(REFEREED RESEARCH)

GRAFTING OF 2-HYDROXY ETHYL METHACRYLATE ONTO WOOL YARNS TO IMPROVE THEIR SHRINK-RESISTANCE AND FASTNESS PROPERTIES

YÜZEYLERİNE 2-HİDROKSİ ETİL METAKRİLAT AŞILAMASI İLE YÜN İPLİKLERİN ÇEKME VE HASLIK ÖZELLİKLERİNİ GELİŞTİRMESİ

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Received: 18.03.2017 Accepted: 15.02.2018

ABSTRACT

In this study, 2-Hydroxy ethyl methacrylate (HEMA) monomer was grafted onto wool yarns via chemically-induced method. Grafting conditions and product characterization were investigated. The effects of grafting temperature, grafting time, monomer and initiator concentrations on grafting yield (GY) percentages were examined and the optimum grafting conditions were determined. Maximum GY value was obtained as 55%. Swelling tests showed that grafting of HEMA negatively affect the swelling percentages of wool grafted yarns. SEM analyses also were performed in order to detect the surface differences between grafted and ungrafted yarns. The dyed fibers were subjected to weather, washing and rubbing fastness tests and higher fastness ratings were observed for grafted yarns, compared to ungrafted samples. Shrinking tests were also carried out to 10%, 20% and 35% HEMA grafted wool yarns and satisfactory results were obtained.

Keywords: Wool yarn, HEMA, grafting, fastness, shrinking

ÖZET

Bu çalışmada, yün ipliklere kimyasal başlatıcılı metodla 2-Hidroksi etil metakrilat (HEMA) monomeri aşılandı. Aşılama koşulları incelendi ve ürün karakterizasyonları yapıldı. Aşılama sıcaklığı, aşılama süresi, monomer ve başlatıcı derişimlerinin aşılama verimi (GY) yüzdesine etkisi araştırıldı ve optimum aşılama koşulları saptandı. En yüksek GY değeri % 55 olarak elde edildi. Şişme testleri, HEMA aşılanmasının yün ipliklerin şişmesini negative etkilediğini gösterdi. Aşılanmış ve aşılanmamış ipliklerin yüzeylerindeki farklılıkları belirlemek için SEM incelemeleri de yapıldı. Boyanmış ipliklere hava, yıkama ve sürtünme haslık estleri uygulandı ve aşılanmış ipliklerde aşılanmamışlara göre daha yüksek haslık değerleri elde edildi. %10, %20 ve %35 HEMA aşılanmış yün ipliklere çekme testleri de yapıldı ve oldukça tatminkar sonuçlara ulaşıldı.

Anahtar Kelimeler: Yün iplik, HEMA, aşılama, haslık, çekme

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1. INTRODUCTION

Wool, a natural protein called α-keratin, has been known as a superior textile material because of their lightness, warmness, softness and smoothness. Natural wool fiber has excellent flexibility and hygroscopicity, which can be widely applied in the field of decorative textiles and clothing materials. Its surface characteristics play an important role in the functional and aesthetic properties of their fabrics [1]. Besides these marvelous properties, dyeability and dimensional stability of wool fibers need to be improved. The difficulty in dyeing of wool fibre is due to its scale (also called cuticle cells) like surface structure [2]. This complex structure makes it difficult for the dye molecules to permeate into the fiber, resulting in low levels of dye exhaustion. A number of studies aimed at improving the dyeability of wool by modifying the wool fibre have been reported.

Heat, moisture and mechanical action are the three factors that negatively affect the dimensional stability of wool fabrics [3]. There are two mechanisms normally associated with the dimensional stability of wool: relaxation shrinkage and wool felting. Shrinking is due to the physical characteristic of wool fibers having scales on the exterior surfaces. When the wool is subsequently taken above its glass transition temperature, by wetting out during laundering or heating using steam, shrinkage in fabrics and garments is observed named relaxation shrinkage. The felting of wool occurs when the fibers are wet and are subjected to mechanical action, as in washing. A successful felt or shrink-resist process has to overcome or reduce the directional frictional effect referred to earlier. One of them is to prevent or inhibit fiber–fiber movement by spot welding the fibers together using a polymer [4].

Graft copolymerization of vinyl monomers using free radical initiation method is commonly used to modify the natural and synthetic fibers. This technique enables the production of new textile materials with desired properties that are based on chemical combinations of natural and synthetic polymers [5]. Grafting reaction is carried out through a number of active free-radical sites on the fiber backbone. These reactive sites could be generated using nonmetal and metal ion oxidizers, organic peroxides and hydroperoxides, aliphatic azo compounds, metal chelates, etc. [6-8]. Vinyl monomers in the medium will attack to reactive sites, leading to graft initiation. Depending on the chemical structure of grafted monomer, the finished product could be obtained in hydrophilic or hydrophobic character, exhibit improved elasticity, water sorbency, ion-exchange capability, heat resistances and resistance to microbiological attack [9]. Such modified fibers found wide application in textile, biomedical and many types of industries [10-11]. Mechanical, physical, chemical and dyeabilitiy properties of wool can also be arranged by this modification method [12].

Many researchers have extensively investigated the graft copolymerization of various vinyl monomers onto wool fibers using different initiation methods [13-19]. In these works, it was generally studied on the factors that affect the grafting yield. The main purpose was to obtain optimum grafting conditions and to control the swelling behaviors of wool fibers. However, literature survey revealed that no work has been reported on graft copolymerization of 2-hydroxy ethyl methacrylate (HEMA) onto wool using benzoyl peroxide (BPO) as initiator. PHEMA is a widely used hydrophilic polymer that has excellent chemical, biological and mechanical properties. Our previous studies were focused on the grafting of some vinyl monomers, such as acrylic acid, acryl amide, crotonic acid, itaconic acid and HEMA on cotton fibers [20-22]. In this study, we aimed to synthesize HEMA grafted wool yarns. The effects of grafting temperature, grafting time, monomer and initiator concentrations on grafting percentages were studied and optimum grafting conditions were determined. Swelling tests and SEM analysis of grafted and ungrafted cotton fibers were also performed. Besides fastness properties, dimensional stability of the grafted samples was also investigated.

2. MATERIAL AND METHOD

2.1. Fiber Preparation

Wool yarn was obtained from the Turkish textile company Boyteks Textile Co. (Bursa, Turkey) The wool yarn is 70 tex X 2 and its average diameter is about 2 mm. The yarn sample about 100 cm total lengths was purified by Soxhlet boiled extraction with acetone (Aldrich) for about 24 hr., followed by washing with cold water and air drying [1] .

2.2. Grafting Procedure

Graft polymerization procedure was performed according to our previous studies [10-11, 20-21]. BPO (Aldrich) was used as an original initiator for HEMA (Aldrich) grafting onto wool yarns. To determine the effect of temperature on grafting yield (GY), we investigated the polymerization reaction by changing temperature from 30 to 70 ºC at constant monomer (M) and initiator (I) concentration values for 4 hours. Appropriate amounts of wool yarn were placed into polymerization tubes containing 4 mL of BPO–acetone (Aldrich) solution and they were put into a water bath at a constant temperature. After thermal equilibrium was reached, 46 mL of a HEMA–water solution was added into the polymerization tubes so that the concentrations of HEMA and BPO in the reaction tube are 0.25 M and 0.04 M, respectively. At the end of 4 hours, the treated yarns were taken out from tubes. The residual solvent, monomer, and homopolymer were removed from grafted yarns by extreme washing with hot and cold water. They were dried at 40 ºC in a vacuum oven for 48 h and weighed.

To determine the effect of time, [I] and [M] on GY, we repeated the grafting procedure, by varying time from 30 to 300 minutes; [I] from 0.02 to 0.10 M and [M] from 0.10 to 0.70 M. All measurements were performed in triplicate. GY values were calculated based on the weight of wool yarns using the following equation [10-11, 20-21, 22-23]:

$$GY\,(\%) = \frac{m - m_0}{m_0} \times 100 \qquad (1)$$

where, m_o is the initial weight of wool fiber before grafting, m is the weight of the grafted wool yarn.

2.3. Swelling Tests and SEM Analysis of Grafted and Ungrafted Wool Fibers

Swelling tests of grafted and ungrafted wool yarn samples were gravimetrically carried out at room temperature. Dried and weighed samples were left to swell in distilled water. Swollen yarns removed from the swelling medium at regular intervals were dried superficially with filter paper and weighed. The measurements were performed until a constant weight was reached for each sample.

Swelling (S) percentage values were determined from the equation given below where m_w is the mass of the swollen yarns and m_d is the mass of the same yarns dried eventually at 40 ºC for 48 h [10-11, 20-21]:

$$S\,(\%) = \frac{m_w - m_d}{m_d} \times 100 \qquad (2)$$

SEM micrographs of grafted and ungrafted yarns were taken to observe the grafting performance by using a JEOL model JSM 840A SEM. The conductivity was supplied by coating the samples with 200 Aº gold-palladium.

2.4. Dyeing of Wool Fibers and Dye Uptake Studies

The commercial-grade reactive dye (Sumifix Supra Blue BRF 150%, CI:Reactive Blue 221, Sumitomo Chemical Co. Ltd, Japan) was used as purchased. Dyeing of grafted and ungrafted wool yarns was carried out using a liquor/wool ratio of 50:1. pH of the dye bath was kept in between 5-6 by using 10% acetic acid (Aldrich). Dye was weighed (2% on the basis of fiber sample weight) and added into the bath. The sample was placed into the bath at 40 ºC and held for 15 min. Then the temperature was step by step raised to boiling temperature. At this temperature the procedure continued for 60 min. and the dyed wool yarns were taken out from the bath, thoroughly washed with cold and hot distilled water. After the samples were boiled in 1% of soap solution for 30 min., they washed thoroughly with distilled water and dried in air [24].

Dye uptake studies were carried out for ungrafted and grafted wool samples. After the dyeing period, the fiber samples were removed from the dye solution and the absorbance of the residual solution was measured at 610 nm using UV– Visible spectrophotometer (Analytikjena Specord 200). The concentration of the dye uptake was determined from the standard curve. Percent of dye absorption was calculated from the following equation:

$$Dye\ Uptake\ (\%) = \frac{C_1 - C_2}{C_1} X\ 100 \qquad (3)$$

where, C_1 is the initial concentration of dye in the dye bath and C_2 is total dye concentration in the residual and rinsing water dye solutions [25].

2.5. Fastness Testing

The weather (including artificial light), washing and staining (rubbing) fastness tests were performed by using Xenon Arc Lamp Method (Atlas, Electric Type, USA) and Crock Meter Method (Atlas, Electric Type, USA), respectively [26-27]. All of the fastness values were determined related to International Standards. Washing fastness test was carried out according to ISO 105 C06/C1S. Staining of the samples was determined based on “Color fastness to rubbing” test numbered as ISO 105 X12. The rubbing and washing fastness tests were assessed according to the international grey scale (1-5), with scales 8 and 5, respectively, ranked the best, while 1 is the most inferior. Color fastness of the samples expose to artificial weather conditions and light were also investigated as described in the ISO 105-B04 standard. This test is named as “Color fastness to artificial weathering: Xenon arc fading lamp test”. This fastness values were determined at both artificial light and weathering conditions and the results were evaluated according to the international blue scale (1-8).

2.6. Dimensional Stability Test

Relaxation shrinkages is the irreversible change in fabric dimensions (shrinkage or expansion) that occurs when a fabric is wet out or exposed to steam. It is caused by the release of cohesively set strains which are imposed on fabrics during the late stages of finishing. In the Fabric Assurance by Simple Testing (FAST) system Relaxation shrinkages is defined as the percentage change in dry dimensions after release in water at room temperature [28].

To obtain relaxation shrinkages, ungrafted and 10%, 20% and 35% HEMA grafted dry wool fibers were cut in 5 cm of length (L_1). They were left into 50 mL of water and soapy water baths for 60 min. at 20 ^{0}C and 40 ^{0}C. At the end of this period, fibers were filtered, washed, dried and weighed (L_2). Relaxation shrinkages (RS) percentages of fibers were determined by using following equation:

$$RS\ (\%) = \frac{L_1 - L_2}{L_1} x\ 100 \qquad (4)$$

4. RESULTS AND DISCUSSION

4.1. Effect of Temperature on Grafting Yield and Swelling

The effect of temperature on graft polymerization of wool yarns was studied at constant grafting condition of 0.25 M HEMA and 0.04 M BPO, within the range of 30-70 ºC. As temperature was increased, the GY also gradually increased, reached to a maximum value and then decreased (Figure 1). Maximum GY was reached as 24% at 50 ºC. The initial increase in GY may be attributed to the increase of the mobility and diffusion rate of monomer and initiator molecules. The decrease in GY at higher temperatures was due to the favored chain-termination reactions and the increase in homopolymer formation. Similar results were also reported in chemically initiated graft co-polymerizations of various vinyl monomers on natural fibers [10-20, 29].

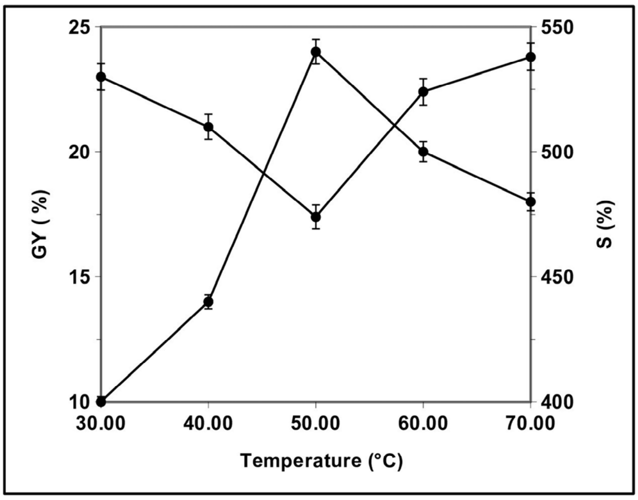

Figure 1. Variation of GY (-●-) and S (-o-) with polymerization temperature (t = 4 h, [M] = 0.25 M, [I] = 0.04 M)

The variations of S% values calculated from Equation 2 are also shown in Figure 1. Swelling values of grafted wool fibers decreased as GY values increases. In general, high grafting yields lead to low swelling percentages. It could be though that the grafting procedure causes partially polymeric covering on the surfaces of wool fibers.

4.2. Effect of the Polymerization Time on Grafting Yield and Swelling

Effect of the polymerization time on GY was investigated by changing time from 30 to 300 minutes at constant grafting condition of 0.25 M HEMA, 0.04 M BPO and 50 ^oC. As given in Figure 2, GY initially increased with time and then reached a saturation grafting value around 3 hours. Maximum GY value was obtained as 28% for 3 h. This deportment could be attributed to depletion in both the monomer and initiator, as well as to the changes in the components of the system as the reaction proceeds [10-21, 29-30].

The variations of S% values calculated from Equation 2 are also shown in Figure 2. By comparison of GY and S% curves, it is seen that HEMA grafting on wool yarns lead to decreasing in swelling values.

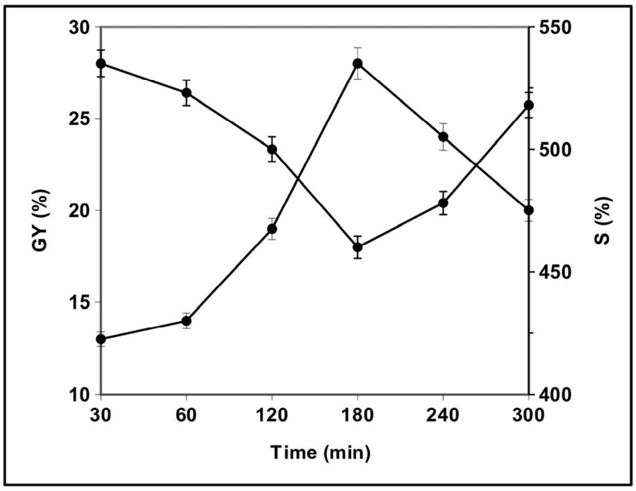

Figure 2. Variation of GY (-●-) and S (-o-) with polymerization time (T = 50 ºC, [M] = 0.25 M, [I] = 0.04 M)

4.3. Effect of Initiator and Monomer Concentration on Grafting Yield and Swelling

Effect of [I] on GY was studied by varying its concentration from 0.02 M to 0.10 M at constant grafting condition (3 h.; [M] = 0.25 M and 50 ^oC). Figure 3 represents the effect of initiator concentration on GY. Evidently, the grafting percentages increased significantly as [I] concentration increased and a further increase decreased GY values. Free radicals occurred as a result of decomposition of BPO taking place in various reactions in polymerization media. The increase in BPO concentration increases the probability of both the hydrogen abstraction from keratin backbone and the chain transfer reactions of PHEMA homopolymers with keratin. However the excessive increase in BPO concentration causes the formation of free radical species via decomposition of BPO ($C_6H_5COO^{\bullet}$ and/or $C_6H_5^{\bullet}$). These free radicals react with keratin macro radicals and growing polymer chains resulting termination or combination reactions; consequently grafting yield decreases [23, 31-32]. Maximum GY value was obtained as 55% for 0.06 M of [I].

Effect of [M] on GY was studied by varying its concentration from 0.10 M to 0.70 M at constant grafting condition (3 h.; [I] = 0.06 M and 50 ^oC). As shown from the results graphed in Figure 4, GY increased first with increasing of [M], reached a maximum and then decreased. As concentration of HEMA increases, the diffusion of monomer molecules into the fiber structure also increases leading to a higher GY. The decrease in GY can be explained by the enhancement of homopolymer formation at high monomer concentrations. Maximum GY value is reached as 55% at 0.25 M of HEMA concentration. The obtained grafting value is satisfactory by comparison with literature [33-34].

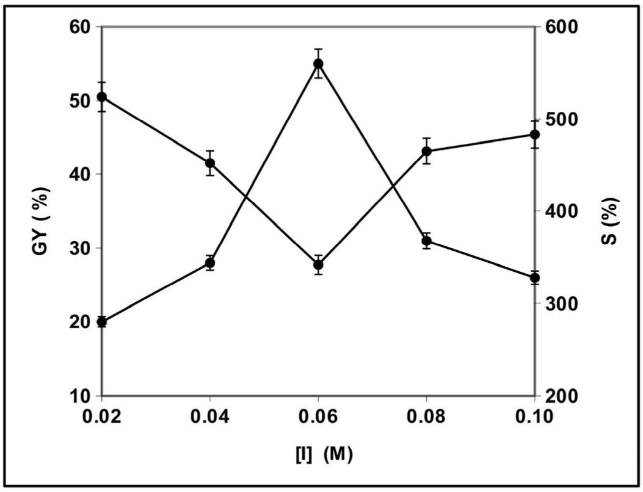

Figure 3. Variation of GY (-●-) and S (-o-) with initiator concentration (T = 50 ºC, t = 3 h, [M] = 0.25 M)

S% values calculated from Equation 2 are presented in Figure 3-4. Similar to Figure 1 and Figure 2, swelling values of grafted wool yarns decreased as GY values increases.

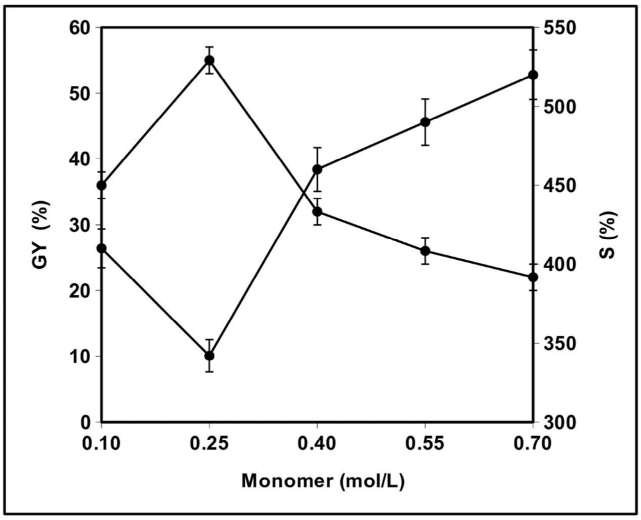

Figure 4. Variation of GY (-●-) and S (-o-) with monomer concentration (T = 50 ºC, t = 3 h, [I] = 0.06 M)

The swelling percentage values obtained for all conditions varied from 342% to 538%. On the other hand the swelling value of ungrafted wool yarns is found as 590%. It can be said that grafting of wool yarns with HEMA lead to decrease in swelling capacity. Although HEMA has hydrophilic character, the wool yarns seem to be more hydrophilic than HEMA. Its scale like structure, numerous water absorption centers and high amorphous regions ratio causes this result.

Due to the grafting processes water attracting groups and amorphous regions of wool are blocked and water absorption capacity decreased.

Depending on the graphs given in Figures 1-4, the optimum grafting conditions providing maximum GY values are determined as 0.25 M of HEMA concentration, 50 ˚C, 3 hours of grafting time and 0.06 M of BPO concentration.

4.4. SEM Analysis

Scanning electron micrographs of ungrafted and grafted wool yarns at two different zoom were presented in Figure 5. Difference in morphology of fiber surface before and after grafting can be evidently observed. Both grafted and ungrafted wool samples present fiber bundles (ribbon like structure). Neither polymer chain nor mound was observed on the ungrafted surfaces (Fig.5 a, c). Some apparent aggregates of PHEMA fibrils on the surface of grafted yarns are a good evidence for the successive grafting process (Fig.5 b, d). The bonded PHEMA fibrils on the wool fibers indicate that the grafting was successfully performed.

4.5. Fastness Properties

The values of rubbing, washing and light fastness of ungrafted and grafted wool yarns are presented in Table 1. Similar weather and dry rubbing fastness values were obtained both HEMA grafted and ungrafted yarns. It seems that the grafting of wool yarns with HEMA not affect their light and dry rubbing fastness properties. On the other hand, washing and wet rubbing fastness ratings increased one step. As expected, grafting process partially covers the surface of wool yarns and causes the blocking of dye attraction groups of wool. In comparisons with the literature, the ratings obtained from fastness tests are satisfactory [35].

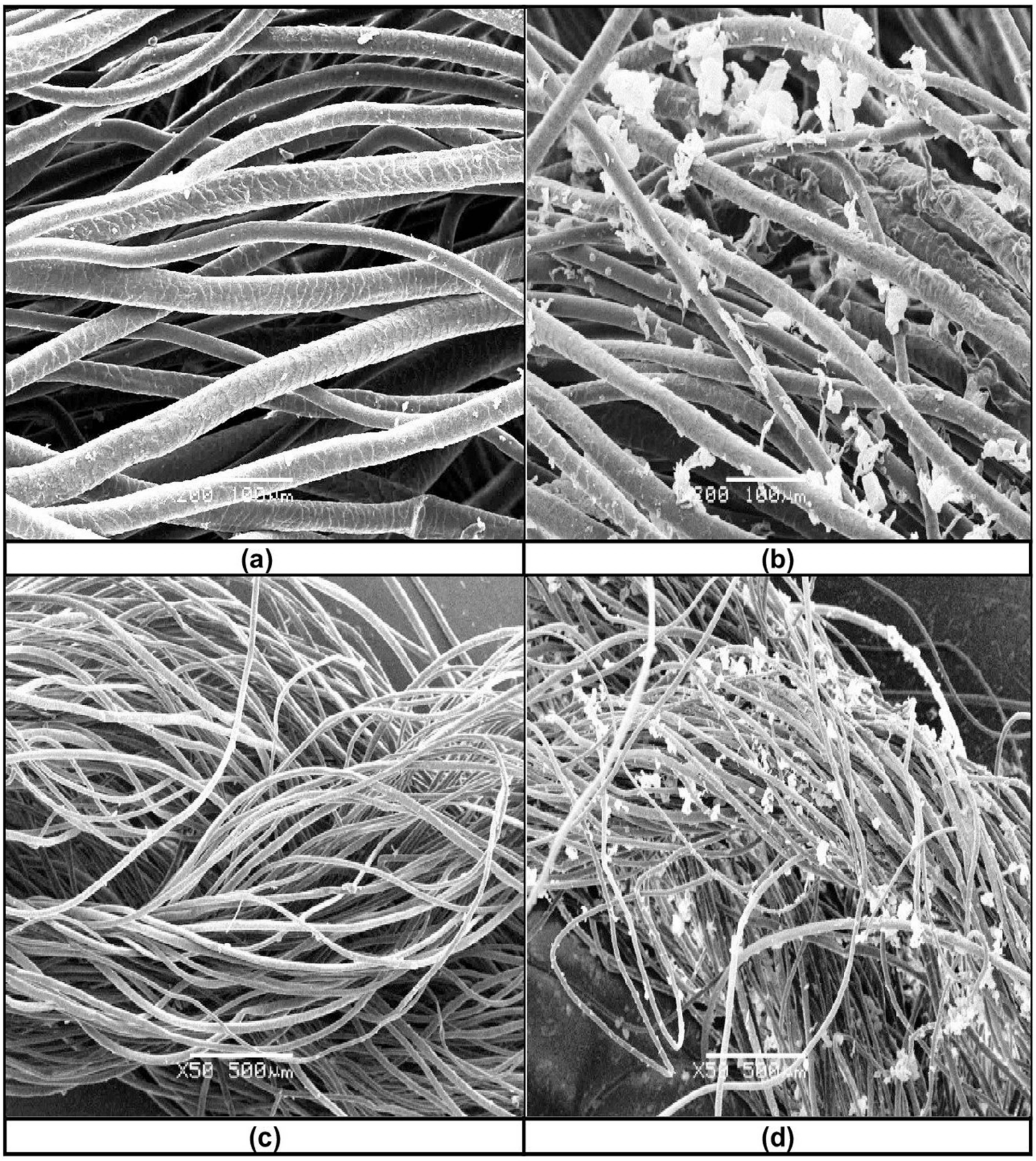

Figure 5. SEM micrographs of ungrafted wool fibers at (a) 50X and (c) 200X; HEMA grafted fibers at (b) 50X and (d) 200 X.

Table 1. The comparative fastness and dye uptake values of the grafted and ungrafted wool yarns

Sample	Light Fastness	Washing Fastness	Wet rubbing Fastness (Staining)	Dry rubbing Fastness (Staining)	Dye Uptake (%)
Ungrafted wool yarns	6	3	3	3	69,3
HEMA grafted wool yarns	6	4	3	4	68,5

As discussed in the previous section, HEMA grafting onto wool yarns decreased the swelling values. Even then, the dye uptake percentages of ungrafted and grafted wool yarns were obtained as similar to each other. It seems that the ungrafted parts of fiber surfaces were enough for adsorption of dye molecules and PHEMA deposition on the wool didn't inhibit the dye uptake.

4.6. Relaxation Shrinking Values

RS percentages of ungrafted and HEMA grafted wool yarns were obtained using Equation 3 and summarized in Table 2. It is clearly seen that the ungrafted wool yarns shrink in all washing conditions. The lengths of washed yarns are nearly 10-14 % shorter than unwashed yarns. The shrinking is more distinct after hot and soapy washing procedure. On the other hand, HEMA grafting is positively affects the dimensional stabilities of wool yarns. The best results were obtained for 35% HEMA grafted wool yarns. The wool fiber lengths have clearly protected from washing effects by grafting procedure.

5. CONCLUSION

The graft copolymerization of HEMA monomers onto wool yarns was performed by using BPO which is an original initiator for HEMA/wool system. The polymerization conditions were investigated and optimum grafting conditions were found as 0.25 M of HEMA concentration, 50 ˚C, 3 hours of grafting time and 0.06 M of BPO concentration. The maximum GY value was obtained as 55%. The existence of graft polymerization was observed in via SEM analysis. Swelling percentage values show that the swelling capacities of grafted wool fibers are lower than the ungrafted wool yarns. Dye uptakes studied were carried out and no significant differences found between dye adsorption values. Fastness tests were performed. Although the grafted and ungrafted wool yarns present similar weather and wet rubbing fastness ratings, the grafted wool fibers had higher ratings of dry rubbing and washing. Shrinking tests were also carried out and satisfactory results were obtained. While shrinking percentages of ungrafted samples reach 14%, no shrinking observed for HEMA grafted wool yarns.

Table 2. RS values of grafted and ungrafted wool yarns in different washing conditions.

Types of Wool Yarns	RS (%)			
	Bath Temperature: 20 ^{0}C		Bath Temperature: 40 ^{0}C	
	In water	In soapy water	In water	In soapy water
Ungrafted	10	14	14	14
10% grafted	No shrinking	4	4	6
20% grafted	No shrinking	4	4	6
35% grafted	No shrinking	No shrinking	No shrinking	No Shrinking

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