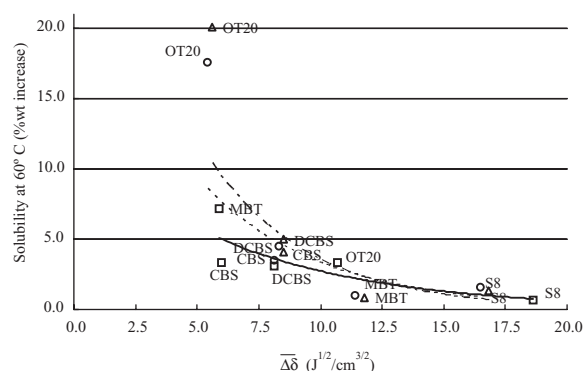


# A Theoretical and Experimental Study on Solubility of Curatives in Rubbers

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The current study provides indications for improving the properties of dissimilar rubber blends. As solubility is a key factor for the distribution and a driving force for the migration of curatives in dissimilar rubber blends, it is of importance to have precise data of their solubilities. The solubilities of (insoluble) sulfur and the accelerators CBS, MBT and DCBS are measured at RT and at 60 °C, in lightly crosslinked SBR, NBR and EPDM. The experimental results correlate well with calculated solubility parameters, as determined using the method of Hoftijzer and van Krevelen.



## Introduction

Attempts to determine the solubility of curatives in rubbers have been made for quite some time. First values of sulfur solubility in natural rubber (NR) were measured by Venable and Greene<sup>[1]</sup> in 1922. Since then, various methods, e.g. equivalent solvents: solvents with similar structure as the rubber polymers,<sup>[2]</sup> weight uptake, microscopy,<sup>[3–6]</sup> radioactively labeled sulfur,<sup>[7–10]</sup> time of flight secondary ion mass spectrometry (ToF-SIMS)<sup>[11]</sup> etc. were used to determine the solubility of curatives, in most cases the solubility of sulfur in rubbers. Amongst all these methods, the method of Morris and Thomas<sup>[12]</sup> is most effective to give reliable solubility results. Crystallization of sulfur is excluded due to the isothermal experimental procedure. Further, the peroxide cure applied in the method limits modification of the chain structure of rubbers, which consequently reduces its influence on the solubility compared to sulfur curing.

Although quite some experimental data have been obtained, an apparent lack of consistence exists due to the drawbacks of each method and the experimental conditions. On the other hand, the wide-spread use of rubber blends stimulates interest in the solubility of sulfur in rubbers other than NR. Especially ethylene-propylene-diene rubber (EPDM) is interesting due to its excellent ozone- and oxygen-resistance. As the distribution and dispersion of curatives other than sulfur in blends of dissimilar rubbers is also vital for the properties of such vulcanized blends, it is of interest to determine the solubility of accelerators in various rubbers, in an attempt to obtain some insight into the mechanistic aspects involved in curing such blends.

The present work is an extension and continuation of results published in ref.[13] as a short communication, which covers an extended experimental study of the solubility of sulfur and various accelerators in styrene-butadiene rubber (SBR), acrylonitrile-butadiene rubber (NBR) and EPDM, slightly pre-crosslinked with peroxide, at room temperature and at 60 °C, making use of the method of Morris and Thomas.<sup>[12,13]</sup> The experimental results are verified with theoretical solubility calculations using the group contribution theory of Hoftijzer and van Krevelen.<sup>[14]</sup>

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The solubility parameters of the rubbers and the curatives involved in this study can be calculated by the method of Hoftijzer and van Krevelen,<sup>[14]</sup> by adding the contributions from all functional groups. The solubility parameter  $\delta$  [ $\text{J}^{1/2} \cdot \text{cm}^{-3/2}$ ] can then be used to predict the mutual solubilities. The solubility parameter can be divided into three parts:

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (1)$$

Where the sub-parameter  $\delta_d$  is the component from the dispersive forces,  $\delta_p$  is the component from polar forces and  $\delta_h$  is from hydrogen bonding. The three components are calculated as follows:

$$\begin{aligned} \delta_d &= \sqrt{\sum F_{di} / \sum V_i} \\ \delta_p &= \sqrt{\sum F_{pi}^2 / \sum V_i} \\ \delta_h &= \sqrt{\sum E_{hi} / \sum V_i} \end{aligned} \quad (2)$$

Wherein  $F_{di}$ ,  $F_{pi}$ , and  $E_{hi}$  are the dispersive force, the polar force and hydrogen bonding contribution from each group;  $V_i$  is the volume contribution from each group.

The mutual solubility between two materials 1 and 2 can be predicted from  $\overline{\Delta\delta}$ , defined as:

$$\overline{\Delta\delta} = [(\delta_{d1} - \delta_{d2})^2 + (\delta_{p1} - \delta_{p2})^2 + (\delta_{h1} - \delta_{h2})^2]^{1/2} \quad (3)$$

For a good mutual solubility the value of  $\overline{\Delta\delta}$  should be small:  $< 5 \text{ J}^{1/2} \cdot \text{cm}^{-3/2}$ .

## Experimental Part

### Materials

In this study, three different kinds of rubbers: S-SBR (Buna<sup>®</sup> VSL 5025-0HM from LANXESS Corp, Germany), NBR (Perbunan<sup>®</sup> 3446F also from LANXESS), and EPDM (Keltan<sup>®</sup> 4703 from DSM Elastomers, The Netherlands) were employed. Zinc oxide and elemental sulfur were purchased from Sigma Aldrich and polymeric sulfur (Crystex<sup>®</sup> HS OT 20) was obtained from Flexsys, Belgium; accelerators (Santocure<sup>®</sup> CBS, Santocure<sup>®</sup> DCBS and Perkacit<sup>®</sup> MBT) were also provided by Flexsys and stearic acid was of commercial type. Dicumyl peroxide (Perkadox<sup>®</sup> BC-40B) was provided by Akzo Nobel, The Netherlands, with a purity of 40%.

### Methods

All the rubber samples were slightly crosslinked by peroxide before the solubility measurements were carried out. The curative formulations are shown in Table 1. The amount of dicumyl peroxide (purity 40%) was varied from rubber to rubber, in order to cure the rubbers to similar

Table 1. Curative formulations for gum rubber compounds.<sup>[1]</sup>

Component	Amount [phr]		
SBR	100	0	0
NBR	0	100	0
EPDM	0	0	100
ZnO	5	5	5
Stearic acid	2	2	2
Dicumyl peroxide 40% pure on inert carrier	1	4.8	6.25

torque levels, i.e. similar crosslink densities. The vulcanization was carried out at 160 °C for only 15 min instead of their optimal vulcanization time  $t_{95}$ , which is 31 min for SBR, 26 min for NBR and 28 min for EPDM. As a result, the levels of crosslinking were kept low, however the vulcanization time should also be long enough to overcome tackiness. The gel content was measured after extraction with toluene in a Soxhlet extractor for 2 d: 96.6% for SBR, 99.6% for NBR, and 98.2% for EPDM.

The vulcanized samples were then cut into sheets with a size of  $10 \times 10 \times 2 \text{ mm}^{-3}$ . These sheets were extracted with acetone in a Soxhlet extractor for 2 d to remove the non-rubber contents. Finally, all the samples were dried in a vacuum oven for 24 h at room temperature. Samples were stored and protected from light before use.

The solubility measurements were carried out in triplicate by placing accurately weighed samples of vulcanizate in a glass bottle such that they were packed on all sides with either sulfur or the accelerators of interest in the form of fine powders. The glass bottle was placed in a thermo-stated oven at room temperature or 60 °C. These are representative temperatures for rubber storage and the temperature generated by mixing on a two-roll mill. The sample weights were measured every day and increases in weight were obtained due to the diffusion of curative molecules into the crosslinked rubber samples. The sample surfaces were cleaned with a sharp blade, followed by treatment with an adhesive tape before weighing in order to remove remaining adhering material. Blank experiments were carried out by inserting rubber samples into the curatives for a few seconds and weighing the sample after the cleaning procedure. The aim of a blank experiment was to check if the cleaning procedure was good enough to remove all the adhered powders from the surface of the samples.

The solubilities of both elemental sulfur and polymeric sulfur (OT20) were measured with these materials as received. Images of elemental sulfur particles from light-microscopy showed that in most cases the particle size was in the range of 25–50  $\mu\text{m}$ ; the particle size of polymeric

sulfur was smaller than 30  $\mu\text{m}$  according the product information provided by Flexsys.

The solubilities of the accelerators *N*-cyclohexylbenzothiazole-2-sulphenamide (CBS), (*N*-dicyclohexylbenzothiazole-2-sulphenamide) DCBS, and 2-mercaptobenzothiazole (MBT) were determined using the same procedure. CBS and DCBS were first ground into fine powders before use. MBT was used as received in powder form. With light-microscopy the particle sizes of the powders were determined: for CBS mostly in the range of 25–50  $\mu\text{m}$ ; 10–25  $\mu\text{m}$  for DCBS; and 5–25  $\mu\text{m}$  for MBT.

## Results and Discussion

First, the solubility parameters of the different elastomers and curatives are calculated based on the method of Hoftijzer and van Krevelen.<sup>[14]</sup> Then the solubilities of the curatives in the different elastomers are presented as percentage weight increase, plotted against time for two temperatures: room temperature (RT) and 60 °C. Finally, these experimental results will be compared with the calculated solubility parameters of the elastomers and curatives.

The example of EPDM is given to illustrate the solubility parameter calculations, by taking the ratio of each monomer into account. The composition of the EPDM used in this study is: 48 wt.-% ethylene, 43 wt.-% propylene and 9 wt.-% ethylidene norbornene. Taking the molecular weight of the monomers into account, the molar ratio was calculated to be: 61:36:3.  $F_{\text{di}}$ ,  $F_{\text{pi}}$ ,  $E_{\text{hi}}$ , and  $V_i$  were summed up from the contributions of the functional groups of each monomer, by taking the molar ratios into account.

The calculated solubility parameter components of the polymers involved in this study are shown in Table 2. It should be mentioned that both the content of more polar groups (e.g. the styrene group in SBR, the acrylonitrile contained in NBR) and the molar ratio of the copolymers influence the polarity and amount of hydrogen bonding in these polymers. Consequently, the solubility parameters for elastomers of different composition will differ to some extent. For example, the solubility parameter of SBR would be  $18.7 \text{ J}^{1/2} \cdot \text{cm}^{-3/2}$ , if the styrene units were of equal molar amounts as the butadiene units in this copolymer.

**Table 2.** Calculated solubility parameter components of rubbers [ $\text{J}^{1/2} \cdot \text{cm}^{-3/2}$ ].<sup>[1]</sup>

	SBR	NBR	EPDM
$\delta_{\text{d}}$	16.6	17.2	16.4
$\delta_{\text{p}}$	0.5	8.6	0
$\delta_{\text{h}}$	0	4.3	0

**Table 3.** Calculated solubility parameter components of curatives [ $\text{J}^{1/2} \cdot \text{cm}^{-3/2}$ ].<sup>[1]</sup>

	S <sub>8</sub>	OT20	CBS	DCBS	MBT
$\delta_{\text{d}}$	33.1	22.0	20.4	21.8	22.5
$\delta_{\text{p}}$	0	0	4.0	2.2	7.5
$\delta_{\text{h}}$	0	0	6.3	6.2	6.8

However, in the case of the SBR used in this study, where the molar ratio of styrene to butadiene monomers is 15:85, the overall solubility parameter is calculated to be  $16.6 \text{ J}^{1/2} \cdot \text{cm}^{-3/2}$ .

The solubility parameters of the curatives are summarized in Table 3. From the values of  $\delta_{\text{p}}$  it can already be deduced that the polarities of the accelerators are much higher than that of sulfur.

The mutual solubilities between rubbers and sulfur or curatives as reflected in the calculated values of  $\overline{\Delta\delta}$ , are given in Table 4. It illustrates the preference of each curative towards the three rubbers used in this study at room temperature:  $\overline{\Delta\delta}$  should be  $< 5 \text{ J}^{1/2} \cdot \text{cm}^{-3/2}$  for good solubility.

No weight increase was observed in the blank experiments. Therefore, the weight up-take of the curatives in the rubber samples purely resulted from the molecules of curatives migrating into the samples. As the experiments lasted for 8 d and were stopped only when no appreciable increase in weight was observed anymore, the final weight up-take can be readily taken as the equilibrium solubility at a certain temperature.

The weight up-take of sulfur ( $S_8$ ) and polymeric sulfur (OT20) increases with time, as shown in Figure 1 and 2. The solubility of sulfur increases with increasing temperature. The percentage weight increase at room temperature for elemental sulfur is in the range of experimental error: below 0.2 wt.-%. It is clear from Figure 1 that the solubility of sulfur is very low at room temperature in all three types of rubber. When the temperature is increased to 60 °C, the solubility increases substantially in SBR and EPDM; however the solubility in NBR rubber remains low. It shows that the preference of sulfur is SBR > EPDM  $\gg$  NBR. Therefore, it can be expected that in case of blends of

**Table 4.** Calculated  $\overline{\Delta\delta}$  between rubbers and curatives at room temperature [ $\text{J}^{1/2} \cdot \text{cm}^{-3/2}$ ].<sup>[1]</sup>

	S <sub>8</sub>	OT20	CBS	DCBS	MBT
SBR	16.5	5.4	8.1	8.3	11.4
NBR	18.6	10.7	5.9	8.1	6.0
EPDM	16.8	5.6	8.5	8.5	11.8

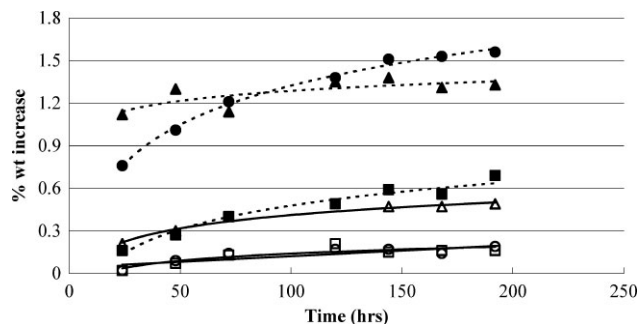


Figure 1. Solubility of sulfur ( $S_8$ ) in SBR, NBR and EPDM gum rubber at room temperature and 60 °C. (○) SBR RT; (□) NBR RT; (△) EPDM RT; (●) SBR 60 °C; (■) NBR 60 °C; (▲) EPDM 60 °C.

dissimilar rubbers, a homogeneous dispersion of sulfur is achieved for the blend SBR/EPDM, while in NBR/EPDM sulfur is expected to accumulate in the EPDM phase.

In Figure 2 it can be seen that the solubility of polymeric sulfur (OT20) is 10-fold higher than that of elemental sulfur for SBR and EPDM. However, it is still poorly soluble in NBR. This can partially explain the reduced blooming tendency of polymeric sulfur. The other reason for reduced blooming is that polymeric sulfur is not migrating, which is not accounted for in this study. A substantial increase in solubility of polymeric sulfur is observed at 60 °C. The preference of polymeric sulfur is EPDM > SBR  $\gg$  NBR. The higher solubility of polymeric vs. elemental sulfur observed in EPDM can be related to the fact that there is about 20% oil mixed in OT20, which has a high solubility in EPDM. However, the solubilities of OT20 in EPDM and SBR are still very close, so that it will still result in a good dispersion of OT20 in a blend of SBR/EPDM. In a NBR/EPDM blend the OT20 will partition more to the EPDM phase than the NBR phase, similar to elemental sulfur.

The solubility measurement of the curatives was also done at the two temperatures: RT and 60 °C. Although a colour change was observed of the curative powders after several days of solubility measurement, DSC analysis of the powders showed no evidence of decomposition at 60 °C. The

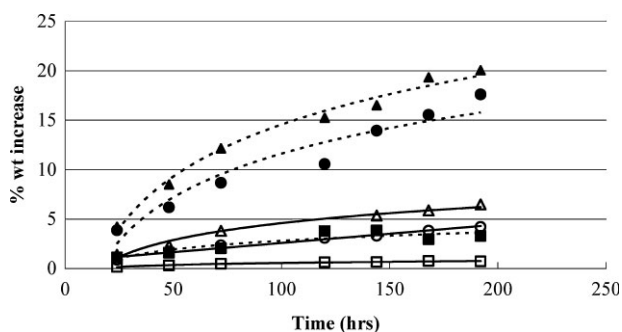


Figure 2. Solubility of polymeric sulfur (OT<sub>20</sub>) in SBR, NBR and EPDM gum rubber at room temperature and 60 °C. Symbols as in Figure 1.

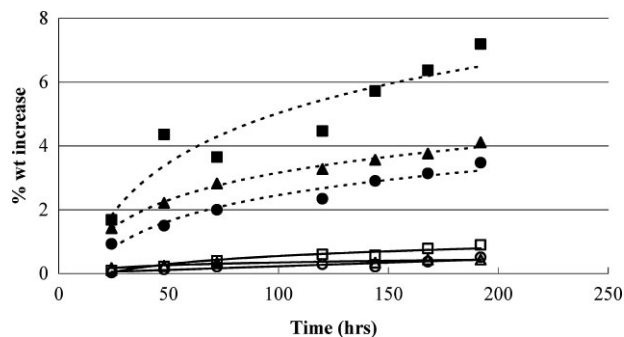


Figure 3. Solubility of CBS in SBR, NBR and EPDM gum rubber at room temperature and 60 °C. Symbols as in Figure 1.

solubility behaviour of CBS in the different rubbers at the two temperatures is shown in Figure 3. The highest solubility of CBS is in NBR at both temperatures. This correlates with the fact that the polarity of CBS is much higher than that of sulfur, as demonstrated by the higher value of  $\delta_p$  of CBS.

The solubility results for DCBS are shown in Figure 4. The highest solubility is found for EPDM at 60 °C, different to CBS. This may be explained by the molecular structures of CBS and DCBS, shown in Figure 5. The decrease in polarity as reflected in the  $\delta_p$  in Table 3 can be attributed to the

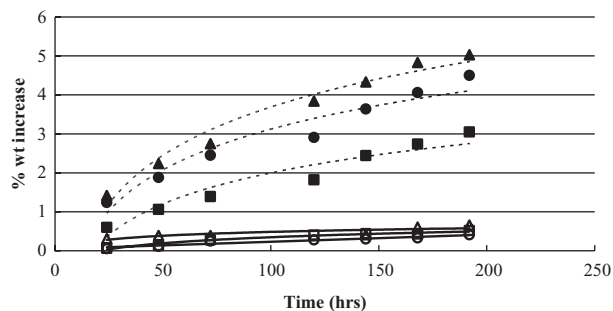


Figure 4. Solubility of DCBS in SBR, NBR and EPDM gum rubber at room temperature and 60 °C. Symbols as in Figure 1.

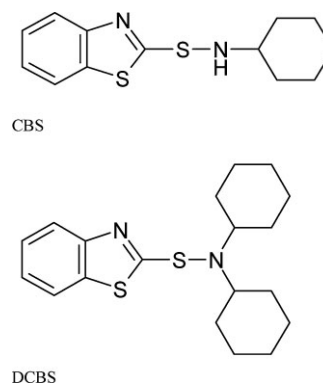


Figure 5. Structure of sulphenamide curatives.

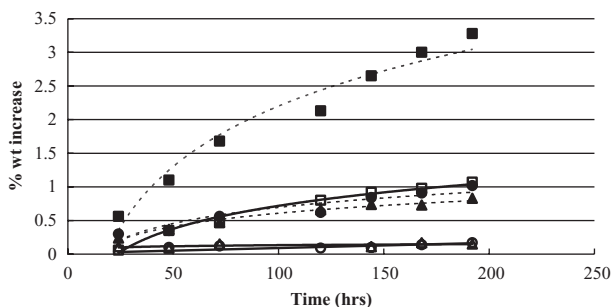


Figure 6. Solubility of MBT in SBR, NBR and EPDM gum rubber at room temperature and 60 °C. Symbols as in Figure 1.

presence of two cyclohexane rings in the DCBS molecular structure.

A solubility measurement was also done for MBT, which is a thiazole-type curative. MBT is a decomposition product of all sulphenamide accelerators. Its solubility is shown in Figure 6. It demonstrates that MBT has the highest solubility in NBR at room temperature as well as at 60 °C. The polarity of MBT is quite high as reflected in the  $\delta_p$  in Table 3, so that it has a preference to partition into the NBR phase in rubber blends like NBR/SBR and NBR/EPDM.

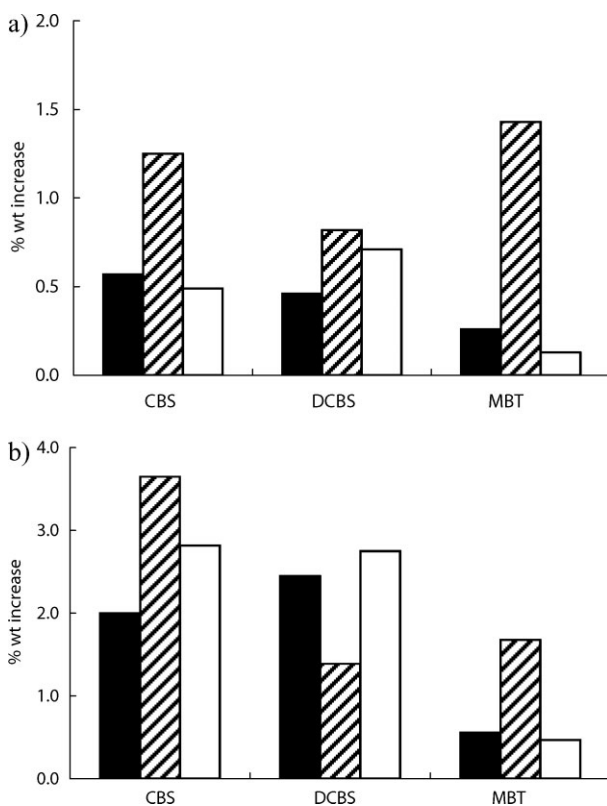


Figure 7. a) Comparison of solubility of accelerators in SBR, NBR and EPDM gum rubber at room temperature.<sup>[1]</sup> b) Comparison of solubility of accelerators in SBR, NBR and EPDM gum rubber at 60 °C.<sup>[1]</sup> (■) SBR; (▨) NBR; (□) EPDM.

A comparative overview of the solubilities, the highest values taken from the measurements, of the three accelerators for a certain temperature is given in Figure 7a and b, for the three rubbers involved in this study. It is clear that CBS and MBT have the highest solubilities in NBR at both RT and 60 °C. The solubility preference of DCBS is quite different from that of CBS. The similar level of solubility of DCBS in SBR and EPDM at 60 °C should be positive for co-vulcanization of SBR/EPDM blends. As the solubility of CBS and MBT in NBR is much higher than in SBR and EPDM, these curatives will tend to accumulate in the NBR phase in NBR/SBR and NBR/EPDM blends.

As stated before, mutual solubility occurs only when the value of  $\overline{\Delta\delta}$  is smaller than  $5 \text{ J}^{1/2} \cdot \text{cm}^{-3/2}$ . This rule can now be used in this study, to check if the calculated  $\overline{\Delta\delta}$ , as shown in Table 4, is sufficiently predictive for the experimental values. In Figure 8a and 8b the solubility data are plotted against the value of  $\overline{\Delta\delta}$  for both RT and 60 °C. Due to the complexity involved in calculating the solubility parameters at 60 °C, especially the solubility parameter components,  $\delta_d$ ,  $\delta_p$  and  $\delta_h$ , the solubility measured at 60 °C is also plotted against the  $\overline{\Delta\delta}$  at room temperature. It is

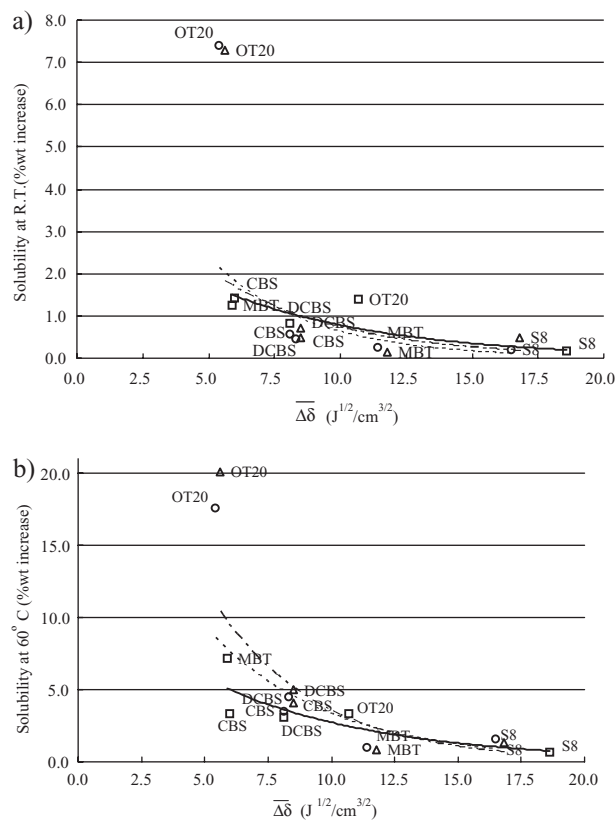


Figure 8. a) Correlation between the calculated solubility parameters and the experimental data at RT.<sup>[1]</sup> b) Correlation between the calculated solubility parameters and the experimental data at 60 °C.<sup>[1]</sup> (⋯○⋯) SBR, (—□—) NBR, (---△---) EPDM.



still possible to observe the same trend in Figure 8b as in Figure 8a. It is clear from Figure 8 that a higher solubility is found with smaller  $\overline{\Delta\delta}$  value, regardless what rubbers or curatives are involved. An extremely high solubility is observed for OT20, but this must most probably be attributed to the 20% oil contained.

## Conclusion

Elemental sulfur does not dissolve well in any of the rubbers investigated. The difference in solubility of sulfur in the different rubbers is more pronounced at higher temperatures (SBR > EPDM  $\gg$  NBR). This is the main reason for cure incompatibility in rubber blends. Polymeric sulfur shows a 10-fold higher solubility than elemental sulfur, although the order is only slightly changed (EPDM > SBR  $\gg$  NBR). This partially explains the ability of polymeric sulfur to prevent blooming.

The solubility of accelerators is much higher than that of elemental sulfur in NBR, SBR and EPDM rubber. CBS and MBT are very polar, which gives them a preference towards NBR rubber (NBR  $\gg$  SBR > EPDM). However, in the case of DCBS, the solubility sequence is SBR > EPDM > NBR, explained by the molecular structure of DCBS, where the two benzene rings cause symmetry and therefore less polarity.

The experimental data of solubility of curatives at room temperature can be correlated with the  $\overline{\Delta\delta}$  values calculated by the method of Hoftijzer and van Krevelen, as shown in Figure 8, where a lower value of  $\overline{\Delta\delta}$  correlates with a higher solubility.

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