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Effect of food chemicals and temperature on mechanical reliability of bio-based glass fibers reinforced polyamide

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ABSTRACT

This paper presents an experimental study to assess the effects of food chemicals and temperature on the mechanical performance of glass fiber reinforced bio-based polyamide. The diffusion of food chemicals was mainly driven by thermal energy, following Arrhenius law in all tested environments. Degradation of mechanical properties and decrease in reliability were assessed, due to the plasticization of polymer matrix. Secondary but not negligible effect on flexural strength degradation is given by the different chemical interaction between polymeric chains and molecules of food chemicals. Colour change was measured and resulted to be positively correlated to diffusion.

Keywords

A. Polymer-matrix composites (PMCs)

B. Environmental degradation

C. Statistical properties/methods

D. Mechanical testing

1. Introduction

The demand for advanced Polyamides (PA) in different industry fields as automotive and transportation, electrical and electronic goods, household and professional appliances, is expected to witness significant growth in the next ten years [1,2]. Among the several grades of commercial available PAs, bio-based ones are fully or partially synthesized from renewable resources, as castor and palm kernel oil, biomass and bio-based acid [3–6]. In industrial applications, these polymers recently gained increasing interests due to their good mechanical (hardness, high toughness, and abrasion resistance), thermal (high melting point and glass transition temperature), [3] and eco-properties. A main limiting factor in the industrial application of polyamides and bio-polyamides is their poor resistance to moisture and water absorption, which can have an impact on the dimensional stability and thermo-mechanical properties of the components [7,8].

Compared to other polyamides, PA 4.10 is proven to be outstanding in thermal resistance [3,5] and low moisture absorption. In particular, it is characterized by a glass transition temperature (T_g = 75 °C) slightly higher than PA 6.10, PA 10.10, or PA 10.12 [3]. For these reasons, glass fiber reinforced PA 4.10 represents an interesting composite material with bio-based matrix to be employed in the industrial field of professional food processing appliances. The professional kitchen environment is characterized by variable operating temperatures, by the presence of aggressive food chemicals [9–11] and by a greater number and frequency of operational cycles experienced by the equipment compared to home kitchen appliances. Many components could deal with the use of polyamide in such context: aesthetic components are among the most used part in professional kitchen environments, and they are the perfect example to consider how technical (such as mechanical, thermal, etc…) and aesthetical properties and durability has to be carefully considered in the design phase [12]. Moreover, other internal components often exposed to harsh chemical environments, such as the ones involved in washing processes [13], are subjected to mechanical properties degradation over their lifetime.

Several studies focused on exploring the influence of environmental conditions (*i.e.*, temperature, moisture, etc.) and reinforcements on the mechanical and thermal behavior of this class of materials [4,14–23]. In particular, previous studies evidenced that the amount of absorbed water in the polyamides is correlated with a strong decrease in the glass transition temperature (Tg) [14,15]. Namely, water absorption in PA composites is influenced by both the amide groups [15], and, inversely, by the weight percentage of glass fiber reinforcements [16]. Despite these studies, the durability of biopolyamides-based composites in direct contact with food chemicals has not been investigated so far. This paper aims at exploring the effect of food

chemicals, with pH ranging from 2.0 to 5.5, water absorption and temperature on the mechanical reliability of glass reinforced bio-based polyamides intended for harsh professional environments.

2. Experimental methods

2.1 Materials

Commercially available PA 4.10 reinforced with 30% of glass fibers in weight was used in this study. From a $148\times210\times3$ mm^3 sheet, specimens were cut into squares of the dimensions $50\times48\times3$ mm^3, and then manipulated based on the needs of the different testing steps.

Food chemicals were chosen in order to optimize the tested pH range and colours of the same foods. For this, following food chemicals were tested: lemon juice (pH = 2.0-2.6), white wine vinegar (following called only vinegar, pH = 2.4-3.4), tomato sauce (pH = 3.5-4.7) and coffee (pH = 5.0-5.5). In order to standardize the testing conditions, commercial food chemicals of the same product batch were used. Water was tested and taken as reference liquid in the comparison among food chemicals absorption.

2.2 Experimental Design

During the experimental planning, the Design of Experiment (DoE) theory was used to build a full factorial design [24] considering time (*t*) and temperature (*T*) as variable parameters, according to Figure 1, using at least 3 replicates for each parameters combination. The same full factorial design was used to generate combinations of aging conditions for every tested food chemical and every pH level related to such chemicals.

To further simplify the experimental design for mechanical testing and reliability evaluation, a second experimental grid was built on the full factorial design, reducing the parameters combinations to a 3x4 factorial design, as illustrated in Fig. 1 with blue circles. A total of 720 samples have been aged, weighted and their colour was measured, and 210 samples were subjected to flexural tests.

2.3 Absorption and diffusivity

Absorption of samples was monitored through weight gain measurements using a precision balance (Kern PKS, 0.001 g accuracy) and using following equation (1) to calculate the weight gain percentage (*WG*):

$$WG = \frac{w - w_d}{w_d} \cdot 100 \tag{1}$$

In Eq. (1), W_d is the weight of "as-received samples", meaning the ones not immersed in any solution but exposed to time and temperature, and W is the weight of immersed samples, both expressed in [g]. Before he testing, all the samples were stored in the same place at the same environmental conditions, in order to reproduce the real starting conditions of new components, where the humidity content is not null due to storage and handling needs.

Diffusion coefficients were calculated assuming that the absorption phenomena followed Fick's law and took into consideration the "edge effects" to calculate the diffusion through the thickness [25]. The model proposed by Shen was used in data redaction [25], according to:

$$D_x = \pi m^2 \cdot \left(\frac{h}{4M_m}\right)^2 \cdot \left(1 + \frac{h}{b} + \frac{h}{d}\right)^{-2} \qquad (2)$$

Where m is the slope of the tangent to the initial linear part of the weight gain-square root of time curve. Moreover, h is the thickness expressed in [mm], M_m is the saturation level experimentally determined as the maximum weight gain, b and d are width and length of specimens in [mm]. The values of M_m were detected through testing at 70°C, considering them as insensitive to the temperature and depending on the moisture content of the environment [25].

2.4 Spectrophotometric measurements

The analysis of colour changes of PA 4.10 samples was carried out by measuring CIELAB parameters (L*, a*, b* and ΔE*) using a spectrophotometer (Konica Minolta CM-2600d). The color difference (ΔE) between the samples was calculated according to the following equation:

$$\Delta E = \sqrt{\Delta a^2 + \Delta b^2 + \Delta L^2} \qquad (3)$$

One-way analysis of variance (ANOVA) was used to evaluate the effects of temperature and food chemicals on color change using Minitab software ver.17 (Minitab, State College, PA).

2.5 Flexural tests

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Flexural tests were conducted using as guideline the testing geometry proposed in ASTM D790-15 standard [26], with support span-to-depth ratio of 13:1 for all samples (due to size limitations of received samples) and cross-head movement speed of 1 mm min^{-1}. Samples width was (10.0 ± 0.1) mm, with (3.0 ± 0.2) mm thickness. Equation (4) [26] was used to calculate flexural strength of tested samples:

$$\sigma_f = \frac{3PL}{2bd^2} \tag{4}$$

where P is the load at break expressed in newton [N], L is the support span in [mm], which in all the tests was fixed at 40 mm, b and d are respectively the width and the depth of tested beams in [mm], and D is the deflection of the centerline of the sample in [mm] at the middle of the support span.

As regards the tangent modulus of elasticity E_B, following equation was used in the calculations:

$$E_B = \frac{L^3 m}{4bd^3} \tag{5}$$

where m is the slope of the tangent to the initial straight-line portion of the load-deflection curve.

All the tests were conducted using an Instron 4411 machine, with 5kN load cell.

2.6 SEM analysis

SEM images of samples fracture surfaces were taken using a scanning electron microscope (EVO 50 SEM, Carl Zeiss), using backscattered electrons detectors.

2.7 Reliability

Reliability evaluation was based on normal probability distribution, considering that mechanical properties of samples showed a central tendency. Reliability values were then calculated using Eq. (6) to obtain the survival probability [27] in function of mechanical properties (indicated as x) of the samples:

$$R(x) = \int_x^\infty \frac{1}{\sqrt{2\pi}\sigma} \cdot e^{-\frac{1}{2}\frac{(x'-\mu)^2}{\sigma^2}} dx' \tag{6}$$

In Eq. (6), σ is the standard deviation and μ is the mean value of experimental data calculated after the data elaboration of flexural tests.

3. Results and discussion

3.1 Absorption and diffusivity

Fig. 2 shows the percentage of absorbed food chemicals vs. time for all the samples at the 3 different temperatures. The saturation level is assumed to be the different at every testing temperature, despite of the high thickness of the samples (3 mm) [2], and it is determined through experimental data. All the samples absorbed very rapidly food chemicals in the first stage (0-4 h), readily reaching the saturation point at 20°C (Fig. 2a) for all chemicals. The amount of food chemicals absorbed at the saturation point increases by increasing temperature: Fig. 2b shows how the saturation point is almost tripled at 50°C, and almost quintupled at 70°C (Fig. 2c), according to the finding reported in [2]. A particular case is given by samples tested with vinegar, showing a quicker absorption rate and higher saturation level. The difference among vinegar absorption and the other food chemicals is more marked at higher temperature, as highlighted in Figures 2 and 3 and in Table 1, as regards both saturation levels and diffusion coefficients. The saturation level of water, lemon, tomato, and coffee are fairly similar, with no significant differences among them. Vinegar shows a significant increase in saturation level compared to water, as showed in Table 1. The interaction between polyamide molecular chains and vinegar will be probably driven not only by hydrogen bonds coordination with the aqueous part of the solution observed also in other polyamides [19,28,29], but also from the chemical interaction between the same molecular chains and acetic acid. All the tested samples showed a Fickian trend of weight gain in time, compared to the shape of *WG* vs. *t* curves of non Fickian diffusion phenomena reported in [14].

As far as diffusion coefficients are concerned, Table 1 shows the effects of the increase in testing temperature, compared to the 20 °C case: an increase of two and three orders of magnitude were detected at 50 °C and 70 °C respectively for all tested food chemicals. In order to evaluate the changes in diffusion coefficients depending on testing temperature and food chemicals, Arrhenius law was used to fit experimentavalues [2]. Figure 3 reports the fitted curves for D_x coefficient calculated from experimental data: no significant differences were detected among different food chemicals.

3.2 Spectrophotometric measurements

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The ΔE variations were statistically evaluated by Fisher's LSD test (α＝0.05). The direct contact between the material and the food chemicals produced significant colour changes at the 3 temperature testing conditions: 20°C (F=24.67, P=0.000), 50°C (F=131.86, P=0.000) and 70°C (F=92.19, P＝0.000). Pearson's correlation revealed that color variation increases by increasing the testing temperatures. In details, a strong correlation was evidenced by comparing the results of the aging test performed at 20 °C vs. 50 °C (r=0.845, P=0.034), at 20 °C vs. 70 °C (r=0.902, P=0.014), and at 70 °C vs. 50 °C (r=0.974, P=0.001). On the contrary, no statistically significant correlation has been found between weight variation [%] and colour change (p> 0.05). While the samples immersed in coffee show detectable colour variation at lower temperature condition (20°C), Figure 4 evidences that only at 70°C strong colour changes could be observed in the all the other samples. For ΔE values lower than 2, indeed, the colour difference between two samples is barely perceivable by the average human eye [30]. Table 2 illustrates the means and standard deviations of color modification of each material at the different environmental condition tested, as well as the differences among groups.

3.3 Flexural tests

The effect of food chemicals absorption on mechanical properties of PA 4,10 reinforced with 30% of short glass fibers is evaluated through flexural tests. In order to compare the performances of reference and aged samples tested with different food chemicals, flexural strength and tangent modulus of elasticity are used. Figure 5 shows the flexural strength distributions of aged samples, grouped by aging parameters. Due to aging conditions, significant differences in the flexural strength were measured: flexural strength decrease was mainly attributed to the temperature conditions, and then to the chemicals. Vinegar was confirmed to be a particular case, with a significantly stronger decrease in flexural strength compared to other chemicals, reaching the 80% of the starting reference value. In the same way, Figure 6 shows flexural modulus of elasticity results on aged samples: similarly to flexural strength analysis, temperature and chemicals influenced the elasticity decrease, even if the scattering of data is higher than previous analyzed mechanical parameter. The maximum decrease in this second parameter is given again by samples aged with vinegar, reaching about the 70% of the starting reference value.

The consistency of these results with the previous absorption curves demonstrated that chemicals diffusion in the materials led to a change in mechanical properties, as done in other studies for different types of composite materials [6,31]. In particular, flexural strength was the most promising mechanical parameter to

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evaluate due to the lower scattering of data. Anyway, the significant decrease in tangent elastic modulus has to be taken into account in order to evaluate the change in fracture behavior of tested material before and after aging. Considering vinegar and its strong impact on mechanical properties decrease, Figure 7 reports load-extension curves of reference samples and the ones aged with vinegar at different temperatures. A change in mechanical behavior at break is clearly visible from the shifting of load-extension curves depending on aging temperature and considering the same aging time: the higher is the temperature, the more plasticization occurred and the fracture behavior becomes more ductile.

The consistency of all previous measurements is again highlighted by Figure 8 for samples aged at 70°C in contact with vinegar: the retained flexural strength can be described by second degree polynomial functions of time, while the weight gain can be described curve with linear functions of square root of time. As regards colour change, isotherm Langmuir equation describes its trend depending on time [32], with higher accuracy with the increase in temperature. The suitability of Langmuir equation and mechanism could be linked to the stress state induced by absorbed food chemicals [33], due to the different coefficients of moisture expansion of fibers and matrix [34].

3.4 SEM analysis

In order to further confirm the change in fracture behaviour, SEM images were taken to evaluate the morphology of fracture surfaces. Figure 9 evidences the plasticization effect hypothesized from flexural tests results. On reference sample (Fig. 9a-c), the fracture surface of polyamide is flat, with presence of debonded fibers (extended pull-out [35]) and some broken fibers in the compressive stress area (Fig.9c). Fracture surfaces of samples aged for 72 hours at 70°C (Fig. 9d-r) highlights how plasticization is evident in the tensile stressed area, with the appearance of shear yielding fibrils and the increase in the numbers of broken fibers and fracture planes. The extreme effect of vinegar is once more evident in the appearance of polymeric matrix fibrils also in the compressive stressed area (Fig. 9r), with decreased brittle behavior of the polymer during the test [21].

The impact of testing times and temperatures is evidenced through Figure 10 for samples aged with vinegar: the increase in temperature is the most impacting effect on fracture surface morphology changes, with appearance of fibrils and increase in voids due to plasticization of the matrix (Fig. 10 f,g). The major finding due to the increase in time is given by the more uniform transverse section of fracture surface: for samples aged for 40 hours (Fig. 10b,d,f) the fracture surface can be divided into two areas with different morphologies, where tensile stressed areas demonstrates higher presence of fibrils and voids compared to

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the flatter surface in the compressive stressed areas (see supplementary material for further details). When the aging time is increased up to 72 hours (Fig. 10 c,e,g), the transverse section shows a more uniform morphology on both tensile and compressive stressed areas: this is consistent with the higher time given to diffusion process to reach the central parts of the samples and the stronger effects of plasticization [36].

3.5 Reliability

In order to quantify the changes in flexural strength and give parameters relevant for the design phase, reliability functions parameters were calculated for every aging condition of samples. Figure 11 shows that these functions are shifted toward lower flexural strength values when testing temperature is increased. Samples aged at 20°C showed a higher change in shape of the function than its shifting (Fig. 11a): this is sign of lower impact of temperature and higher influence of food chemicals in the resulting flexural properties. This observation confirms that the effect of food chemicals on mechanical properties is not negligible at 20°C. Indeed, Figure 11b and 11c show a lower variability in function shape and higher contribution of curves' shifting, due to the crucial role of temperature on flexural properties change. In order to better understand the effect or reliability functions shifting, reliability values were calculated considering an arbitrary flexural stress of 180 MPa for all aging parameters combinations. The reference samples showed 99% reliability, while aged samples decrease this value up to 45% for samples aged at 70°C for 72 hours, with extreme value of 2% when aged at the same conditions in contact with vinegar. From this data, the change in flexural strength is associated with the survival probability of material subjected to the same flexural stress.

4. Conclusions

The effect of food chemicals and thermal aging on the mechanical reliability of bio-based glass fibers reinforced polyamide was investigated in this paper. Based on the results of the study, the following conclusions can be drawn:

1. The diffusion of food chemicals was mainly driven by thermal energy (i.e. following Arrhenius law), with a secondary but not negligible contribution of the chemical interaction between foods and polyamide;

2. The measured change in colour was positively correlated to the weight gain, following a linear trend in time different from the secondary polynomial trend observed for weight gain;

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3. A strong plasticizing effect was induced from chemicals absorption and their interaction with polyamide chains. Degradation of tangent elastic modulus and flexural strength up to 30% was observed, with the change in fracture surface morphology from flat fracture planes and debonded fibers to shear yielding fibrils and broken fibers. This effect was evident for all food chemicals, but stronger in the case of vinegar;

4. Based on mechanical properties statistical elaboration, the reliability curves of aged samples were strongly shifted compared to the reference ones. The influence of food chemicals on flexural strength and tangent elastic modulus degradation was stronger at 20°C, and is partially overlapped from the impact of heat at higher temperatures. This observation was consistent with the positive correlation between diffusion phenomena and mechanical properties degradation.

Previous findings highlight how food chemicals can induce strong changes in mechanical properties of materials that have to be considered in durability evaluation and mechanical design of structural components. The correlation of mechanical properties with reliability is proposed as a good indicator for lifetime assessment of materials when in contact with food chemicals.

Acknowledgments

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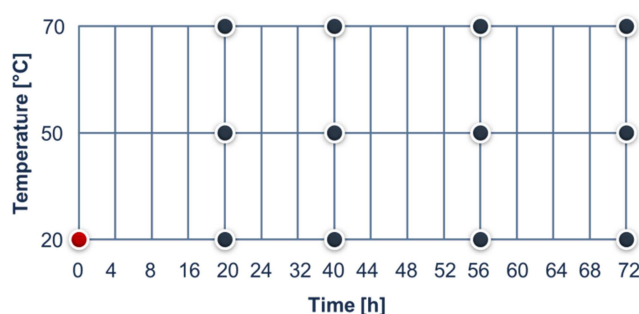**Figures and tables**

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Figure 1: Representation of full factorial design (grid) and reduced 3x4 overlapped design (circles), highlighting reference
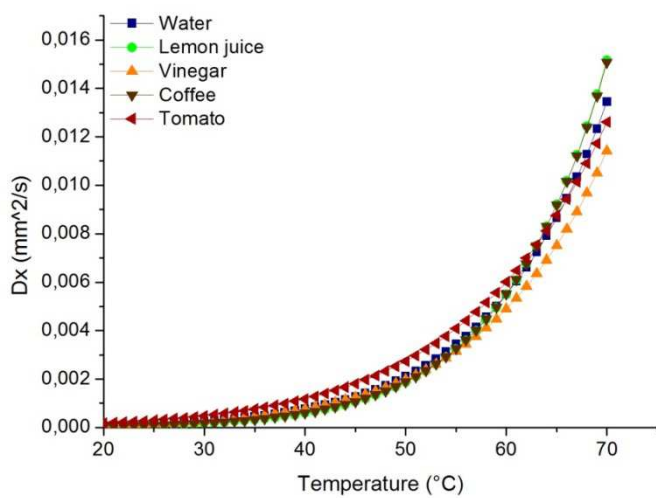
sample at 20°C and 0 hours.

Figure 3: Arrhenius law fits of diffusion coefficients for different food chemicals.
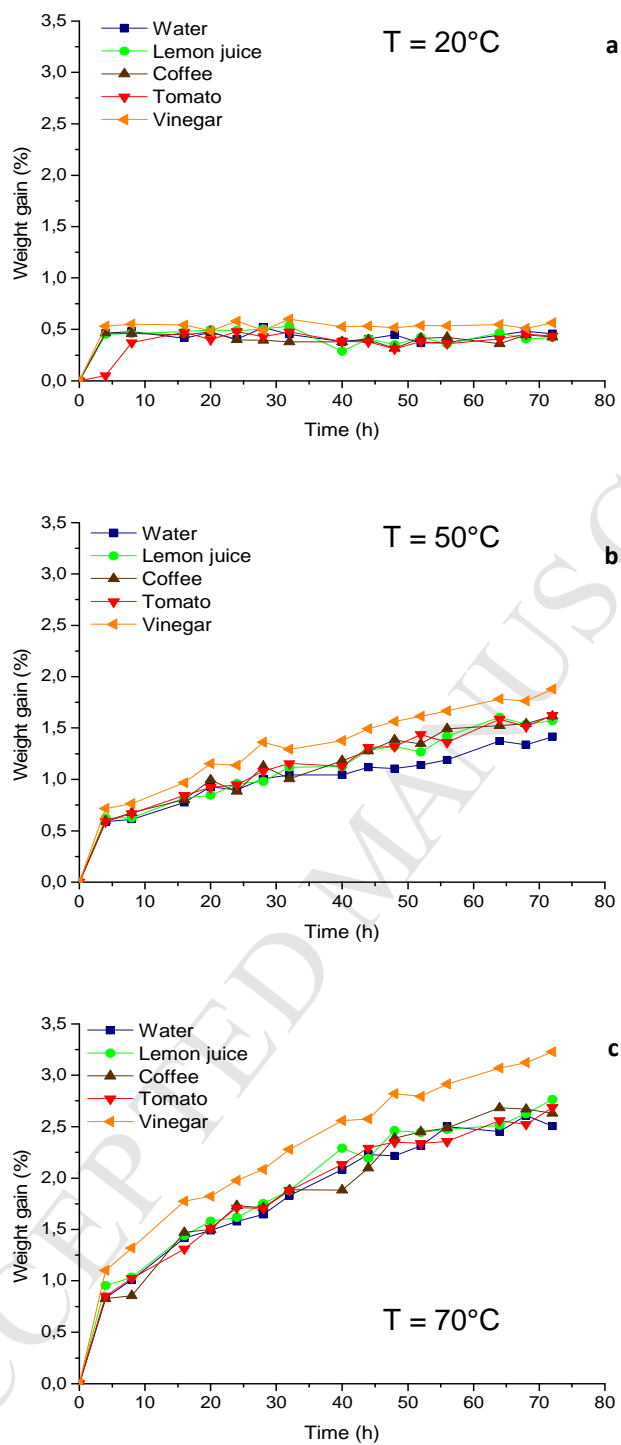
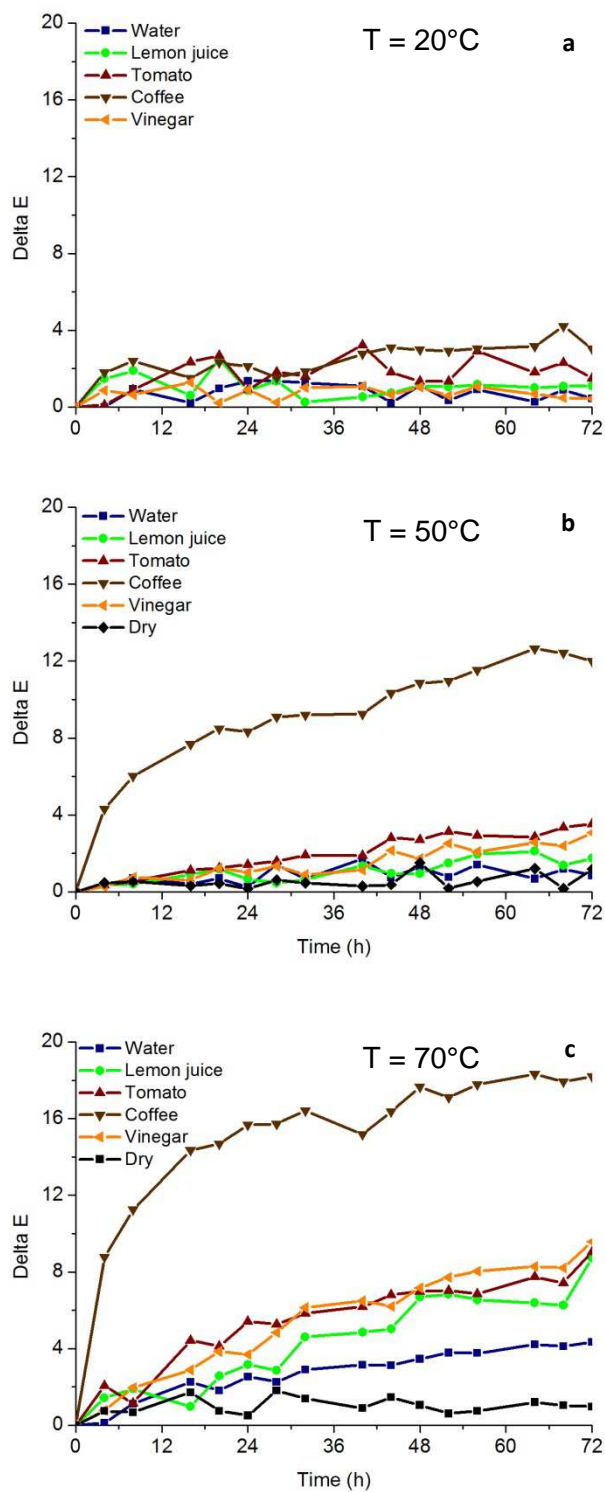*Figure 2: Absorption curves for different food chemicals at 20°C (a), 50°C (b) and 70°C (c) as function of time.*

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Figure 4: Colour change curves (Delta E vector, CIELab colour system) for different food chemicals at 20°C (a), 50°C (b) and 70°C (c) as function of time.
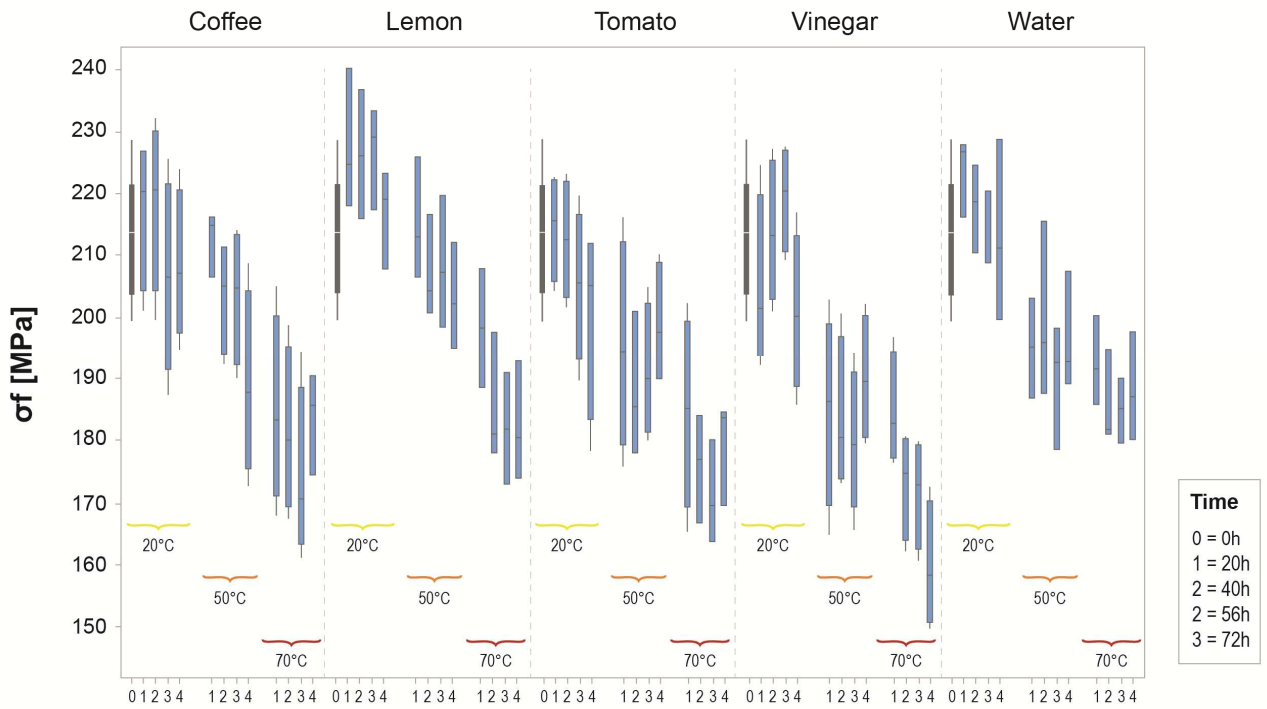
Figure 5: Boxplot of flexural strength grouped based on aging conditions parameters (time, temperature, chemical). Dark grey boxes indicate the reference samples data.
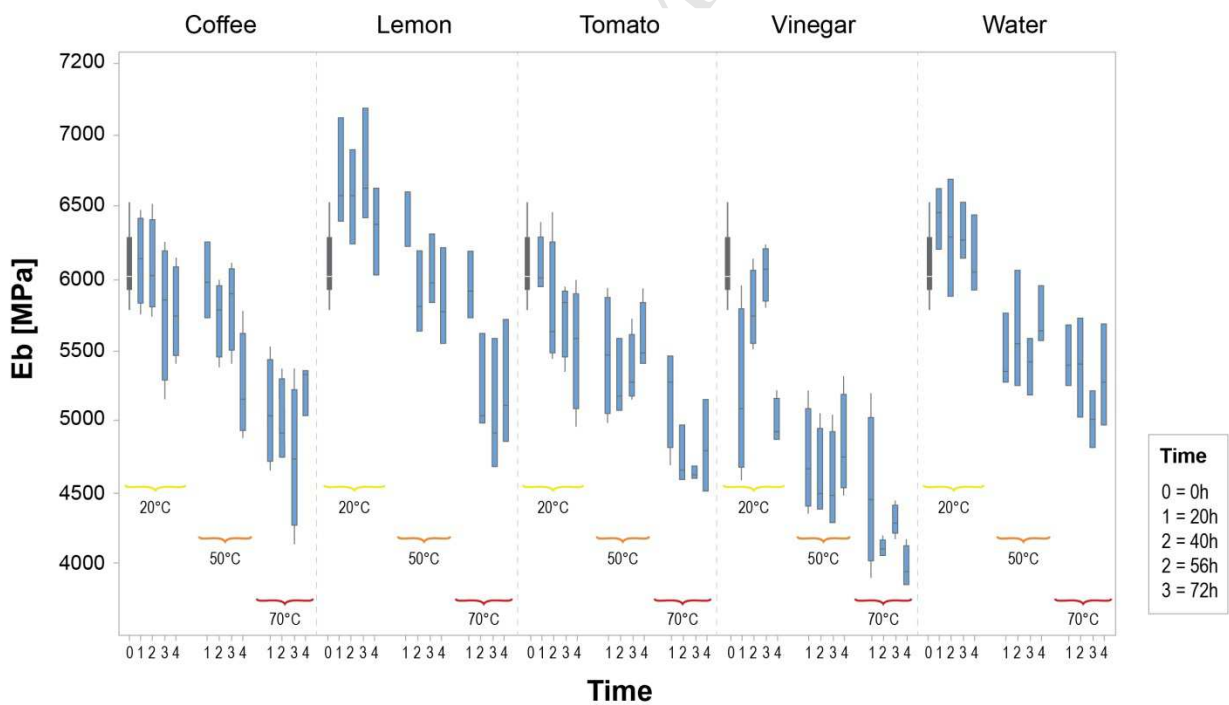

Figure 6: Boxplot of tangent modulus of elasticity grouped based on aging conditions parameters (time, temperature, chemical). Dark grey boxes indicate the reference samples data.
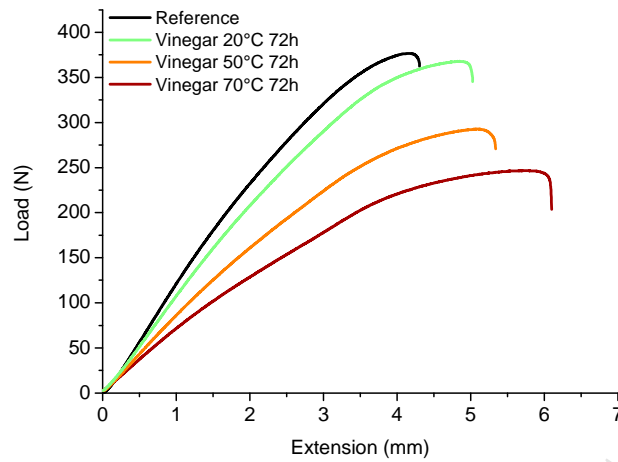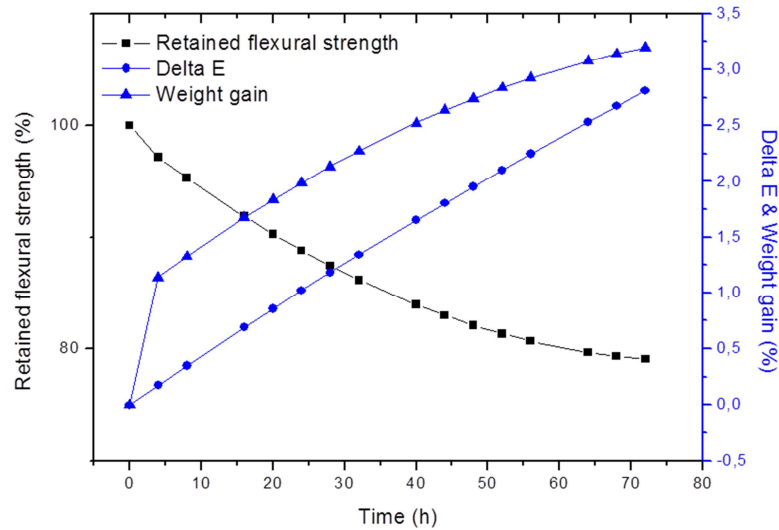
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Figure 7: Load versus extension curves for reference sample and the ones aged with vinegar at different temperatures.

Fitting equation	S
—■— Retained flexural strength $$\frac{\sigma_{f,max}}{\sigma_{f,max,0}} = 0.003401 \cdot t^2 - 0.5280 \cdot t + 99.53$$	0.171072
—◆— Delta E $$\Delta E = 22.7208 \cdot t/(510.099 + t)$$	0.0000026
—▲— Weight gain $$WG(\%) = 0.3600 \cdot \sqrt{t} + 0.2249$$	0.0928100

Figure 8: summarizing plot of fitting curves from experimental data and their equations: retained percentage of flexural strength, colour change (Delta E) and weight gain versus time in the case of samples aged with vinegar at 70°C.
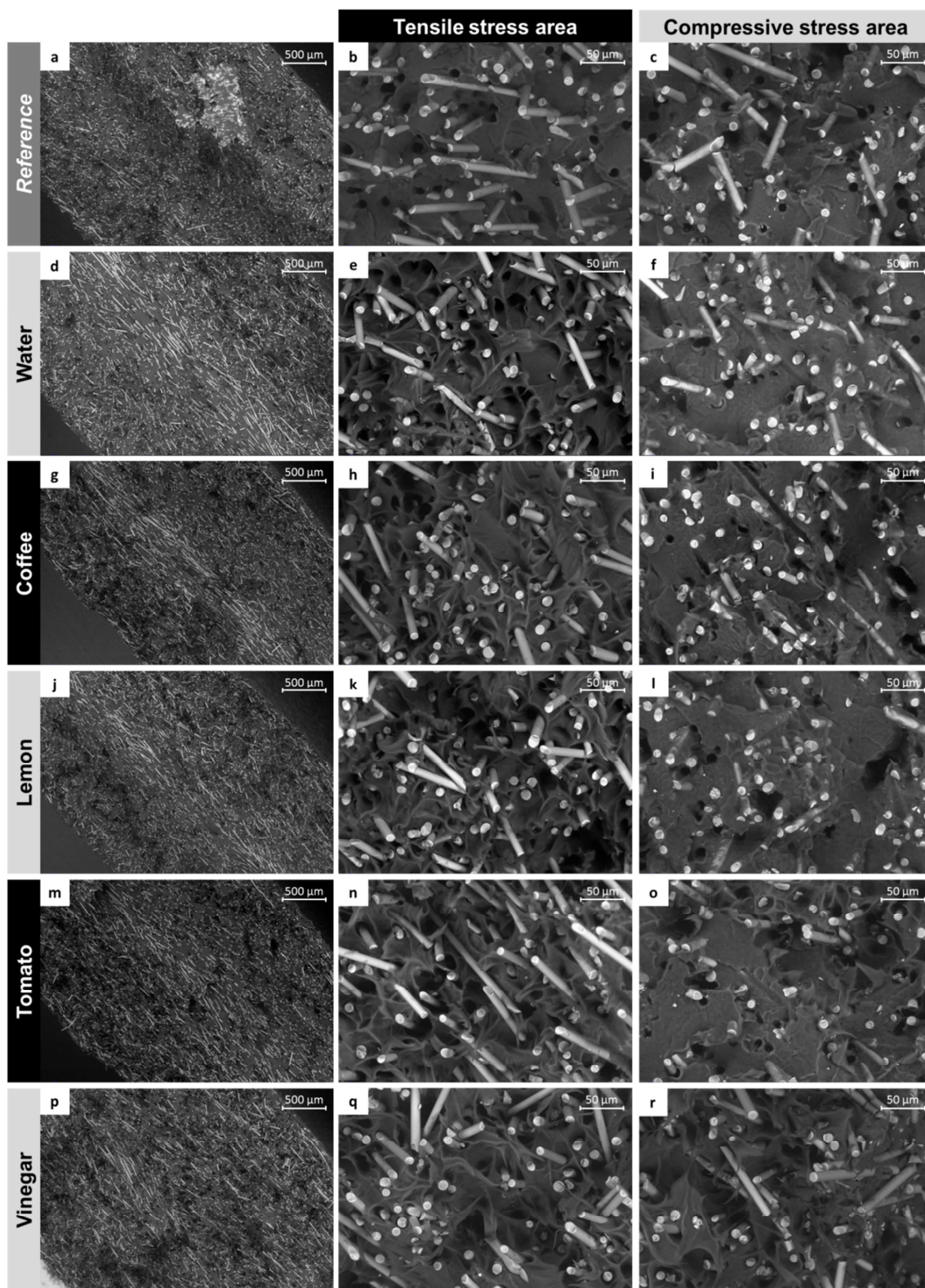
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Figure 9: SEM images (backscattered electrons) of transverse section on fracture surfaces of reference sample (a-c) and the ones aged at 70°C for 72 hours with different chemicals (d-r). Areas where tensile (b,e,h,k,n,q) and compressive (c,f,i,l,o,r) stresses are reported.
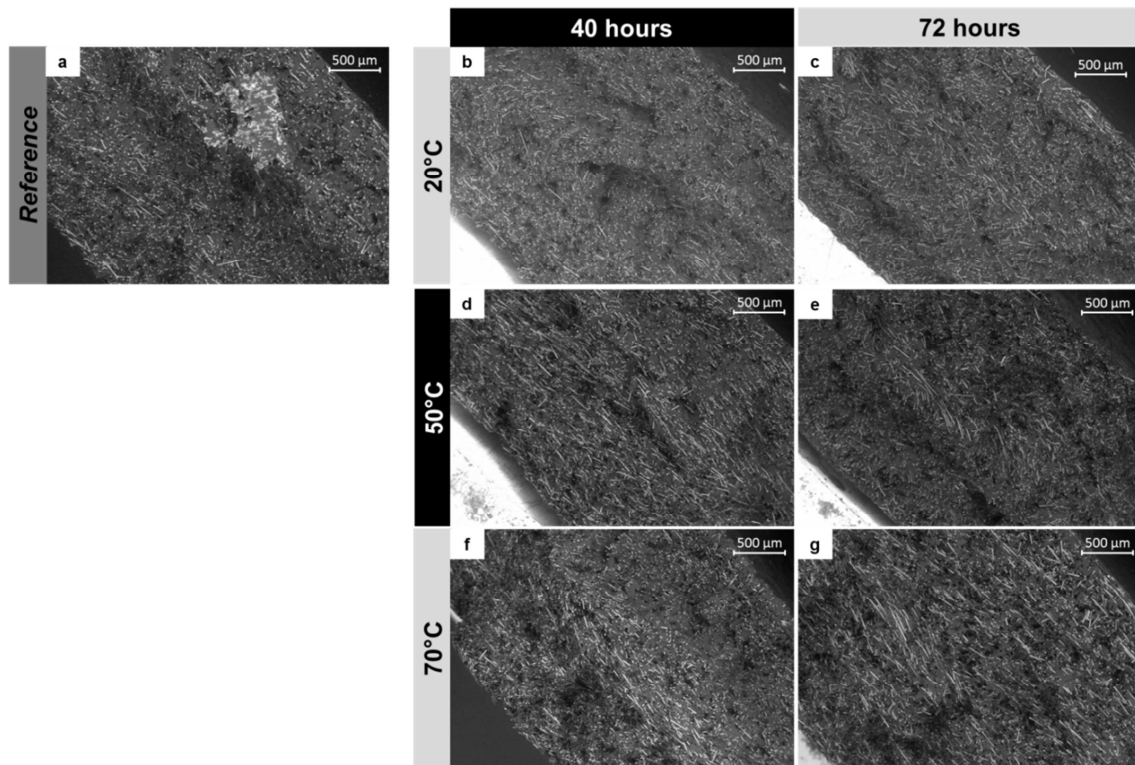
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Figure 10: SEM images (backscattered electrons) of fracture surfaces of reference sample (a) and the ones aged with vinegar at different times and temperatures (b-g).
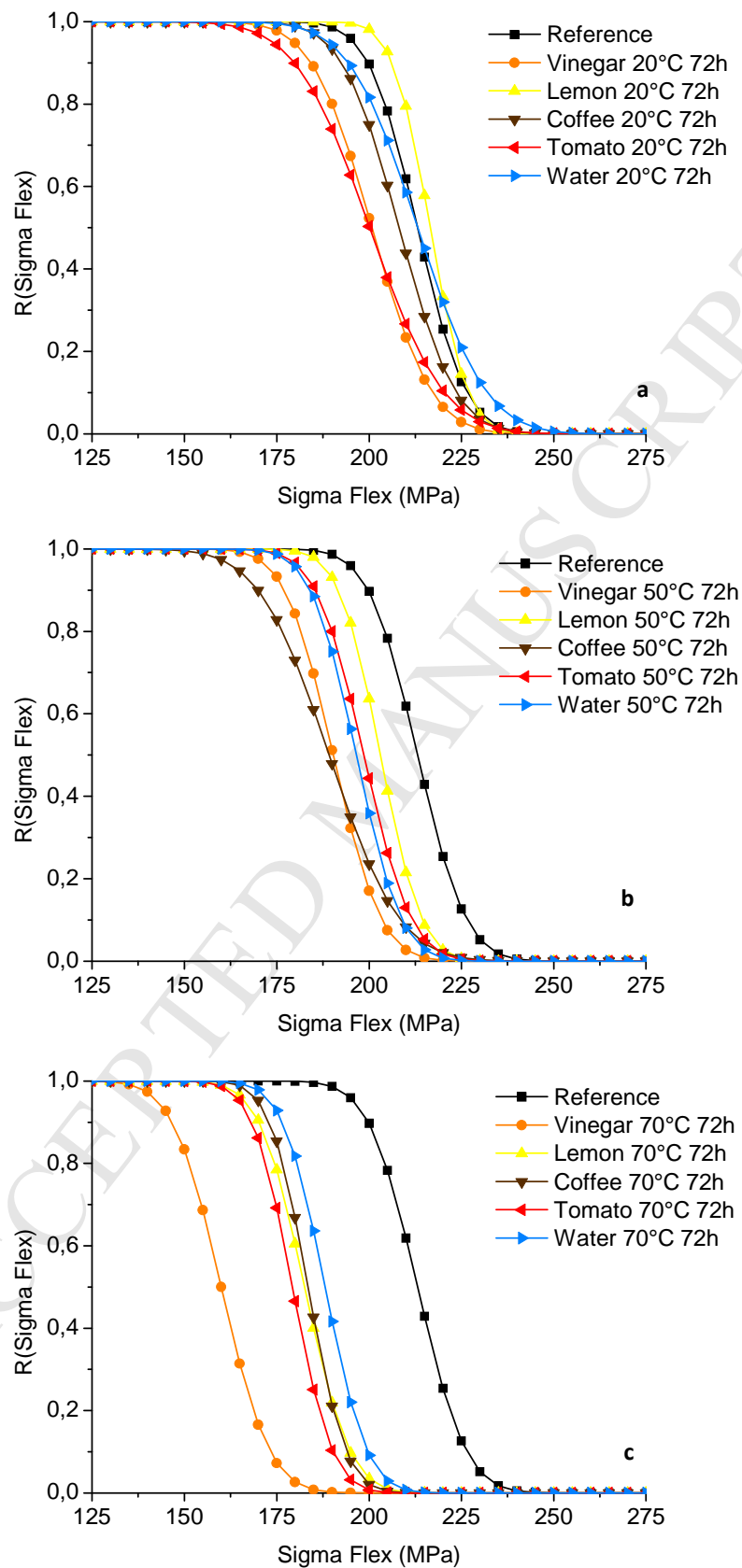
Figure 11: Reliability functions for different food chemicals at 20°C (a), 50°C (b) and 70°C (c) after 72 hours, depending of flexural strength.

Table 1: Diffusion coefficients and saturation levels of tested samples.

Chemical	pH	Saturation level M_m (%)	$M_m/M_{m,water}$	Temperature [°C]	Dx [mm^2 s^{-1}]
Water	7.4 ± 0.1	3.30 ± 0.01	1.00	70	1.156E-02
				50	2.670E-03
				20	7.633E-05
Lemon	2.8 ± 0.1	3.59 ± 0.01	1.09	70	1.051E-02
				50	3.320E-03
				20	3.847E-05
Vinegar	4.0 ± 0.1	4.47 ± 0.01	1.35	70	9.140E-03
				50	2.860E-03
				20	8.248E-05
Coffee	4.2 ± 0.1	3.64 ± 0.01	1.10	70	1.061E-02
				50	3.290E-03
				20	4.050E-05
Tomato	5.3 ± 0.1	3.49 ± 0.01	1.06	70	1.077E-02
				50	3.550E-03
				20	4.124E-05

Table 2: Means and standard deviations of color changes and differences between the materials tested at different environmental conditions. Vertical lines connect groups that are not significantly different (P>0.05) by Fisher LSD Method.

Environmental conditions	Mean ΔE (SD)*		
Temperature / Chemicals	T_{amb}	50°C	70°C
Dry	0	0.568 (0.40)	1.039 (0.39)
Water	0.762 (0.45)	0.884 (0.42)	2.865 (1.16)
Coffee	2.585 (0.72)	9.542 (2.29)	15.694 (2.59)
Tomato	1.778 (0.80)	2.100 (0.99)	5.760 (2.05)
Lemon	1.119 (0.54)	1.105 (0.54)	4.586 (2.25)
Vinegar	0.748 (0.31)	1.589 (0.81)	5.722 (2.52)

∗: Vertical lines connect groups that are not significantly different (P>0.05) by Fisher LSD Method.

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