

Surface properties of extracts from cork black condensate

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Abstract

The insulation corkboard production generates black condensate (BC), a paste-like solid waste. It is hydrophobic and has the potential to be used as protective coating. To evaluate this potential, coatings were prepared from BC extracts and their surface behavior was evaluated by contact angle (CA) measurements. The CA dynamics were recorded as a function of time; advancing CAs were also registered; the approaches were applied according to Fowkes, Owens-Wendt-Rabel-Kaelble (OWRK), and Van Oss to determine the surface energy (SE) for each coating. Depending on the liquid probe, three phenomena were observed: water evaporation, diiodomethane diffusion into the coating, and rearrangement of the chemical groups on the coating surface, when glycerol was dropped onto the surface. Based on the results from the CA dynamics, the applicability of the coatings against hydrophobic environments was limited owing to its affinity to apolar compounds. The results show that the coating prepared by the toluene BC extract was the best coating. The key data were: water CA of 99.3°, total SE (between 37.4 mN m⁻¹ and 40.1 mN m⁻¹), SE polar component (0.1 mN m⁻¹), and the acidic and basic characters were negligible. It can be concluded that the BC extracts have potential for coatings.

Keywords: black condensate; coatings; contact angle; cork; surface energy.

Introduction

Cork is a natural material that constitutes the outer bark of the Oak tree *Quercus suber* L. (Gil and Moiteiro 2002). It

contains a lot of suberin and lignin among other polymers (Pereira 1981, 1988; Bento et al. 1998; Gil and Moiteiro 2002). Suberin is an aliphatic biopolyester and is considered responsible for several of the unique properties of cork, such as its elasticity and low burning rate (Bernards 2002; Silva et al. 2005; Gandini et al. 2006). Cork is usually harvested every 9 years. This process is harmless and the tree regenerates by forming new cork layers rapidly (Gil and Moiteiro 2002).

Stoppers for the wine industry are the main products from cork. The starting point for other applications include the following properties: elasticity, near-zero Poisson coefficient, and thermal and acoustic insulation (Fortes and Nogueira 1989; Rosa and Fortes 1991; Mano 2002, 2007). Different types of agglomerates can be produced from cork, which are mostly applied in the construction sector. For this purpose, cork which is not suited to stopper production is used (Pereira 2007).

The production of the insulation corkboards is based on a treatment of cork granules under superheated steam and pressure. At these conditions, a black liquid is formed that allows for particle agglomeration. However, this liquid is produced in excess, which precipitates as a waxy solid after cooling. This is usually designated as black condensate (BC) and collected as a waste material (Gil 1998).

BC is composed mainly of long chain aliphatic compounds, terpenes, and some aromatic derivatives (Sousa et al. 2006). BC extracts can be used as water repellent materials in wood protection varnishes and coatings (Gil and Pereira 1998). In fact, Gil and Duarte (1998) showed that the coatings from BC reduce the water absorption of *Pinus pinaster* and its shrinking. For a better utilization of BC, a more profound understanding of the surface properties of BC coatings is necessary. Contact angle (CA) measurements are well suited for this purpose.

Measurement of CA as a function of time (dynamic CA measurements) are particularly useful (sessile drop method observed by a high-speed camera). However, there are several limitations to this method. Initial droplet stabilization promotes significant changes in the CA during the first seconds of contact between the droplet and the surface. Advancing CA measurements can avoid this type of problem. In this method, the increasing volume of a droplet is a measure for the determination of the CA. While the droplet is advancing through the surface of the material, a series of images are recorded by the camera. An average CA is calculated from these images.

Surface energy (SE) reveals the affinity of a material to liquids and gases. SE can be determined by CA analysis with different test liquids. There are different theoretical approaches for calculating SE from CA. The Fowkes (1964) approach only considers interactions of the same type

between the surfaces, i.e., it disregards, for example, dispersive-polar interactions. Nevertheless, the dispersive component (D) of the SE (γ) of the solid (s) surface can be determined from the CA (θ) and the D component of SE of the liquid (l):

$$\cos\theta = 2 \cdot \sqrt{\gamma_s^D} \cdot \frac{1}{\sqrt{\gamma_l^D}} - 1 \quad (1)$$

Then it is possible to calculate the SE polar component (P) in the case of a polar liquid probe (e.g., water):

$$\gamma_l(\cos\theta + 1) - 2 \cdot \sqrt{\gamma_s^D \gamma_l^D} = 2 \cdot \sqrt{\gamma_s^P \gamma_l^P} \quad (2)$$

The Owens-Wendt-Rabel-Kaelble (OWRK) approach (Owens and Wendt 1969; Kaelble 1970) considers the SE of each phase as composed by a P and a D component:

$$\frac{(1 + \cos\theta) \cdot \gamma_l}{2 \cdot \sqrt{\gamma_l^D}} = \sqrt{\gamma_s^P} \cdot \sqrt{\frac{\gamma_l^P}{\gamma_l^D}} + \sqrt{\gamma_s^D} \quad (3)$$

Finally, the Van Oss (1993) approach considers that, apart from the dispersive component (LW), there are two main contributions to the polar component (AB) corresponding to an acid (+) and a basic (-) contribution.

$$0 = \gamma_l \cdot (1 + \cos\theta) - 2 \cdot \left(\sqrt{\gamma_s^{LW} \gamma_l^{LW}} + \sqrt{\gamma_s^+ \gamma_l^+} + \sqrt{\gamma_s^- \gamma_l^-} \right) \quad (4)$$

These methodologies are complementary and it is usual to combine them to study specific systems. Therefore, it is possible to collect information ranging from polar and dispersive components and from acidic and basic contributions of the SE.

The surface properties of natural boiled cork have been studied previously by CA determination (Gomes et al. 1993) and by means of inverse gas chromatography (IGC) (Cordeiro et al. 1995). The average water CA was 84° , while the diiodomethane CA amounted to an average of 61° . SEs between 31 mN m^{-1} and 33 mN m^{-1} were calculated. The IGC approach revealed a significant dispersive character on the surface of cork, reaching a value of 38 mN m^{-1} at 40°C .

The surface properties of suberin have also been studied via the CA and IGC approaches (Cordeiro et al. 1997). With the OWRK calculation a SE of 41.5 mN m^{-1} was obtained which includes 4.2 mN m^{-1} of polar contribution, i.e., $\sim 10\%$ of the SE.

The focus of the present work is the characterization of different BCs by their CAs and SEs. A series of CA techniques were studied: monitoring the dynamics of a droplet CA as a function of time without external influence, analysis of the advancing CA of a droplet while increasing its volume with time, and SE calculations based on the advancing CAs. The approaches of Fowkes, OWRK, and Van Oss were used for calculations. The capability of the coating to maintain its surface characteristics was studied by CA dynamics.

Materials and methods

Extraction of black condensate and preparation of the coatings

BC was collected at Amorim Isolamentos industrial site (Vendas Novas, Portugal) as a waste of the insulation corkboard production. The BC particles were milled and subsequently extracted with different solvents. Each experiment was carried out in 25 ml of solvent per g of BC during 30 min at room temperature. Ethanol (Riedel-de Hen, 99.8%), n-hexane (Pronalab, 95%), and toluene (Panreac, 99.5%) were used. A solution of the extract (obtained after filtration of the insoluble part) was spread onto glass plates pre-heated at $\sim 60^\circ\text{C}$, and the temperature was maintained until the solvent was completely evaporated. Whenever necessary, additional droplets of extract solution were added to the surface of the glass plates to fully cover them. The final coating thickness was $\sim 1 \text{ mm}$ in all cases.

FTIR spectroscopy

The components present in the BC extracts were studied by FTIR spectroscopy (Shimadzu IR-Prestige 21; KBr method; range: 4400 cm^{-1} to 400 cm^{-1} ; resolution: 4 cm^{-1} ; 32 scans).

Contact angle measurements

CA dynamics of the BC coatings were determined as a function of time at 23°C and at a relative humidity of 60% with water (Sigma, HPLC grade, droplet volume $1 \mu\text{l}$), glycerol (Fluka, 99%, droplet volume $2 \mu\text{l}$), and diiodomethane (Aldrich, 99%, droplet volume $3 \mu\text{l}$). An OCA15+ contact angle meter (DataPhysics, Germany) and the SCA20 software (DataPhysics, Germany) was used for all surface analyses. Total time of measurements was 10 min and the image acquisition rate was 1 frame min^{-1} . Averaged values and their standard deviations were calculated from five replicated measurements.

Advancing CA measurements were performed at the same conditions as indicated above. Initially, droplets with a volume of $1 \mu\text{l}$ were put in contact with the surface. Afterwards, the volume was increased at a speed of $0.5 \mu\text{l s}^{-1}$, using a ‘‘needle in’’ design, until the drop reached a total volume of $10 \mu\text{l}$. A video was recorded with an image acquisition rate of 1 frame s^{-1} and, based on it, the advancing CA, and the SE with its polar, dispersive, acidic, and basic components were calculated by the approaches of Fowkes, OWRK, and Van Oss.

Results and discussion

Extraction yields and composition of the BC extracts

In Table 1, the yields of extraction and BC solubility for each of the solvents are listed.

Table 1 Yields of extraction of BC and its solubility in different solvents.

Solvent	Yield (%)	Solubility (g l^{-1})
Ethanol	42	13
n-Hexane	23	8
Toluene	55	18

BC is a complex mixture of compounds with different affinities. The extraction yields are between 55% (toluene) and 23% (n-hexane). Ethanol gives rise to 42% of extracts. Based on the principle *similia similibus solvontur*, it is expected that low polarity compounds (long chain aliphatic structures) are better soluble in apolar solvents. By contrast, ethanol should dissolve better compounds with intermediate polarity (lower chain aliphatic alcoholic structures or some phenolic compounds). However, this type of separation is not very strict. None of the tested solvents should dissolve compounds with high polarity, which are soluble only in water. Previous studies showed only $\sim 4\%$ water solubility of BC at room temperature. Compounds present in the water-insoluble fraction are oligomers of suberin, lignin or polysaccharides. The FTIR spectra of the fractions, presented in Figure 1, show high analogy to each other.

In all cases, the presence of $-\text{OH}$ ($3500\text{--}3000\text{ cm}^{-1}$), $-\text{CH}_2-$ (2927 cm^{-1}), $-\text{COOH}$ (1733 cm^{-1}), and $-\text{C}=\text{O}$ groups (1714 cm^{-1}) are visible, which are associated mainly with the long chain suberinic di-acids and ω -hydroxy carboxylic acids. It is also possible that friedelin is present in the BC extracts at percentages up to $\sim 10\%$ of the initial BC (Sousa et al. 2006). The friedelin molecules have a carbonyl symmetric stretching at 1714 cm^{-1} (spectrum obtained with standard sample).

In the spectrum of the n-hexane BC extract, the intensity of the OH band $3500\text{--}3000\text{ cm}^{-1}$ is significantly diminished as the molecules with OH functionalities are not soluble in n-hexane. This is the reason why the yield in n-hexane is low (Table 1).

Contact angle dynamics

BC coatings were prepared on glass plates and analyzed by CA measurements using water, diiodomethane, and glycerol (parameters of SE in Table 2). The CAs of the coatings were

Table 2 Components of the surface energy (SE) of the test liquids.

Test liquid	γ_{total}	γ^{LW}	γ^P	γ^{AB}	γ^+	γ^-
Water	72.8	21.8	25.5	51.0	25.5	25.5
Diiodomethane	50.8	50.8	–	–	–	–
Glycerol	64.0	34.0	30.0	29.9	3.9	57.4

monitored during 10 min to evaluate their behavior after the initial contact period (Figure 2).

Uncoated glass plates (data not shown) were used for comparison. The water CA started at $\sim 30^\circ$ ($t=0$ min) and reached a complete wetting after 7 min. Coated plates showed a water CA (at $t=0$ min) between 95° and 105° (Figure 2a). The monitoring of the water droplet volume with time (Figure 2d) shows a steady decrease at a rate of $0.06 \pm 0.01\ \mu\text{l min}^{-1}$ (control polystyrene surface: $0.05 \pm 0.01\ \mu\text{l min}^{-1}$). This is also consistent with previous results of water evaporation rates being between 0.06 and $0.11\ \mu\text{l min}^{-1}$ (Muszynski et al. 2006). These results show that the variations in the water CA are associated with the interactions between the liquid probe and the air and not between the liquid and the coating. Overall, the dynamics of the water droplet are in accordance with a material of hydrophobic nature that is able to maintain its characteristics as a function of time.

With diiodomethane, a CA slump was observed during the first seconds and a subsequent steeper decrease in the following time (Figure 2b) reaching a plateau after 1 min (n-hexane): 2–3 min (toluene) or 5–6 min (ethanol). Diiodomethane is not expected to evaporate during the test period (10 min). By contrast, the droplet volume (data not shown) decreased $\sim 15\%$ from $t=0$ min until the plateau is reached. This observation is probably as a result of the diffusion of diiodomethane into the coating. A faster diffusion occurs in the case of n-hexane BC coating, whereas slower diffusion

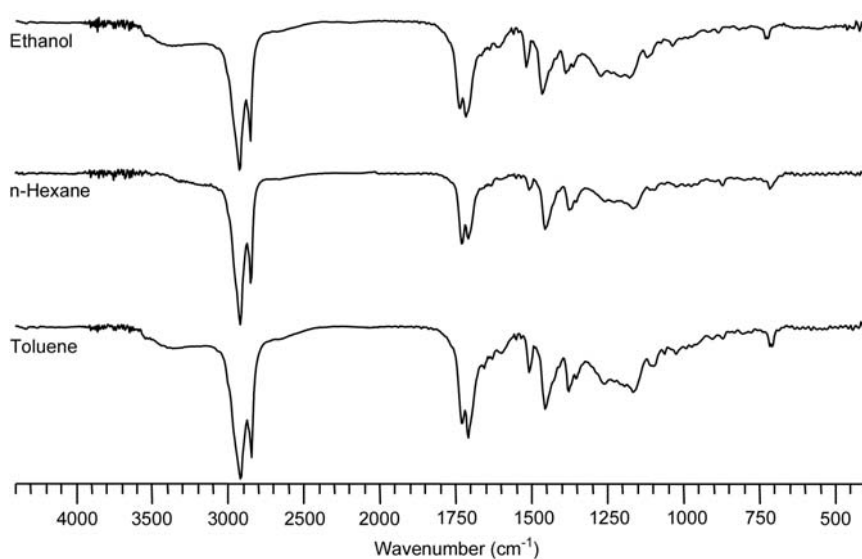


Figure 1 FTIR spectra of the extracts from black condensates obtained by means of different organic solvents.

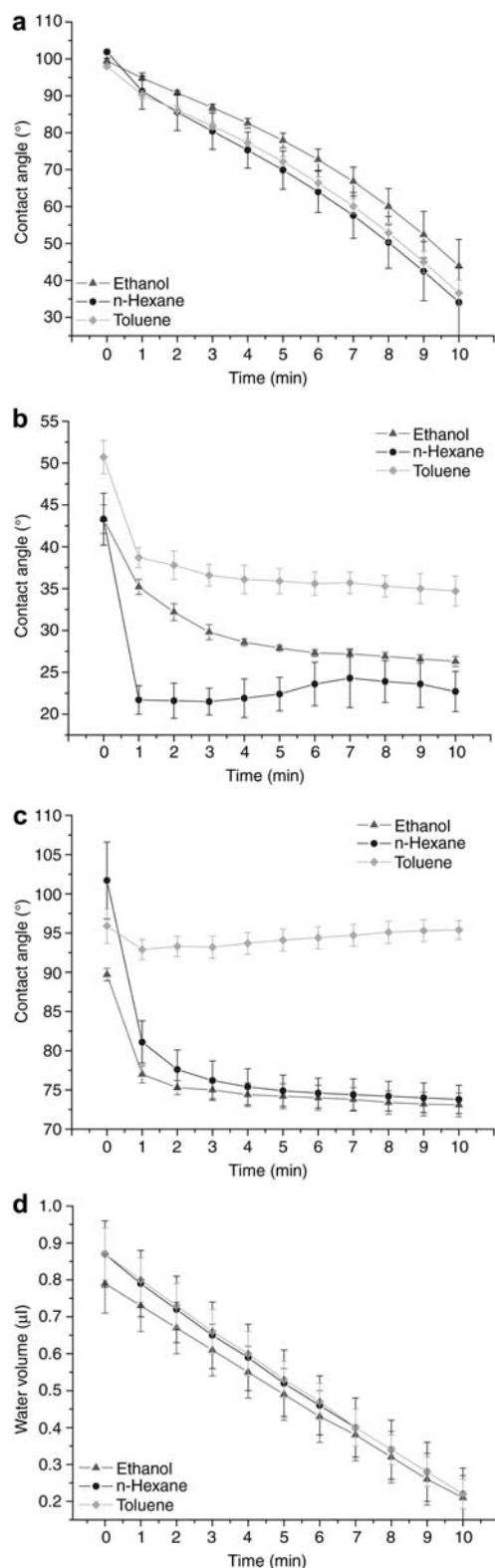


Figure 2 Evolution of the contact angles of water (a), diiodomethane (b), and glycerol (c). Panel (d) shows the water droplet volume as a function of time for the coatings prepared with ethanol, n-hexane, and toluene extracts from black condensates. Error bars are based on standard deviations.

is observed in the case of ethanol BC coating. In general, the dynamics of diiodomethane droplet is consistent with its interaction with hydrophobic coatings. Accordingly, these types of coatings are not suitable as protective layers against apolar liquids.

Glycerol CA dynamics (Figure 2c) reveals that n-hexane BC coating has the largest decrease of CA within the 10 min of experiment ($\sim 28^\circ$), followed by ethanol BC coating ($\sim 17^\circ$) and toluene BC coating ($\sim 0.5^\circ$). Evaporation of glycerol is negligible during 10 min. Moreover, glycerol droplet volume (data not shown) is maintained constant within this time. Initial variation of the CA is related to the dynamic behavior of the surface resulting in a rearrangement of its chemical groups as manifested by a spreading of the droplet and a reduction of the CA. Similar observations were made in other systems (Toselli et al. 2001; Pashkuleva et al. 2008).

CA dynamics ($\Delta t = 10$ min) revealed different phenomena: water evaporation, diffusion of diiodomethane into the coating, and rearrangement of chemical groups. The coating performance is a result of the interaction of these parameters. All coatings seem to be suitable as protection layers against hydrophilic environments, although the diiodomethane results exclude their applicability as protection against hydrophobic environments.

Advancing contact angle

Advancing CAs were determined with water, diiodomethane, and glycerol (Table 3).

n-Hexane BC coating presented the strongest hydrophobic character (highest water CA, 112°), followed by ethanol (106°) and toluene (99°) BC coatings. n-Hexane and ethanol BC coatings had a higher affinity towards diiodomethane (lowest CAs, 33° – 34°). In contrast, toluene BC coating exhibited the lowest affinity with the highest CA (44°). Finally, all BC coatings exhibited similar glycerol CA values between 89° and 100° , showing low affinity to glycerol. CAs obtained by these experiments were used as input values for the calculation of SEs.

Surface energy analysis

SEs of the BC coatings were determined by the Fowkes, OWRK, and Van Oss approaches. Dispersive components (Fowkes approach) were determined from the diiodomethane CAs (Table 3), and values between 39.1 mN m^{-1} and 44.6 mN m^{-1} were obtained. These values are similar to those reported for suberin (Cordeiro et al. 1997) and have the same magnitude as natural boiled cork (Gomes et al. 1993). Polar components (γ_s^P – Fowkes approach) were estimated with the water CAs (Table 3). A residual polarity was observed with the exception of the n-hexane BC coating (2.6 mN m^{-1}).

The OWRK approach (Table 3) revealed a strong dispersive character with minor polar contributions in all BC coatings. n-Hexane BC coating exhibited the highest polar component of 5.4 mN m^{-1} , representing $\sim 10\%$ of total SE.

Table 3 Advancing contact angles (CAs) and surface energies (SEs) of the different black condensate coatings prepared by three solvents.

Solvent	Advancing contact angle with ^a			Fowkes approach ^b		OWRK approach ^c			Van Oss approach ^d		
	Water (°)	Diiodo- methane (°)	Glycerol (°)	SE (mN m ⁻¹)	γ_s^p (mN m ⁻¹)	SE (mN m ⁻¹)	γ_s^p (mN m ⁻¹)	γ_s^d (mN m ⁻¹)	SE (mN m ⁻¹)	γ^+ (mN m ⁻¹)	γ^- (mN m ⁻¹)
Ethanol	106.0 (1.9)	34.4 (0.7)	89.9 (0.6)	43.9	0.8	51.5	49.0	2.5	40.9	0.0	0.0
n-Hexane	111.7 (1.2)	32.8 (1.0)	99.8 (1.5)	44.6	2.6	57.4	52.0	5.4	42.8	0.0	0.0
Toluene	99.3 (0.7)	43.7 (0.8)	89.3 (3.2)	39.1	0.1	40.2	40.1	0.1	37.4	0.0	0.1

Total SE and its polar component (Fowkes approach), total SE and its dispersive and polar component (OWRK approach), and SE and its acidic and basic components (Van Oss approach). ^aStandard deviations are in parentheses; ^bpolar component γ_s^p calculated based on water as polar test liquid; ^cdispersive component γ_s^d and polar component γ_s^p ; ^dacidic component γ^+ and basic component γ^- .

All other BC coatings had polar components below 5% related to their total SE. The lowest value (0.1 mN m⁻¹, 0.2% of the SE) was calculated for the toluene BC coating.

Coatings should dispose of a combination of low SE with a low polar character. Considering these requirements, the toluene BC coating is the best coating. The Van Oss approach demonstrated that the BC coatings do not exhibit acidic or basic character (Table 3). The total SEs (Van Oss approach) have the same tendencies as those obtained with the Fowkes and OWRK approaches. Accordingly, the toluene BC extract is the most promising coating.

Conclusions

CA dynamics of the coatings made of BC coatings confirmed that water evaporates during the test, the groups on the surface groups rearrange in a time range between 1 and 3 min, and diiodomethane diffuses (~15%) into the coating. The last effect limits the applicability of the BC coatings to the protection against hydrophilic environments.

n-Hexane BC coating has the strongest hydrophobic character. However, it also possesses a significant polar component (5.4 mN m⁻¹) revealing its ability to interact with the environment. The behavior of the toluene BC coating is consistent: (1) it is hydrophobic (advancing water CA of 99.3°), (2) it has a low SE (between 37.4 mN m⁻¹ and 40.2 mN m⁻¹), and (3) its polarity is negligible and does not contain acidic and basic components. The studied materials (in particular the toluene BC coating) have similar surface properties as other water-repellent systems, such as paraffin waxes, stearic acid-methylolmelamine derivatives or acrylic coatings (Mirabedini et al. 2006; Cerne et al. 2008). These observations support the applicability of toluene BC extract in coating formulations.

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