

Photodegradation of Decabromo Diphenyl Ether Flame Retardant in Poly (Acrylonitrile Butadiene Styrene) (ABS)

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2 **Photodegradation of Decabromo Diphenyl Ether Flame Retardant in Poly**
3 **(Acrylonitrile Butadiene Styrene) (ABS)**

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5 Hussam Aldoori^{a,b}, Zohra Boubarka^{a,b}, Abdelouahab Nadim^a, Yassine Agguine^a, Said
6 Eddarir^a, Philippe Supiot^c, Corinne Foissac^c, Ulrich Maschke*,^a

7
8
9 ^a Unité Matériaux et Transformations – UMET (UMR CNRS N°8207), Bâtiment C6,
10 Université de Lille, 59655 Villeneuve d'Ascq Cedex, France

11
12 ^b Laboratoire Physico-Chimie des Matériaux-Catalyse et Environnement (LPCM-CE),
13 Université des Sciences et de la Technologie d'Oran « USTO », BP 1505, El M'naouer,
14 31000 Oran, Algeria

15
16 ^c Faculté des Sciences et Technologies, Université de Lille, 59655 Villeneuve d'Ascq Cedex,
17 France

18
19 Corresponding author :

20 Fax : 0033 3 20 43 65 91 ; e-mail : ulrich.maschke@univ-lille.fr

21
22 Emails of the coauthors, in the order of appearance:

23 hussam.aldoori.etu@univ-lille.fr; bouberkazohra@yahoo.fr; nadimabdelouahab@gmail.com;
24 y.agguine@gmail.com; eddarir@yahoo.fr; philippe.supiot@univ-lille.fr;
25 corinne.foissac@univ-lille.fr

27 **Abstract**

28 Decabromodiphenylether (DBDE) is a brominated flame retardant which belongs to the group
29 of polybromodiphenylethers (PBDEs) often used as a fire resistant additive in various well
30 known polymeric systems like polystyrene, poly(acrylonitrile-butadiene-styrene) (ABS),
31 polypropylene, etc. This compound can be considered as a persistent organic pollutant and
32 presents certain risks for the environment owing to the fact that it is bioaccumulable and not
33 biodegradable. A detailed investigation, described here, was carried out on the effect of
34 ultraviolet/visible radiation on DBDE in ABS with the aim to study the photolytic reactions of
35 this molecule in the solid state, in order to improve the economic and ecological treatment of
36 brominated plastic waste from waste electrical and electronic equipment (WEEE). This study
37 presents new aspects of the photochemical degradation of DBDE/ABS systems in the solid
38 state. The photodegradation of DBDE in ABS was followed by Fourier transform infrared
39 spectroscopy (FTIR) as well as by thermogravimetric analysis (TGA). Good agreement was
40 obtained for the results of both analytical methods in terms of the overall photolysis of
41 DBDE.

42
43 **Keywords:** Photolysis; Polybromodiphenylethers; acrylonitrile-butadiene-styrene; UV-visible
44 radiation; Kinetics.

45

46 **1. Introduction**

47 Flame retardants (FRs) are necessary to ensure safety in a wide range of applications such as
48 plastics components of electrical equipments, cars and aircrafts, and the main components of
49 insulation materials, foams in furnitures, mattresses, and textiles [1,2]. Brominated FRs
50 (BFRs) represent the largest market group of FRs due to their low cost and high performance
51 efficiency [2,3]. Polybrominated diphenyl ethers (PBDEs) are well known BFRs with three
52 major commercial formulations: DecaBDE (DBDE), OctaBDE (OBDE) and PentaBDE.
53 However, PBDEs have aroused high environmental concern because of their global
54 distribution and bioaccumulation [4-10]. It has been reported that PBDEs influence liver
55 enzyme activity and act as endocrine disruptors, inducing immunotoxicity and affecting
56 neurological development at a key period of brain growth [11-12]. Marketing and use of
57 PentaBDE and OBDE was banned throughout the EU in 2004 on the basis of the potential for
58 the lower-brominated derivatives to bioaccumulate in the environment [13]. Only DBDE is
59 still commercially available in a few countries worldwide. In the EU, DBDE was limited in
60 use in electric and electronic equipment (EEE) from 2002 until 2005, and from 2005 to 2008
61 it was exempted from the restriction of use in EEE by commission decision 2005/717/EC.
62 Since 30/06/2008, the original Restriction of Hazardous Substances Directive 2002/95/EC
63 (RoHS 1) has been applied again to DBDE, by limiting the concentration of PBDEs to 0.1
64 weight% (wt%). The ROHS II Directive (2011/65/EU) further restricted the use of DBDE in
65 EEE [14]. A new entry 67 was established by the Commission Regulation (EU) 2017/227 in
66 Annex XVII to Regulation (EC) No 1907/2006 of the European Parliament and of the Council
67 (REACH) [15]. Following this entry, DBDE will only be temporally allowed for aerospace
68 and automotive industries, although some exemptions were also given for EEE [16].
69 DBDE remains one of the most important chemical and environmental pollutants of concern
70 since its emissions to the environment occur particularly during both service life and end-of-

71 life phases. Removal of this compound from the environment remains a very difficult
72 challenge because DBDE is highly hydrophobic and has very limited solubility in water [17].
73 Major applications of DBDE are in styrenic polymers, polyolefins, polyesters, and nylons as
74 used in textiles. It is also used as an additive flame retardant mainly in poly(acrylonitrile
75 butadiene styrene) (ABS) and their derivatives, in epoxy oligomers and in engineering plastics
76 for electrical and electronic devices. These bromine derivatives are relatively resistant to
77 physical, chemical or biological degradation. Therefore, it is important to understand its
78 degradation processes and fate in the environment, including both photodegradation kinetics
79 and photoproducts. Research investigations have shown that DBDE can be broken down to
80 produce many lighter-weight PBDEs, including three highly accumulative species associated
81 with PentaBDE [8]. Photolysis is an important degradation pathway for some persistent
82 organic pollutants, including PBDEs, in the environment, and has been reported to occur for
83 PBDE under a variety of conditions [18-21]. Watanabe and Tatsukawa [18] for instance,
84 presented a study on the photolysis of DBDE in a mixture of hexane, benzene, and acetone
85 (8:1:1) employing both sunlight and artificial UV light. Their results indicated that DBDE
86 undergoes photodegradation by reductive debromination and that brominated dibenzofurans
87 (PBDFs) represent the major products from photolysis. Recently, some reports were published
88 on photolysis of DBDE in toluene and adsorbed on silica gel, sand, soil and sediments that
89 showed similar results of photolytic debromination [22-27]. These groups found that the
90 photochemical reaction rate decreased with decreasing bromination degree and that it might
91 also be affected by the positions of the substituted Br-atoms. However, the photolytic
92 decomposition and the effect of photolytic factors on the photodegradation reaction of PBDEs
93 in the solid state have not been well documented in the literature.

94 In the light of the above discussion, since the feasibility of the photolytic degradation in the
95 liquid state has already been shown, this report focuses on the debromination of DBDE in the

96 solid state. In particular, DBDE was dispersed in various concentrations in an ABS (0-30
97 wt%) before undergoing UV-Visible irradiation. These percentages were chosen since they
98 correspond to concentrations of BFRs in polymers from waste EEE.

99 To the best of our knowledge this topic has not been reported before in the literature. In this
100 work two analytical methods were employed in order to compare and correlate the
101 corresponding results. Infrared spectroscopy and thermogravimetric analysis techniques
102 were found to be particularly well adapted since they allow characterization of the solid
103 samples without further treatment.

104

105 **2. Materials and Methods**

106 **2.1 Materials**

107 DBDE (Saytex 102E, purity 98%, CAS: 1163-19-5), 2,2',3,3',4,4',5,5',6,6'-
108 Decabromodiphenylether (BDE-209), (C₁₂Br₁₂O), was purchased from Albemarle Corp.
109 (USA), it was a white to off-white powder.

110 The poly(acrylonitrile butadiene styrene) (ABS) was obtained from a recycling plant situated
111 in the "Région Hauts de France"; mixtures of the ABS with different amounts of DBDE
112 (10wt%, 15wt%, 20wt% and 30wt%) were prepared using a micro-extrusion machine
113 followed by crushing the obtained samples to obtain fine powders. The average diameter size
114 of all powders was between 600 and 800µm.

115

116 **2.2 Photolytic experiments**

117 The irradiation process was carried out at room temperature, using a 150W Xenon light
118 source LC8 from Hamamatsu Photonics France S.A.R.L. together with an optical fiber,
119 characterized by an emission spectrum covering nearly the whole UV-Visible spectrum with a
120 broad maximum in the visible range. The distance between the end of the optical fiber of the

121 UV-Visible source and the sample was kept constant at 3cm.
122 During the photodegradation experiments thin layers of the powdered material (ABS and
123 ABS/DBDE blends) were placed on a flat sample holder which was kept under controlled
124 agitation to renew regularly the sample surface. At the appropriate exposure times, without
125 interruption (i.e., there was no conduction of cumulative experiments), the photodegradation
126 reaction was finished by removing the solid samples from the light exposure and immediately
127 initiating analysis. All experiments were repeated at least two times and averaged values are
128 presented in the corresponding figures.

129 It is well known that irradiation sources generally provide not only a certain amount of
130 photons as function of their UV-Vis spectrum, light intensity and exposure time, but also
131 quite frequently an increase in temperature of the sample medium due to the infrared part of
132 the spectrum. Using the experimental set-up described above, the maximum temperature
133 reached on the surface of the sample was found as $T=50^{\circ}\text{C}$. In order to evaluate eventual
134 thermal degradation effects occurring at this temperature in the absence of light, ABS/DBDE
135 samples underwent an isothermal treatment at $T=50^{\circ}\text{C}$ for one hour in a furnace; these
136 samples were then kept in darkness until analysis was performed by Fourier transform
137 infrared spectroscopy. No thermal degradation of the investigated ABS/DBDE system was
138 detected.

139

140 **2.3 Physico-chemical analysis**

141 2.3.1 Fourier transform infrared spectroscopy (FTIR)

142 FTIR spectra were recorded in transmission mode at room temperature, using a model 2000
143 spectrometer (Perkin Elmer Corp., USA). The spectral range between 400cm^{-1} and 4000cm^{-1}
144 was investigated. The number of accumulated scans was 16 with a spectral resolution of
145 4cm^{-1} . Solid KBr disks of diameter one centimeter and thickness one millimeter were used,

146 formed by mixing 10mg of the powder sample to be analyzed with 90mg of dried KBr. A
147 pressure of 8bars was applied during 5min to prepare the KBr disks.

148

149 2.3.2 Thermogravimetric analysis (TGA)

150 Thermogravimetric analysis (TGA) was conducted using Pyris 1 instrument (Perkin Elmer)
151 exhibiting a mass resolution of 1 μ g. The average mass of the samples was 8mg, placed in
152 Platinum-HT-pans. Thermal analysis of the powder samples was performed under nitrogen
153 atmosphere during a heating ramp of 10°C/min in the temperature range between 20°C and
154 900°C.

155

156 3. Results and discussion

157 3.1 Spectroscopic observations of the photolysis of ABS/DBDE

158 FTIR spectra of ABS, DBDE, and ABS/DBDE blends are presented in Figs. 1 and 2, allowing
159 to identify and to select characteristic bands of DBDE and ABS. In the wavenumber range
160 between 1025 and 1800 cm^{-1} as shown in Fig. 1a, ABS presents bands at 1453 cm^{-1} , 1494 cm^{-1}
161 and 1602 cm^{-1} , all of which can be attributed to C-C stretching vibrations in the aromatic rings
162 of the styrene part in ABS [28]. In the same wavenumber range, DBDE exhibits a broad
163 intense band located between 1250 cm^{-1} and 1370 cm^{-1} , corresponding to asymmetric C-O-C
164 stretching vibrations in the aromatic rings of DBDE [29]. This band, which present no
165 interference with other bands in the DBDE spectrum and does not exist for ABS, can thus be
166 selected to follow the DBDE photodegradation kinetics. With an increase of the concentration
167 of DBDE in the ABS/DBDE blends, the intensity of this band, characteristic of the ether
168 groups, increased correspondingly, as shown in Fig. 1b.

169

Insert Figure 1 here

170

Insert Figure 2 here

171 Figure 2 presents the FTIR spectra of DBDE and ABS in the wavenumber range between 480
172 and 1000 cm^{-1} . Some absorbance bands of ABS and DBDE appear rather close, such as the
173 bands at 966 cm^{-1} (C-H in trans-butadiene part of ABS [30]) and 960 cm^{-1} (C-Br [29] in
174 DBDE); 765 cm^{-1} (CH_2 in vinyl-butadiene and styrene part of ABS [28]) and 761 cm^{-1} (C-C
175 ring [31] in DBDE); and 699 cm^{-1} (C-C ring [32]) and 708 cm^{-1} (C-C ring [31] in DBDE),
176 respectively. In ABS/DBDE mixtures these overlapping bands cannot be used to follow the
177 effects of photolysis. Only the absorbance band at 617 cm^{-1} of DBDE, corresponding to
178 aromatic C-Br vibrations [33], does not interfere with ABS bands and will also be considered
179 in following the debromination process.

180 Insert Figure 3 here

181 The model mixtures ABS/DBDE were subjected to a radiative UV/Vis treatment by the
182 Xenon LC8 lamp at room temperature. The infrared spectral analysis of the impact of the
183 radiation on ABS loaded with 30wt% DBDE is shown in Fig. 3. A relatively strong reduction
184 of the band corresponding to the ether-bond of DBDE was observed after an irradiation time
185 of one hour, accompanied by the appearance of a new band at 1400 cm^{-1} . The kinetics of
186 DBDE degradation was fast in the first few minutes of photolysis, but the reaction rate
187 became relatively slow beyond 10min of irradiation. A fast increase of the peak situated at
188 1400 cm^{-1} in the first ten minutes was also observed. This new absorption band is due to the
189 formation of aromatic C-H-groups belonging to photoproducts of DBDE and, in particular,
190 lower brominated BDE.

191 Insert Figure 4 here

192 In Fig. 4 one notices a significant reduction of the absorbance band at 1080 cm^{-1} , after one
193 hour of irradiation. This band is associated with an aryl-Br valence vibration from DBDE
194 [34]. This can be explained by the change of the chemical environment of the aromatic nuclei

195 of DBDE under the effect of the photolysis. Since DBDE is entirely brominated, one can
196 already see the radiative effect on the debromination of the molecule.

197 Insert Figure 5 here

198 In Fig. 5a one notices a strong reduction of the C-Br absorbance band situated at 617cm^{-1} ,
199 allowing thus to confirm the debromination effects on DBDE during photolysis. In Fig. 5b
200 one observes a slight decrease of the intensities of the absorbance bands situated at 557 and
201 678cm^{-1} , related to C-Br stretching bands (see for example [35]). One should keep in mind
202 that the latter bands interfere with absorbance bands of ABS, in contrast to the peak from
203 DBDE at 617cm^{-1} , which does not interfere with ABS bands (see also Fig. 2).

204 The effect of UV/Vis irradiation was compared between the two systems ABS/20wt% DBDE
205 and ABS/30wt% DBDE, by following the decrease of the absorbance band at 1350cm^{-1} (Fig.
206 6). The conversion values from DBDE to lower brominated species were calculated by taking
207 into account the heights of the peak maxima: $(H_t - H_0)/H_0$, where H_t and H_0 correspond to the
208 peak heights of the irradiated and pristine sample, respectively. It should be mentioned that
209 this approach represents only a fair estimation of the conversion, since the absorbance band
210 considered here might undergo overlapping effects with other bands, especially when
211 photolysis proceeds. In Fig. 6, one notices that the conversion of the band at 1350cm^{-1} of the
212 ABS/20wt%DBDE system was slightly faster and greater than that of the ABS/30wt%DBDE
213 system, showing that the initial concentration of DBDE in the polymer can influence the
214 degradation process.

215 Insert Figure 6 here

216

217 **3.2 Thermal analysis of the ABS/DBDE system before and after photodegradation**

218 The thermograms shown in Fig. 7, obtained by thermogravimetical analysis (TGA), represent
219 the thermal degradation of ABS and an ABS/DBDE mixture (ABS/10wt% DBDE). The

220 thermal behavior of the ABS/DBDE blend was also examined after photolysis (exposure time:
221 60min). The onset temperature (intersection of the tangent of the beginning of the degradation
222 with the base line) of the thermal degradation of ABS was found to be slightly higher than
223 that of the ABS/DBDE blend: The thermal degradation of ABS started at approximately
224 340°C, whereas the ABS/DBDE mixture started to degrade thermally around 300°C. The
225 thermal degradation of the ABS/DBDE mixture and ABS proceeded in two steps, the first
226 important one around 400°C, and the second one around 500°C. In the case of ABS, the latter
227 step can be explained by different factors as indicated in [36], but also by degradation of
228 crosslinked species formed during the first step [37].

229 An important difference in mass loss was observed for the second degradation step when
230 comparing the results from ABS with the ABS/10wt% DBDE mixture before irradiation,
231 indicating that the thermal degradation of DBDE occurred primarily during this step. It can be
232 suggested that DBDE was completely pyrolyzed since the weight loss corresponded to
233 10wt%.

234 Insert Figure 7 here

235 Figure 7 also reveals that photolysis of the ABS/DBDE system resulted in a significant
236 decrease of the second process of the thermal degradation of the sample, compared to the
237 situation before irradiation. These results can be explained by the photolytic degradation of
238 DBDE in the ABS since in the temperature range between approximately 450°C and 600°C,
239 the thermal degradation curve of the irradiated ABS/DBDE system became very close to that
240 of ABS. However, brominated species were still present in the irradiated sample as indicated
241 by the slow decrease of the thermal degradation beyond 600°C up to 900°C, probably due to
242 the presence of aggregates.

243 Interestingly, similar results were obtained from the pristine and irradiated ABS/DBDE blend
244 for the first degradation step indicating that the polymer remained thermally stable after
245 photolysis.

246

247 **4. Conclusions**

248 A simple, effective method was presented to destroy DBDE molecules used as flame retardant
249 and to obtain less harmful molecules in the environment. The proposed method comprises the
250 photo-irradiation of ABS/DBDE mainly by visible light, without prior addition of additives
251 such as oxidants or catalysts like TiO₂. Two analytical methods were employed which were
252 particularly suited for solid state characterization: Fourier transform infrared spectroscopy and
253 thermogravimetical analysis. They allowed us to follow the photodegradation of model
254 mixtures comprised of ABS and DBDE. The results indicated that DBDE could be effectively
255 degraded to a considerable extent in the solid state during the recycling process by UV-
256 Visible irradiation, while the ABS polymer kept its properties, and could thus be reused from
257 brominated WEEE.

258

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264

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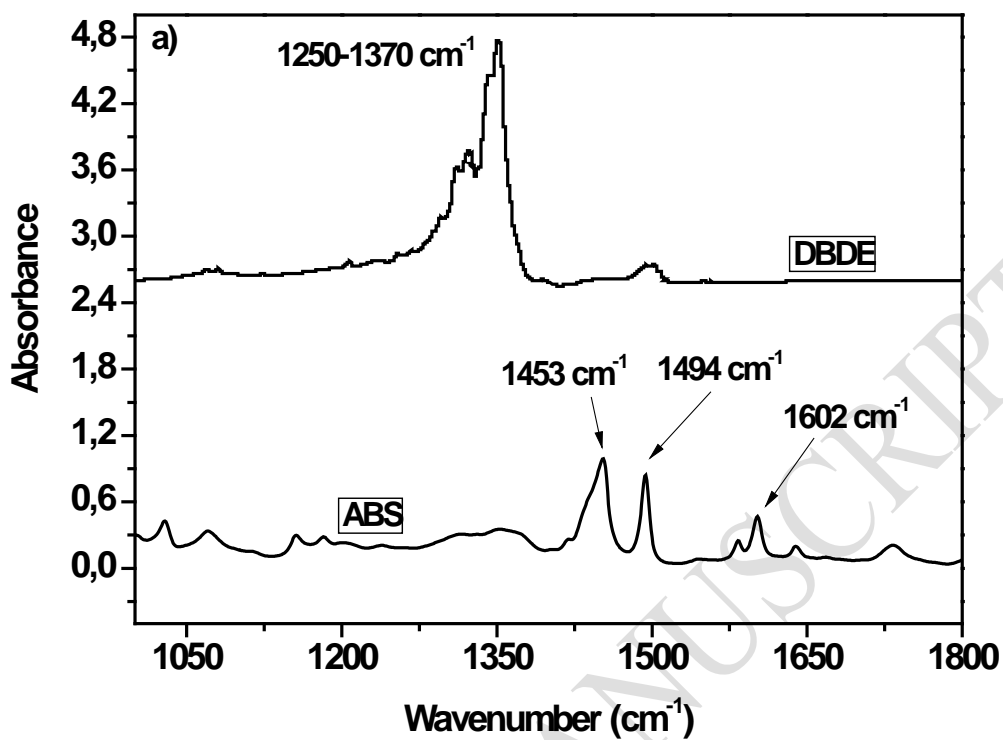
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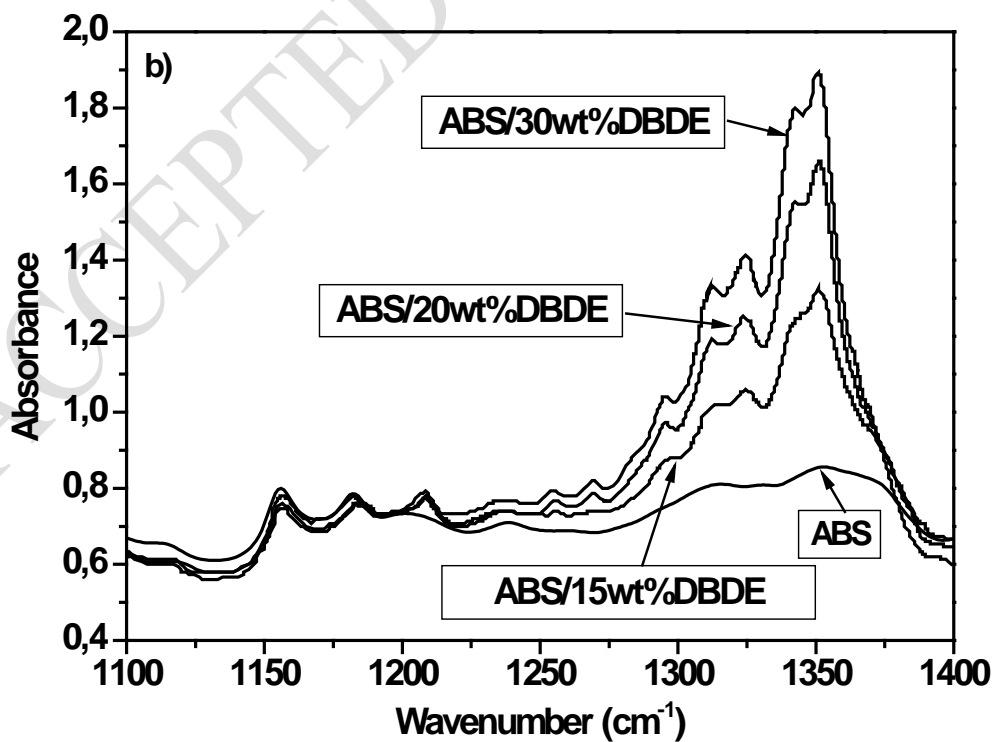
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392 the authors from the direct applications of the research presented in this paper.

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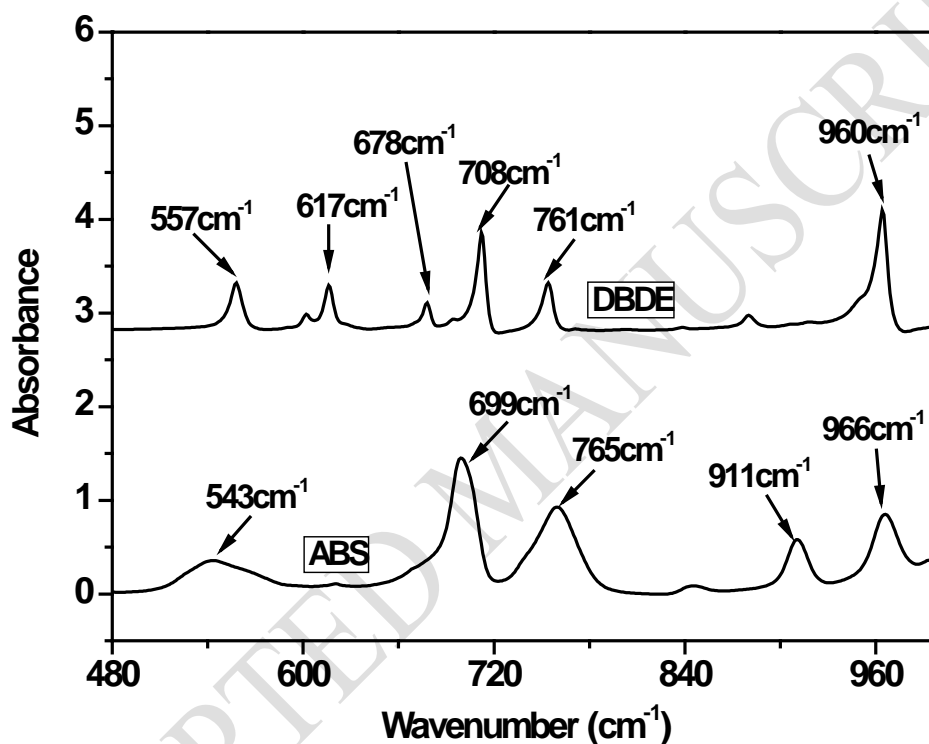
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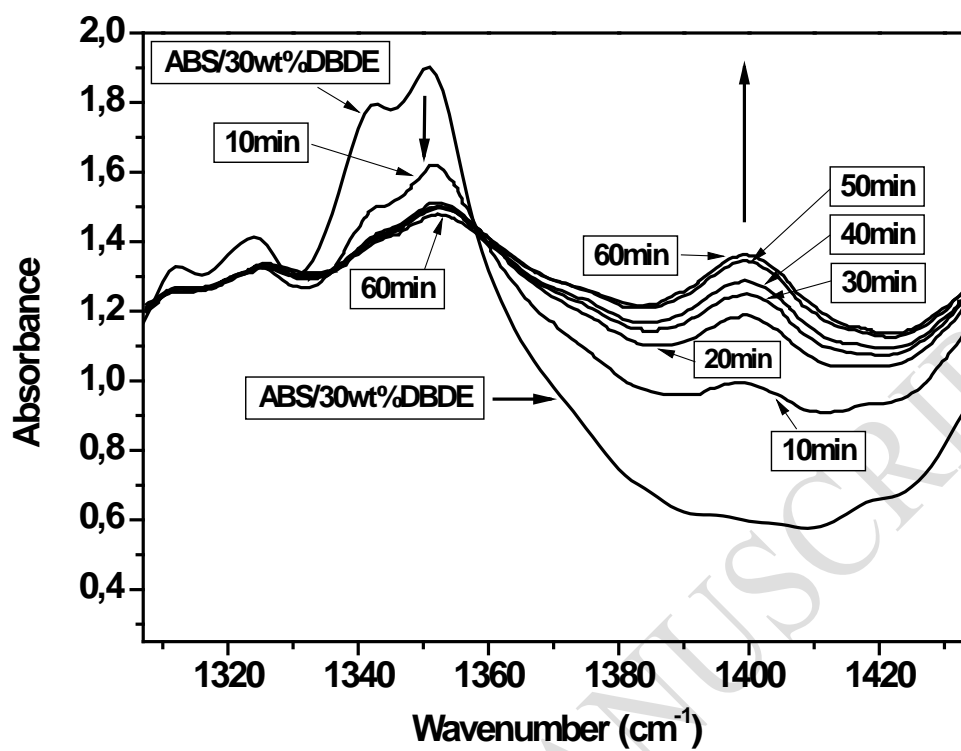
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397 Figure 1: a) FTIR spectra of DBDE, ABS, and ABS/DBDE mixtures in the wavenumber
398 range between 1025 and 1800 cm^{-1} . b) Evolution of the intensity of the ether group band of
399 DBDE in ABS/DBDE mixtures with different amounts of DBDE (15wt%, 20wt% and
400 30wt%).



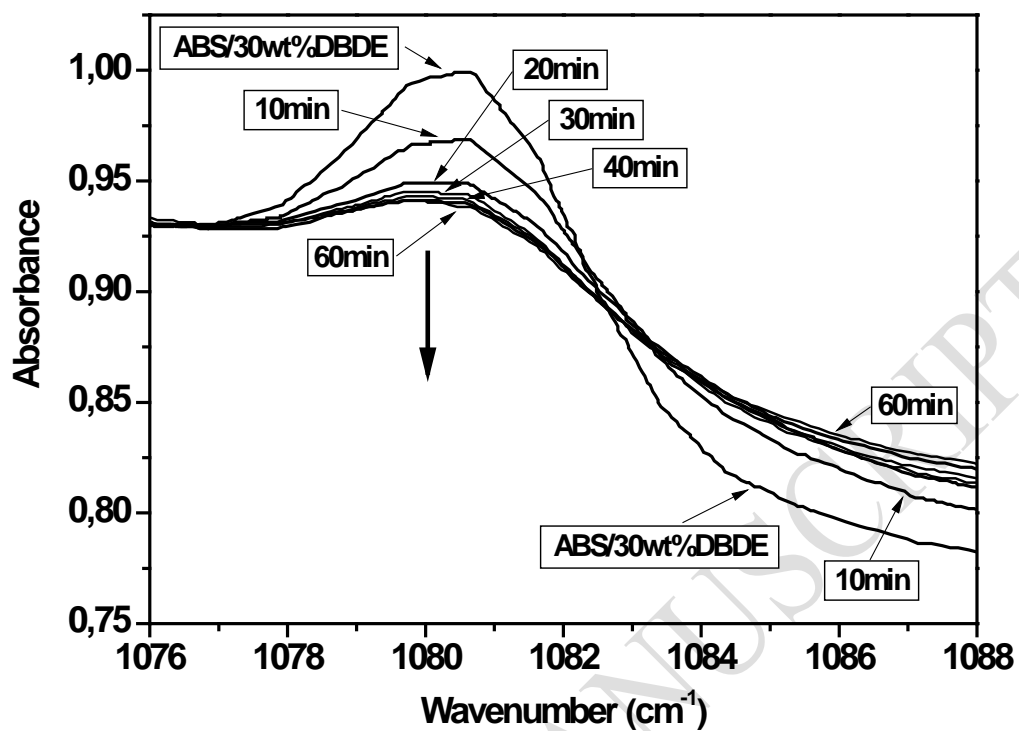
401
402 Figure 2: FTIR spectra of DBDE and ABS in the wavenumber range between 480 and
403 1000 cm^{-1} .



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405 Figure 3: Evolution of the FTIR spectra between 1300 and 1450 cm^{-1} of the ABS/30wt-%

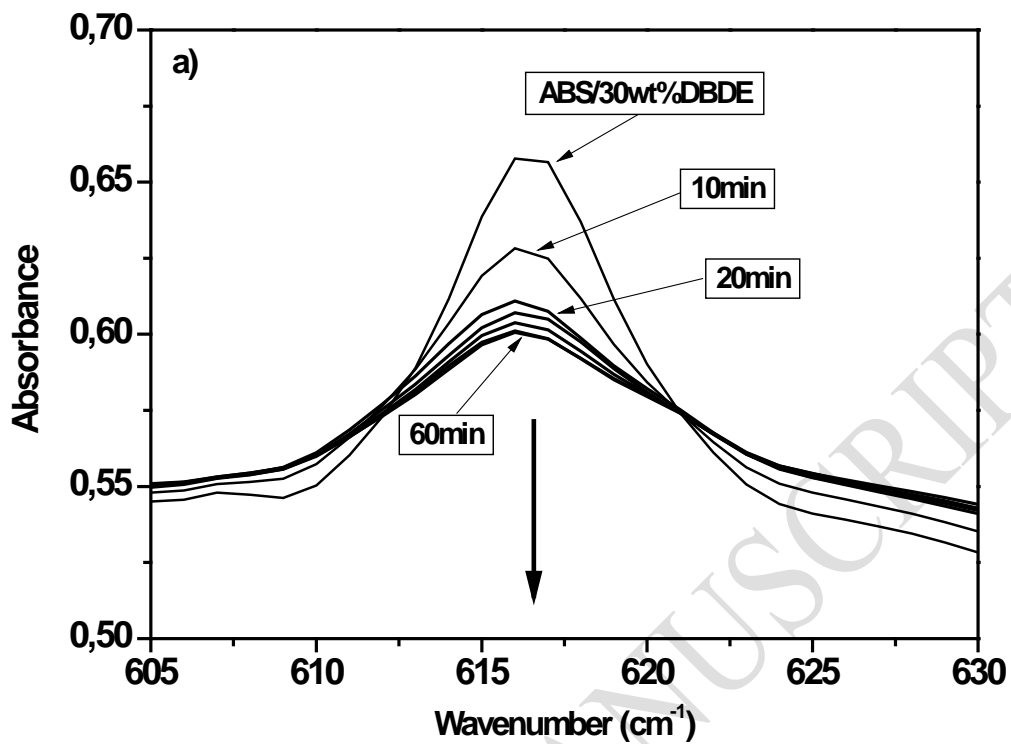
406 DBDE system subjected to radiative UV/Visible treatment as a function of irradiation time.



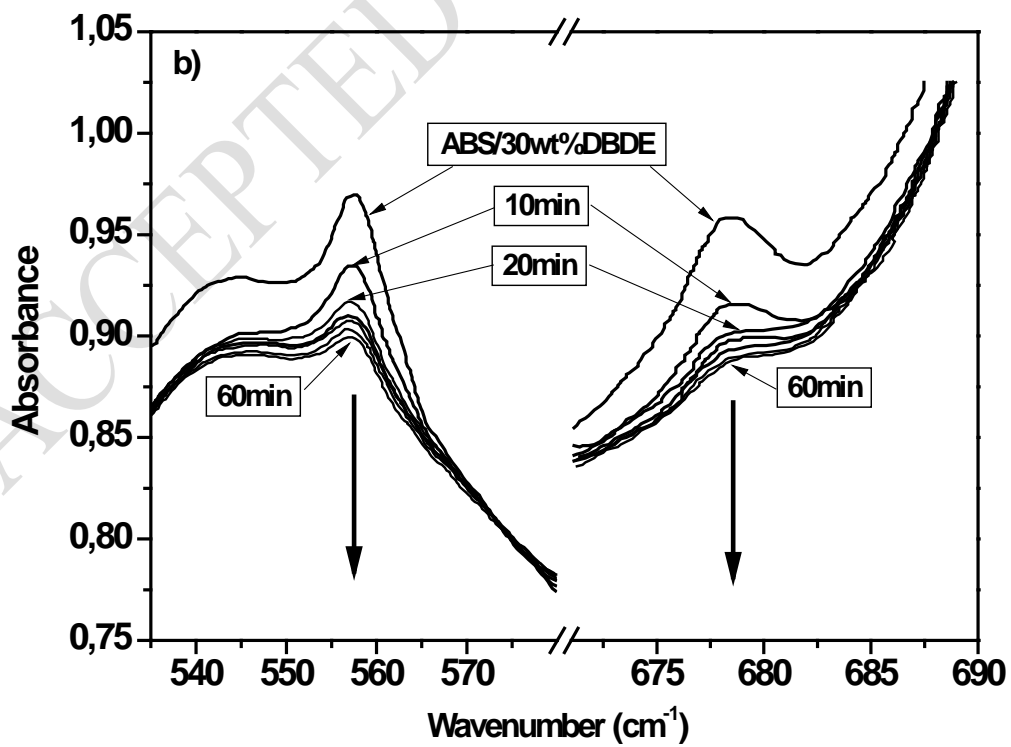
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408 Figure 4: FTIR spectra of ABS/30wt% DBDE as function of irradiation time by UV-visible

409 light, in the wavenumber range from 1076 cm^{-1} to 1088 cm^{-1} .

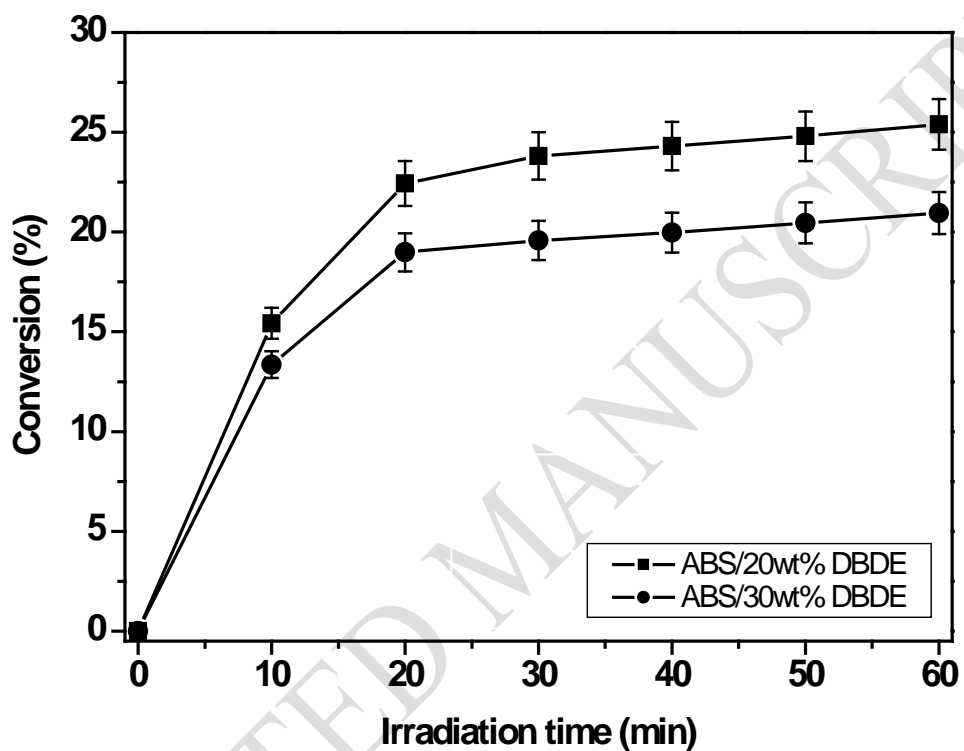


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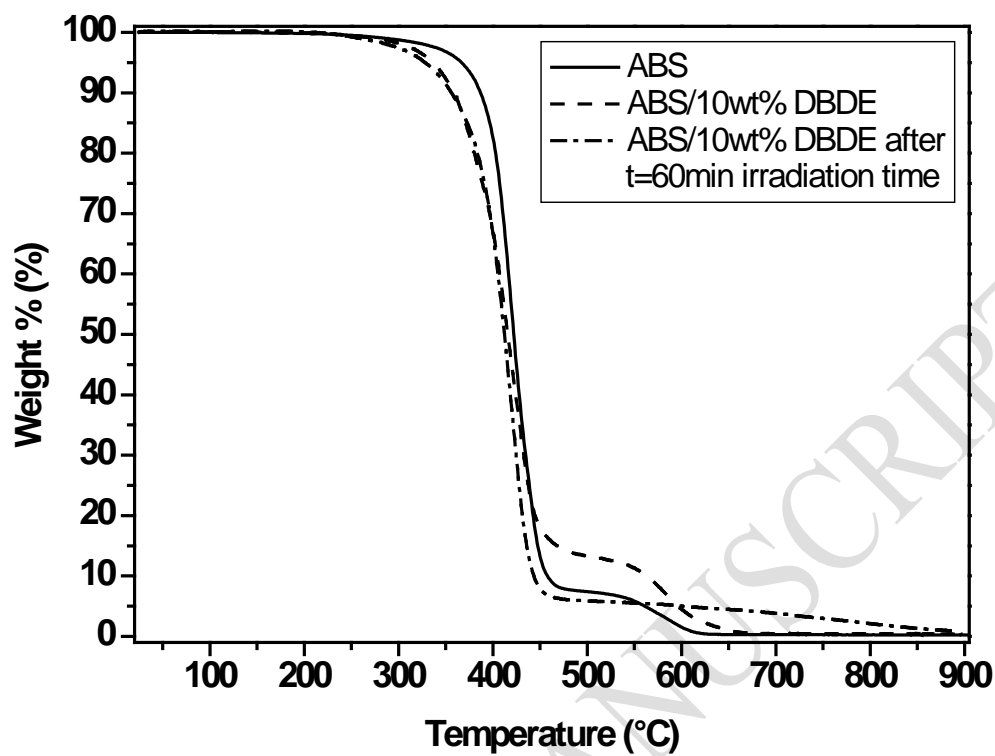


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412 Figure 5: Spectral evolution by FTIR of ABS/30wt% DBDE system during UV/Vis
413 irradiation, in the wavenumber range between a) 605-630 cm^{-1} and b) 535-580 cm^{-1} and 670-
414 690 cm^{-1}
415



416
417 Figure 6: Effect of the DBDE concentration in ABS/DBDE blends on the conversion values
418 of the photodegradation.
419



420

421 Figure 7: TGA thermograms of the pure ABS polymer and the ABS/10wt% DBDE system
422 recorded before and after UV-visible irradiation.

423