

# THE USE OF INFRARED-SPECTROSCOPY TECHNIQUE FOR THE STRUCTURAL CHARACTERIZATION OF ISOTACTIC POLYPROPYLENE FIBRES

## İZOTAKTİK POLİPROPİLEN LİFLERİNİN YAPISAL KARAKTERİZASYONUNDA İNFRA-RED SPEKTROSKOPİ YÖNTEMİNİN KULLANIMI

*İsmail KARACAN*  
*Department of Textile Engineering*  
*Erciyes University*  
*e-mail: ismailkaracan@erciyes.edu.tr*

*Hüseyin BENLİ*  
*Erciyes University*  
*Mustafa Çıkrıkçioğlu*  
*Vocational School,*

### ABSTRACT

Isotactic polypropylene (iPP) fibres were produced by melt spinning method with take-up speeds between 2500 m/min and 4250 m/min. The effect of production parameters on structural parameters such as crystallinity and tacticity is investigated using infra-red spectroscopy together with density measurements. Samples were also characterized using Melt Flow Index (MFI) measurements. Curve fitting of IR spectra yielded accurate peak parameters which are in turn used in the evaluation of tacticity and fractional crystallinity values. Evaluation of isotacticity and atacticity fractions were performed using the absorbance ratios of the IR bands at 998, 841 and 973 cm<sup>-1</sup> (A<sub>998/A973</sub>, A<sub>841/A973</sub>). Isotacticity fractions evaluated from A<sub>841/A973</sub> are generally found to be higher than that evaluated from the ratio of A<sub>998/A973</sub>. Isotacticity fractions show an increasing trend after about the extrusion speed of 3000 m/min whereas atacticity fractions decrease accordingly. Crystallinity fractions obtained from density and infra-red spectroscopy methods are compared. In general, crystallinity fractions obtained from IR-spectroscopy are found to be slightly higher than the density based crystallinity fractions.

**Key Words:** Isotactic polypropylene fibre, Infra-red spectroscopy, Density, Crystallinity, Tacticity.

### ÖZET

İzotaktik polipropilen lifleri eriyikten çekme yöntemi ile 2500 m/dak ile 4250 m/dak arasındaki sarma hızlarında üretilmiştir. Üretim parametrelerinin kristalinite ve taktisite gibi yapısal parametrelerine etkisi infra-red ve yoğunluk ölçümleri ile araştırılmıştır. Numuneler ayrıca eriyik akış indisi ölçümleri ile karakterize edilmiştir. Infra-red eğri analizi hassas pik parametreleri ile sonuçlanmış olup elde edilen pik parametreleride taktisite ve kristalinite oranlarının hesaplanmasında kullanılmıştır. İzotaktisite ve ataktisite oranları 998, 841 ve 973 cm<sup>-1</sup> IR piklerinin pik yükseklik oranlarının kullanımı ile elde edilmiştir (A<sub>998/A973</sub>, A<sub>841/A973</sub>). A<sub>841/A973</sub> oranı ile elde edilen izotaktisite oranları A<sub>998/A973</sub> oranından elde edilen değerlerden genel olarak daha fazla bulunmuştur. İzotaktisite oranları 3000 m/dak üretim hızından sonra artma eğilimi ataktisite oranları ise azalma eğilimi göstermektedir. Yoğunluk ve infra-red yöntemlerinden elde edilen kristalinite oranları karşılaştırılmıştır. Genel olarak, infra-red spektroskopisi yönteminden elde edilen kristalinite oranları yoğunluk esaslı kristalinite oranlarından daha fazla bulunmuştur.

**Anahtar Kelimeler:** İzotaktik polipropilen lifi, İnfra-red spektroskopisi, Yoğunluk, Kristalinite, Taktisite.

Received: 09.09.2010

Accepted: 13.01.2011

### 1. INTRODUCTION

Polypropylene (PP) fibre has been one of the success stories in the past few decades due to its wide range of properties and applications. Due to its low manufacturing cost coupled with excellent mechanical and chemical properties, PP fibres found wide range of use in traditional textiles as well as

in industrial and advanced technological areas. The improvement in mechanical properties of PP fibres together with low density has resulted in an extension of application areas outside the traditional textile end-uses. The last two decade certainly has seen the introduction of PP fibres in various technical and medical related applications.

From historical point of view, one of the earliest studies of melt-spinning of polypropylene was carried out by Sheehan and Cole (1) in the early 1960s. These investigators showed that  $\alpha$ -monoclinic polypropylene is produced under normal air solidification, whereas solidification in cold water prevents crystallization and results in a highly oriented but poorly ordered paracrystalline

smectic structure, which was later referred to as smectic or mesophase form. Later studies (2-6) have emphasized the importance of melt-extrusion conditions on the structure and mechanical properties of the resulting polypropylene fibres. These studies suggested that the structure and properties of fibres can be controlled over a wide range by modifying the production conditions. These studies were restricted to extrusion speeds of less than 1500 m/min. Shimuzu and co-workers (7-10) performed an extensive study of high speed extrusion in the range of take-up speeds from 500 m/min to 6000 m/min. The structure and properties of melt-spun fibres were investigated as a function of take-up speed and extrusion temperature. The effects of annealing these filaments were also studied. Their results show that density and birefringence initially increase rapidly with increasing take-up speed, but the rate of increase decreases substantially above a critical take-up speed that varies with the extrusion temperature (10). The filament tenacities and initial moduli were found to increase, while elongation at break decreased, with increasing spinning speeds.

In a series of publications, Spruiell and coworkers (11-12) dealt with several aspects of the influence of molecular weight and its distribution; they showed that spinnability and the resulting structure and properties are affected by both the weight-average molecular weight ( $M_w$ ) and the breadth of the distribution (polydispersity). In a further investigation (13) they dealt with factors that modify substantially the quiescent crystallization kinetics, such as the influence of the addition of nucleating agents or of copolymerizing with a small amount of ethylene. Misra et al. (14) briefly examined the effects of changing the crystallization kinetics by adding a nucleating agent or by copolymerizing with ethylene. The influence of isotacticity, ethylene comonomer content, and nucleating agent additions on the structure and properties of melt-spun polypropylene filaments was studied for a series of polypropylenes having similar resin melt flow rates (MFI=35), average molecular weights, and polydispersities (15).

Tomka and coworkers in an extensive study (16) showed that fine (<0.6 tex) polypropylene fibres of high strength

can be produced by melt extrusion followed by a two-stage drawing process. In this study, it was confirmed that as-spun paracrystalline fibres of low orientation can be considered to be the best precursors for achieving high strength after a suitable drawing stage. In a further study (17) they showed the effects of heat-treatment, one-stage and two-stage drawing on the structure and properties of the final as-spun fibres. This study showed the effect of increasing the orientation of paracrystalline phase followed by converting this structure to a more stable  $\alpha$ -monoclinic phase. In a series of experimental studies, Suzuki and his coworkers (18-19) used carbon-dioxide laser heating method to produce solid polypropylene microfibre with an average diameter of 1.8  $\mu\text{m}$ . It is claimed that laser-heating allows easier fabrication of microfibers compared with the conventional technology such as the conjugate spinning. Apparently the earlier work (18) produced only the microfibre with a length of 1.5 m length was obtained by using the present  $\text{CO}_2$  laser-thinning apparatus. The researchers considered the result to be very valuable from an industrial point of view and but it was not acceptable from industrial point of view. They then proceeded to the next stage of investigation with continuous production of laser heated microfibre (19).

In an extension of previous studies, Suzuki and Narusue (19) produced an isotactic polypropylene hollow microfibre by using a carbon dioxide ( $\text{CO}_2$ ) laser-thinning method. To prepare the hollow microfibre continuously, the apparatus used for the thinning of the solid fiber was improved so that the laser can circularly irradiate the hollow fiber. An as-spun hollow fiber was laser-heated under various conditions, and the outside and the inside diameter of the fibre decreased with increasing winding speed.

The aim of the present study is to characterize and establish the structure-processing relationships of isotactic polypropylene fibres produced by melt-spinning with an extrusion temperature of 235°C and the extrusion speed range of 2500-4250 m/min using the measurements of MFI (melt flow index), density and infrared spectroscopy with the aim of establishing structure-processing-property relationships.

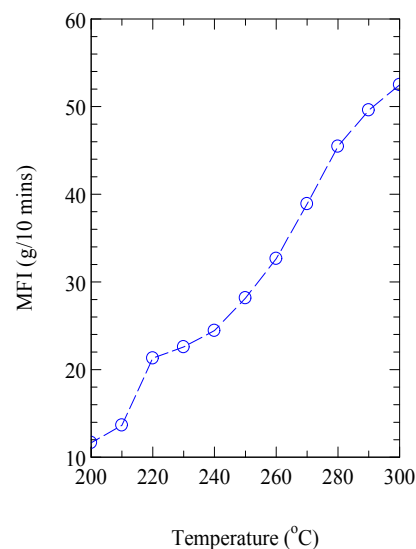
## 2. EXPERIMENTAL DETAILS

### Fibre Production

Melt-spun isotactic polypropylene fibres were produced using Barmag® CF melt-spinning machine operating in an extrusion speed range of 2500 and 4500 m/min. Fibre production details are presented in Table 1. Extrusion temperature was set at  $235 \pm 2^\circ\text{C}$ . Fibre grade polypropylene granules with weight average molecular weight of 179,000 and polydispersity ( $M_w/M_n$ ) of 4.6 obtained from Basell Polyolefins with a nominal MFI of 25 g/10 mins were used during the fibre extrusion stages (Table 2). Melt-Flow Index measurements were carried out according to ASTM D1238 using a load for extrusion of 2.16 kg. MFI measurement was carried out with a temperature increment of  $10^\circ\text{C}$  in the temperature range of 200 and  $300^\circ\text{C}$ . The results are presented in Figure 1.

**Table 1.** Details of the as-spun fibre production parameters

PROCES PARAMETERS		COMMENTS
MFI		25 g/ 10 min
Extrusion Temperature		$235^\circ\text{C} \pm 2^\circ\text{C}$
Take-up speed		2500-4250 m/mins
Cooling Unit Temperature		$18-19^\circ\text{C}$
Air blow speed		40-70 m/s
Spinnerette pressure		60-70 bar
Spinnerette hole number		72
Spinnerette hole diameter (R)		200-400 $\mu\text{m}$
Hole shape		$\Delta$ (Trilobal)
Throughput		9,12 g/mins
Yarn Tension (for 300 denier)		32-33 cN
Environment conditions	Relative humidity	70 %
	Temperature	$15^\circ\text{C}$



**Figure 1.** MFI values against temperature

## Density measurements

Density values were evaluated using a density gradient column operating at 23°C. The column was prepared using isopropyl alcohol ( $\rho = 0.785 \text{ g/cm}^3$ ) and water for the measurement of the density of the as-spun filaments. The samples were allowed approximately 24 hours to reach their equilibrium level of displacement. The fractional crystallinity ( $\chi_c$ ) values of the samples were then estimated using the equation (1).

$$\chi_c = \frac{\rho_c(\rho - \rho_a)}{\rho(\rho_c - \rho_a)} \times 100 \quad (1)$$

Where  $\rho_c$  and  $\rho_a$  are the densities of the crystalline and the amorphous polypropylene. Fractional crystallinity was evaluated from the densities using the crystalline and the amorphous density values 0.936 (20, 21) and 0.850 (21, 22)  $\text{g/cm}^3$ , respectively.

## Infra-red spectroscopy measurements

Perkin Elmer® Spectrum 400 FT-IR spectrometer was employed for infrared measurements using single reflection diamond crystal based GladiATR® model ATR attachment. ATR-IR technique is known to be a surface characterization technique and is known to be sensitive to about a few microns into the surface of the samples. In some cases the depth of beam penetration can be as much as 1.66  $\mu\text{m}$  at 1000  $\text{cm}^{-1}$  for diamond ATR crystals and 0.65  $\mu\text{m}$  at 1000  $\text{cm}^{-1}$  for germanium ATR crystals (23). All the spectra were collected in the mid-IR range (i.e. 4000-400  $\text{cm}^{-1}$ ) with coadded 50 scans collected at a resolution of 2  $\text{cm}^{-1}$ . Finally, all the spectra were analyzed using the OMNIC software® and curve fitting procedures to obtain accurate peak parameters wherever it is appropriate.

## Curve fitting procedure

The infra-red spectrum of isotactic polypropylene in the 1025-775  $\text{cm}^{-1}$  region contains at least six well-defined peaks located at 809, 841, 899, 940, 973 and 998  $\text{cm}^{-1}$ . During the curve fitting stages it was necessary to include additional peaks at 796, 827, 852, 886, 931, and 955  $\text{cm}^{-1}$  to improve the fits in the tail regions of the major peaks. In the second stage, the IR peak located at 973  $\text{cm}^{-1}$  is split into two peaks one at 972  $\text{cm}^{-1}$  and the

other at 974  $\text{cm}^{-1}$ . Curve fitting was restricted to 923-1025  $\text{cm}^{-1}$  region for the second stage. Additional peaks needed to improve the fitting are located at 931, 950, 955 and 966  $\text{cm}^{-1}$ , respectively. All the IR spectra obtained from the extruded as-spun fibres were fitted with a curve fitting procedure developed by Hindeleh et al. (24) to separate overlapping peaks.

## Evaluation of Tacticity

The isotacticity has been measured by means of the absorbance ratios of the IR bands at 841, 973 and 998  $\text{cm}^{-1}$  using the absorbance values obtained during the curve fitting stages. 973  $\text{cm}^{-1}$  band has been used as an internal standard due to its presence in the IR spectrum of melted polymer (25). The absorbance ratios examined in the present investigation are:  $A_{998}/A_{973}$  and  $A_{841}/A_{973}$ . Assuming the absence of syndiotactic propylene sequences in the polymer chain, the tacticity is calculated as the sum of the fraction of isotactic and atactic propylene sequences, hence atacticity is calculated using the equation (2)

$$\chi_{\text{atacticity}} = 1 - \chi_{\text{isotacticity}} \quad (2)$$

## Evaluation of Crystallinity

Certain infra-red bands tend to show absorbance increases following either orientation due to high extrusion speeds, through drawing processes or during annealing stages. The crystalline fraction in the crystalline phase is calculated using the equation (3).

$$\chi_{\text{crystalline}} = \frac{\sum A_{\text{crystalline}}}{\sum A_{\text{crystalline}} + \sum A_{\text{amorphous}}} \quad (3)$$

Where  $\sum A_{\text{crystalline}} = A_{998} + A_{899} + A_{841} + A_{809}$  and  $\sum A_{\text{amorphous}} = A_{974}$ , respectively. Since the sum of the crystalline content and the amorphous content must be equal to unity, the amorphous fraction is evaluated by the equation (4).

$$\chi_{\text{amorphous}} = 1 - \chi_{\text{crystalline}} \quad (4)$$

## RESULTS AND DISCUSSION

### Evaluation and assessment of Melt-flow index (MFI)

Melt flow index, MFI, (or Melt Flow rate MFR) is industrially used to perform

the characterization of the polymer properties for melt extrusion. MFI is usually inversely related to the apparent melt viscosity and the end pressure losses, and therefore MFI gives a coarse indication of the spinnability of the polymer. MFI values are found to be greatly influenced by both the molecular weight and the molecular weight distribution as shown in Table 2. It is shown that an MFI value of 25 g/10 mins used in the present investigation is related to a low molecular weight polymer type with a narrow molecular weight distribution. Sheehan and Cole (1) stated that a polymer with a narrow molecular weight distribution is a useful criteria but not essential for producing high tensile strength polypropylene filaments. Figure 1 shows the MFI values against the extrusion temperature between 220° and 300°C. It is clear that the melt extrudate weight due to the reduced melt viscosity at higher temperatures tend to increase.

### Evaluation and the assessment of the tacticity measurements by IR method

Evaluation of the tacticity in polypropylene is usually performed using solvent extraction,  $^{13}\text{C}$  NMR and FT-IR spectroscopy techniques (26). Solvent extraction method involves extracting soluble atactic fraction after boiling isotactic polypropylene in n-heptane where the remaining matter is insoluble isotactic polypropylene. This method is believed to be expensive, time consuming and is subject to errors.

It is highly likely that small chain segments of isotactic polypropylene may be soluble and may be mistakenly taken into account as atactic fraction. The other possibility may be the presence of small fraction of atactic propylene segments in isotactic polypropylene chains. These possibilities are likely to lead to wrong evaluation of the tacticity values. For these reasons, a more reliable method of determining tacticity is required. Usually relatively simple, rapid, accurate and easy to use method of IR spectroscopy is preferred in research laboratories where  $^{13}\text{C}$  NMR facility is absent.

In the present investigation, for the quantitative characterization of the tacticity of as-spun fibers, the absorbance ratios of the IR bands at 841, 973 and 998  $\text{cm}^{-1}$  are selected,  $A_{998}/A_{973}$ ,  $A_{841}/A_{973}$ . The 998  $\text{cm}^{-1}$  band is

assigned to CH<sub>3</sub> rocking + CH<sub>2</sub> wagging + CH bending vibrations, whereas 973 cm<sup>-1</sup> belongs to strongly coupled CH<sub>3</sub> rocking + C-C chain stretching vibrations. Assignments of IR bands in 1400-800 cm<sup>-1</sup> region is presented in Table 3. 998 cm<sup>-1</sup> absorption band is usually assigned to the crystalline phase, whereas 973 cm<sup>-1</sup> band is assigned to both the crystalline and the amorphous chains in helical conformations and is often used as an internal reference band (25, 27). 973 cm<sup>-1</sup> band is associated with the presence of short isotactic helices apparently still present in the melt or in the atactic material. This peak has been attributed (28) to the superposition of two peaks, the IR peak located at 972 cm<sup>-1</sup> is assigned to the crystalline phase whereas the other IR peak located at 974 cm<sup>-1</sup> is assigned to the amorphous phase. According to Painter et al. (29) the frequencies of the bands in the amorphous phase are likely to be located between the spectrum of helical chains

in the solid state and the molten spectrum. It appears that there is still a portion of helical polymer segments in the amorphous phase. The height of the band at 973 cm<sup>-1</sup> band is found to be essentially insensitive to the structural changes due to the crystallization effects. In many cases, due to their close proximity to each other, the bands at 998, 973 and 841 cm<sup>-1</sup> are used for the orientation measurements (28, 30-31).

Tacticity measurements are performed after obtaining the absorbance values of the relevant IR bands using a curve fitting procedure. Curve fitting is performed in the 1025-775 cm<sup>-1</sup> region, a typical curve fitting of this region is shown in Figure 2 for the sample extruded at 2500 m/min. The isotacticity values are evaluated using the absorbance ratios of A<sub>998</sub>/A<sub>973</sub>, A<sub>841</sub>/A<sub>973</sub> and atacticity values are evaluated using the equation (2). The results are presented in Table 4 and

Figure 3. The results suggest that the isotacticity fractions obtained using the absorbance ratio of A<sub>841</sub>/A<sub>973</sub> is always higher than that of the absorbance ratio of A<sub>998</sub>/A<sub>973</sub> for the samples melt-spun in the extrusion speed range of 2500-4250 m/min. This may be due to the absorption band at 998 cm<sup>-1</sup> being slightly sensitive to less highly ordered phase. In an extensive study, Zerbi et.al (32) showed the existence of ordered helical polymer chain segments in the melt. The spectrum of molten polypropylene showed the existence of a weak band at 998 cm<sup>-1</sup> indicating that during the melting process not all the helices are destroyed. On melting this peak drastically lost its intensity but did not completely disappear. It shows that segments of helical structure still exists in the molten phase. The length of these segments is thought to be about 5 propylene units in the melt.

**Table 2.** Molecular characterization data for polypropylene samples (38)

Code <sup>a</sup>	MFI	M <sub>w</sub> .10 <sup>-5</sup>	(M <sub>w</sub> / M <sub>n</sub> )	M <sub>z</sub> / M <sub>w</sub>	M <sub>v</sub>
<b>High Molecular weight</b>					
narrow	4.2	2.84	6.4	2.59	2.40
regular-broad	5.0	3.03	9.0	3.57	2.42
broad-regular	3.7	3.39	7.7	3.54	2.71
<b>Middle molecular weight</b>					
narrow	11.6	2.32	4.7	2.81	1.92
regular	12.4	2.79	7.8	4.82	2.13
Broad	11.0	2.68	9.0	4.46	2.07
<b>Low Molecular weight</b>					
narrow	25.0	1.79	4.6	2.47	1.52
regular-narrow	23.0	2.02	6.7	3.18	1.66

a: narrow, regular and broad refer to molecular weight distribution

M<sub>w</sub>: weight average molecular weight

M<sub>n</sub>: number average molecular weight

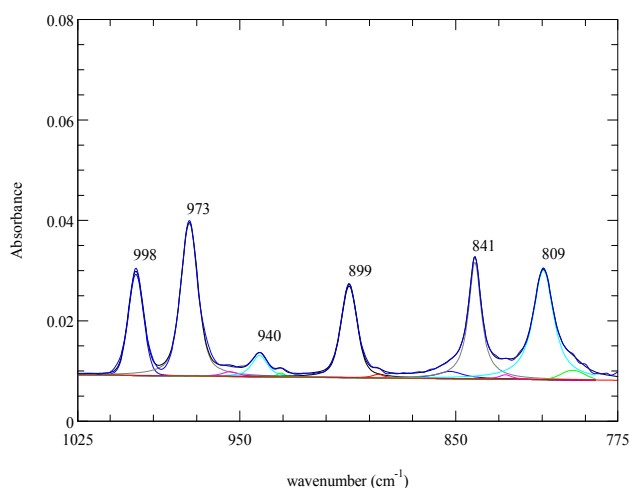
M<sub>z</sub>: z-average molecular weight

M<sub>v</sub>: viscosity average molecular weight

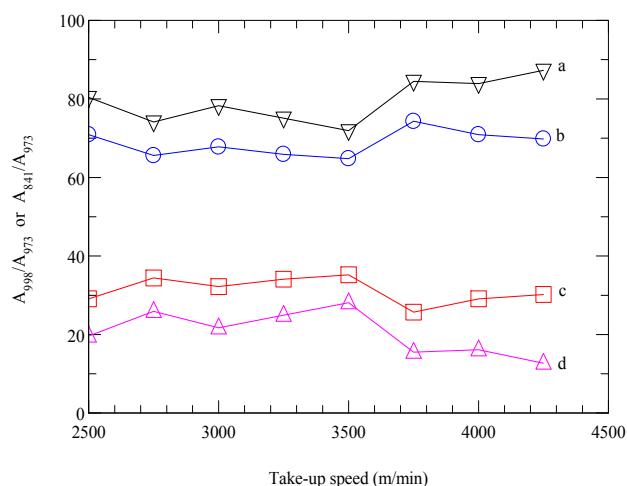
**Table 3.** Assignment of polypropylene infrared absorption bands (39) in the 1400-800 cm<sup>-1</sup> region

Frequency cm <sup>-1</sup>	Phase	Polarization	Assignment
1377	A,C	⊥	CH <sub>3</sub> symmetric bending + CH <sub>2</sub> wagging
1256	A,C	//	CH bending + CH <sub>2</sub> twisting + CH <sub>3</sub> rocking
1220	C	⊥	CH <sub>2</sub> twisting + CH bending + C-C chain stretching
1168	C	//	C-C chain stretching + CH <sub>3</sub> rocking + CH bending
1104	C	⊥	C-C chain stretching + CH <sub>3</sub> rocking + CH <sub>2</sub> wagging + CH twisting + CH bending
1044	C	//	C-CH <sub>3</sub> stretching+C-C chain stretching + C-H bending
998	C	//	CH <sub>3</sub> rocking+CH <sub>2</sub> wagging + CH bending
973	A,C	//	CH <sub>3</sub> rocking + C-C chain stretch
941	C	⊥	CH <sub>3</sub> rocking + C-C chain stretch
900	C	⊥	CH <sub>3</sub> rocking + CH <sub>2</sub> rocking + CH bending
841	C	//	CH <sub>2</sub> rocking + C-CH <sub>3</sub> stretching
809	C	⊥	CH <sub>2</sub> rocking + C-C stretching + C-H stretching

**Key:** C=Crystalline, A=Amorphous



**Figure 2.** A typical curve fitted infra-red spectrum of isotactic polypropylene fibre extruded at 2500 m/min (1025-775  $\text{cm}^{-1}$  range)



**Figure 3.** Effect of extrusion speed on the isotacticity and atacticity of polypropylene fibres a:  $A_{841}/A_{973}$  (%), b:  $A_{998}/A_{973}$  (%), c:  $100 - A_{998}/A_{973}$  (%), d:  $100 - A_{841}/A_{973}$  (%)

On the other hand, the other regularity band at  $841 \text{ cm}^{-1}$  is assigned to a combination of  $\text{CH}_2$  rocking and  $\text{C-CH}_3$  stretching vibrations (Table 3) and shows the lowest peak width in comparison with the other helical bands. This peak has an average half-height width of  $7 \text{ cm}^{-1}$ . It has also been assigned to long helical chains with an average length of 12-14 propylene units (33). Molecular orientation parameters calculated using this peak for isotactic polypropylene films showed excellent agreement and correlation with the X-ray diffraction measurements (28, 30-31). It was suggested that in the absence of the X-ray diffraction data, this peak may be used for the determination of the orientation parameter for the crystalline phase.

The isotacticity fractions obtained from the absorption ratio of  $A_{841}/A_{973}$  varies between 74-87%. Assuming no syndiotactic propylene segments in the polypropylene chains then the atacticity fraction lies in the 13-28% range (Figure 3 and Table 4). The value of the isotacticity fraction tend to show an upward trend after the extrusion speed of 3500 m/min. This may be due to the effect of the orientation and the subsequent increase in the fraction of the ordered material.

#### Evaluation and the assessment of the crystallinity measurements by the density and the IR methods

Infrared-spectroscopy of polymers with crystalline structures are often found to show complicated features due to the

regular structure of the polymer chains. Crystallinity bands are usually classified into four groups as conformational bands, stereoregularity (i.e. tacticity) bands, regularity bands and crystallinity bands (34). In the case of the crystalline isotactic polypropylene structures only the conformational bands and the regularity bands are observed in the mid-infrared spectrum. The regularity bands are dependent upon the conformation of individual chains that arise from sections of the chain which have  $3_1$  helical structure. These features should disappear upon melting the polymer as the helices are destroyed.

Many investigations showed that specific regularity bands are related to the critical length of the isotactic sequences. It was found that the absorption intensity of the  $998 \text{ cm}^{-1}$  band disappears as the sequence length becomes less than 10 monomeric units. The other regularity bands were also found to disappear (35). IR regularity bands of crystallized isotactic polypropylene located at 1220, 1168, 998, 899, 841 and  $809 \text{ cm}^{-1}$  can be defined as helix bands (33). It is shown that (36) only 841 and  $998 \text{ cm}^{-1}$  bands remain for monomeric sequence lengths less than 10 in the IR spectra of isotactic copolymer and deuteropropylene copolymers. Although the  $998 \text{ cm}^{-1}$  band is still observed to exist at  $220^\circ\text{C}$ , its intensity is seen considerably weakened but a small portion is found to remain (37).

The regularity bands at 998, 940, 899 and  $809 \text{ cm}^{-1}$  together with the

amorphous band at  $974 \text{ cm}^{-1}$  are utilized for the evaluation of the crystallinity using the equation 3. This way regularity (i.e. helix) bands are taken into account rather than relying on a single regularity band. In order to establish structure-processing relationships, usually the degree of crystallization (i.e. % crystallinity) is evaluated using analytical techniques such as density, thermal analysis in particular DSC, X-ray diffraction and infra-red spectroscopy methods. IR method, in general, is a method sensitive to crystalline and amorphous phases, whereas X-ray diffraction is only sensitive to crystalline phase. In the present report, density and infra-red measurements are utilized for the evaluation of crystallinity.

The use of density for the evaluation of fractional crystallinity using the equation 1 is now well established, although in many cases questioned due to the use of assumption that the structure is composed of only crystalline and amorphous phases only. The values of density and fractional crystallinity are listed in Table 5 together with the amorphous fraction values. The data presented in Table 5 show increasing density and fractional crystallinity values as a function of increasing take-up speeds. It is believed that due to increasing molecular orientation during the melt-extrusion stages, increases in the density and the crystallinity take place in response to gradual increase in the extrusion speeds.

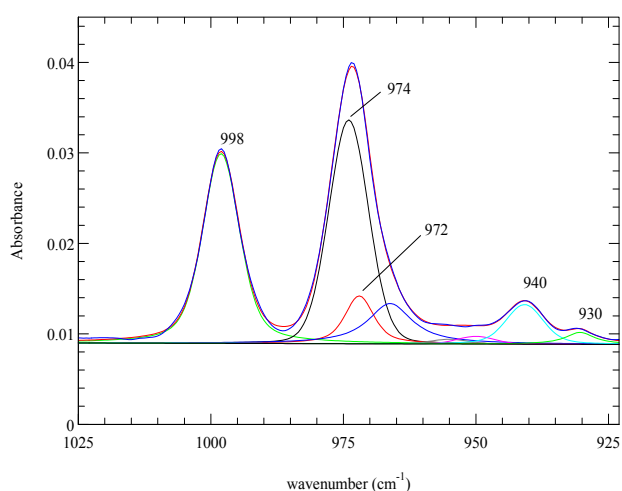
**Table 4.** Isotacticity and atacticity values of isotactic polypropylene fibres

	$A_{998}/A_{973}$	$A_{998}/A_{973}$	$A_{841}/A_{973}$	$A_{841}/A_{973}$
Extrusion speed m/min	Isotacticity %	Atacticity %	Isotacticity %	Atacticity %
2500	70.9	29.1	80.4	19.6
2750	65.6	34.4	74.1	25.9
3000	67.8	32.2	78.3	21.7
3250	65.9	34.1	75.1	24.9
3500	64.8	35.2	71.9	28.1
3750	74.3	25.7	84.5	15.5
4000	70.9	29.1	83.9	16.1
4250	69.8	30.2	87.3	12.7

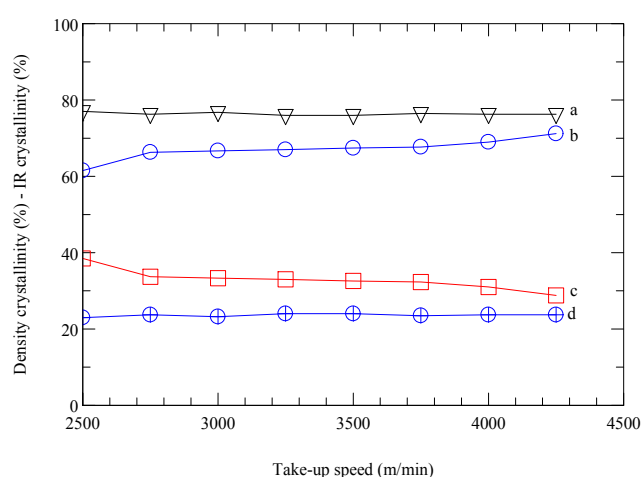
**Table 5.** Comparison of crystallinity values obtained from density and IR-spectroscopy measurements

Take-up speed (m/min)	Density g/cm <sup>3</sup>	Density Crystallinity (%)	Density Amorphous Fraction (%)	FT-IR Crystallinity (%)	FT-IR Amorphous Fraction (%)
2500	0.9009	61.5	38.5	77.0	23.0
2750	0.9051	66.3	33.7	76.3	23.7
3000	0.9055	66.7	33.3	76.8	23.2
3250	0.9058	67.0	33.0	76.0	24.0
3500	0.9061	67.4	32.6	76.0	24.0
3750	0.9064	67.7	32.3	76.5	23.5
4000	0.9075	69.0	31.0	76.3	23.7
4250	0.9095	71.2	28.8	76.3	23.7

Curve fitting in the IR region of 1025-923 cm<sup>-1</sup> is employed for splitting the IR peak at 973 cm<sup>-1</sup> into 972 cm<sup>-1</sup> as crystalline and 974 cm<sup>-1</sup> as amorphous bands, respectively. Figure 4 shows the curve fitting of 1025-923 cm<sup>-1</sup> region for the sample extruded at a take-up speed of 2500 m/min. This way the IR crystallinity can be evaluated using the equation 3. Crystallinity measurements listed in Table 5 and presented in Figure 5 show that the crystallinity values derived from the IR spectroscopy are slightly higher than those obtained using the density measurements as a function of increasing extrusion speeds.



**Figure 4.** A typical curve fitted infra-red spectrum of isotactic polypropylene fibre extruded at 2500 m/min (1025-923 cm<sup>-1</sup> IR region)



**Figure 5.** Comparison of crystallinity fractions of isotactic polypropylene fibres obtained from density and IR measurements. a; IR-crystalline (%), b; density-crystalline (%), c; density-amorphous (%), d; IR-amorphous (%)

It is highly likely that the results will be adversely affected by the assumption that the amorphous density used in the

evaluation of crystallinity from density measurements remains constant. It is most likely that the amorphous density

will increase with increasing extrusion speed. The amorphous fractions obtained from both the density and the

IR measurements are also listed in Table 5 and shown in Figure 5. The values of the amorphous fraction obtained from density measurements show a slight decreasing trend in response to slight increasing crystallinity values. Whereas the crystallinity and the amorphous fractions obtained from the IR measurements do not show much variation in comparison with the density based measurements (Figure 5).

### 3. CONCLUSIONS

Melt-extruded isotactic polypropylene fibres were produced using take-up speeds between 2500 and 4250 m/min. As-spun polypropylene fibres were characterized using melt-flow

index, density and infra-red spectroscopy measurements with the aim of establishing structure-processing relationships. Crystallinity fractions were evaluated and compared using density and infra-red spectroscopy techniques. Curve fitting of infra-red spectra yielded accurate peak parameters which were in turn used in the determination of the tacticity and the crystallinity fractions. Determination and assessment of the isotacticity and the atacticity fractions were performed using the absorbance ratios of the IR bands at 998, 841 and 973  $\text{cm}^{-1}$  ( $A_{998}/A_{973}$ ,  $A_{841}/A_{973}$ ). % isotacticity values determined from  $A_{841}/A_{973}$  are generally found to be higher than that determined from the

ratio of  $A_{998}/A_{973}$ . Both isotacticity fractions tend to increase after about the extrusion speed of 3000 m/min whereas the atacticity decreases accordingly. In general, crystallinity values obtained from the IR-spectroscopy are found to be slightly higher than the density based crystallinity values.

### ACKNOWLEDGEMENTS

The assistance and cooperation of Boyteks A.Ş. (Kayseri) is gratefully acknowledged for the extrusion of polypropylene multifilaments. The financial support of Scientific Research Projects Unit of Erciyes University is very much appreciated (project number FBY-06-74 and FBA-09-955).

### REFERENCES

1. Sheehan W. C. and Cole T. B., 1964, "Production of Super-Tenacity Polypropylene Filaments", *J. Appl. Polymer. Sci.*, 8, pp.2359-2388.
2. Fung P. Y. F., Orlando E., and Carr S. H., 1973, "Development of Stress-Crystallized Morphology During Melt-Spinning of Polypropylene Fibers", *Polym. Eng. Sci.*, 13(4), pp295-299.
3. Kitao T., Ohya S., Furukawa J., and Yamashita S., 1973, "Orientation of Polymer Molecules during Melt Spinning. 11. Orientation of Crystals in As-Spun Polyolefin Fibers", *J. Polym. Sci. Poly. Phys.*, 11, pp1091-1109.
4. Spruiell J. E. and White J. L., 1975, "Structure Development During Polymer Processing: Studies of the Melt Spinning of Polyethylene and Polypropylene Fibers" *Polym. Eng. Sci.*, 15(9), pp660-667.
5. Nadella H. P., Henson M. M., Spruiell J. E., and White J. L., 1977, "Melt Spinning of Isotactic Polypropylene: Structure Development and Relationship to Mechanical Properties", *J. Appl. Polym. Sci.*, 21, pp3003-3022.
6. Minoshima W., White J. L., and Spruiell J. E., 1980, "Experimental Investigations of the Influence of Molecular Weight Distribution on Melt Spinning and Extrudate Swell Characteristics of Polypropylene", *J. Appl. Polym. Sci.*, 25, pp287-306.
7. Shimizu J., Watanabe A., and Toriumi K., 1974, "The High Speed Spinning by Using an air jet nozzle", *Sen-i Gakkaishi*, 30(2), ppT53-T60.
8. Shimizu J., Torid K., and Tamai K., 1977, "High Speed Melt Spinning of Isotactic Polypropylene", *Sen-i Gakkaishi*, 33(6), ppT208-T260.
9. Shimizu J., Tonumi K., and Imai Y., 1979, "High Speed Melt Spinning of Isotactic Polypropylene", *Sen-i Gakkaishi*, 35(10), ppT405-T412.
10. Shimizu J., Okui N., and Imai Y., 1980, "High Speed Melt Spinning of Isotactic Polypropylene", *Sen-i Gakkaishi*, 36(4), ppT166-T174.
11. Lu F. M. and Spruiell J. E., 1987, "The Influence of Resin Characteristics on the High Speed Melt Spinning of Isotactic Polypropylene. I. Effect of Molecular Weight and Its Distribution on Structure and Mechanical Properties of As-Spun Filaments", *J. Appl. Polym. Sci.*, 34(4), pp1521-1539.
12. Lu F. M. and Spruiell J. E., 1987, "The Influence of Resin Characteristics on the High Speed Melt Spinning of Isotactic Polypropylene. II. On-Line Studies of Diameter, Birefringence, and Temperature Profiles", *J. Appl. Polym. Sci.*, 34(4), pp1541-1556.
13. Lu F. M. and Spruiell J. E., 1993, "The Role of Crystallization Kinetics in the Development of the Structure and Properties of Polypropylene Filaments", *J. Appl. Polym. Sci.*, 49, pp623-631.
14. Misra S., Lu F. M., Spruiell J. E., and Richeson G. C., 1995, "Influence of Molecular Weight Distribution on the Structure and Properties of Melt-Spun Polypropylene Filaments", *J. Appl. Polym. Sci.*, 56(13), pp1761-1779.
15. Spruiell J. E., Lu F.-M., Ding Z., and Richeson G., 1996, "The Influence of Isotacticity, Ethylene Comonomer Content, and Nucleating Agent Additions on the Structure and Properties of Melt-Spun Isotactic Polypropylene Filaments", *J. Appl. Polym. Sci.* 62(11), pp1965-1975.
16. Wang I.C., Dobb M.G., Tomka J.G., 1995, "Polypropylene Fibres: An Industrially Feasible Pathway to High Tenacity", *J. Text. Inst.*, 86(3), pp383-392.
17. Wang I.C., Dobb M.G., Tomka J.G., 1996, "Polypropylene Fibres: Exploration of Conditions Resulting in High Tenacity", *J. Text. Inst.*, 87(1), pp1-12.
18. Suzuki A., Narusue S., 2004, "Isotactic Polypropylene Micro.fiber Prepared by Carbon Dioxide Laser-Heating", *J. App. Poly. Sci.*, 92, pp1534-1539.
19. Suzuki A., Narusue S., 2006, "Isotactic Polypropylene Micro.fiber Prepared by Continuous Laser-Thinning Method", *J. App. Poly. Sci.*, 99, pp27-31.
20. Natta G. and Corradini P., 1960, "Structure and Properties of Isotactic Polypropylene", *Nuovo Cimento*, 15, pp40-51.
21. G. Natta, 1955, "Une Nouvelle Classe de Polymeres d' $\alpha$ -Olefines ayant une Régularité de Structure Exceptionnelle", *J. Poly. Sci.*, 16, pp143-154.
22. Natta G., Pino P., Corradini P., Danusso F., Mantica E., Mazzanti G., Moraglio G., 1955, "Crystalline High Polymers of  $\alpha$ -olefins", *J. Am. Chem. Soc.*, 77(6), pp1708-1710.
23. <http://www.piketech.com/technical/crystal-selection-ATR.html>, Accessed on 19th July 2010
24. Hindeleh A.M., Johnson D.J., and Montague P.E., 1983, 'Fibre Diffraction Methods', ACS Symp. No. 141 (Eds. A.D. French and K.H. Gardner), American Chemical Society, Washington DC, p. 149-181.
25. Tadokoro H., Kobayashi M., Ukita M., Yasufuku K., Murahashi S., Torii T., 1965, "Normal Vibrations of the Polymer Molecules of Helical Conformation: Isotactic Polypropylene and Its Deuteroderivatives", *J. Chem. Phys.*, 4, pp1432-1449.
26. Ozzetti R.A., Filho A.P.D.O., Schuchardt U., Dalmo M., 2002, "Determination of Tacticity in Polypropylene by FTIR with Multivariate Calibration", *J. App. Poly. Sci.*, 85, pp734-745
27. Burfield D.R. and Loi P.S. T., 1988, "The Use of Infrared Spectroscopy for Determination of Polypropylene Stereoregularity", *J. App. Poly. Sci.*, 36, pp279-293
28. Karacan I., Taraiya A.K., Bower D.I., Ward I.M., 1993, "Characterization of orientation of one- way and two-way drawn isotactic polypropylene films", *Polymer*, 34(13), pp2691-2701.
29. Painter P.C., Watzek M. and Koenig J.L., 1977, "Fourier transform infra-red study of polypropylene", *Polymer*, Volume 18, 18(11), pp1169-1172.



- 
30. Karacan I., 1999, "Structure-Property relationships in polypropylene fibres", *Polypropylene: A-Z guide*, Ed. J. Karger-Kocsis, Kluwer Academic Publishers, pp 783-789.
  31. Karacan I. and Wang I-C., 1997, "Structural studies of isotactic polypropylene fibres", *Tekstil ve Mühendis*, 11(55-56), pp3-16.
  32. Zerbi G., Gussoni M. and Ciampelli F., 1967, "Structure of liquid isotactic polypropylene from its vibrational spectrum", *Spectrochimica Acta. Part A: Mol.Spec.*, 23(2). pp301-311.
  33. Kissin Yu.V. and Rashina L.A., 1976, "Regularity bands in the IR spectra of C<sub>3</sub>H<sub>6</sub>-C<sub>3</sub>D<sub>6</sub> copolymers", *Eur.Poly.J.*, 12, p p757-759.
  34. Zerbi G., Ciampelli F., and Zamboni V., 1963, "Classification of Crystallinity Bands in the Infrared Spectra of Polymers", *J.Poly.Sci. Part C: Polym.Symp.*, 7(1), pp141-151.
  35. T. Miyamoto, H. Inagaki, 1969, "Structural and Steric Isomerism of Polypropylenes", *J. Polym. Sci., A-2*, 7, pp963-981.
  36. Kobayashi M., Akita K., and Tadokoro H., 1968, " Infrared Spectra and Regular Sequence Lengths in Isotactic Polymer Chains", *Die Makromolekulare Chemie*, 118, pp324-342.
  37. Zhu, D. Yan, H. Yao, P. Zhu, 2000, "In situ FTIR spectroscopic study of the regularity band and partial-order melts of isotactic poly(propylene)", *Macromol.Rapid.Comm.*, 21.pp354-357.
  38. Minoshima, W., White J.L., and Spruiell, J.E., 1980, "Experimental Investigation of the Influence of Molecular Weight Distribution on the Rheological Properties of Polypropylene Melts", *Polym. Eng.Sci.*, 20(17), pp1166-1176.
  39. Jasse B., Koenig J.L., 1979, "Orientational Measurements in Polymers Using Vibrational Spectroscopy", *J.Macromol.Sci.-Rev.Macromol.Chem.*, C17(1), pp61-135.

---

*Bu araştırma, Bilim Kurulumuz tarafından incelendikten sonra, oylama ile saptanan iki hakemin görüşüne sunulmuştur. Her iki hakem yaptıkları incelemeler sonucunda araştırmanın bilimselliği ve sunumu olarak "Hakem Onaylı Araştırma" vasfıyla yayımlanabileceğine karar vermişlerdir.*

---

# Autex2011

## 11th World Textile Conference

### Mulhouse, France

### 8-10 June 2011

The organizers of the 11th World Textile Conference AUTEX2011 have a great honour and pleasure of inviting you to take part in this Conference to be held on 8-10 June 2011, in Mulhouse, France.

The Autex conference provides an excellent opportunity to bring together European scientists and engineers from academy, national research institutes and companies to present and discuss the latest results in the general field of textile materials, technologies, fashion and marketing.

Fortuitously situated near the borders of three countries - France, Germany and Switzerland, Mulhouse owes most of its growth to its textile industry, followed by chemicals and mechanical engineering. From this past, Mulhouse has retained an important heritage: a historical town center and the most important technical museum center in Europe.

In 2011, ensisa is celebrating 150th anniversary of its existence. AUTEX 2011 conference is arranged as one part of anniversary celebration and will be held on the premises of University of Haute Alsace located near the city center.

#### **MAIN TOPICS**

Other topics proposals will be accepted depending on abstract submission

- Composites
- Fashion Design and Garment Industry
- Finishing, Treatments & Coating
- Functional Textiles
- Knitting
- Medical Textiles
- Marketing
- Nano Textile
- Nonwoven
- Polymers
- Simulation and Modeling
- Spinning
- Supply management and Logistics
- Sustainability – Eco-friendly Products Development
- Technical Textiles
- Textile Testing
- Weaving