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Chemical preparation and characterization of conductive poly(methyl methacrylate)/polypyrrole composites

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The processes of the preparation of highly conductive polymer composites of poly(methyl methacrylate) and polypyrrole (PMMA/PPy) have been studied. The composites were prepared by a chemical modification method resulting in a network-like structure of polypyrrole embedded in the insulating polymer matrix. Water was used as a solvent. The content of polypyrrole was determined by elemental analysis varying from 0.25 to 10 wt%. The electrical conductivity of compression-moulded samples depends on the concentration of polypyrrole and reached values of between 1×10^{-9} S/cm to 0.1 S/cm. Highly conductive composites were also obtained from a mixture of coated and non-coated PMMA particles. The PMMA/PPy composites were characterized by elemental analysis, infrared spectroscopy and X-ray photoelectron spectroscopy (X.p.s.). The method of low-voltage scanning electron microscopy was used to study the potential contrast in dependence on the acceleration voltage between areas of different chemical composition. This method can be used to show the perfection of the PPy network structure in the composites. The antistatic properties of PMMA/PPy composites were demonstrated. The stabilizing effect of PPy on the thermal stability of poly(methyl methacrylate) was shown by thermogravimetric analysis. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

The technological applications of electrically conductive polymers are limited by some of their properties. Polyacetylene has good mechanical properties and very high conductivity in a doped state, but poor stability at ambient conditions restricts its utilization[1]. Polypyrrole, polyaniline, polythiophene and other conductive polymers prepared from heterocyclic monomers exhibit high conductivity and stability. However, their mechanical properties, e.g. brittleness and a low level of processability, are inferior compared to conventional polymers.

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[2] with conductive polymers allows the creation of new polymeric materials with interesting electrical properties. Moreover, the problem of surface static charge of poly(methyl methacrylate) can also be solved by blending with conductive polymers. Electrochemically[3,4] or chemically[5,6] prepared polypyrrole, which exhibits conductivity values up to 1000 S/cm, is stable in air.

Conducting polymeric blends have been obtained by the electrochemical polymerization of pyrrole in a poly(vinyl chloride) matrix[7]. However, limitations exist regarding the practical applications of the polymer blends prepared by an electrochemical method. Uniformly thin films of the host polymers are necessary for this process, but it is difficult to prepare such films on a large scale.

Chemical blending provides several possibilities for the preparation of conducting polymer blends. First, PMMA/PPy composite films with a conductivity of about 0.12 S/cm were prepared in 1988[8] using the chemical oxidative polymerization method which involves spreading a water-insoluble 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 X.p.s. was published by Chan et al.[9]. Secondly, Stanke et al.[10] synthesized a graft copolymer film of PMMA and PPy. Later[11], they grafted pyrrole on to a PMMA backbone already containing a pyrrole moiety by oxidative polymerization with $FeCl_3$, but only graft copolymers with very low pyrrole amounts were soluble.

A two-step process, involving an emulsion containing a solution of surfactant in the first phase, was developed in the Ruckenstein laboratory[12,13] for the preparation of polyaniline/poly(alkyl methacrylate) or polypyrrole/poly(alkyl methacrylate). 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.

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The aim of the present paper is to examine the effect of the preparation route on the conductivity of polypyrrole-containing composites. Poly(methyl methacrylate) particles were coated with polypyrrole by the chemical polymerization method and water was used as the dispersion medium. For comparison, blends were prepared by mixing coated PMMA particles with pure PMMA. The prepared composites were characterized by various analytical methods and low-voltage scanning electron microscopy (LVSEM). The stability of PMMA/PPy composites was investigated by thermogravimetric analysis (t.g.a.). Discharging characteristics of PMMA/PPy composites were compared with the behaviour of unmodified materials.

EXPERIMENTAL

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 by emulsion polymerization[14]. Twice distilled water (325 ml) was added as the dispersion medium into a reactor which was equipped with a stirrer and N_2 inlet. Gases dissolved in water were removed by boiling and the water cooled to 50°C and saturated with nitrogen. The components of the polymerization feed were added in the following order:

(1) 9 g of secondary sodium alkane sulfonate emulsifier (E-30, Leuna-Werke, Germany), stirred for 1 h until completely dissolved;
(2) 150 ml of methyl methacrylate (MMA);
(3) 0.65 g of the water-soluble initiator $K_2S_2O_8$;
(4) 0.325 g $Na_2S_2O_4$ catalyst for peroxide decomposition.

A portion (0.075 g) of lipophilic initiator, benzoyl peroxide soluble in MMA, ensured the start of polymerization. The total synthesis time was 60 min. Light scattering and transmission electron microscopy were used to determine the particle size. The diameter of prepared PMMA particles was found to be about 100 nm.

PMMA particles with a cross-linked structure were prepared by the same procedure in the presence of 2 g diallyl phthalate. The average diameter of these particles was about 170 nm.

Preparation of composites and blends

Method I. 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 dispersed polymer particles, varied from 0.25 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/cm² for further investigation. The thickness of the compression-moulded samples was about 0.2 mm.

Method II. Another type of conducting composites was prepared by mixing the coated PMMA particles prepared by Method I with non-coated PMMA particles at room temperature followed by compression moulding.

Instruments

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

Infrared (i.r.) spectra were recorded using the diffuse reflection technique. The powder samples were mixed with KBr. KBr powder was used as the reference. The measurements were made using a FTIR Spectrometer IFS 66 (Bruker, Germany) by means of a reflection unit (Harrick, UK) and MCT detector.

A spectrometer VG ESCA lab 220i (England) was used to acquire photoelectron spectra (X.p.s.) of sample surfaces. Unmonochromatized Mg $K_{\alpha1/2}$ ($h \cdot \nu$ = 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 then 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). Data collection and analysis were performed by an IBM PC using the VG ECLIPSE software routine. The peaks background was subtracted according to the Shirley method[15].

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 morphology of PMMA particles prepared by emulsion polymerization was studied by transmission electron microscopy (TEM). The EM PHILIPS-EM-300 was used for the study.

The microstructure of 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.

Discharge 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.

Samples were prepared in powder form and thermal degradation studies carried out in the presence of nitrogen using the thermogravimetric system TGA 7 (Perkin-Elmer, USA). The sample weight was about 3 mg and the heating rate was 10 K/min.

RESULTS AND DISCUSSION

Figure 1 shows the size and structure of synthesized PMMA particles. The spherical shape and size of about 100 nm was confirmed. The picture also shows that the surface structure of the particles is rough.

The influence of the amount of polypyrrole in the PMMA/PPy composites on their electrical conductivity was investigated using the compression-moulded samples. The composites were prepared by Method I, with the concentration

of monomer varying from 0.25 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. *Figure 2* presents the comparison of the conductivity of PMMA/PPy composites prepared from cross-linked and non-cross-linked PMMA particles. The conductivity of composites prepared from cross-linked PMMA particles at low PPy content was very close to that of composites prepared from non-cross-linked ones, while at a higher PPy content the conductivity was slightly lower. The aim of cross-linking the PMMA particles before their modification with PPy was to stabilize the resulting composite morphology.

Figure 2 also shows that the conductivity of both composite types 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[16] to be about 10^{-13} S/cm. The conductivity of PMMA/PPy composites prepared from non-cross-linked PMMA particles containing 1.12 wt% PPy is 8.8×10^{-9} S/cm. An increase in the content of PPy from 1.12 to 9.9 wt% in PP/PPy composites results in an enormous increase in conductivity by seven orders of magnitude.
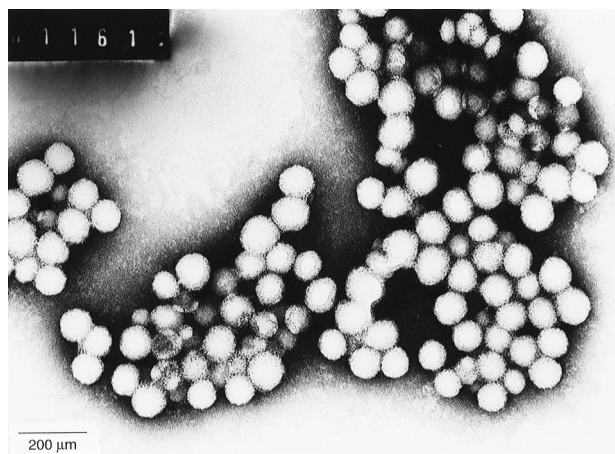
Figure 3 presents a comparison of the conductivity dependence on the PPy content between the two types of composites. The first type of composite samples was prepared using Method I, by the chemical modification of non-cross-linked PMMA. The second type of composites was prepared by mixing a PMMA/PPy composite containing 9.35 wt% PPy with non-coated PMMA (Method II). The prepared samples contained between 0.47 and 7.48 wt% PPy, which relates to the concentration range of 5–80 wt% in the original PMMA/PPy composite prepared using Method I.

The conductivity in both composite types does not significantly differ in the minimum and maximum PPy concentrations, while the conductivity dependence of both composites within the middle concentration range is different. The conductivity of compression-moulded samples prepared by the mixing of coated and non-coated PMMA particles shows a steep gradient within the concentration range of 0.47–2.80 wt% PPy. A further rise in the PPy concentration results in only a small conductivity increase. The maximum difference in the conductivity of the composites prepared by Method I and Method II was observed to be about 2.80 wt% of PPy, which corresponds to a mixture prepared from 70 wt% non-coated and 30 wt% coated PMMA particles. The difference was about four orders of magnitude. This behaviour can be explained by the percolation model. At 30 wt% of coated PMMA particles,

Figure 1 TEM micrograph of synthesized PMMA particles

Figure 3 Conductivity dependence of PMMA/PPy composites on PPy content, (■) composites prepared by chemical modification, (○) composites prepared by mixing of coated and non-coated PMMA particles
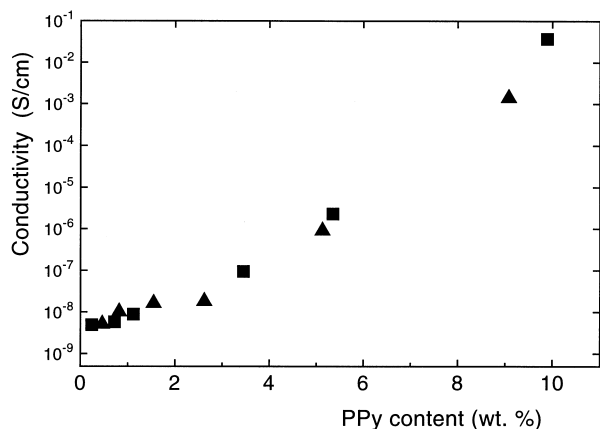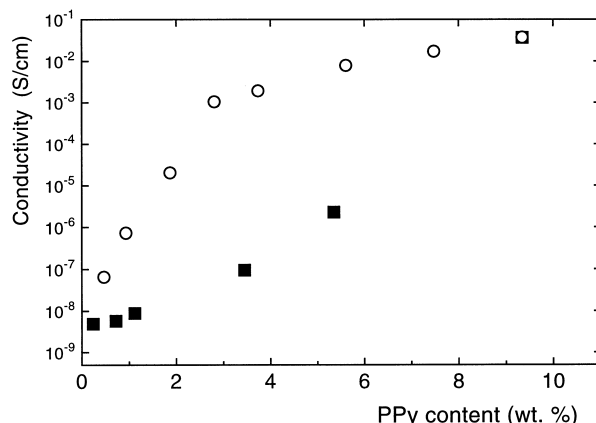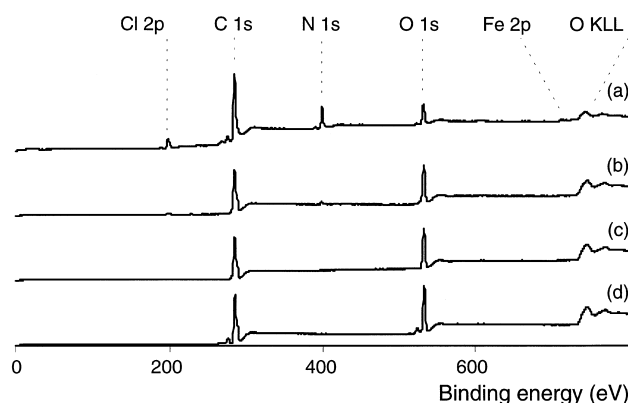

Figure 2 Conductivity dependence of PMMA/PPy composites on PPy content, (■) composites prepared by chemical modification of non-cross-linked PMMA particles, (▲) composites prepared by chemical modification of cross-linked PMMA particles

Figure 4 Survey X.p.s. 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 1 The results of X.p.s. quantitative analysis of chemically synthesized PPy, PMMA and powder PMMA/PPy composites

Sample	[N]/[C]	[O]/[C]	[Cl]/[C]	[Fe]/[C]
PPy	0.160	0.120	0.055	0.004
PMMA	—	0.397	—	—
PMMA/1.12% PPy	0.005	0.385	Traces	Traces
PMMA/9.89% PPy	0.029	0.394	0.012	Traces

an almost perfect network structure is formed. The presented results show that besides the PPy concentration in the samples, the superstructure of the PMMA/PPy composites has a substantial influence on the conductivity of prepared film samples.

The aim of the X-ray photoelectron spectroscopy studies was to analyse the surface layer of the powder PMMA/PPy composite. *Figure 4* shows the X.p.s. spectra of chemically synthesized PPy, PMMA and PMMA/PPy composite powders containing 1.12 and 9.89 wt% PPy. C, N, O, and traces of Cl and Fe were found in both composite samples. Quantitative determinations of the elemental surface composition have been carried out using the spectrometer transmission function and Wagner's atomic sensitivity factors[17]. During the measurements, the spectrometer was working in the constant analyser energy mode with a constant pass energy of 80 eV in the case of survey spectra and 25 eV for resolved spectra.

The quantitative analysis of the samples is given in *Table 1*. The results show the difference between the theoretical PPy structure $(C_4H_3N_1)_n$ and chemically synthesized PPy. The highly resolved C 1s spectrum of PPy is shown in *Figure 5a*. The component peaks I and J result from the two different carbon atoms of the pyrrole units. The ratio of [I]/[J] > 1 indicates a presence of monomer units which are not linked by α-α' bonds[18].

Oxygen in PPy is present in the form of C–O, C–OH (component peak H) and C=O bonds (component peak G). 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[19,20]. The shake-up peaks E and F result from the highly conjugated p_π electron system. The Cl anions act as a doping agent. A small amount of Fe originates from the oxidation agent $FeCl_3$.

The highly resolved C 1s spectrum of PMMA may be divided into four component peaks (*Figure 5b*), where D represents the carbon atoms of the methyl and methylene groups, B the ether bond of the ester group (C–O), A the carboxyl group (COO) and C the β-carbon atom of the carboxyl group (C–COO).

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

The C 1s spectrum of the PMMA/PPy composite containing 9.89 wt% PPy (*Figure 5c*) 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 summarized curve shows that the 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 1*, 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 PP/PPy composites[21], where the surface of the PP particles was quite well covered with PPy. We suggest that pyrrole is also polymerized in the holes of the rough surface of the PMMA particles.

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
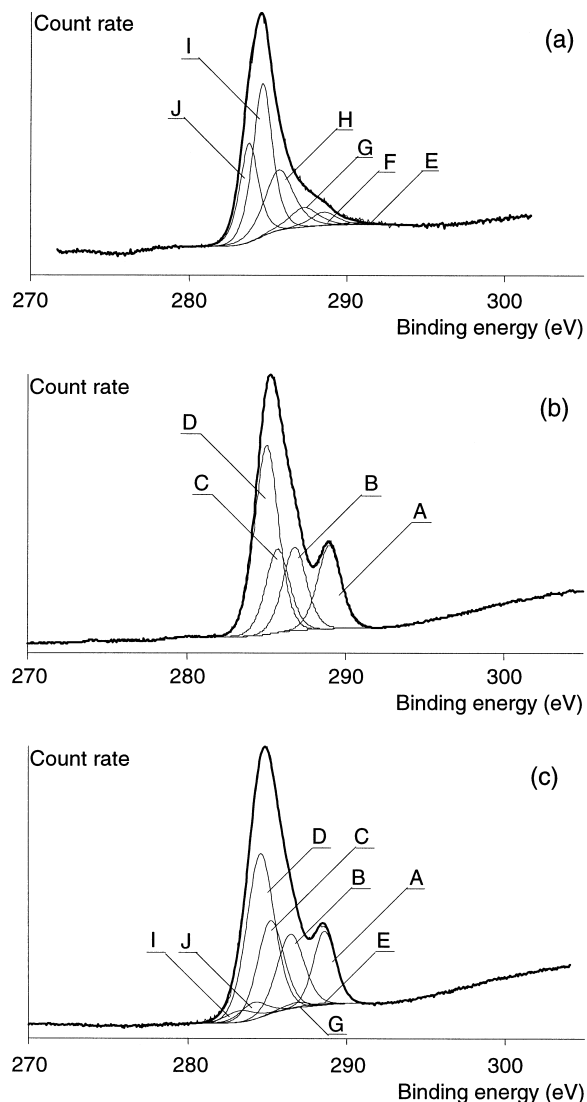

Figure 5 C 1s core-level X.p.s. spectra of (a) PPy, (b) PMMA and (c) PMMA/PPy composite containing 9.89 wt% PPy
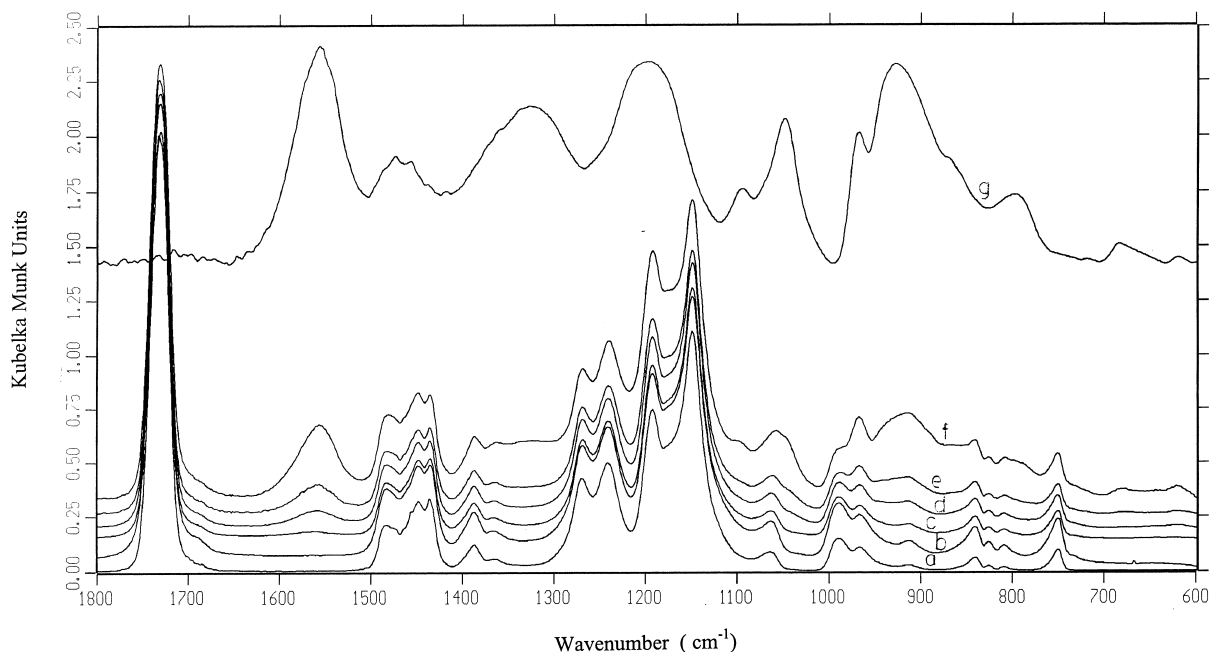
Figure 6 Infrared spectra of (a) pure PMMA, PMMA/PPy powder composites containing (b) 0.24 wt% PPy, (c) 1.12 wt% PPy, (d) 3.45 wt% PPy, (e) 5.35 wt% PPy, (f) 9.89 wt% PPy and (g) chemically prepared polypyrrole

Table 2 Infrared band positions and assignments of poly(methyl methacrylate), chemically prepared polypyrrole and PMMA/PPy composite containing 9.89 wt% PPy

PMMA			PPy			PMMA/PPy	9.89%
λ^{-1} (cm^{-1})	Relative intensity[a]	Assignment	λ^{-1} (cm^{-1})	Relative intensity[a]	Assignment	λ^{-1} (cm^{-1})	Relative intensity[a]
1734	v	ν(C=O)				1734	v
			1558	s	ν_{ring}	1556	m
1486	m	$\delta(CH_2)_b$				1478	m
1451	m	$\delta(CH_3)_b$				1451	m
1438	m	$\delta(CH_3)_b$				1434	m
1388	w	$\delta(CH_3)_b$				1388	w
			1326	m	ν_{ring}	1326	w
1268	m	ν(CO)				1270	m
1241	m	ν(CO)				1240	m
			1197	m	$\nu_{ring\ pulsation}$		
1193	s	ν(COC)				1193	s
1149	s	ν(COC)				1149	s
1064						1163	sh
			1048	m	δ(C–H) + δ(N–H)	1050	m
987	m	$\delta(CH_3)_r$				988	sh
963	w	$\delta(CH_3)_r$					
			969	m	δ(C–N) –C=C-H out of plane	966	m
			928	s	δ(C–H)	925	sh
841	w	$\delta(CH_2)_r$				842	w
			797	m	γ(C–H)	797	sh
753	w	$\delta(CH_3)_r$				751	m
			682	w	γ(C–H)	682	w

[a] v—very strong, s—strong, m—medium, w—weak, sh—shoulder

shows a smaller relative content of COO structures (theory: $[COO]/[C_xH_y] = [A]/[G] = 0.5$; found: $[COO]/[C_xH_y] = [A]/[G] = 0.3476$), while all other peak ratios are nearly equivalent to this one in the C 1s spectrum of pure PMMA.

The modification of PMMA particles by pyrrole polymerization was verified by i.r. spectroscopy. In *Figure 6*, the i.r. spectra of chemically prepared PPy, pure PMMA and five modified PMMA powders containing 0.43, 1.12, 3.45, 5.35 and 9.89 wt% PPy prepared using Method I are shown. Major changes were observed in the region of 1800–600 cm^{-1}.

Table 2 shows band positions and assignments for PMMA, chemically prepared polypyrrole and the PMMA/PPy composite containing 9.89 wt% PPy. The obtained spectra correlate closely with the i.r. spectra of PMMA[22,23] and PPy[24,25].

The spectra of all the PMMA/PPy composites (*Figure 6b–f*) represent a superposition spectrum of pure components. The peak of 1558 cm^{-1} which results from ν ring vibrations of the pyrrole remains unchanged. The increased intensity of this PPy band corresponds to the

increasing amount of PPy in composites as determined by the diffuse reflection technique. It is possible to quantify the amount of PPy in the composites according to the peak area. A calibration curve can be plotted from the peak areas obtained after integration in the region of 1620–1515 cm^{-1} for our five studied composite samples. This calibration curve can be used for the chemical analysis of the amount of PPy in the composite samples.

The potential contrast depends on the acceleration voltage of electrons in the PMMA/PPy composite which contained 9.89 wt% PPy and was studied by low-voltage scanning electron microscopy. This method enables the imaging of non-conducting samples without any metal coating. The principle of this method is to select the electron accelerating voltage so that a balance exists between injected electrons and emitted electrons (secondary
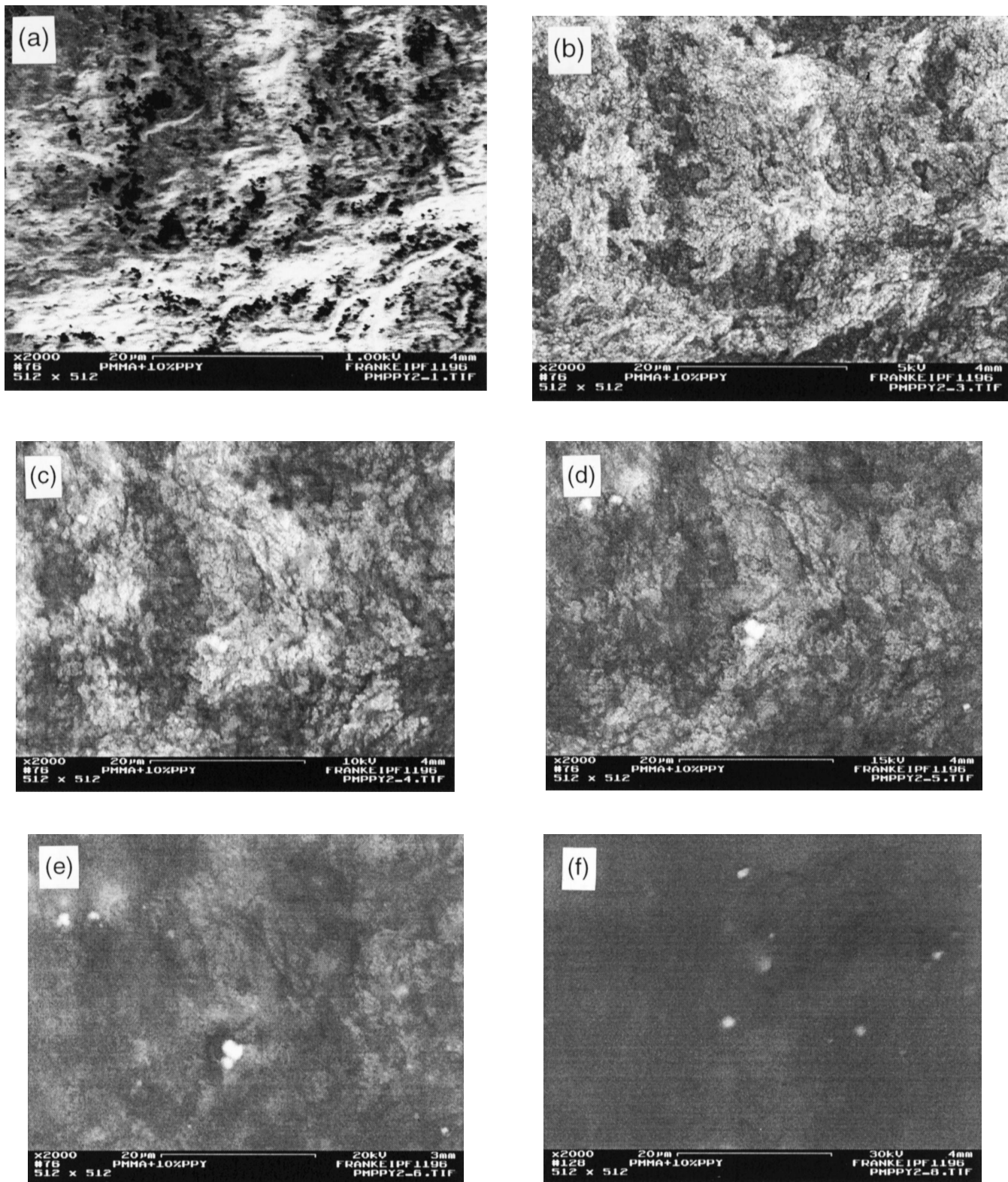

Figure 7 Potential contrast in PMMA/PPy composite containing 9.89 wt% PPy at (a) 1 kV, (b) 2 kV, (c) 5 kV, (d) 15 kV, (e) 20 kV and (f) 30 kV of acceleration voltage
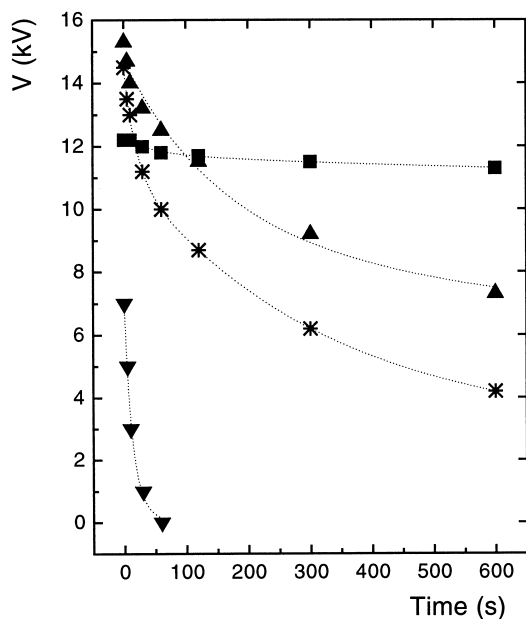
Figure 8 Discharging behaviour of (■) PMMA, (▲) PMMA/PPy composite containing 0.24 wt% PPy, (∗) 0.72 wt% PPy and (▼) 1.12 wt% PPy

Table 3 The discharging characteristic of PMMA and conductive PMMA/PPy composite films prepared by Method I

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

potential contrast created by increasing the acceleration voltage from 2 to 30 kV can be observed in *Figure 7b–f*. The higher the acceleration voltage, the deeper the electron beam entering the sample. Consequently, a larger area of the conducting polymer network is connected to the ground which results in suppression of the charging. At 30 kV (*Figure 7f*) almost all areas are grounded and the potential contrast vanishes. It should be pointed out that, at this voltage, the penetration depth of the electron beam in the samples containing mainly C atoms is approximately 13 μm[26]. For samples containing smaller amounts of PPy, similar effects are observed but larger areas of the sample surface are charged at a comparable acceleration voltage.

In our previous study[27] of PP/PPy composites, different acceleration voltage contrast patterns have been found. The size of PP particles used in the PP/PPy composite was about 37 μm. It is the size of particles, in particular, which can cause different patterns for the same PPy concentration and the same acceleration voltage. In the case of the PMMA/PPy composites, the size of PMMA particles is about 100 nm. The white (non-conducting) areas in the lower accelerating voltage range (up to 15 kV) cover a larger portion of the observed area. However, inside the individual bright patterns, certain irregularities are visible. At 20 kV, the patterns become less visible in the PMMA/PPy sample because the particles are smaller. This was not the case in the PP/PPy sample. There are almost no patterns at 30 kV, both in the PMMA/PPy and PP/PPy composites. This means that no charging occurs in the samples. The electrons drain to the ground completely. The results of this study support the idea that the size of the initial, unmodified particles influences the creation of the polypyrrole-conducting network. However, the final bulk conductivity depends primarily on the kind of conducting polymer and its concentration.

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 *Figure 8*. 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 3*. It should be pointed out, that polymers with $\tau_{1/2}$ lower than 10 s are considered as materials with good antistatic properties[28]. 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 exceeded 1.5 wt%, the discharge time was lower than 1 s, thus no time dependence on surface potential could be registered. At higher concentrations of PPy 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 sufficient to remove any static charge from the

electrons and back-scattered electrons) so that no surface charge occurs. For polymers, the voltage is typically in a range from 0.5 to 1.5 kV depending on the sample material. In *Figure 7a* the real surface of the compression-moulded sheet (200 μm thick) is visible for the PMMA/PPy composite sample.

In the case of partially conducting samples, it is possible to distinguish between conducting and non-conducting surface areas by increasing the acceleration voltage. Thus, non-conducting parts of the sample will be charged and the potential contrast revealed in the image. An increase in the acceleration voltage results in the charging of non-conducting areas which creates a contrast allowing the distinguishing of electrically conducting areas connected to the conducting ground (dark parts of pictures) from areas without any connection to the ground (bright parts) in the composite sample. The bright parts represent the charged areas which may also be partially conductive, but without electrical connection to the ground. The development of the

Table 4 Thermogravimetric characteristics of PMMA, PMMA/PPy composites and chemically prepared PPy

Sample	Temperature of 1% weight loss (°C)	Temperature of 10% weight loss (°C)	Decomposition maximum (°C)	Residue at 450°C (%)
PMMA	203	343	385	1.0
PMMA/0.7% PPy	236	345	391	1.2
PMMA/1.1% PPy	272	353	386	1.2
PMMA/3.5% PPy	238	360	395	3.0
PMMA/5.4% PPy	206	348	399	7.5
PPy	40	170	695	76.0

sample surface immediately. At this PPy concentration, the conductivity of PMMA/PPy composite is about 10^{-8} S/cm.

The samples of pure PMMA, PMMA/PPy powder composites containing various amounts of PPy and chemically prepared PPy were studied by thermogravimetric analysis (t.g.a.). *Table 4* summarizes the results of t.g.a. investigation. The pure PMMA is characterized by a continuous process of weight loss starting at 203°C (1% weight loss). For chemically prepared PPy, the beginning of weight loss was observed at 40°C and was caused by water vaporization. Pure PPy is hygroscopic and water can be absorbed into it[29]. The weight loss proceeded quite steadily, with a residue of about 76% at 450°C. The decomposition of PMMA/PPy composites followed a similar pattern to that of pure PMMA. However, the conducting PPy exerts a small stabilizing effect on the composites. The thermal stability is shifted to higher temperatures with increasing PPy content. The decomposition maximum also increased from 385°C for pure PMMA to 399°C for PMMA/PPy composite containing 5.4 wt% PPy. This is caused by the covering of the surface of PMMA particles by PPy. The PPy layer partially prevents PMMA decomposition. In all composites a residue remained at 450°C. The amount of residue correlated with the PPy content in the composite.

CONCLUSIONS

Conducting PMMA/PPy composites have been studied. The method of chemically oxidative modification of poly(methyl methacrylate) particles by pyrrole enables the obtaining of composites with conductivity in the range of 10^{-9}–0.1 S/cm, depending on the PPy content. Large amounts of material with good antistatic and conductive properties can be prepared in an inexpensive way using this method. One advantage of the presented method is in the use of water as a solvent. It is cheaper and more ecological.

The electrical conductivity of composites which have been prepared by mixing pure PMMA with PMMA particles coated with PPy is enhanced by more than four orders of magnitude when the threshold concentration of coated particles (about 30 wt%) is reached. This fact can be explained by the percolation model.

The results of X.p.s. 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 inside the PMMA particles.

LVSEM study of the PMMA/PPy composites prepared by the described method showed the real image of the conducting network-like structure. The network structure depends on the initial non-conducting polymer particle size. The more perfect PPy conducting network is created by modification of smaller particles.

The threshold concentration of PPy for discharging of composites prepared by chemical modification was found to be about 1.5 wt%. It can be concluded from thermogravimetric measurements that the thermal stability of PMMA is improved by its chemical modification with PPy.

REFERENCES

1. Pron, A., Budrowski, C. and Priluski, J., *Polymer*, 1983, **24**, 1294.
2. Radhakrishnan, S. and Saini, D. R., *Polymer Int.*, 1994, **34**, 111.
3. Warren, L. F. and Anderson, D. P., *J. Electrochem. Soc.*, 1987, **134**, 101.
4. Qian, R. and Qiu, J., *Polymer J.*, 1987, **19**, 157.
5. Myers, R. E., *J. Electron. Mater.*, 1986, **15**, 61.
6. Biswas, M. and Roy, A., *J. Appl. Polymer Sci.*, 1994, **51**, 1575.
7. De Paoli, M.-A., Waltman, R. J., Diaz, A. F. and Bargon, J.J., *J. Polym. Sci., Polym. Chem. Ed.*, 1985, **23**, 1685.
8. Morita, M., Hashia, I. and Nishimura, M., *J. Appl. Polymer Sci.*, 1988, **36**, 1639.
9. Chan, H. S. O., Hor, T. S. A., Ho, P. K. H., Tan, K. L. and Tan, B. T. G., *J. Macromol. Sci.-Chem.*, 1990, **A27**, 1081.
10. Stanke, D., Hallensleben, M. L. and Toppare, L., *Synth. Met.*, 1993, **55–57**, 1108.
11. Stanke, D., Hallensleben, M. L. and Toppare, L., *Synth. Met.*, 1995, **72**, 89.
12. Yang, S. and Ruckenstein, E., *Synth. Met.*, 1993, **59**, 1.
13. Ruckenstein, E. and Yang, S., *Polymer*, 1993, **34**, 4655.
14. Pavlinec, J. and Lazár, M., *J. Macromol. Sci.-Pure Appl. Chem.*, 1994, **A31**, 1469.
15. Shirely, D. A., *Phys. Rev.*, 1972, **B5**, 4709.
16. Ku, C. C. and Liepins, R., in *Electrical Properties of Polymers, Chemical Principles*, Hanser Publishers, Munich, 1987, p. 326.
17. Wagner, C. D., Davis, L. E., Zeller, M. V., Tayler, J. A., Raymond, R. M. and Gale, L. H., *Surf. Interface Analysis*, 1981, **3**, 211.
18. Street, G. B. and Pfluger, P., *J. Chem. Phys.*, 1984, **80**, 544.
19. Lei, J. and Martin, C. R., *Synth. Met.*, 1992, **48**, 331.
20. Kang, E. T., Neoh, K. G., Ong, Y. K., Tan, K. I. and Tan, B. T. G., *Macromolecules*, 1991, **24**, 2822.
21. Omastová, M., Pavlinec, J., Pionteck, J. and Simon, F., *Polymer Int.*, 1997, **43**, 109.
22. Kawasaki, A., Furukawa, J., Tsuruta, T., Inoue, S. and Ito, K., *Macromol. Chem.*, 1960, **36**, 260.
23. Nagai, H., Watanabe, H. and Nishioka, A., *J. Polymer Sci.*, 1962, **62**, S95.
24. Furukawa, Y., Tazawa, Y., Fujii, Y. and Harada, I., *Synth. Met.*, 1988, **24**, 329.
25. Maia, G., Ticianelli, E. A. and Nart, C., *Zeitschrift Phys. Chem.*, 1994, **186**, 245.
26. Seiler, H., *Z. Angew. Phys.*, 1967, **22**, 249.
27. Omastová, M., Košina, S., Pionteck, J., Janke, A. and Pavlinec, J., *Synth. Met.*, 1996, **81**, 49.
28. Vasilenok, Ju. J., *Zashchita polimerov ot staticheskovo zaryada*, Chimia, Leningrad, 1975.
29. Bittih, R., Ely, G. and Woefler, F., *Makromol. Chem., Macromol. Symp.*, 1987, **8**, 51.