Development of a predictive model for choosing cure agents for elastomer blends

Guilherme Cañete Vebber,[1] **Cláudio Nunes Pereira**[2]

[1]Universidade Estadual do Rio Grande do Sul (UERGS), Unidade de Bento Gonçalves, Rua Benjamin Constant, 229, Centro, CEP 95700-000, Bento Gonçalves Rio Grande do Sul, Brazil
[2]Tecnano Pesquisas e Serviços Ltda, ITCientec, Incubadora Tecnológica Cientec, Fundação de Ciência e Tecnologia, Rua Washington Luiz 675, CEP 90010-460, Porto Alegre, Rio Grande do Sul, Brazil
Correspondence to: C. N. Pereira (E-mail: claudio@tecnano.com.br)

ABSTRACT: In elastomer blends with either polarity differences or unbalanced double bond concentration, cure agents have a preferential partition to one of the phases, with a tendency of having overcure in one phase and undercure in the other. To achieve proper vulcanization and improved performance in the final product, it is essential to have a correct balance between solubility and miscibility of each of the various cure agents in the elastomer blend composite. Cure agents with varying polarities and various reactivities have different crosslinking densities in the rubber compound. A homogeneous crosslinking density leads to superior mechanical properties. The method presented in this work includes a new tool based on a genetic optimization algorithm for assessing the partitioning of cure agents in different elastomers and their blends. The quantitative data allowed for a series of analyses of the solubility of the cure agents in the elastomer mixtures of different phases and was validated by correlation with their physico–chemical and mechanical properties of the resulting blend. This is an important tool for planning a cure system in rubber blends and to avoid incorrect partitioning of cure agents and consequent uneven curing of the final compound. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41929.

INTRODUCTION

Rubbers are one of the most widely used groups of materials in engineering products. Their advantages such as elasticity and high damping make them dominant in various applications including tires, dampers, gaskets, seals, and conveyor belts. However, in order to produce its unique material properties, the rubber compound, which is generally a mixture of rubber, vulcanization agent, accelerator, fillers, and several additional ingredients, needs to be vulcanized to form a cohesive rubber based solid.[1]

The interactions between different chemical substances in a polymeric compound, like rubber, are best characterized using thermodynamic models that estimate the interaction energy, promoting the cohesion, adhesion, or separation between different phases. Among the thermodynamic models applied to the development of polymeric formulations, the Hansen three-dimensional model is worth noting. Hansen solubility parameters (HSP) are widely used to predict the affinity between components of paints, plastics, oils, and polymers and other functions.

HSP are numerical constants (δ_d, δ_p, δ_h) associated with intermolecular cohesion forces or energies between molecules of a substance.[2] They therefore represent non polar dispersion or induced dipole forces (δ_d), polar or permanent dipole forces (δ_p) and hydrogen bonding (δ_h). Any substance may be represented by a point $(x, y, z) = (\delta_d, \delta_p, \delta_h)$ in a three-dimensional space, the axes of which are the orthogonal HSP, called "Hansen space." Within the Hansen space, a solute is represented not only by its HSP but also by a solubility radius R_0, thereby defining a "sphere of solubility," within which the substances considered "good solvents" should be included and the substances considered "nonsolvents" should be excluded.[3]

Because of the successful use of Hansen's model in practice, its use has been recently extended for the selection of elastomer cure agents.[4,5] Despite early promising outcomes, there were divergent results, particularly with regard to the correct values of cure agents and sulfur HSP, which are reassessed in this present contribution to the subject.

Previously, it had been shown through the swelling of polymers in organic solvents that, as an elastomer is vulcanized, some of

the HSP change in the resulting compound, increasing the energy dipole and hydrogen bonding (δ_p, δ_h) of the elastomer.[6] This physico-chemical change occurs during the process of rubber vulcanization, in which the elastomer acquires polarity and capacity of an acid–base interaction. Thus, elemental sulfur, a substance with low polarity used in the vulcanization process, transforms into a mixture of several more polar sulfur derivatives, which interact with the unsaturated bonds in rubber.

Substances Involved in the Vulcanization Process

The sulfur molecule (S_8) is essential to promote crosslinking between elastomer polymer chains, a process called vulcanization, due to the use of sulfur and heat. This crosslinking is important to give properties, such as high tensile strengths, high tear energies, and improved dynamic performance to the elastomer base, making it useful for industrial application.

In addition to sulfur and heat, a metal oxide (such as zinc oxide) and a carboxylic acid (typically stearic acid) or a metal soap are added as process activators. Besides these basic ingredients of the elastomer formulation, it is currently common to use cure agents with the aim of increasing efficiency and quality in industrial production. They are responsible for accelerating the process and improving the rheometric curve of elastomer compounds, thus optimizing production time or reducing scorch time, offering security for production and increasing the ratio between disulfide and polysulfide bridges. Therefore, the goal of the cure system is to reach a more efficient and homogeneous cure among different polymeric phases in the elastomer compound, thus resulting in a better finished product.[5]

Vulcanization

The sulfur-based vulcanization is a complex process that involves disulfide or polysulfide molecular chain crosslinking networks, depending on the density and homogeneity of the sulfur and cure agents applied as well as their partition into different elastomer phases in the rubber composition.[5]

It is worth noting that most of these additive molecules are polar, while sulfur has a negligible polar character,[7] so a correct selection of elastomers and cure agents is fundamental, but even so sometimes a compatibilizing agent is necessary. The present study will show that the solubility of the evaluated cure agents in different elastomers is different and is related to their HSP.

In elastomer blends with either polarity differences or unbalanced double bond concentration (difference in molar concentration of double bonds between the rubber phases), cure agents have a preferential partition to one of the phases, with a tendency of having overcure in one phase and undercure in the other. In addition, it must be taken into account that the solubility of activators, such as zinc oxide, which function as vulcanization activators, also interferes with the reactivity of the accelerators within the rubber compound and thus the crosslink kinetics of the sulfur vulcanization. The use of activators and polar fillers would give preferential solubility to polar cure agents. This fact also interferes with the vulcanization of the elastomer compound and has to be taken in consideration when evaluating the vulcanization results. To achieve proper vulcani-

zation and improved performance in the final product, it is essential to have a correct balance between the solubility of each of the various cure agents in the elastomer blend composite. This is valid for the different components in the polymer or elastomer formulation (such as in the case of thermoplastic elastomer blend vulcanizates).

In a review article on elastomer blends, Mangaraj confirms that different cure agents with varying polarities (given as being equivalent to solubility parameters) and various reactivities have different crosslinking densities in the rubber compound.[8] A homogeneous crosslinking density leads to superior mechanical properties. Thus, the correct selection of cure agents and better distribution of the different elastomer phases leads to improved mechanical properties of the compound.

In elastomer development, HSP have also recently been used in the prediction of the partition of reinforcing mineral fillers in composites; for example, Schuster et al. describes the carbon black partition in different elastomer blends and quantitatively correlated the prediction with the HSP.[9]

METHODS

The same elastomers evaluated by Schröder et al.[10] were applied for sulfur or cure agent HSP calculation: ethylene-propylene-diene-terpolymer rubber (EPDM); cis-polyisoprene, named natural rubber (NR); polybutadiene rubber (BR); styrene-butadiene copolymer rubber with 23% (SBR 23) or 64% of styrene (SBR 64); and acrylonitrile-butadiene copolymer rubber with 18% (NBR 18), 34% (NBR 34) or 49% (NBR 49) of acrylonitrile. This study, which presents the solubility or dispersibility of elemental sulfur and various cure agents in these elastomers, is the basis for developing the predictive model. The cure agents studied were: tetramethylthiuram disulfide (TMTD), tetrabenzylthiuramdisulfide (TBTD), tetramethyl thiuram monosulfide (TMTM), N-cyclohexyl-2-benzothiazole sulfenamide (CBS), N-tert-butyl-2-benzothiazyl sulfenamide (TBBS), 2-mercaptobenzothiazole rubber (MBT), dibenzothiazole disulfide (MBTS), zinc diethyldithiocarbamate (ZDEC), zinc dibutyldithiocarbamate (ZDBC), and zinc dibenzyldithiocarbamate (ZBEC).

According to Schröder et al.,[10] the solubility experiments have been carried out using rubber and rubber additives of commercial grade of several suppliers. To measure the solubility limit of a chemical in a selected rubber the chemical was added in steps of 0.5 phr (parts per hundred of rubber) up to 7.0 phr to a rubber sheet on an open mill by Rubicon (roller distance: 150 mm, width: 320 mm) with a temperature setting of 60°C and a friction of 1 : 1.25. The resulting compounds were homogenized and sheeted off at a thickness of ~1 mm. The compounds were pressed in an Agila PE 100 hydraulic laboratory press at 100°C and 180 bar for 15 min between transparent film. The resulting sheets were demolded, cut in two pieces and optically inspected at once with a light microscope by Olympus, type BH2. Below the solubility limits the sheets were always clear. High above the solubility limits the sheets could be opaque or milky. The first half of the sheets was kept at room

temperature in the dark. The second half of the sheets was kept in an hot air oven at 50°C in the dark. The samples were optically reinspected after 24, 48, 72, and 96 h. As soon as the solubility limit of a chemical in a rubber was reached, single crystallites could be seen after a certain period of time. Once formed, these crystals grew in size over the monitoring period.

The polymers, copolymers, and terpolymer elastomers HSP (δ_i) were calculated from the volume fraction (ϕ_j) and the HSP of its n monomer constituents (δ_{ij}), according to the following equations:

$$\delta_i = \sum_{j=1}^{n} \delta_{ij}\phi_j \tag{1}$$

$$\sum_{j=1}^{n} \phi_j = 1 \tag{2}$$

where $i = d$, p, h and δ_d, δ_p, δ_h are the solubility parameters taken from Hansen.[2]

The HSP of the sulfur and cure agents were also estimated, based on the solubility of the cure agents with each rubber experimentally measured by Schröder et al.[10] As the predictive method is based on binary input data (representing the solubility of cure agents in different elastomers), the arithmetic mean solubility between each cure agent and elastomer pair, supplied by Schröder et al., was used as a threshold value. For any cure agent, elastomers with solubility values above/below average were considered soluble/insoluble and their solubility values changed to one/zero. The resulting set of solubilities, combined with the previously derived HSP of the elastomer were used as inputs in a genetic optimization algorithm to calculate the HSP of sulfur and cure agents.[3]

According to the methodology developed by Hansen,[2] the distance in Hansen space from each elastomer to each cure agent is called solubility parameter distance (R_a) and is calculated as:

$$R_a = \sqrt{4(\delta_{d1}-\delta_{d2})^2 + (\delta_{p1}-\delta_{p2})^2 + (\delta_{h1}-\delta_{h2})^2} \tag{3}$$

where (δ_{i1}) are the elastomers and (δ_{i2}) the cure agent HSP components. The constant "4" is justified in theory as a convenient factor for defining spherical regions of solubility.

It is obvious that solubility or high affinity requires $R_a < R_0$, so a RED (relative energy difference) number is often used to quantify R_a distances relative to the solubility radius R_0:

$$RED = \frac{R_a}{R_0} \tag{4}$$

By this definition, RED = 0 is equivalent to no energy difference, RED < 0 indicates high solute–solvent affinity, RED > 1 indicates low affinity and RED = 1 (or around 1) reflects a boundary condition.

To deal with elastomer blends comprising of two elastomers (two distinct phases), the RED distance concept is extended by defining a mixture relative energy distance (mRED). This new parameter measures the average distance of the cure agents to the two elastomer phases, measured by volume or weight fractions (ϕ), according to the available data and RED distances to each elastomer, using the following equation:

$$mRED = \sum_{j=1}^{n} \left(RED_j\phi_j\right) \tag{5}$$

The solubility parameter R_a distances are similarly extended to deal with elastomer blends by defining a mixture solubility parameter distance (mR_a), calculated by:

$$mR_a = \sum_{j=1}^{n} \left(R_{aj}\phi_j\right) \tag{6}$$

After calculating the HSP and solubility radius (R_0) for each cure agent, the quality of the results is first compared using a function called "Datafit," which measures the fraction of elastomers correctly located in relation to the Hansen sphere of solubility of the cure agent. It is variable from 0 (worst possible fit) to 1 (perfect fit). Thus, for perfect matching, good (soluble) elastomers should be inside the sphere, and bad (insoluble) ones outside it. When properly located, good elastomers are called "true positives" and bad elastomers are called "true negatives." When incorrectly located, good elastomers are called "false negatives" and bad elastomers are called "false positives."

The Datafit function is given by:[3]

$$Datafit = \sqrt[n]{(A_1 \times A_2 \times \ldots \times A_n)} \tag{7}$$

where n is the number of elastomer blends (or elastomers) and the A_i quotients are given by:

$$A_i = e^{-[\text{ERROR DISTANCE}(i)]} \tag{8}$$

where ERROR DISTANCE(i) is the error distance of the elastomer blend to the cure agent solubility sphere boundary. When any elastomer blend (i) is correctly located, ERROR DISTANCE(i)=0 and A_i=1; otherwise, ERROR DISTANCE(i) is given by the absolute difference $|mR_{ai}-R_0|$ and $A_i < 1$, where mR_{ai} are the mixture solubility parameter distances, calculated by eqs. (3) and (6), and R_0 is the cure agent solubility radius.

Datafit values are the most important parameters within the optimization process to find HSP elastomer and cure agents. For this task, a genetic algorithm is applied, running in Lab-VIEW (National Instruments) environment.[3] Genetic algorithms are heuristic stochastic global optimization methods that mimic natural processes of biological evolution, such as selection of individuals, mutation, and recombination of genes. In the context of HSP calculation, the genetic algorithm promotes competition between different sets of HSP and solubility radius (four genes corresponding to an individual). Selection of the best individual after several algorithm iteration cycles (the evolution) is guided according to the purpose for which it is applied: Datafit maximization. Therefore, Datafit value is the chosen

Table I. HSP Estimated from Monomers Taken from Ref. 2

Elastomer	δ_d (MPa$^{0.5}$)	δ_p (MPa$^{0.5}$)	δ_h (Mpa$^{0.5}$)	δ_t (Mpa$^{0.5}$)
NR	14.7	1.4	4.1	15.3
BR	14.7	1.7	6.2	16.0
EPDM	16.5	0.7	1.1	16.6
SBR 23	15.6	1.5	5.7	16.7
NBR 18	15.0	4.5	6.3	17.6
SBR 64	17.2	1.3	4.9	18.0
NBR 34	15.3	7.0	6.4	19.0
NBR 49	15.5	9.4	6.5	20.4

individual fitness parameter, just as strength, beauty, intelligence, or immunity could be fitness factors for animal species.

The genetic algorithm starts with a large initial population (usually 10,000), from which the best (1024) are selected to be the first parent set. A percentage (95%) of parents has a percentage (100%) of the four genes mutated by a random top-limited (1) amount before they recombine genes (2 crossover points chosen at random), and generate the next population (8192). From this generation, again the best are selected, having their genes mutated and recombined to produce the following generation. This evolutionary process repeats cyclically until Datafit is higher than a tolerance factor (based on previous tests). At the end of the process, the best individual gives ideal Hansen solubility parameters and radius for the tested elastomer or cure agent.

Besides comparing Datafit values, the final results of the genetic optimization process are evaluated by a truth table, based on the mRED distances and solubilities. This set of evaluation factors comprises the quantity of true positives (TP), true negatives (TN), false positives (FP), and false negatives (FN), as well as sensitivity ($TP/(TN+FP)$), specificity ($TN/(TN+FP)$) and accuracy ($(TP+TN)/(TP+TN+FP+FN)$).

Predictive Model Validation
To validate the predictive method and to illustrate its potential use in the evaluation of elastomer blend vulcanization, an evaluation is made to see if the solubilities between the elastomers and cure agents are predicted by the calculated RED (mRED) distances from each rubber (elastomer blend) to the cure agents. Later, the same distances are correlated with mechanical and physico-chemical properties of the final compound.

RESULTS

Using this methodology, it is possible to estimate the polymers, copolymers, and terpolymer HSP from their monomers, as illustrated in Table I. The total solubility parameters δ_t, also known as Hildebrand solubility parameters, were also calculated from the equation:

$$\delta_t = \left(\delta_d^2 + \delta_p^2 + \delta_h^2 \right)^{1/2} \tag{9}$$

The calculated binary solubilities of the cure agents in each rubber compound are shown in Table II.

Using the previously calculated elastomer HSP data (Table I) and the solubility of sulfur in the various elastomers (Table II), it is possible to estimate the HSP and solubility radius (R_0) of sulfur, as shown in Table III. RED values below 1 signify solubility, while values above are considered insoluble. A set of evaluation factors (true and false positives, true and false negatives, sensitivity, specificity, and accuracy) was also calculated and shown as indicative of the predictive ability of the model in question.

The HSP and solubility radius for the other 10 cure agents, in order of polarity of the cure agents, were calculated from data in Tables I and II. The results presented in Table IV show a great match between elastomers and cure agent solubilities, being perfect for 7 out of 10. It is also observed that, in general, more polar cure agents are soluble in a larger region of the solubility space (higher radii R_0).

Table II. Relative Solubility[a] of the Cure Agents in Each Rubber Compound (Adapted from Ref. 10)

Chemical solubility (phr)	EPDM	NR	BR	SBR 23	SBR 64	NBR 18	NBR 34	NBR 49
Sulfur	1 (1.5)	1 (3.0)	1 (2.5)	1 (3.0)	0 (2.0)	0 (1.5)	0 (1.0)	0 (1.0)
TMTD	0 (0.5)	0 (0.5)	0 (0.5)	0 (0.5)	1 (2.0)	0 (1.0)	1 (3.0)	1 (4.0)
TBzTD	0 (0.5)	1 (2.0)	0 (1.0)	0 (0.5)	1 (3.5)	1 (3.5)	1 (5.5)	1 (6.0)
TMTM	0 (0.5)	0 (0.5)	0 (1.0)	0 (1.0)	1 (5.5)	1 (4.0)	1 (7.0)	1 (7.0)
CBS	0 (2.0)	1 (5.0)	1 (3.5)	0 (1.0)	0 (5.5)	1 (5.5)	0 (5.0)	0 (7.0)
TBBS	1 (2.0)	0 (0.5)	1 (2.5)	0 (0.5)	0 (3.5)	1 (5.0)	1 (5.0)	1 (7.0)
MBT	1 (1.0)	1 (2.0)	1 (2.5)	1 (1.5)	0 (1.5)	0 (2.5)	0 (1.0)	0 (3.0)
MBTS	1 (1.0)	0 (0.5)	0 (0.5)	1 (0.5)	0 (0.5)	0 (0.5)	0 (1.0)	1 (1.5)
ZDEC	0 (0.5)	0 (0.5)	0 (0.5)	0 (0.5)	0 (1.0)	1 (1.5)	1 (3.5)	1 (3.5)
ZDBC	1 (2.5)	1 (3.0)	1 (3.0)	1 (2.5)	0 (4.5)	1 (5.5)	0 (5.5)	0 (7.0)
ZBEC	0 (0.5)	1 (2.5)	0 (0.5)	0 (0.5)	0 (1.0)	0 (1.0)	1 (3.5)	0 (1.0)

[a] Relative solubility is the measured chemical solubility of each cure agent in each tested rubber (in brackets), in parts per hundred of rubber (phr), first divided by the average of all solubilities in the same rubber, then divided by the average of all resulting solubilities of the same cure agent. The results, being higher or lower than unity (soluble = 1, insoluble = 0), are coerced to binary scale (1 or 0).

Table III. Hansen (δ_d, δ_p, and δ_h) and Hildebrand (δ_t) Solubility Parameters, Interaction Radius (R_0), RED Distances to Elastomers, Solubilities, and Some Predictive Factors Calculated for Sulfur (RED Distances to Non Polar Cure Agents are Highlighted in Boldface.)

		Rubber	RED	Solubility
δ_d	15.4	EPDM	0.95	1
δ_p	1.4	NR	**0.48**	1
		BR	0.93	1
δ_h	3.4	SBR 23	0.67	1
		SBR 64	1.12	0
δ_t	15.9	NBR 18	**1.27**	0
		NBR 34	**1.87**	0
R_O	3.0	NBR 49	**2.53**	0
		TP	4	
		TN	4	
		FP/FN	0/0	
		Sensibility (%)	100	
		Specificity (%)	100	
		Accuracy (%)	100	

TP, True Positive; TN, True Negative; Specificity = 100 × TN/(TN + FP). Sensitivity = 100 × TP/(TP + FN). Accuracy = 100 × (TP + TN)/(TP + TN + FP + FN).

Figure 1 shows the solubility interaction between cure agents and different elastomers in the 3D Hansen space. It can be seen in the figure that some cure agents, such as sulfur, are predominantly nonpolar (yellow), some, such as CBS (purple) are mid range in terms of polarity and others, such as MBTS (red) and TMTM (blue), have a broad range of solubility in different rubbers. This does not mean that the solubility of the cure agent inside the Hansen sphere is absolutely equal, but only that the solubility is expected.

The cure agent results of solubility in different elastomers can also be compared by analyzing RED distances from cure agents to elastomers, as presented in Table V, along with truth table parameters (TP, TN, FP, FN, sensitivity, specificity, and accuracy).

From Tables III and V, a comparison can be made between the cure agents with unlike degrees of polarity. For instance, it can be observed, that, as long as the acrylonitrile percentage in the copolymer NBR is higher, the elastomer polarity (Table I) and its RED distance to nonpolar cure agents increases (highlighted in boldface). This is the case for sulfur (Table III), ZDBC, MBT, and CBS (Table V). For all other cases, the cure agents are more polar (Table IV) and there is a preferential partitioning in favor of the NBR phase, as predicted by the lower RED value found by the predictive model (Table V). As a result, the introduction of a secondary cure agent (besides sulfur) gives a better balance in the distribution of crosslinking in the elastomer compound.

For a quantitative study of the influence of curatives in the sulfur vulcanization of elastomer blends, data from Karnika de Silva and Lewan's article were used.[11] The authors studied various blend compositions vulcanized with sulfur and TBBS cure agent with different percentages of the elastomers.

Various blends were made using the elastomers NR and NBR 41 and cured with sulfur and TBBS curative. The tested elastomers and their RED to the cure agent (Table V) are as follows: NR, RED = 1.00; NBR 34, RED = 0.63; NBR 49, RED = 0.51. To estimate the RED of the untested NBR 41 elastomer (RED = 0.57), it was considered the arithmetic mean of NBR 34 and NBR 49 elastomers. To avoid the influence of a third monomer, methyl methacrylate, which is present in the grafted rubber Heveaplus MG30, only samples of elastomers with the same MG30 content (15%) of that monomer were chosen for this analysis.

Table VI presents the calculated mRED distances between the cure agents (S and TBBS) and the various analyzed blends as well as two measured mechanical properties: tensile stress at relative elongation (conventionally referred to as "modulus") and tensile strength (maximum stress that a material can withstand while being stretched or pulled before failing or breaking). The volume fractions ϕ_1 and ϕ_2 refer to the elastomers NR and NBR, respectively. The relationship between each one of the mechanical properties and the corresponding calculated mRED values are illustrated in Figures 2 and 3.

El-Sabbagh and Yehia[12] studied various blends without compatibilization and greater variation in concentration among the

Table IV. Calculated HSP of Different Cure Agents

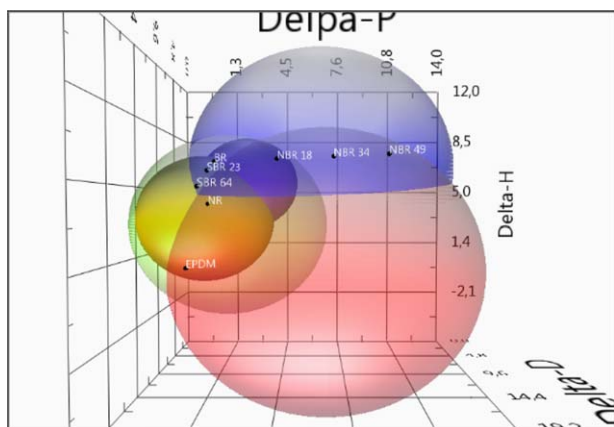| Cure agent	δ_d (MPa$^{0.5}$)	δ_p (MPa$^{0.5}$)	δ_h (MPa$^{0.5}$)	δ_t (MPa$^{0.5}$)	R_O	Data fit
ZDBC	15.2	2.4	3.1	15.7	4.3	1
MBT	15.4	1.3	3.4	15.8	3.4	1
CBS	14.7	3.2	5.1	15.9	2.2	1
ZBEC	15.4	5.8	1.0	16.5	5.5	0.99
ZDEC	15.2	7.0	6.2	17.8	2.7	1
MBTS	16.7	6.6	1.0	18.0	6.6	0.86
TMTM	17.1	6.4	5.7	19.1	5.4	1
TBTD	16.2	11.4	2.0	19.9	10.7	1
TMTD	18.0	6.8	5.4	20.0	6.2	1
TBBS	16.2	11.8	1.5	20.1	11.2	0.96

Figure 1. Positions of the eight tested elastomers in Hansen space and solubility spheres of five cure agents (from the biggest): MBTS (red), TMTM (blue), ZDBC (green), sulfur (yellow), and CBS (purple). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

elastomers NR, SBR 23, and NBR34, which made it possible to analyze the influence of the mRED between CBS cure agent and elastomers in the results of the final compounds. From Table V, the calculated RED distances from the CBS cure agent to the elastomers NR, SBR 23, and NBR 34 were 0.91, 1.12, and 1.89, respectively.

As shown in Table VII, the calculated mRED distances to the elastomer blends were compared to the measured equilibrium swelling, shear modulus (G), and crosslinking density (v), which is shown in Figures 4 and 5. Equilibrium swelling was measured in toluene, according to the ASTM D 471-97 (1998) method and used to determine the crosslinking density by the application of the Flory-Rehner equation. Shear modulus, the ratio of shear stress to the shear strain, was tested according to a standard method [ASTM D412-98a (1998)] using Zwick tensile testing machine (model-1425).[12]

DISCUSSION

Applying the concept of HSP has revolutionized research and development of polymers and oils in many applications in industry. This thermodynamic theory is directly applied to nonreactive polymeric formulations. The accuracy of HSP is given by the study of the dissolution of polymers in various solvents and the larger the amount of tested chemicals with different physico–chemical characteristics encompassing different dipole forces and hydrogen bonding, the better the outcome. Presented results seek to optimize the Hansen sphere of each cure agent distributed in various elastomers in order to cover the greatest number of miscible pairs (RED < 1) and leave outside the sphere as many noncompatible (RED > 0) as possible.[3]

From this viewpoint, the tool is suitable as a predictive method to anticipate the best cure agents for each elastomer with a significant degree of accuracy, optimizing the scientific decision-making process. As the optimization system was fed with extensive experimental data available from Schröder et al.,[10] it is

expected that the results can be transferable to practical situations. The degree of accuracy obtained shows that the tool is important for optimally defining the sphere of compatibility between cure agents and analyzed rubber.

As illustrated in Table III, the resulting sulfur solubility is in general agreement with experimental evidence: BR ≈ SBR ≈ NR > EPDM >> NBR.[13] It can be observed, as expected, that sulfur is more compatible with less polar rubbers. This is in agreement with the results of Terpilowski and colleagues,[7] who found that sulfur has a negligible polar character. The RED values in Table III, although quantitative, should not be read as a declining order of solubility but simply solubility or insolubility. The fact that sulfur was compatible with SBR 23 but not with SBR 64 (Tables II and III) is somewhat surprising, but it derived from the methodology used and the differences in HSP among the types of rubber. Although the elastomers SBR 23 and SBR 64 are copolymers made from the same monomers, the difference in proportion between monomers leads to different HSP (Table I). SBR 64 rubber is predominately less polar (lower δ_p) and has a higher dispersive component (δ_d), which leads to a higher total solubility parameter (δ_t).

In the evaluation of cure agents, as presented in Table V, with the exception of MBTS, there is great agreement between the solubilities found by the genetic algorithm and that was empirically determined by Schröder et al.[10] The match is perfect for most cure agents (ZDBC, MBT, CBS, ZDEC, TMTM, TBTD, and TMTD), which means that there are no outliers (FP or FN) and the method accuracy is 100%. It is almost perfect for the other two cure agents (ZBEC and TBBS), where there is only one outlier.

Another criterion of estimating the effectiveness of predictive solubility of a number of chemicals in relation to a polymer is given by the Datafit number. Its value ranges from zero to one (100% matching), which is achieved in this case when all good (soluble) elastomers are within the solubility sphere and all bad ones are outside it. As noted in Table IV, Datafit values are high even for imperfect correlations, with the lowest being 0.86 for MBTS cure agent.

A higher Datafit does not mean that the predictive model is necessarily better but simply that the product of differences is smaller. Given this situation, it is important to incorporate other concepts in the model to measure the quality of results and method effectiveness, such as number of false positives, number of false negatives, specificity, sensitivity, and accuracy, as shown in Tables III and V.

In vulcanized elastomer blend analysis, Lewan describes partitioning of CBS to the NR phase in the immiscible NR/NBR blends.[14] This is in agreement with the results shown in Table V: as the percentage of acrylonitrile in the copolymer is increased, so its polarity and the difference in relation to the cure agent increases. For the more polar TMTM and TMTD cure agents, partitioning in favor of NBR clearly occurs. The introduction of a secondary cure agent to the primary CBS provided more balanced distribution of crosslinking in the elastomer compound and a consequent improvement in the final mechanical properties.

Table V. Calculated RED Distances Between Cure Agents and Elastomers, Binary Solubilities, and Predictive Solubility Analysis (RED Distances to Non Polar Cure Agents are Highlighted in Boldface and Outliers in Red.)

Rubber	ZDBC RED	ZDBC Solub.	MBT RED	MBT Solub.	CBS RED	CBS Solub.	ZBEC RED	ZBEC Solub.	ZDEC RED	ZDEC Solub.
EPDM	0.88	1	0.93	1	2.66	0	1.12	0	3.18	0
NR	**0.40**	1	**0.47**	1	**0.91**	1	0.92	1	2.26	0
BR	0.77	1	0.93	1	0.81	1	1.10	0	2.01	0
SBR 23	0.68	1	0.69	1	1.12	0	1.14	0	2.08	0
SBR 64	1.08	0	1.13	0	2.39	0	1.36	0	2.65	0
NBR 18	**0.89**	1	**1.29**	0	**0.84**	1	0.91	0	0.94	1
NBR 34	**1.32**	0	**1.88**	0	**1.89**	0	0.92	1	0.11	1
NBR 49	**1.82**	0	**2.52**	0	**2.95**	0	1.08	0	0.95	1
TP	5		4		3		2		3	
TN	3		4		5		5		5	
FP/FN	0/0		0/0		0/0		1/0		0/0	
Spec. (%)	100		100		100		83.3		100	
Sens. (%)	100		100		100		100.0		100	
Accur. (%)	100		100		100		87.5		100	

Rubber	MBTS RED	MBTS Solub.	TMTM RED	TMTM Solub.	TBTD RED	TBTD Solub.	TMTD RED	TMTD Solub.	TBBS RED	TBBS Solub.
EPDM	0.89	1	1.36	0	1.00	0	1.29	0	1.00	1
NR	1.09	0	1.31	0	1.00	1	1.38	0	1.00	0
BR	1.23	0	1.24	0	1.02	0	1.34	0	1.03	1
SBR 23	1.10	1	1.06	0	1.00	0	1.15	0	1.00	0
SBR 64	1.00	0	0.94	1	1.00	1	0.92	1	1.01	0
NBR 18	1.00	0	0.86	1	0.85	1	1.04	0	0.81	1
NBR 34	0.92	0	0.70	1	0.71	1	0.88	1	0.63	1
NBR 49	1.00	1	0.84	1	0.58	1	0.92	1	0.51	1
TP	2		4		5		3		4	
TN	4		4		3		5		3	
FP/FN	1/1		0/0		0/0		0/0		0/1	
Spec. (%)	80		100		100		100		100	
Sens. (%)	66.6		100		100		100		80	
Accur. (%)	75.0		100		100		100		87.5	

Karnika de Silva and Lewan also studied the vulcanization of the incompatible elastomers NR and NBR 41.[11] Various blends were made and cured with sulfur and TBBS cure agent. By applying the predictive model, correlations were made between mechanical properties of the elastomer blends and mRED values of the elastomer to the cure agent. Results show an inverse relationship between mRED and tensile stress at 100% (and 300%) elongation and a direct relationship between mRED and tensile strength (Figures 2 and 3, respectively).

The inverse relationship between mRED and tensile stress could be explained by the simple dependency of the rubber elastic character on the compatibility between elastomer and cure agent. The less the mRED distance, the more compatible the blend compounds. This higher compatibility makes the rubber harder and more homogeneous, increasing its tensile stress values. On the other hand, though with a lower correlation the tensile strength seems to decrease with mRED, contrary to the expected behavior. This anomalous behavior needs a better knowledge of the blend microstructure to be interpreted, but the correlation exists.
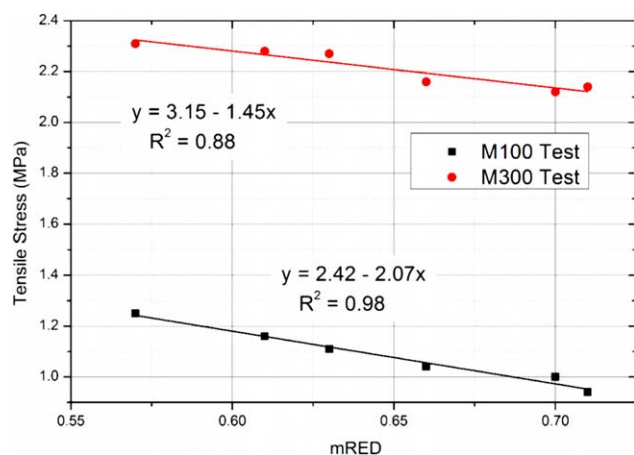
From the work of El-Sabbagh and Yehia,[12] it was possible to analyze the mixture of elastomers NR, SBR 23, and NBR 34, vulcanized with sulfur or the CBS cure agent. From Table VII and Figure 4, it can be seen that the shear modulus (G) and the crosslinking density (v) of the elastomer blend are directly proportional to the mRED distances of the elastomer to the cure agent.

Table VI. Mechanical Properties of NR/NBR 41 Blends Cured with S and TBBS: Tensile Stress at 100% (M100) and 300% (M300) Deformation, and Tensile Strength (Adapted from Ref. 11)

NR:MG30:NBR	ϕ_1	ϕ_2	mRED	M100 (MPa)	M300 (MPa)	Tensile strength (MPa)
60 : 15 : 20	0.60	0.20	0.71	0.94	2.14	24.6
50 : 15 : 35	0.50	0.35	0.70	1.00	2.12	24.9
40 : 15 : 45	0.40	0.45	0.66	1.04	2.16	24.0
35 : 15 : 50	0.35	0.50	0.63	1.11	2.27	23.6
30 : 15 : 55	0.30	0.55	0.61	1.16	2.28	22.4
20 : 15 : 65	0.20	0.65	0.57	1.25	2.31	23.4

This result seems to be inconsistent with the correlation between tensile moduli (M100 and M300) and mRED, shown in Figure 2 and Table VI, because of the inversion in the relationship with mRED. In Figure 2 (Table VI), the tensile modulus of NR/NBR 41 blends cured with mostly TBBS shows an inverse relationship with mRED, while in Figure 3 (Table VII), the shear modulus of NR/SBR 23/NBR 34 blends cured with CBS shows a direct relationship with mRED. To explain this inversion, we suggest that the correlations between mRED and the two analyzed mechanical properties, tensile modulus, and shear modulus, have opposite behaviors because of the cure agents polarity (Table IV): TBBS is very polar compared to CBS, a slightly polar cure agent. We suppose that interactions made by polar intermolecular forces (stronger than dispersive, nonpolar forces) can promote a better crosslinking within elastomers, leading to stiffer rubbers (higher tensile and shear moduli). However, more research is required to understand the role of polar interactions to the vulcanization process and have a definite conclusion.

It is known that mechanical properties of a blend depend on several factors in addition to the crosslinking density of the elastomer and the solubility of the blend. In particular, the continuous phase in the blend contributes significantly to the mechanical properties more than the dispersed phase factor, which depends in part on the density and surface tension of the elastomer phase. In addition, mineral fillers, and other additives interfere with the final compound and can interfere with the balance of the partitioning of the additives used.

The presented method in this work offers a new tool for assessing the partitioning of cure agents in different elastomers and their blends. The quantitative data has been facilitated by a series of analyses of the solubility of the cure agents in the different phases of elastomer mixtures and their correlation with the physico-chemical and mechanical properties of the resulting blend.

In regard to limitations of the method, it is known that the solubility parameters are not very accurate in predictions of very polar substances, which do not follow the regular solutions theory. This theory served as the basis for Hildebrand to introduce the traditional solubility parameter and for Hansen to extend it to the tridimensional parameters, which has been established as a standard for development of formulations in industry. This problem has recently been approached with the introduction of extended solubility parameters (including acidic and basic parameters and their interactions, in a four-dimensional model). The results are still preliminary. The issue of incorporating chemical reactions in the calculation of solubility parameters is still to be achieved.

As the vulcanization process changes the HSP, as discussed earlier and does not allow dissolution in solvents after curing, it is
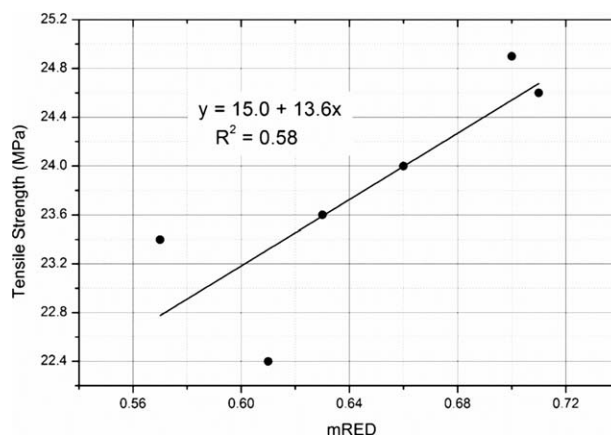

Figure 2. Relationship between calculated mRED of the cure agent TBBS to NR/NBR 41 blends cured with S and TBBS and their measured moduli (M100 and M300). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 3. Relationship between calculated mRED of the cure agent TBBS to NR/NBR 41 blends cured with S and TBBS and their tensile strengths.

Table VII. Equilibrium Swelling, Shear Modulus (G), Crosslinking Density (v), and mRED Distances from Three Elastomers (Elastomer Blends) to the Cure Agent CBS (Adapted from Ref. 12 and Table V)

Elastomer blend	mRED	Equilibrium swelling (%)	G (MPa)	$v \times 10^4$ (mol/cm^3)
S_1 (NR)	0.91	252	0.84	1.86
S_2 75/25 (NR/SBR)	0.98	230	0.93	2.04
S_3 50/50 (NR/SBR)	1.02	208	1.05	2.29
S_4 25/75 (NR/SBR)	1.07	198	1.09	2.12
S_5 (SBR)	1.12	186	1.15	2.48
S_6 75/25 (NR/NBR)	1.16	201	1.42	2.94
S_7 50/50 (NR/NBR)	1.40	158	1.89	3.66
S_8 25/75 (NR/NBR)	1.65	140	2.35	4.30
S_9 (NBR)	1.89	128	2.76	4.76

not possible to calculate the correct values from the solubilization of the polymers or by polymer swelling values.[6] The experimental calculation of HSP and its direct application to vulcanized elastomers becomes unfeasible, which is why the HSP data was estimated from its monomers in the construction of Table I.

Another limitation is the fact that the vulcanization activators and fillers used commonly in rubber compounding are usually polar substances that have a preferential partition to the polar phase and therefore are expected to interact more in these sites. This fact also interferes with the vulcanization of the elastomer compound and has to be taken into consideration when evaluating the vulcanization results.
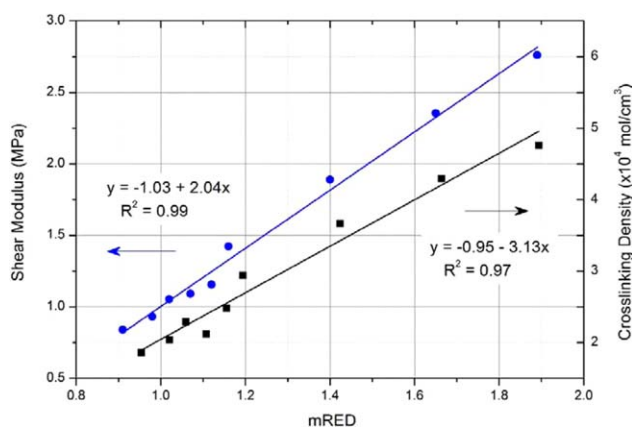

Figure 4. Correlation between calculated mRED distances and measured mechanical and physico-chemical properties of the blend: shear modulus (G) and crosslinking density (v). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
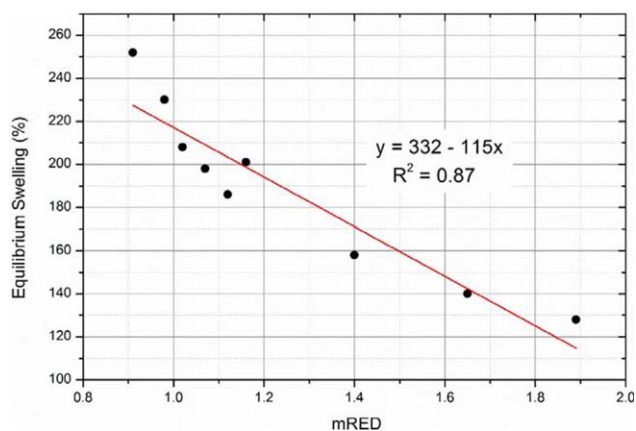

Figure 5. Correlation between the elastomer swelling and mRED distances from the elastomer to the cure agent. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The strength of the HSP model and the approach used in this article concerns its practicability. However, semi-empirical models such as this should not be considered accurate or quantitative. They are important as a guide for suggesting probable directions of compatibility and solubility and are therefore considered important and have been routinely used in the practice of technological development. In the specific case in question, the model makes it possible to indicate the greatest possibility of compatibility of a cure agent and sulfur in various elastomers, using data from Schröder et al.[10]

From these data it is possible, as a trial method, to estimate the solubility of a given cure agent in certain types of rubber with a good level of agreement, which is illustrated by high predictive accuracy values. The methodology presented should be tested as a tool to predict the crosslinking density and partitioning of cure agents in elastomer blends. Empirical results were able to demonstrate the true value of this promising methodology.

CONCLUSION

The correlation method with genetic optimization facilitates the outlining of a Hansen sphere using solubility data of cure agents in different types of rubber. The three-dimensional solubility parameters, together with the interaction radius (distance from one cure agent to the center of the Hansen sphere), allows for the prediction of compatibility of a cure agent with a given elastomer with reasonable accuracy. The method presented in this work includes a new tool for assessing the partitioning of cure agents in different elastomers and their blends. The quantitative data allowed a series of analysis of the solubility of the cure agent in the elastomer mixtures of different phases and was validated by the correlation with the physico-chemical and mechanical properties of the resulting blend. This is an important tool for planning a cure system in rubber blends and to avoid incorrect partitioning of cure agents and consequent uneven curing of the final compound. It was possible to accurately predict the solubility of cure agents in various elastomers or their blends and to correlate relative distances in Hansen space with

mechanical and physico-chemical properties of the elastomer compound using the same methodology.

REFERENCES

1. Khimi, S. R.; Pickering, K. L. *J. Appl. Polym. Sci.* **2014**, *131*, 40008.

2. Hansen, C. M. Hansen Solubility Parameters: A User's Handbook; CRC/Taylor & Francis: Boca Raton, Florida, **2007**; Chapter 1, p 1.

3. Vebber, G. C.; Pranke, P.; Pereira, C. N. *J. Appl. Polym. Sci.* **2014**, *131*, 39696.

4. Guo, R.; Talma, A.; Datta, R.; Dierkes, W.; Noordermeer, J. *J. Macromol. Mater. Eng.* **2009**, *294*, 635.

5. Chapman, A. V.; Tinker, A. J. *Kautsch. Gummi Kunstst.* **2003**, *56*, 533.

6. Nielsen, T. B.; Hansen, C. M. *Polym. Test.* **2005**, *24*, 1054.

7. Terpilowski, K.; Holysz, L.; Chibowski, E. *J. Colloid Interface Sci.* **2008**, *319*, 514.

8. Mangaraj, D. *Rubber Chem. Technol.* **2002**, *75*, 365.

9. Schuster, R. H.; Meier, J.; Kluppel, M. *Kautsch. Gummi Kunstst.* **2000**, *53*, 663.

10. Schröder, A.; Frueh, T.; May, K.; Ruppelt, D.; Alshuth, T. *Kautsch. Gummi Kunstst.* **2008**, *61*, 584.

11. Karnika de Silva, K. G; Lewan, M. *J. Rubber Res. Inst. Sri Lanka* **1998**, *81*, 38.

12. El-Sabbagh, S. H.; Yehia, A. A. *Egypt. J. Solids* **2007**, *30*, 157.

13. Guo, R. Improved Properties of Dissimilar Rubber-Rubber Blends using Plasma Polymer Encapsulated Curatives: A Novel Surface Modification Method to Improve Co-vulcanization. Ph.D. Thesis, University of Twente, Enschede, the Netherlands, **2009**.

14. Lewan, M. V. In NR/NBR Blends—Basic Problems and Solutions. Blends of Natural Rubber: Novel Techniques for Blending with Speciality Polymers; Tinker, A. J., Jones, K. P., Eds.; Chapman & Hall: London, **1998**; pp 68–79.