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FLUORESCENCE INVESTIGATION OF SOME POLYSTYRENE SAMPLES THERMALLY DEGRADED

CARMEN NICULAESCU[1], IOANA BREZESTEAN[1],
CLAUDIU LUNG[1] AND MIHAI TODICA[1,*]

ABSTRACT. The behavior of some samples of commercial polystyrene, thermally degraded, was investigated by UV-VIS and fluorescence methods. Excited with different wavelengths in the domain 315-365 nm, the spectra show a peak located at 409 nm. The amplitude and the shape of this peak change after thermal degradation. Minor changes appear at 200ºC, indicating relatively stability of the samples, but the modifications are more important at 350ºC. At that temperature the samples are affected by oxidation.

Keywords: *polystyrene, thermal degradation, UV-VIS, fluorescence.*

INTRODUCTION

The destruction and the recycling of polymeric materials, without pollutant effects, is one of the important challenges concerning the efforts to preserve the natural environment. One of the simplest methods is the thermal degradation, but often this procedure is followed by the production of secondarily products with pollutant effects, and by dramatically modifications of the physical properties of the initial materials, [1 - 4]. One of the most popular polymers used for the fabrication of a large category of products,

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[1] *"Babes-Bolyai" University, Faculty of Physics, M. Kogalniceanu No 1, 400084 Cluj-Napoca, Romania*
* *Corresponding author: mihai.todica@phys.ubbcluj.ro*

packaging, and most recently for the thermal insulation of the buildings, is the polystyrene. It is known by very high chemical stability, resistance against a large category of solvent, good mechanical and thermal properties and low price of productions. However its large usage is accompanied by the production of huge amount of wastes which must be destroyed or recycling. Burning seems to be the simplest and cheap method of destruction, but this process can be accompanied by great modifications of the physical properties of the initial material. The aim of our study was the investigation by UV-VIS and fluorescence methods of the effects induced by this procedure.

EXPERIMENTAL

For this study we used samples of commercial polystyrene, with the same weight 10g, used as thermal insulation for building. A series of sample was heated 30 minutes at 200ºC, and another one at 350ºC. The samples were investigated by fluorescence methods with FP 8200 JASCO equipment, at different excitation wavelength, 315, 340 and 365nm. The UV-VIS investigation was done with Jasco V-670 system with scan speed 200 nm/min, UV VIS bandwidth 2 nm, and NIR bandwidth 8 nm.

RESULTS AND DISCUSSION

In order to establish the wavelength of the excitation radiation used for the fluorescence investigation we preceded to the UV-VIS analyzes.

Generally, the UV radiation causes the excitation of the electrons from a fully occupied orbital σ and π, or an unrelated orbital in connection with an unoccupied orbital orbital *n*, to an unoccupied antiorbital σ^* and π^*. In organic compounds, the most frequent transitions are $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$, because these compounds contain frequently unsaturated groups with orbital π. [5 - 7]. For a large category of polymers the most important absorption is observed in the domain 200-300 nm, determined mainly by the $\pi \rightarrow \pi^*$ transition of the carbonyl groups, [7, 11]. In our case, at room temperature, the UV-VIS spectrum of polystyrene shows a broad absorption peak centered at 263 nm, with a shoulder at 313 nm. Another peak, with smaller amplitude, is observed at 571 nm, (Fig. 1). The strong absorption in the domain 300nm nm suggests that the most suitable excitation for fluorescence emission should be located in this domain of wavelengths.

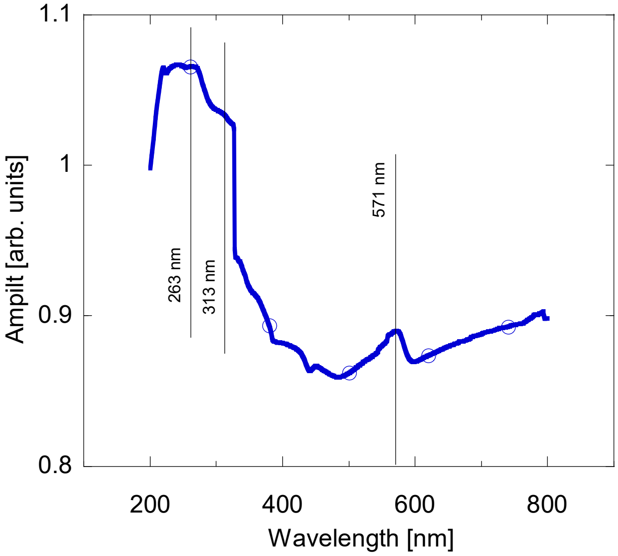

Fig. 1. The UV-VIS absorption of polystyrene at room temperature.

The fluorescence experiments involve the excitation of the electrons from theirs initial state to a high energy level by irradiation with a source of light with well defined wavelength. The return to the initial state can be realized directly by emission of a photon with the same energy as those of the exciting radiation, the resonant fluorescence, or by intermediate states, [7]. In this last case the transitions are accompanied by the emission of photons with energy smaller than those of the excitation. The excitation induces transitions between the lovest vibration level V_{00} of the fundamental state S_0 and one of the vibration level of the upper state V_1, in function of the energy of the incident photon $h\nu_0=\Delta W$. The non-radioactive return to the fundamental state involves transitions between the excited state V_{1*} of the state S_1 and the lowest vibration state V_{10} of the state S_1 through dissipative energy. The energy is used for the excitation of othe vibration modes of the molecule, or by inner molecular friction. Further, the molecule come back to its fundamental state by transitions between the lovest level V_{10} of state S_1 and one of the levels V_{0i} of S_0 state with the emission of a fluorescence photon. Although the excitation is made all the time at the same wavelength, the position of the intermediate state V_{0i} is not all the time the same, that results in the broadening of the spectrum, [8, 9].

We analyzed first the samples in the initial state, using for excitation radiations with 315 nm, 340nm and 365nm wavelength. At 315nm excitation we can observe a broad fluorescence peak located in the domain 350 - 490nm, with a maximum at 409nm. We can observe also a shoulder at 390nm and another one at 470nm, (Fig. 2). The broadening of the spectrum in this domain suggests a large dispersion of the probabilities of transitions between the levels V_{10} of state S_1 and the levels V_{0i} of state S_0.

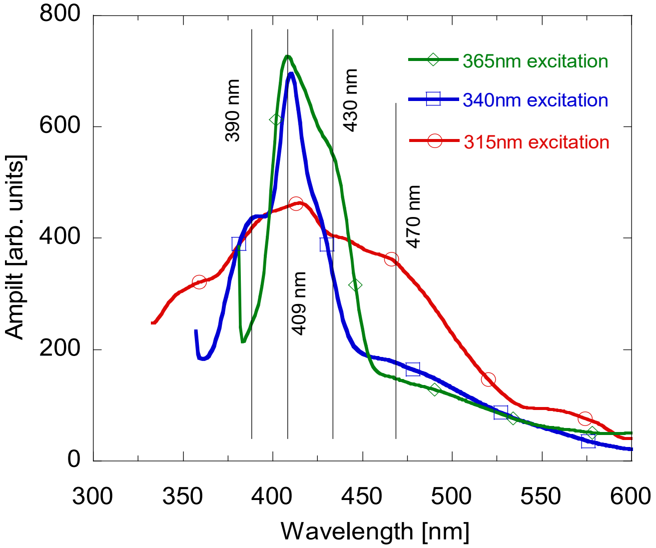

Fig. 2. The fluorescence spectra of polystyrene, at room temperature, excited at 315, 340 and 365m.

At 340nm excitation we can observe a fluorescence peak much narrow but higher, than those observed at 315nm excitation, with a maximum at 409nm. A weak shoulder is observed at 470nm. The narrowing of the spectrum suggests a reduction of the dispersion of the probabilities of transitions between the levels of states S_1 and S_0. At 365nm excitation we observed a fluorescence peak with a maximum at 409nm and a shoulder at 430nm. This peak has almost the same amplitude as the peak observed at 340nm excitation, (Fig. 2). The high amplitude and the narrowing of the fluorescence peak suggest that the most efficient excitation corresponds to 340-365nm wavelength. On the same time we can observe that the position of the maximum of the fluorescence peaks remains unshifted even the excitation changes, in agreement with the theory, [7, 10].

After heating at 200ºC, some changes appear. At 315nm excitation we can observe a weak narrowing and a modification of the shape of spectrum compared with the spectrum obtained at room temperature. The maximum of the peak is observed at 385-390nm, close to the peak 390nm observed at room temperature. The relative amplitude of this peak, compared with the peaks observed at 340nm and 365nm excitation, increases. The shoulder at 470nm remains unshifted. At 340nm excitation we can observe a narrow peak at 409nm and a weak shoulder at 470nm. Except a small modification of the shape and amplitude of the peak, the spectrum is similar with those obtained at room temperature. At 365nm excitation we can observe a large peak centered at 424nm, which is the superposition of the peaks 409nm and 430nm observed at room temperature. Increase of the temperature has as effect the modification of the probabilities of transitions between the levels S_1 and S_0 associated to these peaks, followed by a modification of the intensities of these peaks. The apparent shift of the maximum of the resulting peak from 409nm to 424nm is due to the different contribution of the initial peaks 409nm and 430nm in the superposition. The amplitude of this peak is comparable with the amplitude of the peak 409nm obtained at 340nm excitation. A shoulder at 470nm is observed at the same position like in the case of the excitations at 315 and 340nm, (Fig. 3).

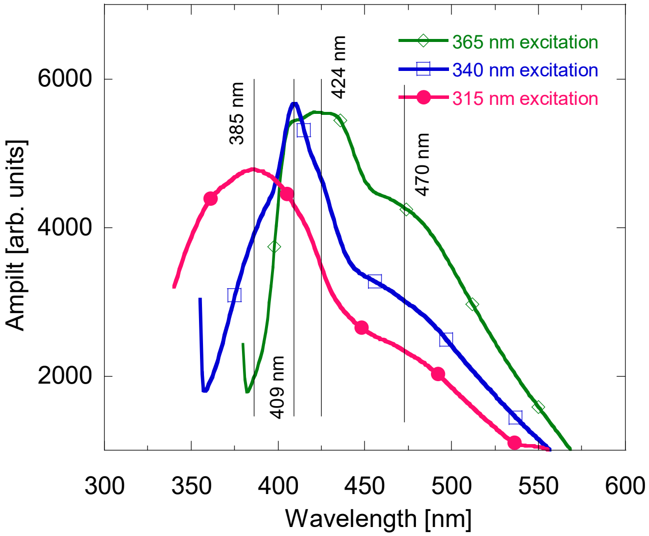

Fig. 3. The fluorescence spectra of polystyrene at 200ºC, excited at 315, 340 and 365m.

The amplitude of all the peaks increases compared with the amplitude at room temperature. However the position of the peaks, considering the effect of the superposition, remains unchanged after heating. We suppose that the electronic levels involved in these transitions are not affected by the heating process.

At 350ºC the general aspect of the spectra is similar to those obtained at room and 200ºC temperatures, except the amplitude of the peaks which is dramatically reduced. All the peaks appear unshifted in this spectrum, with weak modification of theirs shapes, (Fig. 4). All the excitations are followed by a fluorescence emission centered at 409nm. The shape of the peak is determined by the different contribution of the transitions between the states S_1 and S_0 to the fluorescence effect when the frequency of excitation changes. The superposition of the elementary peaks associated to these transitions give rise to the resulting fluorescence spectrum. Increase of the temperature induces modification of the probabilities of these transitions which is reflected by the modification of the general shape of the fluorescence spectrum.

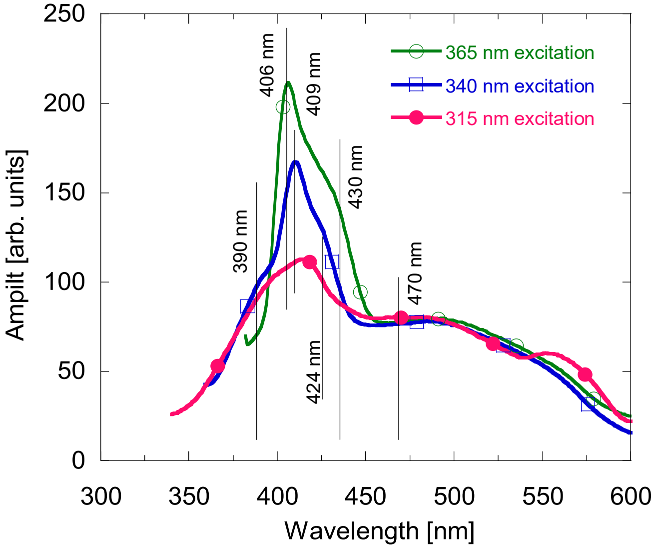

Fig. 4. The fluorescence spectra of polystyrene at 350ºC, excited at 315, 340 and 365m.

However the position of the fluorescence peak remains at 409nm, indicating the fact that the thermal treatment doesn't induced major changes on the electronic energy levels. Only the amplitude decreases with the temperature, fact associated with the irreversible degradation of part of the sample by oxidation. Observing the evolution of the fluorescence peaks in function of excitation we consider that the most stable and efficient fluorescence effect is obtained at 340nm excitation.

CONCLUSION

The behavior of some polystyrene samples thermally degraded was achieved by fluorescence investigation. The excitation was done at 315, 340 and 365nm, in accord with the UV-VIS absorption of these samples.

The fluorescence spectra of the polystyrene excited at different wavelengths contain peaks with widths and amplitudes depending on the frequency of excitation. This behavior is correlated with the probabilities of transitions between the electronic levels involved in the fluorescence emission. The most important peak appears at 409 nm, whatever the frequency of the excitation, but its amplitude depends on the excitation. Taking into account the amplitude and the width of this fluorescence peak, we assume that the 340 nm is the most efficient excitation. Modifications of the fluorescence spectra appear after thermal treatment. The position of the peaks remains unchanged, but the amplitude and the width depend on the temperature. At 200ºC the general aspect of the spectra is similar to those obtained at room temperature, but at 350ºC the amplitude decreases dramatically. We correlate this behavior with the oxidation process of part of the sample. However the stable position of the fluorescence peaks suggests a great stability of the polystyrene even at high temperatures. This property can be taken into account for the recycling of these materials by thermal treatment.

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