Plasma Modifications of Reinforcing Fibers used in Cement Composite Materials

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I would like to dedicate this thesis to my recently deceased grandmother Ludmila Trejbalová. She spent her entire life in education. Therefore, she appreciated my academic achievements and fully supported me during my studies since my childhood to her last moments of life.
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Abstract

This work studied an improvement of fibrous composite materials mechanical properties that are standardly used in the field of civil engineering. At first, the state of the theoretical background of a cohesive synergistic interaction between individual phases is recapitulated. Then, the role of chemical and physical inter-phase interaction is described. Basic types of reinforcing fibers are summarized and their surface as well as bulk properties are characterized. The issues connected with poor adhesion between them and lime- or cement-based matrixes are mentioned. Most of reinforcing fibers, especially those made from glass and different type of polymers, exhibit smooth surface with too high surface free energy. For these reasons, the distribution of tension through fibers across the crack is too poor. Therefore, as the bridging effect fails, residual strength of composite materials is low after exceeding of their elastic limit. The mechanical potential of reinforcement is not exhausted effectively. In order to overcome these limitations, fibers surface modifications were executed by means of low-pressure oxygen plasma. The effect of such treatment provided is twofold; fiber surfaces are roughened by ion bombardment and activated by implementation of active polar groups. The other part of the work summarizes characterization possibilities of micro- and macro-fibers from the perspective of chemical and physical properties. Moreover, different assessments of a fiber/matrix interaction are introduced.

One separate chapter is devoted to modifications of micro-glass fibers with a protective layer, an industrial sizing based on aminosilane. The protective layer was roughened and functionalized using plasma treatment to attain its stronger adhesion to the lime-based matrix. It was shown that treated surfaces were hydrophobized but also mechanically damaged. Because of damage of such protective layer, fibers were exposed to mechanical damaging during mixing with other components of the mixture and thus failed as reinforcement.

The other part of the work deals with plasma modifications of chopped PET fibers. It was found out that surfaces of thus treated reinforcement reached on significantly higher water wettability and indented morphology. Next to that, an increased physical interaction between treated fibers and the cement matrix was proven.

The purpose of the other part of the work was to verify whether the effect of plasma modifications on polymer macro-fibers is stable in time or not. It is possible that the effect would be reduced when fibers are exposed to atmospheric conditions due to interactions between active polar groups on their surfaces and air humidity. Two fiber types standardly used for reinforcing of FRCs were modified by means of plasma treatment. Similarly to previous chapter, required morphology and wettability changes onto fiber surfaces were detected. Moreover, morphology changes
of fibers were detected without any negative impact on fiber mechanical properties after plasma treatment. It was found out that aging development of contact angles is decreased up to reference values after fibers were exposed to atmospheric conditions. On the other hand, it was also found out that the reversible effect within up to 30 days does not influence adhesion between fibers and the cement matrix, because this is, as evaluated, controlled especially by the physical interaction.

The last part of the work summaries all finding obtained during solving results of all previous chapters. It was aimed to find practical application of plasma treated polymer macro-fibers. Thus treated fibers were used as reinforcement in FRCs prismatic specimens and those were then subjected to standardized bending strength tests in order to observe their behavior during post-cracking stage. It was revealed that specimens containing modified fibers exhibited increased residual strength by up to 30% than those with reference fibers. As a result, reduced amount of treated fibers can be applied into FRCs mixture thanks to increased utilization of fibers mechanical properties. Such an approach contributes to improvement of mixture workability and lowers economical burden.
Abstrakt

Název práce česky: Plazmatické modifikace vláknité výztuže používané v cemen-tových kompozitních materiálech

Práce se zabývá výzkumem zlepšení mechanických vlastností vláknových kompozitních materiálů používaných ve stavebnictví. Nejprve rekapituluje teoretickou podstatu kohezivní synergické interakce jejich jednotlivých fází a dokazuje tak význam silných chemických a fyzikálních mezifázových vazeb. Dále popisuje objemové a povrchové vlastnosti základních typů vláken a upozorňuje na fakt, že řadu z nich jejich povrch předispone k nedostatečné vazbě k vápenné či cementové matrice. Většina výztužných vláken, především skleněných a polymerních, totiž vykazuje hladký povrch s příliš vysokou povrchovou energií. Kvůli těmto vlastnostem tak dochází ke slabému přemostění napětí přes vlákna skrz trhlinu v matrice. Výsledný vláknový kompozitní materiál tak dosahuje nízké zbytkové pevnosti po porušení spojitosti matrice, přičemž mechanický potenciál výztuže není plně využit. Ve snaze tyto parametry zlepšit byly aplikovány modifikace vláken pomocí nízkotlakého chladného plazmatu v kyslíkové atmosféře. Tato metoda dosahuje dvojího efektu, vlákna jednak zdrsní prostřednictvím iontového bombardování a jednak jejich povrchy aktivuje, tj., implementuje na ně aktivní polární skupiny, díky kterým dochází k zesílení jejich chemické vazby s vodou. Další část práce sumarizuje možnosti charakterizace povrchů mikro- a makro-vláken z chemického a fyzikálního hlediska a způsoby hodnocení jejich interakce se spojitými fázemi vyztužovaných materiálů.

Samostatnou kapitolu tvoří modifikace povrchů skleněných mikro-vláken, která jsou z výroby opatřena tzv. sizingem, tenkou vrstvou aminosilanu. Tato vrstva byla pomocí plazmatu jemně zdrsněna a funkcializována tak, aby dosáhla vyšší soudržnosti s vápenkou matricí. Ukázalo se, že upravené povrchy byly skutečně hydrofobizovány, ale také mechanicky porušeny. Kvůli ztrátě ochranných vlastností této vrstvy byla vlákna nadměrně poškozena během mísení směsí a jako výztuž následně selhala.

Další část práce se zabývá obdobnými modifikacemi sekaných PET vláken. Ukázalo se, že povrchy upravené výztuže dosahly výrazně větší smačivosti vodou a podstatně vyšší morfologie. Dále bylo ověřeno, že díky těmto změnám vlákna dosáhla větší fyzikální interakce s cementovou matricí.

Účelem další části práce bylo ověřit, zda je efekt plazmatických modifikací polymerních makro-vláken stabilní či nikoliv. Existuje podezření, že se kvůli interakci aktivních polárních skupin se vzdušnou vlhkostí vytrácí. Plazmaticky modifikované byly dva typy makro-vláken standardně používaných pro vyztužování.
vláknobetonu. Podobně jako v předchozích případech byly prokázány žádané povrchové změny, tedy zvýšení smáčivosti a morfologie. Dále bylo ověřeno, že mechanické vlastnosti vláken nejsou modifikacemi příliš dotčeny. Důležitým zjištěním bylo, že se smáčivost modifikovaných vláken postupně navracela k referenčním hodnotám, nicméně tato skutečnost neovlivňovala jejich soudržnost s cementovou matricí. Ukázalo se totiž, že interakce mezi těmito dvěma materiály je řízena především fyzikální vazbou.

Poslední část práce shrnuje poznatky získané ze všech předchozích částí a snaží se najít jejich praktické uplatnění. Plazmaticky modifikovaná makro-vláčna byla použita jako výztuž ve vláknobetonu. Bylo zjištěno, že takto vyztužené vzorky dosahují až o cca 30 % vyšší zbytkové pevnosti během ohybové zkoušky než vzorky obsahující referenční vlákna. Díky vyššímu využití mechanického potenciálu aplikovaných vláken tak může být použito jejich menší množství, což prospívá zpracovatelnosti směsi a ekonomickým aspektům.
Goals

The major goal of the presented research was to modify polymer and glass reinforcing fiber surfaces using a plasma treatment and thus to ensure their strong chemical and physical interaction with lime- and cement-based matrixes. To achieve this goal, it was necessary to divide the thesis into the following sub-goals:

- Study of an importance of an interphase interaction within fibrous composite materials and definition of general surface parameters of standardly used reinforcing fibers in the field of civil engineering.
- Choice of a proper plasma treatment parameters with respect to its applicability and employment for modification of selected reinforcing fibers made from glass or polymers.
- Comprehensive study of modified fibers bulk and surface properties from the chemical and physical point of view. Description of their water wettability, chemical composition, and surface morphology, and mechanical properties.
- Stability assessment of modified fibers surface polarity as a function of time exposure to atmospheric conditions.
- Research of the interaction between modified glass and polymer micro- or macro-fibers and typical matrixes used in civil engineering – based on lime or cement binders.
- Study of mechanical behavior of fibrous composite materials reinforced with modified fibers, focusing on their post-cracking response.
- An application of obtained results within technical practice.
Following the goals listed above, the thesis is divided into 7 main chapters (including appendix), these are as follows:

1. **Introduction and state of art:** This chapter summarizes functional principles of fibrous composites used in civil engineering, in particular those based on lime or cement binders. Standardly applied reinforcing fibers are summarized and characterized. Special attention was paid on a description of an interphase interaction between the individual fiber and the matrix. Principles of interaction failures between the two materials are explained and methods for improvement of the interaction are introduced. Next, possibilities how to assess fibers surface changes and their interaction with matrices are discussed.

2. **Mechanical properties of lime-based mortars reinforced with plasma treated glass fibers:** Within this chapter, industrially sized glass micro-fiber surfaces were plasma treated and functionalised in order to roughen them and thus to ensure their strong adhesion to the lime-based matrix. Although the thesis is focused primarily on the cement matrix, lime-based one was selected in this case because of continuity with other studies ongoing that time on our department. Modified fibers were observed using SEM microscopy to reveal changes in their morphology. Chemical changes were indirectly detected using a contact angle measurement. To reveal the interaction between fibers and the matrix, mechanical destructive tests were conducted on prismatic fiber reinforced mortar samples (amount of reinforcement differed from approx. 0.067 to 3.5 % of matrix volume). Such an approach was employed instead of pull-out tests because of fiber dimensions and fibrillated origin. It was shown that sized fiber surfaces were slightly roughened and activated. Loading tests revealed that bending and compressive strength of lime-based mortars reinforced with treated fibers performed more poorly than those with reference fibers. It can be therefore concluded that the plasma treatment do not bring any benefits in the case of glass fibers being used as reinforcement in lime- or cement-based matrixes. The sizing (present on reinforcing rock-based fibers in most cases) is very sensitive for any treatment. Once the coat is disturbed, its function of fiber protection fails. Because of that reason, future work was focused on polymer fibers modifications.

3. **Impact of surface plasma treatment on the performance of PET fiber reinforcement in cementitious composites:** The aim presented in this chapter is to modify PET short fibers (20 mm long) by means of the plasma treatment in order to activate and roughen their surfaces and thus to support strain-hardening behavior of reinforced cement paste specimens (amount of reinforcement was equal to 2.9 % of matrix volume). A wetting angle measurement revealed that the fiber surface energy was reduced. Fibers were
slightly roughened as found out using SEM analysis. The improvement in adhesion between primary (non-recycled) fibers and the surrounding matrix brought about a more pronounced strain hardening of the specimens tested in four-point bending. The plasma treatment of thinner fibers from recycled PET led to a lower capacity for transferring tensile stresses due to the reduced cross-sectional area of the fibers. The considerable bridging force provided by plasma treated primary PET fibers resulted in the prevention of excessive and abrupt cracking, and limited crack openings. However, the effect of composite multiple cracking behavior was not attained. These findings can be applied in the field of SHCC composites. Nevertheless, their practical potential seems to be poor in the field of civil engineering.

4. **Deterioration of bonding capacity of plasma-treated polymer fiber reinforcement:**
   This chapter is focused primarily on research of plasma deterioration effect on modified polymer macro-fibers and it is considered to be very important from two reasons: (i) after comprehensive literature review, it can not be concluded whether the plasma treatment is stable or not. Therefore, the first purpose of the chapter is to fill that void and find out how atmospheric dust and humidity influence modified fiber surfaces. The second reason (ii) reflects the need of interface enhancement between polymer fibers and the cement matrix in the field of FRCs. Similarly to previous two chapters, plasma treatment was employed to modify surface of polymer macro-fibers standardly used for FRCs reinforcing (length about 50 mm). A microscopy investigation allowed to observe changes in their surface morphology, while changes in chemical bonds were detected by XPS analysis. To quantify the impact of the plasma treatment and its deterioration, water contact angle measurements and pull-out tests were carried out after fibers were exposed to standard atmospheric conditions for certain period. The results indicate that the exposure to atmospheric conditions has a negligible impact on fiber bonding, because surface roughening plays a major role. Therefore, fibers do not need to be incorporated into the cement matrix immediately after their treatment. Anyway, changes happened onto fiber surfaces after modification were considered to be very promising from the practical point of view. Therefore, the topic was extended in the following chapter.

5. **Mechanical properties improvement of fiber reinforced concrete:**
   This chapter uses findings from the previous one and extends them with new results with the focus to their applications. It deals with improvement of FRCs mechanical properties by using plasma modified fibers. Three different polymer macro-fibers were plasma treated and then subjected to pull-out tests from the cement matrix. Based on this experiment, interfacial shear stress between the two materials was revealed and consequently used as a basic input parameter in numerical simulations of bending tests of prismatic notched FRC samples. The aim of the simulation was to reveal whether increased shear stress positively influences bending strength of the specimen, especially during their post-cracking response. Together with numerical simulations and having similar purpose, prismatic notched concrete specimens with dimensions equal to 550×150×150 mm, composed of standard concrete mixture and reinforcement in amount of 0.75 vol. % of the mixture, were made and subjected to standardized bending tests following EN 14845-2. It was shown that residual strength of loaded specimens was improved by up to 30 % by using of treated fibers instead of untreated ones. Such finding has significant practical impact; it is possible to reduce fibers amount applied into FRC mixture and thus to enhance mixture work-
ability and decrease economical burden, while the requirements of the cited standard stay fulfilled.

6. **Conclusions and final remarks:** This chapter summarizes results of the thesis and highlights those that are considered to be the most important.

7. **Contact angle measurement tool based on image analysis (appendix):** During study of reinforcing fibers wettability, new problem arose; how to calculate it with a system capable to utilize wide variety of fiber diameters yet simple enough for possible usage within the civil engineering applications on sites. This chapter describes designation and realization of simple solution for assessment of contact angles on menisci formed around partially submerged fibers into liquid. The hardware system consists of an optical set combined with an open-source software CAMTIA. The fully automatic assessment of contact angles is based on image binarization, identification of regions of interest, boundary smoothing, and contour differentiation. After initial setting of calculation parameters, there is no need for further interaction with the end user. This eliminates the need for expensive commercial solutions or tedious manual placement of tangents, guarantees consistency in the assessment procedure, and allows fast bulk processing of images.
Notation

Abbreviations

- SHCC, Strain hardening cement composites
- FRCC, Fiber reinforced cement composites
- FRC, Fiber reinforced concrete
- ECC, Engineered cement composites
- CFRP, Carbon fiber reinforced polymer
- FRC FCM, Fiber reinforced composites fixed crack model
- CEM, cement
- C-S-H, Calcium silicate hydrate
- ITZ, Interfacial transition zone
- SEM, Scanning electron microscopy
- XPS, X-ray photoelectron spectroscopy
- AFM, Atomic force microscopy
- FEM, Finite element method
- DIC, Digital image correlation
- DSLR, Digital single lens reflex
- CMOD, Crack mouth opening displacement
- PET, Polyethylene terephthalate
- PP, Polypropylene
- PE, Polyethylene
- PVA, Polyvinyl alcohol
- CAMTIA, Contact angle measurement tool based on image analysis
- LVDT, Linear variable differential transformer
- EN, European norm
- ASTM, American society for testing and material
- MOR, Modulus of rupture
- LOP, Limit of proportionality
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Chapter 1

Introduction and state of the art

1.1 Fibrous composite materials

Composites are heterogeneous materials where at least two phases interact to each other. These are differed mainly in chemical composition and both physical and mechanical properties. Such a material can be described as multi-functional synergistic system based on cohesive structure of its phases [1, 2, 3]. Resulting mechanical properties are influenced mainly by:

- properties of individual phases,
- volume amounts and arrangement of individual phases, and
- interaction between individual phases.

In the field of fibrous composite materials, the continual phase is formed by so-called matrix, which often exhibits relatively poor mechanical properties, especially in tensile strength. On the other hand, the discontinual phase, created by reinforcing fibers, is typical for its high toughness and mechanical performance [1, 4, 5]. In this case, resulting composite properties are given by:

- mechanical, surface, and geometrical properties of fibers,
- mechanical properties of matrix,
- amount of both phases, and
- interphase interaction (physical and chemical bonds, snubbing effect and related phenomena).

According to the mechanical theory of pliable continuum, whatever material is deformed under load. When the acting tension overcomes elastic strength limit of the material, its irreversible damage necessarily occurs. In the case of brittle or quasi-brittle materials under tension (caused by external loading, volume contraction, or surrounding conditions), the exceeding of their elastic response is accompanied by creation and development of cracks [6].
Application of fibrous reinforcement gives brittle material an ability of plastic deformation if designed and applied properly. The role of reinforcement is to bridge the crack (such an effect is known as the bridging or sewing effect) and to transfer tensile stress across the crack. The stress is thus dissipated into the broken matrix and the material macroscopic integrity and post-crack load carrying capacity are maintained. Post cracking behavior is driven by amount of bridging stress. If the bridging is capable to transfer higher tensile stress than the matrix does, so-called strain-hardening behavior occurs. This phenomenon is connected to multiple cracking behavior. In the other case, gradual formation of single crack arises (strain-softening) [7]. The principles described here are depicted in Figure 1.1. It has to be stressed out that the rate of stress transferred through fibers depends on their mechanical properties, amount, orientation, and especially on capacity of the interphase physical interaction – friction stress [8].

Figure 1.1: Stress-strain diagram of fibrous composite.

Importance of the interphase physical interaction between the fiber and the matrix is clear from equations for calculation of $\sigma_{\text{LOP}}$ – limit of proportionality and $\sigma_{\text{MOR}}$ – modulus of rupture, both in tensile\(^1\). These were derived by D. J. Kim et al. [10] as follows:

$$\sigma_{\text{LOP}} = \sigma_M (1 - V_f) + \alpha \tau_0 V_f \frac{L_f}{d_f} \quad (1.1)$$

and

$$\sigma_{\text{MOR}} = \lambda \tau_0 V_f \frac{L_f}{d_f} \quad (1.2)$$

where $\sigma_M$ is matrix limit of elasticity; $V_f$, volume amount of fibers; $\alpha$, coefficient reflecting distribution and orientation of fibers; $\tau_0$, shear stress between fiber coats and the matrix; $L_f$, fiber length; $d_f$, fiber diameter; and $\lambda$, coefficient describing fiber embedded length and other parameters relating to single fiber behavior during pull-out.

Note that both of equations listed above do not contain any information about fiber mechanical properties like tensile strength or Young’s modulus of elasticity. The modulus of rupture

\(^1\)Terminology adopted here originated from standard ASTM C1018-97 [9].
is given by the function of fiber volume, aspect ratio, and the physical interaction between the two materials [11].

1.2 Interaction between single fiber and matrix

The post-cracking response of fibrous composite materials described above depends on behavior of the single fiber during pulling out from the matrix. The whole process is divided into two stages (i) debonding and (ii) pull-out. When the chemical interaction is exceeded, tunnel crack between the two materials arises. The frictional stress (recall \( \tau_0 \) from Equations 1.1 and 1.2) is activated by mutual shift between them. If frictional stress is higher than bonding strength, such behavior is called as slip-hardening. Otherwise, that is slip-softening [12, 13]. It is clear that such behavior plays crucial role at the post-crack mechanical performance of fibrous composites.

M. Prinosil and P. Kabele [13] summarized findings of V. C. Li et al. [14] and C. Redon et al. [15] who described the dependence between the fiber free-end displacement and the force defies to it. Until to breaking chemical interaction, the maximal force \( P = P_{\text{deb}} \) is proportional to bonding strength. After that, a tunnel crack is formed between the two materials and the friction is activated \( (P_{\text{pull}}) \), as illustrated in Figure 1.2. The mathematical expressions are following:

\[
P_{\text{deb}} = \sqrt{\frac{\pi^2 E_f d_f^3}{2} \left( \tau_0 u + G_d \right)} \tag{1.3}
\]

\[
P_{\text{pull}} = \pi d_f \tau_0 \left[ 1 + \frac{\beta \left( u - \left( \frac{2\tau_0 L_e^2}{E_f d_f} + \sqrt{\frac{8G_d L_e^2}{E_f d_f}} \right) \right)}{d_f} \right] \times \left[ L_e - u + \left( \frac{2\tau_0 L_e^2}{E_f d_f} + \sqrt{\frac{8G_d L_e^2}{E_f d_f}} \right) \right] \tag{1.4}
\]

\( G_d \) is given by [16]:

\[
G_d = \frac{2 \left( P_{\text{deb}} - P_{\text{pull}} \right)^2}{\pi^2 E_f d_f^3}, \tag{1.5}
\]

and \( \tau_0 \), as a frictional stress after sudden drop following the peak pull-out load, by:

\[
\tau_0 = \frac{P_{\text{pull}}}{\pi d_f L_e} \tag{1.6}
\]

where \( E_f \) is fiber Young’s modulus of elasticity of fibers; \( d_f \), fiber diameter; \( \tau_0 \), interfacial shear stress between the fiber surface and the matrix; \( u \), fiber free-end displacement; \( G_d \), interfacial bond strength; \( \beta \), shear retention factor, parameter describing slip softening/hardening behavior; \( L_e \), fiber embedded length.

1.3 Fibrous composites in civil engineering

Fibrous composite materials frequently used throughout civil engineering are standardly based on inorganic calcium matrixes (cement- or lime-based). These are typical for brittle or quasi-brittle behavior. To eliminate issues connected with their cracking, randomly dispersed fibers
can be added into mixtures. Their amount differ from approx. tenths to units of volume percents. Presence of such fibrous reinforcement can ensure material integrity. Moreover, reinforced composite material could be more resistant against other aggressive agents (water, CO₂, and many others) penetration into its bulk volume.

1.3.1 Fibers

Reinforcing fibers frequently used in the field of civil engineering can be classified into several categories. According to material origin, those are divided into two groups – (i) organic and (ii) inorganic. Organic fibers are then subdivided into biogenic (animal hair and plant-based fibers) and synthetic (polymer, carbon, etc.) [17, 18, 19, 20]. Inorganic fibers are next classified as rock-based (glass, basalt) and others (steel). Other classification reflects fibers diameter and divides them into (i) macro-fibers (those with diameter about hundreds of micrometers) and (ii) micro-fibers (tens of micrometers diameter) [19]. One can also meet groups of (i) high-modulus and (ii) low-modulus fibers. However, the last classification is not relevant for us because the boundary between them is not established.

Organic biogenic fibers are characteristic especially for their relatively low mechanical properties and low chemical stability. On the other hand, those exhibit proper interaction with calcium matrixes thanks to their high water wettability. These fibers are often acclaimed due to low ecological burden [17, 18, 20]. Organic synthetic fibers are represented by many types of polymers, for example: polypropylene, polyethylene, polyvinyl alcohol, polyethylene terephthalate, nylon, etc. These consist of macromolecules which are typical for repetition of one or more atom kinds or their groups (mostly atoms of carbon, hydrogen, oxygen, nitrogen, chlorine, silicon) [21]. Polymer fibers have become popular due to their favorable price and chemical stability. However, their Young’s modulus of elasticity and tensile strength are not as good as in the case of inorganic fibers. Also their chemical and physical interactions with calcium matrixes are unacceptably low; their surfaces are too smooth and represent unfavorable high surface tension [22].
Table 1.1: Basic parameters of selected fibers [20, 28].

<table>
<thead>
<tr>
<th>Fiber type</th>
<th>Diameter [µm]</th>
<th>Spec. weight [g/cm³]</th>
<th>Tensile strength [GPa]</th>
<th>Young’s modulus of elasticity [GPa]</th>
<th>Elongation [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>8–9</td>
<td>1.60–1.70</td>
<td>2.50–4.00</td>
<td>230–380</td>
<td>0.5–1.5</td>
</tr>
<tr>
<td>Nylon</td>
<td>23–4000</td>
<td>1.14</td>
<td>0.75–1.00</td>
<td>4.1–5.2</td>
<td>16–20</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>25–1000</td>
<td>0.92–0.96</td>
<td>0.08–0.06</td>
<td>5</td>
<td>3–100</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>20–400</td>
<td>0.9–0.95</td>
<td>0.45–0.76</td>
<td>3.5–10</td>
<td>15–25</td>
</tr>
<tr>
<td>Kenaf</td>
<td>15–30</td>
<td>1.50</td>
<td>0.35–0.60</td>
<td>40</td>
<td>2.5–3.5</td>
</tr>
<tr>
<td>Steel</td>
<td>100–1000</td>
<td>7.84</td>
<td>0.50–2.60</td>
<td>210</td>
<td>0.5–3.5</td>
</tr>
<tr>
<td>Glass</td>
<td>14</td>
<td>2.68</td>
<td>3.50</td>
<td>72</td>
<td>2–3</td>
</tr>
<tr>
<td>Celulose</td>
<td>-</td>
<td>1.15</td>
<td>0.4–0.62</td>
<td>6.9</td>
<td>-</td>
</tr>
<tr>
<td>PVA</td>
<td>14–650</td>
<td>1.30</td>
<td>0.80–1.50</td>
<td>29–36</td>
<td>5.7</td>
</tr>
</tbody>
</table>

Glass, basalt or generally rock fibers, where SiO₂ is the key mineral, are considered to be representatives of rock-based inorganic reinforcement. These fibers are suitable for reinforcing of subtle constructions and materials due to their small dimensions (diameter standardly about 10–20 µm) and high Young’s modulus of elasticity. Thanks to high toughness, those can reduce crack formation in cement-based matrixes during hardening. Their significant drawbacks include brittleness and chemical instability in high acid or alkaline environment [23, 24]. For example, B. Wei et al. [25] found out in their study that basalt and glass fibers lost up to 10 % and 20 % from their original weight if exposed to 1-hour lasting treatment in 0.2M HCl, respectively. When exposed to 0.2M NaOH, the fiber weight was reduced by approx. 3 % and their tensile strength was reduced by unacceptable 80 %. Most of inorganic fibers are poorly wettable with water [25]. In order to reduce drawbacks described here, fiber surfaces are standardly coated by a thin layer of so-called sizing [26]. Such a treatment unfortunately significantly complicates study of their surface parameters and interaction with any matrixes. Steel fibers belong to the group of others inorganic reinforcement. These fibers reach on very promising mechanical properties and interaction with inorganic matrixes. On the other hand, their cost as well as weight is high [27]. An overview of fibers and their basic mechanical properties are summarized in Table 1.1.

1.3.2 Lime-based composites

Lime-based matrixes can be reinforced with fibers in order to reduce crack width caused by shrinkage and drying or to increase their ductility. Unfortunately, interaction between reinforcing fibers (namely rock-based and polymer) and the matrix is often poor due to problems indicated in Chapter 1.4. In some cases, reinforcement can be even separated from the matrix and thus makes essentially passive aggregate [20, 29, 30]. This phenomenon is demonstrated in Figure 1.3.

1.3.3 Cement-based composites

Fibrous composite materials with the cement matrix are nowadays widespread throughout civil engineering. They are often marked using abbreviation FRCC (fiber reinforced cement com-
The FRCCs are divided into two groups: (i) fiber reinforced concrete (FRC) and (ii) strain hardening cement composites (SHCC, often marked as ECC – engineered cement composites). The main difference between them is influenced by post-cracking behavior [31].

FRC is known since 1874 when it was patented [31]. It is usually reinforced with either steel (high-modulus) or rather polymer fibers (low-modulus) [32, 33]. The amount of reinforcement is mostly less than 1 % of the mixture volume [4, 7]. The role of fibers is to promote specific residual strength to loaded samples after the first crack occurs and thus to ensure macroscopical integrity of broken composite. Residual strength is usually less than elastic (earlier marked as $\sigma_{\text{LOP}}$, Chapter 1.1). The rate of residual strength is assessed in certain stages of crack mouth opening displacement (CMOD). For example, technical standard EN 14889-2 [34] requires FRC to exhibit at least 1.5 MPa and 1.0 MPa at CMOD of 0.5 mm and 3.5 mm, respectively. It is also worth noting that polymer fibers can be applied into concrete to increase its fire resistance. They sublimate during fire loading and thus create porous system where free water steam can diffuse without material destruction (spalling behavior) [35].

SHCCs are reinforced with significantly higher amount of fibers, usually from 3 to 10 % of the mixture volume. Such amount does not allow to apply rough aggregate into mixtures because of their workability. Contrary to FRCs, the role of fiber is to ensure strain-hardening behavior during post-cracking composite loading [4, 10, 27, 36]. Such reinforced materials are extremely expensive, hence their applicability is limited.

Similarly to lime-based matrixes, also those made from cement binders exhibit shortcomings connected with poor interaction (both chemical and physical) with reinforcing fibers. It is caused primarily by fibers surface properties. Consequently, irregular air pores in the interfacial transition zone between the two materials arise. It is clear that frictional stress can not be realized through them, thus fibers are not utilized as they should be. These pores are depicted in Figure 1.4, see the black areas.
1.4 Interface interaction failures

As it has been mentioned, most of reinforcing rock- or polymer-based fibers are typical for their unfavorable surface properties in terms of interaction with lime- or cement-based matrices. Their surfaces are chemical inert (related to mentioned binders) and smooth. Two basic parameters driving the interphase interaction between the two materials are as follows [12, 13]:

- chemical interaction (chemical bond strength),
- physical interaction (frictional bond strength).

High surface tension of fibers causes poor wettability with water [37] (water is always present in discussed matrixes), thus chemical interphase interaction between the two materials is not ensured. In the field of civil engineering, mechanical performance of fibrous composite materials are based rather on physical than chemical interactions. Nevertheless, chemical interactions influence the physical ones [38]. L. Yan et al. [39] demonstrated using electron microscopy that the cement matrix tends to copy fiber morphology even at nano-scale. If the fiber has hydrophilic character, then the contact area with the matrix is increased. Moreover, both chemical and physical bonds get more space where to interact [22, 40]. Anyway, the physical interaction between the two materials is influenced especially by fiber morphology (roughness). Frictional stress is increased with increasing fiber roughness.

It is desirable to have the fiber surface slightly rough and hydrophilic. Otherwise, the synergistic interaction between them and the matrix does not occur. It is required to exhaust fiber mechanical properties as much as possible and thus to reduce amount of fibers applied into mixtures. Such an approach is favorable from economical and technological point of view [36]. Table 1.2 proves that the utilization rate of fibers mechanical potential is in many cases too low. There are summarized results obtained during pull-out test of several types of fibers from lime or cement matrixes. $L_f$ indicates the fiber length, $L_e$ is the fiber embedded length, $P_f$ is force needed for fiber rupture, $P_{pull}$ is force needed for complete fiber pull-out, and $P_{rell}$ is efficiency.

\footnote{Fiber boundless were tested in some cases, therefore, it was not able to determine their diameter.}
### Table 1.2: Pull-out tests results \([12, 13, 16, 41]\).

<table>
<thead>
<tr>
<th>Fiber Material</th>
<th>Diameter ([\mu m])</th>
<th>(L_f) [mm]</th>
<th>(L_e) [mm]</th>
<th>Matrix Material</th>
<th>(P_t) [N]</th>
<th>(P_{pull}) [N]</th>
<th>(P_{rel}) [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acrylic</td>
<td>-</td>
<td>10</td>
<td>5</td>
<td>cement</td>
<td>0.24</td>
<td>0.18</td>
<td>75</td>
</tr>
<tr>
<td>Nylon</td>
<td>-</td>
<td>10</td>
<td>5</td>
<td>cement</td>
<td>0.50</td>
<td>0.15</td>
<td>30</td>
</tr>
<tr>
<td>PVA</td>
<td>40</td>
<td>8</td>
<td>5</td>
<td>lime</td>
<td>1.60</td>
<td>0.5–1.2</td>
<td>31–75</td>
</tr>
<tr>
<td>PP</td>
<td>40</td>
<td>15</td>
<td>7.5</td>
<td>cement</td>
<td>0.75</td>
<td>0.37</td>
<td>50</td>
</tr>
<tr>
<td>Steel</td>
<td>405</td>
<td>32</td>
<td>16</td>
<td>cement</td>
<td>296</td>
<td>170</td>
<td>58</td>
</tr>
<tr>
<td>Glass</td>
<td>-</td>
<td>60</td>
<td>30</td>
<td>cement</td>
<td>900</td>
<td>400</td>
<td>44</td>
</tr>
</tbody>
</table>

Indicator of fiber utilization given by:

\[
P_{rel} = \frac{P_{pull}}{P_t} \times 100\%
\]

### 1.5 Improvements of fibrous composites

In order to enhance mechanical properties of fibrous composites materials, three approaches can be employed \([27, 42, 43]\). All of them are based on theory explained in Chapter 1.1. Those are:

- Improvement of mechanical properties of matrixes,
- Increase of fibers amounts,
- Interphase interaction enhancements.

Mechanical properties of standardly used matrixes and fibers often reached on their economical possibilities in civil engineering. Whatever their other improvement is not effective. Increasing of fibers amounts is generally not possible due to economical and technological aspects. For example, the cost of reinforcement can reach up to one third of FRC total cost \([44]\). Moreover, workability of FRC mixture significantly decreases with increasing amount of fibers. The practical maximum of fiber reinforcement amount is equal to 0.75–1.0 % of mixture volume \([36, 45]\). So the, interphase interaction enhancement seems to be the possibility how to attain mechanical properties of fibrous composites in civil engineering effectively and justifies effort of many researches to deal with the related issues. The biggest area for improvement is presumably in fiber surface modifications.

### 1.6 Fiber surface modifications

In order to ensure strong chemical and physical interaction between reinforcing fibers and the matrix, it is necessary to treat fibers surface. The aim of the treatment is to increase \(P_{rel}\) defined by Equation 1.7 and thus \(\tau_0\) from Equation 1.6. There exist several methods for surface modifications. These are described below in separate subsections.
1.6.1 Mechanical methods

The aim of mechanical treatment is to roughen fiber surface. The effect can be achieved during composite mixture mixing by sharp aggregate edges. It has to be stressed out that such a treatment may lead to fiber damage (critical especially for brittle rock-based fibers) and the whole process is difficult to regulate [39]. It is also clear that the modification affects only physical parameters of fiber surface. Figure 1.5 shows the polymer fiber after mechanical roughening.

It is possible to include also shaping of malleable fibers into the category. This can be done only on steel fibers (twisted fibers – shaped by torsion or hooked fibers – modified by bending) [11].

![Figure 1.5: Damage of the polymer fiber after its surface roughening [38].](image)

1.6.2 Chemical methods

The purpose of chemical treatment is to modify surface layer of the fiber that is directly in contact with the matrix in the interfacial transition zone (ITZ). Such a treatment increases the area of fiber surfaces and helps to achieve required conjunctive transition between the two materials [16, 22].

The specific choice of chemical substance for the treatment is driven by fiber chemical composition. In the case of polymer or glass fibers, strongly alkali water solutions are employed, for example NaOH, Ca(OH)$_2$, H$_2$O$_2$, etc. [40, 46, 47]. Unfortunately, it should be noted that chemical treatment showed to be inapplicable due to demanding time requirements. The whole treatment takes standardly from several hours to days [40]. Moreover, it often affects bulk volume of fibers (not thin surface layer only), hence fibers mechanical properties are consequently significantly decreased. The over-treated fiber by 1 wt. % NaOH water solution is for illustration depicted in Figure 1.6.

1.6.3 Plasma methods

Plasma can be in general described as quasi-neutral ionized gas that is composed of ions, electrons, and neutral particles. These together exhibit collective behavior. Plasma is the first
state of matter [49] and can be created in both atmospheric and low-pressure conditions (tens of Pa) [50, 51]. Plasma methods are suitable (thanks to their thrifty impact on fibers bulk) especially for polymer, carbon, and rock-based fibers surface modifications [52].

It is also worth mentioning that experiments with plasma treatment of solid surfaces have started already in 1960s. R. Li et al. [53] noted that it has been published more than 5200 scientific papers (included in Copendex database) dealing with plasma effects during 1987–1995. Basic principles about plasma modifications of reinforcing fibers have been described approximately 20 years ago by V. C. Li [54, 55].

There are known two basic type of plasma methods, differing mainly in treatment process principle:

- plasma polymerization,
- plasma etching and activation.

1.6.3.1 Plasma polymerization

Plasma polymerization is based on the application of a certain monomeric thin layer directly to fiber surface. The film of controlled thickness and physical properties creates an adhesion bridge with the matrix and ensures an appropriate interaction between both materials [56]. The whole principle is based on activation and defragmentation of certain monomeric molecules through their collisions with highly-energetic electrons. For these purposes, gases with high amount of carbon and hydrogen are used (methane, ethylene, etc.) [57]. The monomeric molecules then adhere onto fiber surface. Created thin film could have nanometers of thickness, as shown in Figure 1.7. This method is proved to be appropriate for rock-based fibers. However, it is also very demanding on time consumption; the treatment takes up to a few minutes and requires low-pressure conditions [58].

1.6.3.2 Plasma etching and activation

This type of plasma treatment has a twofold effect on fibers (especially rock-based and polymeric); their surfaces are modified both chemically and physically [55, 59]. The principle is based on physical and chemical interaction of certain gases (O₂, H₂, Ar, CO₂, NH₃). Plasma decomposes working gas into active species. If fibers are exposed to thus created atmosphere,
their surface bonds could be replaced. Active polar groups are implemented onto their surfaces thanks to chemical bonds between them and the gas. Such a principle modifies fiber surface energy (trend depends on used gas). Consequently, fiber wettability is changed [60, 61].

Physical modification rests in fiber surface morphology treatment by means of the ion bombardment – sputtering effect, which renders the fiber surface rough [50]. This affects only upper thin layers of fiber surfaces, so fiber mechanical properties (depending on intact structure) stay undisturbed or it is minimized.

Although plasma treatment seems to be too complicated for practical purposes, it has found application in many industrial fields. For example, car manufacturer Audi equips dashboard indicator with plasma roughened polycarbonate glass covers in order to reduce light reflection and thus to provide better readability of on-board systems. This technology has shown to be effective also in such cases when it is necessary to print ink on smooth polymer surfaces. The ion bombardment slightly roughs the surface, thus ink adheres easily on it [62]. Both examples are shown in Figure 1.8.

Figure 1.7: Nano-scale layer of a monomer on glass fiber surface [56].

Figure 1.8: Examples of plasma treatment; improving of the print on the PET cap (left) and reducing of light reflectivity of polycarbonate glass covers (right) [62].
1.7 Analysis of fiber surface properties

1.7.1 Physical changes

In order to observe physical (morphological) changes of fiber surfaces after modification, several techniques can be employed. Because changes are visible only on micro- or rather nanoscale, high magnification and resolution are necessary. Scanning electron microscopy (SEM) image analysis fully meets these requirements and all the changes displays properly [37, 63]. Atomic force microscopy (AFM) allows to get information about topography and thus to quantify roughness of fiber surfaces [50].

1.7.2 Chemical changes

Chemical composition of polymer fiber surfaces can be analyzed using X-ray photoelectron spectroscopy (XPS). After peak positions deconvolution, the atomic concentrations of chemical elements on the surfaces can be calculated and presence of implemented active polar groups investigated [50, 64].

It is also possible to determine it using wettability measurement when fibers are exposed to certain polar liquid (for example demineralized water). The interaction between the two materials determines contact angles and allows to calculate surface tension. Water wettability of fibers is a crucial parameter, because it has significant impact on mechanical properties of composite materials based on lime or cement matrixes; these always contain water. Wettability can be observed on three-phase interface (liquid-solid-gas) and expressed at the form of contact angle. The angle is defined by a pair of tangents. The first of them delimits a boundary between solid/liquid, while the second one liquid/gas (gas is in standard situations represented by atmospheric environment) [65]. These principles are analogous for both planar and fiber-shape samples as illustrated in Figure 1.9. The angle depends on surface tension of all described phases; the relationship between them is explained by Young’s equation [65]:

\[ \gamma_{lv} \cos(\Theta_y) = \gamma_{sv} - \gamma_{sl} \]  

(1.8)

where \( \gamma_{lv}, \gamma_{sv}, \) and \( \gamma_{sl} \) is surface tension of following interphases: liquid/vapor, solid/vapor, and solid/liquid, respectively. \( \Theta_y \) is Young’s contact angle.

The contact angle between discussed materials can be determined using two approaches: (i) indirect force-based methods and (ii) direct optical methods.

Indirect methods (Strow, Packed cell, and Wilhelmy) are suitable especially for powders and shortly chopped micro- or nano-fibers. They rest in detection of weight changes of solid samples in contact with liquid. It is necessary to know solid sample geometrical properties, surface tension of liquid, and density of both materials. The change depends on buoyancy and wettability force defined by Wilhelmy as follows [50, 65]:

\[ f = \gamma_{lv} p \cos(\Theta) - V \Delta \rho g \]  

(1.9)

where \( \gamma_{lv} \) is surface tension of liquid; \( p \), circumference of wetted sample; \( \Theta_y \), searched Young’s contact angle; \( V \), volume of liquid adhering onto sample; \( \Delta \rho \), density difference between liquid and gas; and \( g \), gravitational acceleration.
Contrary to indirect methods, direct ones are based on visual observation of the contact angle using an optical goniometer. It is obvious that the three-phase interface must be enough magnified. Such a method provides clear and conclusive results. Unfortunately, it fails if the wettability is extreme. In such case, it is not possible to determine the contact angle properly [65, 66]. The most frequented method is called drop shape analysis. Sessile drop is dosed onto planar solid sample and then its shape is analyzed. Similar approach can be applied also on fibers submerged into liquid [66], see Figure 1.9.

1.8 Analysis of fiber-matrix interaction

When reinforcing fibers are modified and the change of contact angle is proved, it is necessary to verify fibers adhesion to the matrix. There exist two methods; each of them has different advantages and disadvantages, as summarized below.

1.8.1 Pull-out tests

Pull-out tests are based on fiber pulling out from a prismatic specimen of the matrix in direction of its longitudinal axis. The fiber is embedded into the specimen, while its anchor length is as a rule equal to a half fiber length, see Figure 1.10 for illustration. When is the specimen gripped in a static part of loading-frame, the fiber free-end is gripped by a movable part and then pulled-out from the matrix. Two parameters are observed during this tests: (i) fiber free-end displacement and (ii) force resisting to fiber pull-out [12, 13, 16, 41]. Such a method provides clear and valuable results; it answers the question how the two materials mutually interact. Moreover, frictional stress \( \tau_0 \), being necessary input data for fibrous composites numerical modeling, is thus analyzed (recall Chapter 1.2). On the other hand, the method can not be used for fiber bundles, fiberized reinforcement, so-called 3D reinforcement, and in such cases when the fiber is too small or pliable.
1.8.2 Mechanical tests

Mechanical tests are based on usually destructive experiments of specimens made from fibrous composite materials. Tensile, pressure, and most often bending (3- or 4-point) strength tests are employed in order to assess their behavior, especially after the matrix crack occurs. The bridging effect is then analyzed and evaluated [2, 36, 67]. These laboratory methods nearly imitate real conditions. Because of this, they are frequently used through technical praxis. Standardized procedures are described in technical standards. These are usually based on bending tests of notched specimens (dimensions from $40 \times 40 \times 160$ to $150 \times 150 \times 550$ mm), focusing on their residual strength during certain crack opening [68].
2.1 Introduction

2.1.1 Improvement in mechanical properties of mortars

Lime mortars consisting of aggregate, lime, and other secondary admixtures have been used for centuries as a joint material in constructions throughout history for facade plasters, masonry mortars, and filling materials [70]. Nowadays, lime mortars are frequently used for restoring historical buildings because of their compatibility with original materials, technologies, and other favorable properties [71, 72, 73]. To accommodate movement resulting from creep and thermal effects, typical for historical structures, such mortars should have a high rate of ductility [74, 75]. Ductility and other mechanical properties can be improved by (i) proper choice of aggregate (including origin, amount, shape) [72, 76], (ii) amount and type of each component (binder-aggregate ratio) [71, 77], and (iii) additive application (puzzolans, meta-kaolin, crushed bricks [78, 79], and fibrous reinforcement [7, 27, 30]).

Fiber reinforcement can be achieved using a wide spectrum of materials, including synthetic (polymer [29, 80]), natural (plant- or animal-based [17, 20]), and so-called rock-based materials (glass, basalt [25, 81]). Glass and basalt fibers have become popular due to their promising properties such as high Young’s modulus of elasticity and tensile strength, stability in high-alkali environments (if made from alkali-resistant enamel), and favorable costs [31, 82, 83].
The presence of fiber reinforcement improves ductility; however, the compressive and bending strength of such mortars is often negatively impacted.

Santarelli et al. [84] mechanically tested lime mortar samples reinforced with basalt fibers (length 6.35 mm, Ø 10-19 µm). They found that the toughness of samples containing 3 wt. % of fibers increased when compared to samples without reinforcement. However, flexural and compressive strength decreased more than twice in both cases. Iucolano et al. [30] and Asprone et al. [85], using identical materials, examined reinforced lime-based mortars containing basalt and glass fibers (l = 5 and 10 mm, Ø 8-10 and 13 µm, respectively) with weight amounts of 1 and 2 %. The ductility of thus reinforced mortars was enhanced, but compressive strength decreased by up to approx. 35 and 60 % for 1 % and 2 % wt. fiber amount, regardless to the type of fiber employed. Flexural strength decreased by approx. 25 %, in extreme cases. It is worth noting that these problems also hold true for cement-based materials, where conclusions of some studies differ. In such cases, where fiber content did not exceed 2 wt. %, compressive strength or flexural strength were constant or slightly increased [86, 87]. On the other hand, after exceeding this amount, the compressive strength significantly decreased [88]. Iucolano and Asprone et al. [30, 85] attribute this phenomenon to the porosity of a mixture. They pointed out that high fiber content causes the workability of a mixture to deteriorate, resulting in the higher mixture porosity. Moreover, poor adhesion between fibers and the matrix must be also taken into consideration.

2.1.2 Surface sizing

Glass or basalt fibers are abrasive to each other. It is therefore necessary to protect their surfaces by means of sizing, mostly based on the application of polymers such as epoxide, urethane, and polyester [26]. The presence of sizing on fiber surfaces can have a negative impact on fiber/calcium matrix interface interaction as shown by Scheffler et al. [89], who conducted pull-out tests of sized and additionally unsized single glass fibers from a cement matrix, finding that unsized fibers – in some cases – showed better interaction with a matrix then those which were sized. To overcome the unfavorable properties of sizing (such as smooth and low-energy surface, indicated in Figure 2.1 and the variant marked A), most researchers have completely removed sizing from fibers, leaving them to be further modified using plasma polymerization [56, 90, 91], plasma etching [10, 74, 92], chemical oxidative [46, 93], and other techniques. Such approaches are widespread in the field of composite materials based upon an organic matrix (acrylic, resin, or polyester). However, for a calcium matrix, where an aggregate characterized by sharp edges is almost always present, the risk of damage to brittle fibers arises, especially during mixing. Therefore, it is desirable to keep sizing on fiber surfaces but to modify it, in order to roughen its morphology and to increase its free surface energy.

Such principles were adopted by Han et al. [94] and Santos et al. [84], who used plasma etching treatment to roughen and activate sizing on carbon fibers. In their studies, surfaces were roughened (proven using AFM technology) and inter-laminar shear strength between treated fibers and the polypropylene matrix increased. However, it must be noted that too intensive treatment may lead to a reversible effect, which can lead to sizing removal, or fiber stripping.

---

1A layer protecting fiber surfaces against abrasion damage and gives them secondary functions such as protection of fibers from an alkali environment, lubrication (for better homogenization with other phases within a composite material), and compatibility with other materials.
Taking prior recommendations and findings into consideration, modification of sizing should be performed carefully, targeting both slightly roughened and activated sizing surfaces by active polar groups (represented in Figure 2.1 by variant B). Over-treatment of fibers (Figure 2.1, C) results in fiber stripping.

This study employs Han et al. [94] and Santos et al. [84] approaches in order to modify sized glass fibers employed in reinforcing a lime-based matrix.

![Figure 2.1: Principle of sizing modification via oxygen plasma.](image)

2.2 Materials and methods

2.2.1 Glass fibers

Alkali resistant glass fibers – specifically Cem-FIL Anti-Crack HP 12 mm chopped strand fibers from Owens Corning designed for reinforcing concrete, self-leveling floors materials, mortars, and plasters – were used in the present study. Fibers were coated by the manufacturer with sizing based on aminosilane non ionic surfactants (water-insoluble) in order to protect them against surface damage during mixing and to bond individual filaments to strands of approx. 100 pcs. For controlling and prevention of cracking in fresh and hard concrete and mortars, recommended dosage ranges from 1.0 (concrete and mortars) to 70.0 kg/m$^3$ (concrete-glass shells). Basic properties are: filament diameter, 14 µm; number of strands per 1 kg, 2 millions pcs.; tensile strength of strands, 1700 MPa; Young’s modulus of elasticity, 72 GPa; density, 2.68 g/cm$^3$; and elongation, 2.4 %. The fibers are indicated in Figure 4.2.

2.2.2 Lime-based mortars

Three types of lime-based mortars were tested, each of them representing a typical civil engineering application: (i) standard non-reinforced mortar (MR), which can be used for many purposes; (ii) mortar reinforced with a small amount of fibers (MB and MBT), commonly
used as a plaster; and (iii) mortar containing very high amount of fibers (MC and MCT), often employed as a filling material in structures exposed to extreme conditions, e.g., mortar bonding roofs elements such as imbrex and tegula, where preservation of macroscopic integrity is required, even for large deformations.

The reference mortar without fibers (MR) was used in order to compare its mechanical properties to the other two fiber reinforced mixtures. The MB mixtures were reinforced with reference fibers, while MBT was reinforced with plasma treated fibers. In this case, fibers were applied in order to control and prevent the mixture from cracking in both fresh and hardened stages. The amount of reinforcement was 1.8 kg/m$^3$. MC and MCT contained 93.75 kg/m$^3$ of reference and plasma treated fibers, used to create a ductile material. The composition of mortars tested was designed earlier for the reconstruction of historical buildings (Přinosil et al. [95]) and is summarized in Table 2.1. Compared to the composition of common mixtures, metakaolin was added to all mixtures designed in this study to enhance the mechanical properties of the mortars. Finely ground marble powder (grain size range from 0.025 to 0.25 mm) provided an optimum grading curve for high packing density.

Table 2.1: Weight-proportional composition of tested mixtures.

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Lime CL-90</th>
<th>Metakaolin Mefisto</th>
<th>Marble Lavaris</th>
<th>Sand 1 ST2 wt. %</th>
<th>Sand 1 STJ25 wt. %</th>
<th>Plasticizer Malmet HP</th>
<th>Fibers</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>MR</td>
<td>14.54</td>
<td>4.85</td>
<td>8.00</td>
<td>27.85</td>
<td>22.29</td>
<td>0</td>
<td>0</td>
<td>22.47</td>
</tr>
<tr>
<td>MA, MAT</td>
<td>14.51</td>
<td>4.81</td>
<td>7.80</td>
<td>27.96</td>
<td>22.22</td>
<td>0.21</td>
<td>0.07</td>
<td>22.42</td>
</tr>
<tr>
<td>MB, MBT</td>
<td>14.15</td>
<td>4.72</td>
<td>7.65</td>
<td>27.25</td>
<td>21.70</td>
<td>0.38</td>
<td>2.25</td>
<td>21.90</td>
</tr>
</tbody>
</table>

2.2.3 Plasma treatment

Glass fibers were subjected to low-pressure cold oxygen plasma in order to attain the required changes to their surfaces for sizing activation and roughening. Treatment was performed using
an inductively coupled plasma device (Tesla VT 214, 13.56 MHz). Constant plasma parameters were: total power, 100 W; total gas pressure, 56 Pa; and 50 sccm, oxygen flow. Exposition time ranged from 30 seconds to 16 minutes in order to find the required rate of treatment intensity, according to the approach described at the end of Section A.1. Together with fibers, silicate planar wafers (10×10 mm) were treated and their surface changes were then examined to understand how plasma influences silicon containing materials (the glass fibers were composed of more than 25 % Si [25]). Due to the planar shape of the wafers, surface changes on wafers can be observed more precisely than on fibers. These were treated for 4, 8, and 16 minutes.

2.2.4 Wettability measurements

Such measurement of fibers using demineralized water was performed to reveal the impact of chemical changes on the fibers surfaces. These are characterized by the presence of active polar groups (oxygen containing bonds in the case of the oxygen plasma treatment). Their occurrence is based on the assumption that more intensive plasma treatment leads to a higher number of polar groups [63]. Water, being an integral part of calcium – including lime-based – binders as a polar liquid, was chosen for its pure chemical composition. Wettability was quantified with a static contact angle measurement employing an optical direct horizontal goniometer. Individual fibers separated from strands were submerged in water perpendicularly. The menisci of water forming around the fibers were captured using a digital camera and evaluated by an in-house software according to the procedure described in [96]. Wettability of the silicon wafers was assessed by a method known as a sessile drop. The volume of water drops was 5 µl, dosed using a micropipette. Sessile drop shapes were photographed and the contact angles between the drop and planar planes of the wafers were evaluated using a See System device. All measurements were repeated ten times on unused samples to obtain statistically relevant data; results were averaged.

2.2.5 Morphology analysis

Fiber surface morphology changes after plasma treatment were observed with a scanning electron microscope (Merlin, Zeiss). Because sizing layer thickness is under 100 nanometers [26], large magnification (up to 5k×) was necessary to view roughness caused by ion bombardment. To eliminate surface charging during SEM analysis, fibers were coated with a thin gold layer using a plasma sputtering system (BOC Edward Scancoats Six). The thickness of the coating was approximately 10 nm, as measured by a surface profiler (Veeco Dektak 150).

2.2.6 Porosity analysis

Prismatic specimens with the dimensions of 40×40×40 mm (cut from blocks 160 mm long) were dried at 50°C to a constant weight using a dryer machine (Memmert). Each mortar mixture was represented by 6 specimens. The mixture of all mortars was cured and hardened for 28 days at 22 °C and humidity of 95 %. After stabilizing the weight loss of specimens (weighed once every two days), the specimens were saturated with water under low-pressure conditions (vacuum 0.2 kPa) for 24 hours to assess water open porosity following the ČSN EN 1936 [97]
standard. This made it possible to assess the influence of the amount of fibers on open porosity of the specimens. Recall that the phenomenon of porosity increase can be attributed to the use of fibers (see Iucolano [30] and Asprone et al. [85]). Knowing the porosity of all samples helped determining if the porosity of samples containing plasma treated fibers was less than those with reference fibers due to porosity reduction in interfacial transition zones.

2.2.7 Mechanical tests

Two types of destructive tests were performed: (i) a four-point bending test of specimens with the dimensions of 40×40×160 mm, and (ii) a compression test conducted on broken samples. Both tests were made following the ČSN EN 1015-11 standard [98]. A Veb Tiw Rauenstein FP100 (accuracy 0.1 N) loading frame was employed to provide displacement-controlled loading with a constant rate of 0.05 mm/min (bending tests) and 0.3 mm/min during (uniaxial compression). Special attention was paid to the ductility of specimens and assessment of post-cracking behaviors. At this stage, when fibers bridged the cracks and were pulled out of the matrix, flexural toughness provided an overview of fiber/matrix adhesion. When a single fiber pull-out test cannot be performed, this method provides an alternative for observing the mechanical interaction between two materials [99]. Uniaxial compression was carried out to assess the impact of fiber reinforcement on the compression strength of the composites. In both cases, twelve specimens were loaded and results were averaged to obtain statistically relevant data.

2.3 Results and discussions

2.3.1 Wettability measurements

These measurements of the silicon wafers confirmed that the mechanism of surface activation works, even for silicon-based materials. The averaged contact angle describing the interphase interaction between a water drop and reference wafers was 36.3±1.0°. After 4 and 8 minutes of the plasma treatment, wettability increased, i.e., contact angles decreased to 16.3±1.5° and to 7.6±1.5°, respectively. When treatment exceeded 8 minutes, contact angles were too small for optical measurement. These findings revealed the most effective parameters, such as power or gas, for fiber treatment and enabled prediction of how wettability affected the modified fibers. The most representative images obtained during wettability evaluation are given in Figure 2.3; all the results are summarized in Figure 2.5.

Wettability of reference fibers was very poor, as expected; averaged contact angle was 78.3±9.0°. After 1 minute of treatment, the angle decreased only to 70.1±7.0°. The most significant change occurred after 2 minutes of treatment, when the contact angle reached 43.5±7.0°. After additional treatment, wettability increased slightly. Measured contact angles were equal to 39.6±8.0° and 32.6±9.0° after 8 and 16 minutes of the treatment, respectively. Characteristic images obtained during wettability measurement are exhibited in Figure 2.4. Resulting contact angles belonging to specific treatment times are illustrated in Figure 2.5.

In order to reveal the treatment mechanism – i.e., to find the point at which sizing removal
is complete and the surface of glass fibers is stripped and exposed to plasma directly – results were compared to a study by Kim et al. [10] in which they modified unsized basalt fibers using the same approach used in this study. The composition of such fibers is a very similar composition to glass fibers; therefore, the two materials can be compared. Kim et al. [10] found that the contact angle of reference fibers was approx. 70°. Unlike the measurement for sized glass fibers, the angle decreased to approx. 35° already 10 seconds after plasma treatment. Wettability increase with longer treatment was comparable to our results. Based on these observations, it can be conjectured that the sizing of glass fibers was gradually removed from their surfaces during the first 1–2 minutes of treatment. With longer treatment, fibers can be considered to be completely stripped of sizing, which is unacceptable.

![Figure 2.3](image1.png)

**Figure 2.3:** Digital camera photos of the sessile water drop on silicon wafers. From left to right: reference, 4, and 8 minutes of plasma treatment.

![Figure 2.4](image2.png)

**Figure 2.4:** Digital camera photos of fibers protruding from water. From left to right: reference, 1, 2, 8, and 16 minutes of plasma treatment.

### 2.3.2 Morphology analysis

As observed by SEM microscope, the surfaces of reference fibers were covered by obvious layers of sizing that had different thicknesses and morphologies, see Figure 2.6. Sizing was detected between individual filaments, which bonded them together. After 30 seconds of plasma treatment, no noticeable changes on fiber surfaces were detected. Some fiber areas were slightly stripped and sizing was removed from cavities between mono-filaments. Significant changes were detected after 1 minute of treatment, the point at which sizing from treated fibers was roughened and gradually stripped away. Consequently, the modified fibers lost their protection against mechanical damage. As seen in Figure 2.6, D (8 minutes of the plasma treatment), sizing was completely removed from fiber surfaces.

Based on findings from wettability measurement and SEM morphology analysis, it can be concluded that a 60 s treatment period is optimal for the purpose of reinforcement, from both
the chemical and physical points of view. Although wettability increased only by approx. 10–11 %, more intensively treated fibers should not be used, due to excessive stripping.

Figure 2.5: Contact angles measured for fibers and silicon wafers as a function of plasma treatment duration.

Figure 2.6: SEM images of reference (A), 30- (B), 60- (C) and 480-seconds (D) treated fibers.
2.3.3 Porosity analysis

Open porosity of the reference (unreinforced) mortar was 36.1±0.4 %. Practically the same results were achieved with the mixtures reinforced by 1.8 kg/m³ of reference and plasma treated fibers; their porosity was 35.8±0.2 %, resp. 36.2±0.8 %. A high number of fibers (93.75 kg/m³) did not significantly affect the porosity of a mixture. Porosity for these specimens was 38.0±0.2 %, and 36.6±0.4 % for the use of reference, resp. treated, fibers. Results are summarized in Figure 2.7. It is clear that there is no difference between the porosity of mortars reinforced with reference or treated fibers. Similarly, porosity was not significantly influenced by using different fiber amounts. This finding differs from prior research by Iucolano et al. and Asprone et al., who found that by using of 2 wt. % of fibers in mortar mixtures, porosity increased from approx. 35–37 to approx. 52–54 %. It must be noted that they used more accurate mercury porosimetry. On the other hand, the relatively low porosity of all mortars tested in this study can be attributed to the use of finely ground marble powder (grain size 0.025 to 0.25 mm) to fill individual pores.

![Figure 2.7: Open porosity measured on cubic specimens.](image)

2.3.4 Mechanical tests

2.3.4.1 Four-point bending

The specimens reinforced by 1.8 kg/m³ of fibers were extremely brittle; after reaching the elastic limit, localization of damage in the form of a single crack was observed, with no softening in the load-displacement diagram. Such a brittle behavior can be attributed to the low number of fibers which could interlock the opening crack with cohesion. As depicted in Figure 2.8, specimens containing plasma treated fibers exhibited significantly worse behavior than those with reference fibers or non-reinforced samples. The maximal force recorded during loading samples with reference fibers was twice as high as those with treated fibers.
Specimens containing 93.75 kg/m$^3$ of fibers can be characterized as ductile. The elastic limit and ductility of mortars with reference fibers were higher than for the specimens reinforced with plasma treated fibers. While the maximal force recorded during loading reached 2 kN for samples with reference fibers, the force recorded for treated fibers only reached approx. 1.5 kN. The toughness of the samples reinforced with reference fibers was significantly higher than those with treated fibers. For instance, after reaching 1 mm of displacement, residual strength (force recorded during bending) of the samples containing reference fibers was approximately four times higher than the strength observed for treated fibers, as presented in Figure 2.9. Figure 2.10 demonstrates that even reinforced samples (regardless of the amount of fiber used) were broken by a single crack that gradually grew during loading in the post-cracking phase. This proves that crack bridging of fibers is poor due to low adhesion to the matrix, despite surface treatment. For the relatively brittle nature of the material and localization of damage into a single crack, the outer parts of specimens were not affected. Therefore, these could be used for the compression test.

2.3.4.2 Uniaxial compression

Compression tests revealed that there were not any substantial changes in the response of specimens during compression after incorporation of small amounts of reinforcement (MA and MAT). Unreinforced samples and those with reference as well as treated fibers commonly reached the maximal load of approx. 8.5–9.5 kN. Only the loading path beyond the elastic limit of reference samples had higher toughness than the specimens reinforced with fibers. Samples containing treated fibers once again exhibited the lowest ductility and limited strength. Load-displacement curves are presented in Figure 2.11.

For strongly reinforced samples, the resistance to compressive loading was lower in comparison to reference or slightly reinforced samples. Maximal force recorded during loading was 5.5 and 5.9 kN for the samples reinforced with reference and treated fibers, respectively. Such deterioration of mechanical strength can be attributed to an increase in sliding surfaces (i.e., in the interfacial zone between fibers and the matrix) rather than to the increase of porosity caused by using fibers as found by Iucolano et al. [30] and Asprone et al. [85]. It should be noted that the strength deterioration of the strongly reinforced specimens can be also attributed to the presence of defects due to low workability of such mixtures [100]. On the other hand, the reinforced samples exhibited very ductile behavior, which is often more important than high compressive strength. As shown in Figure 2.12, the force recorded after the samples were compressed by 2 mm was still approximately 65% of the maximum strength.

It can be concluded that plasma treatment of sizing did not produce any benefits. For treated fibers, bending and compression strength of loaded samples were lower than for the specimens reinforced with reference fibers. This contradicts findings by Han et al. [94] and Santos et al. [84], who improved mechanical properties of organic matrix based composite materials using similarly treated carbon fibers. For this study, the calcium matrix was probably too rough for treated glass fibers, which likely caused damage and consequent lost of mechanical properties. Due to very brittle behavior, sizing modification proved undesirable. Even slight roughening of sizing resulted in a loss of fiber protection against damage.
Figure 2.8: Load-displacement diagram from four-point bending tests on reference and slightly reinforced mortars.

Figure 2.9: Load-displacement diagram from four-point bending tests on strongly reinforced mortars.
2.4 Conclusion

This study examined the treatment of aminosilane sized glass fibers as a possible technique for increasing cohesion between their surfaces and lime-based mortar matrix. To activate and roughen the surface of sizing, fibers were subjected to oxygen plasma. After finding the most effective configuration of the treatment process, treated fibers were examined from the points of view of chemical as well as physical changes to their surfaces. Activation of surfaces was assessed using contact angle measurements. Morphology changes were observed by SEM microscopy. In order to observe adhesion between treated fibers and lime-based mortars, prismatic samples from these materials were produced and subjected to mechanical testing including both compressive and flexural tests. Two reinforced mixtures were prepared. The first was slightly reinforced (1.8 kg/m$^3$ of fibers) and represented typical mortars for the production of plasters, while the second was strongly reinforced (93.75 kg/m$^3$ of fibers) and represented a commonly
used filling material subjected to ultimate rate of ductility requirements. Open porosity for all hardened mixtures was examined in order to clarify how fibers added into mortar mixtures increase their porosity.

The experimental investigation revealed the following:

- Targeted wettability changes on fiber surfaces were achieved after two minutes of plasma treatment. During treatment, sizing was roughened or completely removed from fiber surfaces as a result of ion bombardment. Regarding chemical and physical changes to surfaces, fibers treated for 60 seconds were used for mortar reinforcement, although wet-tability was only improved by approx. 10–11 %.

- Open porosity was practically identical for all mixtures (included the unreinforced specimens), regardless of fibers used.

- Bending tests revealed that slightly reinforced samples with reference fibers exhibited significantly better bending toughness than those with treated fibers. In compressive tests, samples containing reference fibers had higher resistance to loading than those with treated fibers.

- For strongly reinforced samples, bending tests demonstrated that samples reinforced with reference fibers reached a maximal elastic limit approx. 25 % higher than samples containing treated reinforcement. These samples exhibited almost identical behavior during compressive loading, regardless of the fibers used.

Mortar samples reinforced with any amount of plasma treated fibers exhibited mechanical properties (strength and ductility) which were inferior to those with reference fibers. Although sizing was roughened slightly, fibers were stripped during plasma treatment and thus were exposed to abrasion damage during mixing.
3.1 Introduction

3.1.1 Fiber reinforced concrete

Fiber-reinforced concretes with discrete, short, and randomly distributed fibers have become popular in the construction industry over the past few decades. In some cases, fibers are intended to be the primary or even only reinforcement, while in other cases they only replace a portion of conventional reinforcement provided by steel rebars [19, 101, 102]. In order to reinforce a cementitious matrix, fibers must be easy to disperse in order to ensure uniform distribution, have suitable mechanical properties, and must be durable even with a long-term exposure to an alkaline cementitious matrix [103, 104]. All of the above mentioned properties have been reported for poly(ethylene terephthalate) (PET) fibers [105, 106].

Machovič et al. [40] have revealed that newly-formed multi-molecular layers enable chemical bonding between a PET surface and C-S-H gels in hydrated cements. Moreover, it has been established that PET fibers do not have any influence on the hydration of Portland cement [105]. The use of PET fibers enhances concrete properties and utilizes waste produced by the disposal of PET beverage containers effectively. Current worldwide production of PET products exceeds 6,700 million kg/year and a dramatic increase of production has been reported in China and India [104]. Recently, recycled PET has been utilized as replacement for conventional steel bars or carbon fiber reinforced polymer (CFRP) strips [107, 108, 109], because of
its corrosion-resistant nature and low cost.

PET fibers as dispersed reinforcement in engineered cementitious composites (ECCs) can produce enormous deformations when compared to ordinary Portland cement concrete \[4, 110, 111\]. The key to ensuring the ductility in ECCs is fiber-bridging of cracks. To achieve this strain-hardening behavior, matrix tensile strength must be lower than the maximum bridging stress that can be transferred by fibers \[112\]. The hydrophobic surface of PET fibers results in poor adhesion to any cementitious matrix and can therefore be very limiting \[113, 114\].

### 3.1.2 Modification of reinforcing fibers

To overcome issues mentioned above, various strategies have been employed to modify the surface structure of the fibers in order to make them more hydrophilic. Strategies include wet chemical treatment, flame treatment, mechanical micro-indentation, and various plasma treatments. Wet chemical treatment such as etching in an alkaline environment may cause a significant loss of mechanical fiber strength and the etching intensity is difficult to control. The disposal of waste products from such chemical modifications can introduce environmental burdens \[115\]. Flame or heat treatment causes fibers to become brittle under tensile stresses and can even trigger fatal polymer degradation. Mechanical micro-indentation is usually too rough and can significantly reduce the fiber cross-sections and is extremely difficult to implement on short fibers with small diameters \[114\]. Cold plasma treatment of fibers appears to be the most suitable non-damaging and energy-efficient alternative, with easily controllable outcomes \[2\].

Plasma is a medium consisting of electrons and positively charged ions and it exhibits quite different properties than common substances so is therefore referred to as the fourth state of matter. Plasma is quite rare on earth due to its high energy level, but 99 % of the universe is assumed to consist of plasma \[116\]. Plasma (ion beam) treatments have been employed since the 1980s to modify the surface properties of polymers, primarily in the textile industry. By selecting an appropriate feedstock gas and plasma exposure duration, rapid improvement in polymer surface adhesion, wettability, or dyeability can be achieved without altering original bulk properties \[117, 118\]. The effect of PET fiber plasma treatment is twofold: ion bombardment makes a surface rougher and the activation of polar groups on the fiber surface results in a reduction of surface energy which promotes chemical bonding with surrounding matrix \[57\].

Oxygen plasma treatment can be also considered for improving PET fibers produced directly by cutting beverage bottles. Such technology was proposed and tested by Fotti \[119, 120\] and the outcomes of our study could contribute to cheap and environmentally friendly production \[121\] of hydrophilic fibers with necessary properties. Such reinforcement could be used in concrete to increase ductility in cover layers which protect primary structural rebar reinforcements and thus enhance the durability of reinforced concrete structures.
3.2 Materials and methods

3.2.1 PET fibers

PET fibers 20 mm long were used as the dispersed micro reinforcement. This study focused on the performance of two different sets of fibers from primary and recycled PET (Figure 3.1), with diameters of 400 µm and 260 µm, respectively. Both kinds of the fibers, originally intended for the production of brooms and brushes, were produced by Spokar Company (Czech Republic). The longitudinal grooves along the fibers (Figure 3.2) resulted from the production process.

![Figure 3.1: PET fibers used as cementitious matrix reinforcement.](image1)

![Figure 3.2: Optical microscopy images of untreated PET fibers.](image2)

3.2.2 Reinforced cement pastes

Portland cement CEM I 42.5 R produced at the Mokrá Plant (Czech Republic) was used to produce a cementitious matrix (cement paste) lacking any aggregates. The same water to cement mass ratio, 0.4, was used for preparing all mixes.
Altogether, cement pastes with four types of reinforcing fibers and one lacking any reinforcement were prepared simultaneously in order to obtain results independent of the composition of the cementitious matrix. Each set was represented by 6 specimens. The first, reference mix (R) consisted only of Portland cement and water. Pastes reinforced by primary untreated fibers (PU), primary plasma treated fibers (PT), recycled untreated fibers (RU), and recycled plasma treated fibers (RT) were prepared next. The volumetric fraction of reinforcing fibers was equal to 2% of cement paste weight as suggested by Machovič et al. [40] and Ochi et al. [106], who found that content of PET fibers below 1.5% does not provide strain hardening. On the other hand, Khaloo et al. [122] found that fiber-reinforced concrete strength might be reduced after exceeding a reasonable volume fraction of fibers in the mix, resulting in poor workability and compaction of fresh concrete. Composition, water-cement ratio, and total porosities for all mixtures are summarized in Table 3.1. There were no aggregates or additives in the mixtures, which enabled better identification of the influence of each fiber type influence on effective properties.

Table 3.1: Summary of prepared mixes.

<table>
<thead>
<tr>
<th>Mix</th>
<th>Cement</th>
<th>PET Fibers</th>
<th>Water / Cement</th>
<th>Total Porosity [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>R</td>
<td>CEM I 42.5R</td>
<td>–</td>
<td>0.4</td>
<td>25.1 ± 0.7</td>
</tr>
<tr>
<td>PU</td>
<td>CEM I 42.5R</td>
<td>primary, untreated</td>
<td>0.4</td>
<td>23.5 ± 1.3</td>
</tr>
<tr>
<td>PT</td>
<td>CEM I 42.5R</td>
<td>primary, plasma treated</td>
<td>0.4</td>
<td>26.1 ± 0.2</td>
</tr>
<tr>
<td>RU</td>
<td>CEM I 42.5R</td>
<td>recycled, untreated</td>
<td>0.4</td>
<td>26.2 ± 0.4</td>
</tr>
<tr>
<td>RT</td>
<td>CEM I 42.5R</td>
<td>recycled, plasma treated</td>
<td>0.4</td>
<td>27.0 ± 0.3</td>
</tr>
</tbody>
</table>

Pastes were cast into prismatic molds (40×40×160 mm), which were compacted and unmolded after 1 day of hardening. Curing took place in a controlled laboratory environment at 20±1 °C and the specimens were submerged for 28 days in tap water in order to support a hydraulic reaction. Prior to testing, four specimens of each mixture were cut in half to be tested in compression. The dynamic Young’s modulus was continuously measured using resonance method on the uncut specimens.

3.2.3 Plasma treatment

PET chains with covalent characteristics are chemically inert and hydrophobic. In order to make PET fibers hydrophilic and increase their adhesion to the cementitious matrix, they were subjected to oxygen cold plasma in a vacuum chamber using a Diener Femto PCCE device. Oxygen plasma turned out to be very efficient in reducing the surface energy of polymers, as has been reported by Öktem et al. [123] and Mittal [124]. Oxygen or noble gases must be used during plasma treatment in order to stabilize free radicals formed on the surface being treated [125].

During plasma treatment, the fibers were enclosed in a glass vessel covered by a Petri dish. The dish has no influence on treatment results as demonstrated by Trejbal et al. [126] and prevents blocking of plasma chamber vacuum pumps by stirred fibers. The most suitable treatment duration established was 8 minutes and this exposure ensured a high level of surface roughening with no melting, scorching, and warping of fibers. The process took place at a low
gas pressure equal 110 Pa, with a power supply of 100 W, at frequency of 40 Hz and with gas supply equal to 16.9 sccm.

### 3.2.4 Wettability measurements

In order to quantify surface properties changes due to plasma treatment, static wetting angle measurements were conducted on the PET fiber specimens. As the hydrophobic character of surfaces changes to hydrophilic, wetting angle decreases. A digital single-lens reflex camera was used to optically measure contact angles on the surfaces of fibers half-submerged in distilled water. Measurement equipment included a Canon EOS 600D DSLR camera with a Tamron 70–300 mm objective lens, a gray neutral-density filter, a 50 mm focal length plano convex lens, and a Petri dish filled with distilled water. Backlight illumination was provided by a LED lamp together with a dispersing screen.

Wetting angle was evaluated for each fiber type on six fiber specimens separately using Nemetschek Allplan CAD software. Tangents were placed into the images of the outlines of the fibers and adhering water (Figure 3.3). Values obtained for each fiber are an average of two measurements on mutually opposite sides of the fibers.

### 3.2.5 Morphology analysis

A scanning electron microscope (SEM) was used to investigate the surface of the PET fibers before and after they were subjected to plasma treatment. Gold dust dispersed in the thickness of 10 nm over the surface of the investigated fibers provided the proper electric conductivity required to produce high-quality SEM images.

### 3.2.6 Porosity analysis

Total porosity of the broken pieces was measured after a four-point bending test using the pycnometric method. Each mix was represented with four specimens which had been crushed and ground so that all pores were opened.

### 3.2.7 Mechanical tests

Using the non-destructive resonance method, it was possible to track the evolution of the dynamic Young’s modulus, $E_{\text{dyn}}$, and investigate the influence of fibers on cement paste hardening. Such an approach is more reliable than evaluating elastic stiffness from force-displacement diagrams obtained from quasi-static compression tests [127]. If required, a static modulus of elasticity, $E_{\text{stat}}$, can be estimated according to the relationships determined by Rosell and Cantalapiedra [128] or Malaikah et al. [129], who claim that the $E_{\text{dyn}}/E_{\text{stat}}$ ratio ranges from 0.9 to 1.1.

The measurement of the dynamic Young’s modulus on prismatic specimens using the resonance method is based on the longitudinal vibration equation for beams with a continuously
Compressive and four-point bending tests were carried out using a Veb Tiw Raunenstein loading frame with a 300 kN capacity load-cell. Loading force and displacement records provided by LVDT sensors were gathered with a sampling frequency of 20 Hz. Both tests were displacement controlled in order to capture the descending part of the force-displacement diagram after reaching peak load. Special attention was paid to ductility enhancement and crack-bridging mechanisms, since the main purpose of fiber reinforcement is to facilitate stress transfer across cracks that form within very brittle cementitious matrix. This phenomenon is reflected mainly in post-cracking hardening observed during four-point bending tests.

Testing in four-point bending on 40×40×160 mm specimens was addressed to reveal the effect of fiber reinforcement on the response of cementitious materials to tensile stresses. LVDT sensors, independent of loading frame deformation, were used to provide an accurate deflection measurement. Specimens were symmetrically loaded and the span between cylindrical supports of 11 mm in diameter was equal to 120 mm and 60 mm for the fixed bottom and movable top supports, respectively. Loading rate was set to 0.05 mm/min and 0.15 mm/min in the case of reference and reinforced samples, respectively. A uniaxial compression test was conducted on prismatic 40×40×80 mm specimens (Figure 3.12) at a loading rate of 0.3 mm/min.

### 3.2.8 Crack bridging

The activation and gradual rupture or pull-out failure of individual fibers can absorb and dissipate external energy and stabilize crack propagation. Reduction of the crack opening prevents water and harmful chemicals from entering the matrix, which in turn increases its durability. When designed properly, fibers can efficiently control and arrest cracks promoted by mechanical loading or shrinkage of the matrix [131, 132]. The addition of suitable fibers can significantly alter the behavior of an intrinsically brittle cementitious matrix, creating a tough and ductile material [133].

In order to visualize strain concentrations and the behavior of cracks, digital image correlation (DIC) [134, 135] was employed. This technique overcomes the limitations of conventional contact measurement methods and allowed us to accomplish a full-field monitoring of displacement and strain fields during the four-point bending test. To evaluate displacements and deformations of DIC subsets within individual images, an artificial stochastic pattern had to be applied onto the surface of specimens being tested (Figure 3.8). A non-commercial software, Ncorr [136], together with the in-house postprocessing tool, Ncorr_post [137], was used for DIC calculation and analysis. Cracking patterns were visualized with a map of maximum principal strain in which concentrations can be attributed to the formation of cracks. Virtual extensometers that gather the magnitude of displacement in two arbitrary points were employed to monitor the crack opening and deflection of the tested specimens.

Images used for DIC analysis were taken with a DSLR camera Canon 70D at 10-second intervals in uncompressed format (.raw), yielding approximately 35 px/mm definition. Perfect illumination provided by artificial lighting allowed for a short exposure time (1/125 sec), with the light sensitivity (ISO) parameter set to 100. A focal length (zoom) of 55 mm with a distance between the camera and the observed surface of 80 cm ensured a minimal lens distortion effect.
Setting the subset spacing and radius to 8 px and 32 px, respectively, yielded displacement and strain fields consisting of 840 by 210 discrete values per specimen.

### 3.3 Results and discussions

#### 3.3.1 Wettability measurements

Results from wetting angle measurement demonstrate a positive impact of plasma treatment on the surface of the fibers with respect to their hydrophilic behavior, regardless of PET fiber type (primary or recycled). A summary of results is provided in Table 3.2, the most representative pictures are depicted in Figure 3.3.

![Illustration of wetting angle measurement on primary fibers; from left to right: after 0, 30, 60, and 90 seconds of plasma treatment.](image)

**Figure 3.3:** Illustration of wetting angle measurement on primary fibers; from left to right: after 0, 30, 60, and 90 seconds of plasma treatment.

<table>
<thead>
<tr>
<th>Treatment Duration [min]</th>
<th>Wetting Angle [°]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Primary PET</td>
</tr>
<tr>
<td>0</td>
<td>65 ± 10</td>
</tr>
<tr>
<td>4</td>
<td>27 ± 8</td>
</tr>
<tr>
<td>8</td>
<td>24 ± 7</td>
</tr>
<tr>
<td>16</td>
<td>26 ± 8</td>
</tr>
</tbody>
</table>

#### 3.3.2 Morphology analysis

The surface images with magnifications of 250× and 5000× were taken. Small droplets and longitudinal grooves, result of the fiber production process, are clearly visible in Figure 3.4. Plasma treatment of 8 minutes led to the formation of tiny fissures and holes on the fiber surface (Figure 3.5). An increase of fiber roughness is even more pronounced for fibers made of recycled PET. Exposure to plasma resulted in the formation of a hair-like surface morphology and intense cracking (Figure 3.6).
Figure 3.4: SEM images of untreated fibers from primary PET.

(a) magnification 250 ×
(b) magnification 5000 ×

Figure 3.5: SEM images of fibers from primary PET after 8 minutes of plasma treatment.

(a) magnification 250 ×
(b) magnification 5000 ×

Figure 3.6: SEM images of fibers from recycled PET after 8 minutes of plasma treatment.

(a) magnification 250 ×
(b) magnification 5000 ×
3.3.3 Porosity analysis

It is clear from Table 3.1 that specimens reinforced with plasma-treated fibers contained more pores. This can be attributed to the greater surface area of the fibers and hence their increased ability to retain water. However, this effect is nearly negligible with respect to the scatter of the measured data.

3.3.4 Mechanical tests

3.3.4.1 Young’s modulus

Silva et al. [103] found that the addition of PET fibers in the amount of 0.8 % by volume has no impact on the modulus of elasticity. We reached the same conclusions with our measurements of the specimens containing primary PET fibers. However, incorporating recycled fibers into cement paste led to a reduction in elastic stiffness (Table 3.3). The same phenomenon was generally observed in the case of pastes reinforced by plasma treated fibers. These retained more water on their surfaces and their addition resulted in increased porosity (recall Table 3.1). It can be conjectured that the increase in porosity is responsible for lower stiffness of specimens reinforced by plasma treated fibers (Figure 3.7).

Table 3.3: Development of the dynamic Young’s modulus the cement pastes reinforced by PET fibers.

<table>
<thead>
<tr>
<th>Mix</th>
<th>Average Dynamic Young’s Modulus [GPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>7 days</td>
</tr>
<tr>
<td>R</td>
<td>21.1 ± 1.1</td>
</tr>
<tr>
<td>PU</td>
<td>20.9 ± 0.4</td>
</tr>
<tr>
<td>PT</td>
<td>21.4 ± 0.6</td>
</tr>
<tr>
<td>RU</td>
<td>19.4 ± 1.3</td>
</tr>
<tr>
<td>RT</td>
<td>19.9 ± 2.1</td>
</tr>
</tbody>
</table>

3.3.4.2 Four-point bending

Even a slow loading rate of 0.05 mm/min was not sufficient to capture material softening during bending of reference specimens (Figure 3.9). Their extremely brittle behavior was a consequence of the lack of any reinforcement or aggregate that could interlock and provide the opening crack with cohesion. On the other hand, the constant loading rate of 0.15 mm/min was sufficient for tracking the loading-path beyond the elastic limit in all fiber-reinforced specimens. The crack bridging was, in almost all cases, too strong to allow the specimen separate into two parts and loading was stopped after reaching deflection of approximately 2 mm.

Figure 3.8 demonstrates pull-out failure for non-treated fibers caused by poor cohesion between the smooth hydrophobic fiber surface and the surrounding matrix. Therefore, the capacity of the fibers is not as fully utilized as in the case of treated fibers, which filed more frequently in tension. This is reflected in the significant enhancement of post-peak resistance
of specimens reinforced by primary plasma-treated PET fibers. On the other hand, the elastic limit of thus reinforced specimens was lower than in the case of specimens containing untreated fibers. This can be attributed to higher porosity of the material (recall Table 3.1).

The performance of both untreated fiber types was almost the same, not only in the terms of maximum load but also regarding the hardening observed during the crack opening after reaching maximum load, see Figures 3.10 and 3.11. When discussing treated fiber types, the primary ones are apparently more efficiently used, and this is demonstrated by quite significant hardening. The poor performance of recycled plasma treated fibers in comparison with other fiber types is even more pronounced than it was during the uniaxial compression test. The specimens reinforced by recycled plasma treated fibers exhibited a softening response and their ductility was limited.

3.3.4.3 Uniaxial compression

Force-displacement diagrams are presented in Figures 3.13, 3.14, and 3.15. Silva et al. [103] demonstrated that the addition of PET fibers into cementitious mortars at volumes of 0.4 and 0.8 % has no effect on compressive or flexural strength. However, these conclusions contradict our findings, which are similar to results reported by Ochi et al. [106]: that reinforcement of cement paste with PET fibers significantly increases compressive strength of the material. The fibers enhance resistance of the reinforced composite to the lateral tension which arises from the expansion of unconstrained specimens, thus suppressing transversal splitting.

However, the positive impact of PET inclusions on the resistance of a material subjected to compression should be primarily attributed to their shapes. Choi et al. [120] demonstrated that addition of aggregates made of recycled PET resulted in deterioration of concrete compressive strength. Kou et al. [138] conducted a similar study on concrete with partial replacement of conventional stone aggregates with recycled PET granulate. They found that such concrete exhibited enhanced ductility and resistance to chloride ion penetration, but its compressive
Figure 3.8: Four-point bending test and pull-out failure of recycled untreated fibers during the crack opening.

Figure 3.9: Load-displacement diagrams from four-point bending tests on reference specimens.
Figure 3.10: Load-displacement diagrams from four-point bending tests on specimens reinforced with primary fibers.

Figure 3.11: Load-displacement diagrams from four-point bending tests on specimens reinforced with recycled fibers.
strength and tensile splitting strength were reduced.

Recycled plasma treated fibers, having smaller cross-sectional areas which were further reduced by treatment, failed as reinforcements because the weakened fibers were not capable of efficient stress transfer across the cracks. The incorporation of weak recycled plasma treated PET fibers resulted in a negligible increase in resistance to compressive loading when compared to the reference mix (Table 3.4). On the other hand, the improvement of the interfacial bond between the primary plasma treated fibers and the surrounding matrix resulted in an enhancement in material resistance to uniaxial compression by 36% when compared with the reference mix. In order to increase the compressive strength of cementitious composites, it appears that the incorporation of plasma treated PET fibers with larger diameters into the mix is advantageous.

Figure 3.12: Loading the reference specimen during the uniaxial compression test.

Table 3.4: Results of uniaxial compression tests; $F_{\text{max}}$ and $d_0$ denote the maximum force reached during a test and the corresponding displacement, respectively.

<table>
<thead>
<tr>
<th>mix</th>
<th>$F_{\text{max}}$ [kN]</th>
<th>$d_0$ [mm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>R</td>
<td>59.5 ± 16.7</td>
<td>0.92 ± 0.13</td>
</tr>
<tr>
<td>PU</td>
<td>77.4 ± 7.7</td>
<td>1.04 ± 0.10</td>
</tr>
<tr>
<td>PT</td>
<td>76.7 ± 7.2</td>
<td>0.91 ± 0.08</td>
</tr>
<tr>
<td>RU</td>
<td>81.1 ± 10.8</td>
<td>0.93 ± 0.07</td>
</tr>
<tr>
<td>RT</td>
<td>61.9 ± 6.9</td>
<td>0.90 ± 0.07</td>
</tr>
</tbody>
</table>
Figure 3.13: Load-displacement diagram from compression tests on reference specimens.

Figure 3.14: Load-displacement diagrams from compression tests on specimens reinforced with primary fibers.
3.3.5 Crack bridging

Despite the strain hardening present during bending of the majority of PU, PT and RU specimens, no multiple cracking or branching of cracks was observed and tensile strain localized into a single cohesive crack. The cracking patterns captured with DIC on selected chosen representative specimens are presented in Figure 3.16. Cracks are visualized with a map of maximum principal tensile strain and the numbered marks indicate the positions of virtual extensometers. The first virtual extensometer (1) was located 3 mm from the bottom of the specimens, and the relative extensometer distance was 6 mm. Such a position and spacing allowed documentation of the crack opening without bias from elastic deformations or boundary effects. A second extensometer (2) was located in the vicinity of the supports in order to monitor the true deflection of the specimen.

The relationship between loading force action on the specimens during four-point bending and crack opening is presented in Figure 3.17. The larger force needed for opening of the crack in the case of the primary plasma treated fibers provides clear evidence of more efficient activation of the fibers when compared to primary untreated fibers. The poor cohesion of the crack bridged by recycled plasma treated fibers proves that these are not sufficiently strong enough to reinforce a cementitious matrix. The same conclusions hold when interpreting the DIC measurement results based on the dependence of the crack opening on specimen deflection (Figure 3.18). The enhanced capacity of stress transfer across the cracks bridged by primary plasma-treated fibers ensured increased bending stiffness. As a consequence, specimen deflection was two times lower than the deflection of specimens reinforced by primary untreated or recycled plasma treated fibers.
Figure 3.16: Crack development during four-point bending of selected representative specimens.
Figure 3.17: Relationship between loading force and the crack opening measured with virtual extensometer 1.

Figure 3.18: Relationship between the deflection of the specimen measured with virtual extensometer 2 and the crack opening measured with virtual extensometer 1.
3.4 Conclusion

The investigation of the morphology and performance of primary and recycled PET fibers when untreated and after the oxygen plasma treatment provided valuable findings to be considered in the design of fiber-reinforced cementitious composites. Oxygen plasma treatment proved to be very efficient in altering the surface of PET fibers as demonstrated by microscopy observations and with wetting angle measurements. Surface roughening with ion bombardment together with the activation of polar groups on fiber surfaces resulted in better adhesion of the fibers to the cementitious matrix and stronger interfacial bonding.

Based on the results presented here, it can be concluded that:

- Plasma surface treatment of both fiber types, primary and recycled, significantly increased their roughness, as demonstrated by microscopy images.
- The change of surface morphology made the fibers hydrophilic and led to a reduction of the wetting angle.
- The elastic stiffness of cementitious pastes reinforced by plasma-treated fibers was lower than those reinforced by untreated fibers due to higher water retention for such fibers and a consequently higher porosity of the composite.
- Reinforcement with plasma-treated fibers contributed to elevated compressive and flexural strength for primary fibers.
- Compressive strength was not enhanced by the addition of recycled plasma treated fibers to the reference paste and flexural strength was, if fact, reduced – these phenomena can be attributed to an excessive reduction in the cross-sectional areas of the recycled fibers, which were thinner than the primary ones.
- Plasma treatment of primary fibers ensured better activation and increased hardening after reaching peak load during the four-point bending tests.
- Performance of recycled fibers when subjected to tensile stresses was negatively affected by plasma treatment, resulting in gradual softening of the specimens when subjected to four-point bending.

The considerable bridging force provided by PET fibers, especially the plasma-treated primary ones, resulted in the formation of cohesive cracks and thus prevented excessive and abrupt cracking, thereby limiting the crack opening. A reduced crack opening promotes durability of fiber-reinforced cementitious composites by preventing water and harmful chemicals from entering a matrix. Better activation of fibers and gradual rupture combined with pull-out failure of individual fibers provides absorption and dissipation of external energy and stabilizes crack propagation.
4.1 Introduction

4.1.1 Interphase interaction in FRC

Fiber-reinforced composite materials used in structural engineering are most frequently based on a combination of steel or polymer fibers and inorganic cementitious matrix that exhibits brittle behavior [4]. Discrete, randomly oriented, and uniformly distributed fibers prevent a complete loss of stress transfer across cracks after reaching ultimate matrix strength in tension. Hence, the character of a cementitious material changes from brittle to ductile [19], if designed properly. In engineering practice, the fiber reinforcement is the most frequently utilized for (i) elimination of excessive shrinkage cracking and crack opening, (ii) rendering the reinforced material ductile in tension, and (iii) production of strain-hardening composites.

Strain hardening of a properly designed fiber-reinforced composite allows a multiple cracking as opposed to failing by a single brittle crack [4]. As a consequence, the material retains a macroscopic integrity even after reaching ultimate tensile strength, and a reduced crack opening prevents a penetration of harmful chemical agents. As suggested by Marshall et al. [140], the fiber bridging over cracks in a brittle matrix has the dominant influence on whether the material exhibits multiple cracking. When a fiber-bridged crack opens, the process of fiber extraction from a matrix can be divided into two stages: fiber debonding and pull-out [14, 15]. During the debonding stage, the fiber elastically deforms and the pull-out is restrained by chemical
Deterioration of bond. capacity of plasma-treated polymer fiber reinforc. and mechanical bonding with the surrounding matrix. Once the embedded fiber becomes fully debonded, a bridging force generated by friction stress over the fiber-matrix contact area re-strains the crack opening. The bridging force at both stages is fundamentally influenced by the fiber surface properties [11, 113, 114].

Because an inorganic cementitious matrix contains water, it was conjectured that a fiber surface wettability is an appropriate indicator of the fiber-matrix interfacial bond strength [141]. The limited adhesion of untreated polymer fibers to a cementitious matrix [142] results in easy debonding during fiber pull-out and weakening the interfacial zone due to a formation of micropores within the surrounding matrix [40].

4.1.2 Interphase interaction enhancement

Several strategies have been addressed to increase the fiber hydrophilicity, thus enhancing the interface strength. Cold plasma treatment appears to be the most suitable for its controllable outcomes [2, 55, 143], which is why plasma treatments have been quite extensively employed for a modification of polymer properties since 1980’s, mostly in the textile industry to improve surface adhesion and dyeability of fabrics [117, 118]. Unlike wet chemical treatment, the cold plasma technology can be considered eco-friendly [115] and fast, and plasma-treated fibers do not exhibit an excessive brittleness as in the case of hot air or flame treatments. A mechanical indentation of the fiber surface significantly reduces the effective fiber cross-sectional area and consequently its tensile strength. Therefore, such technology cannot be considered for fibers of small diameters [114].

The effect of plasma treatment is twofold (Figure 4.1): the ion beam bombardment renders the surface rough, while activation of polar groups on the polymer surface reduces the surface energy and promotes chemical bonding with a cementitious matrix [57, 67, 99]. A significant reduction of polymer surface energy caused by plasma treatment was reported by e.g., Öktem et al. [123] or Mittal [124]. Oxygen, or any noble gas, must be present during treatment in order to stabilize free radicals formed on a treated surface [125]. A few authors (e.g., [2, 141, 144]) reported that treatment in a duration of several seconds ensures sufficient surface modification, but the surface wettability was always tested immediately afterwards and not repeatedly in the long term.

![Figure 4.1: Principle of the oxygen plasma treatment modification; polymer surface before (left) and after (right) the treatment.](image)

Activation of chemical bonding cannot be considered permanent due to a reaction of the activated polar groups with airborne dust and air humidity [145]. Therefore, besides determi-
Deterioration of bond capacity of plasma-treated polymer fiber reinforcement is crucial for a successful implementation of the method in the construction industry. After a comprehensive literature review, we are not aware of any study focused on the issue of fiber bonding deterioration in fibers treated by cold oxygen plasma. The purpose of this paper is to fill that void and assess the rate at which the effect of plasma treatment decreases.

4.2 Materials and methods

4.2.1 Polymer macro fibers

The present study is focused on polymer macro fibers, i.e., those with a diameter larger than 0.1 mm and length exceeding 10 mm. These can substitute steel-fiber reinforcement, or even rebars and steel meshes. The tensile strength of such fibers is comparable to those made of steel, while their stiffness is up to 20 times lower. This can suppress the formation of shrinkage-induced cracking at the fiber-matrix interface [146, 147], and therefore enhance the interfacial bond. In contrast to steel fibers, polymer-based ones can be used as concrete reinforcement with no special finishing or cover to prevent injuries caused by their sharp protruding ends. Polymer fibers are also less harmful to shotcreting machines and easy to distribute in a concrete mix [148].

Commonly available materials used in the construction industry were chosen for the study. However, the outcomes are not limited only to the studied fibers, since these are typical representatives of a broad range of available polymer fibers intended for reinforcement of cementitious materials.

4.2.1.1 Coated fibers

Bicomponent elliptic coated fibers (Figure 4.2(a)) made of polyolefin are primarily produced as dispersed reinforcement to concrete. A compliant polymerous coating of a high-modulus high-strength core is declared to increase the adhesion between the fibers and the surrounding matrix. The bond is further enhanced through transverse folds in the surface. The coated fibers were selected to demonstrate whether the plasma treatment affects only the fiber surface, because a modification of the stiff load-bearing core would be translated into a reduction of the fiber tensile strength.

4.2.1.2 Uncoated fibers

Flat and slightly twisted uncoated fibers (Figure 4.2(b)) by a Czech manufacturer, made of a mixture of polypropylene (PP) and polyethylene (PE), were chosen as a cheaper alternative to the coated ones. The surface roughening by transverse folds is negligible, and there is no coating to support bonding with a cementitious matrix. The basic characteristics of both fiber types provided by their manufacturers are summarized in Table 4.1.

\[\text{In this paper, the term tensile strength refers to the maximal tensile force a single fiber can withstand.}\]
Deterioration of bond capacity of plasma-treated polymer fiber reinforcement.

![Coated fibers](image1.png) ![Uncoated fibers](image2.png)

Figure 4.2: Tested fibers commonly used as reinforcement of cementitious materials.

Table 4.1: Basic fiber parameters provided by their manufacturers, except for mass density of uncoated fibers which was assessed based on laboratory measurements.

<table>
<thead>
<tr>
<th>Fiber type</th>
<th>Material</th>
<th>Maximal thickness [µm]</th>
<th>Young’s modulus [GPa]</th>
<th>Length [mm]</th>
<th>Mass density [kg/m³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coated</td>
<td>Polyolefin³</td>
<td>500</td>
<td>≥10</td>
<td>50</td>
<td>910</td>
</tr>
<tr>
<td>Uncoated</td>
<td>PP, PE</td>
<td>480</td>
<td>5.17±0.5</td>
<td>55</td>
<td>~ 913</td>
</tr>
</tbody>
</table>

³ A specific type is not provided by the manufacturer.

4.2.2 Plasma treatment

The hydrophobic polymer fibers were subjected to a low-pressure oxygen cold plasma in order to increase their adhesion to a cementitious matrix. Treatment was accomplished in a vacuum chamber using an inductively coupled plasma device (Tesla VT 214). The fibers were exposed to plasma for different durations (5, 10, 30, 60, 120, 240, and 480 s) in order to determine the most suitable one that provides sufficient surface roughening without melting or excessive warping of the fibers. The process conditions were: 56 Pa, gas pressure; 100 W, RF power; and 50 sccm, oxygen gas flow.

4.2.3 Wettability measurements

The measure of hydrophilicity was quantified by static contact angle measurements using an optical method. The contact angles were evaluated from the images of fibers submerged in demineralized water utilizing an in-house software CAMTIA³. The tangents were placed and angles measured automatically at the outlines of menisci formed due to adhering water (Figure 4.5).

Deterioration of bond capacity of plasma-treated polymer fiber reinforc.

The measurements were performed four times – immediately (in less than 5 minutes at maximum) and 1, 7, and 30 days after plasma treatment. Each measurement was carried on a new set of fibers (each set was represented by six fibers) so that the surface could not be affected by the contact with water during previous measurements.

4.2.4 Morphology analysis

A mechanical surface disruption was observed by a scanning electron microscope (SEM) Maia 3, Tescan. To eliminate surface charging, the investigated fibers were coated with a thin gold layer using plasma sputtering system (BOC Edward Scancoats Six). The sputtering process parameters were as follows: deposition time, 40 s; sputtering voltage, 1.3 kV; current, 35 mA; and total gas pressure, 26.6 Pa. The gold layer thickness was approximately 10 nm, as measured by a profilometer (Veeco DekTak 150). The surface images were acquired at 5000× magnifications.

4.2.5 Weight loss

In order to assess a physical damage due to plasma treatment, the weight loss was measured on sets of fibers exposed to a different treatment duration using a high-sensitivity analytical scale (Kern ABS-N) with accuracy equal to 0.1 mg.

4.2.6 Fiber tensile strength

Tensile strength, or rather load-bearing capacity since the measured force is related to a single fiber and not its area, was tested using a loading frame Veb Tiw Rauenstein FP100. The same equipment was used for pull-out tests described in the following section. The experiment was displacement controlled at a loading rate of 0.8 mm/min until reaching 60 N and 0.6 mm/min afterwards until reaching the ultimate strength. Each set was represented by eight tested fibers.

4.2.7 Chemical analysis

A chemical composition of polymer fiber surfaces was analyzed by X-ray photoelectron spectroscopy (XPS) using an XPS spectrometer (Kratos, AXIS Supra) equipped with a hemispherical analyzer and monochromatic AlKα X-ray source (1486.6 eV). The XPS spectra were acquired from an area of 110×110 µm² with a take-off angle 90°. The survey XPS spectra were recorded with a pass energy of 80 eV, whereas high resolution spectrum scans with a pass energy of 20 eV. CasaXPS software with an implemented linear baseline and Gaussian line shapes of variable widths for a peak fitting was used for spectra processing. XPS peak positions were determined with an accuracy of ±0.2 eV. The atomic concentrations of chemical elements on the surface of polymer fibers were calculated from survey XPS spectra using CasaXPS software.
4.2.8 Pull-out tests

Fiber bonding to a cement paste made of Portland cement CEM I 42.5R was assessed by means of pull-out tests. The paste was prepared with water-to-cement mass ratio equal to 0.4 and cast into $25 \times 20 \times 25$ mm prismatic molds, compacted and unmolded after 1 day of hardening. Curing took place in a controlled laboratory environment at $20 \pm 1 \, ^\circ C$ and relative humidity of 50–60 % for 15 days.

The fiber anchoring length was equal to the height of specimens, i.e., 25 mm. Mortar samples reinforced with any amount of plasma treated fibers exhibited mechanical properties (strength and ductility) which were inferior to those with reference fibers. Although sizing was roughened slightly, fibers were stripped during plasma treatment and thus were exposed to abrasion damage during mixing. The pull-out tests were displacement controlled at a rate of 2 mm/min. The specimens were fixed in self-tightening clamps, while fiber free-ends were anchored by special clamping jaws preventing a notch formation.

Seven sets of specimens, each containing fibers with different combination of plasma treatment duration and exposure to atmospheric conditions, were prepared for both types of fibers. Each set was represented by six specimens. The response of fibers during pull-out testing was evaluated at abrupt the form of force vs. free-end displacement diagrams.

4.3 Result and discussions

4.3.1 Wettability measurements

A mean contact angle on reference (untreated) coated fibers was equal to $55.2 \pm 2.3 \, ^\circ$. Plasma treatment caused an increase in hydrophilicity demonstrated by a reduction of the contact angle to a range between $24 ^\circ$ and $29 ^\circ$, regardless the treatment duration. The deterioration of the plasma treatment effect was quite significant and abrupt – just 1 day after the treatment the contact angles ranged from $38 ^\circ$ to $51 ^\circ$. The values measured after 7 and 30 days were almost identical and approached the contact angles of the reference fibers. The transitory hydrophilization can be attributed to the exchange of surface atoms by oxygen ones. A graphical representation of the results is provided in Figure 4.3.

More hydrophobic uncoated fibers exhibited lower adhesion to water as demonstrated by a higher value of a mean contact angle reaching $82.1 \pm 2.8 ^\circ$ when untreated. After their hydrophilization by plasma treatment, the values of the contact angles ranged between $27 ^\circ$ and $35 ^\circ$. The values did not change substantially even after 1 and 7 days of the exposure to atmospheric conditions, regardless the plasma treatment duration. After 30 days, the contact angles increased to a range from $38 ^\circ$ to $52 ^\circ$ for all the treatment durations, i.e., only 63 % of the reference values. Therefore, it is assumed that the increase in hydrophilicity of fibers is caused by the permanent surface roughening, rather than by the unstable activation of polar groups. The evolution of contact angles is presented in Figure 4.4.
Figure 4.3: Evolution of contact angles measured on plasma-treated coated fibers.

Figure 4.4: Evolution of contact angles measured on plasma-treated uncoated fibers.
4.3.2 Morphology analysis

The surface of reference (untreated) fibers, both coated and uncoated, was smooth with rounded projections, (Figure 4.6). After 30 s of plasma treatment, the surface of fibers was noticeably altered and longitudinal grooves emerged (Figure 4.7). The surface of the fibers treated for 480 s was etched and scaly, and with residues of the coated polymerous coating (Figure 4.8). This corresponds with an atomic force microscopy (AFM) analysis of polypropylene films treated by dielectric barrier discharge by Wang and He [141]. They found that treated specimens were characterized by approximately 15 times greater roughness in comparison with the untreated ones.

4.3.3 Weight loss

It is obvious that plasma treatment causes weight loss (Figure 4.9), which is more pronounced in the case of treatment durations exceeding 60 s. After 480 s, the coated and uncoated fibers lost
Deterioration of bond capacity of plasma-treated polymer fiber reinforce.

2.4 % and 4.7 % of their weight, respectively. This can be attributed to the ion bombardment resulting in a sputtering of the fiber surface. Moreover, the presence of oxygen with broken covalent bonds could cause oxidation of the material.

### 4.3.4 Fiber tensile strength

The results presented in Figure 4.10 indicate that the surface of coated fibers was not significantly damaged, which is in agreement with the results of SEM. The fibers retained their tensile strength, because plasma treatment affected only the fiber coating, and the load-bearing core remained intact.

On the other hand, the uncoated fibers exhibited up to 40 % reduction in their tensile strength after the exposure to plasma for more than 120 s. Based on the weight loss measurements, presented earlier, it is obvious that the strength reduction was not caused purely by the loss of material, but also because of its degradation, since the maximal weight loss reached only 4.7 % and the fiber tensile strength should be proportional to its cross-sectional area. Excessive weakening of fibers could potentially lead their rupturing instead of pull-out and consequent brittle behavior of the composite.
Figure 4.9: Dependence of fiber weight loss on the duration of plasma treatment.

Figure 4.10: Fiber tensile strength after plasma treatment of different durations.
4.3.5 Chemical analysis

The XPS spectra of coated fibers were calibrated on binding energy of 285 eV, which corresponds to a C-C bond [149]. The deconvolution of C 1s peak was made into 4 peaks (Figure 4.11): C-C/C-H (285 eV), C-O (286.6 eV), C=O (287.8 eV), and O-C=O (289 eV) [149, 150]. According to Chen et al. [151], the obtained C 1s XPS spectra of uncoated fibers were fixed at 284.7 eV (C-C/C-H bond). The C 1s peak of a reference uncoated fiber was fitted with two peaks: C-C/C-H (284.7 eV), and C-O (286.3 eV) [151]. Although treated uncoated fibers were deconvoluted into 4 peaks (Figure 4.12): C-C/C-H (284.7 eV), C-O (286.3 eV), C=O (287.9 eV), and O-C=O (288.9 eV) [151, 152].

The XPS analysis of chemical composition of both fiber types was carried out 1 day after oxygen plasma treatment with a focus on the influence of treatment duration. The analysis revealed a dramatic increase of the oxygen content after the treatment (Figure 4.13). Reference coated fibers initially contained a higher amount of oxygen (about 2 at. %), probably due to the fabrication process, whereas uncoated fiber contained about 1 at. %. The comparison of obtained XPS data showed that a prolonged oxygen plasma treatment led to the bonding of 48 at. % of oxygen on the surface of the coated fiber and only 21 at. % in the case of the uncoated fiber.

The chemical bond concentrations on the fiber surface were estimated from deconvoluted high resolution C 1s XPS peaks and summarized in Table 4.2. It was found that reference coated fiber had 7 % of oxygen containing bonds, i.e. C-O, C=O, and O-C=O, while the uncoated one had 2 % (only C-O bonds were identified in C 1s peak). The analysis of deconvoluted C 1s peaks of both polymer fibers revealed the tendency of oxygen containing bonds to change as a function the treatment time.

In the case of coated fibers, 5 s plasma treatment caused a rapid transformation of C-C/C-H bonds into C-O, C=O, and O-C=O bonds, and the total concentration of oxygen containing bonds increased to 17 %. After 30 s plasma treatment of coated fibers, concentration of oxygen containing bonds increased to 21 %. The plasma treatment of coated fibers for 480 s caused another concentration increase of oxygen containing bonds to 34 %. In case of uncoated fibers subjected to 5 s plasma treatment, there was observed an increase in concentration of C-O, C=O, and O-C=O bonds to 14 %. After 30 s plasma treatment the concentrations of oxygen containing bonds decreased to 18 %. More pronounced changes were observed after 480 s of plasma treatment, where the total concentration of oxygen containing bonds increased to 41 %.

4.3.6 Pull-out tests

Regardless the plasma treatment duration, both types of fibers manifested a similar linear behavior during the debonding stage, see representative load-displacement diagrams in Figure 4.14. However, the response of the coated fibers was stiffer, especially in the case of the reference fibers, which can be attributed to more pronounced transverse folds. These folds are also responsible for repeated hardening during pull-out as demonstrated by the jerks in the diagrams, while the response of uncoated fibers was smooth and almost linear.

Next, interfacial shear stress was calculated to provide values normalized by the fiber sur-

---

1 at. % stands for an atomic concentration.
Figure 4.11: Deconvolution of C 1s peaks of coated fibers before and after plasma treatment.

Table 4.2: Concentration of chemical bonds calculated from deconvoluted C 1s XPS peaks.

<table>
<thead>
<tr>
<th>Fibers</th>
<th>C-C/C-H [%]</th>
<th>C-O [%]</th>
<th>C=O [%]</th>
<th>O-C=O [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coated, reference</td>
<td>93</td>
<td>6</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Coated, 5 s</td>
<td>83</td>
<td>13</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>Coated, 30 s</td>
<td>79</td>
<td>14</td>
<td>2</td>
<td>5</td>
</tr>
<tr>
<td>Coated, 480 s</td>
<td>66</td>
<td>22</td>
<td>2</td>
<td>10</td>
</tr>
<tr>
<td>Uncoated, reference</td>
<td>98</td>
<td>2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Uncoated, 5 s</td>
<td>86</td>
<td>8</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>Uncoated, 30 s</td>
<td>82</td>
<td>10</td>
<td>5</td>
<td>3</td>
</tr>
<tr>
<td>Uncoated, 480 s</td>
<td>59</td>
<td>21</td>
<td>5</td>
<td>15</td>
</tr>
</tbody>
</table>
Figure 4.12: Deconvolution of C 1s peaks of uncoated fibers before and after plasma treatment.
face area. Such parameter is crucial when evaluating fiber bridging in cementitious composites. The stress was calculated at distinct stages: (i) when the pull-out force reached its maximum (Figure 4.15), and (ii) when the free-end displacement reached value 3.5 mm\(^1\) (Figure 4.16). The respective values of the interfacial shear stress were calculated as

\[ \tau_{\text{max}} = \frac{F_{\text{max}}}{C_f l_e} \quad \text{and} \quad \tau_{3.5} = \frac{F_{3.5}}{C_f l_e} \]  

(4.1)

where \(F_{\text{max}}\) and \(F_{3.5}\) represent the maximal force and force necessary to reach 3.5 mm free-end displacement, respectively. \(C_f\) is a fiber circumference and \(l_e\) is an embedded fiber length. According to Li et al. [14, 153], the maximal interfacial shear stress, \(\tau_{\text{max}}\), is related mainly to chemical bonding, while the interfacial shear stress at 3.5 mm free-end displacement, \(\tau_{3.5}\), is exclusively related to a surface roughness.

Plasma treatment of the coated fibers had a positive effect on both investigated interfacial shear stresses, \(\tau_{\text{max}}\) and \(\tau_{3.5}\). On the other hand, neither the treatment duration nor the exposure to atmospheric conditions influenced the fiber behavior significantly. Maximal stress, \(\tau_{\text{max}}\), decreased only by 10 % after 7 days of deterioration independently of treatment time (30 or 480 s). The treatment impact was even more accentuated in the case of stress at 3.5 mm free-end displacement, \(\tau_{3.5}\), and the deterioration after 7 days reached 8 % for the both treatment durations.

The behavior of uncoated fibers was similar to that of the coated ones, only the increase in stresses magnitudes was more substantial. After 7 days of exposure to atmospheric conditions, the reduction in maximal stress, \(\tau_{\text{max}}\), was 9 and 12 % for 30 and 480 s of plasma treatment, respectively. In the case of stress necessary to reach 3.5 mm free-end displacement, \(\tau_{3.5}\), 7 days of exposure to atmospheric conditions resulted in 11 and 14 % reduction for 30 and 480 s of plasma treatment, respectively.

\(^1\)A recommendation of EN 14845-2, which requires a residual strength in a fiber-reinforced concrete evaluated at crack mouth opening displacement (CMOD) equal to 3.5 mm [68].
Figure 4.14: Pull-out force-displacement diagrams; reference fibers (top), 30 s treated fibers after 0 days (middle) and 7 days (bottom) of exposure to atmospheric conditions.
Figure 4.15: Comparison of maximal interfacial shear stresses for various treatment duration and exposure to atmospheric conditions.

Figure 4.16: Comparison of interfacial shear stresses at 3.5 mm pull-out for various treatment duration and exposure to atmospheric conditions.
4.4 Conclusion

The main objective of the present study was to assess the rate of bonding deterioration for oxygen plasma-treated fibers. To this purpose, complex coated as well as common uncoated macrofibers were chosen. The plasma induced surface roughening, favorable to bonding, was revealed by microscopy observations. XPS analysis detected chemical bonds that increase the adhesion to liquids. Pull-out strength tests and contact angle measurements were repeated for several days to assess the changes of surface properties when exposed to atmospheric conditions.

Regarding the duration of plasma treatment, we report the following findings:

- The weight loss attributed to the surface damage was proportional to the plasma treatment duration; since the weight loss is associated with a reduction of mechanical strength, the rule “the more, the better” does not apply here.
- The exposure to plasma for more than 120 s led to a quite significant reduction of tensile strength of the uncoated fibers, while the strength of the coated ones was almost independent of the treatment duration.
- For both types of fibers, even the shortest oxygen plasma treatment (5 s) led to a significant increase in oxygen content in comparison to the non-treated fibers, indicating enhanced hydrophilicity; such implication was confirmed by the water contact angle measurements.

Based on the results of pull-out testing and contact angle measurements, it was observed that:

- The contact angles increased over time due to exposure of treated fibers to atmospheric conditions; the coated fibers almost immediately approached values measured on the reference (untreated) specimens, while the uncoated fibers almost retained their enhanced hydrophilicity.
- The bonding strength of the fibers at pull-out increased significantly after their exposure to plasma for 30 s, but there was no further benefit from longer treatment times.
- The interfacial shear stresses, both maximal and at pull-out, were negligibly reduced due to exposure of treated fibers to atmospheric conditions, suggesting that the chemical bonding has a minor impact on the strength of the interface between the fibers and cementitious matrix.

It can be concluded that regardless the type of fibers, there is no need for their incorporation into a concrete mix immediately after cold oxygen plasma treatment. As demonstrated by the wettability tests, the increased hydrophilicity by activation of chemical bonds is not permanent, but the interfacial shear strength almost does not change for fibers exposed to air after their treatment. Therefore, the enhanced bonding to a cementitious matrix can be attributed to an increase in the fiber surface roughness rather than activation of chemical bonds. It was found that prolonged treatment has no positive impact on fiber surface properties and bonding to the cementitious matrix. In order to avoid a significant reduction in tensile strength of fibers, it is advised to treat fibers for less than 1 minute.
Chapter 5

Mechanical properties improvement of fiber reinforced concrete

Based on: J. Trejbal, V. Nežerka, R. Hlůžek and Z. Prošek, Mechanical properties improvement of fiber reinforced concrete, Acta Polytechnica CTU Proceedings, 15th Conference on Special Concrete, paper accepted for publication, 2018. Extended of other results [154].

5.1 Introduction

Fiber reinforced concrete (FRC) has become popular at production of prefabricated concrete materials, shotcretes, and industrial high-loaded floors. Such material is composed from polymer macro-fibers (amount approx. up to 1 % vol. of whole mixture), cement, and aggregate [27, 95].

Technical standards EN 14845-1 and EN 14845-2 [68, 155] describe FRC as structural concrete reinforced with fibers having static effect and fulfilling requirements of EN 14889-2 [34]. During three-point bending test of notched specimens 550×150×150 mm, FRC has to exhibit residual strength at least 1.5 MPa and 1.0 MPa at crack mouth opening displacement (CMOD) of 0.5 mm and 3.5 mm (corresponding deflection 0.47 mm, resp. 3.02 mm), respectively. It is clear that such behavior differentiates the FRCs from strain hardening or engineered composites [95].

D. J. Kim et al. [10] explained that strength limit of a fibrous composite material (including FRC) is a function of fibers volume, fibers length to diameter ratio, and the interfacial interaction between fiber surfaces and the matrix. In the field of FRCs, it means that increasing fibers amount weakens the cement matrix mechanical properties in the stage of elastics response during loading. It is therefore clear that fibers amount should be as small as possible. On the other hand, once the matrix limit of proportionality is overcome and the matrix is damaged by the crack, fibers transfer the acting stress across the crack (crack bridging) and thus ensure macroscopic integrity of reinforced material. Amount of stress transferred via fibers depends
Mechanical properties improvement of fiber reinforced concrete especially on their number and on adhesion between fiber surfaces and the cement matrix. However, adhesion is mostly too poor, especially between polymer fibers and the cement matrix due to fibers smooth and chemically inert surfaces (related to the cement matrix) [12, 16]. Mechanical potential of fibers – tensile strength – is therefore unused. Post-cracking response of FRC is influenced by behavior of the single fiber that is pulled out from the matrix. This phenomenon was described by Ch. Li et al. and C. Redon et al. [53, 156]. The behavior is divided into two stages, the first describes a chemical interaction between the two materials ($P_{\text{deb}}$), while the second one a mechanical interaction activated by fiber movement out of the matrix ($P_{\text{pull}}$), as stated in Equations 1.3, 1.4, 1.5, and 1.6 in Chapter 1.

To avoid issues connected with poor adhesion between the two materials, some researches have applied additional treatment of fibers in order to increase their surface free energy and to increase their morphology, both ensuring improvement of bond with the matrix. For these purposes, several types of treatments may be employed, e.g. chemical (use of high alkali solutions) and physical (mechanical roughening) [38, 39, 157]. The plasma modification has shown to be a promising technology, combining both the chemical (etching) and the physical (roughening caused by a ion bombardment) treatment, as proven by Li et al. from the early 1990s [54, 59] and many other researches later, e.g. [139, 158, 159, 160]. It is also worth noting that such treatment has been extended through many industrial fields over the past few years, especially for the surface treatment (roughening, activating, cleaning) of polymeric materials [161]. Therefore, there is no obstacle to apply such technology during surface treatment of the fibers.

Although a benefit of the fiber surface treatment was proven from the perspective of "surface science" many times, this was not achieved from the practical point of view, including the field of FRCs. To connect theoretical findings with praxis of civil engineering, we studied an influence of plasma modified fibers on mechanical properties of FRC samples using numerical simulations, following EN 14845-1 [155].

5.2 Materials and methods

5.2.1 Polymer fibers

Three types of polymer macro-fibers were used for following experiments. Fibers marked as "Coated" and "Uncoated" were used for research described earlier, within Chapter 4. Recall that these fibers are primarily intended for FRCs reinforcing. As their cheaper alternative, polypropylene fibers made by Czech manufacturer Spokar were also used (see Figure 5.1). These fibers are originally intended for the production of brooms and brushes. Their mechanical properties have been determined experimentally, as reported in [64]. All used fibers geometrical and mechanical properties are summarized in Table 5.1.
Table 5.1: Basic fiber parameters provided by their manufacturers or assessed based on laboratory measurements.

<table>
<thead>
<tr>
<th>Fiber type</th>
<th>Material</th>
<th>Maximal thickness [µm]</th>
<th>Young’s modulus [GPa]</th>
<th>Length [mm]</th>
<th>Mass density [kg/m³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coated</td>
<td>Polyolefin^a</td>
<td>500</td>
<td>≥10</td>
<td>50</td>
<td>910</td>
</tr>
<tr>
<td>Uncoated</td>
<td>PP, PE</td>
<td>480</td>
<td>5.17±0.5</td>
<td>55</td>
<td>~913</td>
</tr>
<tr>
<td>Spokar</td>
<td>PP</td>
<td>305</td>
<td>6.1</td>
<td>55</td>
<td>~900</td>
</tr>
</tbody>
</table>

^a A specific type of polyolefin is not provided by the manufacturer.

5.2.2 Plasma treatment

Fibers were subjected to a low-pressure oxygen cold plasma treatment using device Tesla VT214. Based on finding described in Chapter 4, parameters of the treatment were set as follows: power of RF source, 100 W; gas pressure, 20 Pa; treatment duration, 30 seconds.

5.2.3 Pull-out tests

Prismatic specimens having dimensions equal to 25×20×25 mm were made from cement paste composed of Portland cement CEM I 42.5R, water-to-cement ratio 0.4. Each specimen contained a single fiber in its centerline (fiber embedded length was equal to samples height – 25 mm). Their curing took place in standard laboratory conditions (20±1 °C and relative humidity of 50–60 %) for 15 days. Then, these were subjected to pull-out tests. The experiment was carried out using loading frame Veb Tiw Rauenstein FP100. The specimen was anchored by its matrix body to a static part of the frame, while the single fiber, protruded from the specimen body, was caught by a moving frame part. The loading was displacement controlled at the
constant rate of 2 mm/min and finished after reaching 4.5 mm of fiber free-end displacement. The output of the test was dependence between fiber free-end displacement and force defiant to it.

According to Equation 1.6, maximal interfacial shear stresses were calculated from thus obtained results. Consequently, these were used as basic input values for numerical modeling of FRC bending tests.

5.2.4 Numerical simulation

5.2.4.1 Aim of numerical simulation

Numerical simulations theoretically followed procedure of three-point bending test described in technical standard EN 14845-2 [68]. As already mentioned above, the prismatic notched FRC specimen has to exhibit certain required residual strength during bending test. To avoid lengthy experimental testing, numerical simulation was employed – the aim of the modeling was to reveal whether increased interfacial shear stresses ($\tau_0$, $\tau_s$) obtained during single fiber pull-out tests have positive impact also on bending tests of composite material.

5.2.4.2 FRC FCM model

The fixed crack model for fiber reinforced composites ($FRC FCM$), suitable for representation of individual cracks in plain as well as fiber reinforced cementitious composites – including FRCs – was applied [162, 163]. Mesh of the 2D model, counting 3080 of predominantly triangle linear elements, was created in Salome software [164]. Non-linear numerical analysis was conducted using OOFEM software [165], proceeded in 800 steps. Virtual experiment was controlled by displacement. Solution was searched by Newton-Raphson’s method. The stiffness matrix was compiled in 2D plain-stress preposition. Geometry of the specimen and mesh of finite elements are shown in Figure 5.2. Two calculations for each fiber type were done; the first contained parameters of reference, while the second one 30 seconds plasma modified fibers. The $FRC FCM$ model is based on following main sections:

- Constitutive laws for the matrix;
- Constitutive laws for fibers;
- Pull-out behavior of a single fiber;
- Traction-separation law for fibers;
- Bridging stress and crack stiffness.

5.2.4.3 Constitutive laws for matrix

Constitutive laws for the matrix are given by a traction-separation law, shear stiffness, and shear strength. The traction-separation law is considered to be the most interesting of them
Mechanical properties improvement of fiber reinforced concrete in context to the aim of bending test simulation. It activates when normal stress reaches the tensile strength $f_t$ of concrete. Post-peak behavior $\sigma_m$ described by Hordijk’s softening in case of $\text{softType} = 3$ is for $w \geq w_{\text{max}}$ given by [163]:

$$
\sigma_m = f_t \left[ \left( 1 + \left( \frac{c_1 w}{w_t} \right)^3 \right) \exp \left( \frac{-c_2 w}{w_t} \right) - \frac{w}{w_t} \left( 1 + c_1^3 \right) \exp \left( -c_2 \right) \right], \quad (5.1)
$$

for $w < w_{\text{max}}$:

$$
\sigma_m = f_t \frac{w}{w_{\text{max}}} \left[ \left( 1 + \left( \frac{c_1 w_{\text{max}}}{w_t} \right)^3 \right) \exp \left( \frac{-c_2 w_{\text{max}}}{w_t} \right) - \frac{w_{\text{max}}}{w_t} \left( 1 + c_1^3 \right) \exp \left( -c_2 \right) \right], \quad (5.2)
$$

for $w_{\text{max}} \geq w_t$:

$$
\sigma_m = 0, \quad (5.3)
$$

and

$$
w_t = 5.14G_f/f_t, \quad c_1 = 3, \quad c_2 = 6.93, \quad (5.4)
$$

where $f_t$ is matrix tensile strength; $w$, crack opening; $w_t$, characteristic crack opening; $w_{\text{max}}$, maximum crack opening; and $G_f$, fracture energy of the matrix.

Mechanical properties of the matrix were set to correspond common concrete. These were as follows: Young’s modulus of elasticity $E$, 20 GPa; Poisson’s ratio $\nu$, 0.2; fracture energy of matrix $G_f$, 5.0 N/m; tensile strength $f_t$, 2.5 MPa; parameter describing post-peak behavior $\text{softType}$, 3 – Hordijk’s softening; parameter describing shear stiffness of cracked material $\text{shearType}$, 1 – constant shear retention; shear retention factor $\beta$, 0.001; parameter limiting the magnitude of resulting shear stress acting on crack plane $\text{shearStrengthType}$, 1 – the threshold is set to the value of tensile strength.

In order to distribute loading at points of supports and the point where the force is loaded on the sample during simulated bending tests, adjacent areas were characterized by specific parameters. These parameters followed the extremely tough and high-strength material (isotropic damage model), in particular: Young’s modulus of elasticity $E$, 20 GPa; Poisson’s ratio $\nu$, 0.2; parameter allowing to choose from different definitions of equivalent strain $\text{equivstraintype}$, 0; parameter determining damage law $\text{damlaw}$, 1; strain at peak stress $\epsilon_0$, 1; parameter controlling ductility $w_f$, 1000.

### 5.2.4.4 Constitutive laws for fibers

Constitutive laws for fibers extend the $\text{FRC FCM}$ model. These are influenced by fibers type, their orientation, and volume. In case of $\text{fiberType} = 2$ (short random fibers), once the crack is formed, bridging stress $\sigma_b$ (also called as effective stress) is transfered together by the matrix and fibers [163]:

$$
\sigma_b = \bar{\sigma}_{h,m} \left( 1 - V_t \right) + \bar{\sigma}_{h,f} \bar{V}_t, \quad (5.5)
$$

and overall elastic stiffness is calculated as weighted average of two Young’s moduli:

$$
E = V_t E_t + \left( 1 - V_t \right) E_m, \quad (5.6)
$$
and \( \bar{V}_f \) is given by:

\[ \bar{V}_f = V_f \cos (\theta), \] (5.7)

where \( \bar{\sigma}_{b,m} \) is bridging stress in the matrix (per unit area of crack); \( V_f \), fiber volume ratio; \( \bar{V}_f \), effective fiber volume ratio; \( \theta \), angle between the fiber axis and the crack plain normal; \( \bar{\sigma}_{b,f} \), bridging stress in fibers (per area of fibers); \( E_f \), Young’s modulus of fibers; \( E_m \), Young’s modulus of the matrix.

Constant parameters of the fixed crack model for fiber reinforced composites regarding to fibers type were following: fiber volume ratio \( V_f \), 0.0075; shear modulus of fibers \( G_f \), 1.0 GPa; snubbing coefficient \( J \), 0.5; fiber cross-section shape correction factor \( k_f \), 0.9; class describing type of fiber bond shear strength \( F_{s,\text{type}} \), 0 – constant shear strength; class of reinforcing fibers \( \text{fibertype} \), 2 – short randomly oriented fibers (their behavior during pull-out is indicated in Equations 5.8–5.11); maximal number of cracks \( n_{\text{cracks}} \), 1; exponent related to fiber unloading \( M \), 1, \( \text{fibreActivationOpening} \), 1e-6; lower bond allowing to smoothen the traction-separation law for fibers \( d_{w,0} \), 1e-7; upper bond allowing to smoothen the traction-separation law for fibers \( d_{w,1} \), 1e-7.

Variable input parameters differing according to the fiber type are summarized either in Table 5.1 or in Table 5.2.

**Table 5.2: Variable interfacial parameters differing according to the fiber type.**

<table>
<thead>
<tr>
<th>Fiber type</th>
<th>Shear stress ( \tau_0 ) [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference</td>
<td>Modified</td>
</tr>
<tr>
<td>Coated</td>
<td>1.482</td>
</tr>
<tr>
<td>Uncoated</td>
<td>0.503</td>
</tr>
<tr>
<td>Spokar</td>
<td>0.324</td>
</tr>
</tbody>
</table>

### 5.2.4.5 Pull-out of a single fiber

Pull-out behavior of a single fiber described in the FRC FCM model is based on assumption that the anchoring force \( F_a \), which is equal to the bridging force, is explained as [163]:

\[ F_a = F_0 \exp (f\theta), \] (5.8)

where \( F_0 \) is the resultant of bond shear stress between the single fiber and the matrix and \( f \) is snubbing coefficient reflecting direction of the fiber during pulling. Given the fact that the distribution of bond stress \( \tau_s \) is assumed to be uniform on the fiber surface, therefore, its resultant can be computed as [163]:

\[ F_0 = \pi D_f a \tau_s, \] (5.9)

where \( a \) is length of fiber debonded from the matrix; \( D_f \), fiber diameter; \( \tau_s \), bond shear stress.

As embedded length is decreased with sliding of fibers out of the matrix, the matrix crack is gradually opened. The transitional crack opening is then denoted as \( w^* \) and analytically derived as [163]:

\[ w^* = \frac{L_f^2 \tau_0}{(1 + \eta) E_f D_f}, \] (5.10)
while $\eta$ is given by:

$$\eta = \frac{E_f V_f}{E_m (1 - V_f)},$$  \hspace{1cm} (5.11)

where $L_f$ is fiber length, $\tau_0$ frictional shear stress between the fiber and the matrix during debonding, and other parameters are characterized above.

### 5.2.4.6 Traction-separation law for fibers

Traction-separation law for short randomly oriented fibers formulates secant and tangent stiffness with respect to the crack opening $w$. It must be considered that the crack surface is not perfectly straight. The source of crack surface deformation can be sought in shear stresses in the bond between the matrix and fibers. The crack opening and pull-out are smaller in the vicinity of the fiber. Therefore, the average crack opening is replaced by the effective crack opening $\bar{w}$ which is defined as [163]:

$$\bar{w} = w - \Delta w = L \varepsilon_{cr} - \Delta w,$$  \hspace{1cm} (5.12)

where $\Delta w$ is activation opening parameter; $L$, element size; $\varepsilon_{cr}$, normal cracking strain.

Bridging stress in fibers is then expressed separately for $\bar{w} < w^*$ [163]:

$$\sigma_{b,f}(w) = \frac{g V_f L_f \tau_0}{2 D_f} \left(2 \sqrt{\frac{\bar{w}}{w^*}} - \frac{\bar{w}}{w^*}\right),$$  \hspace{1cm} (5.13)

for $w^* \leq \bar{w} < L_f/2$:

$$\sigma_{b,f}(w) = \frac{g V_f L_f \tau_s(w)}{2 D_f} \left(1 - \frac{2w}{L_f}\right)^2,$$  \hspace{1cm} (5.14)

and for $\bar{w} > L_f/2$:

$$\sigma_{b,f}(w) = 0.$$  \hspace{1cm} (5.15)

Despite of bridging stress in the matrix, stress in fibers does not decrease linearly when the crack is unloading. The implementation uses a power function:

$$\sigma_{b,f}(w) = \sigma_{b,f}(w_{\text{max}}) \left(\frac{\bar{w}}{w_{\text{max}}}ight)^4,$$  \hspace{1cm} (5.16)

where $w_{\text{max}}$ is the maximum crack width, $g$ is snubbing factor, and all other parameters are described above.

### 5.2.4.7 Bridging stress and crack stiffness

Within the composite bridging model, total composite normal traction $\sigma_b$ is obtained by summing up the (nominal) contribution from the matrix $\sigma_{b,m}$ and fibers $\sigma_{b,f}$ [163]:

$$\sigma_b = \sigma_{b,m} + \sigma_{b,f} = \bar{\sigma}_{b,m} (1 - V_f) + \bar{\sigma}_{b,f} V_f = \sigma,$$  \hspace{1cm} (5.17)

where $\sigma_{b,m}$ is bridging stress in the matrix; $\sigma_{b,f}$, bridging stress in fibers; $\bar{\sigma}_{b,m}$, effective bridging stress in the matrix; $\bar{\sigma}_{b,f}$, effective bridging stress in fibers; $V_f$, fiber volume ratio; $\bar{V}_f$, fiber effective volume ratio.
5.2.5 Standardized bending tests

The three-point bending test following the standard EN 14845-2 [68] was employed using loading frame Veb Tiw Rauenstein FP100 at the constant rate of 1 mm/min (experiment was displacement controlled, measured by shift sensor Essa 01). Concrete mixture to be used for production of notched prismatic samples is summarized in Table 5.3. The amount of used fibers corresponds to approx. 0.75% of the mixture volume (density of all fiber was approximately the same). Such amount is supposed to be the maximal permissible with regard to mixture workability and homogeneity, as found out experimentally. Homogenization of the mixture was done by means of concrete mixer Smartest equipped by blades with forced circulation. Its working volume was equal to 80 l, working power 0.2 m³/h. Aggregate, binder, and fibers were mixed together at the first instance. Then, water was added into dry mixture. Mixture was compacted using vibrant table during casting into steel molds. The samples 550 × 150 × 150 mm were stored in standard laboratory condition with no other treatment for 28 days. After demolding, samples were notched using table saw equipped with diamond wheel and then subjected to bending tests. The experiment was interrupted after reaching of 5 mm sample midspan displacement. Each mixture was represented by 5 samples, results were processed and averaged using DiPro software.
Table 5.3: Composition of concrete mixture.

<table>
<thead>
<tr>
<th>Component</th>
<th>Specification</th>
<th>Amount [kg/m³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cement</td>
<td>CEM II 42.5R</td>
<td>490.0</td>
</tr>
<tr>
<td>Water</td>
<td>drinking</td>
<td>161.0</td>
</tr>
<tr>
<td>Water-to-cement ratio</td>
<td>w/c=0.33</td>
<td>-</td>
</tr>
<tr>
<td>Coarse aggregate</td>
<td>fraction 8-16</td>
<td>745</td>
</tr>
<tr>
<td>Medium aggregate</td>
<td>fraction 4-8</td>
<td>100</td>
</tr>
<tr>
<td>Fine aggregate</td>
<td>fraction 0-4</td>
<td>890</td>
</tr>
<tr>
<td>Plasticizer</td>
<td>Sika</td>
<td>4.9</td>
</tr>
<tr>
<td>Fibers</td>
<td>polymer</td>
<td>6.825</td>
</tr>
</tbody>
</table>

5.3 Results and discussions

5.3.1 Pull-out tests

Pull-out behavior of Coated and Uncoated fibers was completely taken from Chapter 4. Results belong to Spokar fibers are shown in Figure 5.3 where dependence between fiber free-end displacement and force resisting to fiber pull-out is depicted. It is clear from the result that the maximal force recorded during pull-out of reference Spokar fiber from the matrix slightly overcame 10 N, while in the case of 30 seconds plasma modified fibers, the force reached on more than 14 N. Thus, interfacial shear stress was increased by approx. 40 %. In the case of Uncoated and Coated fibers, shear stress was improved by approx. 80 and 17 %, respectively. All thus obtained results ($\tau_0$) are summarized in Table 5.2.
5.3.2 Numerical simulation

Despite of original intention, the numerical simulation was in all cases prematurely interrupted already after midspan deflection reached 0.5 mm, instead of 3.02 mm (the second stage on which the directing standard [68] is focused). This was caused by two reasons: (i) the calculation is very time demanding to achieve such deformation due to high number of iterations and (ii) the calculation often collapsed during high midspan deflection. Despite of these limitations, the numerical simulation provided many valuable findings.

The simulations revealed that behavior of all specimens during theoretical loading was practically identical in phases until elastic limit of the matrix was exhausted. On the other hand, samples differentiated to each other in post-cracking phase, as response of pulling out fibers was varied.

It was found out that post-cracking behavior of samples reinforced with Coated fibers was practically the same, regardless to their treatment, as shown in Figure 5.4. This result was expected because these fibers exhibited the poorest improvement in interfacial shear stress if compared to any other ones. On the other hand, residual strength of theoretically loaded specimens was the highest from each other.

In the case of Uncoated fibers, there were detected the most promising results with regard to plasma treatment efficiency. Samples reinforced with treated fibers theoretically exhibited significantly higher residual strength if compared to those with reference fibers. Moreover, post-cracking loading path of modified samples rises more steeply (following clear strain-hardening) than in case of reference ones, see Figure 5.5.

Samples reinforced with Spokar fibers exhibited practically the same behavior as in case of Uncoated fibers. The only difference between them can be seen at deflection of 0.5 mm. While all of theoretically tested samples exceeded the required residual strength 1.5 MPa, those reinforced with Spokar reference fibers not (Figure 5.6). Therefore, these can not be considered as FRC, if the results confirmed also by real bending tests.
Mechanical properties improvement of fiber reinforced concrete

Figure 5.5: Stress during simulated bending as a function of midspan displacement.

Figure 5.6: Stress during simulated bending as a function of midspan displacement.
5.3.3 Standardized bending tests

When results achieved using real bending tests (see Figures 5.7, 5.8, and 5.9) are compared to those obtained by numerical modeling (Figures 5.4, 5.5, and 5.6), some irregularities can be found (common for all cases). The shape of curve obtained during elastic response of loaded samples can be described as bi-linear in case of numerical modeling, while in case of real bending tests, the shape is almost ideally linear. This was probably caused by too fast loading rate; force sensors are not capable to record such fast changes. The other irregularity can be seen in maximal elastic limit of theoretical and real matrixes. The first mentioned are always lower than in case of real ones. This can be caused by variance between theoretical and real matrix mechanical properties or by boundary conditions of supports (those are not ideal in case of experiment). The other clear difference can be observed in a deflection where the matrix is cracked. While in case of numerical modeling the deflection in question is about 0.15 mm, crack formation occurred during approx. 0.5 mm as found by experimental testing. Such behavior is attributed to shift sensor inaccuracy or to seating of sample on supports (pressing of system). The last clearly visible deviation relates to minimal residual strength – the point from where post-cracking paths start. The point is positioned significantly higher in case of real experiment if compared to numerical simulations. This is probably caused by presence of coarse aggregate which can interlock the incipient crack in the real matrix. It has to be also stressed out that many deviations can originated from averaging of curves from bending tests.

However, some similarities between simulation and real experiment were found, especially in case of post-cracking stage. It was shown that there is no importance to treat Coated fibers. Similarly to numerical modeling, the real experiment revealed no improvement in residual strength samples reinforced with plasma treated fibers (Figure 5.7). Such findings were expected and they are in accordance also with pull-out tests results where the shear stress improvement was negligible. These fibers are fitted with sophisticated surface structure – repeated gearing (see Figure 4.2(a)) – which is suppose to be the most effective from the physical interaction point of view. Recall that these fibers exhibited also the significantly highest interfacial shear stresses from each other fibers, therefore, whatever added surface treatment is not necessary.

The residual strength of Uncoated fibers was increased by approx. 30–35% after the plasma treatment, as clear from Figure 5.8. This behavior was predicted by numerical simulation and corresponds also with pull-out tests. These result are supposed to be the most important from the practical point view; it is possible to use lower amount of fibers if treated and thus to reduce economy burden or increase mixture workability, while the requirements stated by EN 14845-2 [68] remain fulfilled.

Samples reinforced with Spokar fibers exhibited the poorest residual strength from all others. On the other hand, the benefit of the plasma treatment was proven in this case, although such material did not meet minimal residual strength (Figure 5.9) of cited standard 14845-2 [68] during deflection of 0.47 mm. However, if focused on the second assessed stage – residual strength during 3.02 mm, the requirement of the standard (at least 1.0 MPa) was achieved with significant reserve.
Figure 5.7: Stress during bending as a function of midspan displacement.

Figure 5.8: Stress during bending as a function of midspan displacement.
5.4 Conclusion

This work dealt with mechanical behavior of fiber reinforced concrete containing reference or surface modified reinforcement during standardized three-point bending tests. Three types of polymer macro-fibers were used and subjected to the low-pressure cold plasma treatment in oxygen atmosphere for 30 seconds to make their surface rough and hydrophobic and thus to promote their adhesion to the cement matrix. Pull-out tests of reference and thus treated fibers were conducted from cement paste in order to examine interfacial shear stress between the two materials. Next, prismatic notched specimens with dimensions $550 \times 150 \times 150$ mm were made from standard concrete mixture containing 0.75 vol. % of reinforcement and these were then theoretically and mechanically tested by means of numerical simulation and standardized bending tests, respectively. The main purpose of both tests was to find residual bending strength of specimens and classify the effect of plasma modified fibers. Finding were as follows:

- Pull-out tests revealed that adhesion between 30 seconds oxygen plasma treated fibers and the cement paste matrix was increased by ca 17–80 % depending on fibers used, if compared to reference ones.

- Numerical simulation of bending tests found that residual strength of loaded prismatic specimens was demonstrably increased only if interfacial shear stress between fibers and the matrix was increased by more than 40 %.

- Significant differences were detected in elastic response of loaded specimens, if the results obtained during numerical simulation and real bending tests were mutually compared. These irregularities were attributed to difficult setting of matrix mechanical properties within numerical testing and too fast loading, inaccurate measurement equipment, and matrix heterogeneity during real bending tests.

- Post-cracking responses of loaded samples were similar if compared to results obtained from numerical simulation with those from experimental testing.
• Real bending tests revealed that residual strength of specimens was increased by up to 12 % and 30 % if interfacial shear stress between fibers and the matrix was increased by 40 % and 80 %, respectively.

• Most of tested samples fulfilled requirements given by technical standard EN 14845-2 [68].

It can be concluded that plasma treatment of polymer reinforcing macro-fibers positively affects the interfacial interaction between them and the cement matrix. This finding can contribute to applying of reduced fibers amount into concrete mixture, while the requirements of relevant technical standards on FRCs mechanical properties stay fulfilled.
Chapter 6

Conclusions and final remarks

The main objective of the thesis focused on the plasma modification of reinforcing fibers used in cement or lime-based composite materials was to enhance the interphase interaction between fibers and the matrix by means of the plasma treatment. It is generally known that a huge number of reinforcing fibers, especially those made from glass or different kinds of polymers, exhibit smooth and chemical inert surfaces. As a consequence of these surface properties, both the chemical and the physical interaction between them and lime- or cement-based matrixes does not occur. Therefore, mechanical potential of reinforcement remains unused and mechanical performance of reinforced composite materials are not as good as they should be. Once is the loaded matrix disinterested by crack, the role of reinforcing fibers is to bridge the crack and thus ensure material integrity. The mechanism of the crack bridging is based especially on the physical interaction between the two materials. It is therefore desirable to have the fiber surfaces rough. It was presented and discussed that plasma treatment seems to be promising technique for an activation and roughening fiber surfaces. The surface of thus modified fibers utilize synergistic effect of physical changes (given by ion bombardment) and chemical changes (given by reaction with working gas).

It can be concluded that all goal of the thesis were accomplished. Within the first chapter, an importance of an interphase interaction within fibrous composite materials and surface parameters together with the focus of lime- and cement-based fibrous composites in the field of civil engineering were reviewed. Process parameters used during plasma treatment with respect to glass or polymer fiber materials were examined. Thus modified fibers were investigated from the chemical and physical point of view focusing on wettability, chemical composition, surface morphology, and determination of fibers mechanical properties. Aging under atmospheric conditions of treated fibers – as an important parameter to real praxis – was also evaluated. Interaction of lime or cement binders with modified glass and polymer micro- or macro-fibers was evaluated by analytical techniques and mechanical behavior of such fibrous composite materials reinforced with modified fibers was studied with the focus on their post-cracking response. Last but not least, an application of obtained results within technical practice was discussed. The most important results are herein concluded.

Plasma treatment was applied during modification of glass fibers sized by thin layer of aminosilane. It was shown that surfaces were activated as proven by means of the water wettability measurement. Their morphology was increased as clear from SEM observation. How-
ever, when thus modified fibers were used in the plaster lime-based mixture, they failed as reinforcement due to their mechanical damage which occurred during mixing with other components. It was shown that the presence of sizing is necessary onto fiber surfaces due to their mechanical and chemical protection and whatever its modification is harmful. Glass fibers are highly abrasive to each other and prone to damage due to their brittle origin. Moreover, the glass melt is poorly resistant to high alkali environment. Therefore, application of plasma treatment showed to be inappropriate due to fibers protective layer destruction.

The plasma treatment showed to be much more beneficial in the case of polymer macrofibers. Several types of them, including PET, PP, and PE, were modified in such way. The findings can be summarized as follows: 30 seconds lasting plasma treatment in oxygen atmosphere is capable to make fiber surface hydrophobic and rough enough. Required morphology changes were proven by SEM analysis, while the chemical ones by means of the wettability measurement and XPS. Moreover, it was shown that the treatment, if done properly, does not affect fiber mechanical properties. Valuable results were also achieved in a question of plasma treatment stability; it was found out that the polarity of modified fibers decreased if fibers are exposed to atmospheric conditions. These results refute claims of those researches who described changes occurred onto polymer surfaces as stable. After proper examination of fiber surface properties, they were subjected to interaction evaluation with the cement matrix. As shown by pull-out tests, modified polymer macro-fibers exhibited improved adhesion with the matrix by up to 80% with respect to untreated fibers.

In the view of promising results obtained during the plasma treatment of polymer macrofibers, practical applicability of them was found. It was shown that these can be enforced in the field of fiber reinforced concrete. In order to verify practical benefits of the polymer macrofibers plasma treatment, FRC specimens containing modified fibers were made and subjected to bending tests, following the relevant technical standards. Results were then compared to those obtained from testing of reference material. It was shown that residual strength of loaded specimens was by up to 30% higher in case of samples reinforced with treated fibers. Thanks to increased adhesion between fibers and the cement matrix, their lower amount can be applied into the FRC mixture, while the requirements of the cited standard remain fulfilled.
References


References


References


References


Appendix A

Contact angle measurement tool based on image analysis


A.1 Introduction

Wettability describes interaction of solids and liquids in presence of a gas. It plays an important role in a huge variety of fields, such as medicine [166], optics [167], chemistry [168], geochemistry [169], electrical engineering [170], health and safety protection [171], textile industry [172], printing [173], ice production [174], etc. In recent years, there has been an increasing interest in the study of superhydrophobic surfaces of solids due to their potential applications in, e.g., self-cleaning, nanofluidics, and electrowetting [65, 175, 176, 177, 178, 179, 180].

Wettability studies usually involve evaluation of contact angles, measured between tangents of a liquid-gas and liquid-solid interface, as primary data indicating the degree of wetting [181]. This information can be used to determine solid surface tension, but its direct measurement is not possible. Therefore, indirect methods have been developed [182, 183, 184, 185, 186], among which contact angle measurement is considered to be the simplest.

Most of the contact angle measurement techniques can be classified into two main categories: indirect force and direct optical methods. Indirect Wilhelmy balance method [187] is based on observing changes in weight (force) of a solid material before and after its contact with liquid [65]. It can be applied to sufficiently stiff planar specimens, rods, wires, tubes, capillaries, or single fibers.

The direct measurement of tangent angles on a sessile drop profile is widely used. In 1940’s Bigelow et al. [188] set up a simple and convenient instrument called telescope-goniometer. The measurement relied on consistency of an operator in the tangent line assignment procedure,
which could not be guaranteed, and the method was not suitable for measuring contact angles below 20° due to the uncertainty in assigning the tangent line to almost flat droplets. The technique has been modified to, e.g., methods using mirror [189], captive bubble method [190], or tilting plate method [191]. However, the main principle has not changed — either sessile drops (liquid resting on planar specimens or horizontal fibers [192, 193]), menisci (submerged planar specimens or vertical fibers), or ultra small droplets are observed and the contact angles are evaluated from the shape of the liquid outline.

Another way of obtaining contact angles is to analyze and fit the drop shape. A profile of a sessile drop can be assumed to be part of a circle, or analyzed using the Laplace equation [194]. With the evolution of computers, the drop shape analysis methods significantly improved, and new methods have been developed [195, 196, 197, 198, 199, 200, 201, 202, 203]. These include, e.g., ADSA (axisymmetric drop shape analysis), where a sessile drop contour line is matched by the best theoretical curve [204], or TIFA (theoretical image fitting analysis), where a whole 2D projection of a drop is fitted [205, 206].

We present an open-source software CAMTIA (Contact Angle Measurement Tool based on Image Analysis) that can be used for a direct evaluation of the contact angles on sessile drops or menisci formed around partially submerged fibers. The purpose is to provide a simple and freely available open-source tool, which allows automatic and consistent bulk evaluation. It avoids a discrepancy in results caused by the operator inconsistency and is reliable even when evaluating contact angles below 20°. To the best of our knowledge, commercial codes allowing such analysis are expensive and not fully automatic.

**A.2 Experimental set-up**

We propose a simple and relatively cheap optical set for acquisition of high-quality images with a sufficient contrast (Figure A.1). The system exploits the same principles as much more expensive state-of-the-art equipment, but consists of commonly available, universal, and easily replaceable components:

- a light source,
- a light diffuser in order to scatter the light and make it homogeneous, e.g., frosted glass,
- a circular aperture in the focal point of a plano-convex lens that restricts the flux, providing a diffused circular light disc,
- a plano-convex lens ensuring cylindrical light flux — its shape allows to eliminate spherical aberration due to unequal distances of the captured objects from the lens,
- a specimen, e.g., a partially submerged fiber or a sessile drop,
- a secondary plano-convex lens allowing to focus on the observed specimen in order to provide sharp images (the sharpness can be adjusted by moving the secondary plano-convex lens along the rail to which all the components are fixed), and
a camera with a photographic lens of maximum possible focal length in order to reach sufficient magnification of the observed specimen; it is favorable to use a lens hood to prevent illumination of the lens from other light sources.

![Optical measurement system diagram](image)

Figure A.1: Optical measurement system consisting of (1) a light source, (2) a light diffuser, (3) a circular aperture, (4) a plano-convex lens, (5) a specimen, (6) a plano-convex lens, (7) a zoom lens, and (8) a digital camera.

Using such an optical system, the specimen is illuminated by a flux of evenly distributed parallel homogeneous soft light. The camera positioning opposite to the light source allows to capture the specimen shadow and its outline can be easily identified within the digital image as described next.

## A.3 Algorithms and program work flow

The images with a sufficient contrast between individual phases are crucial for the calculation procedures implemented in CAMTIA. The program was developed in MATLAB [207] environment and offers a user-friendly graphical user interface (GUI) to execute commands. The program source files and manual with a thorough description of the program structure and GUI controls are provided at the author’s website[^1].

### A.3.1 Binarization of images

The color images are first converted to an 8-bit gray scale by summing up the normalized red-green-blue (RGB) channels according to the CIE 1931 standard as

\[ Y = 0.2126R + 0.7152G + 0.0722B \]

for each pixel. The image is consequently binarized to black and white (b/w) based[^1].

on a user-selected threshold \( T \). The gray-level pixel intensity is converted to 0 for all pixels with \( Y < T \), or to 1 if \( Y > T \).

The resulting b/w images always contain a certain amount of unfiltered small regions resulting from local brightness extremes, depending on the value of \( T \) (Figure A.2). The value can be changed dynamically using a slider in the CAMTIA software. Once the threshold value is set properly, these isolated regions are smaller than the regions of interest and can be identified based on region labeling procedures [208].

![Figure A.2: Effect of the binarization threshold parameter \( T \) on size of unwanted regions; the original image (left) was binarized with \( T \) equal to 0.06 (unacceptable), 0.15 (acceptable), 0.60 (acceptable, but not optimal), and 0.75 (unacceptable) from left to right.](image)

The images taken during experimental testing can be both undexposed or overexposed, when a camera is not set properly. These imperfections can be compensated without any image manipulation by setting the appropriate value of the \( T \) parameter while not compromising the measurement accuracy, as demonstrated in Figure A.3. However, all images within a single batch should have similar brightness distribution histograms.

### A.3.2 Identification of region of interest

After removal of the unwanted regions, the binary image contains noiseless regions representing the liquid level with the object in contact and a contrast background. The outline at the b/w boundary is smoothed based on user-defined smoothing radius using local regression lines [209]. The smoothing radius has to be chosen individually, depending on resolution of images, presence of noise, but also the binarization threshold value. However, its value can be constant for all images acquired using the same camera, experimental set-up, and setting of other parameters. In our particular case, presented in Section A.4, the smoothing radius ranging between 2 and 10 pixels smoothed the boundary reliably, and the tangents snapped to the meniscus/drop corner. After boundary identification (by searching for a change in the binary image column-by-column) it is numerically differentiated, and contact angles are assessed as described next. The program work flow is illustrated in Figure A.4.

### A.3.3 Determination of tangents and calculation of contact angle

The next step is to describe the boundary line by a continuous function \( y = f(x) \) which is numerically differentiated with respect to a local coordinate \( x \), and the contact point \( P[x_P, y_P] \) is found where the derivative \( dy/dx \) reaches its maximum. The contact angle is then evaluated as a tangent angle of a meniscus or a drop inclination \( \theta = \arctan(dx/dy) \), where the differentiation step size in pixels, \( dx \), can be selected and adjusted by a user. There is a small difference in the assessment of sessile drop and meniscus around a fiber specimen in terms of
local coordinate system, see Figures A.5 and A.6. For both configurations, the contact angle is measured at both sides of the specimen.

A.4 System performance

The complete set-up used for the measurements is presented in Figure A.7. We used an adjustable lamp (1) as the light source, which is convenient for selecting the optimum intensity for a required exposure time. The light diffuser (2) ensuring homogeneous light was made of frosted glass. The light flux was restricted by a 10-lamella mechanically operated 0.5–20.0 mm circular aperture (3). The plano-convex lens (4) with focal length of 50 mm was present in order to make the light beams parallel. The measured specimens (5) were either sessile drops of demineralized water resting on a smooth polypropylene (PP) or silica (Si) substrate, or fibers fixed in a chemically inert plastic modeling clay, partially submerged in demineralized water. After fixing all components, the movable plano-convex lens (6) with focal length of 50 mm was adjusted to ensure sharp images. The images were acquired by a high-definition camera (8) Canon EOS 70D (20.2 Mpx) equipped with an APS-C sensor and lens (7) Tamron Temron 70-300 set to focal length of 300 mm. The camera was triggered remotely, and the image stabilization option was switched off, as well as the automatic focusing. A lens hood attached to the camera prevented contamination of images from external light sources.
Figure A.4: Illustration of the program workflow; color to grayscale conversion (top left), generation of a binary image and identification of noise (top right), boundary smoothing (bottom left), and differentiation to assess the contact angles (bottom right).

Figure A.5: Fiber meniscus representation by a continuous function.
Figure A.6: Sessile drop representation by a continuous function.

Figure A.7: Optical measurement system used in the study; the numbering of components corresponds to the scheme in Figure A.1.

Capabilities of the proposed measurement system are presented in Figure A.8. It is clear that in the case of sessile drops the image analysis can, unlike some of the other methods, cope with both hydrophobic and hydrophilic materials. Accuracy of the measurements is demonstrated next.

A.4.1 Validation

CAMTIA was validated by comparing its results with a precise manual tangent placement in CAD software using the same images. Each batch of sessile drops resting on a specific surface (PP, Si) or fibers made of the same material (plasma treated PP, untreated PP) was represented by 10 measurements. In addition, a comparison with commercial tools was also made (Tables A.1 and A.2). These included an advanced drop shape analyzer Krüss DSA30a.

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aPurchased by University of Chemistry and Technology (Czech Republic) for 18,000 EUR.
and a portable instrument See System\(^1\).

The manual tangent placement in CAD software is accurate, yet extremely laborious and tedious. Unlike CAMTIA, DSA30 and See System are limited to assessment of sessile drops only and require an interaction with user to localize a sessile drop and baseline position, but the calculation of contact angles based on curve fitting is automatic.

Table A.1: Results of different tools for direct measurement of contact angles on sessile drops.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Mean contact angle [°] (standard deviation)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CAD</td>
</tr>
<tr>
<td>PP</td>
<td>82.3 (2.4)</td>
</tr>
<tr>
<td>Si</td>
<td>28.6 (4.4)</td>
</tr>
</tbody>
</table>

The results summarized in Tables A.1 and A.2 demonstrate that the full automatization of contact angle assessment in CAMTIA does not compromise the accuracy.

\(^1\)Purchased by Institute of Physics, CAS (Czech Republic) for 3,000 EUR.
Table A.2: Results of different tools for direct measurement of contact angles on menisci around partially submerged fibers.

<table>
<thead>
<tr>
<th>Fiber</th>
<th>Mean contact angle $[^\circ]$ (standard deviation)</th>
<th>CAD</th>
<th>CAMTIA</th>
<th>DSA30</th>
<th>See System</th>
</tr>
</thead>
<tbody>
<tr>
<td>untreated PP</td>
<td>65.8 (10.4)</td>
<td>64.0 (8.1)</td>
<td>×</td>
<td>×</td>
<td></td>
</tr>
<tr>
<td>plasma treated PP</td>
<td>24.6 (4.4)</td>
<td>25.0 (5.9)</td>
<td>×</td>
<td>×</td>
<td></td>
</tr>
</tbody>
</table>

A.5 Conclusion

The open-source software CAMTIA for direct assessment of contact angles based on image analysis is presented. The combination with the proposed optical measurement system provides a universal alternative to expensive commercial solutions. The automatic detection of a fiber/sessile drop boundary within images allows bulk calculation with no need for user interaction, except for initial settings. Moreover, the fully automatic placement of tangents guarantees consistency of results.

High-quality images are essential for a successful analysis. The aperture smaller than $f/8$ should ensure a sufficient depth of field, light sensitivity (ISO) parameter should not exceed 800 in order to avoid noisy images, and it is prudent to keep exposure time below $1/50$ s in order to avoid blurring. If such a camera setting leads to underexposed images, the intensity of the light source should be increased. It is important to check by a shield (common paper suffices) whether the light beam is cylindrical between the plano-convex lenses.

The validation results demonstrate that CAMTIA can be more accurate than semi-automatic commercial solutions. Unlike majority of commercial solutions, CAMTIA is capable of fast assessment of contact angles on both, sessile drop and partially submerged fiber specimens. In addition, CAMTIA can process images from an arbitrary digital camera, which makes the system scalable and versatile.

For its simplicity, low price, and capability of fully automatic assessment we envisage a future use of the proposed solution in research applications as well as in industry. Our future developments will include real-time assessment and implementation of the code in non-commercial programming language Python.