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Investigation of the Effect of Addition of Different Boron Compounds on Thermal Properties of Polyacrylonitrile-co-Vinyl Acetate Fibers Produced by Wet Spinning Method

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ABSTRACT

In this article, the effect of different boron compound additives on the thermal properties of wet spun polyacrylonitrile-co-vinyl acetate P(AN-VAc) fibers was investigated. Different boron compounds (boric acid (BA), borax (B), zinc borate (ZB) and their binary mixtures) were added to fiber spinning solutions in order to improve the thermal characteristics of P(AN-VAc) fibers. For all boron-added P(AN-VAc) fibers except the reference fiber sample, the proportions of (P(AN-VAc)) and boron compounds were kept constant at 90% and 10%, respectively. Boron-free fiber produced from 100% P(AN-VAc) was used as the reference fiber sample. While characteristic peaks of P(AN-VAc) were observed in the Fourier Transform Infra-Red (FTIR) spectra of all fibers produced with or without boron additives, peaks belonging to boron compounds were also observed in the FTIR spectra of boron-added fibers. The results obtained from the measurements of thermogravimetric analysis (TGA) and differential scanning calorimeter (DSC) indicated that there were significant improvements in the thermal resistance of boron-added P(AN-VAc) fibers compared to boron-free P(AN-VAc) fiber. As a result, it was determined that the most effective boron compounds on the thermal resistance of the P(AN-VAc) fibers were ZB, BA and B, respectively.

Farklı Bor Bileşikleri Katkısının Yaş Çekim Yöntemiyle Üretilen Poliakrilonitril-ko-Vinil Asetat Liflerinin Termal Özelliklerine Etkisinin Araştırılması

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ÖZ

Bu makalede, farklı bor bileşikleri katkısının yaş çekim yöntemiyle üretilen poliakrilonitril-ko-vinil asetat P(AN-VAc) liflerinin termal özelliklerine etkisi araştırılmıştır. P(AN-VAc) liflerinin termal özelliklerini geliştirmek amacıyla, lif çekim çözeltilerine farklı bor bileşikleri (borik asit (BA), boraks (B), çinko borat (ZB) ve bunların ikili karışımları) ilave edilmiştir. Referans lif numunesi dışındaki tüm bor katkılı P(AN-VAc) lifleri için (P(AN-VAc)) ve bor bileşiklerinin katkı oranları sırasıyla %90 ve %10 olacak şekilde sabit tutulmuştur. %100 P(AN-VAc)'dan üretilen bor katkısız lifler referans lif numunesi olarak kullanılmıştır. Bor katkılı ve katkısız üretilen tüm liflerin Fourier Dönüşümlü İnfra-Red (FTIR) spektrumlarında P(AN-VAc)'a ait karakteristik pikler gözlemlenirken, bor bileşiği ilave edilen liflerin FTIR spektrumlarında ise ayrıca bor bileşiklerine ait pikler de gözlemlenmiştir. Termogravimetrik analiz (TGA) ve diferansiyel taramalı kalorimetre (DSC) ölçümlerinden elde edilen sonuçlar, bor katkılı P(AN-VAc) liflerinin ısıl direncinde bor katkısız P(AN-VAc) liflerine kıyasla önemli derecede iyileşmeler olduğunu göstermiştir. Sonuçta, P(AN-VAc) liflerinin ısıl direncine en etkili bor bileşiklerinin sırasıyla ZB, BA ve B olduğu tespit edilmiştir.

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1. Introduction

Acrylic fiber, which has the reputation of artificial wool, is one of the most important synthetic fibers, resulting from the wet spinning process of PAN copolymer consisting of acrylonitrile and one or two comonomers, and is widely used in the textile industry (Ren et al., 2017; Guo et al., 2022; Liu et al., 2023). The melting point of polyacrylonitrile is higher than the temperature at which it decomposes. Therefore, PAN can only be produced from viscous concentrated polymer solutions by one of the wet spinning or dry spinning, which are fiber spinning methods. Acrylic fibers have one of the most successful histories of this century, due to their relative low production and material costs, easy processing and ease of handling characteristics (Capone, 1995; Falcai, 1995; Bozdoğan et al., 2000; Tiyek, 2006).

The combustion tendency of acrylic fibers, which have a wide range of uses in clothing and home textiles because of their strength and durability, is the most important factor limiting their use. When the fibers are heated, their physical properties and strength vary, particularly at temperatures above the glassy transition temperature (Frushour, 1995; Wentworth, 1995).

Acrylonitrile (AN) can be produced from petroleum distillation products in easy and inexpensive ways. PAN polymers (Figure 1) are synthesized by radical chain polymerization of AN monomers (Wade and Knorr, 1995; Bozdoğan et al., 2004; Bahrami et al., 2008; Tiyek and Bozdoğan, 2008b).

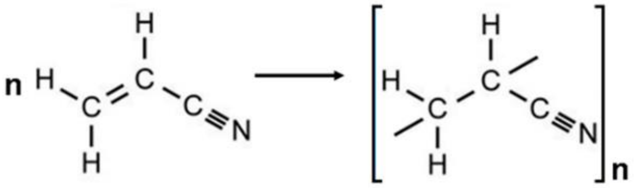

Figure 1. Synthesis of polyacrylonitrile from acrylonitrile

Acrylic fibers containing 100% PAN homopolymers cannot be used commercially due to their poor dye affinity, discoloration when exposed to light and heat over a prolonged period. For this reason, all acrylic fibers contain one or more comonomers between 5 and 15% (Frushour and Knorr, 1985; Wade and Knorr, 1995; Seventekin, 2001; Tiyek and Bozdoğan, 2008a). According to the definition of BISFA, a fiber that contains a minimum of 85% AN in its chemical structure is called acrylic fiber (BISFA, 2000). When PAN is exposed to heat in a vacuum or inert atmosphere, weight loss begins between 250 and 350°C. The main volatile products are hydrogen cyanide and ammonia. In this temperature range, discoloration appears in PAN and a strong exotherm has been identified (David, 1975; Wentworth, 1995). PAN, when heated at normal heating rates of 20 °C/min in DSC, causes cyclization reactions to be a strong exothermic reaction. When the heating rates are increased, the temperature of the decomposition exotherm is shifted to a higher temperature, and a melting endotherm is observed in DSC thermogram before decomposition (Frushour and Knorr, 1985; Frushour, 1995).

PAN homopolymer and the attendant fiber-forming acrylic copolymers fall into the category of high-melting polymers that start to decompose when heated around their melting temperature. PAN exposes a cyclization decomposition reaction at high temperatures in which the neighboring nitrile groups in the structure of PAN react to build aromatic structures of six members. This is a highly exothermic reaction, and this reaction often tends to hide the melting endotherm in thermal analyses (Frushour and Knorr, 1985; Frushour, 1995; Wentworth, 1995).

Another category of PAN fibers is modacrylic fibers, in which the fraction of AN monomers must be less than 85% but greater than 35%. Flame retardant PAN, commonly referred to as modacrylic, is achieved using halogen-containing comonomers. Although they are quite effective as flame retardants, it has recently been thought that halogen-containing materials are ecologically hazardous and environmentally sustainable alternative compounds should be developed. Therefore, improving the flame-retardant properties of organic polymers that are increasingly used both in private and public open spaces is a very important issue, and flame retarding polymers include elements such as P, Si, B, N with naturally flame-retardant properties (Kracklauer, 1978; Lu, 2002; Wyman, 2006). Nowadays, various strategies such as copolymerization (Rahimi-Aghdam et al., 2020), blending (Ren et al., 2017; Peng et al., 2021), finishing (Peng et al., 2020), and surface modification (Liu et al., 2022) have been successfully developed to prepare flame retardant PAN (Guo et al., 2022).

Boron is currently used as a flame retardant in many polymeric systems because it suppresses combustion by sealing the surface of the burning material and blocking its contact with oxygen (Hilado, 1998; Morgan et al., 2000). Boron is considered to carry out most of its flame-retardant function in a condensed state by increasing the amount of char produced by one or both of its decomposition reactions.

In the first mechanism, boron compounds perform the chemical decomposition reactions, producing carbon instead of CO or CO_2 in the condensed phase. It is also claimed that flame retardancy is connected to the formation of a surface layer of preventive char, which acts as a barrier to the access of oxygen to inhibit the oxidation of carbon. In the second mechanism of decomposition reactions, boron compounds form a surface layer of preventive char that insulates burning surfaces by inhibiting the oxidation of carbon by restricting the accessible oxygen and also preventing the gasification of carbon. In both cases a char is formed (Lomakin and Zaikov, 1999; Lu, 2002; Marosfoi et al., 2009; BOREN, 2018). The chemical effect of boron compounds may involve the elimination of impotent hydroxyl groups by dehydration, which causes char formation. The physical effects of boron compounds may include the formation of non-volatile boric oxide, serves as a flux for the carbonaceous residue (Hilado, 1998). Boron compounds are also convenient for decreasing or removing after-grow in halogenated flame-retardant polymeric materials (Lomakin and Zaikov, 1999). Borax and boric acid are well-known as flame retardants, and zinc borate has occurred as an option for antimony oxides in halogenated fire-retardant polymeric materials (Duquesne, 2009).

In this study, boric acid (BA), borax (B) and zinc borate (ZB) were added to P(AN-VAc) polymer solution, and then P(AN-VAc) fibers with and without boron compounds were produced by the wet spinning method. Thereby, it is aimed to improve the thermal properties of polyacrylonitrile fibers. Boron-free P(AN-VAc) fiber is used as a reference sample.

2. Materials and Method

2.1. Materials

Acrylic fibers containing 10% vinyl acetate ($CH_2CHOCOCH_3$) comonomers supplied from AKSA Akrilik Kimya San. A.Ş., Yalova, Turkey was used as polymers in the production of all P(AN-VAc) fibers. N,N-Dimethylformamide ($HCON(CH_3)_2$) (99.5%) used to solve acrylic fibers was supplied from Sigma Aldrich, Germany. Boric acid (H_3BO_3) (99.5%) and borax ($Na_2B_4O_7.10H_2O$) (99.0%) were supplied from Tekkim Kimya San. Tic. Ltd. Şti., Turkey, and zinc borate ($B_2O_6Zn_3$) (85.27%) were supplied from Kimetsan Kimya Maden Metalurji End. Tic. Ltd. Şti., Turkey. Boric acid (BA), borax (B) and zinc borate (ZB) have particle sizes of 13.5-14 μm, 1-1.5 μm and 1.5-2 μm, respectively.

2.2. Method

In this study, the production of P(AN-VAc) fibers was carried out using the wet spinning method. DMF (20%) and water (80%) as coagulants were used to coagulate the spinning solution in the coagulation bath. All P(AN-VAc) fibers were spun as monofilaments in a pilot wet spinning plant (Figure 2) located at the University of Gaziantep Islam Science and Technology. The wet spinning process consisted of a feeding pump, a spinneret system with a single-hole of diameter of 1mm, a coagulation bath, a washing bath and a hot drawing unit. In the wet spinning process, the polymer solution is pumped into a liquid bath containing coagulant through a spinneret submerged in the coagulation bath (Capone, 1995; Bozdoğan et al., 2004; Tiyek and Bozdoğan, 2008a).

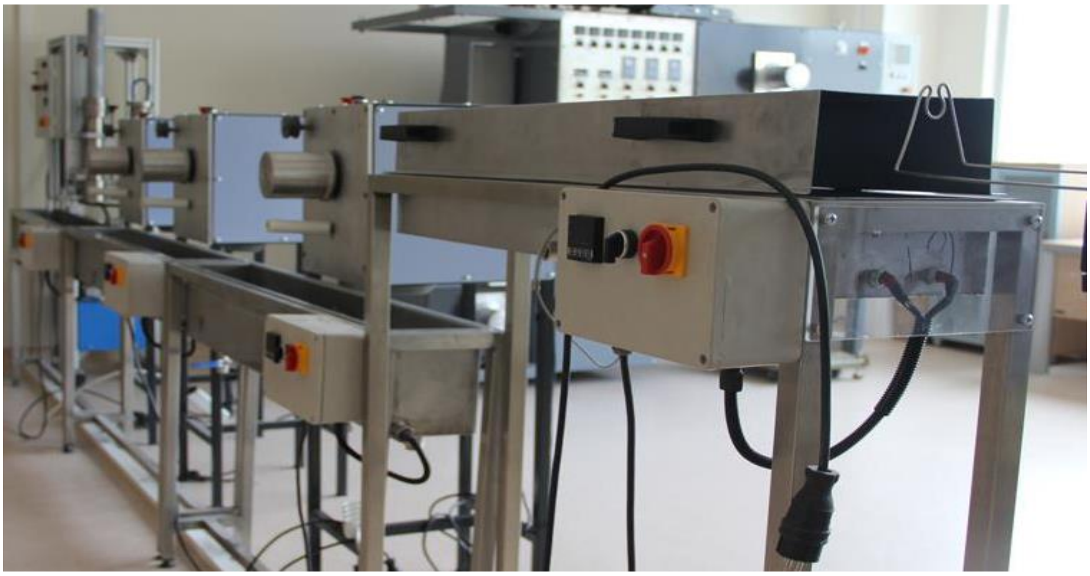

Figure 2. The pilot plant for wet spinning process

The content of spinning solutions used in the production of wet spun fibers and the ratios of the chemicals used in the spinning solution are given in Table 1.

Table 1. Contents of P(AN-VAc) fibers with and without added boron compounds

Sample Code	Fiber Contents (wt. %)			
	P(AN-VAc) (P)	Boric Acid (BA)	Borax (B)	Zinc Borate (ZB)
P-Ref	100	-	-	-
P-BA	90	10	-	-
P-B	90	-	10	-
P-ZB	90	-	-	10
P-BAB	90	5	5	-
P-BAZB	90	5	-	5
P-BZB	90	-	5	5

The production parameters of the wet spinning process are given in Table 2. These process parameters were kept constant in the production of all wet spun fibers.

Table 2. Production parameters of wet spinning process

Parameter	Value
Fiber spinning solution concentration (wt.)	20%
Coagulation bath concentration (wt.)	20%
Coagulation bath temperature	42°C
Washing bath temperature	50°C
Hot drawing unit temperature	48°C
The hole diameter of spinneret	1 mm

2.3. Measurement and Characterization

FTIR spectra of wet spun fibers were obtained from a Perkin Elmer® Spectrum 400 FT-IR/FIR Spectrometer with a diamond protected Attenuated Total Reflectance (ATR) crystal unit in the wavenumbers of 4000 to 400 cm^{-1}. Thermal characterizations of the produced fibers were carried out by

DSC and TGA analysis under a nitrogen atmosphere (Guo et al., 2018). DSC analyses were performed in the range of 30°C and 400°C at a heating rate of 20°C/min by DSC-60 Differential Scanning Calorimeter of Shimadzu. TGA analyses were performed by Exstar TG/DTA6300 Thermogravimetric Analyzer of SII Nanotechnology at a heating rate of 40°C/min. TGA analyzes were carried out in the range of 30°C and 650°C for the 100% P(AN-VAc) fiber (P-Ref) and in the range of 30°C and 950°C for boron compounds added to P(AN-VAc) fibers (P-BA, P-B, P-ZB, P-BAB, P-BAZB, and P-BZB).

3. Results and Discussion

3.1. Fourier Transform Infra-Red (FTIR) Analyzes

The FTIR spectra of P(AN-VAc) fiber samples with and without boron compounds are given in Figure 3. P(AN-VAc) fibers with and without added boron compounds have similar spectra, with the main vibrational peaks around 3394 (-OH asymmetric stretch), 2932 ($-CH_2$ asymmetric stretch), 2860 ($-CH_2$ symmetric stretch), 2247 (-C=N stretch), 1736 (-C=O VAc stretch), 1659 (VAc), 1445 ($-CH_2$ bending), 1369 ($-CH_3$ deformation PVAc), 1235 (-C-O-VAc stretch), 1081 ($-CH_2$ stretch) and 761cm^{-1} (-CH bending). All the peaks are characteristic bands of P(AN-VAc) fibers (Bozdoğan et al., 2000; Tiyek, 2006). In the boron compounds added samples, the band around 810 cm^{-1} was attributed to B-O-H bending, and the bands around 675 and 554 cm^{-1} were also attributed to the O-B-O bending process (Köytepe et al., 2009; Uslu et al., 2011).

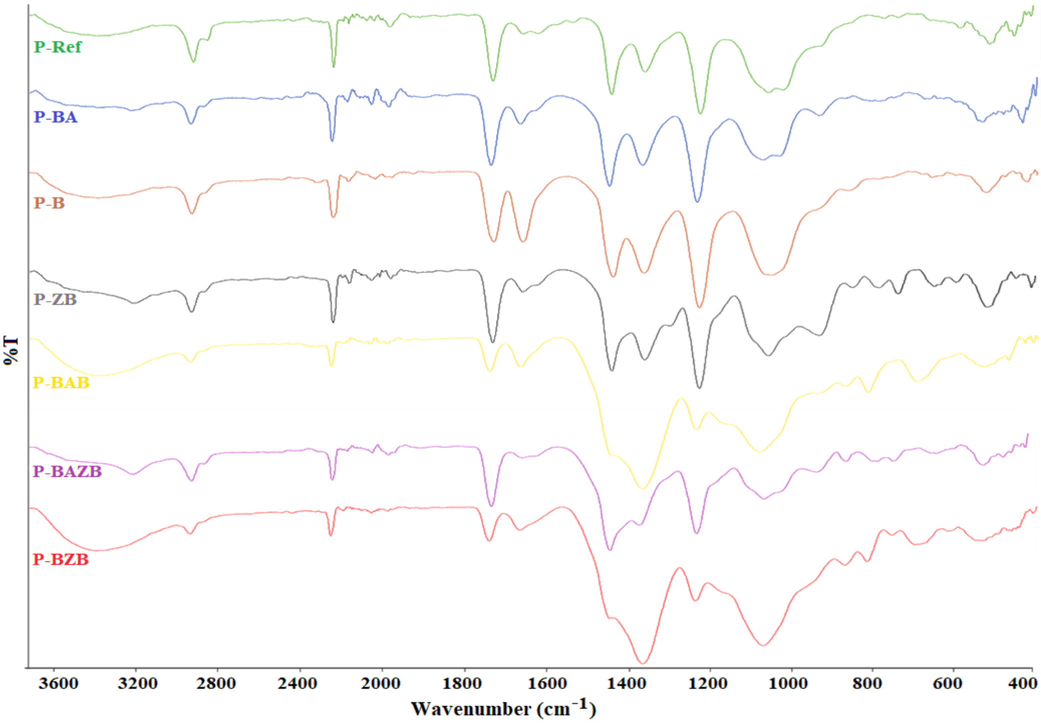

Figure 3. FTIR spectra of wet spun P(AN-VAc) fiber samples

3.2. Differential Scannin Calorimeter (DSC) Analyzes

DSC thermograms of all produced P(AN-VAc) fibers are given in Figure 4.

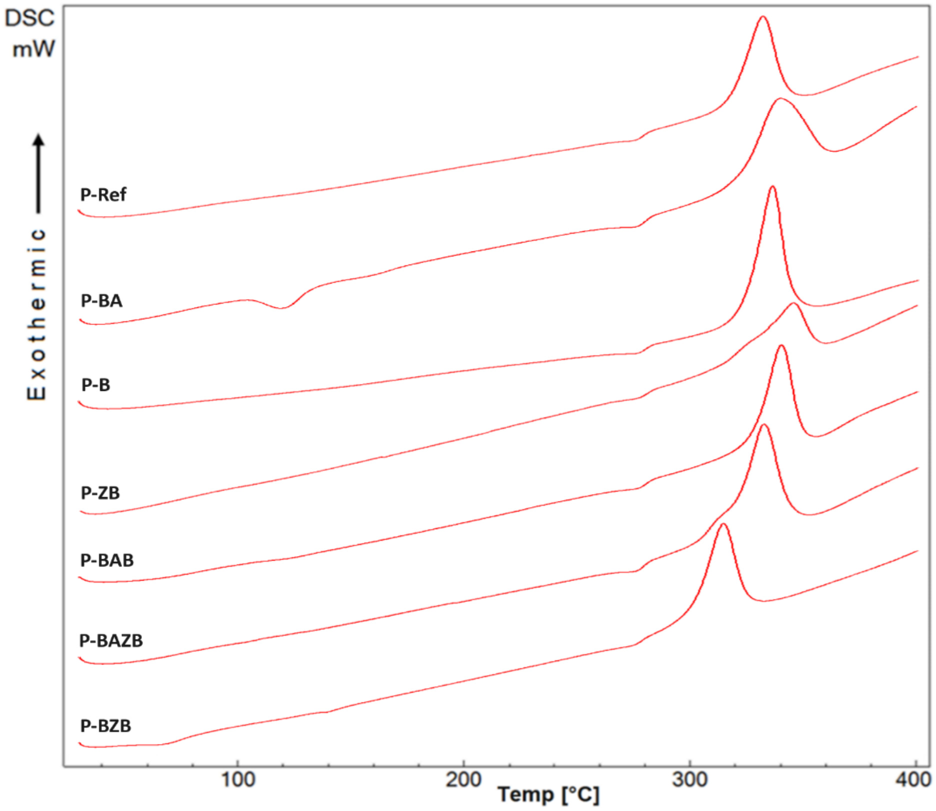

Figure 4. DSC thermograms of wet spun P(AN-VAc) fiber samples

The peaks of endothermic and exothermic are attributed to the melting and thermal degradation of the fibers, respectively. The results obtained from DSC thermograms of wet spun P(AN-VAc) fiber samples are given in Table 3.

Table 3. DSC results of wet spun P(AN-VAc) fiber samples

Sample	Endothermic Peak Temperature (°C)	Exothermic Peak Temperature (°C)	Exothermic Enthalpy (ΔH) (J/g)
PAN	288.53	333.66	-274.79
PAN-BA	287.58	337.87	-340.08
PAN-B	289.28	341.28	-258.34
PAN-ZB	285.48	346.63	-146.75
P-BAB	286.74	341.31	-215.09
P-BAZB	290.73	334.02	-245.01
P-BZB	285.08	315.69	-175.93

DSC thermograms of all samples showed a small endothermic peak located between the temperatures of 285 – 291 °C. These peaks indicate a small amount of melting in the P(AN-VAc) fibers. DSC thermograms of polyacrylonitrile fibers produced from polyacrylonitrile homopolymers composed of 100% acrylonitrile (AN) monomers at the heating rate of 20 °C min^{-1} showed no melting endotherm (Frushour and Knorr, 1985; Frushour, 1995). Therefore, the small amount of melting endotherm in the produced P(AN-VAc) fibers is due to the vinyl acetate (VAc) comonomers present in their structures (Tiyek, 2006).

The DSC thermograms of all samples also showed a strong exothermic peak located between 315 – 347 °C. The exothermic peak temperatures indicate the temperatures at which degradation occurs in the structure of the P(AN-VAc) fibers, and the enthalpy values of the exothermic peaks represent the amount of energy released as a result of the degradation of the P(AN-VAc) fibers. When the P(AN-VAc) fibers are heated, the structure of the polyacrylonitrile is exposed to the degradation reaction of the neighboring nitrile groups in the polymer chain before melting. The degradation in the structure of polyacrylonitrile is expressed by the exothermic peak value (Tiyek, 2006).

It was observed that the exothermic peak temperatures of P(AN-VAc) fibers increased with the addition of boron compounds. The boron compounds, which are most effective at the peak temperatures of the P(AN-VAc) fibers, are zinc borate. It is also understood from these results that zinc in the boron structure has an important role in improving thermal properties.

3.3. Thermogravimetric analyzes (TGA)

In this research, TGA was extensively used for the thermal characterization of all produced fibers. The thermograms of TG (thermogravimetric) (**a**) and dTG (differential thermogravimetric) (**b**) obtained from TGA analyses of wet spun P(AN-VAc) fiber samples with and without boron compounds are given in Figure 5.

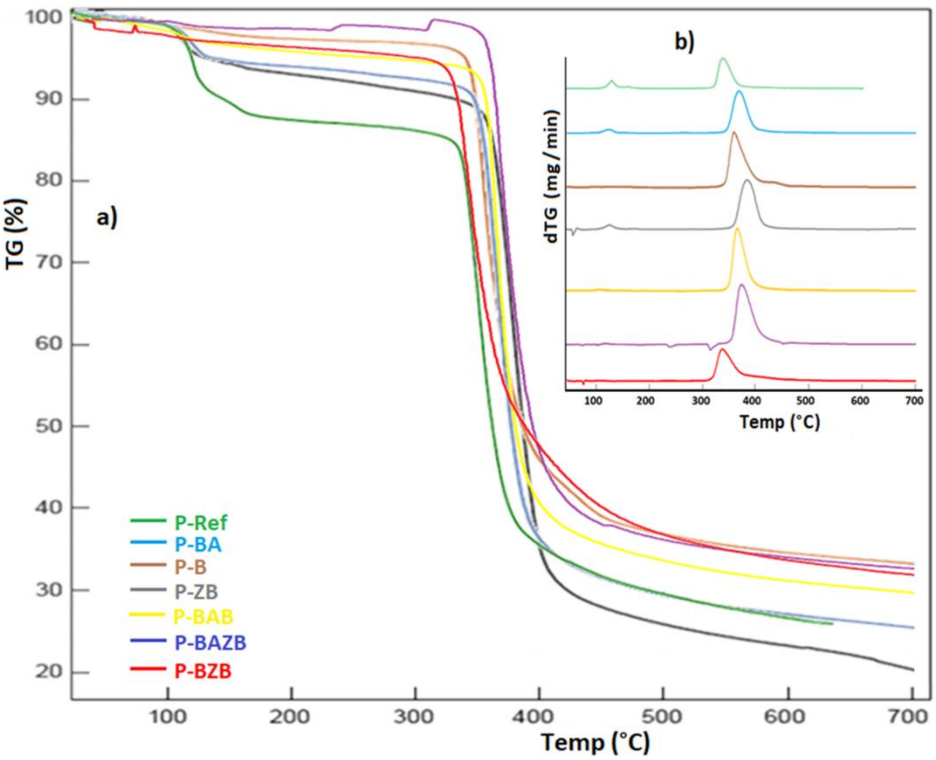

Figure 5. TG **(a)** and dTG **(b)** thermograms of wet spun P(AN-VAc) fiber samples

In general, all samples showed typical and single-step degradation thermograms. The initial weight loss observed in the TGA thermograms is due to the removal of water and other impurities in the fiber structure. Experiences have demonstrated that a relatively steeper and narrower temperature range concerning weight loss demonstrates a faster thermal degradation reaction and results in considerable weight loss which, in turn, results in a lower residual weight fraction (Karacan and Erdoğan, 2012). The TGA results obtained from the thermogravimetric analyses are given in Table 4. Values of the starting temperature (T_i) of initial weight loss (starting dehydration), the starting temperature (T_{ds}) of thermal degradation and the half-life temperature (T_h), the temperature value at which the sample loses 50% of its weight, were obtained from TG thermograms (Figure 5-a), and values of the maximum degradation rate (R_{md}) and the temperature (T_{Rmd}) at which maximum degradation rate occurs were obtained from dTG thermograms (Figure 5-b).

Table 4. TGA results obtained from TG and dTG thermograms

Sample	T_i (°C)	T_{ds} (°C)	T_h (°C)	R_{md} (mg/min)	T_{Rmd} (°C)
P-Ref	40	320	360	1.09	348
P-BA	75	340	378	1.42	372
P-B	50	330	387	1.45	359
P-ZB	75	342	388	1.,36	383
P-BAB	75	334	381	2.53	369
P-BAZB	125	342	394	2.30	374
P-BZB	40	310	388	1.29	347

It has been observed that the boron compounds added fibers have higher thermal degradation starting temperatures (T_{ds}) (except for the P-BZB sample), relatively higher half-life temperatures (T_h) and higher temperatures (T_{Rmd}) at which maximum degradation rate occurs (except for the P-BZB sample) than the reference fiber (P-Ref). That is, the addition of boron to P(AN-VAc) fibers caused the fibers to begin degradation at higher temperatures and to require higher temperatures in order to lose 50% of their weight and achieve maximum degradation rates. The best thermal results were obtained for 10% zinc borate added (P-ZB), 5% boric acid + 5% zinc borate added (P-BAZB) and 10% boric acid added (P-BA) fibers at degradation starting temperature (T_{ds}), for 5% boric acid + 5% zinc borate added (P-BAZB), 10% zinc borate added (P-ZB), and 5% borax + 5% zinc borate added (P-BZB) fibers at half-life temperature (T_h), and for 10% zinc borate added (P-ZB), 5% boric acid + 5% zinc borate added (P-BAZB), and 10% boric acid (P-BA) added fibers at the temperature (T_{Rmd}) at which maximum degradation rate occurs, respectively. These results indicate that the thermal resistance of the boron compound added fibers is better than that of boron-free fiber. That is, the boron additive improves the thermal properties of P(AN-VAc) fibers.

4. Conclusions

The characteristic peaks obtained from the FTIR analysis proved the presence of boron in the fiber. According to the data obtained from DSC and TGA thermal analysis thermograms, the thermal properties of boron compound added fiber samples were higher than the sample of 100% P(AN-VAc) without boron additive. These results indicated that adding boron compounds improved the thermal properties of P(AN-VAc) fibers and were compatible with the literature (Chai et al., 2016). The best thermal properties were obtained for 10% zinc borate added (P-ZB), 5% boric acid + 5% zinc borate added (P-BAZB) and 10% boric acid (P-BA) added P(AN-VAc) fibers, respectively. When boron compounds-added P(AN-VAc) fibers are compared, it was observed that the additive of zinc borate has a more positive effect than boric acid and borax on the thermal properties of the fibers. This means that zinc also contributes to the improvement of thermal properties.

Acrylic fibers are widely used in the textile industry due to light resistance, weather fastness, radiation resistance, and profound warmth retention property. However, PAN fibers exhibit poor thermal stability and high flammability, which extremely limit their potential applications in certain fields where high levels of fire safety are required. Therefore, the flame retardant performance of PAN fibers or fabrics needs to be improved. PAN fibers produced in this study and whose thermal properties were improved by the addition of boron can be more widely used especially in the production of materials that require better thermal properties and fire resistance, in addition to the clothing and home textiles in which they are widely used. In the future, studies can be carried out on the addition of different boron compounds in different ratios or the use of boron with different flame retardant chemicals that can create a synergistic effect.

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Declaration of Conflicting Interests

Authors declare that there is no conflict of interest with any person, institute, company, etc.

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