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The influence of repellent coatings on surface free energy of glass plate and cotton fabric

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ABSTRACT

The aim of this research was to determine the influence of chemical finishes on the surface properties of glass plate, considered as a model homogeneous smooth surface and cotton fabric as a non-ideal heterogeneous rough surface. Microscopic slides and 100% cotton fabric in plain weave were coated with fluorocarbon polymers (FCP), paraffin waxes with zirconium salts (PWZ), methylolmelamine derivatives (MMD), polysiloxanes with side alkyldimethylammonium groups (PSAAC) and aminofunctional polysiloxanes (AFPS). From the goniometer contact angle measurements of different liquids, the surface free energy of the coated glass plates was calculated according to approaches by Owens–Wendt–Kaelble, Wu, van Oss–Chaudhury–Good, and Li–Neumann–Kwok. The results showed that all the coatings decreased the surface free energy of the substrate, which was also influenced by the liquid combination and the theoretical approach used. In spite of the fact that the liquid contact angles were much higher on the coated fabric samples than on glass plates and resulted in the lower values of work of adhesion, a very good correlation between the coatings deposited on both substrates was obtained. The presence of repellent coatings FCP, PWZ and MMD converted the solid surface from polar to highly apolar by masking the functional groups of glass and cellulose. PSAAC and AFPS coatings did not decrease the solid surface free energy to such an extent as the former three coatings due to their monopolar character.

1. Introduction

Chemical textile finishing includes the application of different functional finishes to the fibers such as oil- and water-repellent, softening, antimicrobial, antistatic, flame-retardant, easy-care and soil-release agents to modify the surface properties of fibers [1–5]. This results in a change of the surface free energy, which depends on the chemical structure of the agent used. Surface free energy is an important parameter in evaluating chemical properties of solid surfaces and represents a measure of the solid wettability. It is directly related to the adhesion forces between a solid and a liquid, expressed by the work of adhesion.

Solid surface free energy can be determined only indirectly by measuring dynamic or static contact angles of different liquids using appropriate theoretical approaches. Many experimental methods for contact angle measurements and theoretical approaches for solid surface free energy determination are found in the literature and they should be chosen according to the substrate studied. For porous solids, such as textile fibers, a thin-layer wicking method was recommended by van Oss et al. [6] and Chibowski and González-Caballero [7], where the solid surface free energy components can be determined from the results of liquid penetration rate under the appropriate conditions. The important limitation of this method is its application only to the substrates that are wettable by common liquids. In the case of the low surface energy substrates, their repellency to a majority of polar as well as apolar liquids prevents their penetration into the solid porous structure restricting the method application [8]. In this case, a goniometric technique is still the most appropriate for the liquid contact angle determination with the use of a sessile drop deposited on the solid surface. Consequently, the work of adhesion and solid surface free energy can be obtained from the values of liquid contact angles by using the well-known Young equation [9].

In the determination of liquid static contact angles required for the calculation of surface free energy of textile fibers, we meet some difficulties connected to the morphology and constructional parameters of yarns and fabrics. Namely, a surface of woven fabrics is far from ideally smooth and homogeneous as required by the use of the Young equation. Because of this, the Young contact angle is quite impossible to determine on woven fabric since it is a mixture

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of Wenzel [10] and Cassie and Baxter contact angles [11]. On the other hand, air bubbles trapped inside the roughness grooves could also influence the contact angle value. It should be stressed that the lowest energy of the system is only achieved if the liquid drop is larger than the roughness scale [12,13]. Obviously, when using a goniometric method to determine an equilibrium advancing contact angle, it should be assumed that it is only a close approximation of Young's contact angle, which results in some thermodynamic errors that have to be taken into account.

Despite the textile surface non-ideality, the information about how the presence of chemical finishes influences the fiber properties is very important for textile chemists. While the van Oss et al. and Chibowski and González-Caballero approaches [6,7] are successfully used for calculation of the fiber surface free energy components of wettable porous fabrics on the basis of the thin-layer wicking measurements [14,15], the Zisman approach is recommended for graphical determination of the solid surface free energy for water and oil repellent fibers in terms of critical surface tension. In spite of all advantages of the Zisman theory found in the literature [16,17], its main disadvantage is that the solid surface free energy components cannot be calculated using this theoretical approach. Accordingly, we aimed to demonstrate in this study that repellent finishes could be applied to glass plates as model smooth surfaces to determine the influence of finish chemical structure on solid surface free energy components after the modification. These model systems also proved to be very appropriate for studying the influence of liquid combination and theoretical approach on the values of solid surface free energy components. Afterwards, the surface properties of the coated glass plates were compared to those of the finished fabric samples in order to determine their similarity and consequently discuss the surface properties of the modified textile fibers.

2. Theory

Several approaches are used for the solid surface free energy, γ_S, calculation from the equilibrium liquid contact angles. The most important and widely used are the Owens–Wendt–Kaelble, Wu, van Oss–Chaudhury–Good and Li–Neumann–Kwok approaches. Here, only the basics of the approaches are presented since their theory has been reported many times by others as well as by us [18].

According to the Fowkes theory [19] that interactions between non-polar solid and liquid can only be attributed to London dispersion forces (omitting the spreading pressure, π_e), Owens–Wendt–Kaelbel [20] suggested that dispersive (d) and hydrogen (h) forces may be important across the interface for polar solids (S) and liquids (L). Considering a geometric mean (GM) relationship, the following equation is recommended for γ_S calculation:

$$W_A = (1+\cos\theta)\gamma_L = 2\sqrt{\gamma_S^d\gamma_L^d} + 2\sqrt{\gamma_S^h\gamma_L^h} \qquad (1)$$

where W_A is a work of adhesion, γ_L is the liquid surface tension, and γ^d and γ^h are the apolar and polar components of surface free energy. In order to obtain the γ_S value, the contact angles of two liquids on the solid surface should be measured.

Another two-liquid method for the γ_S determination considers the harmonic mean (HM) relationship and was developed by Wu [21]. In combination with the Young's equation (omitting the π_e), it becomes:

$$W_A = (1+\cos\theta)\gamma_L = \frac{4\gamma_L^d\gamma_S^d}{\gamma_L^d+\gamma_S^d} + \frac{4\gamma_L^p\gamma_S^p}{\gamma_L^p+\gamma_S^p} \qquad (2)$$

where γ^p is a polar component of the surface free energy.

van Oss et al. (VOCG) [22–24] followed the theory of Fowkes using the Lifshitz theory of attractive macroscopic forces. They treated the surface free energy as a sum of the apolar Lifshitz–van der Waals component, γ^{LW}, which includes London dispersion, induction (Debye) and orientation (Keesom) interactions, and a polar component, γ^{AB}, due to electron-donor, γ^-, and electron-acceptor, γ^+, interactions. According to this theory, the solid surface free energy components $\gamma_S^{LW}, \gamma_S^+$ and γ_S^- can be obtained from the following expression:

$$W_A = (1+\cos\theta)\gamma_L = 2\sqrt{\gamma_S^{LW}\gamma_L^{LW}} + 2\sqrt{\gamma_S^+\gamma_L^-} + 2\sqrt{\gamma_S^-\gamma_L^+} \qquad (3)$$

if contact angles of three different, completely characterized liquids are measured on the same solid surface. Empirical evidence suggests that when using Eq. (3), one of the chosen liquids should be apolar.

To reduce the ill-conditioning of the VOCG approach, Della Volpe et al. [25,26] proposed the "multicomponent approach" where Eq. (3) was written in the shape of matrix form $\mathbf{A}_{3\times3}\mathbf{x}_{3\times1} = \mathbf{b}_{3\times1}$:

$$\boldsymbol{A} = \begin{pmatrix} \sqrt{\gamma_1^{LW}} & \sqrt{\gamma_1^+} & \sqrt{\gamma_1^-} \\ \sqrt{\gamma_1^{LW}} & \sqrt{\gamma_2^+} & \sqrt{\gamma_2^-} \\ \sqrt{\gamma_3^{LW}} & \sqrt{\gamma_3^+} & \sqrt{\gamma_3^-} \end{pmatrix}; \qquad \boldsymbol{b} = \begin{pmatrix} \frac{\gamma_1(1+\cos\theta_1)}{2} \\ \frac{\gamma_2(1+\cos\theta_2)}{2} \\ \frac{\gamma_3(1+\cos\theta_3)}{2} \end{pmatrix}; \qquad (4)$$

$$\boldsymbol{x} = \begin{pmatrix} \sqrt{\gamma_S^{LW}} \\ \sqrt{\gamma_S^+} \\ \sqrt{\gamma_S^-} \end{pmatrix}$$

The property of a three liquid combination could be controlled by calculating the condition number, c.n., of matrix **A**, defined as:

$$k\boldsymbol{A} = ||\boldsymbol{A}|| \cdot ||\boldsymbol{A}^{-1}|| \qquad (5)$$

The value of c.n. expresses ill-conditioning in a quantitative way and is therefore an indicator of the stability of the system. Only low c.n. values correspond to a complete and well-balanced set of liquids. Authors recommended the calculation of different vector norms 1, 2 and ∞ to obtain the related values of c.n.:

$$||x||_1 = \sum_{i=1}^{n}|x_i|; \qquad ||x||_2 = \left[\sum_{i=1}^{n}|x_i|^2\right]^{1/2}; \qquad ||x||_\infty = \max_{i=1,\dots,n}|x_i| \qquad (6)$$

The Li–Neumann–Kwok approach [27] known as the equation of state (EQS) is usually called the one liquid approach. For the surface free energy calculation only one liquid with known surface tension is needed. Kwok modified the Li–Neumann's EQS into the form:

$$W_A = \gamma_L(1+\cos\theta) = 2(1-\beta_1(\gamma_L-\gamma_S)^2)\sqrt{\gamma_L\gamma_S} \qquad (7)$$

where the constant β_1 = 0.0001057 $(m^2/mJ)^2$ for all substrates and was determined experimentally as the mean value on several surfaces.

3. Experimental

3.1. Materials

3.1.1. Substrates

We used cleaned microscopic glass plates, also known as soda-lime glass, which is a mixture of silicon dioxide (SiO_2), sodium carbonate (Na_2CO_3) and calcium carbonate ($CaCO_3$). They were purchased from Glaswarenfabrik Karl Hecht KG (Germany).