Spectroscopic properties of HALS doped polycarbonate by fluorescence spectroscopy

Roushdey Salh*

Umeå University, Department of physics, 901 87 Umeå, Sweden

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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.

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

1. INTRODUCTION

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 atoms form bulky stiff molecules that promote rigidity and strength. The bulky chains crystallize with great difficulty, so the polymer is normally amorphous with excellent characteristics such as optical clarity, heat stability and mechanical resistance. These properties make it an ideal material especially for outdoor applications. However, on extended exposure to UV light, PC slowly degrades and turning progressively yellow and loss a lot of its superior physical properties. Over the years, there have been numerous 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 al.,1996; Migahed et al.,2006).

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-4-piperidinyl) 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, Sótonyi et al., 2004). The structure of both Tinuvin 770 and Tinuvin 123 is shown in Fig.1.

In the broadest sense, luminescence is the light emitted by a polymer after it has been excited in various ways. This light is characterized as either fluorescence or phosphorescence depending on the emitting state being either a Singlet or a Triplet state, 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 repeat unit of the polymer, an impurity, foreign molecular additives, oxidation product or degradation product on the polymer chain. Fluorescence (FL) spectroscopy is powerful tool in quantitative analysis owing to its great sensitivity. Luminescence spectroscopy application in polymer science include: identification of different polymers, additives and impurities in polymers, phase separation and polymer miscibility, glass transition temperature, transport properties including permeability, polymer degradation, polymer deformation and failure and also give us an idea about the value of optical band gap (E_g) and the optical absorption spectra within the wavelength detection region. This is achieved through studies of the intensity and lifetime of the luminescence as well as excitation and emission spectra. Different luminescence techniques which used to characterize the properties of small organic molecules has provided an enormous amount of information about the symmetry of the molecule and its electronic excited states and the way it interacts with other molecules in its environment (Bonzanini et al., 2006; Levitsky et al. 2007). Such detailed molecular information also forms the basis for the In-line characterization of organic polymers under production. For many years the luminescence properties of polymers have been measured and compared to those of the small molecule analogue, the polymer repeat unit. The extreme sensitivity of luminescence has led to much valuable information about the role of trace impurities, the processes of interchain interactions (Valencia et al. 2013).

This investigation will be focused on the use of luminescence spectroscopy in the ultraviolet-visible 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.

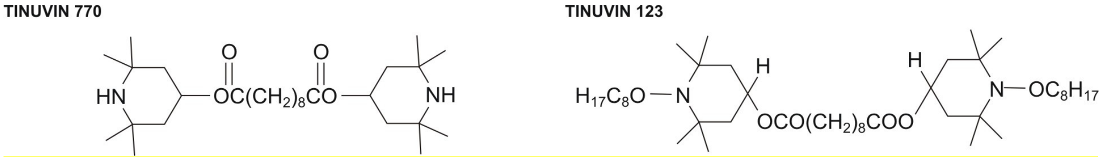

Fig. 1. Chemical name and structure of Tinuvin 770 and Tinuvin 123.

2. EXPERIMENTAL

2.1 Materials and specimen preparation

Commercial Polycarbonate granule, $[–O–C_6H_4–4–C(CH_3)_2C_6H_4–4–OCO–]_n$, with a common brand names Lexan in a semi-crystalline phase with a density of 1.2 g/cm^3, were processed with and without additives “Tinuvin 770 and Tinuvin 123” in different screw speeds (v) and throughputs (δ) as listed in Table 1. Tinuvin 770 white crystalline granules and Tinuvin 123 is a colourless liquid, both are mixed/diluted in large amount of commercial polycarbonate granule to insure the homogenous distribution of both substance during extrusion in Leistritz twin screw extruder. The temperatures at the die were 270±5 °C. Then the samples were pressed at 220 °C to 2 mm thick disks for florescence measurement. The blends got yellow discolored by adding Tinuvin 770 and Tinuvin 123 during extrusion, but they kept their transparency. Also it is important to remark that sample 10 had lower resistance to flow and 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 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 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/m^2 (exposure dose 132192 kJ/m^2) and the sample temperature fixed at 65 °C. For better estimation of sample temperature, the temperatures on the surface of a dummy sample have been measured using a small temperature sensor. The sample had surface temperatures around 60-65oC in different locations within the instrument. The sample-to-lamp distance was 28 cm.

2.2 Molar mass measurement

The molar masses (M) of the samples were determined by size exclusion chromatography (SEC, GPC) in THF using toluene as internal flow marker. The GPC-setup consisted of a Waters 515 isocratic HPLC pump, a TSP AS 100 autosampler, a Waters UV 486 Detector operated at 254 nm and a Waters 410 differential refractometer. Three SDV columns (PSS Polymer Standards Service GmbH, Mainz, Germany) with nominal pore sizes of 10^6, 10^5 and 10^4 Å (30 x 0.8 cm each) were used. Calibration was performed using narrow distributed polystyrene standards. Data acquisition and processing was performed using PSS WINGPC software.

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

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

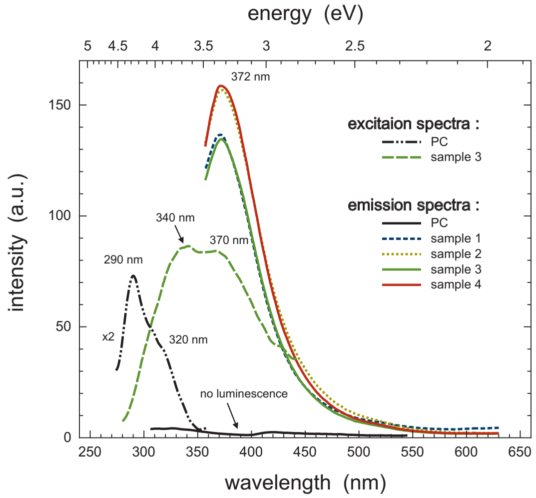

Fig. 2. Excitation spectra (λ_{em}=470 nm) and emission spectra (λ_{ex}=340 nm) of different processed polycarbonate.

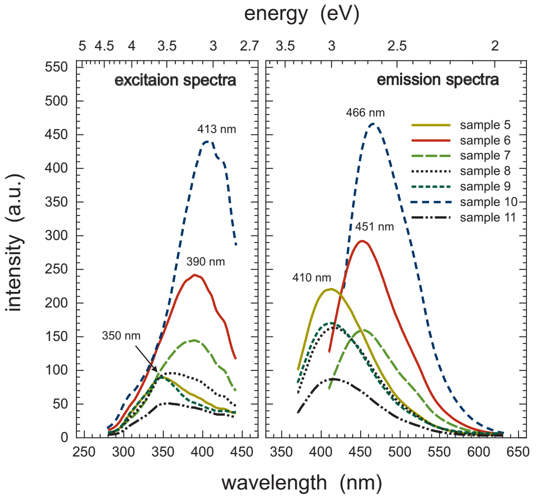

Fig. 3. Excitation spectra (λ_{em}=470 nm) and emission spectra of polycarbonate with different content of Tinuvin 770 and at various processing conditions.

2.3 Fluorescence apparatus and measurement

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 fluorescence, phosphorescence, chemilumines-cence and bioluminescence, equipped with a xenon discharge lamp with pulses equivalent to 20 kW for 8 μs duration and two monochromators (Monk-Gillieson type) for excitation and emission. Pulse width at half height is less than 10 μs. The excitation monocromator cover the range 200-800 nm and the emission monocromator cover the range 200-650 nm. This spectrofluorimeter is provided with FL-Winlab fluorescence software for acquiring and processing the spectral data. The wavelength accuracy and wavelength reproducibility were ±1.0 nm and ±0.5 nm, respectively. Fluorescence measurements were performed using standard excitation and 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 intensity comparability.

3. RESULTS AND DISCUSSION

3.1 Fluorescence and UV-VIS spectroscopy

The excitation and fluorescence spectra were characterized for the PC and for various concentrations of Tinuvin. The spectroscopic scans were measured simultaneously under same experimental conditions. Pristine PC containing no commercial additives absorbs UV light. Excitation scans of the non-processed PC shows a single band at 290 nm besides a shoulder at 320 nm. When PC processed as listed in Table 1, both these bands shifts to lower energies but the second one come to seen more clearly at 370 nm although the maxima remains at 340, as shown in Fig.2. The difference between these bands in both cases is 30 nm which indicates the same formation origin. These two band suggested to be due to the $n \rightarrow \pi^*$ & $\pi \rightarrow \pi^*$ transitions of the carbonyl group, respectively (Gupta et al., 2000).

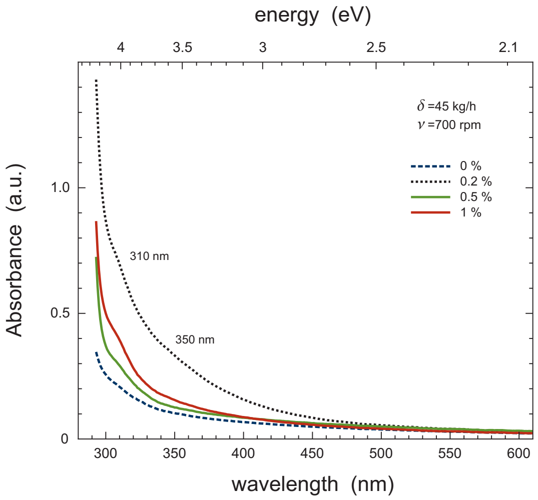

Fig. 4. **UV absorption spectra of pure PC and PC with various Tinuvin 770 concentrations.**

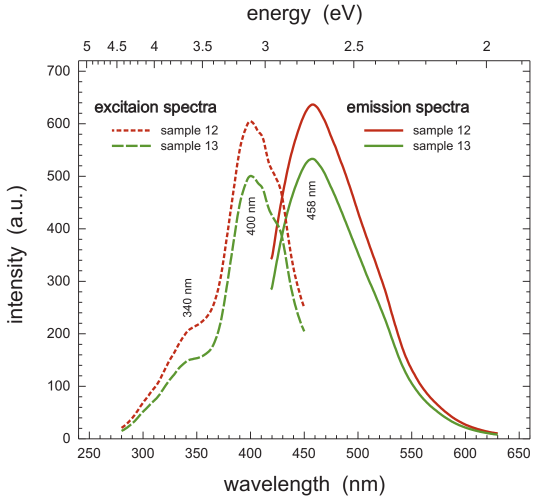

Fig. 5. **Excitation spectra (λ_{em}=470 nm) and emission spectra of polycarbonate doped with Tinuvin 123 at two different processing conditions.**

No obvious influence of the processing parameters on the excitation spectra of PC have been observed, therefore only the spectrum of sample 3 is shown in Fig.2. The pristine PC presents no luminescence (Puglisi et al., 2000), but the processed samples showing a single sharp luminescence band at 372 nm. The intensity of this band raising with higher υ and δ without any shift in band position, these slight changes specifying that PC is stable under different processing conditions. The intensity increases indicates also a distortion of the polymer chains besides a creation of the so called defect states in the band gap (E_g) which leads to new emission bands detection concomitant generally with a shift of the exciting bands usually to lower energies, i.e. lowering of E_g.

Figure 3 presents the excitation and emission fluorescence spectra of processed PC with up to 1% Tinuvin 770 concentration. The hindered amines Tinuvin 770 showed an increase in the intensity and a clear red shift in the excitation (~60 nm) and emission spectra (~40-90 nm).

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. One of the most significant features in Fig.3 is the presence of an intense absorption band centered at 413 nm when the blend (sample 10) processed at higher screw speed (900 rpm) and throughput (45 kg/h). One can suggest that more radicals have been formed during processing which probably reacting with the host polymer. Such a reaction also occurs in samples 6 and 7 where they are processed at lower screw speed (700 rpm) and throughputs (25, 35 kg/h). Here, it is also seen that other bands in the excitation spectra are to be detected at lower energy (2.92 eV). It have tentatively ascribed this spectrum to conjugate structures, i.e. possible formation of carbon clusters, where there is a gradual increase in the formation of a product which absorbs strongly at 2.92 eV. Such product formation appears to be almost saturated at 1% Tinuvin concentration.

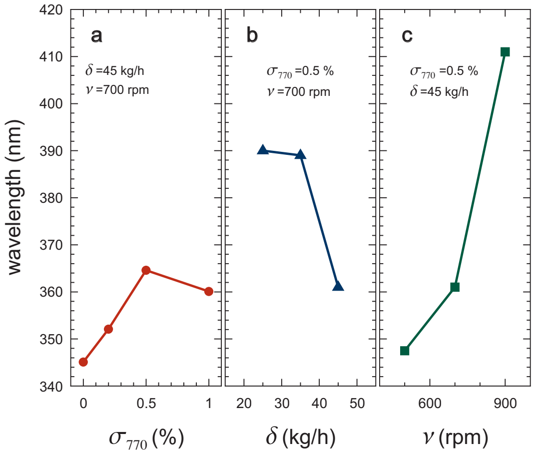

Fig. 6. **Influence of: a) Tinuvin 770 concentration at constant throughput and screw speed b) Throughput at constant Tinuvin770 concentration and screw speed c) processing screw speed at constant Tinuvin 770 concentration and throughput, on the absorption bands of PC.**

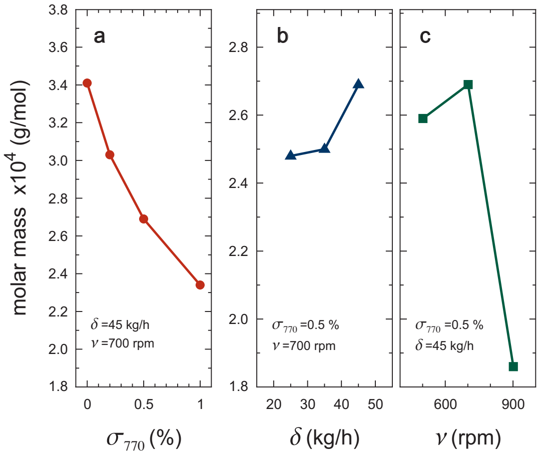

Fig. 7. **Influence of: a) Tinuvin 770 concentration at constant throughput and screw speed b) Throughput at constant Tinuvin770 concentration and screw speed c) processing screw speed at constant Tinuvin 770 concentration and throughput, on the molar mass of the mixture.**

The mechanism of distortion of PC chain that causes new absorption and emission bands are because of the processing procedure. the degradation can be generated due to oxidative processes and/or heat during processing of the polymers. On the other hand, stabilizers can be degraded by reactions that are not related to their consumption during stabilization. All these will lead to radicals formation which will contribute in the new absorption and emission band (Buchberger and Stiftinger, 2012).

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

$$\omega^2 \varepsilon_2 = (\hbar\omega - E_g)^2 \qquad (1)$$

where ε_2 is the optical absorbance. As the shift of the absorption edge can be attributed to an increase of the conjugated structures —C═C— or in other words the appearance of defect states in the optical band, similar results have been recently observed on the spectral analysis of UV irradiated PC films. Fink et al. have described the number of carbon atoms per conjunction length N by $E_g=2\beta\pi/N$ (Fink et al. 1996), there the authors showing indirect 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 more to lower energies between 3.5-3.0 eV for samples with Tinuvin 770 content.

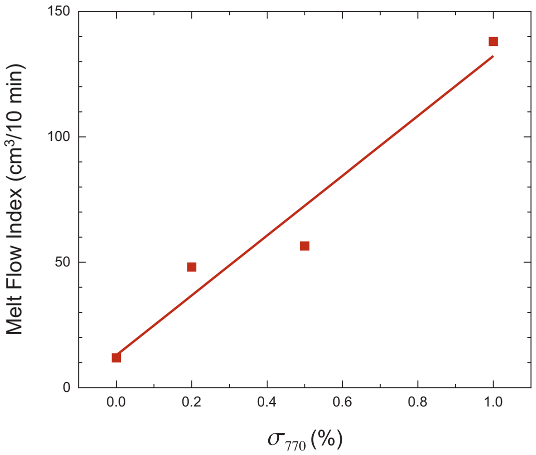

Fig. 8. The melt flow index dependence on concentration of Tinuvin 770.

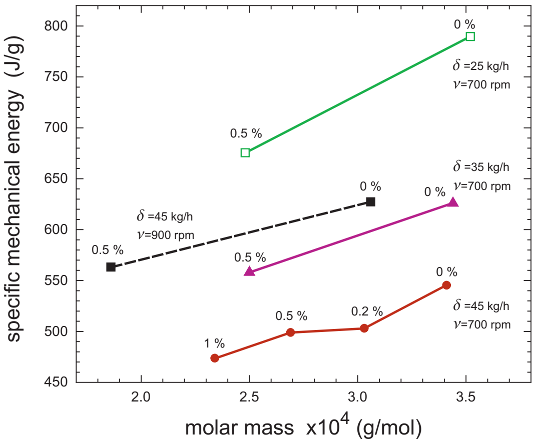

Fig. 9. The SME dependence on M for constant screw speed and throughput but with increasing HALS oncentration from 0 to 1 %.

UV-vis spectrophotometric scans of pure PC and with different Tinuvin 770 content at constant screw speed (ν) and throughput (δ) were measured in the range of 200-800 nm. Figure 4 shows that the absorbance for wavelengths below 400 nm is increasing with increasing Tinuvin 770 concentration. The absorption bands at 320 nm and 355 nm are ascribed to phenylsalicylate and dihydroxybenzophenone, respectively (Rivaton 1995). This figure shows that the absorbance at these wavelengths increases with increasing Tinuvin 770. Figure 5 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 carbon atoms (National Industrial chemicals notification 1992), i.e. the possibility of more or longer conjugated structure which cause the red shift of PC bands, as explained already.

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 3. Tinuvin 770 seems to be destruct PC structure that one cannot detect the irradiation influence.

3.2 Effect of extrusion parameters on PC

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

The dependence of excitation band position and molar mass on concentration (σ), throughput (δ) and screw speed (ν) are shown in Figures 6 and 7. 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.

The molar mass is decreasing drastically with increasing the Tinuvin 770 concentration. Lower viscosity is related with lower molar mass. At constant Tinuvin 770 (0.5%) concentration the molar mass increasing with the throughput and showing a mixed behavior with increasing screw speed. Although direct viscosity measurements have been not 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 index shown in Fig. 8 confirm this observation. The melt are flowing much faster with increasing Tinuvin 770. Furthermore, it is found that adding HALS to polymers shows a drastic effect on delaying the gelation time (Wrobleski et al. 1994). The measured molar masses for pure PC were between 3.5-3x10^4 g/mol, the lowest was when PC processed at 900 rpm. Processing PC with HALS lowering the molar mass to 3-2.3x10^4 g/mol. Sample 10 with 0.5% HALS and 900rpm had the lowest molar mass (1.8x10^4 g/mol) among all samples.

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:

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

where τ is the torque in (Nm) and v , δ are in (1/s) and (g/s), respectively. In Fig. 9 the SME dependence on molar mass is plotted at constant parameters as shown inside the frames. SME is strongly depends on Tinuvin concentration. At higher concentration SME is considerably lower. The degradation of PC is stronger for higher SME (Wang et al., 2008). Similar results were reported for starch ($C_6H_{10}O_5$) (Willett et al., 1997). However, in the current study, the curve for constant throughput does not coincide with the one for constant screw speed, when PC was processed at higher throughput (900 kg/h). This clearly indicates that at higher throughput the *SME* based mechanical degradation is less pronounced for PC. This finding also agrees well with Fig. 7b, where for the high throughput of 45 kg/h less significant dependence of molar mass reduction with screw speed can be seen.

4. CONCLUSIONS

The fluorescence spectroscopy 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 shown that pure non-processed PC has no emission band in the visible range but have an absorption band at 290 nm. Processing under excessive conditions is most likely to produce chains and general degradation which leads to a fluorescence emission. Processed PC with additives shows visible fluorescence bands between 400–470 nm. The intensity of these bands drastically depends on the sample treatment where the luminescence intensity quantitatively characterizes the concentration of defect radicals. PC becomes considerably yellow discolored with higher concentration of Tinuvin 770 or Tinuvin 123 and the PC gets more brittle (higher degradation grade). An increase in screw speed resulted in an increase in specific mechanical energy (SME), higher *SME* led to a remarkable macromolecular degradation. SME is decreasing with increasing Tinuvin 770 concentration.

COMPETING INTERESTS

The author has declared that no competing interests exist.

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