THERMOGRAVIMETRIC, MICROSCOPIC AND MECHANICAL ANALYSES OF PBT AND PET YARNS

PBT VE PET İPLİKLERİN TERMOGRAVİMETRİK, MİKROSKOPİK VE MEKANİK ANALİZLERİ

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ABSTRACT

In this study, thermogravimetric, microscopic and mechanical properties of different types of polyester yarns were investigated and compared. To this goal, PET based regular polyester yarn and polyester yarns modified for various specialities (flame-retardant, UV protective and antibacterial) and PBT yarn were selected. According to the results, it was determined that PBT had a lower Tdi value, higher char residue, lower tensile strength compared to regular PET and similar surface characteristics to regular PET. Among the modification processes, only the flame retardancy process was found to affect the thermal property.

Key Words: PET, PBT, Thermogravimetry, Microscopy, Tensile Strength.

ÖZET

Bu çalışmada, farklı tipte poliester ipliklerinin termogravimetrik, mikroskopik ve mekanik özellikleri incelenmiş ve karşılaştırılmıştır. Bu amaçla, PET esaslı normal poliester ipliği ve çeşitli özellikler (güç tutuşurluk, ultraviole koruyuculuk ve antibakteriyel) kazandırılmak için modifiye edilmiş poliester iplikleri ve PBT ipliği seçilmiştir. Elde edilen sonuçlara göre, normal PET ipliği ile kıyaslandığında, PBT ipliğinin daha düşük Tdi değerine, daha yüksek kömürleşmiş kalıntıya, daha düşük kopma mukavemetine ve benzer yüzey özelliklerine sahip olduğu tespit edilmiştir. Modifikasyon işlemleri arasında ise yalnızca güç tutuşurluk işleminin termal özellik üzerinde değişikliğe sebep olduğu anlaşılmıştır.

Anahtar Kelimeler: PET, PBT, Termogravimetri, Mikroskopi, Kopma Mukavemeti.

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1. INTRODUCTION

Polyester is a well known synthetic fibre that has been around for more than half a century. It is used in all types of apparel, home furnishings, geotextiles, industrial applications, tire reinforcement, and so on. Like other fibers, it is routinely sold in many variants of diameter, cross-section, and luster. It is generally produced by the polycondensation of terephthalic acid and ethylene glycol and this polyester fibre is known as polyethylene terephtalate (PET) fibre (1). Polyethylene terephthalate (PET) fibers have an excellent capacity for physical modification (2). Besides PET fibre, there are also other commercialized polyester fibres synthesized from various monomers such as poly 1,4-cyclohexylenedimethylene terephtalate, poly buthylene terephtalate and poly trimethylene terephtalate (3).

Poly 1,4-cyclohexylenedimethylene terephtalate was originally developed for fibre applications but has found wider utility as a reinforced polymer for injection molding and as a material for crystallized food packaging trays nowadays (4).

Polytrimethylene terephthalate (PTT) is a new type of polymer material produced by the polycondensation reaction of purified terephthalic acid (PTA) and 1,3-propanediol (PDO). As a member of the polyester family, PTT has very similar chemical properties with polyethylene terephthalate (PET) (5, 6).

Poly butylene terephthalate (PBT) is a linear polyester of aromatic nature and has excellent mechanical properties (7). PBT is made by reacting 1,4-butanediol (BDO) with terephthalic acid (TPA) or dimethyl terephtalate (DMT) in the presence of a

transesterification catalyst. PBT is easily made into fibre and monofilament and has been used in some fibre applications. Compared to PET, PBT fibre is more resistant to permanent deformation (4).

Polyester fibers are produced in a variety of forms, broadly classified as staple fibres, textile filament and industrial filament. End-uses for these variants have different requirements in terms of fibre properties and physical geometry, and so different fibre manufacturing processes have evolved according to the special needs of each market segment (4).

Although polyester fibre has good properties like high tensile strength, luster etc., it has inherent characteristics that limit its use in some applications too. For example, low water-absorbing capacity, high pilling tendency, tendency to accumulate static charge, difficulty of dyeing and low abrasion resistance are undesirable properties of the polyester fibres (8).

In many applications, modification of polyester fibre properties is desirable in order to enhance certain features of the product or to enhance the process of converting fibres into finished goods. Polyester can be modified to obtain new or enhanced properties, such as an affinity for cationic dyes, non-flammability, resistance to ultraviolet radiation, increased strength, etc; or to suppress some negative properties, such as reducing the pilling tendency, increasing the absorbing capacity, etc (4, 8).

Polyester melts at around ~265-285°C. The glass transition temperature of amorphous polyester is in the range of 65-75°C, and this can increase to ~125°C after being drawn and partially crystallized, reflecting the reduced rotational mobility of the chain segments. But sometimes, problems can occur with garments made from thermoplastic polymer fibres when exposed to flames; the molten polymer can stick to skin and cause burns. Thermal decomposition of polyester also generates acetaldehyde, which is a flammable gas that feeds combustion. Additives can be used to break the combustion cycle, e.g. endothermic substances that absorb heat; char formers that insulate the flame from the substrate, additives that react with and remove oxygen (e.g. phosphorous), or additives that promote melting and dripping to separate the molten material from the combustion area (4, 9).

UV radiation is also one of the major causes of degradation of textile materials, which is due to excitations in some parts of the polymer molecule and a gradual loss of integrity, and depends on the nature of the fibres. UV absorbers incorporated into the fibres convert electronic excitation energy into thermal energy, function as radical scavengers and singlet oxygen quenchers. The high-energy, short-wave UVR excites the UV absorber to a higher energy state; the energy absorbed may then be dissipated as longer-wave radiation. Alternately, isomerisation can occur and the UV absorber may then fragment into non-absorbing isomers (10).

Antibacterial properties have become important factors for some textile application areas (e.g. sanitary and medical textiles) too. So, incorporation of antibacterial agents like silver, quaternary ammonium compounds, chitosan etc is broadly studied in the literature. In general, the antibacterial agent penetrates the fiber like a dispersion dyestuff and is supported in it by some selected types of carrier. In another method, the bactericide is added during grafting or solid-face copolycondensation of fibres (8).

Briefly, polyester can be modified for a number of reasons and by several different strategies such as to include co-monomers in the polymerization process or additives to the polymer melt before extrusion, topical additive treatments after the fiber is formed and physical/non-additive chemical modifications (1).

Fibers can also be modified via changing fiber cross-sectional shapes. Surface lobes can break up smoothness and reduce glitter, and triangular or 'T' shapes can generate subtle sheen effects to fabrics and yarns. In the literature, it has been mentioned that there are various cross-sectional shapes used to provide visual and tactile effects that are not possible with natural fibres. 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 (1, 4).

In this study, PBT yarn, three PET based modified polyester yarns (flame-retardant, UV protective and antibacterial) and an unmodified PET based yarn were used. Some properties and surface characteristics of these yarns were investigated. The thermal behavior of treated samples was also discussed.

2. MATERIAL AND METHOD

2.1 Materials

The semi-dull modified polyester yarns were supplied from KORTEKS that is an important polyester yarn producer in Turkey. The information about the yarns is given in Table 1.

Table 1. Properties of the yarns

Yarn type	Yarn linear density (dtex)	Number of filaments
Regular PET	167	48
Flame Retardant PET	183	72
UV protective PET	167	48
Antibacterial PET	176	36
PBT	103	24

PET: polyethylene terephthalate.
PBT: polybuthylene terephthalate.

2.2 Methods

2.2.1 Microscopic Analyses

The morphologic features of various modified and unmodified yarns were studied with the help of light microscope (Leica L5 FL stereomicroscope) and SEM (Phillips XL-30S FEG).

2.2.2 Thermogravimetric Analysis (TGA)

The TGA of the fabric sample was carried out using a Perkin-Elmer Diomand in the temperature range of 30–500°C under nitrogen atmosphere. The heating rate was maintained at 10°C/min. The measurements were made under a constant nitrogen flow rate of 20 ml/min.

2.2.3 Mechanical Analyses (Tensile Properties)

The tensile strength and elongation at break properties of the samples were measured using a Statimat material testing machine and tests were conducted according to DIN EN ISO 2062 method.

3. RESULTS AND DISCUSSION

3.1 Microscopic Analysis

To investigate the microstructure of the samples, SEM and polarized light microscope were used. The SEM and microscopic images of the samples are shown in Figure 1 and 2.

From the SEM images, it was clearly seen that the polyester fibre generally had a smooth surface. After the modification processes, it was detected that there were some particles on surface of the fibers and the surfaces were rougher. Also, cross section of the fibres and incorporated materials (e.g. silver particles in Figure 1b) on the fiber surface differed due to change in the spinning process and in the additive material.

From the light micrographs, the cross sectional shapes of the fibres were clearly observed. It was seen that regular and UV additive polyester fibres had circular cross section whereas antibacterial and flame retardant polyester fibres and PBT had pentalobal cross section. It was also seen that PBT fibre had a smooth surface like PET based fibres and this fact confirmed the previous study of Mathew et al (11).

3.2 Thermal Analysis

The thermal behaviors of PBT yarn as well as unmodified and modified PET yarns were investigated by TGA thermograms. The thermal properties of the samples were presented in Table 2.
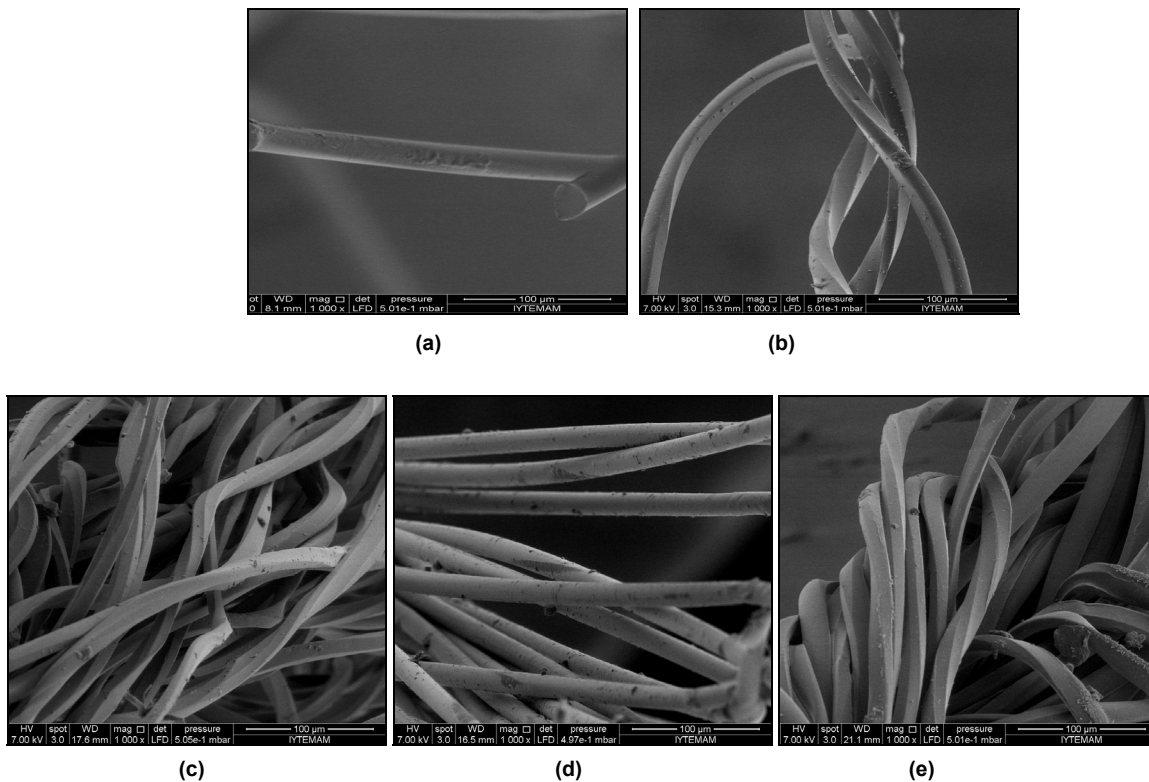

(a) **(b)**

(c) **(d)** **(e)**

Figure 1. SEM images of the samples (a) Regular Polyester, (b) Antibacterial Polyester , (c) Flame-retardant Polyester (d) UV Additive Polyester (e) PBT
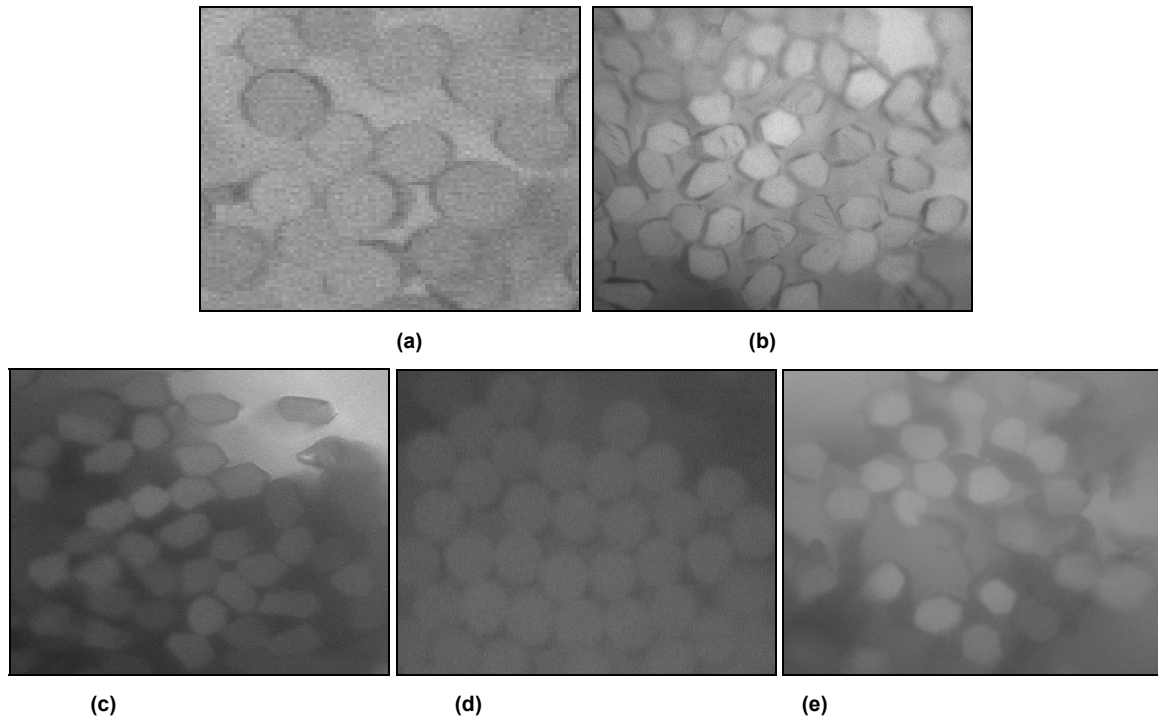
(a)

(b)

(c)

(d)

(e)

Figure 2. Microscopic images of the samples (a) Regular Polyester (b) Antibacterial Polyester (c) Flame-retardant Polyester (d) UV Additive Polyester (e) PBT

Table 2. Thermal properties of the samples

Samples	Onset Temperature for Weight Loss (°C)	Remaining Weight at 500°C (%)
Regular PET	366,39	10,707
Antibacterial PET	374,76	13,262
Flame-Retardant PET	306,80	15,577
UV Additive PET	375,00	13,150
PBT	351,74	13,485

It was observed that all the fibres had different weight-loss stages and onset temperatures. It is generally known that thermal decomposition of polyester usually starts with the scission of the polymer chain and polyester generates benzoic acid, carbon dioxide, carbon monoxide, benzoic acid derivatives, oligomers and polycyclic aromatic hydrocarbons upon high temperature decomposition (9). From the Table 2, it can be said that flame retardant PET undergoes single stage degradation with a single peak at around 306,80°C, whereas the degradation temperatures of other samples are in the range of 350-375°C. This fact is in accordance with the previous studies (9, 12).

In Figure 3, the TGA graphs of the regular PET and flame retardant PET (the most distinctive difference observed ones) are given.

From the data in Table 2, the onset temperature of flame-retardant PET was found to be the lowest one in comparison with the others. In the previous study of Chang et al, the reason of this reduction of T_{di} (initial degradation temperature) was attributed to the fact that the O=P–O bond was less stable than the common C–C bond. Furthermore, it was seen that the char yield increased with phosphorus content, meaning the flame retardancy was improved. The accession to high char yield was estimated to be through two ways. Firstly, flame retardant component interrupted the exothermic processes and suppressed combustion by capturing free radical or secondly, it increased the char yield by redirecting the chemical reactions involved in decomposition in favor of reactions yielding carbon rather than CO or CO_2 and through the formation of a surface layer of protective char (13).

When the UV protective and antibacterial polyester yarns were considered, it was determined that the initial degradation temperature and char residue were slightly higher than the regular PET. For antibacterial polyester yarn, this increase was attributed to the development of intermolecular attraction among the polymer chains by the presence of silver nanoparticles. The improved thermal stability could also be explained through the reduced mobility of the polyester chains. For UV protective yarn, this increase was estimated to be due to the presence of TiO_2 particles in the yarn remained at higher temperatures (14, 15).

When the thermal decomposition behavior of PBT was compared to that of PET, since PBT had high number of methylene groups in the main chain, it was observed that PBT had a low initial degradation temperature (Tdi=351,74°C) and high char residue. These results were in accordance with the involved papers (14-16).
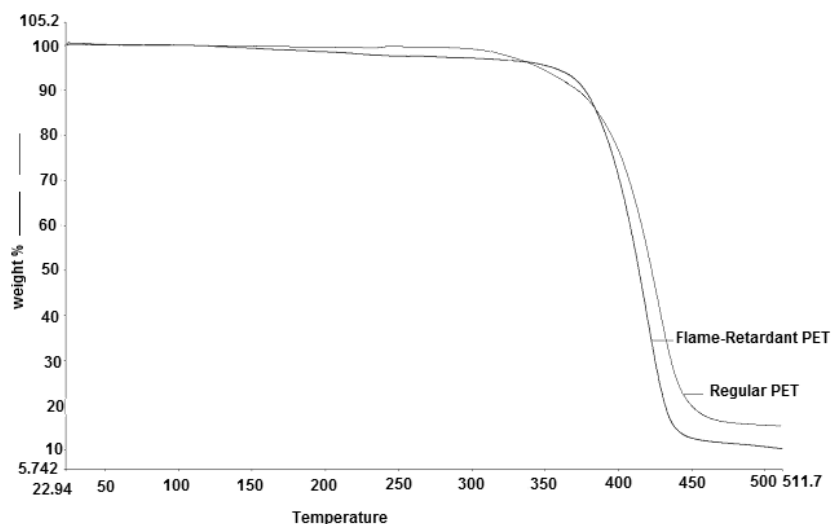
Figure 3. The TGA graphs of the regular PET and flame retardant PET

3.3 Mechanical Analyses

The mechanical properties of the samples are shown in Table 3. Since the yarn numbers were different, it could be considered that this fact could lead to uneven mechanical property comparison. However, it was determined that the flame retardant yarn had the lowest tensile strength, although it was the thickest one. So, it was understood that the difference between the yarn numbers did not affect the mechanical strength significantly. The fact that flame retardant yarn had the lowest tensile strength could be attributed to the weak O=P–O bond and phosphorus content in the yarn. In the related studies, it had been stated that the presence of higher phosphorus content caused lower crystallinity, melting temperature, decomposition temperature and tensile strength but higher residual char after thermal degradation (17, 18). As seen from the Table 3, the second yarn with low tensile strength was found to be PBT. Depending on the different nature, PBT is known to have slightly poorer mechanical properties than PET (4). But the mechanical properties of PBT can be enhanced by hybridization with other fibres (19). When the UV protective and antibacterial PET yarns were considered it could be said that there was no significant difference with regular PET.

Table 3. Mechanical properties of the yarns

Yarn type	Tensile strength (cN/dtex)	Elongation at Break (%)
	(DIN EN ISO 2062/STATIMAT)	(DIN EN ISO 2062/STATIMAT)
Regular PET	3.8 (1.8)	37.8 (3.4)
Flame Retardant PET	2.3 (2.6)	33.1 (6.0)
UV protective PET	3.8 (1.7)	37.4 (4.2)
Antibacterial PET	3.4 (1.4)	22.5 (4.2)
PBT	2.9 (0.4)	32.0 (6.8)

Note: the values in the parentheses are CV%.
PET: polyethylene terephthalate.
PBT: polybuthylene terephthalate

4. CONCLUSION

Five polyester yarns were used to assess the effects of different modifications and components on microscopic, thermogravimetric and mechanical features. Experimental results indicated that the flame retardancy modification had more significant effect on thermogravimetric and mechanical features than that of other samples. Microscopic analyses demonstrated that polyester fibre had a smooth surface. Both the modification processes and difference in chemical composition caused differences like some particles attached on the fiber surface and

increased roughness. From the light microscopy photos, cross section of regular and UV additive polyester fibres was found to be circular whereas antibacterial and flame retardant polyester fibres and PBT was pentalobal in terms of cross section. From the thermogravimetric analyses, it was determined that after flame retardancy process T_{di} (initial degradation temperature) decreased due to the O=P–O bond and PBT had similar thermal behaviors than PET. The findings obtained from mechanical analyses indicated that the physical features of polyester yarns were affected distinctively by applied processes.

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