

Sulfonated Polyetheretherketone/Polypropylene Polymer Blends for the Production of Photoactive Materials

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ABSTRACT: Sulfonated polyetheretherketone (SPEEK) was synthesized via a mono-substitution reaction of PEEK in concentrated sulphuric acid and was blended with polypropylene (PP) in 2–10%w/w concentration to be used for the production of photoactive thermoplastic products. SPEEK and SPEEK/PP blends were characterized using FTIR, DSC, TGA, NMR, rheology, SEM, and EPR. Under UV-Vis irradiation, stable benzophenone ketyl (BPK) radicals were generated by hydrogen extraction from PP. By increasing the amount of SPEEK in the polymer blend a linear increase in the BPK radicals was achieved according to the EPR data. DSC and TGA tests indicated weaknesses in the thermal stability of SPEEK but according to the rheological tests this should not have a major effect on processability. The optimal amount of SPEEK in the blend was obtained at 5%w/w. This concentration provided a good compromise between radical concentration, material processability, and cost. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41509.

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INTRODUCTION

Good indoor air quality is important for health, comfort and well-being. Despite the fact that a lot of efforts have been paid for the abatement of outdoor pollutants,^{1–4} it has been stated that the levels of air pollution inside houses are often two to five times higher than outdoor levels.⁵ Typical sources for indoor air pollution are cleaners, waxes, paints, pesticides, adhesives, cosmetic products, automotive products, and hobby supplies.⁶ Conventional methods to remove the indoors decontaminants are often ineffective, chemically and energetically intensive and suitable only for large systems.⁷ In addition, these intensive chemical treatments can even be the source of new contamination problems.

An effective alternative to conventional methods is represented by photocatalysis. Semiconductors such as TiO₂, ZnO, ZrO₂, CdS, MoS₂, Fe₂O₃, and WO₃ have been examined and used as photocatalyst.^{7–11} Among these, titanium dioxide (TiO₂) has remained as the benchmark against which alternative photocatalysts are compared. TiO₂ is widely used because it is inexpensive, harmless, and its photostability is very high.^{12–14} To enhance the redox potential of the valence-band holes and the

conduction band electrons, particle size must be decreased. Furthermore, the highest surface area to volume ratio enhances their catalytic activity.¹⁵

However, TiO₂ nanoparticles have recently been classified by the International Agency for Research on Cancer (IARC) as an IARC Group 2B carcinogen “possibly carcinogenic to humans.”¹⁶ Therefore, the identification of polymeric photoactive compounds is recommended in order to reduce health concerns induced by nanoparticle handling. Within this study, SPEEK-based (sulfonated polyetheretherketone) polymeric photocatalytic blends have been studied, as an alternative enabling to realize micro- and nanosized materials, such as filaments, particles, and thin layers.

PEEK (polyetheretherketone or poly (oxy-1,4-phenyleneoxy-1,4-phenylenecarbonyl-1,4-phenylene)) is a linear semicrystalline thermoplastic with rather unique set of properties.¹⁷ It has excellent mechanical and thermal properties and chemical resistance. Its water absorption is low, radiation resistance good and flammability low. Because of these properties PEEK is often used in high-tech applications and in extreme environments. The use of PEEK is mainly limited by its high price (100 €/kg).

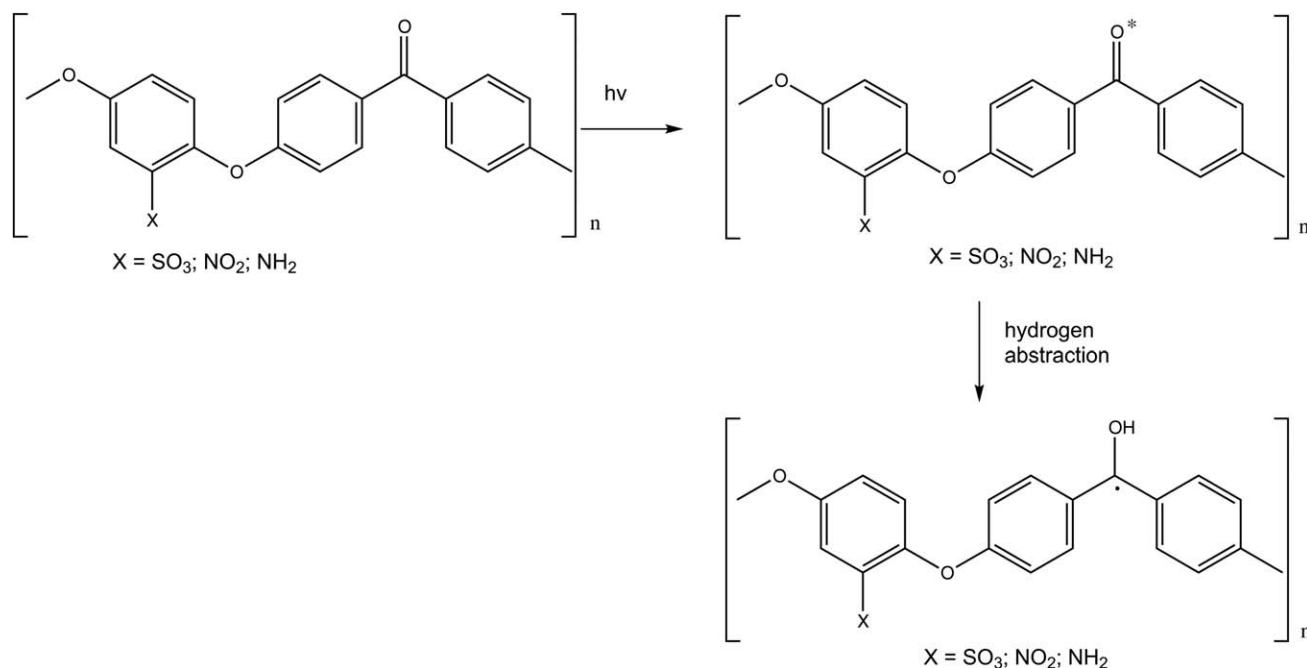


Figure 1. Excitation reaction and radical formation of modified PEEK. X can be SO₃, NH₂, or NO₂.

Sulfonation of PEEK has become a standard procedure and the effects of different parameters are well known.^{18–20} The antimicrobial properties of benzophenone incorporated materials have been studied^{21–23} but not in the case of SPEEK-based polymer blends. SPEEK has been, however, blended (in solution) with polymers such as polyvinyl alcohol (PVA) and polyvinyl butyral (PVB) to be used as a direct methanol fuel cell (DMFC),^{24,25} metal reduction material^{26,27} and for the production of functional thermoplastic materials such as advanced composites.²⁸ On the contrary, the idea to mechanically compound SPEEK with a polyolefin is rather new.

Chemical modifications of PEEK, such as sulfonation, enhance its solubility in organic solvents through electrophilic substitution reactions and promote the formation of benzophenone ketyl radicals (BPK) that could be effectively used to promote photocatalytic reactions. In fact, UV irradiation of a polar benzophenone induces an $n \rightarrow \pi^*$ transition (Figure 1) generating a triplet state that is highly reactive toward hydrogen atom abstraction by forming a stable radical.^{29–31}

A hydrogen transfer reaction is involved in the initial production of the reactant radical and the generation of the final product. The selection of the appropriate hydrogen transfer agent depends on the kinetics of H-atom transfer agent and on the stabilisation of the radical induced by the chemical groups on the acceptor. Polyolefins possess a labile hydrogen atom and can therefore act as efficient chain transfer agents, whilst the sulfonated group stabilizes the radicals.

Within this study PP has been selected as the most promising partner in the photocatalytic activation because it is easy to process, largely available and very cheap polymer. The goal is to develop a new, safe, and affordable photocatalytic polymer

blend that can be used in a wide range of applications (such as the production of filters for air purifier devices, filter masks, curtains, and carpet).

EXPERIMENTAL

Materials

Victrix (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 production of modified benzophenone compounds. In the sulfonation process Carlo Erba (Val de Reuil, France) 98% sulphuric acid (H₂SO₄) was used. The PP grade was Total Petrochemicals (Houston, USA) PPH 4050 homopolymer having a melt index of 3 (2.16 kg, 230°C, g/10').

Synthesis of SPEEK

The sulfonation of PEEK in powder form was carried out in a 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, 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 was 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 weighted, loaded into the compounder and mixed for 5 min at 200°C at a screw speed of 150 RPM.

FTIR

The chemical composition was characterized by ATR (attenuated total reflectance) FTIR spectroscopy. The equipment used was Perkin

Elmer Spectrum One spectrometer in HATR reflection mode. A zinc selenide crystal and a resolution of 4 cm^{-1} were used.

DSC

DSC tests were made with a Mettler Toledo 822 e. Samples were heated in nitrogen (flux 80 mL/min) at a heating rate of 10°C/min . They were heated only once due to the degradative behavior of SPEEK at higher temperatures.

TGA

TGA tests were made with a PerkinElmer TGA 6. Samples were heated from room temperature to 995°C in nitrogen atmosphere with a heating rate of 20°C/min .

NMR

The $^1\text{H-NMR}$ spectra were recorded using a Bruker 200 MHz spectrometer. The spectra were recorded at 60°C , without internal standard and using deuterated dimethyl sulfoxide (DMSO- d_6) as a solvent, with a polymer concentration of about 30 mg mL^{-1} . Experimental data were elaborated with 1D Win-NMR software, applying the Lorentze Gauss enhance function and using appropriate Line broadening and Gaussian broadening parameters in order to improve the peaks resolution.

Rheological Measurements

Oscillatory shear measurements within the linear viscoelastic range (strain amplitude of 10%) were carried out for the samples using an Anton Paar Physica MCR 301 rheometer. All the experiments were performed under a nitrogen atmosphere using a 25-mm plate-plate geometry. The measuring points in the angular frequency range of $0.1\text{--}562\text{ rad/s}$ were recorded with decreasing frequency. Each sample was measured two times and the average of these measurements was used. The time-dependence of viscosity was tested using a constant angular frequency of 10 rad s^{-1} , strain amplitude of 10% and measuring time of 30 min.

Scanning Electron Microscopy

The morphology of PP, SPEEK, and SPEEK/PP blends were investigated by a Philips XL30 scanning electron microscope (SEM). The materials were cut with liquid nitrogen and mounted vertically under the SEM for the investigations. The materials were gold sputtered before investigations in order to increase their conductivity.

Electron Spin Resonance Measurements

Electron paramagnetic resonance (EPR) spectroscopy was used to confirm the free-radical characteristics 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 a UV lamp (effective irradiative power 8 W/m^2 in the range $390\text{--}490\text{ nm}$) at a distance of 11 cm for 15 min. Then the specimen was immediately measured by EPR spectroscopy. The relative radical amount was calculated from the EPR peak areas.

RESULTS AND DISCUSSION

SPEEK Sulfonation and SPEEK/PP Compounding

The processing parameters for PEEK sulfonation were chosen according to a previous study¹⁸ in which a reaction temperature

of 45°C , a reaction time of 3 h and PEEK concentration of 5%w/v provided the highest degree of sulfonation. Sulfonation is an electrophilic aromatic substitution reaction in which a hydrogen atom attached to the PEEK repeating unit is replaced by a sulfonic acid group via a monosubstitution reaction on the benzene ring connected with two ether linkages.¹⁸

SPEEK was compounded with a high viscosity (melt flow index of 3 g/10') PP grade. The selection of this grade was based on the assumption that compounding would decrease viscosity, which indeed was the case according to the rheological tests. Thermal characterization of SPEEK indicates poor thermal stability that had to be taken into consideration during the material compounding: the compounding time and temperature had to be a compromise between proper mixing and as low material degradation as possible. The obtained SPEEK/PP blend had a homogenous character and was brown in colour. An increase of the processing time lead to a darker color, which is a typical sign of thermal degradation.

FTIR

The results of the FTIR analysis correspond with the results from previous studies, where PEEK^{32,33} and SPEEK¹⁸ were characterized. Typical absorption bands of PEEK are 1653 , 1648 , and 1252 cm^{-1} associated with carbonyl stretching frequency, 1490 cm^{-1} characteristic of ring absorption, 1227 cm^{-1} associated with carbon-oxygen-carbon stretching vibration, 863 , 841 , and 700 cm^{-1} associated with ring deformation modes, and 1305 , 1280 , 965 , and 952 cm^{-1} that are related to PEEK crystallinity.

In SPEEK, typical absorption bands associated with sulphuric acid groups are 3440 , 1252 , 1080 , 1024 , and 709 cm^{-1} .¹⁸ The broad band at 3440 cm^{-1} is related to the —OH vibrations of $\text{—SO}_3\text{H}$ and to the absorbed moisture, 1252 cm^{-1} to asymmetric stretching of O=S=O , 1080 cm^{-1} to symmetric stretching of O=S=O , 1024 cm^{-1} to stretching of S=O and 709 cm^{-1} to stretching of S—O .

Literature data¹⁸ suggests that the intensity of aromatic C—C absorption band at 1492 cm^{-1} should decrease and the intensity of the 1472 cm^{-1} band (associated with the aromatic absorption of a substituted ring) increase as the sulfonation degree increases. The FTIR analysis confirms that the intensity of the 1492 cm^{-1} band decreases significantly during the sulfonation. An absorption peak at 869 cm^{-1} , associated with out-of-plane C—H bending of isolated hydrogen in a tri-substituted phenyl ring, appears during the sulfonation.

DSC

Significant changes in the thermal behaviour of the SPEEK polymer in comparison with PEEK were observed in the DSC tests. In PEEK, an endothermic transition peak at 346°C is recorded. In SPEEK, no crystallization peak is observed, which indicates that after the sulfonation reaction a complete amorphous polymer is produced. The T_g (glass transition temperature) midpoint temperature is higher in SPEEK than in PEEK, 225°C and 159°C , respectively (Table I).

In SPEEK/PP blends a single melting temperature (T_m) around 168°C and two different T_g 's around 3°C and 223°C were

Table I. Thermal Properties of PP, PEEK, SPEEK, and SPEEK/PP 2 : 98, 5 : 95, and 10 : 90 Blends Measured by DSC (10°C/min, N₂)

Sample	T_{g1}	T_{g2}	T_m
PEEK	159.4°C	–	346.6°C
SPEEK	–	225.2°C	–
PP	2.3°C	–	168.2°C
SPEEK/PP 2 : 98	3.1°C	221.9°C	169.4°C
SPEEK/PP 5 : 95	2.0°C	225.8°C	167.5°C
SPEEK/PP 10 : 90	2.8°C	219.7°C	168.6°C

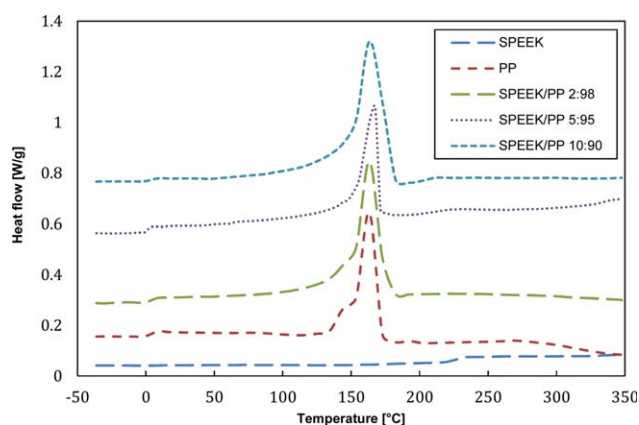
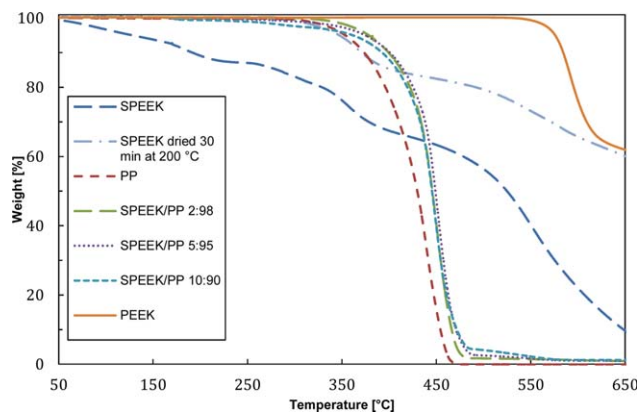
observed. The differences between different blend compositions are rather small. T_m corresponds to the melting temperature of PP whilst it is well known³⁴ that T_g for a homogeneous mixture of bicomponent blends can be considered the weighted mean of the T_g of the single components according to the eq. (1):

$$T_{g\text{mix}} = T_{g1}w_1 + T_{g2}w_2 \quad (1)$$

where T_{g1} and T_{g2} are the glass transition temperatures and w_1 and w_2 the weight portions of the components 1 and 2, respectively. Because the thermal profile shows two different T_g s (Figure 2), this means that an immiscible (heterogeneous) polymer blend is obtained. This result was confirmed by the SEM analysis.

TGA

The TGA analysis in Figure 3 shows that the mass of PEEK remains constant until the decomposition temperature of 580°C, which is rather unique for a thermoplastic polymer. PEEK sulfonation changes the thermal properties of the material totally, lowering the decomposition temperature of SPEEK below 250°C. The mass loss from 50 to 250°C is shown to happen due to chemically and physically bound water, the mass loss from 250 to 450°C is due to the decomposition of acid group which induces the elimination of SO₃ and the decomposition of the –SO₃H group. The mass loss above 450°C is due to the breakdown of the polymer backbone.¹⁸ If the SPEEK is dried 30 min at 200°C, the curve stays at a significantly higher level as a result of the removed water. It is also possible that the

**Figure 2.** DSC curve of SPEEK, PP, SPEEK/PP 2 : 98, 5 : 95, and 10 : 90 (10°C/min, N₂ 80 mL/min). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]**Figure 3.** TGA curve of PEEK, SPEEK dried, SPEEK, SPEEK/PP 2 : 98, 5 : 95, 10 : 90, and PP (20°C/min, N₂). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

drying evaporates some of the most unstable components which change the decomposition behaviour compared with undried SPEEK/PP.

In the SPEEK/PP blend, the mass loss starts earlier with increased SPEEK concentrations. Surprisingly SPEEK/PP seems to have an improved thermal stability compared with neat PP, at least at low SPEEK concentrations. This could be related to the degradation of the SPEEK that promotes clustering of the sulfonated groups, enabling to thermally stabilize the polymer.

The degree of sulfonation (DS) for SPEEK can be evaluated from the weight losses (WL) according to the eq. (2):

$$DS = \frac{WL_m}{WL_t} \times 100 \% \quad (2)$$

where WL_m is the measured weight loss between 250 and 450°C and WL_t the theoretical maximum of the weight loss; the mass of the SO₃ group from the whole unit according to the eq. (3):

$$WL_t = \frac{[SO_3]}{[C_{19}H_{12}O_6S]} \times 100 \% \quad (3)$$

WL_t is thus 21.7% for completely sulfonated samples (exactly one sulfonic acid group per repeating unit is present, Figure 4).

The WL_m measured is 23.7% (Table II), giving a theoretical DS of 109%. The explanation why this value is over 100% is that the acid groups may cause random chain scission reactions, which lead to a loss of phenol groups as well.³⁵ In addition, the limits for SO₃ volatilization can be considered somewhat

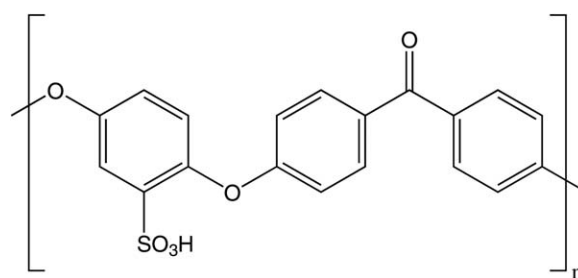
**Figure 4.** The chemical structure of synthesized SPEEK. NMR and TGA studies are confirming that a monosubstituted SPEEK is produced.

Table II. Results of the TGA Analysis for PEEK and SPEEK (20°C/min, N₂)

Sample	Mass loss (%)			Char residue
	50–250°C	250–450°C	450–650°C	
PEEK	0.1	0.0	38.3	61.6
SPEEK	12.4	23.7	53.6	9.6

inaccurate. According to the previous study,¹⁸ the DS (measured by elemental analysis and ¹H-NMR) is around 70–80% with the same processing parameters.

NMR

To confirm that a monosubstitution has arisen, DS has been assessed by ¹H-NMR measurement. In fact, PEEK sulfonation generates a single signal for H proton in ortho position to SO₃H and its intensity is equivalent to the SO₃H group content.³⁶ The ratio between the area of this proton peak (centered at 7.5 ppm) and the area of the other protons corresponds to a degree of sulfonation that equals of 93%. It confirms the achievement of a higher reaction yield compared to previous study¹⁸ and the contribution of acid group random chain scission during thermal degradation.

Rheological Characterization

It is important to know the rheological properties of the SPEEK/PP blend when the material is further processed into an actual product. The results of the rheological tests in Figure 5 show that compounding decreases the complex viscosity. Compounded PP has ~10% lower viscosity compared with neat PP. This is in line with previous studies³⁷ where several extrusion cycles have shown to cause a rapid increase in chain scission reactions and thus a decrease in molecular weight and complex viscosity. SPEEK/PP 2 : 98 has similar viscosity as compounded 100% PP but at a 5 : 95 concentration the viscosity is signifi-

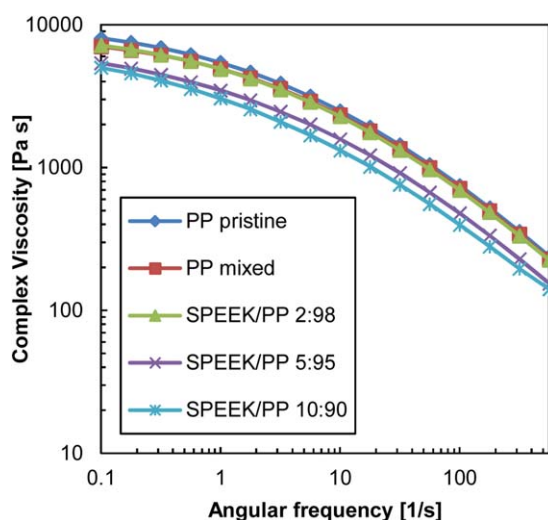


Figure 5. Complex viscosity of PP, PP mixed, and SPEEK/PP 2 : 98; 5 : 95; 10 : 90 (200°C, N₂). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

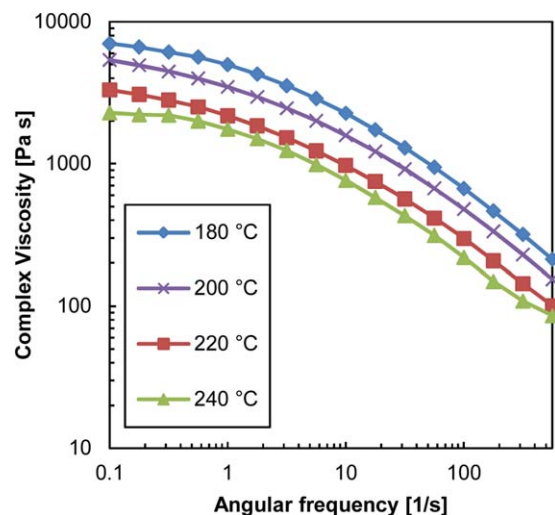


Figure 6. Complex viscosity of SPEEK/PP 5 : 95 (180, 200, 220, and 240°C, N₂). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

cantly lower. The drop in viscosity from a concentration of 5 : 95 to 10 : 90 is relatively small. The decrease in viscosity could be explained by the degradation behavior of SPEEK at elevated temperatures and the following chain scission reactions in the material caused by the decomposition products of SPEEK, such as the acid groups mentioned in the TGA paragraph. A similar degradation has been seen when adding compatibilizing maleic anhydride to PP³⁸ and peroxides³⁹ or nitroxyl radical generators⁴⁰ to PP for rheology control.

There are no significant differences in the shear thinning behavior of SPEEK/PP 5 : 95 blend up to temperature of 220°C (Figure 6). At 240°C the shape of the curve is different from the other curves, indicating that thermal degradation occurs at the end of the measurement. The total measuring time is ~10 min, and the three last points (lowest angular frequencies) take most of this time.

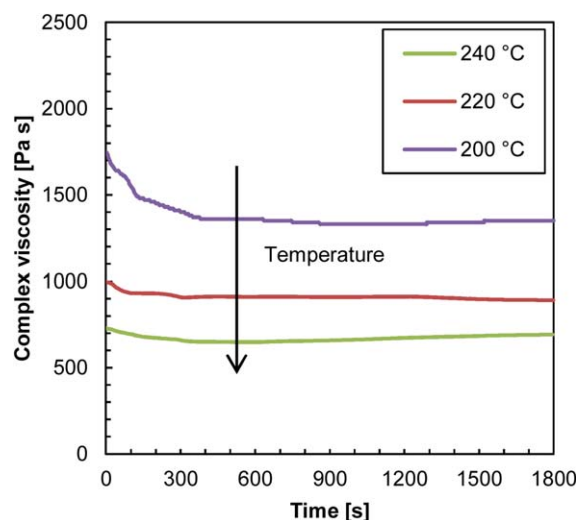


Figure 7. Complex viscosity of SPEEK/PP 5 : 95 as a function of time (200, 220, and 240°C, N₂). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

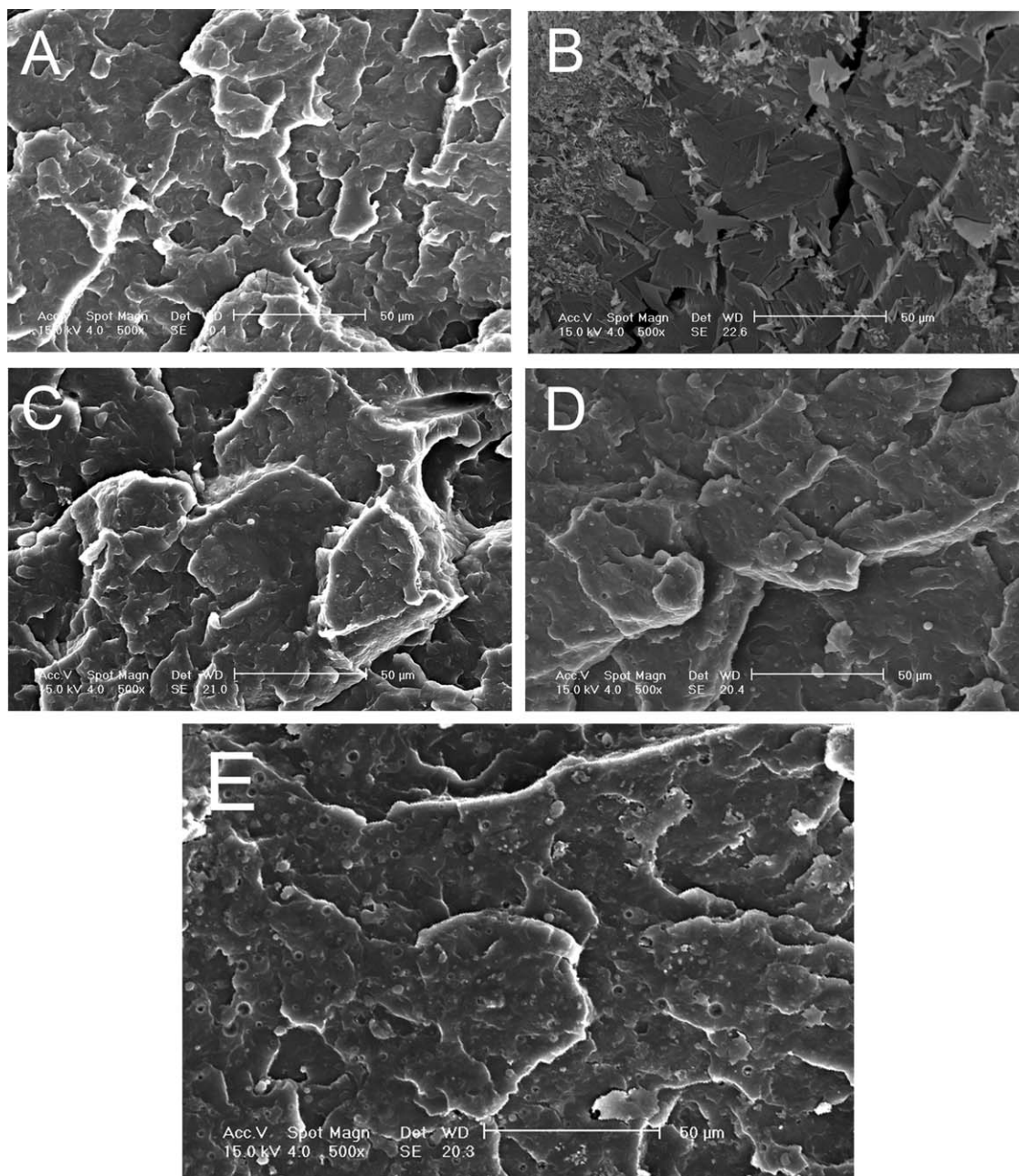


Figure 8. SEM micrograph of PP (A), SPEEK (B), SPEEK/PP 2 : 98 (C), SPEEK/PP 5 : 95 (D), and SPEEK/PP 10 : 90 (E).

Figure 7 shows that viscosity decreases as a function of time, which confirms that thermal degradation occurs. At 200°C the drop is the largest, ~20% during the first 5 min. As a comparison, the drop at 220°C and 240°C is 8–9%. The explanation for this behavior can be found from the measuring setup. It takes a few minutes to melt the material, trim it and then start the measurement. Evidently most of the chemical reactions occur during this time if the temperature exceeds 200°C. This also explains the observed variations in the results with 5 : 95 and 10 : 90 concentrations at 200°C.

The high viscosity PP grade was originally selected to compensate the decrease in viscosity during the compounding and according to these tests the rheological properties of 0–10%w/w

compounds should be sufficient for further processing. Processing times and temperatures are recommended to be minimized in order to avoid thermal degradation of the material.

SEM Analysis

SEM analysis has been carried out for PP [Figure 8(A)], SPEEK [Figure 8(B)] SPEEK/PP 2 : 98 [Figure 8(C)], SPEEK/PP 5 : 95 [Figure 8(D)], and SPEEK/PP 10 : 90 [Figure 8(E)]. There are two different domains in the SPEEK/PP blends which mean that the two polymers are not miscible, even if the shear forces in the compounder seem to be able to homogeneously disperse the photoactive SPEEK polymer into the polypropylene. This result was confirmed by the DSC tests where two separate T_g 's were observed in SPEEK/PP. A typical size of the SPEEK

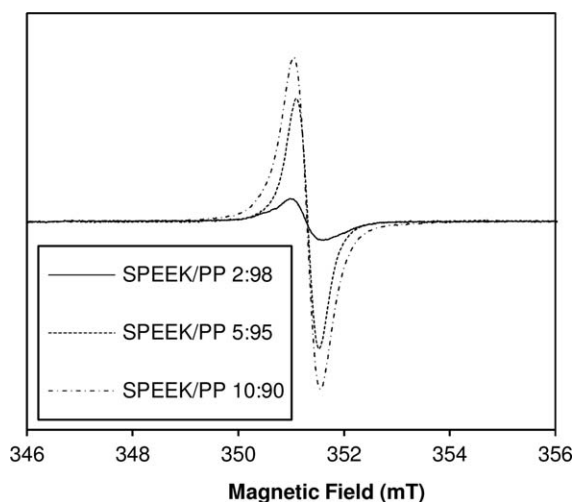


Figure 9. RT X-band EPR spectra of the SPEEK/PP blends (2 : 98; 5 : 95; 10 : 90) recorded after 15 min of irradiation ($\nu = 9.86$ GHz, 0.63 mW power, 0.2 mT modulation amplitude).

particles in the blend seems to be a few micrometers which should not be a problem during the further processing of the material. Even melt spinning of the blend should be possible.

Photochemical Properties

In order to evaluate the photocatalytic effectiveness of the made polymer blends, EPR spectroscopy was performed. Room temperature EPR analysis performed on a transparent casted film made from 100% SPEEK showed that after exposure to UV irradiation for 15 min free radicals are generated. The presence of PP in the SPEEK sample with increasing molar ratio significantly improves the radical formation efficiency. In Figure 9, the room temperature X-band EPR spectra of the SPEEK/PP blends are reported.

X-band EPR spectrum of 100% SPEEK exhibits a single line with a g value of 2.0035 (± 0.0003). The g value obtained for the investigated sample is in agreement with the value reported

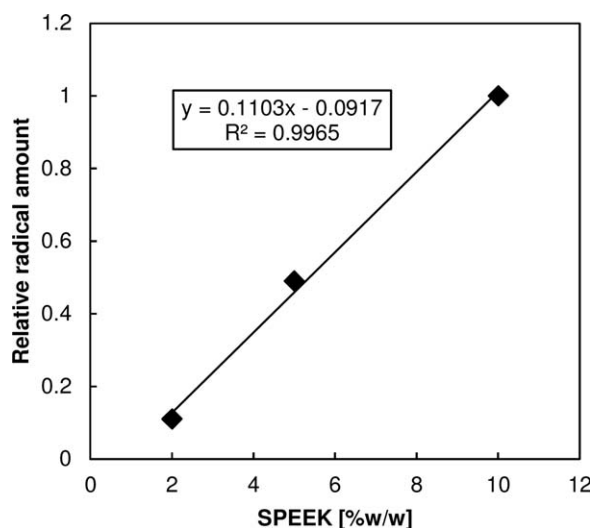


Figure 10. Relative radical concentration as a function of the polymer blend composition.

in the literature for a phenyl ketyl radical of benzophenone.⁴¹ In the EPR spectrums reported for SPEEK/PP 2 : 98, 5 : 95, and 10 : 90, where the donor is polyolefins, the radical signal may derive from the coexistence of both BPK radical and diphenylhydroxy methyl radical. However, the very slight difference in the g values for both specimens does not allow discriminating the single contributions, and the simultaneous presence of the radicals cannot be excluded.

The analysis of the spectral area showed that by increasing the polyolefin content in the range 2–10% a linear increase in the production of the radical is achieved (Figure 10). Higher SPEEK concentrations in the SPEEK/PP blend have not been investigated due to the higher costs of the SPEEK polymer and the high efficiency of the system at low SPEEK content. The relative radical amount of 100% SPEEK was 1/20 of that of SPEEK/PP 10 : 90.

CONCLUSIONS

The combination of SPEEK and PP generates a stable BPK radical formation, enabling to promote the degradation of chemicals. The increase in the radical concentration is almost linear as a function of SPEEK concentration. An optimal amount of modified PEEK in the polymer blend is seen at 5%w/w. This concentration was observed to provide good photochemical properties at a competitive price. The synthesis of SPEEK as well as SPEEK/PP compounding were relatively problem-free and, according to the SEM analysis, SPEEK particles are homogeneously dispersed into the PP matrix. Inferior thermal properties of SPEEK compared with PEEK were evident in the thermal tests, and also the rheological tests showed signs of material degradation as a result of chain scission reactions. Further processing of the material into commercial products should be possible when the optimal processing parameters have been determined.

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