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Characterization of the Cork Surface by Inverse Gas Chromatography

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Inverse gas chromatography (IGC) at infinite dilution has been used to study the surface properties of cork from *Quercus suber*. The dispersive component of its surface energy was determined at different temperatures using *n*-alkanes as probes, and a γ_S^D value of 38 ± 1 mJ · m^{-2} at 40°C was obtained. The surface acid (A)/base (B) properties were also evaluated by using polar probes and the results indicate that cork has an amphoteric character, with a K_A/K_B = 1.1. The advantages of IGC, compared with the technique of contact angle measurements in the characterization of the cork surface, are discussed. © 1995 Academic Press, Inc.

INTRODUCTION

Cork from *Quercus suber* is a natural material with unique chemical (1) and morphological (2) properties, used as such or in composites with polymeric matrices known as cork agglomerates (3, 4). The features of cork composites are obviously very sensitive to the quality of the interface established between the cork granules and the polymeric adhesive chosen to agglomerate them. The detailed knowledge of the surface properties of cork in terms of surface energy and acid/base characteristics is therefore fundamental for the optimization of the performance of industrial cork composites and for the elaboration of new added-value materials.

Contact angle measurements are traditionally used to determine the surface energy of solids and have been recently applied to cork (5). In this investigation, water and methylene iodide were used as liquid probes to determine the dispersive and polar components of the surface energy of cork. These parameters were calculated by using the harmonic and the geometric methods. It was shown that the total surface energy of the cork samples tested was about 32 mJ · m^{-2} and the major component of this energy had a dispersive nature (24 mJ · m^{-2}, i.e., 75%).

The technique based on contact angle measurements can give rise to experimental difficulties and limitations when applied to solid materials possessing porous and/or rough surfaces as indeed is the case with cork. An alternative method available for the characterization of the surface properties of solids without these inconveniences is inverse gas chromatography (IGC) (6). This powerful technique has been used to probe the surface properties of materials such as cellulose fibers (7), paper and wood fibers (8), cellophane (9), textiles (10), glass fibers (11), carbon fibers (12), and polymers, such as polyethylene terephthalate (13) and polyamides (14), to quote only natural and synthetic polymeric materials.

To our knowledge, IGC has never been applied to the characterization of cork surfaces and it was therefore deemed interesting to undertake this type of investigation in the context of a bilateral program aimed at valorizing this remarkable renewable resource. The importance of gaining a thorough understanding of its surface properties by using an original complementary technique stems from the widespread application of cork agglomerates which by definition imply the wetting of its particles with different resins and oligomers.

MATERIALS AND METHOD

IGC experiments were carried out using a DELSI 121 DFL chromatograph with a flame ionization detector and a pyrex column 28 cm × 4 mm, filled with about 1 g of high-quality cork kindly supplied by Champcork Company and ground to 25 mesh in a cutting mill. Samples were conditioned overnight at 70°C in a stream of dry nitrogen. The dispersive component of their surface energy was determined using a series of *n*-alkane probes. The acid/base properties were evaluated using tetrahydrofuran, chloroform, and ethyl acetate as polar probes. The relevant characteristics of these probes, namely, the dispersive component of their surface tension, their molecular surface, and their Gutmann's donor and acceptor numbers (15), are given in Table 1. Propane was used as a marker and the carrier gas was pure nitrogen. All chemicals were commercial samples of the highest purity available.

Zero coverage conditions were achieved by injecting 5-μl aliquots of vapors of the different probes. Under these conditions the adsorbate/adsorbate interactions are negligi-

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TABLE 1

Characteristics of Probe Molecules Used in This Work

	a (Å^2)	γ_L^D (mJ·m^{-2})	DN	AN	Lewis characteristics
C_7H_{16}	57.0	20.3	—	—	Neutral
C_8H_{18}	62.8	21.3	—	—	
C_9H_{20}	68.9	22.7	—	—	
THF	45.0	22.5	20.0	8.0	Basic
$CHCl_3$	44.0	25.0	0.0	23.1	Acidic
Ethyl acetate	48.0	19.6	17.1	9.3	Amphoteric

ble and as a consequence the thermodynamic parameters depend only on the adsorbate/adsorbent interactions.

Experiments were carried out repeatedly at each of the following temperatures: 40, 50, 60, and 70°C ± 0.5°C. Each set of trials was repeated with three columns prepared in the same way. Reproducibility was about 3% among runs both with a given column and between columns.

The IGC method of calculation of the dispersive component of the surface energy of a solid, γ_S^D, and of the acid/base properties of its surface, expressed as the ratio K_A/K_B (see below), has been described in detail elsewhere (6, 16) and will be discussed only briefly here.

The dispersive surface energy, γ_S^D, is given by

$$RT \ln \mathrm{Vn} = 2\,N\,(\gamma_S^D)^{1/2}\,a\,(\gamma_L^D)^{1/2} + \mathrm{Cte}, \qquad [1]$$

where R is the gas constant, T the working temperature, Vn the retention volume, N Avogadro's number, a the probe's molecular surface, and γ_L^D the surface tension dispersive component of the liquid probe.

In order to obtain the acid (K_A) and base (K_B) parameters of the solid surface, the specific free energy ΔG_{sp} for the interaction between the polar probe and the cork surface was evaluated from the plot of RT ln Vn vs $a(\gamma_L^D)^{1/2}$ according to

$$\Delta G_{sp} = RT \ln(\mathrm{Vn}) - RT \ln(\mathrm{Vn_{ref}}), \qquad [2]$$

where Vn is the retention volume of the polar probe and $\mathrm{Vn_{ref}}$ the retention volume obtained from the n-alkane line at $a\,(\gamma_S^D)^{1/1}$ value corresponding to the polar probe.

The specific enthalpy ΔH_{sp} was then obtained using

$$\frac{\Delta G_{sp}}{T} = \frac{\Delta H_{sp}}{T} - \Delta S_{sp} \qquad [3]$$

from the plot of $\Delta G_{sp}/T$ vs $1/T$.

Finally, for each probe, K_A and K_B were derived from

$$\frac{\Delta H_{sp}}{AN} = K_A \frac{DN}{AN} + K_B \qquad [4]$$

as the slope and the intercept of the plot of $\Delta H_{sp}/AN$ vs DN/AN. Here DN and AN are, respectively, Gutmann's donor and acceptor numbers (15) referring to the polar probes.

RESULTS AND DISCUSSION

In order to check the validity of IGC measurements applied to surface characterization, one must be able to show that two phenomena are negligible within the experimental conditions chosen, namely, (i) bulk sorption and (ii) diffusion of probe compounds into the material. These assumptions seem to be verified in the present context by some

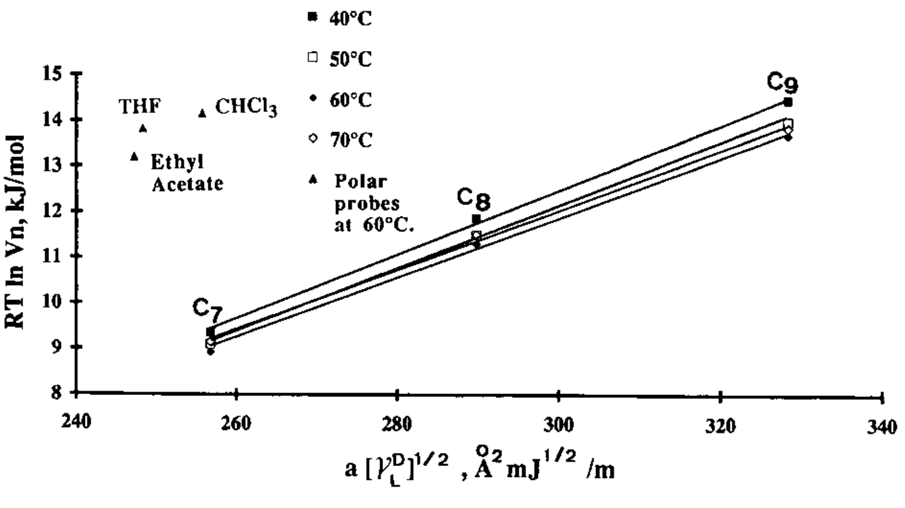

FIG. 1. Plot of RT ln Vn versus $a\,(\gamma_L^D)^{1/2}$ for n-alkane probes at 40, 50, 60, and 70°C and polar probes at 60°C.

TABLE 2

Dispersive Component of the Surface Energy of Cork and Other Cellulosic Materials Determined by IGC and Contact Angle (CA) Measurements

Material	Method	T (°C)	γ_S^D ($mJ \cdot m^{-2}$)	Ref.
Cork	IGC	40	38	This work
		50	35	This work
		60	34	This work
		70	31	This work
	CA	24	24	(5)
Cellulose fibers	IGC	60	44	(7)
	CA	Room	25.5	(7)
Wood fibers	IGC	40	37	(8)

initial observations and error estimations, which will be briefly discussed.

Chromatographic peaks for polar as well as nonpolar probes were sharp, symmetrical, and reproducible. The latter feature was tested in terms of retention time values, with propane as marker and polar and nonpolar probes and resulted in modest fluctuations, viz., about 3.5%. This also applied to tests repeated after the use of different probes, thus excluding problems related to permanent surface contamination. These observations refer to experiments conducted at all temperatures and confirm the applicability of IGC to the surface characterization of cork.

The advantage of using *n*-alkanes as probes is that their interactions with the substrates under investigation are only caused by dispersive forces and, as shown in Fig. 1, γ_S^D can therefore be obtained from the slope of the *RT* ln Vn vs *a* $(\gamma_L^D)^{1/2}$ plot.

The dispersive surface energy of cork was obtained for different temperatures as indicated in Table 2. The value of this parameter extrapolated to room temperature is about 42 $mJ \cdot m^{-2}$, which is much higher than that obtained by contact angle measurements (5). This difference has been observed for other materials, e.g., cellulose (7) (see Table 2) and was probably caused by the influence of the heterogeneity of the cork surface. With IGC, this parameter does not affect the validity of the results because one is dealing with gas–solid molecular contacts which are not sensitive to the macroscopic morphology (roughness) of the surface. As a consequence, the IGC technique provides a more adequate approach to the surface characterization of this type of material than contact angle measurements.

TABLE 3

ΔH_{sp} and ΔS_{sp} of the Polar Probes for the Cork Surface

Probes	ΔH_{sp} $J \cdot mol^{-1}$	ΔS_{sp} $J \cdot mol^{-1} \cdot K^{-1}$
THF	8.4	11.0
$CHCl_3$	6.7	10.7
Ethyl acetate	8.2	14.1

TABLE 4

Acid–Base Characteristics of Cork and Cellulose Surfaces

Material	K_A	K_B
Cork	0.32	0.29
Cellulose (Ref. 7)	0.31	0.24

The acid–base properties of the cork surface were evaluated from its interaction with polar probes. The specific enthalpies, ΔH_{sp}, and entropies, ΔS_{sp}, were obtained by carrying out the IGC measurements at four different temperatures (Table 3). Then K_A and K_B were respectively the slope and the intercept of the plot of $\Delta H_{sp}/AN$ vs DN/AN. The resulting K_A/K_B value of 1.1 (Table 4) implies that cork has an amphoteric nature which should make it compatible with both acidic and basic polymeric matrices. From the structure of the major components of cork, it can be argued that polar moieties such as ester, ether, carboxylic, hydroxy, and, to a minor extent, C=C groups are responsible for this mixed behavior.

CONCLUSIONS

IGC proved to be a good complementary technique for the surface characterization of cork. In fact, the present results indicate that the dispersive component of the surface energy of cork is considerably higher than that determined by contact angle measurements. This does not seem to be an artefact, but rather reflects an intrinsic difference in the mode of probing a surface because other substrates showed the same trend. It follows that depending on the nature of the substance to be added to cork particles, it is important to take into account the values provided by both techniques. It was also shown that the surface of the cork samples investigated has an amphoteric behavior with an equal contribution of acidic and basic character. These properties cannot be studied by simple contact angle observations and emphasize the originality of IGC.

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