Optimization determination of three-dimensional solubility parameters of fluororubber F2603

Hongmei Li¹, Xiaoqin Shi¹, Xuesong Feng² and Liming Dong¹,*
¹School of Chemistry and Chemical Engineering, Xuzhou University of Technology, Xuzhou, China
²Xi'an Modern Chemistry Research Institute, Xi'an, China

Abstract. Turbidity titration experiment on fluororubber F2603 using a variety of good solvents and poor solvents, the minimum volume closure ellipsoidal fit is performed on the 48 cloud point data generated by KY (Kumar and Yildirim) first-order algorithm, thus determining the ellipsoid The ball center is a three-dimensional solubility parameter: $\delta_d=16.63$(MPa)$^{1/2}$; $\delta_r=11.25$(MPa)$^{1/2}$; $\delta_H=12.02$(MPa)$^{1/2}$, and the solubility parameter is 23.40(MPa)$^{1/2}$. The reliability and accuracy of the fitting results are determined by the group contribution method, The solubility parameters have important guiding significance for selecting solvents with superior performance and determining better formulation design.

1. Introduction
Fluoro-polymers have excellent weather resistance, heat resistance, corrosion resistance and so on, which mainly because of the high electro-negativity of fluorine elements and strong fluorocarbon bonds [1]. For example, PTFE, which is referred to as a "plastic king"[2], but the application is limited because it has poor dissolution process-ability and is almost insoluble in all reagents. In order to eliminate this disadvantage, a high molecular elastomeric fluororubber is prepared by copolymerization of a perfluromonomer and a non-perfluoromonomer [3]. The non-perfluoro structure of the main chain destroys the crystallinity of the polymer, making the solvent molecules easily invade the inside of the chain structure, thereby exhibiting solubility characteristics. For example, the fluororubber-26 can be sufficiently dissolved in ketone, ether, ester, amine, ammonia, chlorosulfonic acid, or phosphoric acid solvent. This soluble property broadens the application of such materials, such as anti-corrosion coatings, automotive gaskets, O-rings, oil seals and connecting tubes [4-6]. The solubility parameter is an important parameter to weigh the compatibility between different substances, and is also an important tool to study the solubility characteristics of polymers[7].The solubility parameter of the fluororubber accurately obtained by the solubility parameter theory can quickly and accurately select the polymer solvent and better determine the formulation, which is of great significance.

Since the polymer cannot directly measure its heat of vaporization, its parameters are often obtained by the indirect method of pure solvent method. Liu W.P. used inverse gas chromatography to determine the solubility parameters of fluororubber, but the workload is too large [8]. Liu J. indirectly measured the solubility parameter of fluororubber by intrinsic viscosity method, but the accuracy of the obtained results was poor [9]. Hansen solubility parameter (HSP) [10] can accurately describe the effects of
dispersive force, polar force and hydrogen bond on the solubility parameters of polymers. It is recognized as a scientific method with the good applicability and the selection of solvents by the polymer field [11]. Therefore, it is of great practical value to study the three-dimensional solubility parameters of fluororubber. However, the measurement method of HSP has the disadvantages of requiring large variety of solvents, large workload, long time, high cost, and low accuracy.

In the previous work, a method for accurately fitting the three-dimensional solubility parameter of polymer HSP by turbidity titration has been proposed. The method has the characteristics of simple operation, simple calculation and less solvent[12]. Based on this work, the calculation of the three-dimensional solubility parameters of the polymer was carried out with the commonly used fluororubber F2603 as the object, in order to obtain more accurate three-dimensional solubility parameter results, and provide a theoretical basis for the selection of solvents.

2. experimental part

2.1. Experimental materials

The F2603 produced by Shanghai Sanaifu New Materials Co., Ltd., which was synthesized by copolymerization of 20% hexafluoropropylene and 80% vinylidene fluoride (mol). Its structure is shown in Figure 1:

\[
\begin{align*}
\text{F} & \quad \text{F} \\
\text{C} & \quad \text{C} \\
\text{H} & \quad \text{CH}_2 \\
\text{C} & \quad \text{C} \\
\text{F} & \quad \text{F} \\
\text{F} & \quad \text{F} \\
\end{align*}
\]

Figure 1. Structure of F2603

According to the solubility experiment, it can be determined that the polymer good solvent includes: N,N-dimethylformamide (DMF), N,N-dimethylacetamide (DMAc), Methyl Isobutyl ketone(MIK), Ethyl acetate(EA), acetone, N-methyl-2-pyrrolidone (NMP), methanol, dimethyl sulfoxide (DMSO). Poor solvents include: Benzene, Chlorobenzene(CB), Xylenes, chloroform (CF), tetrachloroethylene (PCE), formamide (FA), 1,1,2,2-tetrachloro Ethane(TCE), water, n-hexane. The solvents were derived from Sinopharm Group, Tianjin Fuchen Chemical Reagent Factory and so on. Analytical purity. All solvents are subjected to water removal and vacuum distillation. The three-dimensional solubility parameters of each solvent were obtained by querying [13].

2.2. Experimental process

F2603 samples 0.1g were accurately weighed and dissolved in 100ml good solvent, then the transparent solution was prepared, 5 ml of the polymer solution was titrated from the poor solvent by using an acid burette, and was identified as the end point of the titration when the solution became cloudy and the turbidity no longer disappeared. The volume of bad solvent was recorded, and tested three times at the same conditions. The average value of the results was finally obtained.

3. Results and discussion

The three-dimensional solubility parameter of cloud point can be calculated by the experimental results according to the document [12]. The calculated three-dimensional solubility parameters of the cloud point are shown in the following Table 1. The coordinates of 48 cloud points were fitted by (Minimum Volume Enclosing Ellipsoid) of minimum volume closure ellipsoid. The result of the fitting is shown in Figure 2.

The fitted ellipsoid sphere can be considered to be soluble and insoluble interface, and the spherical center coordinate is the three-dimensional solubility parameter value of polymer, then the three-dimensional solubility parameter values of F2603 are: $\delta_d=16.63$(MPa)$^{1/2}$; $\delta_p=11.25$(MPa)$^{1/2}$; $\delta$
$\eta=12.02\text{(MPa)}^{1/2}$. According to the theory of three-dimensional solubility parameters of Hansen, the solubility parameters can be obtained: $\delta = 23.40\text{(MPa)}^{1/2}$.

### Table 1. The three-dimensional Solubility parameters of Cloud Point (MPa)$^{1/2}$

| Solvent | Benzene | CB | Xylenes | CF | PCE | FA | TCE | Water | n-Hexane |
|---------|---------|----|---------|----|-----|----|-----|-------|----------|
| DMF     | $\Phi_8/%$ | 80.35 | 79.59 | 84.49 | 63.44 | 90.75 | 72.10 | 78.19 | 71.32 | / |
|         | $\delta_8$ | 17.60 | 17.74 | 17.43 | 17.55 | 17.49 | 17.34 | 17.71 | 16.88 | / |
|         | $\delta_9$ | 12.28 | 12.38 | 12.60 | 11.07 | 13.17 | 18.08 | 12.35 | 14.40 | / |
|         | $\delta_{11}$ | 10.17 | 10.12 | 10.46 | 9.64 | 10.76 | 13.88 | 10.29 | 24.58 | / |
|         | $\Phi_8/%$ | 73.75 | 77.2 | 79.49 | 41.03 | 61.32 | 63.81 | 69.4 | 63.89 | / |
| DMAc    | $\delta_8$ | 17.23 | 17.33 | 16.97 | 17.4 | 16.95 | 71.44 | 16.34 | / |
|         | $\delta_9$ | 9.88 | 10.31 | 10.26 | 7.74 | 9.68 | 18.24 | 9.99 | 13.3 | / |
|         | $\delta_{11}$ | 8.82 | 9.01 | 9.2 | 7.86 | 7.99 | 14.04 | 8.99 | 26.69 | / |
| MIK     | $\Phi_8/%$ | 81.65 | 90.88 | 93.29 | 82.48 | 88.46 | 84.52 | 94.78 | / |
|         | $\delta_8$ | 16.31 | 16.12 | 15.93 | 16.17 | 16.11 | 16.02 | 15.97 | / |
|         | $\delta_9$ | 4.79 | 5.22 | 4.16 | 4.99 | 5.35 | 11.4 | 5.29 | / |
|         | $\delta_{11}$ | 6.56 | 6.89 | 7 | 6.96 | 6.77 | 9.98 | 7.11 | / |
| EA      | $\Phi_8/%$ | 83.77 | 90.79 | 91.74 | 89.79 | 93.19 | 80.05 | 94.24 | 72.13 | / |
|         | $\delta_8$ | 16.01 | 15.85 | 15.69 | 15.75 | 15.71 | 15.85 | 15.71 | 15.5 | 15.18 |
|         | $\delta_9$ | 9.52 | 10 | 9.97 | 9.9 | 10.15 | 14.95 | 10.17 | 12.22 | 7.14 |
|         | $\delta_{11}$ | 6.46 | 6.7 | 6.76 | 6.88 | 6.76 | 10.55 | 6.91 | 23.11 | 4.8 |
| Acetone | $\Phi_8/%$ | 52.16 | 60.67 | 59.5 | 42.75 | 75.26 | 63.21 | 77.42 | 75.81 | / |
|         | $\delta_8$ | 18.19 | 18.4 | 17.84 | 17.89 | 18.07 | 17.71 | 18.18 | 17.43 | / |
|         | $\delta_9$ | 8.88 | 9.95 | 9.51 | 8.38 | 11.04 | 18.66 | 11.09 | 13.29 | / |
|         | $\delta_{11}$ | 5.38 | 5.75 | 5.89 | 6.38 | 6.25 | 12.87 | 6.82 | 21.73 | / |
| NMP     | $\Phi_8/%$ | 76.1 | 79.07 | 87.42 | 58.68 | 78.67 | 47.66 | 91.11 | 68.43 | / |
|         | $\delta_8$ | 15.95 | 16 | 15.44 | 16.27 | 15.84 | 16.23 | 15.46 | 15.23 | / |
|         | $\delta_9$ | 10.73 | 11.11 | 11.51 | 9.63 | 11.22 | 20.79 | 11.84 | 13.58 | / |
|         | $\delta_{11}$ | 19.48 | 19.85 | 2.88 | 17.47 | 19.78 | 20.64 | 21.3 | 30.09 | / |
| Methanol| $\Phi_8/%$ | 64.98 | 66.72 | 71.49 | 64.53 | / | 72.11 | 86.69 | 26.8 | / |
|         | $\delta_8$ | 18.4 | 18.6 | 18.18 | 18.19 | / | 18.07 | 18.45 | 16.33 | / |
|         | $\delta_9$ | 13.22 | 13.62 | 13.88 | 13.3 | / | 19.63 | 15.38 | 16.11 | / |
|         | $\delta_{11}$ | 8.31 | 8.41 | 8.78 | 8.87 | / | 13.25 | 9.69 | 36.57 | / |

“/” means that the two solvents are not soluble in each other.

**Figure 2.** The ellipsoid fitting graph of cloud points
The distance that from the center of the ball to the coordinates of the solvent participating in the fitting experiment was calculated from small to large as follows: DMAc(1.84), DMF (2.67), NMP (5.12), and acetone(5.22), EA(7.70), TCE(9.36), MIK(9.54), Xylenes (15.17), FA (16.51), n-hexane (16.55), benzene (18.96), water (30.67). Theoretically, the closer the distance from the spherical center coordinate to the good solvent, the better the solubility of fluorine rubber samples, and the actual result is consistent with the theory. DMAc value is closest to the spherical center coordinates, and the dissolution effect on the fluororubber sample is also optimal at normal temperature. As can be seen from figure 2, most of the coordinates of cloud points are located in the ellipsoid surface, the coordinates of good solvents are located in the interior of the ellipsoid, then the coordinates of bad solvents are all located in outside the ellipsoid, and the center of the sphere is the point represented by the red circle. According to the above distance calculation results, TCE (9.36) is less than MIK (9.54), however, it was found that MIK is a good solvent in the sphere, TCE is a poor solvent outside the sphere. This undoubtedly proves that the ellipsoid fitting accuracy is better than Hansen’s positive sphere.

Small [14] believes that the cohesive energy density of a polymer is equal to the sum of the cohesive energy densities of all atoms and radicals in the molecular chain. According to this principle, the solubility parameter of the polymer can be calculated from the sum of the molar gravitational constants of all atoms or groups in the macromolecular structural unit. The relationship between the solubility parameter and the molar gravity constant is as follows:

$$\delta = \rho \sum \frac{F}{M_0}$$

where $\rho$ represents the relative density of the polymer; $M_0$ represents the relative molecular mass of the structural unit.

According to the query data, the molar gravity constant of group were as follows: CH$_2$=272.0, CF$_2$=307.0, CF$_3$=561.0, F=84.5[(J/cm$^3$)$^{1/2}$/mol]. The relative density of F2603 was 1.81 g/cm$^3$, the relative molecular mass of the structural unit is 122.8 g/mol, then the solubility parameter is calculated according to formula (1) is:

$$\delta = \rho \sum \frac{F}{M_0} = \frac{1.81[(272.0 + 307.0 \times 2 + 561.0 + 84.5)]}{122.8} = 22.57(J/cm^3)^{1/2}$$

The solubility parameter obtained by the fitting is 23.40 (J/cm$^3$)$^{1/2}$, and the solubility parameter calculated by the group contribution method is 22.57 (J/cm$^3$)$^{1/2}$. The difference between the two is small, indicating that the turbidity titration method is combined with HSP. Theoretical measurement of solubility parameters is reliable and accurate.

4. Conclusion
The three-dimensional solubility parameter value of fluororubber F2603 was obtained by spherical matching method based on turbidity titration method and Hansen HSP theory. The result is: $\delta_d=16.63$ (MPa)$^{1/2}$; $\delta_v=11.25$(MPa)$^{1/2}$; $\delta_H=12.02$(MPa)$^{1/2}$; $\delta_p=23.40$(MPa)$^{1/2}$. The solubility parameter (22.57 (MPa)$^{1/2}$) measured by the group contribution method is similar to the fitting result, which proves the reliability of the fitting result. The turbidity titration fitting HSP three-dimensional solubility parameter method has proved to be an accurate and effective method in this work. it can be extended to the estimation of other polymer solubility parameters.

Table 2. The mathematical expression of ellipsoid

| Vector $c$ | Positive definite matrix |
|-----------|-------------------------|
| $\delta_d=16.63$ | 0.3023 | -0.0505 | 0.0157 |
| $\delta_v=11.25$ | -0.0503 | 0.0280 | -0.0088 |
| $\delta_H=12.02$ | 0.0157 | -0.0088 | 0.0068 |
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