

Mechanical and Electrical Properties of Composites Based on Thermoplastic Matrices and Conductive Cellulose Fibers

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ABSTRACT: Highly pure cellulose fibers were coated with polypyrrole (PPy) and subsequently used for preparation of composites, which reached a certain level of electrical conductivity. The cellulose fibers surface was entirely covered when 20 wt % of pyrrole was used for the modification, as confirmed by scanning electron microscopy (SEM). The cellulose fibers covered with PPy were kneaded with thermoplastic matrices: linear low-density polyethylene (LLDPE), high-density polyethylene (HDPE), and polycaprolactone (PCL). The highest electrical conductivity achieved was for composites based on the PCL matrix. PCL filled with 50

wt % of conducting cellulose fibers reached an electrical conductivity of $6.5 \times 10^{-4} \text{ S cm}^{-1}$. This electrical conductivity falls within the range required for antistatic materials. The mechanical properties of HDPE, LLDPE, and PCL matrices loaded with both treated and untreated cellulose fibers were also investigated. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 133–142, 2006

Key words: composites; fibers; polypyrroles; polyethylene; mechanical properties

INTRODUCTION

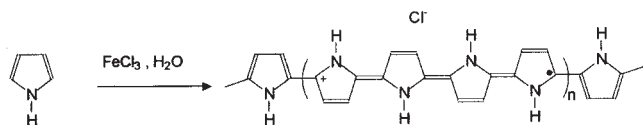
In recent years, there has been a rapid growth in the use of polymeric composites reinforced with natural fibers, yielding an appropriate combination of high performance, great versatility in processing, and favorable cost.^{1–4} Natural fibers have become competitive replacements for inorganic fibers (glass fibers, carbon fibers, etc.) since they offer many advantages, including low density, little damage during processing, biodegradability, high stiffness, noise absorption, easy availability, and renewability as well as relatively low cost. They have some disadvantages compared to synthetic inorganic fibers, such as the lower thermal stability of their properties, and higher water absorption.^{5–6} At present, the use of composites based on polymers filled with natural fibers is increasing mainly in the automobile industry, where many components are produced from these materials.⁷

Polypyrrole (see structure in Scheme 1) belongs to the class of conducting polymers, such as polyaniline, polythiophene, and others, and is known for its high electrical conductivity and good environmental stability. It has been extensively studied because of its various potential applications in batteries, supercapacitors, sensors, microwave shielding, and corrosion protection.^{8–10} The electrical conductivity of polypyrrole (PPy) prepared by chemical oxidative polymerization ranges from 10^{-4} to 100 S cm^{-1} , depending on the specific preparation conditions. Recently, polypyrrole was investigated as a prospective agent for electroconductive coating of different inorganic and organic fibers. More attention was paid to the treatment of carbon and graphite fibers,^{11–13} glass fibers,¹⁴ and partly to polymeric fabrics and fillers.¹⁵ As for natural fibers, little information about their modification with polypyrrole can be found in the literature.¹⁶ Bjorklund and Lundstrom described the synthesis of paper/PPy composites¹⁷ with a conductivity of about 2 S cm^{-1} . Later, the oxidation of pyrrole by iron salts in an aqueous solution of methylcellulose resulting in a colloidal solution of PPy was reported.¹⁸ After cellulose gelation and drying of the product, the conductivity of this material was 0.2 S cm^{-1} . Recently, production of a new conducting composite material based on polyaniline and wood by a simple one-stage synthesis from aniline and wood sawdust was described.^{19,20} However, the preparation of thermoplastic compos-

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Scheme 1 Chemical oxidative polymerization reaction of pyrrole resulting in polypyrrole. Polypyrrole chains bear one positive charge per three or four pyrrole units that is counterbalanced by the anion (so-called *dopant*) from the oxidant.

ites with conducting organic fillers has not been reported in the literature. Only composites of low-density polyethylene (LDPE) filled with Canadian switch grass and coated with polypyrrole were prepared and studied.²¹

The aim of this work is the preparation and investigation of composites based on the filling of a linear low-density polyethylene (LLDPE), high-density polyethylene (HDPE), and a polycaprolactone (PCL) matrix with cellulose fibers, as well as an investigation of the possibility of preparing antistatic materials based on the same polymeric matrices filled with cellulose fibers coated with polypyrrole. Polypyrrole was chosen for modification of the organic filler because of its high conductivity and good environmental stability, and so it can be used as a substitute for metallic conductors or semiconductors in a wide variety of electrical and electronic devices.^{9,10} In this paper, the preparation of electroconductive fibers based on the coating of cellulose with polypyrrole, as well as the influence of conductive cellulose fibers on the electrical conductivity of LLDPE-, HDPE-, and PCL-based composites is reported. The mechanical properties of these composites have also been investigated and compared with the composites filled with untreated cellulose fibers.

EXPERIMENTAL

Materials

Two grades of polyethylene, namely linear low-density polyethylene (MFI = 3.5 g/10 min. with 2.16 kg at 190°C, density = 0.938 g/cm³, specific enthalpy of melting = 155.9 J/g, melting temperature = 130°C) from Sasol Polymers, South Africa, and high-density polyethylene Stamydan HD 9089 V (MFI = 1.7 g/10 min with 2.16 kg at 190°C, density = 0.963 g/cm³, specific enthalpy of melting = 215.6 J/g, melting point = 132.2°C) from DSM, Netherlands, and polycaprolactone CAPA 6800 (MFI = 3 g/10 min. with 2.16 kg at 160°C, density = 1.1 g/cm³, crystallinity = 56%, melting temperature = 58–60°C) from Solvay, UK were used as the matrices for the preparation of the thermoplastic composites.

TABLE I
Some Chemical and Physical Properties of ARBOCEL BWW 40 Cellulose Fibers

Cellulose content	Approx. 99.5%
Average fiber length	200 μm
Average fiber thickness	20 μm
Bulk density	110–45 g/dm ³
Whiteness (absolute value at 461 nm)	(86 ± 5)%
Residue of ignition (850°C, 4 h)	Approx. 0.3%
pH	6 ± 1

Cellulose fibers, ARBOCEL BWW 40 (J. Rettenmaier and Söhne GmbH-Co, Germany), were used as the filler. Some physical and chemical properties of cellulose fibers are reported in Table I [J. Rettenmaier and Söhne GmbH-Co data sheet]. Granulometric parameters of the fibers are summarized in Table II.

For the coating of the cellulose fibers, pyrrole monomer (Merck-Schuchardt, Germany), purified by distillation under reduced pressure and stored in a refrigerator at 4°C, and ferric chloride (FeCl₃; Lachema, Czech Republic) were used.

Cellulose fiber-polypyrrole preparation

Thirty-five grams of cellulose fibers (CF) were dispersed in 1200 mL of distilled water and stirred for 15 min; then an oxidant, FeCl₃, was added and the mixture was stirred for 30 min. Pyrrole was dissolved in 100 mL of water and introduced dropwise into the reaction mixture, which was then stirred for a further 30 min. The molar ratio [FeCl₃]/[pyrrole] was 2.3. After 4 h the cellulose fibers coated with polypyrrole (CF-PPy) were filtered off and rinsed several times with distilled water. The CF-PPy samples were dried at 60°C at atmospheric pressure for 24 h and at 50°C in a vacuum drier for 6 h. The amount of pyrrole used for the modification of cellulose fibers varied from 5 to 20 wt %.

Composites preparation

The composites were prepared by mixing the components in the 30-mL mixing chamber of a Plasti-corder

TABLE II
Granulometric Parameters of ARBOCEL BWW 40 Cellulose Fibers

X ₁	0.6
X ₅	4.7
X ₁₀	8.5
X ₂₀	29.3
X ₅₀	62.8
X ₁₀₀	87.8
X ₁₅₀	95.5
X ₂₅₀	99

X_i, volume % of particles which are smaller than dimension *i* in μm

TABLE III
Elemental Composition (wt %) of Chemically Synthesized Polypyrrole, Cellulose Fibers, Cellulose Fibers Coated with Polypyrrole, and Calculated Real Content of Polypyrrole in CF-PPy Composites

Sample	C	N	H	Real content of PPy
PPy-Cl	55.67	16.18	4.24	100
Cellulose fibers	43.37	—	6.02	0
CF + 5% Pyrrole	44.36	0.78	4.98	4.8
CF + 10% Pyrrole	44.69	1.63	5.01	10.1
CF + 15% Pyrrole	45.21	2.46	5.21	15.2
CF + 20% Pyrrole	45.65	3.33	5.68	20.6

PLE 331 (Brabender, Germany) at 170°C for LLDPE and HDPE, and at 85°C for PCL for 10 min at a mixing speed of 35 rpm. Slabs of 1mm thickness were prepared by compression molding of the mixed composites, using a laboratory hydraulic press SRA 100 (Fontijne, Netherlands) at 2.4 MPa and at 160°C for LLDPE and HDPE, and at 90°C for PCL for 2 min. Dog-bone-shaped specimens of 1 mm thickness with a 35 × 3.6 mm² working area were cut from the slabs.

Characterization techniques

The elemental composition of PPy, CF, and CF-PPy composites was determined by elemental analysis, using an elemental analyzer FISONs EA 1108 provided with an automated result evaluator EAGER 200.

Direct current (DC) electrical conductivity of powder CF-PPy composites was measured at a pressure of 30 MPa by the van der Pauw four-contact method in a home-made polyetheretherketone (PEEK) cell of 9 mm diameter. Tesla Picoamperimeter BM 545 (Czech Republic) and Metra Blansko Multimeter M1T 380 (Czech Republic) were used for measurement of the electrical current and voltage, respectively.

The polymeric composites containing CF modified with PPy were compressed into pellets, 13 mm diameter and about 1 mm thick. Room-temperature DC conductivity was determined by the four-point method in a van der Pauw arrangement, using a Keithley 237 high-voltage source measurement unit and a Keithley 2010 multimeter equipped with a 2000-SCAN 10 channel scanner card. When the conductivity of the samples was below 10⁻⁴ S cm⁻¹, a two-point method using a Keithley 6517 electrometer was used. Before this measurement, circular gold electrodes were deposited on both sides of the pellets.

The morphology of the CF-PPy composites was studied by scanning electron microscopy (SEM), with a Hitachi S-800 microscope (Hitachi, Japan). Powder particles were mounted on an earthed sample holder using a double-sided conducting adhesive tape. The samples were coated with a vapor-deposited gold layer to achieve good quality images and resolution.

The structural and optical properties of the cellulose fibers and fibers covered with PPy were studied using a Fourier-transform Thermo Nicolet NEXUS 870 FTIR infrared spectrometer with a DTGS TEC detector in a moisture-purged environment. All spectra in the range of 500–4000 cm⁻¹ with a 2 cm⁻¹ spectral resolution were obtained from compressed KBr pellets in which CF or CF-PPy powders were evenly dispersed. Sixty-four scans were recorded for each FTIR spectrum. Spectra were corrected for the moisture and carbon dioxide in the optical path.

The mechanical properties were measured at room temperature using an Instron 4301 (Instron, USA) universal testing machine at the deformation rate of 10 mm/min. The final mechanical properties were evaluated from at least six different measurements.

Thermogravimetric analysis (TGA) was performed on about 8-mg samples in oxygen flow at a heating rate of 10°C/min, using a Mettler-Toledo TGA/SDTA 851^e (Mettler-Toledo, USA).

RESULTS AND DISCUSSION

Cellulose fiber-polypyrrole characterization

The cellulose fibers with an aspect ratio of 10 (ratio between length and diameter of the fibers) were modified by chemical oxidative polymerization of pyrrole. The surface of the CF particles was covered with various amounts of PPy, from 5 to 20 wt %, in an attempt to find out the concentration that is necessary to cover the entire surface and consequently to prepare an organic filler with good conductivity. The real content of PPy coated CF was evaluated by elemental analysis. Table III shows the elemental composition of chemically synthesized polypyrrole, cellulose fibers, and cellulose fibers coated with polypyrrole. The weight content of PPy in CF-PPy composites was calculated from detected nitrogen content related to the nitrogen content determined in PPy and synthesized using the same conditions and oxidant. PPy composition was: 55.67 wt % C, 4.24 wt % H, and 16.18 wt % N. In some cases, real content of PPy in CF-PPy composites is

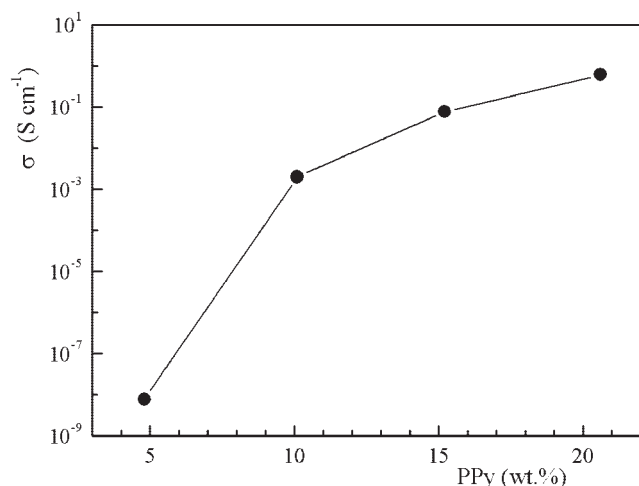


Figure 1 Dependence of the electrical conductivity of coated cellulose fibers on PPy loading.

higher than expected. The reason can be hygroscopic character of polypyrrole, which can contain up to 8 wt % of water, and also oxidation of PPy on fibers surface by air.

Figure 1 shows the dependence of conductivity of CF-PPy on the amount of PPy covering the surface of the original material. When 4.8 wt % of PPy is used the covering is insufficient, and the CF-PPy prepared shows conductivity in the range of $10^{-8}\ S\ cm^{-1}$. With 10.1 wt % of PPy the conductivity of the modified filler increases rapidly by five orders of magnitude. With 15.2 and 20.6 wt % of PPy further enhancement of conductivity of the modified fillers is achieved. The conductivity of CF containing 20.6 wt % PPy is $0.61\ S\ cm^{-1}$. The DC conductivity of pure polypyrrole synthesized under the same conditions, using $FeCl_3$ as oxidant (labeled in the later FTIR study as PPy-Cl), is about $6\ S\ cm^{-1}$. It is known that during pyrrole polymerization, for three or four pyrrole rings in the poly-

mer chain one positive charge is created, which has to be compensated by the anion of the oxidant molecule, in this case by Cl^- , as shown in Scheme 1. Generally powder particles with dimensions of the order of microns coated with PPy are less conductive than PPy, even if their surface is completely covered with the conducting polymer. For the subsequent preparation of composites with a polymeric matrix, we used CF coated with 20.6 wt % PPy.

There is also a macroscopic demonstration of the CF modification by the conducting polymer. During pyrrole polymerization, the white color of cellulose fibers changed to gray or black, depending on the amount of PPy covering the fiber surface. The changes are documented by the optical microscopy of samples in solid state. Unmodified cellulose fibers [Fig. 2(a)] appear semitransparent, whereas CF-PPy containing 20.6 wt % PPy are completely black because the whole CF surface is covered by PPy [Fig. 2(b)]. Modified fibers do not stick together even when high amounts of pyrrole (20 wt %) are used for the modification of CF surface.

Figure 3 reveals the morphologies of unmodified cellulose fibers [Fig. 3(a) and (b)] and CF covered with 20.6 wt % PPy [Fig. 3(c) and (d)]. As shown by the SEM study of the unmodified CF sample, the thickness of the individual fibers is up to $20\ \mu m$ [Fig. 3(b)]; this value corresponds very well with the CF parameters provided by the manufacturer (Table I). The surface structure of CF particles changed after being covered with PPy [Fig. 3(c) and (d)].

The changes in the structure of polypyrrole-coated cellulose fibers after modification by the conducting polymer were studied by FTIR spectroscopy. Figure 4 compares the 4000 to $500\ cm^{-1}$ spectra of CF, PPy-Cl, and CF modified with various amounts of PPy. The spectrum of cellulose is very complicated and is described in Ref. 22. The bands of free or bonded OH vibrations, CH vibrations, C=O stretching of carboxyl

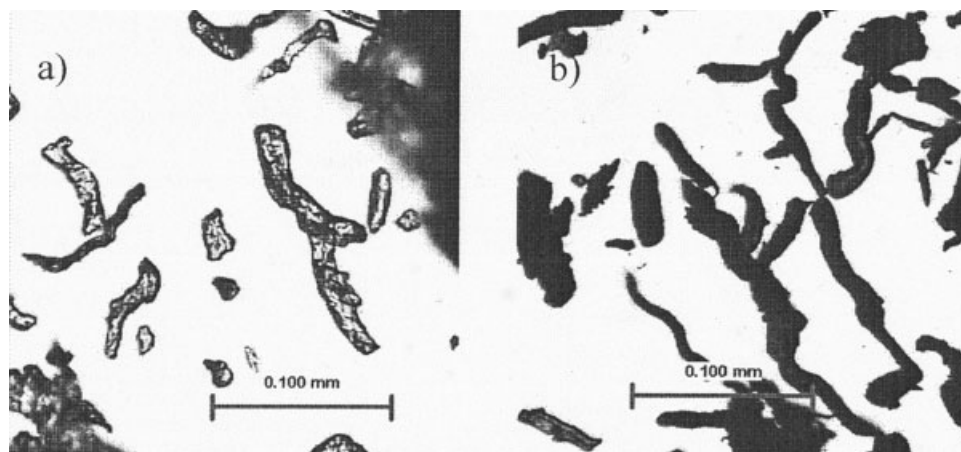


Figure 2 Pictures from optical microscopy study of cellulose fibers (a) and CF-PPy containing 20.6 wt % PPy (b).

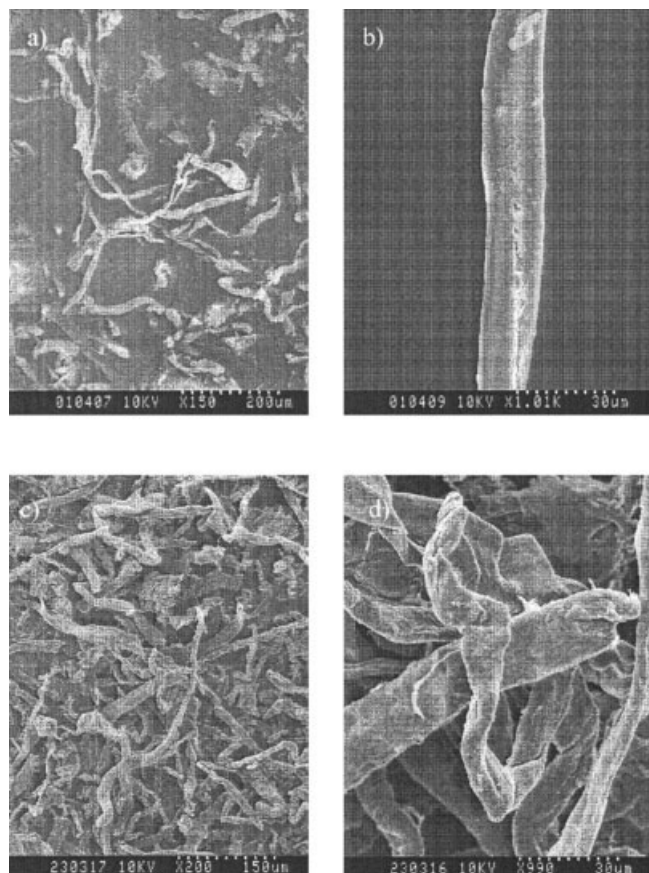


Figure 3 SEM micrographs of cellulose fibers (a), (b) and CF-PPy containing 20.6 wt % PPy (c), (d).

or lactone groups, and COO stretching vibration are observed. In the spectra of CF coated with PPy, the bands of cellulose are partly overlapped by the bands of PPy but they are still well distinguished. For the samples of CF coated with 4.8 wt % of PPy, only the

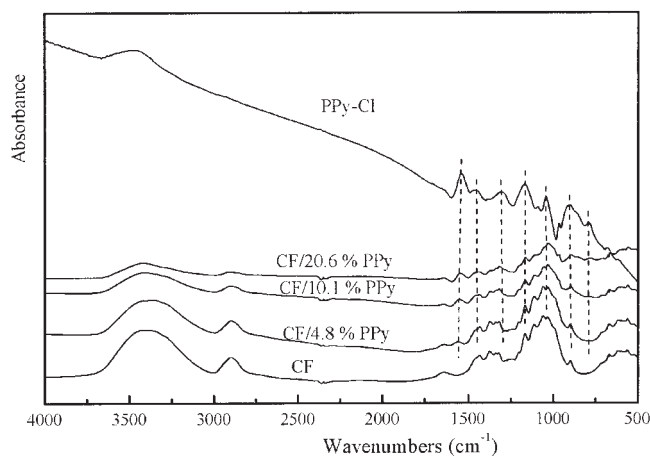


Figure 4 The infrared spectra of cellulose fibers, CF-PPy containing 4.8, 10.2, and 20.6 wt % PPy, and spectrum of pure PPy-Cl.

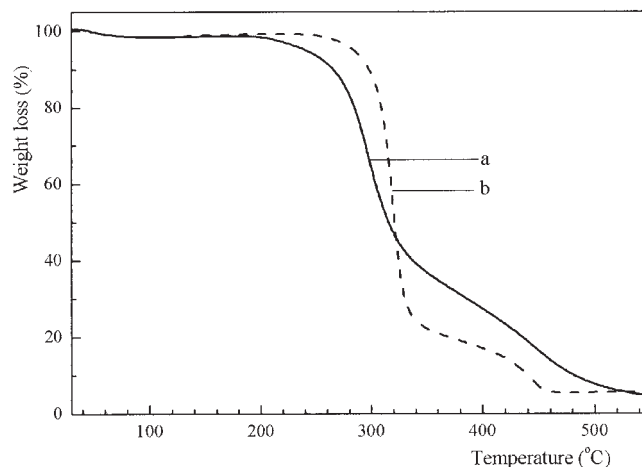


Figure 5 TGA curves of untreated cellulose fibers (a) and CF-20.6 wt % PPy (b) sample.

band of C—C stretching vibrations in the pyrrole ring situated at 1540 cm^{-1} is observed. In the spectra of CF samples with 10.1 and 20.6 wt % of PPy, some of the typical PPy bands can be still identified.²³ Their positions are close to those observed in the spectrum of pure PPy-Cl.

The thermal stability of the cellulose fibers and fibers covered with 20.6 wt % PPy was examined by TGA in oxygen atmosphere. Figure 5 shows the thermal decomposition of the original CF and comparison with the behavior of CF-20.6 wt % PPy. The first weight loss in CF and CF-20.6 wt % PPy samples occurs at temperatures between 30 and 100°C . It is known that both materials are hygroscopic and during the heating to 100°C residual water evaporates. Both samples lose about 1.5 wt % of mass. From the derivation of the TGA curves (not shown in Fig. 5) the maximum decomposition temperature was calculated. The maximum decomposition of CF occurs at 296.9°C . The modified CF-20.6 wt % PPy sample shows a maximum decomposition at a higher temperature, 319.3°C . The reason for the shift of the maximum decomposition temperature of CF-20.6 wt % PPy is the presence of PPy on the CF surface, which makes the material more stable than that with unmodified CF.

To ascertain the influence of thermal aging on the conductivity of CF-20.6% PPy, the material was aged from 30 to 120 min in the compression molding equipment at 2.4 MPa and 180°C . For comparison, the same procedure was performed on pure PPy-Cl. The conductivity values are summarized in Table IV. The conductivity of both samples decreases with increasing aging time, but the decrease in the conductivity is very moderate. The decrease in the conductivity after 120 min aging at 180°C is less than one order of magnitude for both samples. Consequently, it is possible to presume that the mixing time (10 min) used for the preparation of the polymeric composite with CF-

TABLE IV
The Influence of the Aging Time on the Conductivity of PPy and CF – 20.6 wt % PPy

Ageing time (min.)	Conductivity (S cm ⁻¹)	
	PPy-CI	CF-20.6 wt % PPy
0	5.8	0.61
30	1.9	0.21
60	1.4	0.11
120	0.72	0.097

20.6% PPy has no crucial influence on the conductivity of the CF-PPy filler.

Mechanical properties

The mechanical properties of HDPE and LLDPE filled with cellulose fibers covered by 20.6 wt % of PPy were investigated. For a comparison of the mechanical properties of composites containing modified CF, those of the HDPE matrix filled with pure CF were examined. The dependence of stress at break of HDPE filled with untreated and treated cellulose fibers is shown in Figure 6(a). Nonlinear behavior of the dependence is observed in both cases. Stress at break generally depends on the filler concentration in a complex way. The filler can reinforce the polymeric matrix on the one hand, and on the other hand it can suppress the drawability of the polymeric matrix as well as increase the concentration of defects, which can lead to a dramatic decrease in stress at break.²⁴ The actual values of stress at break are the result of these effects. At low filler concentration, a sharp decrease in stress at break was observed as a consequence of the suppression of drawability of the HDPE matrix. The presence of the filler suppresses cold flow as well as orientation strengthening of the matrix. At low filler content, the reinforcing effect of the filler is marginal. The reinforcing effect is more pronounced with the increase in the filler content, while further decrease in deformation has no additional effect on orientation. The reinforcing effect becomes significant at a filler concentration around 10–15 wt %. It seems that CF-20.6% PPy has a more pronounced effect on the reinforcement than untreated CF. This is probably due to an improvement in the interfacial interaction between the polymer and the filler in terms of the PPy layer, since the chemical natures of PE and cellulose are completely different. While polyethylene is a nonpolar and hydrophobic material, cellulose is polar and hydrophilic; these materials are incompatible with each other, and PPy probably improves their mutual compatibility.

The dependence of stress at break of the HDPE and LLDPE matrix filled with CF-20.6% PPy is shown in Figure 6(b). For a better comparison of the two matri-

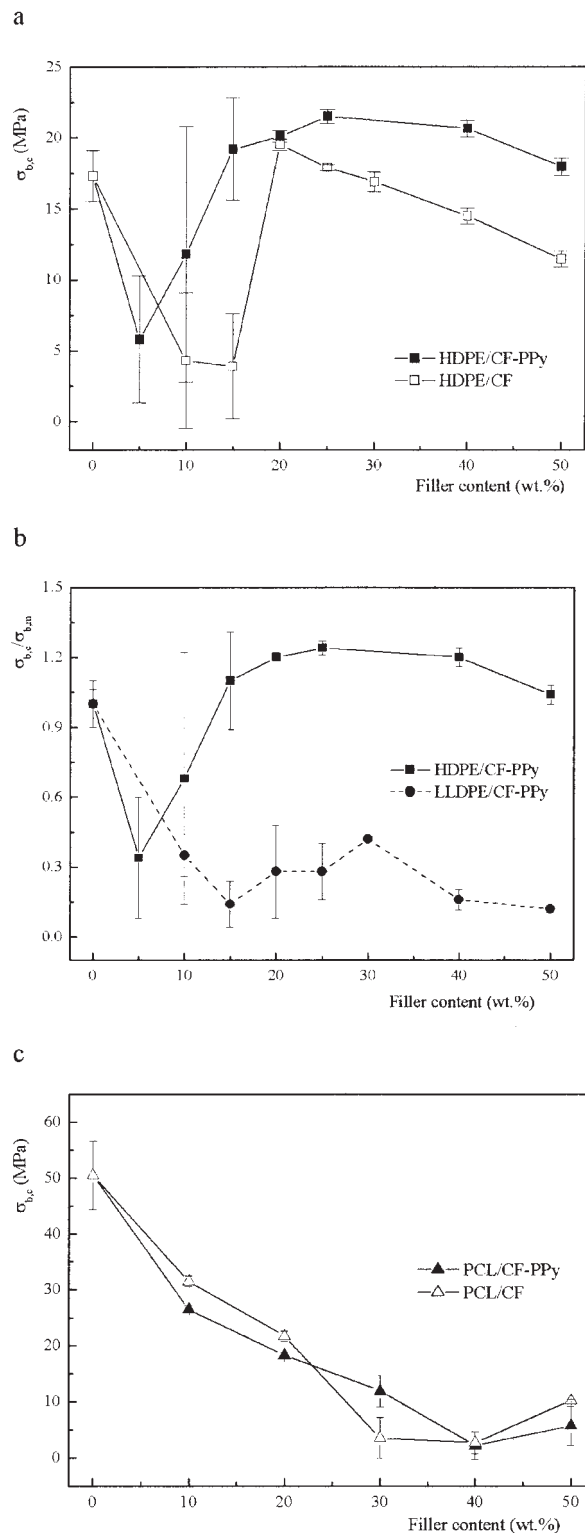


Figure 6 Stress at break ($\sigma_{b,c}$) of the HDPE filled with untreated CF (\square) and CF-20.6% PPy (\blacksquare) (a), ($\sigma_{b,c}/\sigma_{b,m}$) of the HDPE (\blacksquare) and LLDPE (\bullet) filled with CF-20.6% PPy (b), ($\sigma_{b,c}$) of the PCL filled with untreated CF (\triangle) and CF-20.6% PPy (\blacktriangle) (c) as a function of the filler content.

ces, the values of stress at break are expressed as the ratio of stress at break of the composite and of the matrix. As seen in Figure 6(b), the main features of these dependences are the same as in the case discussed earlier. However, the reinforcing effect of the treated cellulose CF-20.6% PPy on the HDPE matrix is much more significant than in the case of the LLDPE matrix. This may be due to the different degrees of crystallinity of the two matrices (59 wt % for LLDPE and 75 wt % for HDPE). The degree of crystallinity of the polymeric matrices was determined as the ratio between the specific enthalpy of melting of the polyethylenes and the specific enthalpy of melting of 100% crystalline PE (288 J/g).²⁵ Since the filler is located only in the amorphous phase, the concentration of the filler relative to the amount of the amorphous phase is higher in HDPE than in LLDPE; consequently, the amorphous part of HDPE is more reinforced than LLDPE because of a higher local concentration of the filler in this phase. Similar behavior was observed in LLDPE and HDPE matrices filled with graphite.^{26,27}

A different behavior is observed for the PCL matrix [Fig. 6(c)]. In this case, stress at break decreases monotonically with increase in the filler content for both coated and uncoated CF. A reinforcing effect of the filler on the matrix was not observed, not even at the highest filler content. Comparison of the absolute values of stress at break of filled PCL shows that these values are slightly higher when treated CF-20.6% PPy fibers are used, probably because the interfacial interaction between PCL and polypyrrole is better than that between PCL and untreated cellulose fibers.

The dependence of Young's modulus of HDPE filled with untreated and treated cellulose fibers on the filler content is shown in Figure 7(a). An increase in Young's modulus with an increase in the filler content was observed in both cases. Similar values for the materials filled with both treated and untreated CF indicate that the surface treatment of CF has a negligible influence on this parameter. Generally, surface treatment has much less influence on the modulus than on the ultimate properties (stress at break and elongation at break). The dependence of Young's modulus of HDPE and LLDPE matrices filled with PPy coated cellulose is shown in Figure 7(b). An increase in Young's modulus was observed in both cases. It seems that the effect of the filler is slightly more pronounced in the case of the HDPE matrix. An increase in Young's modulus with an increase in filler content was observed also for the PCL matrix, as is generally found. This increase was more pronounced for polypyrrole coated cellulose fibers, as seen in Figure 7(c).

The dependences of elongation at break on the filler content for LDPE and HDPE filled with untreated and treated cellulose fibers are shown in Figures 8(a) and 8(b). The dependences are displayed on a semilog

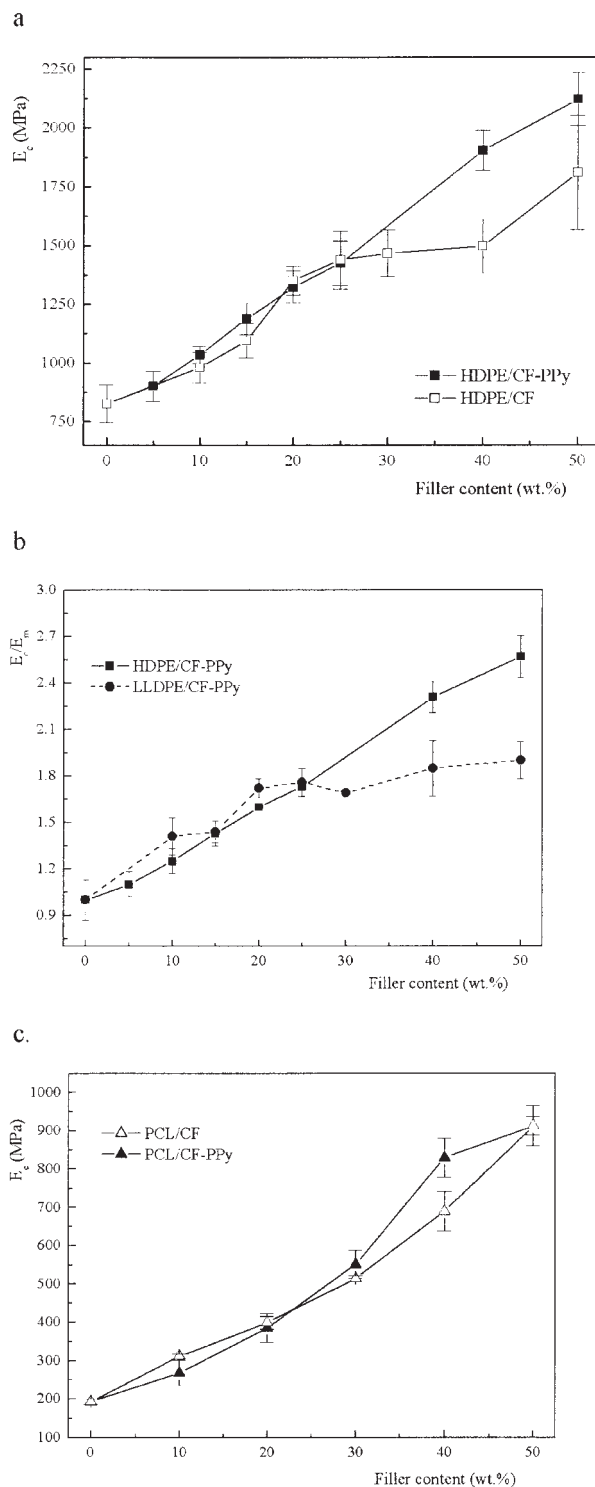


Figure 7 Young's modulus (E_c) of HDPE filled with untreated CF (\square) and CF-20.6% PPy (\blacksquare) (a), (E_c/E_m) of HDPE (\blacksquare) and LLDPE (\bullet) filled with CF-20.6% PPy (b), and (E_c) of PCL filled with untreated CF (\triangle) and CF-20.6% PPy (\blacktriangle) (c) as a function of the filler content.

scale because of the large differences between the values. A steep decrease in elongation at break with an increase in the filler content was observed in all cases.

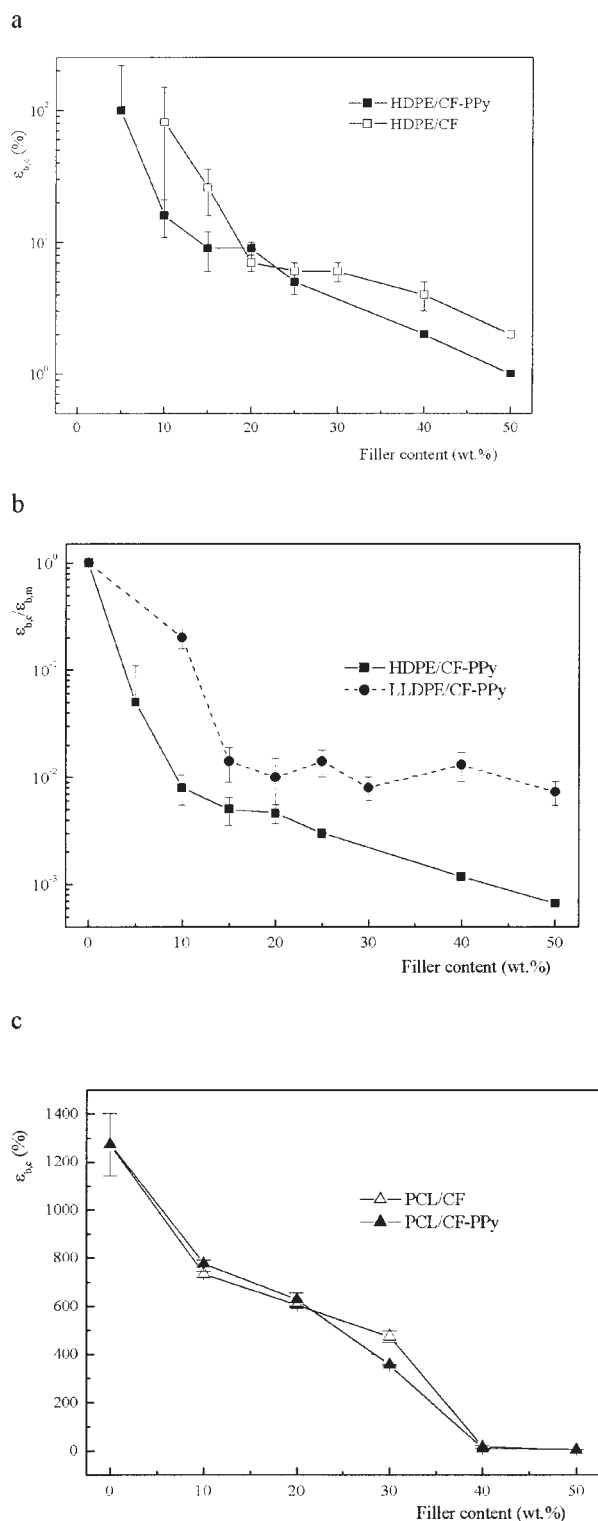


Figure 8 Elongation at break ($\epsilon_{b,c}$) of HDPE filled with untreated CF (\square) and CF-20.6% PPy (\blacksquare) (a), ($\epsilon_{b,c}/\epsilon_{b,m}$) of HDPE (\blacksquare) and LLDPE (\bullet) filled with CF-20.6% PPy (b), and ($\epsilon_{b,c}$) of PCL filled with untreated CF (\triangle) and CF-20.6% PPy (\blacktriangle) (c) as a function of the filler content.

This is a typical behavior for polymers filled with organic or inorganic fillers, since fillers reduce the drawability of polymers.

Figure 8(a) shows that the decrease in elongation at break for composites filled with untreated cellulose is less pronounced than for composites filled with treated material. Generally, parameters that increase the strength of composites reduce their drawability. The surface coating of cellulose apparently leads to an improvement in the interfacial interactions, as we have already discussed for stress at break. On the other hand, it results in a more pronounced decrease in elongation at break. Elongation at break of the filled HDPE matrix decreased more steeply than elongation at break of the filled LLDPE [Fig. 8(b)]. This can be caused by higher local concentration of defects in the amorphous phase of the HDPE matrix. The elongation at break of the filled PCL decreases with an increase in filler content, as shown in Figure 8(c) for both treated and untreated CF, which is a common behavior for filled polymers.

Electrical conductivity

The electrical conductivity measurements on the composites are summarized in Table V. As can be seen, the type of polymeric matrix has a critical influence on the dependence of electrical conductivity on filler content. For the composites based on polyethylene matrices, the filler content has only a small effect on electrical conductivity. Only for composites filled with 50 wt % of CF-20.6% PPy, a reasonable increase in electrical conductivity was observed. On the other hand, in the case of composites prepared using polycaprolactone matrix, the electrical conductivity increases significantly with an increase in the filler content. PCL filled with 30 wt % of CF-20.6% PPy reaches a conductivity of $7.1 \times 10^{-7} \text{ S cm}^{-1}$, and the increase in the CF-20.6% PPy filler content to 50 wt % caused a further increase in conductivity by three orders of magnitude. This can be caused by two factors: firstly, polycaprolactone is more polar than polyethylene and, therefore, coated cellulose fibers are better dispersed therein; secondly, the kneading temperature for the PCL matrix is much lower (85°C) than that for LLDPE or HDPE matrices (170°C). Solid cellulose forms a microcrystalline structure with crystalline regions and amorphous regions. Naturally occurring cellulose crystallizes in monoclinic and sphenoid structures.² An investigation of the thermal properties of microcrystalline cellulose by differential scanning calorimetry and modulated temperature differential scanning calorimetry shows three reproducible step transitions at 132 , 159 , and 184°C .²⁸ It seems that the combination of high temperature and shear forces leads to an aggregation of the cellulose fibers. Fibers stick together and cannot be dispersed properly within a polymeric matrix. This phenomenon suppresses the formation of a well-developed conductive network and results in low electrical conductivity.

TABLE V
Electrical Conductivity of Composites

HDPE/CF-20.6 wt % PPy		LLDPE/CF-20.6 wt % PPy		PCL/CF-20.6 wt % PPy	
Filler content (wt %)	Conductivity (S cm ⁻¹)	Filler content (wt %)	Conductivity (S cm ⁻¹)	Filler content (wt %)	Conductivity (S cm ⁻¹)
0	2.5×10^{-15}	0	1.1×10^{-15}	0	1.8×10^{-13}
10	4.4×10^{-13}	10	4.5×10^{-14}	10	1.6×10^{-11}
20	1.1×10^{-13}	20	4.2×10^{-14}	20	5.9×10^{-11}
25	4.4×10^{-13}	25	8.4×10^{-14}	—	—
—	—	30	8.4×10^{-13}	30	7.1×10^{-7}
40	1.4×10^{-12}	40	1.0×10^{-11}	40	6.7×10^{-5}
50	1.2×10^{-8}	50	1.9×10^{-11}	50	6.5×10^{-4}

CONCLUSIONS

Conductive cellulose fibers were prepared by coating pure cellulose with various amounts of PPy. It was found that coating fibers with 20.6 wt % of PPy is sufficient to obtain material with an appropriate conductivity of 0.61 S cm⁻¹.

A significant influence of the polymeric matrix was found on the electrical conductivity of composites, filled with conductive cellulose fibers. For composites based on polyethylene matrices, the filler content had only a small effect on the electrical conductivity. Only for composites filled with 50 wt % of polypyrrole-coated fibers, a reasonable increase in electrical conductivity was observed. On the other hand, if composites were prepared using a polycaprolactone matrix, the electrical conductivity increased significantly with increase in the conducting filler content. Composites filled with 30 wt % of coated cellulose can be considered as materials with antistatic properties because they reached conductivity level of 7.1×10^{-7} S cm⁻¹.

As regards the mechanical properties of the composites, the behavior of stress at break also depends significantly on the type of polymeric matrix. Nonlinear behavior of stress at break on the filler content was observed for all composites, based on a polyethylene matrix. At low filler concentration a sharp decrease in stress at break was observed, as a consequence of the suppression of drawability of PE matrices. The reinforcing effect became significant at a filler concentration above 10 wt %. Cellulose fibers coated with 20.6 wt % PPy have a more pronounced effect on reinforcement than untreated cellulose fibers. The reinforcing effect of treated cellulose on the HDPE matrix was found to be much more significant than in the case of LLDPE, probably due to a different degree of crystallinity of the two matrices. No significant reinforcing effect was found for the polycaprolactone matrix. The decrease in stress at break with an increase in the filler content was found to be monotonic over the whole concentration range.

An increase in Young's modulus with an increase in the filler content was detected in all cases investigated.

The coating of cellulose fibers with polypyrrole leads to an increase in Young's modulus compared to composites filled with untreated cellulose fibers.

A steep decrease in elongation at break with an increase in the filler content was observed in all composites studied. In the case of coated cellulose fibers, this decrease is more pronounced for the HDPE matrix than for LLDPE. It can be caused by a higher local concentration of defects in an amorphous phase of HDPE. A steep decrease in elongation at break for filled PCL was also observed for both treated and untreated cellulose fibers.

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