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INVESTIGATION OF SOME PROPERTIES OF PET (POLYETHYLENE TEREPHTHALATE) POY YARNS CONTAINING PLASMONIC BORON NANOPARTICLES ADDITIVE

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ABSTRACT

In this study, it was aimed to increase the contribution to the national economy based on boron, which creates a competitive advantage in the development of new technological solutions and to expand the use of boron products. It is necessary to create new generation textile fibers with new usage areas of rich boron resources and to acquire boron products with high added value and new production areas for new markets. Technological and scientific developments in the field of nanomaterials are often used in the functionalization and modification of textile fibers. The usage properties and functions of synthetic yarns can be improved by the utilization of nanomaterials and nano-systems. In this study, PET (Polyethylene Terephthalate) POY (Partially Oriented Yarn) yarns containing different amounts of new generation plasmonic nanocomposite particles [functionalized core-shell nanohybrid nanoparticles (TiNPs@amine- functionalized GQDs@BNNS nanohybrid nanoparticles)] were produced via melt spinning process. Then, the strength, elongation, yarn unevenness, degreasing, etc. properties of PET POY yarns containing boron-based nanocomposite were investigated. With this study, it was ensured that boron-based nanocomposite-doped polyester fibers containing a new generation of plasmonic nanoparticles were developed and produced on an industrial scale.

KEYWORDS

Boron, boron nitride nanoparticle, graphene quantum dots, titanium nanoparticle, polyester, polyethylene terephthalate, PET, fiber spinning, melt spinning, nanocomposite, POY.

INTRODUCTION

Textile products cover many different types of technical applications in construction, automotive, defense, sports, medicine, electronics, marine and similar sectors. In this context, it is expected that the functionalization of polyester yarns will gradually increase. One of the main issues in the realization of the boron policies of Turkey and increasing the competition is that the R&D studies in this field should be oriented towards the commercialization [1]. The idea of innovation and change with globalization, which shows its influence in many fields, is increasing its importance day by day. Innovation has been adopted in developing societies as the key to sustainable development, competitiveness, employment growth, social welfare, and quality of life. According to the literature studies, there are limited number of studies on the use of boron and its derivatives in the textile industry. In order to increase the contribution to the national economy from boron resources; developing new boron products that will spread their use in technological application areas by producing technological solutions that create competitive advantage based on boron, finding new areas of use for existing boron products, obtaining high value-added boron products, developing the industry based on boron in our country, creating new



production areas, increasing employment and the domestic consumption values to higher levels should be increased.

Boron has been utilized in many different fields and has been a material for many industries until today. Boron, which is in group 3A with the symbol B in the periodic table, possesses an atomic number of 5 and an atomic weight of 10.81 [2-7]. In the stable structure, it is found in nature as 19.1-20.3% B¹⁰ and 79.7-80.9% B¹¹ isotope. Boron, accepted as the hardest element after diamond, exists in two different structures as crystal with a density of 2.33 g/cm³ and amorphous with a density of 2.3 g/cm³ [8,9].

It is not found alone in nature and is always found in compounds with oxygen. Although it is included in the structure of more than 150 minerals; in an economic sense, boron minerals are found in the form of hydrate compounds with calcium, sodium, and magnesium elements as an input to many sectors and technology from glass sector to ceramics, from cleaning sector to agricultural products [10]. Although Turkey has 73% of the world boron reserve, the use of boron in technology and industry in Turkey remains very limited [11].

The vast majority of nanomaterials are used in the textile, automotive, aerospace and packaging industries and different methods are involved in their distribution into polymers. Especially if polyester nanocomposite filament fibers doped with nanomaterials are to be made to provide functionality in the textile field, the melt spinning method is one of the most preferred. The fiber melt spinning method is a preferred method in the production of nanocomposite fibers in terms of its suitability for industrial polymer processing methods. In addition, this method is the most widely used nanocomposite production method in practice, as it is inexpensive and environmentally friendly [12].

In this study, it was aimed to create a new generation of boron-based nanocomposite-doped polyester fibers containing plasmonic nanoparticles and to produce them on an industrial scale. TiNPs@amine-functionalized GQDs@BNNS nanohybrid (TiNPs: Titanium nanoparticles; GQDs: Graphene quantum dots; the BNNS: boron nitride nanosheet) doped polyester (PET: Polyethylene terephthalate) nanocomposite fibers and their filament yarns were produced on an industrial scale in large development and production machines. Polyester (PET: Polyethylene terephthalate) polymer was selected as the textile fiber polymer. Since polyester fibers are the most produced and consumed textile fibers in the world. In addition, polyester fiber plays a leading role in the textile fiber industry as a very popular and useful textile fiber with many different end-uses. PET (polyethylene terephthalate) POY (partially oriented yarn) yarns containing varied amount of plasmonic boron nanoparticles additive were industrially produced via melt spinning process. Then, tenacity, elongation, yarn unevenness, oil pick-up etc. properties of PET POY yarns containing plasmonic boron nanoparticles were examined.

MATERIALS AND METHODS

Plasmonic Boron Nanoparticle Production

Synthetic fibers (polyester, polyamide, polyethylene and polypropylene etc.) are widely used in different fields such as textiles. This widespread use is not only due to the properties of these fibers such as high strength and low density, abrasion resistance and chemical resistance. In addition, it is possible to obtain fibers that exhibit properties such as conductivity, thermal resistance, and toughness to be used in some special applications. For instance, the incorporation of nanomaterials such as graphene into fibers changes the mechanical properties of the fibers, while providing many of the functionality required for electrical energy storage and sensor applications [13–16].

Graphene quantum dots (GQDs) are the most important member of nanocarbons. Quantum confinement has different properties such as unique luminescence, chemical stability and high water solubility [15]. Substitution of heteroatoms in graphene is known to adapt the band gap. To change this situation, it is necessary to create sizeless graphene quantum dots (GQDs) [16].

In this study, functionalized core-shell nanohybrid nanoparticles (TiNPs@amine-functionalized GQDs@BNNS nanohybrid nanoparticles) were produced from TiNPs (Titanium nanoparticles), GQDs (Graphene quantum dots) and the BNNS (Boron nitride nanosheet nanoparticles). Titanium (IV)

chloride salt was used for the preparation of Ti nanoparticles (TiNPs). The reduction process was carried out with ascorbic acid. The resulting solution was mixed for 1 hour at a temperature of 15°C. Then, the resulting precipitate was filtered and washed several times with deionized water. Graphene oxide obtained by the Hummers method has been converted into GQDs form. The carboxylic acid groups on the GQDs nanostructures were activated by 249arbodiimide (EDC) and then functionalized with 2-aminoethanethiol (2-AET). After mixing the prepared functionalized GQDs nanostructure on TiNPs in a 1:1 ratio, TiNPs@thiol-functionalized GQDs and boron nitride nanotube (BNNs) were obtained. Obtained BNNs previously prepared TiNPs@thiol-GQDs nanocomposites was treated at 50°C for 2 hours on a water bath on functionalized added during mixing and after washing with deionized water. Then, TiNPs@thiol-functionalized GQDs@BNNs nanocomposites structure was created and shown in Figure 1.

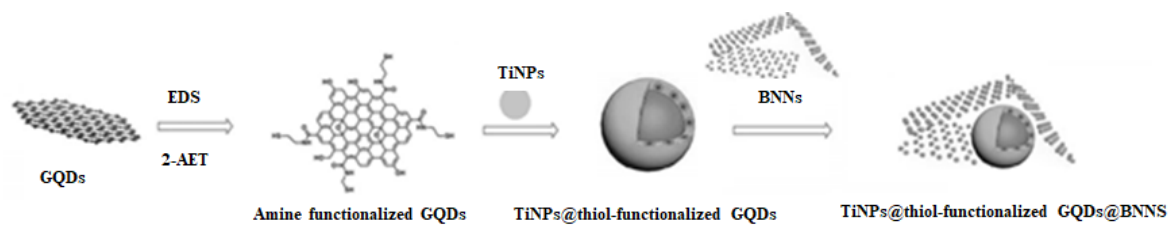


Figure 1. Schematic representation of the resulting functionalized core-shell nanohybrid (TiNPs@amine-functionalized GQDs@BNNs nanohybrid).

Masterbatch Production

Masterbatch was produced with the plasmonic boron nanoparticles and PBT (Polybutylene terephthalate) (Figure 2) using twin screw extruder (Figure 3) according to the melt mixing method with the help of PBT carrier polymer. The rate of active substance plasmonic boron nanoparticle in masterbatch was 10%. (Figure 4).



Figure 2. PBT polymer.



Figure 3. Twin screw extruder.



Figure 4. PBT carrier plasmonic boron nanoparticles added masterbatch.

Melt Spinning Fiber production

PET POY yarns comprising varied amount of plasmonic boron additive were produced according to the melt draft method with polyester (PET: polyethylene terephthalate) material which was in the form of granules. Barmag (Germany) branded industrial fiber melt spinning yarn production machine was utilized for this purpose. Masterbatch containing plasmonic boron was added to the PET polymer with a rate of 1% and 2% using the gravimetric dosing system (K-Tron, Germany) and then the resultant dope were fed to the extruder for melt spinning process. The utilized yarn production parameters are shown in Table 1. PET POY yarns containing varied amount of plasmonic boron were produced industrially under the industrial fiber production conditions (Figure 5). As a result, PET fiber POY yarns containing 1% plasmonic boron nanoparticles (PET POY 1) and 2% plasmonic boron nanoparticles (PET POY 2) were produced. Thereafter, some physical and surface properties of these yarns were investigated.

Table 1. PET POY yarn production parameters.

Production Parameter	CONTROL PET POY (0% BN)	PET POY 1 (1% BN)	PET POY 2 (2% BN)
Masterbatch ratio [%]	-	1	2
PET polymer ratio [%]	100	99	98
Extruder zone 1 [C°]	285	285	285
Extruder zone 2 [C°]	285	285	285
Extruder zone 3 [C°]	285	285	285
Heat transfer fluid [C°]	285	285	285
Winder speed [m/min]	3250/2500	3250/2500	3250/2500
Godet 1 Speed [m/min]	3110/1900	3110/1900	3110/1900
Godet 2 Speed [m/min]	3240/2250	3240/2250	3240/2250
Melt Pump Speed [hz]	26.1	26.1	26.1
Oil Pump Speed [hz]	58	58	58
Fiber Cross section	Round	Round	Round

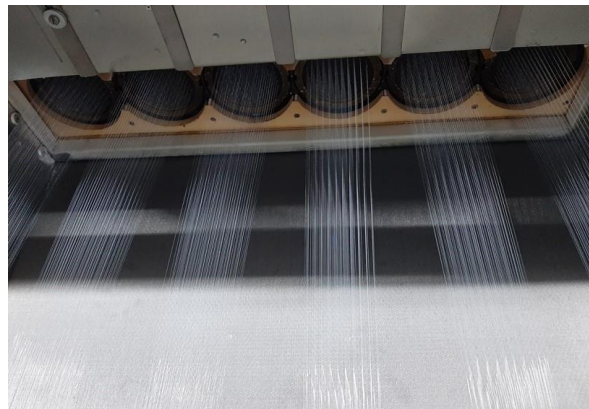


Figure 5. Melt spinning PET fiber production.

In addition, the strength, elongation, yarn unevenness, degreasing, etc. properties of PET POY yarns containing boron-based nanocomposite [Functionalized core-shell nanohybrid nanoparticles (TiNPs@amine- functionalized GQDs@BNNS nanohybrid nanoparticles)] were examined. Content measurement of plasmonic boron nanoparticles in PET POY yarns was also performed.

Yarn count Determination

PET POY yarn count control was performed using the Zweigle yarn reel machine according to the DIN EN ISO 2060 standard.

Tenacity and Elongation Determination

Tenacity and elongation analyses were performed utilizing the Textechno Statimat Me + device according to the DIN EN ISO 2062 standard. Analyses were carried out with 10 replicates for each individual yarn sample.

Oil pick-up Determination

Spin finish oil determination on the PET POY yarns was carried out using Oxford MQA 7020 device according to NMR Method.

Yarn unevenness Determination

Yarn unevenness analysis was performed utilizing Keisokki Evenness Tester according to DIN 53817 standard.

SEM (Scanning Electron Microscopy)

The examination of the PET POY yarn surfaces was carried out using the Hitachi TM3030Plus SEM microscope. Before the yarns were analyzed, their surfaces were coated with 2 micron gold palladium.

ICP-MS (Inductively Coupled Plasma Mass Spectrometer)

In this method, after the elements in the sample were ionized in ICP, they were sent to mass spectroscopy (MS), where they were separated and measured according to their mass/charge (m/z) ratios.

RESULTS AND DISCUSSION

Yarn count, tenacity, elongation, oil pick-up and yarn unevenness properties of PET POY yarns with (PET POY 1: 1% plasmonic boron nanoparticles and PET POY 2: 2% plasmonic boron nanoparticles) and without (CONTROL PET POY: 0% plasmonic boron nanoparticles) plasmonic boron nanoparticles additive, are given in Table 2 and Figures 6-8. Moreover, SEM images of Control PET POY, PET POY 1 and PET POY 2 are displayed in Table 2 and Figure 9. The resultant yarn count values of the Control PET POY yarn, PET POY 1 yarn and PET POY 2 yarn were 287.6, 289 and 290 decitex, respectively (Table 2). Furthermore, the percentage oil pick-up values of the Control PET POY yarn, PET POY 1 yarn and PET POY 2 yarn were very close and were measured as 0.6, 0.81 and 0.74 decitex, respectively (Table 2).

Table 2. Some properties of PET POY yarns with and without plasmonic boron nanoparticles additive.

Properties	CONTROL PET POY (0% BN)	PET POY 1 (1% BN)	PET POY 2 (2% BN)
Yarn count [Decitex]	287.6	289	290
Tenacity [cN/dtex]	2.1	1.91	1.86
Elongation [%]	132.5	121.2	125.3
Oil pick-up [%]	0.6	0.81	0.74
Yarn evenness	0.77	0.91	0.85

* Control PET POY (Control without plasmonic boron nanoparticles additive), PET POY 1 (with 1% plasmonic boron nanoparticles additive), PET POY 2 (with 2% plasmonic boron nanoparticles additive)

The tenacity values of the Control PET POY yarn, PET POY 1 yarn and PET POY 2 yarn were 2.1 cN/dtex, 1.91 cN/dtex, and 1.86 cN/dtex, respectively (Table 2 and Figure 6). Considering these results, the tenacity decreases as the amount of plasmonic boron nanoparticles added to the PET polymer increases. More plasmonic boron nanoparticles content in PET POY yarn resulted in more strength reduction.

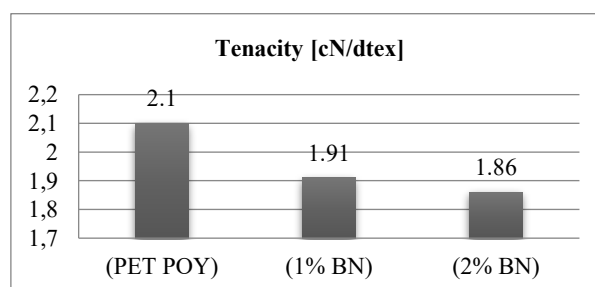


Figure 6. Tenacity properties of PET POY yarns with and without plasmonic boron nanoparticles additive.

The elongation values of the Control PET POY yarn, PET POY 1 yarn and PET POY 2 yarn were 132.5%, 121.2%, and 125.3%, respectively (Table 2 and Figure 7). As can be seen from the obtained yarn analysis values, in contrast to the strength values of PET POY yarn, as the amount of plasmonic boron nanoparticles increased, the elongation increased. However, these values were less than the elongation value of the control PET POY yarn.

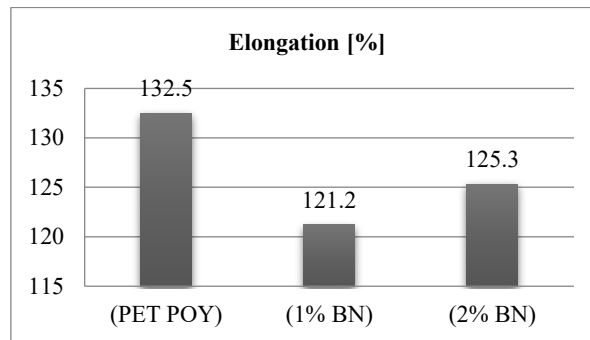


Figure 7. Elongation properties of PET POY yarns with and without plasmonic boron nanoparticles additive.

The yarn unevenness values of the Control PET POY yarn, PET POY 1 yarn and PET POY 5 yarn were 0.77, 0.91, and 0.85, respectively (Table 2 and Figure 8). The lowest yarn unevenness level was monitored in the case of Control PET POY. Looking at the values measured in the yarn unevenness measurement, lower values indicate that the yarn is more even, smoother, and therefore better. PET POY with 1% additive exhibited the highest yarn unevenness value with 0.91 (Figure 8).

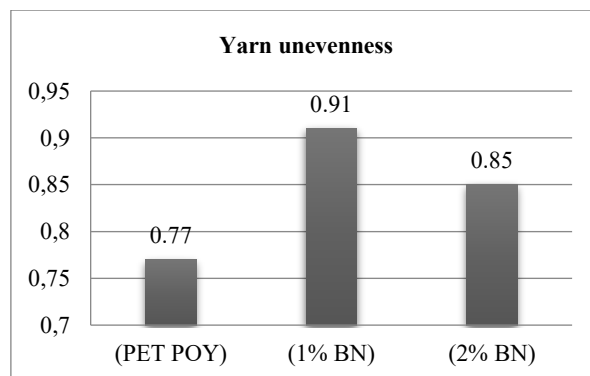


Figure 8. Yarn unevenness properties of PET POY yarns with and without plasmonic boron nanoparticles additive.

Analysis of the amount of B and Ti existence in the PET POY yarns was carried out with the ICP-MS device. According to the ICP-MS analysis, it was clear that there is no B and Ti element in the Control PET POY yarn (Table 3). On the other hand, the presence of B and Ti elements was clearly observed in the results of PET POY 1 and PET POY 2 yarns (Table 3). Higher plasmonic boron nanoparticles content (1% and 2%) resulted in higher Ti and B presence in PET POY yarn. As a matter of fact, according to the results of the Ti presence obtained in the ICP-MS analysis, the amount of plasmonic boron nanoparticles in the PET fiber POY yarn increased approximately 2 times during production with the doubling of the masterbatch dosage.

Table 3. ICP-MS results of plasmonic boron nanoparticle doped and undoped PET POY yarns.

Properties	Control PET (0% BN)	PET POY 1 (1% BN)	PET POY 2 (2% BN)
B content	0	232	243
Ti content	0	141	205

The measured yarn unevenness results were in parallel with the obtained SEM images (Figure 9). Indeed, scanning electron microscope images displayed the presence of some slight deformation and plasmonic boron nanoparticles material on the surface of the polymer (Figure 9). Plasmonic boron nanoparticles presence and observed polymer deformation accumulated on the fiber surfaces resulted in an increase on PET POY yarn unevenness.

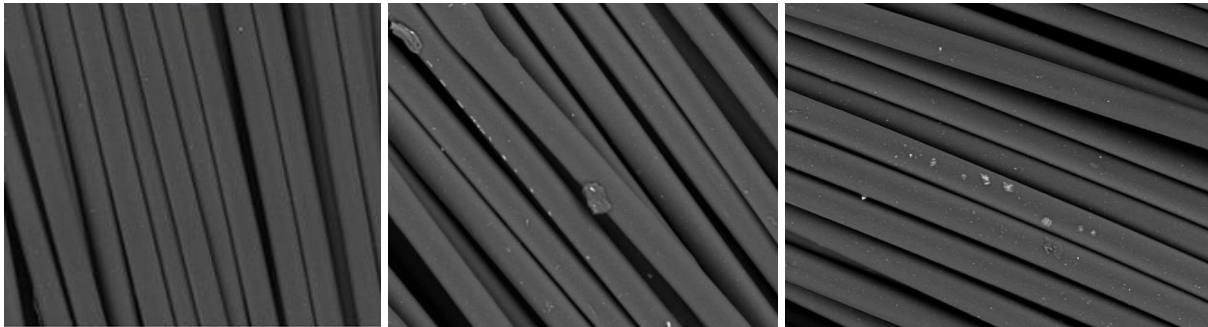


Figure 9. SEM images of Control PET POY (Control without plasmonic boron nanoparticle additive), PET POY 1 (with 1% plasmonic boron nanoparticle) and PET POY 2 (with 2% plasmonic boron nanoparticle).

CONCLUSION

In conclusion, PET POY plasmonic boron nanoparticles doped yarn production was successfully performed in an industrial scale. The presence of plasmonic boron nanoparticle material in the produced PET POY yarns was determined using ICPS-MS. Higher boron and titanium content (2% versus 1%) led to higher B and Ti presence in the PET POY yarn. The amount of plasmonic boron nanoparticles in the PET fiber POY yarn increased approximately 2 times during the production with the doubling of the dosage of the masterbatch according to the results of Ti presence obtained in ICPS-MS analysis. On the other hand, the increase in the amount of plasmonic boron nanoparticles in the PET polymer caused a decrease in tenacity. In a closer look, the tenacity and elongation values decreased, and the yarn unevenness values increased with the addition of the plasmonic boron nanoparticles into the PET polymer when compared to Control PET POY. Moreover, the increased amount of plasmonic boron nanoparticles (from 1% to 2%) in the PET fiber resulted in slightly lower tenacity and slightly higher elongation with slightly lower yarn unevenness. SEM images affirmed the measured yarn unevenness results. Plasmonic boron nanoparticles presence and observed polymer deformation accumulated on the fiber surfaces resulted in an increase on PET POY yarn unevenness.

Overall, this study has shown that functionalized core-shell nanohybrid nanoparticle (TiNPs@amine-functionalized GQDs@BNNS nanohybrid nanoparticle) doped PET POY yarns can be successfully produced under industrial production conditions using the industrial large-scale spinning machines. It is also important to point out that polyester fiber has become the most produced and the most consumed textile fiber in the world and the production, consumption and use of polyester fiber is increasing day by day. Polyester has been used in fashion and home textile production for many years and its production capacities continue to increase. However, with the rapid developments in technology, different production areas such as technical textiles also emerge for polyester fibers other than the traditional application and usage areas.

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