Graft Copolymerization of Benzyl Methacrylate onto Wool Fibers

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ABSTRACT: Benzyl methacrylate (BzMA) was graft copolymerized onto wool fibers by using ammonium peroxydisulphate as the initiator. Grafted samples with different polymer add ons (from 7 to 180%) were obtained by varying the monomer concentration in the reaction system. Following grafting with BzMA, the X-ray diffraction peak at 20.2° slightly moved towards higher spacing values. Birefringence decreased, indicating a lower degree of molecular orientation of grafted wool fibers. The equilibrium regain values of grafted wool decreased with increasing add on. Tensile strength increased in the range 45–77% add on, while elongation at break decreased. Differential scanning calorimetry (DSC) and thermogravimetry (TG) measurements showed a higher thermal stability for grafted wool. Following grafting, the drop of dynamic storage modulus (E') shifted to a lower temperature. Accordingly, the intensity of the loss modulus (E'') peak decreased, indicating that the thermally induced molecular motion was enhanced by grafting. Thermomechanical analysis (TMA) confirmed the increase in chain mobility for the grafted wool fibers. Above 35–40% add on, the presence of homopolymer on the surface of the wool fibers was identified by scanning electron microscopy. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **64:** 343–350, 1997

INTRODUCTION

The chemical modification of wool through graft copolymerization of vinyl monomers can be effective in improving some fiber properties and end-use performance.[1] The internal deposition within the wool of variable amounts of polymer may result in changes in tensile properties, felting shrinkage, abrasion and pilling resistance, hygroscopicity, chemical resistance, thermal stability, dying behavior, etc.[2–5]

Arai and coworkers[6–15] have made extensive work on the graft copolymerization of vinyl monomers onto wool fibers. Grafting, i.e., *in situ* formation of vinyl polymers, can be accomplished by means of the free radical initiation mechanism. Free radicals can be produced by both chemical and physical methods, including the use of redox systems, oxidizing agents, low and high energy radiations, etc.[12,16] The free radical sites formed on the peptide chains backbone may interact with the monomer and initiate the propagation of a grafted chain. Studies on native and modified (reduced, oxidized, alkylated, etc.) wool fibers permitted to ascertain that thiol groups are the preferred grafting sites.[6–8,16]

The location of the grafted polymer chains

within the fiber is influenced by the specific grafting system used (monomer, initiator, reaction conditions, etc.). It has been shown that polymer deposition may occur in the matrix and in the regions between the matrix and the microfibrils, as well as within the microfibril itself.[10,12,14] The "limiting volume" model has been recently developed to describe the stages through which the graft copolymerization of vinyl monomers onto wool proceeds, as well as to explain the changes in dye uptake and tensile properties of grafted wool fibers.[5]

Methyl methacrylate (MMA) has been extensively studied as grafting agent for wool.[1,12,16] However, the application of other methacrylate monomers with different side chain bulkiness, flexibility, and polarity is likely to result in effective changes in wool fiber performance and functionality. The present study deals with the graft copolymerization of benzyl methacrylate (BzMA) onto wool fibers. This methacrylate monomer is characterized by a bulky benzyl side chain. Moreover, the resulting polymer exhibits a glass transition temperature (T_g) sensibly lower than poly(MMA).[17] The changes in physical structure, tensile properties, and thermal behavior, as well as surface morphology of poly(BzMA)-grafted wool fibers with different polymer add ons (from 7 to 180%) were studied as a function of the increasing add on values. It is worth pointing out that the term "grafted" wool is employed to describe the material obtained from *in situ* polymerization and subsequent monomer/oligomer extraction. In fact, it is recognized that the polymer may be not only chemically bonded but also physically held within the fiber structure.

EXPERIMENTAL

Materials

Wool yarn (2/48s) was cleaned by sequential Soxhlet extraction with acetone and ethanol for 12 h, then thoroughly rinsed with distilled water and dried to constant weight before use. Reagent grade benzyl methacrylate (BzMA), purchased from Wako Pure Chemical Ind., was used without any preliminary treatment.

The aqueous grafting system consisted of varying quantities of BzMA monomer (from 35 to 200% on wool fiber weight), nonionic emulsifying agent (10% on BzMA weight), ammonium peroxydisulphate as initiator (3% on BzMA weight), and formic acid (3 mL/L). The material-to-liquor ratio was 1 : 15. The temperature was increased from 25 to 78–80°C over 30 min and then maintained constant for a further 40 min. At the end of the reaction, the grafted wool yarn samples were soaked in a solution containing 1 g/L ninionic detergent at 80°C for 20 min, thoroughly rinsed with water to remove unreacted BzMA, and dried at room temperature before successive measurements.

Measurements

Moisture regain was determined in standard conditions at 20°C and 65% relative humidity (RH).

X-ray diffraction intensity curves were obtained at a scanning rate of 1°/min, with a diffractometer Rigaku Denki Co., Ltd., using the CuKα radiation (λ = 1.54 Å). The voltage and current of the X-ray source were 40 kV and 20 mA, respectively.

Refractive indices were measured with the Beche's line method, using a polarized microscope under the monochromatic light (Na light), in standard conditions.

Tensile properties were measured in standard conditions with a Tensilon UTM-II (Toyo Boldwin Co., Ltd.) tensile tester machine.

Differential scanning calorimetry (DSC) measurements were performed on a Rigaku Denki Co., Ltd. instrument (model DSC-10A) at a heating rate of 10°C/min. The open aluminium cell was swept with N_2 gas during the analysis.

A Rigaku Denki Co., Ltd. instrument (model CN-8361) was used for thermomechanical analysis (TMA). The heating rate was 10°C/min, and dry N_2 gas provided the inert atmosphere.

Thermogravimetric analyses (TG) were run under N_2 on a Rigaku Denki Co., Ltd. instrument. The heating rate was 10°C/min and the temperature range studied was from 25 to 400°C.

Dynamic mechanical (DMA) properties were measured using a Toyoseiki Rheolograph Solid-S. The frequency of oscillation was adjusted to 10 Hz. The temperature range studied was from −50 to 260°C. Samples were heated at 2°C/min. The sample length was 15 mm, with an initial tension of 30 gf.

Scanning electron microscopy (SEM) analysis was carried out with a Jeol JAX-333S microscope, at 10 kV acceleration voltage, after gold coating.
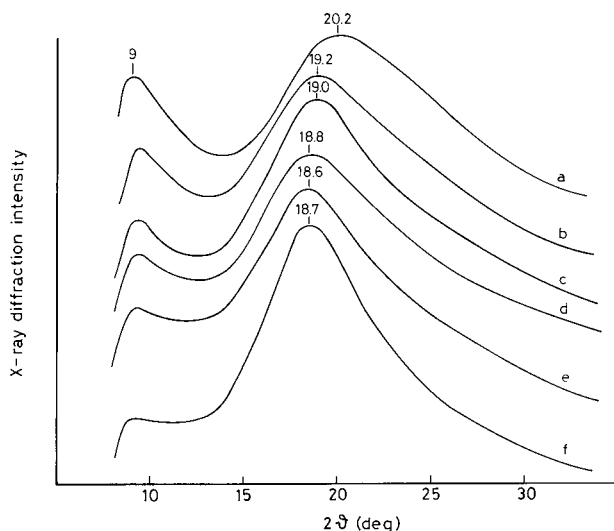
Figure 1 Wide-angle X-ray diffraction curves of untreated (a) and poly(BzMA)-grafted wool fibers. Add on: (b) 34%; (c) 53%; (d) 77%; (e) 92%; (f) 180%.

RESULTS AND DISCUSSION

Crystalline Structure and Molecular Orientation

Figure 1 shows the wide-angle X-ray diffraction profiles of untreated and poly(BzMA)-grafted wool fibers with increasing add on values. The control sample [Fig. 1(a)] showed the typical diffraction pattern of α-keratins,[10] with a prominent 2θ peak at 20.2° and a minor peak at 9°, corresponding to the crystalline spacings of 4.39 and 9.82 Å, respectively. With increasing add on, the position of the minor 2θ peak remained unchanged, though its intensity decreased at higher grafting levels. On the other hand, the major peak shifted towards lower 2θ values (higher spacings) as soon as add on reached 34% [Fig. 1(b)]. This trend was confirmed by the samples with higher grafting levels [Fig. 1(c–f)]. These changes in the 2θ pattern of poly(BzMA)-grafted wool fibers indicate that the deposition of the polymer within the fiber caused little disturbance in the arrangement of the fibrillar elements forming the crystalline regions of wool.[10,12,14]

Optical measurements (Table I) are a useful source of information about the overall fiber structure. Birefringence (Δn) may be regarded as an estimate of the average molecular orientation of a fibrous polymer, because it reflects the orientation of both the polymer chains in the amorphous regions and the polymer crystals in the crystalline regions. Untreated fibers showed a Δn value of 0.01, which places wool within the group of the poorly oriented textile fibers.[18] From the results listed in Table I it is possible to see that grafting induced a marked decrease of birefringence. Δn fell off sharply with increasing add on until about 45%, and then remained fairly constant. The appreciable decrease of molecular orientation should be primarily attributed to the presence of the grafted polymer, which disturbed the arrangement of the keratin chains in the amorphous regions, as well as that of the fibrils in the crystalline regions, as confirmed by the above X-ray data.

The values of isotropic refractive index (n_{ISO}) showed a tendency to increase with increasing add on. Because n_{ISO} is related to structural and morphological features of the fiber, such as crystal content, density, etc., its behavior may account for either an increase in crystallinity or a higher fiber density (the grafted polymer filled the voids within wool fiber).

A common feature emerging from both X-ray and optical measurements is that the most significant structural changes of grafted wool fibers appeared at relatively low add on levels, usually below 50%. This finding may be explained taking into account the stages through which the grafting of BzMA onto wool was found to proceed. As shown by the SEM observations (see below), during the first stage of grafting (<50% add on), polymer deposition occurred mainly within wool fiber, while at higher add ons increasing amounts of polymer formed onto the fiber surface. Accordingly, changes in wool fiber structure arose especially when the polymer grew into the fiber, rather than onto the fiber surface.

Equilibrium Regain and Tensile Properties

Equilibrium regain and tensile behavior are important parameters in the assessment of the properties and functional performance of textile fibers (handle, comfort, maintenance, etc.). Grafting with poly(BzMA) caused a drastic decrease of moisture regain (Table II). This behavior may be attributed to the essentially hydrophobic nature of the grafted polymer, which either masked the groups responsible for binding water or acted as a barrier against moisture diffusion. Moreover, at above 45–50% add on, when homopolymerization at the fiber surface occurred, the polymer might have interfered with moisture absorption.

The values of tensile strength and elongation at break of poly(BzMA)-grafted wool fibers with various add on levels are listed in Table II. The changes in tensile strength, which decreased at

Table I   Optical Properties of Poly(BzMA)-Grafted Wool Fibers

Add On (%)	Refractive Indices		Birefringence (Δn)	Isotropic Refractive Index (n_{ISO})
	($n_{\parallel}$)	($n_{\perp}$)		
0	1.560	1.550	0.010	1.553
34	1.5575	1.551	0.0065	1.553
45	1.558	1.557	0.001	1.557
53	1.558	1.555	0.003	1.556
77	1.558	1.557	0.001	1.557
92	1.5585	1.558	0.0005	1.558
180	1.558	1.557	0.001	1.557

34% add on and then increased in the range 45–77% before falling off at higher add on values, may be attributed to the balance of two opposite effects. Protein fibers are known to be quite sensitive to wet treatments at high temperature.[19,20] The grafting conditions may cause the hydrolysis of some sensitive peptide bonds, resulting in a more or less serious damage of the intrinsic tensile properties. In a recent study on grafted silk fibers,[21] we showed that temperature, acidic pH, and prolonged treatment times played the major role in lowering the fiber strength. Though wool is more resistant than silk at acidic pH, it is reasonable to expect a slight impairment of tensile strength, owing to chemical degradation. On the other hand, the strengthening effect on wool strength brought about by the polymer loaded within the fiber has been reported by various authors.[3–5,22] This effect might depend on various factors, such as the filling of voids within the fiber, and the occurrence of various kinds of polymer–keratin interactions. Strength would, therefore, increase by virtue of increasing the viscosity of the system and the cohesion between the polypeptide chains (the fiber became more homogeneous and crystalline). On account of these effects, the tensile behavior of poly(BzMA)-grafted wool fibers might have been governed by the balance of two contrasting effects, the strengthening effect prevailing in the add on range 40–80%.

Compared to untreated wool, poly(BzMA)-grafted wool fibers exhibited a lower ability to extend when subjected to a strain (Table II). Elongation at break fell off in two sharp steps, one at low (34%) and the other at high (77%) add on values. Grafting resulted in a higher degree of fiber stiffness, attributable to a glueing effect of the grafted polymer, which filled the voids and kept the keratin chains in a fixed position, thus partly inhibiting their movement. Moreover, the higher hydrophobicity of grafted wool fibers and their lower ability to bind water might have contributed to decrease the elongation at break.

Thermal Behavior

The study of the thermal properties of grafted wool fibers involves both scientific and technological aspects. Thermal analysis permits to detect changes in physical (T_g, melting, crystallization, etc.) and chemical (crosslinking, degradation, and other reactions) structure brought about by the interactions between the grafted polymer and wool keratin. In fact, besides other factors, the response to a thermal treatment depends on the structure and morphology of all phases forming the fibrous polymer. Moreover, the study of the thermal behavior is a useful tool for monitoring important processing (heat treatments in dry and wet state) and end-use (wear and maintenance) properties of grafted wool.

The differential scanning calorimetry profile of untreated wool [Fig. 2(a)] showed a broad endothermic transition starting at above 200°C, with a peak at 232°C. This characteristic DSC pattern
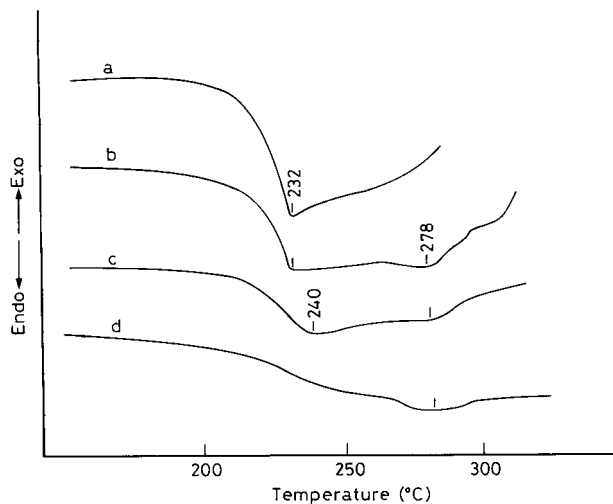
Table II   Equilibrium Regain and Tensile Properties of Poly(BzMA)-Grafted Wool Fibers

Add On (%)	Equilibrium Regain (%)	Tensile Strength (g)	Elongation at Break (%)
0	11.8	346.2 ± 16.8	49.9 ± 0.8
34	9.7	301.0 ± 15.9	39.2 ± 0.9
45	7.2	377.0 ± 16.4	40.0 ± 1.0
53	7.7	338.2 ± 15.0	40.5 ± 1.0
77	6.5	344.0 ± 18.3	28.5 ± 1.3
92	6.1	316.0 ± 17.3	15.7 ± 1.4
180	3.9	286.5 ± 23.0	11.3 ± 1.6

Figure 2 DSC curves of untreated (a) and poly-(BzMA)grafted wool fibers. Add on: (b) 34%; (c) 77%; (d) 180%.

has been assigned to disordering and melting of α-keratin, the width of the endotherm being attributable to the contribution of α-helical material with different thermal stability, belonging to separated fiber domains.[23-29] With increasing add on of poly(BzMA)-grafted wool fibers, the intensity of the endotherm in the high-temperature side increased. A new peak appeared at 278°C [Fig. 2(b)], while the α-keratin peak shifted to 240°C [Fig. 2(c)]. Broadening of the main DSC endotherm continued also at high add on values [Fig. 2(d)], the intensity of the peak at 278°C becoming stronger.

The TG curve of untreated wool [Fig. 3(a)] showed two zones of weight loss. The initial weight loss at approximately 100°C was due to the loss of moisture. Its intensity decreased with increasing add on [Fig. 3(b-d)], in agreement with the behavior of regain data (see Table II). The second strong step of weight loss started at about 180°C. Evolution of simple gases, such as H_2O, CO_2, NH_3, H_2S, should occur at this stage, while a general rupture of disulfide and peptide bonds, leading to wool pyrolysis, is expected to take place at higher temperatures.[24] It is interesting to note that the beginning of thermal degradation coincided with the endothermal effects (melting of α-keratin) shown in the DSC curves. Poly(BzMA)-grafted wool fibers [Fig. 3(b-d)] showed a marked shift towards higher temperature of the onset of thermal degradation. In fact, the values of weight loss at 300°C were 35% for untreated wool, and 25, 18, and 10% for grafted wool with 34, 77, and 180% add on, respectively.

Figure 4 shows the temperature dependence of the dynamic storage (E') and loss (E'') modulus of untreated and poly(BzMA)-grafted wool fibers. The storage component of the dynamic modulus of untreated wool [Fig. 4(a)] decreased slightly in the low temperature range, from −50 to 20°C, and then remained stable until about 165–170°C. At this temperature, corresponding to the T_g of wool proteins,[24] the slope of the E' curve changed and the modulus decreased sharply, owing to the intense thermally induced segmental motion of the keratin chains. Accordingly, the E'' curve
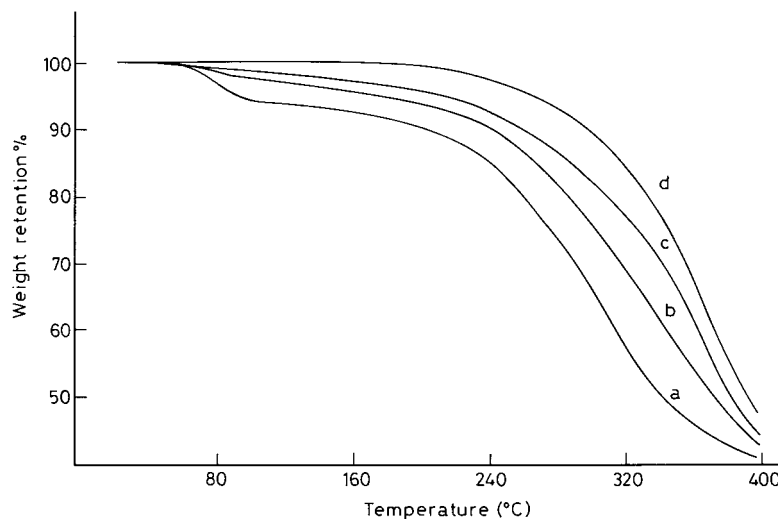

Figure 3 TGA curves of untreated (a) and poly(BzMA)-grafted wool fibers. Add on: (b) 34%; (c) 77%; (d) 180%.
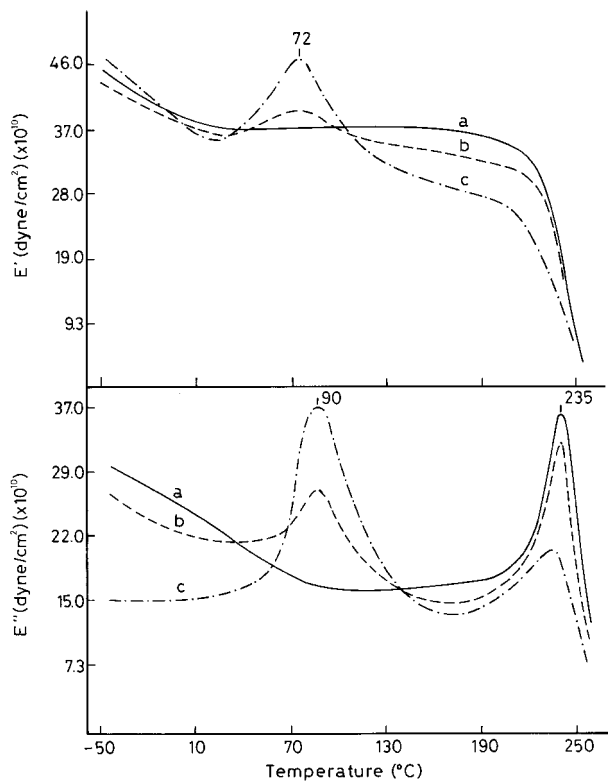
Figure 4   Dynamic storage (E') and loss (E'') modulus curves of untreated (a) and poly(BzMA)-grafted wool fibers. Add on: (b) 34%; (c) 53%.

showed a gradual negative slope until 70° C and a prominent loss peak at 235°C. The latter is attributable to the molecular motion of the protein chains in the α-helix crystallites, because it coincides with melting of α-keratin (see DSC curves), while the low-temperature transitions may be related to motional events in the amorphous matrix of wool fiber.[15] Following grafting with BzMA, the viscoelastic behavior of wool fibers showed significant changes. The main features are the anticipated drop of the storage modulus, the decreased intensity and broadening of the loss peak at 235°C, and the appearance of a new peak below 100°C. The latter increased with increasing add on, suggesting that it may be attributed to the grafted poly(BzMA) chains, i.e., to their glass transition temperature.[17]

The thermomechanical behavior of untreated wool [Fig. 5(a)] was characterized by a slight extension (<1%) from room temperature to about 220°C, followed by a sharp contraction peak with a maximum at 242°C, preceding the final extension due to the beginning of wool backbone thermal degradation. The rapid

shrinkage prior to sample failure was a consequence of melting, because the onset coincided with that of the DSC endotherm attributed to melting of α-keratin. Grafted wool fibers [Fig. 5(b,c)] showed a tendency to extend more easily during heating in the range 25–200°C, while the intensity of the final contraction peak decreased with increasing add on.

The picture emerging from the accumulated thermal data indicates that the thermal behavior of wool was significantly affected by grafting with poly(BzMA). Physicochemical interactions between wool keratin and grafted polymer chains are likely to be responsible for the changes in the thermal response of the fiber. As shown by the DSC and TG results, a higher thermal stability towards treatments at elevated temperature (>200°C) was conferred on wool by grafting, the improvement being evident even at low add ons. Though the appearance of discrete molecular relaxations for poly(BzMA) and wool keratin in the DMA curves of grafted fibers may account for phase separation and incompatibility between the two components of the system, other features of the dynamic mechanical response seem to suggest the occurrence of a certain degree of interaction between the two phases. This comment mainly refers to the enhancement of the molecular motion in both matrix and microfibril domains induced by grafting, as shown by the negative slope and the anticipated drop of the storage modulus, as well as by the depression and broadening of the loss peak. Moreover, the observation that the grafted poly(BzMA) exhibited a T_g value sensibly higher than that of the corresponding homo-
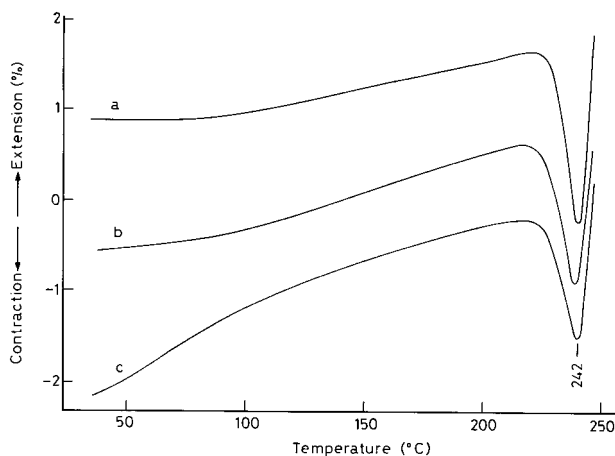

Figure 5   TMA curves of untreated (a) and poly(BzMA)-grafted wool fibers. Add on: (b) 34%; (c) 53%.
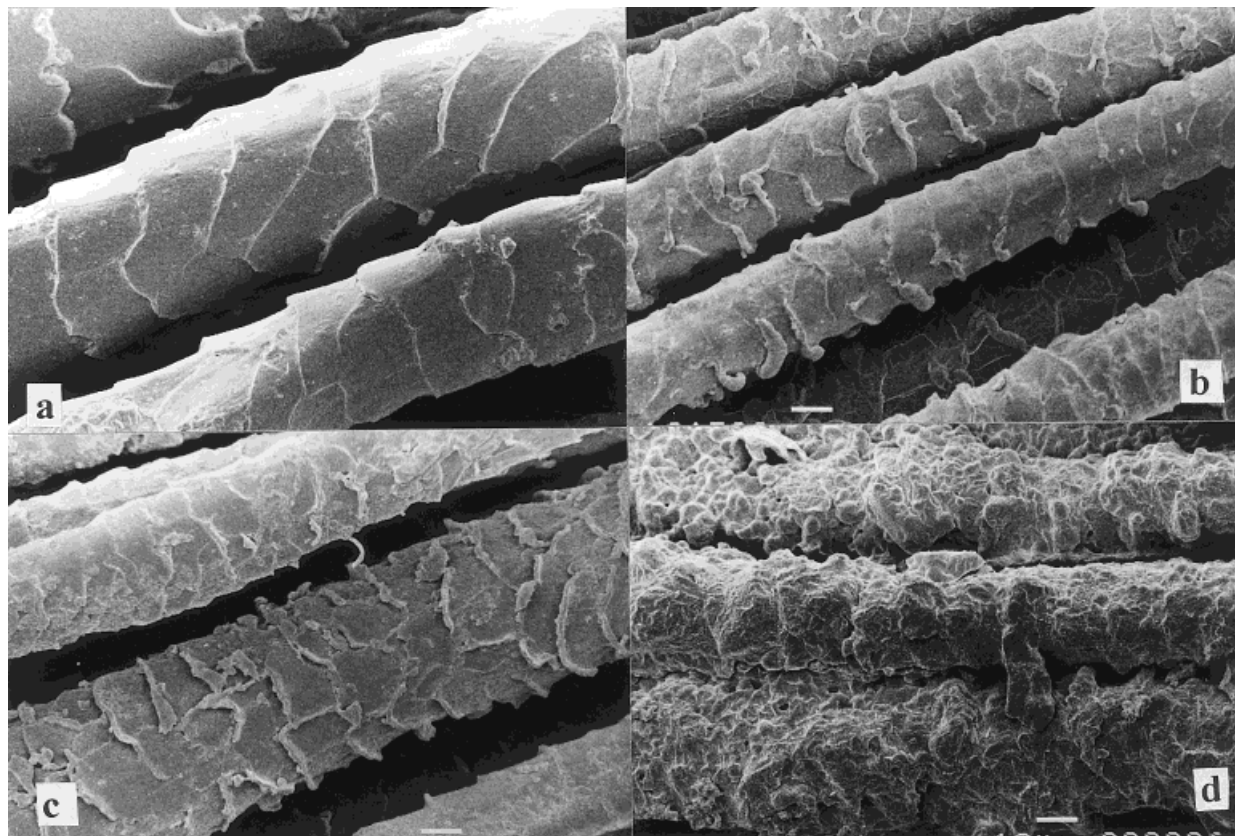
Figure 6 SEM photographs of (a) untreated and poly(BzMA)-grafted wool fibers. Add on: (b) 34%; (c) 72%; (d) 180%.

polymer,[17] might be interpreted as a result of a certain degree of interaction with wool keratin chains.

Surface Morphology

The surface morphology of poly(BzMA)-grafted wool fibers with different add on values was examined by scanning electron microscopy. The typical scale pattern of untreated wool fibers [Fig. 6(a)] underwent slight to drastic modification as a function of the amount of polymer add on. Small deposits of foreign material were visible on the surface of the sample with 34% add on [Fig. 6(b)]. It is reasonable to attribute these deposits to the beginning of homopolymerization, because they increased with increasing add on [Fig. 6(c)]. The sample with 180% add on [Fig. 6(d)] showed the highest degree of scale masking, the fiber surface being almost completely covered by a thick layer of polymer. This is supposed to establish strong interactions with wool, by means of physical and/or chemical bonds, because it is resistant to wet aftertreatments in the presence of surface active agents.

CONCLUSIONS

The results reported in the present study show that poly(BzMA) can be successfully grafted onto wool fibers. As expected, the polymer deposition within the fiber resulted in structural and physico-mechanical changes that did not impair the intrinsic properties of wool. The sensibly higher thermal stability attained by grafted wool fibers is noteworthy. No significant surface polymer deposition was found below 35–40% add on, while extensive homopolymerization took place at higher add on levels, resulting in variable degrees of scale masking. It is reasonable to assume that some surface deposition of the polymer might confer shrink resistance on wool. However, further studies are needed to optimize the grafting conditions in order to attain the desired effects, avoiding negative consequences on wool surface properties and handling.

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