Modeling Solubility Parameters and Permeation Data of Organic Solvents Versus Butyl Gloves from Four Manufacturers

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ABSTRACT: A model based on the combination of Hansen solubility parameter theory and Flory-Rehner polymer solution theory was used to determine the solubility parameters of butyl glove material provided by several different manufacturers using a nonlinear least-square regression. To evaluate the validity of this model, weight gain data were collected for 26 solvents versus butyl gloves from four different vendors. Good correlation was found with R^2 ranging from 0.858 to 0.961, which was attributed to extended weight gain testing and weight gain calculations based on glove sample weight after immersion and postdrying. Steady-state permeation rates (molar steady-state permeation rates), breakthrough times, and lag times for the butyl glove samples against solvents were determined and correlated to solvent-polymer interactive term $\chi\phi_p^2$. A high level of correlation was observed for all glove materials. Correlation was also made with permeation data collected from three of the four glove materials, and a high degree of correlation was found with R^2 ranging from 0.8644 to 0.9369 for steady-state permeation rates (molar steady-state permeation rates), breakthrough times, and lag times. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 3867–3877, 2008

Key words: barrier; chemical protective clothing; elastomers; butyl rubber; hansen solubility parameter

INTRODUCTION

Each year, nearly thirteen million people are exposed to a variety of hazardous chemicals in the workplace, with contact dermatitis being one of most common chemically induced occupational illness, accounting for $\sim$ 10–15% of all occupational illnesses with an estimated annual cost of at $1 billion, according to the National Institute of Occupational Safety and Health's NORA Dermal Exposure Research Program (DERP).[1] Various forms of chemical protective clothing (CPC) have become the most common means of protection against potential chemical hazards. The skin of the hands is routinely exposed to many liquid hazardous chemicals in the workplace. Gloves made of polymeric materials are one of the most common forms of chemical protective clothing used for protection from exposure during handling of chemicals.[2] However, no single polymeric material has been found to be impermeable to all chemicals.[3–5]

Proper selection of chemical protective clothing requires a good understanding of CPC chemical resistance properties in conjunction with assessing the risk of exposure in the selection process. The

material-based rating test methods for CPC usually include degradation, penetration resistance, and permeation resistance testing. Degradation testing is used to determine changes of a material's physical properties (often visual changes) as the result of chemical exposure, whereas the later two allow for the assessment for barrier qualities of a protective clothing material.[6] Investigation of the permeation process draws great interest because the mass transport of a chemical through a barrier membrane takes place on a molecular level and may not be visually noticeable.

To assist end users with proper CPC selection for a specific job function, CPC manufacturers often provide selection guides/charts along with performance data-breakthrough time and permeation rate. However, upon review of manufacturer provided data, direct comparisons are not easily made. Many efforts have been made to establish predictive models based on the chemical and physical properties of various solvents and polymeric materials.[7] These predictive models originated from both solution theory and diffusion theory. Since solubility plays a significant role in overall permeation process, one common approach is to correlate the mutual solubility of a solvent/polymer system with experimental permeation data such as steady-state permeation rate (SSPR) and breakthrough time.[8–12] A major advantage of this approach is that solubility parameters for

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commonly used solvents and many CPC polymers are readily available in literature, allowing convenient prediction of the mutual solubility and therefore the permeation properties for a various solvent/polymer combination.[13–15]

Previous studies have attempted to correlate solubility parameter differences of CPC polymers and solvents directly with experimental permeation data such as SSPR and BT.[8,16] However, Zellers,[9] observed that these correlations were poor and predictions of SSPR and BT were not always accurate, particularly when using the graphical approach for determination of the three-dimensional solubility parameters (3-DSPs) of polymers. Other approaches, such as molecular group-contribution calculations,[17] molecular simulation models,[18] and correlation based on viscosity measurements of polymer solutions,[19] are all mainly semiquantitative or qualitative and have not been applied to crosslinked polymers where quantitative estimates of solvent–polymer solubility are needed.

In a follow-up publication, Zellers,[20] described two methods for determining 3-DSPs for commercially available glove materials. In one method, the polymer's solubility parameters were determined from a weighted average of the 3-DSP's for a range of organic solvents. In the second method, the Flory interaction parameters for all solvent–polymer pairs were calculated by using a modified Flory-Rehner equation where the polymer 3-DSP values were extrapolated from multiple nonlinear regression. Although both of these methods provide reliable estimation of solubility, these approaches require adjustable weight factor(s). For the second approach, polymer specific constants were estimated, including polymer crosslink densities, polymer volume fraction during crosslinking process and a deformation-related variable. Lastly, diffusion coefficients need to be determined separately to estimate permeation performance for a given solvent/polymer system.

The goal of this study represents part of an ongoing effort to develop a universal solubility-based model that can be used to predict the permeation performance of organic solvents versus chemical protective gloves. In a previous publication,[21] this model was described and based on Hansen solubility theory and the polymer–solution theory of Flory and Rehner. Weight gain tests were experimentally obtained for a representative set of organic solvents for four different butyl glove materials. The model fit was initially evaluated for specific brands of butyl gloves. Permeation and solubility data was the combined into a single predictive model. This model does not require estimations of polymer molecular weight or the use of individual weighting factors for specific solvent–polymer combinations. In addition, not only is this model simpler and applicable to many glove materials, but it also does not require the determination of diffusion coefficients, and as previously reported it provides accurate prediction of permeation properties.

THEORETICAL BACKGROUND AND MODEL DESCRIPTION

Hildebrand's solution theory,[22] led to the introduction of cohesive energy density (CED) and solubility parameters, which are useful in predicting polymer–solute interactions. The solubility parameter, δ, is defined as the square root of CED, ΔE is the molar energy of vaporization, and V is the molar volume. Mathematically, this concept is expressed as follows:

$$\delta = \left(\frac{\Delta E}{V}\right)^{1/2} = \text{CED}^{1/2} \tag{1}$$

The CED of a liquid is a numerical value that indicates the energy of vaporization and is expressed as calories per cubic centimeter. It is a direct reflection of the degree of van der Waals forces holding the molecules of a liquid together. One basic assumption of solubility parameter theory is that there exists a correlation between the CED of pure substances and their mutual solubility.

The relative affinity of a polymer and solvent can be assessed using the Hansen's three-dimensional solubility parameters. Hansen expanded Hildebrand's theory by separating the total solubility parameter into three individual parameters dispersive, polar, and hydrogen bonding between the solute and solvent where d represents dispersion, p polar, h hydrogen bonding[23]:

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \tag{2}$$

It is assumed that all three parameters are mutually independent. The Hansen solubility parameter concept can be plotted in three-dimensional space and easily visualized. For a particular solute, its placement in three-dimensional space is based on its values of δ_d, δ_p, δ_h, and the spherical shape surrounding the point defines a ''radius of interaction'' for a solute. Thus, the interaction between the solute and a solvent can be expressed using the following equation:

$$A = [a(\delta_{d1} - \delta_{d2})^2 + b[(\delta_{p1} - \delta_{p2})^2 + (\delta_{h1} - \delta_{h2})^2]]^{1/2} \tag{3}$$

where 1 and 2 stands for the solute and solvent, respectively, and a, b are weighing factors. For polymers, the 3-DSP values are usually assigned based on correlations established between weight gain testing with solvents that have published 3-DSP values.

The weighing factor a for the dispersion parameter difference is commonly set at 4, and the factor b for polarity and hydrogen-bonding terms at 1 to ensure that all three terms are similarly weighed in the model since the dispersion parameter does not vary as widely as the other two terms.[8] It has been reported that better correlations were obtained if $a = 1$ and $b = 0.25$ where used.[11,24,25]

In many applications the A term in eq. (3) is directly used as a semiquantitative index of relative solubility.[8–10] Many attempts have been made to develop relationships between A and permeation data including SSPR and BT. Typically, as A increases, mutual solubility is expected to decrease, and permeation decreases. However, the corresponding correlations are often poor leading to inaccurate predictions of SSPR and BT since quantitative estimates of solubility are required for such predictions.[26]

One successful approach to estimate a polymer's 3-DSP for slightly crosslinked polymers is by combining Hansen three-dimensional solubility parameters and Flory-Rehner polymer solution theory and subsequently applying nonlinear regression. As described by the Flory-Rehner theory,[27] swelling equilibrium is reached for a solvent/polymer system when the chemical potential of the solvent inside the swollen polymer becomes equal to that of the outside phase. Assuming the polymer swells isotropically in the solvent at equilibrium, a modified version of the original Flory-Rehner solution theory is shown where ϕ_p is the volume fraction of polymer in the solvent/polymer system, χ is the Flory-Huggins polymer–solvent interaction parameter, V_m is the molar volume of solvent, ρ_p is the density of the polymer, and M_p is the apparent molar weight between the crosslinks of the polymer.

$$\ln(1 - \phi_p) + \phi_p + \chi\phi_p^2 + \frac{V_m\rho_p}{M_p}\left(\phi_p^{1/3} - \frac{\phi_p}{2}\right) = 0 \quad (4)$$

Because the typical molecular weight of butyl rubber before crosslinking is over 200,000,[28] eq. (4) can be further simplified to the following form by discarding the last term, which is insignificant:

$$\ln(1 - \phi_p) + \phi_p + \chi\phi_p^2 = 0 \quad (5)$$

The polymer–solvent interaction parameter, χ, 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 β) and enthalpic term as follows[29]:

$$\chi = \chi_S + \chi_H \quad (6)$$

and the enthalpic term χ_H can be expressed as follows:

$$\chi_H = \frac{V_m A}{RT} \quad (7)$$

Substituting eqs. (6) and (7) into (5) yields the following equation:

$$\left(\frac{V_m A}{RT} + \chi_s\right)\phi_p^2 = -[\ln(1 - \phi_p) + \phi_p] \quad (8)$$

where χ_s is a constant that is often set between 0.3 and 0.4,[30,31] although a value between 0 and 2.5 has been used, or it can be determined in regression process.[13]

Based on eq. (8), a minimum error solution for the Hansen D, P, and H values for polymers can be determined by nonlinear least-square regression approach using experimental weight gain data. Previous work demonstrated good correlation between Viton and Nitrile glove materials permeation data and $\chi\phi_p^2$.[21] The validity of this solubility-based predictive model will be determined for butyl glove material used in this study.

EXPERIMENT

Materials

Butyl rubber polymer, a copolymer of isobutene (97.5% to 99.5%) and isoprene (0.5% to 2.5%) by $AlCl_3$ initiated cationic polymerization (BF_3 or $TiCl_4$ is used in some processes), is widely used in chemistry protective clothing, inner tubes for tires, engine and auto-body mounts, electrical cable insulation, chemical tank liners, and other industries due to its excellent resistance to corrosive chemicals, vegetable oils, phosphate ester, and some ketones. Butyl rubber is also resistant to aging, moisture and ozone, with excellent flexing properties, tensile strength and tear resistance. For the application of nontacky products, the molecular weights of butyl rubber are at least 200,000.[28]

For the purposes of this study, unsupported, smooth-finish butyl gloves from four different manufacturers were investigated. The four vendors include the following: Best Glove Manufacturing (Glove B, Menlo, GA), Guardian Manufacturing (Glove G, Willard, OH), North Safety Products (Glove N, Cranston, RI), and Renco Corp. (Glove R, Manchester, MA). Manufacturer's specifications of the glove materials are listed in Table I. The densities of butyl glove were determined by displacement as specified in ASTM D792-91. The average density of butyl rubber material used in this study ranged from 1.07 to 1.16 g/cm^{3}.

TABLE I
Glove Materials Manufacturers Specifications

Vendor	Style	Thickness (mil)	Length (inch)	Size	Finish	Hand design
Glove B, Best manufacturing	878	30	14	XL	Smooth	Roll-cuff, Unlined
Glove G, Guardian manufacturing	CP-25	25	14	XL	Smooth	curved
Glove N, North safety products	B174	17	14	L	Smooth	NA
Glove R, Renco corporation	R324B	32	14	L	Smooth	NA

Twenty-six common organic solvents were chosen as the challenge solvents based on varying structure and functionality. Table II lists the physical properties of these solvents including the Hansen three-dimensional solubility parameters, molecular weight, and molar volume that were obtained from standard reference sources.[13,14,32,33] All the solvents were certified ACS reagent grade or higher purity obtained from Fisher Scientific (Pittsburgh, PA), Burdick and Jackson Laboratories, Inc (Muskegon, Michigan) or Sigma-Aldrich (Milwaukee, WI).

Weight gain and weight loss

Commercial butyl rubber glove may contain low molecular weight oligomers and various additives, many of which may be extracted when exposed to solvents. To account for any weight loss due solvent extraction weight gain and loss experiments were conducted in two stages: an immersion stage for obtaining the total weight gain of samples when saturation is reached in various solvents; and an outgassing stage for obtaining postdrying glove sample weights. During the first stage, circular samples with a diameter of 2.5 cm were cut from the flat sections (palm, back, or cuff) of gloves using a stainless steel punch. Visual examination of each glove was performed to eliminate material for any defects such as pinholes or other imperfections. After the initial sample weights were taken, the samples were immersed in 30 mL of solvent in glass bottles with PTFE faced PE-lined closures purchased from Fisher Scientific (Pittsburgh, PA). Sample weights were taken at weekly intervals. Each time samples were picked up and placed between multiple layers of Kimwipes® and a glass rod rolled over it to remove excess solvent on the sample surface. Samples were placed into pretarred screw cap weighing vials to prevent solvent evaporation during weighing. The samples were immediately returned to the original

TABLE II
Three-Dimensional Solubility Parameters, Molecular Weight Molar Volume of Organic Solvents

Solvent	MW (g/mole)	mol. vol. (cm^3/mole)	D (MPa)$^{1/2}$	P (MPa)$^{1/2}$	H (MPa)$^{1/2}$
1,2-Dicholoroethane	98.96	79.4	19.0	7.4	4.1
1,4-Dioxane	88.11	85.7	19.0	1.8	7.4
1-Butanol	74.12	91.5	16.0	5.7	15.8
2-Propanol	60.1	92.0	15.8	5.7	14.5
Acetone	58.08	74.0	15.5	10.4	7.0
Acetonitrile	41.05	52.6	15.3	18.0	6.1
Benzaldehyde	106.12	101.5	19.4	7.4	5.3
Benzene	78.11	89.4	18.4	0.0	2.0
CH$_2$Cl$_2$	84.93	63.9	18.2	6.3	6.1
Chloroform	119.38	80.7	17.8	3.1	5.7
Cyclohexane	84.16	108.7	16.8	0.0	0.2
Cyclohexanone	98.14	104.0	17.8	6.3	5.1
Dimethyl Sulfide	78.13	71.3	18.4	16.4	10.2
DMF	73.09	77.0	17.4	13.7	11.3
Ethanol	46.07	58.5	15.8	8.8	19.4
Ethanolamine	61.08	60.2	17.2	15.5	21.3
Ethyl Acetate	88.1	98.5	15.8	5.3	7.2
Furfuraldehyde	96.09	83.2	18.6	14.9	5.1
MEK	72.11	90.1	16.0	9.0	5.1
n-Butyl Acetate	116.16	132.5	15.8	3.7	6.3
o-Xylene	106.16	121.2	17.8	1.0	3.1
Pentane	72.15	116.2	14.5	0.0	0.0
Pyridine	79.1	80.9	19.0	8.8	5.9
THF	72.11	81.7	16.8	5.7	8.0
Toluene	92.14	106.8	18.0	1.4	2.0

TABLE III
Percent Weight Gain Results for 4 Butyl Rubber Glove Materials[a]

Solvent	Best	SD	Guardian	SD	North	SD	Renco	SD	Literature[20]
1,2-Dicholoroethane	29.7	0.75	32.8	0.17	34.0	0.27	35.79	0.16	40
1,4-Dioxane	14.8	0.28	14.98	0.4	14.0	0.48	15.34	0.36	21
1-Butanol	4.6	0.04	2.97	0.16	2.2	0.23	2.33	0.08	1
2-Propanol	3.2	0.13	1.8	0.05	1.6	0.04	1.59	0.3	NA
Acetone	7.3	0.23	4.37	0.11	4.4	0.19	4.65	0.06	6
Acetonitrile	1.5	0.09	1.05	0.11	0.35	0.25	1.3	0.27	2
Benzaldehyde	12.8	0.92	7.91	0.05	11.4	1.78	12.68	0.2	15
Benzene	119.6	2.18	118.45	2.34	119.3	0.49	121.66	1.98	125
CH_2Cl_2	112.7	0.26	118.34	2.95	117.2	1.07	122.57	0.84	114
Chloroform	410.9	2.9	391.57	11.85	431.3	4.04	419.78	6.34	372
Cyclohexane	294.3	5.92	279.69	7.4	314.7	3.75	292.81	3.1	290
Cyclohexanone	23.7	0.31	24.14	2.06	25.3	0.33	26.54	0.21	31
Dimethyl Sulfide	2.3	0.39	3.33	0.54	1.8	0.38	1.42	0.37	NA
DMF	5.5	1.57	5.21	0.35	2.6	0.31	2.26	0.23	3
Ethanol	2.4	0.04	1.15	0.24	0.57	0.17	1.4	0.33	1
Ethanolamine	2.5	0.42	2.72	0.51	4.9	0.6	2.66	0.31	NA
Ethyl Acetate	12.44	0.06	13.11	0.12	13.4	0.16	14.29	0.29	16
Furfuraldehyde	4.04	0.26	6.24	0.71	3.4	0.21	3.08	0.3	NA
MEK	9.82	0.16	13.61	0.83	9.1	0.13	10.14	0.86	12
n-Butyl Acetate	29.67	0.26	32.8	0.17	33.9	0.18	35.76	0.17	NA
o-Xylene	234.1	4.39	14.98	0.4	291.4	4.23	242.98	5.79	247
Pentane	112.2	2.97	2.97	0.16	107.9	2.63	109.6	0.8	NA
Pyridine	11.98	0.11	1.8	0.05	12.9	0.23	13.39	0.17	NA
THF	168.9	2.35	4.37	0.11	211.7	0.79	193.13	14.36	196
Toluene	189.1	4.59	1.05	0.11	212.3	2.11	185.54	1.42	197

[a] SD, standard deviation based on three measurements.

bottles after weighing. The weighing procedure for each sample was performed less than 1 min. The weight gain stage of the study was carried out for at least four weeks and up to ten weeks. When the weight gain changes were less than 1% for three consecutive weeks, further weight measurements were discontinued. Typically, most samples took one to three weeks to reach maximum weight gain with a few exceptions where solvent absorption took longer to reach equilibrium. Once maximum weight gain was reached, samples were subjected to solvent out-gassing. Diethyl ether was eliminated as a test solvent since it was not possible to obtain an accurate weight measurement.

During solvent out-gassing stage, samples were removed from the solvents and transferred to glass weighing bottles, which were then placed into an electrically controlled oven set at 80°C. For the first set of samples tested, the Best glove samples were dried at 40°C and sample weights were measured every three days. Average outgassing for most samples took 12 days. Since cured butyl rubber remains fairly stable below 100°C, the drying temperature was then raised to 80°C for the remaining sets of samples. At 24-h interval the samples were removed from the oven, allowed to stabilize to room temperature, weighed, and placed back into the oven until the weight changes were less than 1%.

Fractional sample weight gain was calculated at immersion equilibrium relative to the final out-gassed weight whereas weight loss was calculated from the original sample weight minus out-gassed sample weight. The equations are shown below:

$$\text{Weight Gain} = \frac{W_t - W_1}{W_1} \qquad (9)$$

$$\text{Weight Loss} = \frac{W_0 - W_1}{W_0} \qquad (10)$$

where W_0, W_1, and W_t represent initial sample weight, after out-gassing, and sample weight at the elapsed time of immersion. The results of weight gain and weight loss for all glove/solvent exposures are listed in Tables III and IV as weight percent. No sample degradation was observed in any of the glove materials. The standard deviation of weight gain and weight loss for all testing (in triplicate) was not significant.

Permeation test design

Permeation data were collected for a set of solvents with a wide range of Hansen 3-DSP values using a previously described testing procedure, a modification of the widely used and accepted ASTM F739-

TABLE IV
Percent Weight Loss of Four Glove Materials

Solvent	Best	SD	Guardian	SD	North	SD	Renco	SD
1,2-Dicholoroethane	17.0	0.13	5.3	0.03	2.7	0.29	2.8	0.08
1,4-Dioxane	14.9	0.09	2.1	0.07	1.2	0.29	1.4	0.3
1-Butanol	9.3	0.18	4.4	0.26	2.0	0.22	1.9	0.1
2-Propanol	8.3	0.49	3.5	0.05	1.8	0.08	1.7	0.29
Acetone	10.8	0.28	3.9	0.09	2.1	0.09	2.0	0.14
Acetonitrile	1.8	0.11	1.9	0.19	1.6	0.28	1.8	0.33
Benzaldehyde	10.2	0.24	7.3	1.38	−0.4	2.18	2.4	0.22
Benzene	19.3	0.16	8.0	0.12	5.8	0.11	5.2	0.09
CH_2Cl_2	18.7	0.23	7.4	0.28	5.8	0.02	5.0	0.19
Chloroform	18.7	0.07	8.0	0.28	5.7	0.09	5.1	0.21
Cyclohexane	18.7	0.21	7.9	0.29	5.8	0.15	4.7	0.25
Cyclohexanone	17.1	0.13	5.7	0.28	3.3	0.23	3.2	0.09
Dimethyl Sulfide	1.5	0.07	1.4	0.18	1.8	0.15	1.6	0.27
DMF	3.8	1.36	2.0	0.06	2.1	0.18	1.8	0.19
Ethanol	6.4	0.17	3.1	0.23	1.7	0.18	2.0	0.3
Ethanolamine	0	0.32	3.2	0.22	0.1	0.23	1.0	0.43
Ethyl Acetate	16.4	0.14	4.5	1.59	2.4	0.03	3.1	0.14
Furfuraldehyde	3.9	0.11	1.4	0.99	2.1	0.04	1.7	0.2
MEK	16.3	0.06	3.1	0.36	2.4	0.13	2.9	0.2
n-Butyl Acetate	18.1	0.17	7.0	0.04	4.2	0.27	4.0	0.01
o-Xylene	19.0	0.09	8.9	2.42	7.1	0.77	4.7	0.13
Pentane	18.5	0.22	6.9	0.14	5.6	0.13	4.3	0.21
Pyridine	17.5	0.07	5.2	0.32	3.0	0.08	3.3	0.14
THF	19.7	0.14	8.6	0.82	5.7	0.01	5.2	2.23
Toluene	19	0.18	7.8	0.09	6.1	0.21	4.7	0.02
Average	13.0		5.1		3.3		3.1	
Minimum	0.000		1.3		−0.4		1.0	
Maximum	19.7		8.9		7.1		5.2	

SD, standard deviation based on three measurements.

99a for testing of chemical protective clothing.[34,35] The instrument setup incorporated modifications in flow control and temperature as recommended by several authors.[36,37] Open loop configuration was the only configuration used in this study where the collection medium (helium) was passed through the collection side of the permeation test cell to a detection system (GC-FID). During the course of the analysis, continuous flushing of any and all solvent plus extractables first penetrate and subsequently emerge from the other side of the glove membrane during the entire exposure period.

Permeation testing was performed using a Hewlett–Packard 5890 series II Gas Chromatography equipped with a flame ionization detector. A Macintosh computer (Model: 5400/200; Operating System: 9.1) installed with GC WorkMate 2 software (Willstein Software, Wilmette, IL) was connected to the GC system for data acquisition and processing, system control and monitoring. The GC column used was a SPB-5 capillary column, 30 m, 0.53 mm ID, 1.5-μm film thickness (Supelco, Inc., Bellefonte, PA). The flow rates of the carrier gas through 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 250-μL gas-sampling loop (Valco Instrument Co., Inc., Houston, TX) was used for monitoring GC response continuously and for sampling quantitatively.

The permeation cell and all fittings were constructed of 316 stainless steel. Each cell half had an opening with 0.65 cm in diameter, resulting in a 0.33 cm^2 exposure area. A controlled flow of solvent enters the top half of the cell, contacts the outer surface of the membrane, and exits for collection. The collecting medium Helium (flow B) entered the lower half of the cell, contacted the exposed inner surface of the membrane, and exited the cell, where it then entered a sampling valve (Valco, Houston TX) and a gas sampling loop. A flow rate of 0.7 ∼ 0.8 and 7.5 mL/min was used for the solvent and collecting medium, He, respectively.

Test samples were cut from the palm, back or cuff portion of glove (flat surface) using a circular stainless steel cutter. After visual examination and five thickness measurements with a micrometer a sample was mounted between the two cell halves, which was then placed horizontally into a temperature-control device maintained at a constant temperature of 25°C throughout the test.[35] During permeation

TABLE V
Butyl Rubber Experimentally Determined Three-Dimensional Solubility Parameters, χ_s and Correlation Coefficients

	Glove B	Glove G	Glove N	Glove R RencoRenco	Literature[20]
δ_d	18.13	18.51	19.40	18.62	18.4
δ_p	2.71	4.60	1.83	1.64	−5.0
δ_h	7.55	6.68	6.48	5.88	−0.8
χ_s	1.23	1.48	1.34	1.22	0
R^2	0.961	0.926	0.852	0.935	**0.910**

experiments, solvent flows over the surface of sample and carrier gas picks up the solvent penetrating to the other side of the sample film transferring to GC column. The GC response was continuously recorded until a stable permeation state was reached, the sampling loop was purged and the amount of the solvent in the carrier gas was quantified with external standards. The collected permeation data includes: SSPR, BT, and lag time (LT), all of which are extrapolated from the experimental setup. If no breakthrough time (BT) was observed after 24-h period elapsed, it was reported as Not Detected (ND); if BT was detected, SSPR was monitored for a up to 72 h or until stable state permeation was established.

Data analysis

The Hansen solubility parameters D, P, and H (3-DSP) for butyl glove materials were determined from a nonlinear least-squares regression fit of eq. (8), where the term A is defined in eq. (3). Polymer fractional volumes, ϕ_p, were calculated from the experimental weight gains and polymer density. The polymer densities for each of the glove materials and 3-DSP values of the solvent are listed in Table II. A commercially available interactive data analysis program, Data Desk 6.0 (Data Description, Ithaca, NY), was used to obtain the best fit of 3-DSP values. Once the values of D, P, and H were determined, the correlation between $\chi\phi_p^2$ and permeation data steady state permeation rate (SSPR), breakthrough time (BT), and lag time (t_l) was evaluated for all four butyl glove materials.

RESULTS AND DISCUSSION

Glove manufacturers may use different starting materials, manufacturing techniques, additives. Consequently, the 3-DSP values of the butyl glove materials and the chemical resistance typically differ from each other as listed in Table V. Figure 1 is a representative fit of the data, shown as Glove B by

employing eq. (8) and solvent weight gain data, with a correlation of $R^2 = 0.961$. The solubility terms $\chi\phi_p^2$ and the fractional volume term $[\ln(1-\phi_p) + \phi_p]$ exhibited excellent correlation for all four butyl gloves with R^2 ranging from 0.858 to 0.961. Ethanolamine appeared to be an outlier for all glove materials as it may self-associate forming intermolecular hydrogen bonding in the relatively nonpolar polymer matrices, such as butyl rubber.[20] The solubility parameters for the four different butyl rubber gloves tested are listed in Table V, previously reported values for butyl rubber include ($\delta_d = 16.47$, $\delta_p = 0$, and $\delta_h = 0$).[38] Slightly larger positive δ_p, δ_h, and δ_d values may be a result of additives present in the four glove materials; however, since information regarding butyl glove formulation and manufacturing is not available, it remains unclear how it affected the determination of 3-DSP values for each glove material tested. As a comparison, the 3-DSP values for the North glove samples with a different nominal thickness of 16 mil reported by Zellers using a similar nonlinear regression approach but with a shorter immersion period (five days) were 18.4 (δ_d), −5.0 (δ_p), and −0.8 (δ_h).[20] The negative δ_p and δ_h values may be the result of an inadequate immersion time, the determined factor b as 0.16, and the arbitrary setting of $\chi_s = 0$ in the nonlinear regression procedure. In addition, it wasn't clarified whether the weight gain calculation was based on the initial sample weight or postdrying sample weight. If the extraction of oligomers and additives from rubber materials during exposure were ignored, the resultant weight gain may be less accurate.
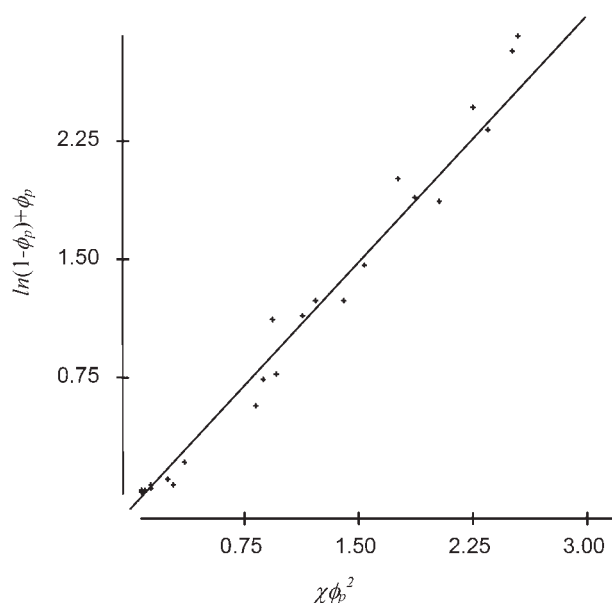

Figure 1 Plot of $\ln(1-\phi_p) + \phi_p$ versus $\chi\phi_p^2$ for Best Glove, $R^2 = 0.961$.

It is more reliable for the purposes of modeling the solubility and for the determination of the 3-DSP values based on the theoretical expressions without using weight factors such as b. As demonstrated in previous work,[21] and in this study, the described nonlinear regression-based approach applied offers more rigorous and effective method to determine 3-DSPs, and allows it possible to predict the solubility of a solvent/polymer system reliably.

Previous attempts have been made to establish a correlation of permeation data, such as SSPRs and breakthrough times, with weight gains, 3-DSP parameters, or other solubility terms. Since the standard free energy change of mixing for a given solvent/polymer systems can be expressed as the following:[14,39]

$$\Delta G_s^R = RT\chi\phi_p^2 \qquad (11)$$

the term, $\chi\phi_p^2$ might provide good correlation with the mutual solubility of polymers/solvents and the natural logarithm of SSPRs, etc.

An initial attempt was made to correlate permeation data obtained in this study against $\chi\phi_p^2$ within each individual glove source. The unit of the permeation rates used was mg/m^2 min. Experimental permeation test data, SSPR, BT, and LT was combined with permeation data (where available) found in the literature,[40,41] for all four glove materials and are listed in Table VI. Several solvents degraded the butyl glove material depending on the manufacturer versus the following solvents: dichloromethane, cyclohexanone, pentane, and toluene all of which are listed as not available (NA). For all the glove samples provided by four vendors, a high level of correlation between ln(SSPR) and $\chi\phi_p^2$ was found with R^2 values ranging from −0.8849 to −0.9894. Figure 2 shows a linear regression fit $\chi\phi_p^2$ and the natural logarithm of normalized SSPR (combined) for the four glove materials in this study, with a correlation of $R^2 = -0.9369$.

This is a significant improvement over earlier work.[42] Unlike many other correlation attempts reported, no arbitrary factor was used in modeling. No outliers were found, and all data was kept for modeling purposes. Overall excellent correlation between the $\chi\phi_p^2$ values and SSPRs could be attributed to improved weight gain/loss tests and nonlinear regression provided a more reliable measurement of three-dimensional solubility parameters of butyl glove materials. Improved correlation was also attributed to the fact that effort was made to collect BT up to 24 h and permeation test was carried out for as long as 72 h so that longer breakthrough-times were incorporated and lower permeation rate data available for modeling as suggested by Bomburger,[43]

and Henriksen.[44] Molar SSPR (nSSPR) versus SSPR was thought to improve the correlation; however, butyl glove material showed no significant improvement. Lack of correlation might be explained by the fact that molar SSPRs versus the natural logarithm of the challenge solvents' molecular weights, in general have molecular weight values very closely related.

The correlation between $\chi\phi_p^2$ to both breakthrough time and lag time were also investigated. An 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. Hansen rationalized that, if the solvent molecule have a similar molecular weight and shape, it is possible to correlate breakthrough times and lag times with barrier properties.[15] Some researchers reported that there was a certain degree of correlation using their predictive models.[8,9,26] Hardy et al. found a high degree of correlation between $\chi\phi_p^2$ and breakthrough times or lag times for Viton®.[21] Given that the challenge solvents have a narrow range of molecular weight and size ranging from 58.08 to 116.16 amu and 63.9 to 132.5 cm^3/mol, respectively, certain degree of correlation can be expected. The determination of breakthrough time in this study was based on a detection limit with signal/noise ratio of 3, and the BTs were normalized to 0.1 μg/cm^2 min as specified in ASTM F 739-99a and ASTM F 1383. This in turn allowed for accurate measurement of breakthrough times for the challenging solvents with very low SSPR such as acetone, ethyl acetate, and n-butyl acetate (comparable to 0.1 μg/cm^2 min). For solvents with high permeation rates (greater than 0.1 μg/cm^2 min) the difference of breakthrough times obtained using the two different criteria was generally smaller than 3%. Good correlation of breakthrough times and $\chi\phi_p^2$ were observed with values of 0.7067, 0.8636, 0.9197, and 0.8120 for Glove B, Glove G, Glove N, and Glove R butyl rubber glove samples, respectively. Shown in Figure 3 is the Linear regression fit $\chi\phi_p^2$ and the natural logarithm of normalized BT for all four glove materials with a correlation of. $R^2 = 0.8644$. This is in comparison to 0.55 reported by Perkins.[42]

Lag time is considered as an important permeation variable since it can be used to calculate the diffusion coefficients of solvents in most rubbery polymer systems.[45] Since the instrument setup in this study allowed continuous monitoring of 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. The correlation results of lag times versus $\chi\phi_p^2$ were 0.7703, 0.7220, 0.9520, and 0.8212 for Glove B, Glove G, Glove N, and Glove R. Figure 4 shows the Linear regression

TABLE VI
Permeation Test Results

Solvent	Glove B	Glove G	Glove N	Glove R	Literature[46,47]
SSPR (mg/m² min)[a]					
Acetone	142	1.74	16.6	ND	**ND,** *15 (0.42 mm)*
Benzene	3500	2985	6383	1799	**1938**
Dichloromethane	6310	NA[a]	NA	NA	**ND,** *6960 (0.40 mm)*
Cyclohexane	9712	3594	8932	2294	**1218**
Cyclohexanone	3048	NA	NA	NA	**ND,** *33 (0.45 mm)*
Ethanol	ND	ND	ND	ND	**ND**
Ethyl acetate	192	45.1	360	26.1	**204,** *204 (0.45 mm)*
Butyl acetate	776	302	986	212	**456.6,** *620 (0.38 mm)*
Pentane	8167	4507	NA	NA	Not tested
Tetrahydrofuran	5893	4002	11644	3893	**6720**
Toluene	7766	5294	NA	NA	**30,660,** *20,200 (0.49 mm)*
nSSPR (mmol/m² min)[a]					
Acetone	2.45	0.030	0.286	ND	
Benzene	44.81	38.22	81.71	23.03	
Dichloromethane	74.29	NA	NA	NA	
Cyclohexane	115.4	42.70	106.1	27.26	
Cyclohexanone	31.06	NA	NA	NA	
Ethanol	ND	ND	ND	ND	
Ethyl acetate	2.18	0.512	4.09	0.296	
Butyl acetate	6.68	2.60	8.49	1.83	
Pentane	113.2	62.47	NA	NA	
Tetrahydrofuran	81.72	55.49	161.48	53.99	
Toluene	84.28	57.46			
BT (min)					
Acetone	287.7	1400.0	409.3	ND	**>480,** *367 (0.42 mm)*
Benzene	30.9	36.6	12.6	77.0	**31,** *20 (0.43 mm)*
Dichloromethane	15.0	NA	NA	NA	**24,** *10 (0.40 mm)*
Cyclohexane	56.4	63.5	17.5	108.7	**50**
Cyclohexanone	60.9	NA	NA	NA	**>960,** *842 (0.45 mm)*
Ethanol	ND	ND	ND	ND	**>480**
Ethyl acetate	131.8	315.0	118.3	647.5	**456,** *455 (0.45 mm)*
Butyl acetate	110.4	217.3	74.0	486.5	**114,** *82 (0.38 mm)*
Pentane	9.2	13.8	NA	NA	Not tested
Tetrahydrofuran	27.6	36.1	9.4	60.7	**27**
Toluene	26.8	30.1	NA	NA	**6,** *17 (0.49 mm)*
LT (min)					
Acetone	957.7	ND	1282.5	ND	
Benzene	41.9	47.3	16.7	100.5	
Dichloromethane	31.5	NA	NA	NA	
Cyclohexane	147.0	87.2	24.3	154.1	
Cyclohexanone	155.8	NA	NA	NA	
Ethanol	ND	ND	ND	ND	
Ethyl acetate	362.2	409.2	379.0	893.9	
Butyl acetate	147.9	268.9	94.9	615.5	
Pentane	24.0	19.1	NA	NA	
Tetrahydrofuran	59.3	48.1	12.4	82.0	
Toluene	62.0	44.3	NA	NA	

Resistance Guide from North Safety Products (value in bold),[46] Forsberg (values in italics).[47]
[a] NA, not available, sample degraded.

fit $\chi\phi_p^2$ and the natural logarithm of normalized LT for all four glove materials with a correlation of R^2 = 0.8868. Lag time values and correlation results are not readily available in literature for butyl glove material.

An attempt was also made to combine all the permeation data together for the samples from Glove G, Glove N, and Glove R and correlate with its individual values of $\chi\phi_p^2$. Glove B sample data was excluded due to its much greater fractional weight losses (13.0% average weight loss versus 5.1%, 3.3% and 3.1% for Glove G, Glove N and Glove R respectively). Permeation data were normalized based on actual thickness of each individual glove sample since the sample thickness was significantly different, with Glove R at 32 mil, Glove G at 25 mil, and North at 17 mil. SSPR (and nSSPR) is often found to be inversely proportional to the thickness and lag
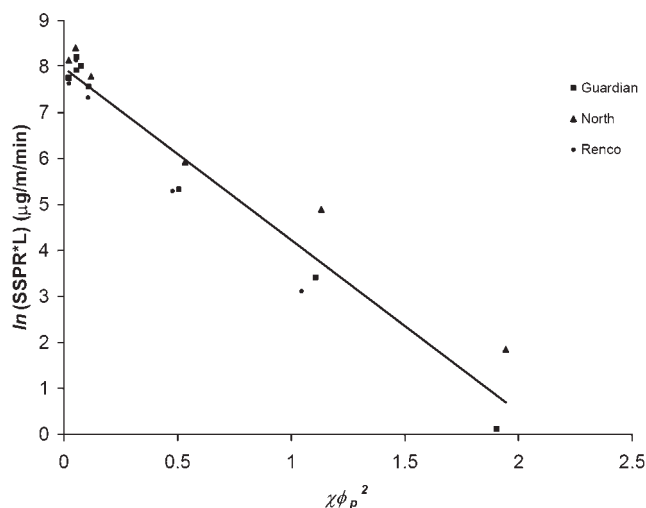
Figure 2 Linear regression fit $\chi\phi_p^2$ and the natural logarithm of normalized SSPR for all four glove materials. $R^2 = -0.9369$.

Figure 4 Linear regression fit $\chi\phi_p^2$ and the natural logarithm of normalized LT for all four glove materials. $R^2 = 0.8868$.

time is related to the square of the thickness, while breakthrough time doesn't have established relationship with sample thickness.[46,47] As shown in Figures 2–4, improved correlations were observed if the thickness normalization was based on SSPR*L, BT/L^2, and LT/L^2 instead of SSPR*L^2, BT/L, and LT/L. Successful correlation was reported using this model for the permeation data of organic solvent against butyl gloves material from three different vendors having a wide range of sample thickness 17–32 mil. With proper thickness normalization of permeation data in conjunction with accounting for weight loss, the $\chi\phi_p^2$ Flory-Rehner based model demonstrated good prediction of permeation properties for butyl gloves from various manufacturers and may serve as
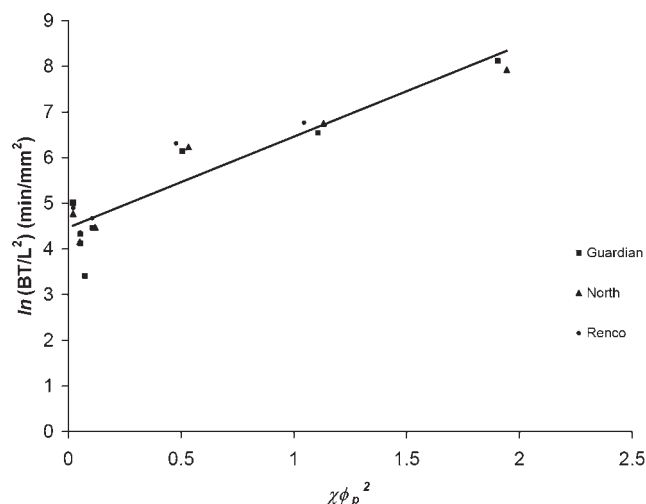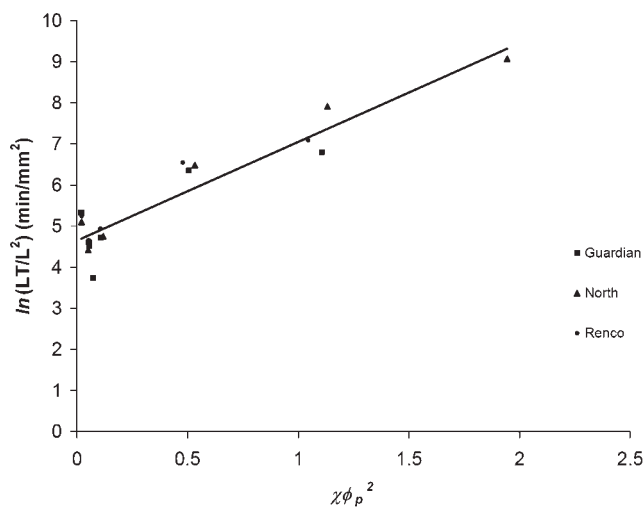
a good chemical resistance performance indicator as compared to what the various manufacturer and published literature provides.

CONCLUSIONS

In this study, an improved nonlinear regression method based on the combination of the Hansen three-dimensional solubility 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 weight factors are required, resulting in a more robust model. An improved weight gain testing procedure is incorporated and proved to be critical to the development of this model. The collected weight gain data showed that it usually takes one to three weeks to reach equilibrium swelling, in some cases, up to five weeks. 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 sample was evidenced during weight gain test, determining weight gain based on the postdrying sample weights should eliminate any possible error source.

The solubility term $\chi\phi_p^2$, a measurement of the standard free energy change of mixing, was found as a good predictor of the permeation properties of butyl glove materials. Strong correlation between SSPRs and $\chi\phi_p^2$ was observed for all four glove materials, and there is no requirement for determining the diffusion coefficient for a specific solvent–polymer system. There also exists a certain degree of

Figure 3 Linear regression fit $\chi\phi_p^2$ and the natural logarithm of normalized BT for all four glove materials. $R^2 = 0.8644$.

correlation for other permeation properties such as breakthrough times and lag times. With proper normalization based on sample thickness, this model should allow reliable prediction of the permeation properties of butyl gloves and future studies will include other commonly used glove material such as nitrile.

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