

NANOCLAY COATINGS ON TEXTILES FOR ADSORPTION OF XENOBIOTICS

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Abstract

Xenobiotics are chemical substances, which are not of natural origin. However they can sometimes be found in organisms. These compounds are for example allergens, pesticides or other mainly harmful substances. Indoor textiles like curtains equipped with an adsorptive functionality can be an approach to minimize the concentration of xenobiotics in ambient air. Furthermore such textiles could be applied as protective clothing, acting as an effective and breathable barrier for airborne substances. An approach to adsorb such substances on textile fibres is presented. This adsorbing capability is achieved by binding modified clay particles to the surface of the fibre. Different approaches to fix those modified clays permanently on textiles were investigated.

Introduction

Natural clays like montmorillonites and hectorites exhibit a three layered structure, where the two outer layers show a tetrahedral and the inner layer an octahedral assembly [1]. The inner layer usually bears aluminium ions. In this work laponite RD was used, which is a commercially available rheologic agent. It contains lithium and magnesium ions in the octahedral inner layer instead of aluminium, resulting in an overall negative charge of the particle. This charge is compensated by sodium ions in the outer sphere. Laponites are like other clay minerals nontoxic, inexpensive and due to their adsorbing capability a preferred material for this approach.

While montmorillonites and hectorites show particle sizes up to 50 µm, Laponite consists of platelets, which are disk shaped with a diameter of 25 nm and 1 nm in thickness [2]. This results in a higher surface area for adsorbing airborne substances. Unmodified clays show an inherent capability of adsorbing water between the layers. This swelling makes them also suitable for use as rheologic agents. Most xenobiotic substances are hydrophobic, so the clays have to be modified to adsorb those substances. This is accomplished by exchanging the sodium ions, which accompany the Laponite® RD platelets, with cationic surfactants. Using this kind of modification, the distance between each layer increases, detected by X-ray diffraction. This interlayer modification allows adsorbing organic molecules.

Sol-gel technology was studied as one method to fix the clay particles on textile surfaces. The sol-gel process was carried out by the use of organosilanes like tetraethoxysilane. This was hydrolysed to yield a reactive silanol as depicted in Fig. 1.

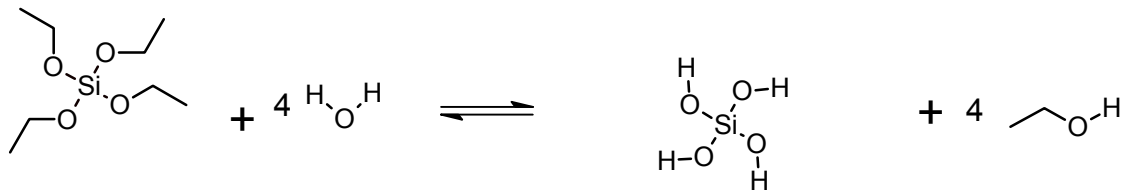


Fig. 1: Hydrolysis of tetraethoxysilane

Depending on the used concentration these silanols can react with each other to form condensed particles as shown in Fig. 2.

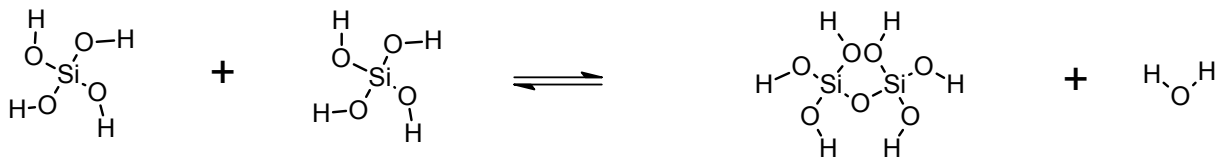


Fig. 2: Condensation of silanol molecules.

This resulting nanosol was then mixed with the adsorptive particles and applied on textiles by padding. When the fabric is dried after the application process, the particles condense to form a film on the fibre. Clays can be embedded into the sol film forming a hybrid layer, because of their hydroxylgroups, which are localized at the edges of the platelets. The nanosol reacts also with hydroxylgroups on cotton fabrics.

For polyester fabrics sol-gel coating is also a possible but not as effective method, so a different process derived from high temperature dyeing was applied. Polyester fabrics, modified Laponite and Dynasytan 9116 (see Fig. 3) were enclosed in a high pressure vessel with ethanol at $4 \cdot 10^5$ Pa.

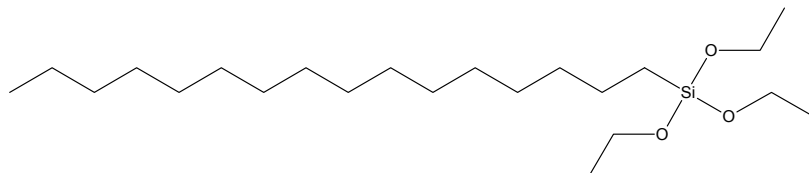


Fig. 3: Structure of Dynasytan 9116

Heating up the pressure vessel above the glass transition temperature of polyethyleneterephthalate allows the alkylchain of Dynasytan 9116 to diffuse into the amorphous regions of the polymeric fibres.

After cooling down the silane is fixed onto the fibre. The process was also carried out without the use of silanes. In this case, the hydrophobic part of the modified clays diffuses into the fibre causing direct fixation to the textile.

Experimental

1. Modification of clays

Clay minerals offer a capability for cation exchange. Due to this property the minerals can also act as storage matrix for cationic detergents like Hyamine 1622 (Fig. 4). The clay material used was Laponite RD, obtained from Rockwood Chemicals. It was dissolved in demineralized water at a concentration of 1 %. In this case no gelation occurs.

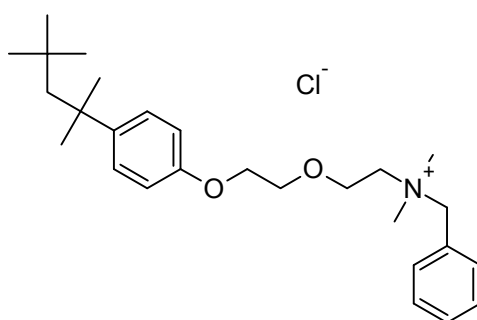


Fig. 4: Structure of Hyamine 1622

Beside Hyamine 1622 octadecyltrimethylammoniumbromide (Fig. 5) was used for modification too. The concentration used was equivalent to 100 % of the cation exchange capacity (CEC) of the clays, which was determined by the Cu-trien method [3]. The detergent solution was added to the clay solution dropwise for three hours and the mixture was stirred for at least three hours.

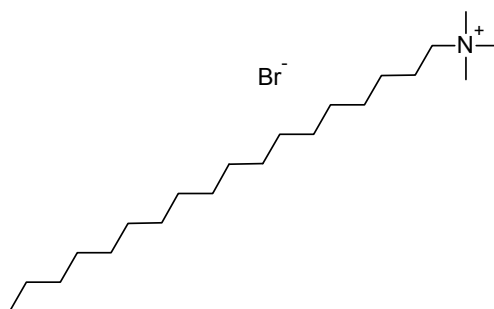


Fig. 5: Structure of octadecyltrimethylammoniumbromide

2. Application of organoclays to textiles

For cotton fabrics the sol gel process was carried out with tetraethoxysilane which was hydrolyzed with triethanolamine. The sol was mixed with 4 % dispersion of organoclays and applied to textile by immersing. The pillared clays were dispersed in the sol directly. After immersing the fabric was padded to remove excess sol. The padded fabrics were dried for at least 10 minutes at 120 °C to allow condensation of the sol. The adsorption of Sudan Red G in the liquid phase and toluene in the gas phase were measured for the finished textiles.

Nonwoven polyester fabrics made of polyethyleneterephthalate were finished by a high-temperature process. The textile was placed in a high pressure vessel, which was heated up to

120 °C. By the use of ethanol as solvent pressure builds up to about $4 \cdot 10^5$ Pa. The organoclay was added as dispersion in water. Also a mixture of silane in ethanol was used together with organoclay dispersion. After 10 minutes in the high pressure vessel the textiles were dried at 120 °C. Finished textiles were also tested by adsorption of Sudan Red G and toluene. All textile samples were rinsed with demineralized water prior to any testing.

Results

The adsorption capability of coated textiles was measured by two methods, the results are shown in Fig. 6. First Sudan Red G uptake was determined in liquid phase by UV-Vis spectroscopy. A Sudan Red G solution in a mixture of 60 % water and 40 % ethanol and a concentration of 20 mg/l was used; the samples of the tested fabrics were at a size of 11.3 cm^2 . The specimens were immersed in the dye solution and after that, the remaining concentration of the dye was measured by UV/Vis-Absorption. The depicted values are the relative amount of dye, adsorbed by the finished textiles. Furthermore, the uptake of toluene from the gas phase was measured by gravimetric analysis. The given values are the mass of adsorbed toluene in relation to the mass of the textile sample. The partial pressure of toluene in air during incubation was $2.9 \cdot 10^3$ Pa; the incubation time was 40 h.

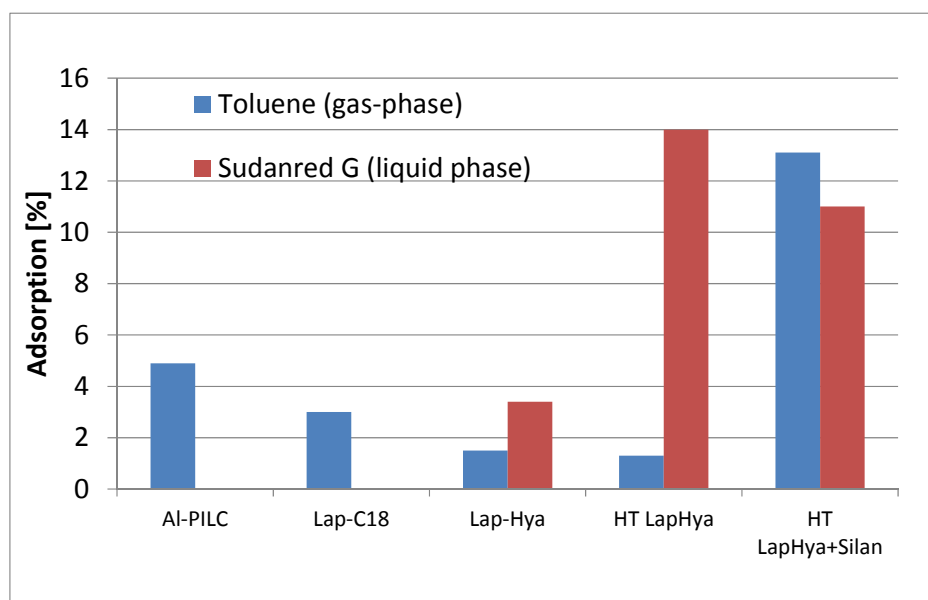


Fig. 6: Toluene and Sudanred G adsorption

Adsorption isothermes were also measured to investigate adsorption characteristics of the textiles (Fig. 7). The isothermes of fabric samples with Aluminium-pillared clays and also the ones with octadecyltrimethylammoniumbromide show condensation in the pores above 80 hPa and 110 hPa respectively. At low partial pressures of benzene both modifications adsorb more benzene, than the hyamine modified samples. However the latter adsorb higher amounts above 60 hPa.

Discussion

Two binding systems were investigated. The sol-gel technology was applied to cotton fabrics, whereas the high temperature process was most effective on polyester fabrics. In this process hyamine modified Laponite was used alone and also in combination with hexadecyltriethoxysilane. There are differences in the adsorption behavior of these samples, depending whether Sudan Red G or toluene is used. This can be caused either by the adsorptive molecule itself or by the different adsorption medium (liquid or gas phase). These effects can be utilized for creating adsorber materials that react specific to adsorptive molecules.

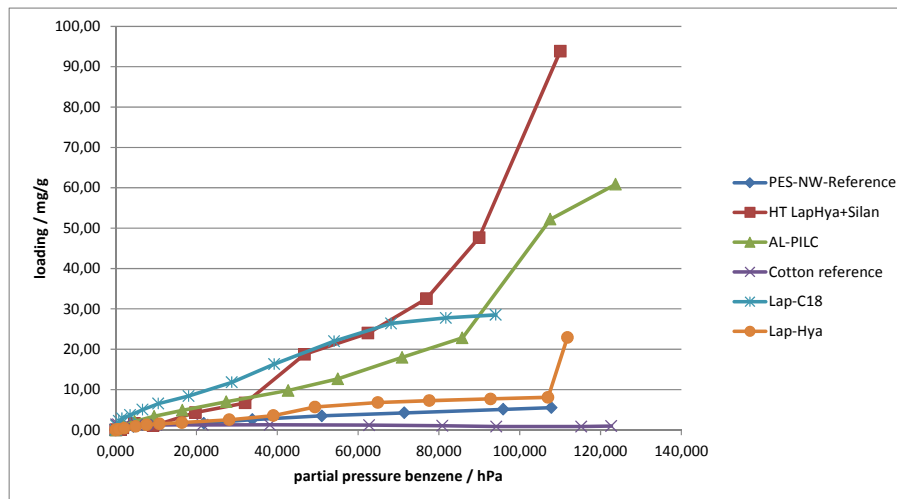


Fig. 7: Adsorption isotherms of finished textiles, all samples are cotton, except the one marked „HT”

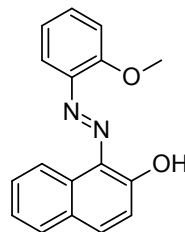


Fig. 8: Sudan Red G

Summary

In this study different ways to fix modified nanoclays on textiles for use as adsorbing agents are presented. For this, a sol-gel process was applied to cotton fabrics and a high-temperature process (HT-process) to polyester nonwoven fabrics. The sol-gel application shows best results on cotton fabrics and the HT-process leads to better results on polyester fabrics. Furthermore a specific adsorptive capacity could be achieved.

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