ANALYSIS OF PYROLYSIS RESIDUES' UV-VIS SPECTRUMS

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Abstract

In the course of the organic matters' anaerobic thermal degradation (pyrolysis) gas, liquid and solid products are formed. In our laboratory solid phase pyrolysis residues of various polymers were examined. The pyrolysis residues were extracted by different polarity solvents. The UV-VIS absorption spectrums of these extracts were saved. Examining of the characteristic area of the spectrums, specific differences were found. The material qualities of the starting polymers, and the condition of the pyrolysis made specific impact on the examined spectrums. On hydrocarbons, in the wavelength range of 200-800 nm, mainly the conjugated double bonded molecules (delocalized π electron system) show absorption. Molecule parts containing hetero atoms and functional groups are also could show absorption in this wavelength range. With this there can be inferred for the molecular fragments' material quality which is the result of the pyrolysis process. For polyamides and polyesters, monomers can be found in the pyrolysis residues by this study. The optical analysis of the solvent extracts of the pyrolysis residues is simple and effective method. Therefore the UV-VIS spectroscopy could be able to do the statistical analysis of the evolving, complex and the various molecules.

Our aim was to test a simple method, the measurement of the optical property of the pyrolysis residues' solvent extract, is able to characterize the pyrolysis process.

Key words: polymer molecules, pyrolysis residues, UV-VIS spectrums.

INTRODUCTION

In case of condensation polymers (polyesters, polyurethanes), the most used chemical recycling methods are the hydrolysis, methanolysis and the ammonolysis (Borda et al., 1999; Sinha V. et al., 2010; Zia K.M. et al., 2007). In case of addition polymers (eg PE, PP, PS, PVC), and plastic waste, they use pyrolysis, gassing and cracking (Maharana et al., 2007; Scheirs, Kaminsky, 2006). In the pyrolysis process the various organic molecules resolve many reaction ways because of the high temperature. In the pyrolysis residue molecules are formed contained varied sized, condensed benzene rings, and/or molecules with conjugated double bonds. The rising amount of easily excitable π-electron systems interacts lights with higher wavelength. Therefore the UV-VIS spectroscopy may suitable for the statistical analyze of the complex and diverse molecules, and to analyze of the pyrolysis process as well. They are used a similar method to study the humus. For the humus form characterization are the rates of the measured absorption of humus extracts at wavelengths of 465 and 665 nm

used (Schnitzer, 1982). This property known as the E4/E6, is in negative correlation with the quantity of condensed aromatic groups (Bravard, Righi, 1991; Stevenson, 1994).

MATERIALS AND METHODS

Six types of pyrolysis residues from polymeric materials (Ultramid, Poliram, PET, ribbon, cellulose, ABS) were analyzed (Table 1).

Table 1

Examined materials

Ultramid	Nylon 6,10	$[- NH(CH_2)_6NH - CO(CH_2)_8CO -]_n$
Polyram	Polyamide	
PET	Polyethylene terephthalate	
Rubber	Polyisoprene	
Cellulose	Polycondensed D-glycose	$[- C_6H_{11}O_5 -]_n$
ABS	Acrylonitrile Butadiene Styrene copolymer	
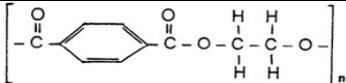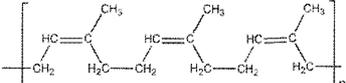
For the test 5-5 g shredded polymer samples were into test tubes weighted. The heat treatment was performed by programmable muffle oven of the laboratory. The tubes with the samples were randomized in a wire basket and put in the oven.

Each plastic samples were annealed in 9 repetitions, for the extracts which were made by 3 solvents, could be produced in 3 repetitions too. As a control, we annealed the solvents as well. The treatments were made with 2 types of temperature program (Table 2).

Table 2

The pyrolysis temperature program

Series	Heating up	Temperature	Keeping
A	150 min.	400 ^{o}C	60 min
B	180 min.	450 ^{o}C	90 min

The oxygen free pyrolysis was ensured by the following factors:
- By the start, beyond the sample we put 5 cm^3 distilled water into the test tubes. The water starts to boil and becomes steam then it squeezes out the air from the airspace above the test tube sample;
- During the temperature rise, the dilation of the gas in the airspace of the test tubes prevents the air from entering;
- The gaseous combustion products leaving the tubes also prevents from the air;

- After the cease of the gas evolution at cooling, the tubes were partly prevented from air entering by aluminum foil plug.

The plugs made of aluminum foil does not lock perfectly the test tubes. They don't prevent the test tubes gases to escape, but hampers effectively the diffusing of the air. Extracts were made from the cooled pyrolysis residues. The following solvents were used: methanol, gasoline and water. 5 cm^3 of solvent were put in each test tube contained pyrolysis residues. Reaching of dissolving balance was subserved by intensive stirring with a shaker. At all raw materials and all solvents 3-3 parallel samples were prepared, the extracts were filtered then measured by a spectrophotometer. If the measured absorbance value exceeds 2.5 then the sample was diluted with its own solvent (we used 10-fold dilution).

The spectrums were saved with a Shimadzu UV-3101PC spectrophotometer, in the range of 200-800 nm by 0.5 nm steps. The measured values were evaluated by excel and orgin programs.

RESULTS AND DISCUSSION

The extracts of various solvents differs widely. The differences based on the polar compounds soluble in polar solvents, and the apolar compounds soluble in apolar solvents. If the residue of the pyrolysis is polar, then it is able to dissociate in ionic form, and its molecules contains acidic and basic groups can be dissolved with polar solvents, water and small-scale methanol. Molecules with apolar hydro carbonic groups dissolve in apolar solvents, for example gasoline. The size of the molecules in all of three solvents, significantly affects on the solubility. The pyrolysis exfoliates the macromolecules forming polymers into smaller molecules.

During the molecule fragmentation, the number of double bonds in the molecules and the polarity of them typically increase. With this the pyrolysis product's solubility in polar solvents increases too. The numbers of the double bonds in conjugated positions are increasing, that of why the π-electrons delocalization are increasing too. The delocalized π-electrons can be excited with electromagnetic radiation with smaller energy (higher wavelength). As it can be seen in the Fig. 1, the water solubility of the molecules formed from the ABS polymers through the pyrolysis is increasing. The three replication's average of the spectrum lines can be seen in this and the further figures. The light absorption of the water-soluble fraction in higher wavelength is also considerable.

Measuring the extract by water, the spectrums showed significant differences in the different materials (Fig. 2). With the increasing wavelength the spectral curves are mostly exponential.

ABS 450 °C
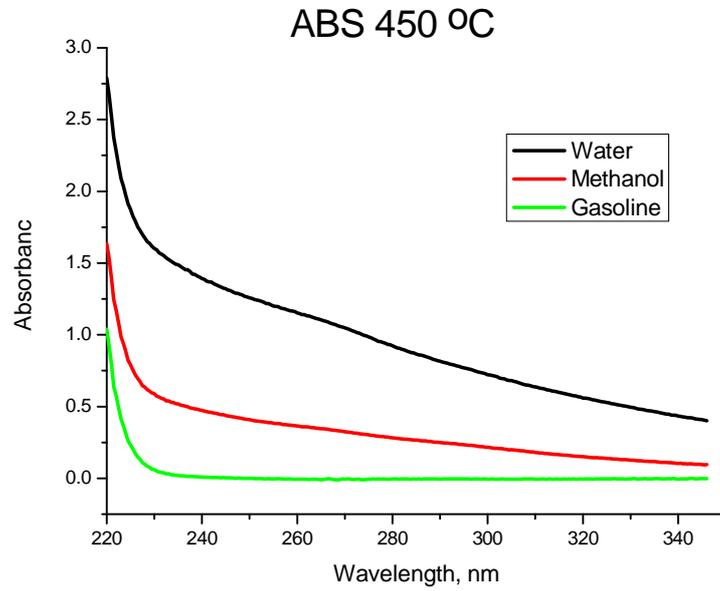
Fig. 1. Influence of different solvents on the absorbance of ABS raw material thermolysed products

400 °C water
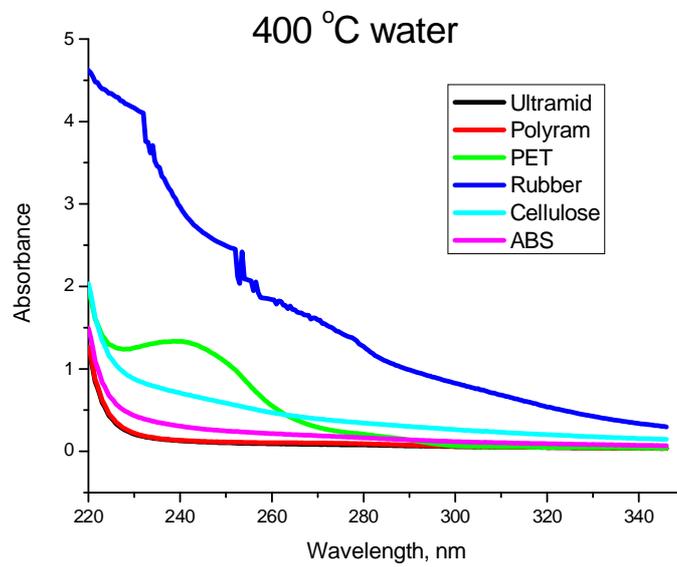
Fig. 2. Spectral features of the different termolysis products' raw materials extraction at 400 degrees
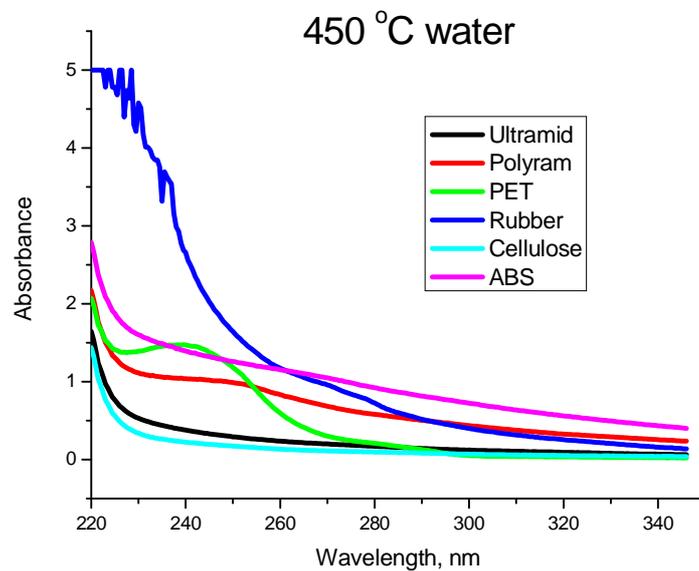
Fig. 3. Spectral features of the different termolysis products' raw materials extraction at 450 degrees
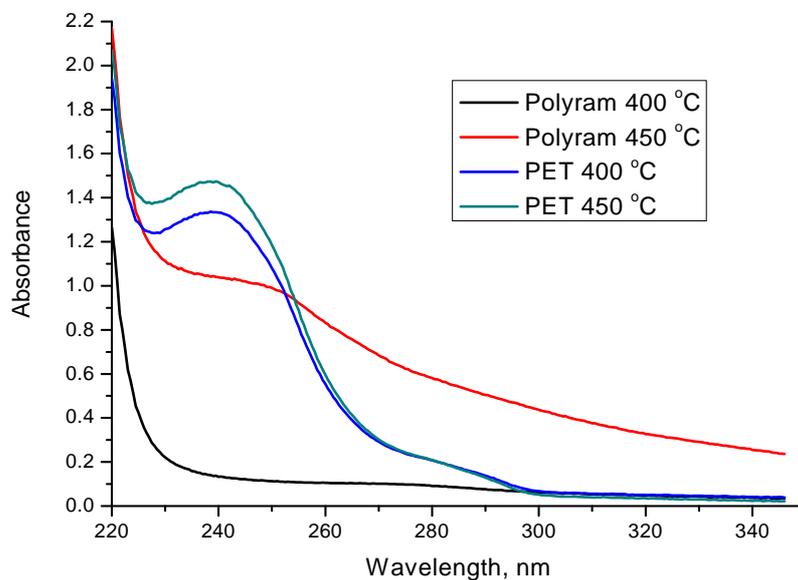
Fig. 4. The effect of the decomposition temperature on the spectrum of the Polyram and PET pyrolysis residue's extract

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Measuring a specific material, it can be proved, that more polar and apolar products formed in some heat measurements, but these rates are changed in depend of the heat measurement. Generally, at pyrolysis with higher temperature, more water soluble products formed in the pyrolysis residue. It can be seen at the example of the Poliram and PET (Fig. 4).

It can be seen at the Polyram, that the number of water-soluble molecules with optically active groups are minimal at 400 degrees. The light absorption of the extract has been greatly increased at 450 degrees. It can mean both the quantitative and the quality change of the extractable materials. It means that the pyrolysis process in the temperature range of 400-450 degrees caused significant change in this material. The Figure 4 shows that the pyrolysis process in case of the PET, has already progressed significantly below 400 degrees. The further 50 °C rise has caused no significant change.

The quality of the material which is formed in the pyrolysis residue from the heat treatment was followed in case of PET. Comparing the extracts made from different solvents (Fig. 5), was experienced that the products from the pyrolsysis dissolved differently but good in water and methanol, but not in gasoline.
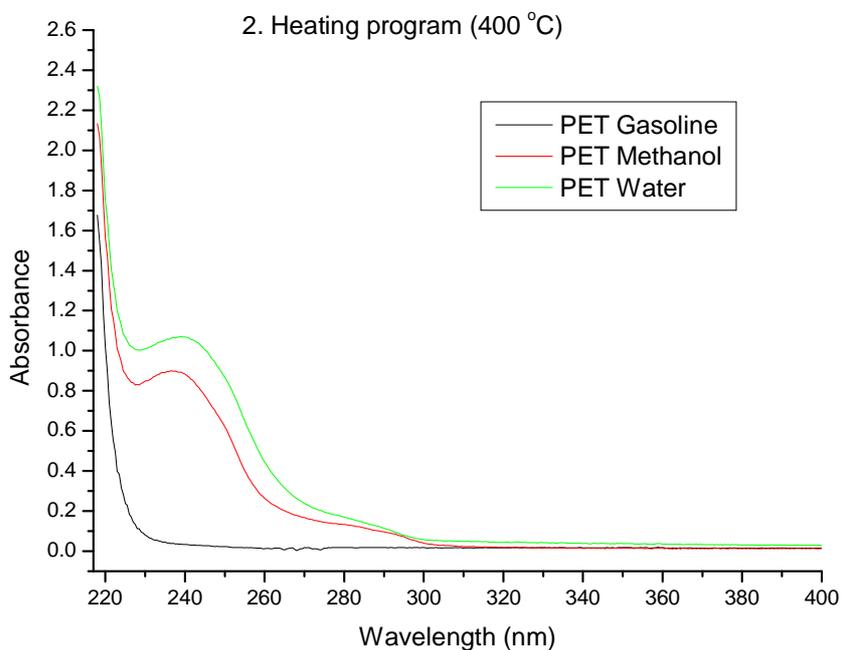
Fig. 5. The light absorption of PET's extracts

We suppose that the PET resolves into its own raw materials, to the ethylene glycol and the terephthalic acid, these materials boil at 197 degrees, so it can't be present at 400 degrees in the pyrolysis residue.
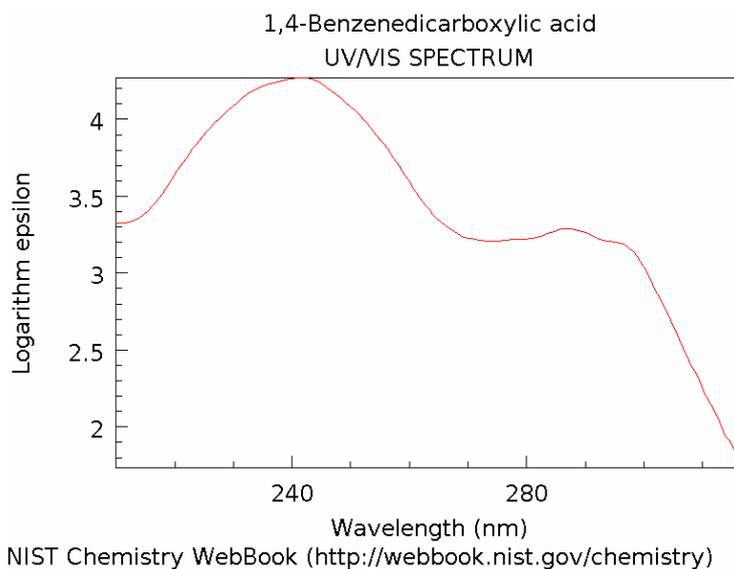
Fig. 6. The spectrum of the terephthalic acid
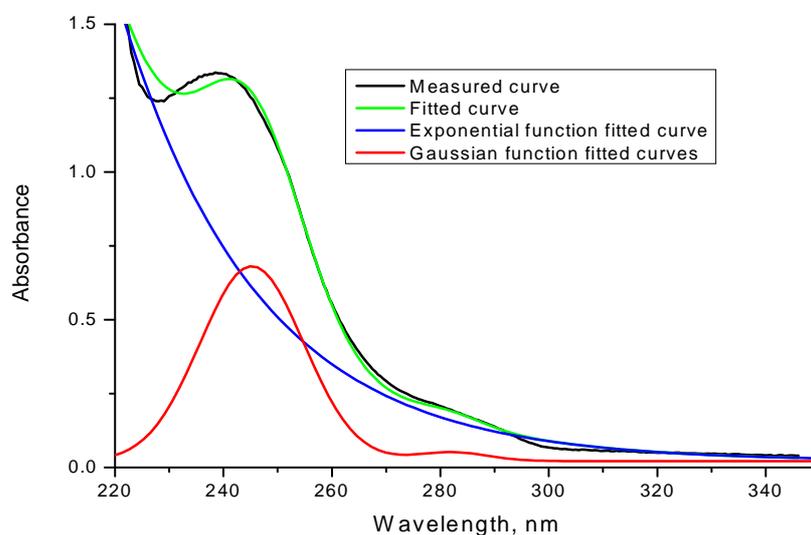
Fig. 7. The spectrum of the terephthalic acid (red curve), the exponential decreasing average curve (blue curve), the sum of the red and blue – fitted – curve (green curve). The measured spectrum is the black curve.

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For the spectrum of the terephthalic acid was searched in the literature (see Fig. 6). This graph's figure is similar to the water extract made from the residue of the PET pyrolysis. If we add the spectrum of the terephthalic acid to the exponential correlation from the average wavelength, then we get the spectrum which is from our measurements (Fig. 7).

We defined the spectrum of the terephthalic acid as the sum of two Gaussian functions, which maximum can be found at 240-250 and at 280-290 nm based on the Fig. 6. The fitted function is the following:

$$y = y_1 + A_1 \cdot e^{-\frac{x}{t_1}} + \frac{A_2 \cdot e^{-\left(\frac{x-xc_2}{w_2}\right)^2}}{w_2 \cdot \sqrt{\frac{\Pi}{2}}} + \frac{A_3 \cdot e^{-\left(\frac{x-xc_3}{w_3}\right)^2}}{w_3 \cdot \sqrt{\frac{\Pi}{2}}}$$

Equation 1. The fitted exponential and binomial Gauss function.

After the fitting the equation parameters were as follows:

Parameter	Value	Error
R^2	0.9951	
y_0	0.0	0.01
A_1	9518.5	2073.30
t_1	25.3	0.63
A_2	15.8	0.59
w_2	19.1	0.47
xc_2	245.2	0.16
A_3	0.5	0.00
w_3	13.2	4.00
xc_3	282.0	0.00

It can be seen at the R^2 parameter, that the shape of the curve with the applied function can be modeled without errors. The Gaussian curve that belongs to the lower wavelength maximum is 20 times bigger than the one that can be seen at higher wavelength. The two maximum points can be found at the expected intervals. According to that the spectrum of the

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terephthalic acid (red curve) added to the exponential decreasing average curve (blue curve), we get a curve (green curve) that fits tight to the spectra of the water soluble products formed in the pyrolysis residue of the PET.

CONCLUSIONS

Hydrocarbon compounds in the 200-800 nm wavelength range shows absorption molecules with conjugated double bond (delocalized π-electron system) mainly. Parts of molecules contain heteroatoms and function groups, both of them can show absorption in this wavelength. We conclude to the molecule fragments formed from the pyrolysis process by optical measurement. In case of polyamides and polyesters, certain monomers can be found in the pyrolysis residue. The pyrolysis process can be observed more efficiently with this simple measurement.

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