The Effect of Sulfonation Treatment on the Structure and Properties of Isotactic Polypropylene Fibers Prior to the Carbonization Stage

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ABSTRACT: The effect of sulfonation treatment was investigated on the molecular structure and mechanical properties of isotactic polypropylene fibers extruded at a take up speed of 2500 m/min. It was found that at extensive sulfonation times, the sulfonated structure showed the characteristic features of carbonized structure as indicated by the results of the density and the X-ray diffraction measurements. Mechanical properties of the sulfonated samples were found to be adversely affected by the sulfonation conditions. Scanning electron microscopy observations showed surface irregularities at low sulfonation times and fiber fractures at high sulfonation times. Polarized infrared spectroscopy measurements analysed by curve fitting procedure showed increasing molecular orientation of long helical chain segments represented by the IR band at 841 cm^{-1} whereas amorphous structure represented by the IR band at 2723 cm^{-1} showed gradual loss of orientation with the progress of sulfonation. IR bands assigned to the sulfonic acid groups formed during sulfonation treatment showed perpendicular polarization and low molecular orientation characteristics indicating the initiation and the development of crosslinking process being perpendicular to the fiber axis direction. Analysis of the equatorial X-ray diffraction traces showed the loss of crystallinity where the paracrystalline phase disappeared faster than the crystalline α-monoclinic phase. During the sulfonation treatment, content of amorphous phase showed gradual increase in line with decreasing crystallinity. In accordance with the loss of crystallinity, apparent crystallite sizes corresponding to the 110, 040 and 130 planes of the α-monoclinic phase also decreased gradually with increasing sulfonation time. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 3375–3389, 2012

Key words: polypropylene; sulfonation; thermal stabilization; IR-spectroscopy; X-ray diffraction

INTRODUCTION

Carbon fibers are now extensively used in polymer-matrix, metal-matrix, and carbon-matrix high performance composite systems[1] in the form of 2-D and 3-D textile preforms, staple fibers, continous rovings, and prepregs.[2,3] The success of the carbon fibers are mainly due to their high tensile strength, high specific stiffness, corrosion resistance, and light weight characteristics for the applications mostly in aerospace, automotive, and in civil engineering projects involving structural and nonstructural systems. Because of high electrical conductivity characteristics, carbon fibers also find applications in electromagnetic radiation shielding applications.[4]

The production of carbon fiber reinforced composites can be performed through the use of compression molding, injection molding, filament winding, tape winding, vacuum bagging, and liquid molding.[5] Carbon fibers can be commercially manufactured from a variety of precursors including viscose rayon,[6] mesophase pitch,[7] and polyacrylonitrile.[8]

Carbon fiber manufacturing involves an initial thermal stabilization stage to prepare the precursor to withstand the high temperatures involved in the subsequent carbonization stage. Carbonization stage is usually carried out in an inert atmosphere[6] usually in nitrogen atmosphere for temperatures up to 1200°C and argon atmosphere for higher temperatures.[1] Carbonization stage may be followed by an optional stage of graphitization up to 2800°C depending on the intended end use.[1]

It is well known that before carbonization stage, thermal stabilization, and chemical resistance of polyolefins, in particular polypropylene, may be improved by means of a process involving crosslinking. Crosslinking of polyolefins can be performed through the use of sulfonation treatment using highly concentrated sulfuric acid,[9–14] fuming sulfuric acid,[15–17] sulfuryl chloride,[18] and chlorosulfonic acid.[19–24]

Crosslinking may also be carried out by alternate means including γ-irradiation, silane grafting, and

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organic peroxide initiated systems. Treatments with these methods may result in several side reactions including chain-scission, which may have adverse effects on the mechanical properties. It is known, for example, that γ-irradiation of polyethylene results in a considerable amount of chain-scission, which eventually leads to a decrease in the fiber strength. Crosslinking by means of organic peroxides, on the other hand, for polyethylene is known to occur without main-chain scission.[25]

Silane crosslinking of isotactic polypropylene is usually carried out by the grafting of silane on to the backbone of polymer chains in a melt compounding process incorporating a silane, for example, vinyl trialkoxy silane, in the presence of a peroxide. During the melt compounding process, the silane grafted polymer is hydrolyzed in warm water and crosslinked by forming Si—O—Si linkages. This process is now widely used for the production of cables and wires.[26]

It is shown that silane crosslinking increases the thermal stability and crystallization temperature of silane-crosslinked polypropylene in comparison with pure polyproplene. Gel content with silane cross linking is either absent[27] or relatively low[26] in the region of 30–35%.

Polypropylene is found to be difficult to crosslink by ionizing radiation due to the fact that the crosslinking and thermal degradation occur at the same time thereby leading to deterioration of physical properties. For these reasons, radiation crosslinking for polypropylene is not performed for wire insulation and heat-shrinkable tubing applications.[28] Ionizing radiation is known to cause chain-scission and crosslinking of polypropylene chains in almost equal proportions whereas crosslinking is said to be the predominant factor in the case of polyethylene.[29]

It is shown that the temperature during the radiation crosslinking is an important parameter. When the temperature during radiation is below the glass transition temperature of polymer, only degradation occurs due to low chain mobility in a glassy state. When the irradiation occurs below T_g, the generated free-radicals are said to be unable to react with each other. Whereas when the irradiaton temperature is raised above the T_g of the polymer, due to the mobility of polymer chains relative to each other, crosslinking is said to occur.

Above T_g, the free radicals formed can react with each other relatively easily by forming new bonds and crosslinking taking place subsequently.[30] This shows the importance of irradiation temperature for polymer mobility. In general, it is known that flexible chain polymers such as polyolefins are easier to crosslink than rigid-chain polymers where crosslinking temperature of rigid chains are higher than the flexible polymers. It is well established that cross-linking can only take place above the melting temperatures of the polymers.[30]

It is well understood that polypropylene experiences chain-scission reactions during the peroxide initiated crosslinking, which eventually results in the lowering of molecular weight and narrowing the molecular weight distributions.[31] According to the published literature,[31] it has been found that the peroxide crosslinking of polypropylene is more complicated than polyethylene due to the simultaneous formation of chain scission and crosslinking, which leads to physical deterioration and eventually poor mechanical properties.

However, the use of coagents together with organic peroxides is shown to speed up the crosslinking of polypropylene. The most frequently used coagents are polyfunctional monomers such as p-benzoquinone, hydroquinone,[32] and pentaerythritol tetra allyl ether,[33] which have been shown to be very efficient coagents for crosslinking.

In an investigation[34] using dicumyl peroxide, a highly efficient crosslinking has been reported in the presence of sulfur being used as a coagent at a temperature of 170°C. In this study, sulfur is said to suppress the undesirable side reactions including polymer chain scission. About 80% gel fraction was obtained when a small amount of sulfur was added to organic peroxide.[35]

The aim of the present investigation is to understand the underlying mechanisms and the effect of sulfonation on the molecular structure parameters including % crystallinity, crystallite size, and molecular orientation together with mechanical properties for the sulfonated isotactic polypropylene fibers extruded at a take-up speed of 2500 m/min.

EXPERIMENTAL DETAILS

Fiber production

The melt spinning of isotactic polypropylene fibers were carried out using Barmag® CF spinning machine operating at an extrusion temperature of 235°C with a constant throughput of 9.12 g/min. In the present investigation, extrusion speed of 2500 m/min was used. Basell Polyolefins isotactic polypropylene granules with a melt flow index of 35 g/10 mins, with weight average molecular weight of 179,000 and polydispersity (M_w/M_n) of 4.6 were used to produce fibers. The melt-extruded filaments were immediately solidified with the assistance of cooling air blow speed of 40–70 m/s and a cooling air blow temperature of 18–19°C. During the melt-extrusion stage, a spinnerrette pressure of 60–70 bar and spinnerrette hole diameter of 200–400 μm was used. The melt-extrusion was performed with environmental conditions having the typical characteristics of 70% relative humidity and 15°C temperature.

Sulfonation procedure

Sulfonation of melt-extruded isotactic polypropylene fiber produced with a take-up speed of 2500 m/min was carried out using highly concentrated sulfuric acid (95–97% conc.) at a constant temperature of 120°C. Sulfonation was performed in a stainless steel heater bath with an electrical resistance controller to vary the temperature up to the desired sulfonation temperature with a heating rate of at least 0.5°C/min. Higher heating rate (i.e., 1°C/min) resulted in a degradation of the sample due to the negative effects of rapid heating. The sulfonation temperature was also externally controlled with an alcohol-based thermometer. The samples were wound onto stainless steel frame with the aim of constraining the samples to prevent shrinkage and subsequently were inserted into the sulfonation bath. The sulfonation bath temperature was then slowly heated to 120°C and kept there for various amounts of times. After the sulfonation treatment for a predetermined time, the samples were taken out, rinsed in three steps by sulfuric acid aqueous solutions with weight percentage of 62.5 (50°Bé), 48.5 (40°Bé) and 35.5 (30°Bé) for 30 min and finally pure water. The rinsed samples were dried at 120°C for 1–2 h until the weight is constant.

EXPERIMENTAL DATA COLLECTION

Infrared measurements

Perkin Elmer® Spectrum 400 FT-IR spectrometer equipped with a KRS-5-based wire grid polarizer was used for infrared dichroic measurements using single reflection diamond based GladiATR® model ATR attachment. In all cases, the fiber sample remained in a fixed North–South direction through the experiments with the aim of using the same area in the two polarization directions and the polarizer was rotated to obtain spectra for different polarization directions. In all cases, 50 interferograms of a sample were averaged and transformed with medium Norton-Beer apodization function. Each sample spectrum was ratioed against a corresponding number of background scans using the same instrument settings. Finally, all the spectra were analyzed using the OMNIC® software and curve fitting procedures where appropriate.

X-ray diffraction

The wide-angle X-ray traces were obtained using a Bruker® AXS D8 Advance X-ray diffractometer system utilizing nickel filtered CuKα radiation (wavelength of 0.154056 nm) and voltage and current settings of 40 kV and 40 mA, respectively. Counting was carried out at 10 steps per degree. The observed equatorial X-ray scattering data in the 5–35° 2θ range

TABLE I
Characteristics of Untreated and Sulfonated Isotactic Polypropylene Fibers

Sulfonation time (hours)	Density g/cm^3	Fiber thickness μm	Fiber thickness loss (%)
0	0.9009	27.74	0
0.5	0.9315	25.94	6.49
1	0.9547	25.67	7.39
2	1.0164	25.60	7.72
3	1.0561	23.76	14.35
4	1.2356	23.75	14.38
6	1.657	22.85	17.63
8	1.696	20.97	24.40

was corrected for Lorentz, polarization and incoherent scatter effects and finally normalized to a convenient standard area.

Density measurements

Density values were evaluated using a density gradient column operating at 23°C. The column was prepared using zinc (II) chloride (ρ = 2.91 g/cm^3) and distilled water for the measurement of the density of the untreated and sulfonated samples. The samples were allowed ∼ 24 h to reach their equilibrium level of displacement. Density gradient column is calibrated by adding a set of known and calibrated densities and plotting a graph of the density of the floats versus the height at which each calibrated float settles after 24 h in the column. The calibration graph is fitted with a linear function, which is then used for the determination of the densities of the unknown samples. The results are accurate to about ± 0.0001.

Care was exercised with the handling of the samples. The samples were clearly identified by tying with different number of knots. The column was prepared by deciding the upper and lower limits of the column densities. For example, for the sulfonated samples with sulfonation time range of 2–4 h, lower and upper density limits of 1.0 and 1.25 g/cm^3 was prepared. In the case of the samples sulfonated for 6 and 8 h, a density column with a higher density range of 1.5 and 1.72 g/cm^3 was prepared. Before the preparation of the density columns, density of each sample was determined on a trial and error basis. The density values obtained from the density gradient column are an average of five readings. The densities (ρ) of the untreated and sulfonated samples are presented in Table I.

Mechanical property measurements

Fiber mechanical properties were measured using Zwick-Roell 1446 tensile tester at room temperature.

A crosshead speed (stretching rate) of 12.5 mm/min was used for all the experiments. The initial length of the sample was set at 25 mm. Careful attention was taken to minimize stretching and slippage of the filaments before testing and while placing the sample in the grips. Tensile modulus was evaluated from the initial slope of the tensile curve. The elongation and tensile strength at break were determined at the position of break. Tensile strength and tensile modulus were calculated in textile units of N/tex. Reported values were averages of at least 10 tests.

Tensile strength in GPa is related to N/Tex by the relation

$$\text{Tensile Strength (GPa)} = \text{Tensile Strength (N/Tex)}$$
$$\times \text{Density(g/cm}^3)\quad (1)$$

Where the densities of the samples used in Eq. (1) are listed in Table I.

Scanning electron microscopy

Surface morphology of the fiber samples was examined using an LEO 440 Scanning Electron Microscope (SEM) with an operating voltage of 10 kV for most specimens and specimen to detector distances ranging from 8 to 12 mm, respectively. Specimen surfaces were coated with gold to enhance the conductivity and to prevent electrostatic charging effects.

EXPERIMENTAL DATA ANALYSIS

X-ray data-curve fitting

All the X-ray diffraction traces obtained from the extruded isotactic polypropylene samples were fitted with a curve fitting procedure developed by Hindeleh et al.[36] to separate overlapping peaks. Each profile is considered to have the combination of Gaussian and Cauchy functions. When the observed and calculated intensity traces converge to the best acceptable parameters, the computer program provides the list of accurate peak parameters in terms of profile function parameter (f), peak height, peak breadth and peak position. In the curve fitting program, profile function parameter also known as peak shape factor is allowed to vary between 0 and 1 and effectively describes the tail region of the profiles. When profile function parameter (f) is equal to unity gives a Gaussian intensity distribution and when equal to zero gives a Cauchy shape. Initially, a value of f equal to 0.5 is given to start the fitting process and then the minimization procedure finds the best peak parameters.

Infrared data – curve fitting

In the present work, the parallel and perpendicular polarization spectra were fitted independently, allowing the peak positions and peak widths to vary freely, using the peak positions previously found using OMNIC® software as a guide to the starting values. Finally, the peak positions and the peak widths obtained from the two spectra were averaged and the parallel and perpendicular spectra were refitted, fixing the positions and the widths at these average values and allowing only the peak heights to vary.

Calculation of orientation parameters of polarized infrared data[37]

Because of the uniaxial orientation nature of fibers arising from cylindrical symmetry, the calculation of orientation parameters obtained from the infrared data analysis can be carried out using the dichroic ratio defined in Eq. (2):

$$D = A_{//}/A_{\perp}\quad (2)$$

where $A_{//}$ and $A_{\perp}$ are the measured absorbance values for radiation polarized parallel and perpendicular to the fiber axis, respectively. To a good approximation, the dichroic ratio is related to the orientation parameter $\langle P_2(\cos\theta)\rangle$ by

$$\langle P_2\rangle = \langle P_{200}\rangle = \langle P_2(\cos\theta)\rangle = \frac{D-1}{D+2}\cdot\frac{2}{(3.\cos^2\alpha - 1)}\quad (3)$$

where θ is the angle between the local chain axis and the fiber axis, and α is the transition moment angle between the associated vibrational mode and the chain axis.

Evaluation of the apparent X-ray crystallinity

Apparent X-ray crystallinity is based on the ratio of the integrated intensity under the resolved peaks to the integrated intensity of the total scatter under the experimental trace.[38] This definition can be expressed as in Eq. (4)

$$\chi_c = \frac{\int_0^\infty \mathbf{I}_{cr}(2\theta)d(2\theta)}{\int_0^\infty \mathbf{I}_{tot}(2\theta)d(2\theta)}\quad (4)$$

The area under the background is considered to correspond to the unoriented noncrystalline scatter. It should be emphasized that apparent X-ray crystallinity is defined between two arbitrarily chosen angles and should be considered an optimum mathematical solution. In this work, apparent X-ray crystallinity was estimated in the 2θ range between 5 and 35°.
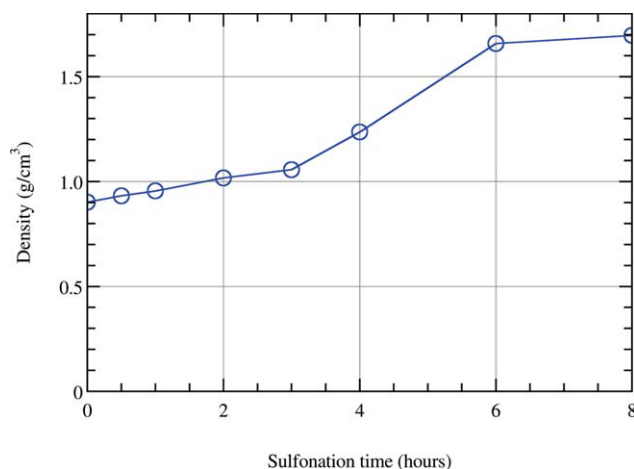
Figure 1 Variation of density values of untreated and sulfonated isotactic polypropylene fibers as a function of sulfonation time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Evaluation of the apparent crystallite size

The peak widths at half-height have been corrected using the Stoke's deconvolution procedure.[39]

Finally, the apparent crystallite size of a given reflection was calculated using the Scherrer equation:

$$L(hkl) = \frac{k.\lambda}{\beta.\cos(\theta)} \tag{5}$$

where θ is the Bragg angle for the reflection concerned, λ is the wavelength of radiation (wavelength of 0.154056 nm), L(hkl) is the mean length of the crystallite perpendicular to the planes (hkl), β is either the integral breadth or the breadth at half maximum intensity in radians, and K is a Scherrer parameter usually taken as 1 for integral breadths and 0.89 for half-widths. Hexamethylene-tetramine compacted at 85°C was used for the instrumental broadening correction.

RESULTS AND DISCUSSION

Fiber thickness variations

Table I shows the change of fiber thickness of sulfonated samples as a function of sulfonation time. The thickness of the sulfonated samples with treatment time of up to 8 h is reduced to 20.97 μm as compared to 27.74 μm of the original untreated isotactic polypropylene fiber. The fiber thickness falls off sharply initially after the sulfonation time of 2 h and further fall continues with sulfonation times of 3, 4, and 6 h, respectively. Most drastic fall is experienced after 8 h of sulfonation time where approximately 25% loss in fiber thickness occurs with respect to the untreated sample thickness (Table I). The drastic

falls in fiber thickness suggest extensive thermal degradation with subsequent loss in mechanical properties as will be mentioned in detail below.

Density of the sulfonated fibers

Table I and Figure 1 show the density values of the untreated and sulfonated samples as a function of sulfonation times ranging from 0.5 to 8 h. Density values increase in an upward trend between 0.5 and 3 h of sulfonation, showing an increase of density from 0.9315 to 1.056 g/cm³ followed by a stepwise increase to 1.2356 g/cm³ for the sample sulfonated for 4 h. After the first half-an-hour of sulfonation treatment, there seems to be considerable sulfuric acid asisted swelling, as a result, more fibrous bulk material becomes accessible to the effects of sulfuric acid and the density increase becomes considerably high (Table I).

A significant increase of density is observed for the samples sulfonated for 6 and 8 h where density values range from 1.657 to 1.696 g/cm³. It is clear that extensive sulfonation times from 6 to 8 h at 120°C seems to have resulted in the carbonization of the samples as indicated by the relatively high density values. According to a patent recently published,[40] for a carbonized isotactic polypropylene fiber, a density of 1.68 g/cm³ is reported to be sufficient for exhibiting sufficiently high conductivity and electromagnetic shielding effectiveness. The same patent also describes the necessary criteria for the isotactic polypropylene precursor prior to carbonization. The precursor is expected to show the characteristics of at least 50% carbon content, a density of 1.38 g/cm³, an oxygen content of at least 4% and a limiting oxygen index of at least 35%. Accordingly, a sulfonation time of 4.64 h should yield a density of 1.38 g/cm³ at a sulfonation temperature of 120°C. It has been reported that a theoretical density value of at least 1.6 g/cm³ is necessary for completely aromatized structure.[41] The increases in the densities confirm the compaction of the whole fiber structures due to the development of extensive crosslinking in the structure of the sulfonated fiber samples.

Assessment of the mechanical properties

Figure 2 shows the stress–strain curves for the untreated and sulfonated samples with sulfonation times between 0.5 and 4 hours. Unfortunately, the samples sulfonated for 6 and 8 h showed excessive thermal degradation, and therefore no mechanical property testing could be performed. Figures 3–5 show the effect of sulfonation on the tensile strength, extension at break, and tensile modulus, respectively. Tensile strength and extension at break
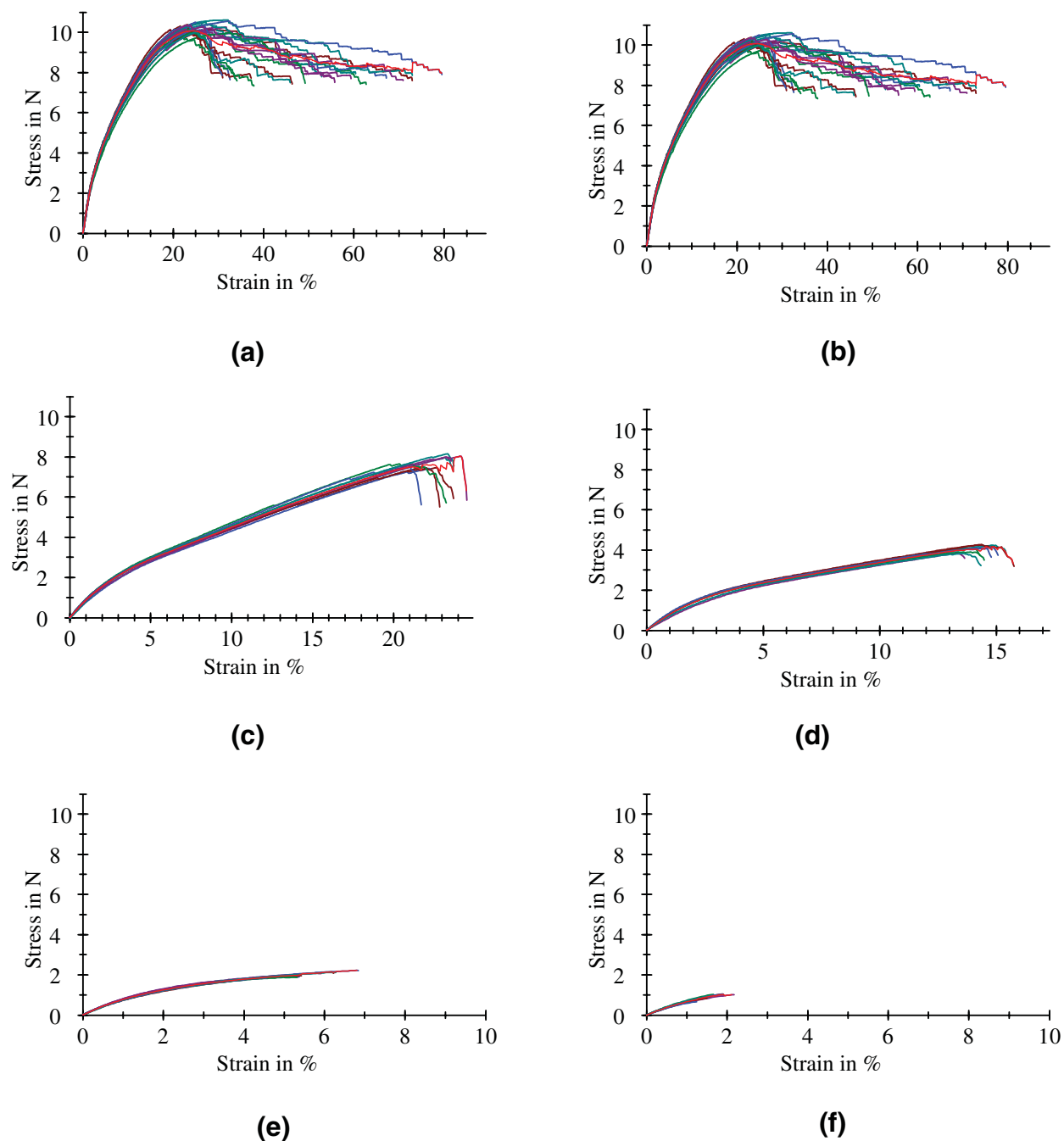
(a)

(b)

(c)

(d)

(e)

(f)

Figure 2 Stress-strain curves of untreated an sulfonated isotactic polypropylene fibers. Sulfonation conditions are indicated underneath each graph. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary. com.]

decreases continuously during the sulfonation reaction, whereas the tensile modulus decreases at first by more than 43.4 % of its original value and then increases with the progress of treatment.

Sulfonation treatment resulted in the loss of tensile strength of the sulfonated samples with progressive sulfonation for the samples sulfonated between 0.5 and 4 h. The tensile strength loss of chlorosulfonated polyethylene fibers has also been reported with the progress of chlorosulfonation.[21] As shown in Figure 3

the same loss trend is observed in the present investigation for the tensile strength as a result of extensive thermal degradation. Extension at break results also show the same trend as that of tensile strength with progressive sulfonation (Fig. 4).

However, the same loss trend is not observed for the tensile modulus results shown in Figure 5 where an initial loss is followed by a steady increase after the sulfonation time of 1 h, possibly due to the formation of intermolecularly crosslinked structure
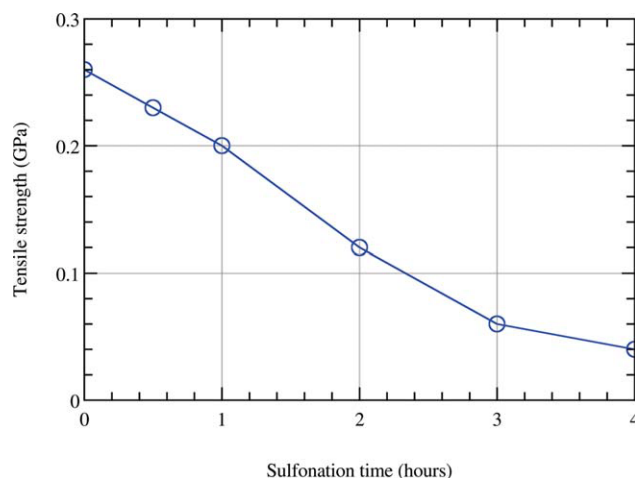
Figure 3 Variation of tensile strength of untreated and sulfonated isotactic polypropylene fibers extruded at a take up speed of 2500 m/min, sulfonated at 120°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 5 Variation of tensile modulus of untreated and sulfonated isotactic polypropylene fibers extruded at a take up speed of 2500 m/min, sulfonated at 120°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

during the sulfonation stage. It is already known that the tensile modulus depends mainly on molecular orientation. The initial loss in tensile modulus shown in Figure 5 suggests that there was a significant molecular orientation loss for the sample sulfonated for 30 min.

Tensile strength loss results are listed in Table II. The results show an initial loss of 11.5% tensile strength after half-an-hour of sulfonation. The tensile strength loss shows an upward trend with progressive sulfonation and reaches an approximate value of 85% tensile strength loss for the sample sulfonated for 4 h with respect to the untreated sample.

A similar trend was observed with the extention at break results. The results presented in Figure 4
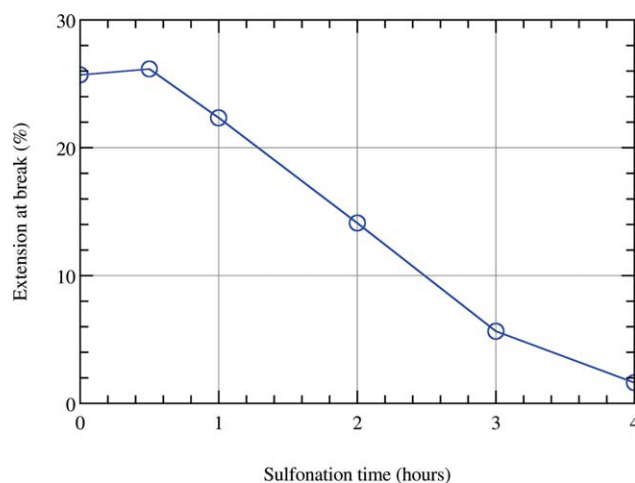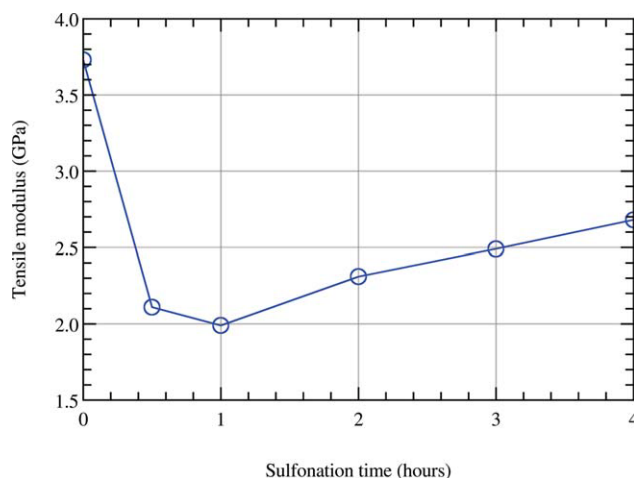

Figure 4 Variation of extension at break (%) of untreated and sulfonated isotactic polypropylene fibers extruded at a take up speed of 2500 m/min, sulfonated at 120°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

shows an initial small increase followed by a steady decrease from an initial value of 25.7% for the untreated sample to 1.6% for the 8 h sulfonated sample.

In essence, the decrease in the tensile strength appears to be due to the thermal degradation initiated chain-scission, whereas the increase in tensile modulus may be attributed to the increase in cross-linking occuring initially in the amorphous regions with gradual progress to the highly oriented para-crystalline regions. After 30 min of treatment, sulfonation results in the swelling of the fibrils resulting in the loss of orientation where the fibrous bulk material becomes available for the sulfuric acid diffusion into the interior parts of the fibers. As mentioned above, in the first half-an-hour, there seems to be considerable loss of molecular orientation with respect to the untreated sample. The loss in molecular orientation may be ascribed to the shrinkage of the fiber, which seems to occur in the beginning of the sulfonation treatment. During this period, the tensile modulus decreases to its minimum value (Fig. 5).

The fiber swelling naturally results in the shrinkage along the fiber axis direction, which eventually leads to a relaxation of extended chain molecules and weakening of the fibrils. This behavior ends up with a reduction in the molecular orientation with a subsequent loss of tensile strength and tensile modulus. Shrinkage of the extended chain molecules may also be brought about by a trans-to-gauche conformational changes as a result of sulfonation treatment.[42]

The structural changes starting with the swelling and sulfonation of the disordered regions ends up with the distortions of the crystalline regions as a

TABLE II
Mechanical Properties of Untreated and Sulfonated Isotactic Polypropylene Fibers

Sulfonation time (hour)	Tensile strength (GPa)	Tensile strength loss (%)	Extension at break (%)	Tensile modulus (GPa)	Tensile modulus loss (%)
0	0.26	0	25.70	3.73	0
0.5	0.23	11.538	26.16	2.11	43.43
1	0.20	23.076	22.34	1.99	46.65
2	0.12	53.846	14.11	2.31	38.07
3	0.06	76.92	5.64	2.49	33.24
4	0.04	84.61	1.62	2.68	28.15

result of sufficiently large internally built up stresses in the proximity of sulfonated regions. At this stage, it is highly likely that the crystalline regions or the surface regions of the crystalline phase exhibit progressive swelling from the surface regions to the interior parts with the subsequent disappearance with the progress of sulfonation as indicated by the loss of crystallinity as shown by the X-ray diffraction results presented below.

After 6–8 h of sulfonation at 120°C, the sulfonated fibers become so weakened due to the extensive sulfuric acid catalyzed swelling that the extended chain molecules shrink considerably to almost fully relaxed state. At this state, the relaxed chain mole-cules lose their molecular orientation along the fiber axis direction and result in the subsequent almost total loss of the mechanical properties with extended sulfonation times.

Assessment of the SEM images

Untreated isotactic polypropylene fiber extruded at 2500 m/min has a trilobal cross-section and a smooth featureless surface. With the progress of sulfonation, surface features are found to be influenced by the sulfonation treatment. After a 30-min exposure to the sulfonation solution, the fiber surface shows a minor damage, which resulted in the loss of tensile strength [Fig. 6(a)]. Extensive damage to the fiber was observed following a 4-h sulfonation treatment as can be seen in Figure 6(b). Fibers exhibited the greatest loss in tensile strength for sulfonation treatments of 6 and 8 h (Fig. 7). After a sulfonation treatment of 8-h complete breakage of the fibers was observed.

With the progress of sulfonation, sulfonated fiber surfaces exhibit cracks along the fibre axis direction [Fig. 7(a)]. A close-up view of one of these fractures shows a crosslinking fibrils shown in Figure 7(b). During the extended sulfonation times of 6 and 8 h, significant amount of sulfuric acid diffuses into the interior regions of the fiber samples and consequently sulfur dioxide (SO_2) and carbon dioxide (CO_2) gases are evolved[10,11] as a result of the sulfonation reactions at 120°C. Part of SO_2 takes part in the crosslinking reactions as part of the sulfonic acid groups (O=S(OH)=O), and the rest is liberated through the walls of the fiber. Built-up pressure caused by the SO_2 and CO_2 groups seems to have caused the rupture of the walls of the fibers during the advanced stages of the sulfonation reactions.

Figure 6 Lateral SEM images of isotactic polypropylene fiber sulfonated at (a) 120°C for 30 minutes; (b) 120°C for 4 h.

Assesment of the polarized infrared spectroscopy results

Qualitative examination of polarized infrared spectra of untreated and sulfonated samples shows that significant structural changes have taken place during the sulfonation tratement. A deeper understanding of structural changes in terms of quantitative
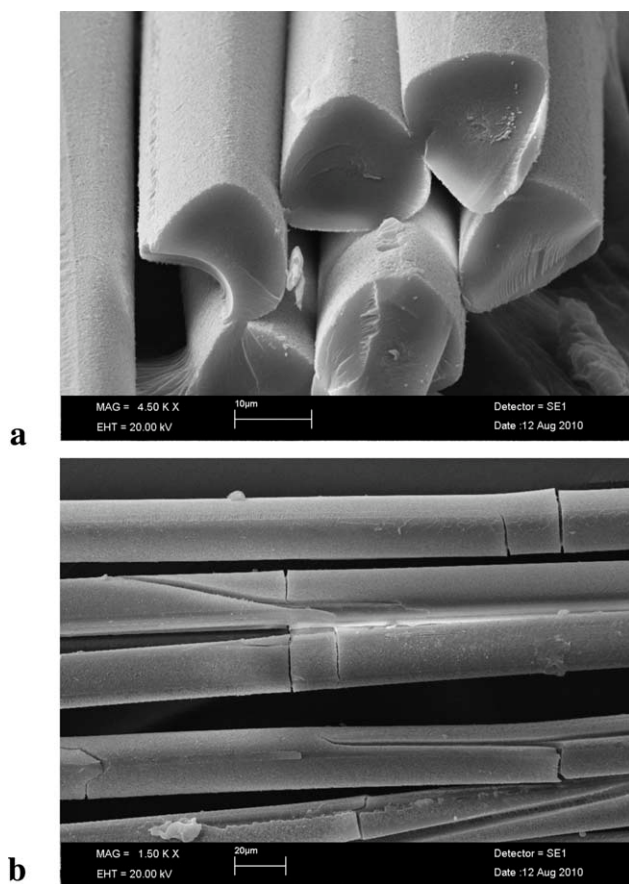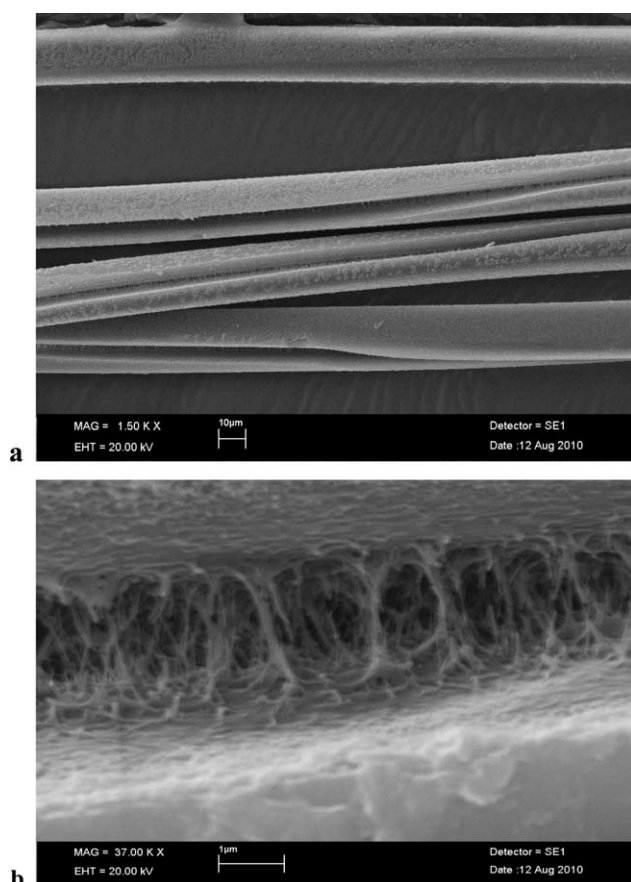
Figure 7 Untreated isotactic polypropylene fiber exposed to the sulfonation solution at 120°C for 6 h. (a) Crack formation along the fiber axis direction and (b) Interconnecting fibrils perpendicular to the fiber axis direction.

assessment of molecular orientation on the effects of sulfonation of isotactic polypropylene fibers may be obtained by analysing the polarized infrared spectra as a function of sulfonation time.

The standard bands of untreated polypropylene occur at 1455, 1377, 1359, 1256, and 1104 cm^{-1} [Fig. 8(a)]. The IR peaks around 1220, 1168, 1104, 1044, 998, 899, 841, and 809 cm^{-1} are the characteristic regularity bands arising from the presence of helical chains.[43] These regularity bands are usually very weak or totally absent in intensity in amorphous polypropylene, which should provide some ideas about the possible molecular changes take place during the sulfonation stage.

Figure 8(a,b) clearly show the polarization directions of both regularity peaks in the 1025–775 cm^{-1} region (Figure 9) and sulfonation related peaks in the 1300–1025 cm^{-1} region. The main regularity peaks located at 998, 973, and 841 cm^{-1} show parallel polarization characteristics whereas sulfonation related peaks show perpendicular polarization characteristics [Fig. 8(b)]. 998 and 841 cm^{-1} IR peaks are usually assigned to crystalline phase, whereas 973 cm^{-1} band is assigned to both crytalline and amor-

phous chains in helical conformations which can be considered as an average band.[44,45]

The regularity band located at 841 cm^{-1} showed the lowest peak width in comparison with other helical bands[46] and has been assigned to long helical chains with an average length of 12–14 units.[43] In a previous study carried out on the characterization of isotactic polypropylene films, molecular orientation parameters calculated using regularity band at 841 cm^{-1} showed excellent agreement and correlation with X-ray diffraction results.[46,47]

It was suggested that in the absence of X-ray data, the IR band at 841 cm^{-1} may be used for the determination of crystalline orientation quite confidentially. As shown in Figure 9(a,b), this peak is very much unaffected by the tails of the sulfonation peaks due to the sulfonic acid groups in the 1280–1000 cm^{-1} range. For this reason, the regularity band at 841 cm^{-1} is chosen for the detailed analysis of the behavior of the molecular orientation corresponding to the crystalline phase using a well established curve fitting procedure.

Figure 10 shows the curve fitting of 915–775 cm^{-1} region corresponding to parallel polarization spectrum of untreated sample. Resolved peak parameters for this fitting are listed in Table III. To improve the fitting, apart from the other regularity peaks at 899 and 809 cm^{-1}, additional peaks at 886, 873, 856, 830, 819, and 796 cm^{-1} were used to improve the fitting but not considered any further. During the curve fitting stages, it is a common practice to add additional peaks to improve the fitting of the tail regions of the peaks. These peaks have nothing to do with the sample or the instrumentation but used purely for practical reasons.

Molecular orientation parameter, $\langle P_2 \rangle$ evaluated for the 841 cm^{-1} peak using eqs. (2) and (3) are shown in Figure 11. Transition moment angle for this peak is taken as 0° (Table IV).

The results show that the molecular orientation corresponding to the crystalline phase arising from the dichroic behavior of this peak, exhibit an increasing trend from a value of 0.72 to 0.85. This peak disappears totally from the polarized IR spectra after 6 h of sulfonation time. It shows that during the sulfonation treatment, crystalline phase shows an increasing molecular orientation with the progress of sulfonation time. It is also clear that the crystalline phase diminishes with the increasing sulfonation time. When all these results are put together, it is clear that the sulfonation results in the gradual elimination of highly ordered crystalline phase, whereas the remaining ordered material exhibits gradually increasing molecular orientation of long chain sequences with the progress of sulfonation.

It has been reported that the IR peak at 2723 cm^{-1} corresponds to the amorphous phase.[48] Figure 12
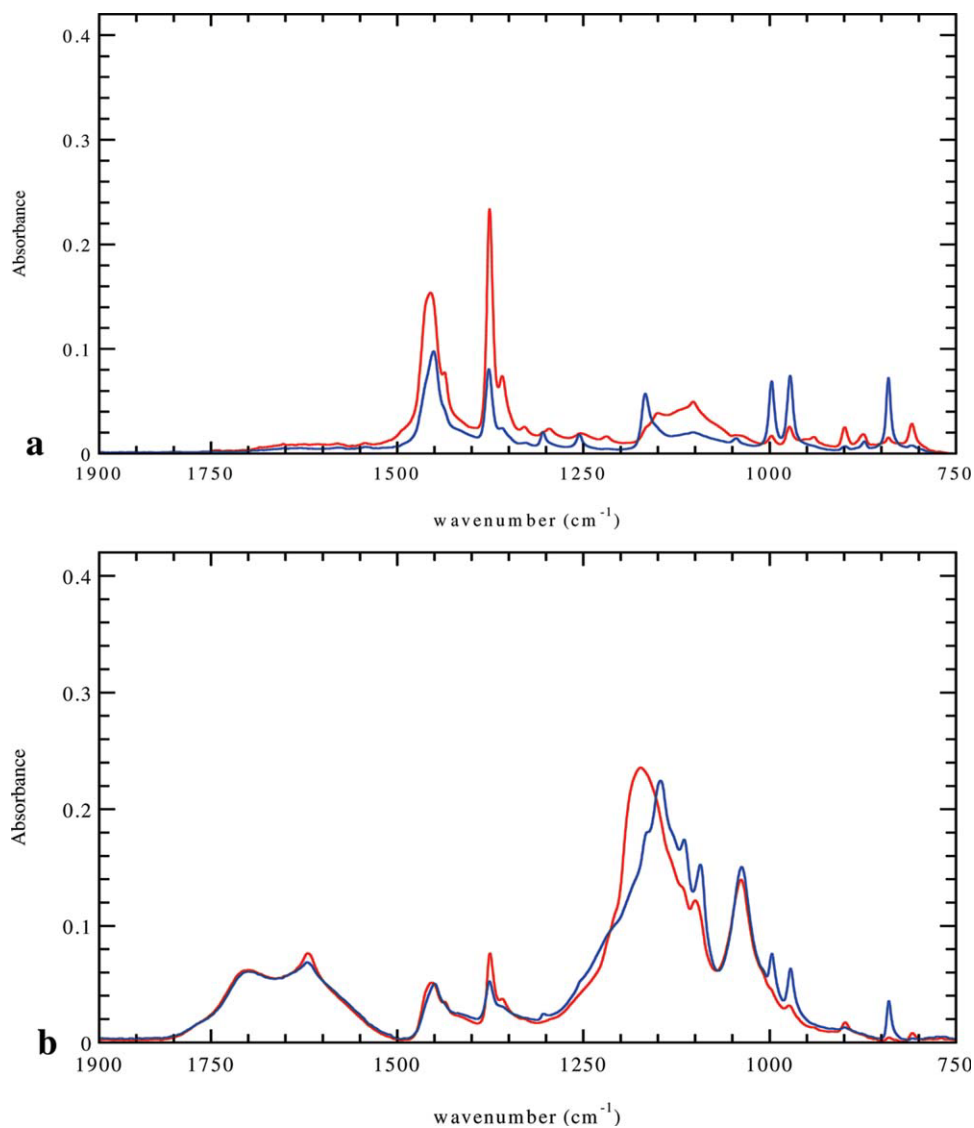
Figure 8 Polarized infrared spectra of untreated (a) and sulfonated isotactic polypropylene fibers (b) 120°C 2 h. Blue line corresponds to paralel polarization and red line corresponds to perpendicular polarization (1900–750 cm^{-1} region). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

shows the dichroic behavior of untreated and sulfonated sample in the 2750–2680 cm^{-1} region. Molecular orientation parameter $\langle P_2 \rangle$ evaluated for the 2723 cm^{-1} peak using Eq. (2) and (3) are shown in Figure 11. Showing perpendicular polarization characteristics, a transition moment angle of 90° (Table IV) has been used for this peak. Being an amorphous peak, the $\langle P_2 \rangle$ values for this peak are lower than the regularity peak at 841 cm^{-1} and show a decreasing trend from 0.58 and 0.41. After 3 h of sulfonation, this peak is lost completely.

Number of characteristic IR bands due to the sulfonic acid groups appear in the 1280–1000 cm^{-1} range. The IR band at 1040 cm^{-1} is assigned to symmetrical O=S=O stretching vibrations, whereas the IR bands centred around 1280–1080 cm^{-1} region can be assigned to asymmetrical O=S=O stretching

vibrations.[16] It is possible to assume that sulfonation reactions give rise to sulfonic acid groups, sultones and sulfate groups as O=S=O contining products.[11]

The polarized infrared spectra of the region assigned to sulfonation reactions show perpendicular polarization characteristics with rather poor dichroism. The IR peak around 1040 cm^{-1} shows a perpendicular polarization characteristic with $\langle P_2 \rangle$ values ranging from 0.19 to 0.00 showing total disorder while exhibiting a decreasing trend (Fig. 11). For this peak, transition moment angle is assumed to be 90° (Table IV). Curve fitting of the IR spectrum in the 1315–930 cm^{-1} region is performed to obtain accurate peak parameters as shown in Figure 13. The IR peak around 1167 cm^{-1} also shows perpendicular polarization characteristics and transition moment angle for this peak is also assumed to be
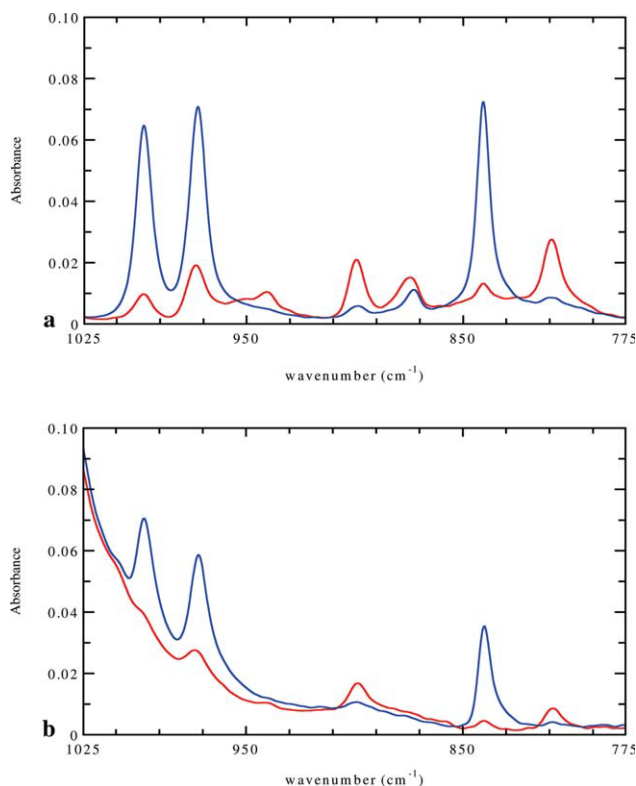
Figure 9 Polarized infrared spectra of untreated (a) and sulfonated isotactic polypropylene fibers in the 1025–775 cm^{-1} region. (b) 120°C, 2 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

90°. The $\langle P_2 \rangle$ values obtained for this peak shows a decreasing trend starting from half-an-hour to 2 h of sulfonation followed by an increasing trend from 3 to 8 h of sulfonation. The molecular orientation values of this peak is found to vary between 0.2 for the 2 h of sulfonation to 0.43 for the 6 h of sulfonation
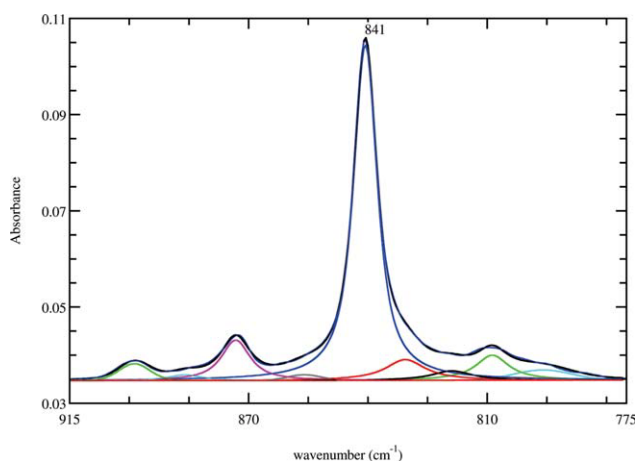
Figure 10 Curve fitting of polarized infrared spectrum of untreated isotactic polypropylene fiber. IR radiation polarized parallel to the fiber axis. 915–775 cm^{-1} region. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE III
Resolved IR Peak Parameters for Untreated Isotactic Polypropylene Fiber Extruded at 2500 m/min (915–775 cm^{-1} Range). IR Radiation Polarized Parallel to the Fiber Axis

Peak no.	Profile function parameter (f)	Peak height	Half-height width cm^{-1}	Peak position cm^{-1}
1	0.85	0.0035	10.7	899
2	0.0	0.0019	10.0	886
3	0.13	0.0084	8.9	873
4	1.0	0.0012	11.7	856
5	0.18	0.0697	7.5	841
6	0.0	0.0043	12.0	830
7	0.0	0.0019	12.0	819
8	0.7	0.0052	10.0	809
9	1.0	0.0021	20.0	796

treatment (Fig. 11). This shows that some sulfonic acid groups characterised by symmetrical O=S=O vibrations forming crosslinks during the sulfonation reaction show totally random orientation whereas those characterised by asymmetrical O=S=O vibrations show relatively higher molecular orientation values.

Assessment of the X-ray diffraction data

Wide-angle X-ray diffraction method has been used to follow the progress of sulfonation and its effect on the crystalline structure. Quantitative analysis of equatorial X-ray diffraction traces have been carried out for the determination of structural parameters in terms of crystallinity and apparent crystallite sizes of the untreated and sulfonated samples. As shown in Figure 14, the equatorial traces in the 5–35° 2θ region show three strong (110, 040 and 130) and three weak (060, 200, and 220) reflections. These reflections are attributed to α-monoclinic phase. During the peak resolution stage, an additional peak around 15.5–16° was needed to improve the fit in the tail regions of the neighbouring peaks. This peak is characterized by a relatively broad half-height width and shows the typical characteristics of a paracrystalline structure. In principle, X-ray diffraction technique is sensitive to the crystalline phase and in some cases paracrystalline phases can also be detected as a broad peak as in the present investigation.

In the published literature, paracrystalline phase was originally known as smectic phase[51–56] and in later years its name was changed to β-hexagonal phase.[57,58] This peak is indexed as (300) in the present investigation in accordance with the published literature.[57,58] The results obtained from curve fitting procedure (Fig. 15) show the presence of polymorphism where α-monoclinic and β-hexagonal phases coexist together with an amorphous phase.
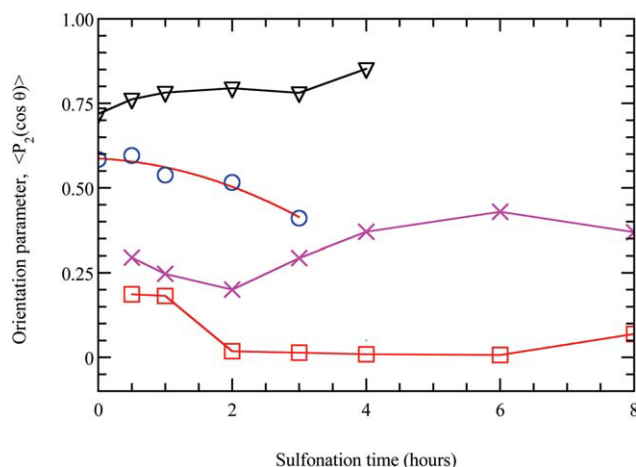
Figure 11 Variation of molecular orientation parameter ($\langle P_2 \rangle$) values of untreated and sulfonated isotactic polypropylene fibers as a function of sulfonation time. ($\triangledown$) 841 cm^{-1}; (o) 2723 cm^{-1}; ($\times$) 1167 cm^{-1}; ($\square$) 1040 cm^{-1}. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The results obtained from curve fitting stages of untreated and sulfonated samples reveal the loss of crystallinity with increasing sulfonation time. Between sulfonation times of half-an-hour and 4 h, α-monoclinic structure (unit cell dimensions of $a = 0.666$ nm, $b = 2.088$ nm, $c = 0.65$ nm, $\alpha = 90°$, $\beta = 99.5°$ and $\gamma = 90°$) is maintained but when the sulfonation time of 6 h is reached a new crystalline structure appears to take place. Tentative assignment of d-spacings obtained from the curve fitting stage leads to a modified α-monolinic phase (unit cell

TABLE IV
Polarization Directions and the Transition Moment Angles of Isotactic Polypropylene Infrared Absorption Bands in the 2800–800 cm^{-1} Region

Wavenumber cm^{-1}	Phase	Polarization	Transition moment angle (°)	Ref.
2725	A	⊥	90	48
1706	–	⊥	90	*
1622	–	⊥	90	*
1455	–	⊥	90	*
1377	A,C	⊥	70	49
1256	A,C	//	0	49
1220	C	⊥	90	48,49
1168	C	//	0	49
1104	C	⊥	90	49
1040	n/a	⊥	90	*
998	C	//	18	49
973	A,C	//	18	49
941	C	⊥	90	*
900	C	⊥	90	*
841	C	//	0	50
809	C	⊥	90	50

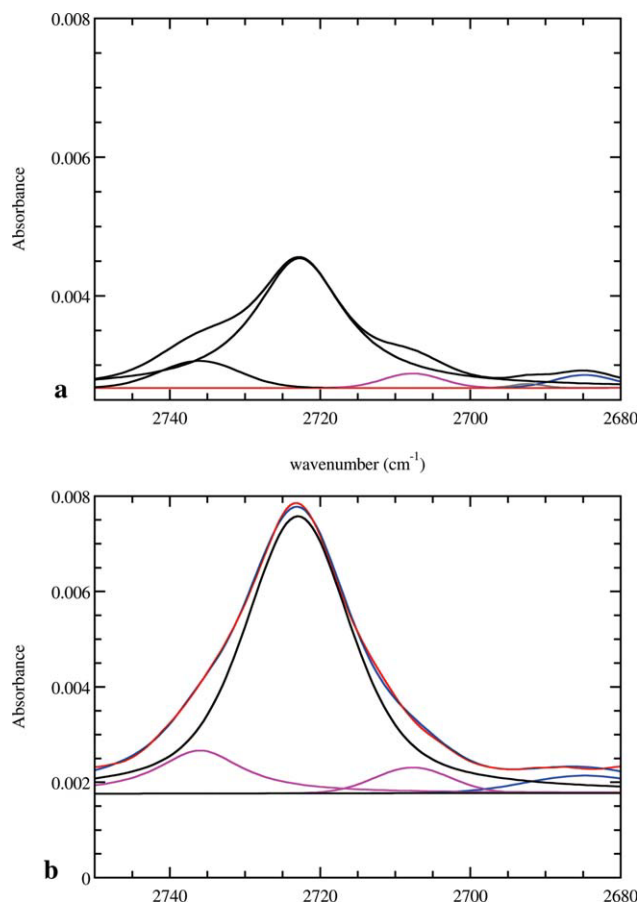Key: C, Crystalline; A, Amorphous; *, Tentative assignment.

a

b

Figure 12 Polarized infrared spectra of untreated (a) and sulfonated isotactic polypropylene fibers in the 2750–2680 cm^{-1} region. (b) 120°C, 2 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

dimensions $a = 0.686$ nm, $b = 2.153$ nm, $c = 0.6504$ nm, $\alpha = 90°$, $\beta = 99.5°$, $\gamma = 90°$). The chain cross sectional area of the modified unit cell in the a–b plane
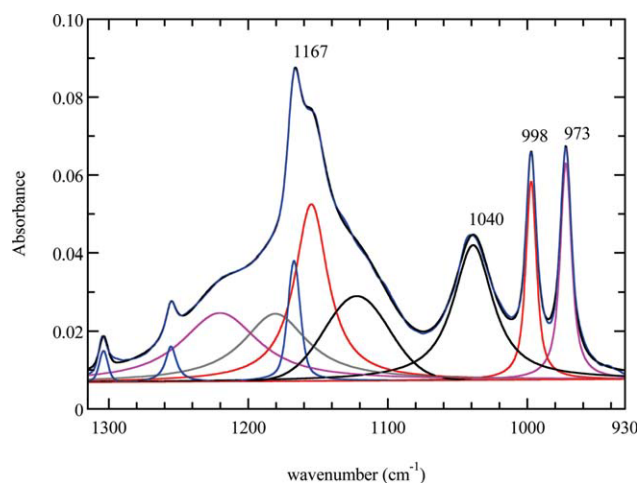

Figure 13 Curve fitting of polarized infrared spectrum of sulfonated (30 min at 120°C) isotactic polypropylene fiber. IR radiation polarized parallel to the fiber axis. 1315–930 cm^{-1} region. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
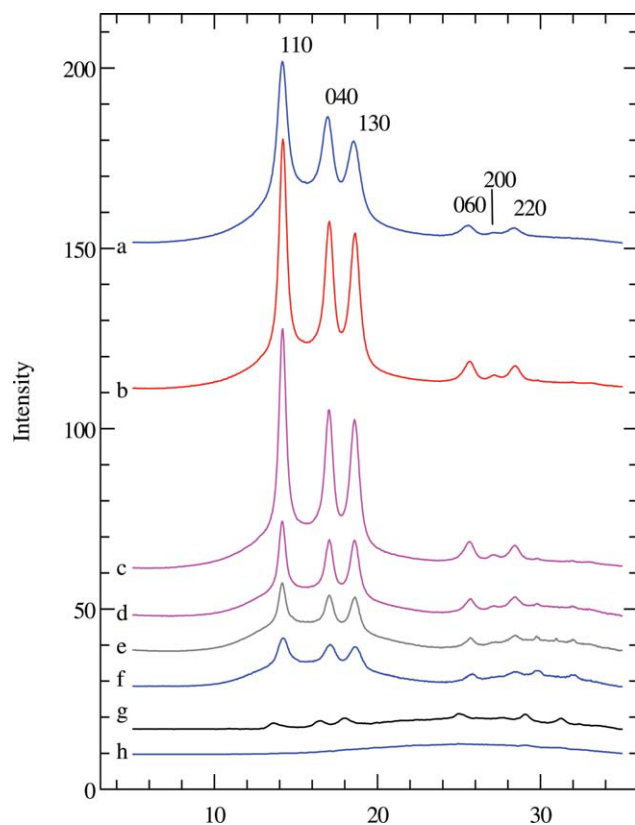
Figure 14 Equatorial X-ray diffraction traces of untreated (a) and sulfonated isotactic polypropylene fibers. (b) 120°C, 30 min; (c) 120°C, 1 h; (d) 120°C, 2 h; (e) 120°C, 3 h; (f) 120°C, 4 h; (g) 120°C, 6 h; (h) 120°C, 8 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

appears to be expanded by an amount of 5.8% from an original value of 0.344 to 0.364 nm.[2]

Sulfonation reaction is shown to have a significant effect on the crystalline structure and the crystallinity of the sulfonated samples. In general, the intensities of the crystalline peaks due to α-monoclinic phase and modified α-monoclinic phase are found to decrease in accordance with increasing sulfonation time up to 6 h. When the sulfonation time of 8 h is reached, both crystalline phases disappear almost completely leaving minor amount behind.

This implies that the crystalline regions within the polypropylene fibers are destroyed with extended sulfonation times which in turn indicates that the amorphous region is greatly enhanced. This is a direct and conclusive evidence that the polymer structure has become much more amorphous in nature with extended sulfonation times.

Results shown in Figure 17 reveal the gradual loss of apparent total X-ray crystallinity evaluated using Eq. (4) with the progress of sulfonation. In fact, α-monoclinic phase is gradually destroyed when the sulfonation time of 4 h is reached and its modified form is destroyed with higher sulfonation times,

whereas paracrystalline β-hexagonal phase is totally lost by the sulfonation time of 6 h. The most impressive improvement has been with the progressive increase of amorphous structure which reaches 97% after 8 h of sulfonation (Fig. 17).

Curve fitting of equatorial traces corresponding to the samples with sultonation times of 6 and 8 h [Fig. 16(a,b)] shows a well defined broad peak centred around a scattering angle of 25° with a d-spacing of 0.355 nm. This shows that highly amorphous carbonized structure exists in the samples with extensive sulfonation times. It is well known that the d-spacing between two graphene layers (d_{002}) in a single graphitic crystal is 0.335 nm.

Depending on the manufacturing conditions and the type of precursors, basic structural units of many carbon fibers may contain irregularly stacked turbostratic layers. It has been reported that irregular stacking of graphene planes in PAN-based carbon fibers may be increased to 0.3434 nm.[1] It is highly likely that the extended periods of sulfonation results in the formation of highly irregularly crosslinked structure which, upon further carbonization may decrease the d-spacing of 0.355 nm to a value closer to the d-spacing of 0.335 nm.

Once the experimental half-height widths are corrected for the instrumental effects, then the corrected half-height widths can be used for the evaluation of
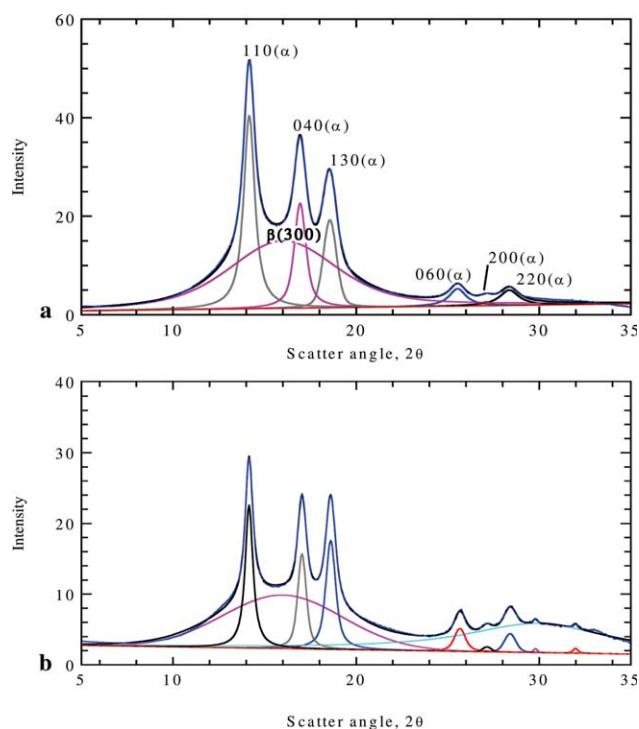

Figure 15 Curve fitting of equatorial X-ray diffraction traces of untreated (a) and sulfonated isotactic polypropylene fibers. (b) 120°C, 2 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
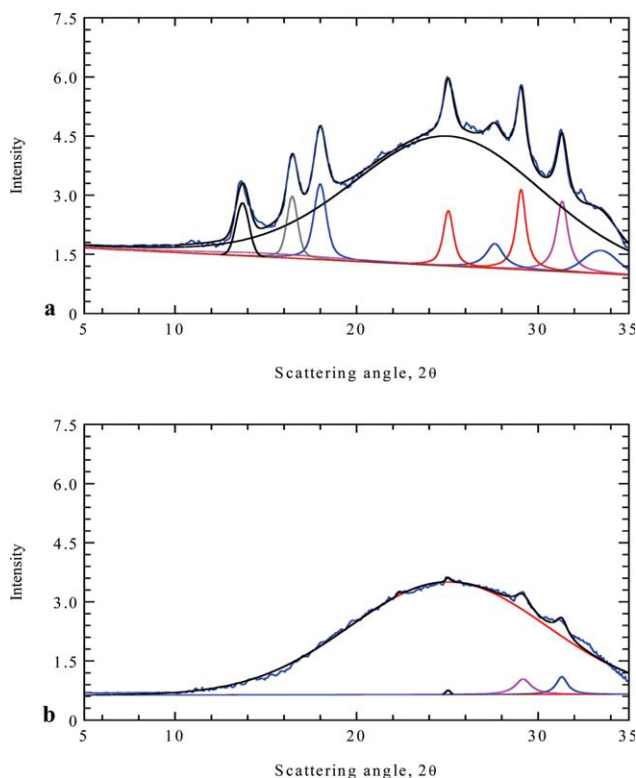
Figure 16 Curve fitting of equatorial X-ray diffraction traces of sulfonated isotactic polypropylene fibers. (a) 120°C, 6 h; (b) 120°C, 8 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary. com.]

apparent crystallite sizes perpendicular to the diffracting planes. For this reason, Scherrers Eq. (5) is used for the determination of apparent crystallite sizes arising from the α-monoclinic structure. Curve fitting of equatorial traces have been used to evalu-
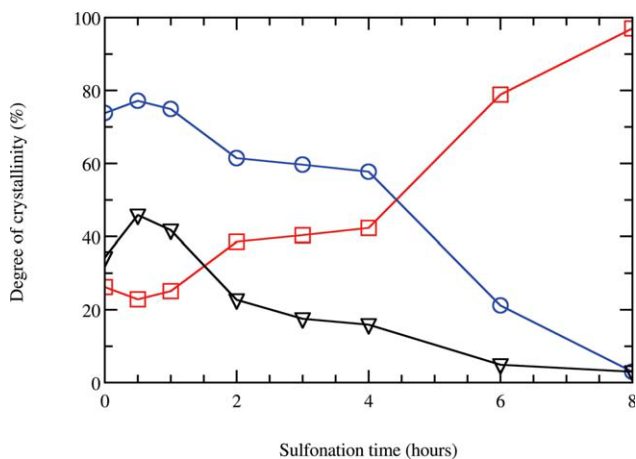

Figure 17 Variation of apparent crystallinity of untreated and sulfonated isotactic polypropylene fibers as a function of sulfonation time. (o) Apparent total X-ray crystallinity (α + β phases); (▽) α-monoclinic phase (until 4 h) and modified α-monoclinic phase (6 and 8 h); (□) amorphous content. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
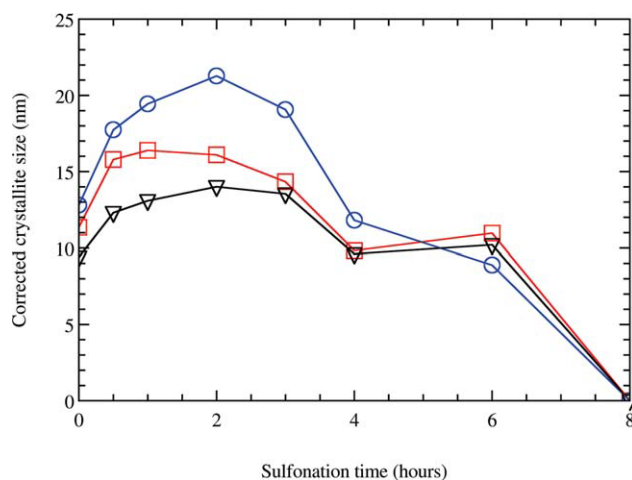
Figure 18 Variation of apparent corrected crystallite sizes corresponding to untreated and sulfonated isotactic polypropylene fibers as a function of sulfonation time. (o) α(110); (□) α(040); (▽) α(130) planes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

ate the apparent crystallite sizes of the untreated and sulfonated samples. The corrected apparent crystallite sizes perpendicular to the 110, 040, and 130 planes of the α-monoclinic and modified α-monoclinic structure are presented in Figure 18.

The crystallite size perpendicular to the 110 planes of the α-monoclinic structure shows a gradual increase up to the sulfonation time of 2 h followed by a gradual decrease. Crystallite sizes due to the (040) and (130) reflections show a similar behavior except that the values show reverse order when the sulfonation time of 6 h is reached (Fig. 18).

CONCLUSIONS

Molecular structure and mechanical properties of isotactic polypropylene fibers were found to be significantly influenced by the conditions of sulfonation treatment. Extensive sulfonation times yielded highly crosslinked and carbonized structure as indicated by the results obtained from the density and X-ray diffraction measurements. Sulfonation conditions also had an adverse effect on the mechanical properties as supported by the SEM observations, which exhibited surface irregularities at low sulfonation times and fiber surface fractures at high sulfonation times.

Analysis of polarized infrared spectra showed increasing molecular orientation of long helical chain segments, whereas amorphous structure showed gradual loss of orientation with the progress of sulfonation. It suggests that remnants of the crystalline structure orients along the fiber axis direction while the sulfonation is in progress. IR bands characteristic of sulfonic acid groups exhibited perpendicular

polarization and low molecular orientation characteristics indicating the formation of crosslinked structure perpendicular to the fiber axis direction.

The results obtained from the analysis of equatorial X-ray diffraction traces showed the loss of crystalline structure where the paracrystalline phase disappeared faster than the crystalline α-monoclinic phase. During the sulfonation treatment, amorphous phase fraction showed gradual increase in line with decresing crystalline fraction. In accordance with the loss of crystallinity, crystallite sizes corresponding to the 110, 040, and 130 planes also showed similar behavior with the progress of sulfonation.

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