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# *Solubility Parameters of Epoxidised Natural Rubber*

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*Solubility parameter values have been obtained for a series of epoxidised natural rubbers (ENR) both by calculation and from equilibrium swelling data. A 41 mole% epoxidised synthetic* cis-*1, 4-polyisoprene was also included in the study; its solubility parameter was determined by the viscosity technique. Solubility parameters increased in a linear manner with the extent of epoxidation. These data can be employed to predict a number of ENR properties e.g. polymer solubility, solvent resistance and compatibility with other polymers. However, any specific solvent/ENR or polymer/ENR interactions such as dipole or hydrogen-bonding forces can lead to erroneous conclusions unless these are also taken into account.*

Epoxidised natural rubber (ENR) is produced by the chemical modification of natural rubber latex with peroxycarboxylic acids. One consequence of the modification is that resistance to swelling by hydrocarbon oils and solvents increases. These solubility characteristics should be reflected in various thermodynamic interaction parameters. Solubility parameters of ENR have been calculated and derived from swelling measurements. The solubility parameter of a 41 mole% epoxidised synthetic *cis*-1,4 polyisoprene has also been determined.

The solubility parameter concept is based on Hildebrand's solution theory[1] and can be related to polymer solvent interaction coefficients and to cohesive energy density, which in turn yields information on intermolecular forces in polymers. This data will be useful in predicting a number of polymer properties, e.g. polymer solubility, compatibility with other polymers and solvent resistance.

The solubility parameter of a low molecular weight liquid can be readily determined from its energy of vapourisation but those of polymers cannot be measured in this way as they cannot be vapourised without decomposition.

The solubility parameters of polymers are determined by studying their interactions with a series of solvents of known solubility parameters and assigning to the polymer the value of the liquid which appears to be the best solvent[2]. This can be achieved by swelling the crosslinked polymer in a series of solvents or the intrinsic viscosity of the polymer can be determined in a series of solvents. In both cases, the solubility parameter of the polymer is assumed to be that of the solvent in which a maximum in the property measured, swelling or intrinsic viscosity, occurs. The values of solubility parameter determined by the above methods can depend on the type of solvents used. This is particularly noticeable when strong hydrogen-bonding solvents are employed which can interact with functional groups in the polymer. A 'three dimensional' solubility parameter has been described[3] to take account of dispersion forces, dipole forces and hydrogen bonding, but in this work a simple approach was taken with care to avoid the use of strong hydrogen-bonding solvents.

Solubility parameter values can also be obtained from a knowledge of the chemical structure and density of the polymer by utilising the concept of molar attraction constants developed by Small[4].

The above methods have been utilised to determine the solubility parameters of a range of epoxidised natural rubbers.

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## EXPERIMENTAL

### Materials

The natural rubber (NR) used was a sample of Malaysian SMR L; 26 mole% and 48 mole% epoxidised natural rubbers (ENR 26 and ENR 48) were obtained from the Rubber Research Institute of Malaysia and 71 mole% epoxidised natural rubber (ENR 71) prepared by epoxidation of NR latex employing peroxyacetic acid solution[5]. The 41 mole% epoxidised synthetic *cis*-1,4 polyisoprene was prepared from Cariflex IR305 (Shell) by reaction with peroxyacetic acid in dichloromethane solution.

Samples for the swelling measurements were taken from 2 mm thick sheets which were produced by crosslinking the rubbers with 1.5 p.p.h.r. of dicumyl peroxide.

Oil resistance measurements *(ISO 1817)* were carried out on vulcanisates produced according to the formulations in *Table 1*.

All the solvents used were of laboratory reagent standard with a purity >99%. Their solubility parameters are recorded in *Table 2*.

Prior to swelling, all the rubber vulcanisates were extracted with acetone in a soxhlet apparatus for 24 h under an atmosphere of nitrogen. The extracted samples were dried to constant weight under vacuum.

### Equilibrium Swelling Measurements

Samples 30 × 5 × 2 mm of the extracted vulcanisates were weighed accurately and then immersed in a glass vessel containing the solvent (30 $cm^3$) at 23°C. The vessels were stored in the dark and periodically the rubber samples removed, dried of excess surface solvent with lens tissue, and weighed in a closed bottle to prevent evaporation. The sample was replaced in the solvent and the process repeated until a constant weight was obtained. The fraction of solvent swollen in the rubber was determined by drying the sample under vacuum.

### Viscosity Measurements

Flow times of solvents of known solubility parameters *(Table 2)* and of solutions of 41 mole% epoxidised *cis*-1,4 polyisoprene in these solvents within the concentration range 0.02 - 0.21 g/dl were measured in an Ubbelohde viscometer at 23°C. Intrinsic viscosities were determined from double plots of $\eta_{sp}/C$ and $\ln\eta_r$ against $C$; $\eta_{sp}$ is specific viscosity, $\eta_r$ is relative viscosity and $C$ is concentration.

## RESULTS AND DISCUSSION

Equilibrium swelling measurements on NR, ENR 26, ENR 48 and ENR 71 gum peroxide vulcanisates were carried out in a range of solvents of known solubility parameters. The results are recorded in *Table 2*. The volume fraction of solvent in the samples, swollen to equilibrium, are plotted against the solubility parameter of the solvent in *Figure 1*. The values of solubility parameter for NR and the ENR estimated by this technique are recorded in *Table 3*. The accuracy of the solubility parameter values determined by this technique depends on the positioning of the curve maximum. In the case of ENR 71 data, it is not possible to determine the maximum with any real accuracy because of a low dependence of swelling on $\delta$ for this polymer.

Solubility parameters can also be obtained from swelling data *via* the modified Flory-Rehner equation:

$$-\ln(1-Vr) - Vr - \chi Vr^2 = \rho Vo\,(Vr^{1/3} - \tfrac{1}{2}Vr)_{/Mc} \quad \ldots 1$$

where $Vo$ = molar volume of solvent
$Vr$ = volume fraction of rubber in the swollen network
$\chi$ = polymer solvent interaction parameter
$Mc$ = average molecular weight of rubber chains between crosslinks
$\rho$ = density of rubber.

From a knowledge of the polymer solvent interaction parameters ($\chi$), solubility parameters ($\delta$) can be calculated from Huggins' equation[6]:

$$\chi = \beta^1 + (Vo_{/RT})\,(\delta_1 - \delta_2)^2 \quad \ldots 2$$

TABLE 1. FORMULATIONS EMPLOYED TO DETERMINE THE OIL RESISTANCE OF POLYMERS

| Item | Formulation | | | | | | |
|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
| Polymer | NR | ENR 26 | ENR 48 | NBR[e] | NBR[f] | NBR[g] | Polychloroprene[h] |
| Zinc oxide | 5 | 5 | 5 | 5 | 5 | 5 | 5 |
| Stearic acid | 2 | 2 | 2 | 2 | 2 | 2 | 2 |
| Antioxidant[a] | 2 | 2 | 2 | 2 | 2 | 2 | 2 |
| S | 1.3 | 1.22 | 1.14 | 0.87 | 0.67 | 0.99 | 0.45 |
| MBS[b] | 1.3 | 1.22 | 1.14 | 0.87 | 0.67 | 0.99 | — |
| TMTD[c] | 0.2 | 0.19 | 0.17 | 0.13 | 0.1 | 0.15 | 0.8 |
| DPG[d] | — | — | — | — | — | — | 0.8 |
| Vulcanisates cured to optimum at 150°C | | | | | | | |
| Modulus at 100% extension (MPa) | 0.84 | 0.80 | 0.83 | 0.83 | 0.82 | 0.85 | 0.82 |
| Modulus at 300% extension (MPa) | 1.97 | 1.80 | 1.80 | 1.13 | 1.05 | 1.23 | 1.38 |
| Tensile strength (MPa) | 20.5 | 21.3 | 23.2 | 3.1 | 2.7 | 3.9 | 16.5 |
| Elongation at break (%) | 640 | 680 | 710 | 800 | 823 | 675 | 830 |
| Oil resistance | | | | | | | |
| Volume swelling (%), 70 h at 100°C | | | | | | | |
| ASTM No. 1 oil | 130 | 31 | 4 | 13 | 3 | 2 | 19 |
| ASTM No. 2 oil | 194 | 104 | 36 | 51 | 16 | 8 | 60 |
| ASTM No. 3 oil | 276 | 190 | 80 | 98 | 40 | 17 | 141 |

[a]Poly 2,2,4-trimethyl 1,2-dihydroquinoline
[b]2-Morpholinothiobenzothiazole-2-sulphenamide
[c]Tetramethylthiuram disulphide
[d]Diphenyl guanidine
[e]18% Acrylonitrile NBR
[f]28% Acrylonitrile NBR
[g]34% Acrylonitrile NBR
[h]Baypren 110

TABLE 2. EQUILIBRIUM SWELLING OF NR, ENR 26, ENR 48 AND ENR 71 GUM PEROXIDE VULCANISATES AT 23°C

| Polymer | Solvent ($\delta$)[a] | Vs | Vr | $\chi$ |
|---|---|---|---|---|
| NR | Pentane [14.4 $(MPa)^{1/2}$] | 0.623 | 0.377 | 0.618 |
| | Hexane [14.9 $(MPa)^{1/2}$] | 0.671 | 0.329 | 0.559 |
| | Octane [15.6 $(MPa)^{1/2}$] | 0.691 | 0.309 | 0.513 |
| | Decane [15.9 $(MPa)^{1/2}$] | 0.678 | 0.322 | 0.510 |
| | Cyclohexane [16.8 $(MPa)^{1/2}$] | 0.792 | 0.210 | 0.433 |
| | Butyl acetate [17.4 $(MPa)^{1/2}$] | 0.642 | 0.358 | 0.589 |
| | Methyl propyl ketone [17.8 $(MPa)^{1/2}$] | 0.505 | 0.495 | 0.736 |
| ENR 26 | Decane [15.8 $(MPa)^{1/2}$] | 0.444 | 0.556 | 0.782 |
| | Cyclohexane [16.8 $(MPa)^{1/2}$] | 0.717 | 0.283 | 0.526 |
| | Methyl isobutyl ketone [17.2 $(MPa)^{1/2}$] | 0.737 | 0.263 | 0.487 |
| | Butyl acetate [17.4 $(MPa)^{1/2}$] | 0.763 | 0.237 | 0.440 |
| | Methyl propyl ketone [17.8 $(MPa)^{1/2}$] | 0.667 | 0.333 | 0.581 |
| ENR 48 | Cyclohexane [16.8 $(MPa)^{1/2}$] | 0.525 | 0.475 | 0.715 |
| | Methyl isobutyl ketone [17.2 $(MPa)^{1/2}$] | 0.788 | 0.212 | 0.448 |
| | Butyl acetate [17.4 $(MPa)^{1/2}$] | 0.789 | 0.211 | 0.422 |
| | Toluene [18.2 $(MPa)^{1/2}$] | 0.830 | 0.170 | 0.376 |
| | Ethyl acetate [18.6 $(MPa)^{1/2}$] | 0.753 | 0.247 | 0.498 |
| | Methyl ethyl ketone [19.0 $(MPa)^{1/2}$] | 0.770 | 0.230 | 0.513 |
| ENR 71 | Butyl acetate [17.4 $(MPa)^{1/2}$] | 0.815 | 0.185 | 0.424 |
| | Methyl propyl ketone [17.8 $(MPa)^{1/2}$] | 0.824 | 0.176 | 0.435 |
| | Methyl proprionate [18.2 $(MPa)^{1/2}$] | 0.806 | 0.194 | 0.477 |
| | Methyl ethyl ketone [19.0 $(MPa)^{1/2}$] | 0.808 | 0.192 | 0.480 |
| | Acetone [20.3 $(MPa)^{1/2}$] | 0.746 | 0.254 | 0.560 |
| | Methyl formate [20.8 $(MPa)^{1/2}$] | 0.755 | 0.245 | 0.558 |

Vs = Volume fraction of solvent

Vr = Volume fraction of rubber

$\chi$ = Solvent polymer interaction parameter

[a]Solubility parameter of solvent[2]

In order to determine the interaction parameter, the number average molecular weight of rubber chains between crosslinks in the vulcanisate has to be established. These can be obtained from $C_1$ values:

$$C_1 = \rho RT_{/2M_c} \qquad \ldots 3$$

$C_1$ values *(Table 4)* were obtained by the standard procedure from stress strain measurements on the unswollen vulcanisates[7]. Bristow and Porter have shown that comparable $C_1$ values are obtained from swollen vulcanisates[7]. The values for $\chi$ presented in *Table 4* were calculated using *Equations 1* and *3*.

Assuming that *Equation 2* represents a valid means of determining solubility parameters, rearrangement gives:

$$\frac{\delta_1^2}{RT} - \frac{\chi}{Vo} = [2\delta_2/RT]\delta_1 - \frac{\delta_2^2}{RT} - \beta^1{}_{/Vo}$$

The slope of the plot of $\delta_1{}^2{}_{/RT} - \chi/_{Vo}$ against $\delta_1$ thus yields the solubility parameter of the polymer. Good straight-line plots *(Figure 2)*

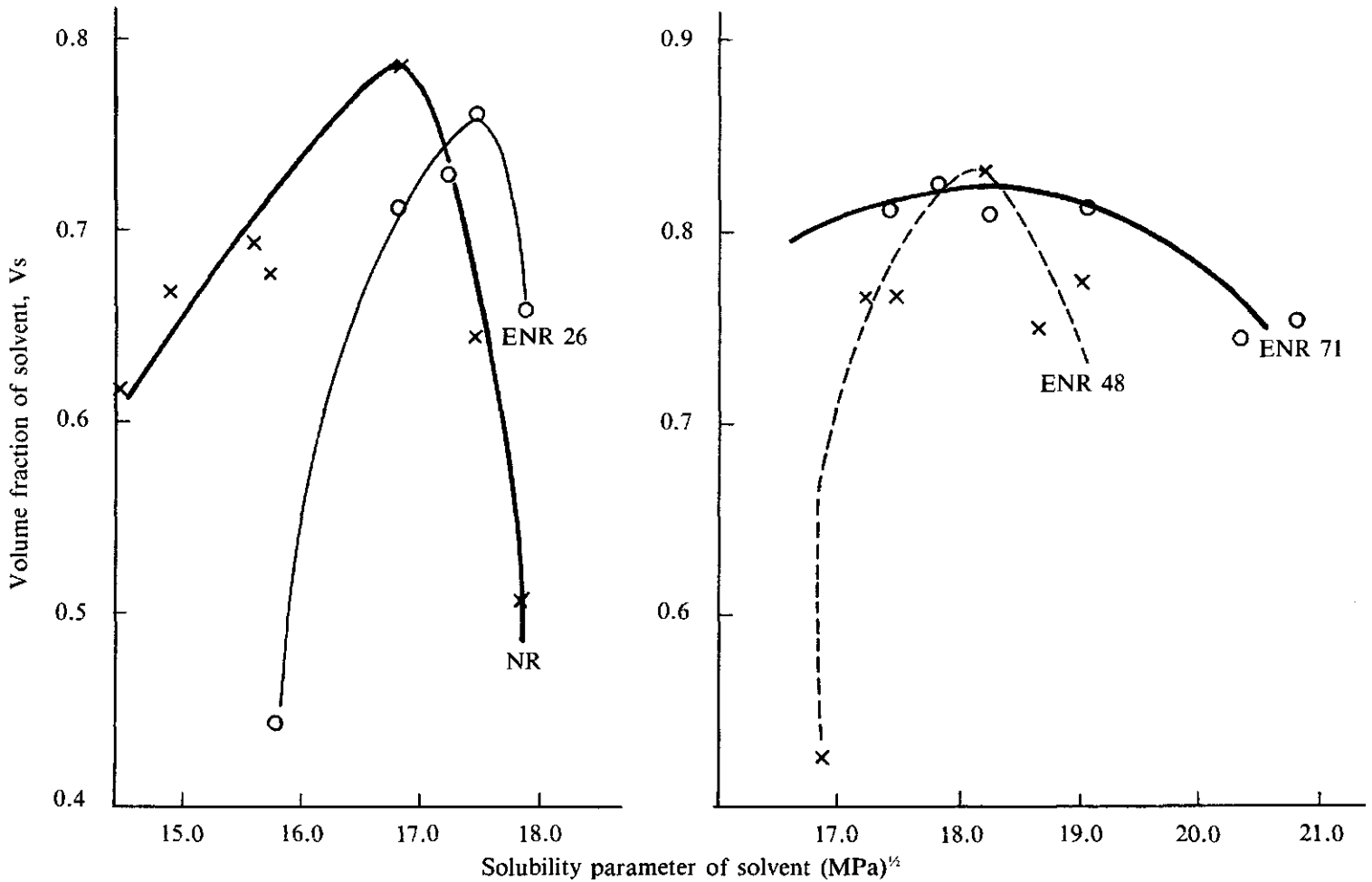


*Figure 1. Equilibrium swelling of gum peroxide vulcanisates of NR, ENR 26, ENR 48 and ENR 71 at 23°C in a range of solvents of known solubility parameters.*

TABLE 3. SOLUBILITY PARAMETERS OF NR AND ENR

| Polymer | Solubility parameter $(MPa)^{1/2}$ A | B | C | D |
|---|---|---|---|---|
| NR | 16.8 | 16.9 | 17.0 | — |
| ENR 26 | 17.4 | 17.4 | 17.6 | — |
| ENR 48 | 18.1 | 18.2 | 18.2 | — |
| ENR 71 | 18.4 | 18.7 | 18.6 | — |
| ENR 41[a] | — | — | 17.9 | 17.8 |

A – Values determined from equilibrium swelling plots

B – Values determined *via* modified Flory-Rehner equation[4]

C – Calculated by Small's method using Hoy's constants

D – Value determined from viscosity measurements

[a]41 mole% epoxidised Cariflex IR305

TABLE 4. ELASTIC PARAMETER, $C_1$ OF THE EXTRACTED PEROXIDE CROSSLINKED RUBBERS USED IN THE SWELLING MEASUREMENTS

| Vulcanisate | $C_1$ (MPa) |
|---|---|
| NR | 0.174 |
| ENR 26 | 0.165 |
| ENR 48 | 0.137 |
| ENR 71 | 0.101 |

were obtained employing the data recorded in *Table 2*. The solubility parameters of NR and the ENR obtained are recorded in *Table 3*.

Solubility parameters of polymers can also be estimated from 'molar attraction constants', a technique which was developed by Small[4]. He assumed that the geometric mean rule holds and thus the contributions of the different groups in the polymer are additive, *i.e.*

$$\delta = \frac{(\Sigma F)}{V}$$

$F$ = molar attraction constant, $V$ = molar volume of a polymeric repeat unit which contains all the different groups.

The solubility parameters of the ENR studied in this paper were calculated employing the molar attraction constants established by Hoy[8] and the results are recorded in *Table 3*.

The solubility parameter of a 41 mole% epoxidised synthetic *cis*-1,4 polyisoprene was also determined, in this case, the viscosity technique[4] was employed. The intrinsic viscosities of the polymer are plotted in *Figure 3*. The solubility parameter of the polymer was assigned as that at which the maximum intrinsic viscosity was observed *(Table 3)*.

All the results are collected together in *Figure 4* which plots solubility parameter against the extent of epoxidation of the rubber. A linear relationship is observed with the solubility parameter increasing with the level of epoxidation.

The resistance of rubbers to hydrocarbon oils is normally measured by determining their volume swell in standard ASTM oils. It is possible to estimate the oil resistance of a rubber from its solubility parameter. This is illustrated in *Figure 5*, where the oil resistance of a series of rubber vulcanisates of similar modulus *(Table 1)* are plotted against their solubility parameters. During this work, it was noted that the literature solubility parameter values[4,9] of polychloroprene cover a wide range, 16.6 $(MPa)^{1/2}$ to 19.2 $(MPa)^{1/2}$. Data obtained from the swelling of polychloroprene, ENR and NBR in ASTM No. 1, 2 and 3 oils *(Table 1)* would indicate a solubility parameter for chloroprene of 17.6 $(MPa)^{1/2}$ to 17.7 $(MPa)^{1/2}$ *(Figure 5)*. The solubility parameter values for NBR were taken from the *Polymer Handbook*[10].

Ply adhesion values between ENR and other polymers have been published[11]. The adhesive strength between NR and a series of ENR can be related to the solubility parameters, as the difference in the polymer-polymer interaction parameters increases, the adhesive strength decreases.

A number of ENR properties can be predicted from solubility parameter values, but this approach needs to be treated with care. For example, the adhesive strength between poly vinyl chloride (PVC) and ENR 50 is high and the two components have been shown to be completely compatible[11], only one glass transition temperature is observed intermediate

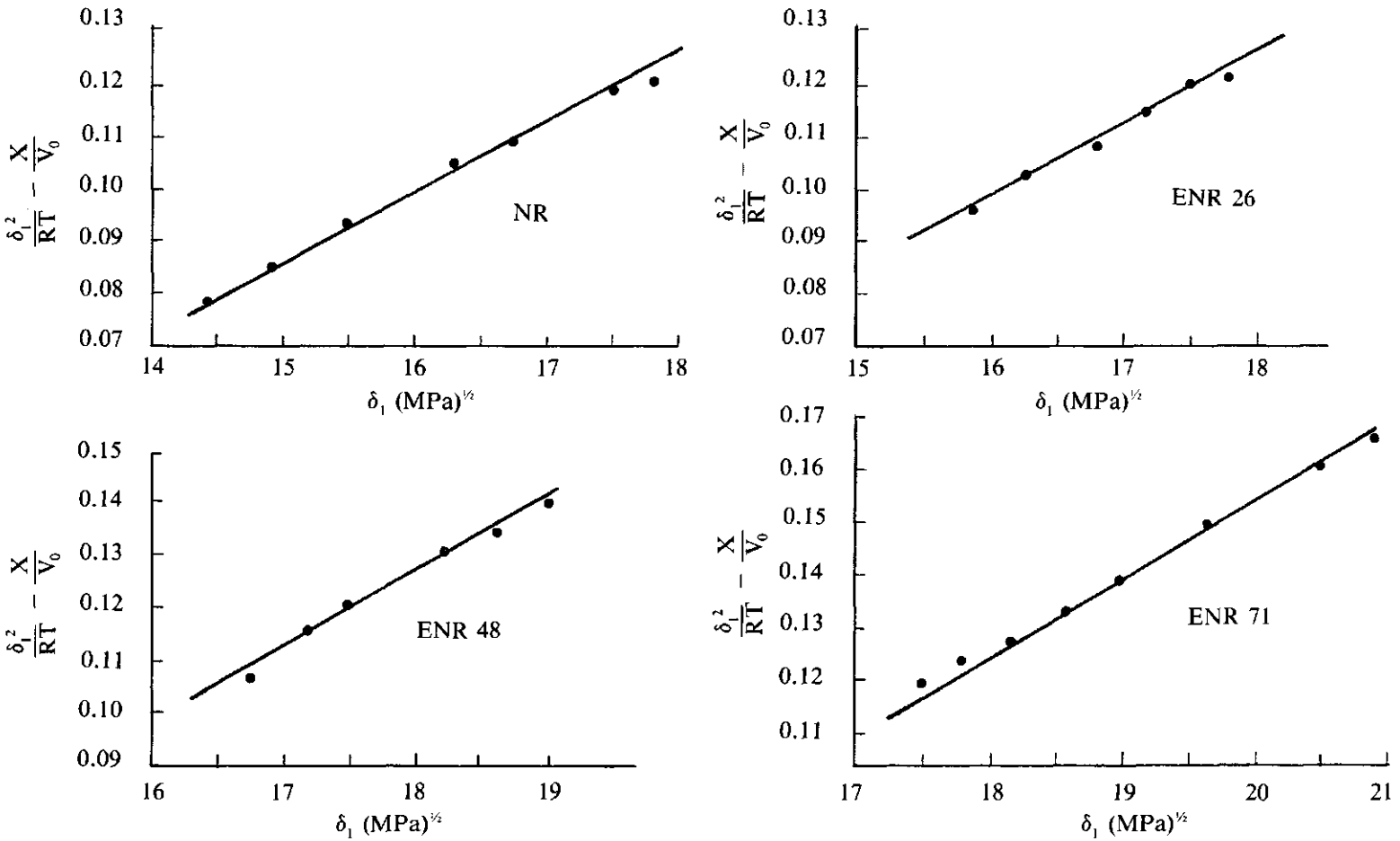


*Figure 2. Modified Flory-Rehner plots of volume swelling data for NR, ENR 26, ENR 48 and ENR 71 to determine solubility parameters.*

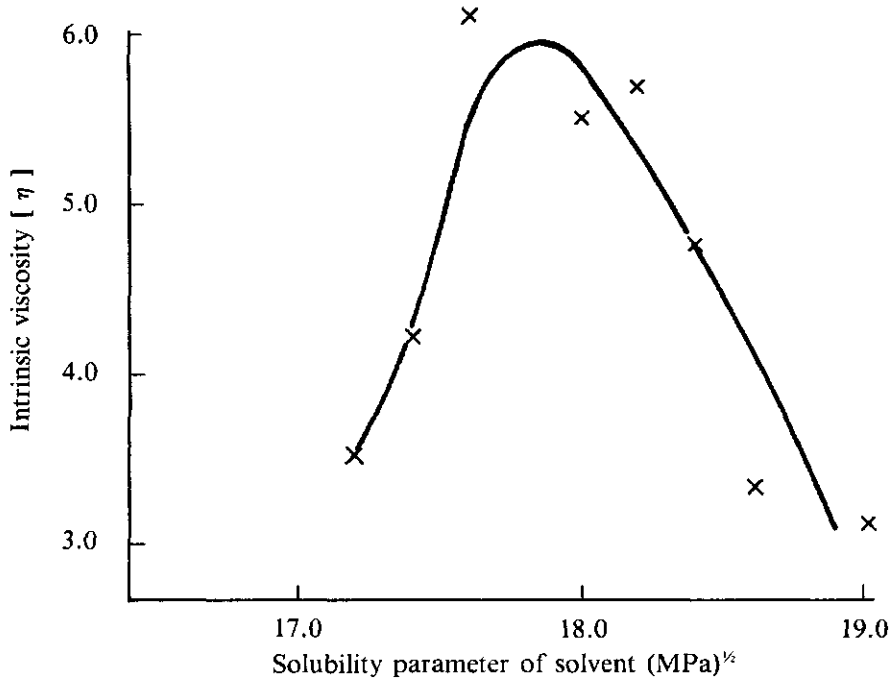


*Figure 3. Plot of intrinsic viscosity of 41 mole% epoxidised Cariflex IR305 in a range of solvents of known solubility parameters.*

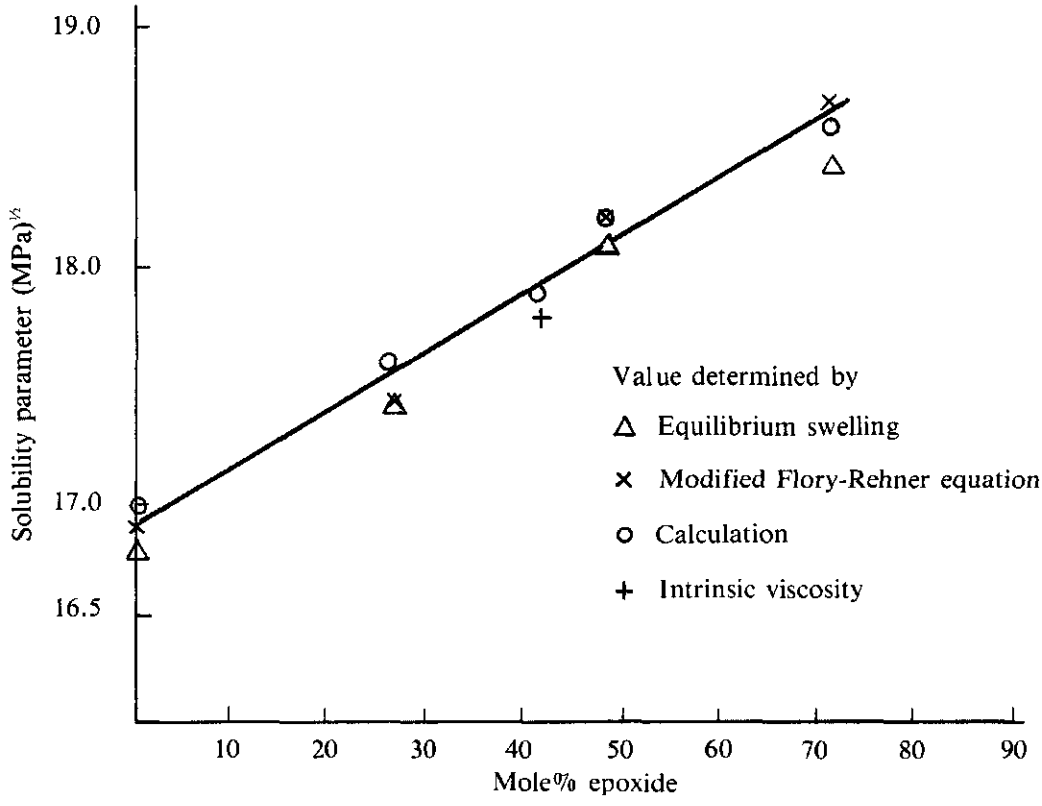


*Figure 4. Dependence of solubility parameters of ENR on epoxide content.*

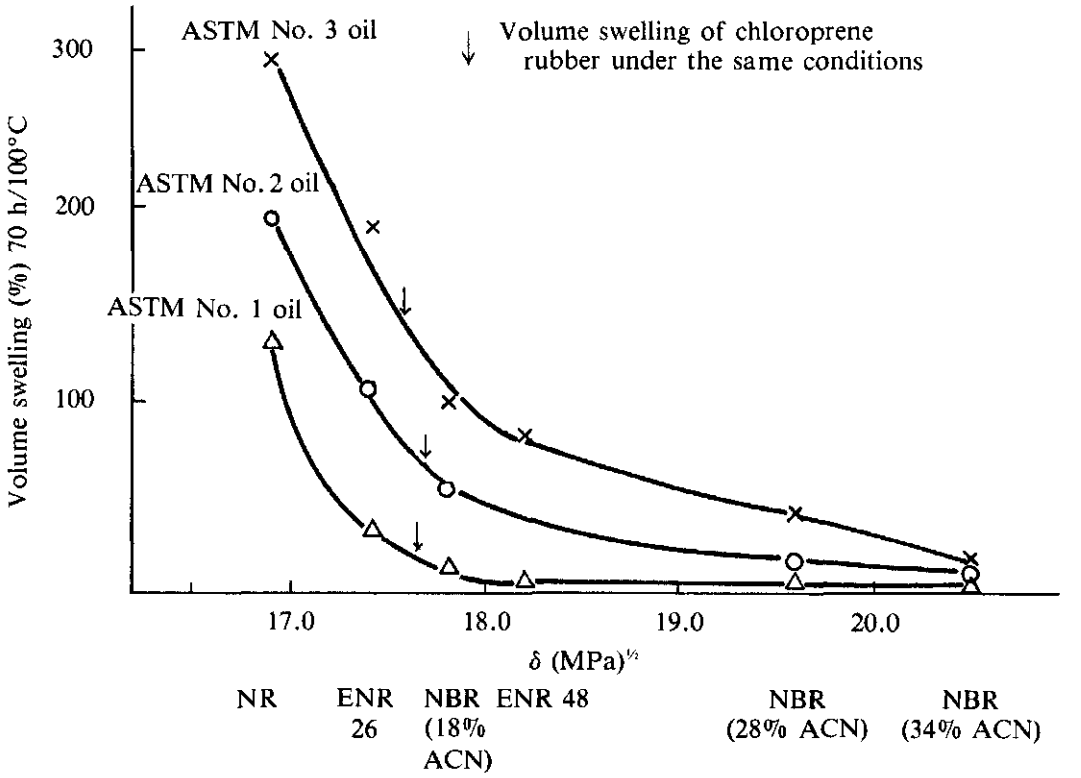


*Figure 5. Volume swelling of a series of ENR and NBR of known solubility parameters in ASTM oils.*

between that of ENR 50 and PVC. The difference in solubility parameters of these materials is 1.3 $(MPa)^{½}$. However, the solubility parameters of ENR 25 and ENR 50 differ by only 0.7 $(MPa)^{½}$, yet the adhesive strength between these two materials is only moderate[11] and they are not compatible, the two individual glass transition temperatures are observed by differential scanning calorimetry.

The unexpected high degree of compatibility between ENR and PVC can be ascribed to polar/polar and/or donor-acceptor interactions between the acidic $\alpha$ hydrogen of PVC and the epoxide groups[12].

Chloroprene rubber and ENR 50 are also completely compatible[13], in this case the difference in solubility parameter is 0.5 $(MPa)^{½}$ but it is known[14] that ENR with a solubility parameter difference of only 0.3 $(MPa)^{½}$ are not compatible and hence specific interactions also probably contribute to the miscibility of chloroprene and ENR 50.

When using solubility parameters of ENR to predict interactions with solvents or other polymers, consideration must be given to the possible involvement of dipole and hydrogen-bonding forces.

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