**Journal of Macromolecular Science, Part A**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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**To cite this Article** Omastová, Maria , Chodák, Ivan , Pionteck, Júrgen and Pótschke, Petra(1998) 'Preparation and Properties of Conducting Polyolefins Composites', Journal of Macromolecular Science, Part A, 35: 7, 1117 — 1126
**To link to this Article: DOI:** 10.1080/10601329808002105
**URL:** http://dx.doi.org/10.1080/10601329808002105

J.M.S.—PURE APPL. CHEM., A35(7&8), pp. 1117–1126 (1998)

# PREPARATION AND PROPERTIES OF CONDUCTING POLYOLEFINS COMPOSITES

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Dedicated to the founder of the Polymer Institute, Professor Milan Lazár, in honor of his 70th birthday.

## ABSTRACT

The method of chemically initiated oxidative modification of polypropylene particles in suspension by pyrrole was used for preparation of conductive polypropylene/polypyrrole composites. Their properties were compared with another type of polypropylene/polypyrrole composites prepared by melt mixing of pure polypropylene with chemically synthesized polypyrrole and with polypropylene/carbon black composites also prepared by melt mixing.

The composites were characterized by elemental analysis and by rheological testing. The antistatic properties of prepared composites were demonstrated. The electrical and flow properties depend on the concentration of filler and on the processing conditions of composites.

## INTRODUCTION

Polyolefins are traditionally used as electrical and thermal insulators. However, research and applications of electroconductive polymer-based materials have increased in the last two decades. The combination of conventional polymers with conductive polymers or fillers enables us to create new polymeric materials with unique electrical properties.

Carbon black, graphite, or other conductive fillers are commonly used as a component of conductive polymer composites [1-4]. Polyolefins blended with a broad range of conductive polymers, such as polypyrrole [5, 6], polythiophene and its derivatives [7], and polyaniline [8] have been investigated as well. In polymer-based conductive composites, the insulating polymeric matrix provides good mechanical properties and processability and the conductive component provides electrical conductivity. Polyolefin- based conductive materials can find, and have found, many interesting applications in the areas such as antistatic plastics, electromagnetic shielding, electrodes for special purposes, and other conductive or semiconductive parts for special application, e.g. in a corrosive environment. Conductive polymer composites have some advantages compared to metals. Their density is lower compared to that of metals and the processing is similar to that of polymers. In addition, it is possible to vary the conductivity of composites by varying the concentration of fillers.

In this paper, polypropylene/polypyrrole (PP/PPy) composites have been prepared by chemically initiated oxidative polymerization of pyrrole on the surface of PP particles in suspension. The properties of these conductive composites were compared with either simple mixtures of polypropylene blended in melt with chemically synthesized polypyrrole or with polypropylene/carbon black (PP/CB) composites prepared by melt mixing. Considering field thermoplastics, a knowledge of processing composites is as important as the data on performance properties. Furthermore, the flow characteristics may, in some cases, bring additional data related to the morphology-supermolecular structure of the material. Therefore, the flow of the PP/conductive fillers was investigated as well as electrical properties.

## EXPERIMENTAL

### Materials

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

TF-411, MFI = 10 g/10 min, $M_w = 2.13 \times 10^5$ g/mol, $M_n = 25\ 100$ g/mol (Slovnaft, Slovak Republic), carbon black (VULCAN® XC-72R, Cabot Corp., U.S.A.), anhydrous ferric chloride (Fluka, Switzerland), and methyl alcohol, analytical grade (Jansen Chimica, Belgium) were used as received. Water was distilled before use.

## Composite Sample Preparation

### *Method I*

Polypropylene particles (5 g) of 30-250 μm in diameter were dispersed in 160 ml of a water-methanol mixture (volume ratio 2.5) and then $FeCl_3$ was added. Pyrrole was dissolved in 20 ml methanol and inserted dropwise under vigorous stirring. The pyrrole concentration range was from 1 to 10 wt%. The molar ratio of $FeCl_3$ to pyrrole was 2.3. All compounds were stirred for 4 hours. The reaction product was filtered off and washed with distilled water and methanol. The prepared polypropylene powder covered with polypyrrole was dried in a vacuum oven at 50°C for 6 hours.

### *Method II*

To investigate the effect of processing on properties of polypropylene chemically modified by polypyrrole, the PP/PPy blends were also prepared by mixing pure PP with chemically synthesized PPy in 50 ml mixing chamber at 40 rpm for 20 minutes at 200°C using a Plasti-Corder kneading machine PLE 651 (Brabender, Germany).

### *Method III*

Another type of conducting composites was prepared by mixing of polypropylene with carbon black in 50 ml mixing chamber at 75 rpm for 10 minutes at 200°C using the Plasti-Corder kneading machine PLE 330 (Brabender, Germany).

### *Analytical Methods*

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

The weight percentage of polypyrrole in the PP/PPy composites was calculated from the nitrogen concentration 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.

For the electrical conductivity measurements, the prepared composites were compression molded at 200°C for 2 minutes under 22.5 kN/cm$^2$. The thickness of the compression molded samples was about 0.2 mm. The electrical conductivity in polymer composites was measured by a standard four probe method. Samples were cut into strips of about 5x25 $mm^2$. Silver paste was used to achieve good electrical contacts of the sample surface with the electrodes of the conduction tester. All measuring instruments (for current and voltage) were connected to a PC in order to collect and calculate the data.

Discharge characteristics of the polymer samples were measured using an integration electrometer POLYSTAT PS-1 (JZD Jizera, Czech Republic). A compression molded specimen in a shape of 1 mm thick disc with the diameter 15 mm was cleaned in *n*-heptane, fixed on a holder and charged in 15 kV electric field (corona discharge). The decrease of the surface electric potential versus time was periodically measured. The periodicity of the potential registration was maintained by sample rotation to the place of measuring sensor location. The charge induced from the moving sample was registered in the form of electric pulses and led to an electronic integrator. The amplified signal from the integrator was connected to a plotter. The time dependence of surface electric potential was measured and plotted.

The rheological behavior of the composite melts at 190°C was studied by means of a Rheometrics RMS 800 rheometer with parallel plates with a diameter of 7.5 mm or 25 mm and a gap of about 1.8 mm in $N_2$ atmosphere. The strain was 20%, the frequency range was from 0.008 Hz to 16 Hz which corresponds to 0.05 rad/s and to 100 rad/s, respectively. The discs were cut from the injection molded specimen or compression molded plates with a thickness of about 2 mm. Before starting the measurement, the sample was preheated at 190°C for 5 minutes. Measurement at various strain indicate that the melts are in the linear viscoelastic region under these conditions.

## RESULTS AND DISCUSSION

The influence of the amount of polypyrrole and carbon black in the composites on their electrical conductivity was investigated. The conductivity comparison of PP/PPy and PP/CB composites is shown in Figure 1. The PP/PPy composites were prepared by chemical modification at the same reaction conditions, while the concentration of pyrrole varied from 1 to 10 wt%. Bulk conductivity of pure PP was found to be about $10^{-16}$ S/cm. Even a very small PPy amount present in composites results in a significant conductivity increase. The increase of the content of PPy from 1.1 wt% to 8.9 wt% in PP/PPy composites results in an enormous enhancement in conductivity up to eight orders of magnitude. The melt mixed

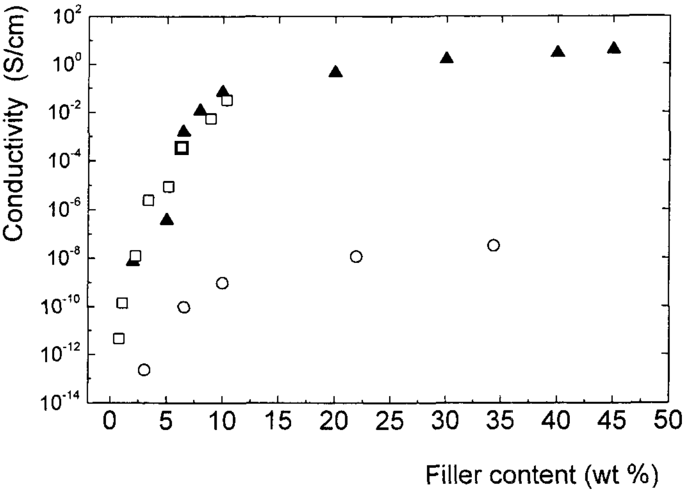

**Figure 1.** Conductivity dependence on filler content of (□) PP/PPy composites prepared by chemical modification, (○) PP/PPy composites prepared by melt mixing, and (▲) PP/CB composites.

PP/PPy composites show considerably lower conductivity than the composites prepared by the chemical modification method. The difference in conductivity is about 7 orders of magnitude for the same PPy concentration and the conductivity values do not exceed $10^{-8}$ S/cm, even when the PPy content is 34.2 wt%. The conductivity of PP/CB composites showed similar tendency to that of PP/PPy composites prepared by chemical modification. The estimated percolation threshold of CB concentration was found to be between 5 and 8 wt%.

Measurements of the surface electric potential provide additional information on antistatic properties of polymer composites. The discharging behavior of pure PP, PP/PPy prepared by Method I, and PP/CB composites are presented in Figure 2. The characteristic parameters of the sample discharging, namely: $\tau_{1/2}$ - the half-life time of leakage of electrostatic charge, and $V_{max}$- the maximum of surface electrostatic potential, are listed in Table 1. It should be pointed out that polymers with $\tau_{1/2}$ lower than 10 seconds are considered as materials with good antistatic properties [9]. A significant difference was observed in the discharging rate of the PP/PPy composites containing 0.44 wt% PPy compared to those with 1.81 wt% or 2.3 wt% PPy. If the concentration of the filler in our samples exceeded 2.5 wt% PPy or 5 wt% CB, respectively, the discharge time was lower than 1 second. Thus, no time dependence of surface potential could be registered. At higher

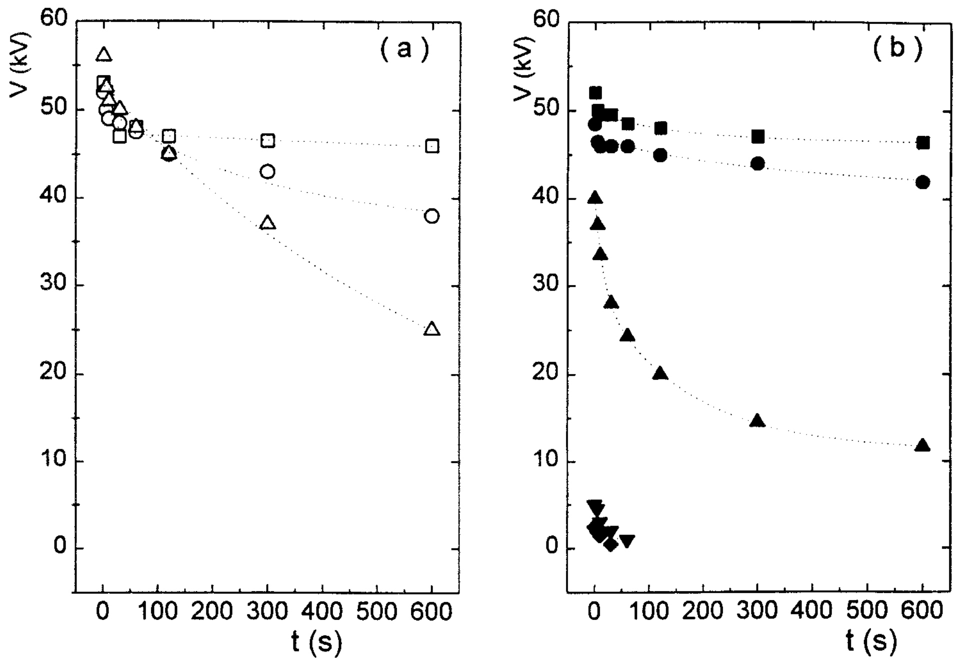

**Figure 2.** Discharging behavior of (a) remolten PP (□), PP/CB composite containing 2 wt% CB (○), 5 wt% CB (Δ), and (b) PP (■),PP/PPy composite containing 0.44 wt% PPy (●),1.23 wt% PPy (▲),1.82 wt% PPy (▼), and 2.37 wt% PPy (•).

TABLE 1. The Discharging Characteristic of PP, Conductive PP/PPy and PP/CB Composites

| PPy content (wt%) | $V_{max}$ (kV) | $\tau_{1/2}$ (s) | CB content (wt%) | $V_{max}$ (kV) | $\tau_{1/2}$ (s) |
|---|---|---|---|---|---|
| 0.0 | 52.0 | - - - | 0.0 | 53 | - - - |
| 0.44 | 48.5 | - - - | 2.0 | 52 | - - - |
| 1.23 | 40.0 | 113 | 5.0 | 56 | 501 |
| 1.81 | 5.0 | 14 | | | |
| 2.30 | 2.5 | 8 | | | |

$\tau_{1/2}$ - the half-life time of leakage of electrostatic charge, and $V_{max}$- the maximum of surface electrostatic potential concentrations of the conductive fillers it was impossible to charge the surface. The content of about 2.5 wt% PPy in PP/PPy composites or about 5 wt% CB in PP/CB composites is the threshold concentration at which the conducting network is sufficient to remove any static charge from the sample surface immediately. It should be pointed out that the conductivity of the PP/PPy composite containing 2.5 wt% PPy is about $10^{-8}$ S/cm.

These results indicate that the above mentioned amount of conductive filler, either CB or PPy in PPy-coated PP particles, is sufficient for a formation of more or less continuous conductive network. On the other hand, a presence of finely distributed PPy does not lead to a formation of such structure, therefore, a conductivity of the PPy composites prepared by the Method II is much lower. Our previous morphology investigations [10] of PP/PPy composites prepared by melt mixing of pure components using low voltage scanning electron microscopy showed that the morphology is a phase-segregated type with large non-conductive areas. This is the reason for the low conductivities of such type of composites.

The modification of the PP with CB or PPy results in an increase of the melt viscosity (Figures 3 and 4). In addition, not only the strength of the solid material, but also the properties of the melts, depend on the kind of filler and processing conditions. The effect of CB on the viscosity is less pronounced than the effect of PPy at the same concentration of the filler. Figure 3 shows the dependence of complex viscosity of PP filled with CB on the shear rate. When adding CB, the viscosity increases with the amount of filler. Parallel to that, the dependency of the viscosity on the shear rate also increases.

PPy containing composites prepared by injection molding (Figure 4) behave similarly to PP filled with CB. An addition of 1.48 wt% PPy leads to the viscosity increases at low shearing rates by a factor of about 2.6 while almost sixfold content of PPy (8.6 wt%) raises the viscosity by a factor of about 4.5 only. At high shearing rates no difference in the viscosity between both type of composites is visible. Similar to the case of PP/CB composites, filling the PP with the filler results in a stronger dependency of the viscosity on the shear rate.

The largest effect of the filler is seen in the composites prepared by compression molding of PP particles coated with PPy (Figure 4). The PPy network formed under these conditions is stable. Its resistance towards the deformation by weak shearing forces results in very high viscosities. Containing less than 1 wt% PPy, the viscosity is increased by a factor of 10, at 8.6 wt% by a factor of 60, both at low shear rates. It is worth mentioning that the differences of the viscosity of the two PP result from the different preparation conditions.

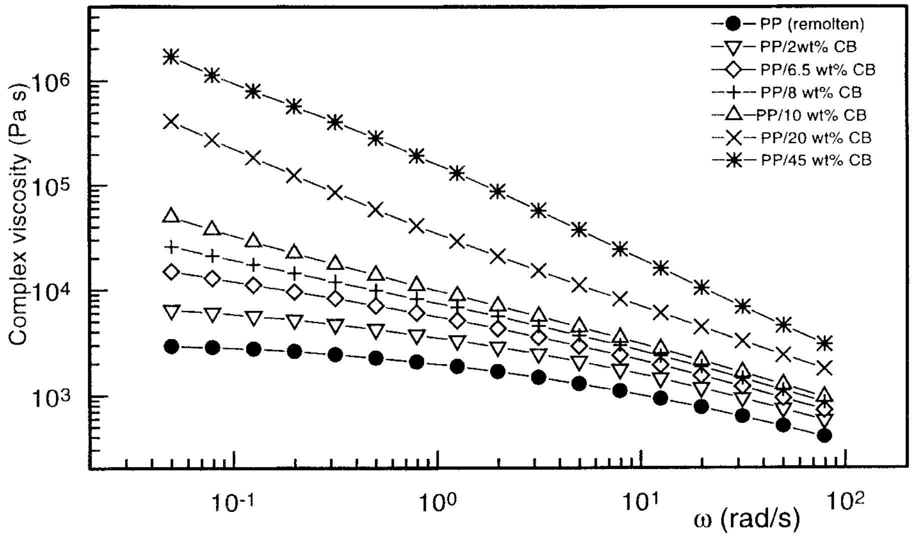

**Figure 3.** Dependence of complex viscosity of PP and PP/CB composites containing various amounts of CB on the shear rate.

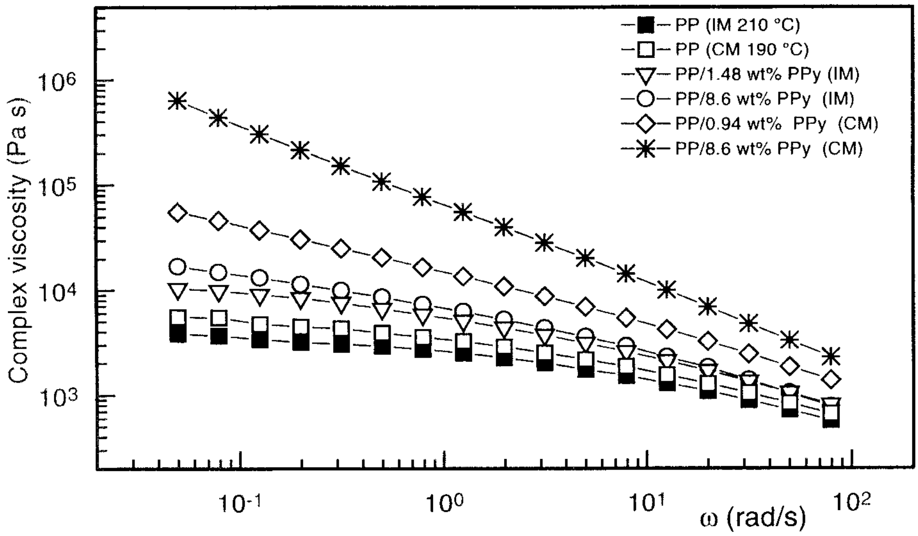

**Figure 4.** Dependence of complex viscosity of PP and PP/PPy composites prepared by injection molding (IM) or compression molding (CM) on the shear rate.

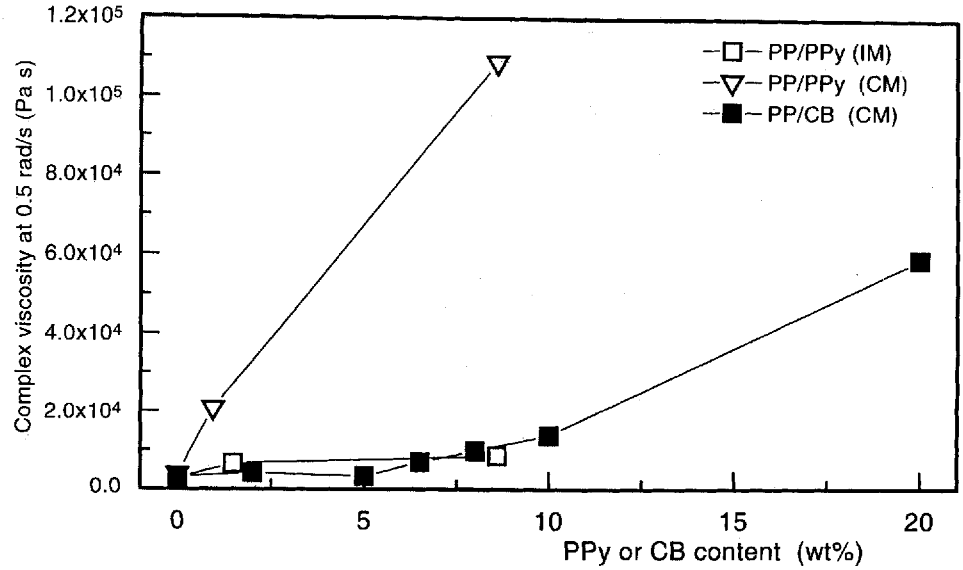

**Figure 5.** Dependence of complex viscosity at 0.5 rad/s on the content of PPy or CB in modified PP composites.

In Figure 5, the melt viscosity at a defined shear rate is plotted over the content on filler and in dependence on the preparation conditions. It is obvious that the use of coated particles has the strongest influence on the viscosity while the influence of the filler in injection molded PP/PPy composites and in CB filled composites behave in a similar manner to each other. The small differences may be caused by the different densities which corresponds to different volume contents on filler and by the variations in the preparation conditions.

## CONCLUSION

A large effect of processing conditions on electrical conductivity of polypropylene/polypyrrole composites was observed. The conductivity of composites prepared by sintering of polypropylene particles covered with deposited polypyrrole is about 7 orders of magnitude higher than the conductivity of the blends prepared by mechanical melt mixing of PP and PPy at the same concentration of the components. The conductivity of sintered composites is comparable to that of PP composites filled with conductive carbon black. The threshold concentrations for rapid discharging the surface were found to be 5 wt% and 2.5 wt% of the filler for PP filled with CB and PP/PPy composites prepared by chemical modification, respectively.

Flow properties of the melt mixed composites (PP/CB and injection molded PP/PPy) are similar. A substantial increase of complex viscosity was observed for compression molded PP/PPy composites. Some kind of temperature resistant network is expected to be formed, which leads to the increase of both viscosity and electrical conductivity of the material.

## ACKNOWLEDGEMENTS

M. O. would like to thank to Regierungspräsidium Dresden for financial support of this work. She is grateful to Ms. Z. Nógellová for PP/CB composites preparation in Brabender.

The authors from the Polymer Institute, Bratislava (M. O. and I. C.) are grateful to the Slovak grant agency VEGA (grant No. 2/1144/96) for financial support of this research.

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