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<td><strong>Author(s)</strong></td>
<td>Zhang, M; Matinlinna, JP</td>
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<tr>
<td><strong>Citation</strong></td>
<td>Journal of Adhesion Science and Technology, 2011, v. 25 n. 19, p. 2687-2701</td>
</tr>
<tr>
<td><strong>Issued Date</strong></td>
<td>2011</td>
</tr>
<tr>
<td><strong>URL</strong></td>
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The Effect of Resin Matrix Composition on Mechanical Properties
of E-glass Fiber Reinforced Composite
for Dental Use

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Short title: Matrix Composition & Mechanical Properties of FRC

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Abstract

The effects of resin matrix composition including bis-phenol-A-diglycidyl dimethacrylate (bis-GMA) -methyl methacrylate (MMA) based or urethane dimethacrylate (UEDMA) -triethylene glycol dimethacrylate (TEGDMA) based composition and storage conditions on the mechanical properties of E-glass fiber reinforced composites (FRCs) were studied. Three experimental groups (‘Exper 1’, ‘Exper 2’, ‘Exper 3’) with differing UEDMA to TEGDMA ratio in the matrix together with a control group (‘Control’) based on bis-GMA-MMA resin matrix were prepared by light-curing. The storage conditions for each group were dry storage at room temperature for 24 h and 30- and 60-day immersion in deionized (DI) water at 37 °C, which further divided each group into three subgroups. For all the four composition groups, mechanical properties including hardness, flexural strength and modulus in both three-point and four-point bending were tested (n=6), together with water sorption and solubility study (n=6) and fracture site scanning with a scanning electron microscope (SEM). The experimental specimens were relatively strong and stiff in three-point bending compared to previous research. The same specimens in three-point bending had a lower flexural modulus and fractured at higher flexural stress than in four-point bending. According to the SEM images after fracture, some resin matrix was still bound to the fiber surface, showing cohesive-interfacial fracture type and relatively stable matrix-fiber adhesion. According to comprehensive analysis, the control group showed superior mechanical performance in most of the tests.

Keywords

FRC, dental materials, E-glass fiber, resin matrix composition, mechanical properties, water sorption and solubility, storage
1. Introduction

As a less invasive, dental tissue saving treatment method than e.g. porcelain fused-to-metal restorations, FRCs have gained more and more interest in dentistry. Their applications fall into three categories: direct-placement splints and fixed partial dentures, direct-placement single-restoration reinforcement, and indirect restorations [1]. More specifically, applications of FRCs include bridges, periodontal splinting, trauma splinting, root canal post, orthodontic retention, and orthodontic splinting [2].

FRC is a composite material made of a plastic reinforced by fine fibers [3], which induce relatively high strength and modulus [4]. It is also called fiber-reinforced polymer (FRP) or glass-reinforced plastic (GRP) [3].

The E-glass fiber is relatively inexpensive and has good mechanical performance. As a promising fiber type in industry, the E-glass fiber was frequently investigated in previous research. Considering its significance in industrial application and for easy comparison with other researches, the E-glass fiber is also adopted in this study.

Matrix has the function of holding fibers together and in place, transferring stresses between fibers and protecting fibers from the outside environment such as chemicals, moisture and mechanical attacks. So matrix would influence the compressive strength, interlaminar shear and in-plane shear properties, interaction between the matrix and the fiber, and processing and defects in the composite [3].

Durable adhesion between fiber and matrix provides good load transmission between the two, which ensures that the load is taken by the stronger fiber and the fiber actually works as the reinforcement. However, if the adhesion is not so durable and some voids appear between the fiber and the matrix, these voids would act as fracture initiation sites in the composite and even facilitate the breakdown of the material [5]. Silane coupling agents are silicon esters and they find applications as
adhesion promoters for coatings and composites [6-14].

Thermosetting plastics are normally used as the matrix for FRC production. Most often unsaturated polyester, and also vinylester and epoxy, are also used. In FRCs with an interpenetrating polymer network (IPN) structure, the matrix consists of a crosslinking polymer, a linear polymer and sometimes photoinitiator to facilitate the polymerization reaction.

A crosslinking polymer is also called a thermoset polymer, referring to multifunctional or dimethacrylate resins, such as bis-GMA, UEDMA and TEGDMA [5]. A linear polymer is also called thermoplastic polymer, referring to monofunctional methacrylate polymers, such as MMA. The linear polymer is added into the crosslinking polymer to reduce the viscosity [15] of the mixture and form an IPN structure [5]. The photoinitiator includes a photosensitizer and a reducing agent. The photosensitizer absorbs visible blue light in the wavelength range of 440-480 nm, thus becomes activated and produces free radicals. These radicals react with reducing agent and produce more radicals. A commonly utilised photosensitizer is camphorquinone (CQ) and reducing agents are 2-(dimethylamino)ethylmethacrylate (DMAEMA), N,N-cyanoethyl methylaniline (CEMA) and dimethyl-p-toluidine (DMPTI). The mixing ratio between photosensitizer and reducing agent varies among different dental FRC products [16].

The bis-GMA-MMA (bis-GMA is needed to form the crosslinking polymer and MMA to form the linear polymer) combination as the resin matrix is widely used. Since bis-GMA is considered to be relatively more cytotoxic and allergenic [17], nowadays the UEDMA-based matrix is gaining more and more interest. In this research bis-GMA-MMA and UEDMA-TEGDMA (TEGDMA added to reduce the viscosity of the mixture) were set as the control and experimental resin matrix
compositions respectively for comparison in mechanical performance.

Water sorption and solubility of dental materials are influenced by various factors. One important factor is the polymer matrix, in which the microscopic voids might cause high water sorption values. High water sorption, in turn, would influence the fiber-matrix interface [18].

Besides, the resin matrix composition has significant effects on FRC mechanical properties [19], which is also the focus of this current study.

The aim of this study was to find a UEDMA-TEGDMA-based resin matrix composition with a desirable combination of mechanical properties for the FRC.

The hypothesis for this study was: the UEDMA-TEGDMA-based experimental FRCs with certain UEDMA to TEGDMA ratios have a superior combination of mechanical properties compared to the bis-GMA-MMA based control group.

2. Materials and Methods

2.1. Materials

The materials used in this study are listed in Table 1.

2.2. Fibre Preparation

The E-glass fibres (R338-2400/V/P, Stick Tech Ltd., Turku, Finland) were already silanized by the manufacturer and kept in a desiccator for 24 h prior to specimen preparation. Then the fibres were sized by immersion in a sizing solution (25 wt% bis-GMA + 75 wt% MMA for the control group; 25 wt% UEDMA + 75 wt%
TEGDMA for experimental groups) for 1 min. The sized fibres were cut into 25 mm long reinforcement with a surgical steel knife for the preparation of test specimens [20].

2.3. Specimen Preparation

Two bundles of the prepared 25 mm long reinforcement were placed along the long axis of the specimen into the mould and embedded into the resin matrix with compositions shown in Table 2. For each composition twelve identical rectangular specimens with dimensions of 2 mm * 2 mm * 25 mm were prepared. Air bubbles were removed carefully by pressing the fibre bundles with a hand instrument. Then the resin matrix was light-cured with a halogen light curing unit (Elipar\textsuperscript{TM} 2500, 3M ESPE, St. Paul, MN, USA) on both sides of the specimens for 3 × 40 s. The average light intensity was 700 mW cm\textsuperscript{-2} measured with Cure Rite\textsuperscript{TM} Model 8000 hand-held radiometer (EFOS Inc., Williamsville, NY, USA), and the wavelength range of the curing unit was 400-500 nm. After light-curing, the specimens were polished with a polishing paper (360 grit) [20, 21].

2.4. Fibre Content Measurement

Six randomly selected specimens were burned in an oven at 700 °C for 1 h. Their weights before and after burning were taken with an electrical balance (EB500HZY-S, A-Tech Global Science Ltd., Hong Kong), which was also used for all other weight measurements in this study. The average (± SD, standard deviation) fiber content was 42.00 ± 0.75 vol%. 
2.5. Storage Conditions

Each of the four groups was divided into three subgroups (n = 12) and stored in the following conditions before mechanical testing: dry storage at 37 °C for 24 h and immersion in DI water at 37 °C for 30 days and 60 days, respectively.

2.6. Water Sorption and Solubility Study

All the four groups with differing matrix composition were subjected to water sorption test according to ISO 3696:1987 (E). The specimens (n = 6) were stored in contact with 15 ml DI water of 37 °C for the following time periods: 0, 4, 5, 6, 7, 11, 15, 22, 36, 40 days. The weights measured at end of these time periods were recorded and plotted in Fig. 1.

2.7. Mechanical Testing

The following mechanical tests were taken (n=6) for each storage subgroup in each matrix-composition group:

2.7.1. Vickers Hardness Test

Vickers hardness test was conducted according to ISO 6507-2. Leitz Micro-hardness tester (Leitz Inc., New York, N.Y., USA) and Leica QGo software program (Leica Microsystems Imaging Solutions Ltd., Wetzlar, Germany) were utilized to carry out the test and calculate the hardness value. A load of 0.245 N and a loading duration of 20 s were used. Because of the viscoelasticity of the specimen, time delay from applying the indenter to the determination of the hardness value was standardized to 10 s [22].
2.7.2. Three-point Bending Test

A universal testing machine (ElectroPuls™ E3000, Instron Industrial Products, Grove City, PA, USA) was used. The span between the two supports was 20 mm and the crosshead speed was 1.0 mm/min during testing. Load and deflection were recorded with Console software (Instron Industrial Products) and load-deflection curve was plotted [20]. The maximum load and slope of the linear portion of the load-deflection curve were used to calculate the flexural strength and modulus according to the following formulae (1) and (2), respectively [23]:

\[ \sigma_3 = \frac{3FL}{2bh^2} \]  \hspace{1cm} (1)
\[ E_3 = \frac{SL^3}{4bh^3} \]  \hspace{1cm} (2)

\( \sigma_3 \): Flexural strength in three-point bending;

\( E_3 \): Flexural modulus in three-point bending;

\( F \): maximum load in the load-deflection curve;

\( L \): span between the two supports;

\( b \): width of the specimen;

\( h \): height of the specimen;

\( S \): slope of the linear portion of the load-deflection curve.

2.7.3. Four-point Bending Test

The same universal testing machine and data recording software program as in three-point bending test were used. The loading span was 10 mm, while the support
span was 20 mm. The crosshead speed was 0.75 mm/min [18]. Load and deflection were recorded to plot the load-deflection curve. Flexural strength and modulus were calculated with the maximum load and the slope of the linear portion in the load-deflection curve according to formulae (3) and (4) respectively [23]:

\[
\sigma_4 = \frac{3FL}{4bh^2} \tag{3}
\]

\[
E_4 = \frac{3SL^3}{17.44bh^3} \tag{4}
\]

\(\sigma_4\): Flexural strength in four-point bending;

\(E_4\): Flexural modulus in four-point bending;

\(F\): maximum load in the load-deflection curve;

\(L\): support span;

\(b\): width of the specimen;

\(h\): height of the specimen;

\(S\): slope of the linear portion of the load-deflection curve.

2.8. Statistical Analysis

The mechanical test results were analyzed with PASW Statistics 18.0 (Statistical Package for Statistical Science Inc., Chicago, IL, USA) software. The level of statistical significance \(p\) was set as 0.05 and \(p\) values less than 0.05 were considered as statistically significant in all the tests. Individual one-way factorial analysis of variance (ANOVA) followed by Turkey post hoc tests was carried out. The dependent variables (hardness, flexural modulus and strength in 3- and 4-point bending tests) were compared with two independent factors (resin matrix composition and storage conditions). Besides, the flexural strength and modulus values obtained in three- and four-point bending were compared with Independent-Sample T test.
2.9. Scanning Electron Microscopy

For all the subgroups with different storage conditions in each composition group, representative fractured specimens after 3- and 4-point bending tests were selected for the scanning electron microscopy analysis. Firstly, the samples were fixed on aluminium sample-holder stubs and sputtered with gold in an ion sputterer (JFC-1100, JEOL, Tokyo, Japan). Then the samples were examined by taking images with a scanning electron microscope (SEM) (XL30CP Philips, Eindhoven, The Netherlands). The working distance was around 20 mm and the acceleration voltage was 10.0 kV [14]. The fracture morphology and adhesion between the fiber and matrix after fracture were observed.

3. Results and Discussion

3.1. Fibre Content of Test Specimens

The average (± SD, standard deviation) fiber content was 42.00 ± 0.75 vol%.

3.2. Water Sorption and Solubility

According to Figure 1, all the four materials showed a relatively sharp weight increase from 0 day to 4 days in water storage, which showed that water sorption of the specimen was faster than dissolution of the soluble substances from the specimen into water. Then from 4 days to 22 days, the specimen weights were more or less stable, which meant that water sorption of the specimen and dissolution of the soluble substances were in equilibrium.

In Lassila et al.’s study [25], the 30 d water sorption for FRCs incorporated with 45 vol% glass fiber were in the range of 0.4 to 2.9 wt%. According to Figure 1, the 30
d water sorption for ‘Control’, ‘Exper 1’, ‘Exper 2’ and ‘Exper 3’ groups were: 0.7 wt%, 2.6 wt%, 1.1 wt% and 1.3 wt% respectively, which were acceptable, even though these were slightly higher values.

Compared with the other three groups, ‘Exper 1’ had the greatest increase in weight during the first 4 days of storage, while the other three materials had relatively similar behavior in water sorption and solubility.

3.3. Hardness

Referring to Le Bell-Rönnlöf’s work [22], in which the FRC specimen with semi-IPN (semi-interpenetrating polymer network) in dry condition had a Vickers hardness value of 18, the Vickers hardness values obtained in this current study are acceptable.

Table 3 shows that under the same storage conditions, the control group had the highest Vickers hardness while the Exper 3 group had the lowest. Moreover, this was with all the three different storage conditions.

In the ‘Control’ and ‘Exper 1’ groups, the hardness decreased from dry to 30 d storage, the decrease of ‘Exper 1’ being more obvious. From 30 d to 60 d storage, the hardness went up for these two groups, with the increase for ‘Exper 1’ again more obvious. In the ‘Exper 2’ and ‘Exper 3’ groups, the trend was a little different: from dry to 30 d, hardness decreased; from 30 d to 60 d, there was no obvious change in hardness. All these trends showed that water storage caused some decrease in Vicker’s hardness of both experimental and control groups.

According to the results of ANOVA test, different storage conditions did not produce any statistically significant difference in the hardness values; while for differing resin matrix composition, the hardness comparison for the four groups suggested the following sequence: ‘Control’ > ‘Exper 1’ = ‘Exper 2’ > ‘Exper 3’.
3.4. Three-point Bending

3.4.1. Flexural Strength

With dry storage (Figure 2 and Table 4), the ‘Control’ group had the highest flexural strength value (605 ± 126 MPa) while the ‘Exper 3’ group had the lowest value (471 ± 36 MPa). After 30-day storage in DI water at 37°C, ‘Exper 2’ had the highest flexural strength (605 ± 44 MPa) while ‘Exper 3’ still had the lowest (408 ± 56 MPa). With 60-day storage in water, ‘Control’ had the highest value (654 ± 83 MPa) while ‘Exper 1’ had the lowest value (463 ± 82 MPa).

In previous researches [20, 21], flexural strengths of E-glass FRCs with bis-GMA-MMA-based matrix in three-point bending were obtained in a range of 180 MPa to 600 MPa. Even though the current work had different components in the FRC specimens from those in previous studies, the consistency showed that the current study results are acceptable. Besides, results on the current experimental specimens suggest that these experimental specimens were relatively strong in flexure.

As storage time increased from 0 day (dry storage) to 60 days, there was no uniform trend in change in strength changing with storage length for the four groups.

According to the ANOVA test, there was no statistically significant difference in flexural strengths with different storage conditions; while for different resin matrix composition groups, the strength order was: ‘Control’ > ‘Exper 1’ = ‘Exper 2’ > ‘Exper 3’.

3.4.2. Flexural Modulus

With dry storage (Figure 3, Table 4), the ‘Control’ group had the highest value (23.9 ± 5.3 GPa) while ‘Exper 1’ had the lowest value (16.7 ± 4.5 GPa). After 30 days storage in DI water, ‘Exper 3’ had the highest modulus value (19.8 ± 5.1 GPa) while ‘Exper 1’
had the lowest value (16.2 ± 0.5 GPa). With 60 days storage, values for the four materials were close to each other, with ‘Control’ the highest (18.8 ± 1.1 GPa) and ‘Exper 2’ the lowest (17.1 ± 0.9 GPa).

For flexural modulus, there was again no uniform trend in change in modulus value with storage conditions for all the four materials.

In Matinlinna et al.’s works [20, 21], flexural modulus of E-glass FRC with bis-GMA-MMA-based matrix in three-point bending was between 18.4 to 9.2 GPa. According to figure 3, values of the experimental specimens obtained in the current study were all near the upper bound of the previous range.

According to the ANOVA test, for different storage conditions, the flexural modulus order was: dry > 30 d = 60 d; while for different resin matrix composition groups, the modulus comparison was: ‘Control’ > ‘Exper 1’ = ‘Exper 2’ = ‘Exper 3’.

3.5. Four-point Bending
3.5.1. Flexural Strength

After storage in water, both 30 d and 60 d storage (Figure 4), the flexural strengths were lower than those in dry storage.

With dry storage, the ‘Control’ group had the highest value (461 ± 50 MPa) while the ‘Exper 1’ group had the lowest value (363 ± 39 MPa). After 30-day storage in DI water at 37°C, ‘Control’ still had the highest flexural strength (400 ± 63 MPa) while ‘Exper 1’ had the lowest (314 ± 22 MPa). With 60-day storage in water, ‘Control’ had the highest value (358 ± 47 MPa) while ‘Exper 2’ had the lowest value (329 ± 28 MPa). Thus, the ‘Control’ group had the highest values after dry, 30-day-water and 60-day-water storage among the four groups.

According to the ANOVA test, comparison for different storage conditions was:
dry > 30 d = 60 d; while for different resin matrix composition groups, the strength order was: ‘Control’ > ‘Exper 1’ = ‘Exper 2’ = ‘Exper 3’

3.5.2. Flexural Modulus

With dry storage (Figure 5), the ‘Exper 2’ group had the highest value (29.9 ± 3.6 GPa) while ‘Exper 1’ had the lowest value (24.4 ± 7.1 GPa). After 30 days storage in DI water, ‘Control’ had the highest modulus value (25.0 ± 2.3 GPa) while ‘Exper 3’ had the lowest value (22.6 ± 1.7 GPa). With 60 days storage, values for the four materials were close to each other, with ‘Exper 1’ the highest (26.8 ± 4.4 GPa) and ‘Exper 2’ the lowest (24.8 ± 2.5 GPa).

For flexural modulus, there was again no uniform trend in change in modulus value changing with storage conditions for any of the four materials.

According to the ANOVA test, with different storage conditions, the modulus order was: dry > 30 d = 60 d. There was no statistically significant difference in flexural modulus for different resin matrix composition groups in four-point bending.

3.6. Comparison between the Three- and Four-point Bending Test Results

Comparing Figure 2 to 4 and 3 to 5 respectively, flexural strengths obtained in three-point bending were higher than those in four-point bending, with the difference in the range of 56 to 295 MPa, which was statistically significant. One reason might be the sensitivity of four-point bending to surface flaws of the specimen [9], which was reflected in reduced strength values in four-point bending. There might be other reasons. Firstly, the deflections before fracture of the specimens might exceed the range in which the strength calculation formulas are valid. So the strengths obtained with these formulas might not be accurate. Secondly, the specimens were not thin
enough. In other words, the support span to height ratio was not low enough. This might result in localized stresses in the region near the loading points and induce certain shear deformation in addition to the pure flexure in the specimens [26, 27]. Besides, the difference in flexural strength values might also result from differing specimen geometries and dimensions, material inhomogeneity, and surface conditions in the specimen [9, 20].

As for flexural modulus, the values obtained in three-point bending were on average 7 GPa (0.27%) lower than those in four-point bending, which was also statistically significant. This result also agreed with previous research on comparison of flexural modulus values between three- and four-point bending [26, 27].

From the comparison between Figure 2 to 4 and 3 to 5, respectively, it was also found that the groups with extreme (the highest or the lowest) strength or modulus value were not necessarily the same groups in three- and four-point bending in the same storage conditions. For example, the highest strength group of 30 d storage in three-point bending was ‘Exper 2’; while the highest strength group of 30 d storage in four-point bending was ‘Control’, which were not the same composition groups.

As Figure 6 shows, the same specimens in three-point bending had a lower flexural modulus and fractured at higher flexural stress than in four-point bending. In both tests, the curves had similar shape.

3.7. SEM Analysis

Representative SEM images were selected and are shown in Figures 7 and 8. The fracture-site morphology of all four matrix composition groups after different storages was similar. As Figure 8 shows, after fracture, for most specimens with varying matrix composition and storage, some resin matrix was still adhered to the fiber surface,
showing cohesive-interfacial mixed fracture type and relatively durable matrix-fiber adhesion.

3.8. Comprehensive Analysis

As is clear from Table 4, the control group showed superior mechanical performance in most of the tests carried out.

4. Conclusions

- Under the same storage conditions, the control group had the highest Vickers hardness while the ‘Exper 3’ group had the lowest hardness. The hardness range for experimental groups was 13.7-24.0 units.

- Different storage conditions did not exhibit any statistically significant difference in the hardness values. However, for different resin matrix compositions, the hardness for the four groups was significantly different: ‘Control’ > ‘Exper 1’ = ‘Exper 2’ > ‘Exper 3’.

- The experimental specimens were relatively strong and stiff in three-point bending compared to previous research. In three-point bending, for experimental groups, the flexural strength range was from 605 ± 44 MPa to 408 ± 56 MPa, and modulus range was from 16.2 ± 0.5 GPa to 21.5 ± 2.7 GPa.

- In three-point bending, there was no statistically significant difference in flexural strengths with different storage conditions. However, for different resin matrix composition groups, the strengths were significantly different: ‘Control’ > ‘Exper 1’ = ‘Exper 2’ > ‘Exper 3’.

- In three-point bending, for different storage conditions, the flexural moduli were
significantly different and the order was: dry > 30 d = 60 d; while for different resin matrix composition groups, the modulus comparison was: ‘Control’ > ‘Exper 1’ = ‘Exper 2’ = ‘Exper 3’.

• In four-point bending, for experimental groups, the flexural strength range was from 314 ± 22 MPa to 415 ± 44 MPa, and the modulus range was from 22.6 ± 1.7 GPa to 29.9 ± 3.6 GPa.

• In four-point bending, the strength order for different storage conditions was: dry > 30 d = 60 d; while for different resin matrix composition groups, the strength order was: ‘Control’ > ‘Exper 1’ = ‘Exper 2’ = ‘Exper 3’.

• In four-point bending, under different storage conditions, the modulus order was: dry > 30 d = 60 d. There was no statistically significant difference in flexural modulus for different resin matrix composition groups.

• The same specimens in three-point bending had a lower flexural modulus and fractured at higher flexural stress than in four-point bending. The differences were statistically significant.

• According to the SEM micrographs, after fracture, some resin matrix was still adhered to the fiber surface, showing cohesive-interfacial mixed fracture type and relatively durable matrix-fiber adhesion.

5. Summary

As the comprehensive analysis shows, the control group showed superior mechanical performance in most of the tests. Thus, the hypothesis at the beginning was not validated and further research will be carried out to find the mechanically optimized UEDMA-TEGDMA-based resin matrix.
Acknowledgements

Esstech Inc. (Essington, PA, USA) is acknowledged for generously donating UEDMA monomer to this study. Stick Tech Ltd. (Turku, Finland) is gratefully thanked for the E-glass fiber materials. Dr. Eija Säälynöja and Mr. Timo Koski, both from Stick Tech Ltd. are sincerely thanked for their assistance and fruitful discussions.
References


(2000).


Figure 1. Average weight of the specimens in each composition group with storage time in DI water at 37°C.

Figure 2. Flexural strength for the four groups with three storage conditions in three-point bending test.
Figure 3. Flexural modulus for the four groups with three storage conditions in three-point bending test.

Figure 4. Flexural strength for the four groups with three storage conditions in four-point bending test.
Figure 5. Flexural modulus for the four groups with three storage conditions in four-point bending test.

Figure 6. Representative stress-strain curves for three- and four-point bending tests with Exper 3 specimens after 60 d DI water storage at 37 ºC.
Figure 7. SEM image of the fractured surface of a test specimen in the group ‘Exper 3’, tested after water storage in 30 days (the tension side; magnification 100×).

Figure 8. SEM image of the fractured surface of a test specimen in the group ‘Exper 1’, tested after water storage in 30 days (the tension side; magnification 500×).
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Table 2.
Matrix composition (in wt%) for the control and experimental groups.

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<th>Component Group</th>
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<td>19.6</td>
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Key: ‘Exper 1’ = Experimental group 1;
‘Exper 2’ = Experimental group 2;
‘Exper 3’ = Experimental group 3.

Table 3.
Vicker’s hardness for the four groups with three different storage conditions.

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<th>Exper 1</th>
<th>Exper 2</th>
<th>Exper 3</th>
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<td>Dry</td>
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<td>31.99 ± 6.85</td>
<td>22.44 ± 3.12</td>
<td>24.025 ± 8.35</td>
<td>16.42 ± 1.69</td>
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<tr>
<td>30 d</td>
<td></td>
<td>31.04 ± 7.63</td>
<td>17.37 ± 2.54</td>
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<td>13.89 ± 0.79</td>
</tr>
<tr>
<td>60 d</td>
<td></td>
<td>33.802 ± 6.48</td>
<td>21.28 ± 3.10</td>
<td>17.89 ± 1.52</td>
<td>13.73 ± 1.22</td>
</tr>
</tbody>
</table>
**Table 4.** The composition groups with the best mechanical performance for each storage subgroup 7 and 8 now:

<table>
<thead>
<tr>
<th>Mechanical property</th>
<th>Vickers hardness</th>
<th>Flexural strength in 3-point bending test</th>
<th>Flexural modulus in 3-point bending test</th>
<th>Flexural strength in 4-point bending test</th>
<th>Flexural modulus in 4-point bending test</th>
</tr>
</thead>
<tbody>
<tr>
<td>Group with the highest value for each storage subgroup</td>
<td>Control for every storage subgroup</td>
<td>E2 for 30 d; Control for 60 d</td>
<td>E3 for 30 d; Control for 60 d</td>
<td>Control for both 30 d and 60 d</td>
<td>Control for 30d; E1 for 60 d</td>
</tr>
</tbody>
</table>