

EXAMINATION OF THE SURFACE FREE ENERGY AND ACID-BASE PROPERTIES OF CELLULOSE BY THE COLUMN WICKING TECHNIQUE AND THE CRITICAL PACKING HEIGHT/DENSITY*

Qing Shen^{a, b**}, Jian-feng Hu^b and Qing-feng Gu^b

^a State Key Laboratory for Chemical Fiber and Polymer Modification

^b The Central Laboratory of Material Science and Engineering College, Donghua University
Shanghai 200051, China

Abstract The column wicking technique was applied to estimate the surface free energy of cellulose, the importance of which is to obtain a real effective capillary radius, R_{eff} , initially from the plot of Washburn penetration distance versus time. Since the cellulose sample could not be packed with good reproducibility, therefore, R_{eff} can not be obtained readily from the slope of the plot. A method was developed in this paper by uniting all apparent packing heights with a unique value to deduce a real effective capillary radius. Based on the defined critical packing height related to the critical packing density, the surface free energy and acid-base properties of cellulose Sigma C8002 were estimated.

Keywords Column wicking technique, Cellulose, Critical packing height, Surface free energy

INTRODUCTION

The wicking technique has been used to determine the surface energy components of solids^[1–7]. Generally, there are two wicking processes in practice, *i.e.* thin layer wicking and column wicking. A comparison of the two wicking techniques made by van Oss *et al.*^[2], shows that column wicking has a problem of showing different packing density due to some kinds of powder materials, *i.e.* clay can not give good repacking reproducibility^[2]. But thin layer wicking has a problem in sample preparation due to water environment and oven drying conditions generally^[1–7]. Probably, such process and related conditions would affect cellulosic materials as reported elsewhere^[8, 9]. With respect to sample protection, the column wicking technique is obviously better but an improved for understanding of various packing densities is required.

The aim of this work is to apply the column wicking technique to determine the surface properties of cellulose.

In this work, in order to overcome the problem apparent in the application of column wicking as van Oss *et al.* has described^[2], cellulose was packed to different packing heights corresponding to various packing densities. Then, a method was developed to deduce a unique value based on all recorded wicking data and defined it as the critical packing height or the critical packing density, from which the critical effective capillary radius on the basis of the Washburn penetration equation was obtained^[10]. Since these critical packing data are ideal and not easy to repeat practically, a practical packing height related to the critical packing height was simulated. This leads to two effective capillary radii for cellulose packed in a column. In addition, the surface tension and related components can be described in two series based on the van Oss-Chaudhury-Good method^[1, 2] as one of us suggested previously^[11]. Therefore, the surface free energy and acid-base properties of cellulose estimated in this

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** Corresponding author: Qing Shen (沈青), E-mail: sqing@eastday.com or sqing@citic.net

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case correspond to four series. Finally, the surface properties of cellulose obtained in this work were compared to literature values.

EXPERIMENTAL

Raw Materials

To preserve the original properties of cellulose, a commercial cellulose powder, code No. C8002, purchased from Sigma Co. was employed as received without any treatment. The median size of this kind of cellulose is about 50–80 μm in the wet state.

The probe liquids used were commercially available distilled water, hexane, diiodomethane and formamide. The surface tension and related components as well as the viscosity of probe liquids were taken from the literature^[1–7, 11] and are presented in Table 1.

Table 1. Surface properties of probe liquids used in column wicking^a

Probe liquids	γ_L (mN/m)	γ_L^{LW} (mN/m)	γ_L^{AB} (mN/m)	γ_L^{+b} (mN/m)	γ_L^{-} (mN/m)
Distilled water	72.8	21.8	51	39.66 (25.5)	16.39 (25.5)
Formamide	58.0	39.0	19	3.54 (2.28)	25.49 (39.6)
Diiodomethane	50.8	50.8	0	0	0

^a γ_L : the surface tension, γ_L^{LW} : the Lifshitz-van der Waals surface tension component, γ_L^{AB} : the Lewis acid-base surface tension component, γ_L^{+} : the Lewis acid component and γ_L^{-} : the Lewis base component

^b Data in parentheses are cited from the van Oss-Chaudhuty-Good method^[1, 2] and others are from Shen^[11].

Column Wicking

Column wicking was performed in the following manner. A glass standard measuring pipette with an inner diameter of about 3 mm was employed as column. The length of the pipette was cut to about 10 cm to keep the original mark of volume level. In every run, about 200 mg of cellulose powder was weighed and charged into the column manually with the help of a thin bar. In such cases, the cellulose powder was found to be unable to pack into the column uniformly from the bottom to the top by gravitational force as pointed out by van Oss *et al.*^[2] Thus, the packing of cellulose powder obviously presents various packing heights or densities. After packing, the column was placed vertically in a glass container containing the probe liquids to allow wicking to occur spontaneously. The wicking time was recorded using a stopwatch as van Oss *et al.* described^[2], and all wicking experiments were carried out at 25 ± 1 °C. Each reported value was the average of three independent measurements with a standard deviation of about 8%. The wicking experiment was illustrated in Fig. 1.

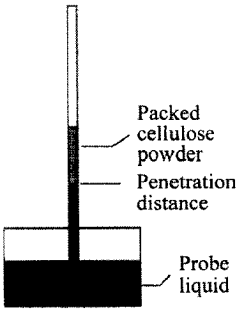


Fig. 1 Illustration of the wicking experiment

RESULTS AND DISCUSSIONS

Characterization of the Critical Packing Height or the Critical Packing Density

According to Washburn^[10], a liquid that penetrates into a porous material is mainly dominated by two properties

of the liquid, *i.e.* the surface tension, γ_L , and viscosity, η . While a contact angle, θ , is usually used to reflect the adhesion between the liquid and solid. The Washburn equation is presented as

$$X^2/t = \gamma_L R_{\text{eff}} \cos \theta / 2 \eta \quad (1)$$

where X^2 is the Washburn penetration distance that was recorded at time t , and R_{eff} is the effective radius of capillary.

The first step in applying the Washburn equation to estimate the surface properties of a solid is to obtain the effective radius of capillary, R_{eff} , which is regarded as an important factor to influence the final values^[1-7]. In principle, R_{eff} can be obtained from the slope of the fitted plot, *i.e.* by taking the Washburn penetration distance, X^2 , as a function of the penetration or wicking time, t . But in such a case the penetration condition must fit $\cos \theta = 1$. It means that one needs to choose a probe liquid with not only low surface tension but also the total surface tension contributed only by the Lifshitz-van der Waals component, $\gamma_L^{\text{LW}[2]}$. By employing hexane as the probe liquid to penetrate cellulose as was done by Dourado *et al.*^[6], the plot of wicking time, t , versus the penetration distance, X^2 , is presented in Fig. 2. Many good linear fits were obviously presented but they cannot yield the effective radius of capillary, R_{eff} , based on the slopes of the lines. Clearly it seems to be impossible to obtain a unique R_{eff} value from Fig. 2 and therefore, a new method to unite the packing heights or packing densities was sought. By taking the inverse Washburn penetration velocity, t/X^2 , as a function of the packing height, h , Fig. 3 shows a phenomenon which attracts our attention because those recorded wicking data obviously present two good linear fits and especially lead to a unique crossing point. Since this unique point is probably related to a critical packing condition (Fig. 3), we defined values related to this point as the ideal critical packing height and density, *e.g.* of about 77.8 mm and 0.306 g/cm³, respectively. Furthermore, these critical packing parameters correspond to an ideal critical effective radius of capillary, R_{eff}^1 *i.e.* 1.22 μm .

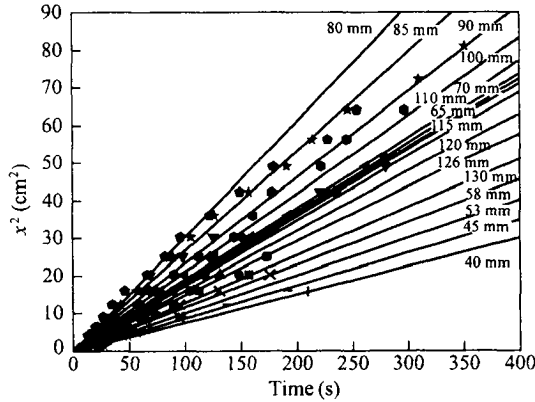


Fig. 2 Washburn penetration distance, X^2 , as a function of time, t , in relation to various cellulose packing heights, h

However, it should be mentioned that these ideal critical packing parameters with height of about 77.8 mm and density of about 0.306 g/cm³ are difficult to prepare in practice. Therefore, a approximate packing height of 78 mm was taken and defined as the practical critical packing height. Correspondingly, this value yielded the practical critical packing density of 0.305 g/cm³ and the practical critical effective radius of capillary, R_{eff}^P of 1.06 μm .

To check the practical critical packing height, the Washburn penetration velocity was plotted as function of the packing density as shown in Fig. 4. It obviously shows a sharp peak which is related to the practical critical packing height, indicating that this simulated practical critical height is reasonable and can be employed to deduce the expected effective radius of capillary for cellulose in this case.

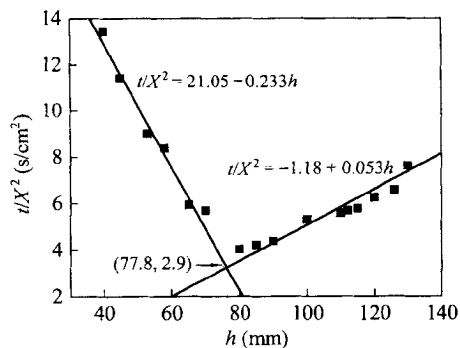


Fig. 3 Relationship between the inverse Washburn penetration velocity, t/X^2 , and the packing height, h , for hexane penetrating into cellulose packed in column to yield the ideal critical packing height, e.g. 77.8 mm, which corresponds to an $R_{\text{eff}}^{\text{I}}$ of 1.22 μm .

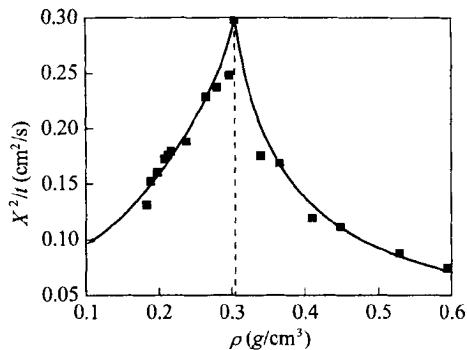


Fig. 4 Washburn penetration velocity, X^2/t , as a function of the cellulose packing density, ρ , to yield the practical critical packing density for cellulose packed in column, i.e. 0.305 g/cm^3 , corresponding to a packing height of about 78 cm

Estimation of the Surface Properties of Cellulose

From Figs. 3 and 4, we obtained two values in relation to the effective radius of capillary. One is the ideal $R_{\text{eff}}^{\text{I}}$ (1.22 μm) and the other is the practical $R_{\text{eff}}^{\text{P}}$ (1.06 μm). The surface properties of cellulose, C8002, therefore can be estimated by means of the Washburn equation^[10] and the van Oss-Chaudhuty-Good equation (Eq. 2)^[1, 2].

$$\gamma_{\text{L}}(1 + \cos\theta)/2 = (\gamma_{\text{S}}^{\text{LW}}\gamma_{\text{L}}^{\text{LW}})^{1/2} + (\gamma_{\text{S}}^{+}\gamma_{\text{L}}^{-})^{1/2} + (\gamma_{\text{S}}^{-}\gamma_{\text{L}}^{+})^{1/2} \quad (2)$$

where the γ represents the surface tension or surface free energy, and the S and L denotes solid and liquid, respectively. The “+” and “-” signs denote the Lewis acid and base component, respectively.

In addition, it is also known that the total surface free energy, γ , is the sum of the Lifshitz-van der Waals, γ^{LW} , and Lewis acid-base component, γ^{AB} , as shown in Eq. (3), and the γ^{AB} could be obtained based on Eq. (4)^[1, 2].

$$\gamma = \gamma^{\text{LW}} + \gamma^{\text{AB}} \quad (3)$$

$$\gamma^{\text{AB}} = 2(\gamma^{+}\gamma^{-})^{1/2} \quad (4)$$

By applying two R_{eff} values and two series of surface tension data as reported in Table 1, Table 2 shows the surface properties of cellulose obtained in this case. Since similar results were also reported in the literature^[6], Table 2 presents these reported values together with our own. In Table 2, the surface free energy of C8002 cellulose is in the range of 56.8–57.5 mN/m and the Lifshitz-van der Waals component is predominant because this component constitutes about 96%–97% of γ_{S} . Moreover, the $\gamma_{\text{S}}^{\text{LW}}$ of C8002 cellulose varies with the effective radius of capillary only and ignores the variety of the surface tension data as described in Table 1. A comparison of data for C8002 in a-d series in Table 2 shows that the application of the surface tension data from Shen^[11] results in reducing the Lewis base and increasing the Lewis acid as compared with the application of van Oss’ data^[1, 2]. However, this is understandable and reasonable as Shen has already described in detail^[11]. Based on Table 2, it is true that cellulose is greater in Lewis base and smaller in Lewis acid, and this conclusion is drawn from the consistency of data obtained in the present work and from that of Ref. [6]. It is quite interesting that the cellulose samples used by Dourado *et al.*^[6] and by us were the same from the Sigma company, but the surface free energy data were obtained using two different wicking technique.

By comparing these data reported in Table 2, it is noted that the surface free energy of C8002 estimated using both the ideal and the practical effective radius values has a similar value to that of Sigmacell 20, but the values are smaller than that of Sigmacell 101 and larger than that of Avicel. Moreover, it is also noted that the

ratio of γ_s^{LW}/γ_s for both Sigmacell 101 and Sigmacell 20 is 92%, is obviously smaller than ours (96%–97%). But the Lewis acid-base component, γ_s^{AB} , of Dourado *et al.*^[6] is obviously greater than ours. It is known that Sigmacell 101 is different from Sigmacell 20^[6]; their γ_s^{LW} are comparatively smaller than our data, indicating that the thin layer wicking process may increase the value of the Lewis acid-base component, γ_s^{AB} , and reduce the value of the Lifshitz-van der Waals component, γ_s^{LW} , of the cellulose. However, it is true that the cellulose we used is different from that used by Dourado *et al.*^[6] with reference to the code number.

Table 2. Surface properties of cellulose estimated in this case and cited from Ref. [6]

Cellulose	γ_s^{TOT} (mN/m)	γ_s^{LW} (mN/m)	γ_s^{AB} (mN/m)	γ_s^{+} (mN/m)	γ_s^{-} (mN/m)	Note
C8002	57.43	55.73	1.70	0.013	56.31	a
C8002	57.41	55.73	1.68	0.020	36.12	b
C8002	57.26	55.07	2.19	0.021	56.16	c
C8002	56.87	55.07	1.80	0.023	36.00	d
Sigmacell	58.98	54.49	4.49	0.110	47.83	e
101	57.18	52.94	4.24	0.110	41.70	e
Sigmacell 20	51.82	51.82	0.00	0.000	50.14	e
Avicel						

^a Values estimated using R_{eff}^P and the surface tension of van Oss-Chaudhury-Good^[1, 2];
^b Values estimated using R_{eff}^P and the surface tension of Shen^[11];
^c Values estimated using R_{eff}^I and the surface tension of van Oss-Chaudhury-Good^[1, 2];
^d Values estimated using R_{eff}^I and the surface tension of Shen^[11];
^e Values from Ref. [6]

CONCLUSIONS

To solve the problem usually attending the use of column wicking process, different packing heights relating to various packing densities were prepared and tested using hexane as the probe. In the plots of t/X^2 versus h and X^2/t versus ρ , a unique packing height and related unique packing density were found which are defined as the critical packing height and density, respectively. Thus, a critical effective radius of capillary can be obtained to estimate the surface properties of cellulose. Results show that the Sigma cellulose (C8002) is greater in the Lifshitz-van der Waals, γ_s^{LW} , and smaller in the Lewis acid-base components, γ_s^{AB} , than other celluloses (Sigmacell 101 and 20)^[6].

This work suggests that the process of thin layer wicking may cause cellulose to increase the Lewis acid-base component and to reduce the Lifshitz-van der Waals component in comparison with column wicking.

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