

Short communication

# Functionalisation of Cotton with Hydrophobic Urea/Polydimethylsiloxane Sol-Gel Hybrid

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## Abstract

A novel organic-inorganic sol-gel hybrid precursor, di-ureapropyltriethoxysilyl [bis(aminopropyl)terminated-polydimethylsiloxane (1000)] (PDMSU), was synthesized and tested as a hydrophobic impregnation for cotton fabrics. Hydrolysis of the precursor was performed with 0.1 mol L<sup>-1</sup> HCl and for deposition 4% sols of PDMSU in EtOH were used. Contact angle measurements revealed the hydrophobicity of the coatings, either on Al substrate ( $\Theta > 100^\circ$ ) or on cotton ( $\Theta \sim 130^\circ$ ). IR attenuated total reflection (ATR) spectroscopy showed that urea groups participate in PDMSU/cotton interface bonding, while 'free' urea groups (1725, 1691 cm<sup>-1</sup>) were noted in the spectra of PDMSU/Al and PDMSU/xerogel samples. The stability of the coatings was determined by repetitive washing. Degradation of the coatings was evidenced from the decrease in contact angle values and the relaxation of the urea-urea associations, leading to the appearance of the new Amide II band (1541 cm<sup>-1</sup>) in the IR ATR spectra.

**Keywords:** cotton, impregnation, hydrophobic, sol-gel, IR spectroscopy

## 1. Introduction

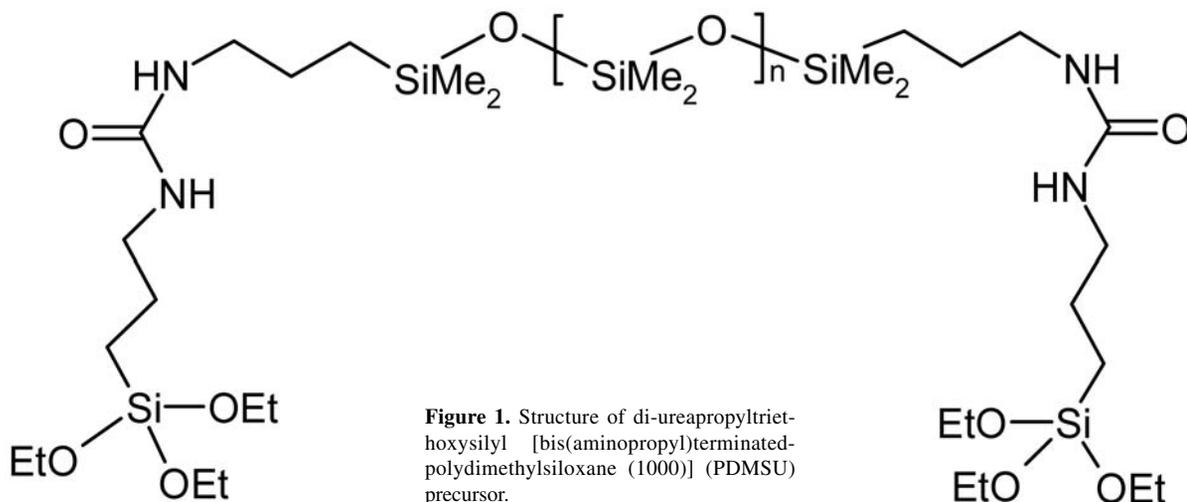
The sol-gel process has been recognized as an appropriate technological approach for impregnation of textiles, imparting them multifunctional properties like durable press finishing,<sup>1</sup> water repellency<sup>2,3</sup> or antimicrobial properties.<sup>4</sup> Usually the sols made of alkyltrialkoxysilanes and/or their mixtures with tetraalkoxysilanes,<sup>5</sup> polysiloxanes with hydrophobic groups, or fluorinated compounds, for example perfluorooctyltriethoxysilane,<sup>6</sup> were employed. In this work we present a novel organic-inorganic hybrid sol-gel precursor (Figure 1), named di-ureapropyltriethoxysilyl [bis(aminopropyl)terminated-polydimethylsiloxane (1000)] (PDMSU), which we used as a hydrophobic material for cotton impregnation. The structural changes of PDMSU coatings on cotton fabrics, exposed to repetitive washing, were followed using the infrared attenuated total reflectance (ATR) spectroscopic technique, suitable for studying surface processes at liquid/solid interfaces.<sup>7</sup>

PDMSU is structurally similar to the ureasils, in which urea groups (-NHCONH-) link end-capped alkoxy-silane groups to various poly(oxyalkylene) chains. The sol-gel process acts on alkoxy-silane groups, creating a silica network of polyhedral silsesquioxane units linking the

organic chains. Urea groups are an important part of ureasils, imparting to them strong luminescence<sup>8</sup> and, by allowing the accommodation of various salts, making them ionically conductive.<sup>9</sup> The active role of the urea groups in establishing the sol-gel network is due to the C=O moiety, which is able to form hydrogen bonding with the N-H moieties of neighboring urea groups, leading to self-assembly.<sup>10</sup> Detailed studies of Amide I and Amide II bands revealed that, apart from highly ordered self-associated urea-urea hydrogen bonded structures, non-bonded C=O moieties and disordered poly(oxyalkylene)-urea hydrogen bonded associations characterize the ureasil sol-gel network.<sup>11</sup> Similarly, also the process of gelling and the deposition of PDMSU sols on cotton fabrics consist of rupture of existing associations and the establishing of new ones. The Amide I and Amide II bands<sup>10,11</sup> of urea groups seemed to be the most suitable ones for providing information about the mechanisms mentioned above.

## 2. Experimental

PDMSU was synthesized from aminopropyl terminated polydimethylsiloxane (ABCR) and 3-isocyanatopropyltriethoxysilane (ABCR).<sup>12</sup> The impregnating sol



**Figure 1.** Structure of di-ureapropyltriethoxysilyl [bis(aminopropyl)terminated-polydimethylsiloxane (1000)] (PDMSU) precursor.

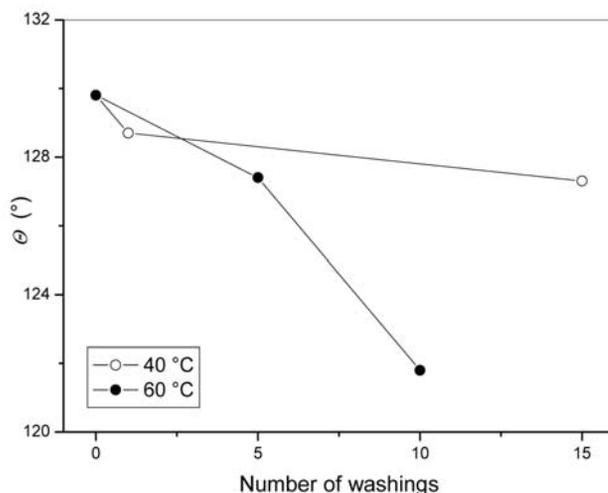
was prepared from PDMSU diluted in EtOH to a concentration of 4% and hydrolysis performed by adding acidified ( $0.1 \text{ mol L}^{-1}$  HCl) water (PDMSU:H<sub>2</sub>O = 1:6). Intentionally, no additional water was added in order to achieve long-term (>1 year) stability of the sols, exploiting the re-esterification reactions evidenced from IR and <sup>29</sup>Si NMR spectral measurements. The latter showed signals at  $-42.0$  ( $T^0(2,1)$ ) and  $-43.7$  ( $T^0(1,2)$ ) ppm, and a single signal attributable to non-hydrolyzed dimers at  $-51.4$  ppm ( $T^1(0,2)$ ),<sup>13</sup> while in the IR spectra the re-esterification reactions were assessed from the presence of the  $-\text{SiOEt}$  band at  $956 \text{ cm}^{-1}$ . PDMSU coatings on an aluminium substrate (AA2024 alloy) (PDMSU/Al) were made by the dip-coating technique (pulling speed  $10 \text{ cm min}^{-1}$ ) and then heat-treated at  $140 \text{ }^\circ\text{C}$  (1 h). The cotton fabrics were soaked in 4% PDMSU/EtOH sols (PDMSU/cotton), afterwards passed through rollers to squeeze out surplus sol and then heat-treated at  $190 \text{ }^\circ\text{C}$  (10 s). Bulk xerogels (PDMSU/xerogels) were obtained after the sols gelled (24 h) at ambient conditions, crushed into pieces and then heat-treated at  $140 \text{ }^\circ\text{C}$  to simulate the curing of the PDMSU/cotton samples.

IR spectra were recorded on a Bruker Model IFS66/S equipped with Silver Gate ATR cell employing a Ge ATR crystal (SpectraTech). <sup>29</sup>Si NMR spectra of xerogels were recorded on a Varian Unity Inova spectrometer equipped with a 3.2 mm magic-angle spinning (MAS) probe. SEM measurements were made on a FE-SEM, Supra 35VP (Carl Zeiss). The contact angles ( $\Theta$ ) for PDMSU/Al coatings were measured on a contact angle goniometer (Kreuss), while for impregnated cotton fabrics the corresponding data were obtained on a dynamic contact angle and absorption tester (FibroDat 500/1100). The impregnated cotton fabrics were washed according to the standard method ISO 105-C01:1989(E) (30 min in a Launder-Ometer) using a soap solution of concentration  $5 \text{ g L}^{-1}$ , previously heated to 40 and  $60 \text{ }^\circ\text{C}$ , to give a liquor ratio of 50:1. Surface energy values were determined us-

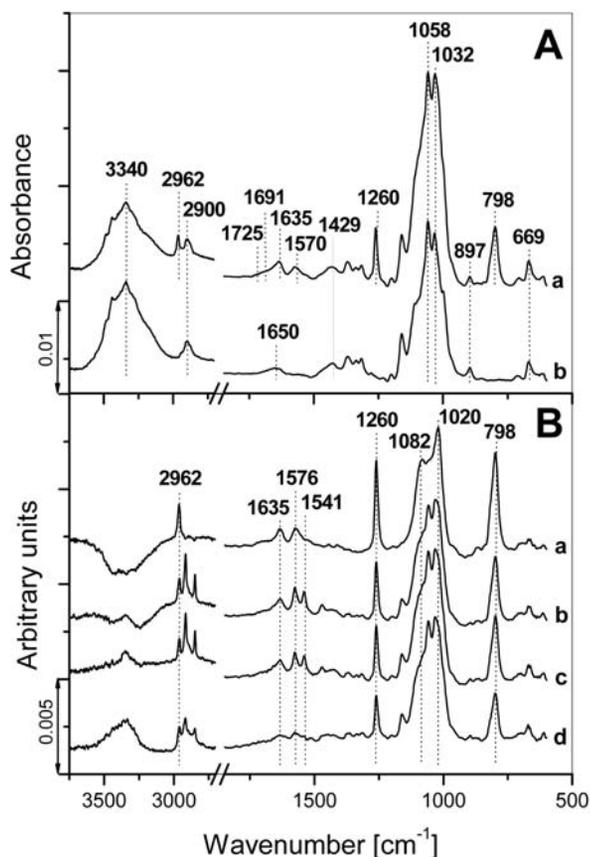
ing the van Oss relation,<sup>14</sup> using contact angle values of a series of testing liquids.

### 3. Results and Discussion

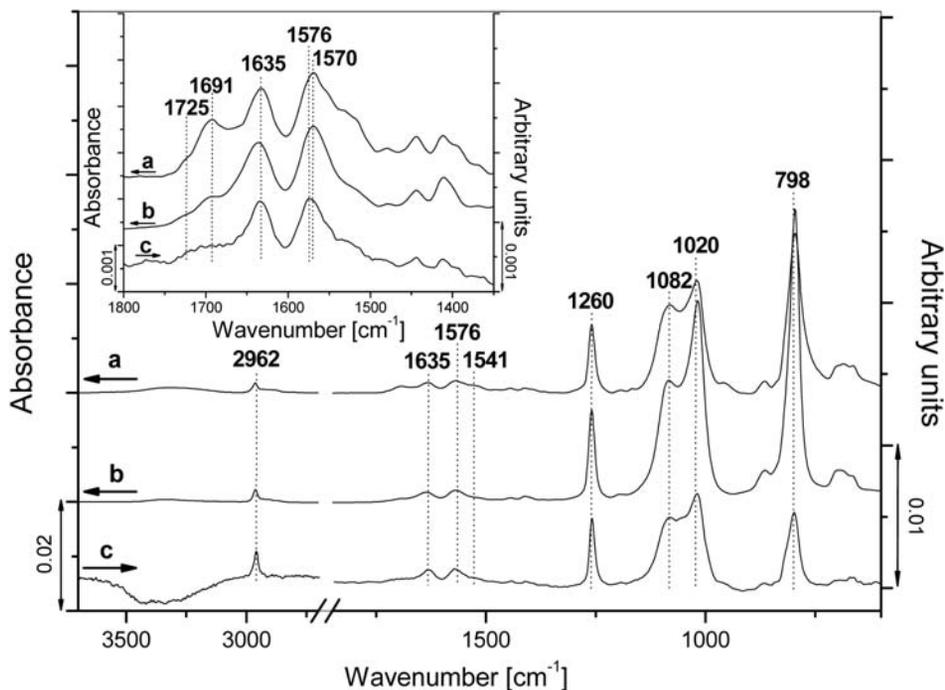
PDMSU/Al coatings were hydrophobic, exhibiting contact angle ( $\Theta$ ) values for water of about  $100^\circ$ . Using the van Oss relation,<sup>14</sup> the components of the surface energy ( $\gamma$ ), i.e. electron-donor ( $\gamma^-$ ), electron-acceptor ( $\gamma^+$ ), apolar ( $\gamma^{\text{LW}}$ ), polar ( $\gamma^{\text{AB}}$ ) and total ( $\gamma^{\text{tot}}$ ) surface energy values were obtained. The PDMSU/Al coatings were not bipolar in nature, showing much smaller electron-donor ( $\gamma^- \sim 0.3 \text{ mJ m}^{-2}$ ) than electron-acceptor ( $\gamma^+ \sim 4\text{--}5 \text{ mJ m}^{-2}$ ) interactions. They exhibited small polar ( $\gamma^{\text{AB}} \sim 4\text{--}5 \text{ mJ m}^{-2}$ ) and apolar ( $\gamma^{\text{LW}} \sim 23\text{--}25 \text{ mJ m}^{-2}$ ) interactions, but  $\gamma^{\text{tot}}$  was not small enough to impart oleophobic properties ( $\gamma^{\text{tot}} \sim 28\text{--}29$



**Figure 2.** Contact angles of PDMSU/cotton washed up to 15-times at 40 and  $60 \text{ }^\circ\text{C}$ . All measurements refer to stationary values obtained 50 s after the application of a water drop. Initial drop volume was  $6 \mu\text{L}$ .



**Figure 3.** A) ATR IR spectra of: a) PDMSU/cotton and b) cotton. B) ATR spectrum of cotton (Ab) subtracted from ATR IR spectra of PDMSU/cotton samples: a) unwashed, b) washed 5-times, c) washed 10-times and d) washed 15-times.

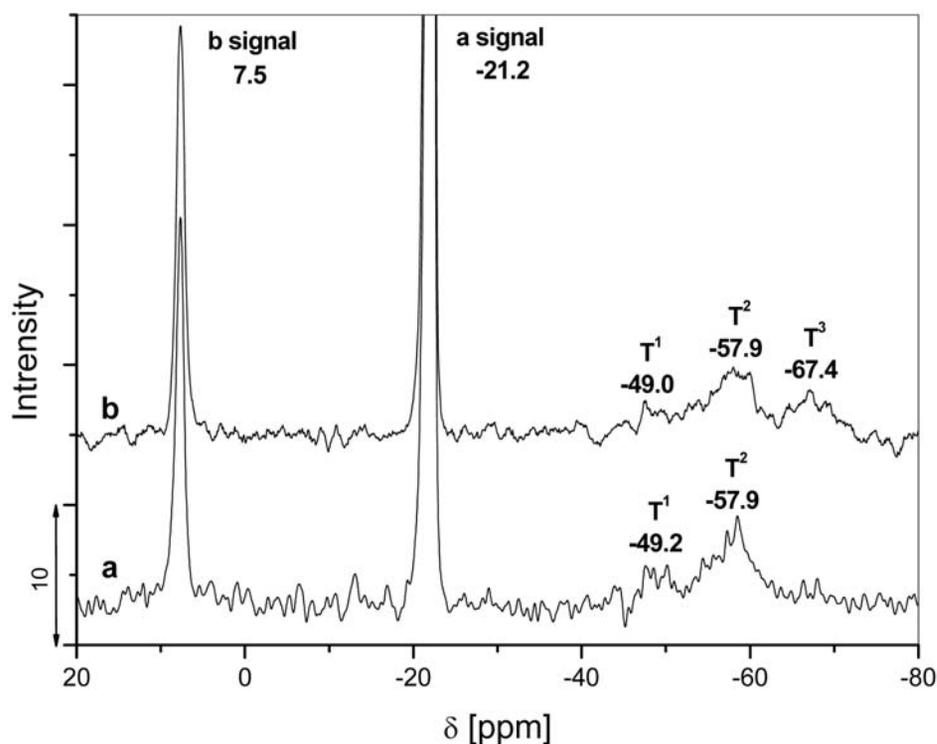


**Figure 4.** ATR IR spectra of: a) PDMSU/Al coating (140 °C), b) PDMSU/xerogel (140 °C) and c) ATR spectrum of cotton subtracted from ATR spectrum of PDMSU/cotton sample. Inset: spectral region between 1800–1350  $\text{cm}^{-1}$ .

$\text{mJ m}^{-2}$ ) to the coatings. The PDMSU/cotton samples exhibited  $\Theta$  values around  $130^\circ$  for water. Washing decreased  $\Theta$  values (Figure 2) to  $\sim 128^\circ$  (40 °C) and  $\sim 122^\circ$  (60 °C), respectively, due to partial degradation evidenced also on SEM micrographs. Expectedly, more severe changes were noted at a higher washing temperature.

The ATR spectra of unwashed PDMSU/cotton samples (Figure 3Aa) revealed the bands of PDMSU at  $1260 \text{ cm}^{-1}$  ( $\delta(\text{Si}-\text{CH}_3)$ ),  $798 \text{ cm}^{-1}$  ( $\text{r}(\text{Si}-\text{CH}_3)$ ) and the  $\text{CH}_3$  stretching band at  $2962 \text{ cm}^{-1}$ , but the  $\nu_{\text{as}}(\text{Si}-\text{O}-\text{Si})$  and  $\nu_{\text{s}}(\text{Si}-\text{O}-\text{Si})$  stretching bands belonging to the polydimethylsiloxane chain modes at  $1082$  and  $1020 \text{ cm}^{-1}$  were blurred by the bands of the cotton fabric.<sup>15</sup> The bands of the urea-urea linkage (Figure 4c) were weak but distinct enough to be seen at  $1635$  (Amide I) and  $1576 \text{ cm}^{-1}$  (Amide II).<sup>10,11</sup>

Difference ATR spectrum obtained by subtracting the spectrum of non-impregnated cotton from the spectrum of unwashed PDMSU/cotton sample did not reveal any bands at  $1725$  and  $1691 \text{ cm}^{-1}$  (Figure 3Ba,4c). These bands can be attributed to “free” urea and the relatively weakly bonded urea-urea associations, and were clearly noticed in the spectra of PDMSU/Al coatings (Figure 4a) and PDMSU/xerogels (Figure 4b). Their absence in the mentioned difference spectrum (Figure 3Ba, 4c) suggested the urea-substrate interface bonding, i.e. bonding of urea groups to cotton. The bands at  $1725$  and  $1691 \text{ cm}^{-1}$  play an important role in the condensation of PDMSU sols; they are intense in the spectra of non-hydrolyzed PDMSU but gradually lose their intensity in the course of



**Figure 5.**  $^{29}\text{Si}$  NMR spectra of PDMSU/xerogels: a) gelled at ambient conditions (24h) and b) heat-treated at 140 °C. The signals at 7.5 ppm (b signal) and -21.2 ppm (a signal) correspond to polydimethylsiloxane chains.<sup>18</sup>

gelling. Surprisingly, they reappeared in the spectra of heat-treated PDMSU/xerogels, suggesting that heat-treatment caused the relaxation of loosely bonded urea-urea aggregates and “free” urea moieties. The reason for this was sought in the condensation of silanol groups, creating various condensation products: open-dimers ( $\text{T}_2(\text{OH})_4$ ), cyclic species ( $\text{T}_4(\text{OH})_4$ ) and various open-polyhedra ( $\text{T}_7(\text{OH})_3$ ) and cube-like condensation products ( $\text{T}_8(\text{OH})_2$ ,  $\text{T}_8$ ) characteristic of other less complex alkyltrialkoxysilane gels.<sup>16</sup> Evidence for the presence of the corresponding species was obtained from the  $^{29}\text{Si}$  NMR spectra (Figure 5) showing the signals at -49.2 and -57.9 ppm for PDMSU gels prepared at ambient conditions, attributable to the  $\text{T}^1$  (25.3%) and  $\text{T}^2$  (74.7%) resonances.<sup>17</sup> The signals changed to -49.0 ( $\text{T}^1$  (18.1%)), -57.9 ( $\text{T}^2$  (55.3%)) and -67.4 ( $\text{T}^3$  (26.6%)) ppm for gels heat-treated at 140 °C, respectively. The build up of the sol-gel network through the formation of  $\text{T}^2$  and  $\text{T}^3$  open- and cube-like species (which was undoubtedly the overwhelmingly dominant process of condensation in the PDMSU hybrid) led to the partial liberation of urea groups. When PDMSU was deposited on a cotton surface and heat-treatment performed, partially “free” urea moieties were used up for cotton-sol-gel network bonding.

Repetitive washing caused loss of the coatings (Figure 3Ba–d), which we inferred from the gradually decreasing intensities of the bands characteristic of PDMSU (2962, 1260, 798  $\text{cm}^{-1}$ ). The region between 1200–1000  $\text{cm}^{-1}$  was blurred due to gradual uptake of water by the

cotton fabrics, also suggested from the appearance of the positive bands in the region 3500–3000  $\text{cm}^{-1}$ .

Washing affected the urea sites (1800–1500  $\text{cm}^{-1}$  region). While the bands at 1635  $\text{cm}^{-1}$  (Amide I) and 1576  $\text{cm}^{-1}$  (Amide II) appeared with decreasing intensity, corroborating the loss of the impregnation, a new Amide II band at 1541  $\text{cm}^{-1}$  was observed. The appearance of this band gave crucial information, indicating breaking and/or relaxing of the hydrogen bonding between urea groups and possibly between the urea groups and the substrate. Their presence in the difference spectra proved that the degradation definitely started at the urea sites and affected the substrate-urea interface bonding.

## 4. Conclusions

Sol-gel PDMSU coatings are promising hydrophobic material for impregnation of cotton fabrics. The synthesis of this organic-inorganic hybrid is straightforward and the stability of its sols is high due to re-esterification reactions. The structure of PDMSU coatings is characterized by a highly cross-linked sol-gel hybrid network consisting of a high amount of polyhedral silsesquioxane condensation species. Heat-treatment favored the reactivity of “free” urea groups to form interactions with the cotton substrate, as shown by the fact that the bands characterizing these groups did not appear in the ATR IR spectra of PDMSU/cotton fabrics.

## 5. Acknowledgements

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## Povzetek

Sintetizirali smo nov organsko-anorganski hibridni prekursor di-ureapropiltrioksasilil [bis(aminopropil)terminiran-polidimetilsiloksane (1000)] (PDMSU) in ga uporabili za hidrofobno impregnacijo bombažne tkanine. Hidrolizo prekursorja smo izvedli z 0.1M HCl, za depozicijo na tkanino pa smo pripravili 4% sole PDMSU v etanolu. Meritve kontaktnih kotov so pokazale, da so prevleke hidrofobne na različnih podlagah, na primer na Al podlagi ( $\Theta > 100^\circ$ ) oz. na bombažni tkanini ( $\Theta \sim 130^\circ$ ). Z IR spektroskopsko tehniko z oslabljenim odbojem (ATR) smo ugotovili, da urea skupine pri vzorcih PDMSU/bombaž sodelujejo pri vezavi na površino tkanine, medtem ko se proste urea skupine ( $1725, 1691 \text{ cm}^{-1}$ ) pojavijo v spektrih PDMSU/Al in PDMSU/kserogelov. Stabilnost hidrofobnih prevlek smo določevali z večkratnim pranjem tkanine. Postopno razgradnjo prevlek dokazuje zmanjšanje vrednosti kontaktnih kotov in relaksacija urea-urea povezav, ki vodi do pojava novega Amidnega II traku ( $1541 \text{ cm}^{-1}$ ) v IR ATR spektrih.