Physicomechanical characterization of polyetheretherketone and current esthetic dental CAD/CAM polymers after aging in different storage media

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ABSTRACT

Statement of problem. Polyetheretherketone (PEEK) can be used to support fixed dental

prostheses (FDPs). However, information about the physicomechanical characterization is

still scarce.

Purpose. The purpose of this in vitro study was to assess the effect of different aging

regimen/durations on roughness, solubility, water absorption, Martens hardness/HM, and

indentation modulus/E_{IT} on different computer-aided design and computer-aided

manufacturing (CAD/CAM) polymers.

Material and methods. Forty standardized specimens of the following materials were

fabricated: PEEK: Dentokeep/DK; hybrid material: VITA Enamic/EN; composite resins:

LAVA Ultimate/LU and an experimental CAD/CAM nanohybrid-composite resin/EX;

PMMA-based: VITA CAD-Temp/CT, Telio CAD/TC, artBloc Temp/AT, and ZENOTEC

ProFix/ZP; a nanofilled-polymer for interim restorations: Protemp 4/CG served as the control

group. Specimens were stored in sodium chloride, artificial saliva, physiological saliva, and

distilled water at 37°C for 1, 7, 14, 28, 90, and 180 days. Roughness, water absorption, HM,

and E_{IT} were investigated after each storage period; solubility was determined after 180 days

only. Data were analyzed using weighted 3/2/1-way ANOVA and the posthoc Scheffé tests

(α=05).

Results. Storage media had no effect on surface roughness and water absorption.

Physiological saliva revealed the highest significant impact on solubility followed by artificial

saliva, sodium chloride, and distilled water. Water absorption increased significantly with

storage duration. PEEK showed the lowest solubility and water absorption values. The highest

solubility was observed for the conventional polymer CG, and the highest water absorption was found for the composite LU. PMMA-based TC, ZP, CG, and AT showed the lowest HM and indentation modulus, followed by CT, and PEEK. The highest values were observed for the hybrid material EN, followed by LU and EX.

Conclusions. The hardness parameters of PEEK were comparable with those of PMMA-based materials.

Clinical implications

With respect to the hardness parameter, PEEK can be recommended as a framework material for FDPs. PEEK is comparable with established PMMA-based materials and displays favorable water absorption and solubility characteristics.

INTRODUCTION

The restorative and prosthetic materials used in oral rehabilitation are subjected to a complex and changing humid and wet oral environment, which is physiologically characterized by natural saliva and its components.[1-3]Polymer networks, in particular, tend to absorb water from the surroundings depending on their specific hydrophilicity and on the humidity of the mouth.[4,5] Potential deleterious effects may arise from pH changes due to cariogenic biofilms in the oral ecology, diet intake, and different enzymes.[6]This can lead not only to esthetic problems in terms of water absorption and discoloration but also to the mechanical weakening of the materials and decreased fracture resistance or increased wear.[7,8]

Novel polymers with different matrix compositions and variable percentages of ceramic and resin fillers are available as monolithic materials fabricated by computer-aided design and computer-aided manufacturing (CAD/CAM) techniques. The manufacturers claim that these materials display improved mechanical properties, lower discoloration rates, and higher wear resistance compared with manually polymerized polymers for interim

restorations due to better manufacturing processes, which encompass high pressures and temperatures leading to better and more constant restoration qualities.[9-12] Therefore, such novel CAD/CAM polymers may be considered as alternative materials to ceramic fixed dental prostheses (FDPs).

The most frequently used CAD/CAM polymers are PMMA-, composite resin-, or polyetheretherketone (PEEK)-based materials. PEEK shows remarkable mechanical properties[13,14] and has been evaluated for use for FDPs in load-bearing areas.[15-17] However, PEEK restorations have a grayish-brown or pearl-white opaque color and need to be veneered with composite resin. Previous studies obtained adequate bond strength to composite resin cements when PEEK surfaces were pretreated and conditioned using adhesive systems contains MMA-monomers.[18-25]

Variations in the composition of CAD/CAM polymers aiming to improve mechanical properties may affect water absorption[9,26,27] and dimensional change. These alterations can be explained by fluid absorption in the polymer matrix due to molecule polarity, especially within the first few days, leading to an overall imbalance between the intermolecular forces.[5,28] Martens hardness enables a physicomechanical characterization of the local mechanical properties of materials, including the elastic and plastic parts under different loading regimens.[29,30] Most of the available studies, however, only determined the reduced mechanical properties of resins after aging in artificial saliva, alcohol, and distilled water.[31,32] To date, only limited information is available on the long-term behavior of contemporary polymers such as PEEK with regard to different aging regimens. The purpose of this study was to determine the physicomechanical characteristics of PMMA, composite resin, and PEEK after different aging regimens and durations with the following assessment methods: roughness, solubility, water absorption, Martens hardness, and indentation modulus. The null-hypotheses tested were that storage media and storage duration would not affect the roughness, solubility, water absorption, Martens hardness, or indentation modulus of the

tested polymers. In addition, the aging of PEEK was compared withPMMA and composite resin materials.

MATERIAL AND METHODS

The investigated materials are summarized in Table 1. From the control group(CG),15 blocks (15×10×10 mm) were fabricated from a silicone mold and polymerized in a pressure pot (Palamat Elite Polymerization Unit; Heraeus Kulzer) at 450 kPa for 20 minutes. Subsequently, 360 specimens were prepared by cutting the blocks into standardized pieces of 10×10×3 ±0.005 mm (n=40/material group) with a diamond saw (Secotom-50; Struers) under water-cooling. The specimens were polished (Tegramin-20; Struers) with a series of silicon carbide papers (SiC) up to P4000 under water-cooling and cleaned in an ultrasonic bath (Ultrasonic T-14; L&R Manufacturing Co) with distilled water for 5 minutes. Specimens from each group were divided into 5 subgroups (n=10) with different storage media: sodium chloride (NaCl; physiologic salt solution 0.9%; B. Braun; pH = 5.7), artificial saliva (KCl 0.4 g/L, NaCl 0.4 g/L, CaCl2, $2H_2O$ 0.906 g/L, NaH_2PO_4, $2H_2O$ 0.690 g/L, Na_2S, $9H_2O$ 0.005 g/L, and urea 1 g/L; pH = 4.7),[33] distilled water (Aqua Bidest.; Kerndl; pH=6.7), and natural extracted saliva (pH=6.85) were used. To represent the diverse bacterial populations, the natural saliva from 10 healthy individuals was collected, and an equal volume of saliva from each of the donors was combined for the experiments. All healthy individuals had natural dentitions without any active caries or clinically diagnosed periodontitis. They had not brushed their teeth in the previous24 hours and had abstained from food/drink intake at least 2 hours before donating saliva. Stimulated saliva was collected during parafilm chewing and kept on ice. It was stored at 37°C, and the media were changed every 14 days. The different pH values were measured on a daily basis (Voltcraft PH-100 ATC; Conrad Electronic). After 1, 7, 14, 28, 90, and 180 days, the roughness, water absorption, Martens hardness, and indentation modulus were measured. Solubility was determined after 180 days.

The surface roughness measurements were made with a profilometer (MarSurf M400+SD26; Mahr GmbH). To achieve accurate and reproducible results, the specimens were fixed in a holding device to keep the surface parallel to the platform of the machine. The 90-degree measuring sensor had a diamond probe tip (diameter 2 μm). The contact force was held at 0.7 mN. Each specimen was measured 6 times with a measuring track of 6 mm set at a distance of 0.25 mm between each track (3×vertically/3×horizontally), and the mean roughness value for each specimen was calculated.

In order to assess the solubility before and after storage, all specimens were stored in a drying chamber (Memmert U30 type with Roth Silica Gel Orange; Carl Roth) at a constant temperature of 37°C until a constant weight was reached. The duration of drying to achieve a constant temperature was approximately 2 weeks for all specimens under investigation. The drying values were analyzed using the specimens' weight, which was measured with a high-precision scale (NewClassic MF Model, MS 104S/M01; Mettler Toledo). Solubility values were then analyzed with the following equation using the weight results before and after drying: $S = m_1 - m_2$; m_1: specimen´s weight before storage; m_2: specimen´s weight after 180 days of storage.

The water absorption during the entire aging period of 180 days was also analyzed on the basis of the weight differences measured always with the high precision scale. The specimens were stored in the drying chamber and weighed until they reached a constant weight. All specimens were then stored in the respective test media in a scaled chamber (Hera Cell 150; Heraeus) at 37°C for storage of 1, 7, 14, 28, 90, and 180 days. On the day of measuring and after cleaning in distilled water for 5 seconds, the specimens were gently wiped with a dry filter paper on both sides and air-dried with oil-free air for 15 seconds before testing. The water absorption was analyzed with the formula: $WA = m_1 - m_3$; m_1: specimen´s weight on the specific storage level; m_3: specimen´s first weight of dried specimens.

The Martens hardness (HM) and indentation modulus (E_{IT}) were assessed using a universal hardness testing machine (Zwick/Roell ZHU 0.2/Z2.5; Zwick). For this purpose, the diamond indenter pyramid (α=136 degrees) of the hardness testing machine was pressed vertically into the specimen´s polished surface with a load of 10 N for 20 seconds.[34] The maximum penetration depth was 0.05 mm. The indenter displacement of the definite test frame represented the total amount of the elastic deformation of the surface along with the plastic depth of the impression.[30] All specimens were tested 3 times, and the values of HM and E_{IT} were calculated (TestXpert V12.3 Master; Zwick) with the following equations (DIN EN ISO 14577)[35]:

$$HM = \frac{F}{A_S\,(h)} = \frac{F}{26.43 \times h^2}$$

HM: Martens hardness (N/mm^2); *F*: Test force (N); $A_S\,(h)$: Surface area of the indenter at distance *h* from the tip (mm^2)

and

$$E_{IT} = (1 - v_s^2)\left(\frac{\sqrt[2]{A_p(h_c)}}{\sqrt{\pi}\,S} - \frac{(1-v_i^2)}{E_i}\right)^{-1}$$

; E_{IT}: indentation modulus, elastic modulus of the indenter (Vickers pyramid); v_s: Poisson ratio of the specimen; v_i: Poisson ratio of the indenter.

Descriptive statistics were calculated, and the normality of data distribution was tested using the Kolmogorov-Smirnov and Shapiro-Wilk test. The Levene test was used to evaluate the assumption of variances' homogeneity. Data were analyzed using the weighted 3-way ANOVA, followed by the posthoc Scheffé test. In addition, the weighted covariance analysis was conducted for water absorption. For solubility defined as the difference between day 180 and initial values, a 2-way weighted ANOVA and two 1-way weighted ANOVAs followed by the posthoc Scheffé test with respect to the 2 factors of material and storage medium were considered. The statistical analyses were performed using a statistical program (SPSS v20; IBM Corp) (α=.05).

RESULTS

The Kolmogorov-Smirnov and Shapiro-Wilk tests indicated the highest rate (79 %) of violations of the normality assumption for surface roughness. The corresponding percentages for solubility, water absorption, Martens hardness, and indentation modulus were equal to 25%, 11 %, 27 %, and 16 %. The violation of the normality assumption was not caused by outliers but rather by measurement rounding, leading to an increased coarseness of the observations in each test group. Additionally, the Levene tests for all dependent variables indicated violation of the variance homogeneity assumption ($P<.001$). The reasons for the increased spread were differences in the dependent variables: surface roughness (EX) solubility (TC, AT, CG), water absorption (ZP), Martens hardness (EN, LU, EX), and indentation modulus (EN, LU, EX). Consequently, weighted statistical analyses had to be considered for all dependent variables.

According to the 3-way ANOVA, the 3-way interaction ($P<.001$) of materials, storage duration, and storage media for surface roughness was significant. It originated mainly in EX showing lower and in AT showing higher initial roughness in distilled water; ZP presented higher roughness for artificial and physiological saliva at day 90. The 2-way interaction between materials and storage duration ($P<.001$) originated mainly in EX having initially higher surface roughness. As far as interaction between materials and storage medium ($P<.001$) was concerned, LU stored in physiological saliva showed the highest roughness. For storage duration and storage media ($P<.001$) artificial and physiological saliva showed higher roughness at day 90 than both the other media. In addition, the tested materials ($P<.001$) and the storage duration ($P<.001$) affected the roughness results (Fig. 1). In contrast, the storage medium ($P=.005$) had no effect on the surface roughness. In general, the lowest surface roughness was observed for the PMMA-based groups TC and ZP, whereas the highest values were found in the EX group ($P<.001$) (Fig. 1). With regard to storage duration, higher surface

roughness was observed at the beginning of the experiment and after 180 days, followed by 90 days of storage and a storage duration of between 1 and 28 days ($P<.001$).

The 2-way ANOVA interaction for solubility was significant ($P<.001$). This interaction originated in the CG and CT and showed lower solubility for artificial and physiological saliva than for NaCl and distilled water in contrast with DK, EN, and EX, which showed practically unchanged solubility independent of the storage medium (Fig. 2). In general, physiological saliva followed by artificial saliva affected the solubility results more than storage in NaCl. Distilled water had the lowest impact on solubility. PEEK (DK) showed the lowest solubility, whereas the highest solubility was observed for the conventional polymer group for temporary restorations (CG). Specimens stored in physiological saliva showed no differences. Significant differences are shown in Table 2.

The 3-wayANOVA for water absorption found a significant 3-way interaction ($P<.001$) among materials, storage duration, and storage media. It originated mainly in the CG showing different progress for NaCl for 1 and 7 days. The 2-way interaction between materials and storage medium ($P<.001$) was significant, but we were unable to detect its main cause. As far as the interaction between materials and storage duration ($P<.001$) was concerned, the CG showed higher water absorption at day 7. For storage duration and storage media ($P<.001$) the interaction at 90 days in distilled water showed lower water absorption. As far as main effects are concerned, the storage medium had no effect on the water absorption results ($P<.001$). However, significant effects of material ($P<.001$) and storage level ($P<.001$) were observed. Therefore, the storage medium groups were pooled, and the results were presented in box-plots with respect to material types and storage media (Fig. 3). In general, the increase of storage time significantly increased the water absorption values ($P<.001$). PEEK (DK) presented the lowest water absorption rates ($P<.001$). The highest values were observed for the composite resin material LU. In addition, the weighted analysis of covariance indicated a significant interaction term between storage duration and material.

Water absorption increase was steeper ($P<.001$) for EN, LU, EX, CT, TC, and AT than for the CG. No difference in the slope of the water absorption for DK and CG with respect to storage duration was found ($P=.999$).

The 3-way interaction for Martens hardness among the materials, storage duration and storage media was found with the 3-way ANOVA ($P<.001$). It originated mainly in EN showing lower HM for artificial saliva at day 90 than at day 180, which contrasted with other materials and storage media. As far as interaction between materials and storage medium ($P<.001$) was concerned, LU showed elevated HM for NaCl and artificial saliva than EN. The 2-way interaction between materials and storage duration ($P<.001$) originated mainly in EN having a differing progress of HM than LU and EX and the rest of the materials. Interaction for storage duration and storage media ($P<.001$) could not be easily interpreted as it appeared to be marginalized with respect to the material. In principle, the groups stored for 90 and 180 days showed lower HM than the non-aged groups ($P<.001$). With respect to the aging media, the specimens stored in artificial saliva presented the lowest HM as compared with specimens aged in distilled water or physiological saliva ($P<.001$). Storage in NaCl produced lower HM than storage in physiological saliva ($P<.001$). The PMMA-based materials (TC, ZP, CG, and AT) showed the lowest HM, followed by CT and PEEK DK ($P<.001$). The highest values were observed for the hybrid material EN, followed by the composites LU and EX ($P<.001$) (Supplementary Fig. 1).

Interpretations of the 3-way interaction ($P<.001$) and the 2-way interactions ($P<.001$) for indentation modulus was similar to those discussed for HM. According to the 3-way ANOVA, material ($P<.001$) and aging medium ($P<.001$) affected E_{IT}. The aging level, however, had no effect on E_{IT} (P=.155). The influence of the material (Fig. 5) and the aging medium was similar to the HM results (Table 3).

DISCUSSION

The highest impact on solubility was found for storage in physiological saliva, followed by artificial saliva, NaCl, and distilled water. This outcome indicates that natural saliva contains components that lead to a higher solubility rate than artificial saliva and especially NaCl and distilled water. Physiological saliva is composed of a complex mixture of secretory organic and inorganic products, whereas water contained 99% in contrast with pure distilled water (100%) with the lowest impact on solubility. All organic and inorganic molecules and solid components are dissolved in the aqueous component and can be different from one person to another and even from one person at different times during the day.[2,3] This might have led to the diverse results in the present study when the extraction of saliva differed minimally in time or composition. In addition to the inorganic part of weak and strong ions (Na^+, K^+, and Cl^-, for example), natural saliva consists of organic parts, including urea and more than 400 types of protein.[2,3] These proteins vary in artificial saliva and possibly reflect the differing results and the higher solubility of natural saliva. To date, little is known about the behavior of the tested materials when stored in artificial and particularly in physiological saliva. Only AT showed no solubility after 180 days of physiological saliva storage. The remaining materials exhibited significant solubility, regardless of the storage media. The lowest material loss was observed for PEEK (DK), the highest for the CG.

The water absorption results were independent of the storage medium. Material and storage duration had significant effects on water absorption. Unsurprisingly, longer storage times resulted in increased water absorption rates, which is corroborated by the composite resin results from a previous study.[4] However, in the case of distilled water and even artificial saliva, water absorption was dependent on storage time and material.[4] Our results support the concept that water absorption generally increases with higher amounts of resin matrix and a lower amount of filler particles. Since the latter cannot absorb water, higher matrix proportions can lead to filler-matrix debonding or even hydrolytic degradation.[4,5,32] In

addition, the more homogeneous a polymer is, the less water is absorbed and the less soluble characteristics it has.[12] As confirmed in this study, industrially fabricated CAD/CAM materials show a reduced risk of porosities and therefore higher and more solid mechanical properties.[16] Another study reported negative effects on surface properties when microhybrid composite resin was stored in saliva, alcohol, and bacterial acid. However, the pH changes seemed not to intensify surface degradation.[5,32] Bacterial contamination in the physiological saliva may also have contributed to additional degradation of the tested specimens. The saliva was not filtered or sterilized to mimic the clinical situation. Furthermore, water absorption and release can cause molecular instabilities, which may lead to crack formations and a decrease in mechanical properties as already mentioned.[28] Water absorption not only affects physical and mechanical properties, especially of composite resins but also decreases surface hardness and the elastic modulus,[4] particularly as reflected in this study.

This study showed that specimens stored in artificial saliva resulted had lower HM values than specimens aged in distilled water or physiological saliva. In general, non- or low-filled materials (PMMA and PEEK) showed the lowest HM, whereas the highest values were found for materials with high percentages of filler particles, such as VITA Enamic, LAVA Ultimate, and the experimental nanohybrid-composite resin (with a filler content of 80%). Therefore, the null hypothesis that storage media and storage duration have no effect on the roughness, solubility, water absorption, HM, and E_{IT} of the tested polymers is rejected.

The most obvious changes in the mechanical and physical properties of polymers can be expected within the first 30 days of testing based on the results of previous studies with a comparable study design.[36,37] Therefore, 4 aging levels in this first month (1, 7, 14, and 28 days) showed assessing distinct hardness changes. Two more measurements after 90 and 180 days were made when more stable values were again expected. Temperature changes to imitate the natural oral environment while drinking and eating were made in distilled water in a thermocycler, which, because of the vaporization process, required a large volume of liquid.

The present study used different media, where physiological saliva especially was difficult to acquire in large volume. For a meaningful comparison of all media, storage in an incubator at a constant temperature of 37°C (clinical mouth temperature) was chosen. Further studies analyzing mechanical parameters at different temperatures would be interesting. Laboratory tests provide only some evidence of reliable values. Clinical studies must be performed to validate the obtained results.

One limitation of this study was the lack of power analysis in its planning stage. When choosing 10 observations, we relied to some extent on the experience of a previous study also based on 10 observations.[37] However, a posthoc power analysis to justify the chosen sample size at least partly was conducted. Given the observed pooled standard deviation of solubility (0.4 mg), the 2-sided 2-sample $t$test has a power of 98% to detect a difference of 0.75 mg (50% of the pooled effect in CG). Note that the observed difference of 1.2 mg between the pooled means in DK and CG is larger and corresponds to an 80% decrease insolubility with respect to the CG.

CONCLUSION

Within the limitations of this in vitro study, it can be concluded that the hardness parameters of PEEK were comparable with those of established PMMA-based materials and that PEEK shows low solubility and water absorption rates. Therefore, PEEK can be recommended for long-term restorations.

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Table 1. Summary of materials, abbreviations, compositions, manufacturers, and Lot numbers

Material group	CAD/CAM materials	Abbreviation	Composition	Manufacturer	Lot No.
CAD/CAM PEEK for definitive restorations	Dentokeep	DK	Ceramic filled (20%) polyetheretherketone (PEEK)	nt-trading	11DK14001
CAD/CAM Hybrid material for definitive restorations	VITA Enamic	EN	Ceramic: 86% SiO_2: 58-63%, Al_2O_3: 20-23%, Na_2O: 6-11%, K_2O: 4-6%, B_2O_3: 0.5-2%, ZrO_2,CaO: < 1% Polymer: 14% UDMA+TEGDMA	VITA Zahnfabrik	34580
CAD/CAM nanohybrid-composites for definitive restorations	LAVA Ultimate	LU	nanoceramic components embedded in highly cross-linked polymeric matrix	3M ESPE	N392139

	exp. CAD/CAM nanohybrid-composite	EX	nanohybrid-compositeresinwith additives filler: 80 wt%	Ivoclar Vivadent	b.28923
CAD/CAM PMMA-based materials for temporary restorations	VITA CAD-Temp	CT	PMMA microfilled	VITA Zahnfabrik	11000
	Telio CAD	TC	99.5% PMMA polymer	Ivoclar Vivadent	R36500
	artBlocTemp	AT	PMMA, OMP = organic modified polymer network	Merz Dental	23408
	Zenotec Pro Fix	ZP	PMMA unfilled	Wieland Dental	0801
Conventional polymer for temporary restorations	Protemp 4	CG	Bis-acrylate composite with nanofillers	3M ESPE	487558

Table 2. Descriptive statistics of all solubility values after 180 days storage in different media for each material separately (Difference between 0 and 180 days in mg)

Material	NaCl	Artificial saliva	Physio. saliva	Distilled water	Impact of storage medium
	Mean ±SD	Mean ±SD	Mean ±SD	Mean ±SD	
DK	-0.23 ±0.08[d/AB]	-0.29 ±0.01[d/AB]	-0.33 ±0.11[a/A]	-0.19 ±0.11[cd/B]	P=.010
EN	-0.38 ±0.15[bcd]	-0.47 ±0.24[cd]	-0.32 ±0.09[a]	-0.45 ±0.17[abcd]	P=.207
LU	-0.58 ±0.3[abc/B]	-0.54 ±0.22[cd/B]	-0.84 ±0.4[a/AB]	-1.01 ±0.24[abc/A]	P=.003
EX	-0.27 ±0.13[cd/B]	-0.45 ±0.23[cd/AB]	-0.48 ±0.2[a/A]	-0.28 ±0.09[bcd/B]	P=.013
CT	-0.95 ±0.36[ab/B]	-1.52 ±0.31[ab/A]	-1.41 ±0.24[a/A]	-0.48 ±0.36[abcd/B]	P<.001
TC	-1.03 ±0.22[a]	-1.02 ±0.6[abc]	-0.99 ±0.37[a]	-1.18 ±0.32[ab]	P=.718
AT	-1.18 ±0.36[a]	-0.74 ±0.85[c]	-0.1 ±0.31[a]	-1.22 ±0.15[ab]	P=.463
ZP	-0.66 ±0.31[abc/B]	-0.86 ±0.47[bc/B]	-1.37 ±0.39[a/A]	-0.78 ±0.29[abcd/B]	P=.001
CG	-1.13 ±0.73[a]	-1.73 ±0.34[a]	-1.78 ±0.34[a]	-1.27 ±0.28[a]	P=.439

[abc] Different letters represent significant differences between CAD/CAM materials within one storage medium.

[ABC] Different letters represent significant differences between storage media within one CAD/CAM material.

Figure 1. Roughness values with pooled storage media results divided into each material and storage day. Error bars represent standard deviation.
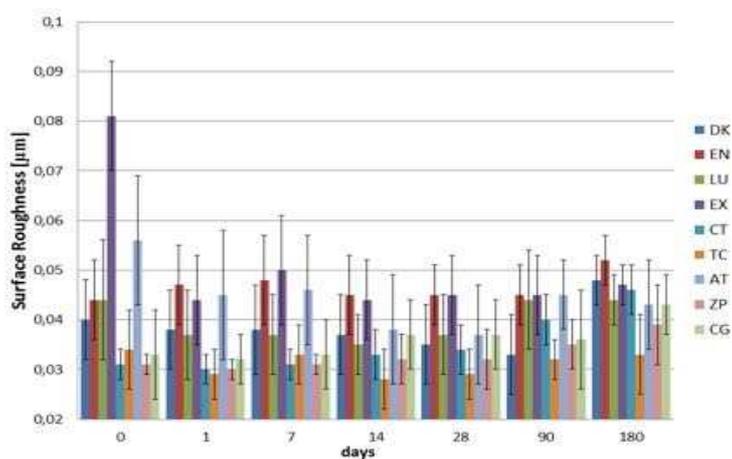

Figure 2. Solubility rates [in mg] differences between initial and after 180 days storage of different materials after immersion in different storage media . Limits of whiskers in boxplots are defined as 10th and 90th percentiles.
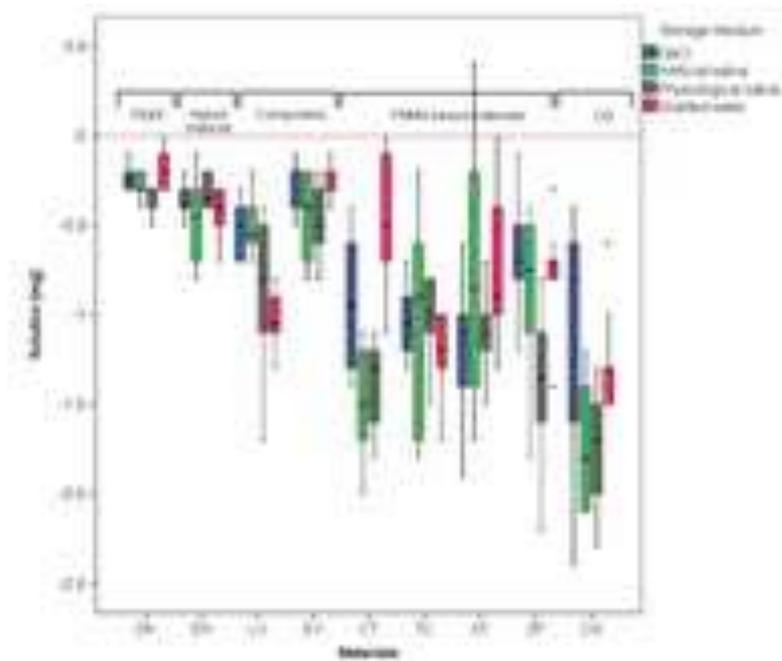
Figure 3. Scatterplot for water absorption values with pooled storage media results.
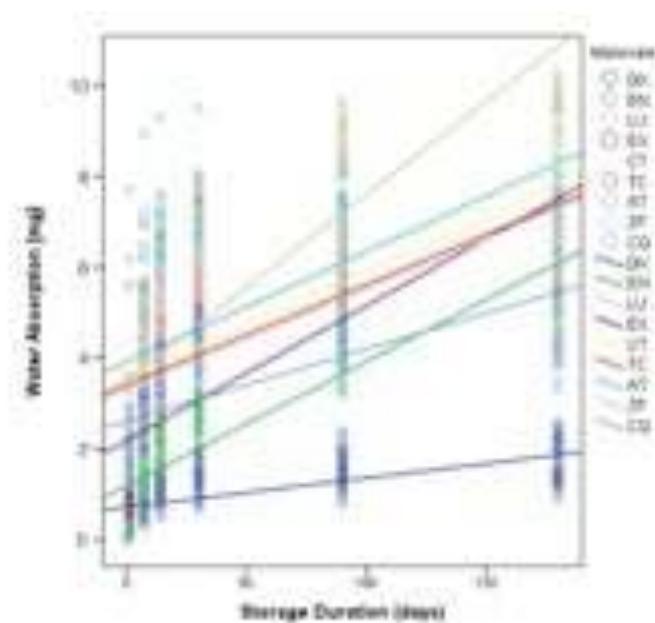

Figure 4. Pooled Martens hardness values for each material separately.Error bars represent standard deviation.
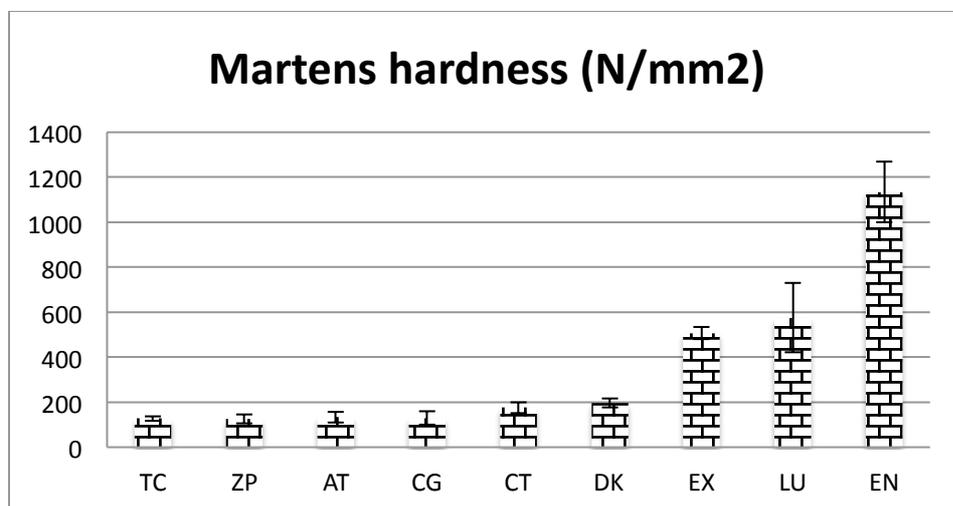
Figure 5. Pooled indentation modulus values for each material separately.Error bars represent standard deviation.