

The Effect of External and Internal Application of Organosilicon Compounds on the Hydrophobicity of Recycled OCC Paper

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There are various applications of organosilicon compounds in papermaking. Additionally, organosilicon compounds have been applied to improve the water resistance of some lignocellulosic materials. The performance, however, of such compounds for the hydrophobation of paperboard is unclear. In this study, an organosilicon solution was internally and externally applied to old corrugated container (OCC) paperboard at ambient temperature. Examination of the infrared spectra of treated paperboard confirmed the presence of CH₂ groups and hydrophobic organic chains of organosilicon in the treated paperboard. Both internal and external treatment of the paperboard helped its resistance to water, though external treatment was more successful in the late reduction of the contact angle of water droplets and also in reducing water uptake.

Keywords: Organosilicon; Hydrophobicity; Contact Angle; Sizing Agent; OCC; Cobb Test

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INTRODUCTION

The hydrophilic nature of paper, paperboard, and some other cellulosic products must be offset for many uses. For this purpose, some chemicals, commonly called sizing agents, are available to reduce paper surface wettability and, therefore, its water absorption. In addition to water repellency, depending on the type of the chemical agent and application process, sizing can also improve paper surface quality, smoothness, paper dimension stability, and other features (Gess and Rodriguez 2005; Hubbe 2007; Samyn 2013).

Sizing agents can be applied internally or externally. In the case of external sizing, various mixtures, including some hydrophobic agents mixed with starch derivatives, are usually applied on the dried paper sheet. The applied chemicals help surface water resistance; as they cover the paper, the contact with the hydrophilic surface of paper is limited or reduced (Gess and Rodriguez 2005). In the case of internal sizing, the chemicals are added to the fiber slurry during papermaking.

Some commonly used chemical agents are alkyl ketene dimer (AKD) (Gess and Rodriguez 2005; Hubbe 2007; Seppanen 2007; Lindström and Larsson 2008; Hutton and Parker 2009; Varshoei *et al.* 2013), alkenyl succinic anhydride (ASA) (Lee *et al.* 2004;

Gess and Rodriguez 2005; Hubbe 2007; Seppanen 2007), various types of anionic, cationic, or soap rosins (Gess and Rodriguez 2005; Hubbe 2007; Rahmaninia *et al.* 2016), and various sizing polymers (Gess and Rodriguez 2005; Hubbe 2007). In addition, other numerous modification methods for improving the hydrophobicity of cellulosic fiber-based paper, such as filling with hydrophobic nanoparticles, wax coating, layer-by-layer, phase separation and enzyme treatment, *etc.*, have been proposed (Huang *et al.* 2011; Cusola *et al.* 2013; Obeso *et al.* 2013; Zhang *et al.* 2014; Li *et al.* 2016; Peng *et al.* 2016). Many studies have attempted to find new formulas with the same performance but with fewer costs, environmental concerns, and process difficulties (Hutton and Parker 2009; Rahmaninia *et al.* 2016).

Organosilicons are a group of materials that have been recently applied to improve the water resistance of lignocellulosic materials, namely wood, and to protect it from fungal attack (Mai and Militz 2004; De Vetter *et al.* 2009). In the paper industry, organosilicons have been used as softening agents, defoamers, and strengthening additives (Ma and Sun 2011). Little knowledge is available about their performance as sizing agents for papermaking. As organosilicons contain the hydrophilic main chain of silicon and side chain of hydrophobic organic groups, it is expected that the structure may help the hydrophobation of paper by changing its surface properties through chemical bonding with hydroxyl groups of the fiber surface, while the hydrophobic side chain is oriented away on the surface. Moreover, in the case of the nano-structured organosilicons, it may have the same effect as the phenomena occurs on lotus leaf, where nano-size hydrophobic spots lay on the surface, therefore water droplets on the leaf surface are expected to tumble down. So, in this study, the potential use of organosilicon compounds for easy applicable hydrophobation of OCC paperboard at ambient temperature was experimented.

EXPERIMENTAL

Materials and Methods

Fibrous samples of old corrugated containers (OCC) were selected at random from a local recycling mill (Kaveh Paper Mill, Saveh, Iran) for repulping. The nano-structured organosilicon with the mean size of about 5 nm (Zycosil[®]) was supplied by Exir Shargh Company (Mashad, Iran).

Old corrugated containers were soaked in tap water (conductivity of 300 $\mu\text{S}/\text{cm}$) for 24 h, and the resulting loose paperboard was torn into smaller pieces for further repulping processing. Slushing, fiber dispersion, and gentle refining of OCC was carried out in a laboratory valley beater according to the TAPPI T 200 sp-10 (2010) test method, up to 300 mL Canadian Standard Freeness (CSF).

For dosing the sizing agent in the fiber slurry (internal sizing), the furnish was diluted to 0.5% (based on fiber oven-dry (OD) weight). The pH was set at 5.5, 7, and 9, representing acidic, neutral, and alkaline paper recycling systems. Various dosages of organosilicon solution (0 to 5% of the oven-dry weight of pulp) were added to the fibrous slurry while stirring with a laboratory stirrer at 750 rpm. After 30 s, the final furnish was transferred to a laboratory manual handsheet maker (PTI Ltd., Austria). The sheets were prepared according to TAPPI T 205 sp-12 (2012), at the basis weight of 130 g/m^2 .

In the case of the surface application of organosilicon on the paperboard, the sheets were first made at a basis weight of 130 g/m^2 at neutral pH, and they were dried and kept in conditioned status until they were dipped into organosilicon solutions of various

concentrations (5, 10, and 15%) for 3 s. The wet sheets were dried on plates and between rings according to TAPPI T 205 sp-12 (2012). Finally, the organosilicon absorption rates were calculated according to the OD weights of the sheets.

FT-IR Spectroscopy

To evaluate possible chemical modifications on the surface of the treated paper, infrared (IR) spectra of the paper sheets were taken on a Shimadzu 8400S FT-IR spectrometer (Tokyu, Japan) equipped with an attenuated total reflection (ATR) apparatus, within 4000 to 400 cm^{-1} at a resolution of 4 cm^{-1} for 32 scans.

Contact Angle

The change in the contact angle of a distilled water droplet (3 μL) with the sheet surface was dynamically measured using a PGX goniometer (Switzerland).

Water Absorption

The sheet reaction to water absorption was evaluated by the Cobb₆₀ test method according to TAPPI T 441 om-13 (2013), in which 100 mL of water was poured into a standard cylinder while the sample sheet covered the bottom transverse section of the cylinder. For a sheet with a previously determined weight, the water uptake amount within a specified time period showed how much water may penetrate into the sheet structure and subsequently be absorbed.

Tensile Strength

To evaluate the tensile index of paper samples, a universal testing machine (model TVT-300Xp, Perten, Sweden) was used according to the ISO 1924-2 (2008) standard method.

RESULTS AND DISCUSSION

Contact Angle

The interaction of a liquid droplet with a solid surface can be described by Young's equation (Eq. 1). This formula indicates the mechanical equilibrium of the drop under the action of three interfacial tensions (Fig. 1): solid-vapor (γ_{sv}), solid-liquid (γ_{sl}), and liquid-vapor (γ_{lv}) (Kwok and Neumann 1999; Shen *et al.* 2000; Yuan and Lee 2013).

$$\cos \theta = (\gamma_{sv} - \gamma_{sl}) / \gamma_{lv} \quad (1)$$

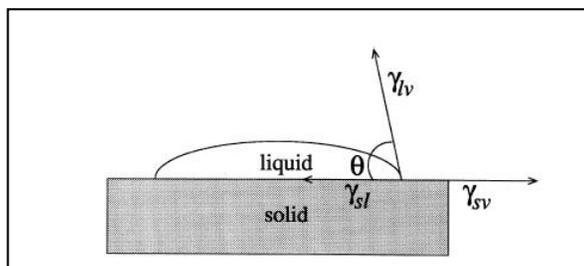


Fig. 1. The action of three interfacial tensions for a liquid droplet on a solid surface

Generally, monitoring the dynamic contact angle of the water droplet with the paper surface revealed the degree to which the sheet surface was hydrophobic and resisted water droplet spreading. Usually, surfaces with contact angles greater than 90° were noted as hydrophobic surfaces, and contact angles greater than 150° indicated a super-hydrophobic surface (Yuan and Lee 2013).

Figure 2 shows the effect of the internal application of the organosilicon solution on the dynamic contact angle of the water droplet with the paper surface. The dynamic measurement of the contact angle was started just after the droplet fell on the surface from the needle of the instrument. As expected, the contact angle of the control paper (untreated) at the starting point (θ_0) was less than 90° , and the contact angle decreased to approximately 10° in few seconds, due to the hydrophilic nature of the surface (Fig. 2). The addition of organosilicon to the pulp slurry increased the contact angle at the starting point by approximately 20° to 30° , and the paper sheets containing more organosilicon were obviously more resistant to the spreading of the water droplet.

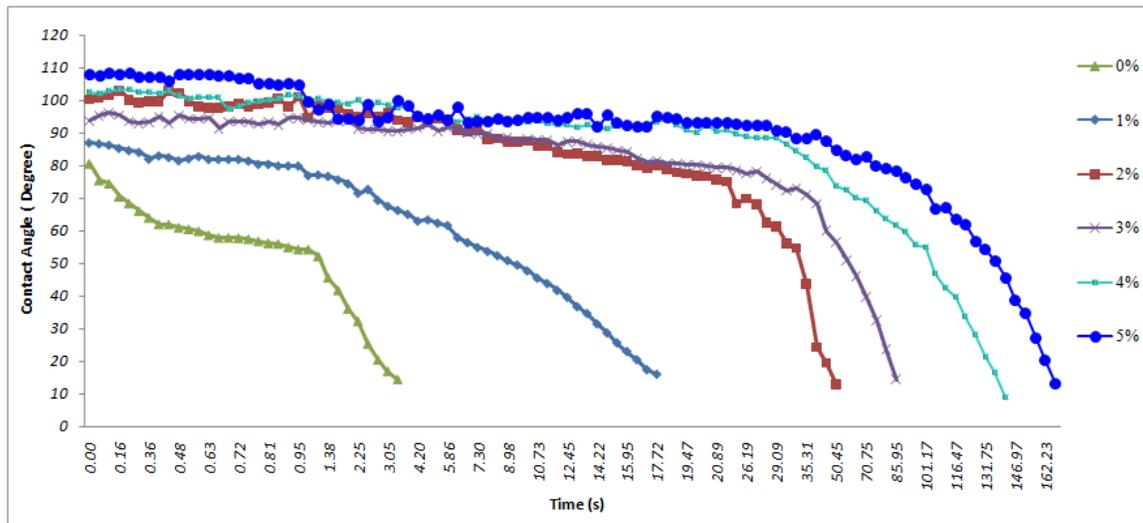


Fig. 2. The contact angle of the water droplet with the paper surface following the internal application of the organosilicon solution

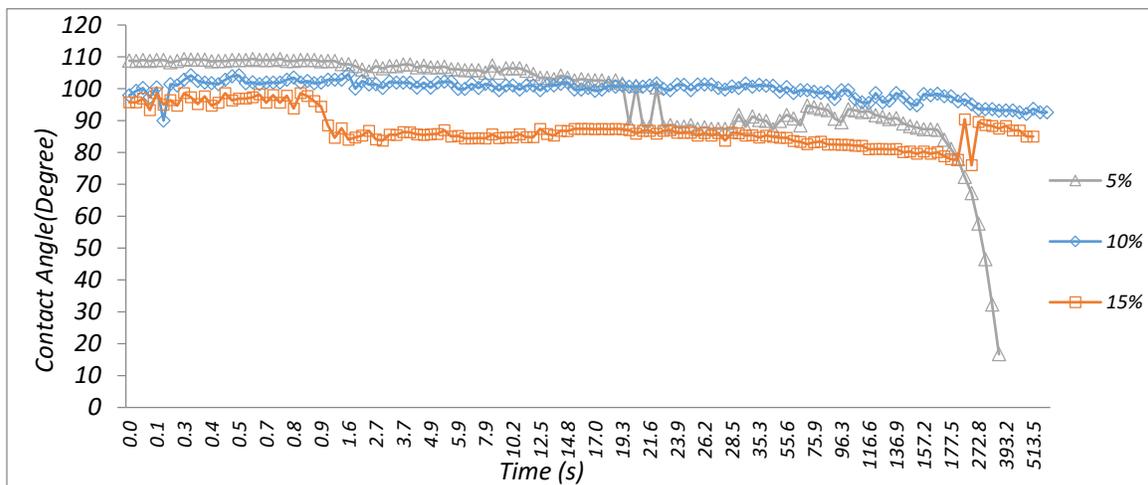


Fig. 3. The contact angle of the water droplet with the paper surface following the external application of the organosilicon solution

In the case of the external application of the organosilicon solution (Fig. 3), the dynamic contact angle at the starting point was nearly the same angle as in the internal application (approximately 100° to 110°), but it took much more time for water droplets to be absorbed and spread out. Therefore, even after 100 s, in all three externally treated papers, the contact angle did not decrease as much as in the internally-treated papers. During the internal treatment, as shown in Fig. 2, the control paper contact angle drastically decreased in only 3 s.

Interestingly, for externally treated papers, the contact angle did not greatly decrease even after 160 s (Fig. 3). Although the contact angle of the externally treated paper sheets with a 5% organosilicon solution dropped after approximately 160 s, the sheets that were externally treated with 10% and 15% organosilicon solutions did not drop until the end of experiment (more than 500 s) (Fig. 3 and Fig. 4).

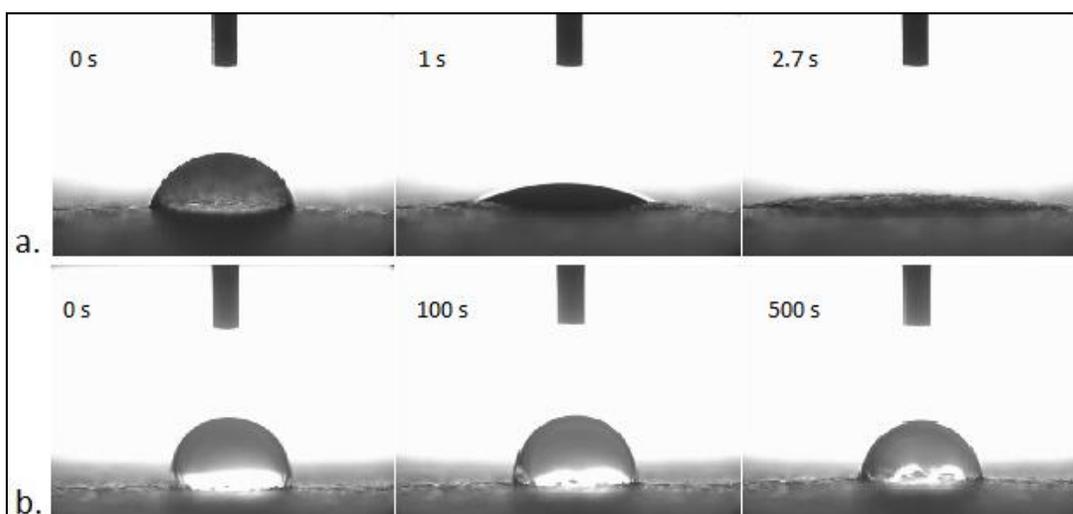


Fig. 4. The differences in the contact angles of the water droplet with the paper surface between (a) the control paper and (b) the paper externally treated with organosilicon

Table 1. Examples of the Contact Angle of Water with Paper Components at Zero Time (θ_0), 15 s (θ_{15}), and 30 s (θ_{30}) (Liukonnen 1997)

Material	θ_0	θ_{15}	θ_{30}
α -Cellulose	26	0	0
Holocellulose	56	0	0
EKP handsheet	43	0	0
Cellophane	34	29	28
Lignin	67	53	49
TMP handsheet	73	30	25
AKD*	107	87	84

*AKD coated on clean glass

For comparison, Liukonnen (1997) studied the contact angle of water with some paper components such as holocellulose, lignin, thermo-mechanical pulp (TMP), eucalyptus kraft pulp (EKP), and AKD (Table 1). The research showed that all paper samples and components had a contact angle of less than 90° with water, except for pure AKD, which was 107° at time zero (θ_0). However, the contact angle of a water droplet on cellophane, which did not have a porous structure, did not decrease as much. In the case of

an α -cellulose sheet with many capillaries and porous structure, the contact angle dropped readily in less than 15 s (Liukkonen 1997). In other words, in addition to surface energy, the structure of the lignocellulosic surface was also of great importance for the contact angle and should not be neglected (Cho and Garnier 2000).

Cobb Test

Although the contact angle is a scientific indicator of the tendency of the surface toward a liquid droplet, the common test that evaluates the performance of a sizing agent in the paper industry is the Cobb test (Gess and Rodriguez 2005). The results of the Cobb test for the internal and external application of organosilicon are shown in Fig. 5 and Fig. 6, respectively.

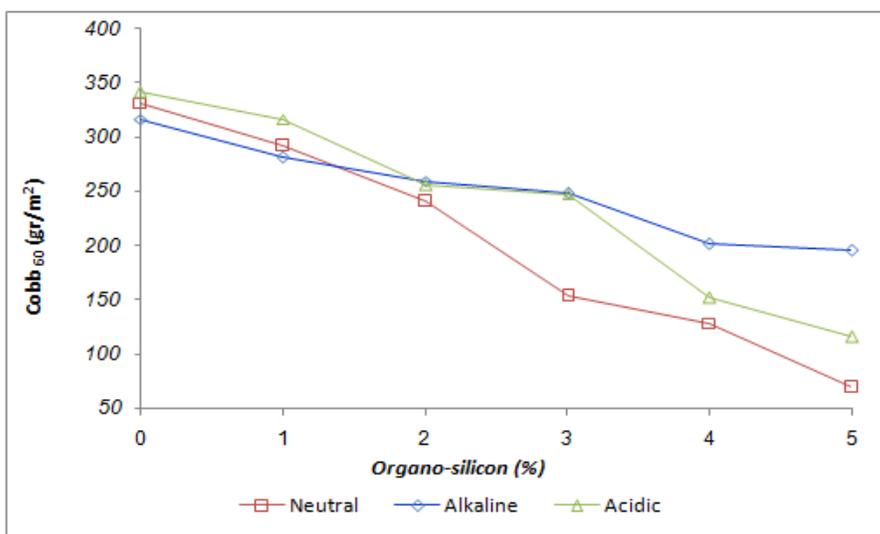


Fig. 5. Cobb test results for internally sized paper at different pH conditions

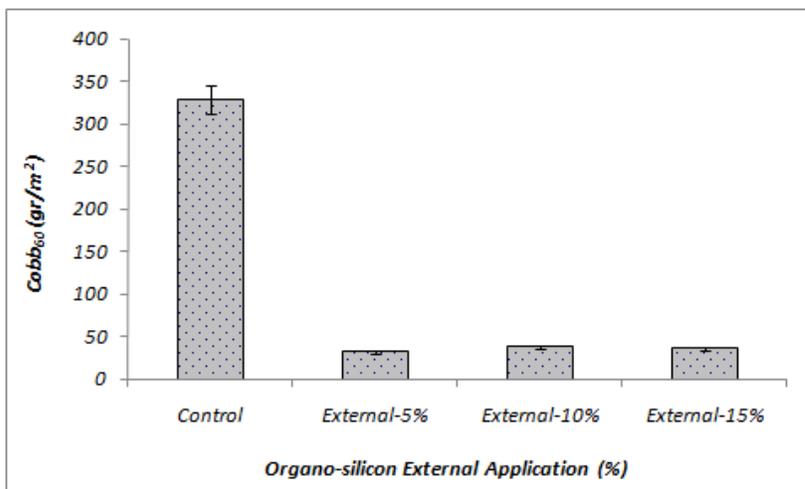


Fig. 6. Cobb test results for externally sized paper at neutral pH

Figure 5 indicates that the application of more organosilicon as an internal sizing agent in all three different pH conditions resulted in lower Cobb data, although all of the Cobb test results were over 50 g/m² (indicating relatively high water uptake). Varshoei *et*

al. (2013) applied AKD as an internal sizing agent in OCC pulp. Their Cobb test results showed that the internal application of AKD (0.25% to 1%) was able to diminish the Cobb (water uptake) to less than 30 g/m².

Figure 6 shows the Cobb test results following the external application of organosilicon to paper handsheets. In contrast with the internal application method, external application resulted in Cobb test data lower than 40 g/m², comparable to AKD, which is a common sizing agent. Also, there was no remarkable difference among 5%, 10%, and 15% organosilicon solutions. Comparing the results of Figs. 5 and 6 revealed that external sizing (external application) with organosilicon was more successful than the internal method.

Organo-Silicon Absorption Rate

As the external treatment of handsheets demonstrated a more desirable performance as a sizing agent, the amount of organosilicon absorbed into paper when applying various (5%, 10%, and 15%) concentrations of the solution was investigated. As Fig. 7 shows, a linear increase in organosilicon uptake was observed. In other words, for each 5% increase in the concentration of organosilicon solution, approximately 1 g/m² of this material was absorbed into the paper sheet (Fig. 7).

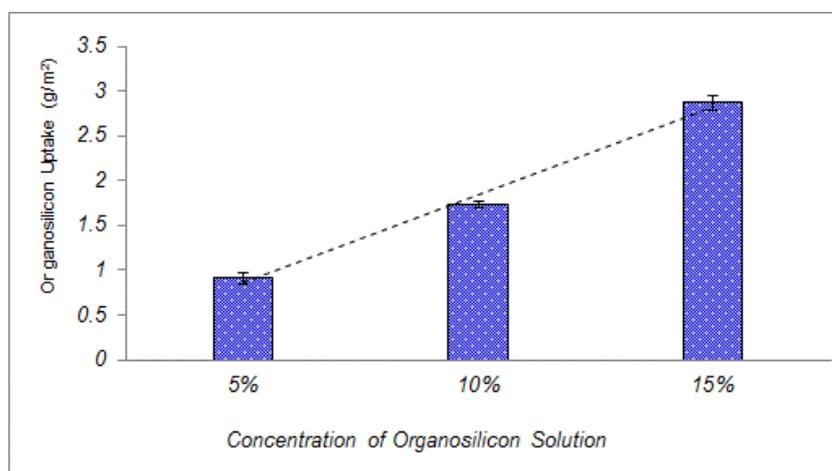


Fig. 7. Organosilicon uptake following external treatment with various concentrations of the solution

Equation 2 was used to compare organosilicon uptake during external application with internal dosing levels. For instance, knowing that the basis weight of the paper handsheet was 130 g/m² and the organosilicon uptake was approximately 1 g/m² (*i.e.* treating with 5% solution) (Fig. 7), the equivalent dosing level was calculated as approximately 0.75% (based on OD weight).

$$\text{Equivalent internal dosage (\%)} = \frac{\text{Uptake } (\frac{g}{m^2})}{\text{Basis Weight } (\frac{g}{m^2})} \times 100 \quad (2)$$

This equivalent dosing level (0.75%) for external usage was less and much more efficient than the 1% to 5% internal dosage of organosilicon. As Fig. 5 shows, the internal application of 1% to 5% organosilicon could not reduce the Cobb to less than 50 g/m².

Tensile Index

Usually, the application of sizing agents in paper negatively affects bonding and, therefore, tensile strength (Gess and Rodriguez 2005). This trend can be observed in Fig. 8. For the same reason, in using more organosilicon either internally or externally, the tensile index suffered. Nevertheless, the reduction in paper strength was more remarkable in the case of the external usage of organosilicon. This could be due to successive rewetting and drying of paper handsheets during external application, which negatively affects the state of bonding between the fibers.

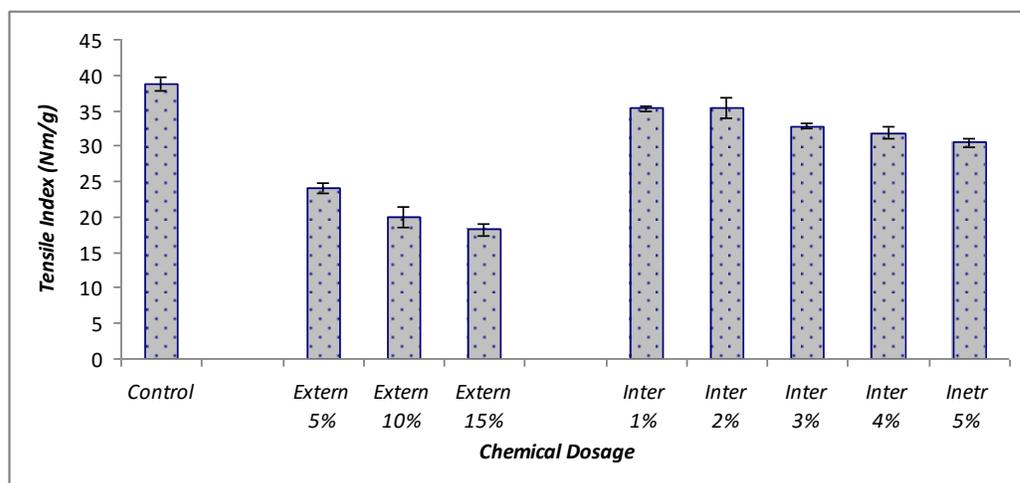


Fig. 8. The effect of internal and external sizing on the tensile index of treated papers

FT-IR Analysis

As previously stated, the FT-IR spectra of the organosilicon compound, an externally treated sheet, and a control (untreated) paper surface were analyzed in order to study possible chemical bonding on the surface of handsheets treated with organosilicon.

Figure 9 shows the FT-IR spectrum of the organosilicon compound. In this spectrum, the peak at 1087 cm^{-1} seems to be related to the asymmetric stretching vibration of Si–O–R bonding, which can be characteristic of the organosilicon compound. Also, the peak at 882 cm^{-1} shows the symmetric stretching vibration of Si–O–R bonding. The observed bands between 2800 cm^{-1} and 3000 cm^{-1} are ascribed to C–H stretching bands (Smith 1960).

Figure 10 compares the FT-IR (ATR) spectrum of the control (untreated) paper with that of the externally treated sample. In this figure, the broad bands positioned in the $3500\text{--}3100\text{ cm}^{-1}$ region along with the peaks at $1160\text{--}890\text{ cm}^{-1}$ can be attributed to hydroxyl (OH), and C–O–C stretching vibration which are observable in most cellulosic materials (Niroomand *et al.* 2016). On the other hand, presence of organosilicon can be confirmed by the increased intensity of –CH₂ stretching in the 2800 cm^{-1} to 3000 cm^{-1} region and Si–O–C symmetric and asymmetric stretching vibration around 800 cm^{-1} and 1100 cm^{-1} . The increased intensity of –CH₂ and alkanes can be due to the hydrophobic organic side chain of organosilicon compound applied for treatment of the paperboard.

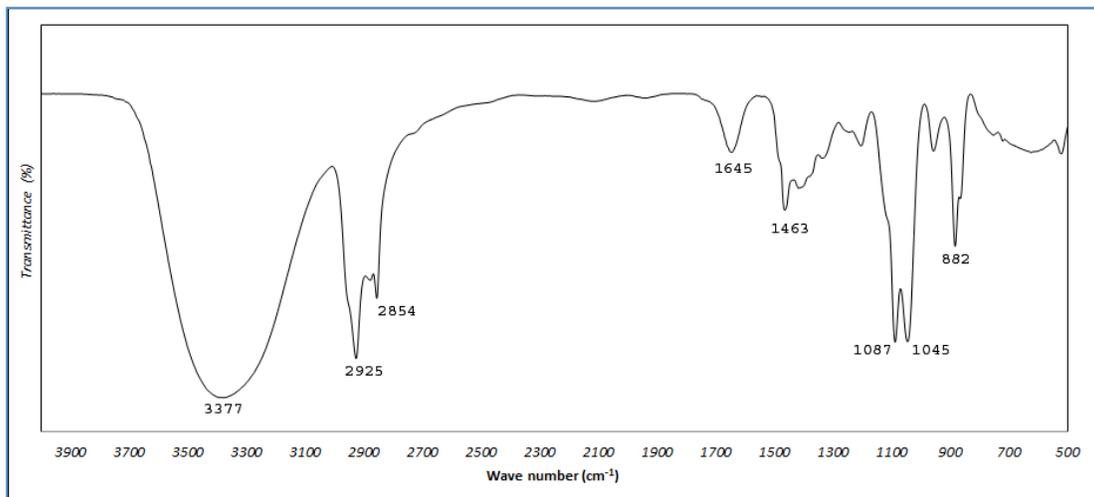


Fig. 9. FT-IR spectrum of the organosilicon compound

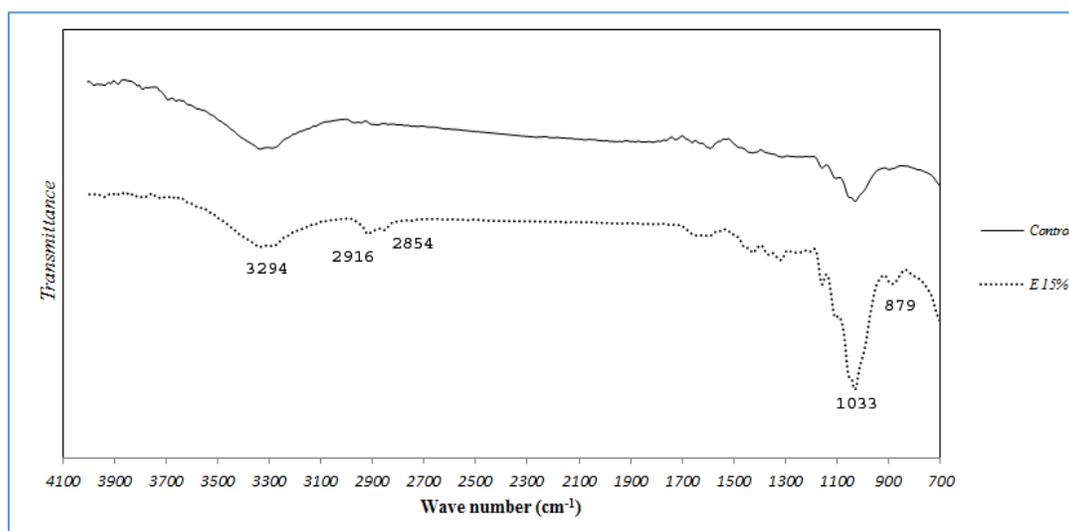


Fig. 10. FT-IR (ATR) spectra of externally treated handsheets and control paper samples

CONCLUSIONS

1. Both the external and internal application of organosilicon in ambient temperature increased OCC paperboard hydrophobicity.
2. Following the external application of the organosilicon solution, promising results were achieved in terms of the Cobb test and contact angle. Against the control sample, the Cobb test results were reduced to less than 40 g/m^2 , and the contact angle did not drastically drop, even after several minutes.
3. Although internal sizing with organosilicon reduced water absorption in the Cobb test and helped water repellency in the contact angle, the results were not as successful as

the available reports about internal application of AKD. Therefore, the external sizing method with organosilicon showed much better performance.

4. Generally, organosilicon acted at ambient temperature through a fast, easy and mild reaction for hydrophobation of paperboard, even in an aqueous medium.

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