Electrokinetic Properties of Polypropylene-Layered Silicate Nanocomposite Fibers

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ABSTRACT: Nanocomposite fibers based on polypropylene (PP) polymer were prepared with different content of nanofiller. Filaments were spun from an isotactic iPP homopolymer. Montmorillonite modified by N,N-dimethyl-N,N dioctadecylammonium cations was used for preparation of PP nanocomposite fibers. A PP grafted with acrylic acid was added as a coupling agent. Nanocomposite fibers were characterized, i.e., the surface morphology of PP nanocomposite fibers was observed and surface properties were defined by electrokinetic properties determination by zeta potential measurements. For particle distribution observation the plasma etching was involved as a method for sample preparation. The addition of nanoparticles has an impact on ZP value of nanofilled fibers, however, isoelectric point IEP is not significantly influenced by different concentrations of nanofiller. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 1276–1281, 2009

Key words: fibers; nanocomposites; plasma etching; electrokinetic properties

INTRODUCTION

There has been intensive research on nanomaterials recently. Several different nanoparticles for nanofilled polymer composites, e.g., layered silicates,[1–8] silica nanoparticles,[9–11] carbon black,[12,13] carbon nanotubes,[14,15] metal-containing nanoparticles,[16] elastomeric nanoparticles,[17] TiO$_2$,[18] etc., have been reported. However, low nanoparticle-loaded polymer composites with improved performance are predominantly produced by injection molding, whereas the spinning procedure is reported less frequently.[19–21]

Because of excellent mechanical properties, high chemical stability, and processability, polyolefins, i.e., polypropylene (PP), and polyethylene represent an appropriate polymer matrix for nanofilled fibers. The most common PP nanocomposites are composed of organically modified silicates, e.g., montmorillonite, and polymeric matrix. The effect of intercalants chemistry and concentration on processing, morphology, and properties of PP nanocomposites was studied by several authors.[22] Nevertheless, in the case of PP, because of incompatibility of polymer and the nanofiller that is conditioned by the absence of polar groups in the backbone of PP, a coupling agent should be added. Therefore, functionalized isotactic PP and syndiotactic PP grafted with maleic anhydride and diethyl maleate, respectively, have been intensively used.[23,24]

The aim of our work was to generally characterize surface properties of nanocomposite fibers composed of organosilicate and PP. In addition, a PP grafted with acrylic acid (PPAA), which is infrequently applied as a compatibilizer in preparation of nanomodified PP fibers, was used. The influence on fiber surface charge due to the contribution of different ionisable moieties from the nanocomposite was studied. Based on amphoteric nanocomposite character, the surface zeta potential could be an estimation of fiber chemical behavior (e.g., ion exchange capacity).

EXPERIMENTAL

Preparing of nanofilled PP fibers

The melt spinning and in-line drawing of PP filaments were performed on an Extrusion Systems Ltd. laboratory spin-draw device. Filaments were spun from a commercial isotactic iPP homopolymer Malen P, S-702 supplied from Basell Orlen Polyolefins, Poland, with MFI = 11 g/10 min – 16 g/10 min and isotactic index 96% (m/m). Commercial product Polybond 1002, a PPAA, supplied from Crompton Corporation, USA, was added as a coupling agent. Properties of Polybond 1002 are melt flow rate at

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230°C 22.1 (15–25) g/10 min, melting point 160°C, specific gravity 0.91 g/cm^3, and acrylic acid content wt = 6%. Ten percent and 20% of PPAA copolymer, respectively, were added. A commercially available montmorillonite (organoclay) MMT modified by N,N-dimethyl-N,N dioctadecylammonium cations (Nanofil 15 from Südchemie, Germany) was used. Nanocomposite fibers with 0.5, 1, and 2% of MMT were prepared.

The polymer was extruded at a rate of 1.7–1.9 g/min through a one-hole spinneret of diameter 2 mm. The temperature of the melt at the spinneret was 200°C, spinning velocity 0.67 m/min. The as-spun filaments were three-stage drawn at 50°C in a continuous spin drawing process with overall draw ratio 1 : 294. Continuously drawn filaments were then additionally drawn to the limiting draw ratio on a Zimmer laboratory draw device. In this subsequent slower stage, the filaments were drawn through a hot plate at the temperature of 115°C with the draw ratio 1 : 3.9 for neat PP and samples containing 10% and 20% PPAA without MMT and samples containing 10% PPAA and MMT nanoparticles. Copolymeric samples containing 20% PPAA and 0.5 or 1% MMT, respectively, were drawn with the draw ratio 1 : 2.5. The draw ratio for nanocomposite fibers prepared with 2% of nanofil was 1 : 2.

Analytical methods

Surface morphology of the prepared nanocomposite fibers was observed by electron microscopy. A JSM–T220 scanning electron microscope (SEM) was used for direct observation of samples. Before inspection, the fibers were coated on a Balzers SCD 050 apparatus with gold according to the standard method for textile fibers to enhance the low conductivity.

The dispersion of particles within the hybrid system is of fundamental importance. A method that is based on selective etching of the polymer using low-pressure weakly ionized highly dissociated oxygen plasma was used for observation of particles.[25] Experiments were performed in a discharge vessel, which was a cylindrical tube of 600-mm length and 40-mm diameter. One side of the tube was connected to a vacuum system that was pumped with a two-stage rotary pump with the pumping speed of 2.2 L s^{-1} and the base pressure of 0.1 Pa. The pressure in the system was measured with a calibrated Pirani gage. The etching was performed at the pressure of 25 Pa cyclically; i.e., five cycles per 1 min with 1-min nonetching interval between the etching process.

The influence of different fiber composition on zeta potential value was investigated. An Electrokinetic Analyzer EKA, A. Paar KG was used for streaming

TABLE I
Linear Density and Tenacity of Nanocomposite Fibers

	T [tex]	Tensile force [cN/tex]
PP	2.24	47.7
PP, 10% PPAA	2.25	50.2
PP, 10% PPAA, 0.5%MMT	2.42	41.8
PP, 20% PPAA	2.27	46.7
PP, 20% PPAA,0.5% MMT	4.62	16.9
PP, 20% PPAA, 1% MMT	4.46	21.9
PP, 20% PPAA, 2% MMT	–	–

potential measurements. The detailed description of the method applied is given in Ref. 26–30.

Unmodified PP and differently modified PP fibers were treated for 24 h in electrolyte solution before zeta potential determination. Potential measurements were always performed in the fiber cell using 0.001 N KCl as electrolyte solution. The adjustment of pH was achieved using 0.1 N NaOH and 0.1 N HCl. The zeta potential ζ was calculated from the streaming potential (U_s) data using the Smoluchowski equation[29,30]:

$$\zeta = \frac{U_s}{\Delta p} \cdot \frac{\eta}{\varepsilon \cdot \varepsilon_0} \cdot \frac{L}{Q} \cdot \frac{1}{R} \qquad (1)$$

where ζ, the zeta potential; U_s, the streaming potential; Δp, the hydrodynamic pressure difference across the plug; η, the liquid viscosity; ε, the liquid permittivity; ε_0, the permittivity of free space; L, the length of the plug; Q, the cross-sectional area of the plug; R, the electrical resistance across the plug. The term (L/Q) consists of two parameters neither of which can be easily measured. In the Fairbrother and Mastin approach the term (L/Q) is replaced by ($R_s \chi_s$), where R_s is the electrical resistance of the plug when the measurement cell is filled with an electrolyte whose specific conductance, χ_s, is accurately known. Thus, eq. (1) becomes:

$$\zeta = \frac{U_s}{\Delta p} \cdot \frac{\eta}{\varepsilon \cdot \varepsilon_0} \cdot \frac{R_s \cdot \chi_s}{R} \qquad (2)$$

Equation (2) is perfectly adequate for most practical systems.

RESULTS

Nanocomposite PP fibers were prepared by addition of different amounts of coupling agent PPAA and organically modified nanoparticles MMT. Mechanical properties of prepared nanocomposite fibers differ according to the spinning process. In addition, the fineness and mechanical properties of nanocomposites fibers are collected in Table I.

The fineness given by the linear density for the fibers, which were drawn in the second drawing

stage with the draw ratio 1 : 3.9 is 2.2 tex increases by the addition of MMT to 2.4 tex. Samples prepared by second-stage draw ratio 1 : 2.5 were thicker and their linear density was above 4.4 tex (4.46 for PP, 20% PPAA, 1% MMT and 4.62 for PP, 20% PPAA, 0.5% MMT, respectively). The higher drawing ratio in the second stage is the ground of better mechanical properties of fibers, which were spun at these conditions (tenacity for neat PP 47.6 cN.tex^{-1} and for copolymer PP, 10% PPAA 50 cN.tex^{-1}, respectively). These results were expected and in accordance with the findings of other authors.[31,32] It was confirmed that by blending neat PP by a small percentage of copolymer, better mechanical properties, mainly because of higher orientation of amorphous domains, is achieved, however, when the amount of added copolymer increases, it influences the mechanical properties negatively.[31,32] The incorporation of MMT lowers fibers tenacity (41 cN.tex^{-1}). Copolymeric samples containing 20% PPAA and 0.5 or 1% MMT, respectively, were drawn by a lower draw ratio and, therefore, their tensile force is adequately lower. The mechanical properties of these two samples are related to the increased amount of added MMT by increasing the filaments tensile force (for the sample with 0.5% MMT tenacity is 16.2 cNtex^{-1} and for the sample with 1% MMT 21.9 cN.tex^{-1}). The additional increase of MMT amount influences the rheological properties, and, therefore, the draw ratio for nanocomposite fibers prepared with 2% of nanofil was 1 : 2.

It should be exposed that the obtained fibers were uneven and, therefore, the mechanical properties results are slightly oscillating. However, from the SEM images presented bellow, we are concluding that the formation of agglomerates and nonhomogeneous distribution of the particles influence the nonuniformity of mechanical properties.

Surface morphology of neat, PP copolymeric and nanofilled PP fibers are shown in Figures 1–3. A smooth fiber surface morphology was obtained, however, some structural differences dependent on chemical constitution (i.e., neat PP or PP with addition of PPAA) are present (cf. Fig. 1). A homogenous distribution of particles in the PP matrix was achieved, although some agglomeration of particles was observed. By the removal of polymer layers by plasma etching (cf. Fig. 2), the inorganic particles are clearly evident and their size can be estimated. A nanocomposite with an average particle size of about 100 nm was obtained, although etched samples demonstrate also the presence of some bigger agglomerates with the dimensions of up to 1 μm (cf. Fig. 3).

The results of electrokinetic properties of nanofilled PP fibers are given in Table II. The influence of different content of copolymer PPAA and nanopar-
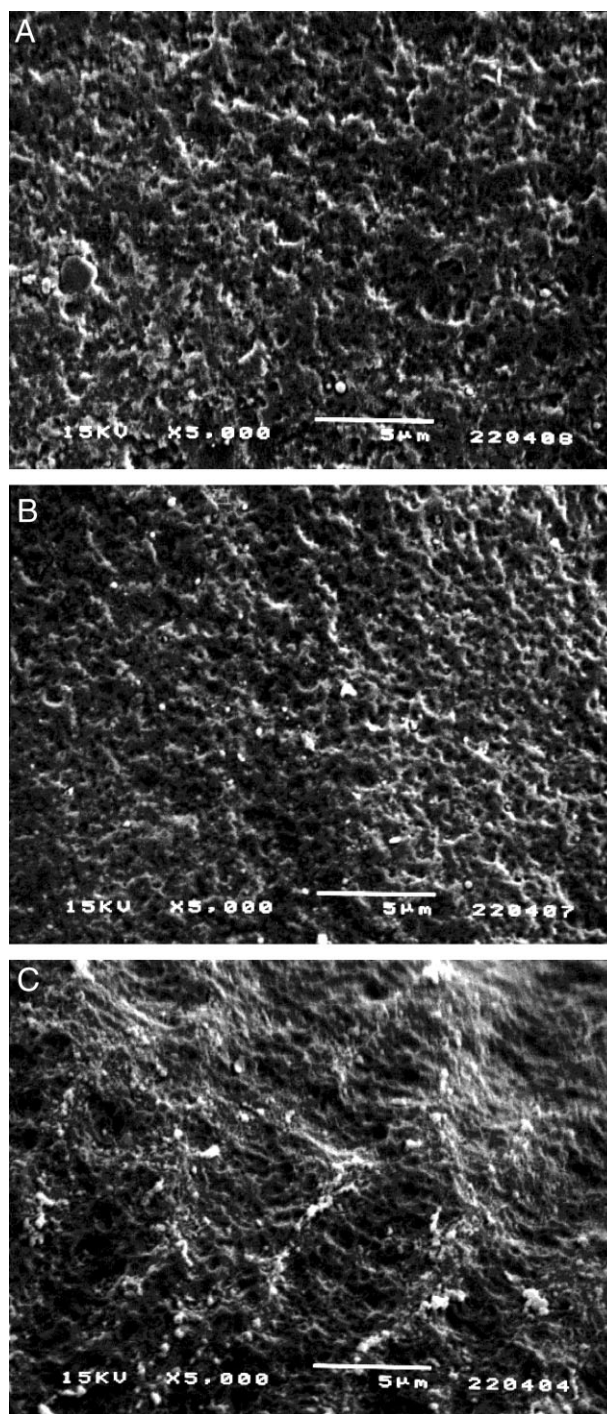

Figure 1 SEM images of plasma etched neat PP (A), copolymeric PP, 10%PPAA (B), and copolymeric PP, 20% PPAA (C) samples.

ticles nanofil on fibers' electrokinetic properties is demonstrated in Figures 4 and 5.

Figure 4 shows the functional dependence pH/zeta potential. A typical plot for a nonpolar polymeric material is observed for the fiber obtained from PP homopolymer because of its nonpolar chemical structure. Fibers prepared from pure PP homopolymer exhibit hydrophobe character with
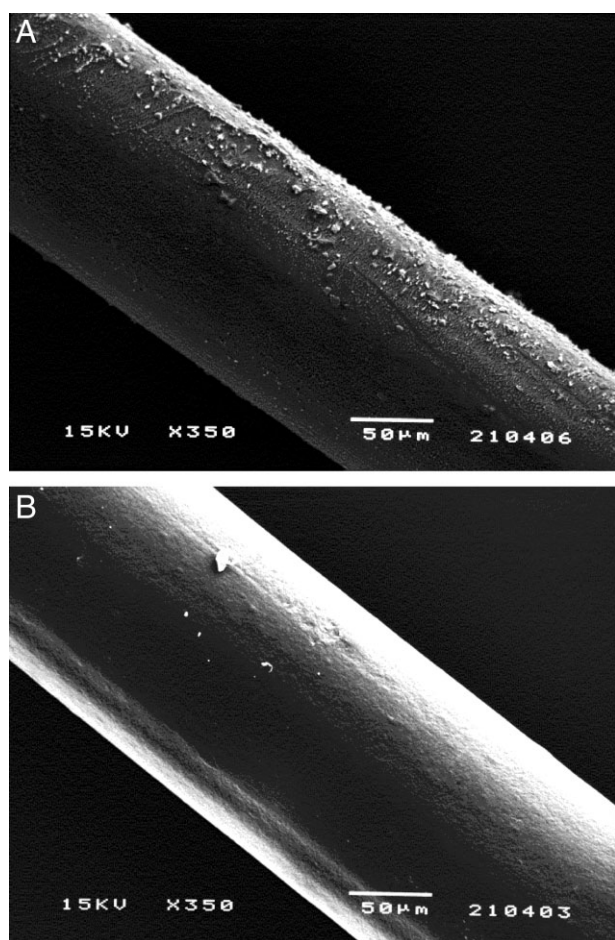
Figure 2 SEM image of nanofilled (A) and plasma etched (B) PP, 10% PPAA, 0.5% MMT fiber sample (magnification 350×).
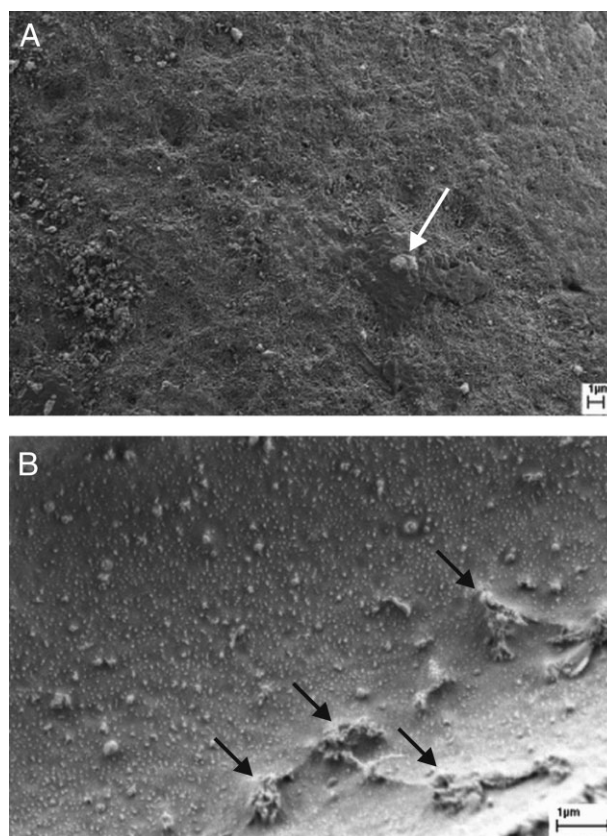

Figure 3 SEM image of plasma etched nanofilled PP, 10% PPAA, 1% MMT (A) and PP, 10%PPAA, 2% MMT (B) fiber (arrows indicate bigger agglomerates).

negative zeta potential value ZP at –25 mV and isoelectric point IE at pH = 3.5. Introduction of polar groups by addition of copolymer significantly influences the ζ/pH diagram. Zeta potential value is drastically decreased for the samples that were prepared by addition of PPAA (ZP = –55 mV for PP fiber with 20% PPAA). The negative zeta potential value is dependent on the copolymer share as expected. For the samples containing PPAA a very slight shift of isoelectric point IE toward acid region is observed. The addition of positively charged modified MMT influences electrokinetic properties in the opposite direction. Zeta potential value is increased (zeta potential value = −8 mV for the PP homopolymer with 0.5% modified MMT) and IP shifts toward neutral region. Electrokinetic properties of nanocomposite fibers are conditioned by both influences. However, modified fibers express a lower ZP value than unmodified fibers and the same IE shift as MMT modified PP fiber without PPAA. Higher concentration of the polar PPAA was expected to dominate the electrokinetic properties of nanocomposites, and results of the ζ-pH function

confirmed that the electrokinetic surface properties are dominated by the PPAA-containing dissociable carboxyl groups.

Figure 5 demonstrates how the content of nanoparticles influences the electrokinetic properties of modified PP fibers. The ζ-pH functions for nanofilled PP fibers containing 20% coupling agent (PPAA) and different content of modified MMT are given. Zeta potential at pH 9 shows a clear picture of the decreasing ZP value (ZP value of copolymer PP fiber with 2% modified MMT = −40 mV and of the

TABLE II
Isoelectric Points IP and Zeta Potential of Nanocomposite Fibers Determined at pH = 3 and pH = 9, Respectively

	ζ at pH=3 [mV]	ζ at pH=9 [mV]	IP
PP	1.75	−24.86	3.26
PP, 0.5% MMT	0.9	−7.0	3.7
PP, 10% PPAA	−0.8	−45.9	2.89
PP, 10% PPAA, 0.5%MMT	4.6	−39.6	3.63
PP, 20% PPAA	1.6	−51.5	3.11
PP, 20% PPAA,0.5% MMT	4.3	−45.9	3.51
PP, 20% PPAA, 1% MMT	4.0	−41.9	3.52
PP, 20% PPAA, 2% MMT	4.2	−32.8	3.68

copolymer PP fiber with 0.5% modified MMT = −25 mV) with decreasing MMT content. However, IE point is not significantly changed by different concentrations of nanofiller.

Despite the fact that PP homopolymer is hydrophobic, there is still some penetration of aqueous solution of electrolyte into the fiber inside, resulting in fiber swelling during the zeta potential measurements. Although the statement is surprising, this phenomenon of small but significant swelling of hydrophobe polymers because of their microstructure was confirmed by Soster and Stana.[33] Especially, in modified nanocomposite fibers containing accessible hydrophilic groups, this phenomenon is more expressed. The adsorption of water or electrolyte solutions causes an interfibrilar swelling of the surface layers and thus the size of active surface is increased, although the nature of dissociable groups is not changed. Because the zeta potential refers to the potential at some idealized plane of shear between the solid and liquid phases when any relative motion is induced between them, the swelling of the solid phase itself causes a reduction of the ZP because of the shift of the shear plane into the liquid phase.[34,35] To avoid these influences the measurements were performed on fibers in a swollen state.

CONCLUSIONS

PP-based nanocomposite fibers were prepared by direct polymer melt intercalation. With the intention to determine the size and dispersion of nanoparticles in the polymer matrix, fibers were plasma etched and SEM observations were performed. Plasma etching represents an appropriate method for preparation of nanofilled samples for microscopical analyses.
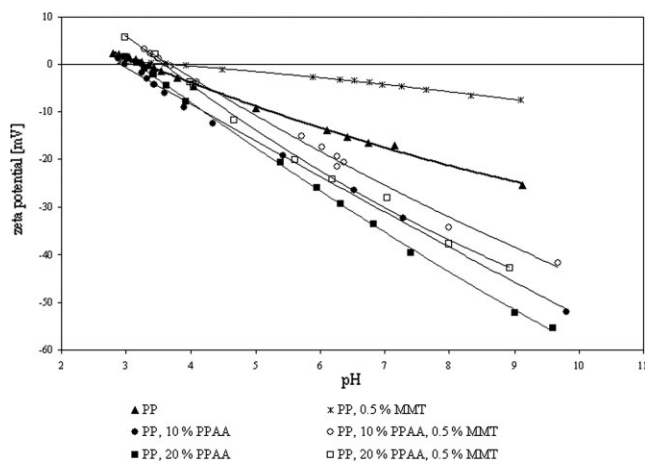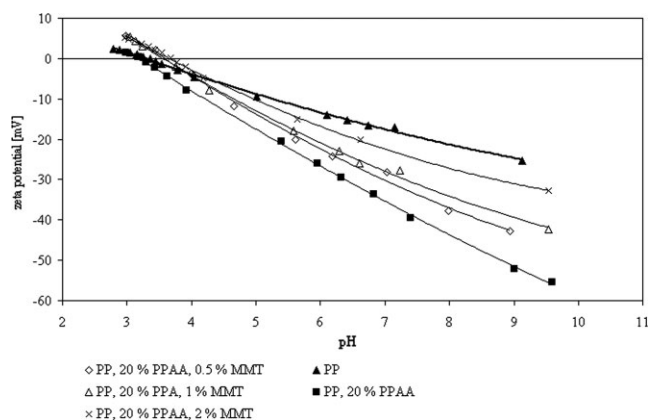

Figure 5 Zeta potential of PP nanocomposite fibers as a function of pH; the influence of the amount of nanofiller on zeta potential values.

The influence of content of nanofiller and coupling agent on electrokinetic properties was studied. PP monofilament fibers exhibit hydrophobe character with negative zeta potential value. The zeta potential value of copolymer PP fiber decreases with increasing PPAA content and the isoelectric point of copolymer samples shifts toward acid region.

Addition of modified montmorillonite, due to the particles electropositive character, affects the reduction of zeta potential value and a slight shift of IE point towards neutral region is observed. Nanoparticles content influences electrokinetic fibers properties, i.e., ZP value is changed, however, IE point is not significantly changed by different concentrations of nanofiller.

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Figure 4 Zeta potential of PP nanocomposite fibers as a function of pH; the influence of PPAA content on zeta potential values.

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