

Preparation of hydrophilic woven fabrics: Surface modification of poly(ethylene terephthalate) by grafting of poly(vinyl alcohol) and poly(vinyl alcohol)-*g*-(*N*-vinyl-2-pyrrolidone)

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ABSTRACT: One of the most industrially important synthetic textile materials, woven poly(ethylene terephthalate) (PET) fabrics, have limitations in the usage of casual apparel applications due to their unwanted hydrophobicity. For that reason, in this study, to impart permanent hydrophilicity to the PET fabrics, hydrophilic poly(vinyl alcohol) (PVA) and a PVA-based copolymer were introduced to the alkaline hydrolysis pretreated PET surface by graft copolymerization for the first time. The graft modification of PET fabric surface was performed with an industrial-adaptable approach. The synthesis of a novel PVA-*g*-(*N*-vinyl-2-pyrrolidone) copolymer was achieved by the introduction of glycidyl methacrylate monomer to the PVA backbone. The structure of the copolymer was evidenced by attenuated total reflection–Fourier transform infrared spectroscopy and ¹H-NMR techniques. The introduction of PVA and copolymer structures with desired functional groups to the PET fabric surface was confirmed with the X-ray photoelectron spectroscopy technique. It was obtained that the contact angle–wetting time of PET fabric (145° and 98 s) could be dropped to 37° and 0.1 s and 64° and 0.7 s after PVA and copolymer grafting, respectively. This suggests that the graft-modified PET fabrics may find the potential of use in the textile applications as the alternative hydrophilic materials. © 2019 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2020**, *137*, 48584.

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INTRODUCTION

The surface modification of synthetic textile yarns/fabrics for desired purposes has been an interesting subject for researchers and industrial institutions. Depending on the properties of the materials used in the modification, functional and high value-added textile yarns/fabrics, which could appeal to many fields of the industry, especially the apparel sector, could be prepared. Among synthetic yarns/fabrics used in textile applications, poly(ethylene terephthalate) (PET) fibers are one of the most preferred materials due to their ability to blend with hydrophilic natural fibers,¹ high mechanical strength,² good strain resistance/easy maintain,¹ and resistance to many chemicals.³ However, their hydrophobic nature and high crystalline structure and absence of suitable functional groups for binding the dyestuffs could limit the usage of PET fibers. These drawbacks hinder their potential to be used as an alternative material for natural and hydrophilic cotton fibers especially during dyeing.³

To remedy the unwanted properties of PET fiber and gain new desired functional groups, and consequently, improve its usage in

different fields, researchers have concentrated on modification of its surface with physical and chemical methods.^{4–6} Among these methods, chemical modification methods such as plasma processing,⁷ graft copolymerization (grafting to polymers and/or grafting from monomers),^{8–10} crosslinking,^{11–13} enzymatic treatment,^{14,15} and aminolysis^{2,16} have been frequently preferred to modify the surface of fibrous PET in the literature. Among them, the graft copolymerization has been one of the most preferred methods in the surface chemical modification, owing to enabling the inclusion of new functional groups to the surface of PET, by requiring of less energy consumption and low-cost chemicals/apparatus. Depending on the properties/functional groups of the selected ingredients in the graft copolymerization (monomers/polymers), the hydrophilicity, dyestuff attraction, soil repellency, antistatic, and antibacterial properties have been reported to be gained to the PET fibers.^{17–19}

In this study, it was aimed to improve the hydrophilicity property of woven PET fabrics, by grafting of hydrophilic poly(vinyl

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alcohol) (PVA) polymer and a PVA-based PVA-*g*-(*N*-vinyl-2-pyrrolidone) (PVA-*g*-NVP) copolymer with free-radical polymerization. In this way, the hydrophilicity of the PET surface, as well as dyestuff-attaching property of PET fabric surface, would also be improved. Hence, in addition to the conventional dyestuffs for PET fiber/fabric dyeing such as disperse dyes, the PET surface could also be dyed with many types of dyestuffs that are suitable for cotton fabrics such as indigo.

Although there have been numerous studies for the graft modification of PET fiber/fabric in the literature,^{2,9,20–24} to our knowledge, no report has been present for the grafting of a PVA based-copolymer or PVA onto PET fabrics. Only in a few studies, the preparation of PET/PVA composites²⁵ and radiation-induced graft copolymerization of vinyl acetate onto PET were reported.²⁶ In the other recent studies, the researchers have focused on the improvement of the other properties of PET fabrics, such as thermoregulating²⁷ and anti-oil staining²⁴ with different materials, such as coating with phase-changing materials and photografting of poly(*N*-isopropyl acrylamide), respectively. In the latter study, the researchers have also performed a prefunctionalization of PET fabric surface by alkaline hydrolysis and carboxylation to enhance the grafting.²⁴ In this study, to obtain certain hydrophilicity imparted PET surface, first, a novel graft copolymer, PVA-*g*-NVP, was synthesized into two steps: (1) metacryloyl groups introducing to PVA and (2) copolymerization of this prepolymer structure with NVP monomer in an organic solvent mixture. Then, this copolymer was grafted onto the alkaline hydrolyzed-PET surface in comparison with its ancestor PVA, by graft copolymerization method that is adapted to the industrial applications. Compared with the conventional solution grafting techniques, this method provides a relatively facile application of the grafting process onto the fabric surfaces and requires fewer amounts of chemicals, solvents, and energy. The changes in the structure, morphology, and surface characteristics of the fabrics were revealed with many techniques in addition to their mechanical properties.

EXPERIMENTAL

Materials

PET fabrics were obtained from SANKO Textile Enterprises Co. ISKO Woven Firm (İnegöl, Turkey). The properties of PET were given in Table I.

PET fabrics 13 cm × 20 cm in sizes were washed in 1 g/L ECE (ECE is defined as non-phosphate standard test detergent without optic whitener) reference detergent, 1 g/L soda, and 1 g/L Primasol deaerator containing aqueous solution at 60 °C. PVA polymers (13.000–23.000 g/mol with 87–89% of hydrolysis; 146.000–186.000 g/mol with 98.5%

of hydrolysis) were obtained from Sigma-Aldrich (Turkey, Ankara). The monomers of glycidyl methacrylate (GMA) and NVP, *N,N,N,N*-tetramethylethylenediamine (TEMED), dimethyl sulfoxide (DMSO), *N*-methyl 2 pyrrolidone (NMP), chloroform, methyl alcohol, acetone, and ethyl alcohol were used as received from Sigma-Aldrich. Initiators of azobis(isobutyronitrile) (AIBN) and benzoyl peroxide (75%) (BPO) were obtained from Merck (Turkey) and used after recrystallization in methyl alcohol and chloroform/methanol [50/50 (V/V)] solvent mixtures, respectively. Other initiators cerium ammonium sulfate (CAS) (Sigma-Aldrich), ammonium peroxydisulfate (APS) (Sigma-Aldrich), and sodium bisulfite (Sigma-Aldrich) were used without further purification.

METHOD

Preparation of Alkaline Hydrolyzed-PET Fabrics

PET fabrics were washed prior to use in experiments, weighed and subjected to alkaline hydrolysis process in 300 g/L of NaOH containing aqueous solution [1/50 (w/V) bath ratio] at 130 °C for 3 min. Fabrics were then washed with plenty of hot water, neutralized with 0.1 M acetic acid solution, and dried at 50 °C under vacuum. Untreated and alkaline hydrolyzed-PET fabrics were donated as UPET and HPET, respectively. The weight loss of the PET fabric after alkaline hydrolysis was gravimetrically calculated as 20%.

Synthesis of PVA-GMA Prepolymer

To synthesize the PVA-*g*-NVP copolymers, first, a PVA-GMA prepolymer was prepared by introducing vinyl methacrylate groups to PVA chains according to a previous method in the literature.²⁸ Briefly, 5.0 g PVA was taken into a two-necked round bottom flask and dissolved in 50 mL of DMSO medium at 70 °C with stirring. After adjusting the temperature to 60 °C, 3.75 g of GMA monomer was added to the solution. Then, with the addition of 0.17 mL of TEMED, the reaction was initiated and preceded for 6 h. At the end of the reaction, the solution was taken to a beaker and precipitated with the addition of excess distilled water to remove the unreacted PVA polymer. The impurities of unreacted GMA, TEMED, and PVA and possible byproducts were removed by the multiple steps of dissolving the prepolymer in 1/1 acetone/ethyl alcohol mixture (V/V) at 60 °C with stirring and reprecipitation with distilled water. The PVA-GMA prepolymer was dried in a vacuum oven at 30 °C and stored in a refrigerator at −5 °C to prevent the formation of possible unwanted byproducts with the effect of heat or light, according to the literature.²⁸

Synthesis of PVA-*g*-NVP Copolymer

The PVA-*g*-NVP copolymer was prepared using the PVA-GMA prepolymer. For this purpose, certain amount of PVA-GMA prepolymer was dissolved in 1:1 acetone/ethanol solvent mixture (V/V) at 60 °C, a certain concentration of AIBN solution in acetone was added and the prepolymer was allowed to interact for some time. After the addition of certain concentration of NVP monomer, polymerization was carried out for 4 h. At the end of the reaction, white colored and precipitated copolymer structure was taken to a beaker and thoroughly washed in hot (1/1) acetone/ethanol solvent mixture (V/V) to remove the unreacted PVA-GMA prepolymer and NVP monomer residues and

Table I. Properties of PET Fabrics

Warp	70/F36 Denier PET
Weft	150/288 Soft lmg Pure PET
Warp density	53.7 warp/cm
Weft density	41.6 weft/cm
Weaving	3/1 Z twill weaving

separated by the centrifugation at 4000 rpm for 15 min. The copolymer was then dried in a vacuum oven at 40 °C for 24 h.

To enlighten the graft copolymer structure with the attenuated total reflection–Fourier transform infrared spectroscopy (ATR–FTIR) and ^1H -NMR techniques, the synthesis of pure PNVP polymer that would be used as a comparison sample was performed under the conditions given below. It was prepared similarly to the copolymer preparation, by the polymerization of NVP with AIBN, except using PVA prepolymer. Briefly, a 1.5 M 8 mL of NVP solution was prepared in acetone/ethyl alcohol (1/1, V/V) with stirring at 60 °C. Then, 0.01 M 2 mL of AIBN solution in acetone was slowly injected into a solution. The precipitated, pure PNVP polymer was washed with cold acetone and then dried in a vacuum oven, stored for use in the further characterization studies.

Graft Copolymerization

UPET and/or HPET fabrics in 20 cm $\times$ 5 cm sizes were put into a wide and flat glass container impregnated with certain concentrations of initiator solutions such as AIBN, BPO, APS, and CAS up to 100% wet pick up and dried. Then, polymer solutions such as PVA (3% w/V, in water) and PVA-g-NVP (3% w/V, in NMP) were also impregnated onto the fabrics at the same volume and kept for a while at drying temperature. After the treatment, the fabrics were washed with either hot water (at 70 °C) or an appropriate solvent/solvent mixture according to the polymer used, dried, and weighed. The graft yields (%) of the fabrics were calculated gravimetrically, by the proportion of the weight increase values of the fabrics to the initial fabric weights.

Characterization

The ATR–FTIR spectra of the samples were taken with a Perkin Elmer Infrared Spectroscopy instrument using the ATR accessory within the range of 4000–650 cm^{-1} . The ^1H -NMR analysis was carried out with 600 MHz Agilent NMR instrument after dissolving the samples at 70 °C in DMSO- d_6 . The elemental compositions of the fabric surfaces after modification processes were determined by X-ray photoelectron spectroscopy (XPS) technique with PHI 5000 VersaProbe instrument using Al monochromatic X-ray anode. The narrow (multiplex) scan results of determined elements were obtained by fitting the most appropriate function after drawing in the Origin Lab Pro 9 program. The changes in surface morphology of the fabrics were revealed from the micrographs taken with Quanta 400F field emission scanning electron microscope (SEM) after coating the samples with Au–Pd. Contact angle measurements before and after modification were performed by Attension Theta Lite Optical Contact Angle Measurement device with the Sessile Drop method. The tensile strength test was employed according to the ASTM D 5034 Standard (Standard Test Method for Breaking Strength and Elongation), by monitoring the behavior of a fabric sample to the applied-tension under warp direction. The tear strength of the fabrics was determined according to the ASTM D 1424 [Test Method for Tearing Strength of Fabrics by Falling Pendulum (Elmendorf) Apparatus], by examining the tearing behavior of a fabric sample in the warp direction by a falling pendulum. In the mechanical tests, the average of the measurements of three different samples

prepared under the same conditions was given as the result of the analysis.

RESULTS AND DISCUSSION

Synthesis of PVA-g-NVP Copolymer

In the first synthesis attempts for the grafting of NVP to the PVA chains, any copolymer formation could not be obtained in an aqueous medium with free-radical polymerization. To the best of our knowledge, no study has been published in the literature for this purpose. In only a few studies, synthesis of block copolymers of vinyl acetate and NVP has been reported with the cobalt-mediated living polymerization and reversible addition-fragmentation chain transfer polymerization techniques.^{29–31} For this purpose, to provide grafting of NVP to the PVA chains by means of free-radical polymerization, first, a PVA–GMA prepolymer was prepared by the chemical modification of PVA with GMA monomer according to a method published in the literature.²⁸ It has been reported that a transesterification reaction between a GMA monomer and PVA takes place in the media of polar-aprotic solvents such as DMSO and DMF, and the vinyl methacrylate side of the GMA is attached to PVA chains from hydroxyl groups of PVA.^{28,32,33} The glycidol side of GMA has occurred as a byproduct during the reaction. When an experimental condition (1/0.75 ratios of PVA to GMA, w/w) yields a high degree of GMA substitution, a yellowish orange colored and adhesive gel-like PVA–GMA prepolymer was obtained unlike a white colored and powdered PVA structure. The possible structure of PVA–GMA prepolymer was illustrated in Figure 1.³⁴

ATR-FTIR

Figure 2 shows the ATR–FTIR spectra of PVA, PVA–GMA prepolymer, PNVP, and PVA-g-NVP copolymer. When the spectrum of the PVA–GMA prepolymer is examined, the bands at 1710, 1630, 1170, and 940 cm^{-1} arise from C=O (ester group) and C=C (vinyl group) bending vibrations, COC (ester group) stretching, and $\text{R}_2\text{C}=\text{CH}_2$ out of bending vibrations, respectively.²⁸ In addition, the absence of the bands at 1255 cm^{-1} (breathing), 908 cm^{-1} (asymmetric deformation), and 845 cm^{-1} (symmetrical deformation) of the

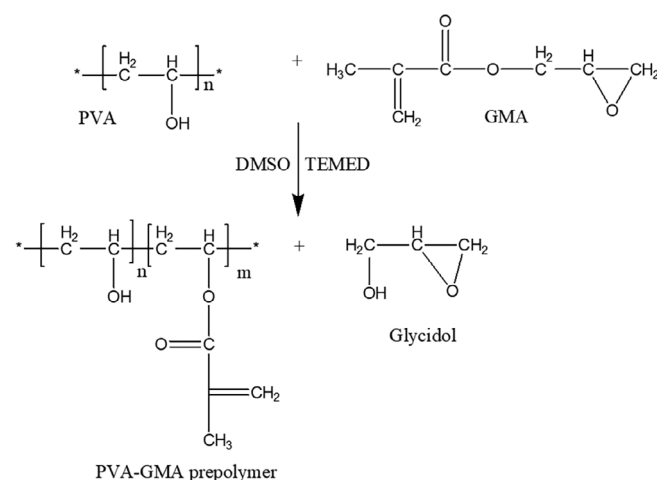


Figure 1. The transesterification reaction of PVA and GMA monomer with TEMED in the medium of DMSO.^{28,32}

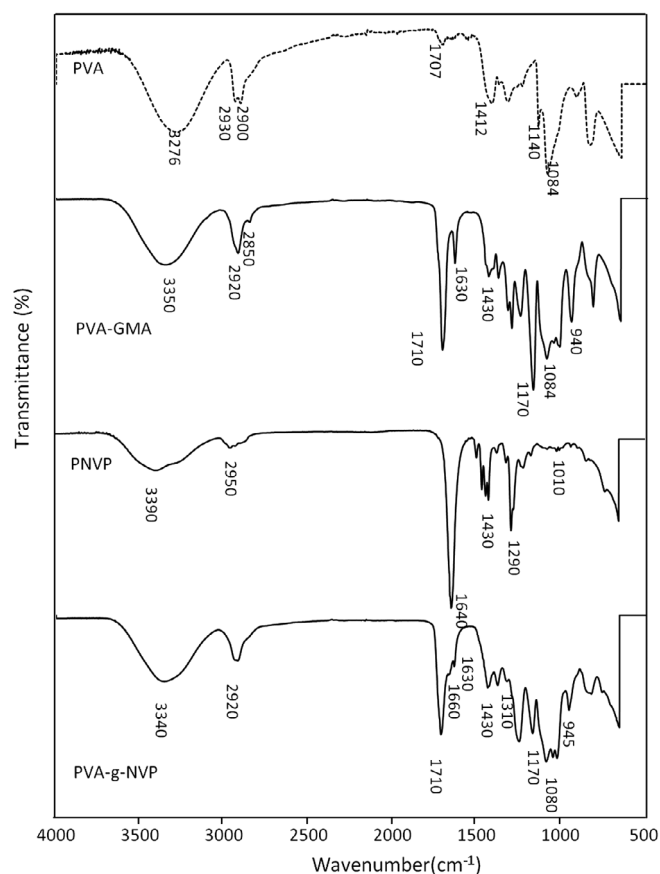


Figure 2. ATR-FTIR spectra of PVA, PVA-GMA, PNVP and PVA-g-NVP copolymer.

epoxide ring of GMA confirm the transesterification reaction of GMA with PVA, in accordance with the literature.

When the spectrum of the PNVP is evaluated, although the sharp band at 1640 cm^{-1} corresponds to the C=O stretching vibration, the bands at 1430 , 1290 , and 1010 cm^{-1} belong to CH_2 bending and C-N stretching vibrations, respectively.³⁵ In addition, the stretching vibrations of asymmetric C-H at 2950 cm^{-1} and associated hydroxyl group at 3390 cm^{-1} are also present in the spectrum of PNVP.³⁶

In the spectrum of PVA-g-NVP, it can be seen that the bands of PVA-GMA prepolymer are preserved and the characteristic bands of PNVP at 1640 and 1290 cm^{-1} are blue shifted to 1660 and 1310 cm^{-1} . This blue shift in C=O stretching vibration was also observed in the PNVP containing studies in the literature,^{36,37} and explained with the changes in π - π conjugations of PNVP chains.³⁷

¹H-NMR

In Figures 3 and 4, the ¹H-NMR spectra of PVA, PVA-GMA prepolymer, PNVP, and PVA-g-NVP are comparatively presented. When all the spectra are investigated, it can be seen that the solvents of $\text{H}_2\text{O}/\text{DMSO}$ present in the polymer structures gave sharp peaks at $\delta = 3.3$ and 2.5 ppm . In the spectrum of PVA, the characteristic proton peaks of -OH, -CH and -CH₂ groups appeared at $\delta = 4.3$ – 4.7 ppm (1H , $I_{4.3-4.7} = 5.03$), $\delta = 3.7$ – 4.0 ppm (1H , $I_{3.7-4.0} = 5.17$), and $\delta = 1.4\text{ ppm}$ (2H ,

$I_{1.4} = 14.2$), respectively. In addition, the protons of -CH₃ group in the acetate side of the PVA chain were observed at $\delta = 1.9\text{ ppm}$ (3H , $I_{1.9} = 2.51$). According to this, when the intensity of the protons of acetate (-CH₃) was proportioned to the intensity values of the total -OH and CH₃ protons [$I_{\text{CH}_3/3}/(I_{\text{OH}} + I_{\text{CH}_3/3})$], the percentage of the acetate residue of PVA can be found as 14% corresponding to a 86% of hydrolysis degree. This value is highly compatible with the real hydrolysis value of the commercial PVA polymer (87–89%) used in the study. Accordingly, it could also be approximately calculated that the $M_n = 13,000$ – $23,000\text{ g/mol}$ (average: $18,000\text{ g/mol}$) of PVA polymer consisted of ~ 310 repeating units of PVA-OH, and ~ 50 units of PVA-OC(=O)CH₃.

In the spectrum of PVA-GMA prepolymer, in addition to the peaks of PVA ($\delta = 4.2$ – 4.7 ppm OH, 1H , $I_{4.2-4.7} = 3.46$), ($\delta = 3.6$ – 3.9 ppm ; CH, 1H , $I_{3.6-3.9} = 3.14$), new peaks appeared belong to the protons of vinyl group ($\delta = 5.6$ and 6.0 ppm ; CH₂, 2H , $I_{5.6-6} = 2.04$) and methyl group of GMA unit ($\delta = 1.9\text{ ppm}$; CH₃, 3H , $I_{1.9} = 6.0$).²⁸ The proton of the CH group of GMA where the GMA monomer is bonded to the PVA chains gave a peak at $\delta = 5.1\text{ ppm}$ (CH, 1H , $I_{5.1} = 1.44$). The absence of the proton peaks of epoxy/oxirane ring -CH₂-[CH-(O)-CH₂] at $\delta = 4.3$ and 3.7 , 3.2 , and 2.8 and 2.6 ppm , respectively, supported the removal of this structure as glycidol during the reaction.²⁸ The GMA functional group percentage (degree of substitution, DS%) of the PVA-GMA prepolymer was also calculated by the proportion of the relative intensity values of the characteristic peaks of GMA (vinyl protons) to PVA (hydroxyl proton). It was found that 37% of PVA chains were functionalized with GMA monomer. According to this, it could be said that the PVA polymer initially having M_n of $18,000\text{ g/mol}$ (~ 310 repeating units of PVA-OH) transformed to 195 units of PVA-OH and 115 units of PVA-GMA, and M_n increased to $\sim 26,000\text{ g/mol}$.

In the spectrum of PNVP (in Figure 3), the relatively wide peaks obtained at $\delta = 3.55\text{ ppm}$ (CH_b, 1H), $\delta = 3.19\text{ ppm}$ (CH_{2e}, 1H), $\delta = 2.20\text{ ppm}$ (CH_{2c}, 1H), $\delta = 1.84\text{ ppm}$ (CH_{2d}, 1H), and $\delta = 1.61\text{ ppm}$ (CH_{2a}, 1H) correspond the protons of CH_b, CH_{2e}, CH_{2c}, CH_{2d}, and CH_{2a} groups, respectively.^{38,39} The widening of the PNVP peaks observed in the NMR spectra was explained with the limited movement of highly soluble PNVP chains in solvents.³⁸

When the spectrum of the PVA-g-NVP copolymer was examined, first, it was noticed that the characteristic peaks of vinyl protons of GMA at $\delta = 5.6\text{ ppm}$ and 6.0 ppm in the spectrum of PVA-GMA disappeared and this suggests that the copolymer formation initiated from this side of the prepolymer. In addition, the peaks of methyl protons of PVA-GMA previously obtained at 2 ppm were observed together with the methyl protons of isobutyronitrile (initiator) at $\delta = 1.1\text{ ppm}$ (CH_{3k}, CH_{3f}, 9H , $I_{1.1} = 34.53$). This finding also reveals the structural changes in PVA-GMA prepolymer. Other peaks obtained in the spectra of PVA-GMA and PNVP were also present in the spectrum. According to this, the number of NVP repeating units grafted to PVA-GMA can be calculated by the proportion of the intensity of methyl protons of PVA-GMA (115 repeating units) in PVA-g-NVP copolymer structure ($I_{\text{CH}_3/9}$) and intensity of CH_{2d} methylene protons of NVP ring in copolymer ($I_{\text{CH}_2/2}$) as shown in the below equation:

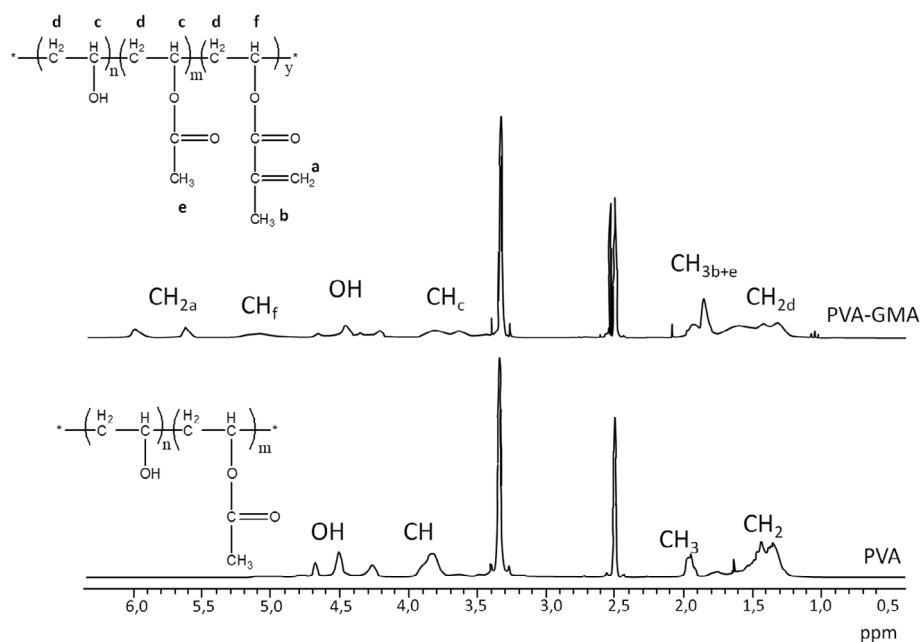


Figure 3. ^1H -NMR spectra of PVA and PVA-GMA.

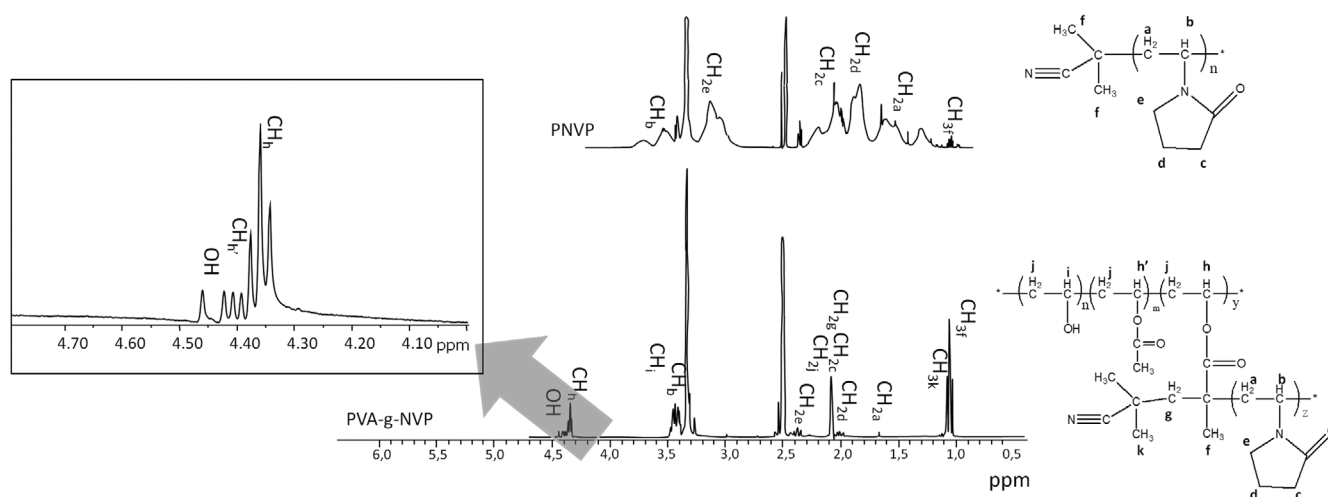


Figure 4. ^1H -NMR spectra of PNVP and PVA-g-NVP.

$$\frac{I_{\text{CH}_3/9}}{I_{\text{CH}_3/9} + I_{\text{CH}_2/2}} = \frac{115}{115 + n_{\text{NVP}}} \quad (1)$$

n_{NVP} represents the repeating unit number of NVP grafted to PVA-GMA chains. Accordingly, the left side of the equation was calculated as 0.659 and the n_{NVP} was approximately found as 60. Considering these calculations, the approximate structure of the graft copolymer and the M_n value can be estimated as $(\text{PVA})_{195}(\text{PVAc})_{50}(\text{PVA-GMA-AIBN})_{115}(\text{PNVP})_{60}$ and 40,240 g/mol, respectively. The possible synthesis scheme is illustrated in Figure 5.

Graft Modification of PET Fabrics

To monitor the effects of initiator type on the graft yield (%) of PET fabrics, five different initiators with different initiator

efficiencies including CAS, APS, APS-bisulfite mixture, BPO, and AIBN were selected. The polymerizations were performed at 120 °C for 10 min, considering the half-life values of the initiators at certain temperatures. That is needed for the decomposition of the initiators to the half concentration. In other words, it was aimed to produce a sufficient amount of radicals that would provide the polymerization at an applicable duration in the industry. The experiments were first carried out with grafting of pure PVA to the alkaline hydrolyzed-PET fabrics in 300 g/L NaOH solutions (HPET). In the first experiments, when the UPET fabrics were used, it was observed that the graft yields (%) were remarkably low (between 0.1 and 1.8%) despite changing the initiator types. When HPET fabrics were used in the experiments, the graft yields (%) of the fabrics took meaningfully changing values, whose results are comparatively plotted in

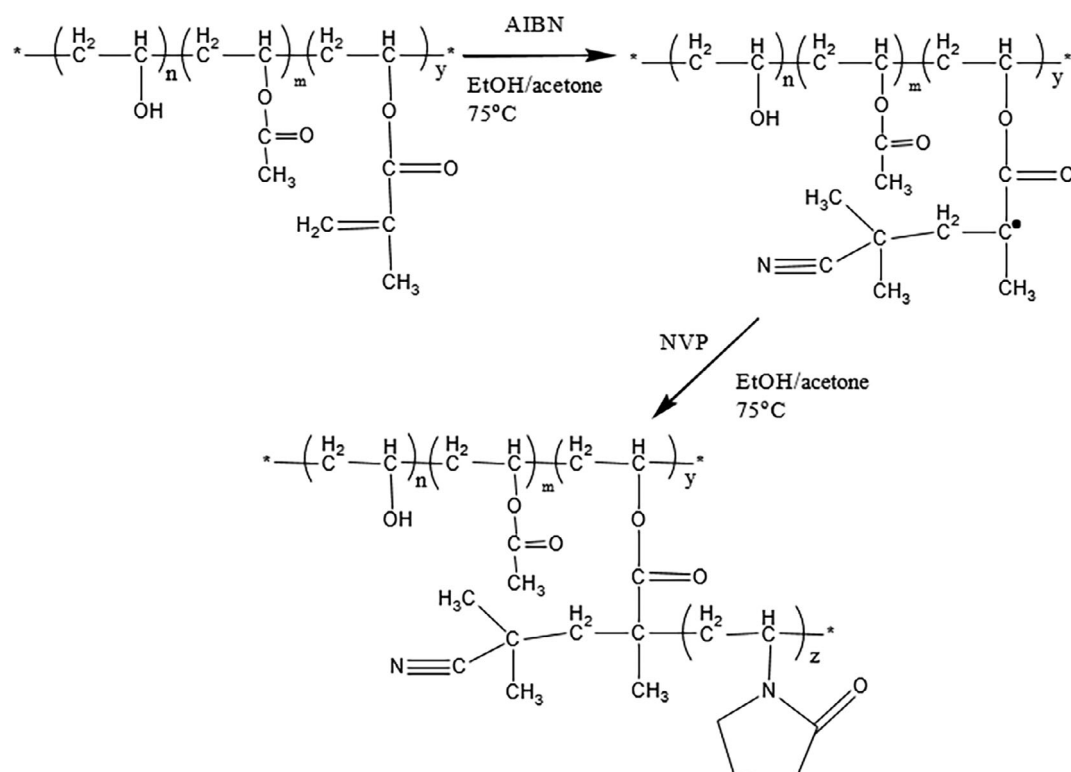


Figure 5. Synthesis scheme for PVA-g-NVP with AIBN initiator.

Figure 6. As seen from the figure, the graft yield (%) values were low when the conventional initiators for PET such as AIBN (0.1%) and BPO (0.2%) were employed in the polymerization. The highest graft yields were obtained in the polymerizations carried out with CAS (4.1%) and APS (3.7%) initiators. When APS was used in the experiment, the color of the PET fabric became pale yellow that would be an unacceptable result for the textile applications. This yellowing of the fabrics after the treatment with APS initiator was also encountered in the literature and this was attributed to the formation of the macroradicals on the fiber surfaces.⁴⁰

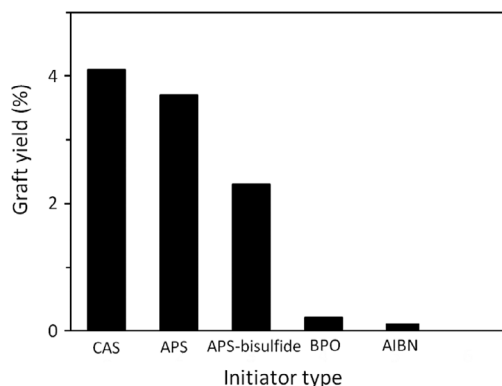


Figure 6. The changes in graft yield (%) of the PET fabrics with initiator types used in the graft polymerization of PVA (PET: HPET, [CAS]: 0.05M, [APS]: 0.07M, [APS-bisulfite mixture]: 0.05M-0.025M, [BPO]:0.02M, [AIBN]: 0.02 M, polymerization temperature: 120 oC, time: 10min).

To prevent the yellowing and obtain high graft yields of the fabrics, the effects of polymerization temperature were investigated using CAS and APS as an initiator, and the results are summarized in Table II. As listed in the table, with the decreasing of polymerization temperatures, the graft yield (%) of the fabrics prepared with CAS decreased and took the value around 1%. For APS initiator, relatively lower graft yields at higher temperatures and higher graft yields at lower temperatures were obtained compared with the CAS. This may be attributed to the intermolecular crosslinking of PVA chains at 120 °C.⁴¹ Consequently, a competitive reaction between grafting and crosslinking may have led to a decrease in the grafting yield of the PVA. However, in all the experiments carried out with APS, the unwanted yellowing of the fabrics could not be avoided and steadily became darker when the temperature was increased. The decrease in the graft yield of

Table II. The Effects of Polymerization Temperature on Graft Yield (%) of PET Fabrics Using APS and CAS Initiators

Temperature (°C)	Graft yield (%)	
	APS	CAS
120	3.6	4.2
100	5.1	1.3
90	2.0	1.5
80	2.9	1.1
70	3.3	1.2

PET: HPET, [APS]: 0.07 M, [CAS]: 0.05 M, time: 10 min.

the fabrics with decreasing temperature could be explained with the decrease in the decomposition rate of the initiator–redox system and reduction of the diffusion of PVA chains to the macroradicals on the PET chains.⁴² As a result, CAS, which is a relatively less known initiators used in the grafting of PET studies,^{43,44} gave the highest graft yields (4.2%) without color changes at the highest temperature.

Figure 7 shows the effects of CAS concentration on the graft yield (%) of fabrics. As seen from the figure, with the increasing of CAS concentration up to 0.1 M value, the graft yield of the fabrics steadily increased and did not change significantly after the value of this concentration. The highest graft yield of the fabrics (6.2%) was obtained with the polymerization carried out using 0.1 M CAS initiator. It could be said that the increase in the CAS concentration leads to the increase in the number of PET macroradicals, and consequently, the numbers of the grafted PVA chains and grafted PVA amounts (graft yield %) also increase. With the further increase of the initiator concentration, the possibility of chain termination reaction between PET macroradicals and initiator radicals may have occurred. As a result of consuming the radicals in the chain termination reaction, the grafting and graft yields may have been deteriorated.^{42,45,46}

After the determination of the graft polymerization condition of PVA onto the PET, the grafting of PVA-g-NVP was also studied using 0.1 M CAS initiator at 120 °C for 10 min. Unlike from the PVA, the PVA-g-NVP copolymer is insoluble in the water and consequently, the grafting of the copolymer to the PET fabrics was performed in NMP solvent, which is a good solvent for the copolymer structure. Compared with the PVA-grafted PET fabrics, the graft yields of copolymer were low and the values were 2.9 and 1.4% for HPET and UPET fabrics, respectively. These lower grafting values of the copolymer may be the result of the difficulty in the approaching of sterically hindered-copolymer structure to the PET macroradicals, and thus, fewer numbers of copolymer chains may have been grafted.

XPS Results

The changes in the surface elemental compositions of the PET fabrics before and after alkali hydrolysis were monitored with XPS spectra, and the results/discussions are presented in Supporting Information Figure S1.

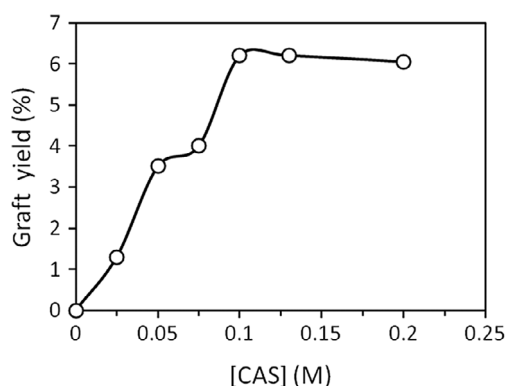


Figure 7. The changes in graft yield (%) of the PET fabrics with CAS concentration (PET: HPET, polymerization temperature: 120 oC, time: 10 min)

In Figure 8, wide and narrow scan XPS spectra of PVA and PVA-g-NVP-g-PET fabrics were plotted and the results are comparatively summarized in Table III. In the wide scan spectrum of PVA-g-HPET fabrics [Figure 8(a)], although no remarkable change was observed in the C1s peak intensity of the PVA-g-HPET compared with HPET fabric, it can be clearly seen that the atomic percentage of C1s decreased, but the peak intensity of O1s, atomic percentage of O1s and relative ratio of O/C significantly increased. The presence of Ce atoms in the wide scan spectrum of PVA-g-HPET and PVA-g-NVP-g-HPET fabrics may have raised from the possible initiator residues that were not removed with washing after grafting.

In the C1s narrow scan spectrum of PVA-g-HPET [Figure 8(b); Table III], it was observed that the relative abundance value (%) of $\text{C}-\text{O}$ binding remarkably increased. In the O1s spectrum, no peak was observed at 529 eV ($\text{O}=\text{C}$ binding type) arising from the ground HPET fabric, but a very high-intensity peak was present at 530.1 eV, corresponding to an $\text{O}-\text{C}$ binding type. This peak indicates the presence of a different $\text{O}-\text{C}$ binding type with a different chemical environment than that of HPET fabric surface. In this case, it could be said that a heavy PVA signal was taken from the surface, after grafting (Table III). Accordingly, it could be said that a new O-C bond was assigned on the PET chain after grafting, and PVA was grafted onto PET fabric through its OH group. It has been reported in the literature that a macroradical formation occurred after the decomposition of the complex between OH group of PVA and Ce^{+4} ions and the graft copolymerization propagated from this point.^{47–50} The possible graft polymerization mechanism of PVA to PET fabric is illustrated in Figure 9.

In the wide scan spectrum of PVA-g-NVP-g-HPET fabrics [Figure 8(a)], the presence of N1s peak with the atomic percentage of 0.8% confirms the presence of NVP structure in the copolymer. When the C1s narrow scan spectrum of copolymer grafted fabric is examined [Figure 8(c)], in addition to the previously identified binding types of $\text{C}-\text{C}$, $\text{C}-\text{O}$, $\text{O}-\text{C}=\text{O}$, $\text{O}=\text{C}$, and $\text{O}-\text{C}$, a new binding type, $\text{C}-\text{N}$, was observed at 283.9 eV.⁵¹ Moreover, it was also noticed in the O1s spectrum that the binding energy corresponding to the $\text{O}-\text{C}$ binding type shifted to 530.5 eV. This finding supports that PVA-g-NVP copolymer was also grafted to the PET surface *via* the O atom in the OH group of PVA. When the relative abundance values (%) are considered, the values for $\text{C}-\text{O}$ ve $\text{O}-\text{C}=\text{O}$ binding types were two times higher when compared with the ground HPET fabric, and this shows that the copolymer in methacrylate structure was present on the surface. According to this, it could be concluded that previously suggested grafting mechanism for PVA could also be valid for grafting PVA-g-NVP copolymer.

SEM Micrographs

In Figure 10, the surface morphology of UPET, HPET, PVA-g-HPET, and PVA-g-NVP-g-HPET fabrics are illustrated. As seen from the micrographs, compared with the smooth surface of the UPET fabric, it is evident that deformation was formed on the surfaces of the PET fabrics after alkaline hydrolysis process. Similar deformation findings defined as craters or pit/corrosion-like structures were also reported in the literature,^{52,53} and the width,

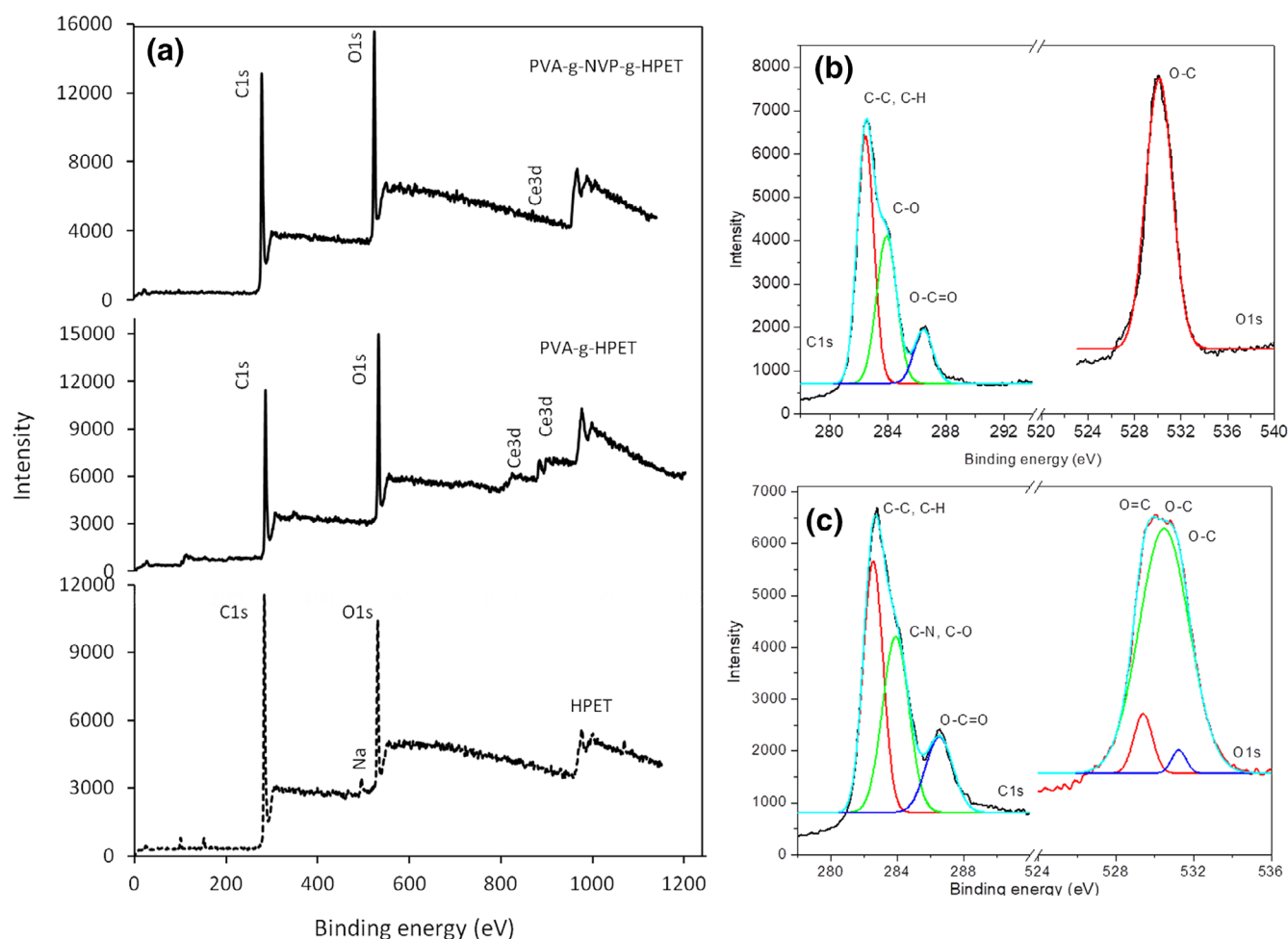


Figure 8. a) Wide scan XPS spectra of HPET, PVA-g-HPET and PVA-g-NVP-g-HPET fabrics, Narrow scan C1s and O1s XPS spectra of b) PVA-g-HPET and c) PVA-g-NVP-g-HPET fabrics. [Color figure can be viewed at wileyonlinelibrary.com]

Table III. Comparative Atomic Percentage and Relative Abundance Values (%) Results of Binding Types Obtained from Narrow Scan XPS Spectra of Relevant Samples

Sample	C1s (%)	O1s (%)	O/C	Relative abundance values (%)				
				C-C	C-O	O-C=O	O=C	O-C
HPET	74.7	22.2	0.30	72.3	19.0	8.7	57.8	42.2
PVA-g-HPET	66.7	31.0	0.47	50.9	36.4	12.7	-	100
PVA-g-NVP-g-HPET	69.3	28.6	0.41	42.7	39.4	17.9	8.2	89.3

diameter, and the frequency of these pits changed depending on the amorphous and crystalline nature of the PET surface.⁵⁴⁻⁵⁶ The presence of these type of pit structures was thought to be efficient in the surface related phenomena such as water absorptivity and/or wetting.⁵⁵

When the SEM micrographs of the PVA-g-HPET and PVA-g-NVP-g-HPET fabrics are examined [Figure 10(c,d)], it is noteworthy that the grafted PVA and PVA-g-NVP layers displayed heavy and homogenous coatings on the PET fiber surfaces. The measurement of the fiber diameters from the micrographs of the relevant samples showed that the diameters are in this ascending

order: HPET (9.17 μm) < UPET (9.77 μm) < PVA-g-HPET (10.14 μm) < PVA-g-NVP-g-HPET (10.31 μm). It is also obvious that the pit/crater structures of the HPET fabrics were almost filled with the PVA and copolymer coating after grafting process, and this suggests that these structures may have helped the homogenous polymer coating on the surface.²⁴ Although the surface of HPET fiber took a film-like and uniform texture after PVA-g-NVP grafting, the texture of the PVA on the HPET gives the impression of granular-like structures was present and concentrated around certain regions. This observation suggests that after the interaction of the PET surface with CAS initiator, the macroradical sites may have formed in certain regions of the

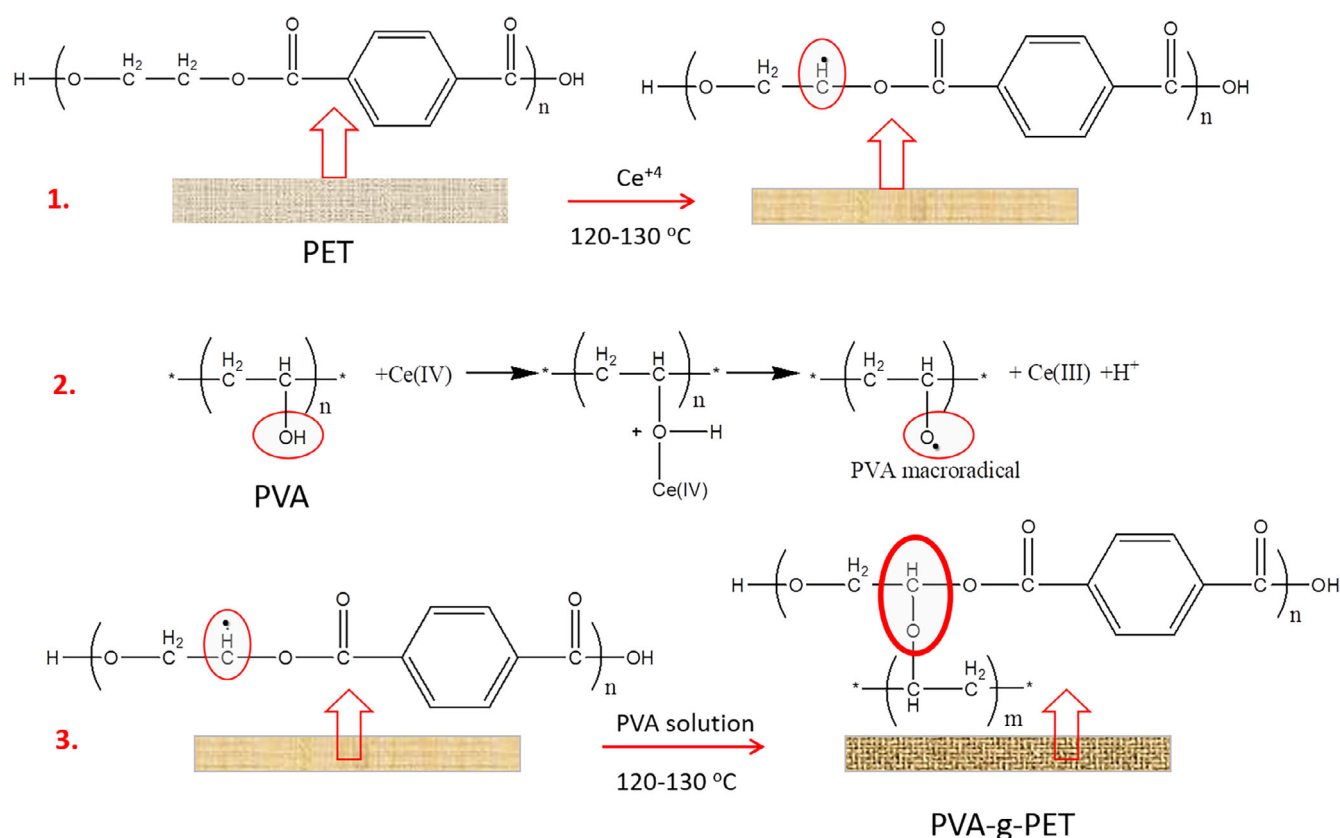


Figure 9. The scheme illustrating the possible grafting mechanism of PVA to the PET fabric. [Color figure can be viewed at wileyonlinelibrary.com]

fabric, and the regional grafting could be provided through penetration of PVA chains to these sites.

Contact Angle Measurements

The effect of graft modification process on the fabric hydrophilicity was monitored with the changes in water contact angle values of samples with wetting time. Because, in the first investigations for the water contact angle measurements, it was observed that the water droplet applied on fabric rapidly disappeared and the time for the disappearance of the water droplet steadily became shorter with the increase in the sample hydrophilicity. Consequently, to determine sensitively the sample hydrophilicity after modification processes, the contact angle values were monitored together with the wetting time and the results are given in Figure 11 and Table IV. As seen from the figure, it can be clearly seen that the hydrophilicity of the PET fabrics significantly increased after PVA grafting, compared with the UPET and HPET fabrics. Although it was evidenced that the graft modification of PVA to the PET fabrics was achieved through OH site of PVA, the higher hydrophilicity value of PVA-g-PET fabrics shows that grafting is found to be more effective on wetting behavior of fabrics compared with the alkaline hydrolysis, despite the porosity/roughness of the surface. Indeed, this also marks the heavy functionalization of the PET surface with grafting as compatible with the XPS results.

The increasing of the hydrophilicity of PET fabric surface after grafting of hydrophilic monomers were also found in the literature, and this was explained with the increase in the number of

large rough sites with the increase in the number of grafted chains on fabric surfaces.^{20,24} Accordingly, it could be said that the texture of the HPET surface became rougher after the graft modification, and this helped the penetration/spreading of a water droplet to the PET surface and shortened the wetting time. When the results of PVA-g-NVP-g-PET surfaces are evaluated, it is seen that both the contact angle and wetting time values were higher than that of PVA-g-PET. But the values were comparable with the values of HPET fabric, and although the contact angle values were lower than that of HPET, the wetting time values were slightly higher. This could be interpreted with a slight decrease in the hydrophilicity of HPET fabrics with the surface modification of water-insoluble PVA-g-NVP copolymer.

Mechanical Properties

To determine the effects of the alkaline hydrolysis process on the mechanical properties of the fabrics, the tensile strength test was applied to the samples and the results are presented in Figure 12.

It can be seen from the stress-strain curves of the UPET and HPET fabrics that the breaking force of UPET fabrics decreased from 634.5 ± 10.5 to 576 ± 9.8 N after alkaline hydrolysis, and no significant change was recorded for the elongation at break values of the fabrics (27.2 ± 4.2 mm). It was also observed that the stress-strain curves of the fabrics were compatible with the almost linear stress-strain curves of the PET fiber, defined in the literature.^{57,58}

When the elastic (reversible) deformation region, where the elongation values showed a linear change under load (corresponding

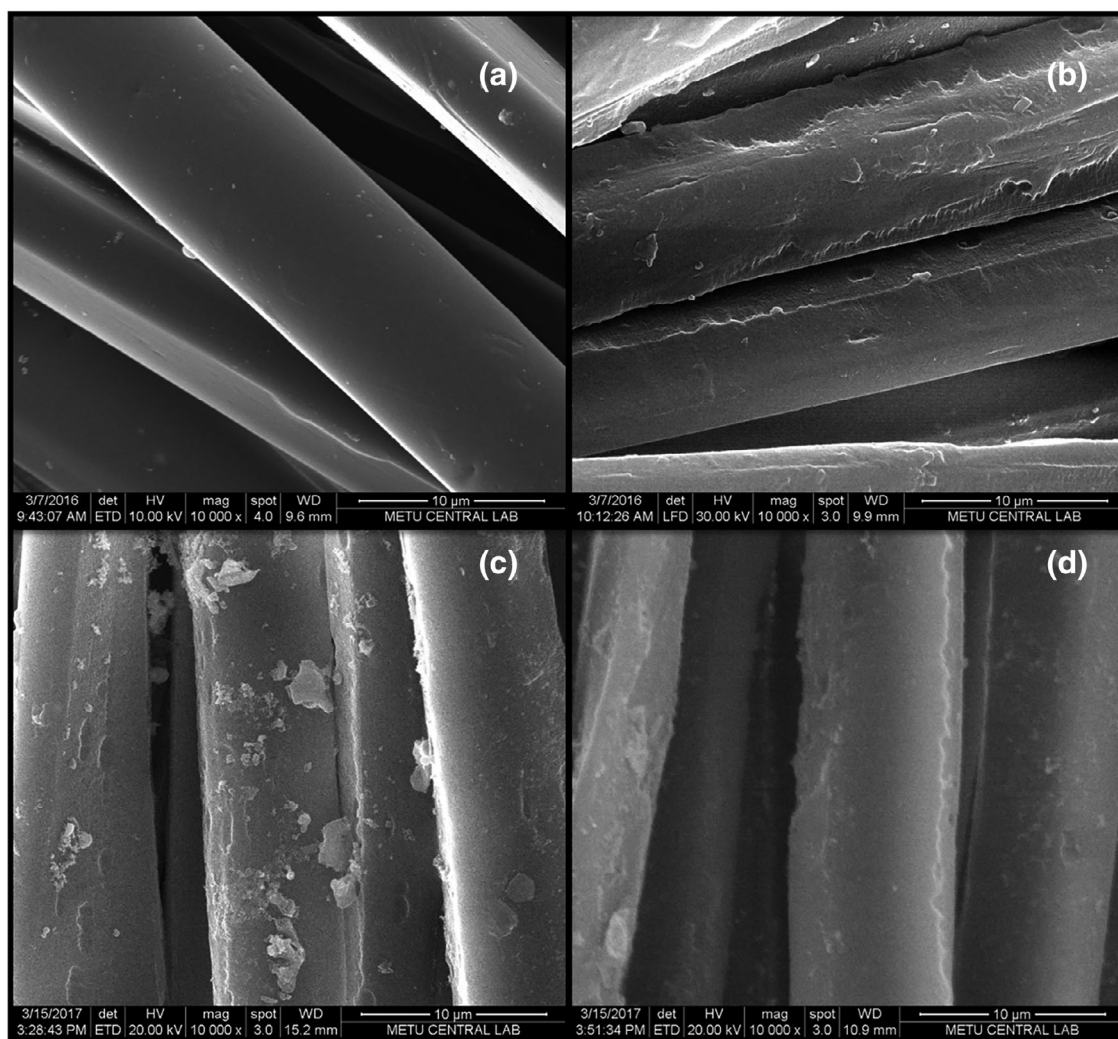


Figure 10. SEM micrographs of a) UPET fabric, b) HPET fabric, c) PVA-g-HPET, and d) PVA-g-NVP-g-HPET fabrics.

to the strain values of 3–6 mm), was investigated, it was observed that the required force to obtain the same elongation value was slightly increased for HPET fabrics and the change was about

15.6% at 6 mm. This could be interpreted as the alkaline hydrolysis process lead to an increase in the elastic modulus of the PET.

The increase in the elastic modulus of the HPET compared with the UPET fabrics up to 6 mm elongation might be attributed to the hydrogen bonds occurred in the chain ends (between the carboxyl and/or hydroxyl sides) of the PET backbone after the alkaline hydrolysis.⁵⁹ Because it has been reported in the literature that the elastic modulus of a polymer was related to the interaction of the polymer chains, the tensile strength was correlated with the molecular weight of a polymer.⁶⁰ During the application of the tensile load in this region, the hydrogen bonds between the polymer chains in the HPET fabrics might be broken. As a result, after 6 mm elongation, the polymer has turned to its normal behavior, and showed a high elongation behavior against applied force and, a decrease in the breaking force depending on the shortening of the chains, as expected.

It was encountered in the literature that the loss of strength observed in the PET fabrics increased by increasing the weight loss/hydrolysis degree of the fabrics after an alkaline hydrolysis process.^{55,61,62} For example, an 8.2% of the loss was observed in

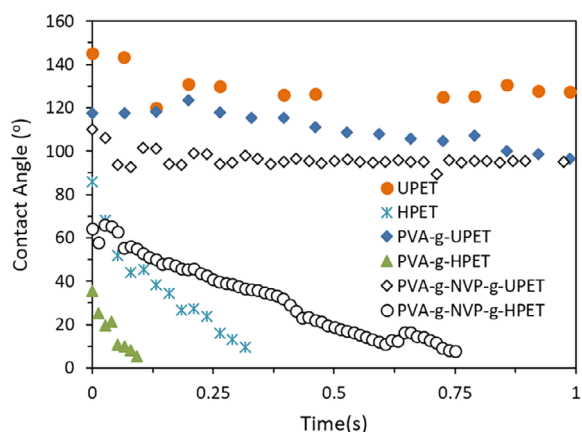


Figure 11. The changes in water contact angle values of the samples with wetting time. [Color figure can be viewed at wileyonlinelibrary.com]

Table IV. Comparative Contact Angle Measurement Results of PVA and PVA-g-NVP-g-PET and HPET fabrics

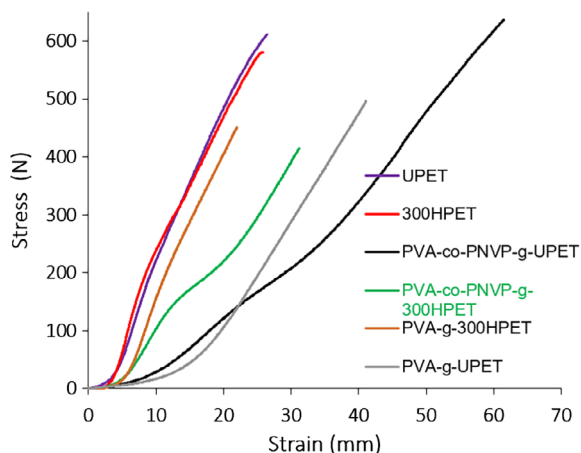
Fabric	PVA		PVA-g-NVP	
	Contact angle (°)	Wetting time (s)	Contact angle (°)	Wetting time (s)
UPET ^a	123.5	15.7	110	57
HPET ^a	37	0.1	64	0.7

^a The contact angle-wetting time values of ungrafted UPET and HPET were 145° and 98 s and 86° and 0.3 s, respectively.

tensile strength of PET fabrics after an alkaline hydrolysis treatment in 5 g/L NaOH solution⁶¹ and this decrease was explained with the nucleation sites, leading to the formation of pits/pores on PET surface. These pit structures formed on the surface of PET under a load effect may have caused the formation of cracks, and this may result in the tearing of the fabrics.⁶³

When the curves of PVA grafted fabrics are evaluated, the breaking force values were recorded as 501.8 ± 5.3 and 455.6 ± 4.3 N for PVA-g-UPET and PVA-g-HPET fabrics, respectively. The elongation at the break values were measured as 36.5 ± 4.5 mm for PVA-g-UPET and 23 ± 1.0 mm for PVA-g-HPET fabrics. When these values were compared with the values of ground HPET and UPET fabrics, while the breaking force values decreased after grafting of PVA, the elongation at the break increased for PVA-g-UPET and slightly decreased for PVA-g-HPET fabrics.

In the elastic deformation region, corresponding to the elongation values of 5–10 mm, it can be seen that the required force to obtain the same elongation value was relatively high in the PVA-g-HPET compared with that of PVA-g-UPET fabric, as obtained for HPET and UPET fabrics. This also marks that the elastic modulus of the HPET fabric increased as a result of achieving relatively higher PVA grafting (%) than that of UPET. The contribution of the grafted PVA chains to the mechanical properties of the HPET fabrics can also be proven from the XPS results of PVA-g-HPET. As the grafting of PVA chains was provided to the PET surface from many grafting sites, the surface of the PET was significantly chemically changed with a different polymer layer.

**Figure 12.** Tensile strength test results of the fabric samples. [Color figure can be viewed at wileyonlinelibrary.com]

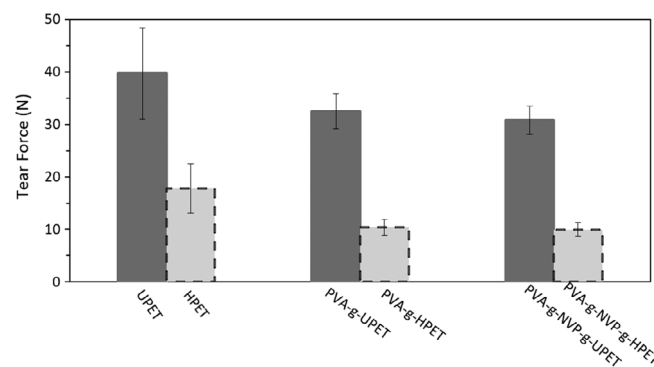
As a result, the mechanical behavior of the HPET fabric also remarkably changed.

Similar mechanical behaviors such as increased elastic modulus and reduced tensile strength were also observed in the literature after the solid-state graft copolymerization of acrylamide to the PVA,⁶⁰ and these behaviors were related to the hydrogen bonding between the grafted chains and polymer backbone. According to this, after changing the nature of the HPET surface with PVA grafting, the possibility of hydrogen bonding would increase,⁶⁴ and thus, the elastic modulus of the PVA-g-HPET also increase.

When the curves of PVA-g-NVP grafted fabrics are evaluated, it can be said that the breaking force and elongation at the break value of the PVA-g-NVP-g-HPET remarkably decreased (422 ± 11 N, 28.7 ± 1.5 mm) compared with the PVA-g-NVP-g-UPET fabric (632.5 ± 3.5 N, 59 ± 3.2 mm). After grafting of PVA-g-NVP to the HPET fabrics, the decreasing of the breaking force shows that the tensile strength of the fabric thoroughly reduced.

From the elastic deformation region that corresponds to the strain values of 5–10 mm, the elastic modulus results of PVA-g-NVP-g-HPET and PVA-g-NVP-g-UPET were in similar trend with those of PVA-g-HPET and PVA-g-UPET fabrics, but with a relatively lower value. This lower elastic modulus of the PVA-g-NVP-g-HPET might have arisen from the lower grafting of the copolymer, compared with the PVA-g-HPET fabrics.

In Figure 13, the tear strength test results of the fabrics are comparatively presented. As seen from the figure, the tear force of the UPET fabric significantly decreased after the modification processes, especially after hydrolysis. For example, after alkaline hydrolysis, a 55.1% of loss of strength was obtained in the UPET fabric. The loss of tear strength values of the graft-modified HPET fabrics was also relatively higher than that of the graft-

**Figure 13.** Tear strength test results of the fabric samples.

modified UPET fabrics. The decrease in the tear strength of the PET fabrics could be explained with the stiffening of the fabrics after the modification. During tear tests, the breaking of the yarns of the PET one-by-one with the applied tear force may have led to a decrease in the tear strength of the fabric.⁵

If the mechanical properties are examined in general, it can be concluded that the breaking force and elongation values at the break of the fabrics tend to decrease after graft modification especially those for HPET fabrics. This case was also encountered in the literature including graft modification of synthetic fabrics such as the polyolefines, and a high loss of tensile strength/elongation at the break was observed for the fabrics with high grafting yields.⁶⁵ The observed strength loss may be related to the limitation of the grafted chain orientation at high graft yields and hardening of the strain.⁶⁶ As a conclusion, when these values are compared with the values of natural cotton and wool fabrics published in the literature,⁶⁷ it can be seen that the values of the graft-modified PET fabrics are still higher. According to this, it could be said that the graft-modified PET fabrics could be used in the textile processing applications.

CONCLUSIONS

With this study, the hydrophobic PET fabric surface was chemically modified with hydrophilic PVA and a novel PVA-g-NVP copolymer, with an industrial-adapted approach including alkaline hydrolysis pretreatment and graft copolymerization. The XPS results evidenced the successful grafting of PVA and the copolymer to the HPET surface. Although the mechanical strength values of the graft-modified PET fabrics reduced compared with untreated PET, the values were higher than those of natural cotton and wool fabrics. This suggests that the fabrics may be still resistive to the further textile processing applications. One of the most important findings of the study was reaching the targeted hydrophilicity/wetting properties of the PET fabrics after graft modification. With the help of these, a synthetic polymer-based textile material could take part in the textile finishing applications where the hydrophilic natural fabrics are required such as casual apparel.

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