

Polymer Properties Associated with Chemical Permeation Performance of Disposable Nitrile Rubber Gloves

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ABSTRACT: Unlike other chemical protective clothing and devices, disposable gloves are not reliably certified to exceed chemical permeation performance standards. In light of generalized chemical compatibility charts, significant variability in performance exists between similar products on the market. This study evaluates whether nitrile rubber composition and uniformity are better associated with the observed product variability in chemical resistance than the available mechanical testing (e.g., tensile strength) done on these products. The independent variables evaluated include two physical, three mechanical, and four compositional parameters. Based on correlation and multiple regression analyses, the factors associated with variation in permeation of ethanol are area density, acrylonitrile content, carboxylation of the base polymer, the amount of extractable oils and oily plasticizers, and polymer uniformity. Increases in area density, acrylonitrile content, and carboxylation improve chemical resistance. Decreases in extractable oils and polymer variability (uniformity) also improve chemical resistance. On average, these combined factors accounted for about 53–67% of the observed variability in permeation, which were moderate but not strong associations. In contrast, tensile strength accounted for about 1% of the observed variability, a negligible effect. These results support the notion that standardized tests and certification criteria need to address polymer composition and uniformity to reduce gaps in performance. However, in light of the lack of strong correlations, further evaluation with tighter control over chemical composition is warranted. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41449.

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INTRODUCTION

Chemical protective clothing (CPC) do not have the same level of certification and workplace protection factors that have been established for respiratory protection devices.¹ These important criteria are missing in most cases and detailed permeation data are often not available, which complicates the selection process. This is especially true for disposable nitrile rubber, or nitrile butadiene rubber (NBR) gloves, which show broad variability in chemical resistance performance between brands and even different lots or batches.^{2,3} Although, the products undergo similar quality control and production testing, those common standardized tests do not adequately predict chemical resistance performance. This further limits the use of chemical compatibility charts and guides in the selection of a suitable polymer material for worker protection.

Determination of those factors affecting chemical resistance will aid in the development of improved materials performance, improved standardized tests, and future certification of disposable gloves. This would improve the protection provided to workers using disposable gloves as a barrier against chemical hazards, and also improve consumer confidence.

Studies have indicated that product variability, acrylonitrile content and area density account for a significant portion of variation with NBR gloves.^{3–5} To determine those factors most associated with performance, additional research is needed to assess the influence of glove composition, such as polymer content, oil/plasticizer content, and inorganic filler content, on chemical permeation.

The purpose of this study was to evaluate whether polymer composition and uniformity properties are better associated with the observed product variability in chemical resistance performance, namely the breakthrough time (BT) and steady-state permeation rate (SSPR). Thirty-seven commercially available disposable NBR glove products were evaluated. In addition, representative samples of general duty, medical grade, low-modulus, and cleanroom

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gloves were included to ensure full coverage of existing product variability. Although these classifications were not directly evaluated, they represent a general indication of polymer formulation modification designed to meet a specific customer need. Permeation testing with ethanol, as a surrogate, was conducted using a previously designed whole-glove permeation testing system.⁶ Various polymer properties were evaluated, including tensile strength, modulus, organic polymer content, inorganic residue content, acrylonitrile ($-C \equiv N$) content, carboxyl (-COOH) content, and polymer uniformity.

This study was designed to address the following questions:

- 1. Are available tensile strength tests sufficient predictors of chemical permeation performance for disposable NBR gloves?
- 2. Are composition and uniformity better predictors of chemical permeation performance for disposable NBR glove products?

The main hypothesis of this study was that variation in chemical permeation was better correlated with glove composition and uniformity than the available measures of polymer mechanical or tensile properties, such as American Society of Testing and Materials (ASTM) Method D 412 and Method D 3187.7,8 The findings and conclusions supported the main hypothesis, and polymer composition and uniformity were better correlated with chemical permeation than tensile strength and related properties. The main factors associated with the observed variation in chemical permeation were area density (physical), acrylonitrile content (compositional), carboxylation of the base polymer (compositional), the amount of extractable oils and oily plasticizers (compositional), and polymer uniformity. However, it must be noted that the correlations were moderate, with the models accounting for only about 53-67% of the variation. By comparison, this was much better than the 1% of variability accounted for by tensile strength. Nevertheless, as these tests were done with available products on the market, further controlled research experiments are recommended to include additional factors that may also play a significant role in the permeation process (e.g., cross-linking density and porosity). This research represents a first step toward reducing product variation, eventual product certifications, and increasing consumer confidence.

EXPERIMENTAL

Gloves

Thirty-seven disposable NBR glove products were tested. A broad spectrum of glove brands and formulations was represented, which included gloves classified as general duty, low-modulus (e.g., soft formulations), medical grade, and cleanroom (i.e., controlled environment). Gloves were medium size with a reported or measured palm thickness of 0.1 to 0.15 mm (4 to 6 mil) on average. Thickness measurements were performed using a previously described method.⁵ Table I summarizes the glove manufacturer, brand, and thickness information.

Permeation Testing

Whole-glove permeation testing was conducted using a previously described system that can also evaluate simulated movement.⁶ Movement was not evaluated in this study. Permeation was per-

formed within a Boekel Model 1340 environmental chamber (Fisher Scientific, Pittsburgh, PA), with chamber dimensions of 29.2 cm \times 25.4 cm \times 30.5 cm. A datalogging MiniRae2000 Photoionization Detector (PID) (Rae Systems, San Jose, CA) with 10.6 eV lamp and internal pump (0.50 ± 0.01 L min⁻¹) was used to collect air concentrations within the chamber, within a closed-loop. Permeation testing was performed with ethanol (Fisher Scientific A407P, Pittsburgh, PA), as a surrogate chemical well suited for permeation testing with NBR, latex and vinyl gloves.⁹

Ambient temperature $(21.4^{\circ}C \pm 1.0^{\circ}C)$ and relative humidity (RH) $(35\% \pm 15\%)$ were recorded during testing. Temperature had a significant effect ($P \le 0.05$) on permeation results. Neither RH nor glove thickness had a significant effect (P > 0.05) on permeation. The multiple regression analyses that follow were all controlled for the temperature variable.

Permeation data were collected for 30 min or until a BT and SSPR could be determined. A longer permeation run was only necessary for glove 3. The datalogger recorded average chamber concentrations at 30 s intervals. The BT, in units of minutes, was determined using a previously described method,⁶ as the first significant increase of 0.4 μg cm⁻² where subsequent readings continued to increase. The SSPR, in units of $\mu g \text{ cm}^{-2}$ min⁻¹, was the slope of the linear portion of permeation curve. At least 10 sequential readings, at 30 s intervals, and a Pearson correlation coefficient criterion of $r \ge 0.95$ ($P \le 0.05$) were used to define the SSPR, the linear, steady-state portion of the permeation curve (Figure 1). Most *r* values were > 0.99 (P < 0.05). Figure 1 illustrates a model permeation curve, from the test data for one permeation run. In addition, an estimation of the area under the curve at 30 min (AUC-30), in min μg^{-1} cm⁻², was used to evaluate the combined effects of BT and SSPR on potential worker exposure. The AUC-30 provides added value in the selection of CPC, as it provides an estimate of potential cumulative worker exposure over time. Calculation and justification of the AUC-30 is provided in a previous study.⁶

Area Density

Area density (AD), a mass-to-area ratio in g cm⁻², was used as an effective measure of density that also takes into account polymer thickness. Area density was more normally distributed and has been shown to correlate well with permeation data.⁵ Area density was determined using a previous method.⁵

Tensile Testing

Tensile strength, in units of MPa, and percent elongation at break tests were conducted using ASTM Method D 412 Standardized Test Methods for Vulcanized Rubber and Thermoplastic Elastomers—Tension.⁷ Tensile testing was conducted using an Admet eXpert 7601 tensiometer with 1 KN vice grips, in accordance with a previously defined method evaluating bidirectional properties.¹⁰ In addition, from the tensile test data, the modulus at 50–100% elongation, hereby termed modulus 50–100%, and the maximum modulus were calculated for each sample. Modulus is the slope of the stress-to-strain curve used in tensile testing. It is a measure of stress (in MPa) versus strain (percent elongation). In a previous study evaluating polymer integrity,¹⁰ maximum modulus was an improved indicator of polymer performance over tensile strength. Additionally, the



Table I. Glove Brand and Thickness

Glove ID	Manufacturer/brand	Average glove thickness (mm \pm SD)	Number of permeation tests performed ^a
1	Ammex Xtreme TM X3	0.08±0.02	20
2	Ansell Micro-Touch [®] NitraFree [™]	0.103 ± 0.006	20
3	Ansell Nitrilite®	0.11 ± 0.01	13
4	Ansell Touch N Tuff [®]	0.109 ± 0.007	24
5	Best [®] Clean-Dex [®]	0.15 ± 0.03	24
6	Best® N-Dex® 6005 (Lot 1)	0.123 ± 0.007	18
7	Best® N-Dex® Free	0.12 ± 0.01	17
8	Cardinal Health Esteem [®] Tru-Blu [™] Stretchy	0.11 ± 0.01	18
9	Fisherbrand [®] Nitrile	0.098 ± 0.009	18
10	Henry Schein Criterion®	0.083 ± 0.009	24
11	High Five [®] Cobalt [®]	0.10 ± 0.01	18
12	High Five [®] Onyx TM	0.12 ± 0.01	24
13	High Five [®] Softwear [™]	0.10 ± 0.02	20
14	Kimberly Clark Kimtech G5	0.090 ± 0.006	24
15	Kimberly Clark KleenGuard G10	0.11 ± 0.02	18
16	Medline Sensicare®	0.09 ± 0.02	18
17	Microflex [®] CE4 System	0.14 ± 0.03	24
18	Microflex [®] Midknight TM	0.11 ± 0.01	18
19	Microflex [®] Supreno [®] SE	0.13 ± 0.01	20
20	Microflex [®] Ultrasense TM	0.095 ± 0.009	18
21	North [®] Chem Soft CE [™]	0.12 ± 0.02	24
22	North® Dexi-Task	0.10 ± 0.02	24
23	Omar Nitrile	0.11 ± 0.02	18
24	PIP Ambi-dex TM	0.11 ± 0.01	18
25	Prima Pro Gentle Guard	0.11 ± 0.01	30
26	QRP [®] Q095 Qualatrile [™] XC	0.12 ± 0.01	45
27	QRP [®] Qualatrile [™] Blue 5	0.11 ± 0.02	24
28	Safety Choice Nitrile	0.11 ± 0.02	20
29	Sempermed [®] SemperSure TM	0.088 ± 0.005	15
30	Tillotson [™] True Advantage [™]	0.096 ± 0.008	18
31	Ansell TNT [®] Blue	0.11 ± 0.01	20
32	Aurelia® Robust®	0.13 ± 0.01	18
33	Best [®] Ultimate N-Dex [®]	0.14 ± 0.01	20
34	Best® Nitri-Care®	0.10 ± 0.01	18
35		0.13 ± 0.01	32
36	Best® N-Dex® 6005 (Lot 2)	0.11 ± 0.01	18
37	Western Safety (Black)	0.12 ± 0.01	17

^aThe number of permeation tests performed was based on the observed variability in permeation parameters during testing and for use in a separate study evaluating the influence of movement on permeation. The sample sizes were adjusted to detect a 10% change in permeation parameters upon exposure to movement, using a Student t test. The large sample sizes were not necessary for this study but the data are included as they serve to reduce variability and improve regression models.

modulus 50–100% represents conditions more closely related to normal use,¹⁰ whereas tensile strength, maximum modulus, and elongation at break are measures associated with conditions near or at complete material failure. All four measures were evaluated to determine which factor was most associated with chemical permeation performance.

Compositional Analysis

Analysis of the polymer composition was performed using a Model Q500 Thermogravimetric Analyzer (TGA) (TA Instruments, New Castle, DE). The samples were first extracted with acetone (Certified ACS grade, Fisher Scientific, Pittsburgh, PA) to remove non-polymer additives, such as oils and oily



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plasticizers,¹¹ which were not easily separated from the main polymer by TGA. Although, a small fraction of non-organic residuals would potentially be removed, the polymers were complex, variable blends and preliminary optimization tests indicated that pre-extraction was necessary to separate organic polymer content from non-polymer additives. The end result was separation of the material into three categories: acetone extraction, inorganic residue and organic polymer content. Serial extractions with 10-mL portions of acetone were carried out in capped glass vials within an ultrasonic bath at $38^{\circ}C \pm 2^{\circ}C$ for at least 1 h. With each extraction, the acetone was removed and the sample dried in a fume hood for at least 5 h and then dried in a vacuum desiccator overnight. The samples were then weighed with an analytical balance. Serial extractions were carried out until no further weight loss was observed. Six extractions were carried out for each sample. The acetone extraction was reported as a percent by weight. The remaining sample was analyzed by TGA using an optimized stepwise isothermal program with temperature isothermal if weight loss exceeded 1% min⁻¹ and ramped if weight loss fell below 0.05% min⁻¹. The program parameters were:

- Ultra High Purity Nitrogen (Airgas, San Bernardino, CA) atmosphere
 - Ramp 20° C min⁻¹ to 650° C
 - Cool 20° C min⁻¹ to 600° C
- Switch to Zero Air (Airgas, San Bernardino, CA) atmosphere
 - Ramp 20°C min-1 to 650°C
 - Isothermal 5 min

Each glove product was analyzed in triplicate. The resulting percent-by-weight data were calculated for each sample:

- 1. Acetone extraction
- 2. Organic polymer content, as weight loss occurring between 290 and $650^{\circ}C$
- 3. Inorganic residue

Infrared Analysis

Infrared analysis of the relative amount of acrylonitrile $(-C \equiv N)$ and carboxylation (-COOH) was performed using a Thermo Nicolet Model 380 FTIR (Thermo Scientific, West Palm Beach, FL). Samples from the palm region were positioned flat and vertically using a cardboard sample support. Triplicate samples were analyzed at a resolution of 4 cm^{-1} and with 32 scans. Relative acrylonitrile content was measured as the peak absorbance (Abs) at 2237 ± 2 cm⁻¹, which is selective for acrylonitrile.¹² Acrylonitrile is a main component of NBR rubber, also known as acrylonitrile-butadiene rubber or NBR, and has been shown to correlate well with chemical resistance.⁵ Relative carboxyl content was measured as the peak absorbance at 1770 ± 2 cm⁻¹, the -C=O stretch.¹³ Carboxylated NBR is known to maintain tensile strength and enhance chemical resistance to oils and solvents.^{14,15} Peak absorbance was evaluated in this study as a comparative measure of these two components. Based on the findings of this study, future work using known formulations and/or reference standards would be effective,



especially with the use of attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy.^{5,16}

Polymer Uniformity

Polymer uniformity was characterized using a previously described and published ATR-FTIR spectroscopy method.^{5,16} ATR-FTIR characterization of polymer uniformity was conducted at 2237 ± 2 cm⁻¹, with 4 cm⁻¹ resolution and 32 scans. Using a stratified, random sampling strategy, 10 samples from the finger (n = 3), knuckle (n = 3), palm (n = 3), and thumb (n = 1) regions were cut from three different glove samples. The sample surfaces were cleaned with ethanol soaked swabs to remove surface residues, dried, and conditioned for 24 h in a constant humidity chamber at $51\% \pm 4\%$ RH and $21.1^{\circ}C \pm 0.5^{\circ}C$. Infrared spectra were collected for both the outer and inner surfaces of the glove samples. Based on previous studies,^{5,16} the manufacturer's specifications for the ZnSe crystal, and the estimated material compression during testing, the estimated depth of penetration using this method was about 25%. A coefficient of variation (CV) was calculated for all measurements combined (n = 60). The CV, in units of percent, was used as an indicator of polymer uniformity.

Statistical Analyses

Sample sizes (Table I), ranging from 13 to 60, were adjusted for product variability to ensure at least a 10% change in BT or SSPR could be determined statistically in a separate research study evaluating whole-glove movement, which was not evaluated in this study. Correlation and multiple regression analyses were performed using Stata versions 11 and 12 (StataCorp, College Station, TX) and IBM SPSS Statistics 19 (IBM, Armonk, NY). Analyses were deemed statistically significant if the *p* value was <0.05. Histograms, Shapiro-Wilks, Shapiro-Francia, skewness, and kurtosis normality tests indicated near normal distributions with a potential outlier in glove 3. The average BT for glove 3 was more than double that of any other glove product and the SSPR was much lower than other products. Thus, a Spearman's correlation analysis was run to control for this effect. In additional all correlations and multiple regressions were run with and without glove 3 to determine if it influenced the analyses (e.g., significantly changed R^2 values). A significant influence was not observed with glove 3, indicating that it was not an outlier and that the data fit into the correlation and regression models. Glove 3 was included in all reported analyses.



The three dependent variables evaluated in this study were BT (min), SSPR ($\mu g \text{ cm}^{-2} \text{ min}^{-1}$) and AUC-30 (min $\mu g^{-1} \text{ cm}^{-2}$). The independent variables evaluated were:

1.	AD	(g	cm ⁻	⁻²)
1 .	1112	15	CIII	

- 2. Tensile strength (MPa)
- 3. Modulus 50-100% (MPa)
- 4. Maximum modulus (MPa)
- 5. Acetone extraction (%)
- 6. Organic polymer content (%)
- 7. Relative acrylonitrile content (Abs)
- 8. Relative carboxyl content (Abs)
- 9. Total CV (%)

RESULTS AND DISCUSSION

Permeation Tests (Dependent Variables)

The permeation data are presented in Table II. Considerable product variation was observed with all three permeation parameters: BT, SSPR and AUC-30. Average BT values ranged from about 7 to 47 min, a sevenfold difference. Average SSPR values ranged from about 3 to 25 μ g cm⁻² min⁻¹, an eightfold difference. Lastly, average AUC-30 values ranged from about 120 to 4900 min μg^{-1} cm⁻², a 40-fold difference, when excluding glove 3. These results are consistent with previous NBR glove permeation studies, showing similar BT and SSPR variability between NBR glove products and brands.^{2,3,5,17} Mickelson and Hall observed up to 10-fold differences in the BT of perchloroethylene through thicker chemically resistant NBR gloves from different suppliers.² Perkins and Pool reported up to twofold differences between batch lots in the permeation of 2-ethoxyethanol acetate through thicker chemically-resistant NBR gloves.³ Up to fourfold differences in the cumulative mass permeated at 125 min, related to BT and SSPR,⁶ were also observed between different glove brands. Forsberg and Keith's compendium of permeation and degradation data for chemical protective clothing show large variations in BT and SSPR between different brands for similar materials.¹⁷ Other studies with similar disposable NBR gloves have found up to a 10-fold difference in normalized BT and 200-fold difference in SSPR between brands.⁵ The need to investigate and understand those factors associated with this variability is justified by these results. Thinner, NBR exam gloves exhibit an equivalent amount of variability with regards to chemical resistance, in comparison to thicker products designed specifically for prolonged chemical resistance.

Physical and Mechanical Properties

The physical and mechanical properties are summarized in Table III. Considerable product variation was observed with each of the properties: AD, tensile strength, elongation at break, modulus 50-100%, and maximum modulus. Average AD ranged from about 8-15 g cm⁻², a twofold difference. Average tensile strength ranged from about 11-34 MPa, a threefold difference. Average elongation at break ranged from about 440-1100%, a 2.5-fold difference. Average modulus 50-100% ranged from about 0.8-4 MPa, a fivefold difference. Average maximum modulus ranged from about 2.3-8.6 MPa, about a fourfold difference. Correlation and multiple regression analyses were later performed and evaluated to determine which of these physical

Table II. Permeation Data (mean \pm SD)

Glove ID	Breakthrough time (min)	SSPR (µg cm ⁻² min ⁻¹)	AUC-30 (min μg ⁻¹ cm ⁻²) ^a
1	6.6 ± 1.8	24.2 ± 6.3	4860 ± 1140
2	10.8 ± 1.5	13.9 ± 2.0	1960 ± 450
3	46.6 ± 4.7	3.2 ± 0.6	0 ^b
4	19.8 ± 2.7	8.3±3.2	250 ± 180
5	15.4 ± 2.3	8.5 ± 2.2	520 ± 290
6	13.5 ± 0.7	16.2 ± 0.6	1300 ± 150
7	13.5 ± 3.5	13.8 ± 2.1	1050 ± 490
8	15.5 ± 1.5	8.0 ± 1.3	440 ± 170
9	8.1 ± 1.4	17.4 ± 0.6	3120 ± 640
10	7.1 ± 1.4	23.1 ± 2.4	4260 ± 790
11	8.1 ± 1.4	25.0 ± 3.9	4460 ± 1080
12	12.0 ± 1.6	12.1 ± 1.6	1200 ± 460
13	9.2±1.7	13.7 ± 0.8	2480 ± 600
14	14.6 ± 3.1	5.1 ± 1.5	370 ± 300
15	12.8 ± 1.3	14.5 ± 2.4	1270 ± 390
16	12.7 ± 1.4	13.7 ± 1.0	1320 ± 440
17	20.1 ± 2.1	4.4 ± 1.5	120 ± 80
18	14.3 ± 1.7	8.8 ± 1.8	600 ± 230
19	19.1 ± 1.7	7.5 ± 1.6	220 ± 110
20	15.6 ± 2.3	11.8 ± 3.6	640 ± 390
21	12.5 ± 1.9	10.6 ± 1.9	990 ± 370
22	12.0 ± 2.6	11.0 ± 2.2	1140 ± 750
23	7.8 ± 0.8	15.1 ± 0.5	3630 ± 460
24	15.3 ± 1.7	9.7 ± 2.2	560 ± 290
25	12.0 ± 2.1	15.5 ± 2.7	1650 ± 810
26	13.7 ± 2.8	12.5 ± 3.0	1040 ± 540
27	17.6 ± 2.9	9.1 ± 3.0	410 ± 280
28	11.2 ± 2.1	11.2 ± 2.3	1140 ± 460
29	10.0 ± 0.9	16.5 ± 2.1	2390 ± 340
30	10.9 ± 1.0	15.4 ± 1.6	1890 ± 460
31	11.5 ± 2.1	17.7 ± 1.9	1910 ± 720
32	14.2 ± 1.1	15.4 ± 2.6	780 ± 230
33	17.0 ± 2.5	11.6 ± 4.7	460 ± 330
34	9.0 ± 0.9	24.4 ± 3.2	3580 ± 660
35	16.7 ± 2.2	9.0 ± 2.6	340 ± 170
36	17.1 ± 1.4	11.2 ± 3.0	360 ± 160
37	11.1 ± 1.1	18.8 ± 1.8	2100 ± 600
All Gloves	13.8 ± 6.0	13.0 ± 5.7	1430 ± 1360

 $^{\rm a}$ AUC-30 min represents the relative area under the permeation curve between the initial breakthrough time (BT) and 30 min. $^{\rm b}$ For glove 3 the BT was beyond 30 min.

and/or mechanical properties were most associated with the observed variability in permeation parameters.

Compositional and Polymer Uniformity Properties

The glove composition and uniformity data are shown in Table IV. Considerable product variability was observed with each of



Table III. Physical and Mechanical Glove Properties (mean \pm SD)

ID	Area density (g cm ⁻²)	Tensile strength (MPa)	Elongation at break (%)	Modulus 50-100% (MPa)	Maximum modulus (MPa)
1	8.5±1.5	14.4 + 4.7	670±133	1.3±0.2	4.9 ± 1.5
2	9.2±1.0	26.1 ± 10.7	846 ±187	1.8 ± 0.6	3.8 ± 1.6
3	11.1 ± 1.2	29.4 ± 5.2	544 ± 96	4.0 ± 0.9	8.6 ± 2.2
4	11.3 ± 0.8	17.8 ±3.6	764 ±100	1.5 ± 0.1	4.5 ± 0.7
5	14.1 ± 1.9	22.9 ± 3.1	785 ± 68	1.5 ± 0.3	5.1 ± 1.0
6	12.8 ± 1.2	30.7 ±7.6	855 ± 169	2.7 ± 0.7	5.3 ± 0.4
7	12.1 ± 1.3	34.3 ± 9.2	1075 ± 203	2.5 ± 0.6	5.2 ± 0.6
8	11.1 ± 1.2	20.6 ± 6.0	681 ± 135	1.8 ± 0.3	5.1 ± 1.4
9	9.4 ± 1.0	13.3 ± 4.6	672 ± 157	1.4 ± 0.2	3.1 ± 1.0
10	8.1 ± 0.7	22.2 ± 6.9	874 ± 173	1.5 = 0.1	2.9 ± 1.0
11	9.4 ± 1.0	16.7 ± 4.4	766 ± 145	1.1 ± 0.1	3.5 ± 0.9
12	11.6 ± 1.4	19.9 ± 6.5	782 ± 141	1.1 ± 0.2	3.7 ± 1.5
13	9.8 ± 0.6	10.8 ± 3.3	724 ± 128	0.99 ± 0.04	2.5 ± 0.8
14	9.2 ± 0.6	23.9 ± 9.1	710 ± 159	2.1 ± 0.4	4.7 ± 2.3
15	11.5 ±1.5	12.2 ± 4.0	611 ± 121	1.5 ± 0.1	2.5 ± 0.8
16	8.8 ± 0.7	18.8 ± 6.0	570 ± 117	1.6 ± 0.1	6.3±1.2
17	13.9 ± 0.5	17.3 ± 3.7	712 ± 114	1.7 ± 0.1	3.4 ± 1.1
18	11.1 ± 1.1	15.4 ± 7.1	577 ± 154	1.5 ± 0.1	5.5 ± 1.5
19	13.6 ± 1.4	19.1 ± 6.4	953 ± 183	1.1 ±0.1	3.7 ± 1.0
20	9.7 ± 1.0	16.4 ± 5.1	656 ± 118	1.2 ± 0.1	3.4 ± 1.5
21	12.1 ± 1.6	15.5 ± 3.8	647 ± 93	1.9 ± 0.4	4.4 ± 0.6
22	9.9 ±1.0	13.4 ± 6.1	487 ± 170	2.4 ± 0.4	3.1 ± 1.2
23	10.1 ± 0.6	20.7 ± 5.1	777 ± 116	2.2 ± 0.1	3.7 ± 1.3
24	11.5 ± 1.0	22.2 ± 7.0	803 ± 146	1.6 ± 0.1	4.2 ± 0.6
25	11.0 ± 1.0	12.6 ± 5.0	665 ± 143	1.4 ± 0.2	2.4 ± 1.1
26	11.7 ± 1.2	18.9 ± 2.8	868 ± 97	1.7 ± 0.2	3.1 ± 1.4
27	11.5 ± 1.4	15.5 ± 7.1	576 ± 155	2.1 ± 0.2	3.5 ± 1.2
28	10.8 ± 2.3	16.3 ± 6.4	955 ± 222	0.8 ± 0.1	2.3 ± 1.2
29	8.4 ± 1.1	27.0 ± 8.6	753 ± 153	2.0 ± 0.2	4.8 ± 1.9
30	9.0 ± 0.9	21.1 ± 6.7	842 ± 148	1.6 ± 0.1	5.4 ± 2.1
31	11.0 ± 1.2	20.1 ± 5.5	771 ± 114	1.7 ± 0.1	4.0 ± 1.3
32	12.9 ± 1.2	12.2 ± 3.6	622 ± 111	1.3 ± 0.2	3.2 ± 0.8
33	14.7 ± 1.3	35.2 ± 4.8	857 ± 70	3.2 ± 0.1	6.0 ± 0.7
34	10.9 ± 1.0	20.8 ± 4.8	927 ± 195	1.3 ± 0.2	4.5 ± 1.1
35	13.6 ± 1.2	13.9 ± 4.3	443 ± 110	3.3 ± 0.3	3.8 ± 0.5
36	11.8 ± 0.8	23.4 ± 11.9	648±241	2.7 ± 0.2	5.6 ± 1.3
37	12.4 ± 0.9	19.1 ± 7.4	767 ± 156	1.3 ± 0.1	5.4 ± 2.1

the properties measured: acetone extraction, inorganic residue, organic polymer content, peak absorbance at 2237 ± 2 cm⁻¹, peak absorbance at 1770 ± 2 cm⁻¹, and total CV. Average acetone extraction amounts ranged from 4 to 16%, a fourfold difference. Average inorganic residue content ranged from about 2–9.5%, a fivefold difference. Average organic polymer content ranged from about 76–91%. Average peak absorbance at 2237 ± 2 cm⁻¹ ranged from about 1.2–2.2 Abs, a twofold difference. Average peak absorbance at 1770 ± 2 cm⁻¹ were either not present or ranged from 0.16–0.78 Abs, greater than a five-

fold difference. The total CV, on average, ranged from about 3–14%, a fivefold difference. As indicated earlier, correlation analyses were later performed and evaluated to determine which of these compositional and/or polymer uniformity properties were better associated with the observed variability in permeation parameters.

Correlation Analysis

The Spearman correlation analysis data for the dependent permeation variables (BT, SSPR and AUC-30) and the independent



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Table IV. Glove Composition^a and Uniformity Data^b (mean \pm SD)

ID	Acetone extraction (%)	Inorganic residue (%)	Organic polymer content (%)	Peak absorbance at 2237 cm ⁻¹ (Abs)	Peak absorbance at 1770 cm ⁻¹ (Abs)	Total CV (%)
1	11.7	7.1 ± 2.9	80.9±2.4	1.18 ± 0.01	0.20 ± 0.01	11.8
2	10.8	3.4 ± 0.5	83.8 ± 0.8	1.37 ± 0.01	-	4.8
3	5.9	5.8 ± 2.9	87.2±2.3	2.17 ± 0.12	0.55 ± 0.04	8.6
4	8.4	1.8 ± 1.9	88.0 ± 1.8	2.14 ± 0.07	0.39 ± 0.02	8.5
5	9.2	2.5 ± 0.5	87.0 ± 0.4	1.89 ± 0.08	-	6.7
6	11.0	5.5 ± 1.3	82.8 ± 1.1	1.79 ± 0.03	0.22 ± 0.03	2.9
7	11.4	7.8 ± 1.9	80.3 ± 2.0	1.69 ± 0.05	-	3.8
8	6.2	2.2 ± 0.7	90.0 ± 0.8	1.49 ± 0.05	0.60 ± 0.02	4.5
9	8.1	4.9 ± 0.9	85.7 ± 1.1	1.31 ± 0.10	0.41 ± 0.11	9.0
10	14.1	9.5 ± 3.3	76.1 ± 2.9	1.43 ± 0.04	-	10.2
11	12.9	5.2 ± 2.9	81.2 ± 2.4	1.26 ± 0.03	0.286 ± 0.002	4.9
12	6.2	3.0 ± 1.6	89.7 ± 1.0	1.39 ± 0.04	0.26 ± 0.01	4.1
13	12.8	5.6 ± 0.6	80.8 ± 0.2	1.42 ± 0.04	0.38 ± 0.01	7.5
14	4.7	7.3 ± 2.9	87.4 ± 1.9	1.56 ± 0.01	0.265 ± 0.004	6.6
15	8.7	8.2 ± 0.9	82.8 ± 0.6	1.39 ± 0.04	0.373 ± 0.004	14.2
16	7.0	2.2 ± 1.1	88.8 ± 0.7	1.56 ± 0.07	0.56 ± 0.04	6.1
17	5.6	3.3 ± 0.6	89.8 ± 0.3	1.87 ± 0.06	0.49 ± 0.02	6.7
18	3.9	5.8 ± 0.5	89.6 ± 0.7	1.48 ± 0.07	0.42 ± 0.02	6.6
19	13.6	3.0 ± 1.0	82.2 ± 0.9	2.04 ± 0.03	0.33 ± 0.01	6.7
20	6.8	2.8 ± 2.5	88.6 ± 2.3	1.45 ± 0.02	0.78 ± 0.01	10.3
21	5.6	6.2 ± 0.9	86.6 ± 0.8	1.65 ± 0.05	0.25 ± 0.01	8.9
22	7.0	9.4 ± 4.0	83.0 ± 3.2	1.25 ± 0.02	0.268 ± 0.001	3.0
23	6.4	7.4 ± 0.4	84.5 ± 0.7	1.32 ± 0.04	0.20 ± 0.01	6.2
24	4.9	6.1 ± 1.2	88.0 ± 0.9	1.47 ± 0.03	0.32 ± 0.01	3.2
25	12.2	5.9 ± 5.2	81.2 ± 4.0	1.77 ± 0.04	0.27 ± 0.01	6.4
26	4.6	2.3 ± 0.7	91.1 ± 0.7	1.65 ± 0.12	0.24 ± 0.02	5.1
27	6.9	5.5 ± 3.1	86.8 ± 2.6	1.39 ± 0.10	0.29 ± 0.02	4.5
28	12.3	6.1 ± 2.5	81.2 ± 2.2	1.48 ± 0.03	-	4.8
29	7.3	4.7 ± 1.4	86.9 ± 1.9	1.27 ± 0.04	-	3.5
30	7.0	6.1 ± 1.8	86.3 ± 1.4	1.40 ± 0.07	-	4.1
31	14.2	4.2 ± 1.9	80.4 ± 2.0	1.63 ± 0.03	0.16 ± 0.01	4.4
32	15.8	5.6 ± 3.6	78.0 ± 2.1	1.89 ± 0.03	0.262 ± 0.005	4.3
33	10.3	4.4 ± 0.1	84.4 ± 0.5	1.67 ± 0.09	0.52 ± 0.06	5.5
34	11.8	8.50 ± 0.02	78.6 ± 0.4	1.51 ± 0.04	-	5.7
35	6.4	6.2 ± 1.4	86.9 ± 1.7	1.67 ± 0.02	0.218 ± 0.003	9.2
36	11.4	6.3 ± 1.7	81.5 ± 1.7	1.77 ± 0.06	0.52 ± 0.03	4.3
37	10.3	8.2±1.7	81.9 ± 1.8	1.57 ± 0.14	0.31 ± 0.05	3.0

^a Glove composition variables include acetone extraction, inorganic residue, organic polymer content, peak absorbance at 2237 cm⁻¹ for relative acrylonitrile content, and peak absorbance at 1770 cm⁻¹ for relative carboxylation of base polymer.

^b Total CV was a polymer uniformity variable.

variables associated with the compositional, physical or mechanical properties are presented in Table V. No strong associations (rho < -0.7 or > 0.7) were observed between the dependent and independent variables. The moderate associations (rho between 0.3 and 0.7 or between -0.3 and -0.7) with the dependent variables included:

- Area density (physical property)
- Acetone extract (compositional property)
- Organic polymer content (compositional property)
- Relative acrylonitrile content (compositional property)
- Relative carboxyl content (compositional property)
- Modulus 50–100% (mechanical property)



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Table V. Correlation Analysis

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	ВТ	SSPR	AUC-30	Tensile strength	Modulus 50-100%	Maximum modulus	Area density	Acetone extract	Inorganic residue	Organic polymer	Acrylonitrile	Carboxyl	Total CV
BT	I	-0.79	-0.96	0.11	0.35	0.27	0.57	-0.34	-0.32	0.45	0.58	0.44	ŋ
SSPR		1	0.88	Ø	-0.31	-0.17	-0.36	0.52	0.23	-0.57	-0.33	-0.35	-0.12
AUC-30			I	-0.08	-0.35	-0.24	-0.54	0.41	0.27	-0.50	-0.54	-0.43	σ
Tensile Strength				I	0.38	0.58	σ	σ	-0.07	0.09	0.10	-0.26	-0.36
Modulus 50-100%					I	0.40	0.22	-0.40	0.18	0.23	0.12	σ	-0.15
Max. Modulus						I	0.18	-0.14	ŋ	0.16	0.13	0.14	-0.16
Area Density							I	-0.12	-0.22	0.18	0.77	0.14	-0.08
Acetone Extract								I	0.11	-0.89	0.08	-0.25	σ
Inorganic Residue									1	-0.51	-0.25	-0.29	a
Organic Polymer										I	ŋ	0.35	σ
Acrylonitrile											I	0.13	0.13
Carboxyl												I	0.16
Total CV													I
Values shown are Spr observed probabilities polymer, acrylonitrile tho ≥ 0.3).	earman' s. Model and cal	s rank orde ate correla boxyl) were	rr correlation c itions between e placed in bo	oefficient (rho the collectior ordered boxes) with all $P \leq 0.0$ is of dependent , for ease of vi	05. Even thoug (BT, SSPR and iewing. Bold = s	h many of th I AUC-30) ai strong assoc	ne correlation nd independe iation (rho ≤ -	s were weak tu nt variables (m -0.7 or rho≥(o moderate, t odulus 50-1(0.7). Italic = v	he large sample s 00%, area densit, veak to moderate	size contribut /, acetone ex association	ed to the low rract, organic rho≤-0.3 or

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Not significant (P > 0.05).

A majority of the moderate correlations were with compositional properties of the polymer, as anticipated based on previous studies.^{5,10} Both relative acrylonitrile content and area density have been shown to correlate well with the chemical permeation of captan through similar disposable NBR gloves.⁵ Area density and modulus have also been shown to have an association with glove integrity (i.e., water penetration through holes) of similar NBR glove products.¹⁰ In contrast, both tensile strength and elongation at break, which are industry standard tests used with disposable NBR gloves in production,^{7,8} showed little to no association in that previous study. The above results support the main hypothesis and indicate that physical and compositional polymer properties are associated with, on average, about 10-30% of the observed variation between glove brands. The combined effects are evaluated with the multiple regression analyses.

Based on an evaluation of the correlation data, the following changes in glove properties are associated with an increase in the BT (positive correlation) and a decrease in SSPR (negative correlation).

- 1. Increases in organic polymer content
- 2. Increases in the area density
- 3. Increases in acrylonitrile content
- 4. Increases in carboxylation
- 5. Decreases in components extracted by acetone
- 6. Increases in modulus 50-100%

Multiple Regression Analyses

A series of multiple regression analyses were run to determine the combination of independent variables predictive of the dependent outcomes. As discussed earlier, glove 3 was not found to be an outlier or influential, thus remained in all the models. A series of stepwise multiple regression analyses with forward, backward, and combined treatments were performed for each set of dependent variables to determine the most predictive model, with the fewest independent variables. All analyses were performed controlling for temperature (*temp*) in degrees Celsius.

For BT, the most predictive model included the following independent variables:

- Area density (AD)
- Acetone extraction (AE)
- Relative acrylonitrile content (AN)
- Relative carboxyl content (CC)
- Modulus 50–100% (M)
- Total CV (CV)

The resulting R^2 was 0.67 ($P \le 0.05$), a moderate association, indicating that about 67% of the observed variation in BT was explained by the following model:

$$BT = (-0.86AD) + (3.1M) + (17.3AN) + (7.1CC) - (0.41AE) - (0.15CV) - (0.74temp) + 9.1$$
(1)

For SSPR, the most predictive model included the following independent variables:

- Area density (AD)
- Acetone extraction (AE)
- Relative acrylonitrile content (AN)
- Relative carboxyl content (CC)
- Total CV (CV)

The resulting R^2 was 0.53 ($P \le 0.05$), a moderate association, indicating that about 53% of the observed variation in SSPR was explained by the following model:

$$SSPR = (-0.31AD) - (9.1AN) - (3.7CC) + (0.95AE) + (0.20CV) + (0.56temp) + 10.2$$
(2)

For AUC-30, which is a function of both BT and SSPR,⁶ the most predictive model included the following independent variables:

- Area density (AD)
- Acetone extraction (AE)
- Relative acrylonitrile content (AN)
- Relative carboxyl content (CC)
- Total CV (CV)

The resulting R^2 was 0.62 ($P \le 0.05$), a moderate association, indicating that about 62% of the observed variation in AUC-30 was explained by the following model:

$$AUC 30 = (-182AD) - (2210AN) - (1194CC) + (171AE) + (106CV) + (182temp) + 1206$$
(3)

The main hypothesis that compositional and uniformity variables were more closely associated with the observed variability in permeation parameters (BT, SSPR and AUC-30) was supported by the correlation and multiple regression analyses. From the correlation analyses, four of the six independent variables that were moderately associated with the dependent variables were compositional properties. Area density, a physical property related to density and thickness, was also moderately associated with the permeation parameters. The only mechanical property exhibiting a moderate association was modulus 50-100%, which is not reported on ASTM test methods or manufacturer specification sheets. Modulus 50-100% may be an improved tensile testing measure over tensile strength and elongation at break, as it relates to polymer performance under conditions closer to normal use. Similar findings were exhibited with the regression analyses, with the addition of polymer uniformity as an important factor in each regression model.

There was agreement between the correlation analyses and multiple regression analyses, with the exception of the organic polymer content and polymer uniformity. First, organic polymer content had moderate associations with all three dependent variables; however, there was a strong association with acetone extraction (rho = 0.89). It stands to reason that as the oil/plasticizer content increases the polymer content will decrease proportionally. The two variables are not mutually exclusive. In the multiple regression model acetone extraction was significant ($P \le 0.05$), whereas organic polymer content was not significant (with P = 0.06 or above) and/or the resulting \mathbb{R}^2 value was lower than with acetone extraction. Ultimately, acetone extraction was more predictive of chemical permeation performance.



Second, polymer uniformity, as total CV, showed little to no association with the correlation analyses, but was a significant factor in all three multiple regression analyses. The large difference in total CV observed between glove products, up to fivefold, is a likely influence behind this divergence.

Thickness may also be a contributing factor associated with polymer uniformity, as three of the four gloves with total CV above 10% (gloves 1, 10, and 20) had average thicknesses less than 0.10 mm. Thinner formulations would be expected to have more problems with uniformity. However, gloves 9, 14, 16, 29, and 30 all had average thicknesses <0.10 mm and total CVs ranging from 3.5 to 9%. Thus, thickness is not a reliable predictor. Instead, area density shows a unique association with polymer uniformity. Although, no correlation exists between AD and total CV, gloves 1, 9, 10, 14, 15, 16, 20, 29, and 30) all exhibit an AD below 10 g cm⁻² and a total CV above 10%. Only gloves 2, 11, and 13 exhibit an AD below 10 g cm⁻² and a total CV below 10%. As exhibited here and in previous studies,^{5,10} AD is a significant polymer property associated with polymer performance and quality.

A similar regression model with seven disposable NBR gloves and permeation of captan, a wettable-powder pesticide, indicated that acrylonitrile content and area density were both predictive of BT and SSPR.⁵ Together acrylonitrile content and area density accounted for about 85–90% of the variation in the normalized BT and SSPR. These associations were not as strong with permeation of a volatile organic solvent (ethanol) in this current study. However, both AD and AN were shown to have moderate associations with BT and SSPR and the variables were significant factors in the regression models for BT and SSPR.

Limitations of the Study

It must be noted that only one test chemical was evaluated in this study, which limits the application to different chemical classes with NBR gloves. Ethanol was selected because it is known to permeate NBR products rapidly without significant degradation, and can be used to evaluate similar natural rubber and neoprene glove products.⁹ While the findings are relevant to similar aliphatic hydroxyl compounds, they may not necessarily apply to different chemical classifications. Lastly, it would have been optimal to control temperature (at body temperature) and relative humidity more closely; however, this study design required a large number of test runs for statistical significance. The presence of a heating element near a flammable solvent posed an additional safety issue.

CONCLUSIONS

As hypothesized, in contrast to tensile properties, the potential predictors of chemical permeation performance were compositional and polymer uniformity properties. Tensile strength and elongation at break, which are industry standard measures of glove quality and polymer performance, were weak predictors of the observed variation in permeation parameters between the glove products. Even though the associations were moderate and not strong, the predictors that should be a focus of future attempts to either certify disposable NBR gloves or reduce the variability in performance include: area density, acrylonitrile content, carboxylation of the base polymer, the amount of extractable oils and oily plasticizers, and polymer uniformity. It must be noted that many of these parameters affect one another; most notably that addition of plasticizers will reduce acrylonitrile content, which has been shown to strongly influence chemical resistance.⁵ Based on the findings of this study, improved permeation performance is potentially associated with (1) increased area density, (2) increased acrylonitrile content, (3) increased carboxylation, (4) decreased amount of acetone extract components, and (5) decreased polymer variation associated with uniformity. Further research needs to include properties of the curing process (e.g., cross-linking density) and other NBR chemical and physical properties that can be measured using standardized tests, such as those present in ASTM Method D 297.^{18,19}

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