(REFEREED RESEARCH)

POTENTIAL USE OF NEW METHODS FOR IDENTIFICATION OF HOLLOW POLYESTER FIBRES

KANALLI POLİESTER LİFLERİNİN TANINMASINDA YENİ YÖNTEMLERİN KULLANIM OLANAKLARI

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ABSTRACT

Today, manufactured textile fibres have many types of chemical structures and finishes and the majority of production processes are new. Therefore, it has been very difficult to identify the different types of fibres in recent times. Even though these fibres may come from a known group of fibres, they do not have the same thermal behaviour, melting point or solubility as classical fibres. So their analysis methods must be more specific than classical fibre analysis methods. The purpose of this study is to investigate various properties of some hollow polyester fibres by new identification methods. For this aim, chemical composition analysis, microscopic analysis, FT-IR and DSC analyses were done. Among these methods, microscopic analyses were found to be most useful in the identification of the hollow PET fibres.

Key Words: Hollow polyester fibers, SEM, FT-IR, DSC, Microscopy.

ÖZET

Günümüzde tekstil lifleri, çok çeşitli kimyasal yapılarda ve yeni tekniklerle üretilmektedir. Bu nedenle değişik tipte liflerin tanınması son zamanlarda oldukça güçleşmiştir. Bu liflerin birçoğu bilinen bir lif sınıfına ait olsa da klasik liflerden farklı termal davranış, erime noktası veya çözünürlüğe sahiptir. Dolayısıyla yeni liflerin analiz yöntemleri klasik lif analiz yöntemlerinden ayrı tutulmalıdır. Bu çalışmanın amacı, bazı kanallı poliester liflerinin yeni tanımlama yöntemleriyle çeşitli özelliklerinin araştırılmasıdır. Çalışmada kanallı poliester liflerinin kimyasal bileşim analizleri, FT-IR ve DSC analizleri yapılmış ve mikroskopik görüntüleri alınmıştır. Bu yöntemler arasından kanallı PET liflerinin tanınması için en uygun olabilecek yöntemin mikroskobik yöntem olduğu tespit edilmiştir.

Anahtar Kelimeler: Kanallı poliester lifleri, SEM, FT-IR, DSC, Mikroskop.

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1. INTRODUCTION

New fibers with various properties have been developed by advanced technologies in recent times. Identification of chemical and physical structures of textile fibers is important since these properties determine how it will perform, and ultimately whether it is acceptable for a particular use. Fiber analysis plays a crucial role in determining product quality and assessing the performance of textile materials. It also provides information about the physical or structural, chemical and performance properties of the fabrics. As consumers become more aware and more demanding of products, the number of tests required for textile materials has grown (1-4).

With the onset of new types of fibers for technical textiles for functional applications, and with the increasing number of innovations taking place in the fiber technology, fiber analysis methods have undergone tremendous changes and there is a need to understand all the procedures before a testing system is adapted to investigate the performance of fabrics.

A number of textile research and testing organizations have published data on new fiber identification methods. There exists a great variety of new procedures for different functional fibers for different end uses. Researchers all over the world have been constantly involved in developing newer methods of fiber identification so as to meet the ever-growing globalization and quality requirements (1).

Since there isn't any international standart involved in identification of functional fibers, a systematic

approach towards integrating the knowledge available in the literature on fiber analyses must be done. This will help all those who are involved in quality assessment and evaluation of textile products to a great extent.

The methods introduced in the literature for fiber analyses have especially been focused on identification of density, viscosity, and solubility properties, microscopic, mechanical and spectrophotometric measurements (1-5). While optical, density, solubility, stain and burning tests are accepted as traditional test methods for fiber identification; SEM (scanning electron microscopy), NMR (Nuclear Magnetic Resonance Spectroscopy), FTIR (Fourier transform infrared spectroscopy), Raman Spectroscopy, X-ray scattering, TGA (Thermogravimetric analysis), DSC (Differential scanning calorimetry) can be thought as relatively new methods. Each of them has some advantages and disadvantages.

In scanning electron microscopy, (SEM) an electron beam is scanned across a sample's surface. When the electrons strike the sample, a variety of signals are generated, and it is the detection of specific signals which produces an image or a sample's elemental composition. The three signals which provide the greatest amount of information in SEM are the secondary electrons, backscattered electrons, and X-rays (6). The instrument is very suitable for different kinds of investigations. It is possible to investigate fiber structure, metal fracture surfaces, rubber and plastic (7).

NMR spectroscopy is one of the principal techniques used to obtain physical, chemical, electronic and structural information about molecules due to either the chemical shift, Zeeman Effect, or the Knight Shift effect, or a combination of both, on the resonant frequencies of the nuclei present in the sample. It is a powerful technique that can provide detailed information on the topology, dynamics and three-dimensional structure of molecules in solution and the solid state (8). For textile application, solid-state NMR and Low-field NMR are commonly used. Solid-state NMR can be used in investigation of the structure of PA 6 filaments, and Low-field NMR can be used in evaluation of crystallization, spinning and chemical finishing ratio (9)

Raman spectroscopy is a spectroscopic technique used to study vibrational, rotational, and other low-frequency modes in a system. It relies on inelastic scattering, or Raman scattering, of monochromatic light, usually from a laser in the visible, near infrared, or near ultraviolet range. The laser light interacts with molecular vibrations, phonons or other excitations in the system, resulting in the energy of the laser photons being shifted up or down. The shift in energy gives information about the phonon modes in the system (10). Raman spectroscopy is commonly used in chemistry, since vibrational information is specific to the chemical bonds and symmetry of molecules. Therefore, it provides a fingerprint by which the molecule can be identified. In textile industry, Raman spectroscopy can be used for determining of dyeing property, density and crystallization degree. Raman spectroscopy can determine less polar functional groups compare to FTIR spectroscopy.

X-ray scattering techniques are a family of non-destructive analytical techniques which reveal information about the crystallographic structure, chemical composition, and physical properties of materials and thin films. These techniques are based on observing the scattered intensity of an X-ray beam hitting a sample as a function of incident and scattered angle, polarization, and wavelength or energy. X-ray diffraction yields the atomic structure of materials and is based on the elastic scattering of X-rays from the electron clouds of the individual atoms in the system. The most comprehensive description of scattering from crystals is given by the dynamical theory of diffraction. Small angle X-ray scattering (SAXS) probes structure in the nanometer to micrometer range by measuring scattering intensity at scattering angles 2θ close to 0°. Wide angle X-ray scattering (WAXS), is a technique concentrating on scattering angles 2θ larger than 5°. WAXS method is used in the identification of crystallization and spinning rate of fibers, determination of crystalline orientation and molecular structure and investigation of physical properties of the filaments (11).

Thermogravimetric analysis or thermal gravimetric analysis (TGA) is a type of testing performed on samples that determines changes in weight in relation to change in temperature. Such analysis relies on a high degree of precision in three measurements: weight, temperature, and temperature change. As many weight loss curves look similar, the weight loss curve may require transformation before results may be interpreted. A derivative weight loss curve can identify the point where weight loss is most apparent. Again, interpretation is limited without further modifications and deconvolution of the overlapping peaks may be required. TGA is commonly employed in research and testing to determine characteristics of materials such as polymers, to determine degradation temperatures, absorbed moisture content of materials, the level of inorganic and organic components in materials, decomposition points of explosives, and solvent residues. It is also often used to estimate the corrosion kinetics in high temperature oxidation (12, 13). Thermogravimetric analysis is preferred especially in high performance fibers in order to measure thermal degradation degree of the fibers in the fabric.

Differential scanning calorimetry or DSC is a thermoanalytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference is measured as a function of temperature. Both the sample and reference are maintained at nearly the same temperature throughout the experiment. Differential scanning calorimetry can be used to measure a number of characteristic properties of a sample. Using this technique it is possible to observe fusion and crystallization events as well as glass transition temperatures Tg. DSC can also be used to study oxidation, as well as other chemical reactions (14, 15). As the temperature increases, an amorphous solid will become less viscous. At some point the molecules may obtain enough freedom of motion to spontaneously arrange themselves into a crystalline form. This is known as the crystallization temperature (Tc). This transition from amorphous solid to

crystalline solid is an exothermic process, and results in a peak in the DSC signal. As the temperature increases the sample eventually reaches its melting temperature (Tm). The melting process results in an endothermic peak in the DSC curve. The ability to determine transition temperatures and enthalpies makes DSC a valuable tool in producing phase diagrams for various chemical systems (11, 15). By this method, it is possible to determine melting enthalpy and temperature, glass transition point and crystallinity of the fiber. The determination of melting temperature is used as a basis for fiber identification. By comparing the measured heat of fusion with the theoretical value, the purity or content can be determined. Similarly the measured heat of reaction can be compared with the theoretical value in order to calculate the extent of reaction, for example with cross-linking reactions. DSC is also useful for characterizing bicomponent fibres, film-forming finishes and coatings (1).

Fourier transform infrared spectroscopy (FTIR) is a technique which is used to obtain an infrared spectrum of absorption, emission, photoconductivity or Raman scattering of a solid, liquid or gas. An FTIR spectrometer simultaneously collects spectral data in a wide spectral range. This confers a significant advantage over a dispersive spectrometer which measures intensity over a narrow range of wavelengths at a time. FTIR technique has made dispersive infrared spectrometers all but obsolete (except sometimes in the near infrared) and opened up new applications of infrared spectroscopy (16). From an FTIR spectrum, particular functional groups can be precisely located at a certain wavelength. Hence, the fibre type, crystallinity, chemical compositions of the fabric surface can be characterized (1). Compared to DSC it has the obvious advantage of being non destructive; compared to WAXD it allows a quick determination of crystallinity, since an IR spectrum can be collected in a few seconds as opposed to the several minutes taken to collect a WAXD diffractogram. IR spectroscopy is therefore a suitable technique when a rapid determination of crystallinity is required, or when a time evolving phenomenon needs to be followed. The main difficulties for the application of the technique are two: firstly, the identification of the bands sensitive to the amorphous and to the crystalline content; secondly, the determination of the absorption coefficient ratio between amorphous and crystal (17). FTIR Infrared spectroscopy is often a useful in the analysis of insoluble or macromolecular substances, cross-linked finishes, fibres, coatings, etc (1).

The main objectives of this work are to introduce the new fiber identification methods and show the some applications of these methods for hollow polyester fibers. Polyester (PES) fibers are a major type of textile raw material having high functional properties. It has an excellent capacity for physical modification (18). Hollow polyester fibers were preferred in the study because they have a great importance on new functional fibers and have been used in technical textiles.

2. MATERIAL AND METHOD

2.1 Material

The properties of the semidull hollow PET fibres used in this study are presented in Table 1. They were gently supplied from Advansa that is an important polyester fibre producer in Turkey.

2.2 Method

The fibres were firstly exposed to chemical solubility tests as described in Ref. 2. According to the test procedure, the types of the fibers are determined by their solubility in certain solvents. Following these tests, light microscope (Leica L5 FL stereomicroscope, 400x magnification), SEM (Phillips XL- 30S FEG, 500x), DSC (Perkin-Elmer/Pyris 6) and FTIR-ATR spectroscopy (Perkin Elmer Spektrum 100) were used as new identification methods. Before SEM analysis, fibres were coated with gold to ensure conductivity.

3. RESULTS AND DISCUSSION

3.1 Microscopic Analyses

After the fibres were proved to be 100 % polyester by chemical solubility tests, microscopic analyses were applied to the samples.

Hollow fibre production by changing the shape of the spinning nozzle is a physical modification of polyester during fibre production to achieve new properties. Synthetic fibers for general commercial application are mostly solid filament or solid fibre yarns. Hollow fibres have benefits for specific applications due to the larger fibre surface/volume ratio.

The fiber cross-section can be modified by changing the shape of the spinneret holes; and while a round section is usual, a myriad of other shapes have been produced, the more common of which would be trilobal or pentalobal. The fiber is solidified by cooling and drawn to encourage polymer chain orientation and crystallinity. The fiber is produced as continuous filaments that can be texturized, or cut into staple lengths. Filaments may be partially drawn (POY) for later draw texturizing, while FOY is fully drawn at the fiber production stage. A change in the shape of the cross section in man made fibres many physical characteristics such as sorption, dyeability, touch, pilling resistance, abration, weight, bulk, thermal properties, insulation capacity, glistering, lustre, covering and opaqueness. Fibre cross section shape also affects the fabric hand (19-23).

Table 1. Properties of the hollow PET fibres

	Aerelle	Air Quallofil	Hollofil	Comforel
Fineness (dtex)	4	5	5	4
Viscosity (dL/g)	0,645	0,603	0,608	0,643
Carboxyl end groups (mmol/kg)	32,4	28,8	24,0	40,0
Diethyleneglycol (DEG) content (%)	0,71	0,86	0,74	0,86

SEM and polarized light microscope were used to visualize the microstructure of the PET micro-porous hollow fibers. Today, the round fiber cross section is the most common shape manufactured by synthetic fiber producers. However, in fiber applications, a round cross section is not always preferred. Other shapes have emerged for a variety of reasons, such as performance, comfort, pilling propensity, bulkiness, tactility, processing, etc. For this aim, various types of specialized section have been developed with special orifices, such as a conventional slit, Y-shape, T-shape or similar shape modified slits, combinations of circle and slit, and various hollow shapes. A non-circular cross-sectional shape of fibers shows properties different from cylindrical fibers with a circular cross section, in bending stiffness, coefficient of friction, softness, appearance and handle (21). When cross-sectional shapes of selected samples in this study are considered, it's clearly seen that all the selected samples have round cross section like regular PET types except core shapes. The cross section of a regular PET fibre is shown in Figure 1.

As presented in Figures 2 and 3, hollow samples have cores that provide thermal comfort. Also, it's clearly seen the wall thickness/hollowness of the PET micro-porous hollow fibers differ from fibre to fibre. For instance, Aerelle and Quallofil have a wide core and thin wall, whereas Comforel has a narrow core and thick wall. On the other hand, Hollofil fibre has four channels to give improved thermal protection.

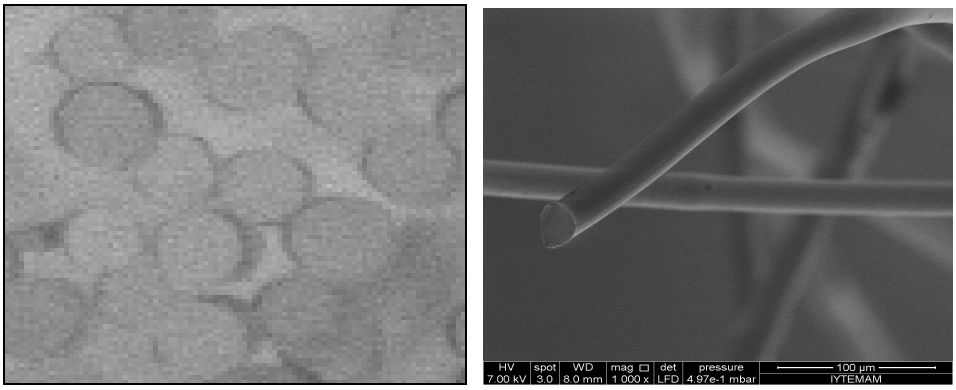

Figure 1. Light microscopic (a) and SEM (b) images of a regular PET fibre

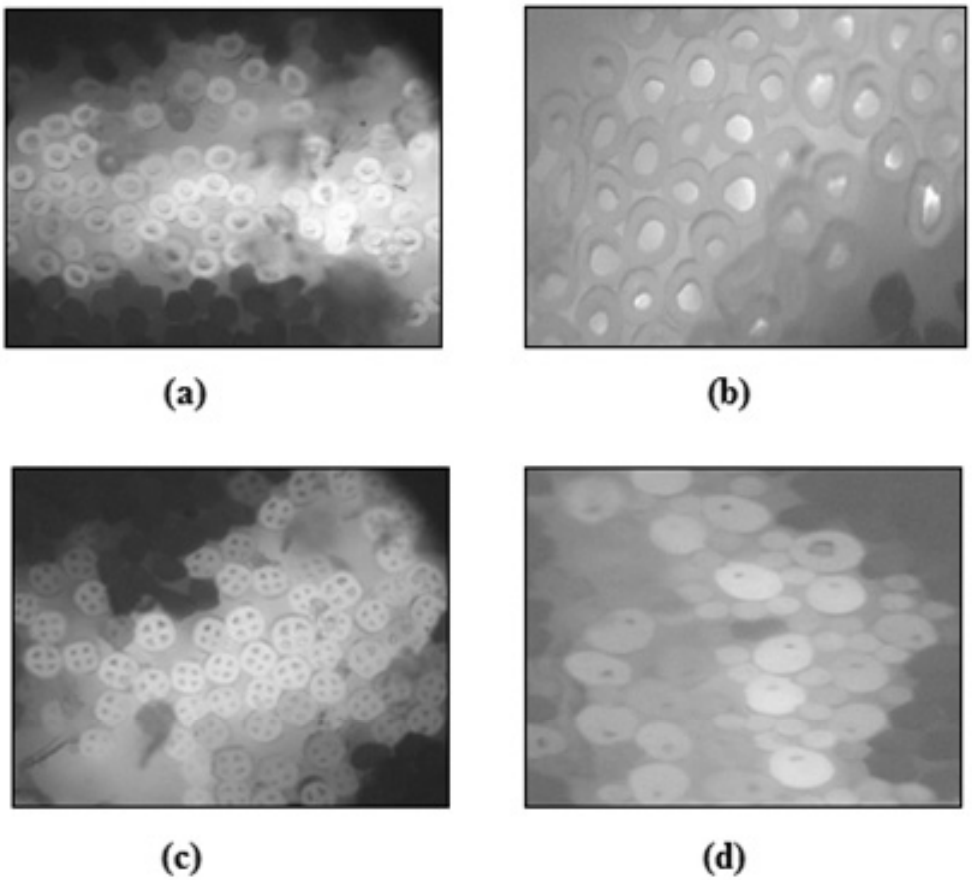

Figure 2. Light microscopic images of the samples (a) Aerelle (b) Air Quallofil (c) Hollofil (d) Comforel

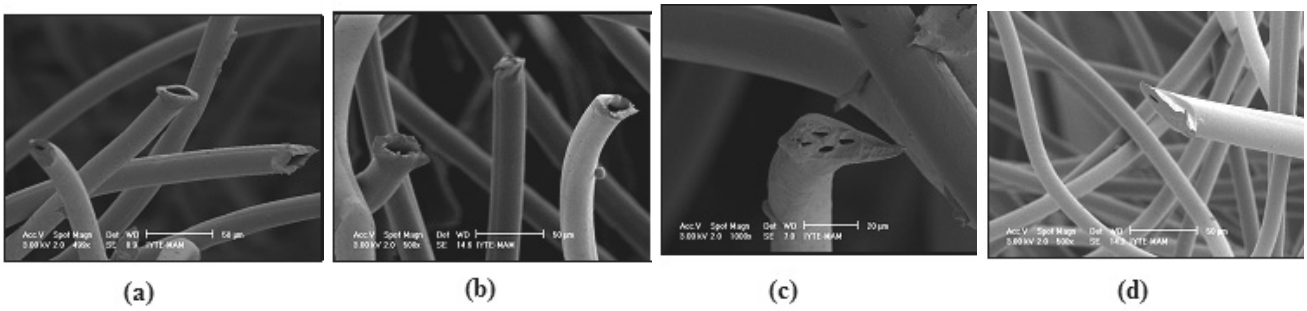

Figure 3. SEM images of the samples (a) Aerelle (b) Air Quallofil (c) Hollofil (d) Comforel

3.2. DSC Analysis

The heat of fusion (enthalpy) and melting point of the fibers were measured by the heating of the samples from 50 to 300°C at 20°C/min on a Perkin-Elmer/Pyris 6 differential scanning calorimeter according to ASTM E 1356-03. The DSC curves of the fibres: (a) Regular PET (b) Aerelle (c) Air Quallofil (d) Hollofil (e) Comforel are presented in Figure 4.

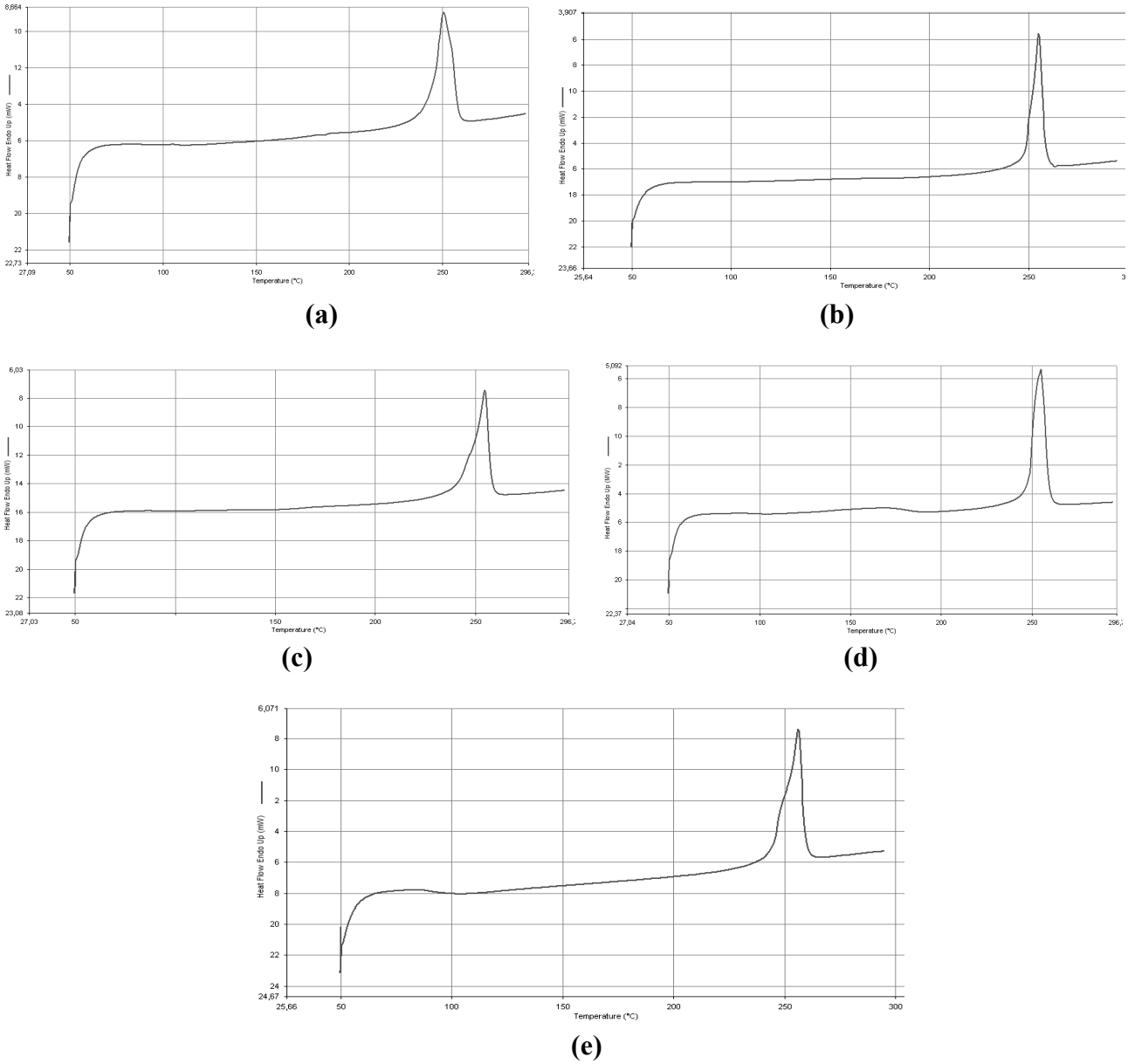

Figure 4. DSC curves of the fibres (a) Regular PET (b) Aerelle (c) Air Quallofil (d) Hollofil (e) Comforel

In the DSC curves of the fibers, due to the melting temperature, the endothermic peak was seen. All five materials gave rise to generally similar thermograms. The melting temperatures of the all fibers were found to be identical (~250-256,5°C).

DSC results can show the net thermal outcome of degradation reactions. A purely gas-phase action would require the production of a large amount of volatile species and the breaking of many chemical bonds, which is an endothermic process (24, 25).

The peak onset temperature and the peak maximum temperature are noted as onset temperature and melting temperature respectively. These values are given in Table 2.

These results underline that regular PET fibre and hollow fibres probably have same mechanism of degradation, and that can be attributed to the modification of polyester during hollow fibre production was physical.

3.3 FT-IR Analysis

The characteristic properties were analyzed using a Fourier Transform Infrared-Attenuated Total Reflection Spectrophotometer (FTIR-ATR), Perkin Elmer, in the region from 4000 to 650 cm^{-1}, with an average of 25 scans and using a resolution of 4 cm^{-1}. In Figure 5, a FT-IR spectrum of the samples are given.

As shown, the most characteristic bands of the PET fibres are 1717, 1242, 1120, 1096 and 726 cm^{-1}. The absorption band at 2874 cm^{-1} is attributed to – CH_2 – groups, 1717 cm^{-1} to carbonyl (C=O) stretching vibration, 1242, 1120 and 1096 cm^{-1} to (C – O) vibrations. The bands between 650 and 900 cm-1 are the characteristic peaks of benzene rings so the distinctive peak in the 726 cm^{-1} is attributed to the benzene rings absorption. The bands at 1560 and 1410 cm^{-1} are phenyl and methylene groups in the PET fibre. These results are consistent with the previous studies about PET fibres (26, 27).

It was found that there is no significant difference between the regular PET fibre and hollow PET fibres since there is no chemical but physical modification in the production of the hollow fibres (see Figure 6)

Table 2. Summary of key DSC temperatures of the samples

	Regular PET	Aerelle	Air Quallofil	Hollofil	Comforel
Onset temperature (°C)	248,96	254,42	254,15	253,73	255,55
Melting temperature of the polymer (°C)	250,28	256,37	256,33	257,34	257,69

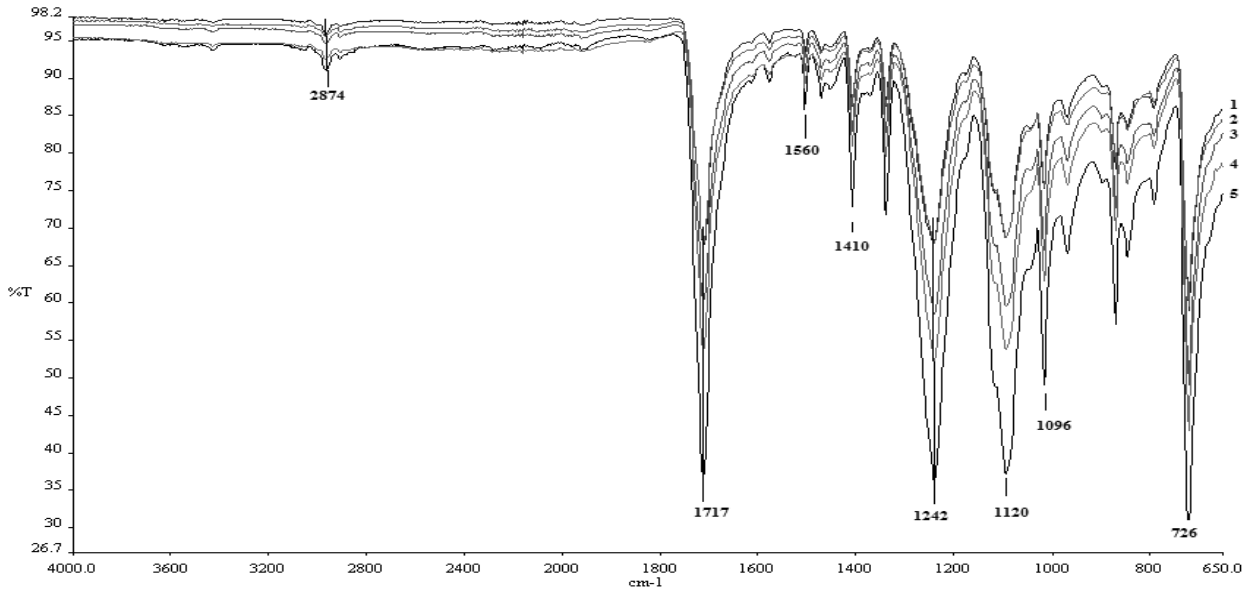

Figure 5. FT-IR spectra of the samples; (1) Regular PET (2) Hollofil (3) Aerelle (4) Comforel (5) Air Quallofil

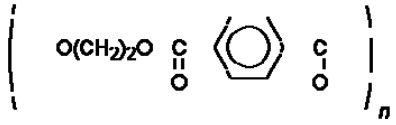

Figure 6. Chemical structure of a Polyester fibre (3)

4. CONCLUSION

This study investigated the use of new methods in the identification of hollow fibres. After the fibres were determined as polyester based by the chemical solubility tests, to find the melting temperatures DSC analysis was performed. The melting temperatures of the all fibers were found to be identical (~256,5°C). From the FT-IR analysis, it was found that there is no difference between the regular PET fibre and hollow PET fibres since there is no chemical but physical modification in the production of the hollow fibres. Microscopic analyses showed that all the samples have round cross section like regular PET types except core shapes. It was also found that Aerelle, Quallofil and Comforel have only one channel and Hollofil fibre has four channels. Among these methods, microscopic analyses were found to be most useful in the determination of the morphological difference between hollow PET fibres and the regular PET fibre.

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