Beeswax/Halloysite microparticles embedded within a geopolymeric layer for the protective coating of steel

Martina Maria Calvino,[a] Lorenzo Lisuzzo,[a] Giuseppe Cavallaro,[a] * Giuseppe Lazzara,[a] Candida Pipitone,[a] Francesco Giannici [a]

[a]*Dipartimento di Fisica e Chimica, Università degli Studi di Palermo, Viale delle Scienze, pad. 17, 90128 Palermo, Italy. giuseppe.cavallaro@unipa.it*

Abstract

A halloysite-based geopolymer filled with microwax particles was designed as a protective layer on steel substrates. Beeswax microparticles were obtained from the clay stabilized Pickering emulsions and they were homogeneously dispersed within the geopolymeric network, thus improving the coating physico-chemical properties. Specifically, this treatment changed the steel's wettability by increasing its hydrophobicity. Moreover, XRF analysis was conducted in order to have details on the chemical compositions.

Keywords

Halloysite, Geopolymer, Coating

1. Introduction

Geopolymers are an innovative and green alternative for construction materials due to the employing of industrial by-products or natural resources with the benefit of the reduction of carbon dioxide emissions [1]. They consist of cross-linked tetrahedral [AlO_4] and [SiO_4] groups with alkali metal cations, and are synthesized by activating an aluminosilicate precursor with a highly alkaline solution [2,3]. Among the precursors, clay minerals as kaolinite and halloysite nanotubes are commonly used given their low cost, eco-friendliness and biocompatibility [4,7]. Geopolymer coatings on metal substrates as protective and thermal barriers for concrete have been reported [8]. In order to guarantee low water adhesion and to reduce the growth of biological species, hydrophobicity is one of the main characteristics of the protective layers [9]. As a matter of fact, it should be noted that geopolymers are inherently hydrophilic because of the hydroxyl groups on their surface. Therefore, microwax particles obtained from Pickering emulsions has been employed [10,12]. In this work beeswax microparticles were embedded within the geopolymeric network to increase the hydrophobicity, obtaining a new protective layer on steel sheets for coating applications.

2. Experimental section

2.1 Geopolymer preparation and treatment of the steel sheets

Beeswax, Halloysite (HNTs), ethanol (≥ 99.5%), acetone (≥ 99.5%) and sodium hydroxide (≥ 98%) are Sigma Aldrich products. Steel sheets are a gift from Puleo SpA, Italy. The beeswax/HNTs microparticles were prepared via Pickering emulsions as reported in literature [10]. Afterwards, a NaOH solution (12 M) was added to the dried beeswax/HNTs microparticles at 1:1 NaOH/HNTs ratio, resulting in a viscous and flowing paste. Prior to any treatment, the steel sheets were degreased in acetone using an ultrasonic bath and washed with deionized water and ethanol. The coating of the steel substrates was performed by brushing the surface with the geopolymeric paste (GP microwax). The final hardening step was carried out by placing the treated steel samples in an oven at 50 °C for 48 hours. Then, samples were washed many times by pouring about 100 mL of water on their surface and by dipping them into 50 mL of water overnight. Finally, the treated samples were dried at room conditions for 5 days before characterization. It is worth to note that the same protocol was used for the treatment of the steel substrates with pure halloysite based geopolymer (GP), without any beeswax addition for comparison.

2.2 Characterization

Optical images of the samples were obtained by a digital microscope (CoolingTech). The wettability was investigated through water contact angle measurements in the sessile drop method, by employing an optical apparatus (OCA 20, Data Physics Instruments) at 25.0 ± 0.1 °C. X-ray Fluorescence (XRF) Spectrometry was carried out by an Olympus Innov-X DS-2000 Delta.

3. Results and Discussion

Optical microscopy was conducted to observe the morphological features of the treated and untreated steel sheets, and to evaluate the effect of the coating layers at a micrometric level (Figure 1).

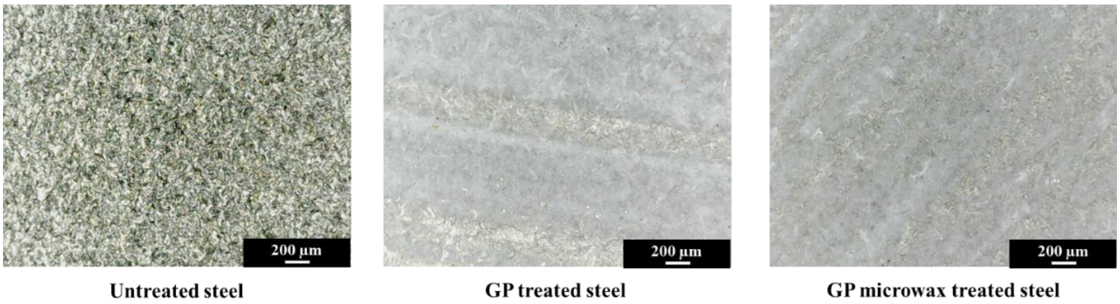

Figure 1. Optical micrographs of untreated steel and sheets coated with HNTs based geopolymer and beeswax/HNTs microparticles based geopolymer.

The surface of the bare steel sheets appears heterogeneous and porous, while it looks smoother and homogeneous after the treatments. This effect can be related to the filling of pores with the coating protective materials, even though some microdomains and aggregation of particles can be observed on both the GP and GP microwax treated steel sheets. Accordingly, we can state that both treatments are effective in reducing the steel porosity although GP and GP microwax are not totally incorporated within the steel structure.

Untreated sheet is hydrophilic and its contact angle is 52.3° without any variation as a function of time (Figure 2). Once the surface is coated with the halloysite based geopolymer, it becomes much more hydrophilic and its contact angle falls to 8.1°. This effect can be related both to the high hydrophilicity of halloysite based geopolymer which can interact with the water via hydrogen bonding with the -OH groups on the surface, and to the smoother surface of the sample [13].

A different behaviour was recorded after coating with the beeswax/HNTs microparticles based geopolymer. For instance, the material is still hydrophilic with a contact angle of 49.2° that barely decreases to 44.3° after

60 seconds before any cleaning step is carried out. Remarkably, the treated steel becomes more hydrophobic after washing the surface with water. The value soared to 83.6° and then it slightly decreased to 74.2° after one minute.

These variations can be most likely related to the excess of halloysite nanotubes. After washing away the excess of clay, the microwax particles on the surface can interact with the water droplet thus enhancing the hydrophobic contribution to the wettability of the material. It should be noted that the addition of hydrophobic beewax can affect the micron-level coating surface structure smoothness.

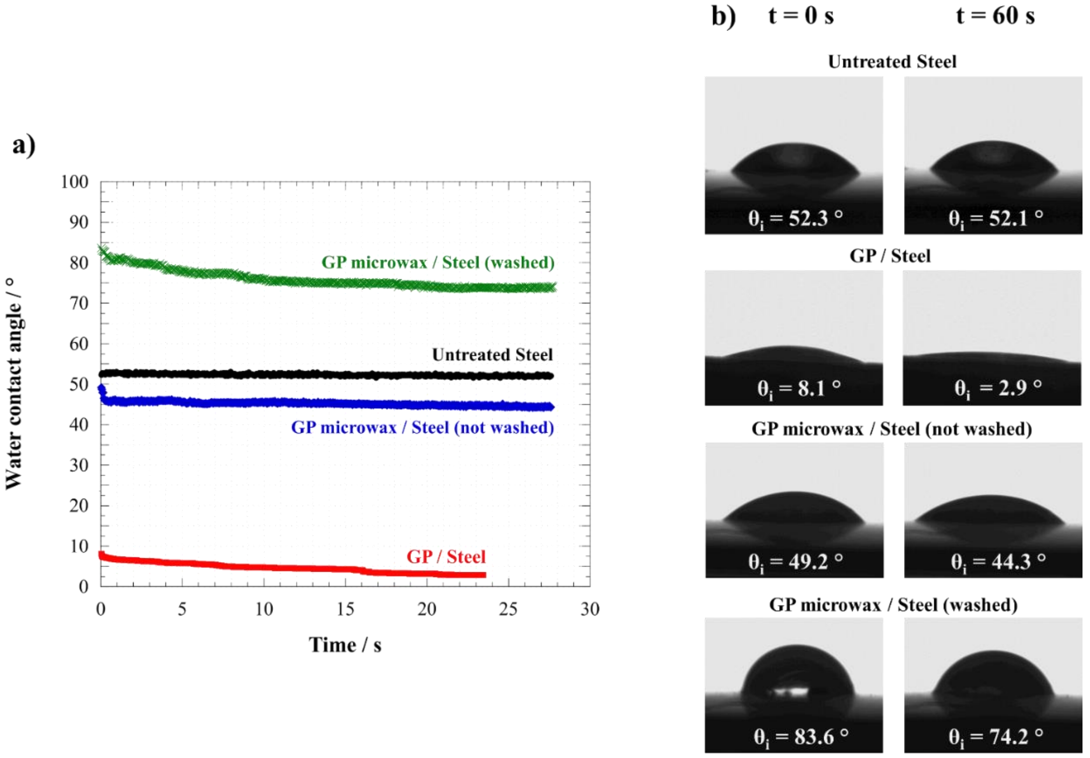

Figure 2. (a) Water contact angle curves as a function of time, (b water droplets profiles at t = 0 s and t = 60 s after their deposition on the surface of the samples.

In order to have more details about the droplet evolution on the surface, the data were analyzed by fitting the curves with the following equation:

$$\Theta = \theta_i \exp(-k_\theta \tau^{n}) \qquad (1)$$

where θ_i is the contact angle at t = 0, k_θ is the constant related to the kinetics of the process and n is a coefficient which describes the mechanism of the water droplet evolution after its deposition on the solid substrate. In particular, values for n range from 0 to 1 on dependence of the absorption and spreading contributions, respectively.

Table 1. Fitting parameters of the water contact angle kinetic evolution.

	K_θ (s^{-n})	n
GP / Steel	0.121 ± 0.007	0.54 ± 0.02
GP microwax / Steel (washed)	0.043 ± 0.006	0.35 ± 0.04

It is clear that the presence of the microwax particles within the coating layer is responsible for a decrease of the process rate, as evidenced by k_0 reduction. Similarly, the mechanism of the water droplet evolution on the treated steel sheet is affected, being the spreading contribution lower compared to the pure halloysite based geopolymeric coating, as suggested by the decrease of n.

Aimed at characterizing the chemical composition of the protective layers on the steel sheets, XRF studies were carried out (Figure 3). It is worth to note that, in the three investigated systems, the most significant peaks are related to the presence of Chromium, Manganese and Iron which are proper components of the bare steel sheet. After the treatment protocols are carried out, instead, Silicon and Aluminum can be detected on the surface. Most interestingly, the intensity of the Si and Al peaks is higher for GP treated steel compared to the steel coated with beeswax/HNTs microparticles based geopolymer (inset in Figure 3).

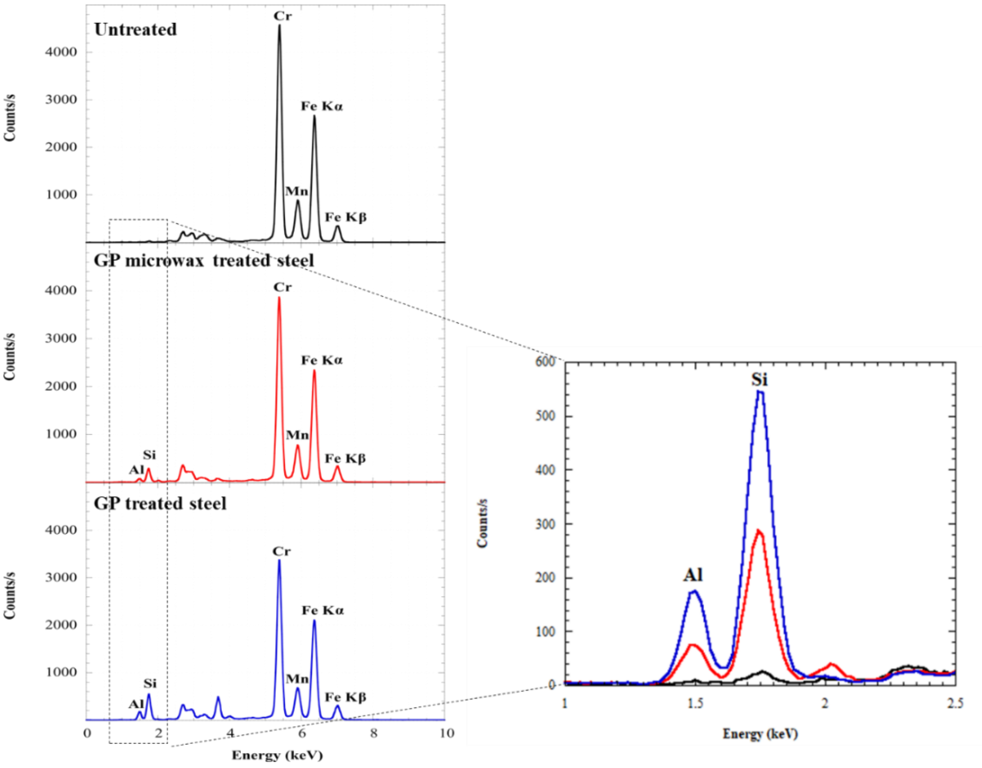

Figure 3. XRF spectra of treated and untreated steel sheets.

Iron and Chromium are the main components of the steel sheets in terms of composition, with 70.85 and 18.10 wt%, respectively. After the treatment protocols, instead, Al and Si are detected significantly. Despite Fe and Cr are still the most abundant elements, the amounts of Al and Si are 11.21 and 11.26 wt%, respectively, for GP microwax treated sample. Besides, the quantities of these elements increase up to 19.57 and 18.62 wt% in the GP treated steel. It should be noted that the Al/Si ratio is ca. 1, which is typical for pristine halloysite [14]. These findings are also in agreement with the contact angle data. Indeed, the higher the amount of nanotubes in the coating layer, the more hydrophilic the surface

4. Conclusions

Halloysite-based geopolymer with beeswax microparticles has been employed as protective layer on steel sheets by brush deposition. For comparison, geopolymeric coating without wax was also reported. After the treatment with both geopolymeric formulations, the steel surfaces appear more homogeneous and smoother. The presence of microwax particles changed the wettability properties of the steel surfaces. In fact, the untreated steel and the GP treated both present hydrophilic values of contact angle. On the other hand, the treatment of the steel sheet with GP microwax enhanced the hydrophobicity features of the material giving new perspectives in protective coating.

Declaration of Competing Interest

The authors declare no competing financial interest or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The work was financially supported by "PON I&C 2014-20, SICAM U-GOV PRJ-0514 – Ricerca Industriale", by "SETI-Sicilia Eco Tecnologie Innovative", Cod.Progetto 2017-NAZ-0204, PO FESR Sicilia 2014/2020 – Azione 1.1.5 and by the University of Palermo.

References

[1] B. Zhang, H. Guo, P. Yuan, Y. Li, Q. Wang, L. Deng, D. Liu, Geopolymerization of halloysite via alkali-activation: Dependence of microstructures on precalcination, Applied Clay Science. 185 (2020) 105375. https://doi.org/10.1016/j.clay.2019.105375.

[2] M. Catauro, G. Dal Poggetto, C. Sgarlata, S. Vecchio Ciprioti, S. Pacifico, C. Leonelli, Thermal and microbiological performance of metakaolin-based geopolymers cement with waste glass, Applied Clay Science. 197 (2020) 105763. https://doi.org/10.1016/j.clay.2020.105763.

[3] T.T. Haw, F. Hart, A. Rashidi, P. Pasbakhsh, Sustainable cementitious composites reinforced with metakaolin and halloysite nanotubes for construction and building applications, Applied Clay Science. 188 (2020) 105533. https://doi.org/10.1016/j.clay.2020.105533.

[4] S. Sadjadi, M.M. Heravi, M. Malmir, Pd@HNTs-CDNS-g-C3N4: A novel heterogeneous catalyst for promoting ligand and copper-free Sonogashira and Heck coupling reactions, benefits from halloysite and cyclodextrin chemistry and g-C3N4 contribution to suppress Pd leaching, Carbohydrate Polymers. 186 (2018) 25–34. https://doi.org/10.1016/j.carbpol.2018.01.023.

[5] G. Gorrasi, R. Pantani, M. Murariu, P. Dubois, PLA/Halloysite Nanocomposite Films: Water Vapor Barrier Properties and Specific Key Characteristics, Macromolecular Materials and Engineering. 299 (2014) 104–115. https://doi.org/10.1002/mame.201200424.

[6] E. Rozhina, S. Batasheva, R. Miftakhova, X. Yan, A. Vikulina, D. Volodkin, R. Fakhrullin, Comparative cytotoxicity of kaolinite, halloysite, multiwalled carbon nanotubes and graphene oxide, Applied Clay Science. 205 (2021) 106041. https://doi.org/10.1016/j.clay.2021.106041.

[7] A. Joshi, C. Montes, S. Salehi, E. Allouche, Y. Lvov, Optimization of Geopolymer Properties by Coating of Fly-Ash Microparticles with Nanoclays, J Inorg Organomet Polym. 25 (2015) 282–292. https://doi.org/10.1007/s10904-014-0105-1.

[8] J. Temuujin, A. Minjigmaa, W. Rickard, M. Lee, I. Williams, A. van Riessen, Fly ash based geopolymer thin coatings on metal substrates and its thermal evaluation, Journal of Hazardous Materials. 180 (2010) 748–752. https://doi.org/10.1016/j.jhazmat.2010.04.121.

[9] Y. Zhang, L. Bai, C. Cheng, Q. Zhou, Z. Zhang, Y. Wu, H. Zhang, A novel surface modification method upon halloysite nanotubes: A desirable cross-linking agent to construct hydrogels, Applied Clay Science. 182 (2019) 105259–105267. https://doi.org/10.1016/j.clay.2019.105259.

[10] L. Lisuzzo, T. Hueckel, G. Cavallaro, S. Sacanna, G. Lazzara, Pickering Emulsions Based on Wax and Halloysite Nanotubes: An Ecofriendly Protocol for the Treatment of Archeological Woods, ACS Appl. Mater. Interfaces. 13 (2021) 1651–1661. https://doi.org/10.1021/acsami.0c20443.

[11] Y. Zhao, W. Kong, Z. Jin, Y. Fu, W. Wang, Y. Zhang, J. Liu, B. Zhang, Storing solar energy within Ag-Paraffin@Halloysite microspheres as a novel self-heating catalyst, Applied Energy. 222 (2018) 180–188. https://doi.org/10.1016/j.apenergy.2018.04.013.

[12] L. Lisuzzo, G. Cavallaro, S. Milioto, G. Lazzara, Pickering Emulsions Stabilized by Halloysite Nanotubes: From General Aspects to Technological Applications, Advanced Materials Interfaces. 2102346 (2022) 1–29. https://doi.org/10.1002/admi.202102346.

[13] L. Lisuzzo, M.R. Caruso, G. Cavallaro, S. Milioto, G. Lazzara, Hydroxypropyl Cellulose Films Filled with Halloysite Nanotubes/Wax Hybrid Microspheres, Ind. Eng. Chem. Res. 60 (2021) 1656–1665. https://doi.org/10.1021/acs.iecr.0c05148.

[14] G. Cavallaro, L. Chiappisi, P. Pasbakhsh, M. Gradzielski, G. Lazzara, A structural comparison of halloysite nanotubes of different origin by Small-Angle Neutron Scattering (SANS) and Electric Birefringence, Applied Clay Science. 160 (2018) 71–80. https://doi.org/10.1016/j.clay.2017.12.044.