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Modification of Polyamide Knitted Fabric using Different Zeolites

Modificiranje poliamidnega pletiva z različnimi zeoliti

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Abstract

The aim of this research was to apply three different types of zeolites and the combination thereof in the form of a very fine powder, together with different chemicals and additives on polyamide knitted fabric according to an industrially acceptable exhaustion procedure in order to study changes in the morphology, optical properties and wettability of surfaces. Zeolites were analysed using Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FTIR) and gas physiosorption. Additionally, the morphology of zeolite-coated surfaces was examined closely using SEM, while changes in molecular-chemical level were examined by means of IR spectroscopy. Optical properties were studied using CIE colour measurement and diffuse reflectance profile determination, while the hydrophilic/hydrophobic character was examined using goniometry. The obtained results show the suitability of the employed exhaustion procedure, depending on the type of zeolite and the composition of the treatment bath. The results also provided evidence of the enhanced wettability of PA fabrics using 4A and 13X zeolites in combination with selected additives.
Keywords: zeolites, polyamide fibres, exhaustion, surface modification, wettability

Izvleček

Namen predstavljene raziskave je bil nanesti tri različne tipe zeolitov in njihovo kombinacijo v obliki zelo finega prahu skupaj z različnimi kemikalijami in pomožnimi sredstvi na poliamidno pletivo po industrijsko sprejemljivem postopku izčrpavanja za študijo sprememb v morfologiji površine, optičnih lastnosti in omočljivosti. Zeolite smo analizirali s pomočjo vrstičnega elektronskega mikroskopa (SEM), Fourierjeve transformacijske infrardeče spektroskopije in plinske fizisorpcije. V nadaljevanju smo podrobno okarakterizirali z zeoliti oplaščene površine s pomočjo SEM, spremembe na molekularno-kemijski ravni s pomočjo IR-spektroskopije, optične lastnosti s pomočjo CIE-meritev in določanjem difuzijskega refleksijskega profila ter hidrofilni/hidrofobni značaj z goniometrijo. Dobljeni rezultati dokazujejo primernost uporabljenega postopka izčrpavanja v odvisnosti od vrste uporabljenega zeolita in sestave obdelovalne kopeli. Prav tako rezultati dokazujejo povečano hidrofilnost PA pletenine pri uporabi zeolitov 4A in 13X v kombinaciji z izbranimi pomožnimi sredstvi.
Ključne besede: zeoliti, poliamidna vlakna, izčrpavanje, površinska modifikacija, omočljivost

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1 Introduction

Polyamide (PA) fibres are linear polymers containing amide bonds, the monomeric units of which are joined through secondary amide (-NHCO-) linkage [1]. This group of synthetic polycondensate fibres is important from a textile-technical and economic point of view due to its favourable properties, such as superior strength characteristics (abrasion resistant), good bacterial resistance, low swelling in aqueous media, excellent dimensional stability when washed, etc. [2]. However, polyamide is relatively hydrophobic in character, with moisture regain of only around four percent [3]. Because of this feature, the ability of polyamide textiles to transport moisture and heat away from the body effectively are limited, while a static charge may also be created on clothing and outfits. Functional surface coatings that address thermal and/or sensorial comfort, which relates to skin contact sensation, have become increasingly important in recent years [4]. The fabrication of multi-functional fibrous materials using various strategies of surface modification with different (nano- or micro-) particles offers excellent potential, either for improving some undesired properties or imparting special functionalities, and developing high-added value products, i.e. textiles for protection, medical and sport activities, technical textiles, etc. [5]. In addition to various nanoparticles that are used for modifying fibre-forming polymers, zeolites of numerous types have attracted increased interest for such kinds of applications on account of their superior heat resistance, high surface area, exchangeable cations and high chemical stability [6, 7]. Because they are non-toxic and non-absorbable by humans, zeolites would be highly promising for the fabrication of multifunctional textiles that are constantly in direct contact with the skin. Through several studies, Grancarić et al. put forth an idea as to how the application of tribomechanically activated natural zeolites could lead to the enhanced antimicrobial and UV protection capabilities of cotton and polyester fabrics [8, 9]. Carran et al. concluded that the surface treatment of wool fabrics with zeolite molecular sieve 5A leads to varied changes in the physicochemical properties of wool [7]. Monteiro and colleagues showed that it is possible to immobilise montmorillonite onto cotton textile efficiently through their functionalisation with organosilanes, which in turn increases washing speed [10]. The promising results of the above-mentioned studies recorded in recent years and a lack of literature in the field of polyamide textiles coated with synthetic zeolites using industrially applicable procedures convinced us to research the viability of fabricating zeolite-modified, fibre-forming polymers with amended water absorption properties. The main objective of our study was therefore to select and characterise three different types of commercially available zeolites and the combination thereof for the further surface treatment of polyamide knitted fabric using a novel dyeing-like exhaustion procedure in order to create a hydrophilic feature. Optical properties were also evaluated, as coating procedures can cause yellowing or colour changes indicating surface damage, and because visual appearance is also a very important parameter.

2 Experimental

2.1 Materials

Three different commercially available zeolites were used in the form of a very fine powder, i.e. 4A, 13X and ZSM-5, as well as a mixture of those three zeolites in a ratio of 60:30:10. The zeolites were industrially synthesized and supplied by the company Silkem from *Kidričevo*.

A series of experiments was carried out using a light-grey 100% polyamide (PA) knitted fabric, which was industrially manufactured by AquafilSLO. Before a series of coating trials was started, the source fabric was washed at a temperature of 40°C for 30 minutes using a neutral non-ionic washing agent, and then rinsed in warm and cold water and dried at ambient temperature.

2.2 Application procedure

Eight previously optimised initial baths were composed of i) 3% owf (of weight of fabric) of an individual zeolite (4A, 13X or ZSM-5) or a mixture of zeolites; and ii) 3% owf of an individual zeolite (4A, 13X or ZSM-5) or mixture of zeolites together with additives (add.) suitable for PA treatment, i.e. 0.3% owf of amphoteric levelling agent (Keriolon A2N, Bezema), 0.5 ml/L of pH-regulator (Meropan OFS, Bezema) and acetic acid (80%) for pH 5–5.5 adjustment.

Individual treatment baths were applied according to the exhaustion procedure at a temperature of 98°C for 60 minutes using a liquor-to-fabric weight ratio of 30:1 (150 mL of deionized water to 5 g of PA) in a sealed stainless-steel treatment pot housed in a Labomat (W. Mathis) laboratory device. The treated samples were rinsed in warm and then cold deionised water, and dried at room temperature. All the zeolite-treated samples were washed at a temperature of 40°C for 30 minutes in a Labomat (W. Mathis) using a solution of 2 g/L of standard reference detergent without optical brighteners, and a liquor-to-fabric weight ratio of 50:1. The samples were then rinsed in tap water and finally dried at room temperature.

2.3 Characterisation of zeolites

SEM analysis was carried out by putting an individual zeolite powder on adhesive carbon tape, which was placed on a brass holder and then observed on an FE-SEM-ZEISS Gemini Supra 35 VP Scanning Electron Microscope (Carl Zeiss NTS GmbH, Germany).
The infrared absorbance spectra of zeolites were obtained using an FTIR System Spectrum GX spectrophotometer (Perkin Elmer) with a Golden Gate ATR attachment and a diamond crystal. The measurements were taken in the range of 4000–650 cm^{-1} wavenumber using 16 scans and a resolution of 4 cm^{-1}.
Additionally, the BET surface area and porosity of an individual zeolite were determined by nitrogen adsorption-desorption isotherms at 77 K using a Tristar 3000 (Micromeritics) system. Prior to these measurements, samples were dried for 24 hours at a temperature of 200°C.

2.4 Fabric's surface characterisation

Scanning Electron Microscopy (SEM) was utilised in order to study the surface morphologies of PA knitted fabrics treated with zeolites. Approximately 1 cm^2 of the fabric was attached to an adhesive carbon band on a brass holder on a FE-SEM-ZEISS Gemini Supra 35 VP Scanning Electron Microscope (Carl Zeiss NTS GmbH, Germany). SEM images were then taken.
The infrared absorbance spectra of zeolite-coated PA samples, relative to a reference sample treated in deionized water under the same conditions, were obtained using an FTIR System Spectrum GX spectrophotometer (Perkin Elmer) with a Golden Gate ATR attachment and a diamond crystal. The measurements were taken in the range of 4000–650 cm^{-1} wavenumber using 32 scans and a resolution of 4 cm^{-1}.
The diffuse reflectance spectra profiles of the untreated (reference) and zeolite-treated PA in the 200–700 nm wavebands were recorded on a Lambda 900 UV-Vis-NIR spectrophotometer (Perkin Elmer) with an integrated sphere at a scanning speed of 450 nm per minute.
CIE measurements of lightness (L^*) and chroma (C^*) of (un)coated samples were made within a spectral range of 400–700 nm wavelengths using a two-ray Spectraflash SF600 Plus spectrophotometer (Datacolor) equipped with an Ulbricht sphere and measuring geometry of d/8° under a standard illuminant D65 (LAV/Spec. Incl.).
The hydrophilic feature of untreated and zeolite-modified fibrous surfaces was studied by contact angle measurement using the sessile drop technique. An individual sample was placed on a horizontal table attached to a mechanical device on a Goniometer (DataphysicApparatus). A micro-drop with the volume of 0.3 µL MilliQ water was poured onto the fabric surface. The drop was illuminated using white diffuse light and observed with a telemicroscope. A clear image of the drop was transferred directly through a CCD-camera showing the drop profile. The contact angle was determined from the tangent to the drop at the three-phase contact line.

3 Results and discussion

3.1 Analysis of zeolites

SEM micrographs of zeolites were taken with the aim of studying the surface morphology of different types of zeolites for the subsequent surface modification of selected polyamide knitted fabric. Those micrographs are presented in Figure 1. Additionally, ATR-FTIR spectra of the zeolites' powder were recorded from a wavenumber of 4000 up to 650 cm^{-1} (Figure 2), while gas physiosorption was determined (Table 1) in order to elucidate the difference between three types of zeolites, as well as combinations thereof.
The SEM micrographs in Figure 1 show structural/formational differences between the used zeolite, namely cubic crystals of zeolite A (a), octahedral crystals of zeolite X (b) and pentasil building blocks

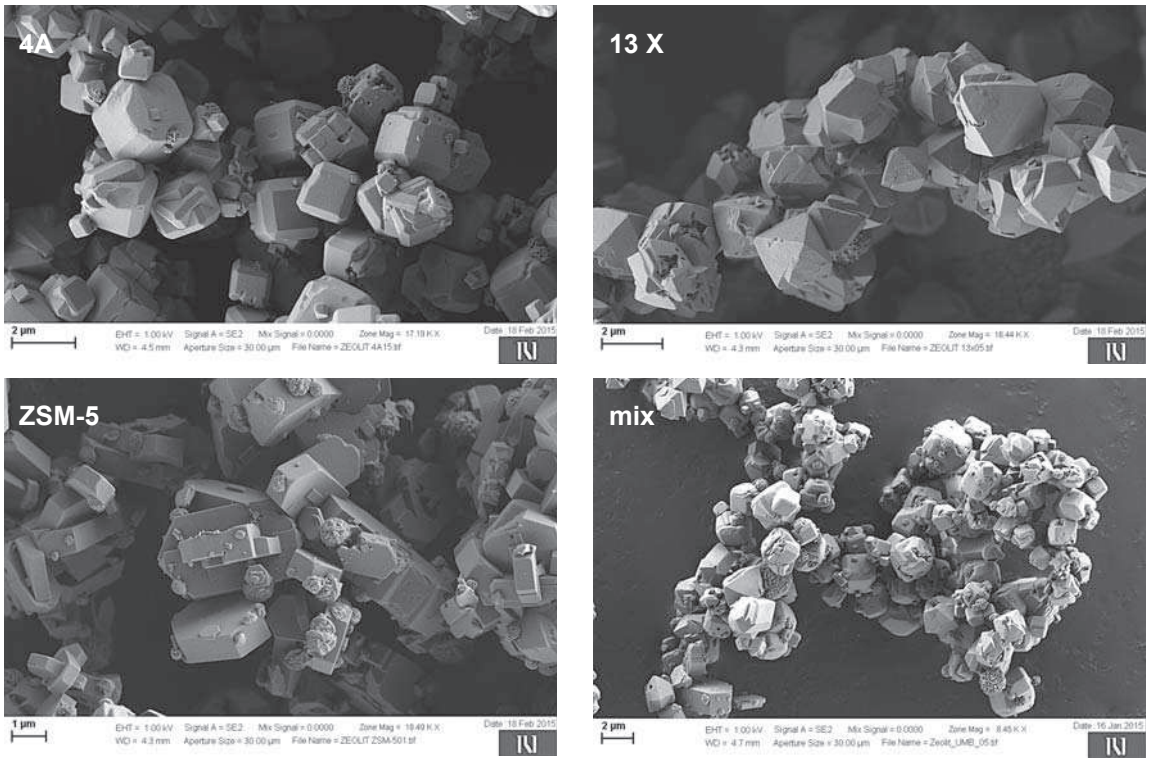


Figure 1: SEM images of selected zeolites

of zeolite ZSM-5 (c), which were all present in the mixture of those zeolites (d) as expected from information provided by the producer. Furthermore, a high amount of sodalite was noticed in all samples, as well as the presence of impurities, probably due to the industrial syntheses and, in the case of the mixture, due to the blending procedure. The examined zeolites are of different sizes, averaging from 1 to 3 µm.

The FTIR spectrum of the zeolites' fine powder, as presented in Figure 2, showed some characteristic bands. The most intensive band within the area of low frequency at wavenumbers of 970 cm^{-1} (4A, 13X

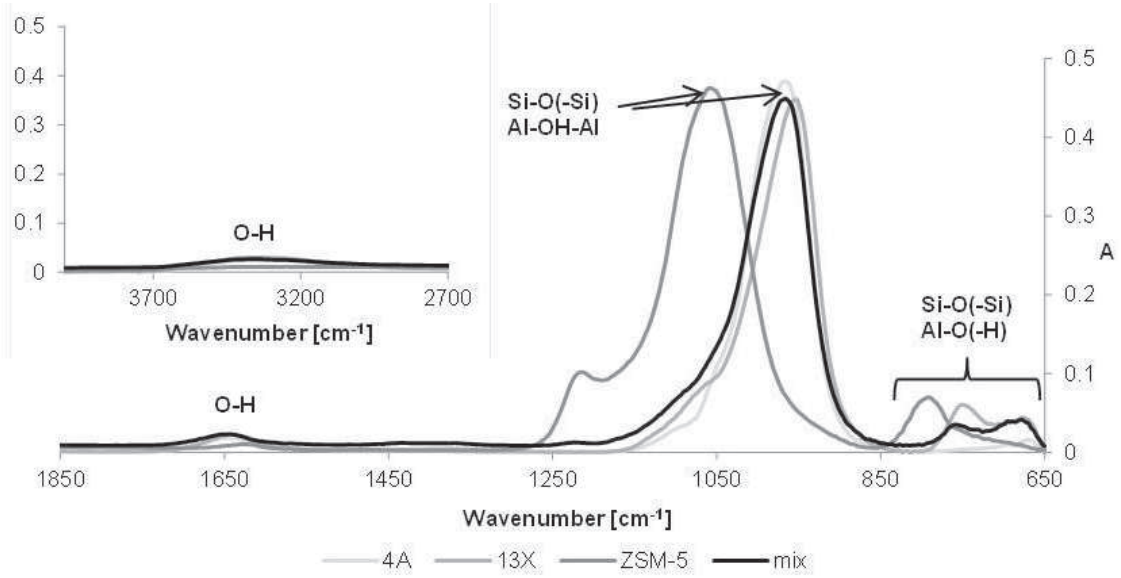


Figure 2: ATR-FTIR spectra of used zeolites

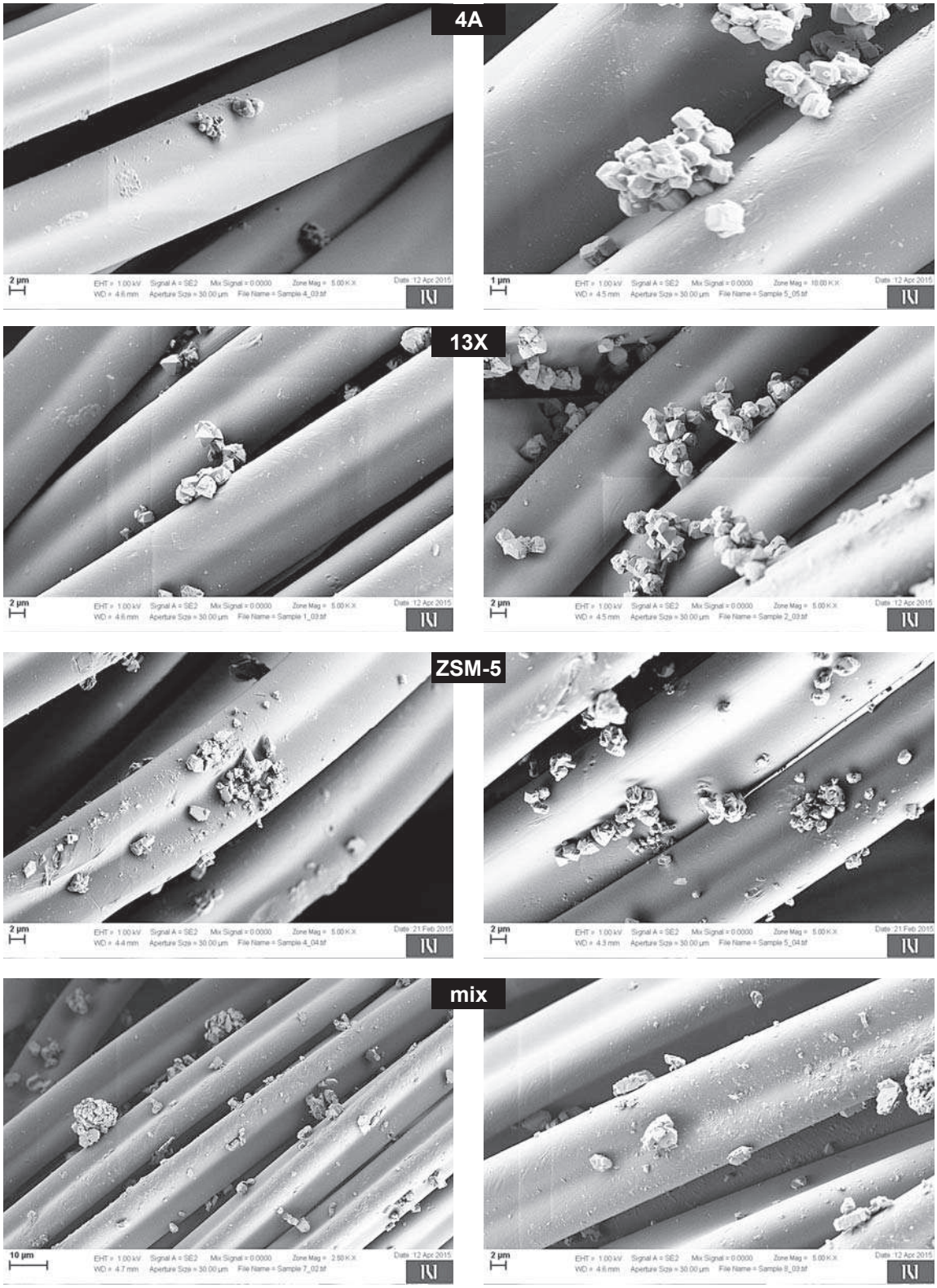


Figure 3: SEM images of PA fabrics coated using 3% owf of zeolites (left column); 3% owf of zeolite mixture with additives (right column).

Table 1: BET surface area and porosity analyses

Sample	S_{BET} [$m^2\ g^{-1}$]	V_{mi} [$cm^3\ g^{-1}$]	V_{tot} [$cm^3\ g^{-1}$]
13X	629	0.290	0.310
4A*	3	–	0.003
ZSM-5	343	0.125	0.178
mixture	204	0.095	0.102

* Sample should be dried at higher temperature using another apparatus.

and ZSM-5) and of 1067 cm^{-1} (mixture of zeolites) was due to Si–O(–Si) stretching vibrations and to bending modes of structural Al–OH–Al, the bands within the range of 680–800 cm^{-1} having been assigned to the 'ring' vibrations of internal oxygen bridges Si–O(–H) and Si–O–Si [11]. Finally, a moderate but wide peak could be observed at a wavenumber of ca. 3340 cm^{-1} and also at 1650 cm^{-1} due to O–H stretching and bending vibrations, respectively, associated with the presence of an interlayer of H_2O.
Table 1 presents typical micropore volume and total pore volume for zeolites ZSM-5 and 13X, while zeolite 4A recorded the lowest values of BET surface and total pore volume, probably on account of filled pores. The aforementioned zeolite should thus be dried at higher temperatures. The three measured parameters were rather low in the mixture of zeolites, as expected, because the ratio of 4A, 13X and ZSM-5 zeolites in that mixture were 60:30:10.

3.2 Morphological analysis of modified PA knitted fabrics

In order to visually establish the amount and equality of four different types of zeolites applied to the surface of PA knitted fabrics according to the exhaustion procedure, the surface morphologies were studied using SEM (Figure 3).
The SEM micrographs in Figure 3 showed different coating morphologies of PA fibres, which were created by applying 3% owf of diverse zeolites (4A, 13X and ZSM-5) and a zeolite mixture, and by different bath compositions, i.e. aqueous dispersions of an individual zeolite (left column) and slightly acidic aqueous dispersions of an individual zeolite, together with proper additives (right column). In the case of aqueous dispersions of zeolite 4A and 13X, an exceedingly low content of micro-particles could be observed over the entire surface of fibres relative to the samples treated with the same zeolites, but in combination with additives in acidic conditions, which matches well with the FTIR and DRS results presented additionally in Figures 4 and 5. When zeolites from pH 5 baths were applied (adjustment by acetic acid), the dealumination of aluminosilicate particles occurred to a minor degree, which was also reported by [7] when applying 5A zeolite molecular sieves on wool fabrics from a 2 wt% aqueous acetic acid solution. According to theory, acid attacks the Al–O–Si framework during dealumination when H+ ions break down the zeolite structure and thus generate large amounts of silanol groups (Si-OH) on a zeolite's surface which could, in our case, interact with protonated $–NH_3^+$ groups of polyamide fibres. As presumed by Gonzales et al. [12], different zeolite structure types (arrangement and pore size) are known to exhibit different accessibility of aluminium atoms in the framework and, consequently, very disparate behaviour towards dealumination. Thus, in our case, zeolite ZSM-5, with a one-dimensional 10-ring pore system, was less prone to dealumination than the three-dimensional 12-ring and 8-ring pore systems of zeolite X and A, respectively.

3.3 Molecular-chemical analysis of modified PA knitted fabrics

The molecular-chemical changes of modified PA knitted fabrics were determined by FTIR, as shown in Figure 4.
In the infrared spectra in Figure 4, typical peak positions for the polyamide were depicted, irrespective of treatment type, including CH_2 asymmetric stretching at 2932 cm^{-1}, CH_2 symmetric stretching at 2858 cm^{-1}, amide I (C=O stretching vibrations) at ~1631 cm^{-1}, amide II (N–H bending and C–H stretching vibrations) at 1531 cm^{-1} and amide III band/CH_2 wagging at 1371 cm^{-1}, as also fully interpreted in [1, 13]. In addition, some characteristic absorption bands are evidently recognised for zeolite-treated PA fabrics, i.e. the peaks

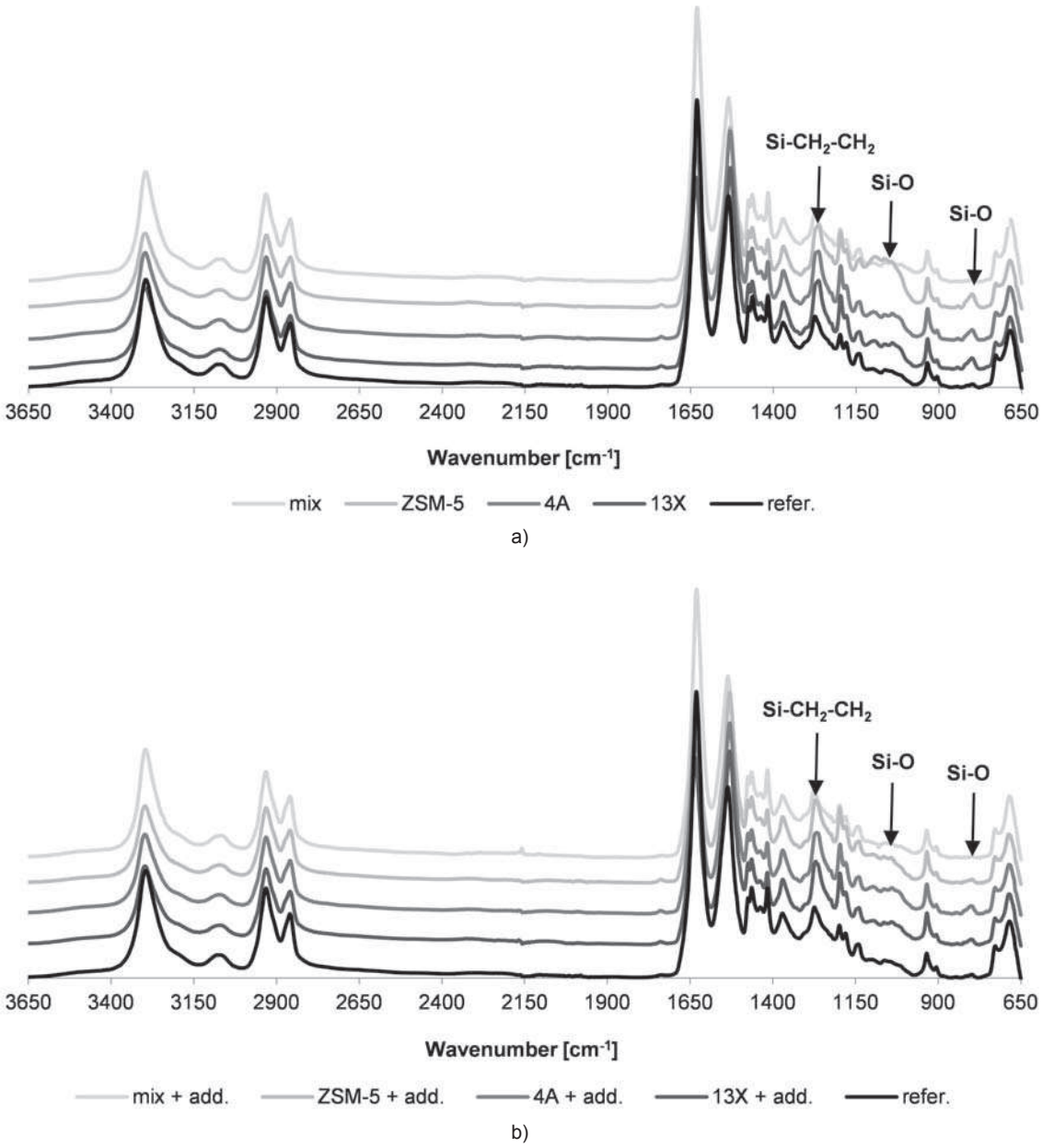


Figure 4: FTIR spectra of untreated (refer.) and coated PA using: a) aqueous dispersions of different zeolites; b) zeolites together with additives

of around 1000 or 1060 cm^{-1} (with respect to the zeolite used) corresponded to stretching vibrations, and at 799 cm^{-1} to the bending Si–O vibrations of Si–O–C [7, 10]. Meanwhile, some peaks became lower, such as the peaks at 1631 cm^{-1} and 3298 cm^{-1}, due to the reduced amino groups or intensified, and the peaks at 1275 cm^{-1} on account of the presence of C–H symmetric bending vibrations of Si–CH_2–CH_2–.

3.4 CIE measurement

A light-grey 100% polyamide (PA) knitted fabric was used for this research. Based on the presumption that zeolites are white pigments and thus applied to the material's surface in an adequate concentration to produce a white colour, the impact of coating of different zeolites on the samples' visual changes was given using CIE lightness (L^*) and chroma (C^*) determination (Figure 5).

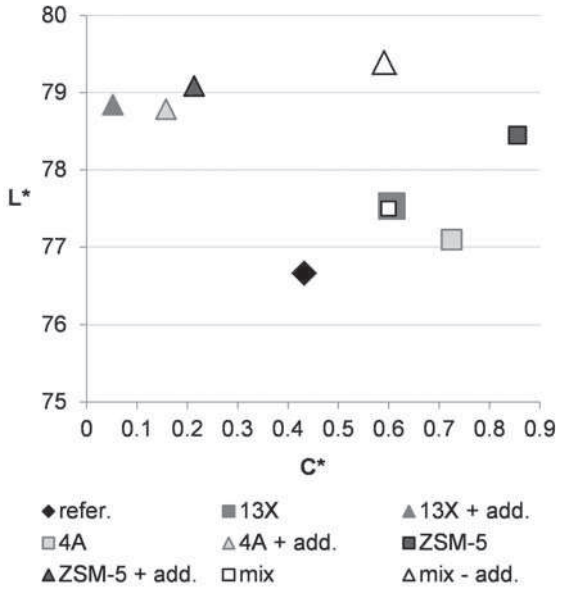


Figure 5: CIE lightness (L) versus chroma (C*) of untreated (refer.) and coated PA using aqueous dispersions of different zeolites and zeolites together with additives (add.)*

The results in Figure 5 revealed visually perceivable changes in lightness (and somewhat less in chroma) between reference and zeolite-coated samples, and between the composition of baths. As expected, samples treated with a slightly acidic (pH 5.5–6.5) aqueous dispersion of zeolites in combination with appropriate additives were brighter (L^* values are higher) and less saturated (C^* values are lower) than the reference sample, implying a higher amount of zeolites on the surface of PA fibres, which could also be perceived from the SEM images. The most chromatic sample was treated with 3% owf of ZSM-5 aqueous dispersion.

3.5 Diffuse reflectance spectra profile determination

The DRS profiles of the polyamide fabrics in both the UV and visible regions (wavelengths between 250 and 700 nm), before and after the modification of zeolites, are illustrated and compared in Figure 6. Figure 6 shows a reflectance curve of bright-grey, untreated fabric (ref.) with one typical absorption peak (reflectance minimum) at a wavelength of 290 nm, which contributed to the optical profile of the polyamide fibres. After the application of zeolites, the optical properties were changed in both UV and visible regions, with respect to the type of zeolite used and the composition of the treatment bath. Also, an extra absorption peak occurred in the UV-A region at 330 nm for all coated samples. Moreover, the obtained results indicate that the reflectance curves of those PA fabrics treated only by zeolites 13X, 4A or ZSM-5 decreased the most in the spectrum's UV region, implying stronger absorption intensity and thus higher UV-ray blocking properties than the reference sample and the samples treated with a combination of individual zeolite and additives.

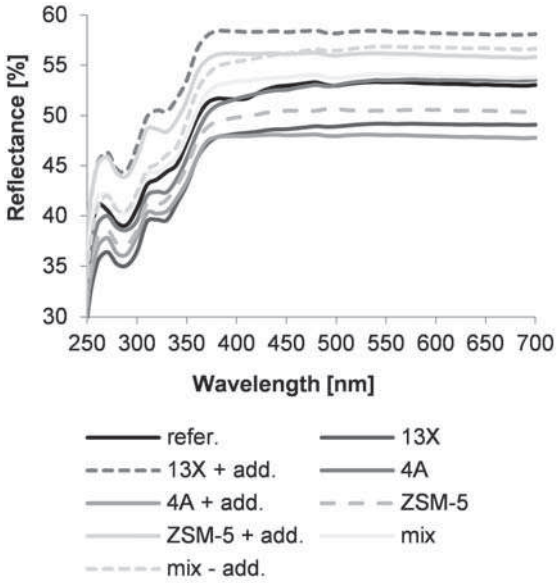
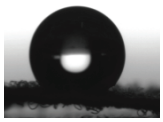
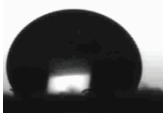
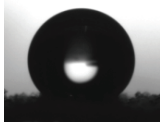
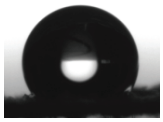
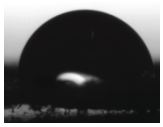
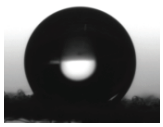
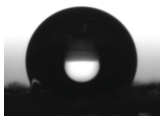


Figure 6: Diffuse reflectance spectra of untreated (refer.) and coated PA using aqueous dispersions of different zeolites and zeolites together with additives (add.)

3.6 Effect of zeolites on the wettability of PA knitted fabrics

In order to improve the comfort of PA knitted textiles for the wearer, the material needs to transport heat and moisture away from the skin. Moreover, hydrophobicity may result in an unfavourable electrostatic charge on textile surfaces, causing garments and outfits to cling to each other [14]. Zeolites form porous structures with cavities and channels that vary between types, giving zeolites the ability to act as adsorbents, catalysts and molecular sieves [7]. Therefore, to assess the role of different types of zeolites and the composition of baths on the wettability of polyamide fabric, contact angles were determined and drop images were scanned by means of goniometry, as presented in Table 2.

Table 2: *Contact angles (CA) of untreated (refer.) and modified PA knitted fabrics*

Sample	Refer.	4A	13X	ZSM-5	mix.
Drop images					
CA [°]	102.9	72.3	67.2	127.5	90.6
Sample	/	4A+add.	13X+add.	ZSM-5+add.	mix.+add.
Drop images	/				
CA [°]	/	44.1	66.2	103.8	86.5

It is evident from Table 2 that the industrially manufactured untreated PA knitted sample has an average contact angle of about 102°. Hydrophilicity increased by reducing the water droplet angle, depending on the type of zeolite particles and whether additives were used. In general, surfaces coated with zeolites in combination with additives had more hydrophilic character than those treated merely with zeolites, probably due to the presence of the levelling agent and acid pH. Carran et al. [7] reported that an acidic condition can cause the dealumination of zeolites, resulting in the breakdown of zeolite structures and thus the generation of a greater amount of –OH containing species, of which some may be bound to the PA surface, while the other caused the enhanced water absorption capabilities of fibres. On the other hand, surfaces treated with ZSM-5 zeolite particles were more hydrophobic than the reference sample. This can be explained by the hydrophobic character of ZSM-5 relative to the hydrophilic character of 4A (25% of water absorption) and 13X (32% of water absorption).

4 Conclusion

The results obtained through surface morphology observation and the identification of specific molecular vibrations of zeolite-coated polyamide knitted fabrics proved the suitability of the employed exhaustion procedure, with respect to the type of zeolite used and the composition of the treatment bath. Moreover, the fabrics' optical properties were changed in both UV and visible regions, i.e. zeolite-treated samples became lighter, while the reflectance curves of those PA fabrics treated only by zeolites 13X, 4A or ZSM-5 decreased the most in the spectrum's UV region, implying stronger absorption intensity and thus higher UV-ray blocking properties than the reference sample. In addition, samples treated with 4A and 13X achieved better hydrophilicity (lower contact angles) than the reference sample. On the other hand, both ZSM-5 treated samples demonstrated a more hydrophobic effect than the reference sample on account of the hydrophobic nature of the zeolite.

Acknowledgements

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