Functionalization of Polypropylene at High Temperature Under Oxidative/Inert Environment

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ABSTRACT: Functionalization of polypropylene (PP) has been investigated using the high-temperature route. The advantage of the high-temperature functionalization is the introduction of cheaper, long-term stable and environmentally friendly routes for generating surface active groups on PP. In this regard, extensive experimental work was undertaken to investigate the influence of the high-temperature (40–360°C) treatment, reaction time, and inert/oxidative gas environments on generation of functional groups on PP. The thermal gravimetric analysis and differential scanning calorimeter techniques were used to study the changes in the temperature of melting/crystallization and the crystallinity of the treated PP samples. Scanning electron microscopic analysis showed that the high-temperature treatment under inert/oxidative affects the surface/morphology of PP samples. Fourier transform infrared (FTIR) was used to examine the surface species formation and the stability of functional groups. FTIR results of the thermally treated PP showed the selective formation of monosubstituted alkenes under inert atmosphere, while the formation of hydroperoxides, carbonyl, lactones, and substituted alkenes stable species was observed under oxidative atmosphere. The changes in the molecular weight of the treated PP under different conditions were evaluated using high-temperature gel permeation chromatography (HTGPC) technique. The extent of functionalization of PP up to 20% or more could be obtained by using the different oxidation conditions. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 1–11, 2012

Key words: polypropylene; functionalization of polyolefin; high-temperature treatment; oxidative/inert atmosphere; FTIR; TGA

INTRODUCTION

Polypropylene (PP), a type of thermoplastic polymer, finds applications in wide range of automotive parts, textiles, instruments, domestic, and industrial products. The global demand for PP, because of its typical physicochemical properties inclusive of acids/bases resistance, has been increasing with a sale of >US$65 billion.[1,2] However, lack in polar functionality onto PP restricts its application in commercial areas. Therefore, much academic and industrial research is directed toward modification of polymers. Polymer modification processes affect the characteristic properties of polymers required for various product applications with respect to the high-temperature stability/impact strength/stiffness and barrier properties. Functionalization of polymers is very important in modifying polymers for industrial applications with wider scope in the areas of adhesion, paintability, printability, as well as compatability with metallopolymers composites and other polymers. Surface treatment is one of the approaches to introduce the functionalities onto polymer.[3–6]

So far, functional modifications of polymers are carried out using various methodologies such as chemical, plasma, corona, ozone, and grafting or combination of chemical and oxidation routes.[7–19] A plasma treatment provides possibilities to refine a polymer surface, enabled by the adjustment of parameters such as gas flows, power, pressure, and treatment time. Degradation of polymer surfaces mainly occurs when a rapid interaction with radicals or ions takes place.[20] Plasma treatment of polymer surfaces causes not only a modification during the plasma exposure but also leaves active sites at the surfaces that are subjected to postreaction aging.[21,22] Corona treatment system (made of several components designed to apply a high-voltage, high-frequency electrical discharge to film) is the most common method of increasing surface energy on substrates to promote adhesion when printing, coating, or laminating.

Efforts in the direction of greener, cleaner routes and cost-effectiveness for polymer functionalization are preferred in commercial applications. In this regard, we aimed to modify PP beads surface or bulk using high-temperature treatments under different gaseous environments. The aim of the present research work is to investigate the

influence of the high-temperature thermal treatment (up to 360°C) on functionalization of PP beads in inert or oxidative environment. The literature on the high-temperature (above melting point of PP) treatment of PP in inert/oxidative atmosphere is scarce and available at lower temperature.[18,19,23–25] Techniques such as thermogravimetric (TG), differential scanning calorimetric (DSC), Fourier transform infrared (FTIR) spectroscopy, scanning electron microscope (SEM), and high-temperature gel permeation chromatography (HTGPC) are employed in analyzing the products of thermally treated PP samples.

EXPERIMENTAL

Functionalized-PP sample preparation

High-temperature oxidative/nonoxidative method was used to functionalize PP. PP beads were thermally treated in the presence of oxidative or inert atmosphere under precisely controlled temperature in the range of 40–360°C and nonisothermal/isothermal conditions. The wide range of temperature was used to know the influence of temperature on PP under oxidative/inert atmosphere. In this study, isotactic polypropylene (Aldrich) beads were used as PP source. High purity air/nitrogen (flow rate 300 mL/min) was used for maintaining the oxidative/inert environment.

Characterization

TGA

The thermal properties of PP at different treatment temperatures were measured by a TA Instruments Q500-TGA. The analysis was preformed with ∼ 8-mg PP sample in a dynamic/isothermal air/nitrogen environment with a heating rate 5°C/min.

DSC

The changes in the temperature of melting (T_m)/crystallization (T_c) and crystallinity of PP samples were investigated using a TA Instruments Q2000 DSC. The DSC analysis was performed over the temperature range of −25–250°C with a heating rate 10°C/min.

FTIR

FTIR analysis on the untreated and treated PP samples was performed with a Thermo Nicolet 6700 FTIR with Smart Orbit Diamond Crystal ATR accessory over wavelength range of 4000–400 cm^{-1} and resolution of 4.0 and 150 scans. The extent of functionalization different groups was obtained by semi-

quantitative estimation of the FTIR peak data. In this method, the exact known amount of samples was used for ATR-FTIR measurements. The FTIR spectra were processed for absorbance, smoothing, baseline, correction, and normalization needed for semiquantitative FTIR analysis, and extent of functionalization was obtained by estimating the peak area/intensities of the functional groups.[26]

SEM

For morphological studies of the unmodified and modified PP samples, a Leica Stereoscan 440SEM with Phoenix EDAX/EDXS was used, and the PP samples were coated with gold.

HTGPC

A PL-220 series HTGPC unit equipped with a refractometer detector and four PL gel Mixed-A (20 μm) columns was used for analysis of untreated and treated polymer samples. The HTGPC analysis conditions were as follows: oven temperature 150°C and autosampler temperature (hot zone) 135°C. The solvent was nitrogen purged 1,2,4-trichlorobenzene (TCB) containing ∼ 200 ppm 2,6-di-t-butyl-4-methyl-phenol (BHT). The flow rate is 1.0 mL/min, and the injection volume was 200 μL. A 2-mg/mL sample concentration is prepared by dissolving the sample in N_2 purged and preheated TCB (containing 200 ppm BHT) for 2.5 h at 160°C with gentle agitation. The GPC column set was calibrated by running 20 narrow molecular weight distribution polystyrene standards. The polystyrene standards were dissolved at 150°C for 30 min under stirring. The narrow standards mixtures were run first and in order of decreasing highest molecular weight component to minimize degradation effect. The equivalent PP molecular weights were calculated by using the Mark-Houwink coefficients for PP[27] and polystyrene.[28]

RESULTS AND DISCUSSION

To functionalize the polymer surface/bulk, PP beads were treated at different temperatures and gas environments.

Effect of the thermal treatment on the PP samples

Influence of the temperature and gas atmosphere on the weight loss of PP was investigated using the thermogravimetric technique. The TGA results of PP samples treated at different conditions are presented in Tables I–III.

The TGA (Table I) results show that in inert atmosphere, PP looses a very small amount of

TABLE I
Influence of the Temperature on the Weight Loss of PP in Nitrogen Atmosphere

Sample	Temperature range (°C) nonisothermal	Weight loss (%)	Sample treated isothermally for 1 h	Temperature range (°C)	Weight loss (%)
PP40N2	25–40	0.0	PP40N2	25–40	0.0
PP140N2	25–140	0.1	PP140N2	25–140	0.2
PP280N2	25–280	1.4	PP280CN2	25–280	2.2
PP340N2	25–340	8.7	PP340CN2	25–340	39.7
PP360N2	25–360	9.2	PP360CN2	25–360	40.5

weight (1.4%) up to 280°C and further, the weight loss increases with the temperature. The maximum weight loss observed for PP was 9.2% at 360°C (without holding the temperature). In inert environment, the isothermally treated PP exhibited higher weight loss as compared with the dynamically treated PP samples. Under isothermal conditions, the weight loss of PP increases from 2.2% at 280°C to 40.5% at 360°C.

PP samples exhibited higher weight losses (Table II) with the thermal treatment temperature in air under nonisothermal conditions as compared with the PP samples treated in nitrogen (Table I). In an oxidative environment, a very small amount of weight loss of 0.7% at 240°C was observed for PP; however, the weight loss of PP significantly increased to $\sim$ 80% at 360°C.

Whereas, when PP was treated isothermally for different periods (Table III), the weight loss of PP was higher than that of the nonisothermally treated samples. The TGA analysis of PP sample thermally treated at different temperatures and period (Table III) shows that the weight loss of PP was nearly same at treatment temperature and period at 140°C, 12 h (weight loss 4.1%) and 160°C, 6 h (weight loss 4.3%), respectively, while the weight loss was nearly double at 180°C for a period of 3 h. These PP samples treated (Tables I–III) at different conditions were further examined by the DSC, SEM, and FTIR for the changes in their properties.

Influence of the treatment conditions on the T_m, T_c, and crystallinity of PP

DSC analysis of the treated PP samples in nitrogen/air shows that the melting and crystallization points of PP are affected. The temperature of melting (T_m) and the temperature of crystallization decreases with increase in the treatment temperature (Table IV). However, the decrease in the T_m and T_c is not so significant for the PP sample treated in nitrogen.

At the treatment temperature of 360°C, the PP sample treated under inert atmosphere exhibited limited decrease of 10% in the T_m and 8% in the T_c, respectively, whereas, for the sample treated in oxidative atmosphere above 280°C, the change in the T_m and T_c was more drastic (26% and 20%), respectively.

The crystallinity is an indication of the amount of crystalline polymer with respect to amorphous content. Crystallinity of a polymer is important from application perspective and is related to the polymeric properties such as melting point, hardness, modulus, long-term stability, tensile, stiffness, and optical clarity. The DSC data were used to calculate the crystallinity of PP samples. The crystallinity of the treated PP samples under oxidative and inert conditions is presented in Figure 1.

The crystallinity was calculated from the DSC data [latent heat of melting of the PP sample and heat of melting of standard PP (207 J/g)].[29] The crystallinity data show that the crystallinity of treated

TABLE II
Influence of the Temperature (Without Holding) on the Weight Loss of PP in Air

Treated-PP sample	Temperature range (°C)	Weight loss (wt %)
PPA40	25–40	0.0
PPB140	25–140	0.1
PPC160	25–160	0.1
PPD170	25–170	0.1
PPE190	25–190	0.2
PPF210	25–210	0.3
PPG240	25–240	0.7
PPH280	25–280	4.5
PPI340	25–340	57.6
PPJ360	25–360	79.6

TABLE III
TGA Data for the PP Samples Treated Isothermally in Air at Different Periods

Sample type	Temperature range (°C)	Temperature hold period (h)	Weight loss (%)
PPA1 40 1 h	25–40	1	0.0
PPB1 140 1 h	25–140	1	0.8
PPC1 160 1 h	25–160	1	0.9
PPE1 190 1 h	25–190	1	2.4
PPF 1 210 1 h	25–210	1	5.0
PPG1 240 1 h	25–240	1	18.9
PPH1 180 3 h	25–180	3	8.3
PPI1 160 6 h	25–160	6	4.3
PPJ1 140 12 h	25–140	12	4.1

Sample	Cycle 1 melting, T_m (°C)	Cycle 2 cooling, T_c (°C)	Cycle 3 melting, T_m (°C)
PP (untreated)	158	111	148
PP sample treated in nitrogen			
PP 140N$_2$	158	110	148
PP280N$_2$	157	108	146
PP340N$_2$	148	108	140
PP360N$_2$	142	101	139
PP sample treated in air			
PP B140	159	110.2	158.5
PPH280	153.1	108.3	152.6
PPI340	135.9	86.4	136.8
PPJ360	117	87.01	116.1

PP samples under nitrogen atmosphere is not significantly affected.

The crystallinity of the PP samples treated in air was drastically affected and significantly decreased with increase in the temperature. The maximum reduction in crystallinity of the sample was observed at 340°C, which is expected due to the partial degradation of PP. However, increase in the crystallinity was observed at 360°C, which could be related to the structural changes occurring in PP at this temperature. For isothermally treated PP samples (for 1 h), the crystallinity loss was much higher than that of those samples of PP treated nonisothermally. This shows that the crystallinity is significantly reduced by holding the sample at high temperatures (>340°C) in the presence of air, which significantly alters the physicochemical properties of PP/degrades PP.

Representative SEM micrographs of the unmodified and modified PP samples are presented in Figure 2. SEM analysis shows that the morphology of PP is not significantly affected by the treatment temperatures up to 240°C [Fig. 2(b)] in inert atmosphere. However, more pronounced surface changes (with number of irregular cracks) were observed at
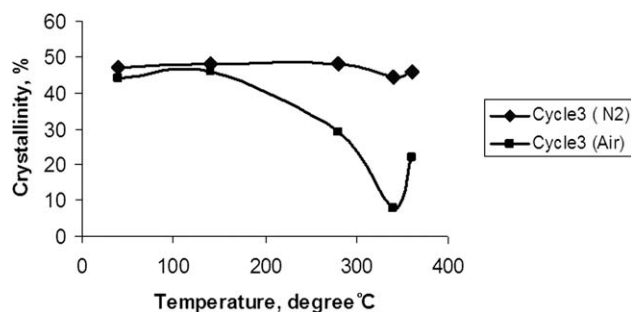

Figure 1 Crystallinity of the treated PP samples in air/nitrogen (without holding the temperature).
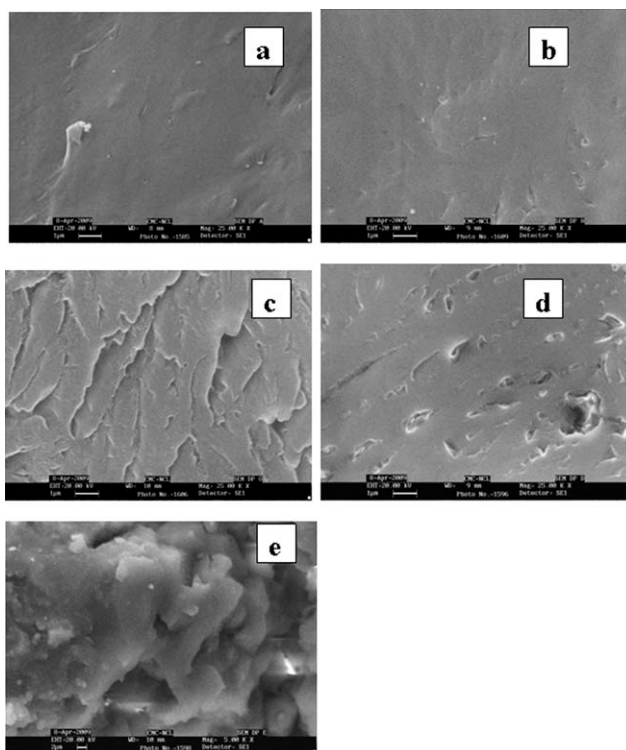
Figure 2 SEM photographs of the untreated PP (a) and treated PP sample in nitrogen at 240°C (b) and 280°C (c) and in air at 280°C (d) and 360°C (e) in air (without holding the temperature).

the temperature of 280°C. Similarly, the thermally air-treated PP samples did not exhibit significant morphological changes up to temperature of 240°C. SEM micrograph [Fig. 2(d)] of the treated-PP sample in air at 280°C exhibits the presence of large number of irregular holes. These holes created would be due to trace of vapor of oligomer from the decomposed PP. The number of holes formation or density of holes was much higher with the PP sample heated at 280°C than in the PP sample treated at 240°C in air. The depth of holes was much more pronounced in the 280°C-treated sample. This indicates that some morphological changes occur in the PP at this temperature.

The SEM results [Fig. 2(e)] show that the morphology of PP at the higher treatment temperature of 360°C (air) is totally changed because of recrystallization/structural changes and larger degree of degradation. The shape and size changes were observed because of the oxidation of PP in air at elevated temperature of 360°C. At these conditions, the TGA results of this PP sample indicated a weight loss of 80%.

FTIR analysis of the modified-PP samples

The thermally treated PP samples were characterized using the ATR-FTIR techniques, so that the
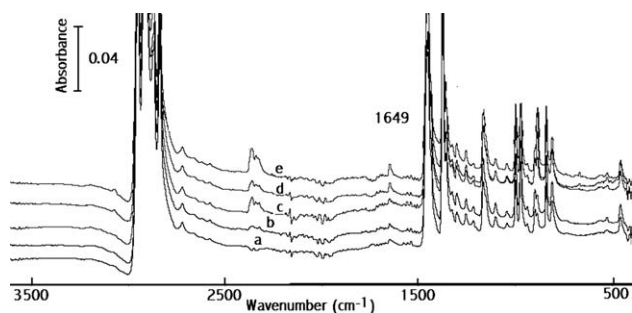
Figure 3 FTIR spectra of PP treated in nitrogen at (a) 40°C, (b) 140°C, (c) 280°C, (d) 340°C, and (e) 360°C (without holding the temperature).

changes in functional/surface/structural with various oxidative/nonoxidative treatments could be observed. Figure 3 shows the influence of temperature (without holding) and nitrogen atmosphere on the functional group(s) of PP. It is interesting to note that when PP is treated at a range of temperatures (40–360°C, without holding the temperature) under nitrogen environment, there were no major changes observed in FTIR spectra up to 280°C. However, above 280°C, new peaks appeared at 1649 cm^{-1} (stretch C=C) and 886 cm^{-1} (bending =C—H) related to monosubstituted alkenes,[30] and a considerable increase in the alkenes absorbance regions was observed at the higher temperatures. The concentration of these alkenes species increased with the temperature in nitrogen environment.

To envisage the effect of isothermal conditions on surface species, the treatment temperature of PP samples was held for 1 h. Influence of isothermal heating on different PP samples in the presence of nitrogen is presented in the Figure 4. Isothermal heating of the PP sample for 1 h also leads to appearance of monosubstituted alkenes at 1649 and 886 cm^{-1}. The concentration of monosubstituted alkenes was higher over the isothermally treated PP
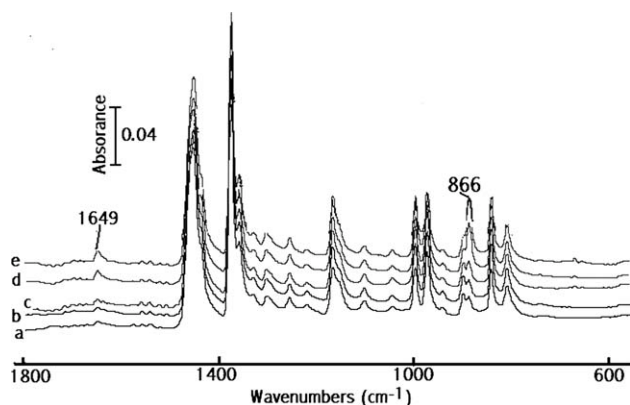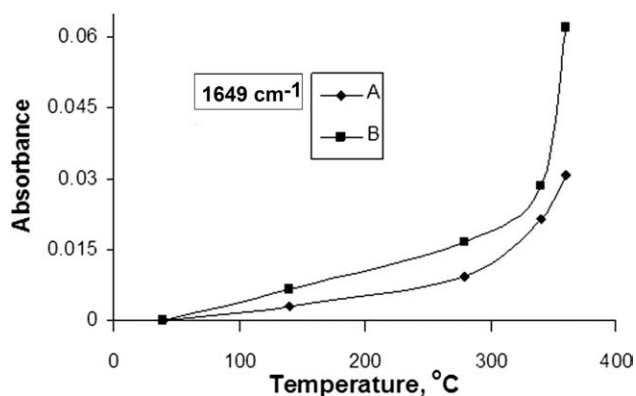

Figure 5 Thermal treatment of PP in the presence of nitrogen (A: without holding the temperature and B: with holding the temperature).

samples than on the nonisothermally treated PP samples. Figure 5 shows the plots of the variation of the absorbance of the monosubstituted alkenes groups. The plots show also the influence of holding the temperature on the concentration of monosubstituted alkenes, which substantially increases above 260°C. It was clearly observed that the holding of the temperature helps to generate higher concentration of monosubstituted alkenes.

FTIR spectra of the PP treated in air under nonisothermal condition (Fig. 6) show that the PP samples do not exhibit significant changes and were stable in the presence of air up to the temperature of <240°C (without holding) as also indicated by the TGA analysis (Table II). However, at the temperature of ≥240°C, new absorption bands at 1776, 1716, and 1648 cm^{-1} were observed, and these bands are related to lactones (1776 cm^{-1}), carbonyl (1716 cm^{-1}), and monosubstituted alkenes (1648 cm^{-1}),

Figure 4 FTIR spectra of PP treated isothermally for 1 h in nitrogen at (a) 40°C, (b) 140°C, (c) 280°C, (d) 340°C, and (e) 360°C.
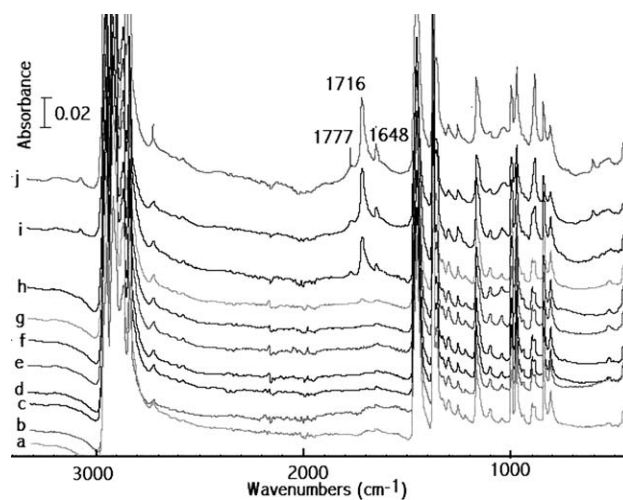

Figure 6 FTIR spectra of PP treated in air at (a) 40°C, (b) 140°C, (c) 160°C, (d) 170°C, (e) 190°C, (f) 210°C, (g) 240°C, (h) 280°C, (i) 340°C, and (j) 360°C (without holding the temperature).
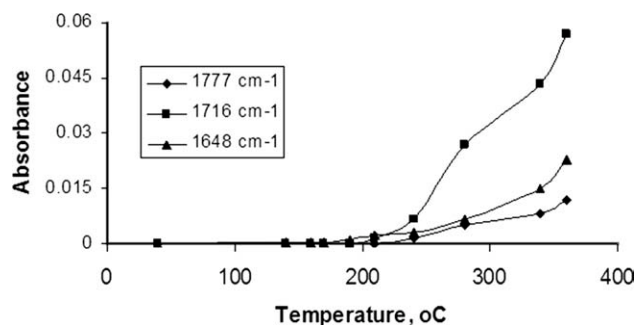
Figure 7 Thermal treatment of PP in the presence of air (without holding the temperature).

respectively.[31,32] The formation of hydroperoxides on the PP occurs above the treatment temperature of $>240°C$.[18] With increase in the treatment temperature, the concentration of hydroperoxides, lactones, carbonyl, and monosubstituted alkenes increased. The carbonyl absorption band at 1716 cm^{-1} in the PP samples treated in the presence of air and high temperature is associated with the development of ketone following beta scission during the oxidation of PP, while lactones are expected to be formed via a cage reaction.[31,32]

Influence of the temperature on the absorbance of the lactones, carbonyl, and monosubstituted alkenes groups is presented in the Figure 7. It can be seen that the absorbance of these groups below 200°C was very low; however, with further increase in the temperature above 200°C, absorbance of these groups increased. Among these three functional groups, the concentration of carbonyl group was relatively much higher than those of lactones and monosubstituted groups.

Figure 8 illustrates the FTIR spectra of the PP treated in air under isothermal conditions. FTIR spectra exhibit the formation of lactones, carbonyl,
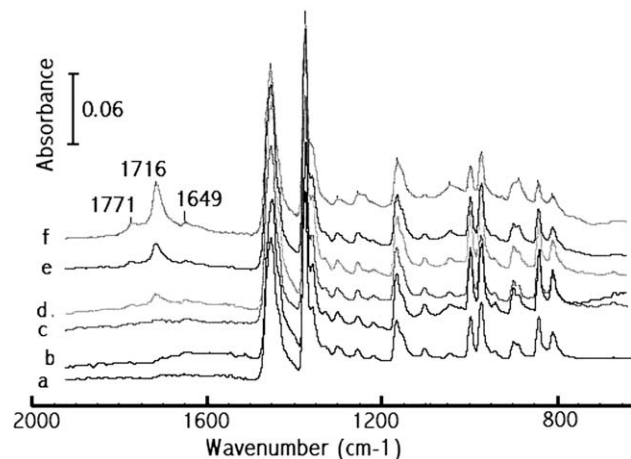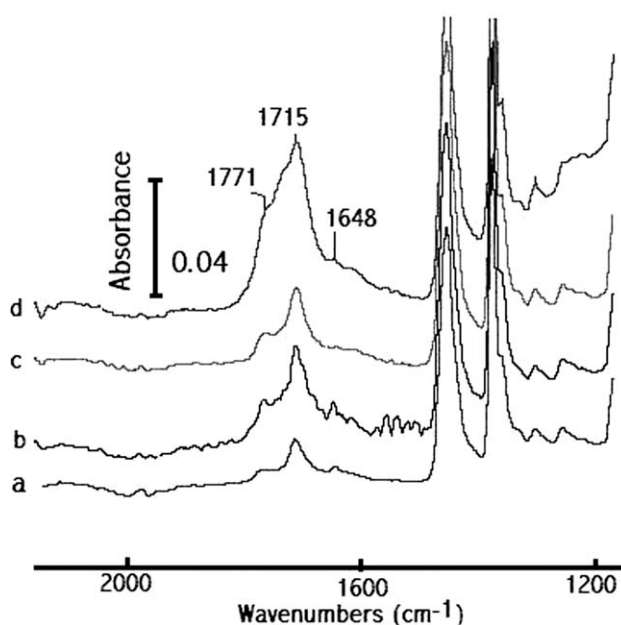

Figure 9 FTIR spectra of the treated PP in air at (a) 210°C for 1 h, (b) 180°C for 3 h, (c) 160°C for 6 h, and (d)140°C for 12 h.

and monosubstituted alkenes above 140°C. Under isothermal conditions, the formation of these species occurs at much lower temperature ($\sim$ 160°C), and the concentration of species increased with the temperature. Also, the concentration of these species formed under isothermal conditions was much higher than the PP samples treated under nonisothermal conditions. At the thermal treatment temperature of 240°C, the carbonyl group formation was three-fold higher than that of lactones and five-fold higher than that of monosubstituted alkenes formations.

The PP samples were treated at different temperatures and isothermal periods to study the influence of the temperature and time parameters on the functional groups. PP samples treated isothermally at 140°C for 12 h, 160°C for 6 h, 180°C for 3 h, and 210°C for 1 h were investigated for their functional changes using FTIR (Fig. 9). These PP samples treated at different temperatures and periods showed the presence of absorption bands at 3400 cm^{-1} (hydroperoxides), 1771 cm^{-1} (lactones), 1715 cm^{-1} (carbonyl), and 1648 cm^{-1} (substituted alkenes). The results show that the temperature and holding period influence the concentration of carbonyl, lactones, and monosubstituted alkenes. The concentration of these species is highest for the PP treated at 140°C for 12 h and lowest for the sample treated at 210°C for 1 h. The TGA analysis of the isothermal-treated PP samples (Table III) showed that the weight loss of the PP treated at 140°C for 12 h was very low (4.1%) as compared with the other treated PP samples. Figure 10 shows the relative percent change in the carbonyl group absorbance with
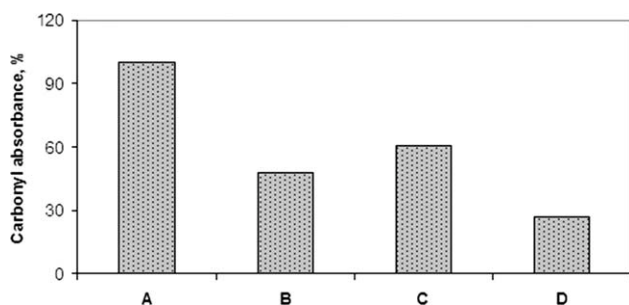

Figure 8 FTIR of the treated PP at (a) 40°C, (b) 140°C, (c) 160°C, (d) 190°C, (e) 210°C, and (f) 240°C isothermally in air for 1 h.

Figure 10 Thermal oxidation of the PP with the temperature and holding period. (A: 140°C for 12 h, B: 160°C for 6 h, C: 180°C for 3 h, and D: 210°C for 1 h).

Figure 12 FTIR of the treated PP in air at 200°C for (a) 1 min, (b) 5 min, (c) 10 min, (d) 1 h, (e) 5 h, and (f)10 h.

varying temperatures and holding period. It can be seen that the higher concentration of carbonyl could be generated at lower temperature with higher holding period without much of compromising the PP properties.

Even at a very low holding period (1 min) (Fig. 11), the concentration of lactones, carbonyl, and substituted alkenes varied with the temperature (266–360°C). At such a low holding period (1 min), the concentration of these species was highest for 360°C followed by 280°C. At lower temperature (157°C, 1 min), mostly alkenes species formation was observed. Influence of the treatment holding period (1, 5, and 10 min) at 280°C (Fig. 11) or at 200°C (1 min, 5 min, 10 min, 1 h, 5 h, and 10 h) (Fig. 12) on PP exhibits increased concentration of the lactones, carbonyl, and substituted alkenes with the time. Comparing the results of Figures 11 and 12, it could be noted that the level of concentration of lactones/carbonyl/substituted alkenes achieved at 280°C could also be obtained at lower temperature 200°C with a particular holding period.

The changes in the absorbance of carbonyl group at 200°C with varying time presented in Figure 13 show that the absorbance of carbonyl group
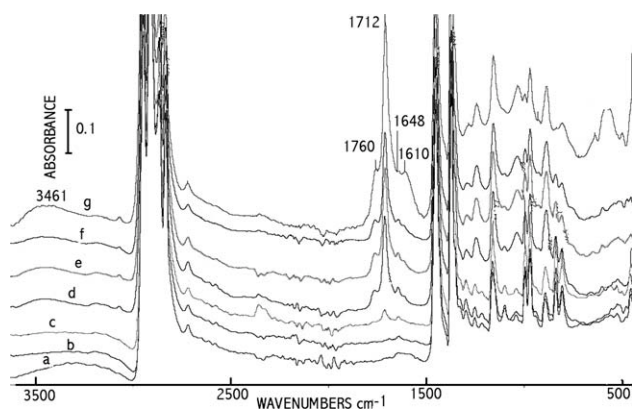
increases with increase in the oxidation reaction period. At initial reaction period of up to 10 min, the absorbance of carbonyl group formed is lower; however above 60 min, the carbonyl absorbance increases linearly with oxidation time. This means that the concentration of carbonyl can be improved and controlled by increasing the reaction period.

Generally, for certain applications, the concentration of carbonyl/substituted alkenes is required on the surface of PP as well as in the bulk sample of PP. The presence of these species on surface and in bulk was investigated by the thermally treating PP sample at 200°C and 280°C for 10 min. FTIR analysis of these samples (Fig. 14) indicates that the carbonyl/substituted alkenes are present on surface of the 200°C- and 280°C-treated PP samples. After FTIR analysis was carried out on external layer of the PP sample, a top layer of ∼ 0.4 mm of surface was removed to check the functional groups present below the surface layer. When the top surface layer of ∼ 0.4-mm thickness was removed, it was observed that the functional groups were present on both the treated samples. However, the concentration of functional groups was lower on inner layer, which is below surface layer. This indicates that the

Figure 11 FTIR spectra of the (a) untreated PP and treated PP at (b) 157°C for 1 min, (c) 266°C for 1 min, (d) 280°C for 1 min, (e) 280°C for 5 min, (f) 280°C for 10 min, and (g) 360°C for 1 min.
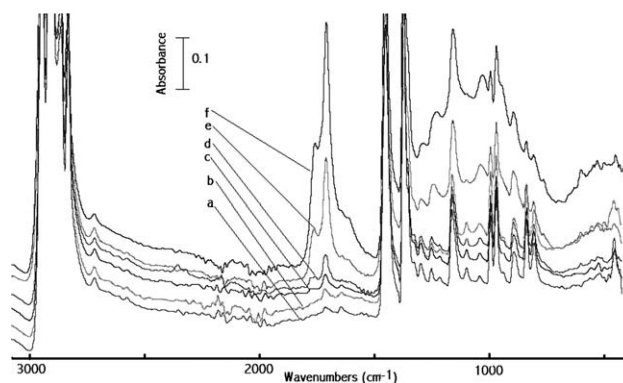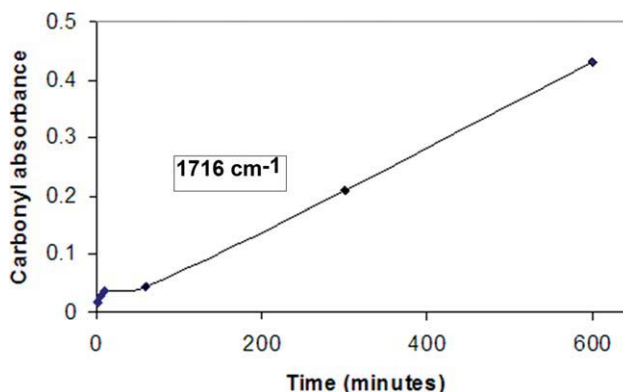

Figure 13 Thermal oxidation of the PP at 200°C with time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
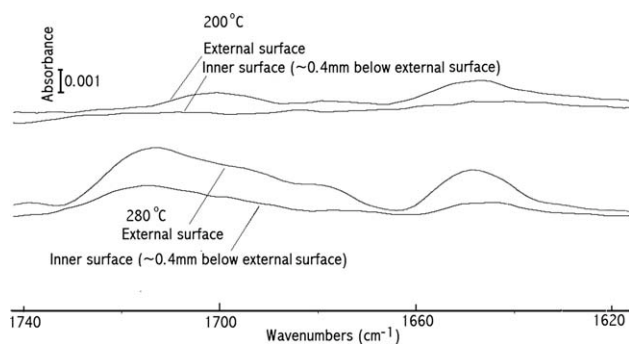
Figure 14 FTIR analysis of the external surface and inner surface of the treated PP at 200°C and 280°C.

Figure 16 FTIR measurements conducted on the same treated PP sample (air, 280°C, 1 min) over a length of time. (a) 1 day, (b) 6 months, and (c) 11 months.

functional groups are also present below surface of the treated polymer, and the concentration and depth of these species can be enhanced/manipulated either by increasing the temperature or holding period.

One of the important criteria for different applications is the stability of these surface species on polymer after functionalization. Therefore, the stability of these species was checked in sweeping nitrogen gas and elevated temperature (>120°C). Generally, polymer functionalization by other techniques leads to lower stability of surface species. For investigating the functional stability in the high-temperature sweeping nitrogen gas (Fig. 15), the thermally treated PP (200°C and 360°C) samples were heated at 120°C for 30 min under the flow of nitrogen (300 mL/min). Comparison of the FTIR results of the high-temperature nitrogen swiped samples [200°C [Fig. 11(a,b)] and 360°C [Fig. 15(c,d)]] with the originally treated samples indicates that the functional species are not lost during the sweeping gas treatment, and most of concentration of this surface species remains nearly similar (with only slight change in peak height of lactones/alkenes peaks).
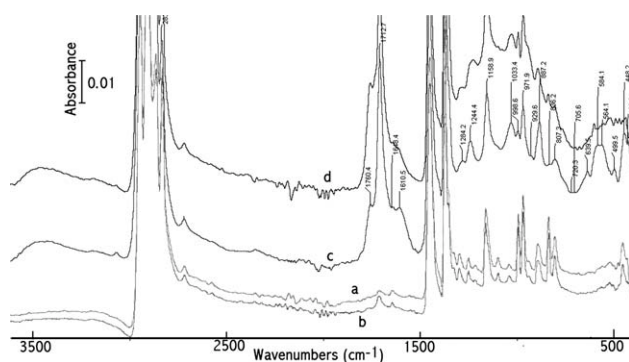
The longer stability period of the surface species formed over the PP samples was also checked for the thermally treated PP sample after 6 and 11 months against 1-day-old sample. In the stability versus time study, PP samples were thermally at 280°C for 1 min in the presence of air, and FTIR measurements were carried out on this sample with time (1 day, 6 months, and 11 months). FTIR analysis (Fig. 16) indicates that the functional species are unaffected with the longer time periods, and functional species formed using the high-temperature thermal techniques are very much stable. Figure 17 shows the percentage changes in the absorbance of carbonyl group with the room temperature holding time of the treated PP sample. The percentage changes in the absorbance of carbonyl group were obtained from the carbonyl peak area of the samples relative to maximum peak area of one of the samples (after processing and normalization of the spectra). It can be clearly seen that there is no much significant change in carbonyl absorbance, indicating the long-term stability of carbonyl group over the treated PP using high-temperature thermal oxidative thermal route.

Figure 15 FTIR spectra of the treated PP at 200°C and 360°C: (a) as treated at 200°C for 1 min in air, (b) after nitrogen sweeping at 120°C for 30 min, (c) as treated at 360°C for 1 min in air, and (d) after nitrogen sweeping at 120°C for 30 min.
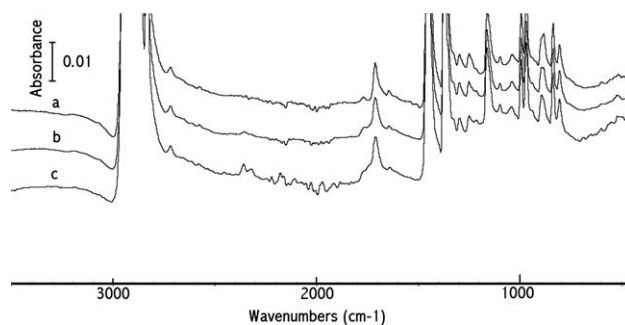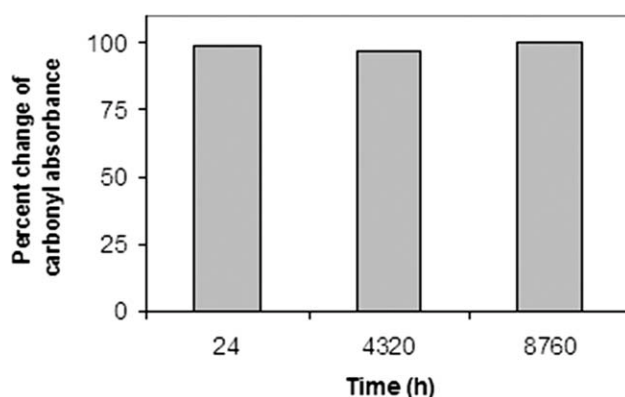

Figure 17 Relative changes in absorbance of carbonyl group of the PP sample oxidized at 280°C for 1 min.

HTGPC Data on the Untreated- and Treated-PP Samples at Different Temperatures in the Presence of Air or Nitrogen

Sample treated in oxidative (air) environment	M_n (g/mol)	M_w (g/mol)	Sample treated in inert (N_2) environment	M_n (g/mol)	M_w (g/mol)
Untreated PP	7710	24,580	Untreated PP	7710	24,850
PP, 200°C, 1 min	5372	21,350	PP, 200°C, 1 min	6924	24,890
PP, 200°C, 1 h	1741	7744	PP, 200°C, 1 h	7317	23,550
PP, 280°C, 1 min	996	3646	PP, 280°C, 1 min	4545	12,240
PP, 360°C, 1 min	777	1202	PP, 360°C, 1 min		

HTGPC analysis

HTGPC technique was used to monitor the changes in the number average molecular weight (M_n) and weight average molecular weight (M_w) for the PP treated at high temperature in oxidative/inert environment. The changes in the M_n and M_w of the treated PP samples are presented in Table V.

The HTGPC analysis of the air/nitrogen-treated PP samples shows that the changes occur in the M_w and M_n values with the temperature and gas environment. In the presence of air, the high-temperature treatment of PP showed significant amount of changes in the M_n and M_w above 280°C. The percentage loss/change of M_n and M_w for the 200°C air-treated PP sample for 1 min was 30% (M_n) and 13% (M_w), while the M_n and M_w drastically decrease for the air-treated PP sample at 280°C (change: M_n: 87%; M_w: 85%) and 360°C (change: M_n: 90%; M_w: 95%) for 1 min. The loss of M_n and M_w was significant for the PP sample treated at 200°C for 1 h compared with that of the PP sample treated for 1 min at 200°C. The suitable temperature range for functionalization (carbonyl/lactones/alkenes) of PP in air can be between ∼ 170°C and 260°C with duration of 1 min. In this range of temperatures, the changes in M_n and M_w are less pronounced.

The treatment of PP in the presence of nitrogen (Table V) illustrates an interesting set of HTGPC (M_n and M_w) results. For the nitrogen-treated sample, the major change in the M_n and M_w occurs at 360°C (50%), while at the temperatures of 200°C and 280°C, the changes are not that significant. Comparison of the M_n/M_w (air/nitrogen-treated PP samples) results indicates that the PP sample is less degraded and more stable in nitrogen than in the presence of air at the higher treatment temperatures. The treatment of PP in the presence of nitrogen can be effectively used for generation of alkenes groups over PP due to lower changes in the M_n/M_w with the temperature.

It is very interesting to note that the use of the high-temperature thermal treatment technique is effective in producing long-term stable functional species suitable for certain applications, where little or no change in function group(s) concentration is needed. Figure 18 shows the extent of functionalization with temperature on the treated PP. The extent of functionalization (lactone/carbonyl/monosubstituted groups, obtained by semiquantitative estimation of the FTIR peak data) varies with the oxidative temperature. By using the high-temperature oxidative route, the extent of functionalization was observed in the range 0.1% to ∼ 22%. At the oxidative temperature of 360°C, the estimated extent of functionalization was ∼ 22%, while at 280°C, the functionalization percent was ∼ 9%. This study shows that the extent of functionalization can be selectively controlled (increased/decreased) by the use of appropriate temperature and oxidative period conditions.

PP is a hydrophobic, low-energy material, and it does not adhere well to other materials. Modification
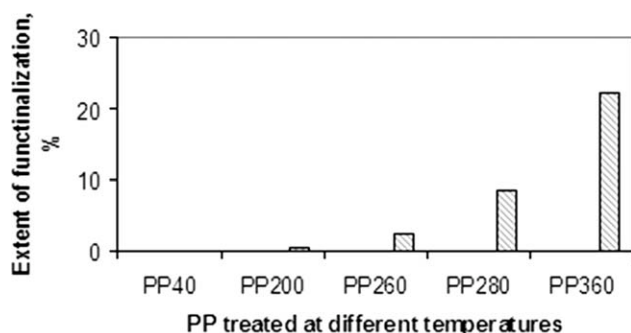
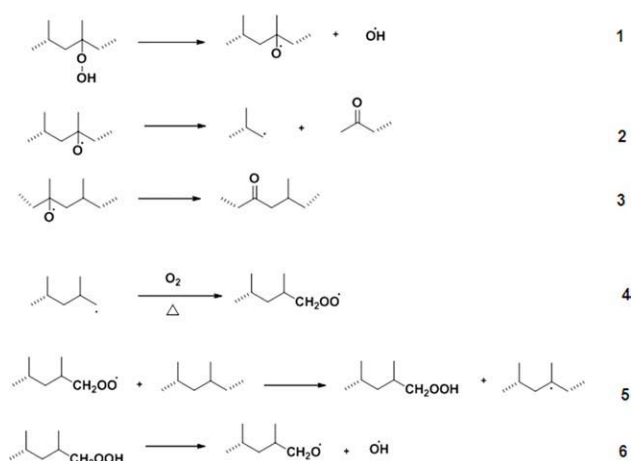**Figure 18** Extent of functionalization on the treated PP.

Figure 19 Formation of functionalities on the oxidized PP.

of surface and or bulk properties helps for its utilization in different applications. The formations of different surface species under different treatment conditions (air/nitrogen, temperature, and period) can act as interlock points for active species present in other materials.[33] The XPS results[34] showed that on the plasma treatment of the polymers, the carbon content decreased and oxygen content increased with introduction of functional groups such as C—O, O=C—O, and C=O on the surface of the treated polymer.

The functionalities that are important to grafting or other reactions are peroxides and carbonyl group. The mechanisms[18,35,36] for formation of hydroperoxides, alkyl radical, ketones, and alkoxy radicals are presented in Figure 19. The oxidation of PP leads to hydroperoxides formation. During the reaction, PP radical reacts with oxygen to form peroxy radicals, which further undergoes a hydrogen abstraction reaction to form alkyl peroxide species bound to PP backbone. Further, the conversion of hydroperoxides within polymer (PP) results in the formation of an alkyl radical, a methyl ketone, and also to an internal ketone [reactions(1)–(3)].

The alkyl radicals react with oxygen to form alkoxy radicals, which can further abstract hydrogen atoms from polymer to form alcohols or other volatile products [reactions(4)–(6)]. For the formation of different oxidative products of polymer, Chien and Kiang[37] reported that the fragmentation of primary and secondary alkoxy radicals proceeds via C—C bond scission with or without the transfer of a hydrogen atom or a methyl group. The alkoxy radicals formed by the thermal decomposition of alkyl peroxide undergo a chain scission or initiate a polymerization. Formation of other radicals on PP backbone occurs if the alkoxy radicals under a chain scission could enact as active grafting sites.

CONCLUSIONS

In summary, functionalization of PP is effective via the cleaner and greener high-temperature and oxidative/nonoxidative routes. The concentration/formation of the functional groups can be selectively controlled by using these thermal methods.

The modification of physiochemical characteristics [such as morphology, crystallinity, thermal (T_m, T_c, and heat of melting/fusion), and functional groups] of PP could be effectively controlled by combination of the high-temperature treatment in the presence of nitrogen or air. The crystallinity of the treated PP inertly is not significantly affected even at the higher temperatures (up to 360°C), while the thermally air-treated PP exhibited substantial reduction in the crystallinity above 260°C.

Selective formation of monosubstituted alkenes groups on PP occurs during the high-temperature treatment under nitrogen gas. In the presence of air, the high-temperature treatment of PP leads to formation of different oxidative products related to hydroperoxides/carbonyl/lactones/alkenes functional groups. Also, the surface/bulk concentration of these functional can be generated/selectively controlled by manipulating the temperature, environment, and treatment period. Depending upon the functional group needs, the extent of functionalization of PP can be achieved by using the high-temperature route in shorter duration. The potential applications of functionalized PP can be demonstrated in the areas of polymer blends/grafting for improving mechanical/electronic properties, metallation, and membranes.

In inert atmosphere and below the treatment temperature of 280°C, the changes in the molecular weight of the PP were not significant. The functional groups generated using this thermal method are substantial, highly stable for a longer period, and also present below the external surface of PP. The formations of desired surface species in PP can act as interlock points for active species present in other materials.

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