Spectroscopic properties of HALS doped polycarbonate by fluorescence spectroscopy

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ABSTRACT

The fluorescence and fluorescence excitation spectra of pure and doped polycarbonate (PC) depending on hindered-amine light stabilizers (HALS: Tinuvin 770 and Tinuvin 123) concentration and different processing conditions have been studied. Non-processed PC has no emission band in the visible range but processed PC with additives show visible fluorescence bands between 400–470 nm. It suggested that PC undergoes a kind of degradation process which lead to the fluorescence emission caused by the transitions from the new distortion-related localized states (defect states) created by processing and the additives. Such defects lead also to the emergence of a new band in the excitation and emission spectra at lower energies, where the symmetry of the bands break near. The intensity of these bands drastically depends on the sample treatment where the luminescence intensity quantitatively characterizes the concentration of defect radicals. An increase in screw speed resulted in an increase in specific mechanical energy (*SME*), higher *SME* led to a remarkable macromolecular degradation.

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Keywords: Luminescence spectroscopy, Polycarbonate, Tinuvin, UV-light stabilizer.

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18 **1. INTRODUCTION**

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20 Polycarbonate (PC) is the most widely used aromatic polymer in various industrial applications. It is a condensation polymer in which benzene rings plus quaternary carbon 21 22 atoms form bulky stiff molecules that promote rigidity and strength. The bulky chains 23 crystallize with great difficulty, so the polymer is normally amorphous with excellent characteristics such as optical clarity, heat stability and mechanical resistance. These 24 properties make it an ideal material especially for outdoor applications. However, on 25 extended exposure to UV light, PC slowly degrades and turning progressively yellow and 26 27 loss a lot of its superior physical properties. Over the years, there have been numerous 28 studies of these degradative processes of PC with a particular attention given to the degradation mechanism at the molecular level (Klein et al., 1981; Ahmad, 1987; Parikh et 29 30 al.,1996; Migahed et al.,2006).

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Improved stability and compatibility of polymers with other additives and polymer systems, reduced volatility and color development are the basic themes of UV stabilizer development in the past year. Particularly notable are new and improved forms of hindered-amine light stabilizers (HALS) have been established. These include high-molecular-weight monomeric and oligomeric HALS, as well as versions that are chemically linked to a monomer backbone or have reactive functionality that binds them to certain polymer systems. There is also a

* Tel.: +46 90 7865702; fax: +46 90 7866673. E-mail address: roushdey.salh@physics.umu.se growing trend toward multicomponent systems combining HALS and UV absorbers to achieve optimal cost performance (Feczkó, 2012). Tinuvin 770 [bis(2,2,6,6-tetramethyl-4piperidinyl) sebacate] and Tinuvin 123 [bis(1-octyloxy-2,2,6,-tetramethyl-4-piperidinyl) sebacate], are among the UV light stabilizer plastic additive used worldwide (National Industrial chemicals notification and assessment scheme, 1992; Ciba Specialty Chemicals Brochure, 1999).

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45 In the broadest sense, luminescence is the light emitted by a polymer after it has been 46 excited in various ways. This light is characterized as either fluorescence or 47 phosphorescence depending on the emitting state being either a Singlet or a Triplet state, 48 respectively. Because of the high efficiency of energy transfer in the solid state, the emitting species is very often not the chromophore that was originally excited but it could be the 49 repeat unit of the polymer, an impurity, foreign molecular additives, oxidation product or 50 51 degradation product on the polymer chain. Fluorescence (FL) spectroscopy is powerful tool 52 in quantitative analysis owing to its great sensitivity. Luminescence spectroscopy application in polymer science include: identification of different polymers, additives and impurities in 53 54 polymers, phase separation and polymer miscibility, glass transition temperature, transport 55 properties including permeability, polymer degradation, polymer deformation and failure and 56 also give us an idea about the value of optical band gap (E_{α}) and the optical absorption 57 spectra within the wavelength detection region. This is achieved through studies of the 58 intensity and lifetime of the luminescence as well as excitation and emission spectra. Different luminescence techniques which used to characterize the properties of small 59 organic molecules has provided an enormous amount of information about the symmetry of 60 the molecule and its electronic excited states and the way it interacts with other molecules in 61 its environment (Bonzanini et al., 2006; Levitsky et al. 2007). Such detailed molecular 62 information also forms the basis for the In-line characterization of organic polymers under 63 64 production. For many years the luminescence properties of polymers have been measured 65 and compared to those of the small molecule analogue, the polymer repeat unit. The 66 extreme sensitivity of luminescence has led to much valuable information about the role of 67 trace impurities, the processes of interchain interactions (Valencia et al. 2013).

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This investigation will be focused on the use of luminescence spectroscopy in the ultravioletvisible region to provide information about the particular properties of modified PC by using Tinuvin 770 and 123, and also to understand polymer breakdown or mechanical degradation during extrusion by means of the specific mechanical energy dependence on the extrusion parameters.

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76 2. EXPERIMENTAL

77 78 2.1 Materials and specimen preparation 79 Polycarbonate, $[-O-C_6H_4-4-C(CH_3)_2C_6H_4-4-OCO-]_n$, in a semi-crystalline phase with a 80 density of 1.2 g/cm³, were processed with and without additives "Tinuvin 770 and Tinuvin 81 123" in different screw speeds (v) and throughputs (δ) as listed in Table 1. Then the samples 82 were pressed at 220 °C to 2 mm thick disks for florescence measurement. The blends got 83 84 yellow discolored by adding Tinuvin 770 and Tinuvin 123 during extrusion, but they kept their 85 transparency. Also it is important to remark that sample 10 had lower resistance to flow and 86 less mechanical stability after solidification. The sample labeled with PC in Table 1 is the pure as received polycarbonate. UV irradiation of samples was carried out for 48 h under dry 87 88 condition (i.e. room relative humidity) using SUNTEST XLS+ model accelerated weathering equipment from ATLAS. The UV light source consists mainly of a Xenon-lamp and optical 89 90 filters to justify the light flux and to eliminate the thermal effect of UV lamp (IR-radiation) for providing constant regulation of sample temperature during UV irradiation. The UV light flux
 used in study was fixed at 765 W/m² (dose 4230 kJ/m²) and the sample temperature fixed at
 65 °C. The sample-to-lamp distance was 28 cm.

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2.2 Fluorescence apparatus and measurement

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97 All fluorescence spectra were obtained on a computer controlled luminescence spectrometer Model LS-55 form (Perkin-Elmer, Norwalk, CT, USA) with the capability of measuring 98 99 fluorescence, phosphorescence, chemilumines-cence and bioluminescence, equipped with a 100 xenon discharge lamp with pulses equivalent to 20 kW for 8 µs duration and two 101 monochromators (Monk-Gillieson type) for excitation and emission. Pulse width at half height 102 is less than 10 µs. The excitation monocromator cover the range 200-800 nm and the 103 emission monocromator cover the range 200-650 nm. This spectrofluorimeter is provided 104 with FL-Winlab fluorescence software for acquiring and processing the spectral data. The 105 wavelength accuracy and wavelength reproducibility were ± 1.0 nm and ± 0.5 nm, respectively. Fluorescence measurements were performed using standard excitation and 106 107 emission scan mode with emission wavelength λ_{em} =470 and excitation wavelength between λ_{ex} =290-466 nm, respectively. Both excitation and emission slits were fixed on 15:10 nm for 108 109 intensity comparability.

111 2.3 Molar mass measurement

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113 The molar masses (M) of the samples were determined by size exclusion chromatography 114 (SEC, GPC) in THF using toluene as internal flow marker. The GPC-setup consisted of a 115 Waters 515 isocratic HPLC pump, a TSP AS 100 autosampler, a Waters UV 486 Detector 116 operated at 254 nm and a Waters 410 differential refractometer. Three SDV columns (PSS 117 Polymer Standards Service GmbH, Mainz, Germany) with nominal pore sizes of 10⁶, 10⁵ and 10⁴ Å (30 x 0.8 cm each) were used. Calibration was performed using narrow distributed 118 polystyrene standards. Data acquisition and processing was performed using PSS WINGPC 119 120 software.

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Sample No.	PC %	Tinuvin 770 σ ₇₇₀ (%)	Tinuvin 123 σ ₁₂₃ (%)	Screw speed v (rpm)	Throughput δ (kg/h)
PC	100	0	0	0	0
1 🔨 🔪	100	0	0	700	25
2	100	0	0	700	35
3	100	0	0	700	45
4	100	0	0	900	45
5	98.8	0.2	0	700	45
6	98.5	0.5	0	700	25
7	98.5	0.5	0	700	35
8	98.5	0.5	0	700	45
9	98.5	0.5	0	500	45
10	98.5	0.5	0	900	45
11	99	1	0	700	45
12	99.5	0	0.5	700	25
13	99.5	0	0.5	700	35

Table 1. list over the samples showing Tinuvin 770 and Tinuvin 123 concentrations and the processing conditions.





128 Fig. 1. Excitation spectra (λ_{em} =470 nm) 129 and emission spectra (λ_{ex} =340 nm) of different processed polycarbonate. 130

Fig. 2. Excitation spectra (λ_{em} =470 nm) 131 and emission spectra of polycarbonate 132 with different content of Tinuvin 770 133 and at various processing conditions. 134

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137 3. RESULTS AND DISCUSSION

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3.1 Fluorescence and UV-VIS spectroscopy 139

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141 The excitation and fluorescence spectra were characterized for the PC and for various 142 concentrations of Tinuvin. The spectroscopic scans were measured simultaneously under 143 same experimental conditions. Pristine PC containing no commercial additives absorbs UV 144 light. Excitation scans of the non-processed PC shows a single band at 290 nm besides a 145 shoulder at 320 nm. When PC processed as listed in Table 1, both these bands shifts to 146 lower energies but the second one come to seen more clearly at 370 nm although the 147 maxima remains at 340, as shown in Fig.1. The difference between these bands in both 148 cases is 30 nm which indicates the same formation origin. These two band suggested to be 149 due to the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions of the carbonyl group, respectively (Gupta et al., 150 2000).

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152 No obvious influence of the processing parameters on the excitation spectra of PC have 153 been observed, therefore only the spectrum of sample 3 is shown in Fig.1. The pristine PC presents no luminescence (Puglisi et al., 2000), but the processed samples showing a single 154 155 sharp luminescence band at 372 nm. The intensity of this band raising with higher υ and δ 156 without any shift in band position, these slight changes specifying that PC is stable under 157 different processing conditions. The intensity increases indicates also a distortion of the 158 polymer chains besides a creation of the so called defect states in the band gap (E_{e}) which 159 leads to new emission bands detection concomitant generally with a shift of the exciting 160 bands usually to lower energies, i.e. lowering of E_{o} .

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162 Figure 2 presents the excitation and emission fluorescence spectra of processed PC with up 163 to 1% Tinuvin 770 concentration. The hindered amines Tinuvin 770 showed an increase in 164 the intensity and a clear red shift in the excitation (~60 nm) and emission spectra (~40-90 165 nm).



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177 However, after processing the mixture at 500 and 700 rpm, there is a gradual increase in the UV absorption between 350-410 nm and a corresponding increase in the emission band. 178 179 One of the most significant features in Fig.2 is the presence of an intense absorption band 180 centered at 413 nm when the blend (sample 10) processed at higher screw speed (900 rpm) 181 and throughput (45 kg/h). One can suggest that more radicals have been formed during 182 processing which probably reacting with the host polymer. Such a reaction also occurs in 183 samples 6 and 7 where they are processed at lower screw speed (700 rpm) and throughputs 184 (25, 35 kg/h). Here, it is also seen that other bands in the excitation spectra are to be 185 detected at lower energy (2.92 eV). It have tentatively ascribed this spectrum to conjugate 186 structures, i.e. possible formation of carbon clusters, where there is a gradual increase in the 187 formation of a product which absorbs strongly at 2.92 eV. Such product formation appears to 188 be almost saturated at 1% Tinuvin concentration.

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190 The absorption bands in the investigated range of wavelength are associated to the $\pi \rightarrow \pi^*$ 191 electron transition (Betz et al., 1994; Calcagno et al., 1992). This type of transition occurs in 192 the unsaturated centers of the molecules i.e. in compounds, containing double or triple 193 bonds and also in aromatics. The excitation of π electron requires small energy and hence 194 transition of this type occurs at longer wavelengths. The optical band can be correlated to 195 the optical band gap E_g by the expression (Tauc et al., 1966; Kumar et al., 2006).

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$$\omega^2 \varepsilon_2 = (\hbar \omega - E_g)^2$$

(1)

199 where ε_2 is the optical absorbance. As the shift of the absorption edge can be attributed to an 200 increase of the conjugated structures -C=C- or in other words the appearance of defect 201 states in the optical band, similar results have been recently observed on the spectral 202 analysis of UV irradiated PC films. Fink et al. have described the number of carbon atoms per conjunction length N by $E_e=2\beta\pi/N$ (Fink et al. 1996), there the authors showing indirect 203 204 proportionality between N and the optical band gap. β is constant. The values of E_{g} is found to decrease from 4.27 eV for pure PC to 3.6 eV for processed PC (samples 1-4) and even 205 206 more to lower energies between 3.5-3.0 eV for samples with Tinuvin 770 content.





209 Fig. 5. Influence of: a) Tinuvin 770 210 concentration at constant throughput 211 and screw speed b) Throughput at constant Tinuvin770 concentration and 212 213 speed c) processing screw screw 214 speed at constant Tinuvin 770 215 concentration and throughput, on the 216 absorption bands of PC.



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UV-vis spectrophotometric scans of pure PC and with different Tinuvin 770 content at 227 228 constant screw speed (v) and throughput (δ) were measured in the range of 200-800 nm. 229 Figure 3 shows that the absorbance for wavelengths below 400 nm is increasing with 230 increasing Tinuvin 770 concentration. The absorption bands at 320 nm and 355 nm are ascribed to phenylsalicylate and dihydroxybenzophenone, respectively (Rivaton 1995). This 231 232 figure shows that the absorbance at these wavelengths increases with increasing Tinuvin 233 770. Figure 4 presents the spectra PC doped with 0.5% Tinuvin 123. It has an excitation maximum at 400 nm and emission maximum at 458 nm. Tinuvin 123 consists of more 234 235 carbon atoms (National Industrial chemicals notification 1992), i.e. the possibility of more or 236 longer conjugated structure which cause the red shift of PC bands, as explained already.

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No significant changes have been observed in Excitation and emission spectra of UV
 irradiated PC-Tinuvin 770 with compare to the result obtained in Figure 2. Tinuvin 770
 seems to be destruct PC structure that one cannot detect the irradiation influence.

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242 **3.2 Effect of extrusion parameters on PC**

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244 One of the most difficult problems associated with assessing the degradation of any polymer 245 is to be able to detect and explain the spectroscopic changes in the absorption and emission 246 spectrum upon exposure to light for short periods of time and the extrusion parameters too. 247 Of course in the case of polycarbonate there have been a large number of papers which 248 have been written over the years using spectroscopic evaluation to monitor the progress of 249 the mechanical and photo decomposition (Rivaton et al. 1986; Lemaire et al. 1986). This 250 section will show the effect of extrusion parameters on the spectroscopic characteristics and 251 the molar mass on PC.

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Fig. 7. The melt flow index dependence
on concentration of Tinuvin 770.

Fig. 8. The SME dependence on M for
constant screw speed and throughput
but with increasing HALS oncentration
from 0 to 1 %.

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The dependence of excitation band position and molar mass on concentration (σ) , throughput (δ) and screw speed (v) are shown in Figures 5 and 6. As one can see that by variation of additive concentration a maximum shift in the excitation wavelength and intensity have been reached at 0.5% Tinuvin 770 concentration, which means that such concentration contribute to degraded polycarbonate instate of stabilizing it against UV radiation. At this concentration: increasing the throughput leads to decreasing the intensity, but increasing the screw speed leads to higher intensity.

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The molar mass is decreasing drastically with increasing the Tinuvin 770 concentration. 272 273 Lower viscosity is related with lower molar mass. At constant Tinuvin 770 (0.5%) 274 concentration the molar mass increasing with the throughput and showing a mixed behavior 275 with increasing screw speed. Although direct viscosity measurements have been not 276 performed but one could roughly recognize during melting and pressing the samples, that samples with high HALS concentration have lower viscosity. Measurements of melt flow 277 278 index shown in Fig. 7 confirm this observation. The melt are flowing much faster with 279 increasing Tinuvin 770. Furthermore, it is found that adding HALS to polymers shows a 280 drastic effect on delaying the gelation time (Wrobleski et al. 1994). The measured molar masses for pure PC were between 3.5-3x10⁴ g/mol, the lowest was when PC processed at 281 282 900 rpm. Processing PC with HALS lowering the molar mass to 3-2.3x10⁴ g/mol. Sample 10 with 0.5% HALS and 900rpm had the lowest molar mass (1.8x10⁴ g/mol) among all samples. 283 284

Further as described earlier in (Wrobleski et al. 1994) the specific mechanical energy (*SME*) where the mechanical impact causing shear and elongational deformation which in turn is related to degradation. For a deeper understanding on how throughput (δ) and screw speed (v) influence the degradation of PC-Tinuvin blends, the values of the *SME* were calculated at different conditions depending on:

$$SME = \frac{2\pi v\tau}{\delta}$$
(2)

293 where τ is the torque in (Nm) and v, δ are in (1/s) and (g/s), respectively. In Fig. 8 the *SME* 294 dependence on molar mass is plotted at constant parameters as shown inside the frames. 295 SME is strongly depends on Tinuvin concentration. At higher concentration SME is 296 considerably lower. The degradation of PC is stronger for higher SME (Wang et al., 2008). 297 Similar results were reported for starch ($C_6H_{10}O_5$) (Willett et al., 1997). However, in the 298 current study, the curve for constant throughput does not coincide with the one for constant 299 screw speed, when PC was processed at higher throughput (900 kg/h). This clearly indicates 300 that at higher throughput the SME based mechanical degradation is less pronounced for PC. 301 This finding also agrees well with Fig. 6b, where for the high throughput of 45 kg/h less 302 significant dependence of molar mass reduction with screw speed can be seen.

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305 4. CONCLUSIONS

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The fluorescence spectroscopy of pure and doped polycarbonate (PC) depending on 307 308 hindered-amine light stabilizers (HALS: Tinuvin 770 and Tinuvin 123) concentration and 309 different processing conditions have been shown that pure non-processed PC has no 310 emission band in the visible range but have an absorption band at 290 nm. Processing 311 under excessive conditions is most likely to produce chains and general degradation which 312 leads to a fluorescence emission. Processed PC with additives shows visible fluorescence 313 bands between 400-470 nm. The intensity of these bands drastically depends on the 314 sample treatment where the luminescence intensity quantitatively characterizes the 315 concentration of defect radicals. PC becomes considerably yellow discolored with higher 316 concentration of Tinuvin 770 or Tinuvin 123 and the PC gets more brittle (higher degradation 317 grade). An increase in screw speed resulted in an increase in specific mechanical energy 318 (SME), higher SME led to a remarkable macromolecular degradation. SME is decreasing with 319 increasing Tinuvin 770 concentration.

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COMPETING INTERESTS

The author has declared that no competing interests exist.

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