

Parameters Controlling the Swelling of Butyl Rubber by Solvents

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ABSTRACT: The method used in the past 30 years for describing the swelling of polymers by solvents is mainly based on the Hansen three-dimensional solubility parameters. However, the subjectivity of its implementation as well as its limited success for several polymers, and in particular elastomers, which constitute choice materials for protective gloves, has been reported by several authors. In this article, data obtained by Zellers et al. with butyl rubber and a list of 53 solvents are analyzed to identify the parameters controlling the swelling of this elastomer. The absence of a global effect of the Hansen affinity, solvent molar volume and saturation vapor pres-

sure, and Flory–Huggins interaction parameter has been confirmed. It was also shown that one of the main factors controlling the swelling of butyl rubber appears to be the chemical class of the solvents. Within these classes, a linear relationship between butyl rubber swelling and solvent saturation vapor pressure was observed, and the correlation with molar volume is almost as good. On the other side, no correlation can be obtained with the Hansen affinity. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 3926–3933, 2008

Key words: swelling; butyl rubber; elastomers

INTRODUCTION

As the use of toxic chemicals has increased over the years as well as the knowledge of their adverse effects on health, polymers have gained a choice place for containing, handling, and protecting from solvents. In the field of personal protective equipment and in particular for gloves, elastomers are widely used thanks to an interesting combination of chemical resistance and mechanical flexibility properties. Among them, butyl rubber offers an excellent protection against most polar chemicals in liquid, aerosol, and gaseous form, resulting from a saturated hydrocarbon structure and a low-network chain mobility.¹ With numerous applications in industrial and military protective equipment, a precise knowledge of its resistance to chemicals is required.

However, due to the huge number of chemicals available and used, a systematic characterization of the effect of every solvent and mixture of solvents on every polymer is therefore not conceivable.

Researchers have thus worked on developing methods for predicting the resistance of polymers to solvents. Hildebrand was the first to introduce the notion of solubility parameter δ , defined as the square root of the cohesive energy density of the compound.^{2,3} According to the mixture theory, two compounds are more miscible if the difference between the values of their solubility parameter, defined as their affinity A , is small.

$$A = (\delta_1 - \delta_2) \quad (1)$$

where δ_1 and δ_2 are the solubility parameters of the two compounds. However, this approach is based on the hypothesis of regular solutions.

To account for the specificity of solvent–solvent and solvent–polymer systems, where polar and hydrogen-bonding interactions are important, Hansen proposed to express the total cohesive energy density of the compound in terms of its dispersion, polar, and hydrogen-bonding contributions.^{4,5} The Hildebrand solubility parameter δ is related to the three Hansen partial solubility parameters (HSP) δ_d , δ_p , and δ_h , corresponding respectively, to the dispersion, polar, and hydrogen-bonding contributions to the total cohesive energy density, according to the following relationship:

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (2)$$

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Using the three HSPs, the affinity between Compounds 1 and 2 is expressed as:

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

where a and b are two empirical weighting factors. Usually, as δ_d values are much smaller and to make the system more symmetrical, it is common practice to set $a = 4$ and $b = 1$.⁶ A later justification of this choice of values for these weighting factors has been provided by Hansen by comparison with the Prigogine corresponding states theory of solutions.⁷

In parallel, other researchers have investigated the problem of swelling through the chemical potential of the polymer–solvent system. The Flory–Rehner model relates the swelling equilibrium to the point where the chemical potentials of the solvent inside the swollen polymer and outside its surface are equal.⁸ The Flory–Huggins parameter χ describes the interaction between the solvent and the polymer. It can be evaluated for example from swelling data^{9,10} or mechanical measurements.¹¹ It was also shown by Hildebrand and Scott¹² that the Flory–Huggins interaction parameter χ can be related to the affinity A calculated from Hildebrand solubility parameters using the following equation:

$$\chi = \chi_s + \frac{V_M A^2}{RT} \quad (4)$$

where V_M is the solvent molar volume. χ_s is a correction term associated with non-negligible entropic effects arising in systems with significant dipolar and hydrogen-bonding interactions. The validity of such relationship was demonstrated both theoretically and experimentally. The effect of various parameters like pressure and temperature on χ was compared with that predicted by the corresponding states theory of Prigogine.¹³ In addition, a good agreement with results obtained for several solvent–polymer systems was observed using Hansen affinity calculated with the three HSPs [eq. (3) with $a = 1$ and $b = 0.25$], especially for nonpolar polymers for which the correction term χ_s can be set to zero.⁷

Working in a three-dimensional reference frame using the three HSPs δ_d , δ_p , and δ_h as coordinates, Hansen observed that, for a given polymer, solvents in which that polymer is soluble can be enclosed in a more-or-less spherical zone.⁷ The coordinates of the center of this solubility sphere were identified with the polymer partial solubility parameters. This graphical method has been used over the last 20 years to characterize the resistance of polymeric protective clothing materials to swelling and permeation by organic solvents.^{14,15}

However, several authors have reported problems with the Hansen approach. First of all, the selection of the criterion differentiating “good” from “bad” solvents, i.e., solvents in which the polymer is soluble or not, does seem to have in certain cases a strong influence on the values obtained for the polymer partial solubility parameters.^{7,16} In addition, Zellers et al.¹⁶ also described how the absence of theoretically justified and experimentally observed linear relationship between the affinity and the mutual solubility of solvents with a given polymer throws doubt on the reliability of the Hansen HSP determination method for polymers. Finally, he reports that the calculated HSP values are highly dependant on the presence or the absence of a few critical solvents, the list of these critical solvents varying for each polymer.

As the Hansen affinity concept does not appear to be sufficient to explain the swelling of polymers by solvents, researchers have looked for other mechanisms affecting the interaction between solvents and polymers during the swelling process. In particular, several authors recognize today the possible influence of adsorption, absorption, and diffusion processes on the swelling of polymers by solvents. For example, the size and shape of test liquid’s molecules, which affect the diffusion coefficient, have been shown to affect the environmental stress cracking of plastics.¹⁷ On the other hand, Zellers et al. have devised two alternative methods to the Hansen graphical technique for the determination of the polymer HSPs.¹⁸ The first one uses the product of the solvent molar volume and the fractional uptake of solvent during swelling as a weighting factor for the solvent. The second one is based on a combination of the Flory interaction parameter and various weighting factors. Other authors have established a linear multiparameter relationship between the logarithm of the polymer swelling and physicochemical characteristics of the organic solvents including the refractive index, relative electric permittivity, Palm’s basicity, Reichardt’s electrophilicity, Hildebrand’s solubility parameters, and molar volume.¹⁹ Finally, McKenna et al. obtained a unique master curve for the variation of the Flory–Huggins interaction parameter as a function of the volume fraction of natural rubber swollen by six different solvents.²⁰ However, no satisfactory solution allowing the prediction of polymer swelling behavior from physicochemical characteristics of the solvent–polymer system has been obtained yet.

EXPERIMENTAL AND THEORETICAL APPROACHES

This article presents a detailed analysis of the influence of various potential relevant parameters on the

swelling of butyl rubber based on measurements carried out by Zellers et al. with a list of 53 solvents.^{16,18} The detail of the experimental procedures is described in his articles. The tested butyl rubber samples were cut out of protective gloves (Model B-161, North, Charleston, SC). Swelling was measured by weighting the samples after 5 days of immersion in the solvent at 25°C and after further drying for 2 days at 70°C. The use of postdrying weight instead of preexposure weight for the determination of butyl rubber swelling was justified by Zellers et al. by the need to exclude leaching additives from the swelling ratio calculation. Indeed, solvents, in addition to swelling polymers, may extract entities from the material. For example, leached-out carbon black, which may be added in protective glove formulations, was associated by the authors with an amber tint appearing in certain solvents during swelling experiments.¹⁶ Zellers et al. reported differences generally smaller than 3% but sometimes larger than 10% between pre-exposure and postdrying weights. As the swelling ratio calculation should only take into account the weight of absorbed solvent, the weight of the additives that have leached out during the swelling process needs to be subtracted from the sample weight.

For the study presented in this article, the three HSPs were used to compute the Hansen affinity between butyl rubber and solvents. In addition, the effects of the solvent molar volume and saturation vapor pressure on butyl rubber swelling were also studied. The data analysis proceeded through successive steps. First, the effect of the three primary parameters on the whole set of solvents was considered. Then, the solvents were grouped according to their affinity and chemical class to try to identify the factors controlling the swelling of butyl rubber. In addition, the variation of swelling as a function of the Flory–Huggins interaction parameter χ was also studied.

RESULTS AND DISCUSSION

For the purpose of our analysis and to provide a more physical description of the phenomenon, the solubility data from Zellers et al. article¹⁸ have been expressed in terms of volume swelling using tabulated physical characteristics for the list solvents. The Hansen affinity between butyl rubber and each solvent was calculated using eq. (3) and the values of the three HSPs obtained by Zellers et al.¹⁶ According to the criterion favored by Hansen in his method for the determination of polymer HSPs,¹⁶ only solvents producing a swelling superior to 10% in butyl rubber (including benzonitrile with a swelling ratio of 9.9%) were considered. For each of these 32 solvents, Table I displays the volume swelling S_v meas-

TABLE I
Values of Butyl Rubber Volume Swelling S_v , Butyl Rubber—Solvent Affinity A , and Solvent Molar Volume V_M and Saturation Vapor Pressure P_{vs} for the 32 Solvents Producing More than 10% Swelling

Solvents	S_v (%)	A (MPa ^{1/2})	V_M^a (cm ³)	P_{vs} (KPa)
Benzonitrile	9.9	6.6	103.03	0.1 ^c
Nitrobenzene	10	8.4	103.4	0.034 ^c
Methyl acetate	11	7.5	79.89	28.8 ^c
Ethyl formate	12	8.8	80.83	32.5 ^c
Benzaldehyde	14	7.1	102.01	0.13 ^b
Methyl ethyl ketone	15	7.4	90.2	12.71 ^b
Diethyl carbonate	16	3.5	122.4	1.42 ^c
Ethyl acetate	18	5.9	98.54	12.49 ^b
Dioxane	20	5.8	86.13	5.08 ^b
Butyraldehyde	23	7.1	90.47	15 ^c
3-Pentanone	28	6.2	106.4	4.9 ^c
1,2-Dichloroethane	32	6.3	79.44	10.5 ^c
Cyclohexanone	33	4.6	104.14	0.58 ^b
Ethyl ether	64	5.9	105.5	71.6 ^b
Methylene chloride	86	5.4	64.43	58 ^c
n-Butylamine	119	5.9	98.76	12.23 ^b
Benzene	142	3.5	89.48	12.69 ^b
Diethylamine	185	5.6	104.23	31.7 ^c
n-Hexane	191	5.9	131.1	20.17 ^b
Tetrahydrofuran	223	6.1	82.44	21.6 ^b
n-Heptane	227	5.3	147.01	6.093 ^b
Toluene	227	2.1	106.56	3.78 ^b
Chloroform	253	3.1	80.66	26.266 ^b
Triethylamine	258	3.0	139.67	9.2 ^c
o-Xylene	275	1.9	121.14	0.88 ^b
1,1,1-Trichloroethane	292	2.2	100.28	16.53 ^c
Mesitylene	299	3.7	139.52	0.33 ^c
Carbon tetrachloride	316	3.5	97.15	15.33 ^b
Methylcyclohexane	369	3.9	128.18	5.73 ^b
Trichloroethylene	371	3.0	90.13	9.2 ^b
Cyclohexane	373	3.7	108.86	13 ^c
Perchloroethylene	391	5.5	102.81	2.466 ^b

^a From Ref. 18.

^b From Ref. 21.

^c From Ref. 22.

ured on butyl rubber as well as the butyl rubber—solvent Hansen affinity A , the solvent molar volume V_M , and saturation vapor pressure P_{vs} at 25°C. The volume swelling values range from 9.9% for benzonitrile to 391% for perchloroethylene. It must be mentioned that, even for such a large swelling ratio, Zellers et al. reported that all butyl rubber samples were recovered intact after immersion.¹⁶

Looking for a general law for butyl rubber swelling

As a first step, the effect of the three selected primary parameters, i.e., the Hansen affinity, solvent molar volume, and saturation vapor pressure, on butyl rubber swelling for the whole group of solvents situated above the 10% criterion was studied. Figures 1–3 display the variation of butyl rubber

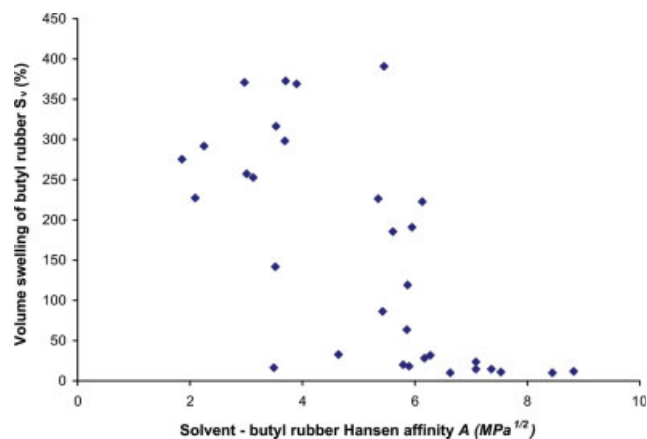


Figure 1 Variation of butyl rubber volume swelling as a function of the butyl rubber-solvent Hansen affinity. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

volume swelling as a function of respectively, the solvent-butyl rubber Hansen affinity, the solvent molar volume, and the solvent saturation vapor pressure. It can be seen that no direct relationship between butyl rubber swelling and any of these three primary parameters can be found, in accordance with what is generally reported in the literature.¹⁹

In addition, the effect of the Flory–Huggins interaction parameter χ was also investigated. As butyl rubber is a nonpolar elastomer, the correction term χ_s in eq. (4) was set to zero. Figures 4 and 5 display the variation of butyl rubber volume swelling as a function of the Flory–Huggins parameter obtained with the affinity calculated respectively, using the Hildebrand expression [eq. (1)] and the Hansen's formalism [eq. (3) with $a = 1$ and $b = 0.25$]. No correlation can be observed in either case.

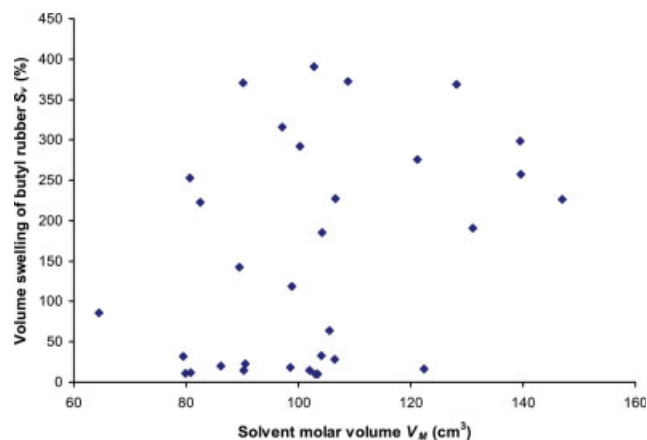


Figure 2 Variation of butyl rubber volume swelling as a function of the solvent molar volume. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

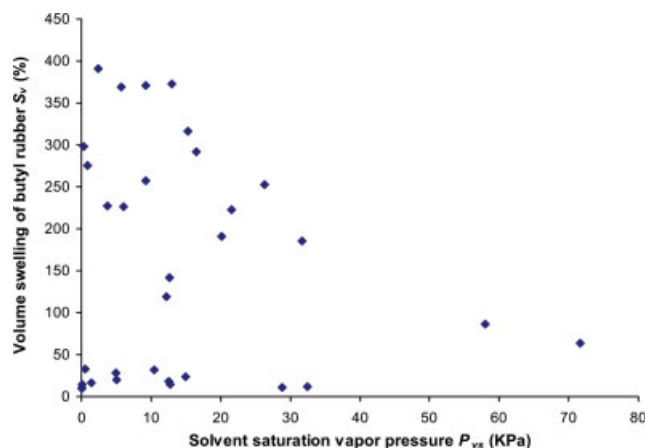


Figure 3 Variation of butyl rubber volume swelling as a function of the solvent saturation vapor pressure. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Grouping solvents according to their affinity with butyl rubber

To evaluate if a better description of butyl rubber swelling can be provided by another combination of the effects of the three primary parameters than the Flory–Huggins interaction parameter, the influence of the solvent molar volume and saturation vapor pressure was studied with solvents of similar Hansen affinity with butyl rubber. Given the characteristics of the solvents, two groups of significant size were assembled, Group I corresponding to an affinity situated between 3 and 4, and Group II between 5 and 6. The lists of solvents included in Groups I and II are provided in Table II, along with their affinity value.

The effect of grouping solvents according to their affinity with butyl rubber on the influence of the

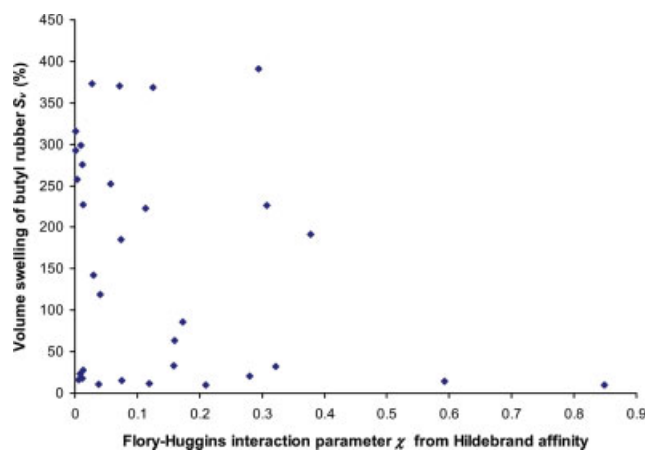


Figure 4 Variation of butyl rubber volume swelling as a function of the Flory–Huggins parameter obtained with the Hildebrand expression for the affinity. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

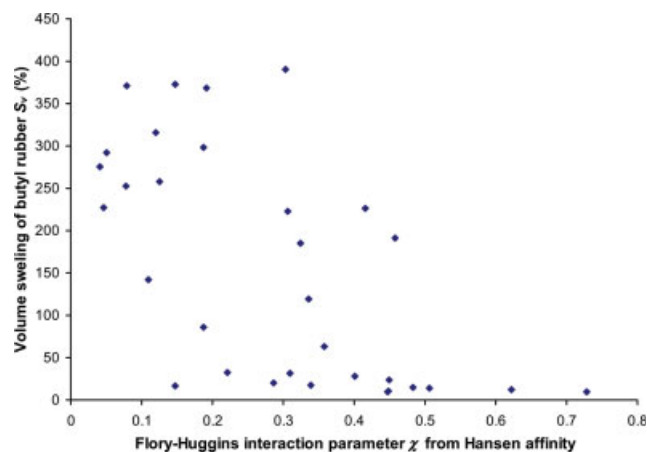


Figure 5 Variation of butyl rubber volume swelling as a function of the Flory–Huggins parameter obtained with the affinity calculated according to Hansen’s formalism. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

two remaining parameters, i.e., the solvent molar volume and saturation vapor pressure, on butyl rubber volume swelling is shown, respectively, in Figures 6 and 7. No real improvement in the distribution shape can be obtained either with the molar volume or the saturation vapor pressure.

Grouping solvents according to their chemical class

When looking for factors controlling the swelling of butyl rubber, it was noticed that, among the 53 solvents tested by Zellers et al., the 10 solvents produc-

TABLE II
List of Solvents with an Affinity with Butyl Rubber Located between 3 and 4 (Group I) and 5 and 6 (Group II)

Solvent	Affinity
Group I	
Triethylamine	3.0
Chloroform	3.1
Diethyl carbonate	3.5
Benzene	3.5
Carbon tetrachloride	3.5
Mesitylene	3.7
Cyclohexane	3.7
Methylcyclohexane	3.9
Group II	
n-Heptane	5.3
Methylene chloride	5.4
Perchloroethylene	5.5
Diethylamine	5.6
Dioxane	5.8
Ethyl ether	5.9
n-Butylamine	5.9
Ethyl acetate	5.9
n-Hexane	5.9

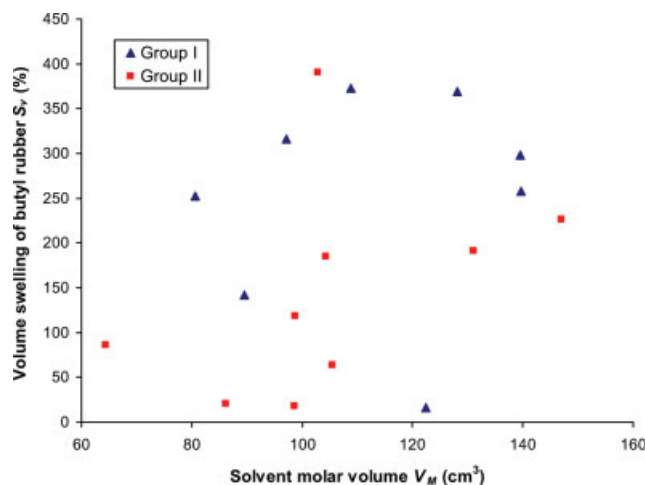


Figure 6 Variation of butyl rubber volume swelling as a function of the solvent molar volume for solvents of Group I (Hansen affinity between 3 and 4) and Group II (Hansen affinity between 5 and 6). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

ing the most important swelling of butyl rubber belonged to only four chemical classes among the 13 covered by Zellers et al. list. As shown in Table III, five of these 10 solvents are chlorinated aliphatics, two of them are aromatic hydrocarbons, two of them are cyclic aliphatics, and the last one is an amine. In the case of good solvents, solvent chemical class thus seems to have a large influence on butyl rubber swelling. As a consequence, it was decided to investigate again the effect of the three primary parameters, the Hansen affinity, solvent molar volume, and

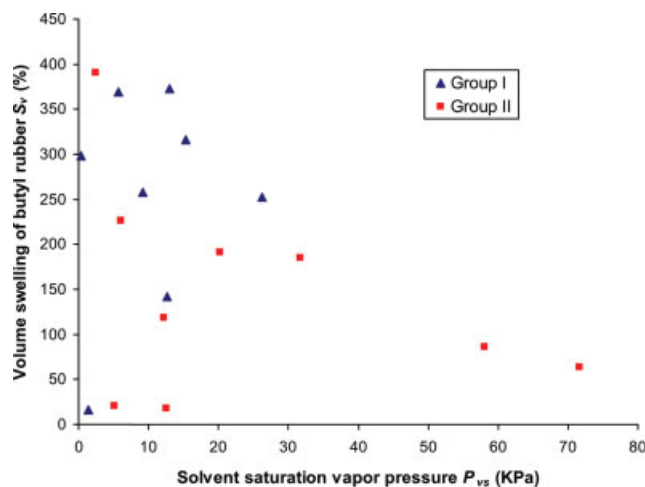


Figure 7 Variation of butyl rubber volume swelling as a function of the solvent saturation vapor pressure for solvents of Group I (affinity between 3 and 4) and Group II (affinity between 5 and 6). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE III
Characteristics of the 10 Solvents Producing the Most Important Swelling of Butyl Rubber

Solvent	Volume swelling (%)	Chemical class
Perchloroethylene	391	Chlorinated aliphatic
Cyclohexane	373	Cyclic aliphatic
Trichloroethylene	371	Chlorinated aliphatic
Methylcyclohexane	369	Cyclic aliphatic
Carbon tetrachloride	316	Chlorinated aliphatic
Mesitylene	299	Aromatic hydrocarbon
1,1,1-Trichloroethane	292	Chlorinated aliphatic
o-Xylene	275	Aromatic hydrocarbon
Triethylamine	258	Amine
Chloroform	253	Chlorinated aliphatic

solvent saturation vapor pressure, as well as that of the Flory–Huggins interaction parameter, whereas grouping solvents by chemical class. As this trend was observed for good solvents, the analysis was restricted to solvents producing a swelling ratio larger than 50% for butyl rubber.

Figures 8–12 show the variation of the volume swelling of butyl rubber, respectively, as a function of the butyl rubber–solvent Hansen affinity, the solvent molar volume, the solvent saturation vapor pressure as well as the Flory–Huggins interaction parameter calculated using the Hildebrand and Hansen affinities, for the list solvents belonging to the chlorinated aliphatic and aromatic hydrocarbon chemical classes. Correlations between swelling and either the Hansen affinity or the Flory–Huggins parameter calculated with the Hansen affinity are not improved when regrouping solvents by chemical class (see Figs. 8 and 12). On the other hand, butyl rubber volume swelling exhibits linear relationships with solvent molar volume and saturation vapor

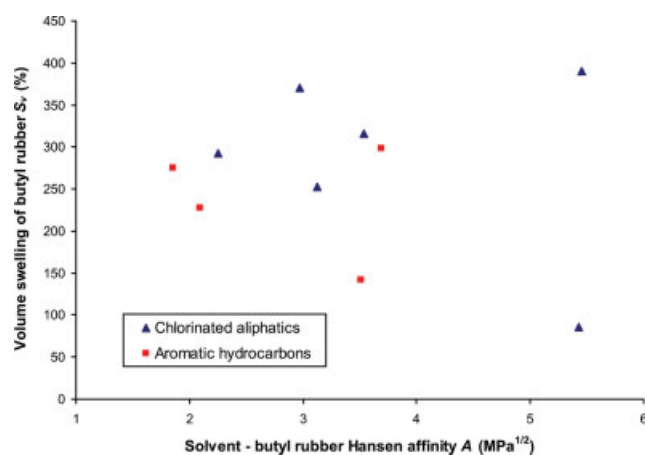


Figure 8 Variation of butyl rubber volume swelling as a function of the butyl rubber–solvent Hansen affinity for chlorinated aliphatic and aromatic hydrocarbon solvents. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

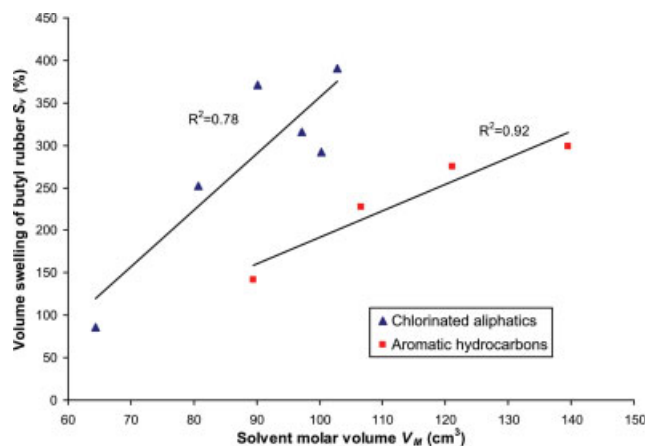


Figure 9 Variation of butyl rubber volume swelling as a function of the solvent molar volume for chlorinated aliphatic and aromatic hydrocarbon solvents. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

pressure for chlorinated aliphatic and aromatic hydrocarbon solvents as shown, respectively, in Figures 9 and 10. Determination coefficients higher than 0.97 were obtained in the case of the influence of the solvent saturation vapor pressure (Fig. 10) whereas they are situated between 0.78 and 0.92 for molar volume (Fig. 9). Concerning the Flory–Huggins interaction parameter calculated with the Hildebrand affinity, a linear relationship is observed for aromatic hydrocarbons but not for chlorinated aliphatic solvents (see Fig. 11). The explanation for such difference in behavior between both classes of chemicals may lay in the fact that three out of the four aromatic hydrocarbons have very similar values for the Hildebrand affinity. In that case, the variation of butyl rubber volume swelling with the Flory–Huggins interaction parameter may eventually be

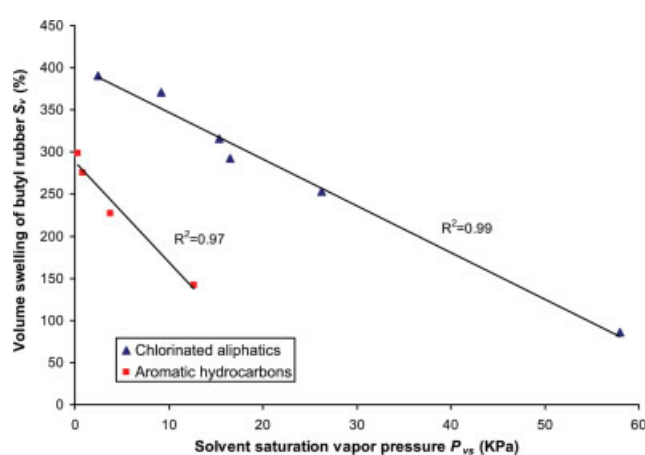


Figure 10 Variation of butyl rubber volume swelling as a function of the solvent saturation vapor pressure for chlorinated aliphatic and aromatic hydrocarbon solvents. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

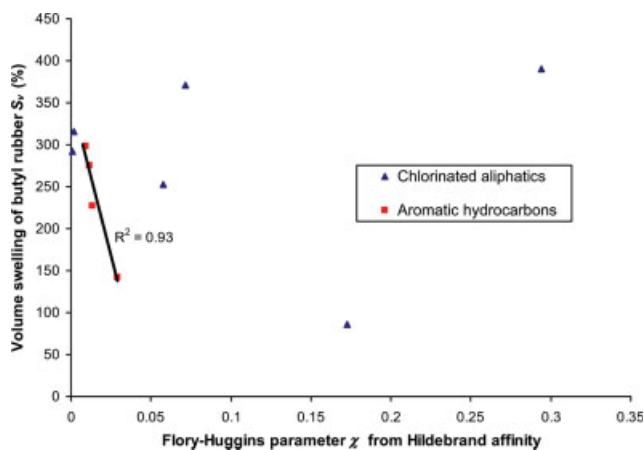


Figure 11 Variation of butyl rubber volume swelling as a function of the Flory–Huggins parameter obtained with the Hildebrand expression for the affinity, for chlorinated aliphatic and aromatic hydrocarbon solvents. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

mostly provided by the molar volume [according to eq. (4)]. On the other hand, Hildebrand affinity values for the list chlorinated aliphatics vary over a wide range. It must be noted that such approach of isolating solvents by chemical class had already been proposed, with more or less success, to correlate elastomer diffusion and sorption coefficients with the solvent molar volume as well as polymer molar swelling with the Dimroth and Reichardt polarity parameters.^{23,24}

A possible explanation for the negative correlation between butyl rubber swelling and solvent saturation vapor pressure observed for chlorinated aliphatic and aromatic hydrocarbon solvents (see

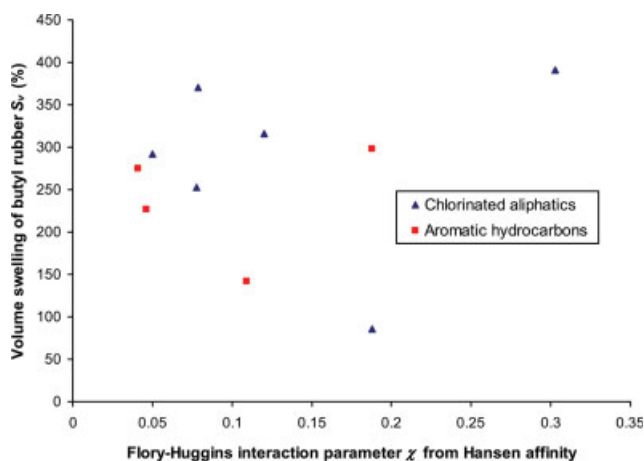


Figure 12 Variation of butyl rubber volume swelling as a function of the Flory–Huggins parameter obtained with the affinity calculated according to Hansen’s formalism, for chlorinated aliphatic and aromatic hydrocarbon solvents. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Fig. 10) is related to the fact that diffusion, which takes part in the swelling process, can be affected by solvent–polymer thermodynamic interactions,²⁵ thus by saturation vapor pressure values. As butyl rubber has an excellent resistance to gas permeation, solvents with a high saturation vapor pressure may have more difficulty diffusing into the elastomer, hence leading to smaller values of the swelling ratio.

On the other hand, the positive relationship that was observed between solvent molar volume and butyl rubber swelling for chlorinated aliphatic and aromatic hydrocarbon solvents within their chemical classes (Fig. 9) raises questions in terms of physical meaning. Indeed, as it has been observed experimentally, larger values of molar volume are expected to hinder solvent penetration into the polymer.¹⁹ However, a negative relationship between saturation vapor pressure and molar volume values has been reported for example by Bel’skii²⁶ for a list of 297 chemicals. This increase in butyl rubber swelling with solvent molar volume is thus consistent with the negative relationship observed between butyl rubber swelling and solvent saturation vapor pressure and shown in Figure 10. In addition, a similar effect of solvent molar volume on butyl rubber swelling can be found in the literature for a series of C₅–C₁₆ alkanes (see Fig. 13, the experimental data are extracted from²⁷ and were taken originally from the work of Bristow and Watson²⁸ carried out on vulcanized butyl-400 commercial polymer). In that case, a first linear increase is observed for three alkanes between C₅ and C₇. It is followed by a drop in butyl rubber swelling before a second linear increase is observed with a smaller slope for three other alkanes between C₈ and C₁₆.

More work is needed to fully understand the phenomena behind the observed tendency relative to

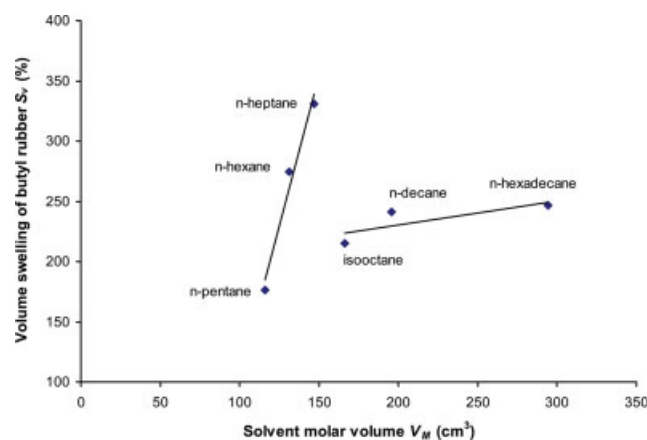


Figure 13 Variation of butyl rubber volume swelling as a function of the solvent molar volume for a series of alkanes (data from,²⁸ lines are provided as a guide to the eye). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the effect of solvent molar volume on swelling observed with butyl rubber. However, a hypothesis can be tentatively proposed to explain the broken line displayed in Figure 13. It is related to the existence of a critical volume for solvent molecules, which depends on the material porosity. When that critical volume has been reached, in agreement with Hansen's concept of surface resistance to molecule absorption,²⁹ solvent penetration into the material can be strongly reduced, leading to a decrease in swelling ratio.

CONCLUSIONS

A detailed analysis of the effect of three primary parameters, the affinity according to Hansen theory, the solvent molar volume, and the solvent saturation vapor pressure, as well as the Flory–Huggins parameter obtained both from the Hansen and Hildebrand expressions for the affinity, on butyl rubber swelling has been carried out using experimental data reported by Zellers et al. for a list of 53 solvents. It confirmed that none of the afore-mentioned parameters produces a definite trend for the whole group of solvents. However, when solvents are grouped by chemical class, strong correlations between butyl rubber swelling and both solvent molar volume and saturation vapor pressure are obtained. This shows that, although solvent chemical class is one of the main factors controlling the butyl rubber swelling process, physical interactions between the solvent and the polymer also have a large influence.

For good solvents within the two chemical classes studied, high saturation vapor pressure values have been associated with a reduced swelling of butyl rubber, possibly in relationship with its high resistance to gas permeation. The observed positive correlation between solvent molar volume and butyl rubber swelling can be explained by the negative relationship between solvent molar volume and saturation vapor pressure. In addition, a hypothesis has been proposed that, when a critical value has been reached for the solvent molar volume, the diffusion process is hindered thus producing a drop in the swelling ratio. This particular behavior may be amplified in the case of butyl rubber because of its low porosity.

These results offer potential tools for trying to predict the swelling behavior of materials used in personal protective equipment when dealing with good solvents. The article also provides some hypothesis on microscopic aspects of butyl rubber swelling by solvents. Further research on this subject should investigate if the correlations observed between butyl rubber swelling and both solvent molar vol-

ume and saturation vapor pressure for chlorinated aliphatic and aromatic hydrocarbon solvents also stand for other chemical classes of solvents. Moreover, such analysis should be reproduced with other types of elastomers relevant for personal protective equipment.

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