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Production of sulfonated polyetheretherketone/polypropylene fibers for photoactive textiles

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ABSTRACT: New photocatalytic fibers made of sulfonated polyetheretherketone (SPEEK)/polypropylene (PP) are melt compounded and melt spun, first on laboratory scale and then on a semi-industrial scale. Fiber spinnability is optimized and the fibers are characterized using mechanical testing, electron paramagnetic resonance (EPR) spectroscopy, and scanning electron microscopy (SEM). According to the results, the fiber spinnability remains at a good level up to 10 wt % SPEEK concentration. Optimal processing temperature is 200°C due to the thermal degradation at higher temperatures. EPR measurements show good and long-lasting photoactivity after the initial irradiation but also decay in the radical intensity during several irradiation cycles. Mechanical tenacity of the SPEEK/PP 5 : 95 fiber is approximately 20% lower than for otherwise similar PP fiber. The fiber is a potential alternative to compete against TiO2-based products but more research needs to be done to verify the real-life performance. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42595.

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INTRODUCTION

The use of photocatalytic textiles in antimicrobial, self-cleaning, and anti-pollution products has increased during the last few decades. These functionalities are based on the highly reactive radicals and oxidants that are generated under band-gap light irradiation. Photocatalysts can be used as an alternative to conventional biocides to prevent the deterioration of textiles caused by insects, fungi, algae, and microorganisms.[1] The self-cleaning property of a photoactive textile is based on the discoloration of organic stains by reactive radicals.[2] Photocatalytic oxidation (PCO) is an emerging technology in air purification, and is also based on the decomposition of harmful substances.[3]

Although several semiconductors have been used as photocatalysts,[4] titanium dioxide (TiO_2) has dominated the research because of its low price, high photostability, and safety.[5] In this study, a photoactive polymer fiber made of sulfonated polyetheretherketone (SPEEK)/polypropylene (PP) blend is manufactured as an alternative to TiO_2-based fibers. According to the previous characterization of the SPEEK/PP blend,[6] the material provides good photochemical properties but has problems in thermal stability. The main competitive advantage of SPEEK/PP is the safety of the material because it does not contain nanoparticles and it has been demonstrated to be biocompatible with minor effect on cytotoxicity induced by residual content of sulphuric acid used in the synthesis.[7] By contrast, the particle size of TiO_2 is reduced to nanoscale to increase the total surface area per volume ratio and thus efficiency. The increased use of nanoparticles in many applications has raised questions about their safety, and recent research suggests that TiO_2 nanoparticles are possibly carcinogenic to humans.[8]

Sulfonated polyetheretherketone (SPEEK) is manufactured through a sulfonation process of polyetheretherketone (PEEK), which is a linear semicrystalline thermoplastic polymer with excellent mechanical and thermal properties and chemical

Additional Supporting Information may be found in the online version of this article.

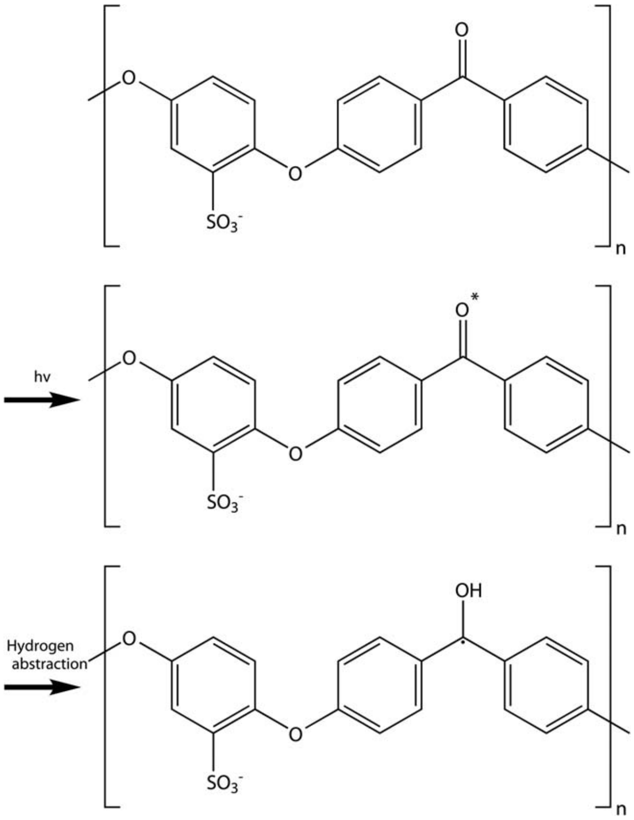

Figure 1. Excitation reaction and radical formation of SPEEK.

resistance.[9] Compared to PEEK, SPEEK alone has poor thermal properties and processability[6] and has to be blended with other polymers.[10–12] The photoactivity of SPEEK is based on the formation of benzophenone ketyl radicals (BPK) in the polymer chain. When polar benzophenone of SPEEK is exposed to UV irradiation, the n-to-π^* transition induces a generation of a triplet state.[11] This triplet state is highly reactive to form a stable BPK radical by abstracting a hydrogen atom (Figure 1). The antimicrobial effectiveness of benzophenone has been previously confirmed with different polymers.[13] PP is an excellent candidate to assist SPEEK in the hydrogen abstraction since it possesses a labile hydrogen atom. Furthermore, PP is an inexpensive commodity plastic widely used in fibers.

The SPEEK/PP fibers are made by first compounding the materials in a melt mixing process, and then melt spinning the compound. During the melt mixing, it is important that the SPEEK particles are homogenously dispersed into the PP matrix and that there remain no large particles or particle agglomerates which could lead to a spinline failure in the melt spinning. It has been observed that when the particle size approaches close to the fiber diameter, the spinning stability is reduced drastically.[14] According to the performed characterization of previously made SPEEK/PP blends, the blend is homogenous with a SPEEK particle size of a few micrometers,[6] which should be small enough for the fiber spinning.

Textile fabrics made of SPEEK/PP filament yarn would have potential for use in photocatalytic textiles. The closest competitor, a PP/TiO_2 nanocomposite fiber, has been evaluated[15] and, according to antimicrobial testing, this blend should have antimicrobial properties in proper compositions.[16] Antimicrobial textiles are currently used in products such as tents, tarpaulins, awnings, blinds, parasols, sails, waterproof clothing, in some consumer textiles, and medical settings.[17] Conventional antimicrobial textiles are based on biocides like silver,[18,19] quaternary ammonium salts,[20] halamine structures,[21,22] triclosan, or zinc pyrithione.[17] These biocides have been criticized due to their limited efficiency, high costs, toxicity, and environmental concerns.[16] A self-cleaning property is desirable especially in the clothing industry and, therefore, the research has focused on that sector.[2,23,24] However, these products are not largely available yet and they raise health concerns due to the nanoparticles they contain. There are many commercial air purifiers on the market that use photocatalytic oxidation to turn harmful substances, including volatile organic compounds (VOCs), into less harmful compounds such as CO_2 and H_2O.[3,25]

In this study, SPEEK/PP-based photoactive fibers are manufactured as an alternative to TiO_2 and conventional methods to provide antimicrobial, self-cleaning, and anti-pollution properties. The fibers are manufactured in a melt spinning process, first on laboratory scale and then on a semi-industrial scale. The fibers are characterized regarding their mechanical properties, photochemical effectiveness, and morphology. Based on the obtained results, their suitability in commercial textile applications is estimated. In addition to the new polymer-based textile material, the novelty of this study is the melt spinning of an unconventional polymer blend containing two totally different components and time-dependent processability.

EXPERIMENTAL

Materials

Victrex (Lancashire, UK) PEEK grade 704 in powder form with an average molar mass of 4.5×10^4 g/mol is the primary source for the synthesis of modified benzophenone compounds. In the sulfonation process, 98% sulphuric acid (H_2SO_4) (Carlo Erba, Val de Reuil, France) was used. The PP grade was PPH 4050 homopolymer (Total Petrochemicals, Houston, USA) having a melt index of 3 g/10 min (2.16 kg, 230°C) according to the supplier's information.

Synthesis of SPEEK

The sulfonation of PEEK in powder form was carried out in a 250 mL reactor in air atmosphere at a constant temperature of 45°C. 5% w/v of PEEK was added to a solution of concentrated sulphuric acid (98%), and the solution was mechanically stirred for a period of 3 h. The obtained SPEEK was then precipitated by dropwise addition of the solution to 500 mL of ice-cooled distilled water. The precipitate was washed till the excess acid was removed and then dried in an oven at 70°C for 12 h.

SPEEK/PP Compounding

The SPEEK/PP blend was batchwise compounded by using a DSM Xplore micro compounder. The equipment has two counter rotating screws and a maximum batch size of 5 mL. The materials were weighed, loaded into the compounder, and mixed for 5 min at 200°C at a screw speed of 150 RPM.

Table I. Processing Parameters for the Laboratory Scale Melt Spinning Process

Number of filaments	1
Die length (mm)	30
Die diameter (mm)	1
Drawing speed (m/min)	100
Spinning path length (m)	0.05
Tex number (g/km)	2-4

The required material amounts are larger in a semi-industrial fiber spinning process, and therefore, the compounding was performed in a Brabender W50 single-screw extruder. The processing temperature was 200°C and the extruder screw speed was 30 RPM. The material was repeatedly processed four times to provide a homogenous compounding quality.

SPEEK/PP Melt Spinning

The laboratory scale melt spinning system was based on a modified Göttfert Rheograph 6000 capillary rheometer.[26] It is a piston-based system for monofilaments with a volume of 26 cm^3 and a maximum processing temperature of 400°C. The most important processing parameters used can be found in Table I.

The semi-industrial multifilament melt spinning of SPEEK/PP 5 : 95 was performed in a Fourne melt spinning system comprised of a single-screw extruder system with a filament count of 1–100. The equipment has the possibility to use heatable godets with different speed settings but these were not used due to the lack of material. The most important processing parameters for this system can be found in Table II.

Electron Paramagnetic Resonance Measurements

Electron paramagnetic resonance (EPR) spectroscopy was used to study the free-radical formation and life time of the photoactive species. Continuous wave (CW) X-band (9 GHz) EPR measurements were carried out at room temperature on a Bruker E500 ELEXSYS Series, using the Bruker ER 4122 SHQE cavity. The sample was placed into a 4.0 mm ID Suprasil tube, exposed to UV irradiation generated by an UV lamp (effective irradiative power 8 W/m^2 in the range of 390–490 nm) at a distance of 11 cm for 15 min. Then the specimen was immediately measured by EPR spectroscopy and the radical was monitored until 16 h. Then, it was irradiated again for 15 min and the radical signal was followed for other 24 h. This was repeated for a total of 10 times. The relative radical amount was calculated from the EPR peak areas by a double integration of the signal, centered at $g = 2.0035 \pm 0.0003$ with a narrow scan of 50 G avoiding Mn(II) contribution.[6]

Table II. Processing Parameters for the Semi-Industrial Melt Spinning Process

Number of filaments	10
Die length (mm)	8
Die diameter (mm)	0.5
Tex number (g/km)	23
Screw speed (RPM)	57
Drawing speed (m/min)	250
Winder traverse (1/min)	198
Spinning path length (m)	4.8

Table III. Spinning Quality Table

Quality	Description
Excellent	No problems in fiber quality or spinning stability.
Good	Fiber spinning was possible but there were problems in the spinning stability or fiber quality and spinning of very thin fibers was not possible.
Not spinnable	Fiber spinning was not possible or the process was stable for a few seconds at best.

Tensile Testing

Tensile tests were performed according to the ISO 2062 standard using ADF brustio Tessile tensile testing machine. A 200 mm clamping length and 1800 mm/min drawing speed were used. A total of 10 measurements per sample were made. Young's modulus was calculated in 0–10% strain. Prior to the mechanical analyses, the samples were conditioned at 20°C and a humidity of 65% for 24 h.

Scanning Electron Microscopy

The morphology of the SPEEK/PP 5 : 95 fibers was investigated by a Philips XL30 scanning electron microscope (SEM). The materials were gold sputtered before investigations in order to increase their conductivity.

Table IV. The Results of the Melt Spinning Tests

Test number	Processing temperature (°C)	SPEEK concentration (%)	Quality
1	180	0	Good
2	200	0	Excellent
3	220	0	Excellent
4	180	5	Good
5	200	5	Excellent
6	220	5	Excellent → good → not spinnable (depending on the residence time)
7	180	10	Good
8	200	10	Excellent
9	220	10	Excellent → good → not spinnable (depending on the residence time)

Figure 2. Melt spun SPEEK/PP 5 : 95 filaments. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

RESULTS AND DISCUSSION

SPEEK Sulfonation and SPEEK/PP Compounding

The SPEEK/PP material has been previously characterized at different blend ratios.[6] According to these tests, the compounding should provide a homogenous blend. The biggest challenge was found in the thermal properties of the blend, and therefore, the blend spinnability was evaluated at different processing temperatures.

SPEEK/PP Fiber Spinning on a Laboratory Scale

The same Göttfert capillary rheometer-based fiber spinning system has been used in previous PEEK melt spinning experiments and the process parameters were thoroughly characterized for PEEK.[26] Although the processing temperatures are very different for the SPEEK/PP blend compared to neat PEEK, the previously found optimal spinning path length (5 cm), capillary dimensions (30/1 mm), and motor speed (100 m/min) for this equipment were used for the SPEEK/PP blend. The goal of these current laboratory scale tests was not to optimize the process as far as possible; instead the aim was to get a good overview of the spinnability at different SPEEK concentrations and temperatures.

For evaluation of the fiber spinning properties, a very simple three-step grading scale was created. The descriptions for different spinning qualities can be found in Table III.

Fiber spinning of the SPEEK/PP blend was easy at best and the fiber quality turned out to be excellent despite the fact that the system has no filters to remove impurities or unmelted particles. Generally an increase in the processing temperature improves spinnability[26–28] and this was evident with the SPEEK/PP blend as well. At 180°C, the spinnability was the worst regardless of the SPEEK concentration. This is not surprising considering how close this temperature is to the melting point of PP. However the processing temperature cannot be increased endlessly because the thermal properties of SPEEK are poor.[6] This was evident at 220°C where spinnability worsened drastically as the residence time increased. At first, the spinnability was excellent but after about 5 min, it had reduced to good and after 10–15 min, it was impossible to keep the

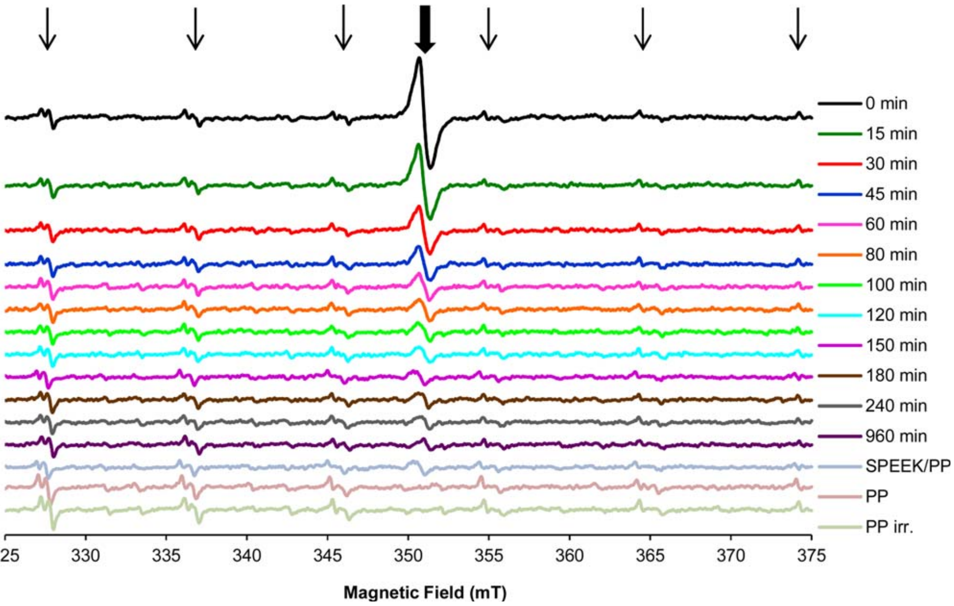

Figure 3. X-band EPR spectra of the sample recorded at different times after the irradiation. $\nu = 9.84$ GHz, 0.1 mT modulation amplitude, 2 mW power, 298 K. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

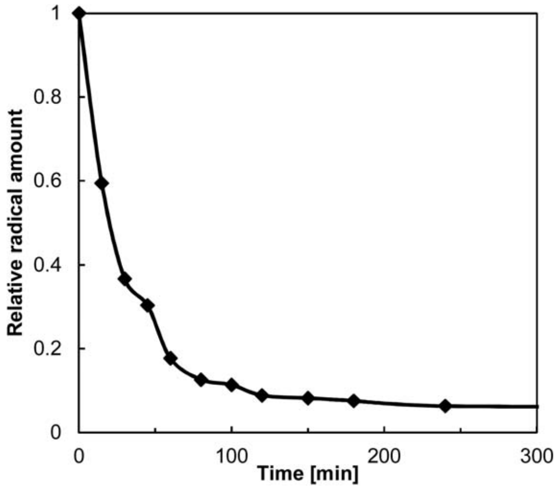

Figure 4. Relative radical amount after the first irradiation compared to I_{max} as a function of time.

process stable at all. The spinnability of PP remained excellent at 220°C so this problem is due to the thermal properties of SPEEK.

The differences in spinnability between different concentrations are small. PP and SPEEK/PP 10 : 90 blend have almost similar spinnability at the same processing temperature (with a short residence time). This is in line with the rheological characterization, where the concentration had only a small effect on viscosity.[6] Although the limits of spinnability were not tested, the best spun SPEEK/PP 5 : 95 blend fibers (at 200°C) were approximately 45 μm in average diameter. This should be easy to improve even further by optimizing the process and the PP grade. The results of the spinning tests can be seen in Table IV.

Semi-Industrial Fiber Spinning of the SPEEK/PP

The goal of the semi-industrial melt spinning was primarily to test the spinnability of the SPEEK/PP 5 : 95 blend under conditions that are closer to the industrial scale, and second, to manufacture a sufficient amount of multifilament yarns for characterization. The fiber properties are more stable in the semi-industrial process as a result of a more stable material flow, a 50 μm filter used to remove impurities, and a more accurate drawing system. The results from the laboratory scale spinning tests were used as a base for the upscaling and therefore a processing temperature of 200°C was used.

The spinnability was excellent from the beginning and no fine tuning was needed for the process to be stable. No broken filament was observed during the spinning of 4 bobbins. According to the SEM micrographs of the previously tested SPEEK/PP bulk blend,[6] the material did not contain any particles larger than a few micrometers, and this was also confirmed by the good spinnability. Figure 2 shows a picture of the bobbins obtained. The photocatalytic filaments have a brown color compared to light-colored PP ones.

Radical Formation

Figure 3 reports the X-band (9 GHz) EPR spectra of the samples recorded at different times after the irradiation. The BPK radical signal, marked as a thick arrow, is detected. The EPR signals, marked as a thin arrow, are the six lines due to Mn(II) impurities. The BPK signal reaches the maximum (I_{max}) immediately after the irradiation, then starts to decay reducing its intensity, and reaches its minimum in 150 min. The radical signal decay has been monitored for 16 h without any further changes in the intensity. A small intensity BPK peak is observed also in non-irradiated SPEEK/PP samples because the photocatalytic reaction is promoted by light sources during material

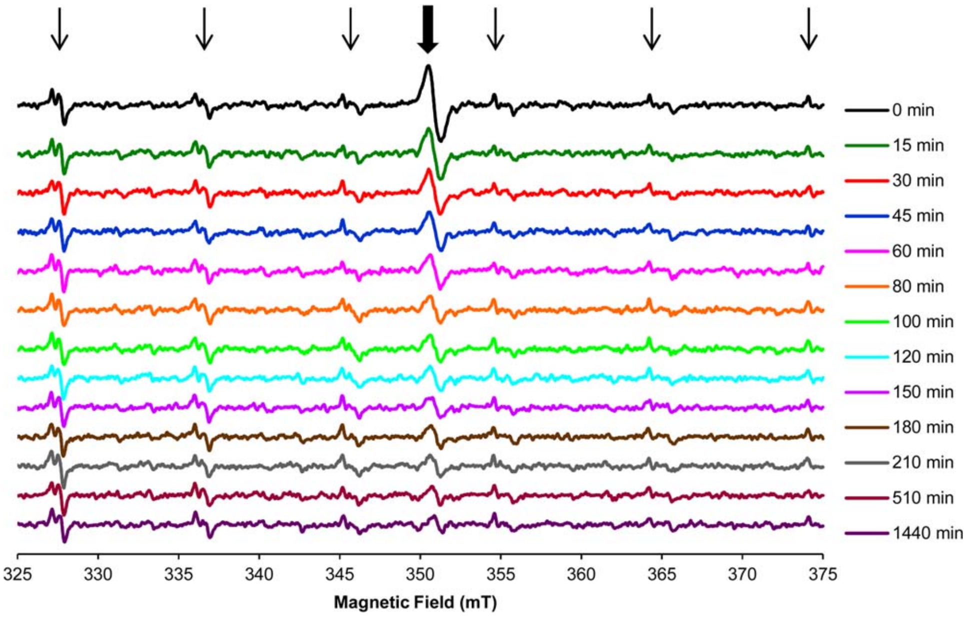

Figure 5. X-band EPR spectra of the sample recorded at different times after the second 15 min irradiation. $\nu = 9.84$ GHz, 0.1 mT modulation amplitude, 2 mW power, 298 K. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

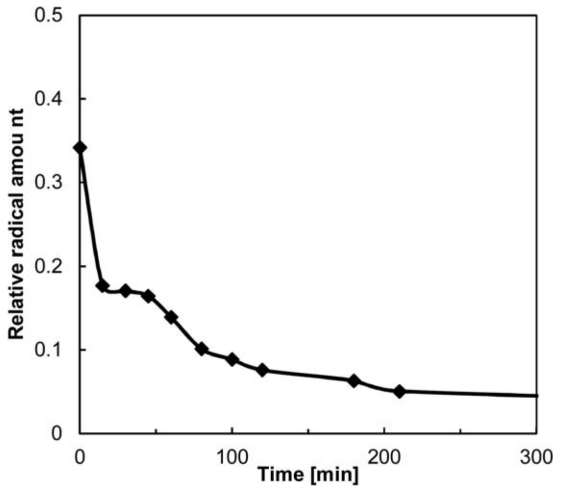

Figure 6. Relative radical amount after the second irradiation compared to I_{max} as a function of time.

handling (cutting of the fibers and displacement in the EPR capillary), demonstrating that material photocatalytic activity is very high. In PP samples, with or without irradiation, this peak was not visible. The reason for the long lifetime of the BPK radicals is their slow dimerization/disproportionation coupling reaction.[29] In the solid state, the mobility of the radicals is slow increasing the life-time.

Figure 4 presents the EPR signal area, obtained by double integration of the experimental spectra, as a function of time. The lifetime of the radical is rather long. After 15 min, the radical intensity is reduced to 59% and after 60 min to 18% of the I_{max}. The residual radical intensity is approximately 5% of the I_{max}.

The same sample was irradiated a second time for 15 min in order to see if the radical was reformed, and its decay was followed. As shown in Figures 5 and 6, the radical is visible again, however, at a lower intensity (approximately one-third of the I_{max}). Based on the previous studies, this result is expected.[29] The radical intensity drops rapidly during the first 15 min. The evolution of the signal was followed for 24 h even though the minimum signal intensity was reached in 3 h.

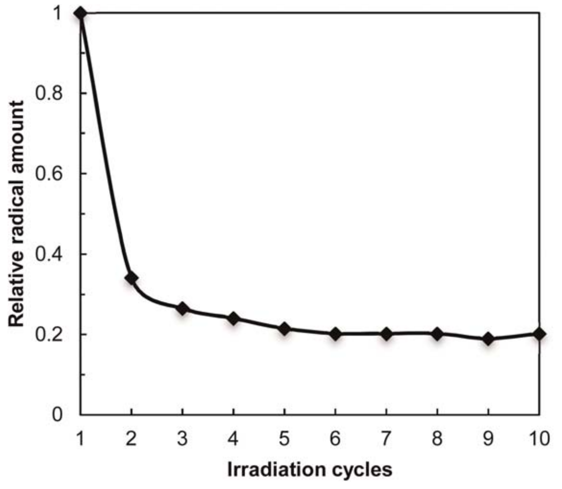

Figure 7. Relative radical amount after irradiation compared to I_{max} as a function of irradiation cycles.

Table V. Mechanical Properties for SPEEK/PP 5 : 95 and PP Filaments

Sample	Tex (g/km)	Tenacity at break (cN/tex)	Strain at break (%)	Young's modulus (cN/tex)
SPEEK/PP 5 : 95	23	9.1 ± 1.2	267 ± 59	19.5 ± 2.9
PP	23	11.6 ± 1.8	268 ± 47	24.7 ± 2.2

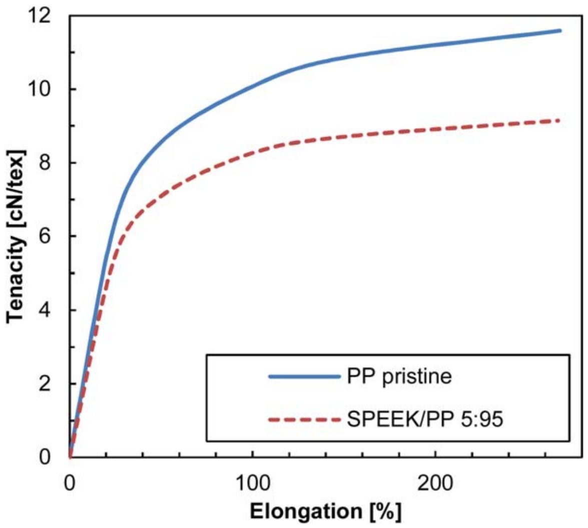

Figure 8. Typical tensile testing curves for PP and SPEEK/PP 5:95. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Relative radical amount was monitored up to 10 continuous irradiation cycles to simulate the fiber effectiveness in use. According to these results (Figure 7), the effectiveness immediately after the irradiation drops significantly during the first few irradiation cycles, and then quickly reaches the residual radical intensity of approximately 15% of the I_{max}. Evidently, the radical formation ability reduces in use and the actual usability has to be verified with, e.g., antimicrobial tests.

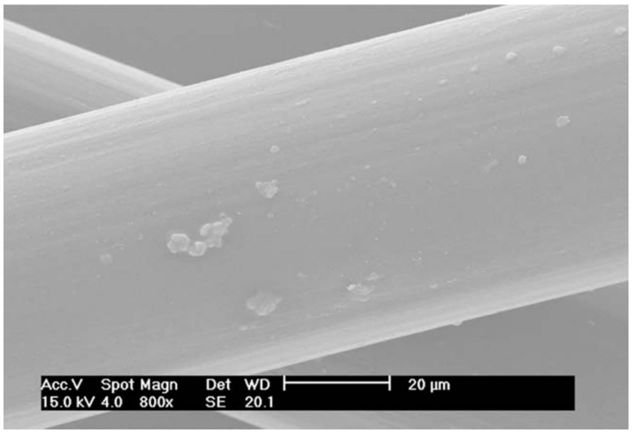

Figure 9. SEM micrograph of the PP fiber.

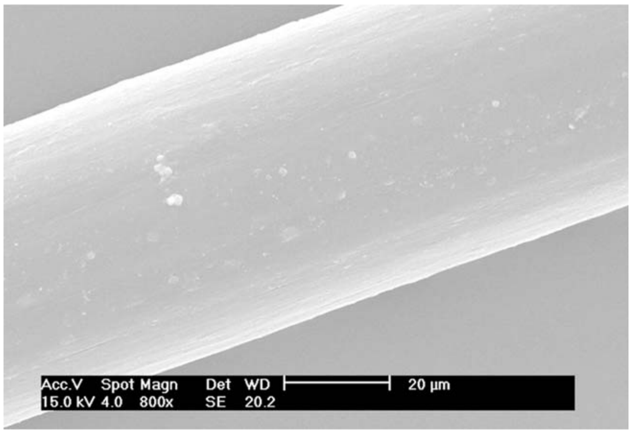

Figure 10. SEM micrograph of the SPEEK/PP 5 : 95 fiber.

Mechanical Properties

The mechanical properties of the yarns are listed in Table V. The mechanical tenacity of the 5 : 95 SPEEK/PP yarn is 20% lower than that of otherwise similar PP yarn. Tenacity values are a little low compared to commercial PP yarns, even with similar linear density.[30] Cold drawing using heatable godets and incrementally increased drawing speed would have improved the orientation of the polymer chains and thus increased the mechanical strength. Unfortunately, the lack of material limited the testing, and only the simplest option, drawing the yarns directly into the bobbin, was performed. Another reason for the low mechanical properties may have been the low melt index of the PP grade used. Even though its use was justified to improve the compounding quality, higher melt index grades are typically preferable in melt spinning. In contrast to the low mechanical strength, the polymer yarns are highly elastic with over 250% strain at break. Typical tensile testing curves for PP and SPEEK/PP 5 : 95 can be found in Figure 8 and the raw data of the measurements in Supporting Information, in Table S1.

SEM Analysis

The analysis of the SPEEK/PP 5 : 95 fibers reveals no problems in the fiber quality. There are only small differences between the surfaces of the PP (Figure 9) and the SPEEK/PP 5 : 95 (Figure 10) fibers according to the SEM micrographs. The surface of the SPEEK/PP 5 : 95 fiber is slightly rougher due to the SPEEK particles. The results are consistent with the previously performed characterization of the blend where SPEEK particles, a few micrometers in size, were found to be homogenously dispersed in the PP matrix. Unfortunately cross-sectional SEM micrographs could not be obtained due to sample manufacturing problems: very thin filaments were too difficult to break using liquid nitrogen.

CONCLUSIONS

The goal of this study was to provide a fiber with sufficient and long-lasting photoactivity and mechanical properties. There were many challenging aspects such as the new polymer blend, thermal degradation of the blend, and small SPEEK particles in the blend that could interfere with the fiber spinning. The overall performance of the fibers is good. Fiber spinnability is good when using optimal processing parameters, most importantly a proper processing temperature of approximately 200°C has to be used. Mechanical properties are only a little affected by the addition of SPEEK and they are sufficient for technical applications. The SPEEK/PP fiber is highly elastic, so the mechanical properties can be further improved by increasing the drawing speed and draw ratio.

UV-induced radicals on the fiber surface were characterized by the EPR technique: stable BPK radical was detected and the characterization of the stability of the radical over several irradiation cycles showed that decay during the first few cycles occurs. This cannot be directly related with the photocatalytic efficiency; however, a reduction on the effectiveness over time is expected as per conventional photoactive materials. The next goal is therefore to estimate the antimicrobial, antipollution, and self-cleaning performance of the final fabrics in order to fully characterize the efficiency of the new fibers.

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