Solubility Coefficients and Fluorinated Rubber Properties

INTRODUCTION

In many cases, the knowledge of the polymer solubility parameters permits one to purposefully choose polymer solvents, softeners, and additives[1] as well as to evaluate the possibility of some intermolecular interactions influencing the technological behavior of a polymer,[2] etc. Considering that the fluorinated rubbers have fragments containing halogen and hydrogen atoms, there is the possibility that hydrogen bonding should take place. At the same time, experimentally determined values of solubility indicate the different values (Ref. 3, pp. 3–33).

EXPERIMENTAL

To investigate this phenomenon in more detail, the authors have determined the solubility parameters and interaction of some solvents with fluorinated rubbers such as SKF-26 ($\sim$70% of globular (weak linkage) fraction, SKF-26-CHM (with no globular fraction), SKF-A (tetrafluor-ethylene–propylene copolymer), and SKF-460 (tetrafluor-ethylene–perflur-methyl–vinyl copolymer). SKF-26 is fluorinated vinylidene and hexaflur-propylene copolymer.

The experiments were conducted using the conventional method of inverse gas chromatography on chromatograph "Colour-102" (Ref. 4, p. 5, 10). Packed columns were used. Insoluble SKF-A and SKF-460 were used as a mechanical mix of crumbed rubber (particle diameter = 0.63 mm) and small glass balls diameter = 0.50–0.63 mm). In some experiments using SKF-26 rubber, satisfactory agreement in results obtained with the packed column and rubber crumb-filled column was found.

As sorbates, n-paraphines (C_8–C_{11}), cyclohexane, toluene, paraxlene, chloroform, n-octane, acetone, and carbon tetrachloride were used.

Experimental temperatures were in the range of 85–115°C with extrapolation to 20°C. By equation $X = \alpha + \beta / T$, according to Ref. 5, the calculation was performed using the method of relative thermodynamical parameters (Refs. 5 and 6, p. 142).

The calculated values of solubility factors were obtained in Tables I and II (Ref. 7, p. 238).

For SKF-26, the experimental value (δ_2) is close to that previously determined by other methods. Values (δ_2) for SKF-26 and SKF-26-OHM are near the calculated

ones obtained without consideration of the hydrogen bond contribution.

RESULTS AND DISCUSSION

Despite general theoretical assumptions,[8] there are no hydrogen links like

$$\begin{array}{cc} F & H \\ | & | \\ A\sim C\sim \quad \sim C\sim B \\ | & | \\ F & \cdots \quad H \end{array}$$
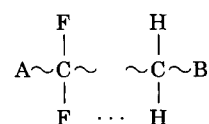
that could be formed in the fluorinated rubbers. It is obvious that the F-atom, having less radius and the greatest electronegativity among all halogens, is insufficient to be active in this reaction, which is exhibited by results of thermodynamical interaction between SKF and chloroform. The high positive parameters (X) are indicative of bad compounding and the absence of special interaction among components. Hydrogen linkages do not build up either in SKF-26 or in SKF-26-OHM, which are different in their molecular mass and structure.

The above consideration does not argue the impossibility of making hydrogen bonds between molecules of copolymers of vinylidene fluoride and other products. In this case, the potential centers of making hydrogen links are atoms of fluorine and hydrogen. The mobility of hydrogen in fragment B can be increased through replacing one hydrogen atom for some polar fragment.

Table II shows the ability of fragment A hydrogen molecules to form hydrogen linkages with the carbonyl group.

Table I   Rubber Solubility Factors (δ_2) at 20°C[a]

| | δ_2 $(mJ/m^3)^{0.5}$ | |
Rubber	Experimental	Calculated
SKF-26	19.4	19.4
SKF-26-CHM	19.8	19.4
SKF-460	13.3	12.2–18.0
SKF-A	20.8	14.1–23.9

[a] The calculated values for SKF-460 are given both with and without considering (lesser value) the polar intermolecular interaction. The same is done with the hydrogen bond energy in SKF-A.

**Table II Interaction Factors for Sorbates and Rubbers at 85°C**

Rubber	n-Octane			Chloroform			Acetone		
	χ_1^∞	$\chi_{1(H)}^\infty$	$\chi_{1(S)}^\infty$	χ_1^∞	$\chi_{1(H)}^\infty$	$\chi_{1(S)}^\infty$	χ_1^∞	$\chi_{1(H)}^\infty$	$\chi_{1(S)}^\infty$
SKF-26	2.55	3.49	−2.94	1.37	4.48	−3.41	−0.31	0.24	−0.55
SKF-26-CHM	2.69	5.97	−3.28	1.37	3.82	−2.45	−0.28	0.48	−0.76
SKF-460	2.69	8.83	−6.15	2.34	9.07	−6.73	1.98	4.30	−2.32
SKF-A	3.06	14.69	−11.63	2.88	12.9	−10.02	3.09	12.36	−9.27

ᵃ χ_1^∞, $\chi_{1(H)}^\infty$, $\chi_{1(S)}^\infty$ are interaction factors and their enthalpy and enthropy components, respectively.

When SKF-26 and SKF-26-OHM react with acetone, the interaction parameter is negative.

The positive value of mixing enthalpy and entropy show better solubility of SKF-26 in acetone with temperature increasing, that is, the system has its upper critical temperature of solubility. This phenomenon is supposed to be connected with the intermolecular reaction between sorbate and rubber, the compounding enthalpy being increased as a result of it. The hydrogen bond formation takes place when a fluorinated rubber reacts with a vinyl group of SKN as well.[9]

SKF-460 does not contain mobile atoms of hydrogen; in terms of thermodynamics, SKF-460 reaction with acetone and chloroform is similar to the reaction with nonpolar n-octane (Table II). It is interesting to note that ether oxygen in the fragment of perfluoromethyl–vinyl ether does not make a link with a mobile atom of hydrogen in chloroform, although simple ethers (for instance, dioxane) are solvents for fluorinated rubbers through making linkage C — H · · · O=. In this case, the electron donor ability of oxygen is likely to decrease because of the influence of adjacent atoms of electronegative fluorine. There is a different reaction scheme when using SKF-A, whose solubility parameter is remarkably higher than the calculated one (with no consideration of H-bond energy). The hydrogen links build up through interaction of components which is promoted with an alternative structure of SKF-A.

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      F
      |
    —C—
      |
      F  ···  H
              |
            —C—
              |
             CH3
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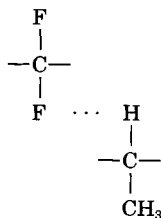
CONCLUSION

The calculated and experimental value of solubility parameters of some fluorinated polymers are determined. It is shown that, in vinylidene fluoride copolymers, the possibility of building up intermolecular H-bonds is not realized because of molecular stiffness and chemical struc-

ture. The tetrafluoroethylene and propylene copolymers as alternatives are featured with strong intermolecular reaction owing to H-bond formation.

We hope our data may be useful to purposefully modify fluorinated elastomers. Particularly, replacing one hydrogen atom in the fragment of vinylidene fluoride for some other substitute can increase the ability to make more hydrogen bonds, thereby increasing polymer resistivity to polar and nonpolar media. This assumption is indirectly proved by the fact that, unlike more highly fluorinated polyvinylidene fluoride, polyvinylidene fluoride is insoluble at ambient temperatures.

References

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