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RESEARCH ARTICLE

THE USE OF THE HANSEN SOLUBILITY PARAMETERS IN THE SELECTION OF PROTECTIVE POLYMERIC MATERIALS RESISTANT TO CHEMICALS

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ABSTRACT

This article focuses on solubility of chemicals on polymeric materials as an approach for selecting the best protective materials. The Hansen three-dimensional solubility parameters (HSP) were used to obtaining the solubility parameters of five of the most used polymer materials from swelling tests with forty chemicals covering a broad spectrum of HSP values. The approach considers that for chemical substances that are soluble in a polymer protective material, this material will not be resistant. Inversely, for polymer materials for which chemical substances are not soluble, the material will be resistant. Based on the experimental data, the Hansen HSPiP software was used to calculate the solubility parameters (the center of the sphere) and radii, R, of the polymer spheres for Nitrile, Neoprene, Natural Rubber, Viton and Butyl Rubber glove materials. Based on the calculated HSP values for the glove materials, the differences with the HSP values (dissimilarity A value following the Hansen approach) for more 1 200 chemical solvents were calculated. The Hansen solubility approach states that for chemicals where the solubility parameter distance (A) of a given chemical to the center of the polymer sphere is higher than the R value, $A/R > 1$, the material will be resistant and inversely, for $A/R < 1$ the material will be not resistant. In this study, a new approach that considers the Hansen Sphere with a modified R was developed. An algorithm that compared the predicted values with close to nine hundred experimental data from the literature, allows defining for each material a zone of uncertainty with minimum and maximum R values. A Software (ProtecPo) was developed that allows the selection of the best glove materials avoiding a dangerous "trial and errors" approach. In any case this software is a substitute of permeation tests to determine the level of chemical resistance to a chemical or mixtures of chemicals.

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INTRODUCTION

Millions of workers worldwide are exposed to a variety of hazardous chemicals that can be absorbed through the skin what is considered the primary route of exposure. NIOSH estimated there are more than 13 million workers in US potentially exposed to chemicals (http://www.cdc.gov/niosh/topics/skin/default.html). Engineering, administrative, and work practice controls can minimize the worker's contact with chemicals (Anderson, 2014). Where these controls are inadequate or difficult to implement, the use of chemical protective materials can minimize the risk of exposure.

Protective materials resistant to chemicals used in glove, footwear and clothing are considered the last line of defense when a chemical hazard cannot be removed from the working environment. These chemical protective materials are made from polymers. The selection of chemical protective materials is a major problem due to the number of chemicals used in industrial operations that are growing day to day and the variety of polymers that can potentially be used. According to REACH, it is estimated that there are more than 100 000 chemical substances, on the market, without considering formulations (REACH, 2007). More than 1000 new chemicals substances are introduced on the market every year, most of them having complex formulations with high potential of dermal exposure. It is well known that no polymeric material exists that protects against all classes of chemicals.

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Permeation test methods have been developed to characterize the resistance of a protective material to chemical substances (ASTM, 2013; ISO6529, 2013). Experimentally, the material chemical resistance is determined by two values; the breakthrough time (BT) that is the time between the first contact between the chemical substance with the external surface of the protective membrane and the detection at its internal surface and the permeation rate (PR), which is the rate at which the chemical permeates the material. There are some Databases containing information on permeation tests for a few numbers of chemical substances and protective materials (Forsberg, 2014). Also, glove and protective material manufacturers provide information on their products for a certain number of the most used chemical substances (http://www.ansellpro.com/download/Ansell_8thEditionChemicalResistanceGuide.Pdf; http://www.showagroup.com/innovation/chemical-resistance). However, all those information's are limited and almost no data exist for other protective materials such as the one used in protective suits, footwears, etc. Chemical safety data sheets often recommends "Use chemical resistant gloves" without any specification.

The goal of this study was to develop a software based on the Hansen Solubility Parameters (Hansen, 2007) to predict the material chemical resistance and to be used as a pre-selection tool of the best protective materials. The experimental data for obtaining the HSP parameters for five of the most used glove materials (Nitrile, Neoprene, Butyl, Natural Rubber and Viton) was limited to 24 hrs swelling tests and calculated using the Hansen HSPiP software. These predictions were compared with the information from glove manufacturers and databases. The software tool is called ProtecPo(https://protecpo.inrs.fr/ProtecPo/jsp/Accueil.jsp?langue=EN).

Theoretical Background

Permeation of a chemical substance through a polymer membrane is considered as a phenomenon that takes place in three steps: an absorption step where the chemical (gas or liquid) comes in contact with the external surface of the polymer membrane and dissolves into the material (some time called the solubility step); the diffusion step where the chemical diffuses through the polymer membrane at a molecular level to reach its internal surface(Hansen, 1988); the desorption step where the chemical evaporates or otherwise leaves the internal surface(Perkins et al., 1985). At this step, the chemical can come in contact with the skin of the protective material user. In the permeation process, the chemical substance diffuses through the polymer membrane, from the highest concentration at the contact surface to the lower concentration on the opposite side.

Following the Fick's first law, the diffusion of a chemical through a polymer membrane can be represented as follow;

$$J = P\frac{(p_1-p_2)}{l} \tag{1}$$

Where J represents the permeation rate, P the permeation coefficient that is a function of the chemical diffusing through a polymer membrane of thickness l, from the higher(p1) to the lower(p2) concentration expressed in terms vapor pressures. Permeation (P) is related to diffusion (D) and solubility (S) coefficients as follow(Crank, 1968);

$$P = DS \tag{2}$$

These parameters can be obtained experimentally through permeation tests. The rate of permeation is directly proportional to how fast the molecules can diffuse as well as their solubility, this establishing the concentration gradient across the film. Considerable effort has been done to develop models to describe chemical permeation through protective materials. In the Hansen eBook(Hansen, 2007;Steven Abbott, 2008), examples are presented that demonstrate that it is possible to simulate the diffusion of chemicals through a given protective glove material with breakthrough times and steady state permeation rates simultaneously in agreement with the experimental data. However the enormous variety of polymers, the use of fillers and additives, the degree of polymer cross linking, etc. makes the task complex. In the present study, the solubility of a chemical into a polymer membrane is considered as the primary criteria in the selection of the best skin protective material.

The solubility approach

It is recognized that the solubility of a chemical in a polymer barrier plays an important role in the chemical permeation. The higher the chemical solubility into the external surface of polymer barrier, the higher the concentration, and consequently the higher the permeation rate and shorter the breakthrough time will be. However, it is important to take into account that no direct correlation exist between the chemical solubility into the polymer barrier and the permeation rate. Other parameters as the molecular volume of the diffusing chemical substance, the polymer crystallinity, the fillers contained into the polymer material, etc. could affect the permeation rate. In this study a primary predictive approach of the resistance of polymer protective materials based on the solubility approach was developed.

The solubility between two substances was described by Hildebrand in 1949 by the concept of solubility parameter. The solubility parameter, δ, of a solvent is the square root of the vaporization energy (ΔE) divided by its molar volume (V)(Barton, 1991).

$$\delta = \sqrt{\frac{\Delta E}{V}} \tag{3}$$

The more similar the solubility parameters of two substances, the higher will be the solubility between them and hence the expression "Like dissolves like". Charles Hansen established that the solubility parameter of a solvent or polymer is the result of the contribution of three types of interactions: dispersion forces, polar interactions and hydrogen bonds (Hansen, 2007; Hansen, 1967).

$$\delta_t = \sqrt{\delta_d^2 + \delta_p^2 + \delta_h^2} \tag{4}$$

δt is the total solubility (Hildebrand) parameter resulting from the contribution of each of the three Hansen solubility parameters (HSP). Thus, each substance can be represented by a point with its three-dimensional coordinates in a figure with δd, δp, and δh axes. The resistance of a polymer material to a chemical can be estimated from the difference in their respective solubility parameters. The more similar the solubility parameters of the chemical and polymer, the more soluble the chemical will be in the polymer, and consequently the less resistant the material will be. To calculate the HSP difference between a polymer and a pure chemical substance, Hansen proposed the following equation:

$$A = \sqrt{4\left(\delta_d^P - \delta_d^S\right)^2 + \left(\delta_p^P - \delta_p^S\right)^2 + \left(\delta_h^P - \delta_h^S\right)^2} \tag{5}$$

A represents the dissimilarity factor, and the superscripts P and S correspond respectively to the polymer and the chemical. For the interaction between a polymer material and a binary mixture of chemicals, A is represented as follows:

$$A = \sqrt{4\left(\delta_d^P - \delta_d^M\right)^2 + \left(\delta_p^P - \delta_p^M\right)^2 + \left(\delta_h^P - \delta_h^M\right)^2} \tag{6}$$

Where

$$\partial_d^M = \delta_{d_1}^{S_1}\varphi_1 + \delta_d^{S_2}\varphi_2\ ;$$
$$\delta_p^M = \delta_{p_1}^{S_1}\varphi_1 + \delta_{p_2}^{S_2}\varphi_2;$$
$$\delta_h^M = \delta_{h_1}^{S_1}\varphi_1 + \delta_{h_2}^{S_2}\varphi_2$$

φ_1 and φ_2 are the volume fractions of solvents 1 and 2 respectively. Figure 1 shows a Hansen solubility sphere. The centre of the sphere corresponds to the HSP parameters δd, δp, and δh of a polymer. These parameters are referred to as D, P, and H, respectively, below. The radius R represents an arbitrary limit considered here to be resistance or not based on sufficient solubility or not. In this example, the polymer is resistant to the pure solvents 1 and 2 (A > R) but not to a mixture of S1 + S2 = M (A < R).

Previous studies demonstrated that for the case of a mixture of two solvents that have a certain degree of solubility into a polymer material, the resistance of the material decreases strongly compared to the resistance to the individual solvents in terms of breakthrough times, permeation rates and swelling (Lara, 1992; Georgoulis, 2005; Perron, 2002). This have been interpreted by the fact that the presence of one solvent in contact with a polymer increases the solubility of the other one (plasticizing effect) (Vahdat, 1993). This phenomena can be qualitatively predicted using equation 6 as was previously demonstrated (Lara, 1992).

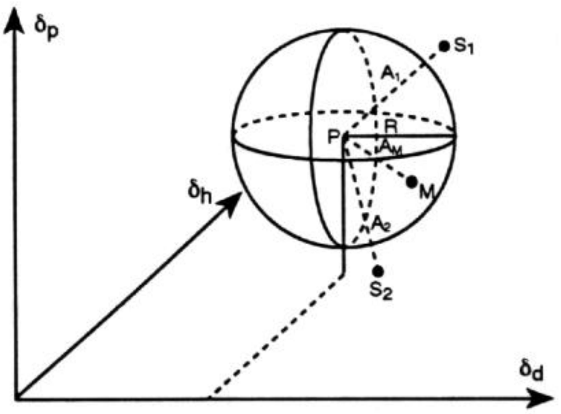


Figure 1. Hansen representation of the polymer solubility sphere

Following this simple approach, the radius of the sphere is such that the polymer material will be resistant to all chemicals that are outside the sphere. Hansen formalized the concept of RED (Relative Energy Difference), given by the following relationship:

$$\text{RED} = A/R \tag{7}$$

Thus, in this model, for RED > 1 the material is considered to be resistant to a solvent, whereas for RED < 1 the material is considered to be not resistant to the solvent. Efforts has been consecrated to associate the solubility parameters to the chemical resistance of protective material (Hansen, 1988). Henriksen in 1982 tried to associate HSP with BT chemical PR with poor success for some materials (r=-0.5) and good for others (r=0.9). Perkins et al. (1985) analyzed the use of HSP for predicting the chemical resistance to single and chemical mixtures and concluded that it is useful for selecting the best protective materials candidates. Furthermore, it has been demonstrated that is not possible to predict the material chemical resistance of solvents mixtures based on data of permeation tests performed with single solvents.

MATERIALS AND METHODS

Glove materials. Commercially available gloves of the most used polymer materials (Nitrile, Neoprene, Natural Rubber, Viton and Butyl non supported gloves) were selected for the swelling tests. A complete list the glove materials submitted to swelling tests is presented in Table 1.

Chemicals. Chemicals having a broad spectrum of Hansen solubility parameters were selected for the swelling tests. A complete list of the chemicals used for the swelling test is presented in Table 2.

Methods – Swelling tests

Pieces of glove materials of 10 mm x 50 mm were completely immersed in 10 mL liquid chemical in a 12mL glass vial closed with caps and maintained at 21 0C for 24 hours. The volume changes and the weight changes were precisely measured as follows; for volume changes measurements; first, the dry sample material was placed into a Petri dish covered with a microscope cover glass. The length and width of the piece were precisely measured with a Vernier caliper TESR with a precision of 0.1 mm. Then, the sample material was placed on a metallic piece covered with a microscope cover glass and the thickness was measured with an Elcometer 456 thickness gauge with a precision of 0.1 mm. The thickness of the material was extracted from the measure of both pieces without the sample. The same procedure was followed after the 24 hrs immersion time. All tests were performed in double.

The volume changes were calculated as follows:

$$Sv = \frac{Vf}{Vi} - 1 \tag{8}$$

Where Sv is the swelling volume change, Vi and Vf correspond to the initial and the final volumes respectively.

The weight changes values (Sm) were obtained by weighting the piece of material before the immersion (Wi) and after the 24 hours immersion time using aMettler-Toledo XPE205 balance with a precision of 1 mg. After the immersion, the material was dried with an absorbent paper to remove the excess of solvent at the surface to obtain the final weight (Wf).

Table 1. Glovematerials

Company/model/thickness	Material	Company/model//thickness	Material
Showa-Best/Nitri-Solve 727/0.41mm	Nitrile	Showa-Best/723/0.5mm	Neoprene
Ansell/Sol-Vex 37-165/0.66mm	Nitrile	Ansell/29-865/0.5mm	Neoprene
Ansell/Canner & Handler 356/ 0.41mm	Natural Rubber	MAPA/Chem-Ply 414 320/ 0.74mm	Neoprene
Viton glove KCL 890 Vitoject (0.70 mm)	Fluoroelastomer	Showa-Best/Chem Master N+L/0.66mm	Neoprene
North/B-131/0.3mm	Butyl		

The weight change was calculated as follows;

$$Sm = \frac{Wf}{Wi} - 1 \qquad (9)$$

Sm values were used to verify the correspondence between the volume changes and the weights changes for each experiment. For any case were non correspondence existed, the tests were repeated.

RESULTS

More than 3000 swelling tests were performed with the forty selected solvents. Using the HSPiP software from the Hansen eBook, the R and D, P, H values for the polymeric glove materials (Nitrile, Neoprene, Butyl Viton and Natural Rubber) were obtained. Figure 2 shows an example of the sphere representation for the calculated R and HSP values for the Natural Rubber glove material. In the data input in the software following the Hansen approach described above, solvents with values Sv>0.5 are considered as good. Solvents with Sv< 0.5are considered as bad solvents. However, it is important to point out that for Sv< 0.5 values does not means that the material will be resistant to the chemical but that the material resistance increases when the Sv decreases to 0.For this project, a good solvent was defined as a chemical to which the protective material is not resistant. Any chemical substance that produces volumes changes Svof the protective material higher than 0.5 is dangerous in terms of its resistance to the chemical. In the data input of to the HSPiP software, all chemical-material pairs that in the swelling tests give values of Sv> 0.5, they are quoted as 1. For chemical-material pairs with Sv< 0.5 are quoted “0”.

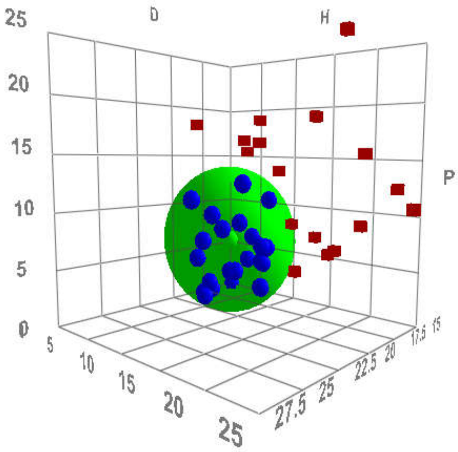


Figure 2. Example of a calculated Hansen solubility sphere for a Natural Rubber glove material

The eBook computer program evaluates the input data following a desirability function that is described as follows (Steven Abbott, 2008):

DATAFIT = (A1 * A2 * …An)1/n

where n is the number of the experimental data. The DATAFIT reaches 1.0 when all chemicals substances that produce Sv> 0.5 are inside the sphere and those Sv< 0.5 are outside the sphere. It is possible that errors for very small or larger molecules or materials containing additives, chemical substances that should be included inside the sphere (RED < 1) fall outside the sphere. For these cases, the chemical substance should be temporally deleted from the data input and recalculation will generate a better correlation and consequentially improved HSP values. Blue dots in Figure 2 correspond to the solvents with HSP coordinates outside the calculated sphere (RED > 1 in Table 3) meaning the glove material is predicted to be resistant. The red dots inside the sphere (RED < 1 in Table 3) correspond to the solvents to which the material is predicted to be not resistant. In some cases, anomalous behaviour could be observed; a solvent to which experimental results show that the material is not resistant, is found to be close but outside of the sphere limit (A > R).

Development of an algorithm based on generic polymer materials

It is well known that chemical protective materials from different companies may have different resistance against the same chemical substance even if the generic polymer used in its manufacture is the same. Differences due to the manufacture process, polymer source, additive contains, degree of polymer reticulation, fillers, etc. may result in differences in the chemical resistance performance. In order to decide the approach to follow in the development of an algorithm allowing to develop a computer tool for the selection of the best chemical protective materials, preliminary tests were performed on materials manufactured with the same generic polymer material from different manufacturers. Swelling tests for two of the most used polymer materials in the gloves manufacture, Neoprene and Nitrile, from different companies, were primarily performed with thirty chemical solvents. Results are presented in Table 4 and Table 5 for Neoprene and Nitrile respectively. The results in Table 4 demonstrated that even if small differences exists between Sv values for the Neoprene gloves from the different manufacturers, the general behavior is the same. These is also true for the case of the Neoprene glove containing Natural Rubber. The same type of results are obtained with the two Nitrile Glove materials presented in Table 5. Based on these results, it was decided to select five glove materials as representative of each generic polymer material; for Natural Rubber, the Ansell/Canner &Handler 356/ 0.41mm glove; for Nitrile, the Ansell 37-165 glove; for Neoprene, the MAPA Chem-Ply 414 glove; for Butyl, the North Butyl B141 glove; forViton,glove KCL 890 Vitoject.

Table 2. Chemical substances used in the swelling tests

#	Chemicalname	δD (MPa1/2)	δP (MPa1/2)	δH (MPa1/2)	MVol (g/mol)
1	2-Propanol	16	6.1	16	76.9
2	Acetone	16	10	7	73.8
3	1-Butanol	16	5.7	16	92
4	Chlorobenzene	19	4.3	2	102
5	Cyclohexanol	17	4.1	14	106
6	o-Dichlorobenzene	19	6.3	3.3	113
7	DimethylFormamide (DMF)	17	14	11	77.4
8	Ethanolamine	17	16	21	60.3
9	Ethylene Glycol MonoethylEther	16	7.2	14	97.5
10	Hexane	15	0	0	131
11	N-Methyl-2-Pyrrolidone (NMP)	18	12	7.2	96.6
12	Nitroethane	16	16	4.5	72
13	Propylene Carbonate	20	18	4.1	85.2
14	Trichloroethylene	18	3.1	5.3	90.1
15	n-ButylAcetate	16	3.7	6.3	133
16	Acetophenone	19	9	4	117
17	γ-Butyrolactone (GBL)	18	17	7.4	76.5
18	Chloroform	18	3.1	5.7	80.5
19	DiacetoneAlcohol	16	8.2	11	124
20	MethyleneDichloride(DCM)	17	7.3	7.1	64.4
21	1.4-Dioxane	18	1.8	9	85.7
22	Di-n-ButylEther	15	3.4	3.2	170
23	Ethylene Glycol	17	11	26	55.9
24	Isophorone	17	8	5	150
25	MethylIsobutylKetone (MIBK)	15	6.1	4.1	126
26	Nitromethane	16	19	6.1	54.1
27	Tetrahydrofuran (THF)	17	5.7	8	81.9
28	EthylAcetate	16	5.3	7.2	98.6
29	Benzene	18	0	2	89.5
30	CarbonTetrachloride (0 Dipole Moment)	18	0	0.6	97.1
31	Cyclohexane	17	0	0.2	109
32	EthyleneDichloride	18	7.4	4.1	80.1
33	DimethylSulfoxide (DMSO)	18	16	10	71.3
34	Ethanol	16	8.8	19	58.6
35	DiethylEther	15	2.9	4.6	105
36	Formamide	17	26	19	39.9
37	Methanol	15	12	22	40.6
38	Nitrobenzene	20	11	3.1	103
39	N-MethylFormamide	17	19	16	59.1
40	Toluene	18	1.4	2	107

Table 3. Example of Calculated RED values using the HSPiP software for the Natural Rubber glove (see Figure 2)

Chemical name	D	P	H	Score	RED
Acetone	15.5	10.4	7.0	0	1.06
Acetophenone	18.8	9.0	4.0	1	0.66
Benzene	18.4	0.0	2.0	1	0.72
1-Butanol	16.0	5.7	15.8	0	1.81
n-ButylAcetate	15.8	3.7	6.3	1	0.70
γ-Butyrolactone (GBL)	18.0	16.6	7.4	0	1.66
CarbonTetrachloride	17.8	0.0	0.6	1	0.72
Chlorobenzene	19.0	4.3	2.0	1	0.43
Chloroform	17.8	3.1	5.7	1	0.53
Cyclohexane	16.8	0.0	0.2	1	0.75
Cyclohexanol	17.4	4.1	13.5	0	1.48
Di-n-ButylEther	15.2	3.4	3.2	1	0.64
DiacetoneAlcohol	15.8	8.2	10.8	0	1.26
o-Dichlorobenzene	19.2	6.3	3.3	1	0.51
DiethylEther	14.5	2.9	4.6	1	0.88
DimethylFormamide (DMF)	17.4	13.7	11.3	0	1.63
DimethylSulfoxide (DMSO)	18.4	16.4	10.2	0	1.83
1,4-Dioxane	17.5	1.8	9.0	1	0.98
Ethanol	15.8	8.8	19.4	0	2.34
Ethanolamine	17.0	15.5	21.0	0	2.81
EthylAcetate	15.8	5.3	7.2	1	0.77
EthyleneDichloride	18.0	7.4	4.1	1	0.41
Ethylene Glycol	17.0	11.0	26.0	0	3.21
Ethylene Glycol MonoethylEther	15.9	7.2	14.0	0	1.61
Formamide	17.2	26.2	19.0	0	3.54
Hexane	14.9	0.0	0.0	1	1.00
Isophorone	17.0	8.0	5.0	1	0.53
Methanol	14.7	12.3	22.3	0	2.88
N-MethylFormamide	17.4	18.8	15.9	0	2.53
MethylIsobutylKetone (MIBK)	15.3	6.1	4.1	1	0.62
N-Methyl-2-Pyrrolidone (NMP)	18.0	12.3	7.2	0	1.15
MethyleneDichloride	18.2	6.3	6.1	1	0.56
Nitrobenzene	20.0	10.6	3.1	1	0.99
Nitroethane	16.0	15.5	4.5	0	1.45
Nitromethane	15.8	18.8	6.1	0	1.92
2-Propanol	15.8	6.1	16.4	0	1.90
Propylene Carbonate	20.0	18.0	4.1	0	1.84
Tetrahydrofuran (THF)	16.8	5.7	8.0	1	0.77
Toluene	18.0	1.4	2.0	1	0.51
Trichloroethylene	18.0	3.1	5.3	1	0.50

Table 4. Swelling tests results (Sv) for Neoprene materials from different manufactures

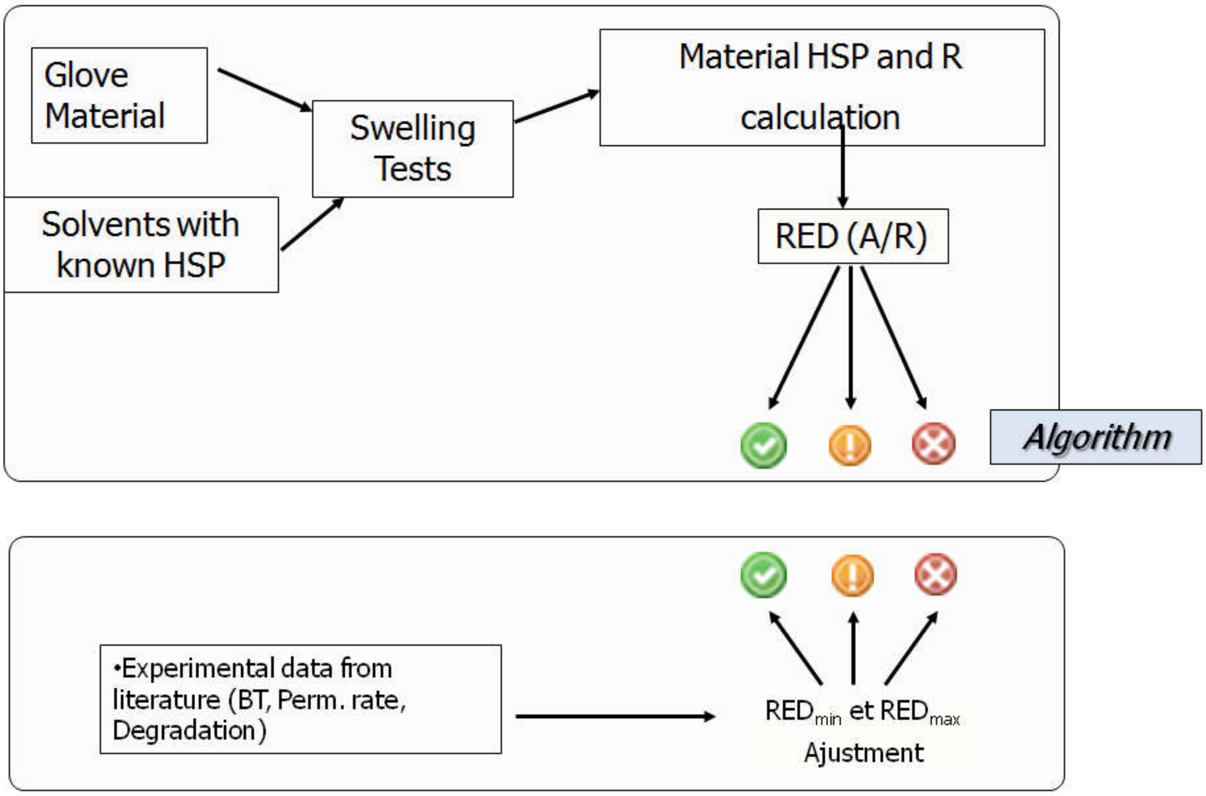
Chemical name	1	2	3	4	Score
Acetone	0.51	0.55	0.38	0.57	1
2-Propanol	0.16	0,18	0.15	0.12	0
Chlorobenzene	4.03	3.76	3.70	3.49	1
Cyclohexane	1.84	1.34	2.45	1.11	1
Cyclohexanol	0.37	0.32	0.34	0.30	0
o-Dichlorobenzene	3.89	3.67	3.65	3.40	1
Di-n-ButylEther	0.87	0.99	0.82	0.94	1
DimethylFormamide (DMF)	0.50	0.76	0.50	0.89	1
Ethanol	0.12	0.20	0.12	0.16	0
Ethanolamine	0.39	0.35	0.36	0.33	0
Nitroethane	0.25	0.27	0.23	0.36	0
Trichloroethylene	4.40	3.49	4.12	2.70	1
n-ButylAcetate	1.83	1.90	1.72	1.76	1
Acetophenone	1.82	2.52	1.70	2.34	1
Chloroform	4.57	3.91	4.29	3.62	1
DiacetoneAlcohol	0.38	0.47	0.35	0.34	0
MethyleneDichloride	3.20	2.98	3.00	2,76	1
1.4-Dioxane	1.98	2.26	1.85	2.10	1
Isophorone	2.43	2.95	2.27	2.73	1
MethylIsobutylKetone (MIBK)	1.70	2.17	1.50	2.00	1
Propylene Carbonate	0.05	0.14	0.05	0.10	0
Tetrahydrofuran (THF)	4.49	3.98	4.21	3.69	1
EthylAcetate	1.32	1.48	1.23	1.28	1
Benzene	3.50	3.52	3.28	3.27	1
CarbonTetrachloride	4.23	3.09	3.86	2.87	1
Cyclohexane	1.84	1.33	2.45	1.14	1
DiethylEther	1.82	1.14	1.71	1.06	1
Formamide	0.45	0.27	0.42	0.25	0
Nitrobenzene	1.52	1.89	1.43	1.76	1
Toluene	4.01	3.31	3.75	3.07	1

1. MAPA Chem-Ply 414; 2.Showa-Best Chem Master; 3. Showa-Best Neoprene 723; 4. Ansell 29-865.

Table 5. Swelling tests results (Sv) for Nitrile materials from different manufactures

Chemical name	1	2	Score
Acetone	1.70	2.90	1
2-Propanol	0.22	0,40	0
Chlorobenzene	3.10	4.10	1
Cyclohexane	0.06	0.25	0
Cyclohexanol	0.05	0.49	0
o-Dichlorobenzene	3.35	4.60	1
Di-n-ButylEther	0.11	0.21	0
Ethanol	0.30	0.40	0
Ethanolamine	0.04	0.48	0
Nitroethane	2.75	1.38	0
Trichloroethylene	2.05	2.80	1
n-ButylAcetate	1.27	1.60	1
Acetophenone	4.60	5.80	1
Chloroform	5.35	7.20	1
DiacetoneAlcohol	1.62	2.02	0
MethyleneDichloride	4.80	6.50	1
1.4-Dioxane	2.20	2.80	1
Isophorone	3.80	5.30	1
MethylIsobutylKetone (MIBK)	1.98	2.80	1
Propylene Carbonate	1.04	1.40	1
Tetrahydrofuran (THF)	2.90	5.10	1
EthylAcetate	1.50	1.60	1
Benzene	1.60	2.05	1
CarbonTetrachloride	0.70	0.75	1
Cyclohexane	0.06	0.25	0
DiethylEther	0.40	0.45	1
Formamide	0.04	0.28	0
Nitrobenzene	3.82	5.80	1
Toluene	1.42	1.60	1

1. Ansell 37-165; 2. Showa-Best Nitri-Solve 727 0.5mm.



BT Green = Sv = 0 and BT > 480 minutes; Yellow = Sv> 0 and < 0.5 and BT < 480 minutes and > 10 minutes; Red = Sv> 0.5 and BT < 10 minutes or material degradation.

Figure 3. Representation of the algorithm

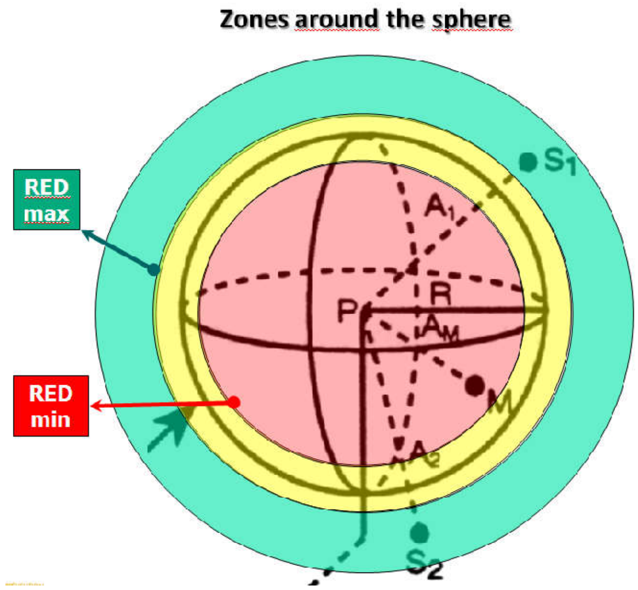


Figure 4. Representation of the three zones concept. The green zone is where the calculated RED values for chemicals indicate the material is resistant. The red zone is for chemicals to which the material is not resistant. Yellow is for a zone of uncertainty where permeation tests should be performed

Table 6. Calculated HSP and R values for the glove materials using the HSPiP software. The REDmin and RED max values were determined as described on the text

Material	D	P	H	R	REDmin	REDmax
1. Natural Rubber	16.4	3.1	4.1	6.8	1.00	2.50
2. Nitrile	20.4	12.4	4.1	13.9	1.00	1.30
3. Butyl	17.3	1.4	2.6	6.3	1.00	1.25
4. Neoprene	19.2	3.9	3.9	10.2	1.00	1.60
5. Viton	15.6	11.3	5.4	7.9	1.00	1.53

Ansell-Canner & Handler 356; 2. Ansell-Solvex 37-165; 3. North Butyl-B131; 4. MAPA Chem-Ply 414 320; 5. Vitonglove KCL 890 Vitoject

Based on the swelling data for these gloves materials, the HSP values were calculated and the results are presented in Table 6.

Development of an algorithm

Figure 3 shows the sequence followed in the development of an algorithm used to estimate the material chemical resistance. Each glove material was submitted to immersion tests with the 40 selected solvents. The swelling results allowed obtaining R and HSP values for the glove materials. Based on these data, the RED (A/R) values were calculated for each solvent-material pair, for all the solvents of the database (close to 1200 solvents). In an iterative process, the theoretical values of RED for each chemical substance-material pair were compared to the permeation data from the Forsberg database (6), thus allowing the level of consistency between the predictions on the material chemical resistance and the literature recommendations to be established. The algorithm used assumes that the radius of the sphere which determines the solubility limit is not a fixed value but can be represented by a zone of uncertainty around the sphere. This concept is represented in Figure 4 by a sphere with three colours; yellow represents the uncertainty zone (where Sv values could be between < 0.5 and > 0). The other zones are green for the chemicals to which the material is predicted to be resistant ($Sv = 0$) and red for chemicals to which the material is predicted to be not resistant ($Sv \geq 0.5$). These are separated by REDmin and REDmax values that are specific for each material. For a material, the REDmin and REDmax values were selected in an empirical way to achieve the highest possible level of consistency. The algorithm developed was validated by comparing its predictions with experimental results found in the scientific literature or in guides published by protective glove manufacturers. This algorithm is rather conservative assuming the worst case scenario; a material is immersed in the chemical during 24 hours. It was developed to give the fewest possible "false-positive results" (meaning a positive recommendation for a material which in fact is not resistant). The algorithm can be refined as new experimental data become available, giving a better and better representation of reality. In the example presented in Figure 4, REDmax is shifted to 1.2 instead of 1, thus predicting with certainty that a material will be resistant to any chemical substance with higher values The 1.0-1.2 YELLOW zone is the one where the predictions are uncertain (intermediate resistance). With these adjustments, it was possible to optimize the predictions and to ensure that they are valid with close to 98% certainty.

Conclusion

Using the calculated Hansen Solubility Parametersand the published experimental permeation data from North Safety Gloves, Ansell Gloves and the Quick Selection Guide from Forsberg, an algorithm based on a new concept was developed to estimate the protective materials resistance to chemicals. The HSP parameters and the sphere radii R for each glove materials were calculated using the HSPiPsoftware based on experimental data obtained in swelling tests using the forty chemicals having a broad spectrum of solubility parameters. The chemical resistance of the protective materials was calculated in a first step using the Hansen RED concept. For RED > 1 the material was considered resistant to the chemicals and inversely, for RED < 1 the material was considered not resistant. In a second step, the predicted data were compared with results from more than 800 permeation tests from the scientific literature, glove manufacturer's data and the Forsberg database. Given that for many cases, differences between the prediction and the experimental data existed, an algorithm was developed to obtain the best correlation between the predicted material chemical resistance and experimental data. The new concept states that the Hansen sphere does not have rigidly defined R limits, and consequently rigidly defined RED values, but a more diffuse boundary zone exists between REDmax and REDmin values. These values were determined for five of the most used protective materials and the predictions were compared with the databases and literature values with success. The software is in the Web as https://protecpo.inrs.fr/ProtecPo/jsp/Accueil.jsp?langue=EN. It can be used to identifying the best protective glove materials against single chemicals and mixtures. This software is useful to select the best protective glove materials against chemicals and thus avoiding a dangerous "trail and error" method. However, in any case the ProtecPo software can be used in substitution tothe permeation tests.

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