



CHARACTERIZATION OF FUNCTIONALIZED POLYPYRROLE

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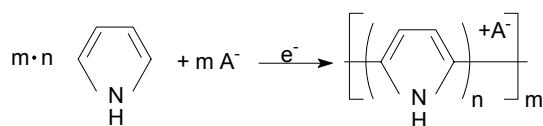
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Polypyrrole (PPY) was functionalized by reaction with glutardialdehyde using sulphuric acid as catalyst. The average size of polypyrrole powder particles was determined by Dynamic Light Scattering (DLS). The samples of functionalized polypyrrole were characterized by different techniques like thermo gravimetric analysis (TGA), differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), X-Ray Photoelectron Spectroscopy (XPS) and Fourier Transform Infrared Spectrometry (FTIR). The functionalization was not done during polymerization process as in other works, but after polymerization. The functionalization purpose was to create binding sites for enzyme immobilization at a distance from the polymer surface.

INTRODUCTION

Since polyacetylene was shown to exhibit high electrical conductivities when properly doped, π -polymers have been studied extensively.¹ During the last decades, conducting polymers (also called conjugated polymers or synthetic metals) such as polypyrrole (PPY) have been studied in great detail because of their rather straightforward preparation methods and reasonable stabilities in air and aqueous media. At the same time, they exhibit environmental stability, high mechanical strength and unique optical and electrical (switchable conductivity between insulator and metal) properties, leading to new possibilities for device fabrication. Polypyrrole and its derivatives, because of their long-term stability of its conductivity, are the leading materials among conducting polymers. Due to its surface properties such as wettability and because of potential

applications in corrosion protection, conductive textiles, antistatic coatings, in the immobilization of biopolymers and growth control of living cells, interest has been recently increased in polypyrrole.¹⁻⁵ PPY and its derivatives can be easily synthesized either by chemical or electrochemical methods (electro polymerization). Electro polymerization usually gives higher polypyrrole conductivity than the chemical methods.⁶ Chemical polymerization is carried out by reacting pyrrole monomer with an oxidant, such as ferric chloride or ammonium persulphate (which is faster than ferric chloride) in a suitable solvent. Electrochemical polymerization is done by oxidation of pyrrole monomer at a suitable anode upon application of a positive potential.^{4,7} The polymerization process in both cases involves the incorporation of certain charged anionic species into the polymer and may be simply described as follows:



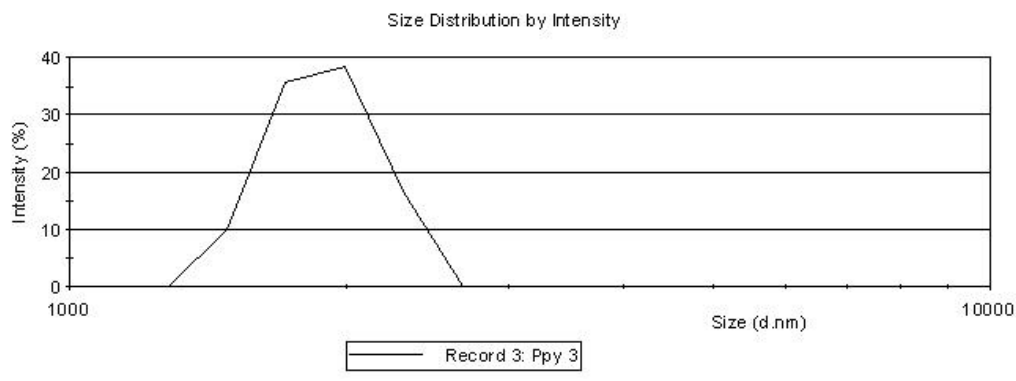
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where A represents the counterion incorporated into the polymer to balance the charge, n is the number of pyrrole monomers per positive charge (usually 2~3), m is the number of the counterion incorporated into the polymer. Polypyrrole exhibits switching properties. After polymerization, polypyrroles exist in their oxidized states. By applying electrochemical stimulation polypyrrole is able of switching between its oxidized and reduced state.⁴ Polypyrrole and its derivatives, *i.e.* pyrrolo [1,2-*a*] quinoline derivatives⁸ and pyrrolo [1,2-*b*] pyridazine derivatives,⁹ were also synthesized. Not only pyrrole derivatives can be synthesized, but also polypyrrole derivatives. Functionalized polypyrrole films have been obtained by electro polymerization in aqueous solution of pyrrole monomer in the presence of hydroquinone monosulfonate (HQS) as functional dopant in order to improve its electrical conductivity.⁸ Also, in order to enhance the electroconductivity, single wall nanotubes functionalized with polypyrrole films doped with poly (*m*-aminobenzene sulfonic acid) were synthesized.⁹

In our work, the functionalization was not done during the polymerization process as in the literature,^{10, 11} but after polymerization. The functionalization was done using glutardialdehyde in order to create binding sites for enzyme immobilization at a distance from polymer surface.

RESULTS AND DISCUSSION

The average PPY particles diameter is about 2.5 μ m with a monomodal distribution as it can be noticed from Fig. 1.



D=2469 nm

Fig. 1 – DLS analyses for polypyrrole powder particles.

In order to prove that PPY functionalization took place and to prove the reproducibility of the functionalization reaction, TGA tests for pure PPY and for three samples of functionalized PPY, prepared in identical conditions, were done. From Fig. 2 it can be observed that functionalized polypyrrole is more stable than pure polypyrrole. This is due to methylene-ammonium salt formation, which is a very stable compound. At the same time, the DTG curves (Fig. 3) confirm that functionalized polypyrrole is more stable than pure polypyrrole, because the temperature assigned to the maximum degradation speed is higher for all samples of functionalized polypyrrole. It can also be noticed that thermal degradation takes place with little differences between the three samples of functionalized polypyrrole, showing the reproducibility of the treatment process. The small differences in DTG of the functionalized samples are due to the concurrence between intramolecular and intermolecular crosslinking.

In order to better compare the thermal decomposition process for the four samples (pure polypyrrole and three samples of functionalized polypyrrole), the following parameters were measured for each sample: the temperature at which thermal degradation begins (T_{onset}) and it ends (T_{offset}), the weight loss, the temperature assigned to maximum degradation speed. These data are given in Table 1 and confirm that functionalized polypyrrole is more stable than pure polypyrrole because: for each sample of functionalized polypyrrole thermal degradation starts at a higher temperature than for pure polypyrrole and the weight loss is higher for pure polypyrrole than for functionalized polypyrrole.

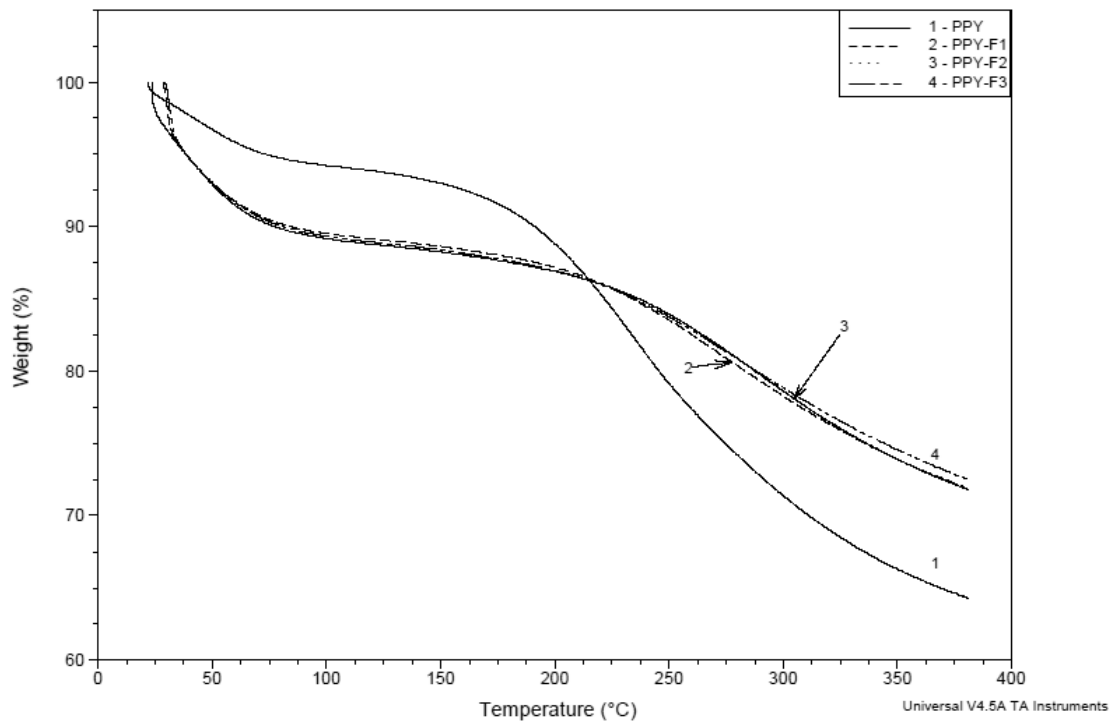


Fig. 2 – TGA curves for pure PPY (1) and three samples of functionalized polypyrrole prepared in identical conditions (2-4).

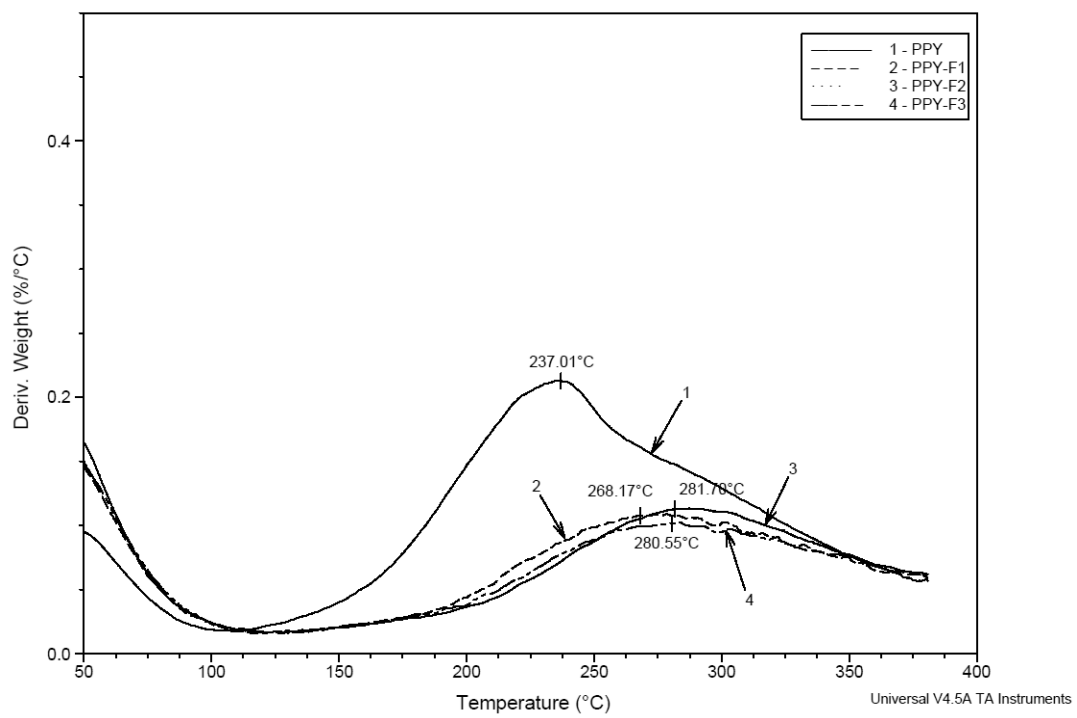


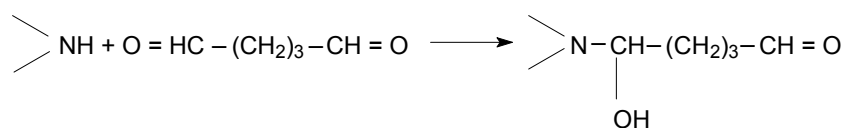
Fig. 3 – DTG curves for pure PPY (1) and three samples of functionalized polypyrrole prepared in identical conditions (2-4).

Table 1

Thermal decomposition data (main peak) for pure polypyrrole and functionalized polypyrrole

Sample	T _{onset} (°C)	T _{offset} (°C)	Weight loss (%)	T _{max} (°C)
PPY	102.40	379.37	29.85	235.51
PPY-F1	126.68	379.68	17.09	275.77
PPY-F2	154.97	380.60	16.35	291.45
PPY-F3	144.82	379.68	15.93	284.69

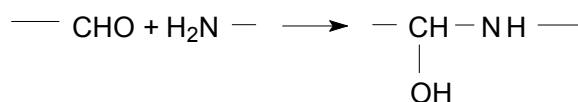
The reaction between CHO groups from glutaraldehyde and –NH groups from polypyrrole may be simply described as follows (Scheme 1):



Scheme 1 – Functionalization reaction of polypyrrole with glutardialdehyde.

The second CHO group is able to react in the same way, leading to cyclization or crosslinking. Reaction conditions must be chosen in such a manner that enough unreacted CHO group remain

for subsequent bonding of the enzyme. The immobilization reaction may be simply described as follows (Scheme 2):

Scheme 2 – Enzyme immobilization reactions between free CHO groups from glutardialdehyde and H₂N groups from the enzyme.

The possibility of a physical glutaraldehyde immobilization was prevented, because the polymer obtained after functionalization was washed with water for several times in order to eliminate the unreacted glutaraldehyde.

In order to further confirm that functionalization modifies the polypyrrole thermal behaviour, the T_g values for pure polypyrrole and the three samples of functionalized polypyrrole were determined.

The influence of functionalization reaction on glass transition temperature (T_g) is revealed by DSC curves (Fig. 4).

The T_g for each sample represents the value which is assigned to the inflection point. The T_g values are given in Table 2. For the T_g values corresponding to the three samples of functionalized polypyrrole, one may notice a slight variation, the values varying between 66-72 °C. Comparing the T_g values corresponding to the

three samples of functionalized polypyrrole to the value corresponding to pure polypyrrole, it appears that functionalization does not lead to significant changes in the T_g value. The low differences between the T_g values assigned to the three samples of functionalized polypyrrole are probably due to the competition between intramolecular and intermolecular crosslinking with glutaraldehyde. Also, because of this competition the temperatures assigned to the amorphous ordering (T_{max}, the temperature assigned to the peak from DSC for cooling processes) are different for the three functionalized polypyrrole samples. At the same time, these temperatures are different from the temperature corresponding to pure polypyrrole, confirming that functionalization reaction took place.

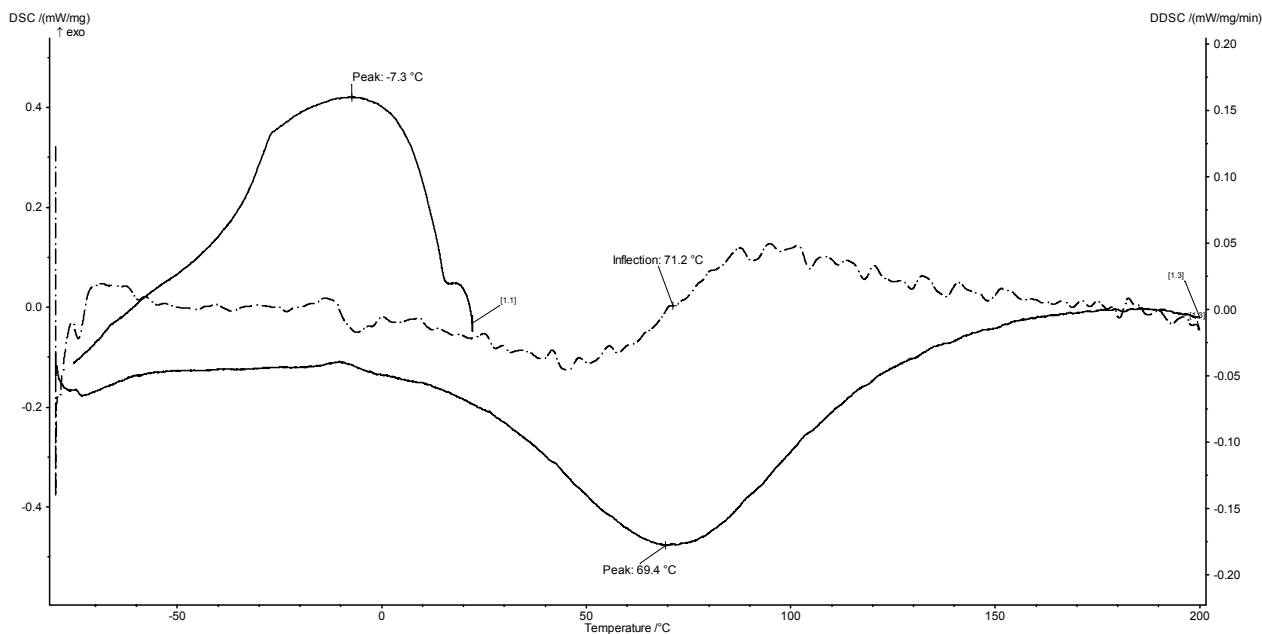


Fig. 4 – DSC curves of pure polypyrrole for heating (curve 1.3) and cooling (curve 1.1) processes and the corresponding first derivative (the curve with broken line) of this sample.

Table 2

T_g values and temperatures assigned to the amorphous ordering (T_{max}) for pure polypyrrole and three samples of functionalized polypyrrole revealed by DSC

Sample	T _g (°C)	T _{max} (°C)
PPY	71.2	-7.3
PPY-F1	66.3	4.9
PPY-F2	69.4	-14.7
PPY-F3	72.3	7.6

In order to further confirm PPY functionalization DMA tests were performed. From Fig. 5 one may observe that samples of functionalized polypyrrole obtained with different catalyst/PPY ratios exhibit different storage modulus compared to pure PPY. This is probably due to change of chemical composition by functionalization. From Fig. 6 it can be remarked that for functionalized polypyrrole the storage modulus decreases compared to pure polypyrrole. The decrease is more obvious for samples prepared with increased amounts of glutardialdehyde, fact which may be due to the increase of aliphatic groups which makes the structure more flexible. Fig. 7 shows that the storage modulus for the sample prepared at highest polypyrrole amount in the reaction mixture (solid/liquid ratio 1/112- curve 1) is much lower in comparison to that for pure PPY (curve 3) and for the samples obtained at lower solid/liquid ratio (curve 4 and 2). This fact shows that the samples prepared at solid/liquid ratio 1/137 and 1/150, because of the small content

of polypyrrole, had not enough available –NH groups for bounding glutardialdehyde and that the solid /liquid ratio is a very important parameter for the functionalization reaction.

In order to emphasize that chemical composition was modified by functionalization, another sample of functionalized PPY was prepared. Before preparing this sample, PPY was heated with distilled water at 70 °C for 30 min., thus a reference with a similar thermal history as the functionalized samples being prepared which was then used for functionalization.

For reference functionalization a liquid phase (mixture of 9.98 mL water, 0.02 mL GLA, 0.136 mL concentrated sulphuric acid) was poured onto 0.1 g reference. Thus, functionalized polypyrrole (PPY-F) sample was obtained. Comparing the elemental compositions from XPS data (Table 3) the following features are observed: the reference exhibits less N, S, O than PPY dry powder and a higher amount of C, for PPY-F the carbon amount is higher than for the reference but it exhibits a less

amount of O, N, S, the reference and PPY-F samples also exhibit a small Si amount which perhaps is due to the dust (SiO_2) from air, absorbed onto the samples surface. The N, S and O content is lower for the reference compared to polypyrrole dry powder, which is due to the fact that after

heating a mixture of polypyrrole and distilled water, the unreacted initiator (APS), is eliminated from polypyrrole. The carbon content increases because distilled water has absorbed CO_2 from atmosphere. These facts mean that before using PPY for functionalizing, it is necessary to purify it.

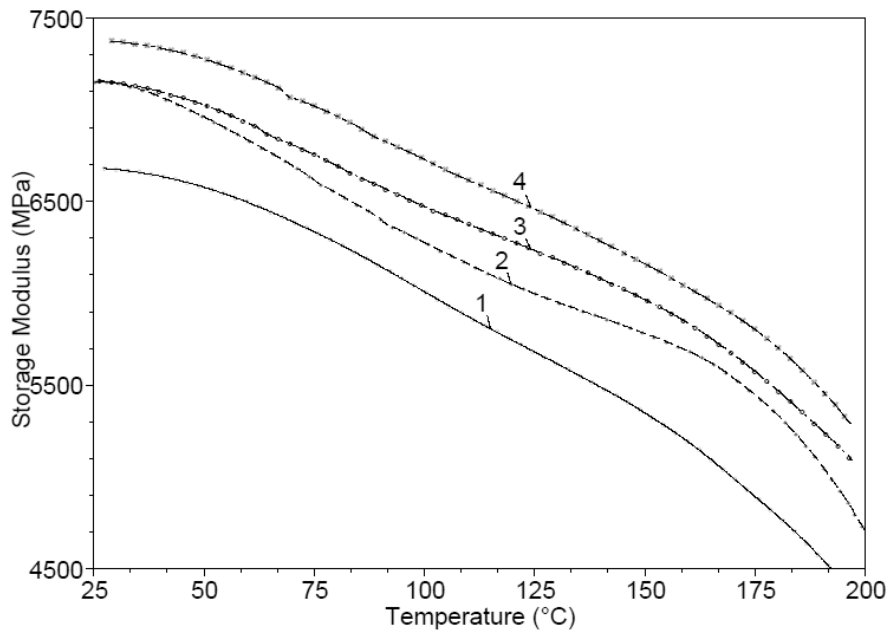


Fig. 5 – DMA curves for pure PPY(3) and for samples obtained with various catalyst /PPY ratios (mL H_2SO_4 /g PPY): 0.163/0.100(1); 0.109/0.100 (2); 0.136/ 0.100(4).

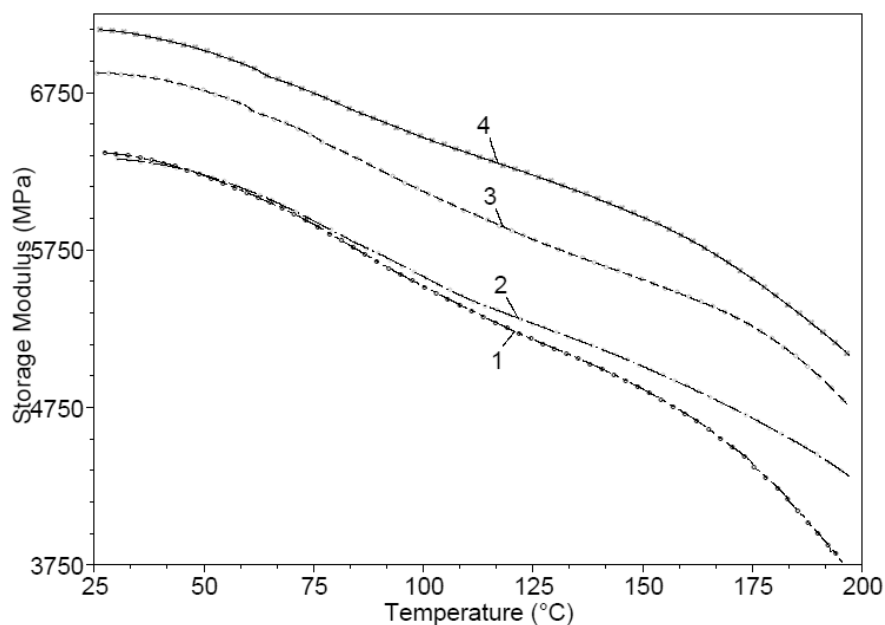


Fig. 6 – DMA curves for pure PPY (4) and samples obtained with various glutardialdehyde/water (GLA/W) ratios: GLA/W=1.50/8.50 (1); GLA/W=1/9 (2); GLA/W=0.25/9.75 (3).

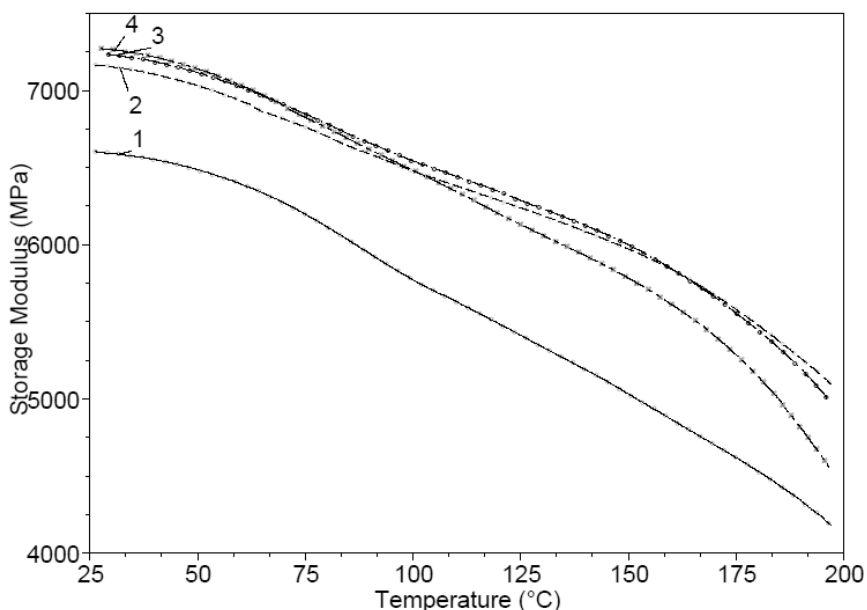


Fig. 7 – DMA curves for pure PPY (3) and samples obtained with various solid/liquid (S/L) ratio: S/L=1/112 (1); S/L=1/137 (4) S/L=1/150 (2).

The C content increase for PPY-F compared to reference is due to GLA bonding, because GLA exhibits a high C content. The N and S amount

decreases after functionalization because GLA does not contain these atoms. All these features show that functionalization reaction took place.

Table 3

Elemental composition for PPY, REFERENCE, PPY-F (mass %)

Sample/Element	O	C	N	S	Si
PPY	25.9	56.8	13.9	3.4	
REFERENCE	19.5	64.7	13.6	1.6	0.6
PPY-F	19.2	65.6	13.6	1.0	0.6

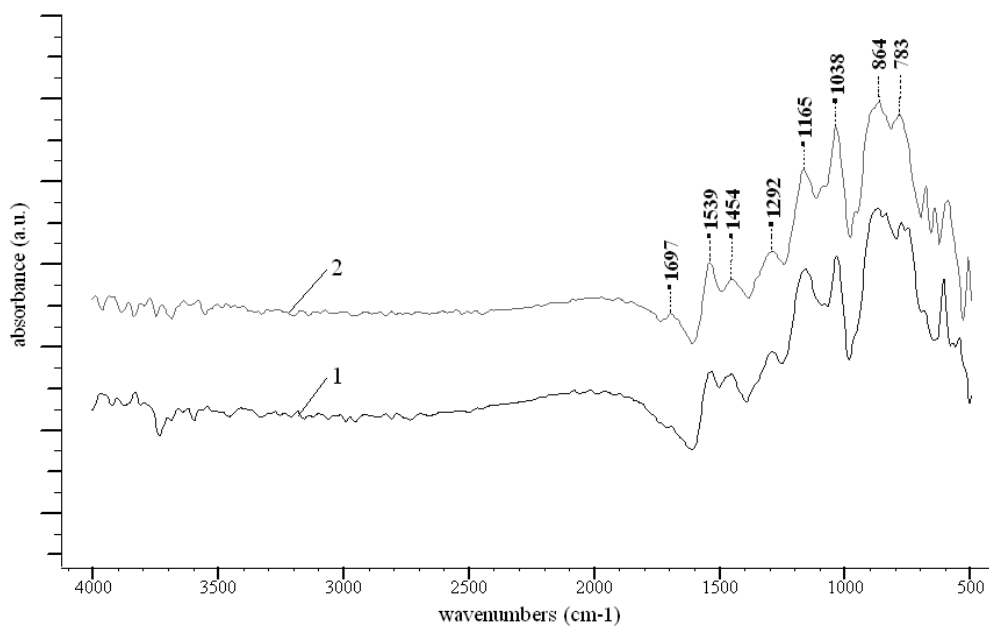


Fig. 8 – FTIR spectra for REFERENCE (1) and PPY-F (2).

In order to further confirm the differences between the pure PPY and PPY-F, FTIR spectra (Fig. 8) were recorded. The FTIR spectra exhibit the characteristic PPY absorptions. Characteristic PPY bands are given by: fundamental pyrrole rings vibrations (1539 cm^{-1} and 1454 cm^{-1}), in plane =C-H bond vibrations (1292 cm^{-1} and 1038 cm^{-1}), and the C-N bond stretching vibrations at 1165 cm^{-1} . The absorption bands from 870 and 780 cm^{-1} can be assigned to outside =C-H bond vibration. PPY functionalization is confirmed by amplitude increase and by the enlargement of the band from 1165 cm^{-1} assigned to C-N stretching vibration. In $600\text{-}1000\text{ cm}^{-1}$ frequency domain a slight change of the absorption bands can be noticed as a consequence of -CH (from PPY) and -CH₂ (from GLA) groups vibration superposition. The absorptions from 1697 cm^{-1} and 660 cm^{-1} can be assigned to unreacted compounds, which were eliminated by heating with distilled water, followed by drying.

EXPERIMENTAL

Materials

Pyrrole (PY) was supplied by Merck and distilled for further purification and then polymerized using ammonium persulphate as initiator in order to obtain polypyrrole (PPY). Ammonium persulphate was provided by Scharlau and used as received. Glutardialdehyde, aqueous solution 50% and sulphuric acid were received from Merck and used without further purification.

Sample synthesis

The PPY was synthesized by oxidative polymerization with ammonium persulphate, using a modification of a method reported in literature.¹² The modified procedure for PPY synthesis was described in our previous paper:¹³ 5mL pyrrole were dissolved in 250mL water; then, 16.4g APS were added stepwise during two hours under continuous stirring, at 5°C. After that, the obtained slurry was filtered, washed and dried in oven at 50-60°C for 6 h.

In order to synthesize functionalized PPY samples, firstly, the liquid phase was prepared by mixing the adequate amounts of water (8-9.75mL), glutardialdehyde (0.25-2mL) and sulphuric acid (0.109-0.163mL) in this order. Then, the liquid phase was poured onto polypyrrole (0.0667-0.1g) solid phase. The mixture thus obtained was heated at 70°C for 30 min., then filtered and washed for five times with distilled water on the filter in order to eliminate the unreacted glutardialdehyde. Three samples of functionalized polypyrrole were synthesized in the same conditions (0.1 g PPY, 8 mL water, 2 mL glutardialdehyde, 0.136 mL sulphuric acid, 70 °C, 30min.). The reference was obtained by heating PPY with distilled water at 70°C for 30 min. For synthesis of a reference functionalized PPY sample (PPY-F) a liquid phase (9.98mL water, 0.02mL GLA, 0.136mL concentrated sulphuric acid)

was poured onto 0.1g reference and the mixture was maintained 30 min at 70 °C.

Sample characterization

Dynamic Light Scattering (DLS). The DLS analyses were registered on a Nano ZS MALVERN (Red Badge) equipment which determines sizes of particles in the range 0.6nm-6µm.

Thermogravimetric Analysis (TGA). The TGA curves were recorded on a Q 500 TA instrument. Each sample was heated from 20 to 400 °C at 10 °C/min heating rate under a constant nitrogen flow rate (100 mL/min).

Differential Scanning Calorimetry (DSC). The DSC curves were registered on a Netzsch 204 F1 Phoenix equipment using a heating rate of 5 °C/min. under a constant nitrogen flow rate (40 mL/min). Each sample was heated from -80 °C to 200 °C and then cooled at -80 °C and reheated at 200 °C.

Dynamic Mechanical Analysis (DMA). The DMA curves were recorded on a Q 800 TA Instrument, at 1 Hz frequency, from 25 °C to 200 °C using a heating rate of 3 °C/min under air. The operating mode was temperature ramp, using powder clamp.

X-Ray Photoelectron Spectroscopy (XPS). The XPS spectra were recorded on a Thermo Scientific K-Alpha equipment, fully integrated, with an aluminium anode monochromatic source (1486.6 eV). The charging effects were compensated by an argon flood gun.

Fourier Transform Infrared Spectrometry (FTIR). The FTIR spectra were registered on a Able Jasco 4100 equipment using 32 scans and 4 cm⁻¹ resolution in 500-4000 cm⁻¹ region. The samples were analyzed using ATR unit.

CONCLUSIONS

At this stage of our research, the polymer functionalization degree is not still well controlled, but some general features appear. By the functionalization of polypyrrole, its stability is increased. The TGA and DTG curves confirm that functionalization reaction takes place and is reproducible. The functionalization is confirmed by the stability increase after functionalization (the maximum degradation temperature increases) as a consequence of methylene-ammonium (very stable compound) formation during functionalization. The functionalization reproducibility is proved by the low differences between the temperatures assigned to thermal decomposition of the three samples of functionalized polypyrrole. The DSC showed that functionalization does not lead to important T_g changes. Anyway, after functionalization the temperature assigned to the maximum at cooling processes changes, confirming that this reaction took place. After functionalization, important thermal stability changes are noticed, showing that functionalization takes place not only at polypyrrole particles surface, but also in the interior of these particles as

our previous paper,¹⁴ by X-Ray Diffraction (XRD), proved. During polypyrrole functionalization the aliphatic groups content increases, leading to a more flexible structure. The higher flexibility causes the storage modulus decreasing, as DMA tests showed. FTIR spectra confirm pyrrole polymerization and polypyrrole functionalization. The XPS analyses prove that after functionalization, the surface elemental composition is modified. The XPS being a surface characterization technique, was used only to show the surface elemental composition changes due to PPY heating with distilled water and to PPY functionalization.

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REFERENCES

1. D.H. Han, H. J. Lee and S. M. Park, *Electrochim. Acta*, **2005**, *50*, 3085-3092.
2. X. Yang, T. Day, Z. Zhu and Y. Lu, *Polymer*, **2007**, *48*, 4021-4027.
3. D. Mecerreyes, R. Stevens, C. Nguyen, J. A. Pomposo, M. Bengoetxea and H. Grande, *Synthetic Met.*, **2002**, *126*, 173-178.
4. B. Xi, "Novel conducting polymer structures for electrochemical actuators", Doctoral thesis, University of Wollongong, Australia, 2005.
5. L. Xu, W. Chen, A. Mulchandani and Y. Yan, *Angew Chem.*, **2005**, *44*, 6009-6012.
6. M. S. Ba-Shammakh, "Electropolymerization of pyrrole on mild steel for corrosion protection", Doctoral thesis, King Fahd University of Petroleum & Minerals, Dhahran, Saudi Arabia, 2002.
7. P. Saville, Polypyrrole Formation and Use, Defence R&D Canada Atlantic Technical Memorandum; DRDC Atlantic TM 2005-04, January 2005.
8. E. Georgescu, F. Dumitraşcu, F. Georgescu, C. Drăghici and M. M. Popa, *Rev. Roum. Chim.*, **2010**, *55*, 217-221.
9. F. Dumitraşcu, C. Drăghici, M. T. Căproiu, D. G. Dumitrescu, M. M. Popa, *Rev. Roum. Chim.*, **2009**, *54*, 923-926.
10. W. Prisanaroon-Ouajai, P. J. Pigram and A. Sirivat, *Jom-J. Min. Met. Mat. S.*, **2008**, *18*, 23-26.
11. K. Wanekaya, Y. Lei, E. Bekyarova, W. Chen, R. Haddon, A. Mulchandani and N. V. Myung, *Electroanal.*, **2006**, *18*, 1047-1054.
12. J. Honey, M. T. Rinku, J. Joe, J. Rani and K. T. Mathew, *Microw. Opt. Techn. Let.*, **2006**, *48*, 1324-1326.
13. T. Sandu, A. Sârbu, S. A. Gârea and H. Iovu, *UPB Sci Bull; Series B*, **2011**, *73*, 123-132.
14. T. Sandu, A. Sârbu, F. Constantin, E. Ocnaru, S. Vulpe, A. Dumitru and H. Iovu, *Revue Roum. Chim.*, **2011**, *56*, 875-882.

