Influence of polysiloxane microspheres on hydrophobicity, structure and mechanical properties of paper materials

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Abstract The aim of the study was to investigate the impact of three types of polysiloxane microspheres on the barrier properties, structure and mechanical properties of paper. An influence of new silicon filler on properties of cellulose paper sheet was analyzed. Polysiloxane microspheres were used as an additive introduced into the network of cellulosic fibers in order to obtain new functional properties of the paper. The following types of microspheres were used in the research: M1 hydrophilic of average diameter 23.5 μm, M2 hydrophobic of average diameter 3.1 μm and M3 hydrophobic of average diameter 23.5 μm. The obtained handsheets were analyzed for changes in apparent density, roughness, tensile strength, bursting strength, and tear resistance. Wettability and resistance to liquid were characterized by contact angle measurement, penetration dynamics analysis and uniformity of liquid penetration measured using an extended liquid penetration analyser. It was found that the presence of M2 (small diameter) microspheres improved significantly the paper’s hydrophobicity without changing the mechanical properties. The addition of M1 and M3 (large diameter) microspheres decreased the mechanical properties of the paper samples and did not improve their hydrophobicity. However, M1 microspheres resulted in increased uniformity of liquid penetration through the paper structure. The presented studies also show that it is possible to obtain paper with high hydrophobic properties only through the filling application when polysiloxane microspheres are used for this purpose. The results also indicate that it is not necessary to hydrophobize the entire material structure in order to achieve its high hydrophobicity.

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Introduction

Paper in its simplest form is a material with a capillary-porous structure. The hydrophilic properties of the cellulosic plant fibers that make up this structure cause the paper to easily absorb water. Considering the functional properties of this material, additional functionality is required for many applications. Proper control of a paper’s resistance to wetting and liquid penetration can be achieved by applying a sizing process. Common methods are based on alkyl ketene dimer (AKD) and alkenyl succinic anhydride (ASA) (Hubbe 2007). Full wet strength can be obtained by coating the surface of the paper with synthetic polymers such as polyethylene and polypropylene. However, these compounds are not biodegradable and neutral to the environment. The properties of paper can also be functionalized by introducing chemical additives called fillers. Fillers are not only used as a replacement for more expensive fibrous material but also contribute specific functionalities to final paper products (Thorn and Au 2009). Depending on the type of filler, they can modify the structural, optical, barrier or other properties of paper. In papermaking, kaolin clays and calcium carbonates are the most commonly used fillers. They are introduced to the paper mainly to improve its brightness and opacity, increase the smoothness of the surface, improve the printability and the dimensional stability of the paper (Holik 2013). Fillers, because of their inorganic origin, also help to reduce the energy demand in the papermaking process (Hubbe and Gill 2016; He et al. 2014). However, their poor binding ability limits their use. Increasing the amount of filler in the paper structure may result in the decrease of both the paper’s stiffness and its strength properties. Moreover, improperly fixed filler on the paper surface can result in dusting and linting during the printing operation. Another disadvantage of the currently used fillers is their low impact on the hydrophobic properties of the paper. Paper, as a porous material consisting mainly of hydrophilic cellulose plant fibers, absorbs water intensively. Excessive liquid absorption not only makes the paper structure weaker but leads to poor printing quality (Borch et al. 2002). Modification of the hydrophilic properties of paper requires additional chemical agents to be added to the fibrous suspension (pulp). The growing requirements related to the need of the production costs reduction calls for the new, more effective control of the absorbency of paper. The modification of the properties of common fillers used in papermaking is one of the methods studied. Such fillers could then be used without the sizing agents (Yang and Liu 2008). For this purpose, cellulose derivatives as a filler modification were used by Wannstrom et al. (2005). Thanks to this, they managed to lower the negative effect of filler loading on sizing. Among many others, research related to the
application of different silicon compounds for filler modification can be found (Gamelas et al. 2011; Song et al. 2012; Lourenco et al. 2014). In the most cases, the use of silicon compounds was associated with the modification of already existing fillers (e.g. precipitated calcium carbonate, TiO₂). Cross-linked polysiloxanes are one of the interesting groups of materials that could also be used as additives to functionalize paper properties. They are characterized by such properties as: non-toxicity, flexibility and heat stability in a wide temperature range, transparency, low flammability, non-toxic combustion products, durability and good mechanical properties (Clarson 2000). Hence the unflagging interest of research groups in them around the world (Calderón et al. 2020; Fawcett et al. 2015; Nowacka et al. 2020). As a result, polysiloxanes are applied in many and various fields of science and production. However, there is no information so far about using cross-linked siloxanes in papermaking, in particular as fillers that can replace sizing agents. In recent years, a growing interest has also been noticed in siloxane materials shaped into nanoparticles, microparticles and microcapsules (Gibson et al. 2008; Liu et al. 2006, 2015; Li 2018; Chai et al. 2018). The Center of Molecular and Macromolecular Studies, Polish Academy of Sciences in Poland developed an original method for the synthesis of polysiloxane microspheres (Fortuniak 2013b). These microspheres were obtained in sol–gel process from the oligomeric divinyl compounds and by cross-linking of polyhydrosiloxanes. The easy and controlled synthesis of all-polysiloxane microspheres, microcapsules and microspheroidal particles (Fig. 1) of various sizes and the wide possibilities of functionalization mean that they can find application as transition metal supports, antimicrobial particles and protein adsorbents and others (Mizerska et al. 2015a, b, 2018; Pospiech et al. 2016a, b). Silicon oxycarbide (SiOC) microspheres obtained in the cross-linked polysiloxanes microspheres pyrolysis process were characterized by high hardness (up to 14 GPa) and a modulus of elasticity above 140 GPa (Szymanski et al. 2019). Ease of modification makes it possible to control the hydrophobic or hydrophilic properties and introduce various functional groups (Mizerska et al. 2015a; Pospiech 2016a, b). In turn, synthesis in the presence of inorganic salts allows highly porous microspheres and microspheroidal particles to be obtained (Pospiech et al. 2017).

Microcapsules with polysiloxane shells and phase change cores also open up a wide spectrum of application (e.g. thermal control in packaging or clothes) (Fortuniak et al. 2013a).

Although there are many reports related to the modification of cellulosic fibers and fillers by silicon compounds to improve the hydrophobic properties (Shen 2012; Song 2013), no information is available about the direct use of siloxane-based microspheres as fillers. Kenaga (1973) introduced thermoplastic
microcapsules into the pulp to obtain a high bulk paper. The increased concentration of microspheres (from 0.88 to 1.65%) caused the bulk and porosity to increase by about 20% and 100% respectively. Mechanical parameters of paper also changed. Cairns et al. (2019) applied small spherical silica particles ($\sim 0.1$–$0.2$ μm) to a clay–latex coating composition. As a result, they were able to improve the paper’s barrier properties using a coating method. Alderfer and Crawford (1997) investigated the effect of the impact of silica nano-spheres fused together in a solid gel structure as the filler used for the ink-jet liquid absorption improvement. Nevertheless, their filler did not replace sizing agent.

The aim of the research presented was to investigate the impact of the various types of polysiloxane microspheres used as fillers on the barrier properties, e.g. the water resistance and air permeability, structure and mechanical properties of paper. In particular, the possibility of using polysiloxane microspheres as a substance that serves both as a filler and a sizing agent was investigated.

**Experimental**

**Chemicals**

Polyhydromethylsiloxane (PHMS) was purchased in ABCR (HMS 991, Mn $4.7 \times 10^3$ g/mol-confirmed by SEC). Polyvinyl alcohol (Mn $7.2 \times 10^4$), dioxane (POCh, analytical grade), 1,3-Divinyltetramethyldisiloxane (ABCR, 97%), Dimethyldimethoxysilane (ABCR, 97%) were used without purification. Pt(0) Karstedt catalyst containing 20 w/w% Pt was obtained from Momentive Performance Materials GmbH, Leverkusen. Commercial bleached kraft softwood (pine) pulp was used in the experiments and was delivered in the form of dry sheets. The average moisture content was 4.3%. The initial pulp parameters were as follows: DP = 1012, $\alpha$-cellulose content = 88.6%, average arithmetic fiber length = 1.79 mm, primary fines content = 10.7%.

**Analytical methods**

$^{29}$Si and $^{13}$C MAS NMR spectroscopy, scanning electron microscopy (SEM)–energy-dispersive X-ray spectroscopy (EDX) were precisely described earlier (Pospiech 2016b). FTIR-ATR was performed on the FT/IR-6200 Jasco spectrometer with an ATR PRO610P-S adapter (Ge crystal).

**Structural, water absorptiveness and mechanical properties of paper samples**

The obtained paper samples were conditioned (according to ISO 187:1990 standard) and tested in accordance with the appropriate ISO standards:

- SR value (ISO 5267-1:1999), L&W Schopper–Riegler freeness tester, Sweden.
- Tensile index (ISO 1924-2:2008), Instron 5564, UK.
- Cobb method (ISO 535:1991), Cobb Tester, L&W, Sweden.
- Elmendorf tear resistance (ISO 1974:1990), L&W Tearing Tester, Sweden.
- Bendtsen air permeance (ISO 5636-3:1992) and roughness (ISO 8791-2:1990), Bendtsen Roughness Tester, TMI Testing Machines Inc., USA.
- Bursting strength (ISO 2758:2001), Mullen Burst Machine, L&W, Sweden.

**Contact angle**

A PGX + Goniometer from Testing Machines Inc. (USA) was used for contact angle measurements. The tests were carried out according to the TAPPI T 458 standard method. Water drop volume was 4 μL.

**Water penetration dynamics**

Water penetration dynamics were measured using a penetration dynamics analyzer (PDA) (Module S 05, emtec Electronics GmbH, Leipzig, Germany). The handsheets were cut into samples, each 21 cm$^2$. Measurements were conducted separately for each sample in distilled water at 20 °C, following the standard procedure described by the manufacturer. The result was an arithmetic average value calculated from the series of 3 measurements.
Uniformity of the material structure in terms of liquid penetration (XLPA method)

A novel method, developed in the Centre of Paper-making and Printing at Lodz University of Technology and described in Olejnik et al. (2018), has been used for the measurement of liquid penetration uniformity through the material structure. Measurement was conducted using an Extended Liquid Penetration Analysrer (XLPA). The main concept of the method is to characterize the liquid penetration by optical examination of both the size and the pattern (texture) of the penetrated area of the paper sample. During the measurement, the liquid was brought into contact with the bottom surface of the paper. Then, the dynamics of the liquid penetration was registered by a digital camera located over the top surface of the examined sample. Finally, the sequence of the recorded images was processed and analyzed to describe quantitatively the phenomenon of liquid permeation through the paper. The recording of the permeation process was carried out with a frame rate of 60 fps. Commercial Hero Blue-Black no. 62 ink was used as the test liquid (viscosity = 1.10 mPa s; surface tension = 40 mN/m). A sequence of images recorded during permeation was analyzed and their brightness was normalized in the range of 0..1. Two parameters—as a function of time from the beginning of permeation—were calculated: the break-through area and the contrast of the image. It was found during earlier studies that a decrease of the normalized pixel brightness to 0.2 or less indicated that the ink had fully penetrated the structure of the paper. This threshold pixel value was defined as $T_r$. The percentage value of the area penetrated (break-through) by the tested liquid was calculated as the sum of the pixels of brightness $T_r$ (or less) divided by the total number of pixels in the image.

A detailed description of the contrast calculation can be found in Pietikäinen and Ojala (1996). From the image analysis point of view, contrast is a parameter which is less sensitive regarding only the pixels brightness, but is very sensitive to dense patterns of pixels with large differences in their brightness. As a result, contrast is a measure of the diversity of adjacent pixels. This means that—for heterogeneous, capillary-porous materials—the contrast will be higher when liquid penetration through the capillary system is more even and unidirectional, e.g. in the “Z” direction with limited sideways flow. In other words, a high contrast value correlates with a high material homogeneity in terms of liquid permeability.

Synthesis of cross-linked polysiloxane microspheres (M1 and M2)

The preparation of polysiloxane microspheres was precisely described earlier (Fortuniak et al. 2013b). Regular microspheres, with diameters ranging from 3.5 to 30 μm (M1, M3—mean value 23.5 μm) and 0.5 to 9 μm (M2—mean value—3.1 μm) were analyzed by $^{29}$Si and $^{13}$C MAS NMR, elemental analysis and SEM. The data obtained in these measurements are presented in Table 1 (the $^{29}$Si NMR spectra are in the supplementary materials, Fig. 1S).

M1—$^{29}$Si MAS NMR ($\delta$ in ppm at maximum): −69.8 MeSi(OSi)$_3$; −60.0 MeSi(OH)(OSi)$_2$; −40.2 MeSi(H)(OSi)$_2$; −23.7 MeSi(CH$_2$)(OSi)$_2$; +4.5 Me$_2$Si(CH$_2$)(OSi) and Me$_3$SiO. $^{13}$CMAS NMR ($\delta$ in ppm at maximum): −3.5, −0.9, +0.6 CH$_3$; +8.5 CH$_2$. Elemental analysis in wt%: C-23.6%, H-6.3%.

M2—$^{29}$Si MAS NMR ($\delta$ in ppm at maximum): −57.9 MeSi(OH)(OSi)$_2$; −38.6 MeSi(H)(OSi)$_2$; −21.2 MeSi(CH$_2$)(OSi)$_2$; +5.7 Me$_2$Si(CH$_2$)(OSi) and Me$_3$SiO. $^{13}$CMAS NMR ($\delta$ in ppm at maximum): −3.9, −2.4, −1.2 CH$_3$; +6.8 CH$_2$. Elemental analysis in wt%: C-25.9%, H-7.0%.

The chemical structure of the microspheres (the amount of SiOH groups) is closely related to their size (Table 1). This effect is explained in (Pospiech 2017). Hydrolysis of SiH groups in PHMS with Pt(0) as catalyst leads to SiOH groups being obtained in the course of the diffusion of water from the continuous phase. However, this diffusion is too slow to hydrolyze most of the SiH groups. In the case of larger particles, they act as nanocontainers for water, which causes the process to take place in a double emulsion W/O/W. As a result, the conversion of SiH groups in larger particles is greater than in smaller ones, so the latter have more unreacted SiH groups and are more hydrophobic.

Modification of surface of polysiloxane microspheres (M3)

M1 microspheres were modified by dimethyldimethoxysilane to change their
hydrophilicity and obtain microspheres of the same size but with hydrophobic surfaces (M3). 4.5 g of M1 microspheres were dispersed in 20 ml of toluene. Dimethyldimethoxysilane (1.76 g, $1.46 \times 10^{-2}$ mol) was added in the presence of allylamine (0.2 g, $4 \times 10^{-3}$ mol) as catalyst. Then the suspension was shaken for 24 hours, controlling the degree of modification by decreasing the silane with gas chromatography. When the concentration of silane stopped changing, the microspheres were separated by centrifugation and flushed by toluene several times. After that, the microspheres were dried under vacuum and analyzed by $^{29}$Si and $^{13}$C MAS NMR, elemental analysis and SEM.

M3–$^{29}$Si MAS NMR ($\delta$ in ppm at maximum): $-67.7$ MeSi(OSi)$_3$; $-57.9$ MeSi(OH)(OSi)$_2$; $-38.1$ MeSi(H)(OSi)$_2$; $-21.5$ MeSi(CH$_2$)(OSi)$_2$; $-12.6$ Me$_2$Si(OSi)$_2$; $+7.0$ Me$_2$Si(CH$_2$)(OSi) and Me$_3$SiO. $^{13}$C MAS NMR ($\delta$ in ppm at maximum): $-6.0$, $-3.1$, $+0.2$ CH$_3$, $+5.5$ CH$_2$. Elemental analysis in wt%: C-25.1%, H-6.2%.

### Table 1 Properties of the polysiloxane microspheres used in the experiments

| Average diameter of microspheres (µm) | Hydrophobic/ hydrophilic properties | Data from $^{29}$Si NMR | AE |
|-------------------------------------|------------------------------------|-------------------------|----|
|                                     |                                    | SiOH [mol%] | SiH [mol%] | C% | H% |
| M1 23.5                             | Hydrophilic                        | 49.4        | 14.4        | 23.6 | 6.3 |
| M2 3.1                              | Hydrophobic                        | 5.0         | 77.93       | 25.9 | 7.0 |
| M3 23.5                             | Hydrophobic                        | 8.7         | 10.27       | 25.1 | 6.2 |

Preparation of paper samples

Pulp samples from bleached pine kraft were prepared according to standard ISO 5263-1 and refined in the PFI mill according to the TAPPI T 248 standard method. The Schopper–Riegler value of the beaten pulp was SR-42 (according to ISO 5267-1:1999). Laboratory sheets of 70 g/m$^2$ with and without microspheres were formed in Rapid-Köthen apparatus (LaborMeks, Poland) according to standard ISO 5269-2:2005. The obtained papers were conditioned according to the ISO 187:1990 standard.

Three types of microspheres were added during the sheet-forming process. M1 were larger (average size about 20 µm) and contained more SiOH groups and hence were hydrophilic. The M3 microspheres were of the same size and showed hydrophobic properties. The third microspheres (M2) were smaller (maximum diameter less than 10 µm) and were hydrophobic (contained more SiH groups). The microspheres were added as dispersed suspension in water (M1 or M3) or in a mixture of MeOH/water (M2).

Retention of siloxane microspheres in the cellulosic fibers network

The retention of microspheres has been specified on the basis of thermogravimetric quantitative analysis of silicon (by heating of the samples in the presence of acid in a platinum crucible). Thermogravimetric analysis indicates that over 40% of the microspheres M1, over 36% of M2 and about 30% of M3 were retained in the fibers network. These values are average of three specimens, with coefficient of variation respectively 6.9% for M1, 5.6% for M2, 6.1% for M3.

### Results and discussion

#### Structural properties of obtained paper samples

Structural analysis was performed by SEM and FTIR-ATR. The distribution of the M1, M2 and M3 microspheres in the paper is presented in the SEM microphotographs in Fig. 2—A, B and C respectively. Clusters of microspheres were observed. In the case of M2, SEM indicated insufficient dispersion of the microspheres in suspension or aggregation in the paper-forming process. The characteristic bands on the ATR spectra confirmed the presence of polysiloxane in the paper sheets (see the Supplementary Materials, Fig. 2S). On all the spectra the Si–O–Si bond peaks (1000–1100 cm$^{-1}$) can be clearly seen.
On the M2 paper spectra the 2100–2200 cm\(^{-1}\) band derived from the SiH bonds present in the microspheres is visible. The peaks between 2800 and 3000 cm\(^{-1}\) are characteristic for Si-O-CH\(_3\) bonds (M3 specimen).

The apparent density of the tested papers was also determined (Tables 2 and 1S in Supplementary Materials). It was generally found that the addition of microspheres resulted in a decrease in apparent density, which means that the paper structure became more porous. The largest decrease in the apparent density (about 20%) was recorded for samples with 10% of M3 microspheres (average diameter: 23.5 μm). This effect is most likely the result of the size and hydrophobic properties of the microspheres. These properties gave rise to repulsive forces between the cellulosic fibers and the microspheres, resulting in the increase of free spaces around them (see Fig. 2c). Smaller-sized microspheres (M2, average diameter: 3.1 μm) formed more packed clusters, so the decrease in the paper’s apparent density was smaller.

It can be assumed that, as the porosity of the paper increases, the air permeability should also increase. This was observed in the case of the M1 microspheres application (Tables 3 and 1S in Supplementary Materials). However, the addition of the small M2 microspheres did not change the air permeability significantly, even for the concentration of 30% (see Fig. 3S in Supplementary Materials). This effect is most likely caused by the size of the particles, which were concentrated in the paper structure in the form of clusters embedded in the pores of the material. As a result, their hydrophobic properties had less effect on the porosity increase of the paper structure.

Effect of introduction of microspheres on hydrophobic/hydrophilic properties of paper sheets

Assuming that the material is solid, its wettability is directly associated with the surface energy (Paula et al. 2003). However, the situation is more complex in the case of capillary-porous structures (e.g. paper). In such case, the wettability cannot be described by a single parameter—the contact angle, for example. Moreover, precise description of the interaction between capillary-porous materials and liquids is very difficult because it is necessary to take into account also a morphological description of the capillary-pore space (Hirasaki 1991). The results obtained indicate that the addition of microspheres to the cellulosic pulp had a significant impact on the wettability of the paper formed from this pulp. The wettability of the paper samples was characterized by four different tests: wettability (Cobb method), contact angle, water penetration dynamics (PDA method) and the

### Table 2 Changing apparent density of paper sheets depending on the type and concentration of microspheres

| Microspheres | 0%  | 10%  | 20%  | 30%  |
|--------------|-----|------|------|------|
| Apparent density | M1  | 0.690 | 0.594 | 0.588 | 0.581 |
| [g/cm\(^3\)] | M2  | 0.681 | 0.672 | 0.672 |
|               | M3  | 0.540 | --    | --    |
uniformity of the liquid penetration through the tested paper samples (XLPA method).

Water absorptiveness (Cobb60)

The Cobb water absorptiveness measurement is one of the simplest methods of determining the degree of hydrophobization of paper materials. In the presented case (Table 4) it was found that the lowest absorptiveness occurred for the M2 microspheres. For M2 concentration of 10%, Cobb60 was equal to 16.5 g/m², and 12.8 g/m² for the concentration of 30%. For the all other paper samples, the increase in basis weight resulting from the absorbed water was over 80 g/m² which means that these samples did not show hydrophobic properties. The coefficient of variation for Cobb60 ranged from 6.1 to 9.4%.

Contact angle measurement

Changes of contact angle with time for the handsheets with M2 are presented on Fig. 3. For all other samples, contact angle was not measurable due to the immediate penetration of water into the material structure. Initial contact angle of all paper samples with M2 microspheres was greater than 100°. In the case of 10% of M2 addition, the decrease of the contact angle after 5 min was about 20°. The differences between the contact angle measurements for the same type of paper indicate the heterogeneity in the microsphere distribution in the paper structure. Moreover, paper containing 20% of M2 microspheres showed a higher initial contact angle and its values were more stable in time comparing to paper containing 10% of M2. Further increase of the amount of M2 from 20 to 30% did not increase the contact angle value (Fig. 3c) but the stability was even better. Taking into account the surface roughness (Table 5), it was found that in the case of paper filled with M2 microspheres, its roughness increased with the increasing amount of microspheres. The sheet with 10% of microspheres had roughness of paper similar to paper without any filler. It can be concluded that high contact angle could be also the result of the surface inhomogeneity and the microroughness of the microparticles (see Fig. 4S in Supplementary Material). As result, the water drops on the surface are pinned in a Cassie-Baxter state. The high contact angle effect can be also explained by the previous SEM observations. It was found that small microspheres anchored in the pores of the paper formed larger clusters. As a result, the total area of the cluster is large and its porosity is low compared to the pores in the paper. The hydrophobicity of the microspheres and the decrease of the average porosity of the paper together resulted in the whole sheet structure becoming hydrophobic (see the results of apparent density in Table 2). This effect was not observed using M3 hydrophobic microspheres. The greater diameter of the particles did not allow the formation of clusters. Consequently, they contributed to the increase of the paper porosity and their total area was not large (compared to the samples with M2). High paper wettability was observed also in the case of M1 microspheres added to paper. However, the high hydrophilicity of these microspheres resulted in a lower porosity of the paper structure (compared to the samples containing M3). In the case of M1, the initial contact angle was comparable to that of paper without microspheres (∼ 50°) however, it quickly decreased and the droplets were fully absorbed by the paper. In

Table 3 Air permeability of paper sheets depending on the type and concentration of microspheres

| Microspheres | 0%   | 10%  | 20%  | 30%  |
|--------------|------|------|------|------|
| Air permeability [ml/min] |      |      |      |      |
| M1           | 121  | 245  | 309  | 379  |
| M2           | 115  | 122  | 136  |      |
| M3           | 968  | –    | –    | –    |

Table 4 Water absorptiveness (Cobb60 values) for paper samples containing different types and amounts of microspheres

| Microspheres | 0% | 10% | 20% | 30% |
|--------------|----|-----|-----|-----|
| Cobb60 value |    |     |     |     |
| M1           | 82.1| 85.3| 83.9| 89.1|
| M2           | 16.5| 12.4| 12.8|     |
| M3           | 81.8| –   | –   | –   |
the case of M3, penetration of water into the material structure was also immediate.

Liquid penetration dynamics analysis (PDA method)

Contact angle analysis was conducted at several points on the surface of the paper, but it did not provide comprehensive information about the dynamics of liquid penetration into the surface. This can be obtained by Penetration Dynamics Analysis (PDA). The main principle of the analysis is based on the effect of ultrasound signal attenuation during its penetration through the paper structure when the surface of the tested material is exposed to water (Skowronski et al. 2005; Skowronski 2010a, b). In general, there are two main stages of liquid interaction with the paper structure can be distinguished: wetting and penetration. In the graph generated when measuring the penetration dynamics, wetting is represented as the wetting time \(\text{Max}(I)\), which is the time between liquid contact and the highest intensity \(I\) of ultrasonic signal registered during the measurement. Liquid penetration begins beyond this maximum value. The faster the liquid penetrates into the paper, the faster the ultrasonic signal decreases. Therefore the slope of the curve beyond the \(\text{Max}(I)\) value can be considered as the penetration speed \(\frac{\Delta I}{\Delta t}\) (Krainer and Hirn 2018; Waldner and Hirn 2020). In the presented research, the time base for penetration speed calculations was 3 s. Results are presented in Table 6; Fig. 4. The coefficient of variation for all cases was similar and ranged from 5.1 to 11.4%.

The longest wetting times were obtained for the M2 microspheres. For M2 concentration of 10%, wetting time was 3.13 s, and 8.7 s for the concentration of 30%. The paper samples with the addition of M3 and M1 microspheres practically did not reveal any barrier to the wetting process. Also, the water penetration speed was the lowest for papers filled with M2 microspheres. This speed was the lowest for the paper with the highest content (30%) of microspheres M2. It can be assumed that these effects were the result of the combined influence of the properties of the microspheres size and their impact on the final structure of the paper.

The addition of larger microspheres (M1, M3) resulted in a decrease of the apparent density and an increase of air permeability. This means that the paper structure was more porous and more absorbent for liquids. The lowest impact on the hydrophobicity was observed in the case of paper with an addition of M3 microspheres.
One can also conclude that the addition of M1 microspheres improved the hydrophilic properties of paper. The shape of the PDA curve in the first three seconds of measurement (Fig. 4b) shows that the surface wetting was faster than in paper without microspheres. It was expected that microspheres of the same dimensions should affect the structure of the paper similarly. However, it was found that the addition of M1 microspheres to the cellulosic pulp resulted in a paper of higher apparent density being obtained. This effect can be explained by the better affinity of the M1 microspheres for cellulosic fibers (see Fig. 5). The presence of −OH groups in the M1 microspheres made the paper structure less porous compared to paper with the addition of M3 microspheres. Consequently, paper with the addition of M1 hydrophilic microspheres showed less wettability than paper with the addition of M3 hydrophobic microspheres.

### Table 6

Wetting time ($\text{Max}_{(I)}$) and water penetration speed ($\Delta I/\Delta t$) obtained from PDA device for paper samples containing different types and amounts of microspheres

| Microspheres | 0%       | 10%  | 20%  | 30%  |
|--------------|----------|------|------|------|
| $\text{Max}_{(I)}$ [s] |          |      |      |      |
| M1           | 0.17     | 0.08 | 0.08 | 0.08 |
| M2           | 3.13     | 7.06 | 8.70 |      |
| M3           | 0.08     |      |      |      |
| Penetration speed = $\Delta I/\Delta t$, \[s^{-1}\] |          |      |      |      |
| M1           | 26.45    | 33.5 | 33.77| 33.75|
| M2           | 1.71     | 0.26 | 0.17 |      |
| M3           | 32.54    |      |      |      |

**Fig. 4** Analysis of the dynamic liquid penetration (distilled water) for tested paper samples (PDA device): a with M2 microspheres; b with M1 and M3 microspheres

Both the contact angle measurement and PDA analysis showed significant differences for papers with M1, M2 and M3 microspheres. The addition of hydrophilic M1 microspheres did not change the paper’s resistance to water compared with paper...
without microspheres. In turn, the addition of M2 microspheres significantly changed the paper’s wettabilities, imparting almost super hydrophobic properties to it. It seemed that the addition of M3 microspheres would also change the hydrophilic properties, but for the papers tested in the research presented, exactly the same results as for M1 were obtained.

Uniformity of the liquid (ink) penetration through tested paper samples (XLPA method)

Unlike the measurement of the contact angle and PDA, the XLPA method allows to measure the interaction of the liquid with the paper over a larger surface area using image texture analysis. As a result, it eliminates the unwanted disturbances related to the influence of local in homogeneities in the paper structure.

Figure 6a, b present the dynamic interaction of the liquid (ink) with the tested paper samples.

Theoretically, if the paper structure were perfectly homogeneous, structural elements (solid particles) of equal sizes and free spaces (pores) of constant size would be distributed evenly. For such a material, the texture of its surface during the penetration of high-contrast liquids will be similar to a chessboard (solid particles—light fields, and evenly filled pores—dark fields). This texture will be characterized by the highest contrast value. Depending on the hydrophobic properties of the material and the level of the structure unevenness, the final result of the liquid penetration (i.e. surface texture) may take a different form and different contrast value. In the case of the investigated paper samples (Fig. 6a), the image of the reference paper surface (without the addition of microspheres) reached its highest contrast value (~ 780) already after approx. 900 ms, and then this parameter quickly decreased. This indicates that the liquid quickly broke through the structure and the surface was completely flooded in an uncontrolled manner. This is confirmed by the results shown in Fig. 6b—the increase in the area penetrated by the liquid for the reference paper was the fastest.

Higher hydrophobic properties were demonstrated by the paper with the addition of 10% M3 hydrophobic microspheres (average size 23.5 μm), although in this case the growth rate of the surface broken through by the liquid was practically identical to that of the reference paper. The highest value of contrast—the highest uniformity in the process of liquid penetration—was obtained for the paper filled with 30% of hydrophilic M1 microspheres (average size 23.5 μm). This paper, at the same time, showed very limited hydrophobicity: its structure was completely flooded with liquid after approx. 4000 ms (Fig. 6b).

It was also observed that paper containing 10% of M3 hydrophobic microspheres was much more wettable than paper containing 30% M1 hydrophilic microspheres. This can be explained by comparing the structural properties of both materials. The paper containing 10% M3 hydrophobic microspheres had the lowest apparent density and the highest air

![Figure 6](https://example.com/fig6.png)

**Fig. 6** Analysis of the liquid (ink) interaction with tested paper samples (XLPA method): a dynamics of the uniformity of liquid penetration; b dynamics of the penetration rate expressed as a break-through area
permeability among all the samples tested. Thus, its porosity was the highest. The more porous structure was more susceptible to liquid absorption. The hydrophobic properties of the microspheres had a minor effect on the reduction of the liquid penetration intensity. On the other hand, the addition of (30% of hydrophilic microspheres caused a similar effect to that observed when other hydrophilic fillers are used in papermaking, e.g. CaCO₃ (Jeong et al. 2009). They increase the evenness of the porous paper structure and reduce the average pore size in this structure (Holik 2013; Hubbe and Gill 2016). As a result, an apparent increase in the paper’s hydrophobic properties can be observed, resulting in a slower penetration of liquid into its structure.

The paper samples filled with 20% and 30% of M2 microspheres (average size 3.1 μm) showed the highest hydrophobic properties. In both cases, the liquid did not break through the structure of these papers (Fig. 6b). Comparing also the contrast changes for both samples containing M2 microspheres (Fig. 6a), it was observed that in the case of the paper with 20% content of these microspheres, there was a greater increase in the texture contrast of its surface during wetting. This indicates that the liquid managed to penetrate more deeply into the paper structure in relation to the sample with 30% content of M2 microspheres. In the case of the latter paper sample, the highest hydrophobicity of the paper was obtained.

Figure 7 shows a view of the surface texture of the tested paper samples, the bottom of which was exposed to the ink (XLPA method). These images were obtained after an equal contact time of 1380 ms. This time corresponds to the maximum contrast value obtained for a paper sample containing 30% M1 microspheres (Fig. 7d). At the same time, this result was the highest among all the samples tested, proving the highest uniformity of liquid penetration through the paper structure. This can be visually observed as a relatively uniform “graininess” of the field broken through with the ink. The presented images confirm the findings represented in Fig. 6a, b.

Effect of introduction of microspheres on mechanical properties of paper sheets

Figure 8a–c presents the basic mechanical properties of the tested paper samples. The tensile index, tear resistance index and bursting strength index were selected for this purpose.

The results obtained indicate that the addition of 10% M1 and M2 microspheres did not affect the tensile index, while the 10% addition of M3 microspheres reduced this parameter by approx. 8 N m/g (compared with the reference paper—Fig. 8a; Table 7). It was also observed that increasing amount of M1 and M2 microspheres resulted in a decrease of the tensile index. Similar results were obtained for the bursting strength index parameter. In the case of the tear resistance index, the addition of all types of microspheres caused a slight decrease in this indicator (the largest decrease was recorded for paper samples with the addition of M2 microspheres). Nevertheless, the highest differences did not exceed 1 mN m²/g. In terms of the concentrations used, no significant effect on the tear strength index was observed. Based on the results presented, it can be concluded that both the size and surface properties of the microspheres used in the experiments have a significant impact on the tensile index and bursting strength index. These analyses indicate that the addition of microspheres interfered with fiber–fiber interactions, which resulted in lowering the strength of the paper structure.

Comparing the same additions of M1 and M3 microspheres, it can be observed that the largest decrease in strength properties was obtained for M3 (hydrophobic) microspheres. The M1 microspheres differed from the M3 microspheres only in their hydrophilic properties of the surface. The addition of M1 microspheres caused a smaller decrease in strength properties. It can therefore be concluded that the hydrophilic particles have a certain ability to form bonds with the paper structure. This property means that it is possible to introduce more of this type of microspheres without significant loss of the strength properties of the paper.

In the case of small hydrophobic particles (M2), the decrease in the mechanical properties of the paper structure was due to the microspheres concentration increase. At low concentrations (10%), indeed, an increase of the tensile index and bursting strength index was observed. Based on SEM analysis, it was found that small particles gradually filled the pores in the fiber network. It can be assumed that the small amount of small diameter microspheres did not have a significant effect on the total bonding area of cellulosic fibers.
Table 7  Mechanical properties of paper sheets depending on the type and concentration of microspheres

|                        | Microspheres | 0%   | 10%   | 20%   | 30%   |
|------------------------|--------------|------|-------|-------|-------|
| Tensile index [N/mg]   | M1           | 76.5 | 72.4  | 69.3  | 62.3  |
|                        | M2           | 78.7 | 70.4  | 61.7  |       |
|                        | M3           | 67.8 |       |       |       |
| Tear resistance index  | M1           | 6.5  | 6.28  | 6.21  | 6.41  |
| [mN m²/g]              | M2           | 5.71 | 6.03  | 5.92  |       |
|                        | M3           | 6.28 |       |       |       |
| Bursting strength index| M1           | 5.6  | 4.72  | 4.93  | 4.51  |
| [kPa m²/g]             | M2           | 5.79 | 5.3   | 4.95  |       |
|                        | M3           | 4.95 |       |       |       |

Fig. 7  View of the paper surface subjected to the XLPA method test after 1380 ms of contact with the ink: a reference paper (no microspheres added); b 20% M2; c 30% M2; d 30% M1; e 10% M3

Fig. 8  Change of mechanical properties depending on types and concentration of microspheres: a tensile index; b tear resistance index; c bursting strength index
However, as the concentration increased, the effects of the mutual repulsion of the hydrophilic fibers and hydrophobic microspheres appeared. Additionally, this effect was strengthened by the ability to create clusters with dimensions significantly larger than the size of typical M1 microspheres (Fig. 2b). To prevent the creation of clusters, surfactant additive can be used as a stabilizer in the suspension. On the one hand, this results in a well dispersed and stable suspension; on the other hand, it causes low retention of microspheres on the fibers network. These effects were confirmed in the SEM and ATR analysis, where no signals from typical SiH groups were observed.

Conclusions

In this study, the effect of three different siloxane microspheres on the mechanical and barrier properties of paper were investigated. Microspheres used in this study had different properties than most common fillers. Moreover, these microspheres could be of different diameters, thanks to which the structure of the material can be controlled. It was found that the type of microsphere (size, chemical structure) and the concentration influenced on the wettability and strength properties of the papers obtained. Small diameter and hydrophobic microspheres, added as a suspension to the cellulosic pulp, resulted in highly hydrophobic properties of the paper. Simultaneously, mechanical properties of the material were maintained. Large diameter hydrophilic microspheres introduced into the paper structure resulted in the increased uniformity of liquid penetration through the paper structure. In turn, large diameter hydrophobic microspheres did not significantly affect the wettability of the paper, but reduced its mechanical properties with respect to the paper sample without the microspheres. However, the impact of the different microspheres on the paper’s mechanical properties was not similar. The addition of 10% of bigger hydrophobic microspheres changed the mechanical properties to the same extent as the addition of 20% of bigger hydrophilic microspheres. The presented studies have also shown that paper with hydrophobic and even super hydrophobic properties can only be obtained by adding polysiloxane microspheres (i.e. without any sizing agent) as the filling application. The results also indicate that, to achieve this effect, it is not necessary to hydrophobize the entire material structure. It is enough to introduce into it the proper amount of hydrophobic particles of a certain size.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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