMETERS AND PERMEATION DATA OF ORGANIC SOLVENTS IN BUTYL GLOVES

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Dissertation

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ABSTRACT

In this work, an improved nonlinear regression method based on the combination of the Hansen three-dimensional solubility parameter theory and the Flory-Rehner theory was successfully applied to estimating the three-dimensional solubility parameters of butyl glove materials. Excellent model fit was observed for all the butyl gloves from four different manufacturers. Unlike earlier work, only a single set of weighing factors were required, resulting in a more robust, convenient, and generally applicable model. Improved weight gain test was critical to the development of this model. The collected weight change data showed that it might take up to five weeks to reach equilibrium swelling for the butyl glove materials immersed in a series of organic solvents. Thus, extended immersion was necessary since equilibrium swelling was assumed in the theoretical context of this model. In addition, since the extraction of oligomers and additives from butyl glove materials was evidenced during weight change test, determining weight gain based on the post-drying glove sample weights should eliminate possible error source.

Since this model is also related to the standard free energy changes of mixing for solvent/polymer systems, it has been demonstrated as a good predictor of the permeation properties of Viton® and Nitrile glove materials. In this work, the model was extended to butyl gloves from four different vendors. Attempts were made to collect permeation property data of the four butyl glove materials against a series of organic solvents, then
correlate it using the described model. Excellent model fit was observed for all four
individual butyl glove materials. With proper normalization approaches based on sample
thickness, it was possible to use this model to correlate the combined permeation data
from different butyl glove materials with different sample thicknesses. The results of this
work further proved the effectiveness of this model in predicting the permeation
performance of chemical protective clothing.
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CHAPTER I

INTRODUCTION

Chemical exposure is considered a major cause of occupational disorders and skin diseases. With advances in the chemical, pharmaceutical, and other industries, many workers have to rely on protective clothing to reduce exposure since their ever-changing work environments prevent the effective implementation of engineering controls. In order to reduce the risk of chemical exposure, personal protective clothing and equipment are used to shield or isolate individuals from chemical, physical, and biological hazards. Since the skin of the hands is particularly susceptible to attack by toxic liquid chemicals, gloves made of polymeric materials are one of the most common forms of chemical protective clothing (CPC) used for protection from exposure during handling of these materials. However, up to now, no single polymeric material has been found to be impermeable to all chemicals.

Proper selection of chemical protective clothing requires a good understanding of CPC chemical resistance properties in conjunction with the integration of risk assessment in the selection process. With test methods standardized for measuring chemical resistance, much CPC performance data has been published and available for end users to make judgments regarding protective clothing. However, a review of these data usually indicates that consistent comparisons cannot be made since these data from different sources are often not compatible with each other. The interpretation of chemical resistance data is often difficult since it is often obscured by poor documentation of
experimental variables and/or differences in test system design. In addition, due to a large number of possible chemical/CPC combinations in the actual work environment, chemical resistance tests are often limited to certain representative chemical solvents/CPC systems. Thus, a predictive model for the permeation characteristics of polymer materials has long been desired.

Since the effectiveness of chemical protective clothing depends on the physical and chemical properties of the polymer material, many efforts have been made to establish predictive models based on these physical and chemical properties.\(^8\) The major models in this field are mainly based on the mutual solubility or diffusivity of solvents in polymeric materials since these two terms play significant roles in the ultimate level of protection from chemical exposure that a CPC can provide. The current study represents part of an on-going effort to develop a generally applicable solubility-based model for predicting the permeation of solvents in chemical protective gloves.\(^9,10\) Such a model should provide excellent correlation between permeation properties and solubility as well as address the problems mentioned above. The butyl glove was selected for this study due to this glove’s wide use in chemical protective clothing. In addition, previous attempts to model the permeation properties of butyl rubber yielded relatively unsuccessful results.\(^11\)
CHAPTER II

LITERATURE

Chemical Exposure

The potential risk of chemical exposure was recognized long time ago and has been a major occupational safety issue for industrial hygienists for many years. According to the National Institute of Occupational Safety and Health (NIOSH), nearly thirteen million people are exposed to a variety of hazardous chemicals in their workplaces every year, which resulted in numerous deaths and occupational injuries, and has cost billions of dollars in economical losses in these industries. Thus, when all other options of safety control are considered inadequate, various forms of chemical protective clothing (CPC) are used to provide protection against potential chemical hazards.

One of the most common forms of chemical exposure is through the use of harmful chemical compounds, which can be in the form of solids, liquids, gases, mists, dusts, fumes, and vapors. Without proper personal protection equipment, the human skin is possibly subjected to an attack by these hazardous materials and chemicals. The routes by which chemicals enter the human body include dermal contacts, inhalation, ingestion, and adsorption; among these routes, dermal contact has been found to be the major route. It has been estimated that skin diseases currently account for 13% of all reported occupational diseases. According to the Bureau of Labor Statistics (BLS), the rate of occupational skin diseases was 81 cases per 100,000 workers in 1997. Dermatitis was
reported to be the third most common cause of compensable temporary total and partial
disability and the sixth most common cause of permanent partial disability in the United
States.\textsuperscript{18} The estimated annual cost may be upward of $1 billion in 2001.\textsuperscript{15}

Skin contact with chemicals causes adverse health effects mainly in two ways.\textsuperscript{19}
The first, and most obvious, are pathological changes when the skin itself is affected. The
most likely effects include allergic and irritant contact dermatitis, which comprises the
bulk of occupational contact dermatitis (OCD). The second way that skin contact can
affect the worker, which is often obscure, happens when potentially toxic chemicals are
absorbed through the skin, adding burden and toxicity to the systemic body and internal
organs. A full understanding of systemic toxicity is far less clear because of the difficulty
in objectively determining of the role of skin absorption, especially if the illness were the
result of chronic exposure.

To reduce skin exposure to harmful chemicals, a number of synthetic protective
barriers, including gloves and other protective clothing, have been developed. It has
become common practice currently to use various forms of chemical protective clothing in
the workplace as protection against these potential chemical hazards.

\textbf{Chemical Protective Clothing}

As the “last line of defense,” chemical protective clothing exists in a variety of
designs, materials, fabrication methods, performance features, and sizes. In order to
make appropriate selections, end users need an understanding of the different types of
chemical protective clothing and their features. It is important to be aware that many
CPCs appear to be similarly designed but may offer significantly different levels of performance. Thus, CPC performance must be carefully evaluated in addition to design and features.

Generally, chemical protective clothing can be classified by its design, performance, and intended service life. Classification of CPC by its design usually reflects how the item is configured or the part of the body area or systems the CPC protects; this classification may provide an indication of specific design features that differentiate CPC items of a similar type. By and large, each type of CPC can fall into the following categories: full-body garments, partial-body garments, gloves, footwear, and face and eye protection. A further means of distinguishing chemical protective clothing by design is to indicate the material used in CPC construction. It is obvious that CPCs made of different materials will provide different performances and wearability. The materials used in chemical protective clothing include the following seven basic types: textiles, unsupported rubber or plastics, microporous film fabrics, adsorbent-based fabrics, coated fabrics, plastic laminates, and combination or specialized materials.

Classification of chemical protective clothing by performance indicates the actual level of performance the CPC can provide. The level of performance can be examined by testing or evaluating the CPC with a standard test related to the type of desired protection. These tests, which are used as demonstrations of protection against intended hazards, often become the basis of claims by the manufacturers for their products. However, manufacturer-claimed performance does not always match the performance in actual usage. In addition, the performance claimed should be applied to all parts of the CPC.
item, and the performance classification should be rated by the weakest element of the CPC design.\textsuperscript{21}

The classification of chemical protective clothing by expected service life is based on the length of useful life that can be expected from the CPC item. The service life of chemical protective clothing generally fits into the following three classes: disposable after a single use; limited use, which means that some cleaning, care, and maintenance is possible, but the CPC may not be reusable under hard physical conditions, or it will degrade eventually after being used and maintained for a certain period; and reusable, in another word, can be readily cleaned and maintained and still continue to provide acceptable performance.\textsuperscript{21}

The selection of chemical protective clothing is often a complicated task that involves many factors and considerations. OSHA’s General Industry Standards on Personal Protective Equipment (29CFR Subpart I) require that an assessment be conducted to identify hazards; then protective clothing (and equipment) selections are made based on the information determined during the assessment. In order to assist end users in the identification of appropriate CPC, NIOSH and other institutions and organizations have developed a number of selection decision guidelines. NIOSH created a selection logic for respirators to help make a choice of a specific respirator type based on specific inputs, such as applications and exposure level.\textsuperscript{22} NIOSH also developed a relatively detailed selection guide for personal protective equipment used during hazardous materials incidents;\textsuperscript{23} this guide provides a number of decision outputs recommending specific types of both respirators and chemical protective suits.
Relatively detailed suggestions are also provided for the emerging area of Bio-Chemical Protective Clothing (BCPC) use. Recently, both NIOSH and the International Safety Equipment Association (ISEA) developed guides for selecting and using particulate respirators.\textsuperscript{24,25} In addition, ISEA has proposed new standards to classify chemical protective clothing and defines the types of CPC based on their integrity and material chemical resistance performance. Several National Fire Protection Association (NFPA) standards were created to specify the types of CPC for relevant situations such as emergency response.\textsuperscript{26} However, a comprehensive selection guide that covers the full range of CPC is not available.

Hand Protection and Chemical Protective Gloves

Hands are at the greatest risk of injury or disease since they are in direct or indirect contact with chemical agents that are common in the industrial environment. It has been reported that 90% of all occupational allergic contact dermatitis was found on the back of the hand and forearm.\textsuperscript{27} However, nearly 50% of the cases of contact dermatitis among homemakers occurred on the palms, whereas in 15% of the cases the back of the hand and fingers were affected.\textsuperscript{28} In a study of dental laboratory technicians, in 93% of the cases of allergic contact dermatitis, the fingertips were primarily involved; whereas, in 80% of the cases of irritant contact dermatitis, the dorsa of the fingers were affected.\textsuperscript{29} Figure 1 depicts the locations of occupational contact dermatitis on the body based on 879 recent Oregon workers’ compensation cases for the period 1988–1992.\textsuperscript{30}
Figure 1. Locations on the body for occupational contact dermatitis (Oregon workers’ compensation cases for the period 1988-1992)

Gloves are the most common form of handwear used to provide protection against injuries to the wearer’s hands and wrists. A protective glove typically falls into one of the following four categories based on the glove’s application:  

1. Resistance to a wide range of chemicals from irritating hand injuries
2. General-purpose gloves that protect against cuts, snags, punctures and abrasion, but not chemicals
3. Product protection such as classroom gloves to prevent contamination
4. Special-purpose gloves for hot/cold
temperatures applications. A protective glove can also be classified into the following three basic types in terms of design: unsupported gloves (including flock-lined gloves), supported gloves, and flat film gloves.\textsuperscript{21} Other design features include the cuff design and the style of the surface finish or design of the grip. The majority of gloves used for chemical protection are in a form of film or coating that covers the entire hand, but some gloves that have partial barriers may be used in less hazardous applications.

Chemical protective gloves are usually manufactured by dip molding or dipping processes.\textsuperscript{21,31} In these processes, forms or molds made of porcelain or metal in the approximate size and shape are immersed in a “rubber solution.” When the form is removed from the liquid, a coating of rubber is deposited and can be further processed into a finished glove. Both unsupported and supported gloves are made this way; however, for a supported glove, a supporting material is placed on the form prior to dipping.

The “rubber solution” mentioned above can be a latex system, a solvent-based solution, or a plastisol. The latex technique, which is environment-friendly and less expensive than the solvent process, is the most common process for the manufacture of chemical protective gloves. In the latex system, rubber particles are suspended as colloid in an aqueous dispersion, in which some non-water-soluble ingredients are added as dispersions or emulsions to stabilize the latex. In order to get the desired physical properties, the latex system is compounded by conventional wet-mixing techniques with additives. Glove film is coagulated, usually by a chemical means such as adding coagulants. Typical coagulants include calcium nitrate, calcium chloride or
cyclohexylamine acetate dissolved in alcoholic solvent or alcohol/water mixtures to concentrations between 10% to 40% w/w. The thickness of the film is controlled by the specific gravity of the coagulant used, the dwell time in the latex, and the latex solids’ content and/or viscosity. Light-weight and medium-weight unsupported gloves can be made in a single dip in most cases.

In solvent processes, a rubber is milled with compounding chemicals into a homogeneous mixture and then dissolved in appropriate solvents. The forms are immersed in this solution, then removed. After the solvents evaporate, a thin film of dried rubber is produced. Repeated dips may be necessary to build up the desired thickness before the gloves are cured. This type of multiple-dipping process results in longer times and uses volatile and flammable solvents instead of water, making this manufacturing process more costly and more hazardous than the latex process. However, multiple-dipping gloves generally have superior chemical-resistance properties over latex gloves made from the same polymer.32

In a plastisol system, a polymer (for example, polyvinyl chloride) is dispersed in a liquid plasticizer. Forms are dipped, withdrawn, and the plastisol allowed to drain. The gloves are then “fused” at a high temperature and removed from the forms. Glove thickness is controlled by adjusting the plastisol viscosity, form temperature, and drain time.

Flat film gloves are made by simply cutting hand silhouettes from plastic film and sealing the periphery with a hot wire device. Some newer manufacturing designs use a
three-piece pattern to create an opposable thumb to improve the hand dexterity of these gloves.

The polymers used in gloves include natural rubber or latex, synthetic rubber, and plastics, such as chloroprene, nitrile rubber, butyl rubber, fluorocarbon rubber, plastics, polyethylene, polyvinyl alcohol, polyvinyl chloride, and ethylene vinyl alcohol.\textsuperscript{33} The chemical resistance performance of a glove is certainly associated with its construction material. However, the performance of certain gloves can vary significantly from the reported generic polymer performance. An examination of the literature has shown that a significant variation in chemical permeation properties was also encountered, such as breakthrough time (BT) and steady-state permeation rate (SSPR) for the same type of material from different manufacturers.\textsuperscript{34, 35} In fact, it was reported that as much as one order of magnitude difference in the permeation data was noticed when similar types of materials were exposed to the same tested chemical.\textsuperscript{36} The important reason is that the specific glove polymer formulation and manufacturing process can vary extensively among manufacturers. Manufacturing quality control is also suspected as one of the major sources causing significant variation statistically on glove performance.\textsuperscript{37} In addition, there are many factors and variables associated with test methods, test conditions, and the nature of tested samples, which can result in inconsistent performance data. Thus, careful consideration should be taken regarding information about gloves and their performance data.
Chemical Resistance Test Methods

Chemical protective clothing including chemical protective gloves can be selected properly only when performance data indicate adequate resistance to chemicals for the duration of anticipated, worst-case exposure. The chemical protective clothing must also demonstrate acceptable integrity for overall protection and provide sufficient strength, durability, and physical hazard resistance. In addition, chemical protective clothing must be functional, allowing the wearer to safely perform the required tasks in an acceptable level of comfort. Such dependability of CPC resistance information mandates the need for rigorous test methods for chemical protective clothing; ideally, the test methods should mimic actual workplace conditions as closely as possible, for the most part.

The study of the development of standard test methodology and reporting did not attract much attention until the late 1970s. Liability issues and the confusion surrounding the measurement of CPC performance prompted an aggressive movement to standardize test methods. Governmental agencies, research institutes and organizations, and manufacturers worked together to address broad issues relating to the test methods for evaluating protective clothing performance. In the USA, the principal forum for these activities has been the American Society for Testing and Materials (ASTM) Committee F23 on Protective Clothing. Within the ASTM framework, the committee endeavored to develop test methods, practices, guidance, classifications and specifications for protective clothing. Subcommittee 13 of Technical Committee 94 within the International Organization for Standardization (ISO) also worked on protective clothing standards. In the mid-1970s, NIOSH sponsored a study on the development of
performance criteria for protective clothing used against carcinogenic liquids in order to facilitate investigation of the performance of protective materials against selected carcinogenic chemicals. Since then, a number of standards that relate either directly or indirectly to chemical protective clothing have been developed. Many of these standards include test methods, but there are also an increasing number of specifications available to the industry for chemical protective clothing. The major areas for test methods and standards include the following:

- Chemical resistance testing,
- Overall product integrity,
- Physical properties,
- Overall specifications, and
- Product functionality.

As a major focus among these subjects, chemical resistance testing methods for protective clothing can be divided into small-scale, material-based tests and full item evaluations. In this section, only material-based test approaches will be discussed, which can be further classified into the following three types, which describe how chemicals may interact with materials:

- Degradation,
- Penetration resistance, and
- Permeation resistance.
Degradation is defined by ASTM’s F-23 Committee as the change in a material’s physical properties as the result of chemical exposure. Usually, physical properties include material weight, dimensions, tensile strength, hardness, or any characteristic related to a material’s performance when used in a particular application. Thus, these tests are used to determine the impact of specific chemicals on materials. Chemical degradation test methods include ASTM D 471, ASTM D 543, ASTM F 1407, and ANSI/ISEA 105. The measurement and observation in degradation tests usually include immersion-based weight change, discoloration, curling, swelling, delamination and disintegration. However, chemical degradation alone cannot fully demonstrate product barrier performance against chemicals. Neither can chemical degradation ascertain the barrier properties of materials. Instead, chemical degradation data are typically used as a screening technique to eliminate a material from consideration for further chemical resistance tests, such as penetration or permeation resistance. As current protective clothing industry practices, most presentations of material chemical degradation resistance are based on qualitative ratings such as “excellent,” “good,” “fair,” “poor,” and “not recommended,” which cannot provide enough information to the end user.

Penetration is defined as the flow of chemicals through closures, porous materials, seams, and pinholes and other imperfection in a protective clothing material on a non-molecular level. This definition is intended to accommodate both liquids and gases but focuses mainly on liquid penetration. In many of the liquid penetration resistance tests, water is used as the challenge although organic solvents can be widely used as well. The
typical properties tested include water repellency, waterproofness, and water resistance. Two fundamentally different approaches used in liquid penetration resistance test methodologies are runoff-based and hydrostatic-based methods. ASTM test methods, including ASTM D751, ASTM D 3393, and ASTM F 903 are all based on the latter. Among the three test methods, ASTM F 903 is used for testing the resistance of protective clothing materials to penetration by liquids, and evaluating material performance against liquid contact from splashes, in which testing liquids other than water are used.

The permeation process is described as a process in which chemicals move through a material at a molecular level, which is caused by the concentration difference in permeating chemicals between the outer and interior sides of the material. Material permeation resistance is generally characterized using breakthrough times and permeation rates. Breakthrough time is defined as the length of time it takes for a chemical to pass or permeate through a barrier membrane until the chemical is first detected on the opposite side, following the initial contact of a chemical with a glove. Breakthrough time measures how quickly a chemical moves through a barrier film and represents the maximum length of time during which the glove could be worn without losing adequate protection. As will be discussed later, the determination of breakthrough time is strongly dependent on the detection limit of the test method and system. Permeation rate is a measurement of the mass flux through a unit area of material for a unit time, which is commonly expressed in units of micrograms per square centimeter per minute. For a given material-chemical combination, the steady state permeation rate is
usually reported. The steady-state permeation rate represents permeation rate at the equilibrium point of the permeation process. In a case when the permeation process does not reach a steady state during the test period, the observed maximum permeation rate is evaluated.

Chemical permeation testing is the most rigorous form of chemical resistance testing. The measurement of chemical permeation resistance is specified in the different standard test methods offered by ASTM, the European Committee for Standardization (CEN), and the International Organization for Standardization (ISO). ASTM test methods include ASTM F 739,53 ASTM F 1383,54 and ASTM F 1407.47 ASTM F 739 was established in 1981 as the first standard test method for measuring material permeation resistance to liquid chemicals, in which the exterior surface of the protective clothing is in continuous contact with a chemical. ASTM F 1383 is a variation of ASTM F 739 that involves testing under conditions of intermittent chemical contact. ASTM F 1407 is basically a simplified form of testing in which permeation is determined gravimetrically. Due to this method’s limited sensitivity, this method is primarily used as a field screening test.

The basic procedure in each permeation test is to charge a chemical into the challenge side of a test cell and measure the concentration of the chemical on the other side of the test cell as a function of time. The permeation test cell specified in F 739-91 is shown in Figure 2, which consists of two chambers. A test sample is located between the chambers, serving as a divider. On one side of the test cell is stored a challenge chemical or mixture, which may be a vapor or liquid at any desired concentration. The
glove material is in continuous contact with the challenge chemical throughout the test. The other side contains a collection medium. In terms of the flow pattern of the collection medium, the permeation test can be either defined as a closed-loop system, in which the volume of the collection medium is fixed, or an open-loop system, in which a stream of collecting medium passes through the cell, picking up the diffused molecules of the permeant continuously for analysis. The selection of a closed-loop or open-loop system is usually dependent on the properties of the challenging chemical and the available detector. Some chemicals such as inorganic substances require closed-loop systems, especially if ion-specific electrodes are used, while, for many volatile organic chemicals, an open-loop system is preferred since it is easily automated. These test configurations are extensively used and sometimes modified in many studies.

Of the chemical resistance data used in reporting protective clothing performance, the majority of the test results are permeation resistance data. However, a review of the data published indicates that consistent comparison often cannot be made and that suppositions for discerning material performance may not be properly based unless an understanding of the test conditions is realized. Although much of the data are reported generically for the material classified, Michelsen and Hall showed significant differences in chemical permeation through elastomers that were generically the same in composition and thickness. This demonstrates that permeation data must be specific to the material/chemical combinations being evaluated, and a complete description of key test parameters, the test material, test chemical, and test system configuration must be included.
Figure 2. ASTM Glass Cell for Liquid Permeation, ASTM F739-91.
Interpretation of permeation data is still a subtle issue. Within the protective clothing industry, many end users may judge the acceptability of a material on the basis of how its breakthrough time relates to the expected period of exposure. In fact, the permeation rate offers a more consistent and reproducible means of representing material permeation and appears to be a better choice for characterizing material performance. The permeation rate shows subtle changes in material characteristics and can be used to determine cumulative permeation when acceptable “dose” levels of the test chemical can be determined. The drawback is that it takes a long time for some material-chemical systems to reach a steady state, and sometimes may exceed the detection limit of the test system. And the lack of widespread data about acceptable dermal exposure levels for most chemicals leads many evaluators to prefer to rely on breakthrough times.

In summary, with the implementation of technical standard test methods, performance data for protective clothing have become more widely available in the past decade. However, guidelines for the use and interpretation of the data continue to be developed. Test methods were developed to provide a basis for evaluating clothing and material effectiveness for protection against a specific hazard. Although the methods are designed to allow comparisons among the relative performances of various products, the influence of other factors must be incorporated into the selection process. Without adequate interpretation guidelines, the selection process can remain confusing for many safety and health professionals, particularly when the test method does not simulate the conditions of actual exposure. In recent years, the development of fast and convenient field-based chemical resistance indicators/testers has attracted much research interest and
certainly will help improve the protection against chemical hazards and minimize the risks associated with the actual use of CPCs.\textsuperscript{60, 61}

Permeation and its Theoretical Treatment

Permeation is not a phenomenon unique to the protective clothing industry but actually takes place in everyday life. For example, when paint is applied and a coating film forms, the solvent remaining must diffuse through the polymer and evaporate to the outside. The manner in which this occurs can affect the finished quality of the product. In the automotive industry, gaskets and seals made of polymer compounds are widely used to prevent various volatile substances and chemicals from coming in contact, where permeation of these volatile substances and the chemicals through the gaskets and seals must be minimized. In the pharmaceutical industry, controlled permeation is used in the applications involving extended-release formulations. If an active drug ingredient is divided into small particles and encapsulated in polymer spheres of varying diameters or certain polymer types, or bound into a specific polymer matrix, the active ingredient will be released at a certain controlled rate over time.\textsuperscript{62} In these examples and other applications of polymers, permeation is a process that must be sometimes minimized, sometimes promoted, and sometimes controlled in order to accomplish a desired effect. A better understanding of this phenomenon certainly enables better prediction and control for the performance and quality of the finished polymer products or other products.

Permeation, as mentioned earlier, is described as a process in which chemicals move through a barrier material at a molecular level, which is caused by the
concentration difference of permeating chemicals between the outer and interior sides of the material. The mass transport in a permeation process can be envisioned as three steps, as illustrated in Figure 3: First, a challenge chemical is absorbed into a barrier material. Second, the species migrates through the amorphous region of the bulk matrix of the barrier material. Third, the species finally emerges from the other side of the sample as gaseous molecules.\textsuperscript{63,64} The whole process will continue as long as the concentration gradient is present. Thus, given an understanding of the mechanism and principle of mass transport of a chemical through a polymer barrier, the relationships between the physical/chemical properties of solvents and polymers should allow certain prediction of the permeation performance of CPC upon exposure to hazardous chemicals. Perhaps most important, an accurate and quantitative prediction should lead to the improvement or better design of chemical protective clothing.

The fundamental basis that led to the understanding of the mass transport of penetrants in polymeric materials is the free volume theory.\textsuperscript{65,66} Theoretical treatment of the permeation process has relied on the concepts of solubility and diffusivity;\textsuperscript{67} the prediction models mainly originated from the solution theory or the diffusion theory.\textsuperscript{68} The solution theory is based on the fundamental principles of thermodynamics. These theoretical models were generally derived from the concept of solubility parameters and the Flory-Rehner solution theory.\textsuperscript{69,70} In these approaches, solubility parameters and polymer-solvent interaction parameters have been widely used to correlate or predict the permeation performance of glove materials. The diffusion theory is another major model
Figure 3. Permeation Process
that is based on the classical Fickian equations. Fickian laws are mathematical approaches widely used in dealing with diffusion phenomenology. In these approaches, the basic physicochemical properties such as the diffusion coefficient and the solubility coefficient are investigated to establish the diffusion mechanism and predict the permeation performance for polymer-solvent systems. Other models include the chromatographic model, solvent polarity index model, and liquid-liquid partition model, which could be used in specific cases. In the following sections, the major concepts and theories will be described in detail.

Solution Process and Solubility

Before a challenge solvent can diffuse through a polymer, the solvent molecules come in contact with the initial “layer” of the polymer. The number of solvent molecules entering this layer is dependent on the solubility of the solvent in the polymer. Thus, the solution step in the permeation process is naturally one of the most important subjects in permeation studies.

The solution phenomenon of a polymer material is more complex than that of small molecules because of its large molecular size and molecular weight. Unlike the solubility parameters of solvents, those of polymers cannot be measured directly since polymers cannot be vaporized. In addition, crystallization regions exist in many polymers, and this will prevent the solution process due to its strong intermolecular interactions unless at temperatures close to their melting points. Thus, the theory of solubility based on the thermodynamics of polymer solutions was developed only for
amorphous or slightly crosslinked polymers with linear structure. The solution process of an amorphous polymer in an organic solvent can be described using an equation of Gibbs free energy of mixing:

$$\Delta G_M = \Delta H_M - T\Delta S_M$$ (1)

where $\Delta G_M$ refers to the free energy change of mixing, $\Delta H_M$ the enthalpy change of mixing, and $\Delta S_M$ the entropy change of mixing. In order for a solution process to occur, a negative $\Delta G_M$ is needed. The more negative the free energy change, the better the solubility. Since the entropy always increases when a polymer dissolves in a solvent ($\Delta S_M > 0$), the sign of $\Delta G_M$ is mainly determined by the sign and magnitude of $\Delta H_M$. In effect, if the intermolecular forces are similar between the polymer and the solvent, the enthalpy change of mixing is quite small (or even negative), resulting in a negative $\Delta G_M$ and good solubility.

In 1919, Hildebrand found out that, based on Raoult’s law, the solubility of a given solute in a series of solvents is determined by the internal pressure of the solvents. This led to Hildebrand and Scott’s development of the solubility parameters of solvents. Later, Scatchard introduced the concept of cohesive energy density (CED) into Hildebrand’s theory, which is defined as the energy of vaporization per unit volume of the polymeric material. In 1936, Hildebrand proposed the square root of the cohesive energy density as a parameter describing the solvent and solute properties in a solution system, assuming that there are only nonpolar molecules in the system. Thus, in such systems, Hildebrand’s concept of the solubility parameter is expressed as follows:
\[
\delta = \left( \frac{\Delta H_v - RT}{V_M} \right)^{1/2} = \left( \frac{\Delta E_v}{V_M} \right)^{1/2} = C_{ed}^{1/2}
\]  

(2)

where \( \delta \) is the solubility parameter, \( \Delta H_v \) and \( \Delta E_v \) are the enthalpy and energy of vaporization, respectively, \( T \) is the temperature, \( R \) is the ideal gas constant, and \( V_M \) is the molar volume. The basic assumption of the solubility parameter theory is that there exists a correlation between the cohesive energy density of pure substances and their mutual solubility. Thus, for an endothermic mixing process in a 2-component system, the following equation can be derived from the solubility parameter theory:80

\[
\Delta H_M = \phi_1 \phi_2 (\delta_1 - \delta_2)^2
\]

(3)

where \( \Delta H_M \) represents enthalpy change of mixing per unit volume, and \( \phi_1 \) and \( \phi_2 \) are the volume fraction of the compound 1 and compound 2, respectively. From the equation, it can be seen that a pair of close values of \( \delta_1 \) and \( \delta_2 \) will yield a small \( \Delta H_M \), thus resulting in good miscibility of these two compounds. Keep in mind here, this equation is valid only for the solution process of amorphous polymers.

However, the solution process becomes more complicated when there exist polar-polar interactions in an interested system. It was reported that the solution process could take place even in the case of a big difference in \( \delta \) values.81 To account for this phenomenon, Blanks and Pransnitz proposed that the solubility parameter based on heat of vaporization was equal to the square root of the sum of the square of non-polar and polar components in polar systems.82 With this assumption, the contribution from the non-polar component could be obtained based on the dispersion energy of evaporation,
while the contribution from the polar component could be obtained from the remaining energy. Witt and Pedersen confirmed Blanks’ work with their precipitation experiments test results. Gardon also evaluated the polar component in cohesive energy density with a focus on the theoretical aspect. His results agreed strongly with those of Blanks except for some corrections needed for chlorinated solvents.

Hansen Three-Dimensional Solubility Parameters

Intermolecular forces include dispersion forces, dipole-dipole forces, and hydrogen bonding forces. Thus, solubility is dependent on these interactions. The introduction of a polar component into the solubility parameters certainly improved the correlation between the solubility parameters and mutual solubility. However, it was found that the calculations based on the consideration of only dispersion and polar interactions were not reliable when hydrogen bonding was present in a system.

Hansen et al. expanded Hildebrand’s theory by introducing hydrogen bonding together with polar interaction component into the system in order to characterize the interactions between paint and solvent. Thus, the total solubility parameter could be separated into three components, and the total cohesive energy density of a substance can be expressed according to the following equation:

$$C_{ed} = \left[ \frac{\Delta E_v}{V_M} \right]^{1/2} = \left[ \delta_d^2 + \delta_p^2 + \delta_h^2 \right]$$  \hspace{1cm} (4)

where $\Delta E_v$ represents the molar heat of vaporization (J/mol), $V_M$, the molar volume (cm$^3$/mol), and $\delta_d$, $\delta_p$, and $\delta_h$ represent the partial solubility parameters contributed by
dispersion, polar, and hydrogen bonding forces, respectively. Combined with the concept of the heat of mixing, the three-dimensional solubility parameters (3-DSPs) can be used to describe molecular interactions between solutes and solvents in a solution. As previously discussed, the contribution from dispersion force interaction is common to all molecules resulting from fluctuations in the temporary dipole moments in non-polar molecules. The second type of interaction is dipole-dipole interactions, including permanent dipole-permanent dipole or permanent dipole-induced dipole interactions. The third component represents the interactions of hydrogen bonding. Thus, the equation for calculating differences in the solubility parameters between the polymer and solvent can be expressed using the following equation:

\[ A = \sqrt{a \left( \delta_{d1} - \delta_{d2} \right)^2 + b \left( \delta_{p1} - \delta_{p2} \right)^2 + \left( \delta_{h1} - \delta_{h2} \right)^2} \]  \hspace{1cm} (5)

where the subscript 1 and 2 are denoted as a polymer and a solvent, respectively, and \( a \) and \( b \) are the empirical weighing factors. The empirical weighing factors are used in order to ensure the similar weight of the three terms in the model since dispersion parameters usually have a smaller variation range than the other two terms. To obtain spherical plots of 3-DSPs, \( a \) and \( b \) were set to be 4 and 1, respectively, although it has been reported that better correlation was achieved when \( a \) and \( b \) are set to be 1 and 0.25, respectively. Using the smaller set of weight factors makes the total difference of the solubility parameters smaller; however, the adjustment has been rationalized for the influence of polar materials inducing dipoles in nonpolar materials that lead to increased interactions. The variable \( A \) in Equation (5) can be used as a semi-quantitative index of relative solubility. Higher differences between the solubility parameters of solvents
and polymer materials usually implies lower mutual solubility, thus better resistance to chemical permeation.

The concept of the Hansen three-dimensional solubility parameters can be visualized using a graphical approach, as shown in Figure 4. The placement of the solutes with certain values of $\delta_d, \delta_p, \delta_h$ is shown in the plot, and a spherical volume of

![Figure 4. Conceptual Diagram of the Three-Dimensional Solubility Parameters.](image)
solubility with $R_A$ as an interaction radius can be obtained. The degree of solution process for a material can be judged by determining the distance to the center of the solubility sphere based on its $\delta_d$, $\delta_p$, $\delta_h$. The solvents close to the center will dissolve the solute fast and better, while the solvents close to the boundary region of the sphere will dissolve the solute rather slowly and poorly. Hansen\textsuperscript{84} successfully employed the concept of three-dimensional solubility parameters in the coating industry to improve paint quality by characterizing the solubility parameters of dye, emulsifiers, pigments, and solvents.

Yet, the concept of 3-DSPs has offered limited application in predicting polymer solubility reliably when quantitative determination of solubility is required. Particularly for crosslinked polymers, there is a lack of a reliable means of determining 3-DSP values using the graphical approach.\textsuperscript{92} The recognized shortcomings of the graphical approach for estimating the 3-DSPs of crosslinked polymers include the following: the lack of a theoretical basis for the assumed linear relationship between $A$ and solubility, the failure to account for the influence of the solvent molar volume and the effective crosslink density of polymers on the correlation between $A$ and solubility, the critical dependence of the graphical determinations on both the uptake criterion chosen to define the spherical solubility zone and the 3-DSP values of only two or three “define” solvents, and the cumbersome nature of the procedures involved. The alternative effective and reproducible methods of estimating a crosslinked polymer’s 3-DSP will be discussed in later sections.
Free Volume Theory

The permeation rate of a chemical through a polymer depends on both the diffusion coefficient and the solubility of the chemical in the polymer barrier. Many theoretical approaches to estimate the diffusion coefficients are based on free volume theory. By definition, free volume within a polymer refers to the empty space between the molecules of the polymer. In other words, free volume is the amount of space the polymer occupies but isn’t actually filled by the polymer chains. The basis of this theory is that the mobility of penetrant molecules in a polymer matrix and polymer segments is dependent on the amount of free volume present in the system. The migration of penetrants can be visualized as a series of unit diffusion steps or jumps during which the penetrant passes over a potential barrier. Before a molecule or jumping unit can migrate in a barrier, the following two requirements must be met: a hole or free volume space with adequate size must be adjacent to the molecule and the molecule must have sufficient energy to move or jump into this void. Molecular vibration creates holes with a size large enough, and the penetrant molecule vibrates with enough energy to jump to the next open space. The frequency of the diffusion steps is controlled by factors including the size and shape of the diffusing species, the intermolecular forces between the polymer chains, the stiffness of the polymer chain, and the tightness of the packing in the structure of polymer.

Cohen and Turnbull originally proposed the free volume theory and gave a simple view of the molecular permeation process. Their basic assumption is that the jumping frequency of diffusants is directly related to the fraction of free volume in the system. Fijita developed his free volume theory in the 1960s based on the assumption that the
free volume available in a solvent-polymer system is the major factor controlling the molecular diffusion rate. In his theory, free volume is defined as the difference between the cage of a molecule and the volume of the molecule itself, analogous to the hole created by the thermal vibration of polymer chain segments. Mass transfer mainly takes place in the free volume region of a polymer membrane. The larger the amount of free volume available, the more room the molecules have for displacement, which also means more room for the permeant to penetrate the polymer. The amount of energy needed for this rearrangement or “hole formation” will successively increase as the size and the shape of the penetrant molecule increase. Vrentas and Duda\textsuperscript{94} investigated free volume theory by correlating and predicting the concentration dependence of the diffusion coefficients. They examined the possible influences of temperature, concentration, and molecular weight on the diffusion process. According to their model, the migration rate is the product of the following two probabilities: the probability that a fluctuation of local density generates a hole of sufficient size and the probability that the jumping unit obtains sufficient energy so that the unit can overcome attractive forces from neighboring molecules. This model gave a reasonable explanation for the dependence of the diffusion coefficients on the concentration.

The models based on free volume theory have been used primarily for polymer-gas systems, but the application of the models for solute-rubbery polymer systems has produced less accurate results.\textsuperscript{87} Due to the limitations of these theoretical models for predicting the diffusion coefficient for these polymer systems, empirical correlations have been made based on other physical properties such as viscosity or kinetic viscosity,
molecular weight, octanol-water partition coefficient, etc. These approaches will be discussed in later sections.

**Fickian Diffusion and Non-Fickian Diffusion**

There are many theories concerning the manner by which a diffusion process takes place. Generally speaking, diffusion is a random movement of molecules such that, if given a certain amount of time, the distribution of molecules tends toward an even concentration over space. For a diffusion process of a penetrant solvent in a polymer membrane to take place, the solvation of the solvent by the polymer must occur when the solvent molecules contacts the polymer surface. As the solvent diffuses through the membrane, a concentration gradient is established that decreases from the highest concentration at the contacted surface to the lowest concentration at the opposite surface where the solvent evaporates and is continuously swept away by a carrier gas or liquid.

Fick’s First Law is a mathematical approach to deal with a process in which the solvent molecules have low solubility in the polymer and the polymer matrix is unaffected by the penetrant molecules. In a one-dimensional diffusion system, Fick’s First Law states that the rate of mass transport across a unit’s cross-sectional area is proportional to the negative concentration gradient normalized to that cross-section:

$$J = -D \frac{\partial C}{\partial x} \quad (6)$$

where $J$ is the mass flux in mg/min•cm$^2$, $D$ is the diffusion coefficient in cm$^2$/min, $C$ is the solvent concentration in the membrane, and $X$ is the distance in centimeters from the contacted membrane surface. The minus sign indicates that diffusion occurs toward the
areas of lower concentration. It should be noted that the flux rate or diffusion rate is dependent upon the concentration gradient and the diffusion coefficient $D$. For a liquid solvent/polymer membrane system, the concentration at the contact surface is equivalent to the solubility of the solvent in the polymer. Diffusion coefficients are observed to be highly dependent on temperature.$^{98}$

Integrating the equation above yields the following equation if the diffusion coefficient $D$ is not dependent on the concentration:

$$J = -D \frac{C_1 - C_2}{L}$$  \hspace{1cm} (7)

where $C_1$ and $C_2$ are the concentrations of permeation upstream and downstream, respectively. As stated previously, $C_2$ is usually 0 and $C_1$ is equal to the solubility of the solvent in the polymer. In the cases where $D$ is a function of concentration,$^{65}$

$$J = - \frac{1}{L} \int_{C_2}^{C_1} D dC$$  \hspace{1cm} (8)

Since the diffusion coefficient in the integral is related to the concentration using some other empirical equations, $\overline{D}$ is used to indicate an overall average diffusion coefficient.

According to Henry’s Law, concentration is related to pressure, as shown in the following equation:

$$C = Sp$$  \hspace{1cm} (9)

where $S$ is the solubility coefficient and $p$ is partial pressure. Thus, by substituting for $C$
in Equation (6) and renaming DS as P, a new equation can be written as follows:

\[ J = -DS \frac{\hat{P}}{\hat{x}} = -P \frac{\hat{P}}{\hat{x}} \] (10)

where P, defined as the permeability coefficient, is the product of diffusion and solubility coefficients. Thus, the permeability reveals the dependency of permeation rates on the solubility and diffusion of penetrant solvents in polymer barriers.

The diffusion model above is rather simple. If the diffusion rate changes as diffusion proceeds, it is defined as non-steady state diffusion. Fick’s Second Law, a second-order differential equation with several different forms, can describe the change in the rate of non-steady-state diffusion. When the diffusion is only limited to one dimension, this type of diffusion can be represented by the resulting partial differential equation:

\[ \frac{\partial c}{\partial t} = D \left[ \frac{\partial^2 c}{\partial x^2} \right] \] (11)

If D is not constant but dependent on the concentration C, as in many polymer-solvent systems, Equation (11) becomes:

\[ \frac{\hat{c}}{\hat{t}} = \frac{\partial}{\partial \hat{x}} \left( D(c) \left[ \frac{\hat{c}}{\hat{x}} \right] \right) \] (12)

where t is the time. The solution for the equation above can be obtained by applying relevant boundary conditions, which will be discussed in the next section.

If the change in dimension and structure of the polymer membrane exceeds to certain extent, Fick’s Second Law no longer holds. When a polymer is in contact with a solvent above its glass transition temperature, the diffusion and the segmental motion of
the polymer chains control the relaxation processes of polymer chain. The transport of small molecules in elastomeric membranes can generally be classified into the following three major categories: (a) Fickian or Case I diffusion, in which the rate of diffusion is much less than the actual rate of relaxation with no dependence on the swelling kinetic; (b) Non-Fickian or Case II diffusion, which refers to a rapid diffusion process compared to concurrent relaxation processes, with a strong dependence on swelling kinetics; (c) Anomalous diffusion, which refers to a process in which the diffusion and relaxation rates are similar, resulting in a minor time dependency. Among the three modes, Case I and Anomalous behaviors are the most commonly observed in elastomers/rubbery polymers, although it is not unusual that non-Fickian diffusion behavior is observed.

The weight change test is a quantitative and convenient experiment method widely used to investigate the sorption and transport of a chemical through a polymeric membrane. After being immersed in a solvent for a certain period, a piece of polymeric glove sample is then drained of the solvent. The change in the weight or the molar volume of the test sample is measured throughout the test, and it can be used to study the absorption and extraction processes and to estimate the diffusion coefficient or other permeation characteristics of a particular glove material.

In many of the published results, an empirical relation of weight change data exists in the solvent/polymer system. By analyzing the sorption data or dynamic swelling results, it can be determined whether the sorption mechanism follows Fickian or other modes. The dynamic sorption uptake results for short times have been determined by a least-squares fit using the following empirical equation:
\[
\frac{M_t}{M_\infty} = K t^n
\]

where \( M_t \) and \( M_\infty \) refer to the mass of solvent absorbed by polymer at time \( t \) and at infinite time, respectively, and \( K \) is an empirical constant dependent on the structure of the polymer and the interaction between the polymer and solvent. The exponential value \( n \) is associated with the transport mechanism and is used to infer the state change in the macro-molecular system. Take the logarithm of both sides, and the above equation can be rearranged as the following:

\[
\log\left(\frac{M_t}{M_\infty}\right) = \log k + n \log t
\]

The equations above are valid for the first 60\% of the final mass of penetrant uptake, and this approach of least-square estimation has showed a good preliminary analysis of the sorption mechanism. The value of both \( n \) and \( K \) can be determined experimentally by using the equation. For \( n \), a value of 0.5 represents Fickian or Case I diffusion, and a value of 1.0 indicates non-Fickian or Case II transport. A value between 0.5 and 1.0 corresponds to anomalous transport, which is the case for most of the observed transport phenomena. When \( n > 1 \), an unusual diffusion mechanism called SuperCase II occurs. The above equation is also applicable for desorption process in which \( M_t \) and \( M_\infty \) represent the weight loss of polymer samples at time \( t \) and at infinite time, respectively. (Note: weight loss here refers to the loss due to the evaporation of penetrant solvents.)
Aminabhavi et al.\textsuperscript{106, 107} extensively investigated the sorption behavior of polymers using the weight change approach. In a sorption-desorption-resorption-redesorption (S-D-RS-RD) experiment, they demonstrated that the weight gain curve for the samples immersed in a solvent trended downward slightly after the sorption equilibrium was reached. Weight losses due to additive extraction by solvents were observed in extended exposure to the chemical solvent. Following the first sorption stage, the immersed polymer sample was desorbed. Then the desorbed sample was again immersed in the solvent for resorption. Based on the weight gain and weight loss data, the diffusion coefficient can be calculated. The S-D-RS-RD experiments represent an effective approach to analyze the polymer-solvent interaction in the sorption process.\textsuperscript{108, 109} The sorption data $M_t$ and $M_\infty$ can be used to classify diffusion mode, evaluate the polymer-solvent interaction, enthalpy, and entropy changes during the sorption process, and estimate diffusion coefficients.

**Determination of Diffusion Coefficient**

The diffusion of solvent molecules into amorphous polymers has been investigated since the early 1940s. A wide range of organic penetrants and a variety of polymers were investigated under a broad range of experimental conditions. The major approaches include the weight gain test and the lag time approach.\textsuperscript{110} Many of the investigations were focused on specific classes of behavior, concentration-independent Fickian diffusion and concentration-dependent Fickian diffusion, diffusion anomalies, and Case II transport.
Further examination of the mechanism of diffusion is often carried out on a microscopic level in order to get a better understanding of the diffusion of small molecules in polymers. For Fick’s diffusion, the rate of approach to equilibrium for a polymer of slab geometry is defined by the diffusion coefficient, and the solvent sorption rate is directly related to the degree of equilibrium swelling of the polymer.\textsuperscript{71}

Incorporating the boundary conditions of a semi-infinite membrane in an infinite solvent bath, Fick’s Second Law can be solved if the diffusion in the x-direction is restricted and the diffusion into the edges of the membrane is ignored. A theoretical mathematical equation is expressed in the following, which can be used to construct sorption curves:\textsuperscript{65,71}

\[
\frac{M_t}{M_{\infty}} = 1 - \left(\frac{8}{\pi^2}\right)^{1/2} \sum_{n=0}^{\infty} \frac{1}{(2n + 1)^2} \exp\left(-\frac{D(2n + 1)^2 \pi^2}{l^2} t\right) \left(1 + \frac{D(2n + 1)^2 \pi^2}{l^2} t\right)^{1/2}
\]

where \(l\) represents the membrane thickness. The absorption kinetics is calculated either by using the model with the numerical or analytical solution. It was determined that the sorption plot showed initial linearity, followed by a plateau region at a later stage of sorption for most of the solvents chosen. For small values of \(t\), the above equation can be simplified to:

\[
\frac{M_t}{M_{\infty}} = \left(\frac{16D}{l^2 \pi}\right)^{1/2} t^{1/2}
\]

Therefore, for Fickian diffusion, the diffusion coefficient can be calculated from the slope of the plot of \(M_t/M_{\infty}\) versus \(t^{1/2}\). Since most polymer/solvent systems have
diffusion coefficients that are concentration dependent, the mean value $\overline{D}$ of the diffusion coefficient is used in the equation above.

On the other hand, for large values of $t$ in a polymer/solvent system in which the concentration of the permeation species approaches zero, Equation (15) can be reduced to:

$$
\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \exp\left( -\frac{D_0 \pi^2 t}{l^2} \right)
$$

where $D_0$ is the diffusion coefficient as the concentration approaches zero. This equation can be rearranged to:

$$
\ln(M_\infty - M_t) = \ln\left(\frac{8M_\infty}{\pi^2}\right) - \frac{D_0 \pi^2 t}{l^2}.
$$

The above equation shows that, plotting $\ln(M_\infty - M_t)$ versus $t$ gives a straight line with a slope of $\theta$:

$$
\theta = -\frac{D_0 \pi^2 t}{l^2}.
$$

Therefore, $D_0$ can be calculated based on the equation above. This equation can be used for systems with a sorption up to 55% of solvents taken up.96

Shen and Springer111 proposed the isotropic diffusion pattern in which the diffusion under equilibrium in all directions is considered instead of in two dimensions, assuming that diffusivity is equal in all directions ($D_r = D_\theta = D_z$). This attempt led to the following equation:

$$
D_{\text{average}} = D_z \left[1 + \frac{h}{r} + \frac{h}{2\pi r}\right]
$$
where \( h \) and \( r \) are the average thickness and average radius of the membrane samples before and after swelling, respectively.

Another procedure for measuring diffusion coefficients is based on the lag time approach. Behind this approach is the solution of Fick’s differential equation as developed by Crank.\(^{112, 113, 114}\) If a film separates two chambers containing a permeable vapor at different pressures, the vapor will permeate from the high-pressure side to the low-pressure side. Before diffusion occurs, the initial concentrations in the film and at the outgoing surface are zero. When a penetrant diffuses through a polymer membrane, there is a transient period from the time the penetrant first enters the film until steady-state permeation is established. As shown in Figure 5, the lag time is the intercept on the time axis obtained by extending the steady-state permeation trendline. If an equilibrium state is instantaneously reached at the interface, the amount \( Q \) of vapor that permeates the film can be given by the following equation:\(^{115}\)

\[
\frac{Q}{lC_1} = \frac{Dt}{l^2} \frac{l}{6}
\]

(21)

where \( l \) equals the thickness of the membrane and \( C_1 \) is the concentration of permeant in the face of the film next to the high-pressure chamber. Rearranging the equation above yields the following:

\[
Q = \frac{DC_1}{l} \left[ t - \frac{l^2}{6D} \right]
\]

(22)
After an initial build-up period as the term \( \frac{l^2}{6D} \) in the above equation, a linear relationship is eventually established at a certain point in time. Lag time \( \tau \) can then be expressed as:

\[
\tau = \frac{l^2}{6D}
\]  

(23)

Thus, diffusion coefficients can be determined by using the following rearranged equation:

\[
D = \frac{l^2}{6\tau}
\]  

(24)

Similarly, Ziegel et al. developed an empirical correlation to estimate the diffusion coefficient of solvents in polymers.\(^\text{116}\) Instead of lag time, they used the time it took to achieve half of the steady-state permeation rate. The equation used in their approach is:

\[
D = \frac{l^2}{7.199t_{1/2}}
\]  

(25)

where \( t_{1/2} \) is the time needed to reach half of the steady state permeation rate.

Variables in Permeation Processes

Polymer swelling is an important factor that affects permeation processes. Swelling is a process in which a polymer material absorbs a quantity of a solvent when it contacts with the solvent.\(^\text{117}\) Although most glove materials made of crosslinked polymers do not dissolve in chemical solvents, the materials can swell by taking up certain amounts of solvents. When polymer chain mobility is promoted due to swelling, it allows the chains to extend and separate, resulting in additional free volume spaces, a
Figure 5. Steady-State Permeation Rate, Breakthrough Time and Lag Time
decreased energy barrier required for a permeant molecule to jump from one space to the next and increased solvent transport. In addition, constrained swelling of polymer materials leads to stress and certain losses of mechanical properties such as tensile strength and tear/puncture resistance, etc. Thus, it is highly unlikely that for a swelling polymer/solvent system, the diffusion coefficient is constant. Instead, polymer swelling is considered a cause of deviation from the Fickian mechanism for a diffusion process.

Molecular size and shape are known to affect diffusion rates. As might be expected from diffusion theory, the larger a molecule, the less likely that holes large enough will be formed to allow the molecule to diffuse. Consequently, diffusion coefficients are usually smaller as the molecule becomes larger in a homologous series. Larger molecules also possess less kinetic energy, so the speed at which the molecule is able to jump to the next hole is less than that of a smaller molecule.

One of the physical properties of polymers is crystallinity. If an interaction occurs among polymer chains in some regions of a polymer material that are oriented effectively parallel to each other, then the possibility of the formation of a hole of a certain size is reduced. This commonly occurs in polymers with a high degree of crystallinity, for example, high-density polyethylene, which has a greater crystallinity than low-density polyethylene. Plasticizers are also widely used in polymer formulations and processing, which soften these polymers, increase the space between polymer strands, and make the polymer more pliable. While increased crystallinity usually decreases the diffusion coefficient, the addition of a plasticizer increases the diffusion coefficient. However, plasticizer influence can be rather complex in reality. For example, a chemical may have
an initially high permeation rate, but over time, the chemical may interact with the plasticizer and leach it from the polymer. As more plasticizer is leached away, the permeation rate begins to decrease because the polymer strands get closer together. This is one example of how additives to polymers can cause non-Fickian diffusion, as mentioned previously.\textsuperscript{123}

Another polymer property that affects diffusion is crosslinking. Many crosslinking accelerants are organic, or crosslinks can occur directly between reactive sites on two polymer chains forming covalent bonds. Crosslinking typically delays the diffusion process because the polymer chains are pulled close together with limited chain movement. However, if the crosslinking agent is a large organic molecule and can interact with solvents, the effect on diffusion can be more like that of plasticizers. The net result may be non-Fickian diffusion as well.\textsuperscript{124}

Two additional variables must be considered in the permeation process: the temperature of the solvent/polymer system and the thickness of the polymer. Changes in temperature may affect permeation by several mechanisms.\textsuperscript{38} Increased temperatures may increase the solubility of the challenging chemicals in the polymer materials or by increasing the vapor pressure of the chemicals. The rate of the diffusion steps in the permeation process can also increase with rising temperature, according to the Arrhensius equation type of relationship. Therefore, a small change in temperature may exhibit a significant breakthrough time and permeation rate. Since many actual uses of gloves occur at higher than ambient temperatures, the gloves coming in contact with solvents in
these applications should be selected properly with respect to the actual temperatures of the solvents.

Thickness is another important variable, which often has a significant effect on permeation.\textsuperscript{125, 124} Permeation rates and breakthrough times reported for a glove with a given thickness will not be applicable to another glove with a different thickness. Thickness normalization is considered to be an effective method to correct for thickness effect. Generally, the normalization approach is to multiply or divide permeation data with sample thicknesses or the square of the thickness. Steady-state permeation rate is often found inversely proportional to the thickness, and the lag time is related to the square of the thickness of the membrane. However, these relationships hold true only for Fickian diffusion, so in many cases its use is incorrect, and, more importantly, there is no relationship between the breakthrough time and thickness. Consequently, one should be very careful when applying thickness correction factors.

Development of Predictive Models

Numerous investigations have focused on estimating the diffusion coefficient since the permeation rate is dependent on this parameter. Due to the limits of the theoretical basis and the complexity of the permeation phenomenon, a satisfactory correlation cannot be achieved without empirical correlations between diffusion or permeation characteristics and physical properties of polymer-solvent systems. For example, in the study by Colletta \textit{et al.}\textsuperscript{38} of the derivation of short-term diffusion coefficients for nine carcinogens in order to predict the permeation resistance of protective clothing, they

45
concluded, unfortunately, that, due to the complexities associated with permeation through “filled” elastomers, accurate diffusion coefficients could not be determined, and modeling was impractical.

Southern and Thomas\textsuperscript{126} studied the diffusion of various liquids in natural rubber, and they concluded that the diffusion coefficient depends mainly on the liquid’s viscosity. In Schwope and Reid’s\textsuperscript{120} investigation of the correlation among the diffusion coefficient and properties representative of the size and shape of the solute molecules, they found out that their best correlations were with molecular weight. However, Khinnavar and Aminabhavi\textsuperscript{127} did not observe a consistent relationship between the diffusion coefficient and the size of solvent molecules in their experiments because the solvent and polymer they used possessed different chemical groups with varying complexity. Vahdat\textsuperscript{128} investigated the diffusion characteristics of several solvents through elastomers at different temperatures and showed that the diffusion coefficients are mainly dependent on kinetic viscosity. Vahdat\textsuperscript{71} also used sorption/desorption experiments to determine solubility and an expression for the diffusion coefficient in terms of concentration; however, the result of estimating the steady-state permeation rate of ethyl acetate in a few gloves and garments was a lack of representation.

A number of studies on solubility obtained by conducting weight gain tests showed interesting predictive results. The weight gain of a polymer was a measurement of the solubility of the solvent in the polymer. When the weight gain and solubility were high, short breakthrough times were usually observed; however, the reverse was not so consistently true, and no correlation study was performed. Weeks and McLead\textsuperscript{129}
conducted correlation studies of weight gain and breakthrough times. They tested commonly available polymer materials used in CPC against Arichlor 1254 and other chloroethanes; however, no correlation coefficient was reported. Holcombe\textsuperscript{130} studied the weight gain of Viton\textsuperscript{®} after immersion in six different chemicals. When the natural logarithm of these values was correlated with the breakthrough time, a correlation coefficient of 0.9 was obtained. The US Coast Guard\textsuperscript{131} developed a predictive model to test a chemical protective suit, which was based on the solubility phenomenon and Fick’s diffusion laws. Even though some uncertainty was noticed in the data set, the solubility parameters obtained in this study were found to be reliable for prediction.

Since 3-DSPs are available for many common organic solvents and polymeric materials, one might think that if a solvent and polymer have similar 3-DSP values, the solvent should be highly soluble in the polymer, thus resulting in a high permeation rate. Henriksen\textsuperscript{90} used this concept in correlation studies of permeation parameters. The preliminary work with permeation data from other researchers indicated that the natural logarithm of the steady-state permeation rate, when correlated with polymer and solvent 3-DSP differences, gave correlation coefficients ranging from 0.5 to 0.7, indicating a possible dependence of permeation on solubility. Bomberger\textsuperscript{35} \textit{et al.} used permeability coefficients, mainly derived from Nelson’s work,\textsuperscript{63} to correlate with 3-DSP differences of solvent and polymer pairs. This work yielded correlation coefficients ranging from 0.5 to 0.98. Perkins \textit{et al.}\textsuperscript{132} also modeled permeation data using the 3-DSP for the polymer Viton\textsuperscript{®}. Their work yielded a correlation coefficient of 0.69 for $\ln$ (BT) and a correlation of 0.65 for $\ln$(SSPR) when correlated against 3-DSP differences of the polymer and
solvent. In another study, Perkins\textsuperscript{11} also used solvent molecular volume and polymer thickness in combination with 3-DSP differences to predict permeation parameters. He observed that the 3-DSP differences were the most significant variable for both the breakthrough time and steady-state permeation rate, while molecular volume was found to be significant only in the breakthrough time studies; thickness was significant in predicting the steady-state permeation rate but not the breakthrough time. However, the overall correlation was poor, and it was suggested that 3-DSP might only serve in semi-quantitative applications.

Since the accurate measurement of solubility parameters is critical to improve the correlations and prediction capacity of the model based on solubility parameters, Zeller \textit{et al.}\textsuperscript{91} developed a model by incorporating the Flory-Rehner theory into the Hansen solution theory. Variables such as solvent molar volume, exposure temperature, and the degree of crosslinking in the polymer were also incorporated in the model since it is believed that the omission of these critical variables resulted in failure in the previous modeling attempts. The weighing factors a and b were determined empirically for each solvent group in order to minimize the variation in solubility interactions associated with one single set of 3-DSP values. A nonlinear regression technique was used to provide a more reliable approach to determine the 3-DSP of glove materials with minimum overall deviation. To use Zeller’s original model to estimate permeation data such as BT and SSPR, the solubility data was used to determine the values of solubility coefficient S and equilibrium diffusion coefficient D first. Then the calculated S and D values were used to estimate the BT and SSPR values using the Fickian diffusion equation. A comparison
was made between the modeled and experimental permeation data, and the modeled BTs were found to have been slightly overestimated by a factor of two or three, while modeled SSPRs were less accurate within a factor of six. This was a fairly successful attempt.

Hardy et al\textsuperscript{9, 10} described an improved predictive model based on the combination of the Hansen solubility theory and the Flory-Rehner solution theory and successfully applied it to estimate the solubility parameters of Viton\textsuperscript{®} and nitrile polymeric materials using a nonlinear least-square regression technique. In this model, the determination of polymer solubility parameters did not rely on the estimation of the polymers’ molecular weights or the use of individual weighting factors for particular solvent-polymer combinations. Weight gain tests were extended up to 12 weeks to ensure that equilibrium was established, resulting in a high level of correlation, with correlation coefficients ranging from 0.956 to 0.9913. With more reliable solubility parameters obtained, Hardy et al were able to apply their solubility-based model to correlate the permeation data, including SSPR, BT, and LT, of organic solvents in Viton\textsuperscript{®} and nitrile polymeric materials with a high level of correlation in their study. This was a significant improvement from all previous solubility-based models.

The goal of this study is to employ Hardy lab’s approach to determine the solubility parameters of butyl gloves from four different manufacturers using extended weight change test. The solubility-based model derived from the Hansen solubility theory and the Flory-Rehner solution theory as described in Hardy’s approach was used to correlate the permeation data of organic solvents in the butyl gloves. This is the first time that this
predictive model has been applied to butyl glove materials manufactured by different manufacturers and the predictability of this model was examined.
CHAPTER III

EXPERIMENT

Theoretical Background and Model Description

As discussed previously, the solution theory described by Hildebrand is based on the discovery that the solubility of a given solute in a series of solvents is determined by the internal pressures of the solvents.\(^{78}\) This theory led to the introduction of the concept of cohesive energy density and solubility parameters, which are useful in predicting the solubility of low-molecular-weight solutes and polymers in solvents. Mathematically, this concept is expressed as follows:

\[
\delta = \left( \frac{\Delta E}{V} \right)^{1/2} = C \varepsilon d^{1/2} \quad (26)
\]

where \(\delta\) is defined as the solubility parameter equal to the square root of cohesive energy density, \(\Delta E\) is the energy of vaporization of a polymer to a gas at zero pressure, and \(V\) is the volume of the polymer. The basic assumption of the solubility parameter theory is that there exists a correlation between the cohesive energy density of pure substances and their mutual solubility.

Hansen et al.\(^{84}\) expanded Hildebrand’s theory by introducing hydrogen bonding together with a polar interaction component into the system in order to characterize the interactions between a solute and a solvent. Thus, the total solubility parameter could be
separated into three components, and the total cohesive energy density of a substance can be expressed according to the following equation:

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2$$  \hspace{1cm} (27)

where $\delta_d$, $\delta_p$, and $\delta_h$ represent the partial solubility parameters contributed by dispersion, polar, and hydrogen bonding forces, respectively. The contribution from dispersion interaction is common to all molecules resulting from fluctuations in the temporary dipole moments in non-polar molecules; and the second type of interaction is dipole-dipole interactions, including permanent dipole-permanent dipole or permanent dipole-induced dipole interactions in polar molecules; the last one represents the interactions of hydrogen bonding.

Hansen also used a three-dimensional graphical approach to plot and visualize this concept. For a particular solute, its placement in three-dimensional space is represented according to its values of $\delta_d$, $\delta_p$, $\delta_h$; a spherical shape surrounds the point and defines a “radius of interaction” for that solute. Thus, the interaction between the solute and a solvent can be expressed using the following equation:

$$A = \left[ a \left( \delta_{d1} - \delta_{d2} \right)^2 + b \left[ \left( \delta_{p1} - \delta_{p2} \right)^2 + \left( \delta_{h1} - \delta_{h2} \right)^2 \right] \right]^{1/2}$$  \hspace{1cm} (28)

where $d$ represents dispersion, $p$ dipole interaction, $h$ hydrogen bonding; 1 and 2 are the solute and solvent, respectively, and $a$, $b$ are weighing factors. For polymers, the 3-DSP values are usually assigned based on correlations established from weight gain testing with solvents whose values are published. The weighing factor $a$ for the dispersion parameter difference is commonly set as 4, and the factor $b$ for polarity and hydrogen-
bonding terms as 1 to ensure that all three terms are similarly weighed in the model since dispersion parameters usually vary in a smaller range compared to the other two terms.\(^2\)

It was reported that better correlations for polymer-solvent solubility were obtained if \(a=1\) and \(b=0.25\), in which using the smaller weighing factors led to smaller differences of term A and higher estimates of solubility. It was rationalized that adjustments for the increased solvent/solute interactions resulted from the induced dipoles of nonpolar molecules by polar molecules.\(^87,88,89\)

Estimating 3-DSP values of polymers can be achieved based on a graphical method\(^135\) or approaches that use viscosity measurements of polymer solutions,\(^136\) molecular group-contribution calculations,\(^137\) and molecular simulation models.\(^138,139\) However, all these approaches cannot be applied to crosslinked polymers to estimate solvent/polymer solubilities quantitatively. Alternatively, the approach used in this work is to combine Hansen three-dimensional solubility parameters and the Flory-Rehner solution theory,\(^70\) and use a nonlinear regression technique to obtain 3-DSP values with minimum overall error. Assuming a polymer swells isotropically in a solvent at equilibrium, a modified version of the original Flory-Rehner solution theory is shown in Equation (29), which takes the swelling process and free energy change of mixing into account:\(^140\)

\[
\ln (1 - \phi_p) + \phi_p + \chi \phi_p^2 + \frac{V_m \rho_p}{M_p} \left( \phi_p^{1/3} - \frac{\phi_p}{2} \right) = 0, \quad (29)
\]

where \(\phi_p\) is the volume fraction of polymer in the solvent/polymer system, \(\chi\) is known as the Flory-Huggins polymer-solvent interaction parameter, \(V_m\) is the molar volume of
solvent (cm$^3$/mole), $\rho_p$ is the density of the polymer, and $M_p$ is the apparent molar weight between the crosslinks of the polymer.

Because the typical molecular weight of butyl rubber before crosslinking is over 200,000,\textsuperscript{141} Equation (29) can be reasonably further simplified to the following form by discarding the insignificant last term:

$$\ln(1 - \phi_p) + \phi_p + \chi \phi_p^2 = 0 \quad (30)$$

The polymer-solvent interaction parameter, $\chi$, which describes the change in free energy when mixing a solvent and a polymer, can be defined as the sum of the entropic term (Flory combinatorial entropy correction factor $\beta$) and enthalpic term, as follows:

$$\chi = \chi_s + \chi_H \quad (31)$$

and the enthalpic term $\chi_H$ can be expressed as follows:

$$\chi_H = \frac{V_m A}{RT} \quad (32)$$

Substituting Equations (31) and (32) into (30) yields the following equation:

$$\left(\frac{V_m A}{RT} + \chi_s\right)\phi_p^2 = -[\ln(1 - \phi_p) + \phi_p], \quad (33)$$

where $\chi_s$ is a constant that is often set in the range between 0.3 and 0.4,\textsuperscript{142} although a value between 0 and 2.5 has been used, or it can be determined in regression process.\textsuperscript{143, 144} By examining both sides of the equation above, it can be observed that there are only two variables for different solvent-polymer systems ($\chi_s$ is set constant): $A$ and $\phi_p$, while all the other terms are constants if all the experiment will be carried out at a constant temperature. Thus, the Flory interaction parameter for a given solvent/polymer
system can be related to mutual solubility using this equation. It was reported that a reliable approach is to estimate a polymer’s solubility parameters by correlating the weight gain data of the polymer in a set of organic solvents using nonlinear regression for some polymer materials.

Previous work\textsuperscript{9, 10} has demonstrated a correlation between $\chi \phi_p^2$ and permeation properties such as steady-state permeation rates and the breakthrough time. This correlation is based on the fact that $\chi \phi_p^2$ is a good measurement of free energy change in a solution process. The success of this model applied to correlating permeation data and $\chi \phi_p^2$ for Viton\textsuperscript{®} and nitrile gloves prompted the research interest to test the validity of this model for butyl glove materials. This work will represent part of the effort to examine the possibility to use this model to predict the permeation performance of polymeric materials against chemical solvents.

Materials Used

Butyl rubber polymer, a copolymer of isobutene and isoprene monomers shown in Figure 6, has been widely used in chemical protective clothing and other industries due to the polymer’s excellent resistance to chemicals, aging, moisture, and ozone, and low permeability. The content of isoprene usually ranges from 0.5 to 2.5\% for crosslinking, while the molecular weight of butyl rubber used for non-tacky products is usually over 200,000.\textsuperscript{141}

In this work, unsupported, smooth-finish butyl gloves from four different manufacturers were investigated as permeation barrier membranes. The four vendors of
butyl gloves are Best Glove Manufacturing (Menlo, GA), Guardian Manufacturing (Willard, OH), North Safety Products (Cranston, RI), and Renco Corporation (Manchester, MA). The detailed specifications of the four gloves are listed in Table 1. All the glove samples were cleaned up with Kimwipes® without any further treatment.

The selected challenging permeants were 26 common organic solvents representing a variety of functional groups, polarities, and H-bonding. The 3-DSPs of these solvents are available from standard literature sources. All chemicals used in this work were certified A.C.S. reagent grade or higher purity. Among them, 2-propanol, acetone, benzaldehyde, and heptane were obtained from Fisher Scientific (Pittsburgh, PA). Cyclohexane, tetrahydrofuran, and chloroform were obtained from Burdick & Jackson Laboratories, Inc (Muskegon, Michigan). 1-Propanol and 2,2,4-trimethylpentane were obtained from Aldrich (Milwaukee, WI). The chemicals were all used without further purification. Listed in Table 2 are the properties of these solvents, including the three-dimensional solubility parameters, molecular weight, and molar volume.

Weight Gain and Weight Loss

Commercial butyl rubber glove contains oligomers and various additives, many of which may be extracted when it contacts solvents. When a glove sample is immersed in a solvent and absorption equilibrium is reached, the weight gain calculation should be based on the net weight of the solvent absorbed and the glove sample mass on dry basis, which may be less than the initiate sample weight before immersion. Thus, the weight change experiment was conducted in two stages: immersion stage for obtaining the total
Table 1. Specification of Four Butyl Gloves

<table>
<thead>
<tr>
<th>Vendor</th>
<th>Style</th>
<th>Thickness (mil)</th>
<th>Length (inch)</th>
<th>Size</th>
<th>Finish</th>
<th>Hand design</th>
</tr>
</thead>
<tbody>
<tr>
<td>Best Manufacturing</td>
<td>878</td>
<td>30</td>
<td>14</td>
<td>Extra Large</td>
<td>Smooth</td>
<td>Roll-cuff, Unlined</td>
</tr>
<tr>
<td>Guardian Manufacturing</td>
<td>CP-25</td>
<td>25</td>
<td>14</td>
<td>XL</td>
<td>Smooth</td>
<td>curved</td>
</tr>
<tr>
<td>North Safety Products</td>
<td>B174</td>
<td>17</td>
<td>14</td>
<td>10</td>
<td>Smooth</td>
<td>NA</td>
</tr>
<tr>
<td>Renco Corporation</td>
<td>R324B</td>
<td>32</td>
<td>14</td>
<td>10</td>
<td>Smooth</td>
<td>NA</td>
</tr>
</tbody>
</table>

Figure 6. Structure of Butyl Rubber Polymer
Table 2. Three-Dimensional Solubility Parameters, Molecular Weight and Molar Volume of Organic Solvents. 134, 142

<table>
<thead>
<tr>
<th>Solvent</th>
<th>MW (g/mole)</th>
<th>mol. Vol. (cm³/mole)</th>
<th>δ_d (Mpa)^1/2</th>
<th>δ_p (Mpa)^1/2</th>
<th>δ_h (Mpa)^1/2</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2-Dichloroethane</td>
<td>98.96</td>
<td>79.4</td>
<td>19.0</td>
<td>7.4</td>
<td>4.1</td>
</tr>
<tr>
<td>1,4-Dioxane</td>
<td>88.11</td>
<td>85.7</td>
<td>19.0</td>
<td>1.8</td>
<td>7.4</td>
</tr>
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<td>1-Butanol</td>
<td>74.12</td>
<td>91.5</td>
<td>16.0</td>
<td>5.7</td>
<td>15.8</td>
</tr>
<tr>
<td>2-Propanol</td>
<td>60.1</td>
<td>92.0</td>
<td>15.8</td>
<td>5.7</td>
<td>14.5</td>
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<tr>
<td>Acetone</td>
<td>58.08</td>
<td>74.0</td>
<td>15.5</td>
<td>10.4</td>
<td>7.0</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>41.05</td>
<td>52.6</td>
<td>15.3</td>
<td>18.0</td>
<td>6.1</td>
</tr>
<tr>
<td>Benzaldehyde</td>
<td>106.12</td>
<td>101.5</td>
<td>19.4</td>
<td>7.4</td>
<td>5.3</td>
</tr>
<tr>
<td>Benzene</td>
<td>78.11</td>
<td>89.4</td>
<td>18.4</td>
<td>0.0</td>
<td>2.0</td>
</tr>
<tr>
<td>CH₂Cl₂</td>
<td>84.93</td>
<td>63.9</td>
<td>18.2</td>
<td>6.3</td>
<td>6.1</td>
</tr>
<tr>
<td>Chloroform</td>
<td>119.38</td>
<td>80.7</td>
<td>17.8</td>
<td>3.1</td>
<td>5.7</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>84.16</td>
<td>108.7</td>
<td>16.8</td>
<td>0.0</td>
<td>0.2</td>
</tr>
<tr>
<td>Cyclohexanone</td>
<td>98.14</td>
<td>104.0</td>
<td>17.8</td>
<td>6.3</td>
<td>5.1</td>
</tr>
<tr>
<td>Diethyl Ether</td>
<td>74.12</td>
<td>104.8</td>
<td>14.5</td>
<td>2.9</td>
<td>5.1</td>
</tr>
<tr>
<td>Dimethyl Sulfide</td>
<td>78.13</td>
<td>71.3</td>
<td>18.4</td>
<td>16.4</td>
<td>10.2</td>
</tr>
<tr>
<td>DMF</td>
<td>73.09</td>
<td>77.0</td>
<td>17.4</td>
<td>13.7</td>
<td>11.3</td>
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<td>Ethanol</td>
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<td>58.5</td>
<td>15.8</td>
<td>8.8</td>
<td>19.4</td>
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<tr>
<td>Ethanolamine</td>
<td>61.08</td>
<td>60.2</td>
<td>17.2</td>
<td>15.5</td>
<td>21.3</td>
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<tr>
<td>Ethyl Acetate</td>
<td>88.1</td>
<td>98.5</td>
<td>15.8</td>
<td>5.3</td>
<td>7.2</td>
</tr>
<tr>
<td>Furfuraldehyde</td>
<td>96.09</td>
<td>83.2</td>
<td>18.6</td>
<td>14.9</td>
<td>5.1</td>
</tr>
<tr>
<td>MEK</td>
<td>72.11</td>
<td>90.1</td>
<td>16.0</td>
<td>9.0</td>
<td>5.1</td>
</tr>
<tr>
<td>n-Butyl Acetate</td>
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<td>132.5</td>
<td>15.8</td>
<td>3.7</td>
<td>6.3</td>
</tr>
<tr>
<td>O-Xylene</td>
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<td>121.2</td>
<td>17.8</td>
<td>1.0</td>
<td>3.1</td>
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<td>14.5</td>
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<td>0.0</td>
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<tr>
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<td>80.9</td>
<td>19.0</td>
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<td>5.9</td>
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<td>THF</td>
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<td>5.7</td>
<td>8.0</td>
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<td>Toluene</td>
<td>92.14</td>
<td>106.8</td>
<td>18.0</td>
<td>1.4</td>
<td>2.0</td>
</tr>
</tbody>
</table>
weights of samples saturated with solvents; and out-gassing stage for obtaining post-drying glove sample weights. During the first stage, circular samples with a diameter of 2.5 cm were cut from the flat section of gloves. Each sample was visually examined for any obvious defects like pinholes or other imperfections. After the samples were weighed using an analytical balance, they were immersed into 30 ml of the 26 solvents in screw-tight glass bottles. Then sample weights were taken on a weekly basis. Each time when the sample weights were taken, the samples were picked up and placed between layers of Kimwipes®️, a roller pressed gently to remove excess solvent on the sample surface quickly, and then the samples were transferred into pre-tarred weighing vials with caps in order to prevent solvent evaporation during weighing. The samples were then put back into the bottles immediately. The total time taken in the procedure was less than a one-minute interval. The weight gain stage was carried out for at least four weeks and up to 10 weeks, until the weight changes were less than 1% for three consecutive weeks. Mostly, the samples reached their maximum weights within one to three weeks, with a few exceptions. Once a maximum weight was reached, the sample went to the second stage.

During the second stage, the samples were taken out from the solvents and placed into an electrically controlled oven at 80 °C (For the first set of samples tested, the Best glove sample was dried at 40°C and sample weights were measured every three days. It took as much as 12 days to dry the sample. Since the typical curing temperature for butyl rubber is between 149 and 171°C, the drying temperature was then raised to 80 °C for
the remaining sets of samples). At an interval of 24 hours, the samples were pulled out, cooled down to room temperature, weighed, and placed back into the oven until the weight changes were less than 1%. The weight gains were obtained by calculating the fractional gains of the sample weights at equilibrium compared to the weights after they were out-gassed. The weight losses were the fractional losses of the sample weights calculated by using the initial sample weights and the final weights at the end of the out-gassing stage.

The densities of the glove samples were measured according to the method specified by ASTM D792-91. In triplicates, each brand glove sample was measured according to the test method. The average density ranged from 1.07 to 1.16 g/cm³.

Instrument and Permeation Setup

The instrument used in this work was a Hewlett-Packard 5890 series II Gas Chromatograph equipped with a flame ionization detector. A Macintosh computer (Model: 5400/200; Operating System: Mac OS 9.1) installed with GC WorkMate 2 software (Willstein Software, Wilmette, IL) was connected to the GC system for data acquisition, system control and monitoring, data storage, and data processing. The GC column used was a SPB-5 capillary column, 30m, 0.53 mm ID, 1.5 μm film thickness (Supelco, Inc., Bellefonte, PA). The flow rates of the carrier gas in the analytical column (flow A) and in the permeation cell (flow B) were measured using a dual-channel electronic flow sensor (EFS), which were calibrated using a bubble flow meter. A 10-
port, 2-position sampling valve equipped with a gas-sampling loop (Valco Instrument Co., Inc., Houston, TX) was used for sampling gaseous samples quantitatively.

Permeation tests were carried out in an open-loop configuration, similar to the ASTM F739-96 chemical permeation method. The setup incorporated modifications that
were recommended by several authors in that both temperature and flow are controlled.\textsuperscript{146, 147} Figure 7 shows the sketch of the test setup and associated equipment. A permeation cell, shown in Figure 8, consists of two hemi-cells, 79 mm in diameter and 30 mm in height, which are separated by a glove sample during the permeation tests. The sample exposure area was 0.33 cm$^2$. During the permeation experiments, solvents flowed over the surfaces of the samples, and the carrier gas picked up the solvents penetrating to the other side of the sample film into the GC column.
Permeation Tests

The GC instrument parameters were set as following:

- Oven temperature: 150°C
- Injection Port: 200°C
- Detector Temperature: 250°C
- Carrier Gas/Flow Rate: He/\(~\text{7.5 cm}^3/\text{min}\)
- H₂/Air (Detector): ~35 cm³/min /~300 cm³/min
- N₂: 20 cm³/min
- Split/Non-split: Non-split

Test glove samples were taken from the palm, back, or cuff portion of the glove (flat surface) using a circular stainless steel cutter. After visual examination for any defects and five thickness measurements in the center area of a glove sample, it was mounted between the two permeation hemi-cells. A set of O-rings made of fluorocarbon/Viton® (Parker Seals, KY) was used to provide a tight seal between the two chambers. Then the cells were bolted tightly and connected to the solvent tubing and sampling gas tubing. Helium was used as carrier gas, and flow rates were set 7.5 ml/min. The perme cell was then horizontally placed into a container equipped with a temperature-control device for at least 30 minutes before a permeation test started. Throughout each permeation test, the temperature was controlled within 25 ± 0.5°C. A 1000 mL Omnifit® liquid chromatography solvent bottle (Cambridge, United Kingdom) with three two-way valves in the screw cap was used as the permeant reservoir. The
valves were used to control the solvent flow from the reservoir to the permeation cell and the air vent. Another bottle was placed under the outlet tubing from the cell to collect waste solvents.

Once a stable baseline was established, the permeation test was started by switching the valve, allowing solvent to flow into the permeation cell. The flow rate of the solvents was set up at ~0.7-0.8 ml/min, and the GC response was recorded continuously. During the permeation experiments, solvents flowed over the surface of the samples and the carrier gas picked up the solvents penetrating to the other side of the sample film into the GC column. The GC response recording continued until a stable GC response curve was reached. Then in triplicate, the sampling loop was purged with five-minute intervals for re-equilibrium. At the end, three injections of 0.1 μl of the test solvent were made as an external standard, allowing the amount of the solvents in the carrier gas to be quantified. The permeation data, including the steady-state permeation rate, breakthrough time and lag time, could be calculated by processing the collected data.

Data Processing Methods

The Hansen solubility parameters $\delta_d$, $\delta_p$, and $\delta_h$ for each butyl glove material were determined based on Equation (33). A nonlinear least-square regression technique was used in this data treatment to ensure the best fit of the solubility parameters. The implementation of this treatment was carried out using Data Desk 6.0® (Ithaca, NY), an interactive data analysis program. To facilitate batch processing the data, an in-house
data processing template on the platform of Data Desk 6.0® was written so that the result of the nonlinear least-square regression modeling could be conveniently obtained with minimum deviation by inputting weight gain data and density together with molecular weight, molar volume, temperature, and ideal gas constant.

All GC response raw data in the permeation tests were stored on the Macintosh computer, which were extracted as ASCII format using GC Work Mate 2. Microsoft® Excel 2000 was used to process the data to determine the steady-state permeation rates, breakthrough times, and lag times. Modeling and correlating permeation data against solubility terms was performed using Excel 2000. Single-factor ANOVA data analysis was conducted by also using the data analysis tools available in Excel 2000.
CHAPTER IV

RESULTS AND DISCUSSION

Weight Gain and Weight Loss

Weight change tests, which provide a simple, quantitative approach for assessing material degradation resistance, have been widely used in testing material chemical resistance. In this study, unsupported, smooth-finish butyl gloves from four different manufacturers were evaluated against 26 common organic solvents. Some highly volatile solvents such as diethyl ether were rejected since it evaporated too fast to allow accurate measurements of sample weights during the test. The weight change experiments included two primary stages: immersion stage, which were carried out by immersing the glove sample in organic solvents for extended period, and outgassing stage, in which the glove samples from the immersion stage were dried in an oven and sample weights were taken. Weight gains are defined as the fractional weight changes of the soaked samples compared to post-drying samples, and weight losses here are defined as the fractional weight changes of pre-immersion samples compared to post-drying samples. The calculation equations are shown below:

\[
\text{Weight Gain} = \frac{W_i - W_1}{W_1},
\]

\[
\text{Weight Loss} = \frac{W_0 - W_1}{W_0},
\]
Figure 9. Examples of Weight Change During Immersion and Drying Stages

where $W_0$, $W_1$, and $W_t$ represent initial sample weight, post-drying weight, and sample weight at the elapsed time of immersion.

To illustrate a sample weight change during the two-stage tests, some examples of the weight change plots are given in Figure 9. Weight change curves were found to generally follow a similar pattern as reported previously. Initially, the weights of most samples increased at relatively fast rates by absorbing the solvents into the material specimens; the weight gain was often visually noticeable since many of the samples
swelled. Within one to three weeks, the sample weights approached equilibrium in most cases. Then the sample weights started to decrease or increase slightly over time, and reached equilibrium. Weight losses of the original glove materials were evidenced when the sample weights after drying were less than their initial weights. During the immersion stage, two processes, the absorption of solvents and the extraction of additives and oligomers from gloves, proceeded simultaneously. Once the solvent absorption process approached equilibrium and the additive extraction was nearly complete, stable sample weights were reached.

Extended immersion is necessary in order to obtain accurate and reliable weight gain data since polymer solution process may take much longer time than that of small molecule solutes. In the selection guide of chemical protective clothing it was stated that weight gain tests usually last for 8 hours.\textsuperscript{148} The longest weight gain test reported was 14 days (not including Evan’s and He’s studies).\textsuperscript{150} However, in the current study it was found that 8 hours immersion period was far from adequate to obtain accurate sample weight gains at or close to equilibrium for many solvents. As shown in Table 3, it might take up to five weeks (plus additional two weeks to confirm) for certain combinations of solvents/glove samples to reach equilibrium immersion state.

The results of the weight gain and weight loss data are listed in Table 4 and 5, and the molecular weights, molar volumes, and solubility parameters of all the solvents tested are listed in Table 2. No sample disintegrated at the end of the weight change tests. As
Table 3. Examples of Glove Sample Weight Change During Immersion Stage

<table>
<thead>
<tr>
<th>Glove</th>
<th>Solvent</th>
<th>Sample Weight (grams) at Immersion Times of</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Initial</td>
</tr>
<tr>
<td>Best</td>
<td>1-Butanol</td>
<td>0.3724</td>
</tr>
<tr>
<td>Best</td>
<td>Pyridine</td>
<td>0.3607</td>
</tr>
<tr>
<td>Best</td>
<td>Benzaldehyde</td>
<td>0.3613</td>
</tr>
<tr>
<td>Best</td>
<td>THF</td>
<td>0.3389</td>
</tr>
<tr>
<td>Guardian</td>
<td>n-Butyl Acetate</td>
<td>0.3267</td>
</tr>
<tr>
<td>Guardian</td>
<td>Benzaldehyde</td>
<td>0.3216</td>
</tr>
<tr>
<td>Guardian</td>
<td>Ethyl Acetate</td>
<td>0.3242</td>
</tr>
<tr>
<td>North</td>
<td>1,2-Dichloroethane</td>
<td>0.1817</td>
</tr>
<tr>
<td>North</td>
<td>Benzene</td>
<td>0.1856</td>
</tr>
<tr>
<td>Renco</td>
<td>Chloroform</td>
<td>0.4301</td>
</tr>
<tr>
<td>Renco</td>
<td>Cyclohexane</td>
<td>0.4242</td>
</tr>
</tbody>
</table>

shown in Table 4, the standard deviations for all the samples were insignificant, though there were some variations in sample thickness in each triplicate. Based on this observation, it could be concluded that sample thickness had an insignificant effect on weight gain and weight loss in the weight change tests given the extended immersion time. The benefit of extending the sample immersion period in the organic solvents is that it ensured consistent and reproducible measurement of weight changes, minimizing the influence from dynamic change of the sample weight and other interferences. Another benefit of the extended immersion is that it also ensured that the equilibrium was reached so that the weight gain data collected reflected the interaction between polymers and solvents more accurately. The table shows that the weight gain data of the glove samples from four vendors were comparable with each other; the nature of the interaction
between the chemical solvents and the polymer had a dominant effect on the weight gain results and solution behavior of the glove materials.

Weight loss was observed for most of solvent/glove material combinations. Listed in Table 5, the average weight losses were 0.130, 0.051, 0.033, and 0.031 for Best, Guardian, North, and Renco gloves, respectively. The maximum weight losses were 0.197, 0.089, 0.071, and 0.052, respectively. In order to eliminate the effect of additive and oligomer extraction as potential error source, determination of weight gains was based on the glove material masses after immersion and outgassing of solvents as shown in the previous calculation equation for weight gain. For Best Gloves the extraction effect was found to be tremendous while the samples from the other manufacturers showed moderate weight losses. Larger weight losses are expected to adversely affect the permeation performance for the sample from Best.

In the chemical protective glove industry, material degradation resistance and chemical resistance can be evaluated by performing weight change tests. In Table 6 the ratings of four butyl gloves are listed using a common rating system based on weight change. Although all the butyl gloves provided excellent degradation resistance against about 10 solvents, the gloves were not recommended for eight organic solvents. In general butyl gloves perform well against polar compounds, especially those containing strong hydrogen bonding interactions, but perform poorly against nonpolar organics and alkyl chlorides. This agrees quite well with the rule of “likes dissolve likes.”
The effects of the sample sources on the weight gains and weight losses were examined as well (See Table 7 and 8). The single-factor ANOVA test performed on all the weight gain data yielded an F-value of 0.0230, much less than the $F_{\text{crit}}$ of 2.699 (Alpha equal to 0.05). The p-value equaled 0.9953, which suggests that all the butyl gloves were similar to each other in terms of solution behavior. Such a high level of correlation on these weight gain data sets could be attributed to the major composition of butyl rubber in all the finished products (for example, North glove sample contains about 76% w/w of butyl rubber). The results of the ANOVA test performed on the weight loss data resulted in an F-value of 37.90, compared to the $F_{\text{crit}}$ of 2.699 (Alpha equal to 0.05), and the p-value of $3.02\times10^{-16}$. Even after the weight loss data from Best Gloves were excluded, the results of F-value, $F_{\text{crit}}$, and p-value were 7.725, 3.124, and 0.000914, respectively. The low correlation of the weight loss data is possibly due to the fact that different manufacturers might use quite different starting materials or add different amounts and types of additives, etc. Different recipes and different manufacturing procedures might result in different tolerances to organic solvents in terms of weight losses. In short, the single-factor ANOVA test results of the weight gain data demonstrated how similarly the glove samples perform in terms of overall solubility behavior, while the results of the weight loss data revealed how differently the glove samples resist solvent extraction and how different the glove samples are in terms of recipes and manufacturing processes. Certainly, the impact of weight loss on the permeation performance of glove materials against organic solvents could be expected to
Table 4. Fractional Weight Gain

<table>
<thead>
<tr>
<th>solvent</th>
<th>Best</th>
<th>SD</th>
<th>Guardian</th>
<th>SD</th>
<th>North</th>
<th>SD</th>
<th>Renco</th>
<th>SD</th>
<th>Literature</th>
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<tbody>
<tr>
<td>1,2-Dichloroethane</td>
<td>0.2969</td>
<td>0.0075</td>
<td>0.3280</td>
<td>0.0017</td>
<td>0.3403</td>
<td>0.0027</td>
<td>0.3579</td>
<td>0.0016</td>
<td>0.40</td>
</tr>
<tr>
<td>1,4-Dioxane</td>
<td>0.1482</td>
<td>0.0028</td>
<td>0.1498</td>
<td>0.0040</td>
<td>0.1402</td>
<td>0.0048</td>
<td>0.1534</td>
<td>0.0036</td>
<td>0.21</td>
</tr>
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<td>1-Butanol</td>
<td>0.0456</td>
<td>0.0004</td>
<td>0.0297</td>
<td>0.0016</td>
<td>0.0216</td>
<td>0.0023</td>
<td>0.0233</td>
<td>0.0008</td>
<td>0.01</td>
</tr>
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<td>2-Propanol</td>
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<td>0.0013</td>
<td>0.0180</td>
<td>0.0005</td>
<td>0.0164</td>
<td>0.0004</td>
<td>0.0159</td>
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<td>NA</td>
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<td>0.0401</td>
<td>1.0794</td>
<td>0.0263</td>
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<td>0.0080</td>
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</tr>
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<td>0.0011</td>
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<td>0.0023</td>
<td>0.1339</td>
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Table 5. Fractional Weight Loss

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<thead>
<tr>
<th>solvent</th>
<th>Best</th>
<th>SD</th>
<th>Guardian</th>
<th>SD</th>
<th>North</th>
<th>SD</th>
<th>Renco</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2-Dichloroethane</td>
<td>0.1703</td>
<td>0.0013</td>
<td>0.0534</td>
<td>0.0003</td>
<td>0.0271</td>
<td>0.0029</td>
<td>0.0284</td>
<td>0.0008</td>
</tr>
<tr>
<td>1,4-Dioxane</td>
<td>0.1485</td>
<td>0.0009</td>
<td>0.0208</td>
<td>0.0007</td>
<td>0.0116</td>
<td>0.0029</td>
<td>0.0138</td>
<td>0.0030</td>
</tr>
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<td>1-Butanol</td>
<td>0.0930</td>
<td>0.0018</td>
<td>0.0437</td>
<td>0.0026</td>
<td>0.0201</td>
<td>0.0022</td>
<td>0.0186</td>
<td>0.0010</td>
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<td>2-Propanol</td>
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<td>0.0352</td>
<td>0.0005</td>
<td>0.0181</td>
<td>0.0008</td>
<td>0.0173</td>
<td>0.0029</td>
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<td>0.0028</td>
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<td>0.0207</td>
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<td>Acetonitrile</td>
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<td>0.0011</td>
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<td>0.0164</td>
<td>0.0028</td>
<td>0.0177</td>
<td>0.0033</td>
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<tr>
<td>Benzaldehyde</td>
<td>0.1015</td>
<td>0.0024</td>
<td>0.0726</td>
<td>0.0138</td>
<td>-0.0042</td>
<td>0.0218</td>
<td>0.0236</td>
<td>0.0022</td>
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<tr>
<td>Benzene</td>
<td>0.1933</td>
<td>0.0016</td>
<td>0.0799</td>
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<td>0.0011</td>
<td>0.0518</td>
<td>0.0009</td>
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<td>CH2Cl2</td>
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<td>0.0744</td>
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<td>Chloroform</td>
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<td>0.0021</td>
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<td>Cyclohexane</td>
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<td>0.0025</td>
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<td>Cyclohexanone</td>
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<td>0.0023</td>
<td>0.0321</td>
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<td>0.0179</td>
<td>0.0015</td>
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<td>DMF</td>
<td>0.0379</td>
<td>0.0136</td>
<td>0.0195</td>
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<td>0.0209</td>
<td>0.0018</td>
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<tr>
<td>Ethanol</td>
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<td>0.0023</td>
<td>0.0102</td>
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<td>Ethyl Acetate</td>
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<td>0.0311</td>
<td>0.0014</td>
</tr>
<tr>
<td>Furfuraldehyde</td>
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<td>0.0099</td>
<td>0.0206</td>
<td>0.0004</td>
<td>0.0174</td>
<td>0.0020</td>
</tr>
<tr>
<td>MEK</td>
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<td>0.0006</td>
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<td>0.0241</td>
<td>0.0013</td>
<td>0.0288</td>
<td>0.0020</td>
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<tr>
<td>n-Butyl Acetate</td>
<td>0.1813</td>
<td>0.0017</td>
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<td>0.0004</td>
<td>0.0416</td>
<td>0.0027</td>
<td>0.0396</td>
<td>0.0001</td>
</tr>
<tr>
<td>O-Xylene</td>
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<td>0.0887</td>
<td>0.0242</td>
<td>0.0714</td>
<td>0.0077</td>
<td>0.0474</td>
<td>0.0013</td>
</tr>
<tr>
<td>Pentane</td>
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<td>0.0561</td>
<td>0.0013</td>
<td>0.0428</td>
<td>0.0021</td>
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<td>Pyridine</td>
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<td>0.0007</td>
<td>0.0523</td>
<td>0.0032</td>
<td>0.0300</td>
<td>0.0008</td>
<td>0.0325</td>
<td>0.0014</td>
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<td>THF</td>
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<td>0.0572</td>
<td>0.0001</td>
<td>0.0523</td>
<td>0.0223</td>
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<tr>
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<td>0.0611</td>
<td>0.0021</td>
<td>0.0472</td>
<td>0.0002</td>
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<tr>
<td><strong>Average</strong></td>
<td>0.1299</td>
<td></td>
<td>0.0513</td>
<td></td>
<td>0.0326</td>
<td></td>
<td>0.0310</td>
<td></td>
</tr>
<tr>
<td><strong>Minimum</strong></td>
<td>0.0000</td>
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<td>0.010</td>
<td></td>
</tr>
<tr>
<td><strong>Maximum</strong></td>
<td>0.197</td>
<td></td>
<td>0.089</td>
<td></td>
<td>0.071</td>
<td></td>
<td>0.052</td>
<td></td>
</tr>
</tbody>
</table>
Table 6. Performance Rating of Butyl Glove Based on Weight Gain

<table>
<thead>
<tr>
<th>Rating</th>
<th>Percent Weight Gain</th>
<th>Number of Solvents</th>
</tr>
</thead>
<tbody>
<tr>
<td>Excellent</td>
<td>0-10%</td>
<td>Best 10, Guardian 11, North 10, Renco 10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Good 4, Guardian 3, North 4, Renco 4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fair 3, Guardian 1, North 1, Renco 1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Poor 0, Guardian 2, North 2, Renco 2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Not Recommended 8, Guardian 8, North 8, Renco 8</td>
</tr>
</tbody>
</table>
Table 7. Single-Factor ANOVA Test for Weight Gain

ANOVA: Single Factor for Weight Gain

<table>
<thead>
<tr>
<th>Groups</th>
<th>Count</th>
<th>Sum</th>
<th>Average</th>
<th>Variance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Best</td>
<td>25</td>
<td>18.1989</td>
<td>0.727956</td>
<td>1.187102</td>
</tr>
<tr>
<td>Guardian</td>
<td>25</td>
<td>17.8907</td>
<td>0.715628</td>
<td>1.109383</td>
</tr>
<tr>
<td>North</td>
<td>25</td>
<td>19.8162</td>
<td>0.792648</td>
<td>1.442371</td>
</tr>
<tr>
<td>Renco</td>
<td>25</td>
<td>18.7269</td>
<td>0.749076</td>
<td>1.243658</td>
</tr>
</tbody>
</table>

ANOVA

<table>
<thead>
<tr>
<th>Source of Variation</th>
<th>SS</th>
<th>df</th>
<th>MS</th>
<th>F</th>
<th>P-value</th>
<th>F crit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Between Groups</td>
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<td>0.028609</td>
<td>0.022968</td>
<td>0.995254</td>
<td>2.699394</td>
</tr>
<tr>
<td>Within Groups</td>
<td>119.58033</td>
<td>96</td>
<td>0.001439</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>119.66616</td>
<td>99</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 8. Single-Factor ANOVA Test for Weight Loss

ANOVA: Single Factor for Weight Loss

<table>
<thead>
<tr>
<th>Groups</th>
<th>Count</th>
<th>Sum</th>
<th>Average</th>
<th>Variance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Best</td>
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<td>3.2473</td>
<td>0.129892</td>
<td>0.004495</td>
</tr>
<tr>
<td>Guardian</td>
<td>25</td>
<td>1.282246</td>
<td>0.05129</td>
<td>0.000622</td>
</tr>
<tr>
<td>North</td>
<td>25</td>
<td>0.81556</td>
<td>0.032622</td>
<td>0.00044</td>
</tr>
<tr>
<td>Renco</td>
<td>25</td>
<td>0.774969</td>
<td>0.030999</td>
<td>0.000201</td>
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</tbody>
</table>

ANOVA

<table>
<thead>
<tr>
<th>Source of Variation</th>
<th>SS</th>
<th>df</th>
<th>MS</th>
<th>F</th>
<th>P-value</th>
<th>F crit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Between Groups</td>
<td>0.1636399</td>
<td>3</td>
<td>0.054547</td>
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<td>2.699394</td>
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<tr>
<td>Within Groups</td>
<td>0.1381782</td>
<td>96</td>
<td>0.001439</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
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<td>99</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>
be dramatic. From the point of glove recipe development, it might be feasible to boost
glove chemical resistance performance by minimizing maximum weight loss of glove
materials.

3-DSP and Polymer-Solvent Interaction Parameters

Attempts have been made to establish a correlation of permeation data, such as
steady-state permeation rates and breakthrough times, with weight gains, 3-DSP
parameters, or solubility. Since the standard free energy change of mixing for a given
solvent/polymer systems can be expressed as the following:\textsuperscript{134, 142}

\[ \Delta G_s^R = RT \chi_p^2, \] (34)

it was strongly expected that \( \chi_p^2 \) might provide a good correlation with the mutual
solubility of polymers and solvents, the natural logarithm of steady-state permeation
rates and possibly other permeation data. Thus, the first step in this study was to obtain
\( \chi_p^2 \) and the Hansen 3-dimentional solubility parameters, using a similar approach that
Zellers and others used in their studies.\textsuperscript{9, 92}

From Equation (33), it can be seen there are two variables, \( A \) and \( \phi_p \). The value of
\( \phi_p \) could be derived from experimental weight gain data obtained at room temperature
according to the following equation:

\[ \phi_p = \frac{1/ \rho_p}{W_s / \rho_s + 1/ \rho_p} \] (35)

where \( W_s \) is fractional weight gain, \( \rho_p \) the densities of butyl glove materials in gram/cm\(^3\),
and \( \rho_s \) the densities of the organic solvents in gram/cm\(^3\). Since the 3-DSP values of all
the solvents tested are available in Table 2, the 3-DSPs for the butyl glove materials were determined by incorporating the fractional weight gain data along with the following variables: the density of each glove material, molecular weight, molar volume, and the 3-DSP parameters. Data Desk 6.0® (Ithaca, NY) was used to achieve the best fit of the model for weight gain data using a nonlinear least-square regression technique. There were differences in detailed regression approaches between Zellers’s approach and the current work. The major difference is that in Zellers’ regression approach, a slightly different equation was used to perform nonlinear regression which involved the determination of polymer crosslink densities, polymer volume fraction during crosslinking process and a deformation-related variable; weighing factor $a$ was assigned as 1 and $b$ was determined using multiple nonlinear regression in order to achieve the best fit; $\chi_s$ was set at 0 instead of the commonly used value of 0.34, the later of which was used in our model. It can be expected that this would lead to slightly different regression results.$^92$

In Figures 10 to 13, the plots of $ln(1-\phi_p)+\phi_p$ against $\chi\phi_p^2$ were obtained by using the weight gain data for the solvents/butyl glove samples from four vendors in this study after nonlinear least-square regression optimization. The plots represent the relationship between the solubility terms and the fractional weight gain data. The optimized results of $\delta_d$, $\delta_p$, and $\delta_h$ for the four butyl glove materials were listed in Table 9. The solubility terms and the fractional weight gain data exhibited an excellent fit with the correlation coefficients ranging from 0.858 to 0.961. The high correlation obtained in this study is
mainly attributed to the improve weight change test. In the literature, the weight change
tests typically lasted from hours to days, and the longest immersion period was reported
as 14 days. In this study, the immersion tests were performed for five to 10 weeks so
that the equilibrium of solvent absorption was achieved or close to being achieved by
extending the immersion period of the glove samples in the solvents. Since equilibrium
swelling was assumed in the theoretical context of this model, extended immersion was
necessary to ensure that equilibrium is achieved. In addition, since the extraction of
oligomers and additives in glove materials was evidenced from weight loss test and some
of the original sample was lost, calculating weight gain based on the glove material mass
after immersion and drying should eliminate possible error source. Among the solvents
tested, Ethanolamine appeared to be an outlier for all four glove materials due to
unknown cause, however, amines were reported difficult to be modeled well in many
attempts and it was suspected that amines may be self-associating in the relatively
nonpolar polymer matrices.

The obtained solubility parameters for the four samples are quite different
compared to that of pure butyl rubber ($\delta_d=16.47$, $\delta_p=0$, and $\delta_h=0$). The difference in
the obtained 3-DSP values (especially the $\delta_h$ values) compared with pure butyl rubber
could possibly be attributed to the theoretical expressions used in this study. In the
described model, assigning a value of 1 for weighing factor $a$ and 0.25 for $b$ could
potentially cause the obtained solubility parameters to vary to great extent. It could also
be attributed to large amounts of additives present in each individual sample and the
crosslinking of polymer chains in glove materials that might have significant influence on
Figure 10. Plot of $-\ln(1-\phi_p) + \phi_p$ against $\chi \phi_p^2$ for Best Glove, $R^2 = 0.961$
Figure 11. Plot of $ln(1-\phi_p) + \phi_p$ against $\chi^2\phi_p$ for Guardian Glove, $R^2 = 0.926$
Figure 12. Plot of $\ln(1-\phi_p) + \phi_p$ against $\chi \phi_p^2$ for North Glove, $R^2 = 0.858$
Figure 13. Plot of $\ln(1 - \phi_p) + \phi_p$ against $\chi \phi_p^2$ for Renco Glove, $R^2 = 0.935$
Figure 14. Plot of \(-\ln(1-\phi_p) + \phi_p\) against \(\chi \phi_p^2\) for All Gloves, \(R^2 = 0.903\)
Table 9. Results of Three-Dimensional Solubility Parameters and Correlation Coefficients

<table>
<thead>
<tr>
<th></th>
<th>Best</th>
<th>Guardian</th>
<th>North</th>
<th>Renco</th>
<th>All</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\delta_d)</td>
<td>18.13</td>
<td>18.51</td>
<td>19.40</td>
<td>18.62</td>
<td>18.74</td>
</tr>
<tr>
<td>(\delta_p)</td>
<td>2.71</td>
<td>4.60</td>
<td>1.83</td>
<td>1.64</td>
<td>2.71</td>
</tr>
<tr>
<td>(\delta_h)</td>
<td>7.55</td>
<td>6.68</td>
<td>6.48</td>
<td>5.88</td>
<td>6.70</td>
</tr>
<tr>
<td>(R^2)</td>
<td>0.961</td>
<td>0.926</td>
<td>0.858</td>
<td>0.935</td>
<td>0.903</td>
</tr>
</tbody>
</table>

polymer solution behavior in organic solvents. Since information regarding the glove recipe and manufacturing processing is not available, it remains unclear how these affected the 3-DSP determination of glove materials. The 3-DSP values for the North glove samples (with different thicknesses) reported by Zellers, using a similar nonlinear regression approach but with a shorter immersion period (five days), were 18.4 (\(\delta_d\)), -5.0 (\(\delta_p\)), and -0.8 (\(\delta_h\)). The negative \(\delta_p\) and \(\delta_h\) values could result from inadequate immersion time, the factor \(b\) determined as 0.16, and the arbitrary setting of \(\chi_s = 0\) in the nonlinear regression procedure. In addition, Zellers didn’t clarify whether the weight gain calculation was based on the initial sample weight. If the extraction of oligomers and additives from rubber materials during exposure was ignored, the resultant weight gain would be less accurate. Lastly, it should be mentioned again that high degree of
model fit indicated that the described nonlinear regression approach is still a more general, rigorous method to model solubility in order to derive the 3-DSP values based on the theoretical expressions without the need to determine the value of weighing factor \( b \). The accuracy achieved has been proved sufficient for many potential applications such as predicting the mutual solubility of solvents/polymers and the permeation properties of chemical protective gloves.

From the results of single-factor ANOVA test on the weight gain data from the four vendors, it was found that there was no significant difference among weight gain data for different groups of butyl gloves, and the four gloves exhibited similar solution behavior. Thus, it was necessary to examine the effectiveness of this model if all the butyl gloves were treated as generically the same butyl glove. Figure 14 shows the plots of \( \ln(1-\phi_p) + \phi_p \) against \( \chi \phi_p^2 \) and in Table 9 listed are the obtained \( \delta_d \), \( \delta_p \), and \( \delta_h \) when all the weight gain data were combined together. A high level of correlation of 0.903 implies similar solution behavior for all four glove materials. Presumably, butyl rubber, the major component in these glove materials, still plays a dominant role in determining the material solution properties. This made it possible to use \( \chi \phi_p^2 \) as a general predictor of the mutual solubility of solvents in butyl gloves regardless the sample sources.

In summary, the extended weight change test described in this work could be considered as improvement from traditional weight gain test, based on which more accurate and reliable determination of mutual solubility and 3-DSP values is possible. Correlating permeation properties of butyl glove material with solubility or solubility terms obtained in this study should offer certain advantage over the previous attempts.
Permeation Data Processing and Permeation Behavior

Permeation tests were performed on different solvent/butyl glove combinations using the test method and setup described previously. Compared to ASTM F739-96, The Permeation Resistance Test Method for Chemical Protective Clothing, the permeation experiment setup in this study was modified slightly in order to monitor GC response continuously throughout the test and have better control of the test temperature. In addition, a continuous solvent flow through the permeation cell allowed all the extracted ingredients to be flushed out. Since it was suggested that low permeation rates/long breakthrough times were highly desired to improve the fit of predictive models, the solvents selected in this study were intended to cover a wide range of $\chi\phi^2_p$. However, due to the sensitivity of the test method/system, it was found difficult and sometimes impossible to obtain permeation data experimentally for those solvents with $\chi\phi^2_p$ values greater than 1.5. For example, the permeation of ethanol was not detected over 48 hours. Acetone merely showed penetration through the samples from all the vendors except Renco, but the lag time for acetone/Guardian couldn’t be determined. Thus, a $\chi\phi^2_p$ value about 1.5 to 1.9 appeared to be the upper limit in a permeation experiment based on the test method/system in the current study.

Figure 15 to 18 show some examples of permeation plots (GC response versus time) for different combinations of solvents/polymers. In the literature, five typical permeation behaviors were reported; however, in this study, Type A was observed in most cases as shown in Figure 15 to 17, which represents a typical case that the glove
sample retained its physical integrity throughout the testing and steady-state permeation was established at the end. Only in a few cases was Type B observed, which was similar to Type A except that when an equilibrium was reached or about to be reached the GC response continued to increase or decrease slightly over time as shown in Figure 18. The Type B pattern is attributed to slight physical or chemical changes in the polymer materials in contact with solvents, which was evidenced by the swelling exposed areas of the glove samples at the end of the tests and weight losses in the weight change tests.

The most interesting permeation data are steady-state permeation rates (SSPR), breakthrough times (BT), and lag times (LT). The steady-state permeation rates were calculated by using the following equation:

$$SSPR = \frac{M \times F}{V \times A}$$ (36)

where SSPR is expressed in mg/m$^2$$\cdot$min, M refers to the mass of permeant in mg at steady-state, F is the flow rate of the collection medium through the permeation cells (mL/min), V is the volume of the sample loop (mL), and A is the sample exposure area (m$^2$). The molar permeation rate, defined as the moles (or millimoles) of a chemical that permeates through a glove sample and is expressed in mmol/m$^2$$\cdot$min, can be obtained by dividing the permeation rate by the molecular weight of the challenging solvent. It was suggested that using molar steady-state permeation rates might improve the correlation results using the predictive models. Therefore, molar steady-state permeation rates were also investigated in the current study. Both steady-state permeation rates and molar steady-state permeation rates are listed in Table 10.
Figure 15. North / Benzene Permeation Curve (Type A Permeation Behavior)
Figure 16. North / Cyclohexane Permeation Curve (Type A Permeation Behavior)
Figure 17. North / Tetrahydrofuran Permeation Curve (Type A Permeation Behavior)
Figure 18. Best / n-Butyl Acetate Permeation Curve (Type B Permeation Behavior)
Table 10. Permeation Test Results

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Best</th>
<th>Guardian</th>
<th>North</th>
<th>Renco</th>
<th>Literature&lt;sup&gt;155&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>142</td>
<td>1.74</td>
<td>16.6</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
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<td>6383</td>
<td>1799</td>
<td>1938</td>
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<td>Ethyl Acetate</td>
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<td>118.3</td>
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<td>THF</td>
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<td>84.28</td>
<td>57.46</td>
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</table>
As mentioned earlier, breakthrough time refers to the time it takes for a chemical to penetrate a barrier membrane until it is first detected on the opposite side following the initial contact of a chemical with a glove. It represents how quickly a chemical moves through a barrier film and represents the maximum length of time during which the glove could be worn without losing adequate protection. Since the determination of breakthrough times is strongly dependent on the sensitivity and detection limit of the test system and method, ASTM F 739 requires that a breakthrough time must be reported along with the analytical sensitivity. However, reporting of analytical sensitivity alone is still insufficient to allow proper interpretation of the test results. The analytical sensitivity of the detector may have little or no relevance to test method/system sensitivity, while the latter is defined by analytical sensitivity, the surface area of the clothing material sample, and the collection medium flow rate (for open-loop systems). Currently, ASTM F 739 and ASTM F 1383 specify reporting of the normalized breakthrough time in addition to actual breakthrough time, where normalized breakthrough time is defined as the time when the permeation rate is equal to 0.1 μg/cm²•min. Among the challenging solvents tested, acetone and ethyl acetate only showed low steady-state permeation rates (comparable to 0.1 μg/cm²•min). Thus, a more sensitive detection criterion for BT determination was required to allow accurate measurement of the breakthrough times for these solvents. In this work, the limit of detection was set as signal/noise ratio at 3 instead of using normalized breakthrough times. This was justified not only for low permeation rates but for high permeation rates as well since the difference of breakthrough times between using 0.1 μg/cm²•min and
signal/noise ratio of 3 was found generally smaller than 3% for those solvents with high permeation rates (>>0.1 \( \mu \text{g/cm}^2 \cdot \text{min} \)).

Shown in Figure 19 is the plot of permeation rate versus time for the benzene/North permeation test as an example of breakthrough time determination. Since dead volume existed between the points of the permeation cell and the detector on GC, an adjustment to the breakthrough time was made by subtracting a time offset of 0.25 min (\( \frac{\text{Dead Volume of 2.01 mL}}{\text{Flow Rate of 8.0 mL/min}} = 0.25 \text{ min} \)). Listed in Table 11 are the limits of detection for all the solvents tested based on the instrument setup and test conditions in this study.

Lag time is considered as another important permeation performance variable since it can be used to calculate the diffusion coefficient of a solvent/polymeric membrane system. In the previous chapter, the theoretical basis of calculating diffusion coefficients from lag times was discussed as shown in Equation (24), and it was found to be suitable when applied to rubbery polymers.\(^{154}\) Since the instrument setup in this study allowed continuous monitoring of GC response, the cumulative permeation curves were readily obtained. The determination of lag time is shown in Figure 20 by plotting cumulative permeation against time and extrapolating the linear portion of a cumulative permeation curve to where it intersects the x-axis (time). Adjustment due to dead volume similar to that made to breakthrough times was made to lag times.
Figure 19. Sample Determination of Breakthrough Time for North/Benzene
Figure 20. Permeation Curve and Cumulative Curve for North/Benzene
Table 11. Detection Limits

<table>
<thead>
<tr>
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<th>Detection Limit (mg/m²•min)</th>
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<td>0.0035</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.0016</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>0.0008</td>
</tr>
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<td>Ethyl Acetate</td>
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</tr>
<tr>
<td>n-Butyl Acetate</td>
<td>0.0035</td>
</tr>
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<td>Pentane</td>
<td>0.0044</td>
</tr>
<tr>
<td>THF</td>
<td>0.065</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.0040</td>
</tr>
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</table>

Modeling of Permeation Data

The permeation test results are listed in Table 10, together with the permeation rates and breakthrough times published in the literature for the butyl glove from North Safety Products. The results were reported as the averages of triplicate runs. Lag times are not readily available in the literature. By examining these data, the following can be observed:

- First, the permeation results from the literature were based on the same glove samples from North Safety Products with a thickness of 17 mil. The breakthrough times obtained in the current study were found to be shorter than those in the literature. The determination of breakthrough time is dependent on test methods and instrument setup, and the shorter BTs obtained are possibly due to the better sensitivity and detection limit of the test method/system in this
study. On the other hand, the steady-state permeation rates were found to be slightly greater than those in the literature.

- High variability in permeation data was observed among the glove samples from the four vendors in this study. As discussed in the review section, high variability was reportedly one of the major issues in permeation tests of chemical protective gloves. Given that all the permeation tests were performed under the same experimental conditions, solvents could penetrate one glove sample much faster than another glove sample with a magnitude of one order, in terms of SSPR, BT, or LT. Certainly, a direct comparison of these glove samples was not objective since the sample thicknesses were different, but it still indicated that the glove source is an important variable to consider when a sample is evaluated for its permeation performance.

- In general, non-polar or slightly polar solvents such as benzene, cyclohexane, and THF, for example, can permeate through the glove samples at much faster rates than polar chemicals. As a solvent containing strong hydrogen bonding interaction, ethanol, didn’t show permeation through any of the glove samples. The overall permeation results agreed with the weight gain tests: the higher the weight gains, the faster the steady-state permeation rates and the shorter the breakthrough times and lag times.

- The permeation performance seems related to the sample’s weight loss data. The SSPR values decreased in the following order of the Best, Guardian, and Renco glove samples (North was excluded due to its much thinner sample
thickness), while the breakthrough time increased. It is reasonable to assume that greater weight loss could create more free volume in the polymer material to facilitate solvent movement, thus resulting in a much bigger permeation rate and faster breakthrough time. In practice, weight loss information may serve as another good indicator of permeation performance for a specific glove material.

An initial attempt was made to correlate the permeation data against $\chi\phi_p^2$. The plots of $\chi\phi_p^2$ against the logarithm of the steady-state permeation rates are shown in Figure 21 to 24. The unit of the permeation rates used here was milligrams per square meter per minute. For all the glove samples from the four vendors, a high level of correlation between $\ln(\text{SSPR})$ and $\chi\phi_p^2$ was found with $R^2$ values in ranging from 0.8849 to 0.9894. Unlike many other correlation attempts reported, none of any factor was used in modeling. No obvious outlier was found, and there was no rejection of any data. The overall excellent correlation between the $\chi\phi_p^2$ and steady-state permeation rates could be attributed to the following facts:

- In this study, SSPR is possibly governed by the solubility terms of the solvents in the glove materials. Since the permeation coefficient is the product of the diffusion coefficient and the solubility coefficient, a wide range of $\chi\phi_p^2$ made solubility coefficient the more significant variable.

- From the plots, it can be observed that the leverage effect of the points of acetone and ethyl acetate was tremendous. As suggested by Bomburger\textsuperscript{35} and Henriksen,\textsuperscript{90} correlation could be improved if low permeation rates data were
available for modeling. Without such data, the correlation results would certainly have been worse.

- The improved weight gain test and nonlinear regression technique provided a more reliable measurement of 3-DSPs and the solubility term $\chi \phi_p^2$ with minimum overall variation for all the solvents tested in this work, making it possible to improve such a correlation based on solubility. Molecular weight and shape are known to affect diffusion rates. In this study, the tested solvent molecules have relatively close molecular weight and size, ranging from 58.08 to 116.16 amu and 63.9 to 132.5 mL/mole, respectively.

The conversion from SSPR to mol_SSPR was expected to improve the correlation as some researchers suggested; however, a slight deterioration was observed instead. Actually, the deterioration in correlating the molar steady-state permeation rates was observed also by other researchers in their studies, and was attributed to the nature of logarithmic fit and the narrow range of the molecular weights of the challenging solvents.$^9,10$ The real cause for the slightly worse correlation is still not clear. In fact, using mol_SSPR can be considered an attempt to normalize permeation rates by molecular weight, but the influence of the molecular weights on the permeation rates may not be so straightforward and can vary from different systems to systems of solvents/polymer materials. While the unit commonly used in permeation rates is $\mu g/cm^2 \cdot min$ or $mg/m^2 \cdot min$, the most suitable unit for characterizing permeation rates remains unclear in order to obtain best correlation results.
Figure 21. Plot of $\ln(\text{SSPR})$ versus $\chi\phi_p^2$, Best Glove, $R^2 = 0.885$

Figure 22. Plot of $\ln(\text{SSPR})$ versus $\chi\phi_p^2$, Guardian Glove, $R^2 = 0.989$
Figure 23. Plot of $\ln(\text{SSPR})$ versus $\chi_{p}^{2}$, North Glove, $R^2 = 0.982$

Figure 24. Plot of $\ln(\text{SSPR})$ versus $\chi_{p}^{2}$, Renco Glove, $R^2 = 0.973$
Figure 25. Plot of $\ln(\text{mol\_SSPR})$ versus $\chi\phi_p^2$, Best Glove, $R^2 = 0.861$

$$y = -2.795x + 4.590$$
$$R^2 = 0.861$$

Figure 26. Plot of $\ln(\text{mol\_SSPR})$ versus $\chi\phi_p^2$, Guardian Glove, $R^2 = 0.975$

$$y = -4.110x + 4.013$$
$$R^2 = 0.975$$
Figure 27. Plot of $\ln(\text{mol\_SSPR})$ versus $\chi_{\phi_p}^2$, North Glove, $R^2 = 0.961$

Figure 28. Plot of $\ln(\text{mol\_SSPR})$ versus $\chi_{\phi_p}^2$, Renco Glove, $R^2 = 0.949$
Figure 29. Plot of $\ln(BT)$ versus $\chi_{\phi^2}$, Best Glove, $R^2 = 0.707$

Figure 30. Plot of $\ln(BT)$ versus $\chi_{\phi^2}$, Guardian Glove, $R^2 = 0.864$
Figure 31. Plot of $\ln(BT)$ versus $\chi_\phi^2$, North Glove, $R^2 = 0.920$

Figure 32. Plot of $\ln(BT)$ versus $\chi_\phi^2$, Renco Glove, $R^2 = 0.812$
Figure 33. Plot of $\ln(LT)$ versus $\chi^p_\phi^2$, Best Glove, $R^2 = 0.770$

Figure 34. Plot of $\ln(LT)$ versus $\chi^p_\phi^2$, Guardian Glove, $R^2 = 0.722$
Figure 35. Plot of $\ln(LT)$ versus $\chi^2_{\phi}$, North Glove, $R^2 = 0.952$

Figure 36. Plot of $\ln(LT)$ versus $\chi^2_{\phi}$, Renco Glove, $R^2 = 0.821$
The correlation between $\chi \phi p^2$ and both breakthrough time and lag time were also investigated. The attempt to correlate breakthrough times or lag times with the solubility terms doesn’t mean there is a valid theoretical basis for such a correlation. It was rationalized that, if the solvent molecules have a similar molecular weight and shape, it is possible to correlate breakthrough times and lag times with barrier properties\textsuperscript{133}. Previously some researchers reported that there was a certain degree of correlation using their predictive models. Evans\textsuperscript{9} and He\textsuperscript{10} found a high degree of correlation between $\chi \phi p^2$ and breakthrough times or lag times for Viton® and nitrile gloves in their study. Listed in Table 12, the correlation results of breakthrough times versus $\chi \phi p^2$ were 0.707, 0.864, 0.920, and 0.812 for the Best, Guardian, North, and Renco glove samples in this study. Although other factors such as solvent viscosity, molecular weight and shape, and polymer swelling can affect the permeation process, the good results obtained did establish that solubility does play an important role in the overall permeation process, probably as a governing factor.

Lag time is considered an important permeation variable since it can be used to calculate the diffusion coefficients of solvents in most rubbery polymer systems\textsuperscript{154}. Since the instrument setup in this study allowed continuous monitoring of the GC response, the cumulative permeation curves were readily obtained and lag time was determined by extrapolating the linear portion of a cumulative permeation curve to where it intersects the time, x-axis. Figure 33 to 36 represents the correlation results of lag times versus...
Table 12. Correlation Results of Permeation Data Against $\chi^{2}_{\phi}$

<table>
<thead>
<tr>
<th></th>
<th>Best</th>
<th>Guardian</th>
<th>North</th>
<th>Renco</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\ln (SSPR)$</td>
<td>0.885</td>
<td>0.989</td>
<td>0.982</td>
<td>0.973</td>
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<tr>
<td>$\ln (SSPR*L)$</td>
<td>0.886</td>
<td>0.989</td>
<td>0.982</td>
<td>0.975</td>
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<tr>
<td>$\ln (\text{mol}_{SSPR})$</td>
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<td>0.975</td>
<td>0.961</td>
<td>0.949</td>
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<tr>
<td>$\ln (\text{mol}_{SSPR*L})$</td>
<td>0.864</td>
<td>0.976</td>
<td>0.961</td>
<td>0.953</td>
</tr>
<tr>
<td>$\ln (BT)$</td>
<td>0.707</td>
<td>0.864</td>
<td>0.920</td>
<td>0.812</td>
</tr>
<tr>
<td>$\ln (BT/L^2)$</td>
<td>0.771</td>
<td>0.865</td>
<td>0.918</td>
<td>0.845</td>
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<tr>
<td>$\ln (LT)$</td>
<td>0.770</td>
<td>0.722</td>
<td>0.952</td>
<td>0.821</td>
</tr>
<tr>
<td>$\ln (LT/L^2)$</td>
<td>0.815</td>
<td>0.717</td>
<td>0.949</td>
<td>0.854</td>
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</tbody>
</table>

$\chi^{2}_{\phi}$. The obtained $R^2$ values were 0.770, 0.722, 0.952, and 0.821 for Best, Guardian, North, and Renco.

The correlation results for the Best glove samples were worse than those for this sample’s peers. Reexamining the weight gain and permeation data, one should notice that, while the Best glove sample showed weight gain comparable to that from other vendors, greater steady-state permeation rates and shorter breakthrough times were generally observed. This could be partially attributed to the fact that the Best glove had the highest
weight losses, as previously discussed. On the other hand, six out of the eleven organic solvents selected against the Best glove sample in permeation tests have weight gains greater than 1 (high swelling), which corresponds to $\chi_p^2$ values less than 0.21. As discussed in the literature chapter, high swelling of a polymer and high weight loss are claimed as the major causes for deviation from the Fickian mode. It is possible that high swelling and high weight loss might also be less favorable to attempt any correlations.

The SSPR, breakthrough times, and lag times results from the North glove samples were excellent. One of the factors that led to the strong results was this sample’s low weight losses against most of the solvents tested here, which allowed the collected permeation data based on the North glove sample with relatively stable composition. In addition, the North glove samples were only 17 mil, the thinnest among the tested gloves. It was a reasonable assumption that the stable states of both the glove’s physical/chemical composition and permeation state could be established faster than the thicker samples during the tests. Furthermore, the thinner thickness made it possible to obtain accurate permeation data for solvents with low permeation rates such as acetone, which has the biggest $\chi_p^2$ among the tested challenging solvents.

Normalization of Thickness

In a previous section, a direct comparison of permeation data was made among the samples from the four vendors, and high variation was observed. One factor that contributed to such variations was sample thickness. According to the literature, thickness
does have a significant influence on the permeation performance of chemical protective gloves.\textsuperscript{124} For the butyl gloves from the four vendors, the claimed sample thicknesses were different, with Renco at 32 mil the thickest, Best at 30 mil, Guardian at 25 mil, and North at 17 mil, the thinnest. In fact, not only was a certain variation between the actual sample thickness found and the claimed thickness, but there was also noticeable thickness difference among the test samples from the same vendors. Thus, the normalization of permeation data based on sample thicknesses ought to be an effective approach to make a fair comparison and improve modeling of the permeation data.

According to some theoretical treatments in the literature,\textsuperscript{124,125} SSPR (and mol\_SSPR) is often found inversely proportional to the thickness (as shown in Equation 8), and lag time is related to the square of the thickness of the membrane (as shown in Equation 23). These relationships hold true only for Fickian diffusion; there is no relationship in theory for breakthrough times. It was reported that, for rubbery polymer/solvent systems, the transport of solvents usually follows either Fickian diffusion pattern or anomalies pattern at a temperature above the polymer’s glass transition temperature.\textsuperscript{100} Thus, the common empirical approach to normalize permeation data should be carried out carefully. Usually, the normalization procedure is to multiply or divide permeation data with sample thickness or the square of sample thickness as shown below:

\[
\begin{align*}
SSPR_{\text{normalized}} &= SSPR \times L, \\
BT_{\text{normalized}} &= \frac{BT}{L}, \\
LT_{\text{normalized}} &= \frac{LT}{L}, \\
SSPR_{\text{normalized}} &= SSPR \times L^2, \\
BT_{\text{normalized}} &= \frac{BT}{L^2}, \\
LT_{\text{normalized}} &= \frac{LT}{L^2}.
\end{align*}
\]
The first attempt was conducting thickness normalization within each group of butyl glove samples from the same vendors. Better correlation results were observed if the thickness normalization was based on $SSPR\times L$, $BT/L^2$, and $LT/L^2$ instead of $SSPR/L^2$, $BT/L$, and $LT/L$; the detailed results are listed in Table 12. $SSPR$ (and mol_$SSPR$) was found less sensitive to thickness variation, and, in all the four vendors’ samples, slight improvement or no improvement in correlation was found. Since the thickness variations were still in a narrow range within each set of sample groups and the correlation before normalization was already very high, these results are not considered strong evidence of the improvement from the thickness normalization. In terms of breakthrough time and lag time, noticeable improvement was generally found, and this indicates that both breakthrough time and lag time are sensitive to thickness variation. Furthermore, $SSPR\times L$ and $LT/L^2$ were found to be a more effective normalization approach, which suggested that Fickian diffusion took place more likely in most of the tested butyl glove/solvent systems.

Considering that the sample thicknesses the vendors claim ranged widely from 17 to 32 mil, it would be interesting to see the effectiveness of normalization based on thickness across the sample set groups. In fact, it should be a meaningful attempt to correlate all the permeation data of the four butyl gloves against their solvent-polymer interaction parameters. In Figure 37 to 44, the correlation results before and after thickness normalization are shown. The thicknesses used in normalization were the actual measurements of each individual test sample. Significant improvements were noticed in
Figure 37. Plot of $ln(\text{SSPR})$ versus $\chi^2_{p}$ for All Glove Samples, $R^2 = 0.835$
Figure 38. Plot of $\ln(\text{mol}_{\text{SSPR}})$ versus $\chi_p^2$ for All Glove Samples, $R^2 = 0.810$
Figure 39. Plot of $\ln(BT)$ versus $\chi^4 \phi_p^2$ for All Glove Samples, $R^2 = 0.617$
Figure 40. Plot of $\ln(\text{LT})$ versus $\chi^2_{\phi_p}$ for All Glove Samples, $R^2 = 0.677$
$y = -3.561x + 8.274$

$R^2 = 0.866$

Figure 41. Plot of $\ln(\text{SSPR}\times L)$ versus $\chi\phi_p^2$ for All Glove Samples After Thickness Normalization, $R^2 = 0.866$
Figure 42. Plot of $\ln(\text{mol}_{\text{SSPR}} \cdot \text{L})$ versus $\chi\phi_p^2$ for All Glove Samples After Thickness Normalization, $R^2 = 0.843$
Figure 43. Plot of $\ln(BT/L^2)$ versus $\chi^2_{\phi_p}$ for All Glove Samples After Thickness Normalization, $R^2 = 0.768$
Figure 44. Plot of $\ln(\frac{LT}{L^2})$ versus $\chi_{\phi}^2$ for All Glove Samples After Thickness Normalization, $R^2 = 0.841$
Figure 45. Plot of $\ln(\text{SSPR} \cdot L)$ versus $\chi^2$ for All Glove Samples Excluding Best Glove After Thickness Normalization, $R^2 = 0.937$
$y = -3.640x + 3.497$

$R^2 = 0.913$

Figure 46. Plot of $\ln(\text{mol\_SSPR\_L})$ versus $\chi\phi_p^2$ for All Glove Samples Excluding Best Glove After Thickness Normalization, $R^2 = 0.913$
Figure 47. Plot of $ln(BT/L^2)$ versus $\chi^\phi_p^2$ for All Glove Samples Excluding Best Glove After Thickness Normalization, $R^2 = 0.864$
Figure 48. Plot of $\ln(LT/L^2)$ versus $\chi^2_{\phi_p}$ for All Glove Samples Excluding Best Glove After Thickness Normalization, $R^2 = 0.887$
all the permeation data, especially BT and LT. Thus, $SSPR^*L$, $BT/L^2$, and $LT/L^2$ can be considered an effective approach of normalization due to the thickness discrepancy.

Given the undesirable high weight losses of the samples from Best, correlation of the permeation data from the Guardian, North, and Renco samples (excluding Best) was also conducted. As shown in Figure 45 to 48, the $R^2$ for SSPR, mol_SSPR, BT, and LT were 0.937, 0.913, 0.864, and 0.887, respectively. This is considered a successful correlation using this model for the permeation data of organic solvent against butyl gloves, which were from three different vendors and have a relatively wide range of sample thickness from 17 to 32 mil. With proper thickness normalization of permeation data in conjunction with a reasonable requirement on weight losses, this $\chi_\phi^2$-based model could demonstrate good predictive capacity of permeation properties for butyl gloves from various sources and serve as a good chemical resistance performance indicator.
CHAPTER V

SUMMARY

In this study, a predictive model based on solubility was extended to estimate the solubility parameters of butyl gloves and predict the permeation properties of organic solvents in butyl gloves. The Hansen three-dimensional solubility parameter theory and the Flory-Rehner solution theory were used as the basis of this model in this study. Butyl gloves from four different manufacturers were tested in this study in order to evaluate the model fit for butyl glove materials and determine the influence of glove source on the model fit.

The solubility of organic solvents in butyl gloves was determined by performing weight change tests, which consist of immersion and out-gassing stages. Since it was expected that the equilibrium solubility would improve the estimate of the solubility parameters of the butyl gloves, in this study the immersion stage was extended for up to 10 weeks until the weight of the soaked glove samples approached equilibrium. Weight loss was observed when the post-drying weight of the glove samples from the immersion stage was examined, indicating the extraction of oligomers and additives from the glove samples into solvents. Therefore, determination of weight gains should be based on the glove material mass after immersion and outgassing of solvent in order to eliminate the effect of additive and oligomer extraction as potential error source. The improved weight change tests were proven to offer a reproducible and reliable approach to obtain the
solubility, making it possible to improve the reliability of the predictive model. Single-factor ANOVA analysis on the weight gain data was performed, and it indicated that all the glove materials had a similar solution behavior due to the major content of butyl rubber; on the other hand, single-factor ANOVA analysis on weight loss results revealed a possible significant discrepancy in the glove recipes and processing techniques, which would affect the chemical resistance performance of the butyl gloves.

The solubility term $\chi_\phi^2$, as a measurement of the residual free energy change of mixing, was obtained by incorporating the solubility data of the organic solvents in the butyl gloves into a combined equation of the Hansen 3-DSP and Flory-Rehner solution expressions; a nonlinear least-square regression analysis technique was used to ensure overall minimum error of the polymer’s solubility parameters. A high level of correlations was found for all four butyl gloves. The obtained 3-DSPs of each butyl gloves varied with each other and pure butyl rubber to a certain degree, suggesting that different gloves might show slightly different performance levels against organic solvents. Nevertheless, this approach was proven applicable for estimating reliable and accurate solubility of butyl glove materials.

The permeation tests were performed using a variety of commonly used chemical solvents against all four butyl gloves on a modified open-loop permeation test system compared with ASTM F739-96, *The Permeation Resistance Test Method for Chemical Protective Clothing*. These solvents represented a wide range of function groups and polarities. An attempt was made to collect permeation data for the solvents with a wide range of $\chi_\phi^2$ values since it might improve the model fitness. However, it was still not
feasible experimentally for certain solvents due to the detection limits of the test system and method. In addition, a significant variability in permeation data due to glove source was observed, especially in breakthrough times and lag times.

Generally, the correlation of permeation data against $\chi \phi^2_p$ yielded good results. Steady-state permeation rates were found strongly correlated to $\chi \phi^2_p$ for all the butyl gloves from different vendors, suggesting a high dependency of steady-state permeation rates on $\chi \phi^2_p$. Good model fits were also observed for breakthrough times and lag times, indicating that solubility does play a role, probably a governing factor, in the overall permeation process. Normalization of the permeation data with sample thickness was conducted, and $SSPR \ast L$, $BT/L^2$, and $LT/L^2$ was found to be the proper normalization procedure. Although the improvement in correlation was not obvious within each sample group, significant improvement was observed when thickness normalization was performed on the combined permeation data of the tested butyl gloves from all four vendors. Furthermore, after excluding one set of permeation data from one brand of butyl gloves due to its much bigger weight loss, excellent modeling results were obtained.

In conclusion, the predictive model based on the Hansen three-dimensional solubility theory and the Flory-Rehner theory was successfully applied to butyl gloves. Based on this model and improved weight change tests, the three-dimensional solubility parameters were obtained with overall minimum error using a nonlinear regression approach. The solubility term $\chi \phi^2_p$ was found to be strongly correlated with permeation
properties such as steady-state permeation rates, breakthrough times, and lag times, and it could serve as a permeation performance indicator of CPC materials. With this model, only a single set of weighing factors is needed, and there is no requirement for determining the diffusion coefficient for a specific solvent-polymer system. With proper normalization based on sample thickness, this model should allow easy and reliable prediction of the permeation properties of butyl gloves.
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