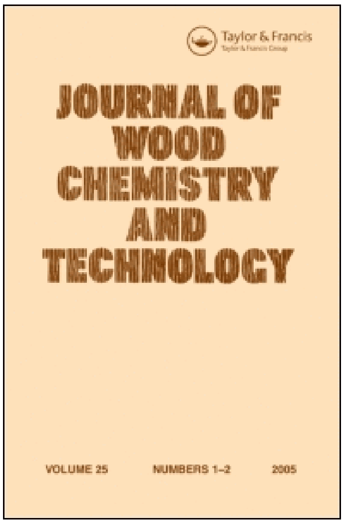

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THE SOLUBILITY PARAMETER OF CELLULOSE AND ALKYLKETENE DIMER (AKD) DETERMINED BY INVERSE GAS CHROMATOGRAPHY

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ABSTRACT

The partial solubility parameters of cellulose and AKD (Alkylketene dimer) treated paper were determined by inverse gas chromatography. The Snyder/Karger-Hansen interaction model was used, where $-\Delta E^A = V_i\delta_d^i + \delta_p^i\delta_p^J + \delta_h^i\delta_h^J)$. The adsorption internal energies of a series of n-alkanes and five polar probes were measured. From the ΔE^A values of n-decane, acetone and THF, which give the largest normalized determinant M(n), the partial solubility parameters of the stationary phases were calculated. The partial solubility parameters of cellulose were: $\delta_d = 8.27$; $\delta_p = 8.00$; $\delta_h = 13.88$; $\delta_t = 18.03$ cal$^{1/2}$/cm$^{3/2}$. AKD treated paper gave $\delta_d = 8.10$, $\delta_p = 12.35$, $\delta_h = 7.96$, and $\delta_t = 16.78$ cal$^{1/2}$/cm$^{3/2}$.

INTRODUCTION

In a composite material two polymeric materials in which one of the components acts as the adhesive binder, while the other forms the substrate matrix, are consolidated. Glass, carbon, and aramide fibers are the most commonly used reinforcing fibers for high performance materials. These fibers provide elasticity, high tensile strength, dimensional stability and durability[2]. Cellulosic fibers have also been used as a substrate matrix to make light, strong and less expensive composites.

The compatibility of the matrix and polymeric fibers is of major importance for making good composite materials. However, incompatibility of the matrix and polymer occurs in many cases. To overcome incompatibility between two phases, coupling agents are frequently used. Vinyl polymers[3,4], and dichloro-s-triazine derivatives[5] have been employed as coupling agents for cellulose. Modification of cellulose fiber with a compound containing one or two long alkyl chain(s) has also been found to promote adhesion[6]. Alkylketene dimer (AKD) may also be used as coupling agents for cellulose reinforced composites since it forms chemical bonds with cellulose and renders the cellulose fibers hydrophobic.

Solubility parameters have been widely used to explain polymer-polymer miscibility[7]. In predicting polymer-polymer miscibility the assessment of the specific interaction defined by the proton donor - proton acceptor concept is very important since the use of the one-component solubility parameter approach is virtually useless unless only dispersive interactions are present[7]. It has been shown that the specific interactions of polar probes on cellulose and AKD are very significant indicating that polar and hydrogen bonding components of the solubility parameter must be incorporated to describe its miscibility[8].

The aim of this paper is to determine the solubility parameters of cellulose and AKD treated paper by the inverse gas chromatography technique. With this information the behavior of the cellulose fibers in manufacturing composite materials may be predicted more accurately.

EXPERIMENTAL

The stationary phases were prepared by passing strips of Whatman No. 1 filter paper through a clean Telex punch machine to obtain small uniform discs with the diameter of 1.8 and 1.1 mm now called confetti. The confetti was extracted with tetrahydrofuran (THF) to remove extractives. The specific surface area of confetti was determined independently by nitrogen adsorption with a Quantasorb™ equipped with a thermal conductivity detector. The BET specific surface area of the untreated stationary phase was 1.10 m^2/g before THF extraction and 1.19 m^2/g after. In view of the work of Gurnagul and Gray[9] these values may be low by as much as 50% if krypton were used for the B.E.T. measurements. The AKD treated column was prepared by sizing the confetti with a solution of AKD in n-heptane. The AKD (Aquapel 364) was supplied by Hercules Inc., and the ketene is a 60:40 mixture of stearic and palmitic acid chains. It was recrystallized from acetone solution three times prior to use. The n-heptane was allowed to evaporate in a vacuum oven at 65°C with occasional gentle stirring. The prepared confetti were packed into a thoroughly washed teflon tubing with an inner diameter of 0.58 cm. The dry weights of the stationary phases of pure cellulose and AKD treated paper were 4.44 and 7.45 g, respectively. The treated paper contained 1.025% of ketene (unreacted).

A Varian 1740 gas chromatograph with dual FID's was used. The detailed description of the GC apparatus is given in previous paper[8].

Retention volumes of n-alkanes and five polar probes including tetrahydrofuran (THF), chloroform, benzene, acetone and ethyl ether were determined at infinite dilution. Skewed peaks were observed for the polar probes. Eq. [1] was used to get the true retention time in this case.

$$t_R = t_I + (t_F - t_{max}) \qquad [1]$$

where t_I and t_F are the points at the base line determined by drawing tangent to the leading and the trailing side of the peak, respectively, and t_{max} is the retention time at the peak maximum. More than four measurements were made at the highest sensitivity of the FID detector and the average retention time was used for calculating retention volumes. The carrier gas flow rate was 21.8 ml/min and 27.0 ml/min for the cellulose and the AKD treated paper respectively. The pressure drop across the column was 20.5 and 27.3 mm (H_2O) for cellulose and the AKD treated paper respectively. Only vapor was injected into the columns[8].

THEORETICAL CONSIDERATION

Solubility Parameters

The original solubility parameter, δ, was defined by Hildebrand and Scott[10] as the square root of the density of the energy of cohesion for substances as shown in Eq. [2].

$$\delta = \left(\frac{\Delta E^{v}}{V}\right)^{1/2} = \left(\frac{\Delta H^{v} - RT}{V}\right)^{1/2} \qquad [2]$$

where ΔE^{V} is the internal energy of evaporation, ΔH^{V} is the enthalpy of vaporization, V is the molar volume, R is the ideal gas constant, and T is the temperature.

This solubility parameter has been extended to incorporate various interaction as well as London dispersion interaction. Blanks and Prausnitz[11] extended the treatment to polar (but non-hydrogen bonding) systems. Hansen[12] expanded to the three-dimensional system by subdividing the solubility parameters into dispersion (d), polar (p), and hydrogen bonding components (h). This is based on the assumption that the energy of evaporation can be divided into its component such as dispersion (E_d), polar (E_p), and hydrogen-bonding (E_h).

$$\Delta E^{v} = E_d + E_p + E_h \qquad [3]$$

This gives

$$\frac{\Delta E^{v}}{V} = \frac{E_d}{V} + \frac{E_p}{V} + \frac{E_h}{V} \qquad [4]$$

or

$$\delta_t^2=\delta_d^2+\delta_p^2+\delta_h^2 \qquad [5]$$

where δ_t is the total solubility parameter.

The solubility parameter provides a simple way to predict and correlate the cohesive and adhesive properties of materials from a knowledge of the properties of the individual components. For example, two materials with similar δ values are miscible while immiscibility results if they have different δ values. The measurement of the solubility parameters for liquids is quite simple. Determination of the enthalpy of vaporization of the liquids is readily available experimentally. However, for polymers alternative methods need to be employed because it is impossible to vaporize the material without chemical degradation. Consequently, several indirect methods have been used for polymeric materials to estimate their energy of interaction including swelling, and internal pressure measurement[13]. Recently, gas chromatography was proposed to measure the solubility parameters of polymers, which employed the determination of the internal adsorption energy of probes[14,15]. This has been developed based on thermodynamic principles.

The energy of mixing, ΔE^M, which can be obtained from the difference between the condensation energy for the solution and for the pure liquids is given by Eq. [6], if the intermolecular force is solely due to London dispersion forces

$$\Delta E^M=\frac{n_iV_in_jV_j}{n_iV_i+n_jV_j}(\delta_i-\delta_j)^2 \qquad [6]$$

where n is the moles of compounds, V is the molar volume of the component, and i and j denote solute and solvent, respectively. The partial molar energy of solution of component i can be obtained from Eq. [6] by partial differentiation with respect to n_i.

$$\left[\frac{\partial \Delta E^M}{\partial n_i}\right]_{n_j} = \Delta E_i = V_i \phi_j^2 (\delta_i - \delta_j)^2 \qquad [7]$$

where ϕ_j is the volume fraction of the solvent[16]. If the concentration of component i is infinitely low, ϕ_j approaches 1.0 and Eq. [7] simplifies to

$$\Delta E_i = V_i (\delta_i - \delta_j)^2 \qquad [8]$$

Eq. [8] was applied to the prediction on band migration in gas chromatography by Keller et al.[17]. They extrapolated this to gas-solid chromatographic system in which the concentration of the solute, i, is low, and derived an equation for the energy of adsorption, ΔE^A, on the adsorbent solid, j

$$-\Delta E^A = V_i \left[(E_{ij})_d + (E_{ij})_o + (E_{ij})_{in} + (E_{ij})_{hb}\right] \qquad [9]$$

where E_{ij} is the energy density (cohesive pressure) acting between i and j. This equation takes into account every possible interactions, including dispersion (d), orientation (o), induction (in), and hydrogen bonding (hb), occurring in adsorption process. For interaction which obeys the law of geometrical means such as dispersion and orientation interactions, E_{ij} is given by

$$E_{ij} = (E_{ii})^{1/2} (E_{jj})^{1/2} = (\delta_i \delta_j) \qquad [10]$$

where E_{ii} and E_{jj} are the densities of the energy of cohesion of pure i and j. More complicated relationships between E_{ij} and the solubility parameters result for the induction and hydrogen bonding interactions.

Eqs. [9] and [10] may be used to obtain the solubility parameters of a solid adsorbent. Even though Eq. [9] describes the adsorption process very accurately, Hansen's three solubility parameters (δ_d, δ_p, δ_h) are more commonly employed because of the controversy involved in the definition and calculation of the hydrogen bonding term in Eq. [9][18,19].

If the law of geometric means is obeyed by slightly polar molecules, from Eqs. [5], [9] and [10]

$$
\begin{aligned}
-\Delta E^A &= V_i\left[(E_{ij})_d + (E_{ij})_p + (E_{ij})_h\right] \\
&= V_i\left(\delta^i_d\delta^j_d + \delta^i_p\delta^j_p + \delta^i_h\delta^j_h\right)
\end{aligned}
\qquad [11]
$$

Therefore from Eq. [11] it is possible to determine the solubility parameters of the solid, j, by measuring the energy of adsorption for various probes whose molar volume and the solubility parameters are known. Then depending upon the number of probes used, n, a set of linear equations with three unknowns (β_d, β_p, β_h) are obtained as shown in Eq. [12].

$$
\begin{aligned}
-\Delta E^A_1 &= \beta_d V_1 \delta_{1d} + \beta_p V_1 \delta_{1p} + \beta_h V_1 \delta_{1h} + \epsilon_1 \\
-\Delta E^A_2 &= \beta_d V_2 \delta_{2d} + \beta_p V_2 \delta_{2p} + \beta_h V_2 \delta_{2h} + \epsilon_2 \\
\vdots \quad & \quad \vdots \qquad \vdots \qquad \vdots \\
\vdots \quad & \quad \vdots \qquad \vdots \qquad \vdots \\
-\Delta E^A_n &= \beta_d V_n \delta_{nd} + \beta_p V_n \delta_{np} + \beta_h V_n \delta_{nh} + \epsilon_n
\end{aligned}
\qquad [12]
$$

where β's are the values of partial solubility parameters (dispersion, polar and hydrogen bonding) of the adsorbent, ϵ's are experimental error and V and δ are molar volume and the solubility parameter of the probe molecule, respectively. By applying a matrix algebra to Eqs. [12] the best linear unbiased estimates (BLUE) of the β may be calculated according to Eq. [13]

$$\begin{pmatrix}-\Delta E_1^A\\ -\Delta E_2^A\\ \\ \vdots\\ \\ \vdots\\ \\ -\Delta E_n^A\end{pmatrix}\begin{matrix}=\\ =\\ \\ \\ \\ \\ \\ =\end{matrix}\begin{pmatrix}V_1\delta_{1d} & V_1\delta_{1p} & V_1\delta_{1h}\\ V_2\delta_{2d} & V_2\delta_{2p} & V_2\delta_{2h}\\ \\ & \vdots & \vdots\\ \\ & \vdots & \vdots\\ \\ V_n\delta_{nd} & V_n\delta_{np} & V_n\delta_{nh}\end{pmatrix}\begin{pmatrix}\beta_d\\ \\ \beta_p\\ \\ \beta_h\end{pmatrix}+\begin{pmatrix}\epsilon_1\\ \\ \epsilon_2\\ \\ \epsilon_3\end{pmatrix} \qquad [13]$$

$$Y = X\beta + \epsilon$$

The left hand side of the above equation is a column vector containing n adsorption energy values of n adsorbates measured experimentally. The first matrix on the right side of the equations with dimensions of (n, 3) contains information on the probes.

It is possible to choose any number of probes above three for obtaining the estimate of the absorbent solubility parameters. However, to improve the precision of the calculation, the size of the matrix or the number of probes should be minimized[14]. To obtain three solubility parameters, the minimum number of the probes needed is three. However, many combinations of the probes are possible. Thus, the selection of probes should be made which gives the best estimate. This can be done by comparing the determinant $|X^tX|$. When the determinant is maximum, the best estimate of the parameters, β, is obtained. Since the determinant changes with the number of the probes, for comparison between different matrix with different number of probes, a correction should be made as shown in Eq. [14] to get the normalized determinant M(n).

$$M(n) = \frac{|X^tX|}{n^k} \qquad [14]$$

where k is the number of the parameter estimates of the model.

Determining the Energy of Adsorption

To determine the solubility parameters of the adsorbent the energy of adsorption of several probes need to be determined. The internal energy of adsorption, ΔE^A, is related to the specific retention volume according to Eq. [15]

$$\ln V_g(T_c) = -\frac{\Delta E^A}{RT} + C \qquad [15]$$

where $V_g(T_c)$ is the specific retention volume at column temperature T_c, and C is a constant. The specific retention volume at T_c is defined as the net retention volume at T_c for unit weight of stationary phase. Therefore, by plotting $\ln V_g(T_c)$ against 1/T, the energy of adsorption can be obtained from the slope.

RESULTS AND DISCUSSION

The solubility parameters and the molar volume of the probes used are listed in Table 1. The values are obtained from Hansen[12]. Other polar adsorbates such as various alcohols (methanol, ethanol, and 1-propanol) which show high hydrogen bonding property, and acetonitrile which has high polarity have been suggested as good probes for the measurement of the solubility parameters by gas chromatography[15]. However, the law of geometrical means is more applicable to the less polar adsorbates.

Table 2 shows the normalized determinants for various combinations of the probes. This has been calculated with the use of SAS (Statistical Analysis System) program. Three probes, n-decane, acetone and THF were found to give the largest normalized determinant of 4.51×10^{14} as shown in Table 2.

Table 1. Molar volume and solubility parameters of probes[12]

No.	Probe	Molar volume (ml/mol)	Solubility parameters $cal^{1/2}/cm^{3/2}$ δ_d	δ_p	δ_h	δ_t
1	n-Hexane	131.6	7.24	0.0	0.0	7.24
2	n-Heptane	147.4	7.42	0.0	0.0	7.42
3	n-Octane	164.0	7.55	0.0	0.0	7.55
4	n-Nonane	180.0	7.65	0.0	0.0	7.65
5	n-Decane	195.9	7.72	0.0	0.0	7.72
6	Benzene	89.4	8.95	0.5	1.0	9.15
7	Ethyl ether	105.0	7.05	1.4	2.5	7.62
8	Chloroform	81.0	8.65	1.5	2.8	9.21
9	Acetone	74.0	7.58	5.1	3.4	9.77
10	Tetrahydrofuran	81.7	8.22	2.3	3.9	9.52

The energy of adsorption of all probes are listed in Table 3 and Table 4 for the cellulose and AKD treated paper columns, respectively. The values of $\Delta(\Delta E^A)$ calculated by comparing the experimentally measured and calculated adsorption internal energy of probes were less than 8% for both columns as shown in Table 3 and 4.

Internal energies of adsorption of three probes, n-decane, acetone and THF, were used for the calculation of the solubility parameters of the cellulose and AKD according to Eq. [13] to obtain the best estimate.

Table 2. The value of the normalized determinants of the information matrix as a function of probes.

n	Probes*	$\|X^tX\|x10^{-16}$	$(n)^3$	M(n)
10	1-10	10.41	1000	1.04×10^{14}
9	2-10	9.25	729	1.27×10^{14}
9	1-4,6-10	7.50	729	1.03×10^{14}
9	1-8,10	0.03	729	3.56×10^{11}
8	3-10	7.73	512	1.51×10^{14}
7	3-5,7-10	7.04	343	2.05×10^{14}
7	4-10	5.78	343	1.68×10^{14}
7	3-5,6-8,10	1.91	343	5.57×10^{11}
6	3-5,7,9,10	5.27	216	2.44×10^{14}
6	4,5,7-10	5.16	216	2.39×10^{14}
5	4,5,7,9,10	3.86	125	3.09×10^{14}
5	3-5,9,10	3.04	125	2.44×10^{14}
4	4,5,9,10	2.23	64	3.48×10^{14}
4	5,7,9,10	2.12	64	3.31×10^{14}
4	4,7,9,10	1.76	64	2.75×10^{14}
3	4,9,10	1.01	27	3.74×10^{14}
3	5,9,10	1.22	27	4.51×10^{14}

* From Table 1

The partial solubility parameters of cellulose obtained were: δ_d = 8.27; δ_p = 8.00; δ_h = 13.88; δ_t = 18.03 $cal^{1/2}/cm^{3/2}$. AKD treated paper gave δ_d = 8.10, δ_p = 12.35, δ_h = 7.96, and δ_t = 16.78 $cal^{1/2}/cm^{3/2}$. This shows that δ_h is a major partial solubility parameter of cellulose while δ_p is important for AKD treated paper. AKD treatment, thus, reduced the hydrogen

Table 3. Adsorption internal energy of probes for cellulose

Probe	$-\Delta E^A$, kcal/mol		$\Delta(\Delta E^A)$, %
	Measured	Calculated	
n-Heptane	8.34	9.04	7.74
n-Octane	9.60	10.24	6.25
n-Nonane	11.16	11.39	2.02
n-Decane	12.51	12.10	-3.39
Benzene	8.54	8.22	-3.89
Ethyl ether	10.70	10.94	2.19
Chloroform	9.44	9.91	4.74
Acetone	11.15	11.48	2.87
Tetrahydrofuran	11.48	11.15	-2.96

Table 4. Adsorption internal energy of probes for AKD treated paper

Probe	$-\Delta E^A$, kcal/mol		$\Delta(\Delta E^A)$, %
	Measured	Calculated	
n-Hexane	7.14	7.72	7.51
n-Heptane	8.37	8.86	5.53
n-Octane	9.55	10.03	4.79
n-Nonane	10.75	11.15	3.59
n-Decane	12.26	12.25	0.00
Benzene	7.70	7.74	0.52
Ethyl ether	9.93	9.90	-0.30
Chloroform	9.47	8.98	-5.46
Acetone	11.21	11.21	0.00
Tetrahydrofuran	10.30	10.30	0.00

bonding property of cellulose greatly. The importance of the polar component of the solubility parameter of AKD may be attributed to the lactone ring. Upon exposure to a polar environment the lactone rings are exposed and interact more favorably with the polar probes. The observation of significant specific interactions between AKD and polar probes is also indicated elsewhere[8]. In contrast to these results microcrystalline cellulose was found to have $\delta_d = 9.5$, $\delta_p = 6.2$, $\delta_h = 15.3$ and $\delta_t = 19.2$ cal$^{1/2}$/cm$^{3/2}$ by gas-solid chromatography[14]. It appears that δ_p is more significant in cotton cellulose while δ_h seems to be more important in microcrystalline cellulose.

Finally, we would like to highlight, that while we have discussed the solubility parameters for a cotton cellulose and an AKD treated cotton cellulose, the latter is for all practical purposes AKD itself since the paper is more than fully covered. Thus, the δ values for the AKD treated paper applies to bulk AKD.

CONCLUSIONS

The partial solubility parameters of cellulose and AKD treated paper were determined by inverse gas chromatography. The Snyder/Karger-Hansen interaction model was used, where $-\Delta E^A = V_i(\delta_d^i\ \delta_d^j + \delta_p^i\ \delta_p^j + \delta_h^i\ \delta_h^j)$. The adsorption internal energies of a series of n-alkanes and five polar probes were measured. From the ΔE^A values of n-decane, acetone and THF, which give the largest normalized determinant M(n), the partial solubility parameters of the stationary phases were calculated. The partial solubility parameters of cellulose obtained were: $\delta_d = 8.27$; $\delta_p = 8.00$; $\delta_h = 13.88$; $\delta_t = 18.03$ cal$^{1/2}$/cm$^{3/2}$. AKD treated paper gave $\delta_d = 8.10$, $\delta_p = 12.35$, $\delta_h = 7.96$, and $\delta_t = 16.78$ cal$^{1/2}$/cm$^{3/2}$. These values indicate that δ_h is a major partial solubility parameter of cellulose while δ_p is important for AKD treated paper. The greater polar component of solubility parameter in AKD was attributed to the presence of the lactone ring.

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