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1 **Monitoring of abiotic degradation of photo-crosslinked silicone acrylate coatings: The fate of the photo**
2 **initiator**

3

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11

12 **Abstract**

13 Photocrosslinked silicone acrylates are used in a variety of applications, such as printing inks adhesives or
14 adhesive release liners. Their production requires the use of a photoinitiator. Even if the photoinitiator represents
15 a minor mass in the photocurable formulation (2 to 10%), it is used in excess and residual amounts may therefore
16 remain in the polymerized products and possibly migrate into the environment during the use of the products
17 and/or at their end-of-life stage. Little is known on the possible degradation of silicone acrylate which may
18 increase the potential release. The present study investigated the release of Darocur 1173, the most commonly
19 used photoinitiator, from silicone matrix and the effect of accelerated photoageing on the extent of the
20 phenomenon.

21 Leaching tests in water were conducted on thin coated plastic film (release liners) made of a mixture of
22 polypropylene and polyethylene. Results showed that 44% of Darocur 1173 photoinitiator initially used in
23 silicone formulation was released from silicone matrix in the leaching test. Accelerated photoageing obtained by
24 UV irradiation of the films for up to 200 h was found to favor photoinitiator degradation but also induced a
25 strong and fast oxidation of silicone coated liners as compared to uncoated ones.

26

27 **Key words:** Silicone acrylate, coating, photoinitiator, Darocur 1173, leaching, photoageing, service life

28 Introduction

29 Adhesive release liners have a wide range of applications in everyday-life products such as labels, diaper
30 closures, medical wound dressings, or health and beauty products (Benedek 2004). They facilitate the transfer of
31 the adhesive from the liner. Photocrosslinked acrylate silicone coatings are widely used in this domain for their
32 unique ability to be applied and cured on various substrates and their lower release forces as compared to other
33 types of coatings. The production of self-adhesive labels accounts for 70% of the overall consumption of
34 adhesive release liners in the world. About 20 billion square meters of release liners are produced annually
35 worldwide out of which about 10% use UV photocuring technology. The annual growth of the global release
36 liner market is approximately 4 to 5%; whereas the radiation cured release liner market growth is about 7 to 8%
37 (Stadtmüller and Oestreich 2000).

38 During the UV curing process at industrial scale in this field of application, radical photoinitiators are generally
39 applied in excess in order to favour their reactivity, usually at concentrations ranging from 2 to 10% (by weight
40 of the total photocurable formulation). Within the large group of known photoinitiators structures, α -
41 hydroxyalkylphenones have gained much interest due to their high reactivity, thermal stability and universal
42 applicability (Seidl et al. 2006; Kaczmarek and Vukovic-Kwiatkowsk 2012; Belaidi et al. 2013). Darocur 1173
43 (2-hydroxy-2-methyl-1-phenylpropan-1-one) is the most widely used molecule in this group. It is commonly
44 used with silicon acrylate formulations (Gruber 1992). It has been reported that only about 10% of the
45 photoinitiator is converted during photocuring (Wipo Green 2015). The coated products therefore contain
46 residual amounts of acrylate monomers and photoinitiator (Gruber 1992; Jang et al. 2005; Green 2010) which
47 after curing may migrate (Green 2010) to the surface of the film and be released into environmental media if the
48 polymerized products are contacted with water during their use and / or at their end-of-life stages. This
49 phenomenon limits the use of UV curable coatings for applications in food, medicine and pharmaceutical
50 packagings (Ye et al. 2006).

51 The products containing adhesive release films may be exposed to potentially aggressive environmental factors
52 during their use and at their end-of-life stage. For example, in outdoors applications, adhesive release liners are
53 exposed to UV light, temperature, oxygen, and moisture. These conditions may alter the chemical structure and
54 functional properties of polymers (Colin et al. 2015) and increase the release of the residual photoinitiator,
55 resulting in potential environmental or health impacts. Yet, very little is known on the fate of silicone in the
56 environment (Laubie et al. 2012), and to our knowledge no work has been yet published on silicone acrylates

57 coatings or Darocur 1173. The objective of this study was to generate knowledge and data on these issues.
58 Laboratory-scale experiments were conducted under controlled conditions to assess the fate of model
59 photocrosslinked silicone acrylate coatings deposited on plastic films. The experimental approach was designed
60 to evaluate the effect of some factors considered as representative of the conditions that the real products may be
61 exposed to during the use or the end of life of coated materials, namely the contact with aqueous solutions
62 (leaching) and photodegradation are likely to occur. The aim of the leaching tests was to investigate whether
63 untransformed residual photoinitiator remaining within the silicone coating could migrate into solution when the
64 samples were contacted with water. This information is key to the evaluation of potential environmental
65 pollution. Accelerated photoageing tests were performed to assess whether the residual photoinitiator could be
66 degraded or not by UV irradiation.

67 **Materials and methods**

68 **Tested material**

69 The experiments were done on model materials specifically prepared for the study, consisting in plastic films
70 coated with photocrosslinked silicone acrylate. UV curable silicone acrylate was prepared by mixing 98% (w/w)
71 silicone acrylate oil provided by Bluestar Silicones company (700-800 cPs at 25°C, $M_n=8000$, $M_w = 20000$
72 g/mol, $D = 2.4$) and 2% (w/w) photo-initiator 2-Hydroxy-2-methyl-1-phenylpropane-1-one (Darocur 1173, 97%,
73 MW 164.2 g/mol, hydrosolubility 13.3 g/L at 20°C, CAS N° 7473-98-5) purchased from BASF. The chemical
74 structure of silicone acrylate oil is $MD_{85}D^*M_{7.5}$ (with D^* motif= $SiMe(CH_2)_3OCH_2CHOHCH_2OCOCHCH_2$)
75 (**Fig.1**). The mixture was stirred for 30 min at room temperature until a homogeneous liquid phase was obtained.
76 The formulation was coated as a 1 μm -thick layer on 20 μm -thick extruded films composed of 57% PP, 33% PE
77 and 9% TiO_2 (called GLD2) corresponding to a covering weight of 3.62 g/m^2 . To obtain a reasonably low
78 coatweight, films were coated on a pilot coater equipped with 5 roll coating head set up (Rotomec Brand), placed
79 on a conveyor moving at 100 m/min (corresponding to a residence time of about 0.2 seconds under UV
80 irradiation) and then irradiated with UV light at 280 nm using a mercury lamp (UV HONLE Princoncept) set at
81 100 W/cm^2 . The residual O_2 concentration under the lamp was less than 20 ppm to avoid any inhibitive action of
82 O_2 on the reactive species.
83 Coated films were recovered immediately at the exit of the machine and the amount of coating deposited (g/m^2)
84 was measured by X-ray fluorescence. Based on the dosage used for the formulation, 1.44 g of coated film

85 contained 5 mg of Darocur 1173 (PI). It should be noted that coated films were NOT washed before the study
1 because at the industrial scale, coated films are not washed after photocuring and they are directly put into coils
2
3
4 87 and intended for various applications. A control sample was also prepared with silicone acrylate coating of 10
5
6 88 μm thickness on glass slide which represents a photo-chemically inert support.
7
8
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11 90 **Darocur structure and analysis**

14 91 The chemical structure of Darocur 1173 (PI) is given in **Figure 2**.

17 92 A drop of Darocur 1173 was analyzed by FTIR-ATR. Its spectrum, shown in **Figure 3**, exhibited intensive
18
19 93 hydroxyl absorption $\nu\text{O-H}$ (with maximum at 3455 cm^{-1}), bands at $2800\text{-}3100\text{ cm}^{-1}$ range, at 1598, 1446, 1366,
20
21 94 $957, 719\text{ cm}^{-1}$ assigned to aliphatic and aromatic C-H (stretching and bending), 1670 cm^{-1} (carbonyl C=O
22
23 95 vibration) and 1170 cm^{-1} (C-O-C vibrations).

25 96 Thus, only two bands (1670 and 1598 cm^{-1}) could be detected on the FTIR spectra of coated films since they are
26
27 97 not masked by silicone bands (**Figure 6**).

30 98 **Evaluation of Darocur leaching**

33 99 Batch leaching tests were performed by contacting thin coated film samples (GLD2) with leaching solutions of
34
35 100 different natures. An aliquote sample of 1.44 g of coated film (calculated to contain 5 mg of PI) was cut into
36
37 101 small pieces of 1 cm^2 and introduced into 50 mL high-density polyethylene flasks (HDPE) containing 20 mL of
38
39 102 leaching solutions. The leaching solutions used were (i) de-ionized water (pH= 6; $18\text{ M}\Omega/\text{cm}$, Veolia water STI),
40
41 103 (2) acidic aqueous solution (pH=2 with HCl; Chimie-Plus Laboratories, 37%) and (iii) alcaline solution (pH=12
42
43 104 with NaOH; Chimie-Plus Laboratories, 98%). The flasks were placed in an orbital shaker operated in the dark at
44
45 105 9 rpm and room temperature (25°C) over 15 days. Experiments were performed in triplicates. Blanks were
46
47 106 prepared in triplicates with uncoated GLD2 films and treated in the same manner as the assays. The solutions
48
49 107 were sampled at different times and analyzed for released PI by UV spectrophotometry. Leached coated films
50
51 108 were also analyzed by UV spectrophotometry in order to detect any residual photoinitiator.

54 109 **Photodegradation**

57 110 Assays were done using an accelerated photoageing chamber SEPAP 12.24 with the following settings: λ : 290
58
59 111 nm ; temperature of exposed surface: $60 \pm 1^\circ\text{C}$ controlled by air circulation according to EN16472 standard.
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63
64
65

112 Coated silicone GLD2 films (GLD2-PI) and uncoated GLD2 films (blanks) were exposed to UV irradiation at
113 the same time in two separated SEPAP 12.24 chambers for 200 h corresponding to 1 year exposure under South
114 of France outdoor conditions (45° South exposition). The degradation of tested films was assessed by FTIR
115 spectrophotometry and UV/visible according to ISO 10640 standard. Samples were analyzed at 50, 100, and 200
116 h.

117 **Analytical methods**

118 **EDXRF analysis of silicone coating**

119 The Rigaku NEX QC is a Benchtop Energy Dispersive X-ray Fluorescence (EDXRF) spectrometer which was
120 used for elemental analysis of silicon in film coatings on solid substrates.

121 In EDXRF, low energy “soft” X-rays (1-50 keV) are emitted from an X-ray tube. These source X-rays enter the
122 sample and cause the atoms in the sample to fluoresce their own characteristic low energy “soft” X-rays. These
123 fluorescent X-rays are captured by the detector and counted by a multi-channel analyzer. The NEX QC software
124 then calculates the concentration of each element present in the sample.

125 The X-ray analysis gives a signal proportional to the Si-atoms concentration in the coating. Calibration curves in
126 X-ray units are used to calculate the actual silicone coat.

127 **UV spectrophotometry**

128 Darocur 1173 (PI) was analyzed using a Jasco V 630 Spectrophotometer at a wavelength of 247 nm. Quartz cells
129 of 1 cm path length were used, and the respective leaching solutions were used as a reference. A calibration
130 range of PI was prepared in each tested solution from 1.56 mg/L to 20 mg/L. The calibration curve was linear
131 with optical density ranging from 0 to 0.89. Samples were diluted before analysis, if necessary, to be within this
132 range of absorbance.

133 The film samples were analysed using a PERKIN-ELMER 650S UV/visible spectrophotometer. Fragments of
134 1.5 cm² of films were used and spectra were recorded at a resolution of 2 nm.

135 **FTIR Spectrophotometry**

136 Small fragments of coated or uncoated films whose section could be as small as 1000 μm² were used for FTIR
137 spectrophotometry. A Thunderdome Nicolet MAGNA IR 600 analyzer was used. The IR beam entering the

138 spectrophotometer was focused on a predefined 1000 μm^2 zone of the small fragments and FTIR spectrum was
139 recorded in the ATR mode with a resolution of 4 cm^{-1} . Small fragments whose surface was 1.5 cm^2 were also
140 analyzed by FTIR spectrophotometry using a NICOLET IS10 analyzer where spectra were recorded in the
141 transmission mode with a resolution of 4 cm^{-1} .

142 **Results and discussion**

143 **Leaching tests**

144 Leaching tests results were expressed in mg of photoinitiator released per gram of silicone coating introduced
145 (mg/g). Results are shown in **Figure 4**. It can be seen that Darocur was leached at significant concentrations
146 from coated GLD2 films under all the conditions tested. Blanks with uncoated GLD2 films did not release any
147 compound which may have interfered with the analysis of Darocur (**data not shown**). Leaching of Darocur
148 from coated films was affected by the pH of the leaching solution. Around 27% of Darocur 1173 used in the
149 formulation of the films were leached in 15 days in de-ionized water (pH=6) and the alkaline solution (pH=12),
150 whereas around 44% were leached under acidic conditions (pH=2). Similar results were reported previously by
151 the authors on the leaching behavior of coated LDPE films (Ouali et al. 2017) and by Laubie et al.2012 using
152 different silicone elastomers and regarding catalyst concentration in leaching solution.

153 Green, 2010, reported that Darocur 1173 was readily extracted by various solvents using Soxhlet extraction of
154 the cured coatings. The small size of the molecule (164.2 g/mol) was probably favorable to its migration within
155 the coating, allowing its leaching into the solution.

156 The leaching tests therefore confirmed that the dosage of Darocur used in the formulation of the silicone
157 acrylates was largely in excess. The photo-initiator did not react entirely, and residual amounts were therefore
158 available to be released into the leaching solutions. Although an excess of photo-initiator is needed to guarantee
159 a good reticulation of silicon acrylates. The dosage of the photoinitiator used in the formulation of silicone
160 acrylates should be optimized on an industrial scale in order to check if the use of an amount less than 2% would
161 keep the desired physico-chemical properties for the final material (coating).

162 After completion of the leaching tests, the films were sampled and analysed by UV/visible spectrophotometry.
163 Darocur absorbance was measured at 245 nm and the residual concentration of Darocur was evaluated from the
164 ratio between the absorbance at 245 nm and the films' thickness. The same protocol was applied to samples

165 taken before the leaching tests. Results showed that only a small fraction of Darocur was leached over the 15
166 days of the assays (**Fig.5**). The residual amounts of Darocur after leaching test were about 76% of initial load at
167 pH=2, 91% at pH=6 and 95% at pH=12. These observations indicated that most of Darocur used in the
168 formulation was not consumed in the photo-reticulation process and retained within the coatings. Further studies
169 would be needed to determine whether the retention was stable over time, or whether Darocur leaching was
170 kinetically limited by its diffusion through the coating and / or at the interface with the leaching solution. **Figure**
171 **5** also showed that lowest residual concentration of Darocur was observed after acid leaching, which confirmed
172 the stronger leaching observed in the acidic solution (**Fig. 4**).

173 However, this analysis was quantitative only on small representative pieces of the sample (coated GLD2)
174 leached; therefore it was not possible to estimate the percentage of residual photoinitiator in the total mass of the
175 tested films. Thus, only a qualitative trend of the residual photoinitiator in the leached films can be compared to
176 the photoinitiator released in solution.

177 **Accelerated photoageing**

178 FTIR/transmission analysis of the evolution of coating and GLD2

179 An initial characterization of uncoated and coated films by FTIR-Transmission (**Fig.6**) showed characteristic
180 bands of polyolefin (PE/PP). Silicone acrylate coating showed the same profile with a strong absorption of
181 specific bands at 1261, 1094, 1022, 802 cm^{-1} and an ester band at 1738 cm^{-1} characteristic of C=O bounds of the
182 acrylic ester group. The specific bands of absorption of Darocur 1173 (hydroxyl group) were slightly visible
183 only at 3450 cm^{-1} .

184 The main modifications observed after 50 h, 100 h and 200 h of photo-ageing of uncoated and coated GLD2
185 films were represented respectively on **Figure 7(a)** and **Figure 8(a)**. FTIR spectra analysis of uncoated films
186 showed hydroxyl group formation near 3400 to 3200 cm^{-1} , acidic and anhydride group formation respectively
187 near 1715 cm^{-1} and 1780 cm^{-1} (**Fig.7(a)**). These results revealed the photochemical oxidation of the backing
188 material (PE/PP). FTIR spectra of coated GLD2 films (**Fig.8(a)**) showed the oxidation of silicone acrylate
189 coating and probably the residual photoinitiator which resulted in an increase of absorbance around 3200 cm^{-1}
190 linked to the hydroxylated photoproducts and an increase of carbonylated photoproducts at 1738 cm^{-1} .

191 Lacoste et al. 1996 showed that the photooxidation of phenylated silicone during 180 h of SEPAP exposure
192 induced chain scissions and oxidation of phenyl ring which created new IR absorption bands consistent with the

193 presence of phenolic groups, carboxylic acids and esters that were probably formed from the oxidation of
194 phenolic groups. Our results showed that silicone acrylate coatings were vulnerable to further degradation since
195 carbonyl groups (probably from Darocur) are known to be photo-sensitive (Feldman 2002). Other studies on the
196 degradation of acrylic-silicone matrix reported that under photo-irradiation at wavelengths above 295 nm, the
197 degradation was initially due to the presence of chromophore impurities capable to absorb UV light and
198 propagate oxidation (Colin et al. 2015) whereas acrylic resins did not absorb at these wavelengths. The
199 chromophore groups include carbonyl and unsaturated bonds C=C (Youcif and Haddad 2013). In the same
200 context, several studies have also shown that UV irradiation coupled with di-oxygen application induced
201 oxidative reactions yielding to the formation of hydro-peroxide functions (Ranby and Rabek 1975; Gardette
202 2000).

203 Indeed, the presence of photoinitiator with carbonyl groups has a strong effect on the photo-degradation
204 mechanism. The spectrum of sunlight penetrating the earth's surface ranges from 290 to 3000 nm with UV light
205 in the range of 295-380 nm. While saturated compounds possessing bonds such as C-C, C-H, and O-H will
206 absorb light at wavelengths below 200 nm, both carbonyl groups such as those in Darocur and conjugated double
207 bonds have absorption maxima between 200 and 300 nm (Feldman 2002).

208 The surface of uncoated films was analyzed in a domain specific of the possible chemical evolution. Results
209 obtained before and after UV irradiation (50 h, 100 h and 200 h) are shown in **Figure 7(b)**. They highlight a
210 strong PE/PP backing oxidation.

211 Same analyses were done on the surface of coated GLD2-PI films and coated glass slides. The obtained IR
212 spectra were normalized to a constant analyzed thickness in order to make them comparable. The collected
213 spectra shown in **Figure 8(b)** confirmed clearly the oxidation of coated films, which was observed after 50 h of
214 SEPAP exposure and increased over time. Before irradiation ($t = 0$), spectra from GLD2-PI films exhibited a
215 peak at 1738 cm^{-1} which was not visible in the spectra collected from uncoated GLD2 films as expected because
216 there is no silicone on uncoated films (**Fig.7(b)**). This peak corresponded to acrylate groups of the silicone
217 coating. During irradiation, this band appeared on uncoated GLD2, explained by the oxidation of the support and
218 the formation of ester groups, this band also increased on the coted GLD2 film which could be explained by the
219 band of acrylates to which is added that of the formed ester groups from the oxidation of the support GLD2.

220 A large peak was also observed at 1715 cm^{-1} after photo-ageing of both coated and uncoated films,
221 corresponding to the formation of the main product of PE/PP photooxidation. This peak was present as a
222 shoulder in the spectra from coated films before photoageing (**Fig.8(b)**). This observation was attributed to the

223 oxidation of GLD2 backing during the photocrosslinking process conducted on a Rotomec pilot coater, probably
224 under the effect of silicone coating and photoinitiator system.

225 FTIR/ATR analysis of the evolution of coating

226 The analysis of the surface of coated films by FTIR-ATR (**Fig.9**) did not reveal any band at 1715 cm^{-1} after
227 photoageing, indicating that this signal matched well with GLD2 backing's oxidation. Finally, the spectra
228 obtained at $t=0$ from silicone coating on glass slides (used as a reference) (**Fig.10**) revealed no peak at 1715 cm^{-1} ,
229 thereby confirming that this band was not related to silicone coating. At $t = 0$, acrylate band (1738 cm^{-1}) was
230 more intense, with a slight shoulder at 1715 cm^{-1} for coated GLD2 films whereas the absorption of acrylates was
231 wider and without shoulder for coated glass slides. All of these results allowed to conclude that the PP/PE film
232 was slightly oxidized during the coating / photocrosslinking process, and the oxidation was further increased
233 during photo-ageing.

234 FTIR-ATR spectra of coated films (GLD2-PI) were rather focused on silicone acrylate coating oxidation which
235 was more easily observed than with transmission mode (**Fig.9**) and mainly characterized by an increasing of the
236 ester band absorption of carbonylated photoproducts at 1738 cm^{-1} .

237 In order to compare oxidation rates of coated and uncoated films, the absorbance measured at 1715 cm^{-1}
238 (corresponding to the formation of the main critical photoproduct) was plotted vs. exposure time to irradiation in
239 **Figure 11**. It can be seen that coated films (GLD2-PI) exhibited a higher degree of oxidation as compared to
240 uncoated films. This oxidation could be attributed to the presence of TiO_2 in the coated and uncoated GLD2
241 films. A higher degree of oxidation of coated films could be linked to the residual photoinitiator. However, other
242 tests were carried out on GLD2 films without TiO_2 and the results (data not shown) showed the same level of
243 oxidation for coated and uncoated films and the difference in behavior between coated and uncoated films is
244 mainly related to the presence of residual photoinitiator.

245 In our study, $\text{Abs}_{1715\text{ cm}^{-1}}$ of uncoated films was increased by 13% after 200 h of SEPAP exposure (**Fig.11**),
246 revealing a significant level of oxidation.

247 Photo-ageing therefore clearly showed that silicone acrylate coating could promote the photooxidation of coated
248 films as compared to uncoated ones, probably because of the presence of residual photoinitiator within the
249 silicone matrix.

250 **Fate of Darocur 1173**

1
2
3 251 During coating under UV radiation, the photoinitiator generates free reactive radicals that interact with the
4
5 252 functional acrylic groups of silicone thus initiating the crosslinking of the formulation following a chain reaction
6
7 253 initiated by these free radicals. Also, the photolysis of Darocur 1173 generates two free radicals (benzoyl radical
8
9 254 and alpha hydroxy alkyl) that react with the dual connection of acrylates functions, recombine to regenerate
10
11 255 Darocur 1173 or undergo a rearrangement to produce photoproducts mainly benzaldehyde (Green 2010).

12
13 256 The degradation of residual Darocur 1173 was monitored during photoageing process.

14
15 257 FTIR-Transmission analysis of coated films allowed to identify only the bands at 1598 cm^{-1} and 1631 cm^{-1}
16
17 258 corresponding to the aromatic ring of Darocur and which are absent on uncoated GLD2 films (**Fig.12**).
18
19 259 Phenomena of smaller magnitudes were also observed like the decrease of absorbance of band absorption of
20
21 260 Darocur aromatic ring at 1600 cm^{-1} , 1598 cm^{-1} and Darocur hydroxyl group at 3446 cm^{-1} which revealed the
22
23 261 degradation of residual Darocur 1173 in the silicone coating (**Fig.13**).

24
25 262 Coated films were analyzed by UV spectrophotometry in transmission mode before photo-ageing and after 100 h
26
27 263 and 200 h of SEPAP exposure. The large absorption of TiO_2 , between 200 and 400 nm unfortunately masked
28
29 264 any possible band which may have revealed the evolution of Darocur structure since Darocur absorbance was in
30
31 265 the same range (**Fig.14(a)**). Uncoated films showed no band of absorption at 247 nm, which confirmed the
32
33 266 absence of any molecule capable of interfering with the analysis of Darocur (**Fig.14(b)**).

34
35
36 267 It was therefore concluded that the whole amounts of residual Darocur 1173 remaining in the silicone acrylate
37
38 268 coatings after photocuring were completely degraded under the photo-ageing conditions implemented.

42 269 **Conclusion**

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45
46 270 This study investigated the effects of leaching and photo-degradation on the fate of silicone acrylates coatings
47
48 271 and the potential release of residual photo-initiator Darocur 1173 remaining within the coating after the photo-
49
50 272 crosslinking process.

51
52 273 Leaching experiments on coated plastic films showed that the dosage of 2% Darocur 1173 used in the
53
54 274 formulation of silicone acrylates provided an excess of photo-initiator which did not react completely during
55
56 275 photocrosslinking. In practice, this observation means that if the coated films are put into contact with water, the
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58 276 excess photo-initiator may migrate from the silicone matrix into the water. Leaching experiments showed that
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277 Darocur was partially leached, but the major fraction remained within the silicone coating under the
1 experimental conditions tested. Leaching was facilitated under acidic conditions.
2

3
4 279 When exposed to accelerated photoageing, the coated films revealed a strong oxidation as compared to uncoated
5
6 280 films. Results showed that the residual Darocur was also degraded during photo-ageing, which may reduce the
7
8 281 risks of possible environmental impacts associated to the release of Darocur.
9

10
11 282 Significant differences were observed when comparing silicone coated and uncoated films. Silicone coated films
12
13 283 were found to be more sensitive to abiotic degradation than uncoated films. The differences observed were
14
15 284 probably related mainly to the presence of residual amounts of photo-initiator and TiO₂ within the coating, which
16
17 285 could accelerate the oxidation process of the silicone coating.
18

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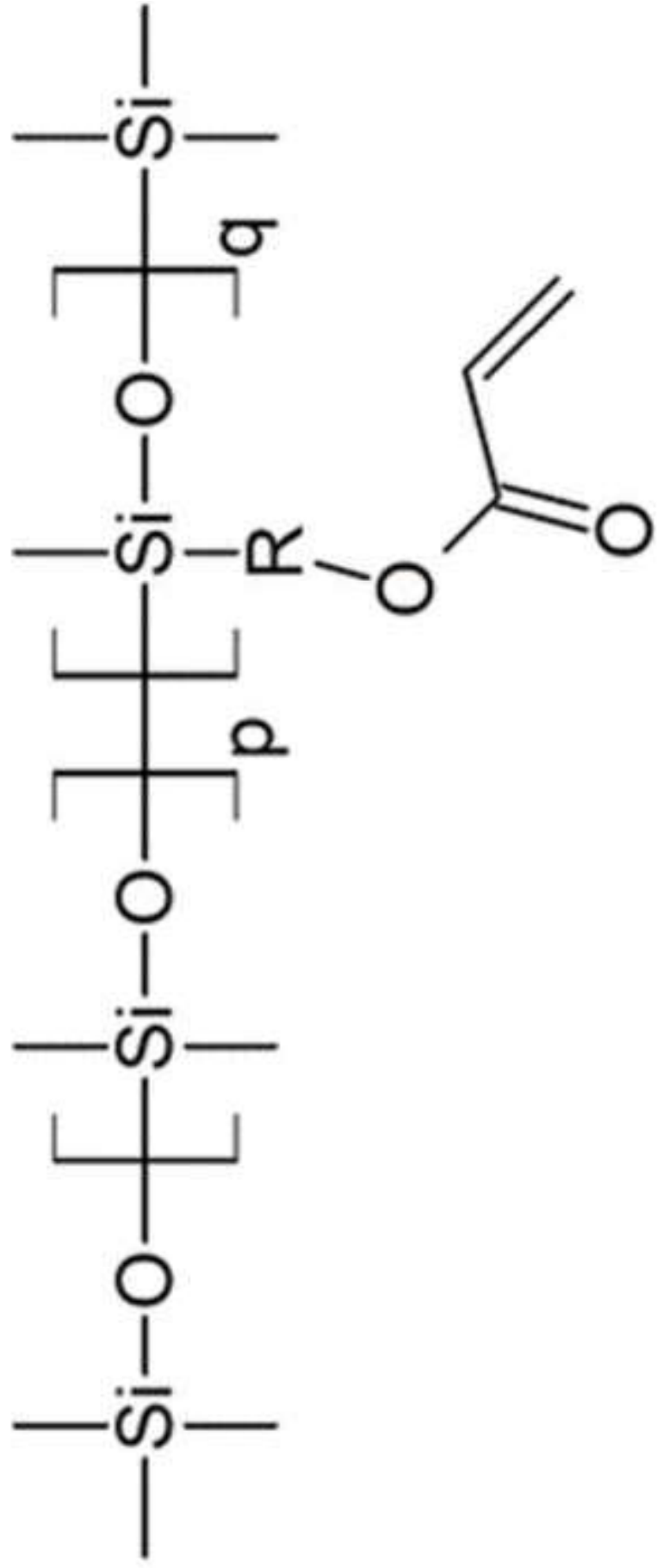
20 21 287 **Acknowledgements**

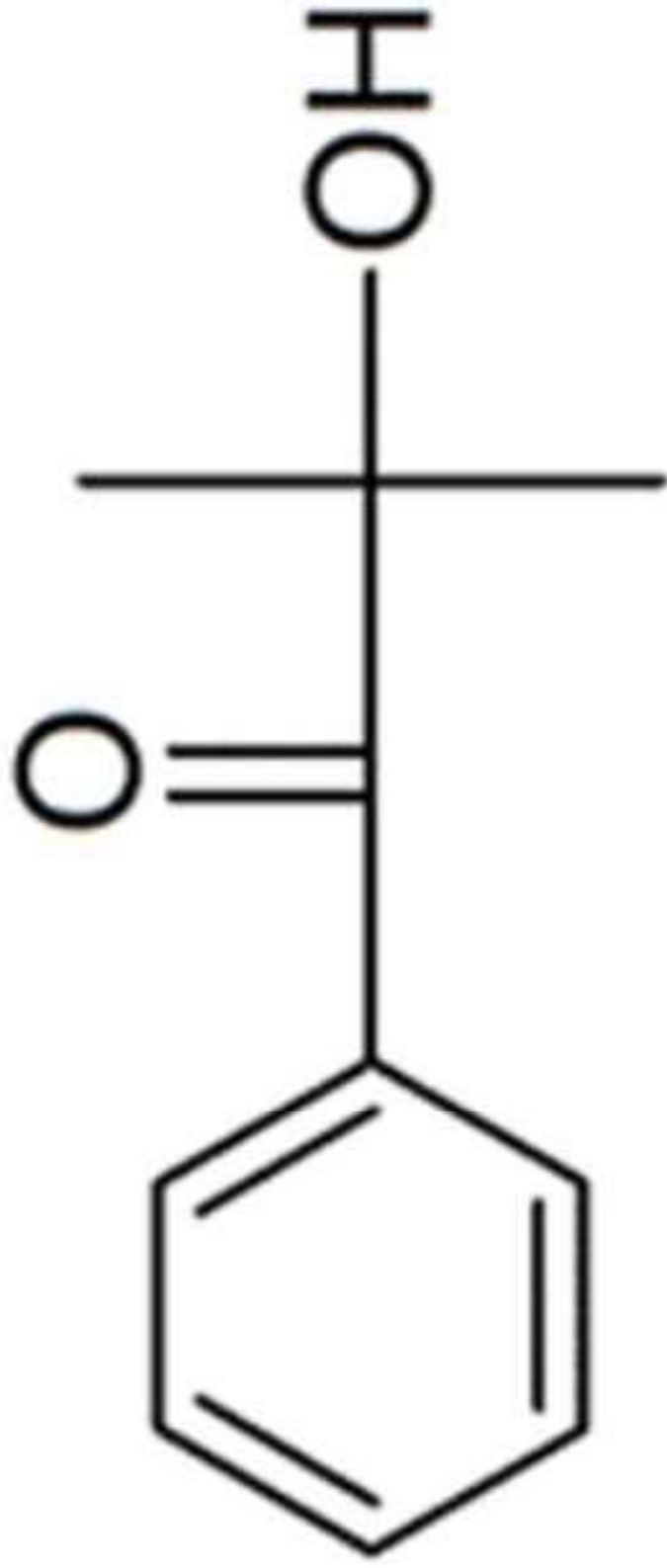
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31 292 photoageing experiments”.
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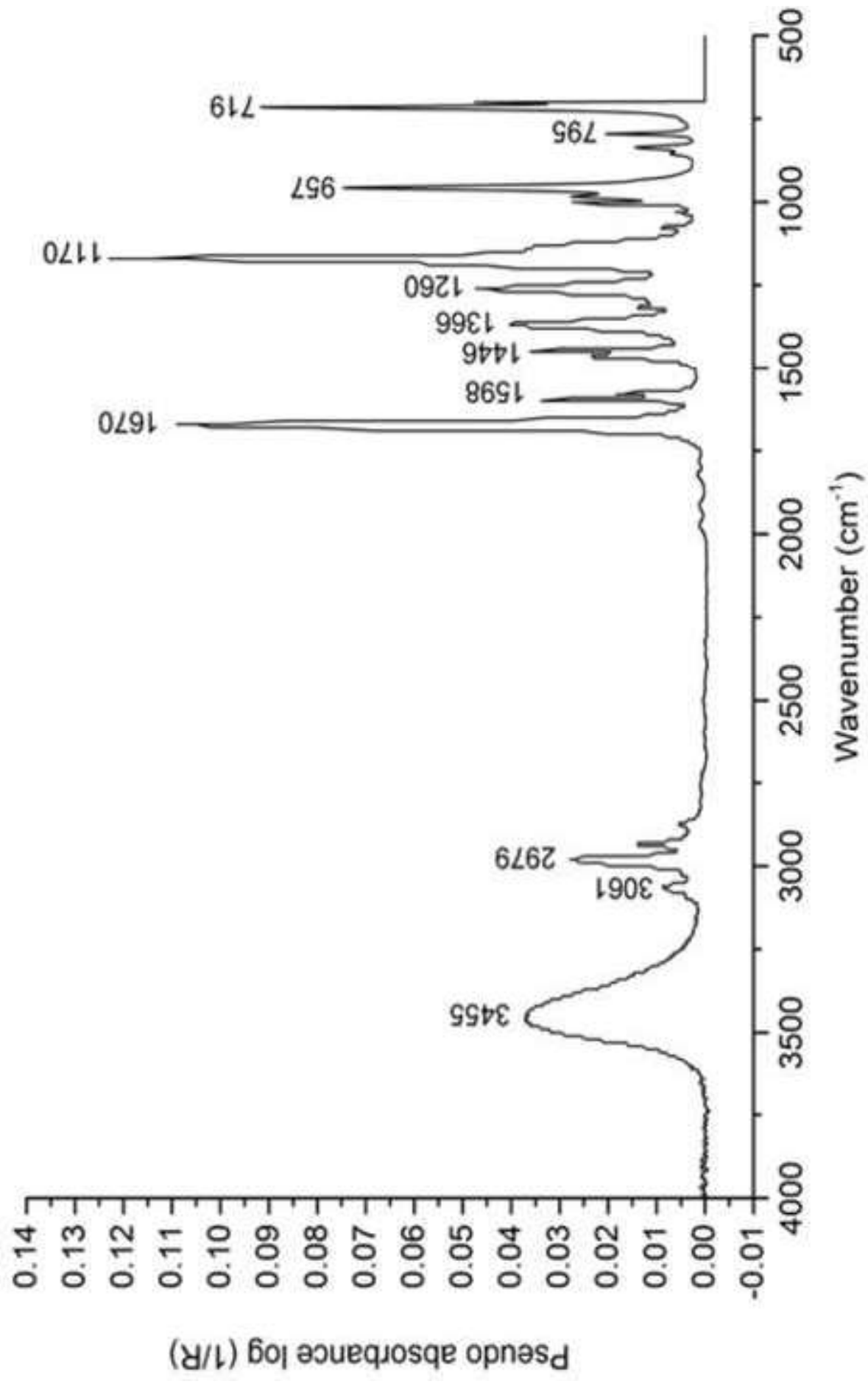
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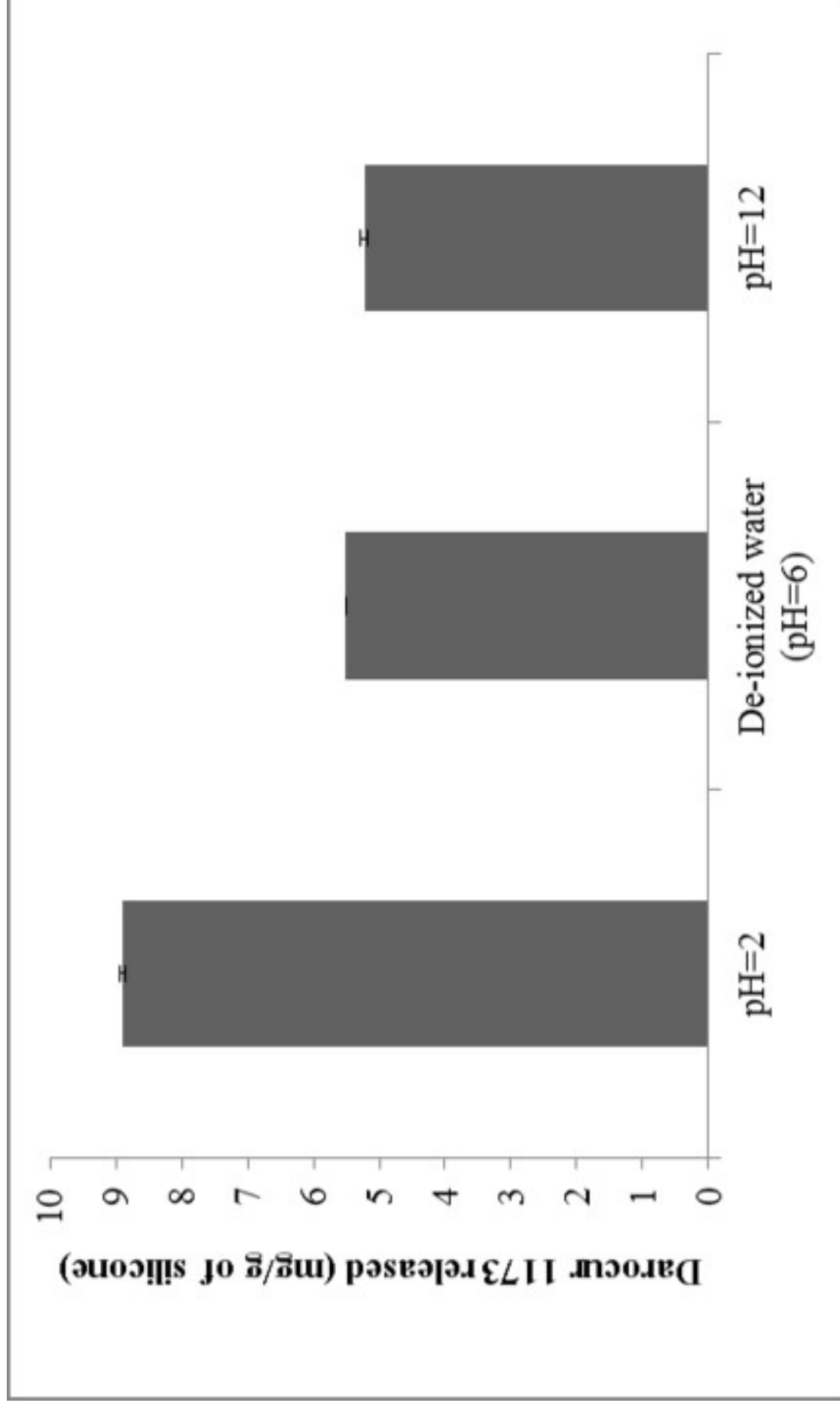
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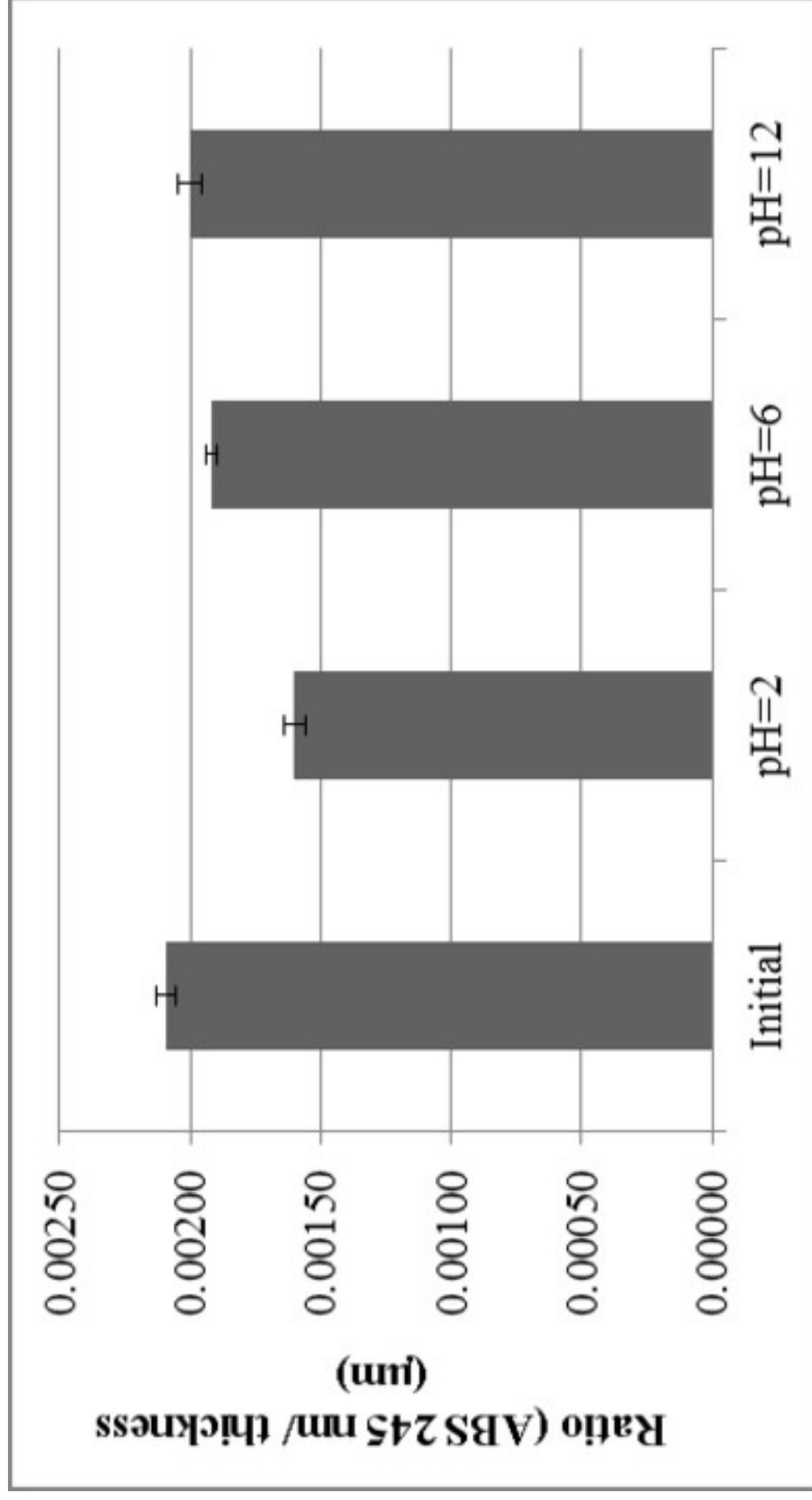
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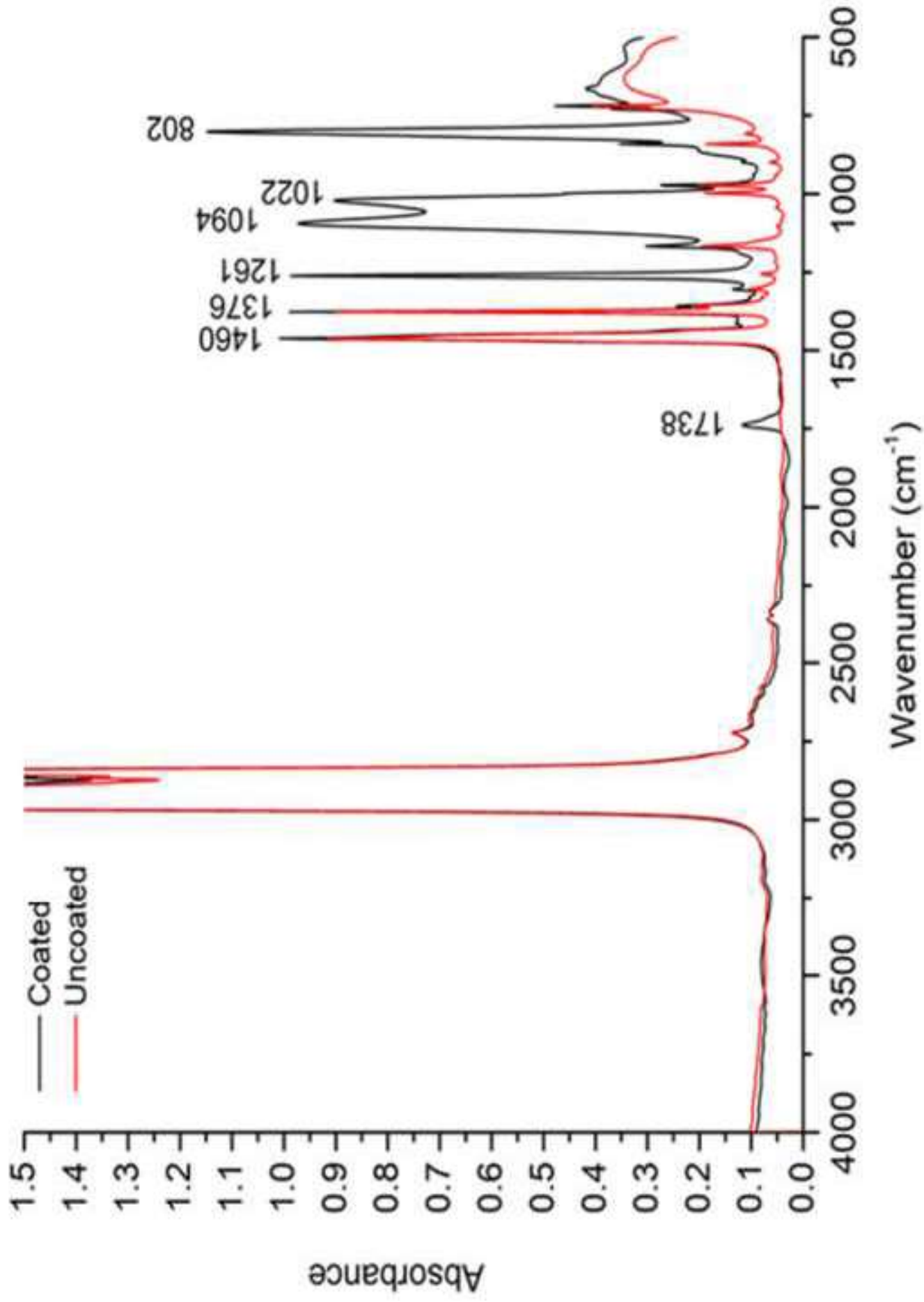


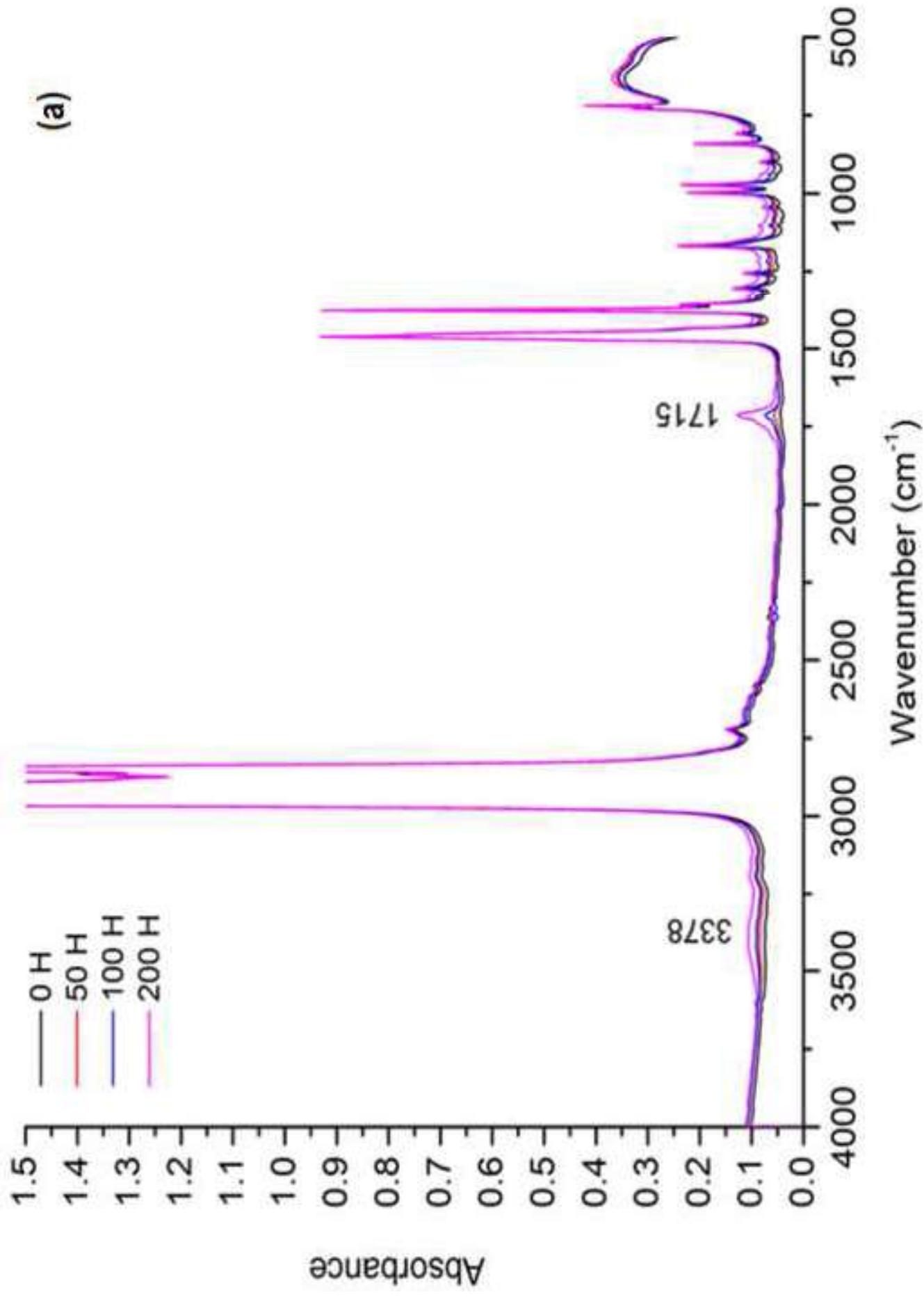


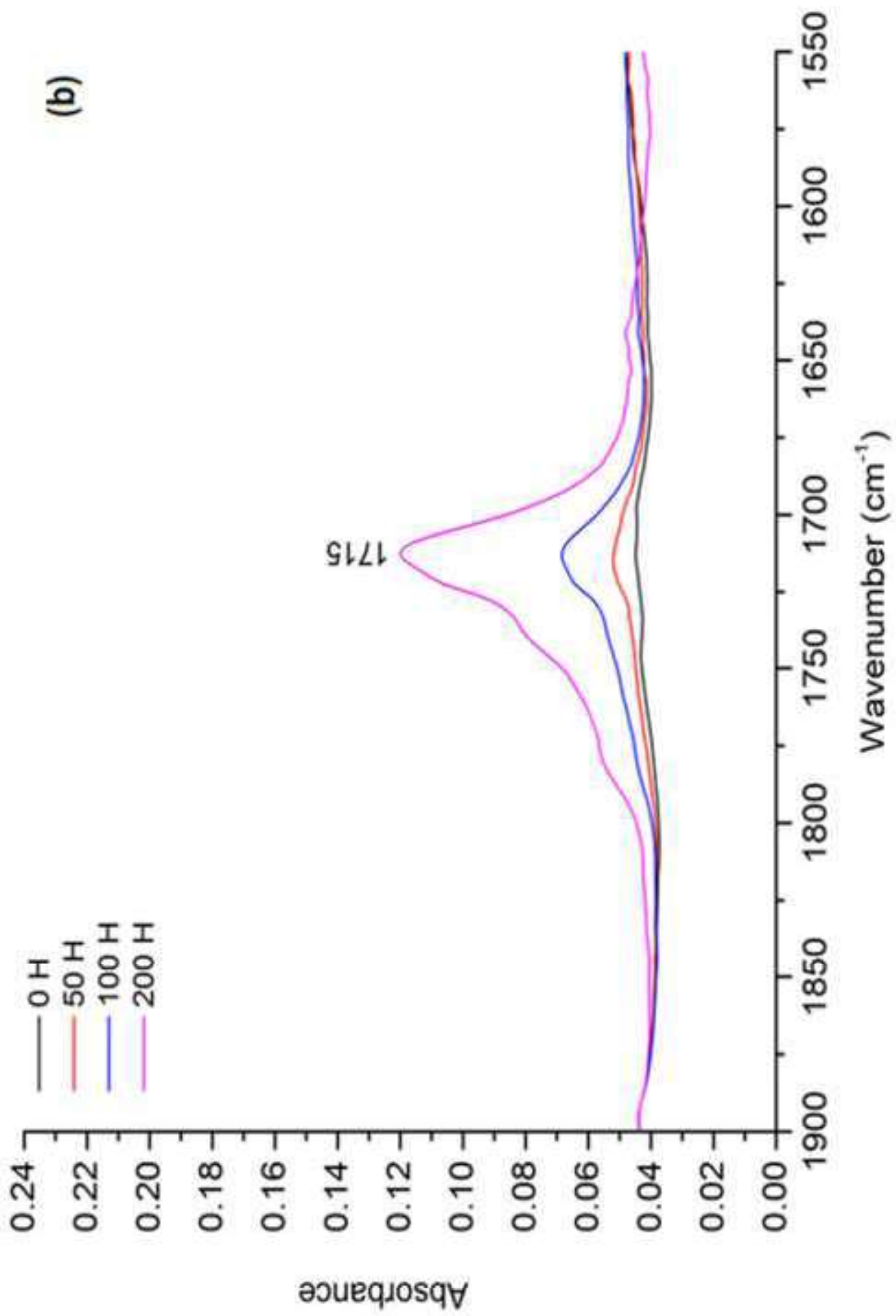


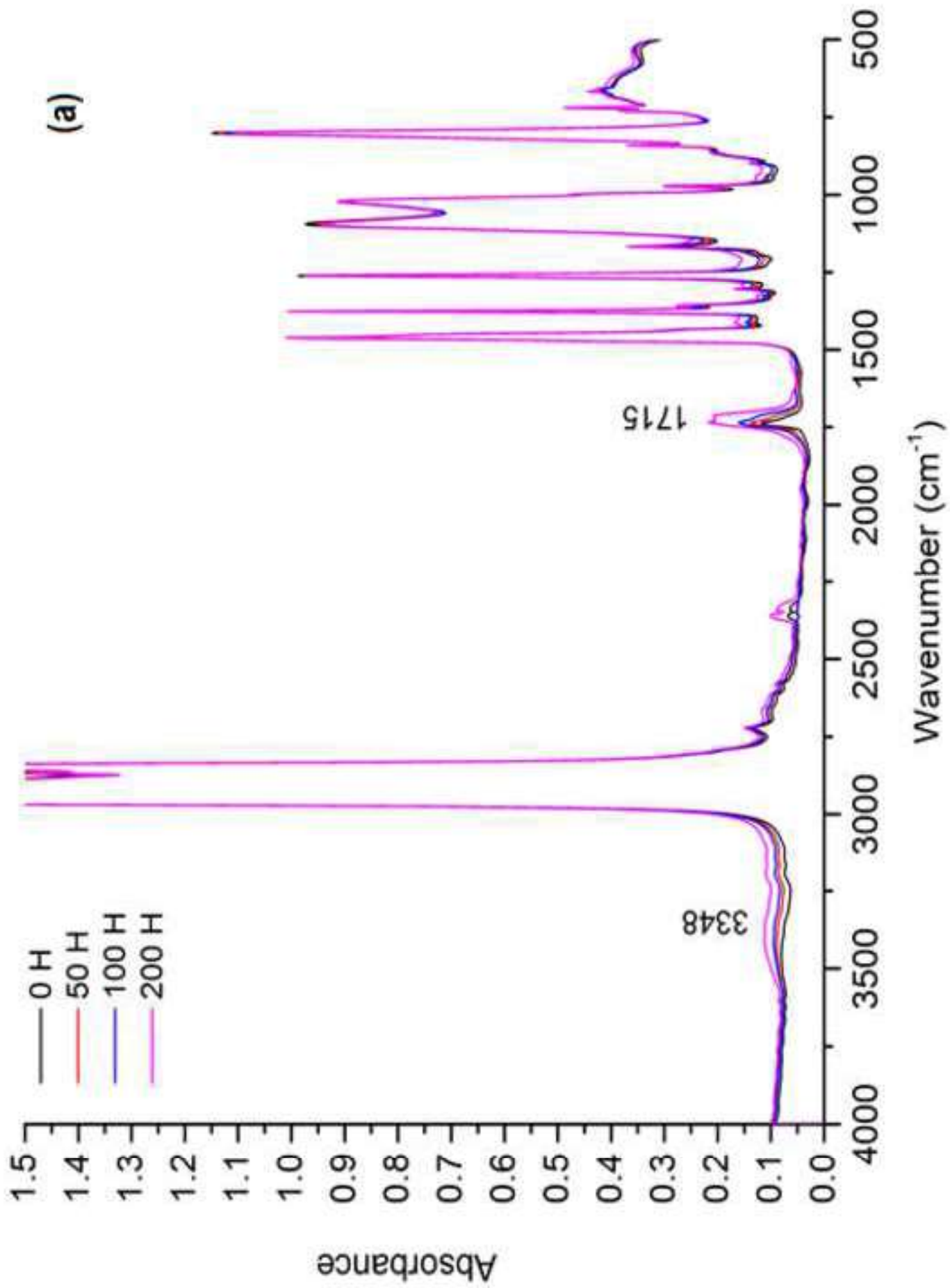


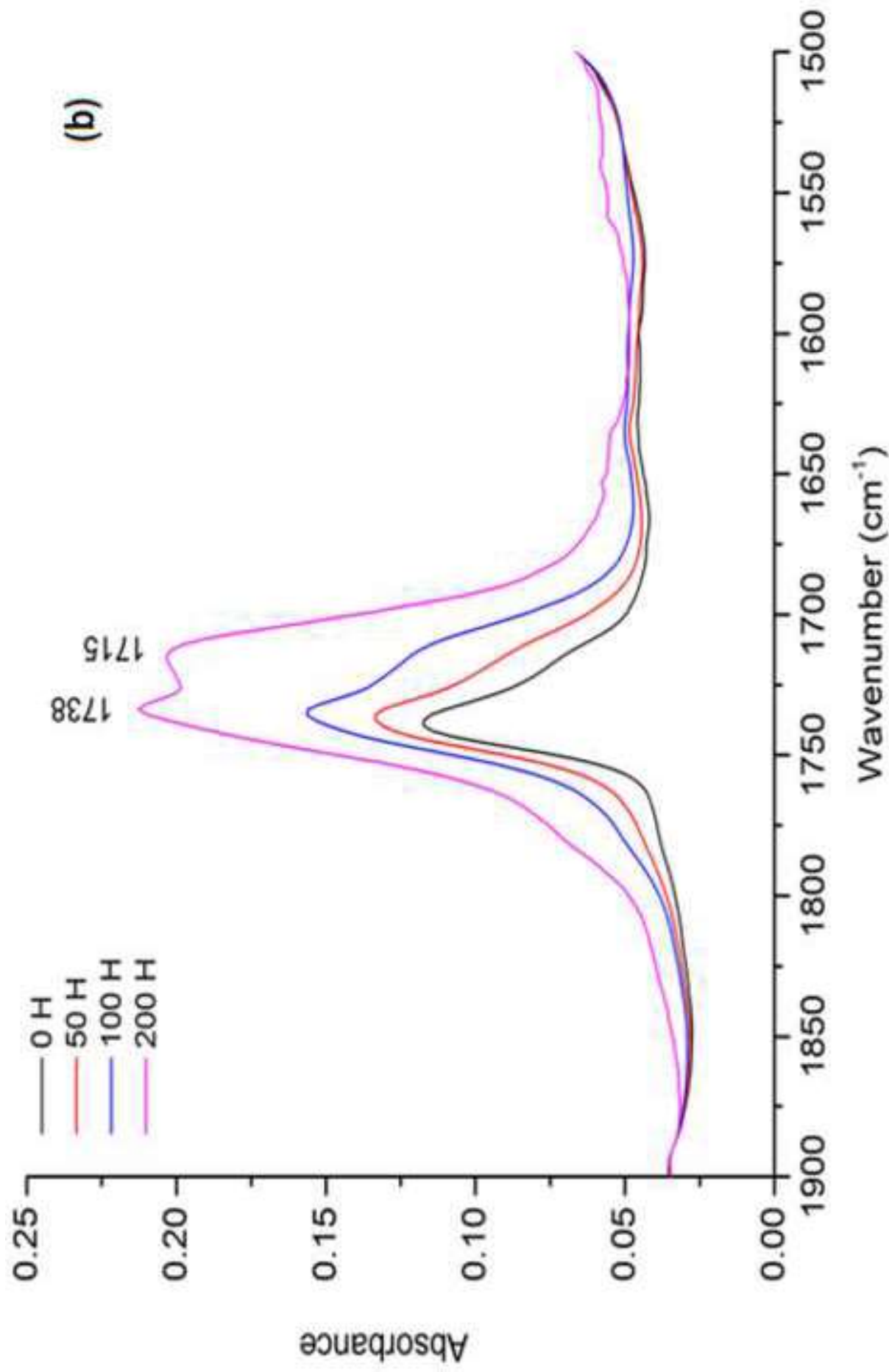


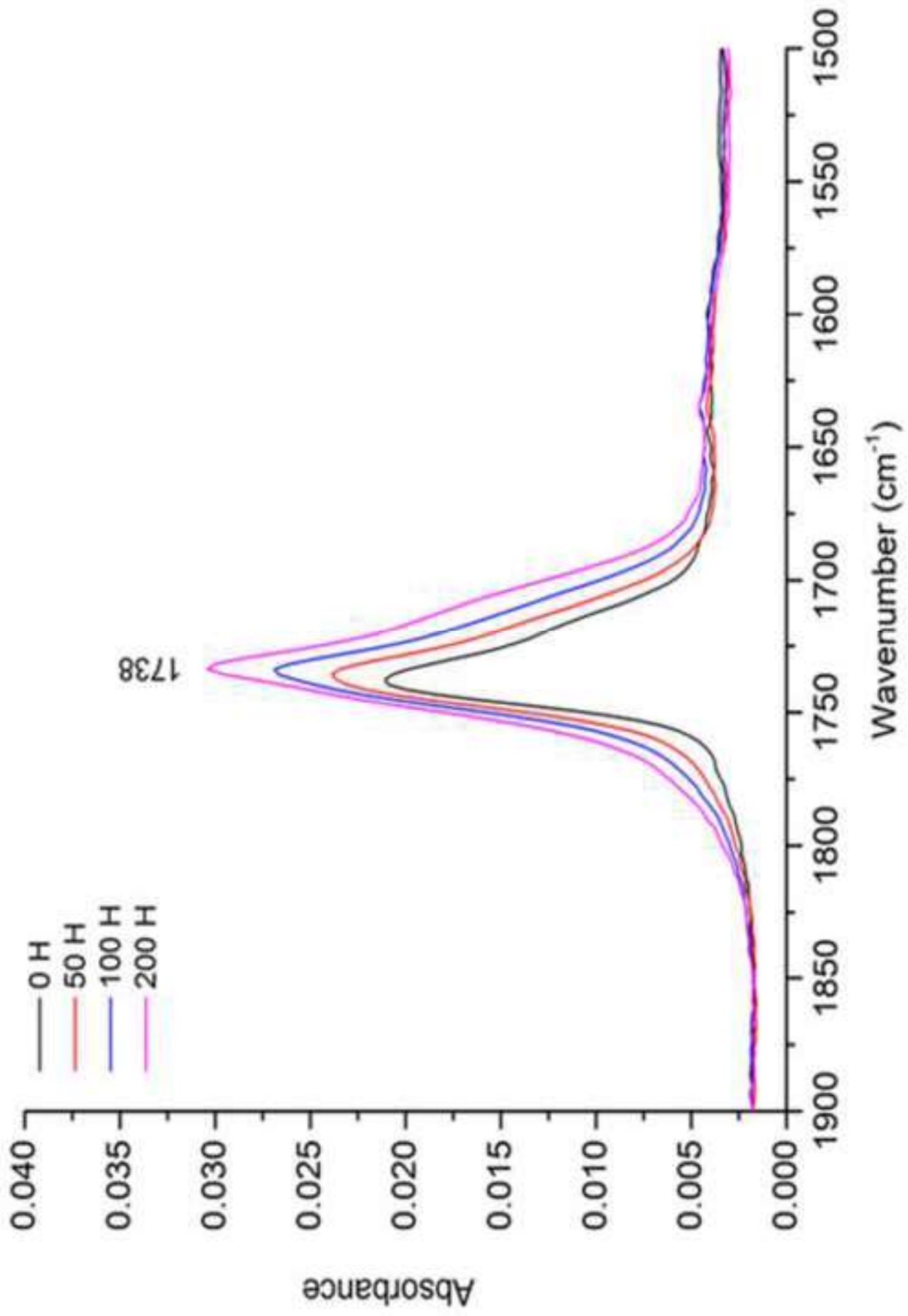


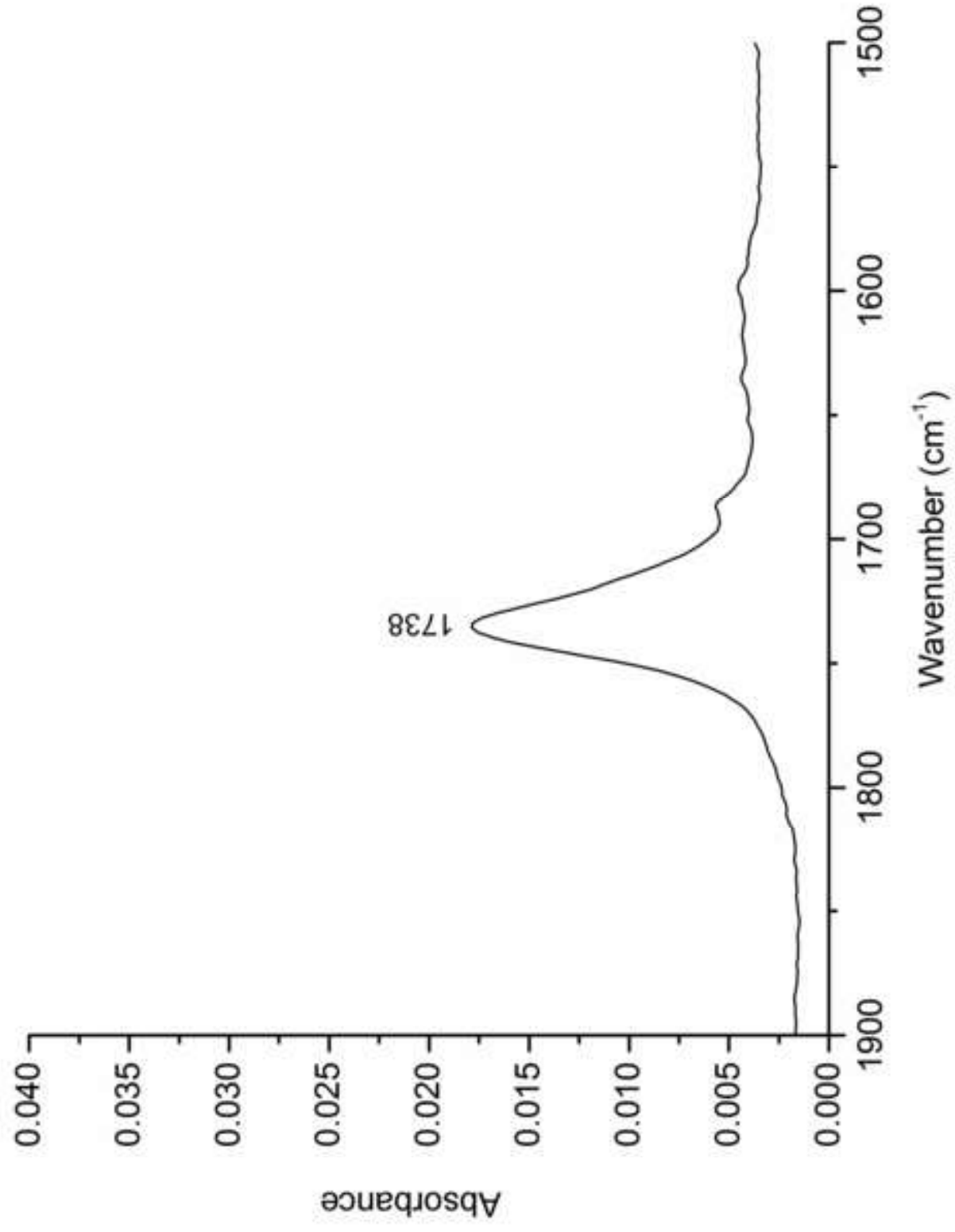


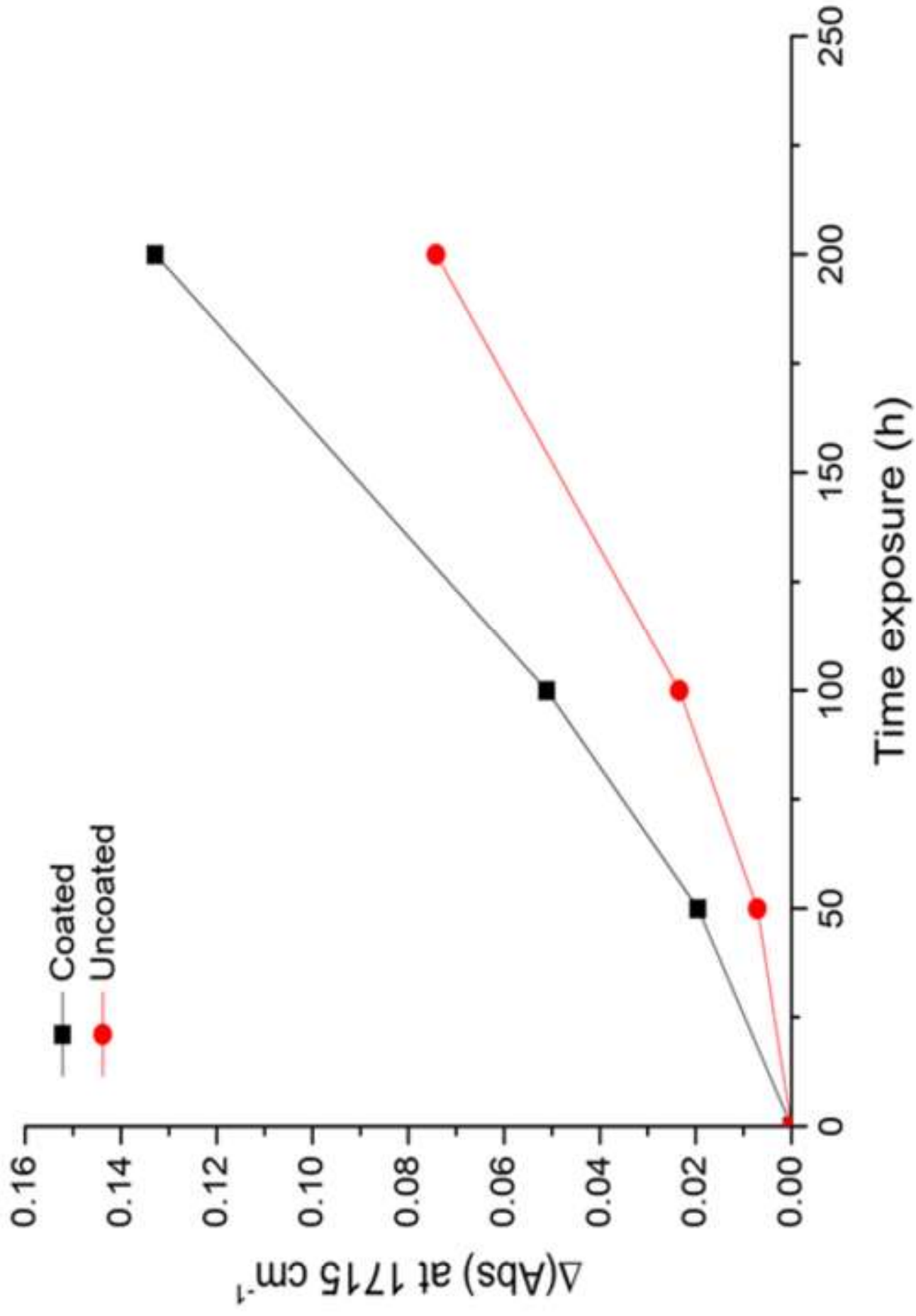


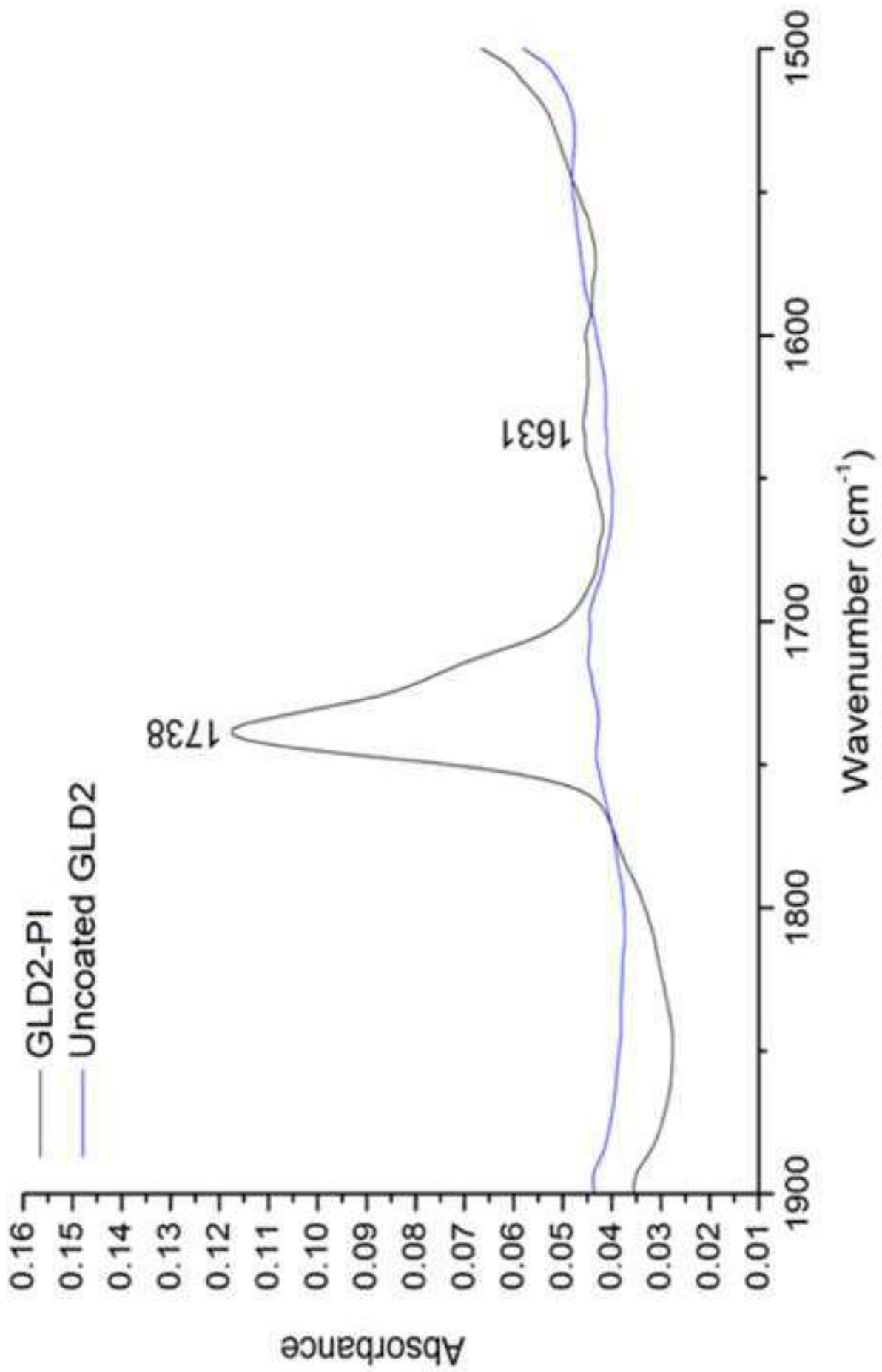


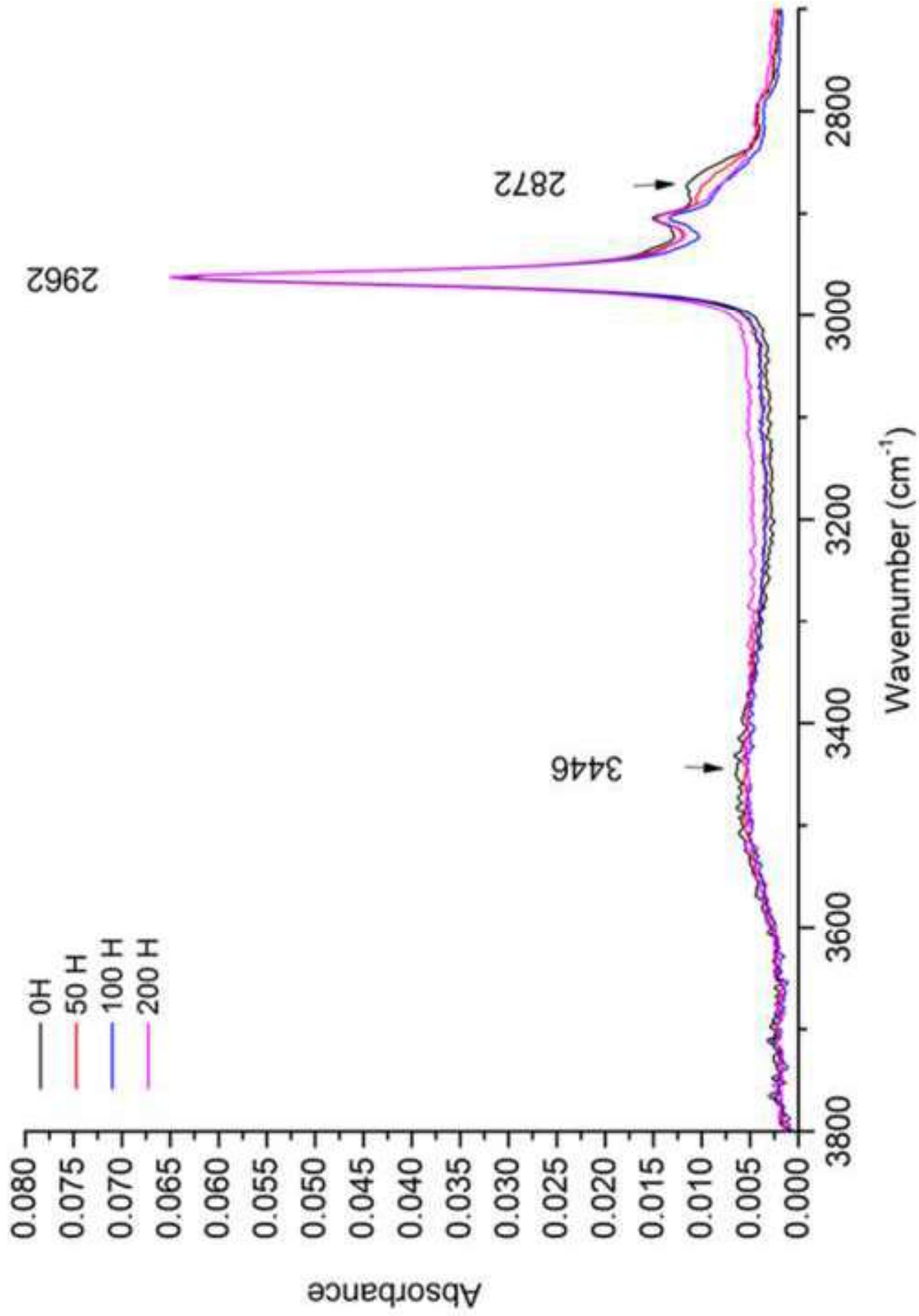


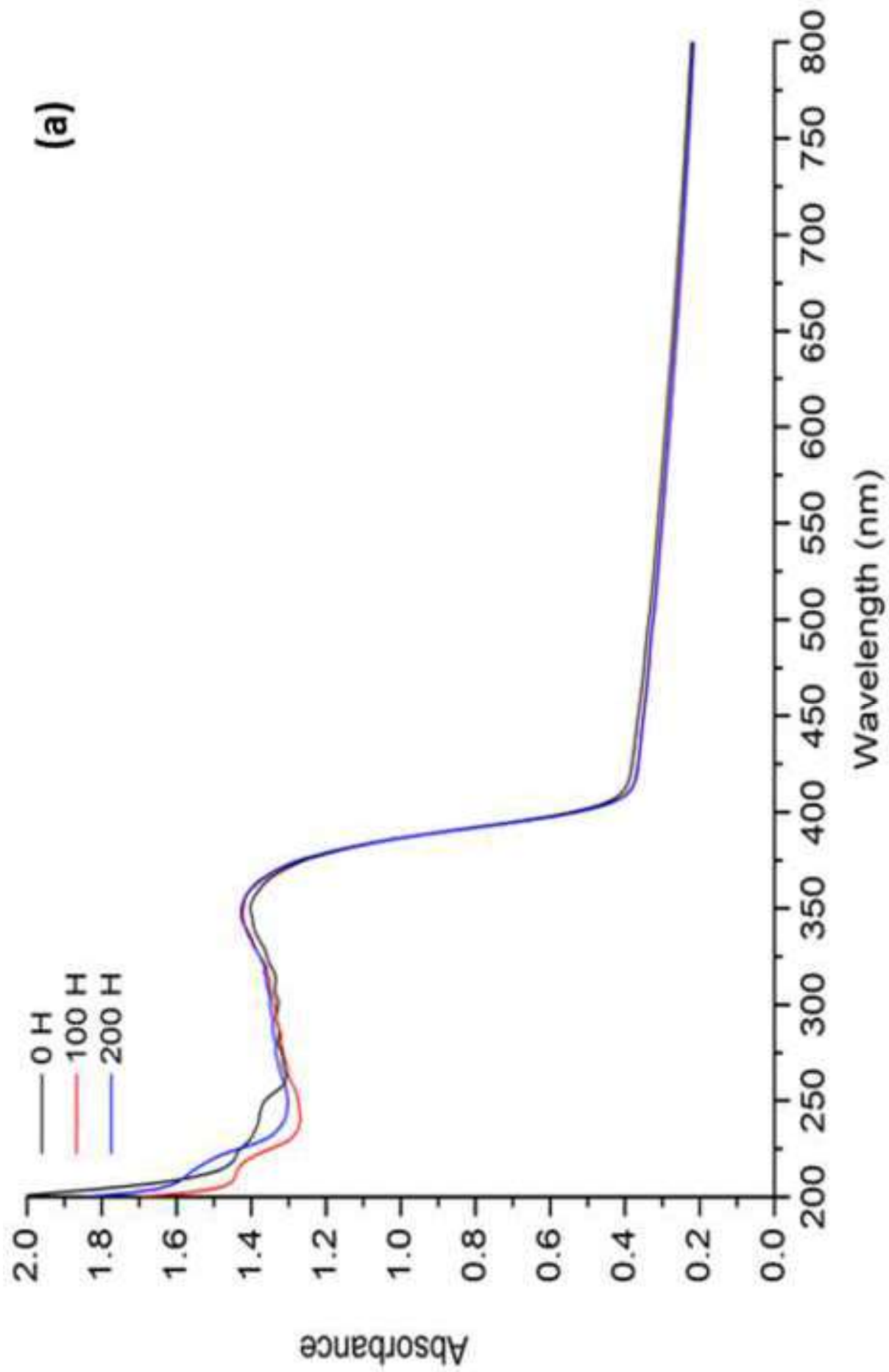












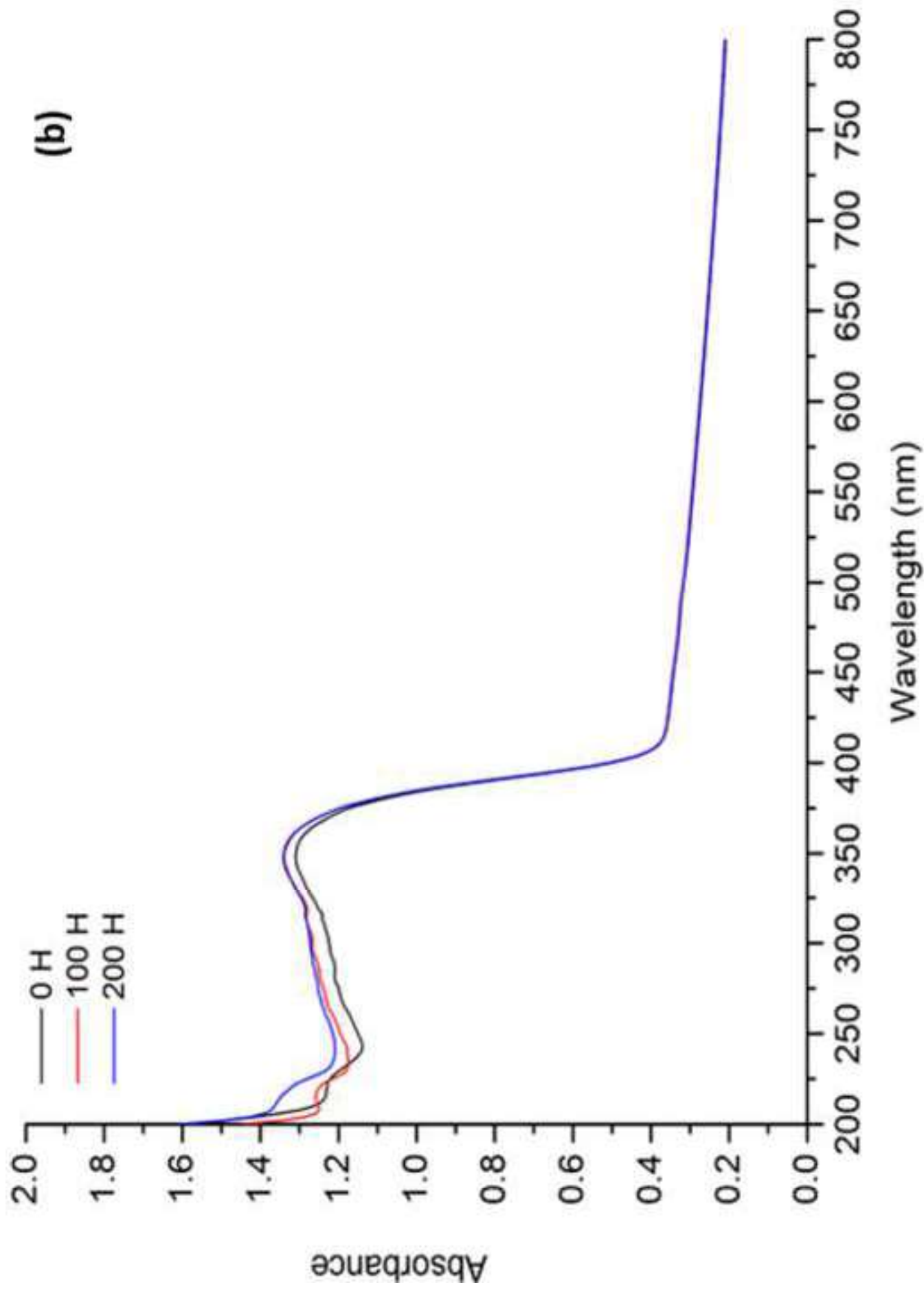


Figure Captions

Fig.1: Chemical structure of silicone acrylate oil (M motifs = Me_3SiO , D motifs = Me_2SiO_2)

Fig.2: Chemical structure of Darocur 1173

Fig.3: FTIR/ATR analysis of Darocur 1173

Fig.4: Leaching of Darocur 1173 (PI) after 15 days from GLD2 coated films in acidic solution (pH=2), de-ionized water (pH=6) and basic solution (pH=12)

Fig.5: Residual Darocur after leaching of coated GLD2 films at different pH

Fig.6: FTIR/Transmission analysis of coated GLD2-PI and uncoated GLD2 films before SEPAP exposure

Fig.7: FTIR/Transmission spectra of uncoated GLD2 films (a) after photo-oxidation in SEPAP 12.24 and carbonyl domain evolution (b)

Fig.8: FTIR/Transmission spectra of coated GLD2-PI films (a) after photo-oxidation in SEPAP 12.24 and carbonyl domain evolution (b)

Fig.9: FTIR/ATR analysis of carbonyl domain evolution of coated GLD2-PI after photo-oxidation in SEPAP 12.24

Fig.10: FTIR/ATR analysis of carbonyl domain evolution of coated glass slides before photoageing

Fig.11: Comparative rates of oxidation of coated and uncoated GLD2 films over exposure time to photo-ageing, estimated by the absorbance measured at 1715 cm^{-1}

Fig.12: FTIR/Transmission spectra of coated GLD2-PI and uncoated films before SEPAP exposure.

Fig.13: FTIR/Transmission spectra of coated GLD2-PI after 50 h, 100 h and 200 h of SEPAP exposure.

Fig.14: UV/visible spectra of coated GLD2-PI films (a) and uncoated films (b) after 100 h and 200 h of SEPAP exposure.