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Hydrophobic Silica Sol Coatings on Textiles—the Influence of Solvent and Sol Concentration

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Abstract. Hydrophobic silica sol coatings on textiles were investigated with respect to the influence of the solvents and the concentration of the sol. For this purpose, two silica sols, prepared with the hydrophobic additives octyltriethoxysilane and perfluoroctyltriethoxysilane were diluted by different solvents: water, ethanol and aceton.

In case of using pure water for dilution, the hydrophobicity of coated textiles decreases drastically with increasing dilution of the applied sol. For coatings on polyester fabrics or mixed fabrics made from polyester and cotton, the use of the organic solvents ethanol or aceton leads to significant hydrophobicity even in case of strong dilution down to a sol concentration $<1\%$. The hydrophobic effect of coated polyamide textile is less. The reason for different hydrophobicity of coated textiles resulting from the use of water instead of organic solvents is explained by different surface morphologies of the coatings deposited on the textile fibres, as observed by REM. In case of using organic solvents the coatings contain a more flat morphology which covers the fibres completely. In contrast, sols with higher water content lead to less adhesive coatings with crack formation.

The use of a combination of water with less inflammable organic solvents such as di(propylene glycol) n-propyl ether (Dowanol™ *DPnP*) in hydrophobic silica sols yields textile coatings with good hydrophobicity, even in case of low sol concentration. For practical application of textile coatings, especially silica sols with high water content are of interest, due to less risk of inflammation and lower ecological impact. Therefore, the use of water diluted hydrophobic silica sols with small amounts of *DPnP* offers a chance for textile refinement by the sol–gel technique.

Keywords: hydrophobicity, textiles, coatings, sol

1. Introduction

Sol–gel coatings on textiles have been used to provide textiles with new properties, e.g. coloration, UV protection, biological or medical applications [1–7]. A subject of special interest are water- and oil repellent textiles [8, 9] which can be used for example to prepare antiadhesive wound bandages [10, 11].

An earlier study reports on the hydrophobic properties of sol–gel coatings on textiles with respect to different hydrophobic additives [9]. Altogether the effect of 10 different additives were investigated as function of additive concentration added to the silica sol. It was determined that especially additives containing long alkyl chains or fluorinated groups lead to well hydrophobic properties of the coated textiles. This previous paper reports mainly on nanosols containing a high amount of the organic solvent ethanol. The presence of organic solvent has the advantage of shorter drying time and lower curing temperature, resulting in less energy consumption and reduction of processing time [12]. In contrast to these advantages, for practical applications aqueous media are usually favoured, because they are non-inflammable and environmentally more accepted. Therefore it is interesting to develop an aqueous sol–gel system for hydrophobic coatings.

The now presented paper reports on sol–gel systems for the preparation of hydrophobic coatings on textiles containing different types of solvents, especially water. In contrast to the earlier study, the investigations are performed as function of sol concentration. As hydrophobic additives octyltriethoxysilane and perfluoroctyltriethoxysilane are used, because they yield well hydrophobic properties on textiles [9].

For preparation of water containing sol–gel systems few statements have to be made. A sol–gel system with a high amount of water for hydrophobic coatings has to fulfil generally two conditions. First, the hydrophobic additive has to be stable in the aqueous sol–gel system. Second, the aqueous sol–gel system containing the hydrophobic additive has to be miscible with water in any ratio of water and sol. It is not trivial to meet both conditions, because of the insufficient solubility of hydrophobic compounds in water and the lower stability of hydrophobic sols in contact with water. In principal, there are two strategies for preparation of such aqueous sol–gel systems:

(i) An ethanolic sol–gel system is prepared and then diluted with water. Afterwards the ethanol is evaporated and replaced by water, so the inorganic nanosol particles are dispersed in pure water [13].
(ii) The inorganic alkoxy precursor is hydrolysed in diluted aqueous acid or base without any addition of organic solvent [14]. In this case, the amount of ethanol in the resulting sol–gel system (e.g. 40 vol%) can be further diluted with water to increase the flashpoint. Also the remaining ethanol can be evaporated and replaced by water. The present paper discusses both strategies with respect to the water repellent properties of coated textile fabrics.

2. Experimental Part

2.1. General

Tetraethoxysilane (TEOS) and octyltriethoxysilane were obtained from ABCR, perfluoroctyltriethoxysilane from Degussa-Hüls AG.

Di(propylene glycol) n-propyl ether (Dowanol™ *DPnP*) was obtained from Sigma-Aldrich.

2.2. Sample Preparation

The hydrophobic sol 1 with a solid content of 13 wt-% was prepared by hydrolysis of tetraethoxysilane (TEOS) and octyltriethoxysilane (weight ratio 40:1) in 0.05 molar HCl_{aq}. For hydrolysis a mixture of all ingredients was stirred for 24 h at room temperature. The sol 2 was prepared analogously with perfluoroctyltriethoxysilane instead of octyltriethoxysilane. Before coating, these sols were diluted by using different solvents (water, ethanol, aceton) or a mixture of water and di(propylene glycol) n-propyl ether (Dowanol™ *DPnP*—flashpoint 87°C) in a ratio 3:1. In one case, the ethanol resulting from hydrolysis of sol 1 was evaporated and replaced by water. This nanosol was further diluted by using water. Besides coatings on glass, three types of textiles were used for dip-coating (polyester PES −85 g/m^2, polyamide PA −113 g/m^2 and a mixture of polyester and cotton PES/CO −201 g/m^2). After dip-coating with silica sols the samples were dried for 2 hours at room temperature and annealed for 1 h at 120°C.

2.3. Methods

For contact angle measurements a Surftens instrument (OEG GmbH, Germany) was used. The contact angle on coated glass was determined with water. To investigate the water repellency of the coated textiles two types of tests were performed. First, the water uptake of the textile under full contact with water was determined. Textile fabrics of 20 cm × 20 cm were placed in

300 ml distilled water for 1 minute. Second, a common "spray test" was performed. In this test, 250 ml water is sprayed on the coated textile fabrics (20 cm × 20 cm) during 30 s via a spray nozzle and from a distance of 16 cm. The textile fabrics are fixed on a device under an angle of 45°. The uptake of water by the textile sample during this procedure was determined using a balance.

To determine the amount of silicon deposited on the fabrics, the textile samples were leached in $NaOH_{aq}$. The amount of silicon in the leaching solution was measured by ICP (Zeiss, Jena). Scanning electron microscopy SEM was used to investigate the surface topography of coated PES/CO fabrics. All measurements were performed after sputtering with gold using a Topcon-microscope ATB55.

3. Results and Discussion

3.1. Hydrophobic Sol–Gel Coatings on Textiles

First investigations on coatings resulting from sol 1 were performed by contact angle measurements on coated glass (Fig. 1). The sol 1 was applied as dilution with water, ethanol or aceton. Even in case of strong dilution and a remaining solid content less than 1%, high water contact angles were observed. Sol 1 contains 40 vol-% of ethanol after hydrolysis. If this ethanol resulting from hydrolysis is evaporated and replaced by water, a further dilution of the sol by water leads to a significant decrease in hydrophobicity (Fig. 1).

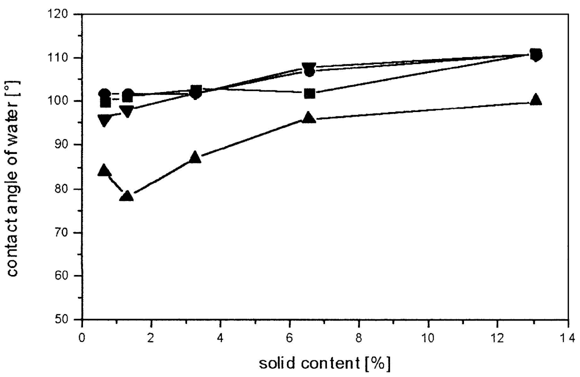

Figure 1. Water repellent properties on coated glass substrates as function of the concentration of sol 1 for different types of dilution (ethanol ■; aceton ▼; water ●; after ethanol evaporation dilution with water ▲).

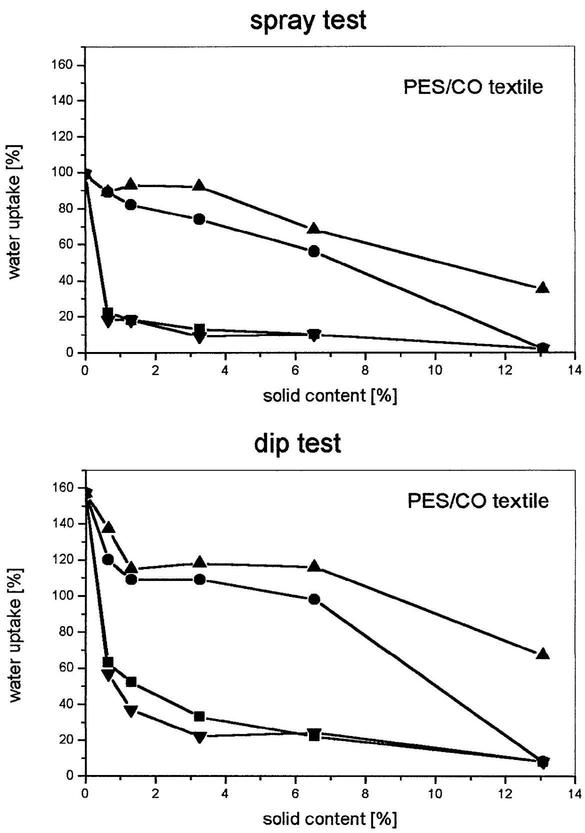

Figure 2. Water repellent properties on coated textile fabrics (polyester/cotton PES/CO) as function of the concentration of sol 1 for different types of dilution (ethanol ■; aceton ▼; water ●; after ethanol evaporation dilution with water ▲).

Analogous coatings were investigated on PES/CO textiles using spray- and dip-tests (Fig. 2). With decreasing sol concentration the amount of water uptaked by the textile increased but this amount is significantly influenced by the type of solvent used for the dilution of the sol. The coatings resulting from sol 1 diluted with ethanol or acetone lead to a small water uptake of textiles after spraying or dipping even in case of a sol concentration <1%. In contrast to this, the same sols containing water as solvent result in coatings, which are not able to prevent a high water absorption. If the ethanol is evaporated from sol 1 before dilution with water, the water uptake is the highest corresponding to the lower contact angles measured on glass. The same trend was also observed, if the coatings were performed on PES fabrics. In this case, the use of sol 1 diluted with ethanol leads to more water repellent textiles than the application of sol 1 diluted with water (Fig. 3). In contrast, coated PA fabrics contain different properties.

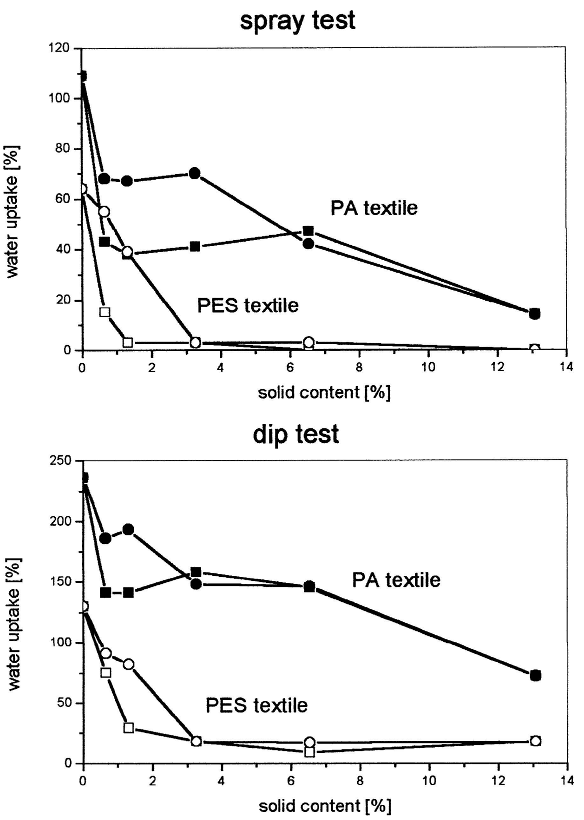

Figure 3. Water repellent properties on coated textile fabrics—with sol 1 (polyamide PA/full symbols and polyester PES/open symbols) as function of sol concentration for different types of dilution (ethanol ■; water ●).

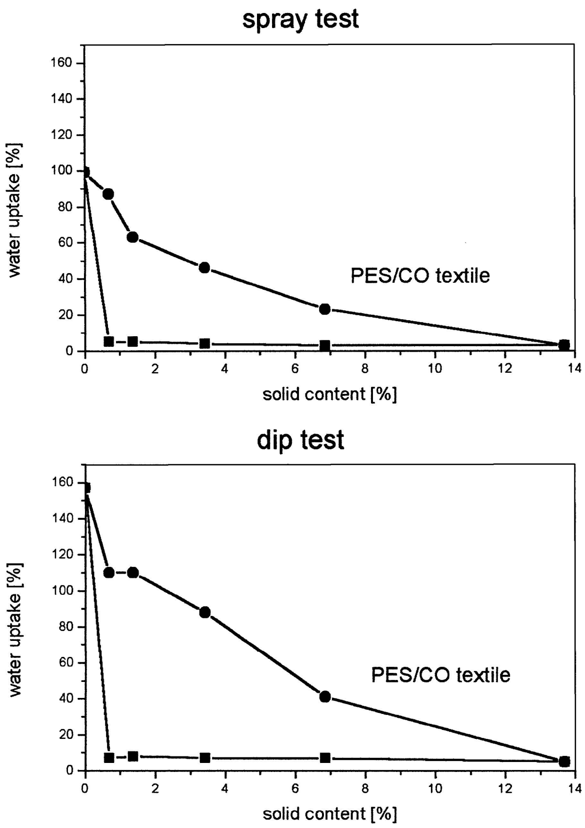

Figure 4. Water repellent properties on coated textile fabrics—with sol 2 (polyester/cotton PES/CO) as function of sol concentration for different types of dilution (ethanol ■; water ●).

Even PA textiles with coatings from undiluted sol 1 contain a higher water uptake, which increases with further dilution of the sol.

Analogously coatings on PES/CO fabrics were performed with sol 2 prepared with perfluoroctylsilane instead of octylsilane as hydrophobic additive (Fig. 4). The coatings resulting from sol 2 show high hydrophobicity even in case of high dilution performed with ethanol down to sol concentrations $<1\%$. The excellent hydrophobicity in comparison to sol 1 can be explained by the lower surface energy of the fluorinated additive. Nevertheless even with sol 2 the hydrophobic properties of coated textiles decrease drastically with increasing water content of the sol.

Based on the experimental work, it has to be concluded that the two described hydrophobic silica sols lead to water repellent coatings especially on PES or PES/CO textiles, while the hydrophobic effect is less on PA fabrics. If the sols are diluted by organic solvents like ethanol or acetone water repellent coatings can be prepared even with low sol concentration. In contrast, the same sols lead to significant lower water repellent properties in case of dilution with water.

Therefore it has to be stated that the type of used solvent is an important parameter for preparation of hydrophobic coatings on textiles using the sol–gel technique, beside other parameters like sol concentration, hydrophobic additives used or types of coated textile. This result is new and further investigations have to be performed to determine the influence of solvent on the formation of hydrophobic coatings on textiles.

3.2. Influence of Solvent on Formation of Hydrophobic Coatings on Textiles

Up to now it has to be stated that hydrophobic silica sols with the same sol composition but different added solvents lead to different hydrophobic properties after coating on textiles. Recently it has been reported for silica sol coatings spin-coated on silica wafers that the type of used solvent does not influence the molecular structure but can indicate a different morphology of the coatings [15]. Analogously for the reported case of textile coatings, where the different solvents were added to the hydrolysed silica particles, no influence of the solvent on the coating composition should be expected. Therefore, it has to be investigated whether the amount of deposited silica on the textiles is determined by the type of used solvent and, therefore, could be responsible for different water repellent properties. For this, the amount of silicon deposited from sol 1 on PES/CO, PES and PA was determined as function of sol concentration (Fig. 5). It is shown that the amount of silicon deposited is clearly determined by the concentration of the used silica sol but not by the solvent used for the dilution of the sol. In contrast, the coatings on the fibres itself show structural differences as function of sol concentration and different solvents under microscopic view (Fig. 6). In case of sol 1 on PES/CO textiles, bigger agglomerates can be observed on the fibres, due to the high solid content of 13% and the

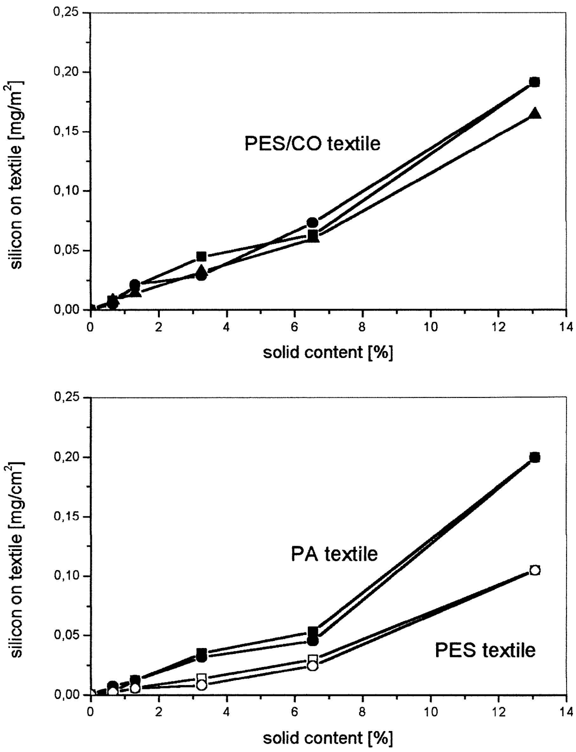

Figure 5. Amount of silicon on coated PES/CO, PA and PES after coating with sol 1 diluted with different kinds of solvent (ethanol ■; water ●; after ethanol evaporation dilution with water ▲) Ver.

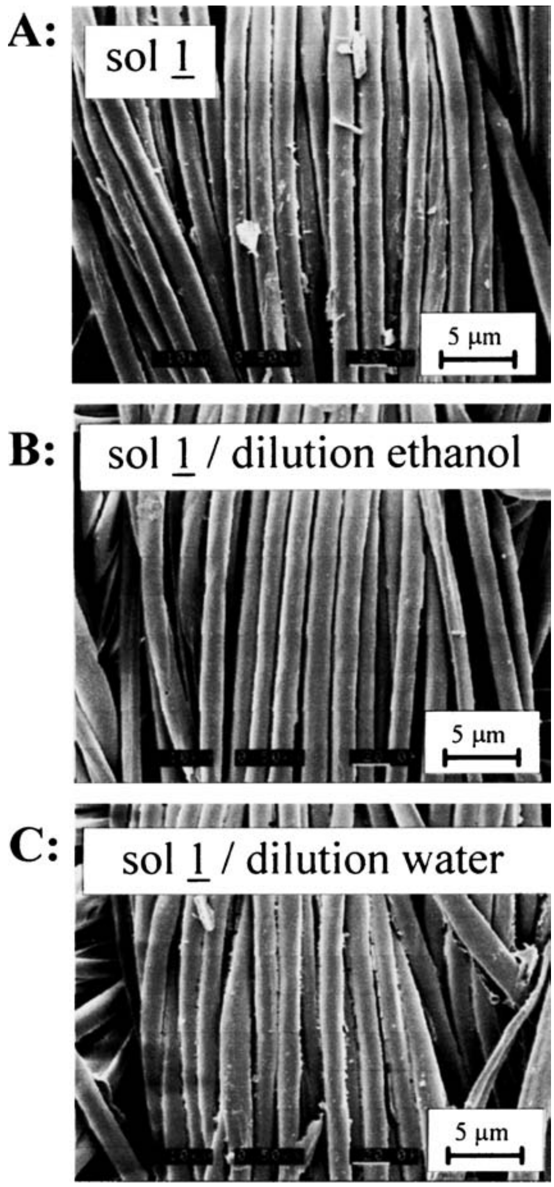

Figure 6. SEM figures of coated PES/CO fabrics; A: coating with sol 1 (sol concentration 13%); B: coating with sol 1 diluted in ethanol (sol concentration 3.3%); C: coating with sol 1 diluted in water (sol concentration 3.3%)

amount of 0.2 mg/cm^2 deposited silicon. Because of the high sol concentration, besides fibre coating also bigger agglomerates were deposited on the textile and the fibres are glued together resulting in less flexibility of the textile fabric. If sol 1 is applied as dilution with only 3% solid content, the coated textiles keep their flexibility and the structure of the deposited silica coating is determined by the solvent used for dilution.

In case of dilution with ethanol, the coatings seem to be more flat and regular than by use of water, due to better film formation for sols diluted with ethanol. The coating resulting from the aqueous diluted sol shows crack formation. It has to be stated that the type of used solvent does not influence the amount or the composition of the silica coatings deposited on textiles. Therefore, it can be assumed that different interactions of the organic textile fibres with the sol solvents may be a reason for the different hydrophobicity. The organic solvents could lead to swelling of the organic textile fibres, resulting in enhanced adhesion of silane compounds on the fibre surface [16]. Organic solvents have also lower surface tension and therefore provide a better wetting of the surface and a better film formation. These reasons may lead to a flatter coating and less crack formation, so the fibres are fully coated and protected against water exposure. The coatings resulting from the aqueous diluted sol contain cracks and therefore the fibres are not fully protected against water exposure. This assumption is supported by the fact that the aqueous diluted sols coated on glass substrates show a good hydrophobicity in comparison to the poor hydrophobicity observed on textile coatings.

3.3. *Combination of Water-Based Sols with Less Inflammable Organic Solvents*

Because of the advantages of water-based sol–gel systems, due to their non-flammability and better environmental acceptability, there exists a great demand to develop water-based sols for hydrophobic textile coatings. For practical applications instead of pure water the dilution of the sol can be also performed with a mixture of water and an organic solvent which is less volatile and inflammable but ensures a hydrophobicity in a wide range of sol concentrations. It was observed that the dilution with a mixture of water and *DPnP* is very advantageous.

Although the use of this solvent combination (volume ratio 3:1) leads to insufficient values of hydrophobicity in case of sol 1, very good hydrophobicity can be obtained on all three types of investigated textiles (Fig. 7) with sol 2. The better hydrophobicity with sol 2 may be explained by the inherent lower surface energy of the fluorinated additive in comparison to the non-fluorinated variant of sol 1.

In summary hydrophobic sol–gel coatings on textiles can be obtained through the use of silica sols with high water content in combination with small amounts of

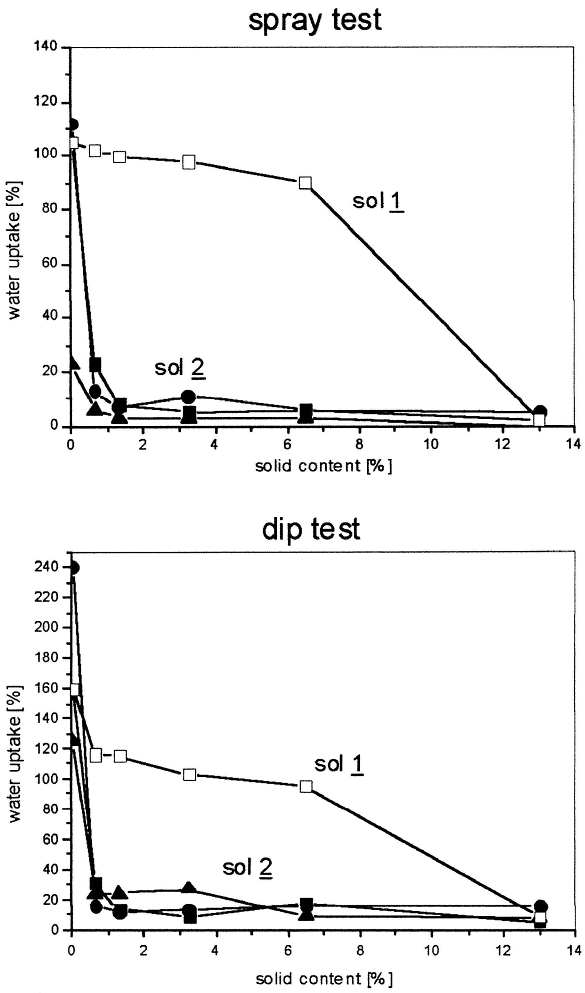

Figure 7. Water repellent properties on coated textile fabrics (polyester/cotton PES/CO ■; polyamide PA ●; polyester PES ▲), preparation with sol 1 (open symbols) and sol 2 (full symbols) diluted with a mixture of water: *DPnP* (volume ratio 3:1)

water-miscible organic solvents with a high flashpoint. Due to the advantages of these aqueous systems, these silica sols can lead to new practical applications for textile coatings.

4. Conclusions

This study concerns the preparation of water repellent textiles, obtained by coating with hydrophobically modified silica sols. The investigations were performed as function of the four different parameters: added solvent, sol concentration, type of textile and type of hydrophobic additive. It was presented that the hydrophobic properties of coated textiles are significantly determined by the used solvent and sol concentration. In case of low sol concentration and the use of organic solvents good hydrophobic properties can be performed on polyester fabrics or mixed fabrics made from cotton and polyester. Less hydrophobic properties were determined on PA textiles. In contrast modified silica sols with the same sol composition but containing water instead of organic solvents lead to low hydrophobicity of coated textile. Therefore it has to be concluded that the solvent is an important parameter for the preparation of hydrophobic sol–gel coatings on textiles. While the amount of silica is not influenced by the type of solvent, the morphology of the sol–gel coating on textile fibers is determined by sol concentration and solvent used and could be the reason for different hydrophobic properties. The combination of hydrophobically modified silica sols with water and high flash-point water-miscible solvents such as di(propylene glycol) n-propyl ether (*DPnP*) can result in textiles with significant hydrophobic properties and may lead in future to pratical applications of textile finishing.

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