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Title: Effect of refining degree on particle size, sensory and rheological characteristics of anhydrous paste for ice creams produced in industrial stirred ball mill

Article Type: Research paper

Keywords: nut and cocoa cream; particle size distribution; viscosity; textural profile analysis; grinding energy

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Abstract: Refining of an anhydrous hazelnut and cocoa based paste for ice cream in a stirred ball mill was characterized in terms of energy use and product viscosity, particle size and sensory characteristics. With a specific milling power of 0.03 kW per kg of paste, the fineness of practical interest, 22.4-30.4 μm , was reached in 225-150 min, respectively. The pastes showed a time-independent pseudoplastic behavior with n and K in the range 0.62-0.69 and 14.2-27.2 Pa sn, respectively. The particle size distribution (PSD) curves, as determined by laser diffractometry, were mainly unimodal, with 90% percentiles $[D(v,0.9)]$ higher than the micrometer readings, suggesting the presence of flat particles, as confirmed by scanning electron microscopy. Most of the textural attributes showed a small difference among the samples with fineness 22.4-30.4 μm , thus suggesting a product with fineness, $D(v,0.9)$ and specific energy equal to 30.4 μm , 41.8 μm and 0.074 kWh/kg, respectively, as optimal.

UNIVERSITÀ DEGLI STUDI DI NAPOLI FEDERICO II



CENTRO DI ATENEIO PER L'INNOVAZIONE E LO SVILUPPO NELL'INDUSTRIA ALIMENTARE

Naples, January 09th 2017

Dear Editor of *LWT - Food Science and Technology*,

Enclosed is a revised copy of the manuscript entitled "Effect of refining degree on particle size, sensory and rheological characteristics of anhydrous paste for ice creams produced in industrial stirred ball mill" by Marcello Fidaleo, Stefania Mainardi, Vincenzo Armini, Roberto Nardi, Silvana Cavella and myself.

According to reviewers and Editor's comments, we modified the paper and we separately prepared the replies for each of them. Thank you for all the suggestions, they helped us to improve the paper.

I look forward to hearing from you on the suitability of this revised version for publication on *LWT - Food Science and Technology*.

SINCERELY,

DR. NICOLETTA A. MIELE

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Nicoletta Antonella Miele

Reply to Editorial

Dear Editor

In this file, we responded (in italic fonts) to your suggestions, point by point.

1. Each highlight should have a bullet point before it.
N. We added them.
2. Line 26: "needed energy" should be "energy use"
N. We modified as you suggested in the abstract.
3. Line 40: % should be g/100 g
N. We changed the % in g/100 g
4. Line 84-85 and elsewhere: The composition % should be changed to g/100g. The % unit for composition and concentration is not accepted in LWT.
N. We modified the unit format in all the manuscript.
5. Line 95: The room temperature should be specified in degree Celcius.
N. We wrote: "....samples of 1 kg of refining paste were withdrawn and stored at 20°C...."
6. Line 154, 155 and other locations: "M" for molar concentration should be changed to mol/L
N. We modified the unit format in all the manuscript.
7. % v/v is not accepted in LWT, write mL/100mL or convert to mL/L.
N. We used mL/100 mL instead of % in all the text
8. Figures: The key of symbols should be written in the captions' text and not below the x-axis. Also, the variables/symbols used for axes labels must be defined in the captions' text because the figures should be self explanatory.
N. We improved the resolution of all the figures, removed legends and added the definition of symbols and variables in the caption's text.
9. The scale bar on micrographs is not legible. Either make them legible or write it in the caption's text.
N. We preferred to use the original micrographs including the scale bar, but we only improved the resolution and dpi.

Thank you for your advice and comments to our work. They were useful to clarify all the paper and make it suitable for the publication in your journal.

Best regards

Nicoletta Antonella Miele and coauthors

Reply to Reviewer 1

Dear Reviewer

In this file, we responded (in italic fonts) to your comments and suggestions, point by point.

1. The manuscript reads well but needs further revision.
N. thank you for your interest in the manuscript!
2. Line 48-49: The sentence is vague. "they should not be spreadable" should be changed to "they are not spreadable". "should be more liquid" should be written as "become more liquid". "at environmental temperature" should have a specified temperature range.
N. According to your suggestion we modified lines 49-50 as following "... but they are not spreadable across a wide temperature range and become more liquid than a spread at 20-25°C....."
3. I do not find a list of figure captions which is required.
N. Sorry for that. We added figure captions
4. Line 93: The recycling mass flowrate of 4640 kg/h seems very high. Please check it again.
N. We double checked the recycling mass flow rate value and confirmed that it is 4640 kg/h. This value was supplied by the manufacturer but also measured experimentally. Considering that the mass of refining cream is about 400 kg, this mass is recycled to the mill about $4640/400 = 10.8 \text{ h}^{-1}$, that is almost 11 times in an hour.
5. Sensory: Specify the hours of training given to train the judges.
N. At line 136 we added the following sentence: "Judges were trained for 10 hours."
6. Line 202: "a Casson viscosity almost always increasing with" is vague. Write it as "that Cason viscosity increased with"
N. We modified as you suggested at line 204: "...The authors found Casson viscosity increased with the increase of milling time."
7. Line 249: "big" should be "large"
N. We used large instead of big.

*Thank you for your advice and comments to our work. They were useful to clarify all the paper.
Best regards*

Nicoletta Antonella Miele and coauthors

Reply to Reviewer 2

Dear Reviewer

In this file, we responded (in italic fonts) to your comments and suggestions, point by point.

1. This paper reported the refining process of anhydrous hazelnut and cocoa based paste using ball mill. The report is of practical value for industry and worth publishing.

N. Thank you for your interest in the manuscript!

2. The figures are of poor quality. It is strongly recommended to replace with much higher quality figures.

N. We strongly improved the quality and dpi of all the figures.

3. Line 164, 169: "mill ball" or "ball mill"?

N. Sorry for that. Ball mill is correct.

Thank you for your advice and comments to our work. They were useful to clarify all the paper.

Best regards

Nicoletta Antonella Miele and coauthors

Highlights (3-5 points, maximum 85 characters including spaces)

1. Refining of a hazelnut and cocoa based paste in stirred ball mill was characterized.
2. The refining pastes showed a time-independent pseudoplastic behavior.
3. The particle size distribution curves were mainly unimodal.
4. Most texture attributes showed small changes in the fineness range 22.4-30.4 μm .
5. A product with fineness equal to 30.4 μm appeared as optimal.

TITLE

**Effect of refining degree on particle size, sensory and rheological characteristics of anhydrous
paste for ice creams produced in industrial stirred ball mill**

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**Keywords: nut and cocoa cream; particle size distribution; viscosity; textural profile analysis; grinding
energy.**

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24 *Abstract*

25 Refining of an anhydrous hazelnut and cocoa based paste for ice cream in a stirred ball mill was
26 characterized in terms of energy use and product viscosity, particle size and sensory characteristics.
27 With a specific milling power of 0.03 kW per kg of paste, the fineness of practical interest, 22.4-30.4
28 μm , was reached in 225-150 min, respectively. The pastes showed a time-independent pseudoplastic
29 behavior with n and K in the range 0.62-0.69 and 14.2-27.2 Pa s^n , respectively. The particle size
30 distribution (PSD) curves, as determined by laser diffractometry, were mainly unimodal, with 90%
31 percentiles $[D(v,0.9)]$ higher than the micrometer readings, suggesting the presence of flat particles, as
32 confirmed by scanning electron microscopy. Most of the textural attributes showed a small difference
33 among the samples with fineness 22.4-30.4 μm , thus suggesting a product with fineness, $D(v,0.9)$ and
34 specific energy equal to 30.4 μm , 41.8 μm and 0.074 kWh/kg, respectively, as optimal.
35
36

37 **1. Introduction**

38 Nut creams can be defined as complex systems made up of different solid particles (sugar, cocoa
39 powder, milk whey, milk powder, nuts, etc.) dispersed in a continuous fluid (oil) (Glicerina et al.,
40 2013). They include nut butters and nut spreads that contain at least 90 and 40 g/100 g nut ingredients
41 (Shakerardekani et al., 2013), respectively, but also other nut based products, like sweet creams used as
42 filling, anhydrous pastes for ice cream preparation or spreadable products, such as hazelnut chocolate
43 based spreads. Textural, color, and flavor properties of these products play a major role in consumer
44 appeal, buying decisions and eventual consumption (Di Monaco et al., 2008). Depending on the
45 specific product, the most desired characteristics are a good spreadability across a wide temperature
46 range, a creamy taste, no fat-phase separation and a good oxidative stability.

47 Anhydrous pastes based on nut creams used for the preparation of ice creams are close to nut based
48 spreads for the recipe, but they are not spreadable across a wide temperature range and become more
49 liquid than a spread at 20-25°C, this being obtained by varying their fat phase composition (Birkett,
50 2009). They could also resemble a filling cream, that is generally fat and sugar based and represents an
51 important component in different confectionary foods, in which it provides taste, texture and adhesion
52 of the baked items (Miele et al., 2015).

53 The production process of nut creams requires a step for the reduction of solid particle size. The main
54 aim of this unit operation, called refining, is to reduce the solids to a specific particle size that depends
55 on the specific product. For example, in the case of chocolate, the size of largest solid particles has a
56 direct influence on rheological (flow properties) and sensory (mouthfeel grittiness) properties.
57 Chocolate with particle size above 35 μm becomes gritty or coarse in the mouth resulting in lower
58 acceptability (Petković et al., 2013).

59 Refining is mainly carried out with roll refiners, typical of the chocolate industry, or, more recently and
60 for small productions, with stirred ball mills. In this last process, nut cream ingredients to be milled are

61 fed into a jacketed tank containing the grinding media, typically stainless steel balls. The refining
62 product and the balls are then agitated by a rotating shaft with arms. The product can also be recycled
63 through the ball mill several times (Alamprese et al., 2007). During this process of mixing, grinding
64 and recirculation, the size of the solid particles reduces and their surface is wrapped by the fat phase
65 (Petković et al., 2013), conferring to the cream its rheological and textural properties.

66 The rheological behavior of this kind of product is affected both by several process parameters
67 (temperature, agitation rate, milling time) (Petković et al., 2013) and by formula composition
68 (Lončarević et al., 2016; Glicerina et al., 2013). These factors act also on the particle size distribution
69 of the product under refining (Lončarević et al., 2016). The same considerations can be applied to
70 chocolate refining in stirred ball mills (Alamprese et al., 2007; Lucisano et al., 2006). Since the particle
71 size of the product affects overall perception of the final product, it is really important to optimize this
72 attribute (Birkett, 2009). An accurate definition of target particle size of the product and corresponding
73 method of measurement are essential, especially to avoid. Not only does overgrinding reduce
74 productivity but also has significant implications for energy consumption, considering that the energy
75 required to reduce particle size rises dramatically as particle size set point decreases.

76 In literature, it was not possible to find any work dealing with the refining of anhydrous paste for ice
77 cream or similar products in stirred ball mills. Thus, the main objective of this work was to evaluate the
78 effect of stirred ball mill refining degree on particle size, sensory and rheological characteristics of this
79 product and also on specific energy consumption.

80 **2. Materials and methods**

81 **2.1 Materials**

82 Cocoa and hazelnut based anhydrous paste samples were produced in an Italian confectionery factory
83 using an industrial plant (Mazzetti Renato Srl, Italy) as described below. The following formulation

with reference to 100 g of paste was used: seed oil (27 g), hazelnut paste (8 g), cacao powder (11 g), milk powder and derivatives (7.5 g), lecithin (0.6 g), sugar (31 g), ice sugar (14 g), other (0.9 g).

2.2 Grinding equipment, operation and energy consumption

The paste production line allowed the production of 2400 kg for each production cycle. It was composed of a mixer, a holding tank, three ball mills and a tank to store the refined paste. The stirred ball mills (model WAFA400, Mazzetti Renato Srl, Italy) allowed the production of batches of 400 kg of paste. They consisted of jacketed cylindrical tanks containing 9.5-mm diameter stainless steel balls, a vertical shaft with horizontal arms for stirring and a recycling pump. Refining was carried out at a starting temperature of 42 °C, at an agitator shaft speed of 50 rpm, recycling the mass through the bed of balls at a flow rate of 4640 kg/h.

At various time intervals (60, 90, 120, 150, 195, 225 min) during the process, samples of 1 kg of refining paste were withdrawn and stored at 20°C in air-tight plastic containers before being used for the sensory analysis, the determination of the rheological behavior and measurement of the particle size. At the same time intervals the electric current flowing into the motor connected to the vertical shaft was measured by a digital clamp meter (model ELD200N, Eldes Instruments Srl, Italy).

The power (P) absorbed by the asynchronous three-phase motor connected to the stirring shaft assembled with the ball mill was calculated according to Eq. (1) (Alamprese et al., 2007):

$$P = VI\sqrt{3}\cos(\phi) \quad (1)$$

where V and I are the electric voltage and current and $\cos(\phi)$ is the power factor of the motor (0.84 in this case).

The specific energy (E) consumed by the ball mill for grinding as a function of time (t) was calculated according to Eq. (2):

$$E = \frac{\sum_{i=1}^{i=n} VI_i\sqrt{3}\cos(\phi)t_i}{M} \quad (2)$$

107 where the summation index i refers to the refining time interval, I_i and t_i to the corresponding electric
108 current and time, M to the mass of refining paste.

109 **2.3 Particle size measurement**

110 A Mastersizer laser diffraction particle size analyzer equipped with Hydro 3000 dispersion unit
111 (Malvern Instruments, Worcestershire, UK) was used. About 0.1 g of paste was analyzed at ambient
112 temperature ($20 \pm 2^\circ\text{C}$). The sample was added into the disperdant (vegetable oil) until 18–20%
113 obscuration was obtained. Stirring was conducted to ensure that particles were independently dispersed.
114 Size distribution was quantified as relative volume of particles in size bands and presented as size
115 distribution curves. Several indexes of the particle size distribution (PSD) based on the volume of
116 particles were estimated, including the volume weighted mean $D[4,3]$, and the 10, 50 and 90
117 percentiles $D(v,10)$, $D(v,50)$ and $D(v,90)$, respectively.

118 For each refining time two different samples were analyzed and for each sample 15 measurements were
119 performed.

120 In the production area, the micrometer method was used to measure the particle size of refining paste.
121 Samples of the refining paste were withdrawn from the ball mill and analyzed immediately in five
122 replicates by a digital micrometer (model IP65, Mitutoyo, IL, USA). A second measurement procedure
123 consisted in dispersing the paste sample (approximately 1 g) in 1 g of white mineral oil before being
124 placed on the jaws of the micrometer (Lucisano et al., 2006).

125 **2.4 Viscosity measurement**

126 Viscosity of paste samples was determined by a rotational rheometer ARES-LS (Rheometrics Inc.,
127 Piscataway, NY). The flow curves were carried out at 30°C using a plate-plate system. In steady state
128 conditions, after a pre-shearing of 500 s at 2 s^{-1} , the apparent viscosity was measured as a function of
129 increasing shear rate from 2 to 50 s^{-1} (I ramp) within 180 s, then of decreasing from 50 to 2 s^{-1} (II ramp)
130 (Glicerina et al., 2016). Between the two ramps samples were sheared for 30 s at 50 s^{-1} .

131 The obtained flow curves were fitted with the model of Ostwald de Waele (Power Law model), as
132 reported by Glicerina et al. (2013). Three replications for each sample were performed.

133 **2.5 Sensory analysis**

134 Texture profile was performed with a panel of nine trained judges. Judges were trained for 10 hours.
135 Approximately 10 g of each sample was served in two different containers (plastic petri dishes and
136 cups), identified by three-digit random codes and presented in a monadic sequential order. The
137 assessors were provided with a knife and with a spoon for each sample.

138 One visual, four non oral and three oral texture attributes were scored on 10 cm unstructured lines with
139 references. Attribute definition, evaluation techniques and references are described in Table 1 and most
140 of them have been kept from Di Monaco et al. (2008). Tests were run in separate booths at 20°C. As a
141 blocking factor, the preservation temperature, 4 or 20°C, of samples for 4 h before sensory evaluation
142 was used. Assessors evaluated the samples when they reached the temperature of 20±1°C.

143 **TABLE 1**

144 Descriptive data were collected over six sessions; the samples were split into two blocks, separately
145 for each preservation temperature, and inside each block each sample was tested following a
146 randomized design with two replications. Data were collected by means of "Fizz Acquisition" software
147 (Biosystèmes, Couternon, France).

148 **2.6 Microstructure analysis**

149 Microscopy investigations were conducted on samples at different refining time (60, 90, 120, 150, 195,
150 225 min). Digital images were collected by using a LEO EVO 40 scanning electron microscope (SEM)
151 (Zeiss, Germany) with a 20 kV acceleration voltage. Sample preparation was a modified version of the
152 procedure used by Worrasinchai et al. (2006). The paste samples were encapsulated in 2.5 g/100 g agar
153 at 45°C, and then cut into 3–4 mm cubes. The gel samples were fixed overnight in 2 mL/100 mL
154 glutaraldehyde in 0.1 mol/L phosphate buffer (pH 7), rinsed several times in fresh buffer and then fixed

overnight in 2 mL/100 mL osmium tetroxide with 0.1 mol/L phosphate buffer. After washing the samples with buffer, they were dehydrated in a graded series of aqueous ethanol solutions (50, 70, 90, 95, 99 and 100 mL/100 mL, 30 min in each). The samples were then critical point dried through CO₂. Dry sections were fractured and torn with a blade and fragment were mounted on aluminium SEM stubs, and coated with gold.

2.7 Statistical Analysis

One-way analysis of variance (ANOVA) and multiple comparisons (Duncan or Tukey) were used to evaluate if differences among the sample means were statistically significant ($p \leq 0.05$). The statistical software SPSS for Windows version 17.0 was used for data analysis (SPSS Inc., Chicago, IL, USA).

3. Results and discussion

3.1 Grinding kinetics and energy consumption

The time course of the paste refining process in the ball mill is reported in Figure 1.

FIGURE 1

From Figure 1a, it can be seen that the particle size, as determined by the micrometer, decreases rapidly before reaching a critical time point of 2 h, corresponding to a particle size of $36.0 \pm 1.6 \mu\text{m}$, after which it assumes an asymptotic trend making it difficult to obtain any further desirable reduction in size. Despite ball mill refining rate depends on several factors such as the feed characteristics and mass, the grinding media mass and size and the stirring rate, this asymptotic behavior was observed also by Lucisano et al. (2006) in the case of chocolate refining. Figure 1b reports the time course of the power required by the ball mill, showing that a power of 10.9 kWh was required at the beginning of refining, 11.9 kWh at the end and that a maximum of 12.4 kWh at 90 min of refining was present. Since the variation range of power was quite small, 10.9-12.4 kWh, the corresponding specific energy increased almost linearly with time. To obtain a paste with a target fineness of $22 \mu\text{m}$ a specific energy of 112.3

178 kWh/Mg was required. Because of the abovementioned asymptotic trend, the desired target level of
179 fineness exerts a strong effect on productivity and on milling energy costs, especially if pastes with
180 particle size smaller than 30 μm are desired. Thus, an accurate definition of target fineness and
181 corresponding method of measurement are essential, especially to avoid overgrinding as a way in
182 industrial practice to assure that the product is in specification. For example, in chocolate production,
183 overgrinding makes it necessary to increase the quantity of cocoa butter to obtain the desired viscosity
184 of the final product and this increases production costs. For these reasons, several chocolate producers
185 (Blasco, 2013) but also the cement industry (Pugh, 2014) switched from conventional fineness
186 measurement techniques to laser diffraction particle size analysis to provide more sensitive product
187 characterization to improve the grinding process and avoid overgrinding. Also, there have been some
188 studies aimed at reducing the ball mill refining time in the production of chocolate (Alamprese et al.
189 2007).

190 3.2 Viscosity

191 All the paste samples exhibited a pseudoplastic behavior, as shown in Figure 2, where the apparent
192 viscosity of the pastes decreased as the shear rate increased from 2 to 50 s^{-1} .

193 **FIGURE 2**

194 Table 2 reports the Power Law model parameters, n and K , estimated for each paste, together with the
195 corresponding average coefficient of determination (R^2).

196 **TABLE 2**

197 All samples were characterized by n values in the range 0.6-0.7 typical of pseudoplastic fluids. The K
198 values were in the range 15-27 Pa s^n and tended to increase as refining proceeded, with some exception
199 such as the peak in K , and in the apparent viscosity, as shown in Figure 2, at 90 min of refining
200 corresponding also with a peak in the power absorbed by the mill motor (Figure 1b). This is in line with
201 the rheological behavior of solid dispersions such as chocolate (Birkett, 2009). Lončarević et al. (2016)

202 used a laboratory ball mill to produce a spreadable cocoa cream with different refining degree and
203 containing varying amounts of lecithin of different origins (sunflower, rapeseed and soy lecithin). The
204 authors found Casson viscosity increased with the increase of milling time. This was reported also by
205 Afoakwa et al. (2008) who investigated the effects of particle size distribution and composition on the
206 rheological properties of dark chocolate, where it was observed that an increase in particle size resulted
207 in a decrease in Casson plastic viscosity.

208 For what regards the magnitude of the flow model parameters obtained, the composition of the product
209 under study in terms of fat, cocoa, hazelnut paste, sugar and lecithin is similar to cocoa spreads (Di
210 Monaco et al., 2008). However, the type of fat may differ and this results in different rheological
211 parameter values, as reported by Glicerina et al. (2013) who found that increasing the level of
212 hydrogenated fats in nut spreads results in increased consistency and apparent viscosity. Finally, from
213 repeated shear rate sweep tests it was possible to establish that all the tested samples showed no
214 tixotropic behavior (data not reported).

215 *3.3 Particle size distribution*

216 The PSD curves obtained for the pastes refined for different amounts of time reported in Figure 3
217 appear unimodal.

218 **FIGURE 3**

219 As stated by Bolenz and Manske (2013), unimodal PSD are more typical for ball mill refining products
220 in contrary to many roller milled products which present a multimodal PSD. They studied the effect of
221 fat content during grinding on PSD and flow properties of milk chocolate. The PSD curves obtained for
222 chocolate, refined in ball mills were unimodal and not affected by fat content. Unimodal distributions
223 in ball mills were also observed by Bolenz et al. (2014) in the refining of milk chocolate. Table 3
224 reports the percentiles of the PSD as well as the volume mean particle size ($D[4,3]$).

225 **TABLE 3**

226 It can be observed that increasing the milling time resulted in a statistically significant negative effect
227 on $D(v,0.9)$ and on the other percentiles. The samples obtained at 195 and 225 min of milling presented
228 statistically different $D(v,0.9)$ mean values equal to 37.6 and 35.2 μm respectively. Thus 30 min of
229 milling allowed a reduction in particle size of only 2.4 μm , confirming the low refining rate at low
230 particle size. $D(v,0.9)$ values correlated with micrometer readings as reported in the literature (Beckett,
231 2008) but their absolute values were higher than the micrometer readings. This is consistent with the
232 results of Bolenz et al. (2014) and Bolenz and Manske (2013) who refined white chocolate in ball mills
233 until a micrometer reading of 22 μm was reached and estimated for their samples $D(v,0.9)$ ranging
234 from 28.14 to 30.50 μm . As underlined by Glicerina et al. (2014) and Pieri et al. (2006) this may be due
235 to the fact that the laser diffraction method considers the solid particles as spheres while they may be
236 more similar to flat particles, like disks. Thus the micrometer method estimates a figure linked to the
237 thickness of the flat particles, that is their smallest dimension, which in chocolate seems to correlate
238 better with consumers acceptability compared to the other particle dimensions because once in the
239 mouth particles will tend to orient along their flattest axis (Pugh, 2014). The micrometer readings of
240 paste samples diluted with oil were lower of approximately 30% compared to the samples as such. This
241 is most likely due to the fact that in diluted samples the effect of overstacking (the presence of small
242 particles stacked together with large flat particles) is reduced.

243 *3.4 Microstructure*

244 SEM was employed in an attempt to evaluate the size and morphology of particles. In fact, the PSD
245 curves obtained by laser diffraction are based on the useful and convenient assumption that every
246 particle is a sphere. This technique, like many others, reports values that are equivalent spherical
247 diameters and thus not directly useful to define the particle size to which our palate is most sensitive.
248 Micrographs obtained by SEM show that anhydrous pastes differ in morphology, size and distribution
249 of particles (Figure 4).

FIGURE 4

Sample refined for 120 minutes (Figure 4a) presented a wide distribution of big flat particles, not continuously distributed in the fat phase. Samples refined for 195 minutes (Figure 4b) presented very small particles of different morphology and size well distributed in the continuous phase. Finally the micrograph of the most refined samples (Figure 4c) showed a continuous matrix in which it is possible to find both small particles and some aggregates made by flat and round particles.

Thus, the SEM technique revealed that the refining pastes contained particles with different shape, size and distribution, all elements that supposedly affect the graininess and the flouriness, and not the spreadability, as reported by Di Monaco et al. (2008). The presence of different particle morphologies is consistent with the type of solids present in the paste, primarily cocoa solids, sugar, milk and hazelnut solids. Cocoa solids are not crystalline, and they can therefore be found in almost any shape. Sugar (sucrose) is a monoclinic crystal which means it usually will be found in a uniform shape but in differing dimensions and sizes. Milk solids particles may appear in a variety of shapes and sizes depending upon how it is processed (Pugh, 2014). Hazelnut particles should behave as cocoa particles.

3.5 Sensory Analysis

Texture is one of the most important factors determining food choice, especially for foods with semi-solid or solid textures. A broad range of terminology has been used to describe different food products and their respective evaluation techniques. In some cases, the attribute name and definition are similar across studies; however, it is assessed by different evaluation techniques (Pascua et al., 2013).

In the present study only some texture properties of pastes were evaluated by assessors. A two-way analysis of variance showed that refining time affected almost all the considered texture attributes ($p < 0.001$), while storage temperature had an effect only on oily separation ($p=0.028$). Furthermore, the two factors did not interact. For those reasons the texture attributes of anhydrous pastes reported in

Figure 5 were averaged across storage temperature at each refining time. Only for the attribute oily separation, the scores were not averaged.

FIGURE 5

Figure 5a shows how the storage temperature affects oily separation of the different anhydrous pastes; when the different samples had been held for 4 h at 20°C, the assessors did not find any difference among samples, while for the other storage condition, some differences among samples were underlined. In particular, increasing refining time from 60 min to 150 min reduced significantly oily separation.

The refining time significantly affected graininess between fingers ($p < 0.001$), fluidness ($p < 0.001$), adhesiveness to the spoon ($p < 0.001$), flouriness ($p < 0.001$) and graininess in the mouth ($p < 0.001$), while spreadability ($p=0.114$) and meltability ($p=0.671$) did not significantly change during the refining operation. Figure 5b-h illustrates a general decrease in graininess between fingers, fluidness, flouriness and graininess in the mouth as the refining time increases while the reverse is observed in terms of adhesiveness to spoon. For the graininess between fingers, it was drastically reduced after 120 min and then it seemed to not vary (Figure 5b). The samples registered medium- high spreadability values (between 5 and 7) on the 10 points scale (Figure 5c). The fluidness also decreased, but after 90 min it reached the minimum value and then increased, but at the end it reduced again (Figure 5d). Adhesiveness to the spoon tended to increase during refining time, even if it reached the maximum after 90 min and at the end, after 225 min (Figure 5e). Meltability of the samples was around 5 for all the refined pastes (Figure 5f). The flouriness significantly decreased after 150 min, with some differences among samples at increasing refining times (figure 5g). Graininess in the mouth is the most discriminant textural attribute for the refining time. At 60 min of refining time, the anhydrous pastes presented a high graininess, around 7, and then they were perceived significantly less grainy as the refining time increased, with the lowest graininess detected, less than 1,

297 for the samples refined for 195 min (Figure 5h). Indeed, graininess in the mouth discriminated better
298 the samples than graininess between fingers, in particular at 195 min of refining time, the graininess of
299 the samples was really low as well as the flouriness.

300 So it is possible that the meltability and the spreadability did not change during refining time because
301 they are mainly affected by the fat composition and/or type and amount of emulsifier (Lončarević et al.,
302 2016; Glicerina et al., 2013), but in the present study they were the same for all the samples.

303 Adhesiveness to the spoon of the samples seems to follow the same trend of consistence index (K),
304 estimated from flow curves. Comparing particle sizes detected by sensory evaluation with the same
305 estimated by laser diffraction method, some differences can be underlined. For both data sets the
306 evaluated particle size reduced as the refining time increased, but this did not hold true for the most
307 refined sample (225 min). So we could hypothesize that refining time significantly decreased the
308 average particle size, but after 225 min some small aggregates were formed and they were detected by
309 sensory analysis and confirmed by microscopic observation, but not by the laser diffraction or
310 micrometer method. The reason for the discrepancy between sensory data and particle size data may be
311 explained by considering that only the micrometer readings were carried out as soon as the paste was
312 produced while the SEM analysis and the sensory evaluation were carried out only after 30-45 days of
313 storage at room temperature, during which some re-aggregation could have taken place in the most
314 refined sample. In all probability, this could not be detected by laser diffraction because the method
315 requires stirring and re-dispersion of the sample with consequent aggregate breaking. In fact, laser
316 diffraction measurements correlated with micrometer readings. Re-aggregation phenomena in ball mill
317 chocolate refining have been observed at high refining times (Alamprese et al., 2007). This seems to
318 confirm the more proneness of the most refined sample to re-aggregation.

319 **4. Conclusions**

320 Starting from a company's need to reduce the refining time of an anhydrous hazelnut and cocoa based
321 paste for ice cream, the present study analyzed the viscosity, particle size and textural sensory attributes
322 of the refining paste. After 150 min of refining at a milling power of 0.3 kW per kg of refining paste,
323 the fineness reached a value of 30.4 μm and assumed an asymptotic trend afterwards, making it
324 difficult to obtain further reduction of particle size by prolonging the refining time. Since any further
325 increase in refining time did not result in significant and important changes in many textural attributes,
326 in particular the graininess in the mouth, it can be concluded that the optimal degree of refining is 150
327 min at a power of 0.3 kW, corresponding to a paste with fineness, $D(v,0.9)$ and specific energy equal to
328 30.4 μm , 41.8 μm and 0.074 kWh/kg, respectively.

329

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Table 1. Texture profile analysis: attribute definition, evaluation techniques and references

Attribute	Type	Definition	Evaluation techniques	Scale	References
Oily separation	Visual	Streaks due to the oil separation	Look at the sample and evaluate the amount on the streaks on the sample surface	No streaks at all (0)- a lot of streaks (10)	0= commercial topping; 10= unrefined paste
Graininess between fingers	Non oral texture	Presence of coarse sugar crystals	Evaluate the amount of the grains by manipulate it between two fingers	No grains (0) many grains (10)	0= commercial topping; 10= unrefined paste
Spreadability	Non oral texture	Property of the sample to be spread over a flat surface	Evaluate the ease to spread the sample. Use the rask and the knife to perform the test	0=difficult; 10=easy	1= butter; 10= unrefined paste
Fluidness	Non oral texture	Force required to mix the sample	Dip the spoon in the cup and evaluate the force required to mix the sample.	0=not very fluid; 10=very fluid	0= frozen paste; 10= unrefined paste
Adhesiveness to the spoon	Non oral texture	Property of the sample to stick to a surface	Dip the spoon in the cup and then turn of 90° the spoon and evaluate the amount of sample attached to the spoon	0=not adhesive at all; 10=very adhesive	0= unrefined paste; 10= butter and sugar mix
Meltability	Oral texture	Speed of fat melting	Put a spoon of sample in the mouth between tongue and palate and evaluate its melting rate	0=not meltable at all; 10=quickly meltable	2= dark chocolate; 8= butter
Flouriness	Oral texture	Presence of flour due to cacao or other particles that interact with saliva	Evaluate how floury the sample is perceived in the mouth	0=not floury at all; 10=very floury	0= white chocolate; 10= unsweetened cocoa powder
Graininess in the mouth	Oral texture	Presence of big sugar crystals	Evaluate the amount of grains in the mouths	No grains (0) many grains (10)	0= commercial topping; 10= unrefined paste

Table 2. Flow parameters of pastes at different refining times: flow index (n), consistency index (K) and determination coefficient (R^2).

Refining time (min)	n (-)	K (Pa s ⁿ)	R² (-)
60	0.688±0.012 ^c	14.240±0.908 ^a	0.995±0.003
90	0.677±0.009 ^c	22.293±0.665 ^d	0.997±0.000
120	0.658±0.003 ^b	17.448±0.455 ^b	0.996±0.000
150	0.637±0.007 ^a	21.476±0.547 ^d	0.996±0.001
195	0.631±0.006 ^a	19.656±0.397 ^c	0.996±0.000
225	0.62±0.008 ^a	27.161±0.693 ^e	0.997±0.001

Data represent means ± standard deviations of three replicated determinations. Values in the same column followed by different letters differ significantly at $P<0.05$ level (Duncan's method).

Table 3. Micrometer readings without and with dilution in oil and particle size distribution parameters of pastes at different refining times.

Refining time (min)	micrometer (μm)	Oil - dilution (μm)	D(v,0.1) (μm)	D(v,0.5) (μm)	D(v,0.9) (μm)	D[4;3] (μm)
60	129.8 $\pm$ 69.2 ^f	67.4 $\pm$ 28.4 ^e	2.52 $\pm$ 0.04 ^f	11.82 $\pm$ 0.23 ^f	68.29 $\pm$ 5.01 ^f	25.46 $\pm$ 1.82 ^f
90	46.4 $\pm$ 6.3 ^e	30.4 $\pm$ 2.1 ^d	2.59 $\pm$ 0.02 ^e	11.24 $\pm$ 0.15 ^e	55.82 $\pm$ 2.06 ^e	21.91 $\pm$ 0.81 ^e
120	36.0 $\pm$ 1.6 ^d	25.4 $\pm$ 1.1 ^{cd}	2.46 $\pm$ 0.02 ^d	10.29 $\pm$ 0.15 ^d	46.93 $\pm$ 2.15 ^d	18.85 $\pm$ 0.83 ^d
150	30.4 $\pm$ 2.1 ^c	21.6 $\pm$ 1.1 ^c	2.35 $\pm$ 0.06 ^c	9.70 $\pm$ 0.25 ^c	41.78 $\pm$ 1.39 ^c	17.08 $\pm$ 0.58 ^c
195	25.2 $\pm$ 1.1 ^b	17.0 $\pm$ 1.0 ^b	2.29 $\pm$ 0.02 ^b	9.15 $\pm$ 0.09 ^b	37.59 $\pm$ 1.17 ^b	15.63 $\pm$ 0.46 ^b
225	22.4 $\pm$ 0.5 ^a	14.0 $\pm$ 0.7 ^a	2.25 $\pm$ 0.01 ^a	8.89 $\pm$ 0.07 ^a	35.12 $\pm$ 0.67 ^a	14.76 $\pm$ 0.28 ^a

Data represent mean values $\pm$ standard deviations. D(v,0.1), D(v,0.5), D(v,0.9) represent PSD quintiles, D[4;3] represents the weigh mean diameter based on the PSD. Micrometer readings and PSD measurements were replicated 5 and 30 times, respectively. All values in the same column followed by different letters were significantly different at $P < 0.05$ (Tukey's and Duncan's method for micrometer readings and PSD parameters, respectively). For the micrometer data the inverse of fineness was used as response to satisfy ANOVA assumptions (normality and constant variance of residuals).

Figures

Figure 1. Time course of the refining process of 400 kg of paste in the stirred ball mill:

- (a) fineness $\blacklozenge$ (f) and temperature $\blacksquare$ (T) as a function of refining time (t);
(b) power $\blacklozenge$ (P) and specific energy $\blacksquare$ (E) as a function of refining time (t). P and E values were calculated by using Eq.s (1) and (2), respectively, from measured electric current data.

Figure 2. Apparent viscosity (η) as a function of shear rate ($\dot{\gamma}$) for pastes at different refining times.

Symbols refer to experimental data while the continuous lines where calculated by using the Power Law model with the parameter estimates reported in Table 2.

- | | | |
|------------------------|-------------------|--------------------------|
| $\blacksquare$ 60 min | $\bullet$ 90 min | $\blacktriangle$ 120 min |
| $\blacksquare$ 150 min | $\bullet$ 195 min | $\blacktriangle$ 225 min |

Figure 3. Particle size distribution of pastes at different refining times.

Different lines refer to experimental data

- | | | |
|-----------|-------------|---------------|
| — 60 min | - - 90 min |120 min |
| — 150 min | - - 195 min | 225 min |

Figure 4. Micrographs of pastes refined for 90 (a), 195 (b) and 225 (c) min.

Figure 5. Textural sensory evaluation of pastes at different refining time and pretreatment temperatures.

- (a) oily separation, for all the samples at two storage temperature, 4 $\blacksquare$ and 20 ° C $\blacklozenge$; (b) graininess between fingers; (c) spreadability; (d) fluidiness, (e) adhesiveness to the spoon, (f) meltability, (g) flouriness, (h) graininess in the mouth, respectively, of all the refined pastes (60-90-120-150-195-225 min), averaged for storage temperature.

Data represent means $\pm$ standard deviations of 18 replicated determinations (9 assessors x 2 replications). Values followed by different letters differ significantly at $P<0.05$ level (Duncan's method).

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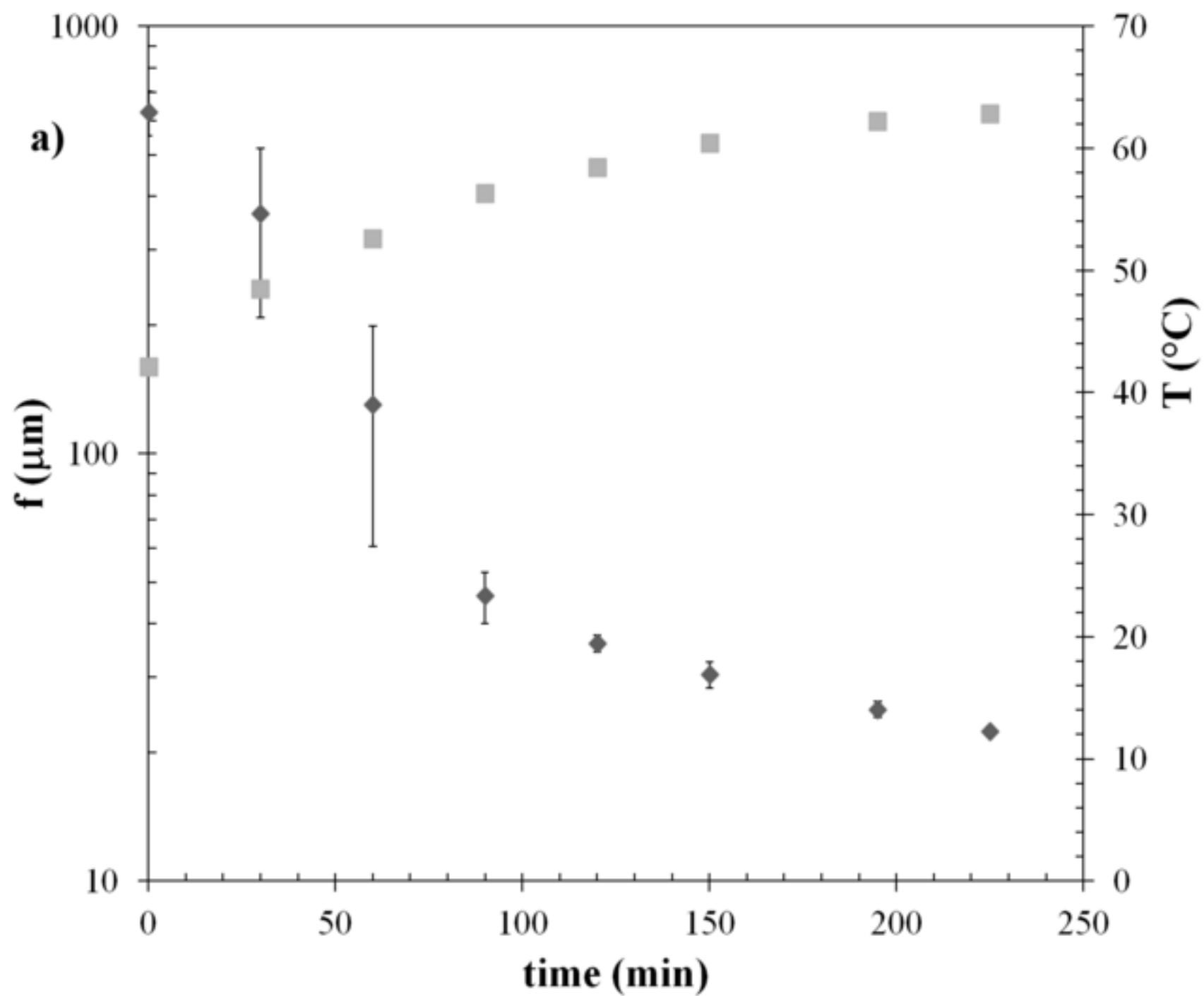


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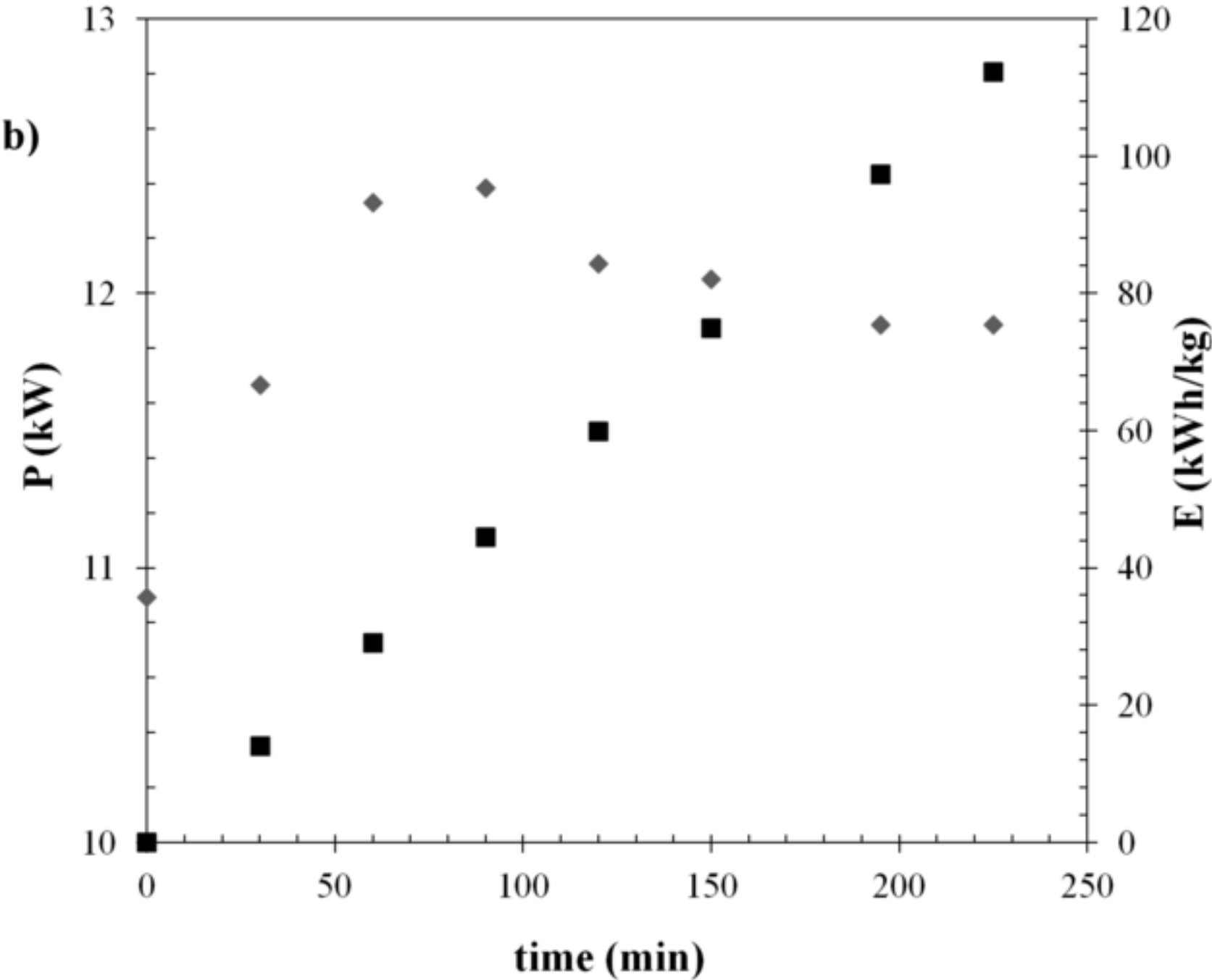


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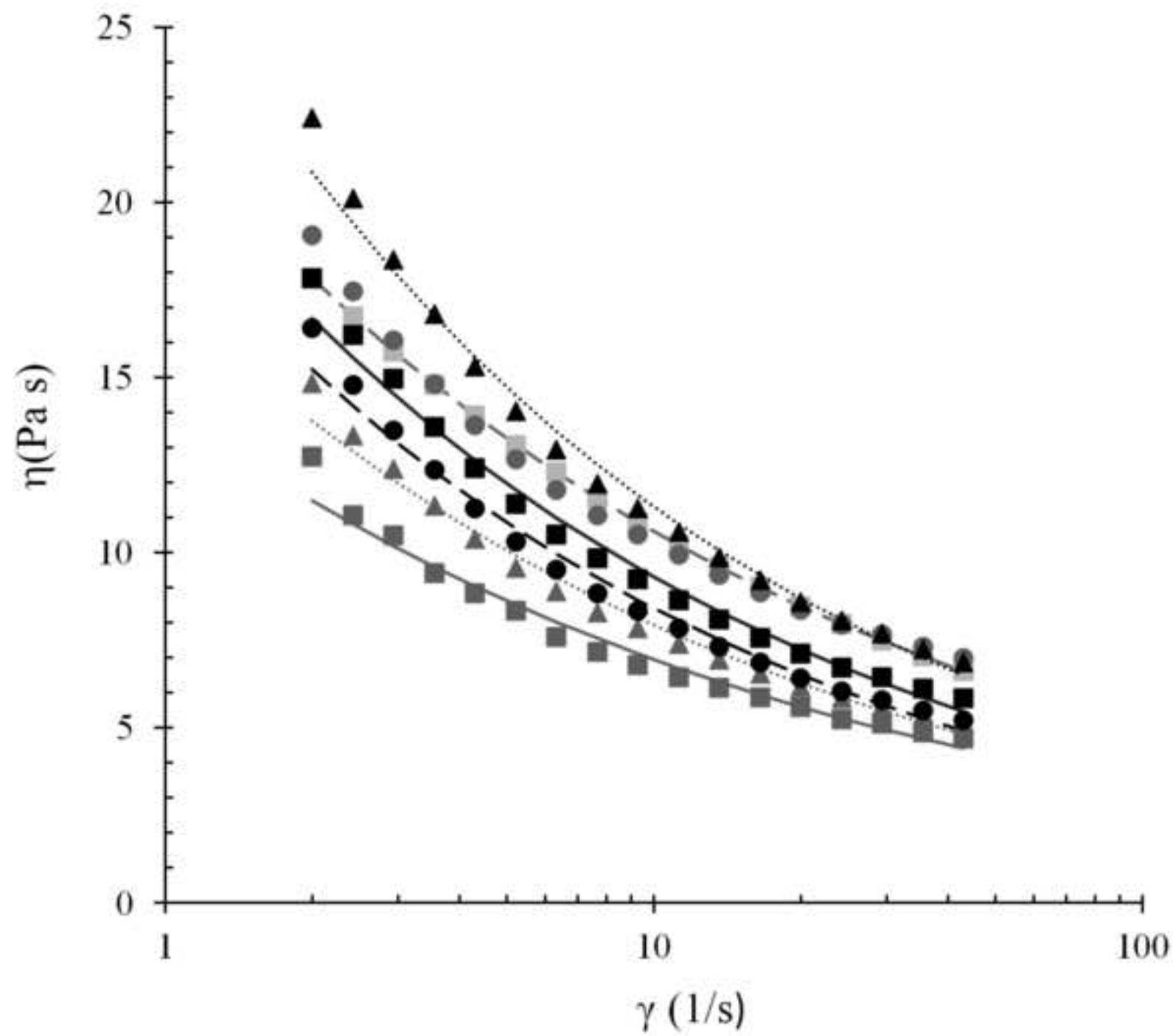


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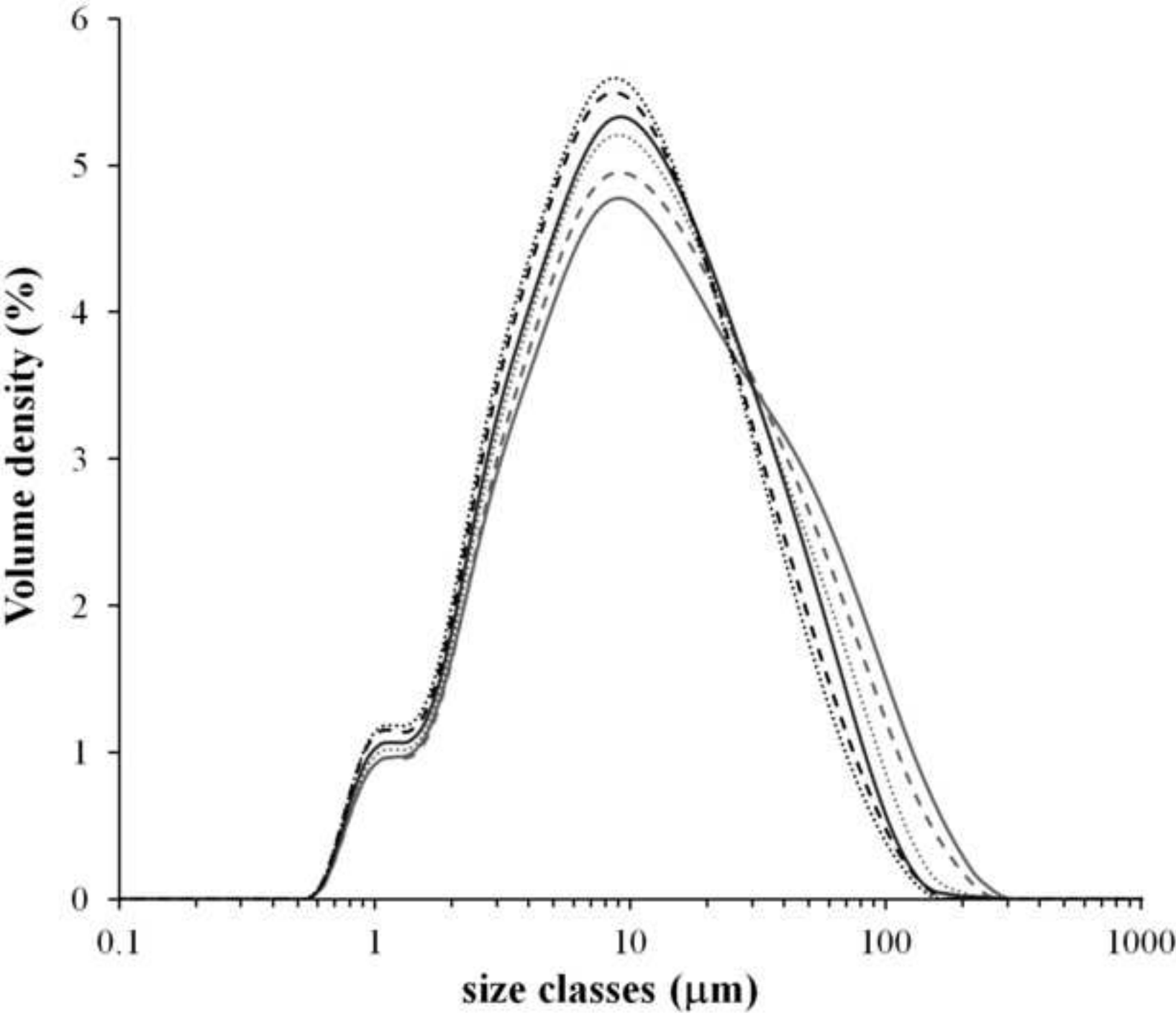


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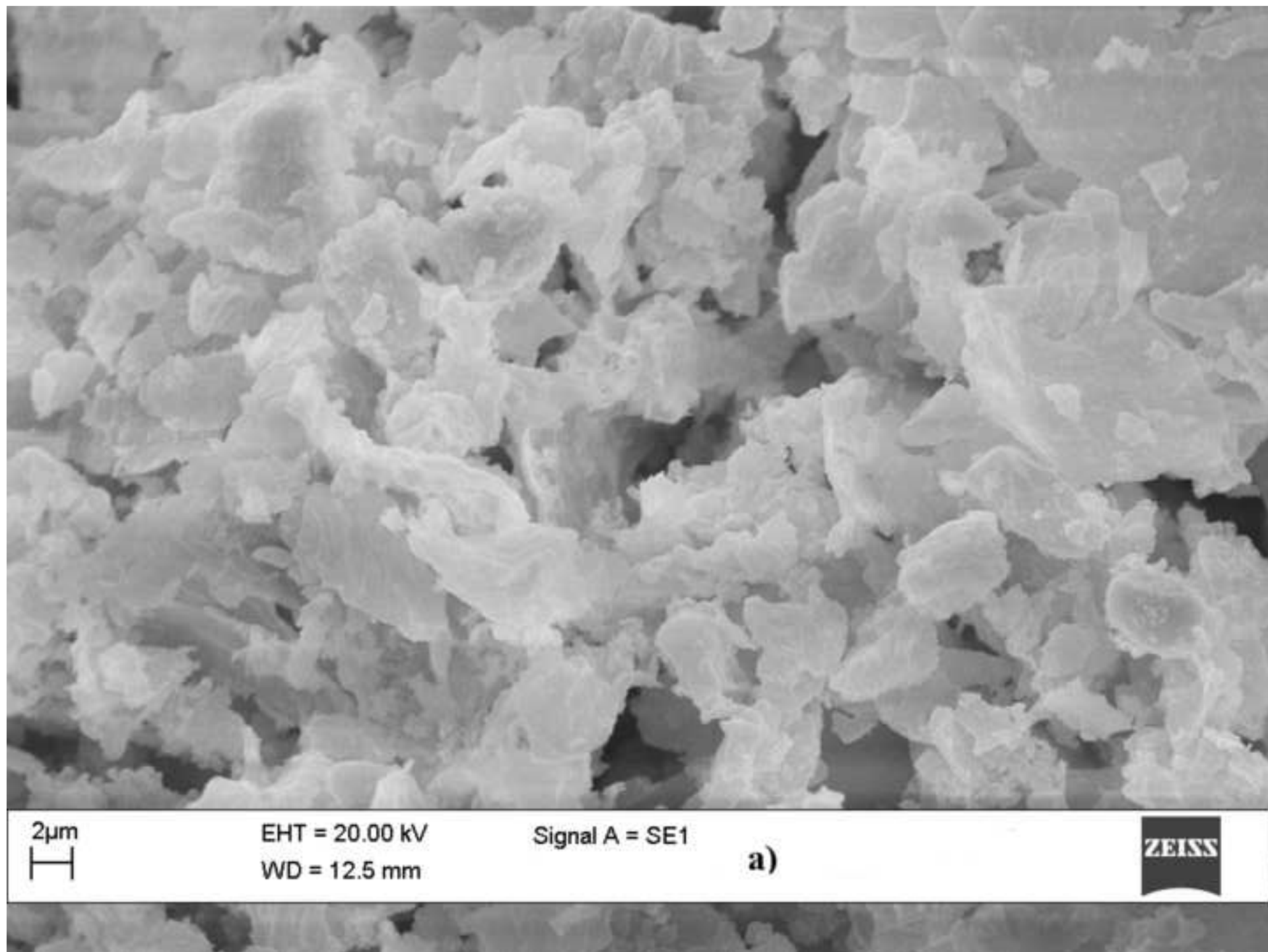


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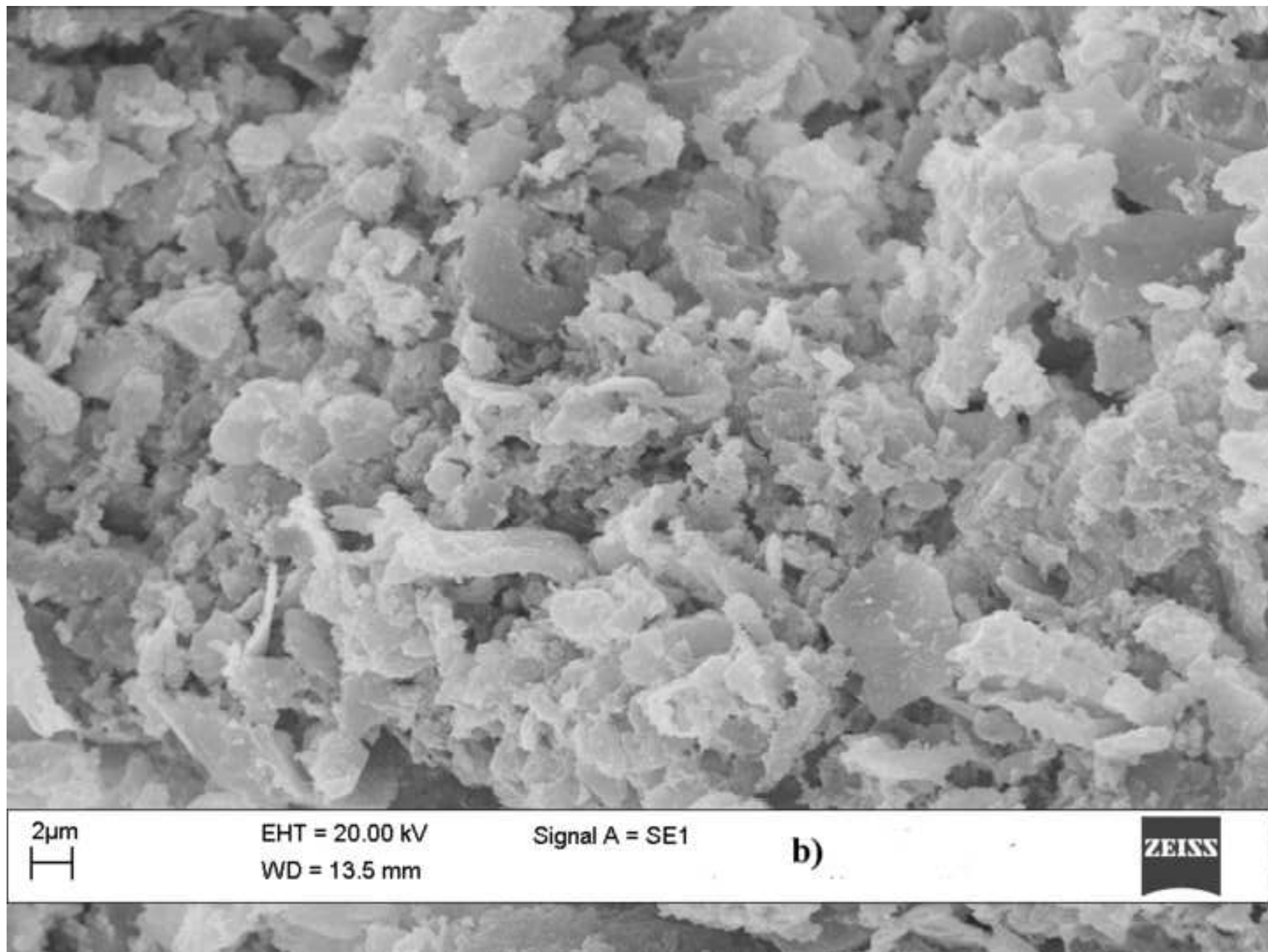


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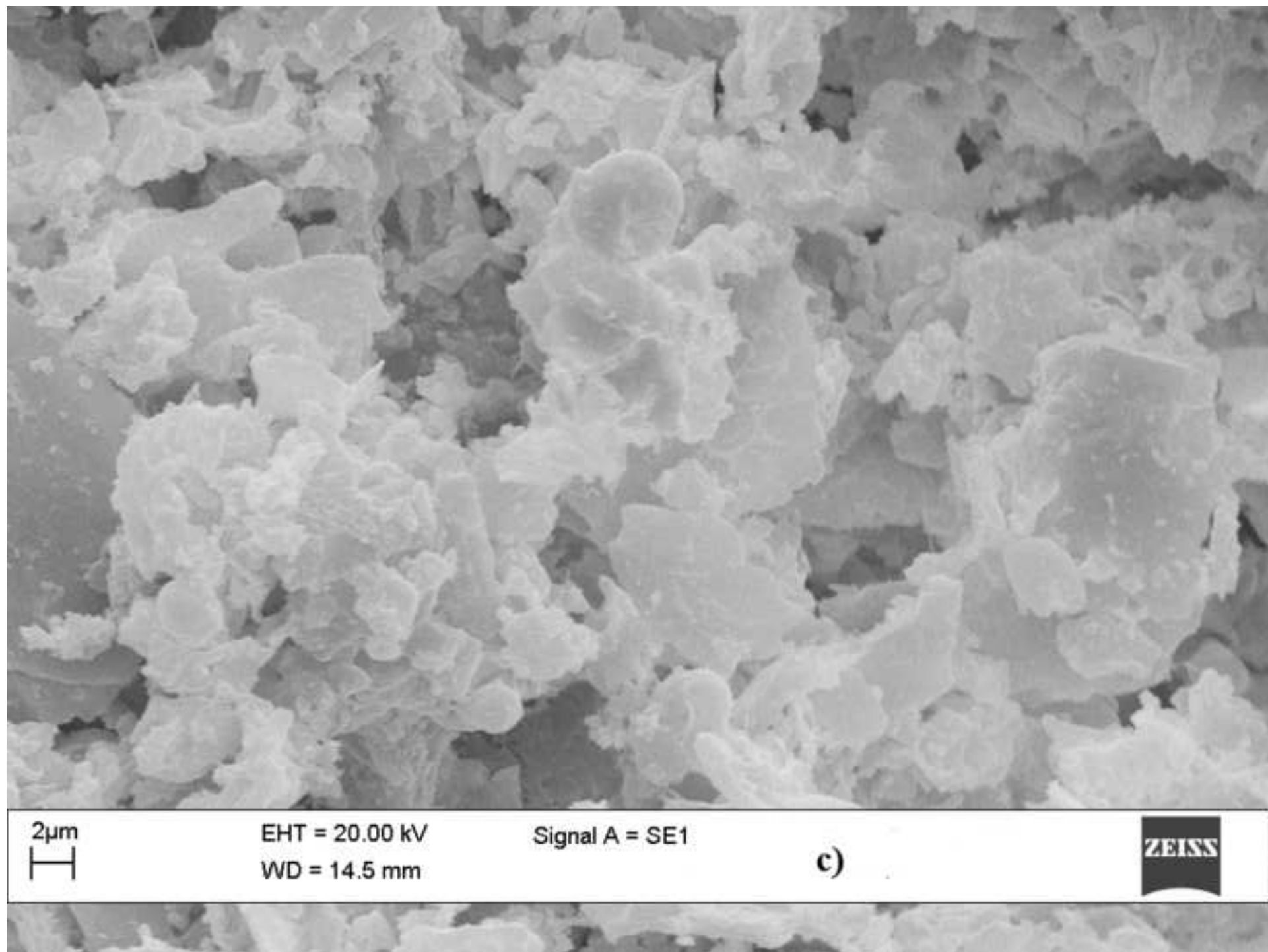


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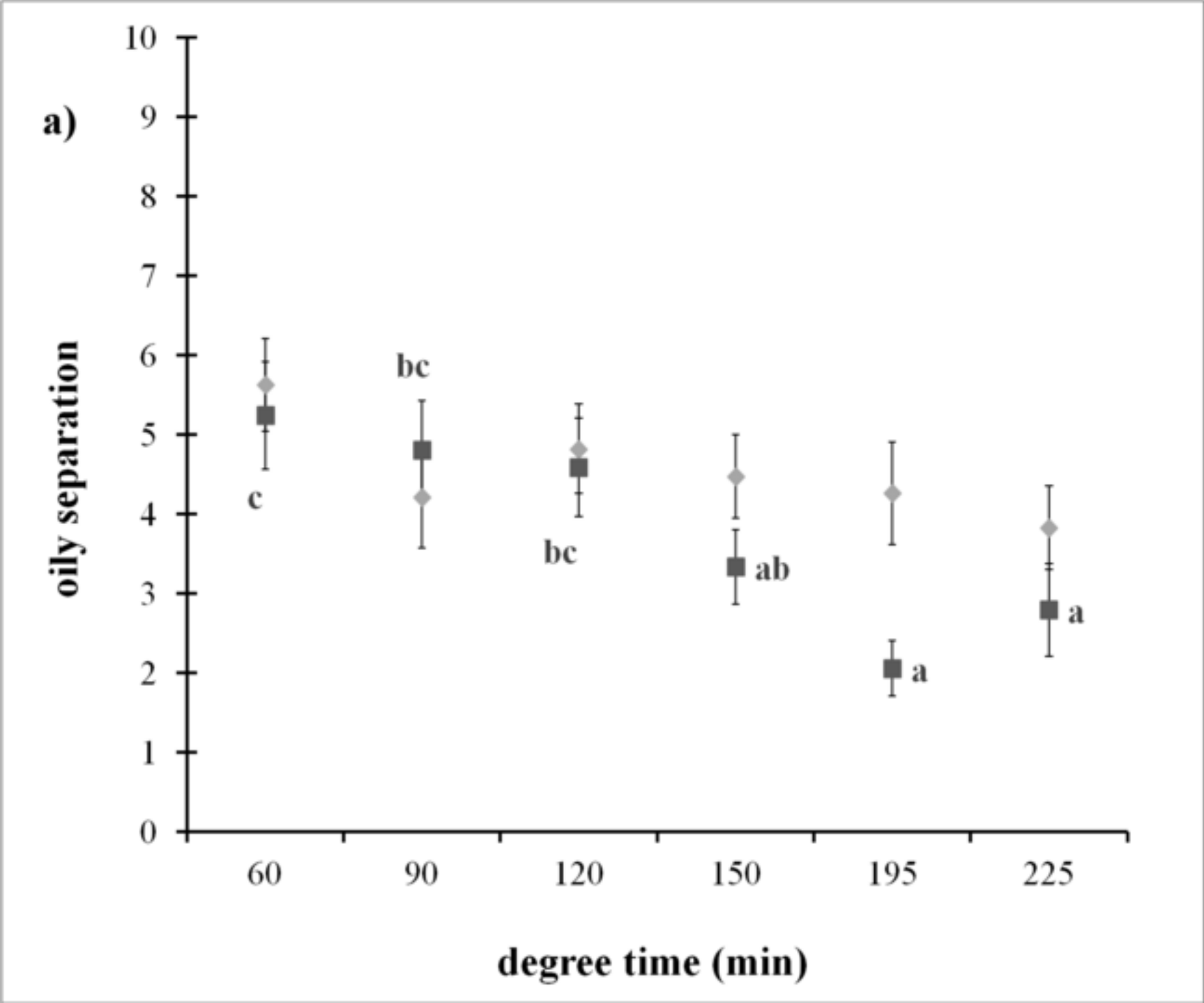


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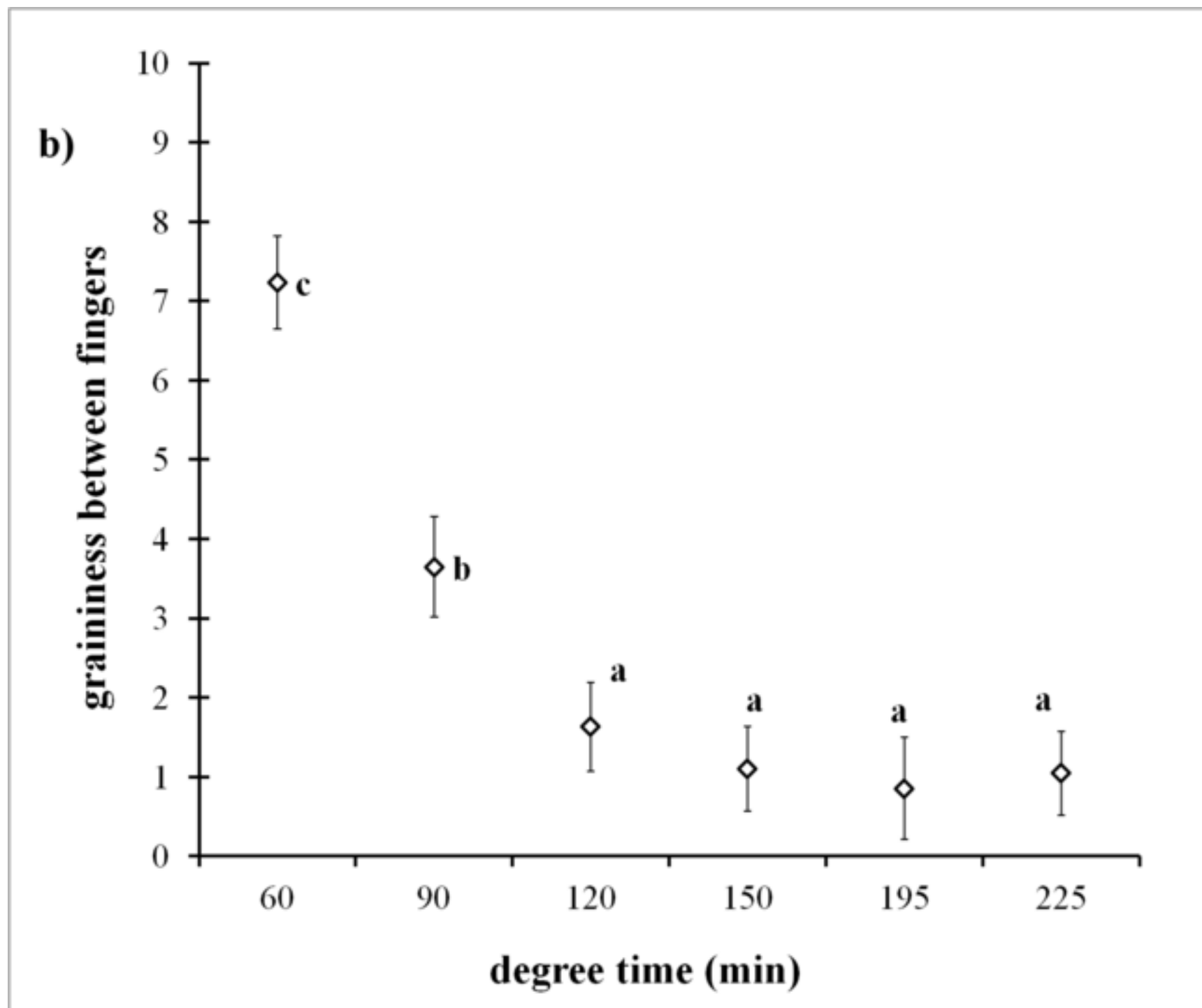


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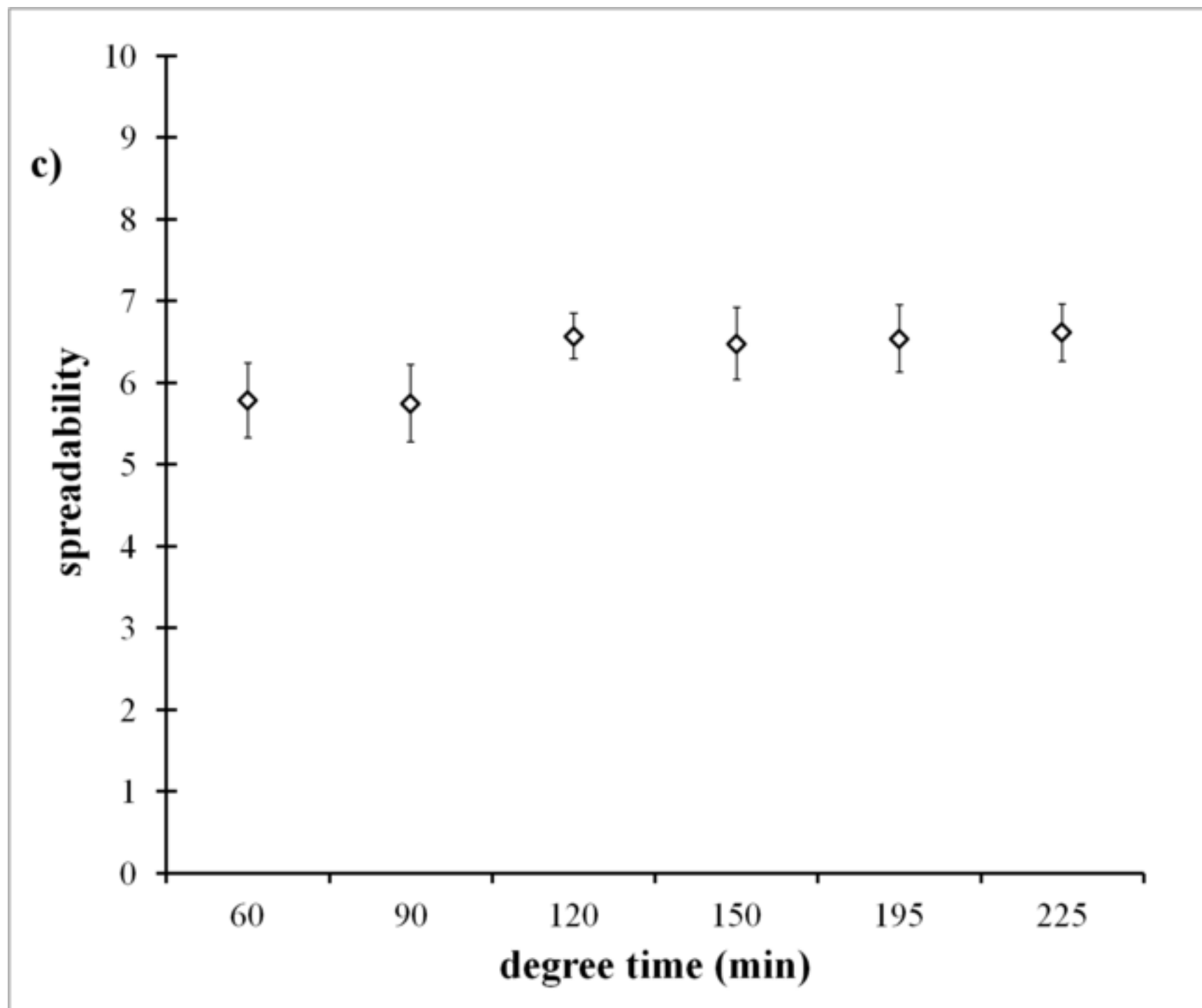


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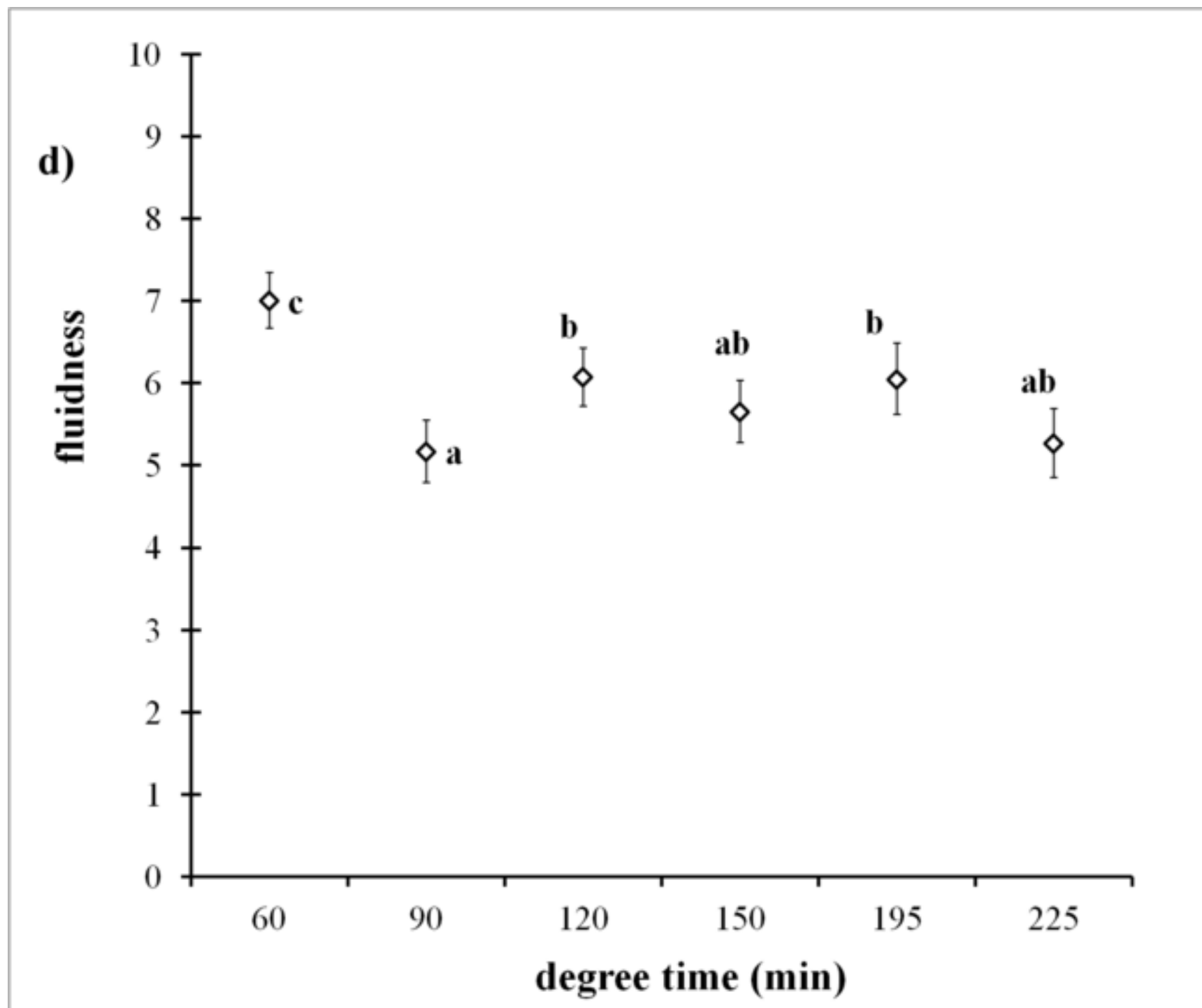


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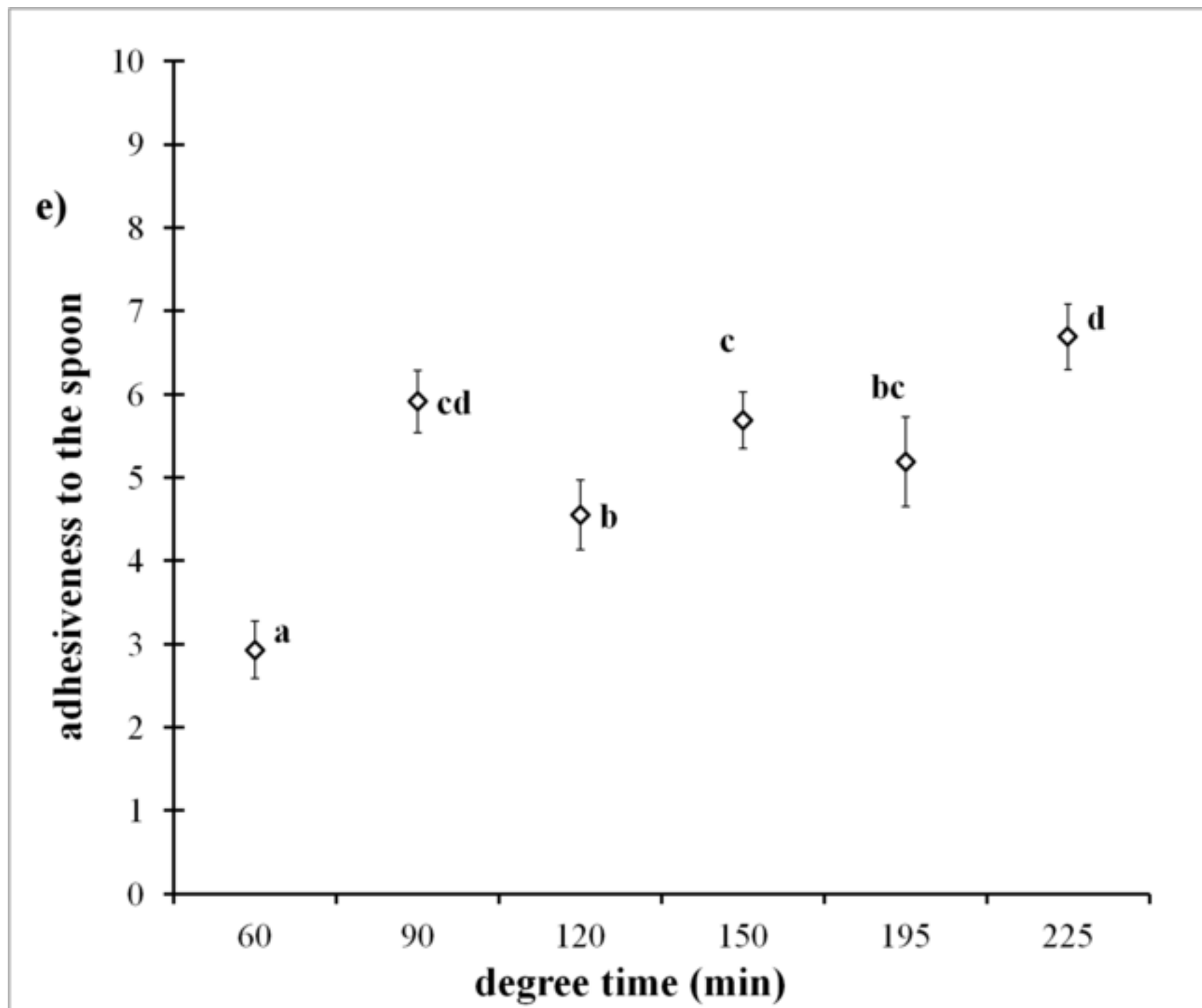


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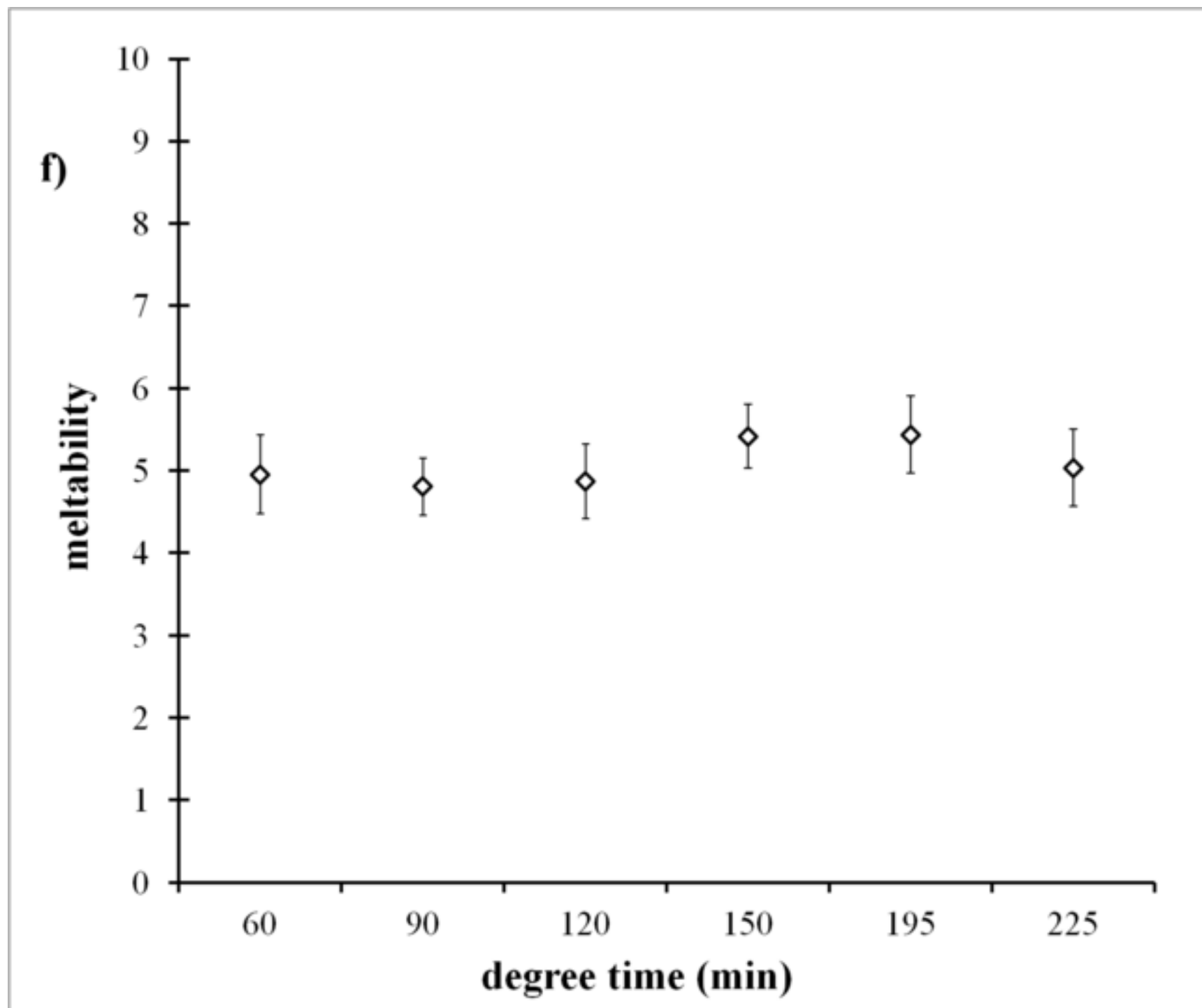


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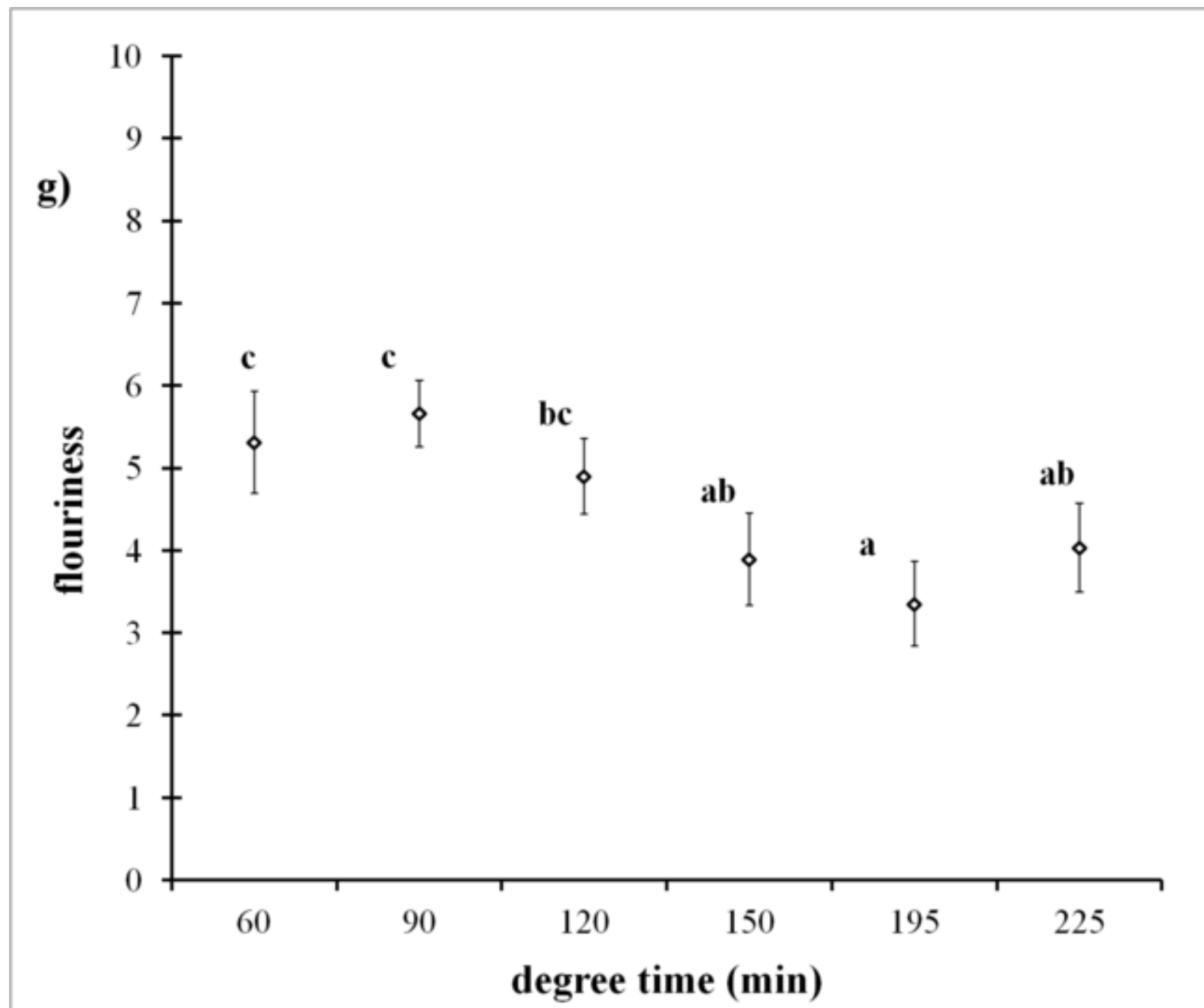


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