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Effect of plasticization on the photodegradation of poly (para-methoxystyrene) films

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Abstract The influence of dibutyl phthalate, dioctyl phthalate, dimethyl terephthalate, diethyl terephthalate, and dioctyl terephthalate-plasticizers on poly (para-methoxy styrene) photodegradation was investigated by UV–vis, fluorescence, and FT-IR spectroscopic methods. The increase in irradiation time caused an increase in the absorption band of the polymer and an increase in the absorption of new band at longer wavelength, thus indicating a possibility of photodegradation of polymer films. The study on poly (para-methoxy styrene) photodegradation was also compared to varying phthalate and terephthalate plasticizers in order to provide an understanding of its photodegradation vis the presence of phthalates and terephthalates plasticizers. The decrease in the excimer fluorescence upon the increase in the time of exposure to UV-radiation provides an evidence for the degradation of polymeric chains through a chin scission processes. The increase in the photodegradation of the polymer increased with the increase in the bulkiness of added plasticizer molecule. IR-spectra of irradiated pure and blended polymer films indicated that the photodegradation of the polymer occurred, by the formation of new absorption bands, and the increase in the intensity of other bands.

Introduction

Polystyrene (PS) is very important polymer that has many excellent properties such as high electrical resistance, and good mechanical properties under various conditions. However, since PS degrades easily at high temperature and upon exposures to light, the needs of preparing new polystyrene derivatives to improve the thermal- and photostabilization is of a greater interest. Some of the works that are interested in this area is the use of stabilizers and plasticizers that can cause less degradation to the polymer upon exposure to thermal and light energies, as well as the improvement of mechanical properties of the polymer [1–4].

The photodegradation of polystyrene [2–6] and substituted polystyrene [7, 8] have been extensively studied by both theoretical and experimental approaches. The results obtained for photodegradation of polystyrene indicate that these processes are more complicated than what has been predicted by theoretical aspects [3]. The difficulties in presenting a satisfactory mechanism for photodegradation of polystyrene can be attributed to the fact that the mechanism of degradation differs in terms of structure and state of the polymer.

The mechanism of interaction of photon energy with polymeric chromophores involves complex physical and chemical reactions. The photodegradation is triggered by the formation of free radicals by UV-irradiation. The photon energies associated with the light absorbed at UV-region are sufficient to break many of the chemical bonds present in the polymeric chains. Therefore, the main processes which arise from photo-irradiation are chain scission, cross-linking, and photo-oxidation [9]. Photodegradation of polymers, on the other hand, is in most cases initiated by abnormal groups, which can be introduced into polymer backbone during their manufactures. Such structures as initiator fragments, chain branching points, peroxy, and carbonyl groups are present in polymer backbone in very low concentrations. Some of these groups do not directly weaken the polymer chain but provide

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initiation points for peroxidation by atmospheric oxygen. The formed peroxy and hydroperoxy groups are truly weak links, and their radical decomposition products initiate photodegradation processes [1, 10].

Many investigations concerned with the degradation of PS [11–15] and substituted polystyrene [16–18], showed that most of substituted polystyrene are more easily photodegradable than PS, owing to the relatively weak bonds in substituted polystyrene. Recently, studies of thermal degradation of ring-substituted polystyrene have showed that degradation characteristics are sensitive to ring substitution, in particular, electron-withdrawing groups (Cl, and Br) that tend to reduce the thermal stability, largely by producing depolymerization radicals [15, 19].

A previous study on the photodegradation of substituted polystyrene in solution, showed a new fluorescence bands at longer wavelength, which may indicate new products formed as a result of photodegradation [20]. The formation of hydro peroxides, as primary photoproducts, is well established. Several types of secondary reactions are reported to involve direct photolysis, decomposition by energy transfer, and intermolecular decomposition which might lead to the formation of carbonyl and hydroxyl compounds [21–23]. Numerous structures have been reported on the bases of IR and visible analysis [24–26]. Among these structures are aromatic ketones formed by decomposition of tertiary hydroperoxide [27]. Aliphatic ketones have also been reported, as they would be formed by oxidation of the secondary carbon atom on the polymeric backbone. Oxidation of the aromatic ring has been also postulated to lead to the formations of aldehyde type structures [3, 27]. However, the main evidence for the formation of these photo products is the position of the IR absorption maxima in the C=O domain [25].

The purpose of the present work is thus to study the effect of added phthalate and terephthalate plasticizers on the photodegradation of pure and blended poly (*para*-methoxystyrene) (PMXS) in solid films. Plasticization with terephthalate showed a lower degradation towards UV-irradiation in comparison with that of phthalate plasticizers. The effects of UV-irradiation on plasticized and non-plasticized PMXS solid films were followed by absorption, fluorescence, and FT-IR spectroscopic techniques.

Experimental

Materials

The sample of poly (*para*-methoxystyrene) (PMXS) was supplied by Across-Organics with high-purity, and with ($M_W = 24{,}900$). Only spectroscopic grade dichloroethane (DCE) was used in preparation of solid films, and found to give no detectable absorption in range 250–400 nm. It was purchased from Fluka GMBH and used as received. The used plasticizes are dimethyl terephthalate (DMT), diethyl terephthalate (DET), dioctyl terephthalate (DOT), dibutyl phthalate (DBP), and dioctyl phthalate (DOP). These were of high-purity of about 99.8%, and were purchased from Across-Organics. All used plasticizers were found to have no absorption in the region of absorption or emission of poly (para-methoxystyrene) of 260–500 nm.

Preparation of plasticized polymeric solid films

PMXS thin films with thickness of approximately 0.02 mm were prepared by solution casting of 20 wt% polymer in DCE on a spectroscopic window (quartz plate of 1.0 mm × 20 mm diameter). Also 0.02 mm thick PMXS-plasticizer films, with different wt% plasticizers were prepared by solution casting a 20 wt% polymer in DCE solvent. These films were used to get better insight into the possibility of photodegradation of the polymer during irradiation. The films were dried in a vacuum oven at 300 K for 6 h, to ensure the complete removal of solvent traces [18].

Irradiation of solid films

Polymeric solid films were exposed to UV-radiation for different intervals of time, from (0.0–4.0 h), using a JASCO spectrometer with a built in Hydrogen-Xenon lamp (6808-J007A model number ESC-333), supported with monochromator of holographic grating with 1,800 groves/mm. The irradiations of solid films were carried out in thermostated solid sample holder in presence of air, and at 298 K. A 265 nm monochromatic light was selected for irradiation of solid films, with intensity of 4.9 mW/cm^2. Each polymeric film was exposed to UV-irradiation for different intervals of time.

Fluorescence measurements

Fluorescence spectra were recorded on JASCO-FP 6500 spectrofluorometer for each of the prepared films. All measurements were preformed under the same conditions of temperature, and excitation and emission slits width to avoid any influence on the physico-chemical properties of PMXS films. The excitation wavelength was 265 nm, and the emission wavelength range was 270–500 nm. All fluorescence spectra were obtained by using a thermostated solid sample holder.

UV-absorption spectra measurements

The UV-absorption spectra for PMXS solid films were recorded before and immediately after the exposure to

UV-irradiation, with a Cary 100 Bio UV–visible Spectrophotometer.

Measurements of FT-IR-spectra

For IR-measurements, polymer solid samples were irradiated for different intervals of time; then the IR-spectra were recorded for the irradiated and non-irradiated polymer films on a KBr disk on NICOLET-MAGNA-IR-560-Spectrometer.

Results and discussion

Absorption spectra of plasticized and non-plasticized PMXS solid films

The effects of UV-light irradiations on the efficiency of photochemical processes in films of pure PMXS, as well as in films with wt% of (1–4%) of added phthalates and terephthalate plasticizers were studied by measuring their absorption spectra. The analysis of UV-absorption spectra of non-irradiated and irradiated PMXS films, as presented in Fig. 1, has shown that during the exposure of pure PMXS solid films to UV-radiation for different intervals of time at 265 nm, a small increase in the intensity of the absorption band took place with the increase in irradiation time.

It was found that short-wavelength UV has sufficient energy to cleave the bonds in the polymeric chains with the production of free radicals. The produced radicals can initiate further reactions with molecular oxygen, which result in the splitting of the molecular chains, and producing new fragments. Irradiated plasticized PMXS solid films had also shown a higher increase in the intensity of the absorption spectra, and a change in the structure of the absorption band, with the increase in irradiation time. It was reported that the UV-spectra of irradiated PS containing additives, displayed an increase in the intensity of absorption at 310 nm region, and was chosen as a measure of the photodegradation of PS solid films [28]. This effect was attributed to the formation of a carbonyl group adjacent to phenyl group of PS. The presence of plasticizer molecules in the blended PMXS film also increased the absorption intensity and change in the structure of the absorption band, as presented in Fig. 2.

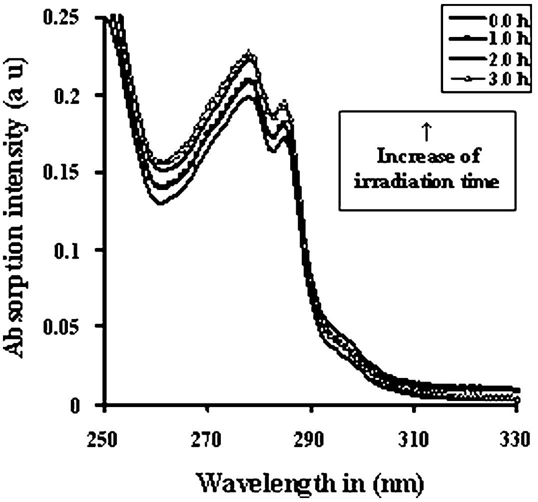

Fig. 1 Absorption spectra of irradiated and non-irradiated PMXS films, at irradiation time of 0.0, 1.0, 2.0, and 3.0 h (from bottom to top), ($\lambda_{\text{ext}} = 265$ nm)

The presence of oxygen distinctly increased the efficiency of absorption and accelerated the photo-oxidation of polymeric chains, which led to the formation of macroradical species [29]. Radicals thus formed may recombine to give conjugated π-electron system. The conjugated species are usually presumed to be poly phenyl cross-linked products, which result from phenyl radical recombination after direct bond scissions [30]. As can be seen in Fig. 2, a new absorption band at about 290 nm is noticed, where its intensity increases by the increase in the mass percent of added dimethyl terephthalate plasticizer. The formation of such new absorption band may be attributed to the formation of low-molar mass products, as a result of the reaction between radicals through abstracting hydrogen atoms of the methylene groups in irradiated PMXS film. This suggests that added plasticizers alter both the photochemical stability of PMXS and the process which led to the increase of absorption, such as photodegradation (with scission of bonds in the polymer chains) or photo-transformation (with changes in the conformation of DMT molecules). Moreover, the increase of absorption of irradiated DMT doped PMXS films, and the increase in the intensity of the absorption band at 290 nm, suggest that

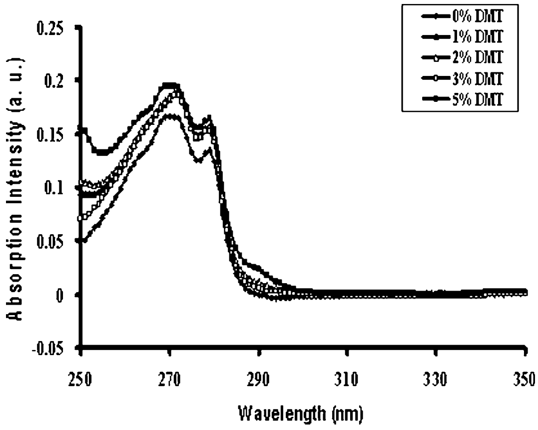

Fig. 2 UV-absorption spectra of PMXS films irradiated at 2.0 h as function of added DMT plasticizer (from bottom to top)

photo-oxidation and photodegradation processes are the main dominating processes in the irradiated polymer.

Irradiation time effect on the quenching of excimer fluorescence of PMXS solid films

A number of studies have provided information about photodegradation of *para*-substituted polystyrenes in solid films [31–33] and in solutions [20]. Therefore, the effect of irradiation on the degradation of PMXS has been examined by fluorescence technique. The fluorescence spectra were obtained for PMXS films, photo-irradiated in the presence of air as well as the non-irradiated polymer solid film at 265 nm, and are presented in Fig. 3.

In a recent work [34], PMXS gave strong excimer fluorescence band centered at about 324 nm, and gave relatively very weak monomer fluorescence band in solid films, as only the polymer chromophores absorb in the region 260–295 nm. Irradiation of the polymeric film at different exposure time was accompanied by the gradual decrease in excimer emission band. However, the excimer fluorescence band shifts from 324 nm to about 329 nm when solid films of PMXS were irradiated for 0–80 min. It seems that the quenching of excimer emission of the irradiated films occurs as a result of photo-oxidation and photodegradation of polymeric chains. The band shift can be explained by the formation of the conjugated double bonds during the photodegradation by hydrogen abstraction process [34, 35]. The shift in emission band of irradiated PMXS films is in good agreement with that reported with irradiated polystyrene and poly (vinyl chloride) solid films [36]. Tovborg and Kops [37] pointed out that quenching of polymeric emission might be attributed to the energy transportation of the oxides formed by the photo-oxidation of UV-radiation. Wu et al. [38] also studied the photo-oxidation of polystyrene by fluorescence spectra and proposed that the quenching of polystyrene fluorescence was attributed to the quenching effect of the peroxides formed during UV-irradiation.

Irradiation time effect on excimer fluorescence of plasticized PMXS solid films

The effect of UV-irradiation on degradation of polystyrene and substituted polystyrenes receives a considerable attention, mainly due to their industrial importance [7, 8]. However, the photodegradation of some substituted polystyrenes has been studied extensively but no work on photodegradation of plasticized PMXS has been reported. The presence of plasticizers in solid films of PMXS would result in quenching of both monomer and excimer emissions and in increasing the fluorescence intensity of a longer range band of the exciplex emission [35]. The latter was increased as the amount of added plasticizer increases; no attempt was made to study the irradiation effect on the degradation of PMXS in the presence and absence of plasticizers [34]. For all the quenching processes, there was no change in the shape of the fluorescence spectra, or change in the absorption spectra of PMXS-quencher system, even with high concentration of added plasticizers, as seen in Fig. 4.

In an earlier study, it was found that the absorption spectra for PMXS containing a verity of DOT plasticizer showed that at excitation wavelength of 265 nm, DOT molecules do not absorb and only the PMXS chromophores are excited [35]. The absence of any change in the position of the absorption spectra, or the formation of a new absorption band at longer wavelength indicated the absence of a ground state complex formation [35]. The irradiation time effect on fluorescence quenching of blended PMXS with 4.0% of DMT is shown in Fig. 5.

As can be noticed in Fig. 5, the band centered at 324 nm is representing the excimer fluorescence, where the band at

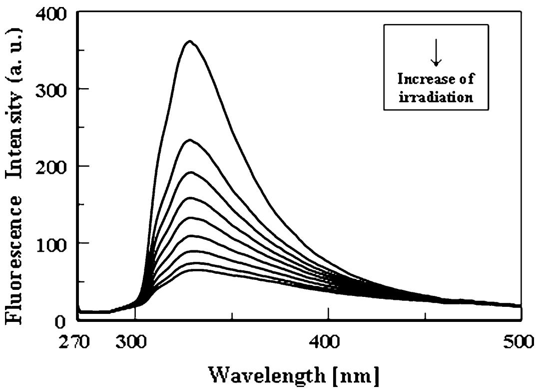

Fig. 3 Fluorescence spectra of PMXS films as a function of UV-aerated exposure time at $\lambda_{ext} = 265$ nm (Irradiation time for spectra from top to bottom, at 0.0, 10, 20, 30, 40, 50, 60, 70, and 80 min)

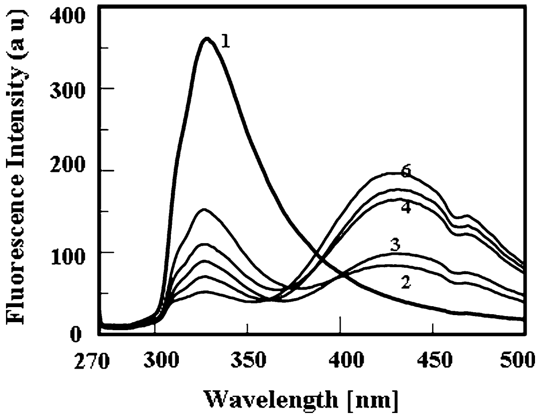

Fig. 4 Steady-state fluorescence quenching of PMXS by DOT in solid films. The mass% of added DOT are: (1) 0.0%, (2) 1.0%, (3) 2.0%, (4) 3.0%, (5) 6.0%, and (6) 8.0%, at $\lambda_{ext} = 265$ nm

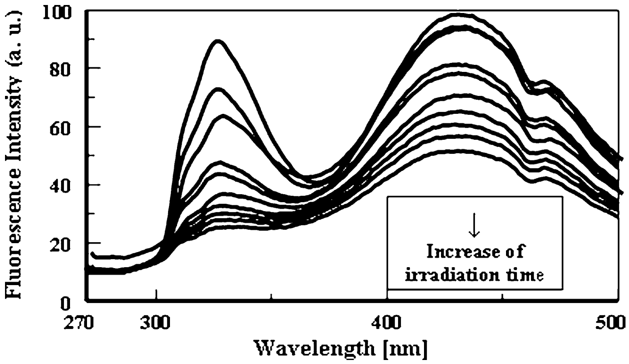

Fig. 5 Fluorescence spectra of PMXS films plasticized with 4.0% DMT at irradiation time of 0.0, 10, 20, 30, 40, 50, 60, 70, 80, and 90 min

429 nm is representing the exciplex fluorescence. Although no isopiestic point was observed, both excimer and exciplex emissions were quenched by irradiation of plasticized PMXS solid films at different intervals of exposure time. We also observed a small red shift in the excimer fluorescence band during irradiation of polymeric films. The efficiency of fluorescence quenching with irradiation time for the non-plasticized PMXS showed a larger value than that found for plasticized polymer. Hence, increasing the time of irradiation of blended PMXS showed a smaller decrease in the intensity of both excimer and exciplex emissions in solid films, as can be seen from Fig. 5. This indicates that the irradiated polymer chains may well undergo photo-oxidation, as well as chain scission, which lead to a reduction in the intensity of both emissions with the increase in time of irradiation.

The comparison of the quenching efficiencies of blended PMXS with different mass percent of DMT to that of pure PMXS films is shown in Fig. 6.

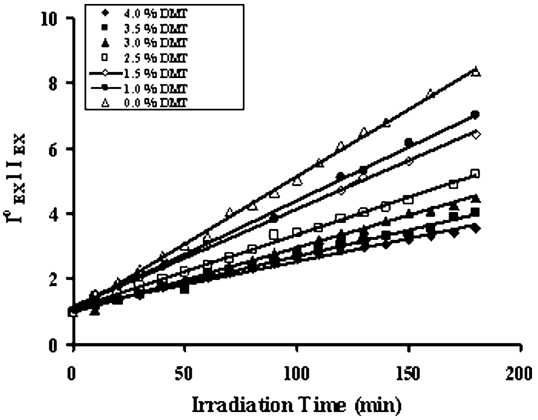

Fig. 6 Effect of plasticizer concentrations of DMT on fluorescence quenching of PMXS films at different irradiation time at ($\lambda_{\text{ext}} = 265$ nm)

Table 1 Effect of amount of added DMT on the efficiency of excimer fluorescence quenching of PMXS films

$\lambda_{(\text{emis})}$ (nm) (max)	DMT-plasticizer (%)	Time (min)	$\left(I^{\circ}_{\text{EX}}/I_{\text{EX}}\right)$ Irradiated	k_{PQ}
327	0.0	120	8.34	0.041
327	1.0	120	6.99	0.033
328	1.5	120	6.46	0.029
329	2.5	120	5.20	0.022
329	3.0	120	4.45	0.019
330	3.5	120	4.02	0.016
331	4.0	120	3.56	0.013

It was reported that blending of PS with other polymers or with stabilizers and plasticizers may offer opportunities to improve stability, and reduce brittleness of the polymer. So far, many PS blends containing poly (vinyl acetate) have been reported [1, 38]. It was found that the processes of photo-oxidation and photodegradation were accelerated in blends compared to pure PS.

As is evident in Fig. 6 and Table 1, the ratio of $\left(I^{\circ}_{\text{EX}}/I_{\text{EX}}\right)$ decreases with the increase in the amount of added DMT plasticizer, and also increases with the increase in the time of irradiation, where I°_{EX} is the intensity of excimer emission of unirradiated doped or pure polymer film, and I_{EX} is the intensity of excimer emission of doped or pure polymer film after exposure to different interval of time. It was found that excimer fluorescence of PMXS solid films was readily quenched in the presence of ground state plasticizer molecules, and increased with the increase in added plasticizer [35]. The efficiency of the fluorescence photo-quenching rate constant k_{PQ} was found to decrease with the increase in added amount of plasticizers and with the increase in time of irradiation. It has been reported that the photo-stability of PS was reduced by the addition of polymeric additives, which depends on the chemical structure of the additive [28]. Chain scissions and changes in the molecular weight distribution were the main reactions resulted from the photo-oxidation of irradiated plasticized PS films [3]. It was also found that the increase in the bulkiness of the additives increases the fluorescence quenching efficiency as seen in Fig. 7.

The comparison of the change of the ratio of $\left(I^{\circ}_{\text{EX}}/I_{\text{EX}}\right)$ for pure PMXS film to that of blended PMXS with 4.0% by mass of DMT, DET, DOT, DBP, and DOP is shown in Fig. 8.

In general, blended PMXS films with phthalates plasticizers gave higher fluorescence quenching efficiencies than that obtained with unblended polymer, while blended PMXS films with terephthalates plasticizers gave lower fluorescence quenching efficiencies than that obtained with unblended polymer. The presence of plasticizer molecules

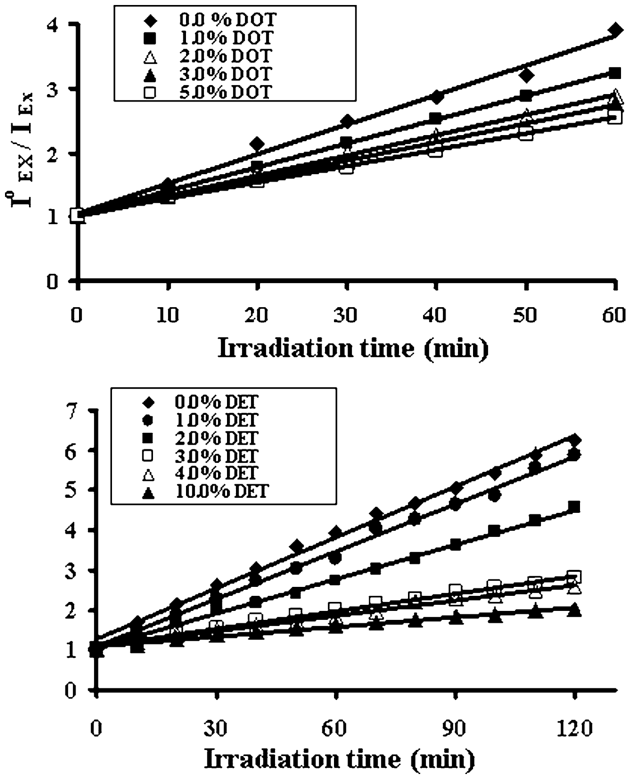

Fig. 7 Effect of added mass percent of (**a**) DET, and (**b**) DOT on fluorescence quenching of PMXS films at different irradiation time at ($\lambda_{ext} = 265$ nm)

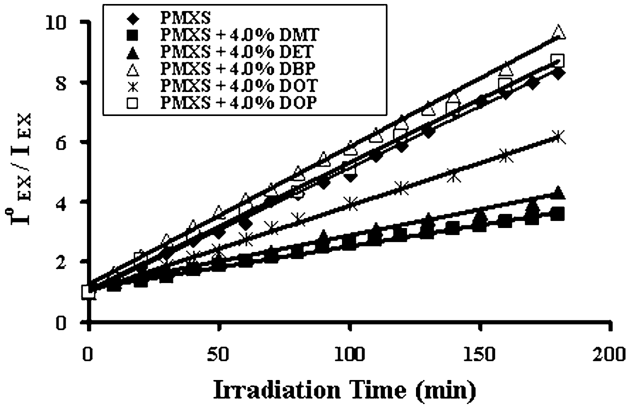

Fig. 8 Effect of plasticizers molar mass on fluorescence photo-quenching of PMXS films at different intervals of exposure time, ($\lambda_{ext} = 265$ nm)

in the polymer matrix was found to cause a lowering in the activation energy during the thermal degradation of PMXS films [16]. It was attributed to the lowering in the charge transfer character of the excimer conformation. As can be seen from Fig. 8, the photo-quenching of excimer fluorescence was increased with the increase in molar mass of the used terephthalate plasticizers, a fact that correlates well with that obtained for the thermal degradation of plasticized PMXS solid films [16]. The trend of increase in the efficiency of excimer fluorescence quenching is DOT > DET > DMT. Phthalate plasticizers, DBP, and DOP showed higher efficiency of photo-quenching than what was obtained by terephthalate plasticizers. This behavior may indicate that there is a higher stability for the (terephthalate-PMXS)* excited complex than that of (phthalate-PMXS)* excited complex [16]. It is more likely that the bulkiness of the doped plasticizer molecules can lower the stability of the formed energy transfer complex, and also to the exciplex activation energy for exciplex formation of charge transfer character.

The comparison for the efficiency of fluorescence quenching $\left(I^{\circ}_{EX}/I_{EX}\right)$ and the photo-quenching rate constant (k_{PQ}) values, for the irradiated pure and blended PMXS films are shown in Table 1.

In the effect of concentration of added quencher on the fluorescence quenching process, Stern-Volmer plot is normally used for quenching process to evaluate some kinetic parameters like quenching rate constant and quenching cross-section [38]. Assuming that we can apply this theory for photo-quenching process, where the quenching process is affected by the amount of absorbed radiation, then,

$$I^{\circ}_{EX}/I_{EX} = 1 + (k'_{PQ} \times A \times t) \qquad (1)$$

where (A) = number of (photons/s) absorbed by polymeric chromophores.

t = time of irradiation.

If we assume that the number of photons emitted from the source of light per second (photons/s) during irradiation is (A), and is constant value during irradiation, then (k'_{PQ} A) = k_{PQ}:

$$I^{\circ}_{EX}/I_{EX} = 1 + (k_{PQ} \times t) \qquad (2)$$

where k_{PQ} is the photo-quenching rate constant.

In the photo-quenching processes, if we assume that the number of photons absorbed by polymer chromophores/s, is constant, and then we can plot $\left(I^{\circ}_{EX}/I_{EX}\right)$-values against times of irradiation (t). From this plot, similar to that of Stern-Volmer, we can evaluate the photo-quenching rate constant k_{PQ}, for irradiated pure and PMXS blended with the used plasticizers, as shown in Table 2.

From k_{PQ} values for pure and plasticized PMXS films, DBP plasticizer showed a higher value of photo-quenching rate constant compared to that plasticized with terephthalate plasticizers, where DMT plasticizer gave the lowest value of quenching efficiency.

FT-IR spectra of irradiated and non-irradiated PMXS solid films

It has been reported that irradiation of polystyrene solid films resulted in changes in the FT-IR absorption spectra

Table 2 Relative intensities of the ratio $\left(I^{\circ}_{\mathrm{EX}}/I_{\mathrm{EX}}\right)$ and k_{PQ} values for excimer fluorescence spectra of pure and blended irradiated PMXS films

$\lambda_{(\mathrm{exc})}$ (nm)	$\lambda_{(\mathrm{emis})}$ (nm) (max)	Plasticizer (4.0%)	Time (min)	$\left(I^{\circ}_{\mathrm{EX}}/I_{\mathrm{EX}}\right)$ Irradiated	k_{PQ}
265	327	–	120	8.33	0.041
265	329	DMT	120	3.55	0.014
265	330	DET	120	4.34	0.017
265	330	DOT	120	6.30	0.029
265	333	DBP	120	9.66	0.046
265	331	DOP	120	8.63	0.043

[39]. The formation of the absorption peak at 275 nm in the irradiated solid films has been attributed to polyene sequences with three–six conjugated double bonds [39–41].

In the irradiated PMXS solid films, a decrease in the fluorescence intensity as well as a small increase of the absorbance at longer wavelength 290–305 nm were observed, and is due to the formation of new chromophores. In order to confirm the presence of photodegradation products in the irradiated PMXS films, solid films of this polymer were irradiated for 0.0 and 2.0 h in the presence of air, and at 298 K, then the FT-IR spectra were recorded before and after irradiation, as shown in Fig. 9.

Figure 10 shows the FT-IR spectra of the blended PMXS film with 4.0% DET and the irradiated blended PMXS films with 4.0% DET for 0.0 and 2.0 h, at 298 K.

As can be noticed in Fig. 9, modifications occur in different bands in the FT-IR spectra of the irradiated PMXS film. The increase of the bands at (2,994, 2,920, 2,833 cm^{-1}), can be assigned to formation of more conjugated double bonds or to increase in the aromatic structure of the polymer backbone. The irradiated PMXS film at 265 nm shows that the photo-oxidation led to the formation of a new band centered around 1,714 cm^{-1}, as well as enhancement in the intensity of the bands; 1,610, 1,511, and 1,501 cm^{-1} as shown in Table 3.

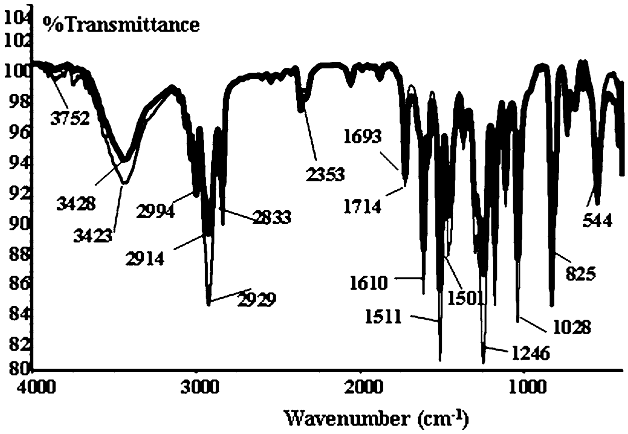

Fig. 9 FT-IR spectra for PMXS film at 298 K, (*solid line*) and PMXS film irradiated for 2.0 h at 298 K, (*fade line*) ($\lambda_{\mathrm{ext}} = 265$ nm)

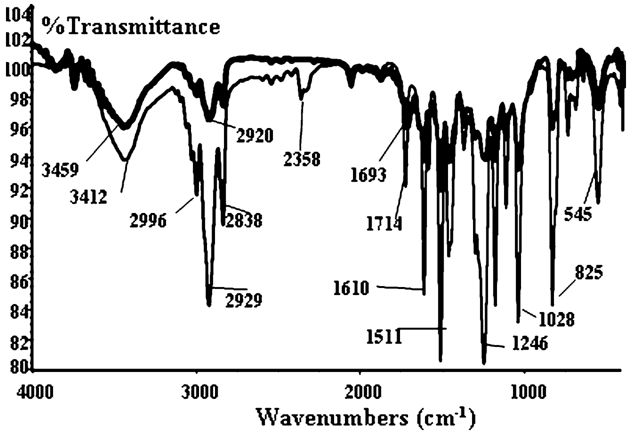

Fig. 10 FT-IR spectra for PMXS + 4.0% DET (*solid line*) and irradiated PMXS + 4.0% DET (*fade line*) for 2.0 h at 298 K ($\lambda_{\mathrm{ext}} = 265$ nm)

The increase of the absorption band around 1,714 cm^{-1}, with the increase in irradiation time is evidence of the creation of new photo-oxidation products. However, the interpretation of this band is not simple because of the overlapping of the different types of carbonyl species in the same frequency range. It is generally accepted to attribute the absorption band for C=O stretching vibration at (1,705–1,715 cm^{-1}), to saturated and unsaturated ketones and aldehydes [39, 41]. The increase in the FT-IR absorption bands at 1,610 and 1,511 cm^{-1} indicate modifications in ring substitution; it means that the aromatic rings loose their symmetry throughout photo-oxidation processes [29].

The FT-IR spectra also make it possible to draw some conclusions about photodegradation of irradiated PMXS and irradiated DET doped PMXS films. As can be seen in Fig. 10, there was an increase in the intensity of the absorption bands at the range (3,428–825 cm^{-1}) upon blending PMXS film with 4.0% DET. This increase in the absorption intensities even larger than that observed in case of irradiated pure PMXS film at 265 nm for 2.0 h. The formation of carbonyl compounds is found to increase by irradiation and by blended PMXS films as found on the bases of increasing absorption of the band around 1,714 cm^{-1}. The other observation in the IR-spectrum is the large increase in the relative absorption in the region (1,610–1,028 cm^{-1}), in comparison with that of unblended PMXS film. This may indicate that there is an increase in the number of (C=C) that resulted from hydrogen abstraction during chains-scission process.

Table 3 FT-IR band position in irradiated and non-irradiated Pure PMXS and blended PMXS with DET, at ($\lambda_{ext} = 265$ nm)

Polymer	Band (cm^{-1})	Time of irradiation (h)			Type of vibration	Intensity
		0.0	1.0	4.0		
PMXS	3,750	–	3,754	3,754		Increased
PMXS	3,428	3,428	3,430	3,423		Increased
PMXS	2,994	2,994	2,994	2,994	(C–H), stretching vibration of benzene	Decreased
PMXS	2,914	2,914	2,921	2,929		Increased
PMXS	2,833	2,833	2,833	2,833	C–H stretch in aldehydes	Increased
PMXS	2,353	–	–	2,353	Conjugated double bonds	
PMXS	1,714	–	1,714	1,714	C=O stretch vibrations, carboxylic acids-dimeric forms	Increased
PMXS	1,610	1,610	1,610	1,610	C=C stretch	Increased
PMXS	1,511	1,511	1,511	1,511	Mono substitution of benzene ring	Increased
PMXS	1,246	1,246	1,246	1,246	C–O–C stretching vibration	Increased
PMXS	825	825	826	825	Conjugated double bond	Decreased
PMXS/DET[a]	3,428	3,428	3,425	3,423		
PMXS/DET[a]	2,996	2,996	2,996	2,996	(C–H), stretching vibration of benzene	Increased
PMXS/DET[a]	2,920	2,920	2,925	2,924		Increased
PMXS/DET[a]	2,358	–	–	2,358		
PMXS/DET[a]	1,714	–	1,714	1,714	C=O stretch, carboxylic acids-dimeric forms	Increased
PMXS/DET[a]	1,610	1,610	1,614	1,614	C=C stretch	Increased
PMXS/DET[a]	1,511	1,511	1,511	1,511	Mono substitution of benzene ring	Increased
PMXS/DET[a]	1,454	–	1,454	1,454		Increased
PMXS/DET[a]	1,246	1,246	1,248	1,250	C–O–C stretching vibration	Increased
PMXS/DET[a]	1,028	1,028	1,030	1,030		Increased
PMXS/DET[a]	825	825	825	825	Conjugated double bond	Increased

[a] PMXS blended with 4% DET plasticizer

Conclusions

Based on the obtained values of fluorescence quenching for the irradiated plasticized and non-plasticized PMXS solid films, the conclusions can be summarized as follows:

1. Irradiation of pure and blended PMXS films with light of a frequency absorbed by only polymeric chromophores resulted in a small increase in the absorption band, with the increase of exposure time of pure PMXS films. On the other hand, irradiation of blended PMXS with plasticizers caused change in the shape of the absorption spectra, as well as, formation of a new absorption band at longer wavelength, indicating a possibility of photodegradation of the polymeric backbone by chain scission as well as photo-oxidation of polymeric chromophores.
2. Blending of PMXS films with DMT, DET, DOT, DBP, and DOP plasticizers resulted in the formation of exciplex emission. Irradiation of blended PMXS films with terephthalate and phthalate plasticizers showed that terephthalate additives caused less fluorescence quenching effect in comparison with that caused by phthalate plasticizers. The photo-degradation effect was found to increase with the increase in bulkiness of the plasticizer molecule.
3. IR spectra of PMXS and blended PMXS irradiated films showed a formation of new absorption bands, and the disappearance of some other absorption bands. This can indicate that the photodegradation of the polymer has occurred. The formation of C=O is the main indication of photo-oxidation at the peak centered at 1,714 cm^{-1}. It is clearly seen that there is a difference in most of the peak position and their relative intensities, which means that photo-degraded products are not the same during the degradation process.

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