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The hydrophilic modification of acrylic textile fibers by grafting of 2-hydroxyethyl methacrylate and investigation of the imparted properties

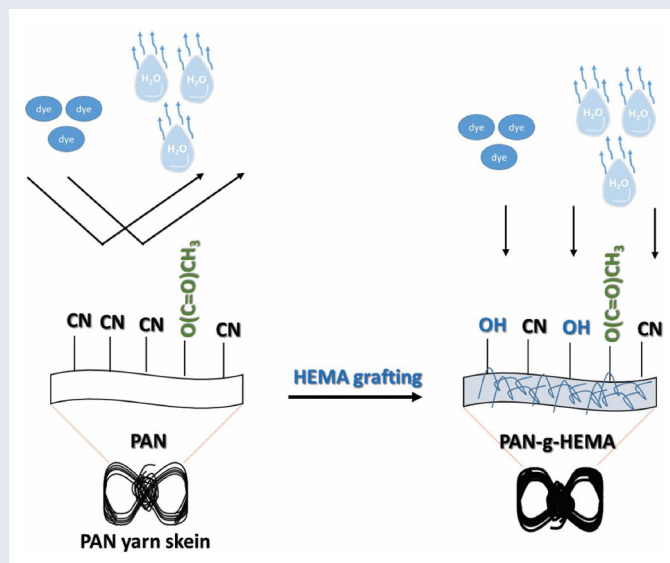
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ABSTRACT

In this study, to mimic the hydrophilic character of cotton, the industrially prominent polyacrylonitrile (PAN) fibers were enriched by polar OH-groups via the graft copolymerization technique. For this purpose, the grafting of the 2-hydroxyethyl methacrylate (HEMA) was ensured in the high graft yields (~95%). The effects of polymerization conditions such as the solvent selection, initiator type and concentration, monomer concentration, polymerization temperature, and time were investigated for the highest graft yield, where the fiber's dimensional stability is preserved. The changes in the structural, thermal, and morphological properties of PAN-g-HEMA fibers were executed by ATR-FTIR, ¹H-NMR, TGA, and SEM techniques. Depending on the modified fibers' grafting yields, the changes in the tensile strength, elongation at break, moisture, and water retention properties were investigated. It was obtained that the moisture absorption of PAN fiber (2%) reached 15.7% after grafting (95% graft yield). The dyeability of the modified fibers was studied with a direct dye (Direct Black 38), which is conventionally employed for cellulose dyeing, by monitoring with the L*a*b* color measurements and K/S color strength. 0.049 g of dye was adsorbed by 1 g of PAN-g-HEMA fiber containing 68% of HEMA at pH 11 for 120 min.

GRAPHICAL ABSTRACT



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KEYWORDS

Polyacrylonitrile fiber; grafting; 2-hydroxyethyl methacrylate; hydrophilicity; dyeability; moisture absorption

1. Introduction

PAN is one of the most industrially prominent polymers used to manufacture many different textile materials ranging from apparel to technical textiles due to its desired properties, such as high chemical, mechanical and environmental stability, ease for fiber spinning, and keeping warm by imitating natural wool, and low moisture absorption when necessary.^[1,2] However, its low hydrophilicity causing

unwanted low sweat release and low dyeability with specific dye molecules restricts comfort properties when preferred for apparel purposes. For that reason, many attempts have been made to improve the properties of PAN using many different physical and chemical methods, such as atmospheric plasma treatment,^[3] layer by layer assembly,^[4] graft modification of various monomers,^[5–7] the introduction of chemical functional groups (amine, amidoxime, amide),^[8–10]

and conversion of its -CN groups to the other chemically attractive groups, such as -COOH.^[11] Among them, the graft modification technique is a versatile method for permanently imparting the desired properties of the grafted agents. By this method, various monomers and polymers, such as HEMA,^[5] allylamine,^[7] acrylamide,^[6] phosphorous-containing acrylates,^[12] poly(ethylene imine),^[13] natural soybean protein,^[14] casein,^[15] cotton,^[16] were reported to be grafted onto PAN to open new application fields, including trace metal adsorption, dye removal, CO₂ adsorption, flame retardancy, and hygroscopicity.

This work aims to include the advantageous properties of a hydrophilic character to the PAN fibers by mimicking the natural cotton surface and preserving the fiber texture through the grafting of the HEMA monomer. With the help of this, the good desired properties of natural cotton fibers, such as high moisture absorption, water retention, and reactive dyeing, are targeted to be gained to a synthetic textile entry. The preferred hydrophilicity source of this study, the HEMA monomer, contains the polar-hydroxyethyl (-CH₂CH₂OH) side group that may also impart resilience to the PAN fiber due to its vinylic structure,^[17,18] which is an essential parameter for the comfort/handling property of textile material. The graft of the HEMA monomer onto the other textile products, such as natural silk, was found to improve the fiber's moisture content and dyeing properties, with a negligible effect on the mechanical properties.^[17,19] Thus, during the improvement of the PAN hydrophilicity, the mechanical properties of the PAN may also be retained. Other studies also report the graft modification of synthetic or natural textile substrates to improve hydrophilicity by preserving the mechanical properties of the textiles.^[20–24]

Although the numerous studies mentioned above reported the graft modification of PAN fibers for different purposes, in most studies, the researchers have mainly focused on improving the chemical attractiveness of PAN surface to employ it for environmental issues, such as heavy metal adsorption, flame retardancy, or dye remediation.^[5,13,25,26] For example, in a recent study, flame retardancy was reported to be gained to the PAN fibers after grafting of HEMA by UV-induced polymerization that is quite different compared to our study. There has been less focus on the dyeing properties of PAN after a hydrophilic graft modification^[6] in the literature. The imparted hydrophilic characters such as moisture content, water absorption, and dyeability with an alkaline dye were investigated after the grafting of -NH₂ groups containing acrylamide monomer to the PAN backbone.^[6] Unlike these published works, in our study, we intended to ensure mimicking the surface of cotton fibers by gaining the polar -OH groups of HEMA monomer to the PAN chains. Additionally, we investigated the dyeing and coloring properties of the modified PAN fibers using a direct dye, which is conventionally preferred for dyeing cellulose products, and monitored their durability against detergent washing. Finally, we considered the dimensional stability of PAN fibers by monitoring the mechanical properties of the fibers even at the quite high graft yields.

2. Materials and method

2.1. Materials

PAN fibers (87% PAN, 13% poly(vinyl acetate)) (AKSA Co. TURKEY) were washed with acetone (Merck) under reflux for 2 hours at a boiling temperature to remove impurities. Benzoyl peroxide (Bz₂O₂) (Merck) and azobis(isobutyronitrile) (AIBN) initiators (Merck) were used after twice crystallization from the solvent mixture of chloroform/methanol (50/50) by volume. Other chemicals, HEMA monomer (Merck), ammonium peroxydisulfate (APS) (Sigma-Aldrich) and cerium ammonium nitrate (CAN) (Sigma-Aldrich) initiators, solvents of ethanol (Merck), ethyl methyl ketone (Merck), and methanol (Merck), Direct Black 38 (C₃₄H₂₅N₉Na₂O₇S₂, 781.73 g/mol) (Burboya, Turkey), HCl (37%) (Merck), and NaOH (Merck) were directly employed in the studies. In the second stage of the color measurement analysis of dyed fibers, phosphate, optical brightener, and protease-free and sodium aluminum silicate (32.5%) based European Colorfastness Establishment (ECE) reference detergent is employed according to the International Organization for Standardization (ISO) 105-C08:2010 standard.^[27]

2.2. Methods

2.2.1. Preparation of PAN-g-HEMA copolymer fibers

The PAN fibers (0.3 ± 0.0005 g) made into a skein were taken into two-necked round-bottom flasks, whose temperature was fixed at different temperatures (60–90 °C) under reflux. The polymerization was initiated by adding 5 mL of different initiator solutions at different concentrations (1.2 × 10⁻⁴ M–1.0 × 10⁻¹ M). Then, 15 mL of HEMA monomer solution prepared at different concentrations (0.05–0.6 M) in different solvents (e.g., acetone, methanol, and methyl ethyl ketone (MEK) solvents mixtures with water) was added onto the fibers to ensure thorough wetting in the monomer solution. At the end of the determined polymerization time, the fibers removed from the mixture were washed with ethanol in a soxhlet for 24 h to remove the initiator, monomer residues, and PHEMA homopolymer. Then, the copolymer fibers were dried in a vacuum oven at 55 °C until reaching the constant weight. The increase in dried fibers weights was calculated gravimetrically according to the following equation (Equation 1).

$$\text{Graft yield (\%)} = \frac{w_c - w_f}{w_f} * 100 \quad (1)$$

The w_c and w_f correspond to the weights of copolymer and PAN fibers, respectively. The effects of varying conditions such as initiator type, polymerization solvent type, initiator concentration, monomer concentration, polymerization temperature, and time on the grafting yields were investigated in detail. In each investigation parameter, three different samples were employed (number of samples, $n = 3$) to obtain a mean value with a standard deviation. A schematic representation for the preparation route of a

PAN-g-HEMA copolymer fiber is given in supplementary file Figure S1.

2.2.2. Dyeing process of PAN-g-HEMA copolymer fibers

The graft modified PAN-g-HEMA fibers dyeing process was conducted using the Direct Black 38 dye, a conventional direct dye used in the dyeing of hydrophilic cotton fibers.

To determine the dyeing bath pH, different Direct Black 38 dye solutions were prepared in the different pH values ranging from pH 1 to 11. For this purpose, the acidic calibration graph was plotted from UV-Vis spectra by adding 0.5 M aqueous HCl solution to the dye solutions prepared at a particular concentration for pH 1, pH 3, and pH 5. The alkaline calibration graph (pH 9 and 11) was also obtained by adding 0.1 M NaOH solution to the dye baths.

The graft-modified copolymer fibers dyeing process was carried out by placing a copolymer fiber sample to the 30 mL different concentrations of Direct Black 38 solutions (0.06 g/L–1.2 g/L) prepared at different pH values between pH 1 to 11 at 85 °C under reflux for 0–120 minutes. UV-vis measurements monitored the absorbance values of the samples taken from the dyeing solutions at the end of specific periods. The dyeing results were evaluated by considering the absorption values recorded in the 260–700 nm wavelength range. The dye intake amounts of the copolymer fibers were calculated as $m_{\text{dye}}/m_{\text{fiber}}$ (with units of g of dye/g of fiber). The samples were abbreviated as M1 to M11 depending on the dyebath pH. A similar dyeing procedure was also employed for untreated PAN fibers for comparison.

2.2.3. Moisture absorption and water retention processes of PAN-g-HEMA copolymer fibers

To examine the moisture absorption of graft-modified fibers, a copolymer fiber sample with four different graft yields ranging from 23% to 95% of each were dried in the oven for 48 h to reach constant weighing. Five hundred milliliters of distilled water containing beaker was placed in the center of the closed system to provide 65% relative humidity in the chamber. Then, the fiber samples were orderly put around the beaker and allowed to absorb moisture for different periods ranging from 1 h to 7 days at 25 °C. The moisture absorption values (%) of the samples were calculated gravimetrically according to Equation 2.

$$\text{Moisture absorption (\%)} = \frac{w_{\text{wet}} - w_{\text{dry}}}{w_{\text{dry}}} * 100 \quad (2)$$

w_{dry} and w_{wet} correspond to the dry and wet weight of copolymer fibers, respectively. Each experiment set was repeated twice by employing two different copolymer fiber samples, and the results were presented by taking the mean values of these four different measurements.

The fiber samples water retention properties were examined by putting the fibers in the oven for 48 h and then keeping them in distilled water at 25 °C for 2 and 3 h. Completely wetted fibers were isolated from the water, placed between two filter papers, thoroughly compressed to remove the water, and weighed. The fibers' water retention

values (%) were determined gravimetrically, taking into account the fibers' initial and wetted weights.

2.2.4. Color measurements

The color measurements of the modified fibers dyed in solutions with different pH values were carried out before and after washing with detergent, with a Minolta 3600d Spectrophotometer at a D65 light source with an observation angle of 10°. The results are given according to the Commission Internationale de l'Eclairage (CIE) $L^* a^* b^*$ space. Here, in the vertical coordinate given according to the mathematical system, L^* is the lightness/darkness, the horizontal a^* and b^* are the chromaticity coordinates (Supplementary file, Figure S2). The magnitudes of a^* , b^* , and c^* give information regarding the vividness and saturation of the color, respectively.

The ΔE color distance value was used to determine the color difference before and after washing with the detergent for the fibers dyed at different pH degrees. A sample dyed at pH 1 (with the lowest dyeing efficiency) was taken as a reference, and the ΔE color distance was calculated according to Equation 3.

$$\Delta E = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2} \quad (3)$$

The K/S color strength of the dyed samples was obtained using the Kubelka-Munk equation given in Equation 4.

$$\frac{K}{S} = \frac{(1 - R)^2}{2R} \quad (4)$$

Here, K, S, and R correspond to the Absorption, Scattering, and Reflectance coefficients, respectively.

2.3. Characterization

The structural analysis of the samples was revealed by ATR-FTIR spectra recorded using a Perkin Elmer Spectrum 100 spectrophotometer in the wavelength range of 500–4000 cm^{-1} . The structural changes that occurred in the graft copolymer fibers were determined by ^1H -NMR spectra taken in DMSO- d_6 solvent in Agilent 600 MHz Premium Compact NMR instrument. The UV-Vis spectra of the samples taken from solution at particular periods during the dyeing processing of graft modified PAN-g-HEMA copolymer fibers were measured with the Shimadzu UV-1700 UV-Vis Spectrophotometer. The surface morphology changes of PAN fibers were imaged through the fiber samples coated with 3 nm of Au-Pd using the Quanta 400 F FE-SEM Instrument. The thermal stability of samples was determined by the TGA measurements, using a Perkin Elmer Diamond Thermal Analyzer at a heating rate of 5 °C min^{-1} under the N_2 atmosphere between 30 and 750 °C. The mechanical properties of the PAN fiber-containing HEMA at different percentages (3 samples for each) were measured at 20 °C and 65% relative humidity using Instron 4411 Tensile Strength Instrument by following the requirements of TS EN ISO 2062:2010.^[28] The mechanical test results were evaluated by means of analysis of variance (ANOVA) method.

Table 1. The changes in graft yields (%) of PAN-g-HEMA copolymer fibers with the initiator types used in the polymerization (number of samples, $n = 1$).

Initiator type	Graft yield (%)
Bz ₂ O ₂	63.3
CAN	24.0
AIBN	9.6
APS	5.2

([HEMA]: 0.25 M, [Initiator]: 5×10^{-3} M, polymerization temperature: 80 °C, time: 120 min).

3. Results and discussion

3.1. Graft copolymerization conditions

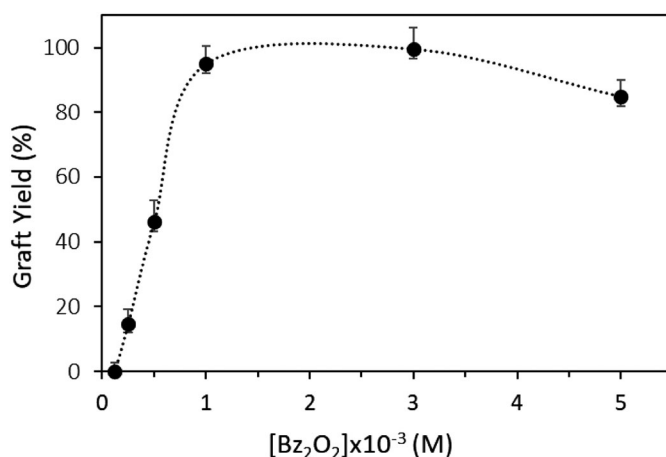
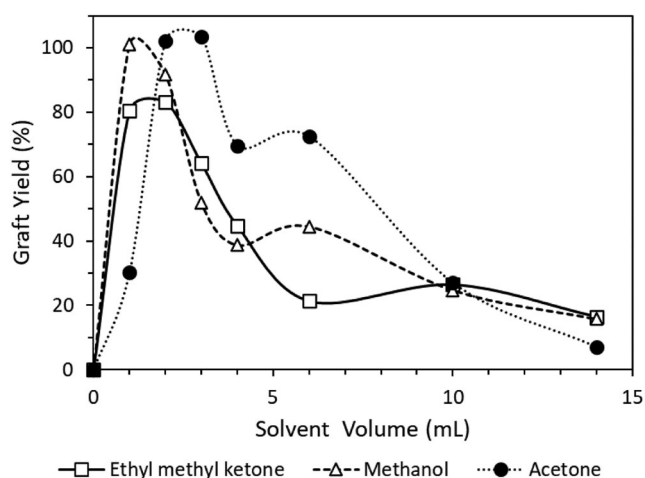
3.1.1. Initiator type

The first attempts for densely and homogeneously grafting of HEMA on the PAN fiber aim to determine the experimental conditions by systematically changing the polymerization conditions to achieve the highest grafting yields. For this purpose, firstly, experiments with different initiator types were carried out to determine the initiator for radical addition polymerization. Accordingly, the polymerization reactions were conducted using redox oxidants such as APS, CAN and radical initiators such as AIBN and Bz₂O₂, and the results are presented in Table 1. As seen in the table, the copolymer fiber with the highest graft yield (%) was obtained when Bz₂O₂ was employed in the polymerization, as compatible with the studies reporting the graft copolymerization of vinyl monomers to the fiber materials in the literature.^[6,29] Consequently, further grafting investigations continued with the usage of Bz₂O₂.

3.1.2. Initiator concentration

To further examine the effects of Bz₂O₂ concentration on graft yields (%) of PAN fibers, the polymerization reactions were conducted by adding different Bz₂O₂ solutions ranging from 1.2×10^{-4} M to 1.0×10^{-1} M constant HEMA concentrations at 80 °C for 120 min. The results are depicted in Figure 1. Accordingly, with the gradual increment of the initiator concentration up to 1.0×10^{-3} M, the graft yield values also showed an increasing trend and then stayed nearly constant with a slight decrease. This case can be explained by the chain growth and termination reactions proceeding simultaneously in the polymerization medium. At further initiator concentrations, the termination reaction rates possibly dominated the growth ones, and thus, this may have caused a slight decrease in the grafted HEMA amount on the PAN fiber.

The free radicals increased by increasing initiator concentration form more polymeric radicals on the PAN chain that are suitable for grafting, by eliminating hydrogen atoms from the chain. These free radicals also play a significant role in the formation of HEMA homopolymers. In addition to these possibilities, the acceleration of termination reactions is a typical situation as the radical species formed in the medium will increase excessively with the increase in the initiator concentration. By further increasing the Bz₂O₂ concentration after a particular value, the dominating termination reactions that occurred together with the growth reactions slow the graft polymerization on the PAN fiber.

**Figure 1.** The changes in graft yield (%) values of PAN-g-HEMA copolymer fibers with Bz₂O₂ concentration ([HEMA]: 0.25 M, polymerization temperature: 80 °C, time: 120 min, $n = 3$).**Figure 2.** The changes in graft yields (%) of PAN-g-HEMA copolymer fibers with the solvent volumes added to the water (total volume: 20 mL, [HEMA]: 0.25 M, [Bz₂O₂]: 1×10^{-3} M, polymerization temperature: 80 °C, time: 120 min).

Therefore, decreasing in grafted HEMA content may have been observed.^[5,30]

3.1.3. Polymerization solvent selection

It has been known that the nature of the solvent/solvents mixture used as the polymerization medium has an indisputable effect on the polymerization of vinyl monomers.^[31,32] Therefore, to determine the effect of solvent type on graft yield (%) of PAN fibers, solvents such as acetone, methanol, and methyl ethyl ketone (MEK) were chosen, known to be suitable solvents for the initiator Bz₂O₂. Accordingly, the graft copolymerization reactions were performed by dissolving Bz₂O₂ in a total of 20 mL of solvent-water mixtures in the different volume proportions, and the pooled results are presented in Figure 2. As seen in the figure, when the volume of solvents was selected as 2 mL corresponding to the volume ratio of 10/90, it was observed that the graft yields (%) of the copolymer fibers became the highest values. The values were 103.5%, 91.7%, and 83.2% for acetone, methanol, and MEK, respectively. With the further increment of the solvents' volume ratio, the graft yields

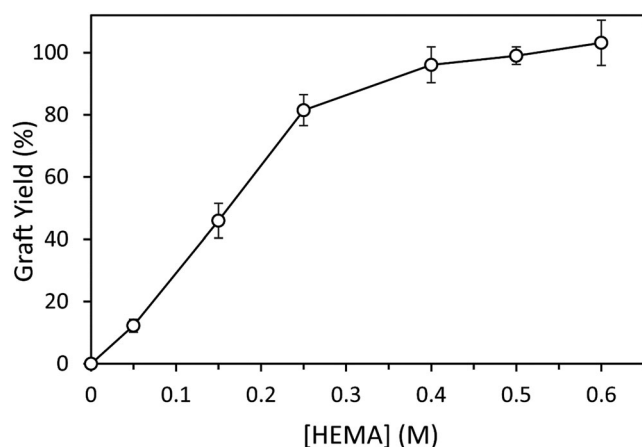


Figure 3. The changes in graft yields (%) of PAN-*g*-HEMA copolymer fibers with the HEMA concentration ($[Bz_2O_2]$: 1×10^{-3} M, solvents: 10/90 acetone/water, total volume: 20 mL, polymerization temperature: 80 °C, time: 120 min, $n = 3$).

gradually decreased for all the solvent mixtures. Although a solvent mixture of 5/95 methanol/water also gave a high graft yield value (101.2%), since a stiff and brittle copolymer fiber structure was obtained in all methanol/water mixtures, the 10/90 acetone/water mixture was chosen as a polymerization medium, and the further experiments were continued in this solvent mixture. Similar results were also reported for the graft copolymerization of vinyl monomers onto fibrous samples in the literature,^[33] such as the use of a 10/90 (V/V) acetone/water mixture for grafting of methyl methacrylate onto poly(ethylene terephthalate) fibers.^[31]

3.1.4. Monomer concentration

Figure 3 illustrates the change in graft yields (%) of PAN-*g*-HEMA copolymer fibers with HEMA concentration. It was found that the graft yield (%) values increased steadily by increasing the monomer concentration and remained almost constant after a particular concentration value (0.4 M). This situation can be related to an increase in the active monomer centers, and thus, the possibility of adding more HEMA molecules to the PAN fiber structure, increasing graft yield values (%). Also, a significant increase was observed in viscosity due to homopolymer formation dominance in the medium at high monomer concentrations, meaning that preventing active center and monomer diffusion to PAN fiber structure, graft yield value can be unchanged. Additionally, since more solvent and time are required to remove the homopolymers that physically adhered to the fiber, HEMA concentration (0.25 M), at which 81.5% grafting yield was obtained, was determined as the most appropriate concentration.^[5]

3.1.5. Polymerization temperature and time

The effect of polymerization temperature and time was monitored on grafted HEMA yields (%) of the copolymer fibers, and the polymerization reactions were conducted at varying temperatures ranging from 60 to 90 °C, whose results are plotted in the supplementary file Figure S3. At 60 °C, even as the time was prolonged to 145 min, the graft

yields of the copolymer fibers could be reached 0.23%, suggesting that the copolymerization could not be achieved at this temperature. This situation may also be correlated with the low decomposition rate of the Bz_2O_2 at 60 °C because it cannot form sufficient amounts of radicals that initiate graft sites on the PAN backbone. Consequently, the values obtained over 70 °C were evaluated in the figure. At 70 °C, by the increment of polymerization time, the graft yields of the fibers also showed a steady increase and took the highest value at the 120th min (65.6%). At 80 °C, the graft yields reached over 90% values at 90th min and remained almost unchanged with increasing time. When all the results are evaluated, one can see that the graft yield values obtained at 90 °C took relatively lower values than those of 80 °C, which can be related to the decreased initiator activity and increased termination reaction rate at an elevated temperature.^[6,34] Accordingly, the graft polymerization reactions were continued at 80 °C for further investigations.

3.2. Characterization results

3.2.1. ATR-FTIR spectra

The ATR-FTIR spectra of pure PHEMA, untreated PAN, PAN-*g*-HEMA copolymer fibers grafted by 53% and 89% are provided in Figure 4.

In the spectrum of pure PHEMA, while the expanded band around $3100\text{--}3600\text{ cm}^{-1}$ (3412 cm^{-1}) belongs to the $-\text{OH}$ stretching vibration, the bands that arose at 2947 cm^{-1} and 1717 cm^{-1} correspond to the stretching vibrations of aliphatic CH_2 and $\text{C}=\text{O}$ of ester groups, respectively. The bands observed at 1152 cm^{-1} , 1246 cm^{-1} , and 748 cm^{-1} correspond to $\text{C}-\text{O}-\text{C}$ and $\text{C}-\text{O}$ bonds' stretching vibrations and out-of-plane stretching vibration of $\text{C}-\text{O}$ bond, respectively.^[5,35,36] The band at 1073 cm^{-1} is also associated with the $-\text{OH}$ deformation.^[5]

In the spectrum of untreated PAN fiber, the respective bands obtained at 2919 cm^{-1} and 2242 cm^{-1} evidence the presence of aliphatic CH_2 and $\text{C}\equiv\text{N}$ groups.^[5] The bands at 1736 cm^{-1} and 1232 cm^{-1} are attributed to the stretching vibrations of $\text{C}=\text{O}$ and $\text{C}-\text{O}-\text{C}$ groups of poly(vinyl acetate) units, present in fewer amounts in the fiber structure compared to the PAN.^[37] The band at 1452 cm^{-1} also arises from the bending vibrations of CH_2 units.^[38]

In both spectra of copolymer fibers, the characteristic $-\text{CH}_2$ and $\text{C}\equiv\text{N}$ bonds of untreated PAN fiber and $-\text{OH}$, CH_2 , $\text{C}=\text{O}$, and $\text{C}-\text{O}$ bonds of pure PHEMA polymer are also encountered with slight wavenumber shifts, intensity, and bandwidth differences. Besides, the increase in the intensity and bandwidth of the bands similar to the HEMA spectrum with the increasing graft yields may prove the more entrance of HEMA to the PAN fiber structure.^[5]

3.2.2. $^1\text{H-NMR}$ spectra

To further illuminate the PAN-*g*-HEMA copolymer structure, the $^1\text{H-NMR}$ spectra of the samples prepared in a δ_6 -DMSO solvent were taken, and the results are shown comparatively in Figure 5 with their possible structures. At first

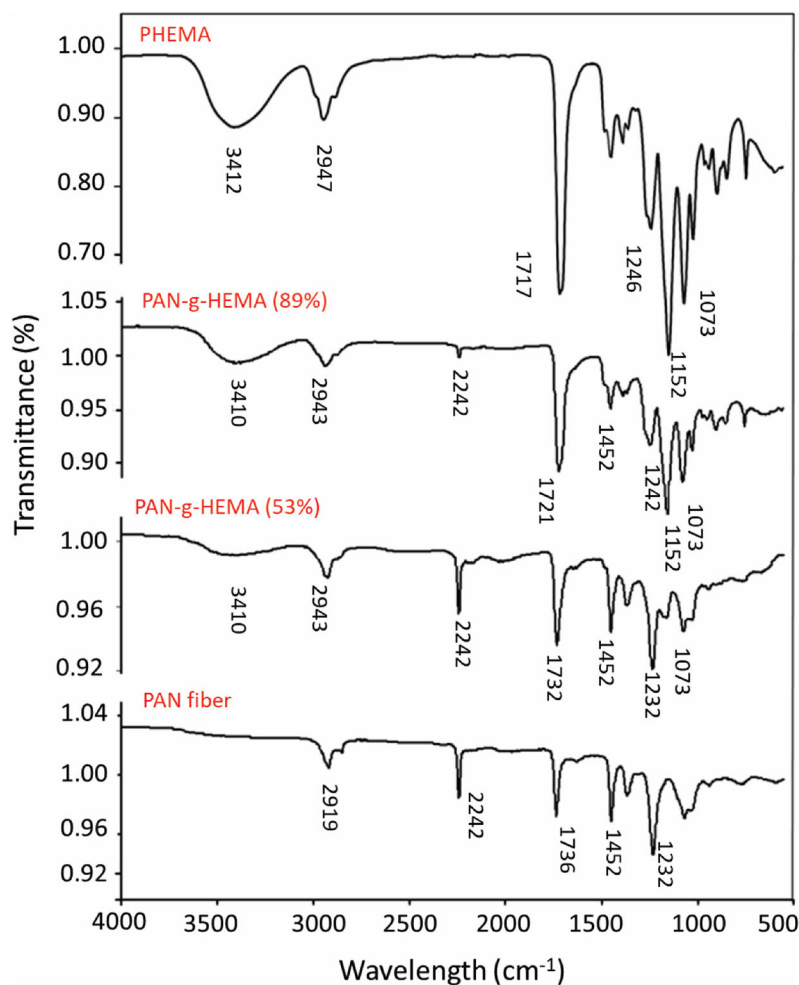


Figure 4. ATR-FTIR spectra of pure PHEMA, untreated PAN fiber, and PAN-g-HEMA copolymer fiber with 53% and 89% graft yields.

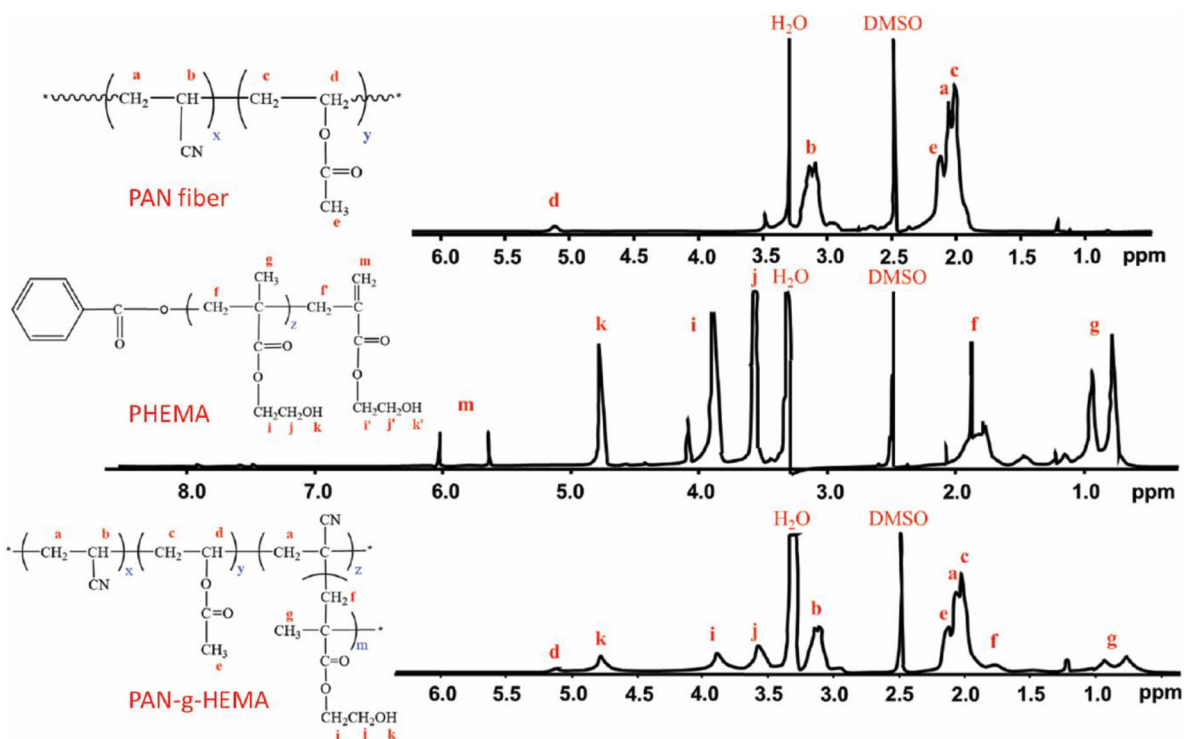


Figure 5. ^1H -NMR spectra of untreated PAN fiber, pure PHEMA, PAN-g-HEMA with 89% graft yield.

glance at the spectra, it is observed that the high-intensity signals of the H₂O protons absorbed into the polymer structure and the DMSO protons remaining from the analysis appeared in all three samples at $\delta = 3.3$ ppm and $\delta = 2.5$ ppm, respectively.

In the spectrum of PAN fiber, the proton peaks belong to $-\text{CH}$ and $-\text{CH}_2$ groups were obtained between $\delta = 3\text{--}3.2$ ppm (CH_b , 1H, $I_{3\text{--}3.2} = 18.28$) and $\delta = 2.05$ ppm (CH_{2a} , 2H, $I_{2.05} = 16.98$), respectively. Additionally, the proton peaks of $-\text{CH}$, $-\text{CH}_2$, and $-\text{CH}_3$ groups present in the poly(vinyl acetate) units of PAN fiber structure also arose at $\delta = 5.1$ ppm (CH_d , 1H, $I_{5.1} = 0.95$), $\delta = 2.0$ ppm (CH_{2c} , 2H, $I_{2.0} = 16.98$), and $\delta = 2.1$ ppm (CH_{3e} , 3H, $I_{2.1} = 12.13$), respectively.^[39]

In the spectrum of pure PHEMA polymer, the characteristic proton peaks of OH groups were obtained at $\delta = 4.8$ ppm (OH_k , 1H, $I_{4.8} = 10.52$).^[35,40] The other respective determinative peaks, including methylene protons of COO-CH_2 and CH_2OH groups, were also observed at $\delta = 3.9$ ppm (CH_{2i} , 2H, $I_{3.9} = 20.87$) ve $\delta = 3.6$ ppm (CH_{2j} , 2H, $I_{3.6} = 20.35$).^[35,40] While the methylene protons present in the main polymer chain gave a peak between $\delta = 1.9\text{--}2.1$ ppm (CH_{2f} , 2H, $I_{1.9\text{--}2.1} = 19.04$), the methyl group protons appeared between $\delta = 0.7\text{--}0.9$ ppm (CH_{3g} , 3H, $I_{0.7\text{--}0.9} = 26.45$).^[41] Due to the possible termination disproportion mechanism of the polymerization, the protons of double-bonded CH_{2m} groups that might be formed at the end of the polymer chain were obtained between $\delta = 5.6\text{--}6.05$ ppm (CH_{2m} , 2H, $I_{5.6\text{--}6.05} = 2.5$). Finally, the low-intensity peaks arose between 7.5 and 7.9 ppm (CH , 1H, $I_{7.4\text{--}7.9} = 0.45$) correspond to the protons of $-\text{CH}$ groups present in the Bz_2O_2 structure.^[42]

When the spectrum of PAN-g-HEMA (89% graft yield) copolymer fiber is examined, it is observed that the presence of characteristic proton peaks of PAN fiber and PHEMA could be detected but in the low-intensity values. The overlapping of the proton peaks of the grafted fiber with its components supports the successful grafting. The possible reason for the low intensity of the peaks can be interpreted as analyzing a diluted copolymer solution because the copolymer fiber was less soluble in the δ_6 -DMSO solvent. This situation may also prove the formation of a copolymer structure since both of the copolymer components can be easily dissolved in the DMSO solvent individually.

The structural composition of the PAN-g-HEMA copolymer fiber was also estimated by considering each component's determinative proton peak intensity value. Accordingly, the content of HEMA grafted to the PAN structure was calculated according to Equation 5:

$$\text{HEMA (\%)} = \frac{I_{\text{OH (HEMA)}}}{I_{\text{OH (HEMA)}} + I_{\text{CHb}} + I_{\text{CH}_{3e/3}}} * 100 \quad (5)$$

After considering the intensity values of each characteristic peak, the HEMA (%) content of the PAN-g-HEMA was calculated as 28.8%. It can be seen that the obtained HEMA (%) content of the copolymer fiber is lower compared to that of gravimetrically calculated graft yield (89%). The observed difference might result from the low dissolution of

the copolymer structure in the δ_6 -DMSO that only enables the analysis of the low molecular weighted-fraction of the copolymer fiber. The other possible explanation might be the possible physical adhesion, strong secondary interactions (i.e., H-bonding), and the formation of inter/intramolecular crosslinks of HEMA chains onto PAN fiber, in addition to the grafting.^[35]

3.2.3. SEM micrographs

SEM micrographs recorded at different magnifications of untreated PAN fiber and PAN-g-HEMA copolymer fiber with 80% HEMA grafted are given in Figure 6. As seen in Figure 6a, the untreated PAN fiber surface has a smooth and straight texture containing a longitudinal grooved structure. After grafting HEMA, the surface of copolymer fiber preserved its smooth appearance (Figure 6c) and was homogeneously coated by HEMA with a thin film-like coverage that can be easily identified from the micrograph taken at higher magnification (Figure 6d). It is also apparent that the copolymer's fiber surface lost its longitudinal grooved structure after grafting. The diameter of the PAN fiber (20.5 μm) was determined to increase to 22.2 μm after graft modification.

3.2.4. TGA curves

Thermograms of untreated PAN fiber, pure PHEMA, and 80% HEMA grafted-PAN-g-HEMA copolymer fiber samples are presented in Figure 7, showing the weight loss values and degradation temperatures recorded in the N₂ atmosphere between 30 and 750 °C. It is known that nitrile groups of PAN undergo cyclization and carbonization and leave residual weight due to the burning of PAN fiber under the N₂ atmosphere.^[43] These afore determining steps were also encountered in the thermogram of PAN fiber. Accordingly, in the thermogram of untreated PAN fiber, it is seen that PAN exhibits a two-step thermal degradation behavior. In the first step, there was a rapid weight loss in the 280–350 °C range (302 °C) due to the degradation of PAN. The total weight loss at the end of the first step was calculated as 46.6%. In the second step (395 °C), a weight loss of 24.4% was observed due to the irreversible carbonization of the cyclized PAN chains. At 700 °C, the graphitized PAN left 29% of the residual weight.^[5]

In the thermogram of pure PHEMA polymer, two-step thermal decomposition was recorded between 100 and 500 °C (around 170 °C, at 378 °C), and at 700 °C, no residual weight was determined for PHEMA.

It can be seen that the PAN-g-HEMA copolymer fiber exhibited a thermal behavior between PAN fiber and PHEMA with 4 stages of thermal degradation. In the first stage, 1.6% weight loss occurred up to 107 °C, which was understood to come from removing water and solvent remaining in the copolymer structure. The following three stages proceed in the same order as the PAN fiber. In the second stage, due to the cyclization of the nitrile groups and the removal of volatile compounds, 3% of weight loss occurred.^[44] The third step in the thermal degradation of

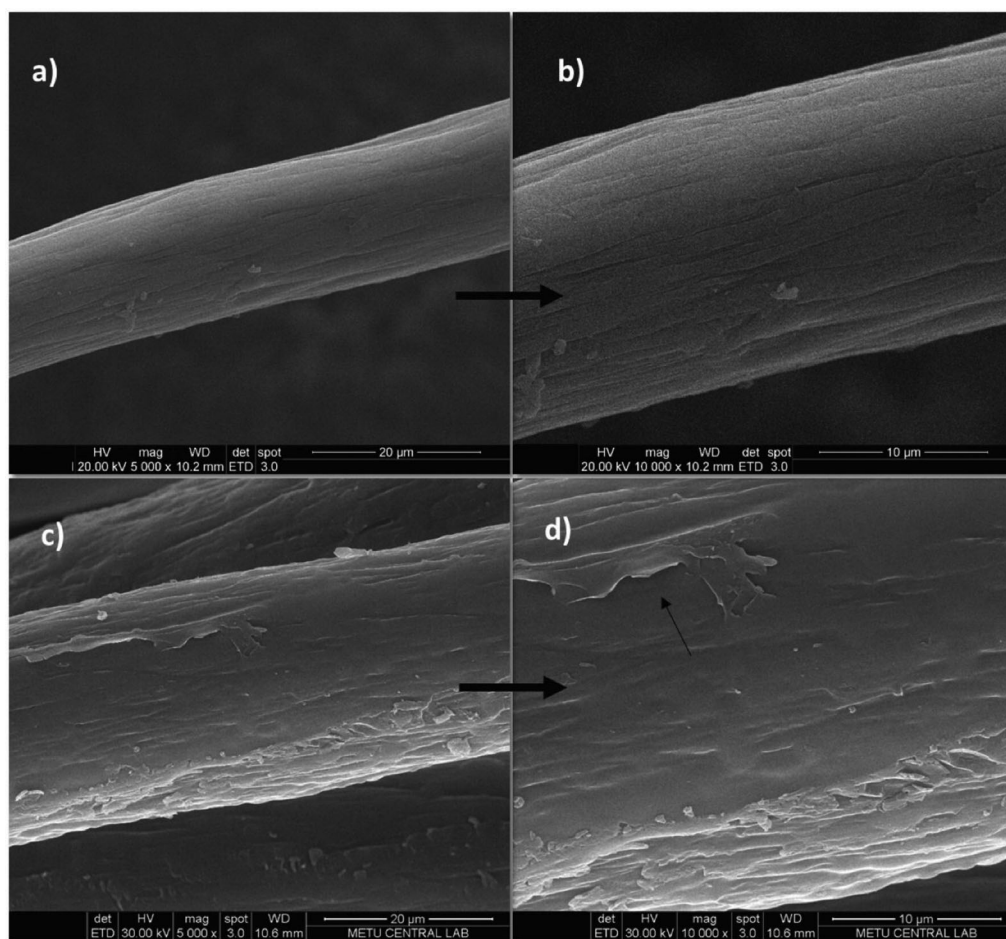


Figure 6. SEM micrographs of (a) and (b) untreated PAN fiber, (c) and (d) PAN-g-HEMA copolymer fiber taken at different magnifications.

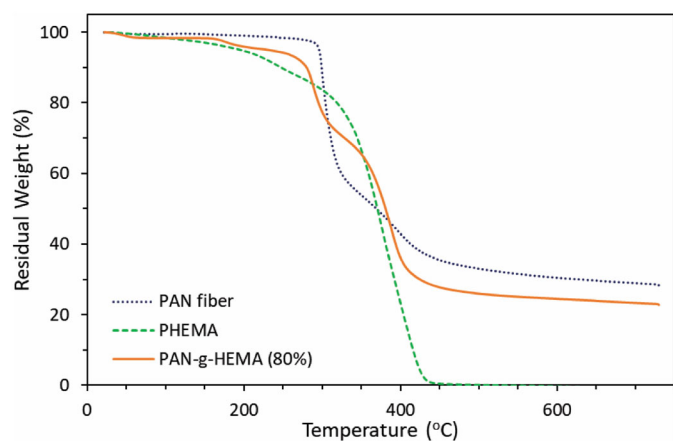


Figure 7. TGA curves of untreated PAN fiber, pure PHEMA polymer, and PAN-g-HEMA copolymer fiber contain 80% HEMA.

the copolymer, with 25.1% rapid weight loss observed at 220 °C. However, in this step, it is seen that the total weight loss of the copolymer (29.7%) became lower than that of pure PAN fiber (46.6%). In the last step, the weight loss of 46.9% of the copolymer starting at 322 °C is attributed to dehydrogenation caused by decomposition resulting from thermal decomposition. As a result, PAN-g-HEMA copolymer fiber also left 23.3% residual weight at 700 °C, similar to pure PAN fiber. As a result of thermal analysis, it was

concluded that the residual weight (23.3%) and thermal decomposition temperature formed by the degradation of the grafted copolymer fiber took lower values when compared to that of untreated PAN fiber. This situation may be associated with the more degraded part of the fiber after grafting, as compatible with the literature.^[5]

3.2.5. Mechanical properties

The tensile strength and elongation at break values of PAN-g-HEMA fibers with different graft yields are given in Figure 8. When Figure 8a is examined, it is seen that the tensile strength value of untreated PAN fiber is found as $1004 \text{ cN} \pm 71$. It is also noteworthy that the tensile strength of the copolymer fibers took close values to that of untreated fiber, demonstrating that the grafted HEMA chains did not lead to a significant alteration in the properties of PAN fiber. This case was also statistically evaluated by the ANOVA method, and at 99% significance level ($p < 0.01$), the calculated F value for tensile strength measurements between changing graft yields (%) was found 1.26, which is lower than the critical F value of 4.46. This shows that the graft yields (%) have no statistical significance with each other. It was also obtained that the grafting process has no statistically significant when compared to the tensile strength values of an untreated PAN fiber with a 68.6%

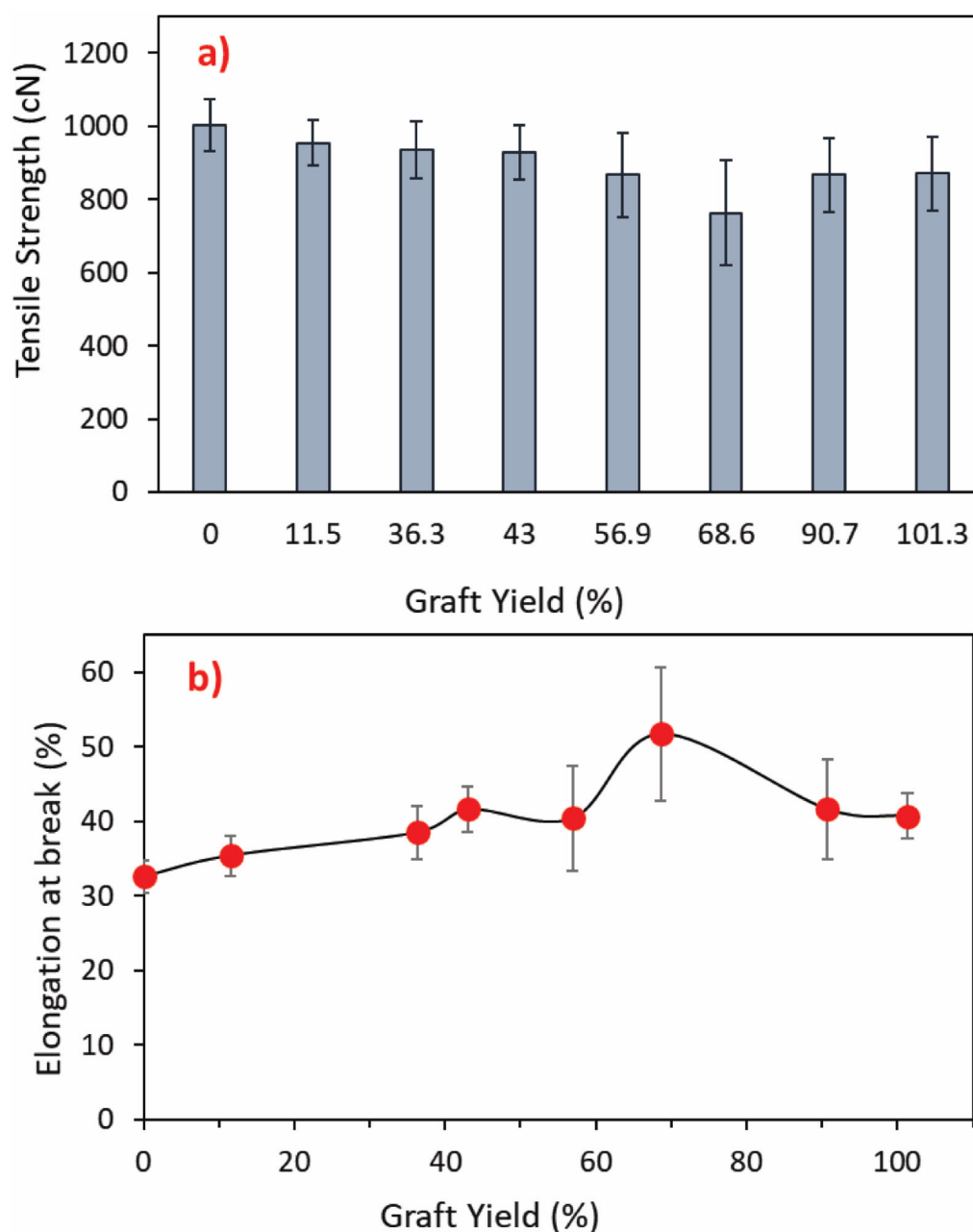


Figure 8. (a) The change in tensile strength values and (b) elongation at break values of PAN-g-HEMA copolymer fibers with varying HEMA graft yields (%) ($n = 3$).

grafted PAN, taking into account the calculated T value of 2.62 and T critical value of 4.60.

Although an increase in the mechanical properties of HEMA-grafted cotton fiber was reported in the literature,^[45] we did not observe such a tendency. When the elongation values are considered (Figure 8b), it can be seen that the elongation values of graft modified fibers also took close values to that of an untreated fiber. When the results are considered statistically, it was obtained that the elongation at break (%) values showed the same trend as that of the tensile strength, and both the F calculated (2.51) and T calculated (3.61) values were found lower than that of the F critical and T critical values, respectively. This finding concludes that the graft modification process almost preserved the fiber's mechanical properties.

3.3. Moisture absorption and water retention results

Figure 9 represents the moisture absorption values of untreated PAN and PAN-g-HEMA fibers with different grafting yields depending on their exposure time in a humid environment. As can be seen in the figure, it is clearly seen that the moisture absorption value of pure PAN is relatively low and is increased by eight times thanks to the rising grafting yield. This situation can be explained by integrating –OH functional groups to the PAN fiber structure through HEMA grafting. Besides, the increasing moisture absorption values of copolymer fibers with HEMA graft yields evidence of successful grafting. For example, the moisture absorption value of 2% of pure PAN fiber reached 15.7% after grafting 95% of HEMA onto the fiber. This increase in the moisture absorption ability of PAN fiber can

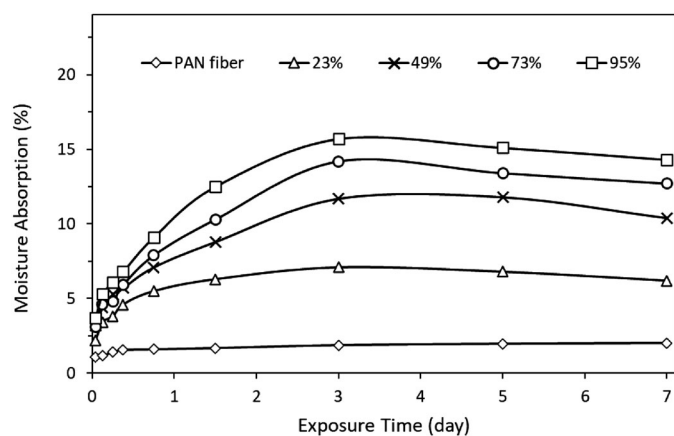


Figure 9. Moisture absorption (%) values of untreated and PAN-g-HEMA copolymer fibers containing different graft yields with exposure time ($n = 4$).

Table 2. The water retention values of the PAN-g-HEMA copolymer fibers with varying graft yields ($n = 1$).

Sample	Water retention (%)
Untreated PAN fiber	252
23% grafted	298
45% grafted	308
73% grafted	394
95% grafted	376

also be understood from the SEM micrographs because it has been reported that the increase in the moisture absorption has a remarkable influence on the fiber diameter increase.^[46,47] When the change of moisture absorption values in an environment with 65% relative humidity was examined, it was observed that the highest value (%) was reached on the 3rd day, regardless of the graft yields. However, it can be said that these values remained approximately constant with a slight decrease in the examinations after three days. It can be concluded that the graft modified fiber reached moisture saturation, and thus it is not very meaningful to examine after three days.

The water retention values of untreated PAN fiber and PAN-g-HEMA copolymer fiber with varying HEMA graft yields (%) are comparatively listed in Table 2. Accordingly, it can be seen that the water retention capability of the PAN fiber is significantly improved compared to an untreated sample even at a low graft yield such as 23%, and reached saturation with the increasing of HEMA graft yield up to 73%, in accordance to reports in the literature.^[48] This tendency of the graft copolymer fibers was also consistent with the study's moisture absorption findings, which can be related to PAN fiber's increased hydrophilic –OH moiety.^[49] The slight decrease in the water retention value of the PAN-g-HEMA fiber at the densest grafting condition (95%) may arise from the possible decrease in the free –OH groups due to the formation of inter/intramolecular crosslinks.

3.4. Dyeability study results

The effect on PAN fiber dyeability of hydrophilicity property imparted to fiber with the PAN-g-HEMA copolymer fiber

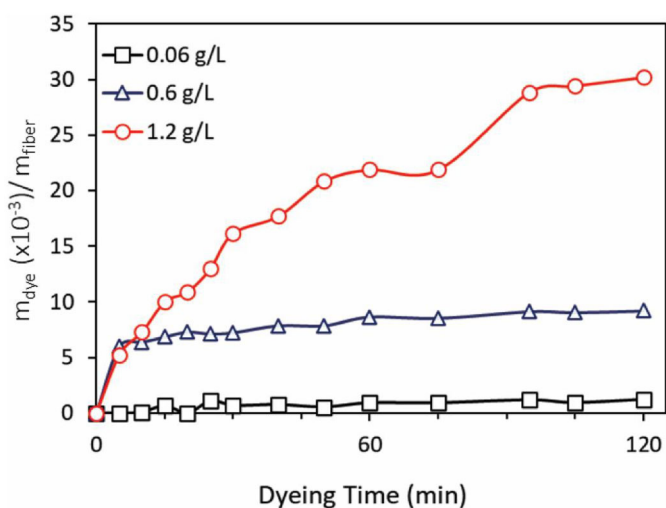


Figure 10. The changes in dye uptake values of PAN-g-HEMA copolymer fibers with the dye concentration between 0 and 120 min dyeing time (HEMA graft yields: 80–90%).

prepared was monitored through a dyeing process by a direct meta dye (Direct Black 38). This dye is conventionally applied to the hydrophilic cellulosic samples such as cotton, linen, rayon, and paper^[50,51] since their dye fixation ability is high through hydrophilic –OH groups. Thus, it was aimed to mimic the dyeing characteristic of natural cotton fibers with a PAN-g-HEMA copolymer fiber. Accordingly, the images of the dyed PAN-g-HEMA copolymer fibers with the different HEMA graft yields obtained after dyeing with Direct Black 38 at pH 5 are provided in Figure S4 in the Supplementary file. When the samples are visually examined, it was viewed that the increase in the amount of grafting affected the dye fixation but was not individually sufficient to obtain a high dye uptake. For this reason, the conditions under which the highest dye uptake was obtained were determined by changing the dye concentration and pH values of the dyeing bath in the dyeing experiments.

In the first attempts for the dyeing investigations, the copolymer fibers with HEMA graft yields of 80–90% were employed, and the effect of concentration was studied by changing the dye concentration between 0.06 g/L and 1.2 g/L and keeping the pH constant. Then, the dye uptake of the copolymer fibers was calculated as $m_{\text{dye}}/m_{\text{fiber}}$ through the UV-Vis measurements (Figure 10). As can be seen, it was observed that the dye uptake values of the copolymer fibers gradually increased with dye concentrations. At the lowest dye concentrations (0.06 g/L), the color shade of the fibers was relatively weak due to the low penetration of the dye. When the concentration was raised to 0.6 g/L, the dye uptake values increased by six times and rapidly reached saturation at the early stages of dyeing (5 min). At the highest dye concentration, the highest dye uptake values were obtained but at a slow pace. The highest dye uptake of Direct Black 38 was recorded as $30.2 \times 10^{-3} m_{\text{dye}}/m_{\text{fiber}}$, which can be evaluated as entirely satisfactory compared to the similar dye uptake values published in the literature.^[52,53]

The changes in dye uptake values of copolymer fibers with changing graft yield values are shown in Figure 11.

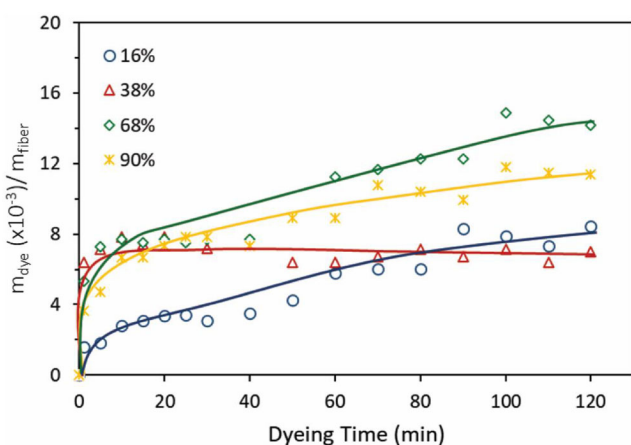


Figure 11. The changes in dye uptake values of PAN-g-HEMA copolymer fibers with the HEMA graft yield between 0 and 120 min dyeing time (pH = 5, [dye]: 1.2 g/L).

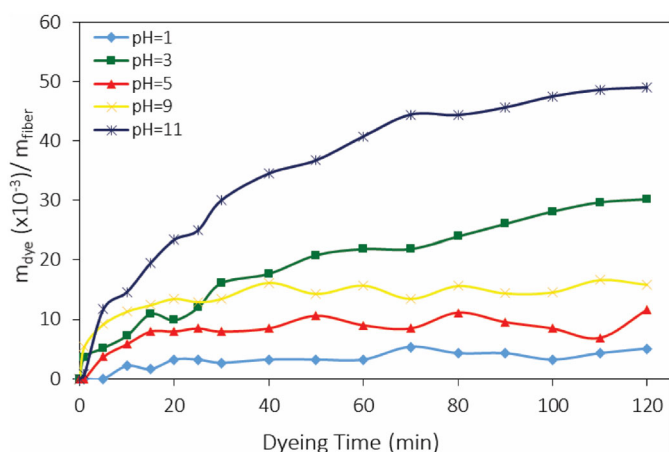


Figure 12. The changes in dye uptake values of PAN-g-HEMA copolymer fibers with changing dye bath pH values ([dye]: 1.2 g/L, HEMA graft yield: 80–90%).

With the increase of dyeing time, dye uptakes of all the copolymer fibers containing different graft yields increased up to 60 min and did not significantly change with time over 90 min. Among all the copolymer fibers, the dye uptake values became relatively the highest in the 68% of the HEMA graft yield containing series. The highest value in this serial was measured at 100 min as $14.9 \times 10^{-3} m_{\text{dye}}/m_{\text{fiber}}$.

It is known that the pH of the dye bath is an effective parameter for the increase of dye fixation onto the substrates in the literature.^[50,54] For that reason, to increase the dye molecule penetration onto the copolymer fibers, the dye bath pH was varied, and the results, including the dye uptake values of the samples, are illustrated in Figure 12. As seen from the figure, the dye uptake values of the copolymer fibers were remarkably influenced by the pH change. For example, although all the samples showed an increasing tendency with time, the dye uptake values took relatively the lowest values at the lowest pH value (pH 1). Interestingly, the highest dye uptake values of the copolymer fibers were recorded at pH 3 and pH 11, as $30.2 \times 10^{-3} m_{\text{dye}}/m_{\text{fiber}}$ and

$49.0 \times 10^{-3} m_{\text{dye}}/m_{\text{fiber}}$, respectively. Consequently, pH 11 was found as the most appropriate condition for dyeing the PAN-g-HEMA copolymer fibers with the Direct Black 38.

The increase in the dye uptake values of the copolymer fibers at the elevated pH values may be correlated with the increase of chemical interaction of dye molecules with the copolymer fiber surface through facilitated ionization of the dye.^[55] Because at the higher pH values, the dye molecule may be more likely to dissociate, resulting in strong interactions, such as ion-dipole and H-bonds. The increment of pH value of the dye baths yields to the increase of negatively charged sites either on the target dye adsorbed-surface or the dye molecule,^[54,55] and this may have increased the fixation of the dye on the hydrophilic copolymer fiber. Accordingly, further investigations were continued with the dyeing series of pH 11 and pH 3.

The CIE $L^*a^*b^*$ color measurement and K/S color strength test results of the dyed fibers at the different pH values are listed in Table S1 (Supplementary file). The photographic images of the samples can also be seen in Figure S5 (Supplementary file). The table shows that the K/S values of the dyed copolymer fibers remarkably changed with the pH of the dye baths, and it was observed that the highest K/S values were obtained for the samples dyed at pH 3 and 11, which confirm the dye uptake investigation results. This situation can also be visualized from the optical images of the dyed samples because the samples (dyed at pH 3 and pH 11) with the highest K/S values also had the highest color shades (the lowest L^* values corresponding to the dark shades). The dyed sample at pH 1 exhibited the lowest dyeing performance with the lowest K/S value.

The $L^*a^*b^*$ color measurement and K/S color strength test results after applying detergent washing-rinsing-drying processes for five cycles of copolymer fibers dyed at different pH values are presented in Table S2 (Supplementary file). The appearances of the dyed samples after the detergent washing process are also provided in Figure S6 (Supplementary file).

When the K/S values of the samples are examined, it can be seen that the color shades of the samples remarkably lightened after applying a repeated detergent washing procedure. However, the fiber that almost retained its color shade was the sample dyed at pH 11 (M11), with a K/S value of 20.720. According to K/S color strength, the order of dyed fibers was M11, M5, M3, M9, and M1. This case can also be evidenced from the images of the samples given in Figure S5 (Supplementary file).

The ΔE value is also found a practical method for comparing the distance between two color tones. In the study, the dyed sample at pH 1, which has the lowest dye uptake, was chosen as the reference sample to differentiate the color shades of the dyeing. Accordingly, it was observed that there were no noticeable color tones between the samples after the detergent washing, even a remarkable difference in their K/S and L^* values. The ΔE value of the M3 sample dyed at pH 3 was slightly high compared to the other samples. This finding may have arisen from the difference between the samples' a^* and b^* color space values.

4. Conclusion

It was outlined with the present study that an industrially available synthetic textile material, PAN fiber, was practically gained hydrophilicity property by the graft modification technique. The grafting of the HEMA monomer was ensured in the high yields (~95%) using the copolymerization process with the Bz₂O₂ initiator in the solvent mixture system. The ATR-FTIR and ¹H-NMR spectra results evidenced the structural changes that occurred after the grafting of HEMA. SEM micrographs displayed the homogenous and thin film-like coverage of HEMA on the PAN fiber that led to the loosing the longitudinal grooved structure. The thermal analysis results revealed the slight thermal stability lowering of PAN-g-HEMA copolymer fibers in terms of thermal decomposition temperature. The tensile strength and elongation at the break (%) test results approved the negligible weakening in the mechanical properties of PAN after the grafting. The most outstanding results of the study were relevant with hydrophilicity, such as moisture absorption and water retention, and dyeability with a direct dye, suggesting the potential of a synthetic PAN fiber to be used in the different applications where natural cotton fiber can take part in, such as manufacturing of breathable apparels in the future.

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