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An investigation on the surface properties of lyocell-based carbon fiber with inverse gas chromatography

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Abstract The surface thermodynamic properties of two types of cellulose-based carbon fibers (LYCF and RCF from lyocell and rayon precursors, respectively) were studied by inverse gas chromatography (IGC). It was found the molar free energy of adsorption ($\Delta G_{\mathrm{m}}^{\mathrm{ads}}$) of *n*-alkane probe molecules on the LYCF surface is higher than that of RCF at different temperatures. The interaction of probes on the surfaces of LYCF and RCF becomes stronger with the increasing in the chain length of the *n*-alkane probes. Simultaneously, the ln K_{s} is linear to $1/T$, where K_{s} and T are the constant of Henry's law and temperature, respectively. Similar results were obtained by using Dorris–Gray method (area per methylene unit) and measured probe areas. The results indicate that LYCF and RCF are different in the surface morphology and physical chemistry properties, which suggests that LYCF is a more promising cellulose-based carbon fiber material.

Introduction

The surface properties of carbon fiber play a key role in its application as a reinforcing material for the polymer matrix composites. More specified, the physiochemical nature of the surface of the reinforcing fiber is important due to that it determines the adhesion between the reinforcing fiber and the polymer matrix [1–3], and the mechanical properties of the resulted composites. It is well known that the fiber/matrix interface is a key factor that influences the properties of the composites. For example, a good level of adhesion is required for effectively transferring the external loads from the matrix to the reinforcing fibers. Among the numerous factors in the design of composites, the thermodynamic properties and the morphology of the fiber surface should be seriously considered.

The principle of inverse gas chromatography (IGC) was proposed by Kiselev in 1967 [4]. The applications of IGC in material science become growing interest with the simultaneously developing in its theory in the last decades [5]. In conventional gas chromatography (GC), the analyzed samples flow into the column after vaporization and are separated on the surface of the stationary phase and then each separated components are determined by a detector. However, it is impossible for only using conventional GC to characterize of the non-volatile liquid samples and solid samples such as polymers. IGC provides a possibility to characterize these samples by directly coating the liquids or the solid polymer solutions on the surface of the material of stationary phase or using the solid polymer as the stationary phase [6]. The physical chemistry nature of the stationary phase can be characterized by measuring the retention time of the probe molecules with low boiling point. Therefore, IGC is also named as the probe chromatography technique in some literatures [7]. IGC is an ideally technique to study the adsorption at very low coverage (infinite dilution) and is valuable in the characterization of the materials surface, especially for polymers, copolymers, polymer blends, paints and coatings, living macromolecules, pulp and fiber, composite catalyst, etc. [2, 5].

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LYCF, a novel carbon material, has some unique aggregating structures and mechanical properties [8]. However, few work has been carried out on its surface morphology and physical chemistry properties, which limits it applications such as being used as reinforcing carbon fibers. In this work, the surface thermodynamic properties of LYCF were studied by IGC and compared to those of RCF. The thermodynamic parameters obtained from IGC data were further discussed based on the interaction between the probes and the carbon fiber surface.

Fundamental principles

The thermodynamics nature on solid material surface

The chromatographic retention behaviors of the probe molecule on the surface of the stationary phase relate directly to its thermodynamic interaction with the surface in gas chromatography, the probe molecules retention behaviors are characterized by the adjustive retention volume (V_n), which can be calculated accurately from the flow rate of the carrier gas at the column exit (F_0), the retention time of the probe molecule (t_r) and the dead time (t_0). Considering the flow phase as a soap bubble and taking account of the gas compressibility, V_n can be given by [5, 9]:

$$V_n = jF_0(t_r - t_0)\frac{T_c}{T_f}\left(\frac{p_0 - p_{H_2O}}{p_0}\right), \tag{1}$$

where, j is the James-Martin correction factor in gas compressibility, T_c and T_f are the temperature of the column and flow phase, respectively, and p_0 and p_{H_2O} are the pressure at the column outlet and the vapor pressure pure water at T_f, respectively. All these parameters can be obtained from experiments.

In case of IGC fiber chromatographic column, the flow resistance is quite low and the gas compressibility effects can be negligible ($j = 1$). When IGC measurements are conducted under infinite dilution, the interactions between probe molecules can be eliminated. Therefore, the mole free energy of adsorption of the probes at the stationary phase surface relates to V_n as

$$\Delta G_m^{ads} = -RT\ln(V_n) + C, \tag{2}$$

where R is the universal gas constant, T is the absolute temperature, C is the constant that depends on the reference state. Equation 3 may derivate from Eq. 2 as the following form

$$\frac{\partial(\ln V_n)}{\partial(1/T)} = -\frac{\Delta G_m^{ads}}{R} + C'. \tag{3}$$

Thus $\ln V_n$ is linear to $1/T$ in the specified temperature range and the slope represents the mole free energy of probe.

The interaction parameter between the probe molecule and the stationary phase material

The interaction parameter between the probe molecule and the stationary phase material can be derived from Flory-Huggings' theory [10]:

$$\begin{aligned} x_{12} = {} & \ln[(RT\cdot v_2)/(p_1^0\cdot V_g^0\cdot V_1)] - 1 + [V_1/(v_2 M_{2n})] \\ & - p_1^0\cdot(B_{11} - V_1)/RT, \end{aligned} \tag{4}$$

where, V_1 and v_2 are the mole volume of probe molecule at the experimental temperature and the specific volume of stationary phase material at column temperature, respectively; V_g^0 is the specific retention volume; p_1^0 is the saturated steam pressure of pure probe molecule at the column temperature; M_{2n} is the number average molecular mass of the material that has interaction with the probe; B_{11} is the second Rayleigh coefficient of the probe molecule. V_1, p_1^0 and B_{11} can be found in literatures. In this work, the molar mass of the stationary phase, LYCF or RCF is quite high. Therefore, Eq. 4 can be simplified as

$$x_{12} = \ln[(RT\cdot v_2)/(p_1^0\cdot V_g^0\cdot V_1)] - 1 - p_1^0\cdot(B_{11} - V_1)/RT \tag{5}$$

by which the interaction parameter of probe molecule on the surface of LYCF and RCF columns can be estimated. A larger χ_{12} corresponds to a weaker the adsorption of the probe on the stationary phase surface.

Dispersive component of the surface energy

Based on Fowkes' work [11], the adhesion work (W_a) between probe molecule and a solid material is mainly governed by two independent interactions, the dispersive forces and the acid–base interactions, and can be written as

$$W_a = W_a^D + W_a^{AB}. \tag{6}$$

The superscripts D and AB note the dispersive and acid–base interactions, respectively. If non-polar molecules, such as n-alkanes, are used as probes, W_a^{AB} can be neglected and the interaction between the surface of fiber stationary phase can be considered as the pure dispersion force. In this case, the dispersive component of surface energy of the stationary phase material can be calculated by [12]

$$\gamma_s^D = \frac{-RT\left(\ln\frac{V_{n(C_{n+1}H_{2n+4})}}{V_{n(C_nH_{2n+2})}}\right)^2}{4(N\cdot a_{CH_2})^2\cdot\gamma_{CH_2}}. \tag{7}$$

where, N is the Avogadro's number, $a_{-CH_2} (= 0.06\,\text{nm}^2)$ is the area of an ethylene unit ($-CH_2$) adsorbed on the surface of stationary phase [13]. γ_{CH_2} can be estimated by the surface tension of a linear polyethylene melt as a function of temperature (t, °C) following the method in literature [12]. $\gamma_{CH_2} = 35.6$ mJ/m^2 at 293 K by extrapolation and $d\gamma_{CH_2}/dT = -0.058\,\text{mJ/m}^2\text{K}$. Similar values can also be obtained by extrapolating to the to infinite chain length of the n-alkanes [12]

$$\gamma_{CH_2} = 36.8 - 0.058t. \tag{8}$$

Experimental sections

Materials

LYCF and RCF were prepared by the procedure reported elsewhere [14, 15]. All probe molecules: n-hexane, n-heptane, n-octane, and n-nonyl alkane are chromatography grade from Shanghai Reagent Co., China and used as received.

Preparation of carbon fiber column

Carbon fiber columns were prepared by pulling intact fiber bundles through a stainless steel column 50 cm in length and 3.0 mm in internal diameter. The excess carbon fiber at both ends was cut. The load of carbon fiber in the column was around 1.1 g. A tightly packed stainless steel IGC column normally contains up to 60,000 single carbon fiber threads.

Chromatographic analysis

Adsorption measurements were carried out by IGC at infinite dilution by using a GC-16A gas chromatography equipped with a C-R3A data processor and a hydrogen flame ionize detector (FID) (Shimadzu Corporation Japan). Chromatographic conditions are given below: the temperatures of the vaporize room and the examination is both kept at 200 °C. The flow rate of the carrier gas, N_2 (99.9999%) is 20 mL/min and the injection volume 0.2 μL. The retention volume of the probe on the surface of carbon fiber columns was measured isothermally in the range of 338–393 K. Prior to analysis, the columns of bare fiber materials were conditioned at 423 K for 6 h and IGC columns with sized fibers were treated for the same period at 383 K. The residence times of an un-retained compound, such as methane, etc., was used to determine the dead time (t_0) of the system. The temperature difference between the column (T_c) and the flow-meter (T_f) and the water vapor pressure of the bubble (p_{H_2O}) were calibrated according to the literature [5]. The pressure of the column outlet was measured by a U-mode mercury manometer.

Results and discussion

Adsorption and the mole free energy of adsorption (ΔG_m^{ads}) for probe molecules on the surface of carbon fibers

Unlike conventional adsorption techniques, IGC allows the measurement of adsorption data down to very low vapor concentration, where the surface coverage approaches to zero and the interactions of adsorbate–adsorbate can be neglected. In this work, symmetrical chromatographic peaks were obtained for all n-alkanes samples and the peak maximum position is independent on the amount of the injected probe molecule. In this case, the adsorption should be in the linear part of isotherm (Henry's law) and the retention volume of the different n-alkanes could be measured at the peak maximum. The constant of Henry's law (K_s), which characterizes the adsorption equilibrium, relates directly to the retention volume (V_n) as

$$V_n = K_s \cdot A, \tag{9}$$

where A is the total surface area of stationary phase that can be measured by Brunauer–Emmett–Teller's theory. The thermodynamic functions of the adsorption process at infinite dilution can be calculated from K_s. For an equilibrium process, the derivation of the free energy of adsorption (ΔG_m^{ads}) with temperature is given by the Gibbs–Helmholtz equation (Eq. 10). The standard differential heat (q_d) is numerically equal to the opposite of enthalpy of the process in the case of zero coverage (or infinite dilution) conditions

$$\left[\frac{\partial(-\Delta G_m^{ads}/T)}{\partial(1/T)}\right]_p = \left[R\frac{\partial(\ln K_s)}{\partial(1/T)}\right]_p = q_d. \tag{10}$$

The adsorption entropy (ΔS_m^{ads}) can be calculated by Eq. 11 with known ΔG_m^{ads} and K_s

$$\Delta S_m^{ads} = -\frac{q_d + \Delta G_m^{ads}}{T}. \tag{11}$$

Figure 1 shows the linear dependence of lnK_s as a function of (1/T) obtained for the adsorption of n-alkanes on the carbon fiber samples. The results indicate that the slope of the plot keeps at constant in the experimental temperature range. Moreover, it is shown that the

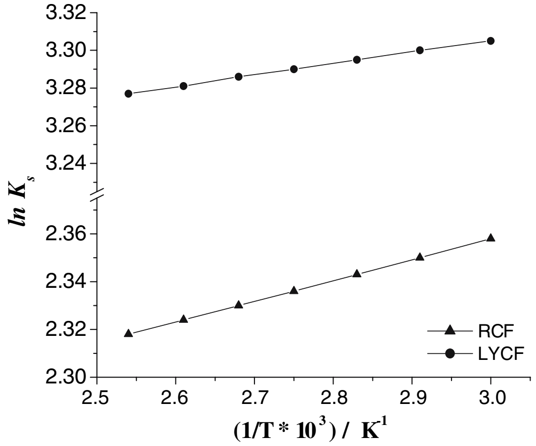

Fig. 1 Variation of ln K_s with (1/*T*) for the adsorption of *n*-nonyl alkane on LYCF and RCF samples

adsorption entropy is independent on the temperature, which is consisted with the linearity of lnK_s vs. (1/*T*) (Fig. 1).

Since the fact that carbon fiber is a solid material, the probe molecules does not easily penetrate into internal the carbon fiber and most of them are absorbed on the fiber surface during normal IGC analysis. Figure 2 shows the dependence of the retention volumes on temperature for different *n*-alkanes on the carbon fiber column. The results show clearly that the retention volume of the probe molecules increases with the increasing in the chain length (the number of carbon atom) of the *n*-alkanes at the same temperature, indicates a stronger absorption with increasing chain length of the *n*-alkanes. Moreover, plotting lnK_s vs. (1/*T*) results a good linear relationship in all cases and the mole absorption free energy for different probe molecules on the carbon fiber surface can be calculated by the slope of the line.

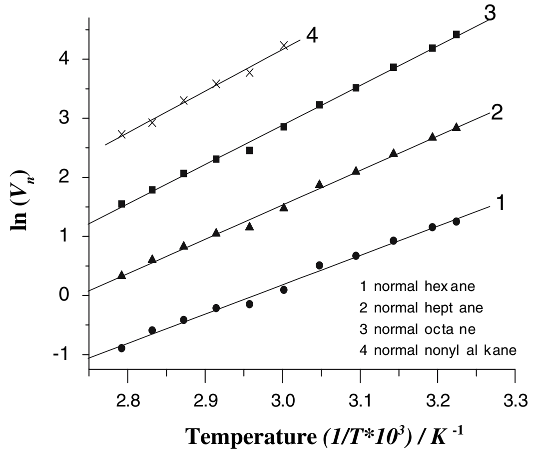

Fig. 2 Variation of the adjustive retention volume (V_n) with temperature (1/*T*) for the adsorption of different probes on LYCF sample

Table 1 The thermodynamic properties of *n*-alkanes on the different carbon fiber surfaces (free energies and entropy of adsorption at 343 K)

Thermodynamic parameter		*n*-alkane				
		C_6	C_7	C_8	C_9	C_{10}
$-\Delta G_m^{ads}$ (kJmol^{-1})	LYCF	24.25	27.24	34.37	36.17	40.13
	RCF	27.22	31.40	36.58	41.07	45.42
$-\Delta S_m^{ads}$ (J K^{-1} mol^{-1})	LYCF	23.46	28.65	32.82	38.02	42.94
	RCF	54.49	56.47	59.04	61.13	64.43
q_d (kJ mol^{-1})	LYCF	32.30	37.07	45.63	49.21	54.86
	RCF	45.91	50.77	56.83	62.04	67.52

Table 1 lists the thermodynamic parameters of some non-polar probe molecules on the surfaces of two kinds of carbon fiber materials. The results indicate that the mole free energy of adsorption is different for the same *n*-alkane on the surface of LYCF and RCF. The results of these parameters on LYCF surface are greater than those on the RCF surface under the same condition, which indicates that the surface physical chemistry properties and structures of LYCF and RCF are different.

The dispersive component of the surface energy for carbon fiber (γ_s^D)

The value of $RT\ln V_n$ can be obtained from the chromatography retention volume of different *n*-alkanes probe molecules on the surface of carbon fiber in the packed column. The value of $RT\ln V_n$ as a function of the carbon atom number of *n*-alkanes is shown in Fig. 3. The results indicate that the value of $RT\ln V_n$ has a linear relationship with the carbon atom number of *n*-alkanes at different temperature. It should be indicated that only one or several –CH_2 units are different among the used *n*-alkanes. Hence, the value of ΔG_{-CH_2} at different temperature can be calculated by the slope of these right lines. Moreover, the value ΔG_{-CH_2} also shows a good linear relationship with temperature (Fig. 4) and the value of ΔG_{-CH_2} at different

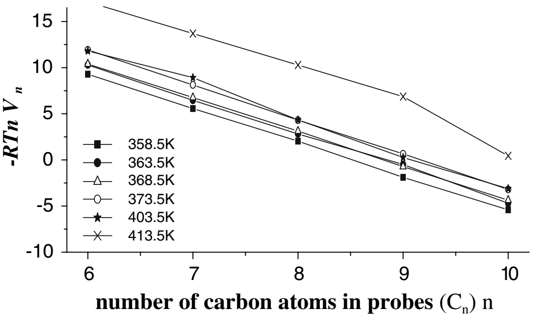

Fig. 3 Variation of the adjustive retention volume (V_n) with the carbon atom number in *n*-alkanes

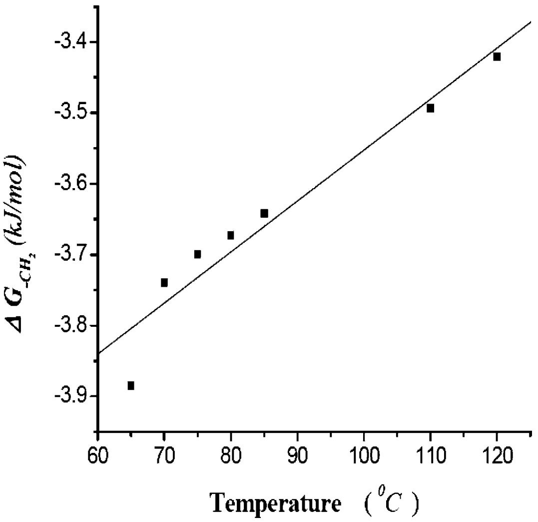

Fig. 4 Variation of $\Delta G_{-\mathrm{CH}_2}$ with temperature

temperature can be obtained. Due to those non-polar probe molecules, *n*-alkanes, were used in the work, the interaction between the probes and carbon fiber surface is mainly attributed to the dispersive interaction and the probe–probe interaction can be neglected under infinite dilution situation. Therefore, the dispersive component of the surface energy for carbon fibers at different temperature can be calculated by Eqs. 7, 8.

In this work, two methods was used to evaluate the γ_s^D values of *n*-alkane probes, Dorris–Gray's method based on $a_{(-\mathrm{CH}_2)}$ and $\gamma_s^D(-\mathrm{CH}_2)$ and Schulltz's method [2] with measured *a* values. Similar γ_s^D values were obtained by these methods (Table 2). The data in Table 2 also showed that the dispersive component of surface energy for the Lyocell-based carbon fiber is smaller than that for Rayon-based carbon fiber.

The interaction parameter x_{12} between probe molecule and carbon fiber

For those small probe molecules, the adsorption behaviors on the surface of solid materials are achieved by the inter-molecule interaction and the strength mainly depends on the physical-chemistry nature of solid material and slightly relates to the structure of the small molecules. Table 3 lists the interaction parameters (x_{12}) of the probe molecules on the surface of carbon fibers at different temperature. The results show that the interaction parameter x_{12} decreases with the increase of the carbon chain length of the probe molecules at the same temperature. While x_{12} increases with the increase of the experimental temperature for the same probe molecules. Moreover, the x_{12} values of *n*-alkane on LYCF surface are higher than those on RCF surface under the same chromatographic conditions. Therefore, it can be concluded that a lower the temperature or a longer the carbon chain of the probe molecule corresponds a stronger interaction between *n*-alkanes and carbon fiber surface. The adsorption ability of *n*-alkanes on LYCF surface is weaker than that on RCF surface, indicates a different surface structure between LYCF and RCF.

Table 2 Dependence of dispersive component of the surface energy γ_s^D (mJ m^{-2}) with temperature *T* (K) for the different carbon fibers under study

Fiber		*r*	γ_s^D (mJ m^{-2})*	
			Method 1	Method 2
LYCF	$\gamma_s^D = 82.19–0.153T$	09924	37.34	37.57
RCF	$\gamma_s^D = 107.51–0.166T$	0.9993	58.85	56.34

*Values extrapolated at 293.15 K

Method 1 on the basis of a $_{-\mathrm{CH}_2}$ (0.06 nm^2) and γ_s^D (–CH$_2$); method 2: with measure a values [7]

Table 3 Interaction parameters of between probe molecule and carbon fiber (x_{12}) at different temperature

	Interaction parameter (x_{12})				
	40°	50°	60°	70°	80°
RCF					
Normal hexane	3.985	4.020	3.969	4.299	4.374
Normal heptane	3.420	3.500	3.609	3.858	3.996
Normal octane	2.843	2.987	3.152	3.427	3.552
Normal nonyl alkane	–	–	2.800	2.975	3.194
LYCF					
Normal hexane	4.001	4.090	4.394	4.346	4.531
Normal heptane	3.448	3.589	3.935	3.901	4.061
Normal octane	2.917	3.090	3.486	3.468	3.605
Normal nonyl alkane	–	–	3.015	3.033	3.182

Conclusions

Surface properties of two kinds of cellulose-based carbon fibers from different precursors, rayon and lyocell fiber, have been investigated by IGC. It was shown that IGC is useful for characterizing the surface properties, such as the mole free energy of adsorption ($\Delta G_m^{\mathrm{ads}}$) and the Henry's law constant (K_s) for characterizing the adsorption equilibrium, the dispersive component of surface energy (γ_s^D) and the interaction parameter (x_{12}) between probe molecule and the carbon fiber, etc. The results indicated that the cellulose-based carbon fibers from rayon and lyocell are different in surface properties. The logarithm of Henry's constant lnK_s as a function of (1/*T*) shows a linear relationship for the adsorption of *n*-alkanes on the carbon fiber samples.

The dispersive component of surface energy of RCF is higher than that of LYCF. A lower temperature or a longer carbon chain length of the probe corresponded to a smaller x_{12} value, indicated a stronger interaction between *n*-alkanes and the carbon fiber surfaces. The ability of adsorption of *n*-alkanes on LYCF surface is lower than that on RCF surface.

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