

Surface Chemical Modification of Polypropylene Fiber Waste by H₂SO₄: Mechanistic Investigation and Application as Cation-Exchange Adsorbent

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ABSTRACT: In this work, polypropylene (PP) fiber waste was modified by the reaction with concentrated H₂SO₄. IR, TG, Raman, CHN, acid titration, SEM, and XRD suggested that sulfuric acid at about 105°C reacts with PP to produce mainly surface sulfonic groups. The kinetic experiments showed that these SO₃H groups decompose to form SO₂ gas leading to an aromatization of

the polymer to form amorphous and graphitic carbon. Adsorption isotherms of the cationic model molecule methylene blue showed that the modified PP fibers have a great potential as ion-exchange adsorbent. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 3586–3591, 2010

Key words: polypropylene; fibers; H₂SO₄; cation exchange

INTRODUCTION

Polypropylene (PP) has become one of the most important polymer in the past two decades because of its excellent mechanical properties, high-chemical stability and processability. However, because of low-surface energy, lack of reactive sites and sensitivity to photo or thermal oxidation, the PP properties are insufficient for some applications. Therefore, surface chemical modification of PP to introduce new properties such as wetting, dyeing, adhesion, friction, and biocompatibility is important. Moreover, alternative routes to transform PP waste into new materials is of considerable interest because the reuse and recycling show some limitation and low-economical attractiveness.

Chemical modification of PP has been scarcely investigated and only few works can be found in the literature. For example, high-energy electron beam irradiation is necessary to create radical reactive points on the PP surface. These dangling radicals can then react with different molecules such as sulfonated styrene (CH₂=CHC₆H₄SO₃Na), acrylic acid (CH₂=CHCOOH) Mohr's salt ((NH₄)₂Fe(SO₄)₂·6H₂O) and styrene.¹ Other examples of radical-based functionalization have been reported using thiol reaction with the unsaturation end of the PP chain²

and the reaction with maleic anhydride initiated by radicals.³

To develop a simple process to modify the adhesion properties of PP, different sulfonation reactants, for example, fuming acid and H₂SO₄/HNO₃, have been investigated.^{4,5} Molecular orbital calculations and some experimental evidence suggested that the sulfonation of PP proceeds via electrophilic addition of SO₃.⁶ Although these reports indicated that other reactions than sulfonation could be taking place, no further investigation was carried out.

In this work, a detailed study of the reaction of PP fibers with concentrated H₂SO₄ revealed the presence of a complex mechanism involving sulfonation, oxidation, decomposition, and aromatization to form carbonaceous structures. Under controlled reaction conditions, a high concentration of cation exchange sites are introduced on the PP fibers. The combination of the fiber structure and the surface ion-exchange properties produced an excellent material with great potential for application in waste water treatment.

EXPERIMENTAL

The reactions were carried out with 1 g of PP fibers from oil absorbent cloaks with 20 mL concentrated H₂SO₄ (98%, VETEC) and magnetic stirring at 105 ± 1°C for times varying from 20 min to 12 h. After reaction, the PP fibers were extensively washed with distilled water at 70°C until neutral pH in the rinsing water was obtained. The obtained fibers were dried at 70°C for 12 h. TG/DTG/DTA analyses were

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carried out in a DTG60 SHIMADZU with heating rate 10°C min⁻¹ in N₂ (200 mL min⁻¹). IR spectra were obtained in a Perkin-Elmer spectrum GX FTIR using an ATR system. Gas analyses by IR used a NaCl window gas cell. CHN elemental analyses were carried out in a Perkin-Elmer model CHN-PE-2400. Raman spectroscopic analyses were made in a Renishaw Instrument with excitation wavelength of 633 nm equipped with confocal imaging microscope. SEM images were obtained in a JEOL-JSM-840 A. XRD patterns were obtained in a Rigaku Geigerflex using a Co radiation. The acid site numbers (ASNs) were determined using 20 mg of PP reacted with NaOH, 0.01 mol/L (50.00 mL) for 30 min in a sealed flask. The excess NaOH was titrated with a HCl, 0.005 mol/L. Gas formed during reaction was measured in a volumetric system connected to the reaction flask. The volume was converted to the number of mol (*N*) considering the pressure (*P*), the ideal gas constant (*R*), and the temperature (*T*) using the equation $PV = NRT$.

The adsorption tests used the cationic probe dye methylene blue at 50, 80, 100, 250, and 500 ppm (50 mL) with 20 mg of PP for 24 h. The dye adsorption was determined from UV/Vis measurements at 570 nm in a Shimadzu UV/Vis MINI. The analyses of hydrogen in the gas formed in the reaction were carried out in CHEM BET 3000 Quantachrome Instruments equipped with a thermal conductivity detector (TCD).

RESULTS AND DISCUSSION

The reactions of PP fibers with H₂SO₄ were carried out at 105°C for 20 min up to 12 h. The reactions led to a darkening of the fibers with formation of a gas. Reflectance infrared spectroscopic analyses of the obtained polymers are shown in Figure 1.

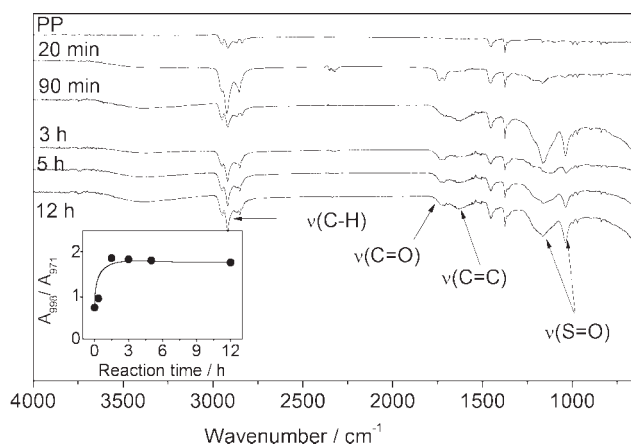


Figure 1 ATR IR analyses of the PP fibers after reaction with H₂SO₄ at 105°C at different times (detail: area ratios for the bands at 998 and 971 cm⁻¹).

TABLE I
CHN Analyses of the PP Fibers after Reaction with H₂SO₄

Material	C (%)	H (%)	Others (%)
PP	84.3	14.8	0.9
PP (20 min)	81.7	14.6	3.6
PP (90 min)	67.9	11.0	21.1
PP (3 h)	67.8	11.3	20.9
PP (5 h)	73.8	12.4	13.8
PP (12 h)	74.6	13.2	12.4

The original PP fibers showed bands at 2700–3000 cm⁻¹ related to C–H vibrations of –CH–, –CH₂–, and –CH₃ groups.⁷ On H₂SO₄ treatment even after 12 h these C–H bands were still present suggesting that the H₂SO₄ reacts only with part of PP. On the other hand, after reaction with H₂SO₄ new bands at 1220 and between 1040 and 665 cm⁻¹ likely related to S=O stretching of –SO₃H appeared. Weak bands located at about 3300–3400 cm⁻¹ are likely related to –OH present in –SO₃H or H₂O molecules adsorbed on the material. A band at about 1750 cm⁻¹ suggests the formation of C=O probably due to carboxylic acids, –COOH. Also another relatively broad band at 1575–1625 cm⁻¹ indicates the formation of C=C unsaturations.

The bands at 971 and 998 cm⁻¹ have previously been assigned to the amorphous and crystalline PP, respectively.⁸ The area ratio A_{998}/A_{971} strongly increased up to 90 min reaction suggesting that the amorphous PP has reacted preferentially with H₂SO₄. For reactions longer than 90 min, the area ratio does not change significantly.

The ASN formed on the PP fibers was determined by simple titration with NaOH/HCl. The obtained results showed that the original PP did not have any acid site. On the other hand, the reaction with H₂SO₄ for 20 min, 90 min, and 3 h increased the ASN to about 0.5, 4.6, and 5.3 mmol g⁻¹,

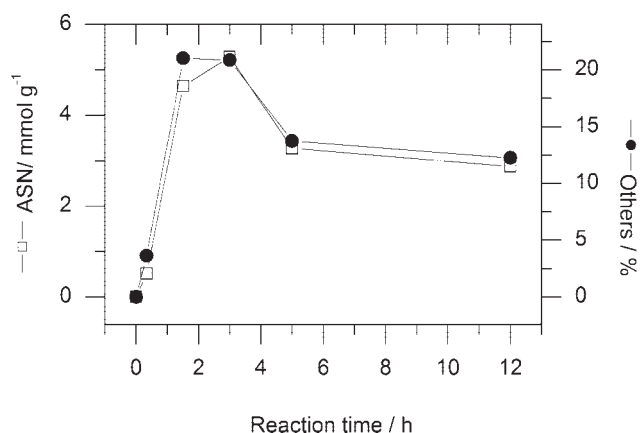


Figure 2 Acid site number (ASN) and %others for the PP reacted with H₂SO₄ at 105°C for different times.

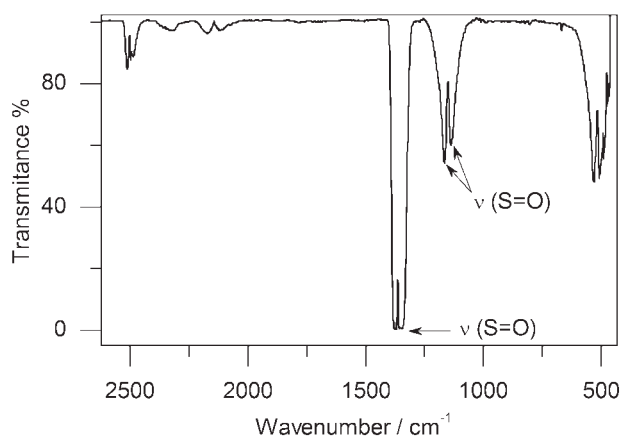


Figure 3 Infrared spectra of gas sample collected from the reaction of PP with H_2SO_4 at 105°C .

respectively. For longer reaction times the acid sites seem to decompose, as after 5 and 12 h, the ASN decreased to 3.2 and 2.8 mmol g^{-1} , respectively.

Table I shows the CHN analyses of the PP fibers after reaction with H_2SO_4 .

The obtained results showed the presence of only carbon and hydrogen but no nitrogen. Nondetectable elements (others), likely oxygen and sulfur, should also be present. It can be observed that after H_2SO_4 reaction up to 3 h, the %C and %H strongly decreased whereas %others increased likely related to the formation of SO_3H and small amounts of COOH . After 3 h reaction, the %C and %H increased again and %others decreased suggesting that these acid groups might be decomposing.

Figure 2 shows a very good correlation between the ASN and the %others in the prepared materials. These results clearly show that %others is correlated to S and O introduced in the PP as acid sites.

During the reaction of PP fibers with H_2SO_4 , it was observed the formation of large amounts of gas. Analyses of this gas by a TCD suggested the presence of a low-thermal conductivity gas which

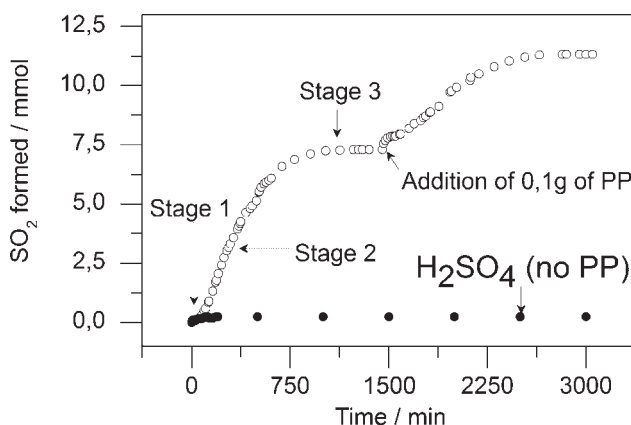


Figure 4 Formation of SO_2 gas in the reaction of PP fibers with H_2SO_4 at 105°C (●, pure H_2SO_4 and ○, PP + H_2SO_4).

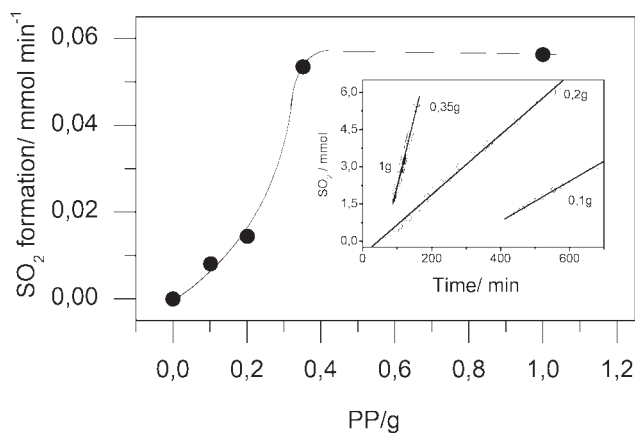


Figure 5 Effect of PP amount in the SO_2 formation rate.

excluded the formation of H_2 via protonation of C—H bond.

IR spectra of the gas presented bands at $1135\text{--}1160\text{ cm}^{-1}$ and $1335\text{--}1370\text{ cm}^{-1}$, which clearly showed the formation of SO_2 but not SO_3 (Fig. 3).

Figure 4 shows the kinetics of SO_2 formation during the reaction.

It can be observed that no significant amount of SO_2 is formed by the decomposition of pure H_2SO_4 (no PP). On the other hand, in the reaction of PP with H_2SO_4 a rapid SO_2 evolution is observed. In the first minutes of reaction, the SO_2 formation is slow (Stage 1) but gradually increases to reach a plateau from 100 to 750 min (Stage 2). After 750 min, the formation of SO_2 stops (Stage 3). At this point, if 0.1 g of PP is added, the SO_2 formation begins similarly to Stages 1, 2, and 3 again. In a separate experiment more H_2SO_4 was added in Stage 3 but no SO_2 was further formed. These results clearly indicate that H_2SO_4 is in excess and that PP limits the reaction. The effect of the amount of PP in the SO_2 formation rate was investigated (Fig. 5). The detail in Figure 5

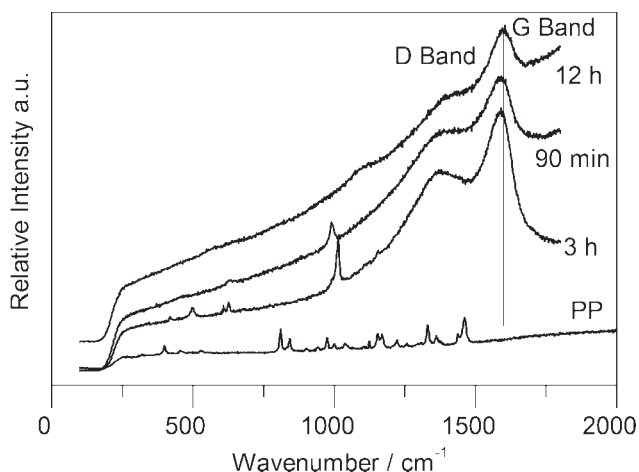


Figure 6 Raman spectra for the PP after reaction with H_2SO_4 for 90 min, 3 h, and 12 h.

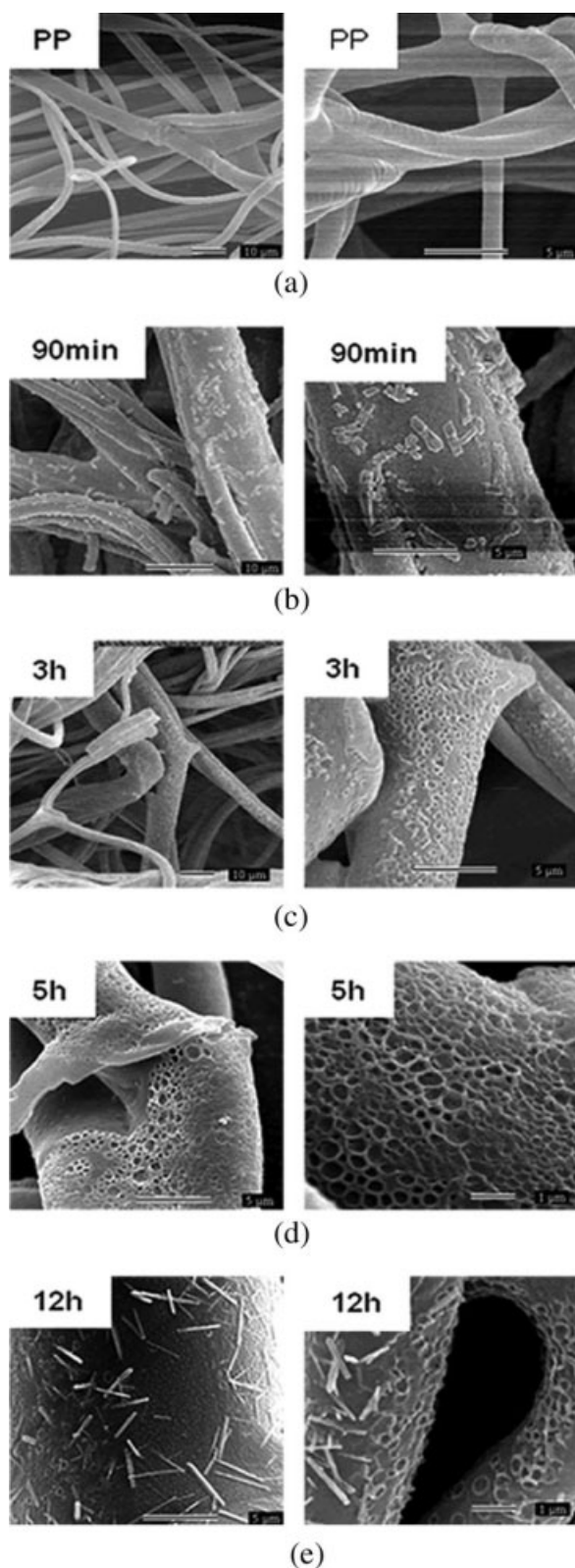


Figure 7 Scanning electron microographies for (a) PP and after reaction with H₂SO₄ for (b) 90 min, (c) 3 h, (d) 5 h, and (e) 12 h.

shows the SO₂ formation for different amounts of PP used in the experiment. The linear behavior of these curves suggests a kinetic based on a zeroth order pro-

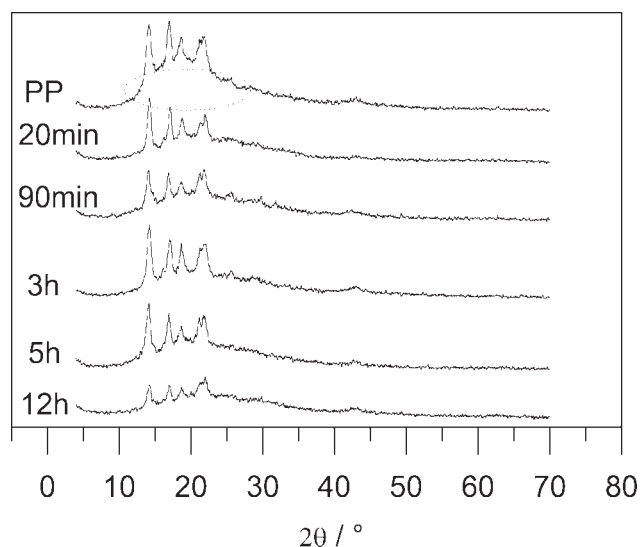


Figure 8 XRD patterns for the PP after reaction with H₂SO₄.

cess. To obtain the SO₂ rate constants the slope of the gas formation curves were calculated.

It can be observed that the SO₂ formation rate strongly increased up to 0.35 g/20 mL H₂SO₄ but does not vary significantly for higher amount of PP.

In all experiments, ~1.5 mmol of SO₂ was formed per 1 mol of PP.

Raman spectra for the obtained materials are shown in Figure 6.

The spectrum for pure PP showed typical bands at 1160, 974, 840, and 805 cm⁻¹.^{9,10} After reaction with H₂SO₄ new broad bands appeared at 1590 and 1360 cm⁻¹. These bands are related to ordered and disordered sp² carbon in polyaromatic structures. The band at 1590 cm⁻¹, called G band, is related to more organized graphitic structures. The band at 1360 cm⁻¹ called D band is related to amorphous carbon or defects in graphitic structures.¹¹

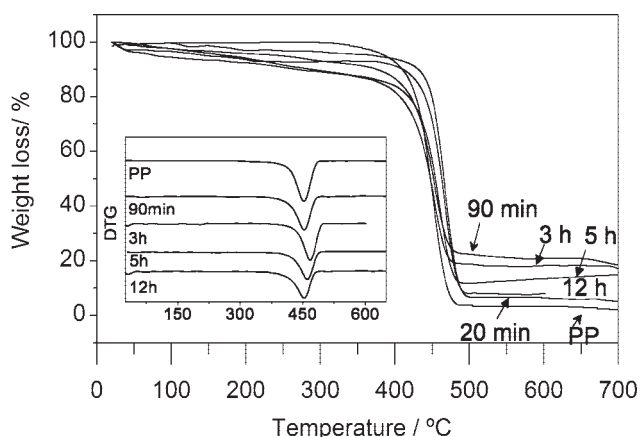


Figure 9 TG analyses of PP reacted with H₂SO₄ in N₂.

These results clearly suggest that carbonaceous structures are formed during the reaction with H_2SO_4 . In fact, after reaction, the PP becomes completely black in color. It is interesting to note that the relative intensity of the G compared with the D band increases suggesting the formation of more organized graphitic structures.

SEM analyses of the PP showed the presence of smoothed surface regular fibers with diameters varying from about 2–8 μm Figure 7(a). Figure 7(b–d) show SEM images of the PP after reaction with H_2SO_4 for 1.5, 3 h, 5 h, and 12 h.

In all cases, the PP fiber structure is maintained even after 12 h reaction. After 90 min reaction, the PP fiber is clearly covered with 1–5 μm rectangular structures. After 3 and 5 h, reaction pores/cavities were formed on the PP fiber surface whereas with 12 h reaction needle shaped structures are also present on the PP surface.

Powder XRD for the PP (Fig. 8) showed diffraction peaks between 10 and 25° are related to the α -monoclinic PP crystalline phase.^{11,12}

After reaction with H_2SO_4 , no significant change in the XRD peaks can be observed up to 5 h reaction suggesting that the reaction takes place on the surface of PP fibers and preferentially at the amorphous parts. On the other hand, after 12 h reaction, the XRD peaks decrease in intensity suggesting an attack on the crystalline parts of the polymer.

TG analyses for PP (Fig. 9) shows a single weight loss at about 450°C related to the thermal decomposition of the polymer chain.

TG curves for the PP after reaction with H_2SO_4 showed small weight losses at temperatures lower than 400°C likely related to the decomposition of $-SO_3H$ and $-COOH$ groups formed in the reaction. It is interesting to observe no significant change for the PP decomposition temperature even after 12 h reaction with H_2SO_4 . PP loses about 100% during TG analysis at 750°C. As PP reacts with H_2SO_4 , a

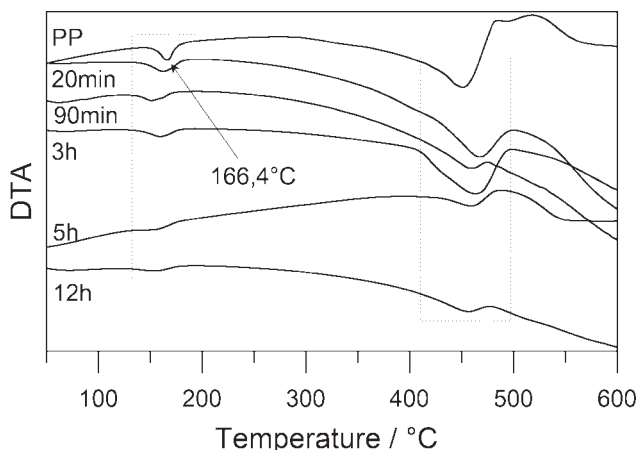


Figure 10 DTA for PP after reaction with H_2SO_4 .

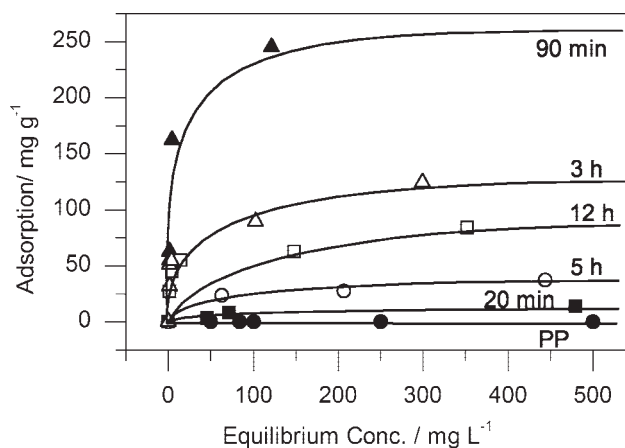


Figure 11 Adsorption isotherms of MB on PP fibers after reaction with H_2SO_4 for different times.

carbonaceous residue is formed by thermal decomposition. This carbonaceous residue reaches 20% for the PP (90min) but decreases for longer reaction times. These results suggest that the formation of carbonaceous residues is related to the presence of the functional groups, for example SO_3H and $COOH$. Likely, these functional groups thermally decompose to form reactive intermediates which will lead to the aromatization of the polymer.

DTA profile shown in Figure 10 showed two endothermic events at about 166 and 451°C related to the melting and decomposition of PP, respectively.

A melting point of PP at 166°C indicates a 60–80% on isotacticity.⁸ Even after 12 h reaction with sulfuric acid, the endothermic peak related to the PP melting is still present, reinforcing the idea of surface reaction.

To investigate the adsorptive properties of the reacted PP fibers, the dye methylene blue (MB) was used as a probe molecule. MB is a cationic molecule which should interact mainly with SO_3^- groups created on the PP fibers by the reaction.

Adsorption isotherms of MB on the different PP are shown in Figure 11.

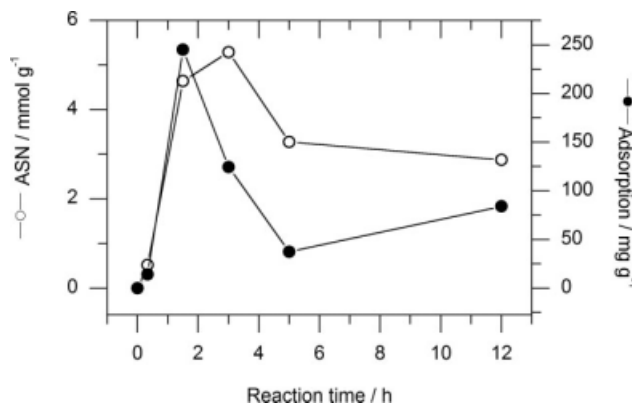


Figure 12 MB adsorption and ASN for the PP reacted with H_2SO_4 for different times.

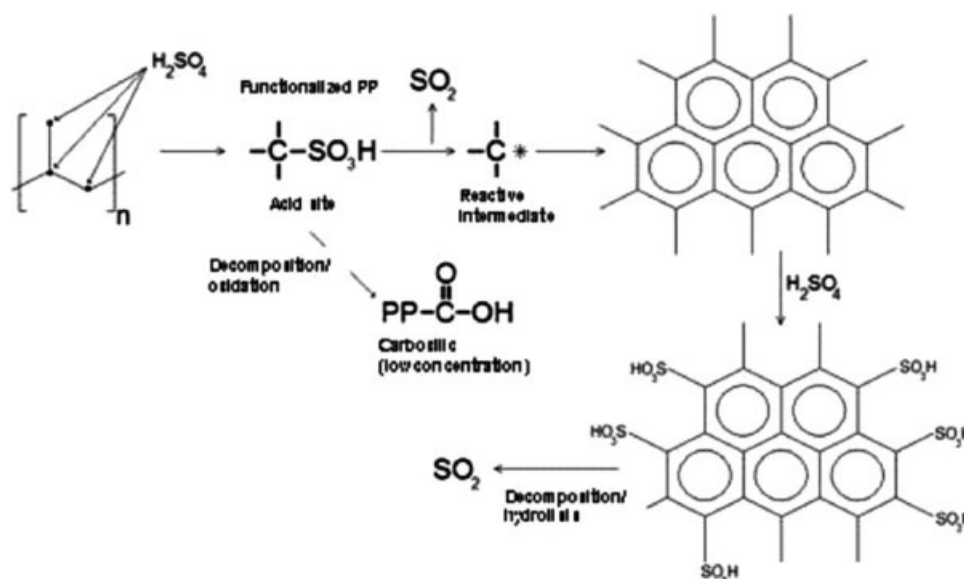


Figure 13 Schematic representation of the reaction mechanism proposal of PP fibers with H₂SO₄.

The original PP does not adsorb any significant amount of MB. After reaction with H₂SO₄ for 20 min, a small increase on the MB adsorption is observed. On the other hand, 90 min reaction with H₂SO₄ produced a remarkable increase on the adsorption capacity of the PP fibers to ~250 mg g⁻¹. It is interesting to observe that for longer reaction time with H₂SO₄, a gradual decrease on the adsorption of MB is observed. This decrease in adsorption is likely related to the decomposition of sulfonic groups leading to a decrease on the number of adsorption sites. Figure 12 clearly shows a relationship between the adsorption capacity with the number of acidic groups on the PP surface.

The results obtained in this work clearly show that three or more processes take place on reaction of PP fibers with H₂SO₄. Figure 13 presents a simplified proposal with the main processes during the reaction of PP fibers with H₂SO₄.

In a first step, H₂SO₄ attacks the surface of PP fibers producing sulfonic groups. The formation of sulfonic groups have been observed before.^{1,4}

The sulfonation reaches a maximum near 90 min to 3 h. Sulfonic groups formed also decompose to form SO₂ as detected by IR. As result of this decomposition two other processes take place: the formation of carboxylic groups and aromatization producing carbonaceous materials. It can be envisaged that the formed polyaromatic structures can also be easily sulfonated by H₂SO₄.⁶ IR, TG, and XRD results suggested that all these processes take place mainly on the PP surface. SEM analyses showed an attack on the PP surface and the segregation of different materials on the PP surface. The kinetics experiments suggested that at some point the PP surface passivates after reaction with H₂SO₄.

Even under excess of H₂SO₄ no further reaction takes place.

CONCLUSION

PP fibers react with sulfuric acid in a complex process involving sulfonation, oxidation, decomposition to SO₂, and aromatization to grafitic and amorphous carbon. The modified PP fibers show good cation-exchange properties, especially with 90 min reaction, due to the large concentration of surface sulfonic groups. Based on this process, PP fiber waste can be transformed by a low cost and technically simple reaction with H₂SO₄ into materials with great potential for the treatment of wastewaters.

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