POLITECNICO DI TORINO
Repository ISTITUZIONALE

Development of glass-stalks-unsaturated polyester hybrid composites

Original
Development of glass-stalks-unsaturated polyester hybrid composites / Taurino, R.; De Bortoli, L. S.; Schabbach, M. L.; Bondioli, F.. - In: COMPOSITES COMMUNICATIONS. - ISSN 2452-2139. - 22:(2020), p. 100428. [10.1016/j.coco.2020.100428]

Availability:
This version is available at: 11583/2847048 since: 2020-09-29T16:34:40Z

Publisher:
Elsevier Ltd

Published
DOI:10.1016/j.coco.2020.100428

Terms of use:
openAccess

This article is made available under terms and conditions as specified in the corresponding bibliographic description in the repository

Publisher copyright
Elsevier postprint/Author's Accepted Manuscript

© 2020. This manuscript version is made available under the CC-BY-NC-ND 4.0 license
http://creativecommons.org/licenses/by-nc-nd/4.0/.The final authenticated version is available online at:
http://dx.doi.org/10.1016/j.coco.2020.100428

(Article begins on next page)

21 December 2022

Manuscript Details

Manuscript number	JCOMB_2019_2905
Title	DEVELOPMENT OF STALKS-UNSATURATED POLYESTER HYBRID COMPOSITES
Article type	Full Length Article

Abstract

The aim of this study is to investigate the possibility to use agro-residues of the vinification process as a cheaper and eco-friendly fillers to prepare unsaturated polyester composite for interior design building sector. The selection of stalk fibers, as an alternative ligno-cellulosic material from agricultural residues, is based on the high volume and seasonal availability throughout the year. In this work stalks-unsaturated polyester hybrid composites were manufactured and completely characterize to evaluate their mechanical, chemical and physical properties. The presence of stalk fibers, up to 50 wt%, increased Young's Modulus preserving a satisfactory tensile strength and hardness in comparison with the pure resin properties. Samples with functionalized stalk fibers were also produced in order to improve the filler-matrix adhesion. The final results showed that stalk fibers from winemaking can be satisfactory used as natural fiber resource to produce composites for furniture.

Keywords	unsaturated polyester resin; natural fibers; agro-waste; composite
Manuscript region of origin	Europe

Corresponding Author	Rosa Taurino
Corresponding Author's Institution	University of Parma
Order of Authors	Rosa Taurino, Leticia De Bortoli, Luciana Schabbach, federica bondioli
Suggested reviewers	Andrea Dorigato, marco sangermano
Opposed reviewers	Isabella Lancellotti

Submission Files Included in this PDF

File Name [File Type]

LETTER Composite Part B.docx [Cover Letter]

TEXT (Composite Part B).docx [Manuscript File]

Fig. 1.pdf [Figure]

Fig. 2.pdf [Figure]

Fig.3.pdf [Figure]

Fig.4.pdf [Figure]

Fig.5.pdf [Figure]

Fig.6.pdf [Figure]

Fig.7.pdf [Figure]

Fig.8.pdf [Figure]

To view all the submission files, including those not included in the PDF, click on the manuscript title on your EVISE Homepage, then click 'Download zip file'.

UNIMORE
UNIVERSITÀ DEGLI STUDI DI MODENA E REGGIO EMILIA

Dipartimento di Ingegneria "Enzo Ferrari"

Sede
Via Pietro Vivarelli, 10 · 41125 - Modena, Italia
T +39 059 2056177 · F +39 059 2056180

www.unimore.it
www.ingmo.unimore.it

Modena, 27th June 2019

Dear Editor,

I have the honor to submit You the work titled: "**Development of stalks-unsaturated polyester hybrid composites"** by Taurino R. et al., that I would like You to consider for publication on the "Composites Part B": Engineering.

This work highlights the potentiality of agro-residues of the vinification process (stalk fibers) as eco-friendly fillers to prepare unsaturated polyester composite for interior design building sector. In this work stalks-unsaturated polyester hybrid composites were manufactured and completely characterize to evaluate their mechanical, chemical and physical properties.

Even if a lot of natural fibers were used in association with both thermoplastic and thermoset matrix to substitute polymers or fiberglass composites, to the authors' knowledge, there is not literature that studied the use and the effect of agro-residues of the vinification process on the final properties of unsaturated polyester hybrid composites.

For this reason, our research investigates the role played by stalk fibers concentration and presence of silane coupling agent, on the final physical and mechanical properties.

The experimental results showed as the presence of stalk fibers, up to 50 wt%, increased Young's Modulus preserving a satisfactory tensile strength and hardness in comparison with the pure resin properties. The final results showed that stalk fibers from winemaking can be satisfactory used as natural fiber resource to produce composites for furniture.

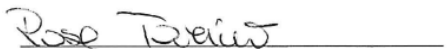
For all of these aspects, in the authors' opinion this manuscript should receive consideration for publication in the "Composites Part B: Engineering".

We confirm that the present manuscript has never been published previously.

Thank You for Your attention.

Sincerely yours,

Dr. Rosa Taurino



DEVELOPMENT OF STALKS-UNSATURATED POLYESTER HYBRID COMPOSITES

R. Taurino*[a], L.S. De Bortoli[b], M. Shabbach[b], F. Bondioli[c]

[a]Department of Engineering "Enzo Ferrari", University of Modena and Reggio Emilia, Via Vivarelli 10, 41125 Modena, Italy

[b]Department of Engineering, Federal University of Santa Catarina (UFSC), Campus Blumenau, 89036-256, Blumenau, SC, Brazil

[c]Department of Applied Science and Technology, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Torino, Italy

corresponding author e-mail: rosa.taurino@unimore.it

Author ID: http://orcid.org/0000-0001-7834-9948

Abstract

The aim of this study is to investigate the possibility to use agro-residues of the vinification process as a cheaper and eco-friendly fillers to prepare unsaturated polyester composite for interior design building sector. The selection of stalk fibers, as an alternative ligno-cellulosic material from agricultural residues, is based on the high volume and seasonal availability throughout the year. In this work stalks-unsaturated polyester hybrid composites were manufactured and completely characterize to evaluate their mechanical, chemical and physical properties. The presence of stalk fibers, up to 50 wt%, increased Young's Modulus preserving a satisfactory tensile strength and hardness in comparison with the pure resin properties. Samples with functionalized stalk fibers were also produced in order to improve the filler-matrix adhesion. The final

results showed that stalk fibers from winemaking can be satisfactory used as natural fiber resource to produce composites for furniture.

Keywords: unsaturated polyester resin, natural fibers, agro-waste, composite

1. Introduction

In the last 15 years there has been growing research interest in natural fibers as reinforcing materials in composites due to not only to the increasing environmental awareness but also to their specific properties, price, health advantages, and recyclability [1].

Natural fiber composites are indicated to application in components subjected from light to moderate loadings. Typical applications include civil construction, furniture, packing, and mainly the automotive industry [2–3] where natural fibers were used in association with both thermoplastic and thermoset matrix to substitute polymers or fiberglass composites [4-6].

In particular, the insertion of natural fibers in the industrial, building, and commercial market sectors has experienced a growth rate of 13% over the last 10 years with an annual use of approximately 275 million kilograms [7].

Due to their large availability throughout the world and low cost, sisal, flax, jute, coconut, and ramie are the most used reinforcing fibers. Other alternative fibers for the manufacturing of composites can be the agricultural residues such as wheat cereal straws [8], rice husk [9], bagasse [10] and kenaf [11], to mention a few examples. In this scenario, the search for local alternatives from agro residues is of extreme interest. For example, one of the most primary sectors that generate millions of tons of agro-waste

per years in many European Countries, such as Italy, France, Spain, Germany and Portugal, is the wine industry. In Italy the annual potential production of wine residues is about 0.5 T as dry matter, more than 60% deriving from grape marcs and stalks. According to the European Council Regulation (EC) 479/2008 regarding the common organization of wine market, grape marc and lees must be sent to alcohol distilleries. Anyway, the Italian code D.M. 301 December 2008 (Art. 5) reports a list of cases whereby the wine makers are not obliged to give by-products to the distilleries. On the basis of this legislation, the study of new solutions to recycle and/or valorize winery waste became possible and valuable [12].

In recent years, several researches have been demonstrated that winery wastes could be used as additional sources. Indeed, winery wastes can represent an alternative source for obtaining natural antioxidants [13], soil conditioner for fertilizer production [14], or for the recovery of tartaric acid [15], while Taurino *et al*. [16] manufactured lightweight bricks from wine wastes by controlling the nature and concentration of those additives. In this work, the possibility to use grape stalks in the composites manufacturing industry for the production of composites for furniture was investigated. In particular, the effect of filler content, ranging from 10 to 50 wt%, on the mechanical, physical and chemical properties of the obtained materials was evaluated. Moreover, since natural fibers commonly exhibit a relative high moisture absorption and a poor compatibility with polymer matrix, the influence of silanization on the interfacial matrix-fiber properties and thus on the final composite properties was studied. In fact, a high adhesion between fiber and matrix is essential for an efficient stress transfer, i.e. to permit the crack propagation and prevent a premature failure and/or fracture of the material. [17]. With this goal a silane coupling agent, commonly adopted to improve the

composite adhesion between unsaturated polyester resin and bacterail cellulose [18] or wood fiber and an unsaturated polyester matrix [19], was used and the obtained results carefully evaluated.

2. Experimental section

2.1. Materials

The natural fiber used as composite filler was stalk fibers collected as winemaking waste. The stalk fibers, furnished by a cooperative wine-growers association located in the Emilia-Romagna Region (Italy), were completely characterized before their use in the matrix. An unsaturated polyester resin supplied by Carlo Ricco & F.lli company was used as composite matrix. The catalyst used to provide the crosslinking reaction of unsaturated polyester resins was methyl ethyl ketone peroxide (Mekp), and cobalt bis(2-ethylhexanoate) (Co) was used as accelerant.

According to the material data sheet, the polyester resin used in this research has a density of 1,2 g/cm³, a hardness Shore D of 64, a Young Modulus of 230 MPa, and a tensile strength of 7 MPa. Glass microspheres S.22, supplied by 3M company, with a particles size of 75 μm, were added to improve the mechanical and chemical properties of composite panels.

2.2 Wine waste preparation

In order to remove all the residual moisture, the as-received stalk fibers were dried at 80ºC for 6 hours. In fact, the removal of moisture from fibers is an essential step for the preparation of composites to avoid fiber swelling within in the matrix [20].

In order to obtain a more homogeneous material and a better fiber dispersion, the dried stalks were grounded with a grinder (IKA A10 model) at 20000 rpm for 30 seconds and passed through a 2 mm sieve to obtain a grain size distribution smaller than 2 mm.

Figure 1 shows the aspect of the stalks, before (a) and after (b) the grinding and sieving steps. The morphology of the obtained powders was observed by a Scanning Electron Microscopy (ESEM Quanta 200, FEI Company) coupled with energy dispersion spectroscopy equipment (EDS INCA-350, Oxford Instruments, UK). The micrograph (Figure 1c), obtained with an accelerating voltage set at 20 kV, reveals that the stalk fibers are characterised by heteregoneous and irregular particles, both in size and in shape.

2.3 Composites preparation

To optimize the composite preparation, the research was performed in two main steps. In a preliminary phase, composites with different amount of wastes (Table 1) were prepared to verify the effect of filler concentration on the curing reactions of polyester resin and on the chemical, physical and mechanical properties. Therefore, the results of this preliminary phase were used to select the optimized filler concentration and thus to evaluate the effect of the salinization step.

In the first step, the resin was dissolved in styrene and then mechanically mixed with the catalyst and the accelerant to obtain a homogeneous solution. The glass microspheres and the milled stalks were added during the mixing. The samples were produced by casting into silicone moulds (Figure 2). The samples were left on the mould, at room conditions, for 24 hours. To optimize the post-curing process samples R100 sample was treated at 80°C for 6 hours or at 100°C for 2 hours to complete the cross-linking reaction.

In the second step, in order to increase the compatibility between fillers and resin and to avoid the presence of pores [21], an air release agent (BYK A-555) (ANB) and vinyltriethoxysilane (VTS) were added to the resin. Table 1 reports the list and the composition of the obtained samples.

It is necessary to underline that, in agreement with the DSC results here not reported, Mekp and Co concentration in the composites was increased, at higher fillers concentration, to complete the cross-linking reaction as already reported in several works [21-23].

2.4 Sample Characterization

Differential scanning calorimetry analyses (DSC) were carried out on the liquid resin and on R100 samples obtained after different curing process to define the appropriated curing treatment and to calculate on each sample the obtained cross-linking degree. The analyses were carried out using a TA DSC2010 instrument. In the first DSC run, the sample was heated up from 0 to 200°C at a constant heating rate of 20°C/min, held at 200°C for 1min and then cooled down to 0°C at a cooling rate of 20°C/min. This procedure was repeated in a second run in order to check for any further exothermic energy flow and provide the reference for the subsequent evaluation of the reaction enthalpy.

In order to evaluate the effect of new kind of fillers on the mechanical properties, standard tensile tests were carried out according to the standard ISO 527-2 by using a 2 kN load cell, at a crosshead speed of 5 mm/min, in environmental condition of temperature and relative humidity by a dynamometer testing machine TesT GmbH model 112,2 kN (Erkrath, Germany). The average of at least five samples was reported for each formulation.

Shore D hardness testing was carried out in accordance with ASTM D 2240-86 and ISO 868 using a durometer AFFRI Hardness Tester (REMET). The minimum dwell time of 1s was used in order to minimise creep effects and tests were carried out at 23±1°C. Measurements were taken at regular intervals at least 12 mm from the edge of the specimen and 10 mm apart. These requirements ensure to minimize the stress fields

arising from the indentation at the edges and bottom surface of the sample. The average of at least six readings was taken for each specimen.

The evaluation of the water absorption was carried out according to ASTM 570-98; the samples were left in water for 24 hours at a temperature of 23±1°C, and the weight change was measured.

To analyse the resistance in boiling water, the samples were left for 2 hours in water at 100°C. After removing the water excess, the samples were weighted and the water absorption (wt. %) was calculated by comparing the initial and the final weight.

The chemical durability was evaluated according to ASTM D543-14 by immersing the samples into acid solution (10 vol% of HCl) for 7 days at room temperature. The specimens were completely submerged into HCl solution. It is important to note that in this procedure all composite faces were exposed to acid environment, while, in real conditions only one face of composite structures could be exposed. Afterwards, they were washed with clean water and dried at room temperature. Durability was analyzed by the measurement of weight change.

Finally, the microstructure of the samples was observed on fracture surfaces using a scanning electron microscopy (ESEM Quanta 200, FEI Company) using an accelerating voltage of 20 kV. The samples were gold-coated in a sputter coater before collecting the images.

3. Results and Discussion

3.1 Curing step optimization

DSC thermograms of liquid resin and R100 samples before and after post-curing processes both at 80 and 100°C, are reported in Figure 3.

DSC thermogram of pure uncured resin (Figure 3a) shows two exothermic peaks at around 100 and 140°C. Even though there are several controversial interpretations about the origin of these exothermic peaks [24-25], the first peak can be attributed to the polymerization initiated by a redox decomposition of methylethylketone peroxide (MEKP), and the second one to the polymerization initiated by the thermal decomposition of MEKP at higher temperatures.

After the curing process at room temperature (Figure 3b) the sample is almost completely cured with a cross-linking degree of 95,5%. The exo peaks completely disappear after the post-curing processes at 80 °C (6 hrs) and 100°C (2 hrs). However, after post-curing at 80°C, the sample was yellowish and translucent while, after the post-curing step at 100°C, the sample colour changed from yellow to brown as a result of an incipient degradation. After these preliminary results, to avoid the thermal degradation of resin and eventually of stalk fibers, a post-curing at 80°C for 6 hours was applied to all the prepared composites.

3.2 Composite characterisation

Table 2 shows the mechanical properties of neat polyester and of obtained composites. It can be observed that the hardness of composites with stalks fibers (Table 2) is slightly lower than that of R_{100} and $R_{100}S_0$ samples, while there are no differences among the composites with different stalks concentration. Moreover, the modulus of the composites containing stalks is much greater than that of both pure resin and polyester/glass sphere composite. It can be observed that increasing stalks fibers waste content up to 50%, the modulus increases by 73% when compared to pure polyester resin, while the elongation at break decreases by 92% when the fiber content increases up to 50%. This is in

agreement with the literature because the stalk fibers hinder the movement of the polymer chains promoting the stiffening of composites. [26].

On the contrary, the composites tensile strength is not influenced by the stalk fibers concentration. In particular, the tensile strength of resin increases, as expected, after the addition of glass microspheres but then decreases as the stalks fiber content is increased. The final mechanical results can be ascribed to the intrinsic tensile strength of fibers [27], to the presence of residual porosity and to weak bonds between resin and stalks fibers. This last one can be likely a result of reduced mixing efficiency [28], [29].

Figure 4 reports the chemical durability of pure resin and composites. As expected, the glass microspheres increase the chemical resistance in acid of pure resin. Regarding the effect of fibers, the weight change increases as the fiber concentration is increased even though composites with fiber concentration lower than 20 wt% are characterized by a durability similar or even higher than that of pristine resin. Higher weight change was measured for the composites containing 30, 40 and 50 wt% of stalks fibers. Probably, at these concentrations, the quantity of resin is insufficient to completely wet the fibers so the acid solution easily dissolves digestible matters of stalks fibers, such as hemicellulose and cellulose [26].

Figure 5 shows the water absorption results obtained after 2 hours in water at boiling temperature and after 24 hours at room temperature. All the composites show similar or lower water absorption, after 24 hours at environmental temperature, with respect to the pristine resin. The results in boiling water are less satisfactory. Infact, the weight percent of water absorption increases from 0% for pure resin to 15,9% for composite with 50 wt% of stalks. Probably the boiling water causes stalks phase swelling and produces tensile stress across the resin/fibers interface that causes interface debonding and then increases

of water absorption. Infact, as already reported, stalks fibers are cellulosic fibers, hydrophilic materials that can absorb moisture between 5 and 10% and thus affect physical and mechanical properties [21]; [25].

3.4 Effect of silanization

Figure 6 reports the stress-strain curves for $R_{60}S_{40}$ and $R_{50}S_{50}$ composites before and after silanization. Both manufactured composites were found to be brittle as they underwent a sudden failure. However, it was observed that after silanzation there is a decrease in Young's Modulus and an increase in percentage of elongation at break and energy at maximum load, indicating an increase in the ductility of the composites. This could be due to the formation of flexible polysiloxane (Si-O-Si) from selfcondensation reaction of silane [21] as also confirmed by the decrease of hardness (Table 2) and Young Modulus of silanized samples.

Moreover, the better interaction between matrix and fibers after silanization results in a better stress transfer, in particular for sample $R_{60}S_{40Si.}$ These results mean that silane functionalization of fibers has an effect on increasing the toughness of fiber composites. Synergistically, silane functionalization of fibers increases the resistance to fracture when receiving external forces, because silane as a coupling agent provides higher and close interfacial reactivity between fibers and matrix.

As shown in Figure 7, the chemical treatment of fibers by a coupling agent decreases the absorption of the samples in boiling water and acid solution with respect to the unsilanized samples. A better interaction between fibers and matrix is thus provided by the silanization. On the other hand, the treatment of the fibers with coupling agent didn't

lead to a significant variation of the water resistance after long time (24 hours) at environmental temperature.

Finally, figure 8b shows that there is not pull out mechanism form resin matrix after silanization process suggesting a positive interaction between resin and stalk fibers as confirmed by the mechanical and chemical properties.

4. Conclusions

The objective of this experimental study was to evaluate the potential use of agro-residues of the vinification process for the fabrication of composites for interior design building sector.

In particular, stalk-unsaturated polyester hybrid composites were manufactured by casting with different amount of stalk-fibers (ranging from 10 to 50 wt%) to verify the effect of filler concentration on the chemical, physical and mechanical properties of the polyester resin.

The results showed as the presence of stalk fibers increases mechanical properties like tensile modulus preserving satisfactory mechanical properties in comparison with the pure resin properties. The physical and chemical tests, instead, showed a poor matrix-fiber adhesion, and thus a lower chemical resistance, especially in water, for composite samples.

A better interaction between fibers and matrix was provided by a silanization step that improve the filler-matrix adhesion, decreasing the absorption of composites in water and acid solution. The good interface, additionally, provided higher stress transfer and toughness of fibers composites.

These preliminary experimental results suggested that stalk fibers from winemaking could find an application as new potential natural fillers to produce composites for furnitures reducing the consumption of raw materials, in an environmentally friendly and cost effective way.

Acknwledgments

Authors are thankful to all the partecipants in the project SOSTINNOVI Grant number: PG/2015/737442 “Sostenibilità e innovazione nella filiera vitivinicola”- Project co-financed by 2014-2020 POR FESR, Emilia Romagna Region (www.sostinnovi.eu).

References

[1] Atiqah A, Maleque MA, Jawaid M, Iqbal M. Development of kenaf-glass reinforced unsaturated polyester hybrid composite for structural applications. Comp. Part B: Eng. 2014;56:68-73

[2] Ho MP, Wang H, Lee JH, Ho CK, Lau KT, Leng JS, Hui D.Critical Factors on Manufacturing Processes of Natural Fibre Composites. Composites: Part B 2012; 43:3549-3562.

[3] Sathishku mar TP, Navaneethakrishnan P, Shankar S.Tensile and Flexural Properties of Snake Grass Natural Fiber Reinforced Isophthallic Polyester Composites. Composites Science and Technology, 2012;72:1183-1190

[4] Deepaka K, Prabhakar Vattikutia SV, Venkatesh B. Experimental Investigation of Jute FiberReinforcedNano Clay Composite. In 2nd International Conference on Nanomaterials and Technologies (CNT 2014). Proced. Mat. Sci. 2015;10:238-242

[5] Shaikh and S A Channiwala. To Study the Characteristics of Jute Polyester Composite for
Randomly Distributed Fibre Reinforcement. Proceedings of the World Congress on Engineering 2010, Vol II WCE 2010, London, (2010)

[6] Mueller DH, Kaobjilowski A. New Discovery in the Properties of Composites Reinforced with Natural Fibres. J. Ind. Textiles 2003;33:111-130

[7] Report NFCM. Natural fiber composite market report. Little Falls, Kline and Company, New Jersey, 2004

[8] Wang D, Sun XS. Low density particleboard from wheat straw and corn pith. Ind Crops Prod 2002;15:43-509

[9] Leiva P, Ciannamea E, Ruseckaite RA, Stefani PM. Medium-density particleboards from rice husks and soybean protein concentrate. J Appl Polym Sci 2007;106:1301-6

[10] Xua X, Yaob F, Wub Q, Zhoua D. The influence of wax-sizing on dimension stability and mechanical properties of bagasse particleboard. Ind Crops Prod 2009;29:80-5

[11] Kalaycıoglu H, Nemli G. Producing composite particleboard from kenaf (Hibiscus cannabinus L.) stalks. Ind Crops Prod 2006;24:177-80

[12] Angel J, Albena Y, Stoyan D. Effect of wheat starw and sunflower seeds husks as pore forming agents on the properties of porous clay bricks. J Chem. Tech. and Met. 2017;52:885–891.

[13] González-Paramás AM, Esteban-Ruano S, Santos-Buelga C, et al. Flavanol Content and Antioxidant Activity in Winery Byproducts. J. of Agric. Food Chem. 2004;52:234–238.

[14] Arvanitoyannis IS, Ladas D, Mavromatis A. Potential uses and applications of treated wine waste: A review. Int. J.of Food Sci. and Tech.. 2006; 41:475–487

[15] Yalcin D, Ozcalik O, Altiok E, et al. Characterization and recovery of tartaric acid from wastes of wine and grape juice industries. J. of Therm. Anal. and Cal. 2008;94:767–771.

[16] Taurino R, Ferretti D, Cattani L, Bozzoli F, Bondioli F. Lightweight clay bricks manufactured by using locally available wine industry waste. J. of Build.Eng. (in press)

[17] Faruk O, Bledzki AK, Fink HP, Sain M. Biocomposites reinforced with natural fibers: 2000–2010. Progr. in Polym. Sci. 2012;37:1552-1596

[18] Thakur VK, Thakur MK. Processing and characterization of natural cellulose fibers/thermoset polymer composites Carbohydr. Polym. 2014;109:102–117

[19] Zhang Hh, Cui Y, Zhang Z. Chemical Treatment of Wood Fiber and Its Reinforced Unsaturated Polyester Composites. J. Vinyl Addit. Technol. *2013*;19:18–24

[20] Wang B, Panigrahi S, Tabil L, Crerar W. Pre-treatment of flax fibres for use in rotationally molded biocomposites. J. Reinf. Plast. Compos. 2007;26:447-463

[21] Taurino R, Lancellotti I, Tatàno F, Carchesio M, Pozzi P. Mechanical and chemical resistance of composite materials with addition of anaerobic digestate. Comp Part B: Eng.2016;92:259-264

[22] Sen S,Nugay N. Uncured and cured state properties of fly ash filled unsaturated polyester composites. J.Appl.Polym.Sci. 2000;77;1128-1136

[23] Paauw M, Pizzi A. Some filler effects on cross-linking of unsaturated polyesters J Appl. Polym. Sci. 1993;50:1287-93

[24] Popescu C. Integral method to analyze the kinetcis of heterogeous reactions under non-isothermal conditions. A variant on the Ozawa Flynn-Wall method. 1996;285:309-323.

[25] Martin JL. Kinetic Analysis of Two DSC Peaks in the Curing of an Unsaturated Polyester Resin Catal7:62-70yzed With Methylethylketone Peroxide and Cobalt Octoate. Pol. Eng. And Sci. 2007; 4

[26] Silva RV, Ueki MM, Spinelli D, Bose Filho WW, Tarpan JR. Thermal, Mechanical, and Hygroscopic Behavior of Sisal Fiber/Polyurethane Resin-based Composites. J. Reinf. Plast. Comp. 2010; 29: 1399-1417

[27] Oksman I, Mathew AP, Langstrom R, Nystrom B, Joseph K. The influence of fibre microstructure on fibre breakage and mechanical properties of natural fibre reinforced polypropylene. Compos. Sci. Technol. 2009; 69: 1847-1853

[28] Roe, P. J.; Ansell, M. P. Jute-reinforced polyester composites. J. Mater. Sci. 1985;20: 4015-4020

[29] Vaxman A, Narkis M, Siegmann A, Kenig S. Void formation in short-fiber thermoplastic composites. Polym. Comp.1989;10:449-453

Figure captions

Figure 1. Image of stalks fibres before (a) and after the grinding (b) and SEM micrograph after the grinding (c).

Figure 2. $R_{70}S_{30}$ samples for mechanical a) and physical–chemical b) tests.

Figure 3. Differential scanning calorimetry (DSC) thermograms (hexo up) of a) liquid resin, b) R_{100} sample before post-curing, c) R_{100} sample after post-curing at 80°C for 6 hours and d) R_{100} sample after post-curing at 100°C for 2 hours.

Figure 4. Chemical resistance of the resin and its composites after 7 days of immersion in acid solution.

Figure 5. Water absorption of resin and its composites

Figure 6. Stress-strain curves of composites a) $R_{60}S_{40si}$, $R_{60}S_{40,}$ and b) $R_{50}S_{50si}$, $R_{50}S_{50}$.

Figure 7. Water absorption (WW) and chemical resistance of composites $R_{40}S_{60}$ and $R_{50}S_{50}$, before and after silanization.

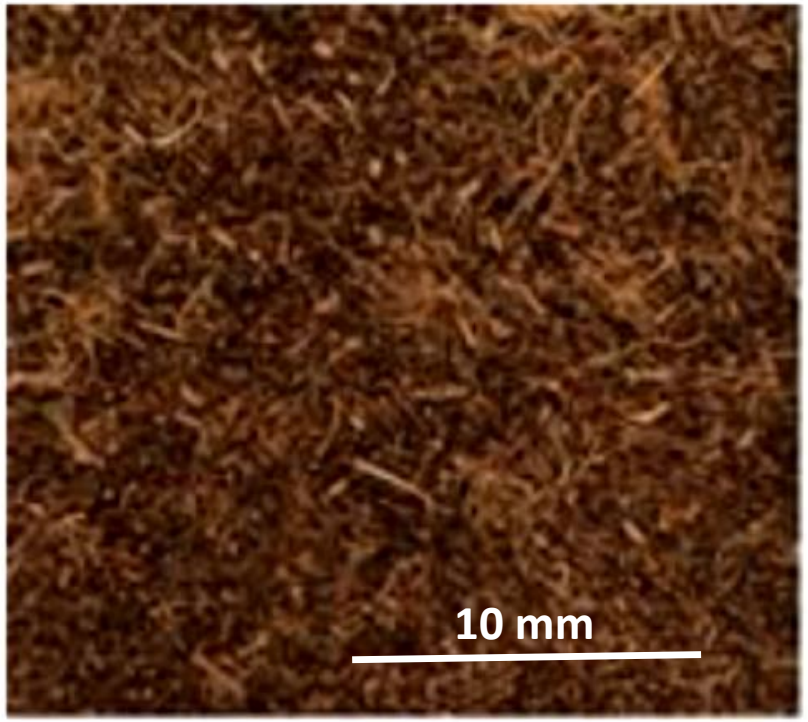
Figure 8. ESEM images of fracture surface of a) $R_{60}S_{40}$ and b) $R_{60}S_{40Si}$ composites

Table 1 – List of the samples and their compositions.

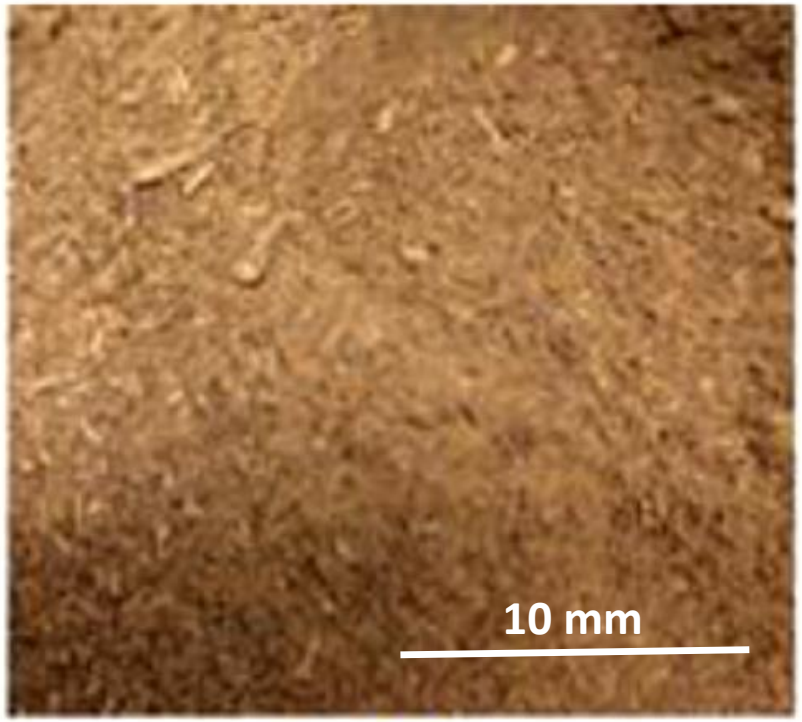
Samples	R70 (g)	Styrene (g)	Glass microsphere (g)	Stalk (g)	Co %wt	Mekp %wt	VTS %wt	ANB %wt
$\mathbf{R_{100}}$	100	35	0	0	0.3	2	0	0
$\mathbf{R_{100}S_{0}}$	100	35	5	0	0.3	2	0	0
$\mathbf{R_{90}S_{10}}$	90	31.5	5	10	0.3	2	0	0
$\mathbf{R_{80}S_{20}}$	80	28	5	20	0.3	2	0	0
$\mathbf{R_{70}S_{30}}$	70	24.5	5	30	0.6	4	0	0
$\mathbf{R_{60}S_{40}}$	60	21	5	40	0.6	4	0	0
$\mathbf{R_{60}S_{40Si}}$	60	21	5	40	0.6	4	1	0.3
$\mathbf{R_{50}S_{50}}$	50	17.5	5	50	0.9	6	0	0
$\mathbf{R_{50}S_{50Si}}$	50	17.5	5	50	0.9	6	1	0.3

Table 2 – Mechanical properties of polyester and composites after optimized post-curing.

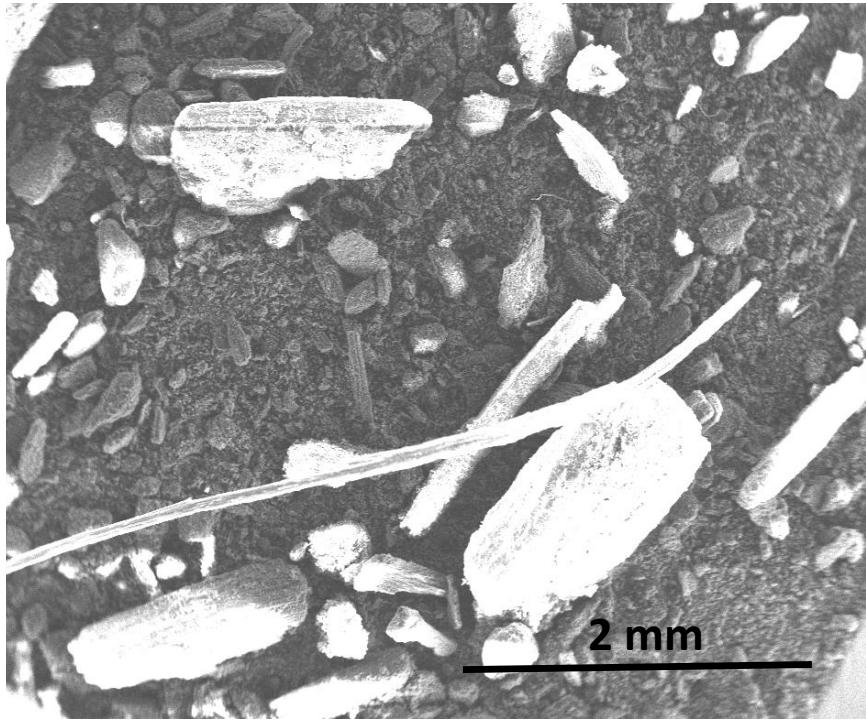
Samples	Tensile modulus (E_t) (MPa)	Tensile strength (σ_t) (MPa)	Elongation at break (ε_b) (%)	Hardness (Shore D)
R_{100}	288±34	13.0±1.0	36±7	73±1
$R_{100}S_0$	325±5	15.9±1.1	9.7±1	73±1
$R_{90}S_{10}$	337±47	15.1±0.2	7.7±0.4	68±1
$R_{80}S_{20}$	360±17	9.7±1.9	3.7±1.1	67±1
$R_{70}S_{30}$	462±39	11.2±1.1	4.3±0.5	67±2
$R_{60}S_{40}$	478±38	10.9±1.3	3.8±0.6	69±2
$R_{50}S_{50}$	498±33	10.5±0.5	2.9±0.4	68±1
$R_{60}S_{40Si}$	403±40	11.6±1.0	4.3±0.5	69±2
$R_{50}S_{50Si}$	399±27	9.8±0.6	3.9±0.5	61±2



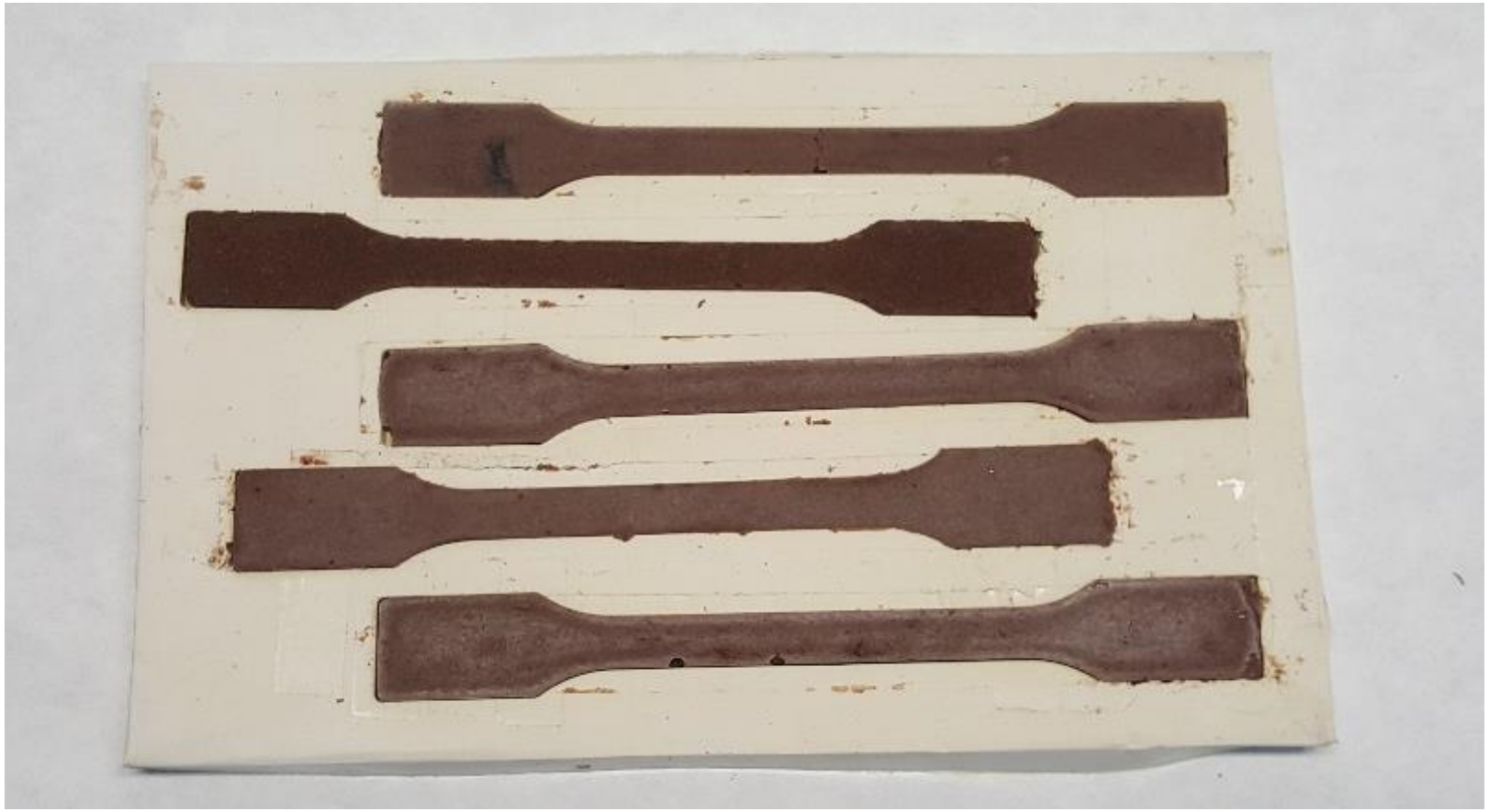
a)



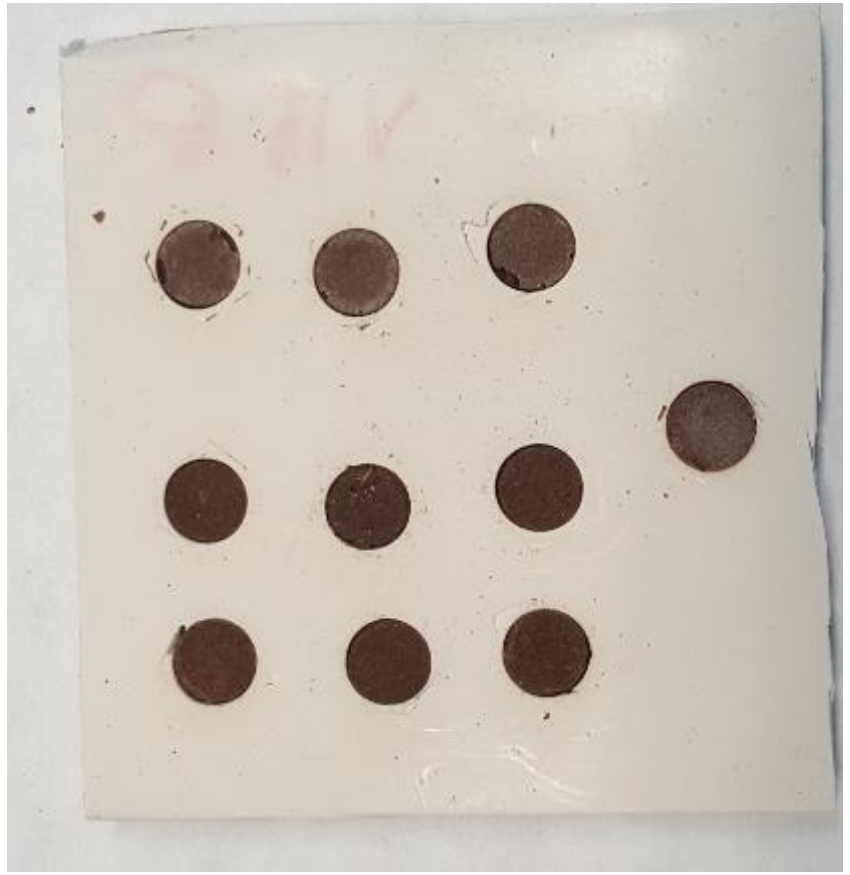
b)



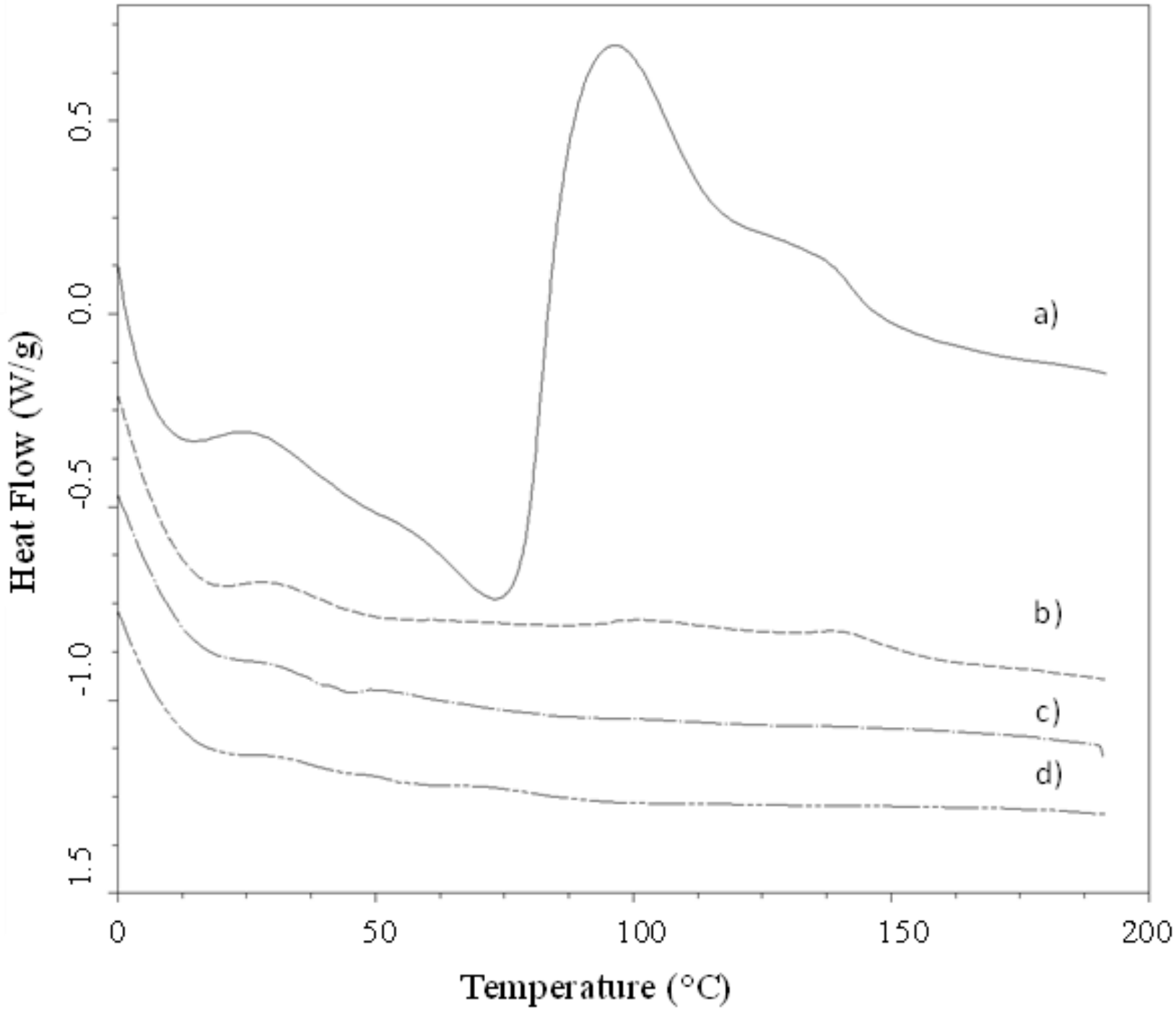
c)

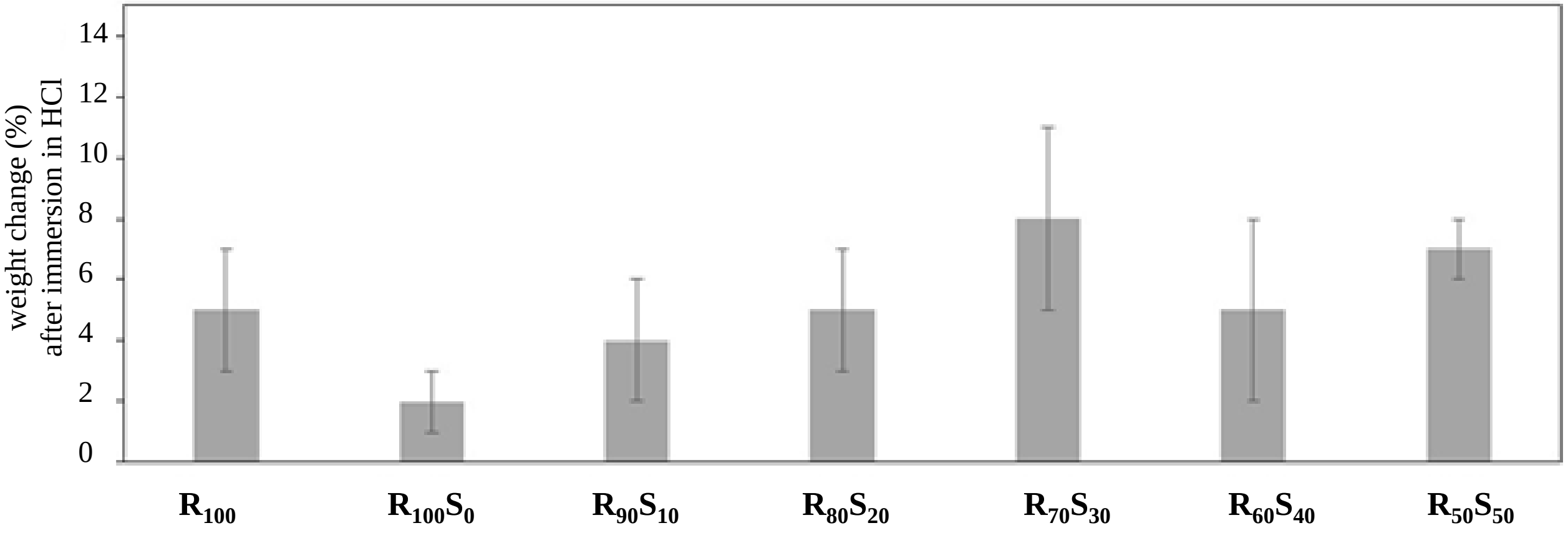


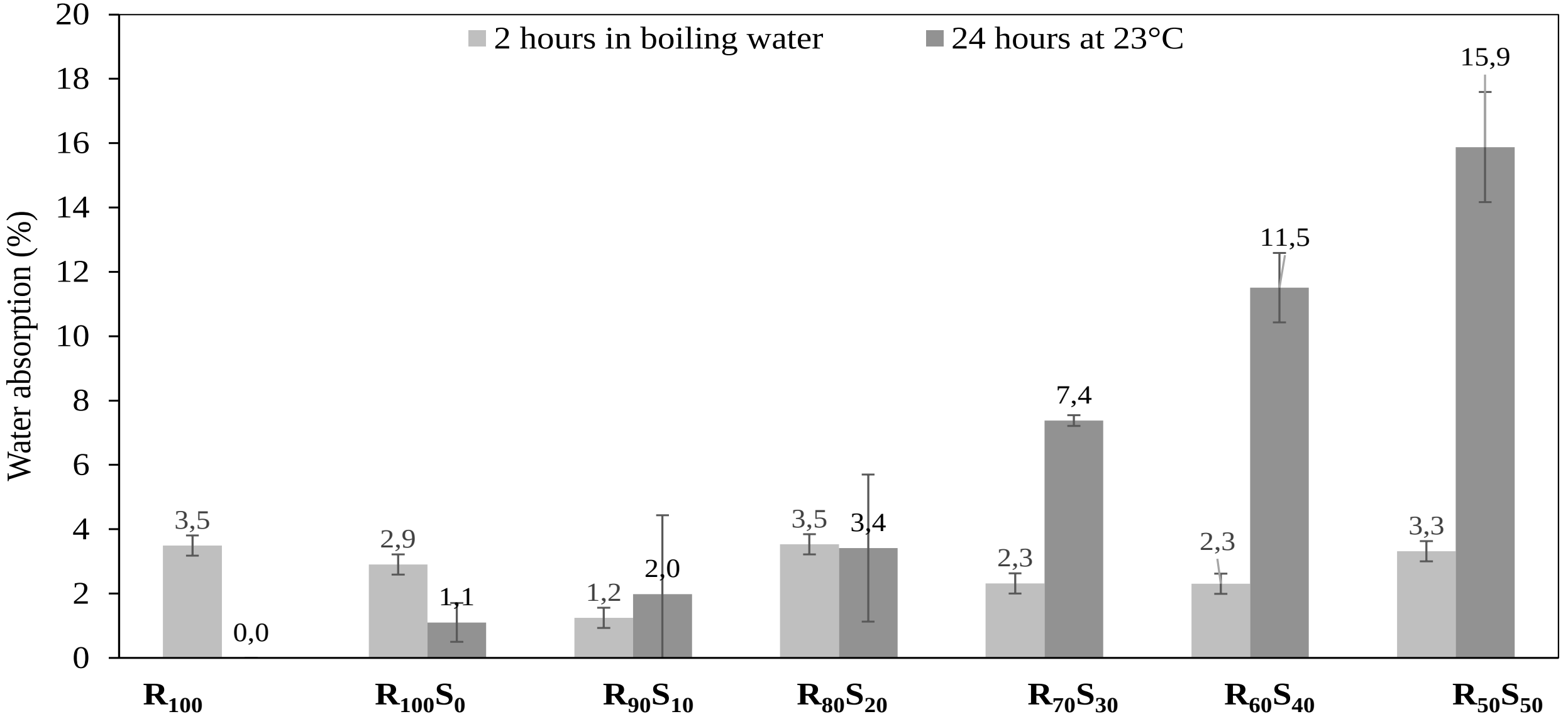
a)

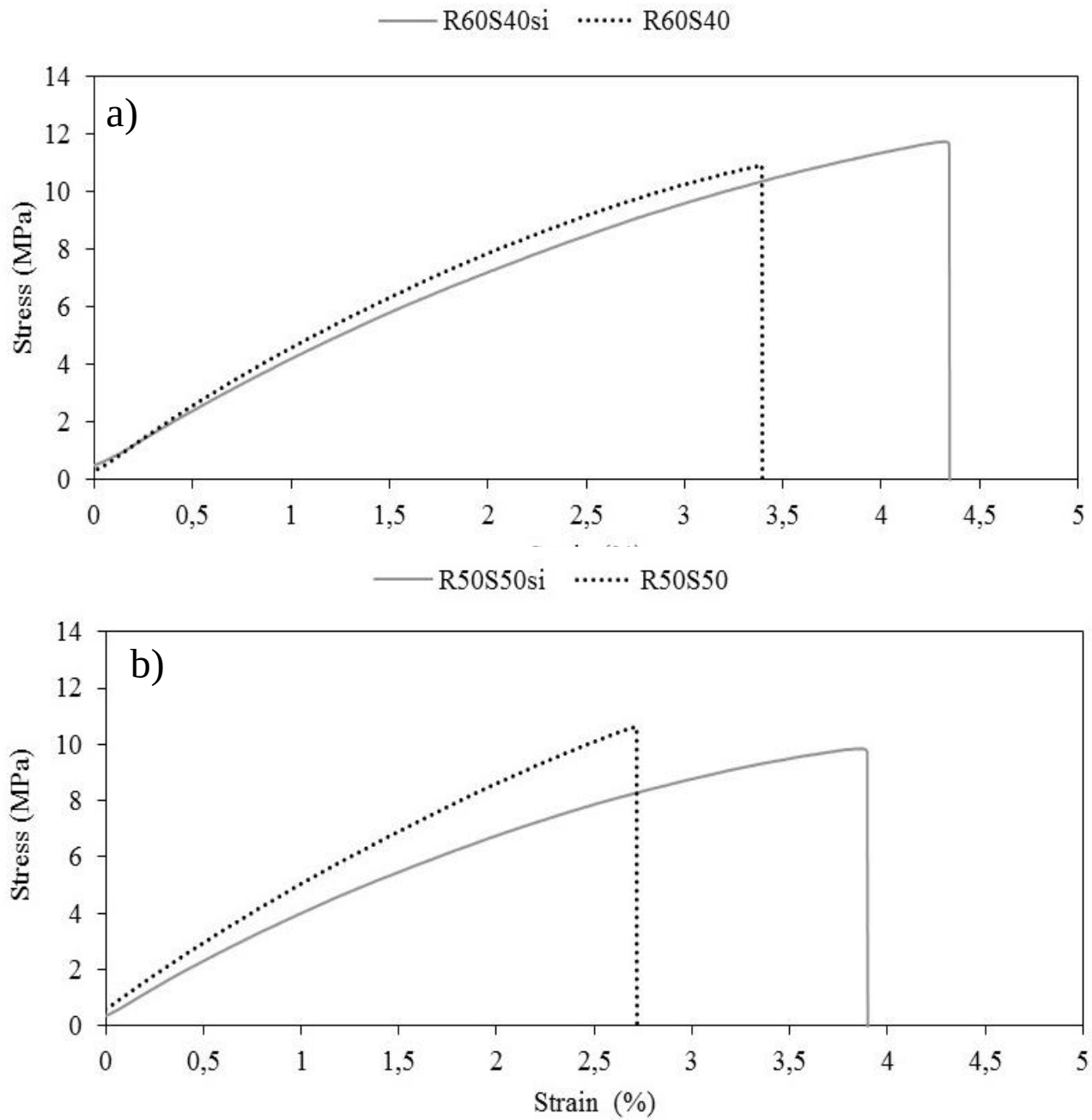


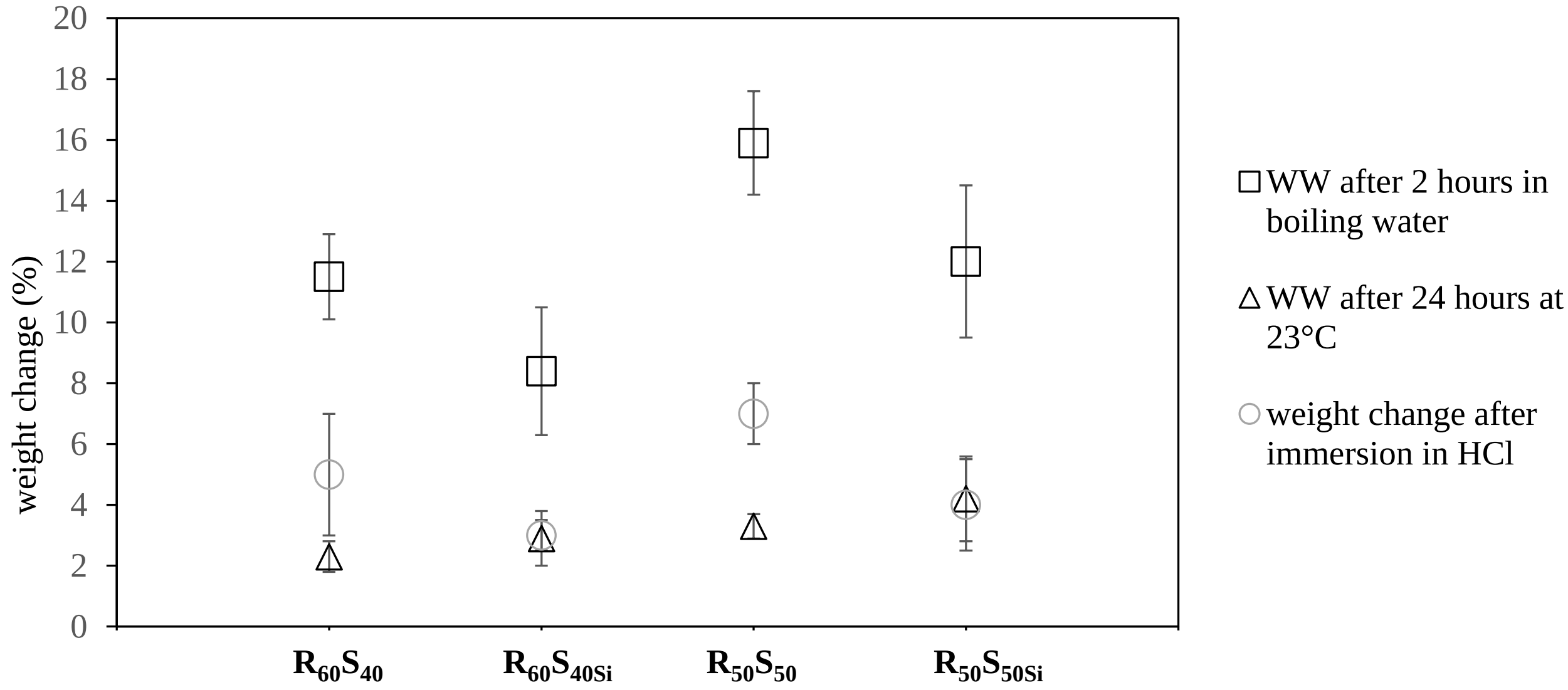
b)

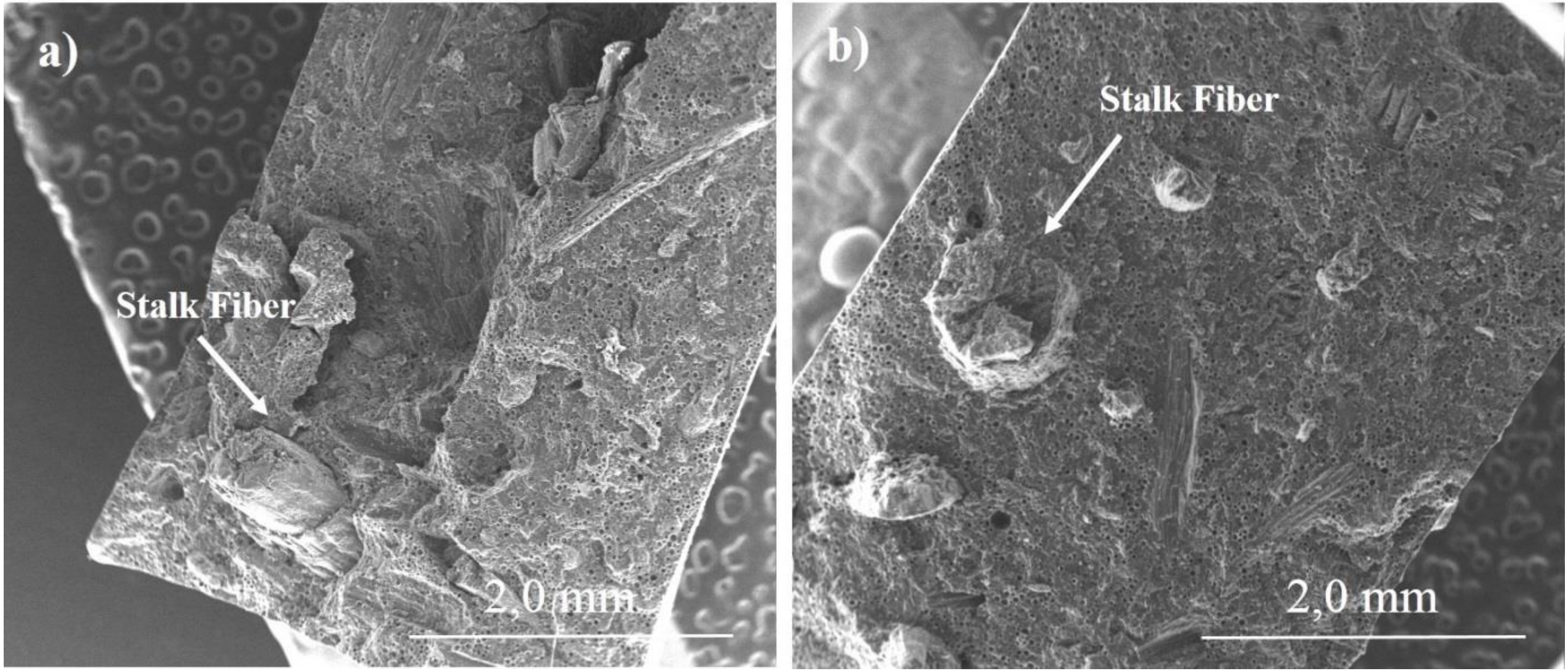

Heat Flow (W/g)
0.5
0.0
-0.5
-1.0
1.5
0
50
100
150
200
Temperature (°C)
a)
b)
c)
d)


weight change (%)
after immersion in HCl
14
12
10
8
6
4
2
0
R100
R100S0
R90S10
R80S20
R70S30
R60S40
R50S50


2 hours in boiling water
24 hours at 23°C
Water absorption (%)
20
18
16
14
12
10
8
6
4
2
0
3,5
0,0
2,9
1,1
1,2
2,0
3,5
3,4
2,3
7,4
2,3
11,5
3,3
15,9
R100
R100S0
R90S10
R80S20
R70S30
R60S40
R50S50


R60S40si
R60S40
a)
Stress (MPa)
0
2
4
6
8
10
12
14
0
0,5
1
1,5
2
2,5
3
3,5
4
4,5
5
R50S50si
R50S50
b)
Stress (MPa)
Strain (%)


20
18
16
14
12
10
8
6
4
2
0
weight change (%)
R60S40
R60S40Si
R50S50
R50S50Si
WW after 2 hours in boiling water
WW after 24 hours at 23°C
weight change after immersion in HCl


a)
Stalk Fiber
2,0 mm
b)
Stalk Fiber
2,0 mm