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

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Abstract

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

Keywords: Photolysis; Polybromodiphenylethers; acrylonitrile-butadiene-styrene; UV-visible radiation; Kinetics.

1. Introduction

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

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

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

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

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

2. Materials and Methods

2.1 Materials

DBDE (Saytex 102E, purity 98%, CAS: 1163-19-5), 2,2',3,3',4,4',5,5',6,6'-Decabromodiphenylether (BDE-209), ($C_{12}Br_{12}O$), was purchased from Albemarle Corp. (USA), it was a white to off-white powder.

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

2.2 Photolytic experiments

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

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

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

2.3 Physico-chemical analysis

2.3.1 Fourier transform infrared spectroscopy (FTIR)

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

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

2.3.2 Thermogravimetric analysis (TGA)

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

3. Results and discussion

3.1 Spectroscopic observations of the photolysis of ABS/DBDE

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

Insert Figure 1 here

Insert Figure 2 here

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

Insert Figure 3 here

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

Insert Figure 4 here

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

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

Insert Figure 5 here

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

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

Insert Figure 6 here

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

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

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

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

Insert Figure 7 here

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

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

4. Conclusions

A simple, effective method was presented to destroy DBDE molecules used as flame retardant and to obtain less harmful molecules in the environment. The proposed method comprises the photo-irradiation of ABS/DBDE mainly by visible light, without prior addition of additives such as oxidants or catalysts like TiO_2 . Two analytical methods were employed which were particularly suited for solid state characterization: Fourier transform infrared spectroscopy and thermogravimetical analysis. They allowed us to follow the photodegradation of model mixtures comprised of ABS and DBDE. The results indicated that DBDE could be effectively degraded to a considerable extent in the solid state during the recycling process by UV-Visible irradiation, while the ABS polymer kept its properties, and could thus be reused from brominated WEEE.

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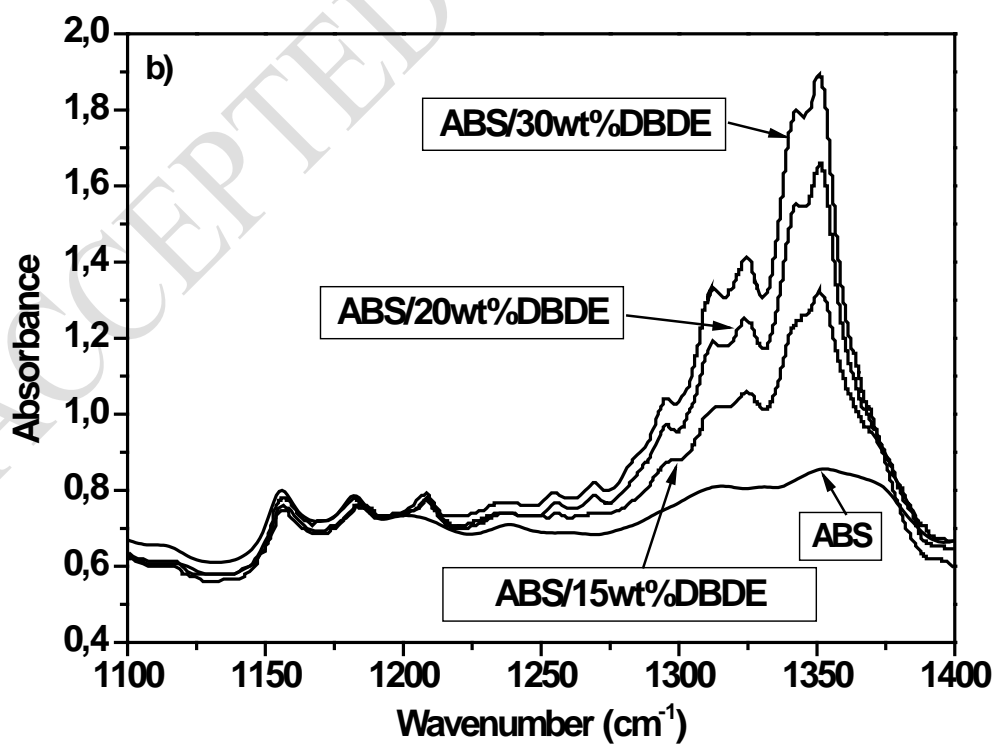
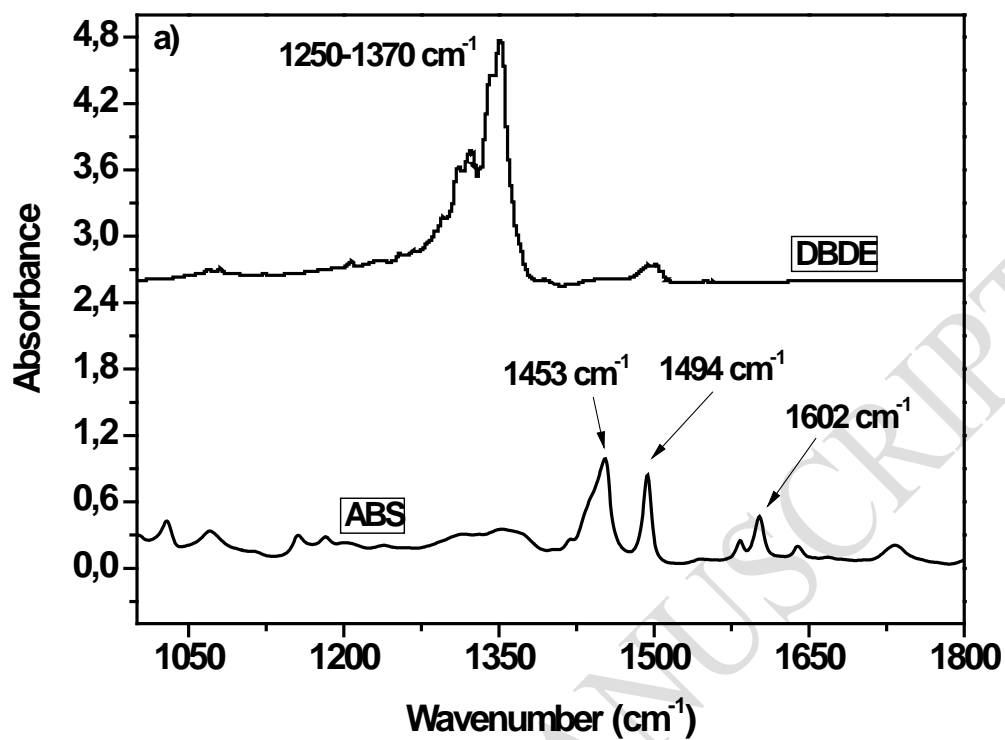
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391 Disclosure statement. This is to acknowledge that no financial interest or benefit has arisen to
392 the authors from the direct applications of the research presented in this paper.

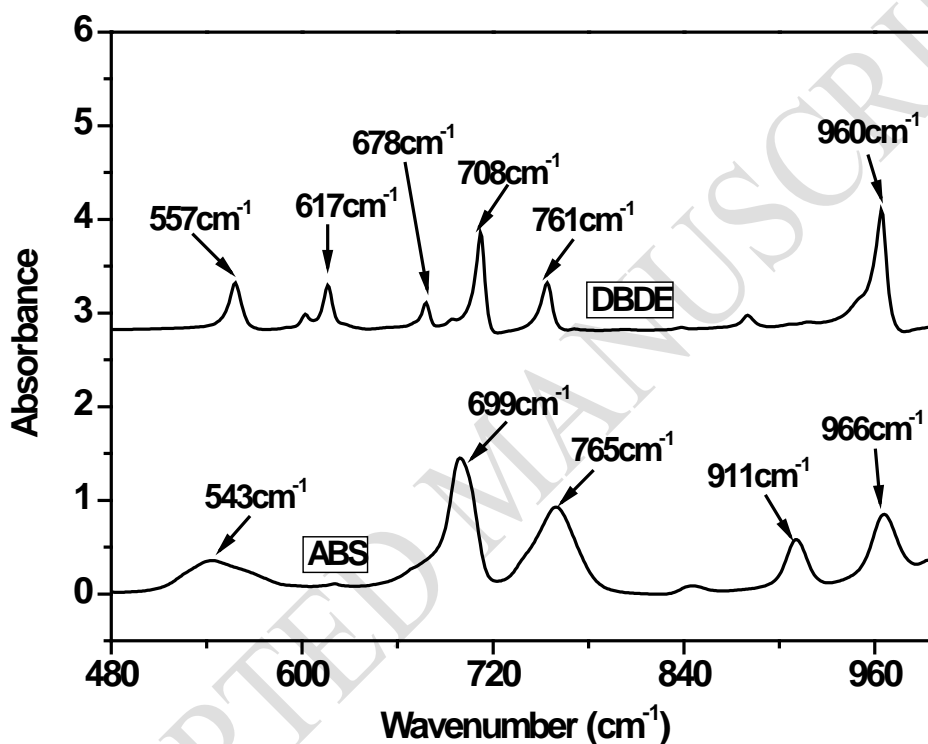
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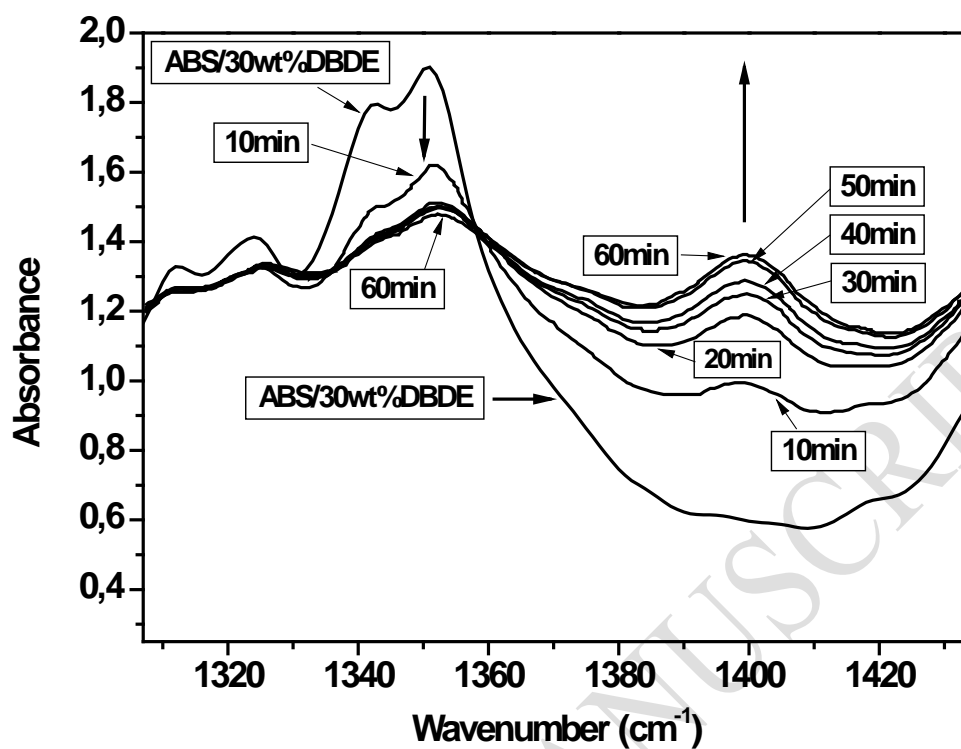


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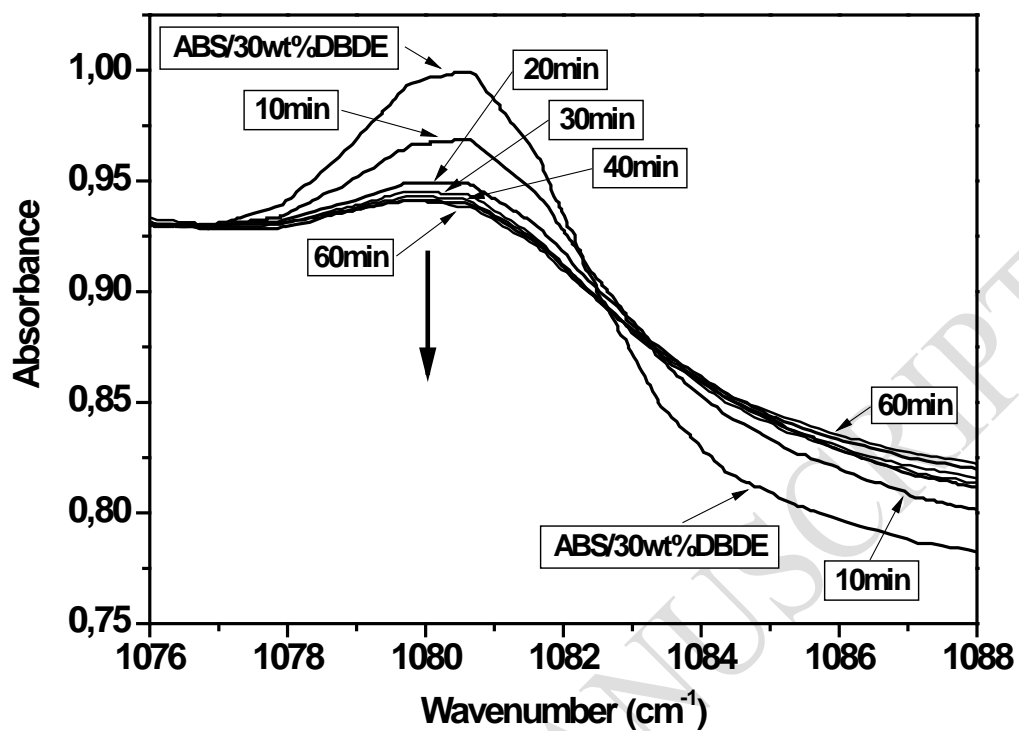
397 Figure 1: a) FTIR spectra of DBDE, ABS, and ABS/DBDE mixtures in the wavenumber
398 range between 1025 and 1800 cm^{-1} . b) Evolution of the intensity of the ether group band of
399 DBDE in ABS/DBDE mixtures with different amounts of DBDE (15wt%, 20wt% and
400 30wt%).



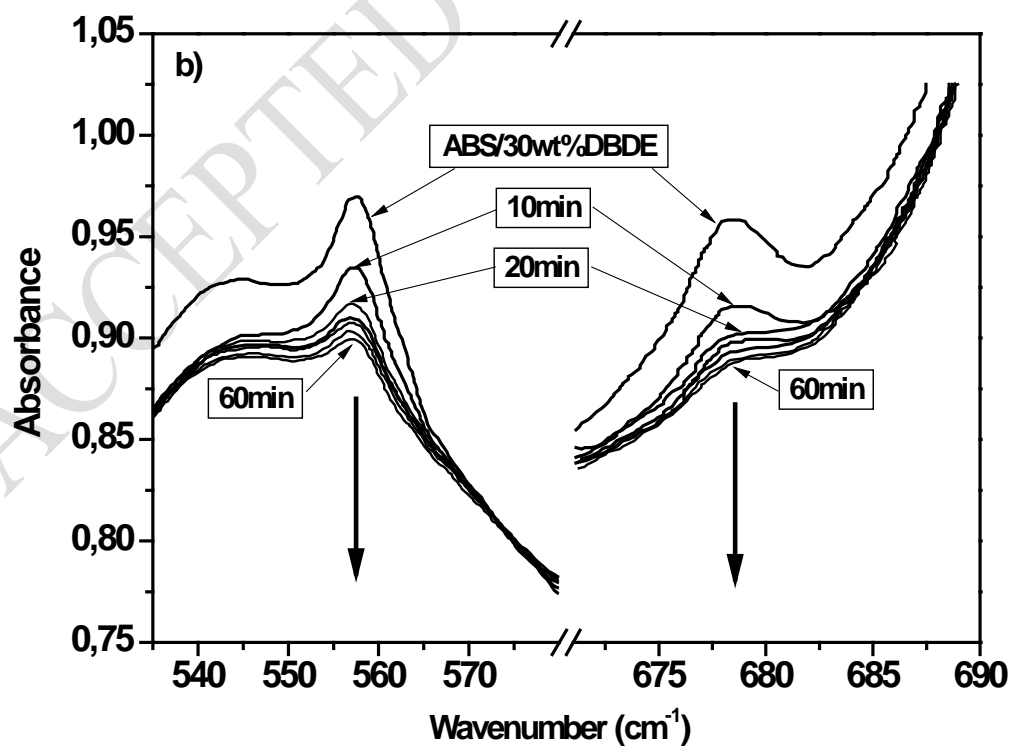
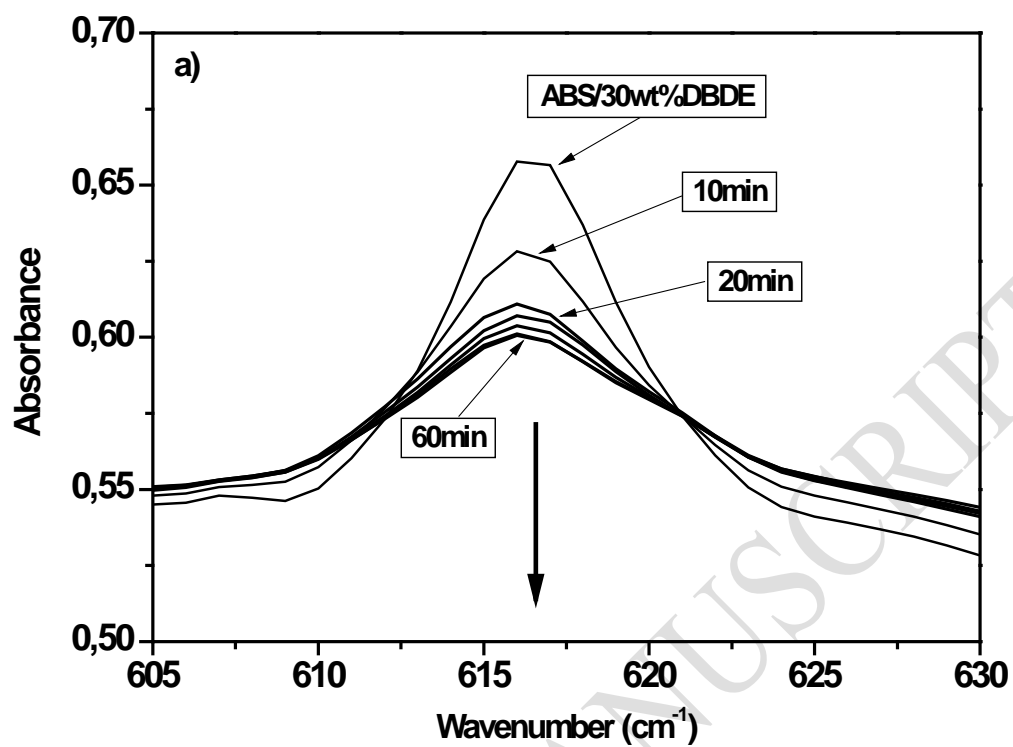
401
402 Figure 2: FTIR spectra of DBDE and ABS in the wavenumber range between 480 and
403 1000 cm^{-1} .



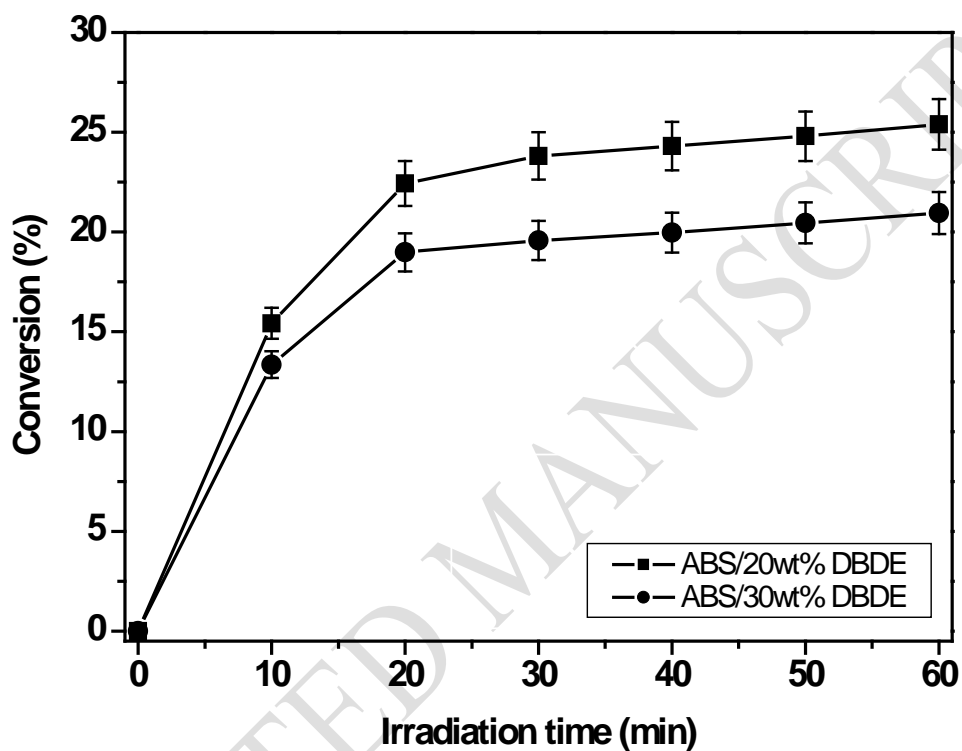
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 405 Figure 3: Evolution of the FTIR spectra between 1300 and 1450 cm^{-1} of the ABS/30wt-%
 406 DBDE system subjected to radiative UV/Visible treatment as a function of irradiation time.



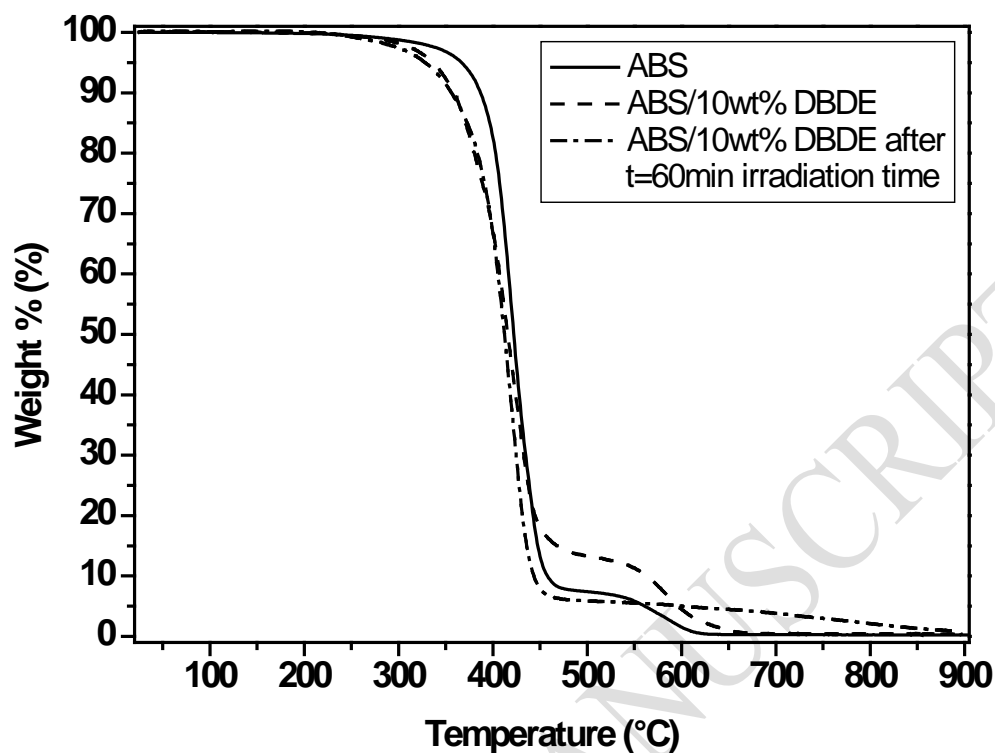
407
 408 Figure 4: FTIR spectra of ABS/30wt% DBDE as function of irradiation time by UV-visible
 409 light, in the wavenumber range from 1076 cm^{-1} to 1088 cm^{-1} .



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