JOURNAL OF MATERIALS SCIENCE **35** (2000) 1743–1749

Surface characterizations of conductive poly(methyl methacrylate)/polypyrrole composites

M. OMASTOVÁ*
Polymer Institute, Slovak Academy of Sciences, Dúbravská cesta 9, 842 36 Bratislava, Slovak Republic
E-mail: upolmaom@nic.savba.sk

F. SIMON
Institute of Polymer Research Dresden, Hohe Strasse 6, 01069 Dresden, Germany

The composites of poly(methyl methacrylate) and polypyrrole (PMMA/PPy) were prepared by a chemical oxidation of pyrrole in a PMMA latex medium resulting in a network like structure of polypyrrole embedded in the insulating polymer matrix. Water was used as the dispersion medium. The content of polypyrrole was determined by elemental analysis as varying from 0.25 wt.% to 10 wt.%. The electrical conductivity of prepared composites depends on the concentration of polypyrrole and reached values of between 1×10^{-9} S/cm to 0.1 S/cm The surface of powder form of PMMA/PPy composites was characterized by X-ray photoelectron spectroscopy (XPS) and by scanning electron microscopy (SEM). The antistatic properties of compression moulding form of composites were tested.

1. Introduction

Several attempts have been made to improve the poor mechanical properties of conductive polymers by forming blends or composites with other polymers. A combination of conventional polymers or copolymers [1] with conductive polymers allows the creation of new polymeric materials with interesting electrical properties. Moreover, blending with conductive polymers can also solve the problem of surface static charge of poly(methyl methacrylate). Electrochemically [2] or chemically [3] prepared polypyrrole (PPy), which exhibits conductivity values up to 1000 S/cm, is stable in air. A large numbers of studies using XPS has been devoted to the characterization of chemically or electrochemically synthesized PPy [4–6].

First PMMA/PPy composite films with a conductivity of about 0.12 S/cm were prepared in 1988 [7] using the chemical oxidative polymerization method which involves spreading a water-immiscible solvent solution of pyrrole and PMMA on the surface of the aqueous solution containing $K_2S_2O_8$. The detailed characterization of these films using the elemental analysis, thermogravimetry and XPS was published by Chan *et al.* [8]. Later Stanke and co-workers [9] synthesized a graft copolymer film of PMMA and PPy. A two-step process, involving an emulsion containing a solution of surfactant in the first phase, was developed in the Ruckenstein's laboratory [10, 11] for the preparation of polyaniline/poly(alkyl methacrylate) or polypyrrole/poly(alkyl methacrylate) composites. Pyrrole was present in the organic solvent. The electrical conductivity of the composites reached a value of about 6 S/cm when the PPy content was higher than the percolation threshold (10 wt.% PPy). The type and concentration of the surfactant also affected the conductivity. The authors also concluded that a single step procedure leads to composites with very low conductivities. Chehimi *et al.* [12, 13] used XPS study to determine the surface composition of absorption of PMMA on chlorine and tosylate-doped PPy from neutral, acidic and basic solvents. Over the last decade XPS has became an established technique for the characterization of polymer surfaces [14, 15]. Preparation of micro- and nano-sized conducting materials received much scientific and technological attention because of possible applications. Yassar *et al.* already in 1987 reported that chemically synthesized PPy could be deposited *in situ* onto polystyrene latex particles [16]. Later polyaniline (PAni) was used for preparation core-shell conducting dispersions [17, 18]. Wiersma *et al.* at DSM Research have demonstrated that sterically-stabilizes latex particles can be coated with PPy or PAni in aqueous media to form composite latexes with good colloid stability [19, 20]. Armes *et al.* [21] described the preparation PPy- and PAni-colloidal silica composites, but the deposition of conducting polymer was non-uniform process. Lascelles and co-workers reported the synthesis of micrometer-sized PPy-coated polystyrene latexes [22].

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[*] Author to whom all correspondence should be addressed.

0022–2461

Peruchot *et al.* [23] examined the surface of one of these latexes containing 8.7% PPy by XPS, confirming uniform nature of the PPy overlayer. Latest results showed that polyaniline coating are much less uniform than the PPy overlayer on polystyrene latexes [24].

In our work pyrrole is polymerized by chemical oxidation in a poly(methyl methacrylate) latex medium. The result of first investigation of powder form of prepared composites using SEM led to more detailed study of surface characterization of both, powder and compression moulded forms of composites. The prepared composites were characterized by XPS. Surface discharging behaviour of PMMA/PPy composites was compared with the behaviour of virgin PMMA.

2. Experimental procedure

2.1. Chemicals

Pyrrole (Merck-Schuchardt, Germany) was distilled twice under reduced pressure and stored in a refrigerator at about 4 °C before use.

Poly(methyl methacrylate) particles were synthesized in our laboratory by emulsion polymerization [25] in water as a dispersion medium containing sodium dodecyl sulfonate as an emulsifier. Light scattering and transmission electron microscopy was used to determine the particle size. The diameter of prepared PMMA particles was found to be about 100 nm.

2.2. Preparation of composites

An emulsion containing 5 g poly(methyl methacrylate) was diluted with 25 ml of water and then $FeCl_3$ dissolved in 10 ml water was added. Pyrrole was dissolved in 5 ml of water and inserted dropwise under vigorous stirring. The pyrrole concentration, relating to the amount of the dispersed polymer particles, varied from 0.25 wt.% to 10 wt.%. The molar ratio of $FeCl_3$ to pyrrole was 2.3. The reaction mixture was stirred for 4 h at room temperature. The polymer product was precipitated from the emulsion by freezing the latex, washing with distilled water and filtering off. The prepared composites were dried in a vacuum oven at 50 °C. The prepared powder composite samples were compression moulded at 220 °C for 2 min. under 22.5 kN/cm^2 for further investigation. The thickness of the compression moulded samples was about 0.2 mm.

2.3. Instruments

The particle size of synthesized PMMA was determined by light scattering. A BI-90 Particle sizer (Brookhaven Instruments Corp., USA) was used.

The weight percentage of polypyrrole in the composites was determined by elemental analysis using an elemental analyser CHNS-O EA 1108 (Carlo Erba, Italy).

The electrical conductivity in the polymer composites was measured by the standard four probe method. Samples were cut into strips of about 5 × 25 mm. To achieve good electrical contacts a small gold pattern was sputtered on the sample surface. All measuring instruments (for current and voltage) were connected to a PC in order to collect and calculate the data.

The microstructure of PMMA and PMMA/PPy composites was observed using a low voltage scanning electron microscope DSM 982 Gemini (Zeiss Oberkochen, Germany). Samples without any metal coating were glued to an electrically grounded sample holder using double faced conductive tape. Light microscopy study was performed using Laborval 4 light microscope (Carl Zeiss Jena, Germany) connected with video system.

A spectrometer VG ESCA lab 220i (England) was used to acquire photoelectron spectra of sample surfaces. Unmonochromatized Mg $K_{\alpha 1/2}$ ($h\nu = 1253.6$ eV) radiation was used as the excitation source. The power of the source was 300 W at 20 mA. The typical base pressure was lower than 10^{-9} mbar. The binding energy (BE) scale of the spectra was set on the Cu $2p_{3/2}$ peak ($BE = 932.67$ eV) and the Au $4f_{7/2}$ peak ($BE = 84.00$ eV). An IBM PC using the VG ECLIPSE software routine performed data collection and analysis. The peaks background was subtracted according to the Shirley method [26]. Quantitative determinations of the elemental surface composition have been carried out using the spectrometer transmission function and Wagner's atomic sensitivity factors [27]. During the measurements, the spectrometer was working in the constant analyser energy mode with constant pass energy of 80 eV in the case of survey spectra and 25 eV for resolved spectra.

Surface discharging characteristics of the polymer samples were measured using an integration electrometer POLYSTAT PS-1 (JZD Jizera, Czech Republic). A compression moulded 1 mm thick disc of the polymer sample cleaned in n-heptane was fixed on a holder and charged in a 15 kV electric field (corona discharge). The decrease of the surface electric potential over time was periodically measured and plotted.

3. Results and discussion

3.1. Conductivity of PMMA/PPy composites

The influence of the amount of polypyrrole in the PMMA/PPy composites on their electrical conductivity was investigated using the compression moulded samples. The concentration of polypyrrole in the composites varied from 0.25 wt.% to 10 wt.%. The PPy content was calculated from the nitrogen content obtained by elemental analysis, which was compared to the nitrogen value of chemically prepared pure PPy. PPy prepared in our laboratory contained 15.7 wt.% N. Fig. 1 shows that the conductivity of composite increases with the increasing weight percentage of polypyrrole. Even the presence of a very small amount of PPy in the composites results in a significant conductivity increase. The bulk conductivity of pure PMMA has been found [28] to be about 10^{-13} S/cm. The conductivity of PMMA/PPy composites containing 1.12 wt.% PPy is 8.8×10^{-9} S/cm. An increase in the content of PPy from 1.12 wt.% to 9.9 wt.% in PP/PPy composites results in an enormous increase in conductivity by seven orders of magnitude.

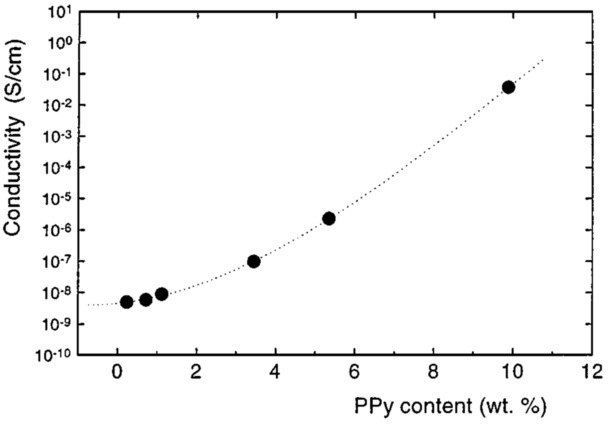


Figure 1 Conductivity dependence of PMMA/PPy composites on PPy content.

3.2. Morphology of PMMA and composites

In Fig. 2a the surface structure of PMMA powder particles is shown at magnification 10 000-times. The surface of unmodified PMMA particles is rather rough. In Fig. 2b only small differences are visible on micrographs of PMMA/PPy powder composite containing 5.35 wt.% PPy compared to morphology of virgin PMMA. The picture is sharper as a result of higher conductivity of surface, where some amount of PPy is present. However, typical PPy cauliflower-like morphology was not observed.

The covering of PMMA particles with PPy using chemical modification reaction is already visible from composite appearance. The colour of powder particles changed from white (virgin PMMA) to grey or dark grey in composites, depending on quantity of PPy present in composite sample. Fig. 3a and 3b from light microscopy study of virgin PMMA and PMMA/PPy composite containing 1.12 wt.% PPy provided further evidence for it.

3.3. XPS analysis

The primary aim of the X-ray photoelectron spectroscopy studies was to analyse the surface layer of the powder PMMA/PPy composite. Besides this, also the study of the pure components, PMMA and PPy powders was carried out.

Fig. 4 shows the XPS spectra of chemically synthesized PPy, PMMA, and PMMA/PPy composite

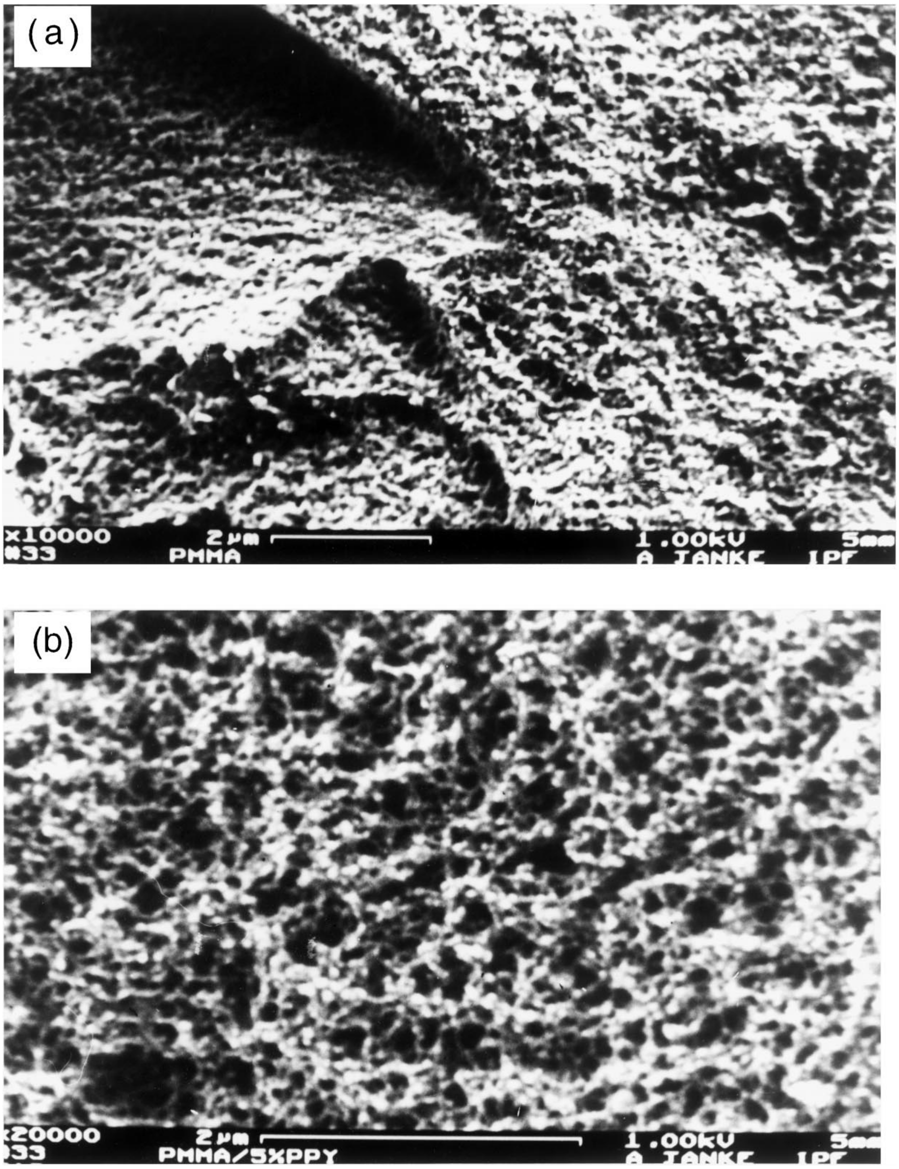


Figure 2 SEM micrographs of (a) PMMA, and (b) PMMA/PPy composite powder particles containing 5.35 wt.% PPy.

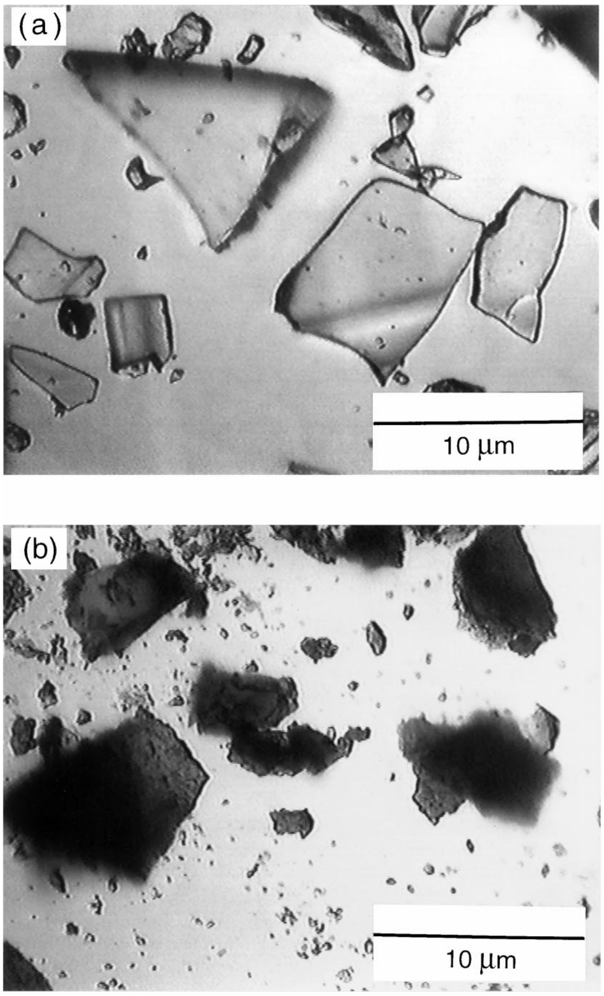


Figure 3 Cross-polarized optical micrographs of (a) PMMA particles, and (b) PMMA/PPy composite particles containing 1.12 wt.% PPy.

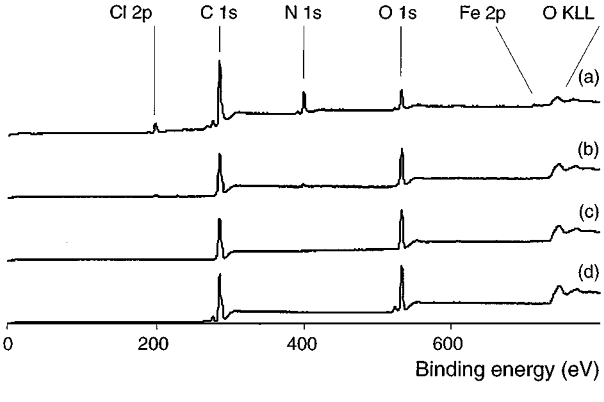


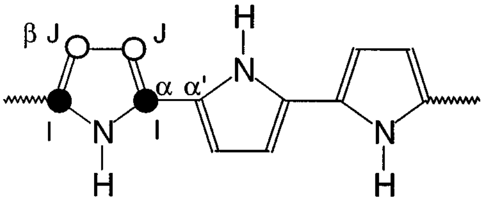
Figure 4 Survey XPS spectra of (a) chemically synthesized PPy, (b) powder PMMA/PPy composite containing 9.89 wt.% PPy, (c) PMMA/PPy composite containing 1.12 wt.% PPy, and (d) PMMA.

TABLE I The results of XPS quantitative analysis of chemically synthesized PPy, PMMA, and powder PMMA/PPy composites

Sample / Ratio	PPy	PMMA	PMMA/1.12% PPy	PMMA/9.89% PPy
[O] : [C]	0.1198	0.3971	0.3854	0.3937
[N] : [C]	0.1596	—	0.0047	0.0293
[Cl] : [C]	0.0551	—	—	0.0116
[Fe] : [C]	0.0040	—	Traces	Traces

powders containing 1.12 wt.% and 9.89 wt.% PPy. C, N, O, and traces of Cl and Fe were found in both composite samples. The survey spectrum of PPy powder shows the expected peaks of polypyrrole: C (as C 1s, C KVV) and N (as N 1s, N KLL). In addition, oxygen (as O 1s, O $KL_{23}L_{23}$ [O KL1], O $KL_{23}L_1$ [O KL2], O KL_1L_1 [O KL3]), chlorine (as Cl 2p, Cl 2s) and iron (as Fe 2p, Fe 3p, Auger series Fe LMM) were found. The quantitative analysis of the samples is given in Table I. In contrast to the theoretical atomic ratio $[N]:[C]_{theo} = 0.25$, the value $[N]:[C]_{real} = 0.1596$ was found in PPy prepared in our laboratory. The reasons of the excess of carbon may consist in the presence of impurities from hydrocarbons and carbon-oxygen compounds showing by the oxygen peak.

It is important to note that the sample did not show an electrical charging during the measurements. The highly resolved C 1s spectrum of PPy is shown in Fig. 5a. This spectrum shows a wide tail at higher binding energies (BE). The spectrum was decomposed into six component peaks named E, F, G, H, I and J. The maximum of J is situated at BE = 283.7 eV. In contrast to paraffin (BE = 285.00 eV) the delocalized p_π electron system PPy shifts the component peak J to ΔBE = 1.3 eV to lower BE. The second component peak of the PPy structure (I) is shifted from F to ΔBE = 0.85 eV. The structure elements of J and I are given in Scheme 1 [4, 29]:



Scheme 1

According to Scheme 1 the intensities of J and I should be the same. However, I has a higher both count rate and line width.

The atomic ratio [N] : [C] determined by means of the high-resolution C 1s spectrum is given by Equations 1 and 2.

$$\frac{N}{C} = \frac{[\text{Peak I}]}{2 \cdot \sum[\text{Peak i}]} = 0.1977 \qquad (1)$$

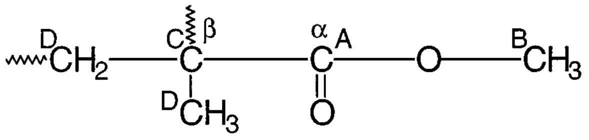
$$\frac{N}{C} = \frac{[\text{Peak J}]}{2 \cdot \sum[\text{Peak i}]} = 0.1211 \qquad (2)$$

The comparison between the [N] : [C] ratios from Equationqs 1 and 2 and $[N]:[C]_{real}$ from the survey spectrum shows that I is too large and J is lower than expected. The differences in line width of peaks I and J were discussed in the literature [4]. In real structure of PPy the presence of α–α' bonds together with crosslinked structures (partial involvement of the β–carbons in ring bonding), saturated rings and terminated pyrrole units were confirmed. The mean value of Equations 1 and 2 ($[N]:[C]_{mean\ value} = 0.1594$) corresponds very well with $[N]:[C]_{real}$.

The third component peak H is much wider as I and J. That peak results from hydrocarbon and carbon-oxygen compounds containing oxygen with a low oxidation number (C–OH, C–O–C). Component peak G represents carbon-oxygen compounds of higher oxidation number (C=O, COO). These bonds may be formed during the polymerization process as a consequence of both the presence of water in the solution and the reaction of atmospheric oxygen with polypyrrole [30, 31]. In the reference [4] three different shake-up peaks have been described. According to the BE the component peaks E and F were interpreted as shake-up peaks. The shake-up peaks E and F result from the highly conjugated p_π electron system. The third shake-up peak at $BE \approx 295$ eV was not detected.

From the survey spectrum of PMMA (Fig. 4) the determined atomic ratio $[O]:[C]_{real} = 0.3971$ corresponds very well with the theoretical ratio of $[O]:[C] = 0.4$. Impurities were not detected in the surface region.

According to the structure formula (Scheme 2) the C 1s spectrum was decomposed into 4 component peaks (Fig. 5b) corresponding the following structure elements:



$$\sim\!\!\sim CH_2-C(CH_3)-C(=O)-O-CH_3$$

Scheme 2

The peak areas of A ($\underline{C}OO$), B ($\underline{C}$–O–$\underline{C}$) and ($\underline{C}$–COO) were equal. This result is in a good agreement with the structure shown in Scheme 2. Furthermore, the BEs found correspond well with data published in the literature [15, 32]. The atomic [O] : [C] ratio determined from the high-resolution spectrum is almost equal to that found in the survey spectrum (Equation 3).

$$\left.\frac{[O]}{[C]}\right|_{C1s} = \frac{2\cdot[\text{Peak A}]}{[\text{Peak A}]+[\text{Peak B}]+[\text{Peak C}]+[\text{Peak D}]} = 0.3777 \qquad (3)$$

The ratio of [component peak A] : [component peak D] should be 0.5 (Scheme 2). However, a small excess of hydrocarbon (D) was found.

The O 1s spectrum of PMMA (Fig. 6) shows the two component peaks of C–$\underline{O}$–C and C=$\underline{O}$ bond having the same intensity.

The spectra of the both investigated composite samples show features of pure components (PMMA and PPy). PPy was detected by the N 1s peak (Fig. 7). The PPy peak is rather small while PMMA structures are clearly dominant. This is shown by the almost unchanged [O]/[C] ratio (Table I). However, the relative intensity of the N 1s peak in composite samples (Fig. 4) increases with increasing PPy content in the composites.

In Fig. 8 the C 1s spectrum of the PMMA/PPy composite containing 9.89 wt.% PPy was separated into two subspectra, one for PMMA (peaks D, C (partially), B, and A) and one for PPy (peaks I, J, C (partially), E, and G). The intensity ratios of the individual component peaks were fitted to those of the pure polymers, PMMA and PPy. The summarised curve shows that the

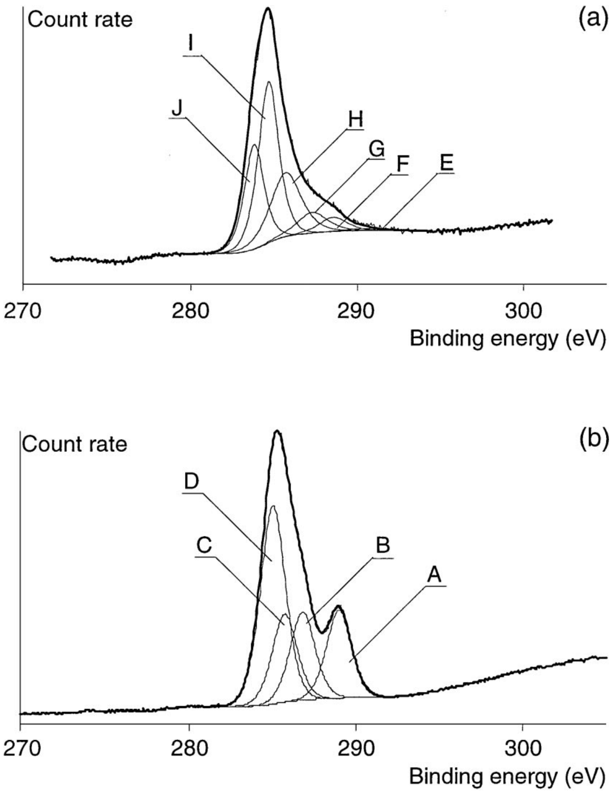


Figure 5 C1s core-level XPS spectra of (a) PPy, and (b) PMMA.

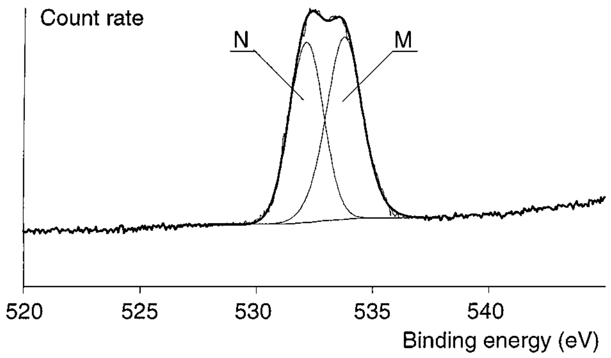


Figure 6 O1s core-level XPS spectrum of PMMA.

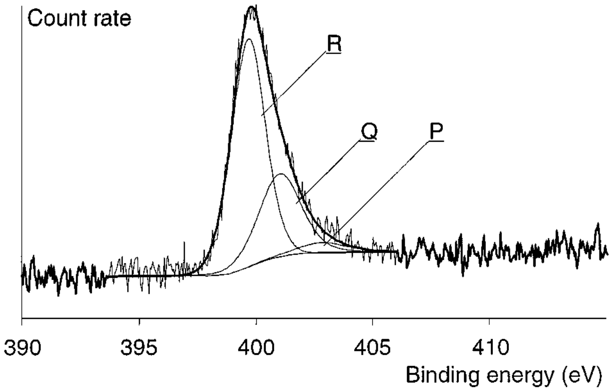


Figure 7 N1s core-level XPS spectrum of PMMA/PPy composite containing 9.89 wt.% PPy.

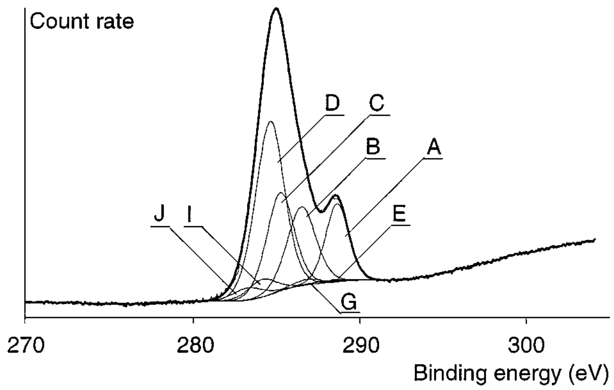


Figure 8 C1s core-level XPS spectrum of PMMA/PPy composite containing 9.89 wt.% PPy.

separation of the peaks corresponds well with the actual measured curve.

A PPy content of 0.0332 was calculated from the survey spectrum of PMMA/PPy composite containing 9.89 wt.% PPy using the ratio [PPy]/[PMMA] (in contrast to the [N]/[C] ratio, given in Table I, where the C content of the PPy is also considered). Additionally, a PPy content of 0.0319 was calculated from the ratio [PPy]/[PMMA] using the convoluted core-level C 1s spectra. The small amount of PPy detectable at the surface is in contrast to our results obtained for the polypropylene/polypyrrole composites [33] where the smooth surface of the polypropylene particles containing about 10 wt.% PPy was completely covered with PPy. Also from the comparison of these results can be concluded that pyrrole is polymerized in the holes of the rough surface of the PMMA particles. The surface of PMMA particles is rough and very corrugated as showed the pictures from transmission electron microscopy study, published recently in our article [34].

TABLE II The surface discharging characteristic parameters of PMMA and conductive PMMA/PPy composite films

PPy content (wt.%)	0.0	0.24	0.72	1.12
$V_{\max}$ (kV)	12.2	15.3	14.5	7.0
$\tau_{1/2}$ (s)	—	540	209	10

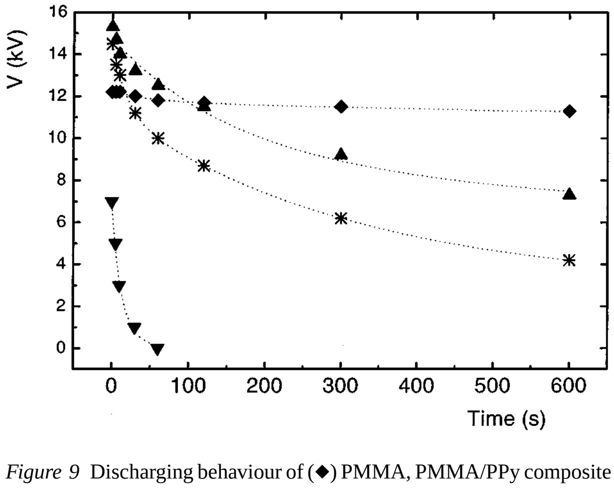


Figure 9 Discharging behaviour of (◆) PMMA, PMMA/PPy composite containing (▲) 0.24 wt.% PPy, (✱) 0.72 wt.% PPy, and (▼) 1.12 wt.% PPy.

In the subspectrum of the PPy part, the ratios of the component peaks correlate closely with the ratios in the spectrum of pure PPy. The subspectrum of the PMMA part shows a smaller relative content of COO structures (theory: $[\mathrm{COO}]/[\mathrm{C}_x\mathrm{H}_y] = [\mathrm{A}]/[\mathrm{G}] = 0.5$; found: $[\mathrm{COO}]/[\mathrm{C}_x\mathrm{H}_y] = [\mathrm{A}]/[\mathrm{G}] = 0.3476$), while all other peak ratios are nearly equivalent to this one in the C 1s spectrum of pure PMMA.

3.4. Surface discharging properties

Measurements of surface electric potential provide additional information on the antistatic properties of polymer composites. The discharging behaviour of pure PMMA and PMMA/PPy composite films is presented in Fig. 9. The characteristic parameters of the sample discharging, $\tau_{1/2}$- the half-life time of leakage of electrostatic charge, and $V_{\max}$- the maximum of surface electrostatic potential, are listed in Table II. It should be pointed out, that polymers with $\tau_{1/2}$ lower than 10 seconds are considered as materials with good antistatic properties [35]. There is a significant difference in the discharging rate of the composites containing 0.24 wt.% PPy compared to those with 1.12 wt.% PPy. It was found that if the concentration of PPy in our samples reached value 1.5 wt.%, the discharge time was lower than 1 second thus no time dependence on surface potential could be registered. At this PPy concentration in composites it was impossible to charge the surface. The content of about 1.5 wt.% PPy in composites is the threshold concentration at which the conducting PPy network is dense enough to remove any static charge from the sample surface immediately. At this PPy concentration the conductivity of PMMA/PPy composite is about 10^{-8} S/cm.

4. Conclusions

1. The chemical oxidation polymerization of pyrrole in a poly(methyl methacrylate) latex medium enables the obtaining of composites with conductivity in the range of 10^{-9} to 0.1 S/cm, depending on the PPy content. The advantage of the presented method is possibility of using water as a solvent.

2. The results of XPS analysis of PMMA/PPy powder composites showed that the PPy content at the surface of the particles is smaller than the overall PPy content determined by elemental analysis. This indicates that pyrrole is polymerized also interior of the PMMA particles.

3. The creation of PPy conducting network-like structure in the PMMA/PPy composites results in removing of the static charge from the sample surface. The threshold concentration of PPy for discharging of composites prepared by chemical modification was found to be about 1.5 wt.%.

Acknowledgement

The research was supported by the Grant Agency for Science of the Slovak Academy of Sciences (GAV-2/5032/98). M. O. would like to thank to the Institute of Polymer Research Dresden and to Saxon

Ministry of Art and Sciences for the support of this work.

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Received 6 April 1998
and accepted 9 September 1999