

Mechanism on the Permeation of Ethanol in Nitrile Gloves Studied Using Positron Annihilation Lifetime Spectroscopy

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ABSTRACT: Positron annihilation lifetime spectroscopy (PALS) was applied to study the mechanism of ethanol diffusion through commercial nitrile rubber gloves. Even though the untreated raw samples were very different in their colors and area densities (g/cm^2), the correlation between the ethanol diffusion coefficient from permeation test and the free volume from PALS measurement is well consistent with the Vrentas-Duda model. Via combining the PALS technique and the Vrentas-Duda theory, it is revealed that (a) the diffusion coefficient is correlated to the number of free volume holes rather than the average size of holes, (b) the diffusion process is not regulated by the size of ethanol molecule but by the size of critical volume for polymer segments to migrate, (c) nitrile group does not present in the free volume hole where the diffusion of ethanol molecule takes place, but is embedded in polymer matrix, and therefore, does not directly interact with ethanol molecule, and (d) nitrile group affects the average size, but not the number of free volume holes. The experiment demonstrates that the PALS technique, being mainly used in pure academic researches, might have application in the glove industry due to its ability in measuring terminal free volume quantities, which are directly related to the permeation of small organic molecules through protective gloves. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41282.

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INTRODUCTION

Nitrile butadiene rubber (NBR) is widely used in manufacturing chemical protective clothing, such as protective gloves in chemical labs and other fields. It has been well realized that the gloves from different manufactures and even the different batches from the same manufactures exhibit a marked difference in the permeation of small organic molecules through them.^{1–3} For instance, Mickelson et al.¹ found that the permeation of perchloroethylene showed 10-fold difference for the gloves from different suppliers, meanwhile, Perkins et al.² reported that permeation of 2-ethoxyethanol acetate could vary up to 2-fold for the gloves from the same supplier but at different batches. Therefore, the exploration of those factors affecting the permeation of small organic molecules is of interest to environmental scientists and engineers. Because NBR is polybutadiene copolymerized with nitrile group (CN), the chemical composition, especially the CN group content is of primary interest. Many studies show that the chemical resistance of NBR gloves increases with the increasing CN group content,^{4,5} particularly

for nonpolar molecules such as fuel and oil.^{6–8} Phalen et al.⁹ reported the permeability of captan, a slightly polar molecule widely used as a pesticide, is closely related to the content of CN group and the area density (in g/cm^2) of glove samples. This result indicates that both chemical composition (CN content) and physical property (area density) play roles in regulating captan permeation through glove samples. However, some others, e.g., Mueller et al.,¹⁰ found that the permeability rate of polar solvents such as methanol and methyl ethyl ketone increases with the increasing CN content, indicating a decrease in permeation resistance. It must be noted that both methanol and methyl ethyl ketone are not recommended for use with NBR due to chemical degradation and/or incompatibility, which could be a factor in the previous study.¹¹ Nevertheless, the reason why CN group in gloves has different effect on some polar molecules needs to be answered. Furthermore, the abovementioned studies presented, more or less, phenomenological correlation between the permeability of organic penetrants through gloves and CN group content within, yet the underlying mechanism has not been investigated. The aim of this research is to

address this issue and to study the diffusion of ethanol in NBR gloves from the standpoint of free volume at the atomic scale.

It is generally believed that the permeation of a liquid through a polymer thin film such as a glove is described by a physical quantity, permeability (P), of the liquid through the film. The permeability of a liquid through a polymer film is believed to be determined by two factors: solubility (S) and diffusivity (D) of the penetrant via the relation of $P = S \times D$. Between those two, D is believed to be much more sensitive to the microstructure, generally described as the free volume, of a polymer. The relation between diffusivity (D) and fractional free volume (f_v) was first proposed by Cohen and Turnbull¹² and later on was further studied by Vrentas and Duda et al.,¹³ which will be elaborated in the next section.

Free volume in polymers can be well characterized by using positron annihilation lifetime spectroscopy (PALS). This technique utilizes the quantum effect of a positron, the antiparticle of an electron, inside a material and relates its lifetime with the size of a free volume hole. A positron emitted from a positron source, usually isotope ²²Na, has a large kinetic energy. When entering into a material, the positron will lose most of its kinetic energy and be thermalized in several picoseconds. During the process of the thermalization, the positron can ionize some molecules via collision, creating a series of plasma spurs that are composed of electrons, molecular ions and neutral molecules. In the last spur, the kinetic energy of the positron is low (corresponding to room temperature) and may catch an ionized electron and form a bound positron-electron state, positronium (Ps). Based on the spin coupling, $\frac{1}{4}$ of Ps will be para-positronium (p-Ps) with anti-parallel spins (total spin $S = 0$) of electron and positron and $\frac{3}{4}$ of Ps will be ortho-positronium (o-Ps) with parallel spins (total spin $S = 1$) of electron and positron. Upon formation, positronium will diffuse into the open space, free volume holes, inside the material due to the lower electric potential inside. Para-positronium (p-Ps) has an intrinsic lifetime of 0.125 ns in both vacuum and materials. In contrast, ortho-positronium (o-Ps) has an intrinsic lifetime of 142 ns in vacuum, but is shortened to several ns due to the so-called pick-off annihilation because of the overlap of wave function of o-Ps with the electron layer inside the free volume hole. In a simple Tao-Eldrup model, the free volume holes are treated as the solid spherical voids with a thin electron layer. Using a particle-in-a-box model, the wave function of positronium inside holes can be easily obtained and the pick-off annihilation rate of o-Ps can be calculated. The well-established and also widely applied relationship between the lifetime of o-Ps and hole radius is,

$$\frac{1}{\tau} = 0.2\text{ns} \left[1 - \frac{R}{R + \Delta R} + \frac{1}{2\pi} \sin \left(\frac{2\pi R}{R + \Delta R} \right) \right] \quad (1)$$

where τ is the lifetime of o-Ps in materials, R is the average radius of holes, and ΔR is an empirical value, which is taken as 1.66 Å.

For decades, PALS has been demonstrated to be one of the most powerful techniques to characterize the free volume holes in amorphous materials where application of other techniques

such as X-ray and neutron diffraction is limited due to the lack of short range ordered structures. Because free volume is considered to be the most important parameter in polymers relating to the permeation of small molecules, PALS technique, in conjunction with permeation testing, was utilized to study the mechanism of permeation and diffusion of small molecules in a variety of model polymers and polymeric thin films.

In this project, we applied this technique to study commercial nitrile gloves and to explore the correlation between free volume and the permeation of organic solvents. The purpose was two-fold: first, we explored the diffusion mechanism of small molecules in nitrile gloves and second, we extended the application of PALS to the environmental and occupational hygiene industry. The latter one is of importance, because so far glove manufacturers and US government agencies have not established standards designed to address the quality of protective gloves in terms of their resistance to organic solvents. As stated previously, the same grade of nitrile gloves from different providers can exhibit different permeation results. This is also true for different batches or lots from the same provider.² This suggests that critical characteristics regulating diffusion of small molecules have not been revealed. We hypothesized that this parameter might be free volume holes within those gloves. Therefore, this work will not only shed the light on the mechanism of diffusion of small molecules in those commercial gloves, but also may provide an effective and standard method to evaluate and control the quality of commercial gloves.

In this article, we reported our results on the permeation of ethanol through commercial NBR gloves and the characterization of the free volume holes using positron annihilation lifetime spectroscopy. We studied the correlation between the diffusion coefficient of ethanol and the free volume in gloves, and interpreted those results using the Vrentas-Duda model. Furthermore, we explored the diffusion mechanism of ethanol in NBR gloves and made suggestions for improving the quality of protective nitrile gloves.

EXPERIMENTAL

Glove Samples and Penetrant Chemical

The samples were disposable and powder free NBR gloves purchased from Thermo Fisher Scientific (Chino, CA). All eight samples were Microflex brand assumed to have similar formulation ingredients, additives and engineering process. Among them, four samples (CE4, Midnight, Supreno and Ultrasense) were purchased in 2009 and the other four samples (CE5, Freeform, Ultraform and Xceed) were purchased in 2012, to determine if different batches varied. All samples were tested with no further treatment in accordance with the experimental purpose, which was designed to study the commercial samples directly.

Ethanol was chosen as the penetrant for the following four considerations. First, ethanol can permeate NBR products rapidly without significant degradation, and is often used to evaluate natural rubber and neoprene glove products.¹⁴ Second, ethanol is a relatively small organic molecule that is widely used in the industry and labs. Therefore, if gloves can effectively inhibit the penetration of this molecule, they will certainly prevent the

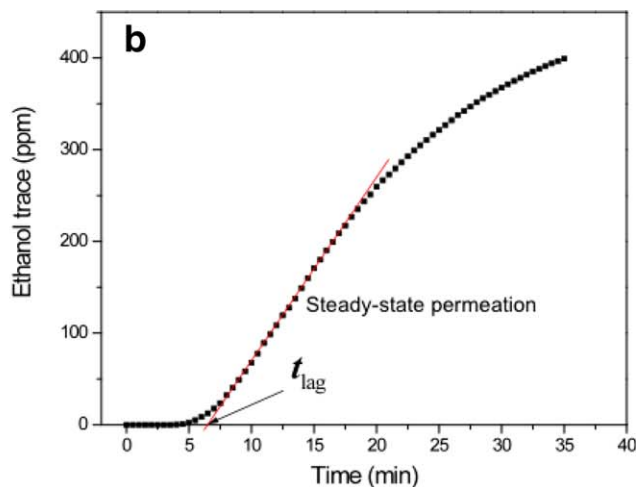


Figure 1. (a) Setup of permeation test. (b) Curve of permeation test. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

penetration of other large organic molecules. Third, ethanol is a polar molecule with a highly polar OH group and the CN group in glove samples is also polar. If there is a direct interaction between CN group and OH group, the effect of CN group content on the diffusion of ethanol will be more obvious than that only generated from the free volume change. And fourth, ethanol has a low toxicity, which makes it safer to work with. Analytical grade ethanol (99.99% purity) was acquired from Sigma-Aldrich (St. Louis, MO) with no further purification.

Permeation Test

The permeation equipment and tests were similar to those in previous experiments as shown in Figure 1(a).^{15,16} Around 200 mL ethanol was filled into the gloves and then sealed by pushing the PVC coupling against the PVC end cap tightly. The PVC end-cap was fixed at the ceiling of the permeation test chamber. The permeation of ethanol was monitored using a MiniRae2000 Photoionization Detector (PID) (Rae Systems, San Jose, CA), which is sensitive to trace ethanol content. The PID was calibrated using 100 ppm isobutylene before the test. One average datum point was recorded every 30 s and the whole test duration was about 35 min until the saturation plateau was approached, as shown in Figure 1(b). The lag time (t_{lag}) of ethanol within the glove material was determined via a linear fit of the steady-state permeation rate (SSPR) illustrated in Figure 1(b). The diffusion coefficient of ethanol within the glove material was calculated via the equation,¹⁷

$$D = L^2 / 6t_{\text{lag}} \quad (2)$$

where D is the diffusion coefficient, L is the thickness of a glove, and t_{lag} is the lag time.

Positron Annihilation Lifetime Measurement

Positron annihilation lifetime spectroscopy was acquired in the Department of Chemistry and Biochemistry at California State University, San Bernardino. The detailed explanation of PALS setup can be found elsewhere.¹⁸ The brief description of this experimental setup is given as follows: A commercial ^{22}Na

isotope positron source (POSN-22, Eckert & Ziegler Isotope Products, Valencia, CA) with an intensity of 40 μCi , which is sealed in thin tungsten foils, was sandwiched between two stacks of glove samples. Each stack of samples included around 20 pieces of 2.0 cm \times 2.0 cm films cut from commercial gloves (Microflex) to ensure the complete annihilation of positrons inside gloves. Accompanying the generation of a positron, a 1280 keV γ photon emits from the ^{22}Na source, marking the birth of the positron. This γ photon was acquired by the first detector (homemade) and processed by a constant fractional differential (CFD, Ortec 583B) to generate a start signal. Meanwhile, the positron will be quickly thermalized in a few pico-seconds and then either annihilate inside a free volume hole with a lifetime of several tenth nanoseconds or form a positronium, which also eventually annihilates inside a hole with several nanoseconds, giving another γ photon with the energy of 511 keV. This γ photon was acquired by the second detector (homemade) and processed by the second CFD (Ortec 583B) to generate a stop signal. Both start signal and delayed stop signal were transmitted into time-amplitude-converter (TAC, Ortec 567) to generate a voltage signal with the amplitude proportional to the time difference between the start and stop signals. Then the voltage signal was analyzed via a multichannel analyzer (MCA, Ortec Easy-MCA-2k) to generate a digital signal that was recorded by a computer with an Ortec acquisition program.

In the PALS measurement, a total 1.0 million counts for each spectrum were taken for statistical reliability. The spectra were analyzed using two different programs, PATFIT and MELT, with different algorithms. The PATFIT (Positron Fit) program is a least-squares method and treats an ideal spectrum as the sum of several discrete lifetime components,

$$s(t) = \sum_i \lambda_i I_i e^{-\lambda_i t}$$

where λ_i is the annihilation rate and is related to each lifetime as $\lambda_i = 1/\tau_i$, I_i is the relative intensity of each component and therefore,

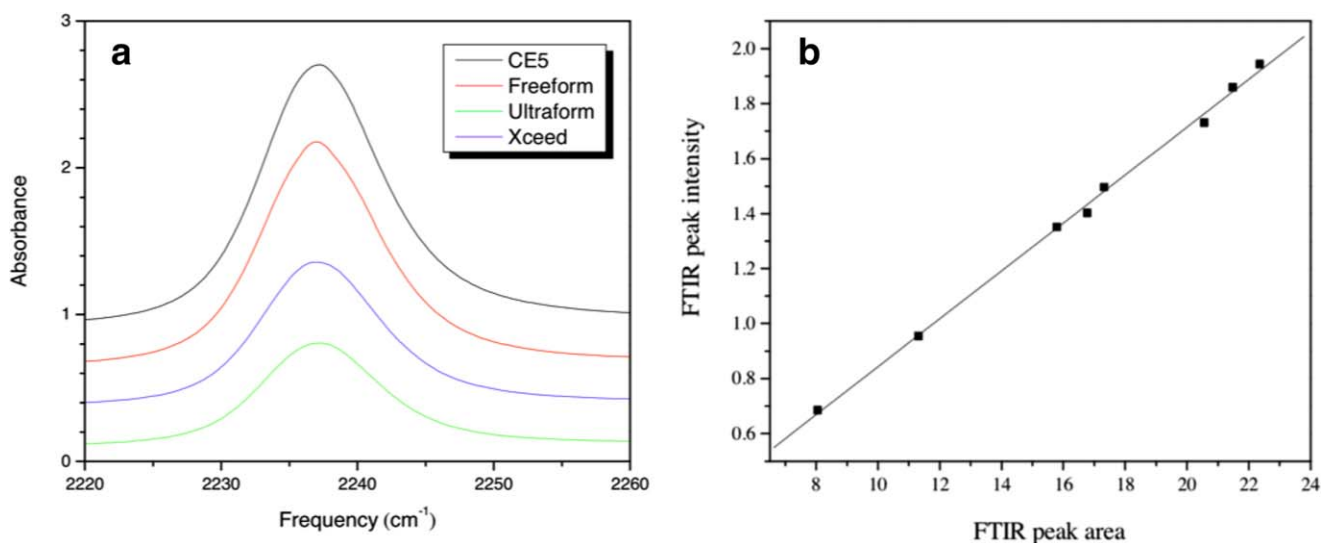


Figure 2. (a) CN vibrational mode (2237 cm^{-1}) in FTIR of batch 2 samples. (b) Correlation the peak intensity and the peak area in FTIR. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$\sum_i I_i = 1$$

The components are selected based on a plausible physical model: usually 3 or 4 lifetime components are input, the first one refers to the rate of intrinsic annihilation of p-Ps and its lifetime is fixed as 0.125 ns. The second one refers to the annihilation rate of free e^+ . The third and/or fourth one refers to the annihilation rate of o-Ps, depending on the trapping state and reflecting annihilation of o-Ps inside free volume holes.

Meanwhile, MELT (Maximum Entropy for Life Time analysis) analyzes a spectrum on the ground of a quantified maximum entropy method and treats it as a continuous distribution of annihilation rate (λ),

$$s(t) = \int_0^{\infty} \lambda I(\lambda) e^{-\lambda t} d\lambda$$

Similarly, the intensity function $I(\lambda)$ is regulated as,

$$\int_0^{\infty} I(\lambda) d\lambda = 1$$

The observed experimental spectrum $y(t)$ is the convolution of the ideal spectrum $s(t)$ and the instrumental resolution function $R(t)$, which is taken as a Gaussian function, as,

$$y(t) = R(t) \otimes (N_{\text{tot}}s(t) + B)$$

where N_{tot} and B are the total count and the background of a spectrum, and \otimes denotes a convolution of the decay integral with the resolution function.

Measurement of CN Content Using FTIR

The relative content of CN group was determined by using transmitting Fourier Transform Infrared (FTIR) spectroscopy with Jasco FTIR spectrometer (Model FT/IR 4200). The clear peak at 2237 cm^{-1} was assigned as the CN vibrating adsorption, as shown in Figure 2(a).

The FTIR sample was cut from the central palm of each glove and thickness of the sample was measured using micrometer.

Because transmittance of infrared light is affected by sample thickness, the absorbance of infrared signal was normalized to that with the same thickness based on Beer-Lambert's law. In addition, the intensity of the CN peak (2237 cm^{-1}) is linearly correlated with the area under the peak, as shown in Figure 2(b); therefore, either measure can be used to indicate the relative CN group content. In this work, the intensity of the peak was used to determine the CN group content in glove samples.

Measurement of Glove Sample Thickness

Thickness of the sample was important in this experiment since FTIR was normalized based on thickness and the diffusion coefficient of ethanol was also calculated using thickness (eq. 2). The thickness of a sample was measured using two different methods for the purpose of comparison. The first method was a direct measurement of the central part of gloves using micrometer. The second method was indirect using a NaCl salt solution with varying density. A $2.00\text{ cm} \times 2.00\text{ cm}$ square film was cut from the palm of a glove and weighed on an analytical balance to 0.1 mg. A saturated NaCl solution with the density of 1.25 g/mL was prepared. Because this density is higher than that of a glove sample ($\sim 1.1\text{ g/mL}$), the polymer film was initially floating on the top of the saturated NaCl solution. Then distilled water was slowly added into the solution to adjust its density. When the density of the solution was equal to that of the polymer sample, the sample was suspended inside the solution, following a small disturbance to overcome the surface tension of the NaCl solution. The final density of the NaCl solution was determined by weighing the 5.00 mL aliquot on the same analytical balance. From the density, mass and area of the polymer film, the thickness of the sample was calculated. It was found that the two methods generated similar results. For example, the thickness of Midnight was 0.0102 cm using a micrometer and 0.0105 cm using the NaCl density method, each within about 3% of each other. Therefore, for ease of measurement, the direct measurement with a micrometer was applied in all subsequent measures of thickness.

RESULTS AND DISCUSSION

Cohen–Turnbull and Vrentas–Duda Free Volume Theory on Diffusion of Molecules

Intuitively thinking, the diffusion of small organic molecules inside polymers must require some free volume space to enable those molecules to move from one site to another. The pioneering work to formulate this idea was presented by Cohen and Turnbull¹² and later modified by Fujita,¹⁹ as described in the following equation,

$$D = A \exp(-B/f_v) \quad (3)$$

Here D is the diffusion coefficient of organic molecules in a polymer, A is a constant related to the size and shape of the small molecules, B is a constant related to both small molecules and polymers and f_v is the fractional free volume.

The above relationship was applied successfully to study the diffusion of gas molecules inside polymers at room temperature.^{20–22} However, due to the simplicity of the model, there are some limits when applying this equation. First, it does not account for diffusion coefficient dependence on temperature and penetrant concentration.^{23–25} Second, the constants A and B do not provide a clear physical representation. Consequently, a modified free volume theory, proposed by Vrentas and Duda,^{26–28} provides an improved model of penetrant diffusion over a large concentration and temperature range. According to this model, the solvent self-diffusion coefficient (D_1) in a polymer matrix and the polymer/penetrant binary mutual diffusion coefficient (D) above the glass transition temperature (T_g) are described as,

$$D_1 = D_0 \exp\left(-\frac{E}{RT}\right) \times \exp\left(\frac{-\gamma(\omega_1 \hat{V}_1^* + \xi \omega_2 \hat{V}_2^*)}{\omega_1 K_{11}(K_{21} - T_{g1} + T) + \omega_2 V_F}\right)$$

$$D = D_1(1 - \phi_1)^2(1 - 2\chi\phi_1)$$

Here, D_0 is a pre-exponential factor, E is the critical energy which a penetrant molecule has to overcome in order to migrate to the next site, γ is an overlap factor because the same free volume hole can be occupied by more than one penetrant molecules, \hat{V}_1^* is the specific critical hole volume for a solvent molecule required for a diffusion to jump, \hat{V}_2^* is the specific critical hole volume for a polymer segment to migrate to the neighbor site, ω_1 and ω_2 are the weight fractions of the solvent and the polymer, ξ is the ratio of the molar volume of the solvent jumping unit to that of the polymer jumping unit, K_{11} and K_{21} are the free volume parameters of the solvent, V_F is the hole free volume of the polymer, ϕ_1 is the solvent volume fraction in the solvent/polymer system, and finally χ is the solvent–polymer interaction parameter which can be estimated using Flory-Huggins equation.²⁹

When the penetrant concentration is very low in the polymer system, which occurs with chemical permeation through gloves, the diffusion coefficient of the penetrant in the polymer gloves may be described via the following reduced format,

$$D = D_0 \exp\left(-\frac{E}{RT}\right) \times \exp\left(-\frac{\gamma \xi \hat{V}_2^*}{V_F}\right) \quad (4)$$

Total specific free volume V_F can be expressed as,

$$V_F = V \times f_v \quad (5)$$

Here V is the specific volume and f_v is the fractional free volume of the polymer respectively. If we substitute V_F into eq. (4), we will obtain,

$$D = D_0 \exp\left(-\frac{E}{RT}\right) \times \exp\left(-\frac{\gamma \xi \hat{V}_2^*/V}{f_v}\right) \quad (6)$$

By comparing eqs. (3) and (6), we may obtain that,

$$A = D_0 \exp\left(-\frac{E}{RT}\right), \quad B = \gamma \xi \hat{V}_2^*/V$$

The physical meaning of A and B in Cohen–Turnbull equation is now clear. A is related to the interaction (E) between penetrant molecule and polymer as well as the temperature (T), retaining Arrhenius format. B is related to the size of free volume hole required for the diffusion jump of both solvent molecules and polymer segments. Therefore, from Vrentas–Duda, we can see that mutual diffusion coefficient is determined not only by the fractional free volume f_v but also by the size of free volume holes required for diffusion jumping of both penetrant molecules and polymer segments.

When above T_g (rubbery state), the fractional free volume is generally expressed as,

$$f_v = f_g + (\alpha_l - \alpha_g)(T - T_g)$$

where f_g is the fractional free volume at T_g , α_b and α_g are the thermal expansion coefficients above and below T_g , respectively. Often f_v is determined from the William–Landel–Ferry (WLF) equation in the viscosity experiment, where f_g is taken as the universal value of 0.025. Once f_v is determined, the specific free volume (V_F) can be calculated by using eq. (5).

The above method to determine f_v and V_F is at macro-scale and provides only the overall values, and hence miss important detailed information. For instance, f_v and V_F arise from the combination of two factors: size of free volume holes and number of the free volume holes. Therefore, albeit small hole size and large hole number could generate the same f_v and V_F as large hole size and small hole number, they might play very different roles in terms of the diffusion of small solvent molecules.

An alternative way to assess the f_v and V_F is from the atomic scale using positron annihilation lifetime spectroscopy (PALS). As described above, by far this is the most promising technique to directly observe micro-vacancies at the atomic scale in polymers.³⁰ PALS not only provides the average free volume hole size at atomic scale (several Å), but also resolves the hole-size distribution at this scale. The latter is important to study molecular diffusion in polymers because the same average hole-size could correspond to a different size distribution and therefore the percentage of holes allowing for molecular/diffusant migration could be quite different. This will be further elaborated in the following section. The specific hole volume (V_F) assessed at macro-scale correlates well with the average hole volume obtained at atomic scale via PALS technique.³¹ The fractional free volume (f_v) is obtained by the empirical equation,

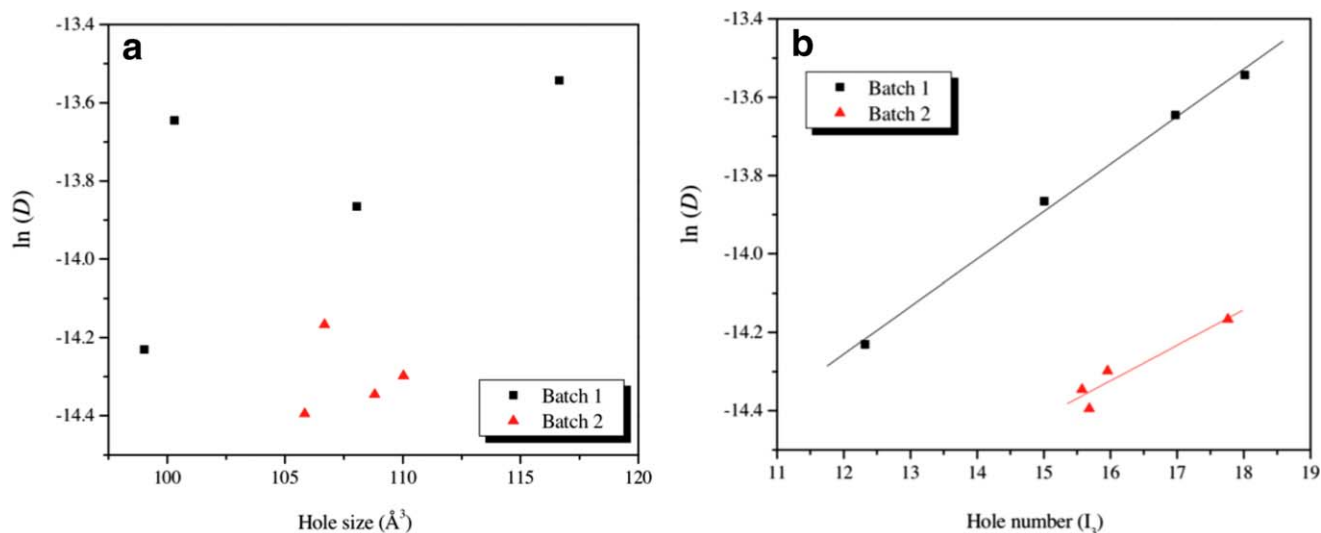


Figure 3. (a), $\ln D$ vs. V_f (Average volume of holes). (b) $\ln D$ vs. I_3 (Number density of holes). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$f_v = CV_f I_3$$

Here V_f is the volume of a hole calculated directly from radius in eq. (1), I_3 is the relative intensity of o-Ps which was proposed to sample the concentration of free volume holes, and C is an empirical constant. C is generally related to polymer type, due to positronium formation sensitivity to the chemical environment. Therefore, the value of C is often determined by comparing PALS data with the free volume values estimated using equation-of-state (EOS) of Simha-Somcynsky (SS) hole theory via the bulk pressure-volume-temperature (P - V - T) experiment.^{32–34} Even though C ranges from 0.001 to 0.002 for many polymers, it is generally taken as 0.0018.³⁵ In this study, we use this same value.

The PALS technique has been used to study the diffusion of gases in polymeric materials. There are two different correlations: $\ln D$ versus V_f and $\ln D$ versus f_v . As more polymers were studied, the later correlation $\ln D$ versus f_v became more obvious.^{36–40} In contrast, studies on the diffusion of solvents in polymers using this technique showed a more complicated scenario, indicating the correlations between $\ln D$ and V_f or f_v could be positive, negative or near zero, depending on the interaction between the solvents and polymer molecules.^{41,42}

As far as we know, most (if not all) of the previous research used standard model polymers. In this article, we will apply PALS technique to a more practical system, protective gloves. We selected gloves from Microflex due to the diversity of their available glove types (e.g., light duty versus heavy duty formulations) and previous work done with the diffusion of ethanol through these products. The gloves are majorly composed of polybutadiene copolymerized with different contents of nitrile group (CN).

Correlation of PALS Data with the Diffusion Coefficients of Solvents

Figure 3(a) shows the correlation between the diffusion coefficient of ethanol and the average size of free volume holes (V_f),

which is calculated from positron lifetime data. Figure 3(b) shows the relation of $\ln D$ versus the intensity of positronium (I_3), which samples the number density of free volume holes. From Figure 3(a), there is no definite correlation between the diffusion coefficient and the free volume hole size (V_f), as seen in other articles.^{42,43} This suggests that glove samples with larger average hole sizes do not necessarily transport the small ethanol molecules better. Meanwhile, as shown in Figure 3(b) there is a near linear correlation between the coefficient (indicated by $\ln D$) and the number density of free volume holes (indicated by I_3) in the first batch of samples (CE4, Midnight, Supreno, and Ultrasense) and a slight correlation for the second batch of samples (CE5, Xceed, Ultraform, and Freeform). This suggests that the average size of free volume holes does not affect the permeation of small ethanol molecules but rather the number of free volume holes does. This will be further explained along with the hole size distribution in the next section. In addition, from Figure 3, there are two distinct differences between these two batches of glove samples. First, both free volume hole sizes and number densities in the second batch of gloves are much closer to each other, which means they have similar free volume holes inside the polymer matrix. Second, the overall diffusion coefficients of ethanol molecules in the second batch of gloves are much smaller than those in the first batch of gloves for the similar range of hole intensity (I_3), as shown in Figure 3(b). This might be due to the fact that, on average, one free volume hole in the second batch of gloves can be available to more small ethanol molecules, as will be discussed further.

In order to apply Vrentas-Duda, the correlation between $\ln D$ and fractional free volume f_v was plotted, as shown in Figure 4. The resulting linear relationships between $\ln D$ and the fractional free volume ($1/f_v$) are strong. This is consistent with many other referenced results, which showed that for many polymers fractional free volume ($1/f_v$) has a better correlation with the diffusion coefficient. Also, the consistency between Figures 3(b) and 4 indicate that for glove samples the variation of fractional free volume arises from the number of holes, rather than from the

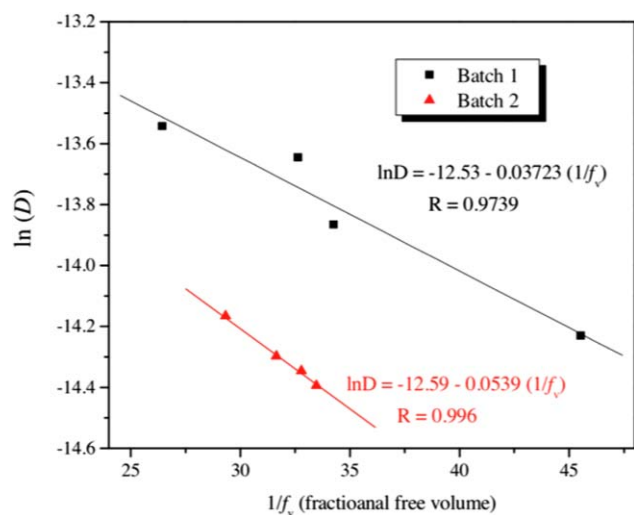


Figure 4. Correlation between diffusion coefficients and fractional free volume (f_v). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

size of holes. This difference can only be differentiated by PALS technique, which could separate hole size and hole numbers, as aforementioned. It is interesting to note that the two fitted lines have close intercepts (-12.53 and -12.59), but different slopes (-0.03723 and -0.0539). Using the Vrentas-Duda free volume model, we discovered new insights on the mechanism of the diffusion process of ethanol molecules within a glove matrix. From eq. (6), we may obtain,

$$\ln D = \ln D_0 - \frac{E}{RT} - \frac{\xi \hat{V}_2^* / V}{f_v} = \left(\ln D_0 - \frac{E}{RT} \right) - \left(\gamma \xi \hat{V}_2^* / V \right) \left(\frac{1}{f_v} \right) \quad (7)$$

Because all measurements were carried out at room temperature and both D_0 and R are constants, the intercepts, from fitting the means the E , are same for both batches of the samples, as shown in the following,

$$\text{Intercept} = \ln D_0 - \frac{E}{RT}$$

According to the Vrentas-Duda model, E is the energy required for organic molecules to overcome the interaction with the local polymer segments in order to jump to the nearby free volume holes. It is reasonable to assume that E is related to the chemical environment of the free volume holes where the organic molecule resides. The same E indicates that chemical structure of the internal wall of holes is not modified by the addition of additives like pigments or the copolymerization of nitrile groups. Therefore, it is concluded that either nitrile groups are embedded in the polymer matrix and only butadiene segments construct the free volume holes, or their interaction with ethanol molecules are same as that of butadiene units. Since nitrile group (CN) is polar and CH bond in butadiene backbone is non-polar, their interactions with polar ethanol are different. Hence the presence of CN groups inside the volume holes would significantly modify E and further change the diffusion coefficient. This should reduce the diffusion coefficient due to

the strong polar-polar interaction between nitrile (CN) groups and ethanol molecules. It has been demonstrated that the polarity of polymer unit plays a very important role in the transportation of small molecules.^{42,44,45} For instance, Soles et al.⁴² tested the diffusion of polar water molecules inside epoxy resin cured with different curing agents and found that the diffusion coefficients of H_2O in resins containing less polar ether and ester linkages are around one magnitude higher than those in their counterpart amine resins. Another evidence to support the above claim is that there was no swelling effect during the permeation test of ethanol. It is well known that if the interaction between polymer segments and solvent molecules were larger than that between polymer segments, a swelling effect would present.⁴⁶ In this study, it is obvious that the interaction between CN group in polymer chain and OH group in ethanol is stronger than that between CN group and CH_2 group on polymer chain. Therefore, if CN presented in free volume holes, the swelling effect would be seen easily. This might also explain why for some gloves the permeation of a polar solvent increases with the increase of CN content while for other gloves it decreases, as observed by e.g., Mueller et al.¹⁰ Depending on the location of CN group, if the CN group presents in free volume holes and directly interacts with the penetrant, the effect on the diffusion coefficient will be different.

The interaction energy E can be determined by conducting the experiment at different temperatures (T) and obtaining the relation between the above intercept versus ($1/T$). Then, E can be compared with Flory-Huggins interaction parameter (χ) of interaction between poly(butadiene) and ethanol. This will be done in future experiments.

Meanwhile, the slopes of fitting lines in Figure 4 are quite different. On the basis of eq. (7), the slope is related to the hole properties as shown in the following,

$$\text{Slope} = \gamma \xi \hat{V}_2^* / V$$

Here γ is the overlap factor of the free volume hole, ξ is the ratio of the molar volume of solvent jumping unit to that of the polymer jumping unit, \hat{V}_2^* is the specific volume required for polymer segments to jump to the next hole site and V is the specific volume of glove samples.

For the two batches of samples, the specific volumes are almost identical ($1.01 \text{ cm}^3/\text{g}$ to $1.04 \text{ cm}^3/\text{g}$). Because the polymer jumping unit is composed only by the soft butadiene part, both ξ and \hat{V}_2^* should be similar for those two batches of samples. Therefore, the difference in diffusion coefficients might be caused by the parameter γ , the overlap factor indicating that the same free volume hole is available to several diffusing molecules. According to the Vrentas-Duda equation, a larger γ will induce a smaller diffusion coefficient probably due to the trapping effect. This is consistent with our observation in Figure 4: the slope of the second batch (0.0539) is much larger than that of the first batch (0.03727) and correspondingly, the overall diffusion coefficients of the second batch is much smaller than those of the first batch. The different γ might be induced by the different engineering processes in the glove production and/or the degradation of the samples after three years.

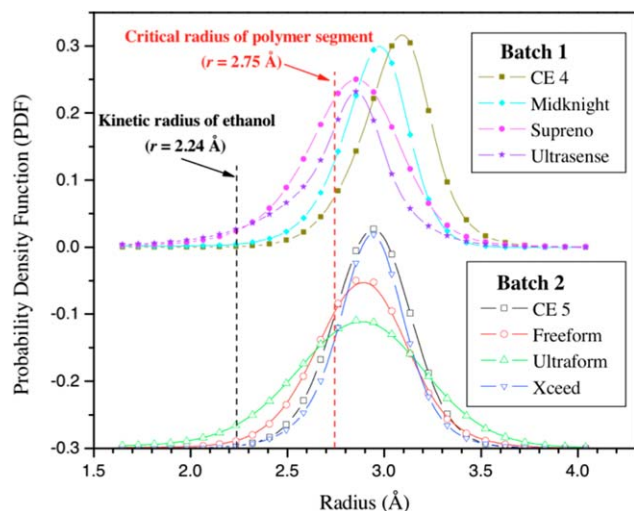


Figure 5. Distribution of free volume hole size for two batches of glove samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The critical volume (\hat{V}_1^*) for the diffusant molecule to jump should be same as the volume of the ethanol molecule,⁴⁷ which has a kinetic radius of 2.24 Å. As seen in Figure 3, the corresponding volume of ethanol ($\sim 47 \text{ \AA}^3$) is much smaller than the smallest average volume of holes in polymers ($>100 \text{ \AA}^3$). This means that almost all free volume holes are large enough to accommodate ethanol molecules and hence ethanol diffusion in the samples is not regulated by their own size, but by the critical value for polymer segments to jump, as discussed further below.

The specific volume ($\hat{V}_{2,m}^*$) for butadiene segments to jump in polybutadiene (both *cis*- and *trans*-) is $0.954 \text{ cm}^3/\text{g}$,⁴⁸ equivalent to the critical volume of 85.6 \AA^3 for one jumping unit via the relation,

$$\hat{V}_2^* = \hat{V}_{2,m}^* M_2 / N_A$$

Here M_2 is the molecular weight of the butadiene structural unit ($-\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2-$) and N_A is Avogadro's number. If the jumping unit of the polymer segment is simply taken as a sphere, the corresponding radius is 2.75 Å.

Figure 5 shows the free volume hole size distribution for the two batches of samples. It can be seen that the average hole sizes in the second batch of samples are much closer to each other. This is consistent with the PATFIT results shown in Figure 3. Another interesting point seen from Figure 5 is that the kinetic diameter of ethanol is much smaller than most of the polymer holes. If only judged by the free volume hole size, it appears that all the ethanol molecules would easily permeate through the glove films; however, in reality this is not the case. This is because diffusion is the mutual movement of both ethanol molecules and polymer segments, not just the migration of ethanol molecules. For the same reason, the interstitial free volume, which is the static free volume, does not contribute to the diffusion of small molecules; whereas, the hole free volume, which is the dynamic free volume, contributes to the diffusion process. From the free volume size distribution curve in

Figure 5, it can be seen that only those holes with a radius larger than 2.75 Å contribute to the diffusion of ethanol molecules and therefore the intensity of such holes, corresponding to the area under the curve, should be related directly to the diffusion coefficients. This confirms the observation in Figure 3: the diffusion coefficients are not related to the average hole size because from Figure 5 the average hole sizes for all samples are larger than the critical radius of 2.75 Å. Additionally, the diffusion coefficients are almost linearly related to the intensity of o-Ps (I_3) as shown in Figure 3(b), corresponding to the total number of the free volume holes. This is because the total number of free volume holes should be loosely proportional to the number of holes above the critical volumes.

One paradox in Figure 5 is that the overall percentage of free volume holes above the critical radius in the second batch of samples is larger than that in batch 1 samples; however, the diffusion coefficients of ethanol molecules in latter are lower. This might be due to the larger overlap factor, γ , in the second batch of samples, as discussed before. The different overlap factor might be due to the different engineering process and/or the degradation of the gloves after 3 years.

Correlation of Nitrile (CN) Content with Free Volume Data

The CN group content in each glove sample was determined using FTIR as described before. Because different glove samples have different thicknesses, we normalized the FTIP peak height to a thickness of 0.1 mm, which is close to the thicknesses of all samples, based on Lambert-Beer's law, $\text{Abs} = adc$ with a is a constant, d is the thickness, and c is the concentration of the absorbents. There is no clear correlation between the CN group content and the fractional free volume (f_v) as well as the number density of free volume holes, as shown in Figure 6(a,b).

However, there is a correlation between the CN group content and the average free volume hole size, as shown in Figure 7. From Figure 7, the CN content is negatively correlated to the average free volume hole size, that is, a higher the CN group content results in a smaller average free volume hole size. This is understandable when we consider the chemical structure associated, as shown the below diagram, with our previous discussion on the location of CN groups inside polymer matrix. Because CN is polar and the N atom is partially negative, the nearby CN groups have mutual repulsive Columbic force. Furthermore, from our discussion on the diffusion of polar ethanol molecules within the polymer, we conclude that CN group does not present in free volume holes but is embedded in the matrix. Therefore, the repulsive Columbic force from the polar CN groups on different polymer chains might "squeeze" the free volume holes and thus reduce the average hole size (V_f). However, this repulsive force is not strong enough to divide free volume holes, inducing more hole numbers.

It is worth noting that in the permeation test the diffusion coefficient of ethanol has a strong relationship with the fractional free volume (f_v), rather than with the average of free volume hole size (V_f). Therefore, we may conclude that the CN group content in glove samples does not solely and/or directly determine the permeation of small organic molecules through them, other factors such as the engineering process, degradation, and

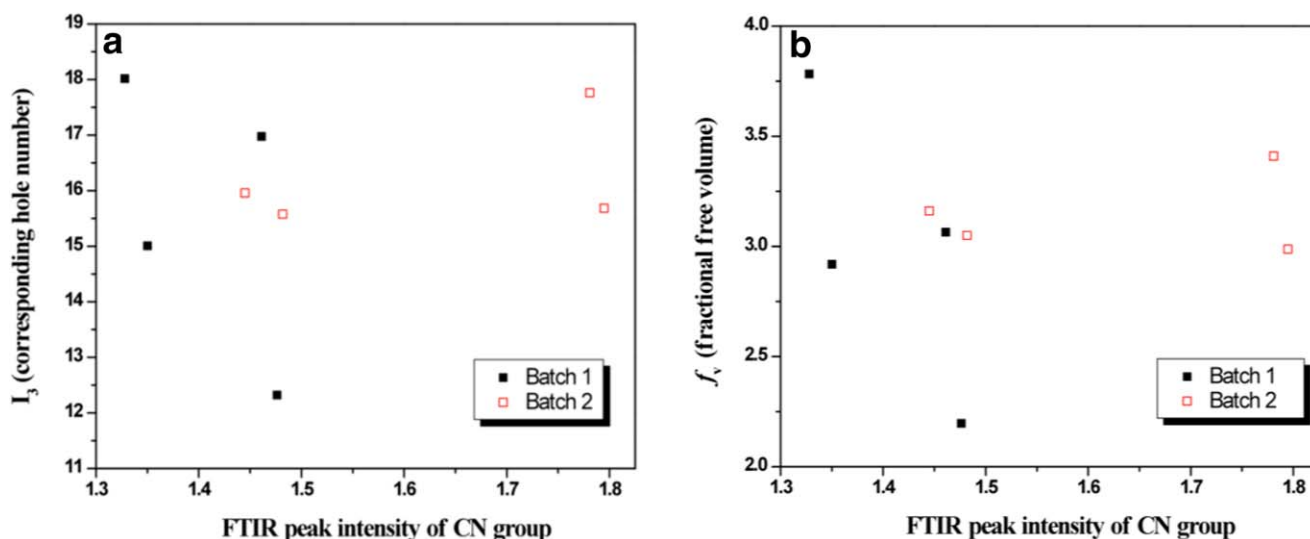


Figure 6. (a) Correlation between $\text{C}\equiv\text{N}$ peak height and the hole number density (I_3). (b) Correlation between $\text{C}\equiv\text{N}$ peak height and the fractional free volume (f_v). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

other ingredients such as pigments may also play an important role. This is consistent with the results from Phalen et al.,⁹ which demonstrated that permeation is related to both CN content and area density.

Also, from Figure 7 for the second batch of samples, free volume hole size is less sensitive to the modification of CN content, which is reflected in the slope of the fitting line. The slope of the first batch of samples is almost 10 times larger than that of the second batch of samples (101.9 vs. 9.953). The large reduction of free volume size in the first batch with the increase of CN content may indicate that the CN group might accelerate the degradation of gloves, as the CN group is relatively reactive.

It is interesting to further compare two samples with similar CN content. First, let us compare two samples from the same batch, for instance, Supreno and Ultrasense from the first batch,

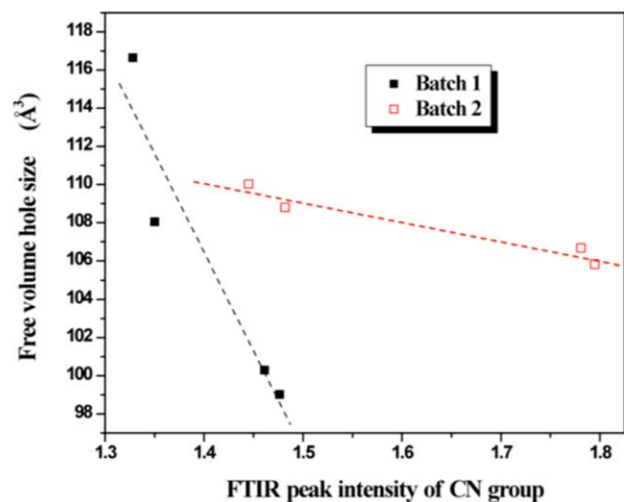


Figure 7. Correlation between FTIR $\text{C}\equiv\text{N}$ peak height and the average free volume hole size. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

or Ultraform and Xceed from the second batch. For example, Supreno and Ultrasense have almost the same CN group content, as seen in Figure 6, and this corresponds to almost identical average free volume hole size. However, the free volume hole size distributions are quite different: Ultrasense has much narrower distribution than Supreno and therefore has a lower diffusion coefficient for small ethanol molecules (6.60×10^{-7} vs. 1.18×10^{-6} cm^2/min). This indicates that the diffusion coefficient is determined not only by the free volume hole size but also the hole size distribution for the same batch of products. This is understandable as, from Figure 5, the hole size distribution is correlated to the area under the curve above the critical size (2.75 \AA), corresponding to the number of holes that are available for the diffusion process. Second, we can compare the two samples with similar free volume hole properties from two different batches, for instance, Supreno from the first batch and the Ultraform from the second batch. Both samples have almost the same average free volume hole size as well as the same hole size distribution; however, the diffusion coefficient of ethanol in Ultraform is smaller than that of Supreno (6.17×10^{-7} vs. 1.18×10^{-6} cm^2/min). This confirms that for the different batches of gloves, other factors such as additives, engineering process, etc., might also play important roles in regulating the diffusion and penetration of small organic molecules through the glove film. However, from the current data, it is not clear how these factors affect the diffusion of small organic molecules, especially since the chemical interaction between the polymer and ethanol is similar (E is same in Vrentas-Duda equation) and the free volume hole properties (average size and distribution) are also similar. These might change other properties, such as the size of hardness/softness domains in the polymer matrix.

CONCLUSIONS

Positron annihilation lifetime spectroscopy was applied to study the diffusion mechanisms of ethanol through commercial NBR gloves at the atomic level. Eight commercial gloves samples from

the same supplier, but at two different batches in time, were tested. Four samples were from an old batch purchased in 2009 and the remaining four were from a new batch purchased in 2012. The following conclusions were drawn from permeation test and positron annihilation lifetime spectroscopy measurement:

- The basic Vrentas-Duda model can well describe the diffusion of small organic molecules in commercial glove samples even with different additives (e.g., different pigments) and different engineering processes (e.g., inducing different area density).
- For the same batch of samples, the diffusion coefficients of ethanol are strongly correlated to the fractional free volumes in samples; however, such correlations are very different for the different batch of samples, probably due to the different engineering process or degradation of the gloves over time.
- Diffusion coefficient is directly correlated to the fractional free volume, which is mainly caused by the number of free volume holes rather than the average size of free volume holes.
- The diffusion process is determined by the critical volume available for polymer segments to migrate, not on the small size of ethanol molecules.
- CN groups in polymers do not present on the inner surfaces within the pores, but are embedded in polymer matrix, so they do not directly interact with ethanol molecules.
- The CN group content affects pore size, but not fractional free volume, which is directly correlated to diffusion coefficient.
- Engineering process, degradation and other additives, rather than CN group content, play a larger role in the diffusion process.

In conclusion, positron annihilation lifetime spectroscopy measures the final overall free volume holes at the atomic scale for samples with different components. The results are consistent with the free volume theory on molecule diffusion in polymers. This experiment demonstrated that the PALS technique, which has been a powerful tool in studying the free volume of polymers via model samples in research labs, can be extended to the study of commercial samples and therefore might be used as a quality control tool for glove products within industry. The use of this technique can be significantly broadened.

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