# Surface analysis of poly(ether imide) by inverse gas chromatography

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In this work, the surface properties of poly(ether imide) (Ultem) were analyzed by inverse gas chromatography. Four *n*-alkanes (*n*-C7, *n*-C8, *n*-C9 and *n*-C10) were chosen as nonpolar probes to characterize the surface dispersive free energy at different temperatures. The retentions of tetrahydrofurane, dichloromethane, chloroform, ethyl acetate and diethyl ether on Ultem were measured in the temperature range from 303.2 K to 328.2 K by inverse gas chromatography. The dispersive component of the surface free energy, $\gamma_S^D$ of studied adsorbent surface was estimated using retention times of different nonpolar organics in the infinite dilution region. Thermodynamic parameters of adsorption (free energy, $\Delta G_A^S$, enthalpy, $\Delta H_A^S$ and entrophy, $\Delta S_A^S$), dispersive components of the acid, $K_A$ and base, $K_D$ constants for the Ultem were calculated. The results mean that Ultem was a strong basic polymer.

## 1. Introduction

For the last 15 years new poly(ether-imides) have been introduced as thermoplastic materials to produce adhesives, self-slanding films, and interlayer dielectrics. Initial goal has been the production of melt-processable polyimides without taking into account the enhanced solubility provided by two oxygen atoms and other flexible bonds. In electronics, poly(ether-imides) are extensively studied as interlayer dielectrics for multichip modules in which electrical conductors are grown by electroless plating. Another important application is the fabrication of adhesive layers for flexible circuits and TAB laminates [1]. Commercial Ultem which is an high performance polymer with a $T_g$ of 215 $^0$C is an amorphous thermoplastic with the following characteristics: high heat resistance, strength, and modulus; inherent flame resistance with low smoke evolution; high dielectric strength, stable dielectric constant and dissipation factor over a wide range of temperature and frequencies; transparency; amenable to conventional molding processes [2-4]. Chemical formula of Ultem is illustrated in scheme 1.
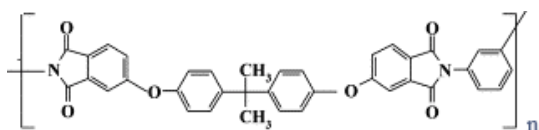


*Scheme 1. Chemical structure of Ultem*

The surface properties of polymers influence their adhesive properties, permeability, biocompability, wettability, coating ability and corrosion. The presence of acidic and basic centers on the polymer surface increases the specific intermolecular interactions with solvents and other polymers. So it is very important to determine the surface energy and the quantity of acid-base character of polymer. For this reason, in the present study, the surface free energy and acid-base characteristics of Ultem were utilized through measurements of net retention volumes of several probe molecules and by use of adsorption on principle in inverse gas chromatography (IGC). The basic tools for IGC are inexpensive, widely available and well suited for routine laboratory applications. IGC data may be collected quite rapidly over extended temperature ranges. IGC is an efficient and versatile method to evaluate the surface properties of various materials such as organic materials [5], natural materials [6] and polymers [7,8]. Ultem relation with used polar and nonpolar solvents was tested at temperatures between 303.2 K and 328.2 K.

## 2. Experimental

Hewlett-Packard 5890 Model, series II gas chromatography with a thermal conductivity detector was used to measure the retention time of the solvents in this study. Data acquisition and analysis were performed by means of HP-3365 software. The column was stainless steel tubing with 3.2 mm o.d. and 1 m in length. The Ultem was coated on the support by slowly evaporation of chloroform as stirring the Chromosorb W in the Ultem solution. Trace amount of solvent which was taken by

Hamilton syringe as 1 μL, poured and diluted with air five times was injected into the chromatograph at infinite dilution. The column was conditioned at 260 $^0$C for 24 h under helium atmosphere.

The probes were high purity grade n-alkanes such as, n-heptane (Hp), n-octane (O), n-nonane (N), n-decane (D) and other acidic, basic and amphoteric probes such as tetrahydrofurane (THF), dichloromethane (DCM), chloroform (TCM), ethyl acetate (EA) and diethyl ether (DEE) used without further purification. The all studied solvents and support materials being Chromosorb-W(AW-DMCS-treated, 80/100 mesh) were supplied from Merck AG. Inc.  Silane treated glass wool used to plug the ends of the column was obtained from Alltech Associates, Inc., respectively.

## 3. Inverse gas chromatography theory for surface characterization

IGC is an adaptation of conventional gas chromatography that is used in the characterization of material surfaces. The adsorbate net retention volumes, $V_N$ were calculated from the expression:

$$V_N = Q \cdot J \cdot (t_R - t_A) \cdot T / (T_f) \tag{1}$$

where $t_R$ is the adsorbate retention time, $t_A$ is the retention time of air, $Q$ is volumetric flow rate measured at column outlet and at ambient temperature $T_f$ (K), $T$ is the column temperature (K) and $J$ is James-Martin gas compressibility correction factor [9]. The interactions experienced between an adsorbate and an adsorbent can consist of two components-specific and dispersion forces [10]. Dispersion forces, also known as London forces, are present between all molecules, regardless of their identity. Specific forces generally rely on some compatibility between the structures of the interacting molecules, either physically or electronically.

The surface free energy of the adsorbent, $\gamma_S$ (J/m$^2$), may therefore be split into dispersion, $\gamma_S^D$ and specific, $\gamma_S^S$ components, corresponding to the dispersion and specific interactions, given by Eq. (2).

$$\gamma_S = \gamma_S^D + \gamma_S^S \tag{2}$$

Similarly, the free energy of adsorption can be split into dispersion and specific components Eq. (3)

$$\Delta G_A = \Delta G_A^S + \Delta G_A^D \tag{3}$$

For the n-alkanes homologous series, it is assumed that there are no specific interactions [11], hence Eq. (4)

$$\Delta G_A = \Delta G_A^D \tag{4}$$

The dispersive component of surface energy was determined using both Dorris-Gray and Fowkes methods. The adsorption energy for the n-alkanes increases with the number of carbon atoms in the chain. According to Dorris and Gray, the increment, corresponding to the adsorption energy of a methylene group, $\Delta G_{A[CH_2]}$ is given by [12]

$$\Delta G_{A[CH_2]} = -RT \ln\left(\frac{V_{N,n}}{V_{N,n+1}}\right) \tag{5}$$

where $V_{N,n}$ and $V_{N,n+1}$ are the retention volumes of two n-alkanes having n and n+1 carbon atoms in their chain. This parameter is independent of the chosen state of the adsorbed molecule. Thus at constant temperature, for a series of alkane probes, a plot $RT \ln V_N$ versus the number of carbon atoms should give a straight line from which $\Delta G_{A[CH_2]}$ can be found.

The methylene adsorption energy can also be defined as [13]

$$\Delta G_{A[CH_2]} = 2 N_A \, a_{[CH_2]} \sqrt{\gamma_S^D \gamma_{L[CH_2]}^D} \tag{6}$$

where $N_A$ is Avagadro's number, $a_{[CH_2]}$ is the surface area covered by one methylene group (0.06 nm$^2$) and $\gamma_{L[CH_2]}^D$ is the surface free energy of a surface consisting of methylene groups, i.e. polyethylene, given by

$$\gamma_{L[CH_2]} = 35.6 + 0.058(293.2 - T) \tag{7}$$

Thus using Eqs.(5)-(7) and the experimentally determined values of $V_{N,n}$ and $V_{N,n+1}$, the dispersion component of the surface free energy, $\gamma_S^D$ may be calculated.

The free energy of adsorption, $\Delta G_A$ may also be defined in terms of the retention volume of the probes [13]

$$\Delta G_A = -RT \ln(V_N) + K \tag{8}$$

$T$ is the column temperature and $K$ is a constant for a given column.

Consequently, the equations may be combined to give the Fowkes equation [14]

$$-\Delta G_A = RT \ln(V_N) = 2Na(\gamma_S^D)^{0.5}(\gamma_L^D)^{0.5} + K'' \tag{9}$$

Thus for a series of n-alkane probes, a plot of $RT \ln V_N$ against $a(\gamma_L^D)^{0.5}$ will give a slope of $2N(\gamma_S^D)^{0.5}$. Values of $a(\gamma_L^D)^{0.5}$ of apolar solvents are found in the literature [14,15]. The values of $a(\gamma_L^D)^{0.5}$ used in this study are presented in Table 1.

*Table 1. Values of $a(\gamma_L^D)^{0.5}$ for the selected n-alkane solvents.*

| Probe | $a$ (x$10^{-10}$m$^2$) | $\gamma_L^D$ (mJ/m$^2$) | $a(\gamma_L^D)^{0.5}$ (m$^2$(mJ/m$^2$)$^{0.5}$) |
|-------|------|------|------|
| Hx | 57.0 | 20.3 | $2.57\times10^{-18}$ |
| O | 62.8 | 21.3 | $2.90\times10^{-18}$ |
| N | 69.0 | 22.7 | $3.28\times10^{-18}$ |
| D | 75.0 | 23.4 | $3.63\times10^{-18}$ |

The specific component of the free energy is determined from the n-alkane plot of $RT\ln V_N$ against $a(\gamma_L^D)^{0.5}$. The distance between the ordinate values of the polar probe datum point and the n-alkane reference line gives the specific component of the surface free energy, $-\Delta G_A^S$. An equation may be written for this procedure,

$$-\Delta G_A^S = RT\ln\left(\frac{V_{N,n}}{V_{N,ref}}\right) \qquad (10)$$

where $V_{N,n}$ and $V_{N,ref}$ are the retention volume for the polar probe and the retention volume for the n-alkanes' reference line, respectively.

Values of $a(\gamma_L^D)^{0.5}$ the Gutmann's modified acceptor number, $AN^*$ and donor number, $DN$ of the polar probes used in this study are presented in Table 2 [16,17].

*Table 2. Values of $a(\gamma_L^D)^{0.5}$, $DN$ and $AN^*$ for the selected polar solvent.*

| Probe | $a$ (x$10^{-10}$m$^2$) | $\gamma_L^D$ (mJ/m$^2$) | $a(\gamma_L^D)^{0.5}$ (m$^2$(mJ/m$^2$)$^{0.5}$) | $AN^*$ (kJ/mol) | $DN$ (kJ/mol) |
|-------|------|------|------|------|------|
| DCM | 31.5 | 27.6 | $1.65\times10^{-18}$ | 16.4 | 0.0 |
| TCM | 44.0 | 25.9 | $2.24\times10^{-18}$ | 22.7 | 0.0 |
| THF | 45.0 | 22.5 | $2.13\times10^{-18}$ | 2.1 | 84.0 |
| DEE | 47.0 | 15.0 | $1.82\times10^{-18}$ | 5.9 | 80.6 |
| EA | 48.0 | 19.6 | $2.13\times10^{-18}$ | 6.3 | 71.8 |

The adsorption of a polar probe onto the adsorbant surface leads to a change in the enthalpy of the system and the entropy of the system. These factors are related to the energy of adsorption by the equation,

$$\Delta G_A^S = \Delta H_A^S - T\Delta S_A^S \qquad (11)$$

Here, $\Delta H_A^S$ is the adsorption enthalpy by Lewis acid-base interactions, $\Delta S_A^S$ is the adsorption entropy Lewis acid-base interactions and $T$ is the column temperature.

For each polar probe, $\Delta H_A^S$ and $\Delta S_A^S$ can be determined from a plot of $-\Delta G_A^S/T$ against $1/T$.

The surface Lewis acidity and basicity constants, $K_A$ and $K_D$, may be calculated from the equation,

$$-\Delta H_A^S = K_A DN + K_D AN^* \qquad (12)$$

$K_A$ and $K_D$ are obtained from a plot of $-\Delta H_A^S/AN^*$ versus $DN/AN^*$ with $K_A$ as the slope and $K_D$ as the intercept. Parameters $K_A$ and $K_D$ reflect the ability of the examined surface to act as an electron acceptor and electron donor, respectively [14,15].

## 3. Results and discussion

The sorption properties of Ultem were investigated at infinite dilution conditions by IGC between 303.2 K and 328.2 K. The net retention volumes, $V_N$ of the nonpolar, polar and amphoteric solvents on the Ultem was obtained using Eq.(1) and graphical results were given in Fig. 1a and 1b, respectively.
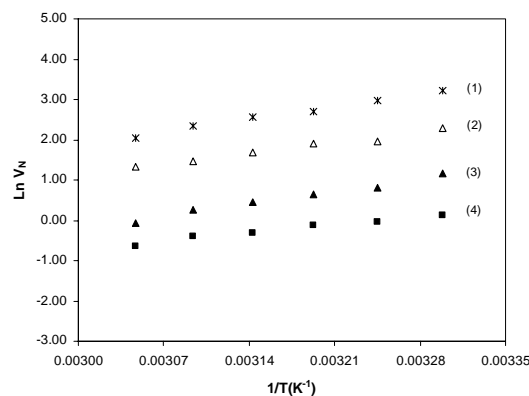


*Fig. 1a. The retention diagram of non-polar solvents adsorbed onto Ultem (1)-D, (2)-N, (3)-O and (4)-Hx.*
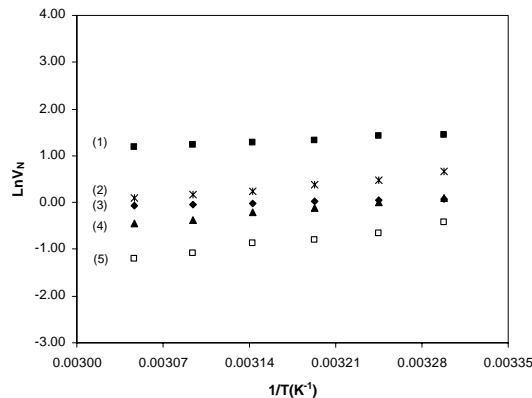


*Fig. 1b. The retention diagram of polar solvents adsorbed onto Ultem (1)-DCM, (2)-EA, (3)-TCM, (4)-THF and (5)-DEE.*

The dispersive component of the surface energy of Ultem was determined from Eq.(5) and the slope derived from the plot of $RT \ln V_N$ of n-alkanes versus their carbon atoms, at various temperatures, as illustrated in Fig. 2. The slope of the line corresponds to the free energy of adsorption of a methylene group, $\Delta G_{A[CH_2]}$. The variation of $\gamma_S^D$ and $\gamma_{L[CH_2]}$ with temperature were calculated from Eq.(6) and (7), respectively. The results of $\Delta G_{A[CH_2]}$, $\gamma_{L[CH_2]}$ and $\gamma_S^D$ were listed in Table 3. As observed, the dispersive component of surface energy of Ultem do not change significantly between 303.2 K and 328.2 K.
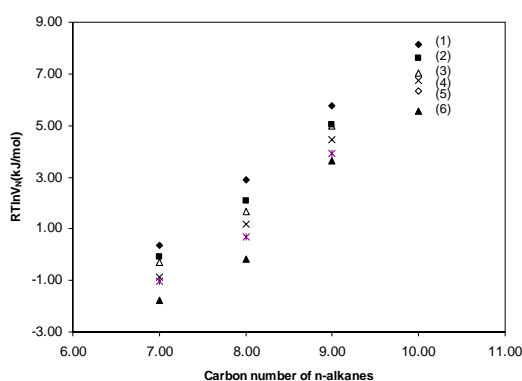


Fig. 2. The plot of $RT \ln V_N$ versus carbon number of n-alkanes (1)-303.2 K, (2)-308.2 K, (3)-313.2 K, (4)-318.2 K, (5)-323.2 K and (6)-328.2 K.

Table 3. The adsorption energy of a methylene group, $\Delta G_{A[CH_2]}$, the surface free energy of a surface consisting of methylene groups, $\gamma_{L[CH_2]}$ and dispersion component of surface free energy, $\gamma_S^D$ values calculated by Dorris-Gray method for Ultem determined at studied temperatures.

| T(K) | $\gamma_{L[CH_2]}$ (mJ/m²) | $\Delta G_{A[CH_2]}$ (10⁶ mJ/mol) | $\gamma_S^D$ (mJ/m²) |
|---|---|---|---|
| 303.2 | 35.02 | 2.62 | 37.56 |
| 308.2 | 34.73 | 2.60 | 37.32 |
| 313.2 | 34.44 | 2.54 | 35.83 |
| 318.2 | 34.15 | 2.60 | 38.03 |
| 323.2 | 33.86 | 2.54 | 36.38 |
| 328.2 | 33.57 | 2.58 | 37.88 |

From the Fowkes equation (Eq. 9, referred to as Schultz and Lavielle approach by some authors) [14,18,19], a plot of $RT \ln V_N$ as a function of $a(\gamma_L^D)^{0.5}$

will yield a slope of $2N(\gamma_S^D)^{0.5}$ and intercept $K''$. The linearity was obtained by the n-alkenes at the studied temperature ranges. An example of the pattern of results obtained was given in Fig. 3 for the isotherm at 303.2 K. Values of $a(\gamma_L^D)^{0.5}$ of apolar solvents are found in the literature [14,15]. The values of $\gamma_S^D$ at studied temperature ranges were given in Table 4.
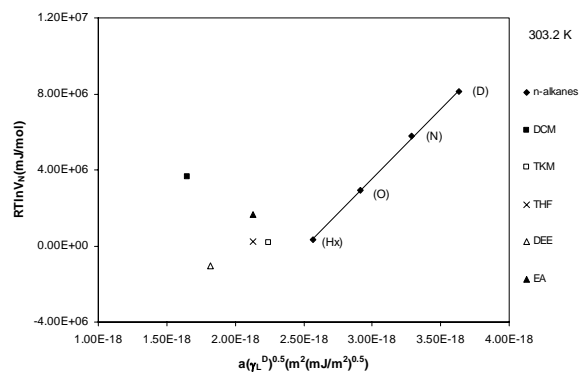


Fig. 3. A plot of $RT \ln V_N$ vs. $a(\gamma_L^D)^{0.5}$ for n-alkanes and polar probes on Ultem at 303.2 K.

Table 4. $\gamma_S^D$ values calculated by Fowkes method and slope at studied temperatures.

| T(K) | Slope (x10²⁴) | $\gamma_S^D$ (mJ/m²) |
|---|---|---|
| 303.2 | 7.36 | 37.41 |
| 308.2 | 7.31 | 36.89 |
| 313.2 | 7.14 | 35.22 |
| 318.2 | 7.33 | 37.04 |
| 323.2 | 7.14 | 35.13 |
| 328.2 | 7.26 | 36.38 |

The values of $\gamma_S^D$ calculated according to Dorris-Gray and Fowkes approaches are very close each other at the studied temperature ranges. The surface energy of Ultem film had been measured to be approximately 35 to 40 mJ/m² [20], depending on grade and the side of the film measured. It was seen that the $\gamma_S^D$ data found in this study are comparable with the literature values.

The specific component of the surface free energy, $-\Delta G_A^S$, is calculated using the difference between the calculated value of $RT \ln V_N$ and that which was derived using the equation of the linear fit of the n-alkane reference line.

The variation of free energy of specific interactions, $\Delta G_A^S$ between Ultem and polar probes for studied temperatures is given Table 5.

Table 5. The variation of free energy of specific interactions, $-\Delta G_A^S$ (kJ/mol) between Ultem and polar probes for studied temperatures.

| T(K) | DCM | TCM | THF | DEE | EA |
|---|---|---|---|---|---|
| 303.2 | 7.35 | 0.48 | 1.17 | 0.90 | 2.57 |
| 308.2 | 7.34 | 0.66 | 1.14 | 0.39 | 2.34 |
| 313.2 | 7.48 | 0.95 | 1.20 | 0.37 | 2.49 |
| 318.2 | 7.61 | 1.17 | 1.19 | 0.34 | 2.39 |
| 323.2 | 7.62 | 1.34 | 0.96 | -0.02 | 2.42 |
| 328.2 | 7.64 | 1.53 | 1.00 | -0.24 | 2.50 |

By plotting the values of $-\Delta G_A^S / T$ against $1/T$, the adsorption enthalpy, $\Delta H_A^S$ and the adsorption entropy, $\Delta S_A^S$ were determined for each studied polar probe and the results were given in Table 6.

Table 6. Values of the enthalpy, $-\Delta H_A^S$ and entropy, $\Delta S_A^S$ of adsorption on Ultem for the polar probes.

| Probe | $-\Delta H_A^S$ (kJ/mol) | $\Delta S_A^S \cdot 10^3$ (kJ/molK) |
|---|---|---|
| DCM | 10.59 | 5.48 |
| TCM | 20.21 | 3.64 |
| THF | 5.03 | 4.08 |
| DEE | -3.52 | 2.38 |
| EA | 5.72 | 4.47 |

The value of $\Delta H_A^S$ indicates the strength of the interaction between the solvent and the surface of the Ultem. The strength of interaction increases in the order: TCM<DCM<EA<THF<DEE.

The values of $K_A$ and $K_D$ were calculated using Eq.(12). The plotting $-\Delta H_A^S / AN^*$ versus $DN / AN^*$ with $K_A$ as the slope and $K_D$ as the intercept (Figure 4).
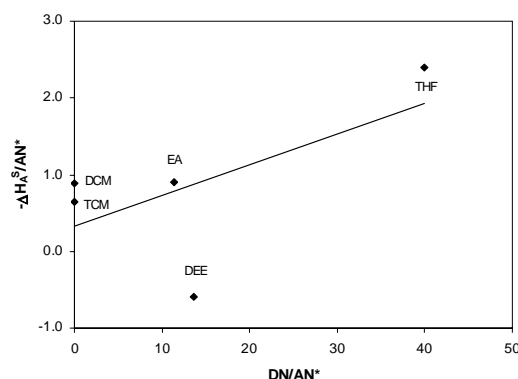


Fig. 4. The plot of $-\Delta H_A^S / AN^*$ versus $DN / AN^*$.

The values of $K_A$ and $K_D$ are found to be 0.040 and 0.328, respectively. According to the values obtained for $K_A$ and $K_D$, the surface of Ultem is basic character between 303.2 K and 328.2 K.

## 4. Conclusions

The aim of this study was the investigation of adsorption properties, surface and Lewis acid-base characteristics of Ultem of technological importance by means of IGC at infinite dilution, in the temperature range from 303.2 K and 328.2 K. The $\gamma_S^D$ values of Ultem change ranges from 37.56 to 37.88 mJ/m$^2$ (Dorris-Gray approach) from 37.41 to 36.38 mJ/m$^2$ (Fowkes approach). The values of $\gamma_S^D$ of Ultem do not change significantly between 303.2 K and 328.2 K. The values of $\gamma_S^D$ of Ultem obtained in this study are in agreement with the literature values. The values of $K_A$ and $K_D$ parameters indicated that Ultem surface is basic nature as 8.20.

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