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### ► To cite this version:

Hussam Aldoori, Zohra Boubarka, Abdelouahab Nadim, Yassine Agguine, Said Eddarir, et al.. Photodegradation of Decabromo Diphenyl Ether Flame Retardant in Poly (Acrylonitrile Butadiene Styrene) (ABS). *Journal of Macromolecular Science Part B Physics*, 2020, *Journal of Macromolecular Science Part B Physics*, 59 (10), pp.609-620. <10.1080/00222348.2020.1763607>. <hal-03104368>

**HAL Id: hal-03104368**

**<https://lilloa.hal.science/hal-03104368v1>**

Submitted on 8 Jan 2021

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HAL Authorization

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2 **Photodegradation of Decabromo Diphenyl Ether Flame Retardant in Poly**  
3 **(Acrylonitrile Butadiene Styrene) (ABS)**  
4

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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), (C<sub>12</sub>Br<sub>12</sub>O), 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  $400\text{cm}^{-1}$  and  $4000\text{cm}^{-1}$   
144 was investigated. The number of accumulated scans was 16 with a spectral resolution of  
145  $4\text{cm}^{-1}$ . 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 $\mu$ 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 $^{\circ}$ C/min in the temperature range between 20 $^{\circ}$ C and  
154 900 $^{\circ}$ 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 $\text{cm}^{-1}$  as shown in Fig. 1a, ABS presents bands at 1453 $\text{cm}^{-1}$ , 1494 $\text{cm}^{-1}$   
161 and 1602 $\text{cm}^{-1}$ , 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 $\text{cm}^{-1}$  and 1370 $\text{cm}^{-1}$ , 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 $\text{cm}^{-1}$ . Some absorbance bands of ABS and DBDE appear rather close, such as the  
173 bands at 966 $\text{cm}^{-1}$  (C-H in trans-butadiene part of ABS [30]) and 960 $\text{cm}^{-1}$  (C-Br [29] in  
174 DBDE); 765 $\text{cm}^{-1}$  ( $\text{CH}_2$  in vinyl-butadiene and styrene part of ABS [28]) and 761 $\text{cm}^{-1}$  (C-C  
175 ring [31] in DBDE); and 699 $\text{cm}^{-1}$  (C-C ring [32]) and 708 $\text{cm}^{-1}$  (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 $\text{cm}^{-1}$  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 $\text{cm}^{-1}$ . 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 $\text{cm}^{-1}$  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  $\text{cm}^{-1}$ , 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 

198 In Fig. 5a one notices a strong reduction of the C-Br absorbance band situated at  $617\text{cm}^{-1}$ ,  
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  $678\text{cm}^{-1}$ , 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  $617\text{cm}^{-1}$ , 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  $1350\text{cm}^{-1}$  (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  $1350\text{cm}^{-1}$  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 

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 TiO<sub>2</sub>. 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

#### 259 **Acknowledgements**

260 This work was accomplished in the framework of an international research program. The  
261 authors gratefully acknowledge the support of the Algerian Ministry of Higher Education and  
262 Scientific Research, the University of Sciences and Technology of Oran/Algeria, the French  
263 Centre National de la Recherche Scientifique, and the University of Lille/France.

264

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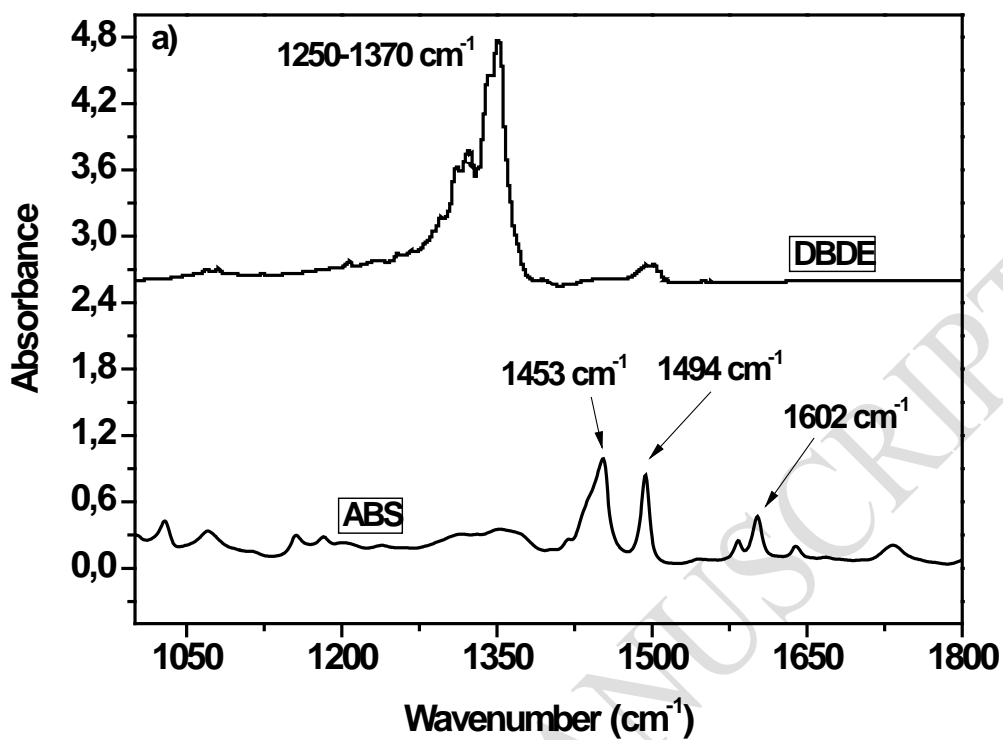
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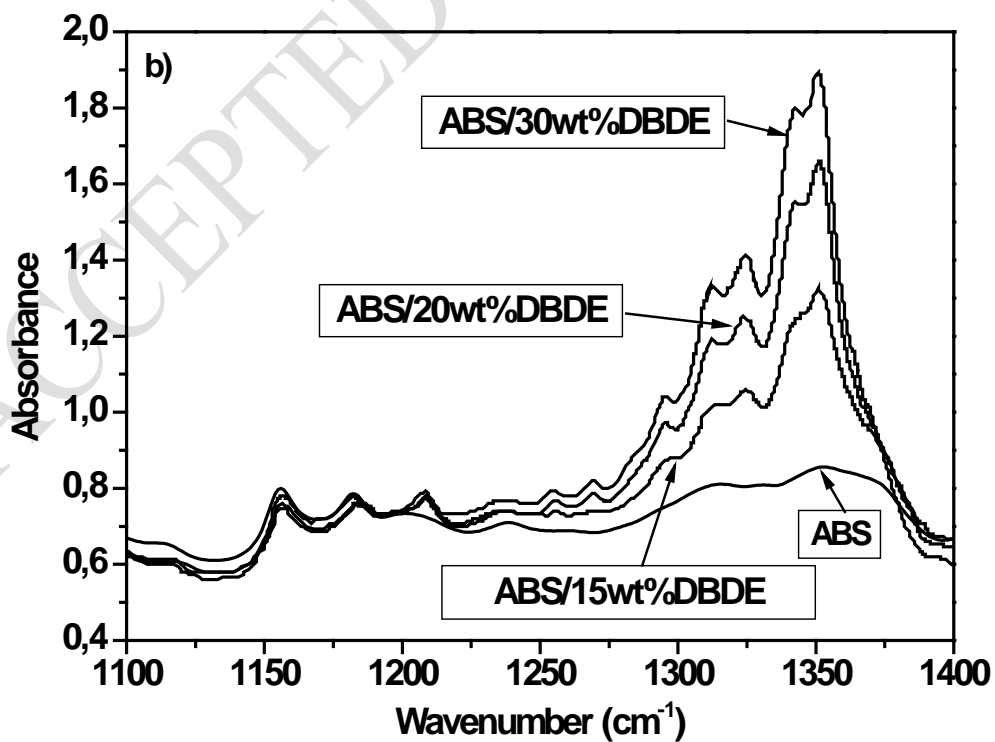
391 Disclosure statement. This is to acknowledge that no financial interest or benefit has arisen to  
392 the authors from the direct applications of the research presented in this paper.

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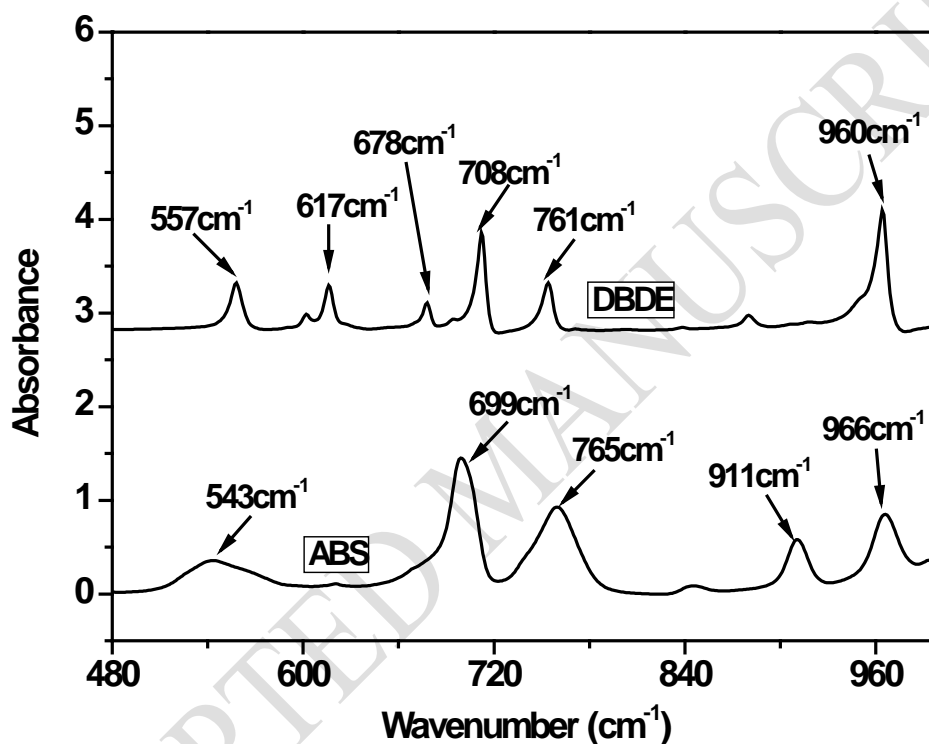
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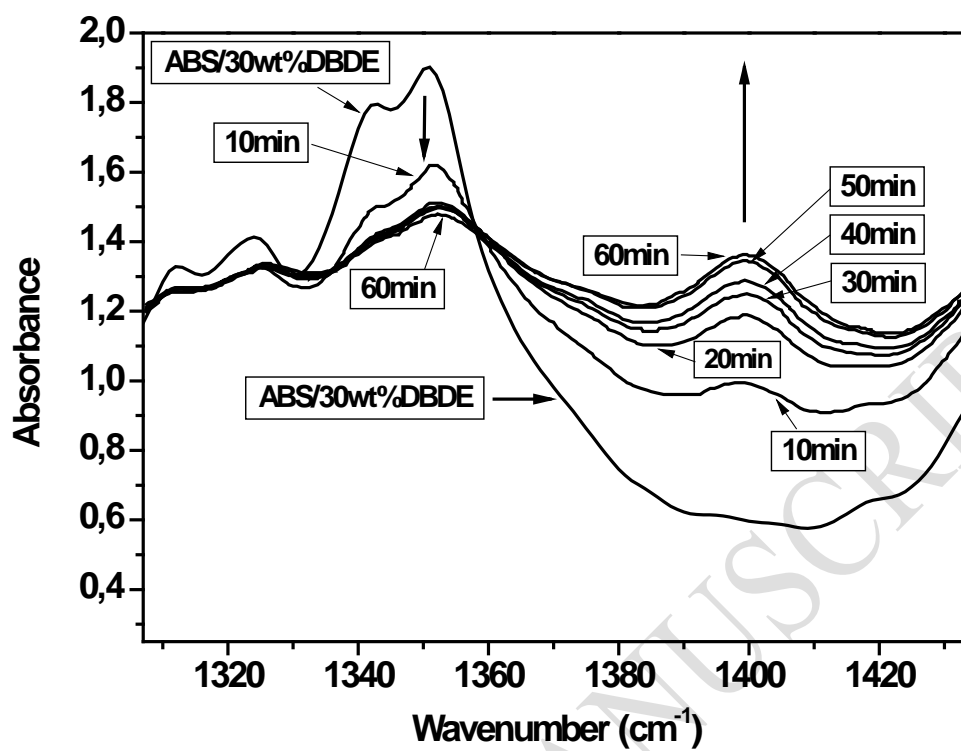
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397 Figure 1: a) FTIR spectra of DBDE, ABS, and ABS/DBDE mixtures in the wavenumber  
398 range between 1025 and 1800 $\text{cm}^{-1}$ . b) Evolution of the intensity of the ether group band of  
399 DBDE in ABS/DBDE mixtures with different amounts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



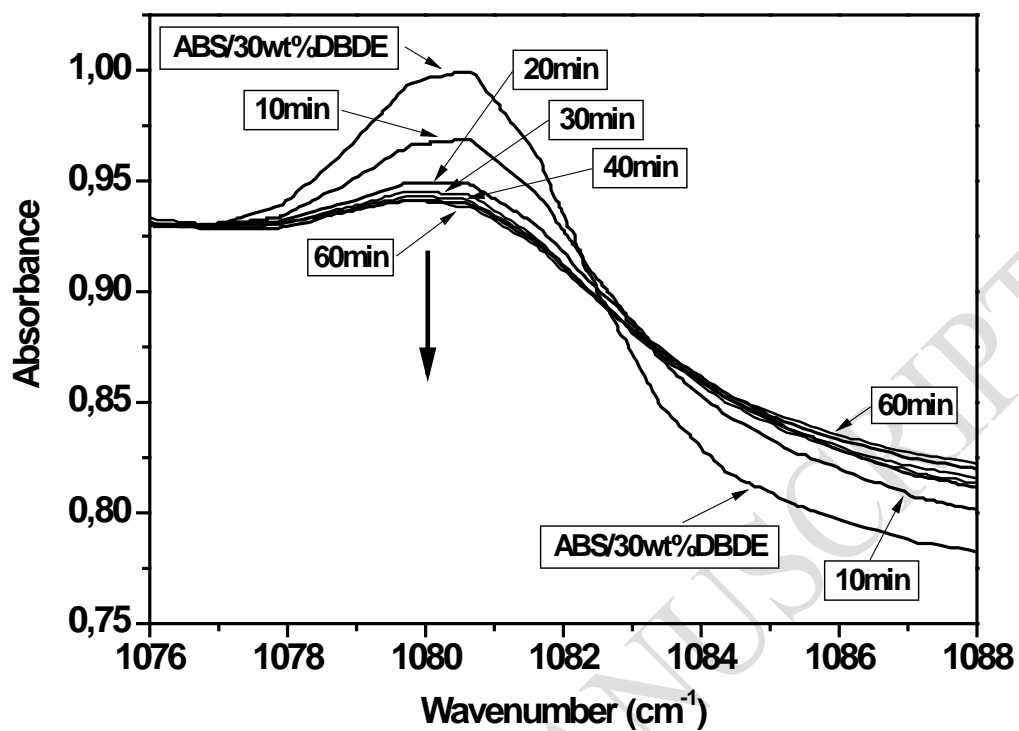
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402 Figure 2: FTIR spectra of DBDE and ABS in the wavenumber range between 480 and  
403 1000 $\text{cm}^{-1}$ .



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

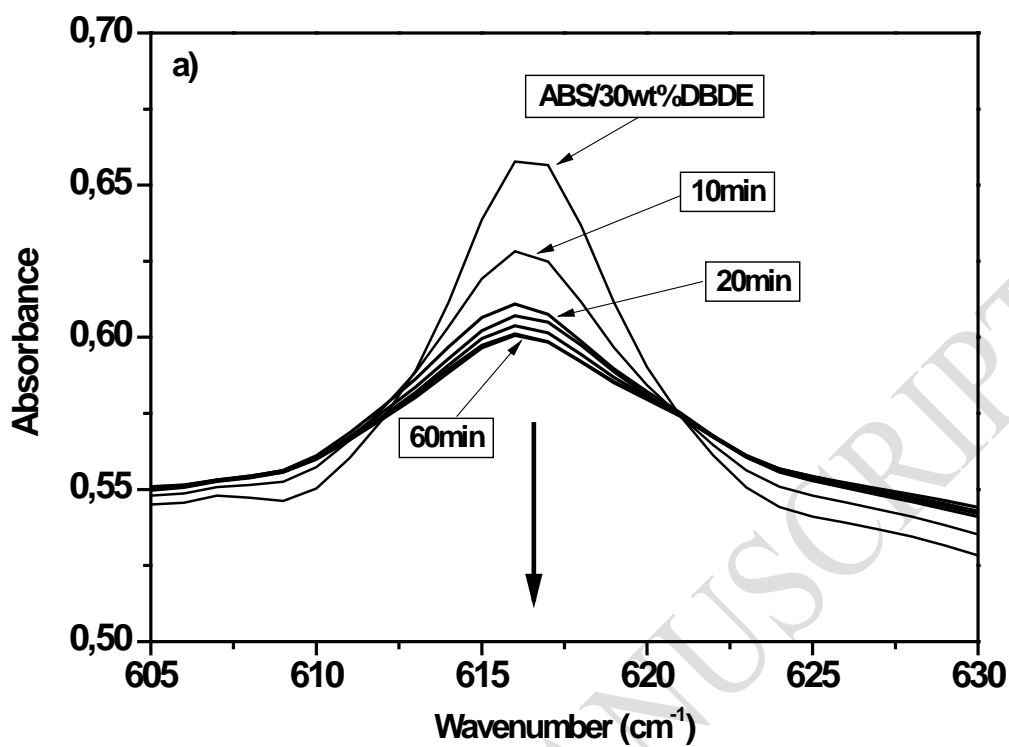
406 DBDE system subjected to radiative UV/Visible treatment as a function of irradiation time.



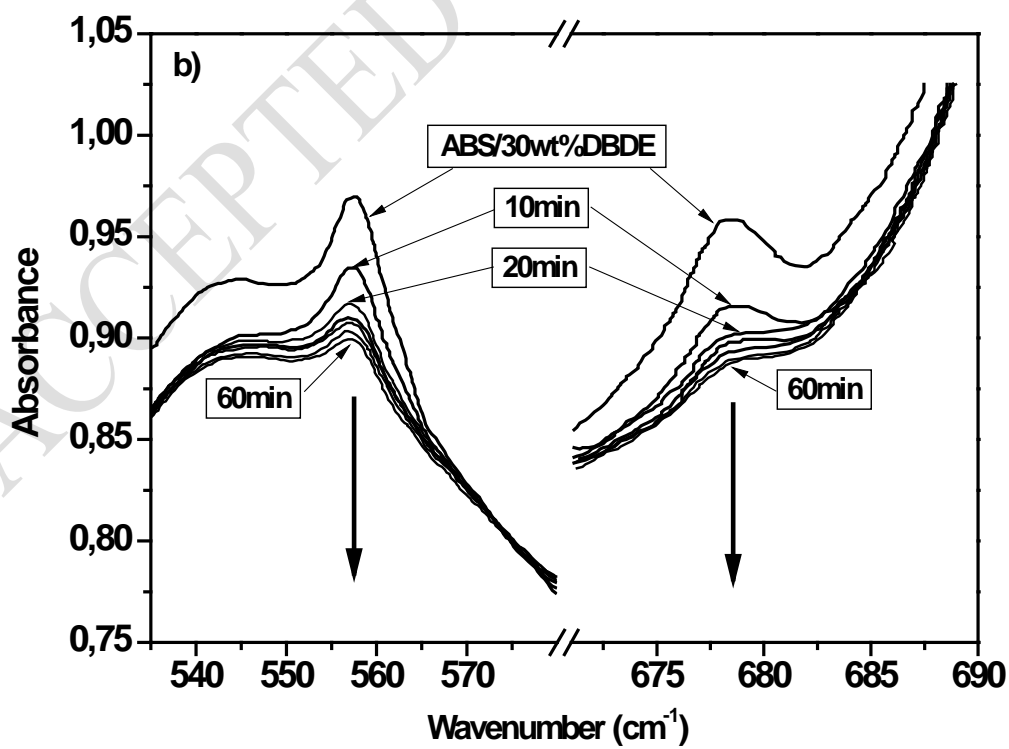
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408 Figure 4: FTIR spectra of ABS/30wt% DBDE as function of irradiation time by UV-visible

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

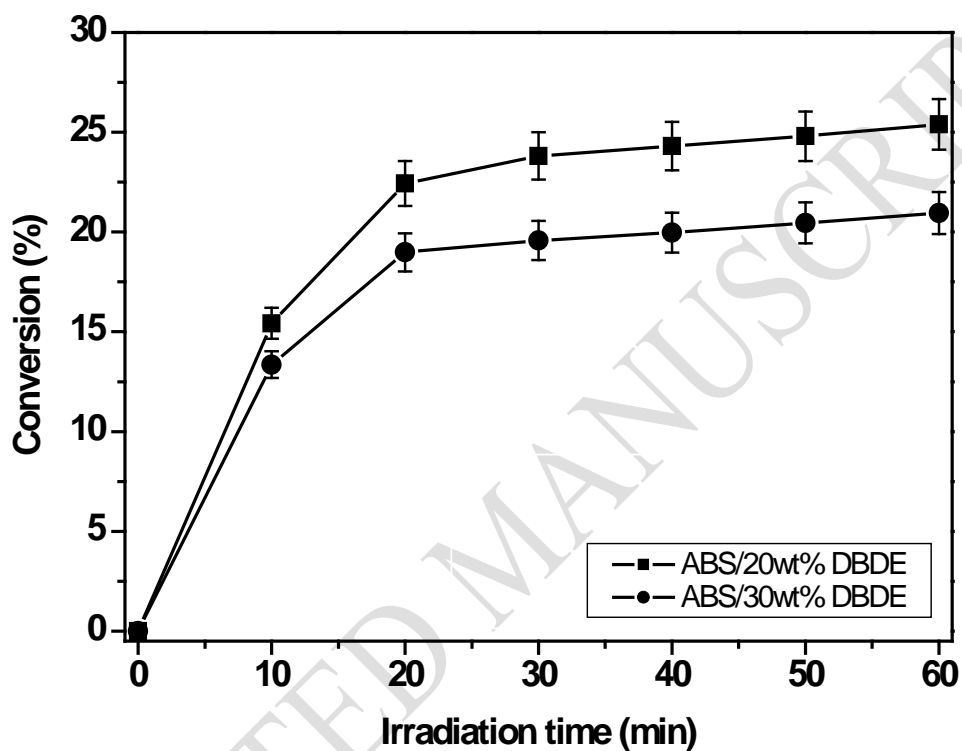


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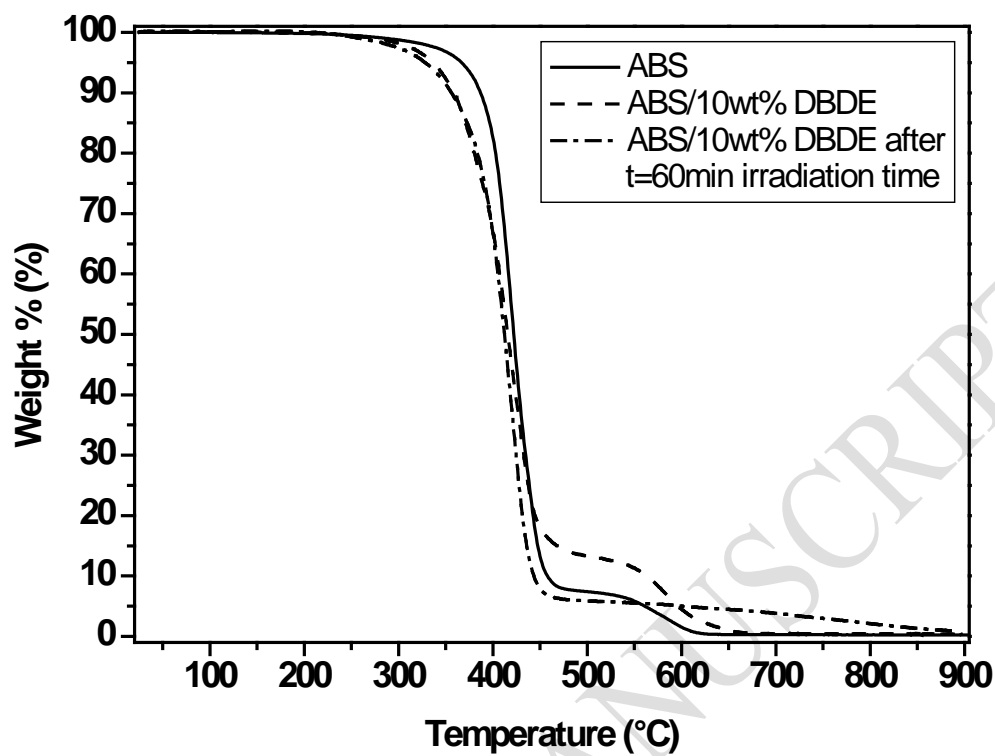


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412 Figure 5: Spectral evolution by FTIR of ABS/30wt% DBDE system during UV/Vis  
413 irradiation, in the wavenumber range between a) 605-630  $\text{cm}^{-1}$  and b) 535-580  $\text{cm}^{-1}$  and 670-  
414 690  $\text{cm}^{-1}$   
415



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