

Characterization of the surface tension and solubility parameter of epoxy resin by using inverse gas chromatography

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Abstract : Inverse gas chromatography (IGC) was used to measure the surface tension and solubility parameter of E51 epoxy resin in this work. By using the Schultz method, decane, nonane, octane and heptane were chosen as the neutral probes to calculate the dispersive surface tensions (γ^D). Based on the Good-van Oss equation, the specific surface tension (γ^{SP}) of E51 epoxy resin was calculated with the acidic probe of dichloromethane and the basic probe of toluene. The results showed that the γ^D and γ^{SP} of the E51 resin decreased linearly with the increase of temperature. According to the Flory-Huggins parameters (χ) between the resin and a series of probes, the solubility parameters (δ) of E51 resin at different temperatures were estimated using the method developed by DiPaola-Baranyi and Guillet. It was found that the values of δ of the E51 resin were 11.78, 11.57, 11.48 and 11.14 MPa^{1/2} at 30, 40, 50 and 60 °C, respectively. The dispersive component (δ_D) and the specific component (δ_{SP}) of solubility parameter at different temperatures of the E51 resin were investigated according to the relationships between surface tension, cohesion energy and solubility parameter. The results showed that the values of δ_D were higher than those of δ_{SP} for the epoxy resin, and both of them decreased with the increase of temperature.

Key words : inverse gas chromatography (IGC); surface tension ; solubility parameter ; epoxy resin

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反气相色谱法测定环氧树脂的表面张力和溶解度参数

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摘要 : 采用反气相色谱(IGC)测定了环氧 E51 树脂在 30、40、50 和 60 °C 下的表面张力和溶解度参数。采用 Schultz 法, 以正癸烷、正壬烷、正辛烷和正庚烷为非极性溶剂探针, 计算了不同温度下环氧 E51 树脂的色散表面张力。根据 Good-van Oss 方程, 以甲苯为碱性探针, 二氯甲烷为酸性探针, 计算得到环氧 E51 树脂的极性表面张力。结果表明, 环氧 E51 树脂的色散表面张力和极性表面张力均随着温度的升高而线性降低。根据不同溶剂探针与树脂间的 Flory-Huggins 相互作用参数, 采用 DiPaola-Baranyi 和 Guillet 方法计算得到环氧 E51 树脂在不同温度下的溶解度参数, 其在 30、40、50 和 60 °C 下分别为 11.78、11.57、11.48 和 11.14 MPa^{1/2}。根据表面张力、内聚能和溶解度参数的相互关系, 计算得到不同温度下溶解度参数的色散和极性分量。结果发现, 环氧 E51 树脂的溶解度参数的色散分量大于极性分量, 且均随着温度的升高而降低。

关键词 : 反气相色谱 ; 表面张力 ; 溶解度参数 ; 环氧树脂

Epoxy resin has been widely used in adhesives, paints, electronics and composite industries due to its excellent adhesion, chemical resistance, good electrical insulating and mechanical properties [1]. The normal parameters, including vis-

cosity, epoxy equivalent and relative molecular mass, are chosen to characterize epoxy resin. However, the existing reports on the surface tension and solubility parameter, which are closely related to the surface and interface properties of

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epoxy resin , are few in the published literature.

The surface tension has been shown to be closely connected to the wettability of epoxy resin , and it can be thought of the sum of the dispersive surface tension (nonpolar components) and the specific surface tension (polar components). The surface tension of typical liquid epoxy resin can be readily measured by dynamic contact angle meter and tensiometer (DCAT) using the Wilhelmy balance method [2] , however , one insufficiency of this method is that it does not allow for the calculation of the dispersive and specific component of surface tension. The solubility parameter , in conjunction with solution theory , has found many practical applications in the prediction of solubility and compatibility of polymer mixture. The polymer solubility parameter can be generally deduced from swelling or viscosity measurements , or it can be estimated from group additivity contribution method or computer simulation [3]. After the introduction and subsequent theoretical developments , the application of inverse gas chromatography (IGC) in the material sciences has grown rapidly. With the variety of well characterized probes , IGC can readily give consistent and realistic estimates for surface energy , solubility parameter and other properties of materials under investigation , and the reliability of the technique has been proven by many studies [4 - 9].

In this study , the retention times in IGC of 8 probes , including decane , nonane , octane , heptane , toluene , dichloromethane , ethanol and acetone , were measured at different temperatures on the stationary phase of passivated glass wool coated with E51 epoxy resin. And the dispersive surface tensions , the specific surface tensions , the Flory-Huggins parameters of the probes and resin , and the solubility parameter of E51 epoxy resin were calculated.

1 Experimental

1.1 Materials

The sample tested in this study was bisphenol-A epoxy resin E51 (Shanghai Research Institute of

Synthetic Resins). The solvents used in IGC were supplied by Sigma-Aldrich , USA. All these adsorbates were high performance liquid chromatographic grade or high purity solvents , and were purchased from J&K Chemical Ltd.

1.2 Apparatus and procedure

IGC experiments were carried out at infinite dilution using an SMS-iGC (UK). The neutral probes were decane , nonane , octane and heptane ; the polar probes included toluene , dichloromethane , ethanol and acetone. Data relating to all probes are presented in Table 1. The E51 was first dissolved in acetone (1% , mass fraction) , and the passivated glass wool (supplied by SMS , UK) was immersed in the solution of E51 for 24 h. And the glass wool was desiccated for 48 h in vacuum at 60 °C , then packed into the SMS standard passivated glass column with an internal diameter of 4 mm and a length of 300 mm. The amount of the coated glass wool was 0.2 g. Methane was used as a non-interacting marker for the measurement of dead-time. Helium was used as the carrier gas , and the flow rate was 10 mL/min. The data calculation was made by the SMS-iGC analysis software (v1.2.5).

Table 1 Properties of the probes

| Probe | Property | Surface tension/ (J/m ²) | Cross sectional area/m ² |
|-------------------|----------|--|--|
| <i>n</i> -Heptane | neutral | 0.0234 | 7.5 × 10 ⁻¹⁹ |
| <i>n</i> -Octane | neutral | 0.0227 | 6.9 × 10 ⁻¹⁹ |
| <i>n</i> -Nonane | neutral | 0.0213 | 6.3 × 10 ⁻¹⁹ |
| <i>n</i> -Decane | neutral | 0.0203 | 5.73 × 10 ⁻¹⁹ |
| Toluene | basic | 0.0285 | 4.6 × 10 ⁻¹⁹ |
| Dichloromethane | acidic | 0.0245 | 2.45 × 10 ⁻¹⁹ |
| Ethanol | acidic | 0.0211 | 3.53 × 10 ⁻¹⁹ |
| Acetone | basic | 0.0165 | 3.4 × 10 ⁻¹⁹ |

2 IGC theory

The retention time was the primary information in gas chromatography [10 - 13] , and it can be converted into the retention volume , which is directly related to the various physico-chemical properties of the material.

The net retention volume V_R^0 can be determined by Equation 1 :

$$V_R^0 = \frac{j}{m} \cdot F \cdot (t_R - t_0) \frac{T}{273.15} \quad (1)$$

where, T is the column temperature, m is the sample mass, F is the carrier gas flow rate, t_r is the retention time taken for the probe and t_0 is the dead time, j is the James-Martin correction, which depends on the pressures at the column inlet and outlet.

As described in the method of Schultz [14] :

$$RT\ln V_R^0 = 2aN_A\sqrt{\gamma_s^D\gamma_L^D} + \text{const} \quad (2)$$

where, N_A is the Avogadro constant, R is the gas constant, a is the cross sectional area of the adsorbate, γ_s^D and γ_L^D are the surface tensions of the adsorbent and the adsorbate, respectively.

So, the dispersive surface energy can be derived from the slope of a series of alkanes $RT\ln V_R^0$ plot to $a(\gamma_L^D)^{1/2}$.

The activity coefficient Ω can be obtained from the retention volume [15 ,16] :

$$\ln\Omega = \ln \frac{273.15R}{p^0 M_1 V_R^0} - p^0 \frac{B_{II} - V_1}{RT} \quad (3)$$

where, p^0 is the saturation pressure, M_1 is the molecular mass, B_{II} is the second virial coefficient and V_1 is the molecular volume of the probe molecule at column temperature.

The Flory-Huggins parameter χ can be derived from Equation (4) :

$$\chi = \ln\Omega + \ln \frac{\rho_1}{\rho_2} - \left(1 - \frac{V_1}{V_2}\right) \quad (4)$$

where ρ is the liquid density and V is the molecular volume.

Using the approach from DiPaola-Baranyi and Guillet [5] a linear equation can be formed :

$$\frac{\delta_1^2}{RT} - \frac{\chi}{V_1} = \left(\frac{2\delta_2}{RT}\right) \cdot \delta_1 - \left(\frac{2\delta_2^2}{RT} - \frac{\chi_s}{V_1}\right) \quad (5)$$

where, δ_1 is the solubility parameter of the probe molecule, δ_2 is the solubility parameter of the resin, χ is the entropic contribution to the Flory-Huggins parameter and V_1 is the molar volume of the probe molecule. If the left-hand side versus δ_1 yields, δ_2 can then be determined from the slope.

3 Results and discussion

3.1 Surface tension

The dispersive surface tension can be calculated from the measured net retention volumes of a series of n -alkane probes according to the Schultz

method. As can be seen from Fig. 1, the values of $RT\ln V_R^0$ at each temperature increase as the increase of the probe carbon number. It should be considered that the n -alkanes adsorption takes place by only dispersive forces, which change linearly with the carbon number of the n -alkanes. The dispersive surface tensions of E51 were 32.98, 30.98, 29.39 and 25.71 mJ/m² at 30, 40, 50 and 60 °C, respectively.

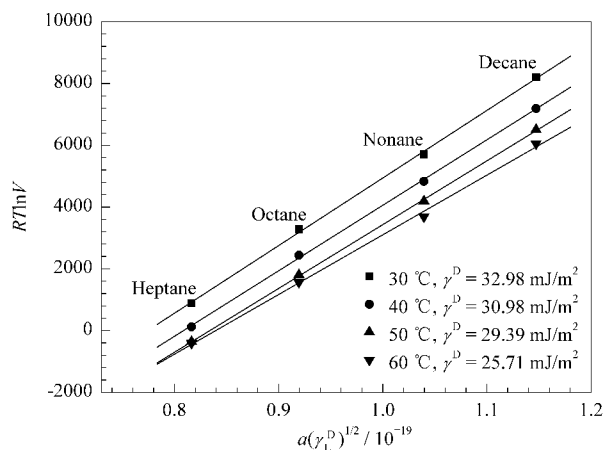


Fig. 1 Dispersive surface tensions for E51 at different temperatures

The specific surface tension represents the contributions of molecular forces other than the dispersive force, which include the hydrogen, polar, and acid-base interactions. The specific surface tension can be estimated theoretically from the specific free energy of adsorption (ΔG^{SP}) of polar probes with different acid-base properties. The interactions between polar probes and the substrate involve both dispersive and specific interactions. As proposed by Schultz, $RT\ln V_R^0$ for each probe plotted against it is $a(\gamma_L^D)^{1/2}$. The distance between each polar probe's point and the straight alkanes line represents the specific interaction, ΔG^{SP} . The values of ΔG^{SP} of the acidic probe of dichloromethane and basic probe of toluene were calculated and are listed in Table 2. As can be seen from Table 2, the ΔG^{SP} s for dichloromethane and toluene decrease as the temperature increase.

Table 2 ΔG^{SP} for dichloromethane and toluene tested on E51

| Probe | J/mol | | | |
|-----------------|---------|---------|---------|---------|
| | 30 °C | 40 °C | 50 °C | 60 °C |
| Toluene | 5197.22 | 5101.13 | 4977.03 | 4332.35 |
| Dichloromethane | 9241.29 | 8913.99 | 8756.41 | 7375.66 |

The specific surface tension can be deduced from the Good-van Oss method [17], as can be seen from Equation (6) :

$$\Delta G^{SP} = 2aN_A(\sqrt{\gamma_L^+ \gamma_s^-} + \sqrt{\gamma_L^- \gamma_s^+}) \quad (6)$$

where γ_L^+ and γ_L^- are the electron acceptor and donor parameters of the probe molecule , γ_s^+ and γ_s^- are the electron acceptor and electron donor parameters of the stationary phase surface. The γ_L^+ of the basic probe of dichloromethane is 124.58 mJ/m² , and the γ_L^- of the acidic probe of toluene is 16.23 mJ/m². The γ_L^- of the acidic probe of dichloromethane and the γ_L^+ of the basic probe of toluene are zero. The γ_s^+ and γ_s^- for the resin can be calculated from Equation (6) , and then the specific surface tension was obtained from Equation (7). The specific surface tensions of E51 were 13.07 mJ/m² , 12.37 mJ/m² , 11.86 mJ/m² and 8.69 mJ/m² at 30 , 40 , 50 and 60 °C , respectively.

$$\gamma_s^{SP} = 2 \sqrt{\gamma_s^+ \gamma_s^-} \quad (7)$$

The total surface tension (γ^T) of E51 can be obtained from the sum of the dispersive surface tension (γ^D) and the specific surface tension (γ^{SP}). As shown in Fig. 2 , the total surface tensions decrease linearly with the increase of temperature , and the dispersive surface tension and the specific surface tension show the same tendency. This phenomenon agrees with the results in early works in which they were measured by DCAT technique [2]. The results indicated that IGC can be used as a valuable tool for the characterization of the epoxy resin surface tension.

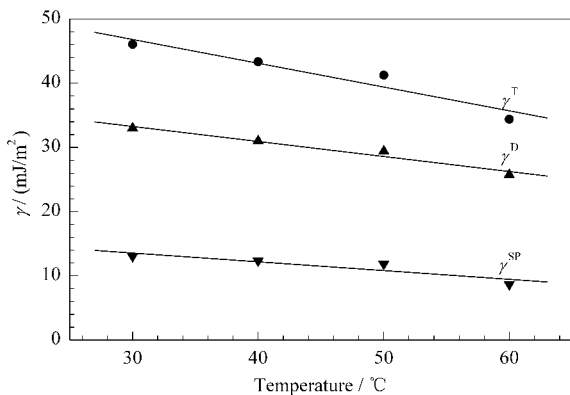


Fig. 2 Surface tensions for E51 at different temperatures

3.2 Solubility parameter

The measured solubility parameters of the resin were based on the nonane , octane , heptane , toluene , ethanol and acetone probes , which have different solubility parameters. The retention volume can be converted into an activity coefficient , which is used to calculate the Flory-Huggins interaction parameter. The Flory-Huggins interaction parameters between probes and resin at different temperatures are summarized in Table 3. The Flory-Huggins interaction parameter decreases with the increase of temperature illustrating that the interaction abilities between the probes and resin get weaker.

Table 3 Flory-Huggins interaction parameters (χ) between probes and resin at different temperatures

| Adsorbate | 30 °C | 40 °C | 50 °C | 60 °C |
|-----------|-------|-------|-------|-------|
| Nonane | 6.194 | 6.073 | 5.874 | 5.610 |
| Octane | 6.239 | 6.139 | 5.969 | 5.636 |
| Heptane | 6.079 | 5.932 | 5.690 | 5.275 |
| Toluene | 5.153 | 5.067 | 4.910 | 4.755 |
| Ethanol | 6.152 | 6.084 | 5.949 | 5.827 |
| Acetone | 5.112 | 5.096 | 4.951 | 4.964 |

As shown in Fig. 3 , the solubility parameters of E51 were calculated from Flory-Huggins interaction parameters of a series of probes using the method developed by DiPaola-Baranyi and Guillet. The solubility parameters of the epoxy resin at different temperatures (30 , 40 , 50 and 60 °C) were 11.78 , 11.57 , 11.48 and 11.14 MPa^{1/2} , respectively.

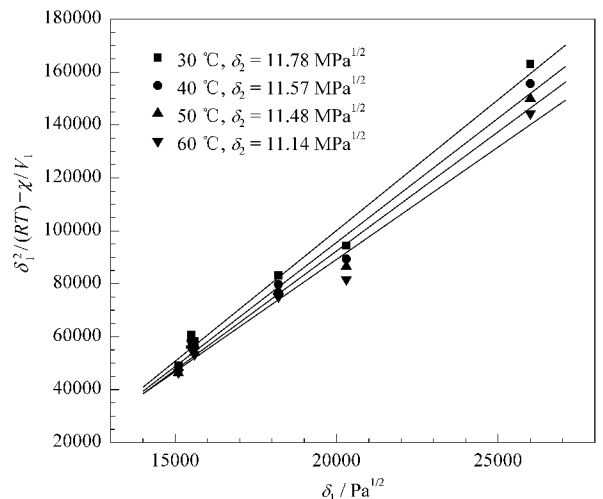


Fig. 3 Solubility parameters for E51 at different temperatures

The solubility parameter (δ) for the polar polymer is generally divided into dispersive (nonpolar) component (δ_D) and specific (polar) component (δ_{SP}).

$$\delta^2 = \delta_D^2 + \delta_{SP}^2 \quad (8)$$

The solubility parameter is the square root of $\Delta E/V$, where ΔE is the cohesive energy density and V is the molar volume of the solvent. It can be shown that the cohesive energy density can be divided into dispersive and specific components (ΔE_D and ΔE_{SP} , respectively), the relationship between the surface energy and the solubility parameter can be described by Equation (9) and Equation (10) [2].

$$\left(\frac{\delta_D}{\delta}\right)^2 = \frac{\Delta E_D}{\Delta E} = \frac{\gamma^D}{\gamma^T} \quad (9)$$

$$\left(\frac{\delta_{SP}}{\delta}\right)^2 = \frac{\Delta E_{SP}}{\Delta E} = \frac{\gamma^{SP}}{\gamma^T} \quad (10)$$

The δ_D and δ_{SP} of E51 at different temperatures were calculated from Equation (9) and Equation (10) respectively, and are summarized in Table 4. The δ_D values of E51 were higher than those of δ_{SP} for E51 resin.

Table 4 Dispersive, specific solubility parameters of E51 at different temperatures

| Temperature/ °C | $\delta_D/\text{MPa}^{1/2}$ | $\delta_{SP}/\text{MPa}^{1/2}$ |
|-----------------|-----------------------------|--------------------------------|
| 30 | 9.97 | 6.28 |
| 40 | 9.78 | 6.18 |
| 50 | 9.69 | 6.16 |
| 60 | 9.63 | 5.60 |

4 Conclusions

IGC was used to characterize the dispersive surface tensions, the specific surface tensions and the total surface tensions of epoxy resin at differ-

ent temperatures. The results showed that the dispersive surface tension of epoxy resin was higher than the specific surface tension, and both of them decrease with the increase of temperature. The solubility parameters of E51 decreased little with the increase of temperature. The value of dispersive component showed higher than that of the specific component. This method is expected to be available for the research of wettability and compatibility of other epoxy resins.

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