

Formation of Poly(methyl methacrylate) Thin Films onto Wool Fiber Surfaces by Vapor Deposition Polymerization

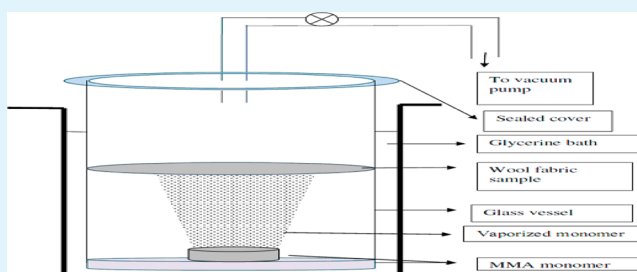
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ABSTRACT: Chemical vapor deposition (CVD) polymerization is a useful technique because of the possibility of forming very thin film of pure polymers on substrates with any geometric shape. In this work, thin films of poly(methyl methacrylate) or PMMA were formed on the surfaces of wool fabrics by a CVD polymerization process. Various polymerization initiators including dicumyl peroxide, *tert*-butyl peroxide, and potassium peroxydisulfate have been investigated to polymerize methyl methacrylate onto the surfaces of wool by the CVD polymerization. The wool fabrics were impregnated with initiators and were then exposed to MMA monomer vapor under vacuum at the boiling temperature of the monomer. Wool fabrics with vapor-deposited PMMA surfaces were characterized by elemental analysis, TGA, FTIR, disperse dye absorption, contact angles measurement, AFM, and SEM. PMMA-coated wool fabrics showed higher contact angle and absorbed more dyes than that of the control wool. It was evident from the results obtained by various characterization techniques that MMA was successfully polymerized and formed thin films on the surfaces of wool fabrics by all initiators investigated but the best results were achieved with *tert*-butyl peroxide.

KEYWORDS: chemical vapor deposition, poly(methyl methacrylate), thin film, wool, disperse dye



1. INTRODUCTION

Chemical vapor deposition (CVD) polymerization is a very attractive polymerization technique. It enables one to fabricate a thin film of polymer by evaporating and polymerizing monomers toward a substrate. It can produce thin films of very pure polymers on complicated shaped substrates which is difficult to achieve by traditional polymerization techniques. CVD polymerization is a one step process directly polymerizing a monomer without any purification and without using any solvent. Monomers are directly converted into a polymeric film without any subsequent drying or curing steps. The types of polymers synthesized by this technique may include oligothiophene-based polyamide,¹ poly(vinylcarbazole),² poly(vinyl methyl siloxane),³ poly(glycidyl methacrylate),⁴ poly(methylmethacrylate),⁵ poly(α -methylstyrene),⁶ polyimine,⁷ fluorocarbon polymers,^{8,9} poly(oligothienylene vinylenes),¹⁰ and poly(phenyl quinoxaline).¹¹ Unlike other thin film techniques such as sputtering CVD, it can also be used to produce nanofibers,¹² nanotubes,¹³ and monoliths.¹⁴ Chemical vapor deposition (CVD) and physical vapor deposition (PVD) polymerizations are used widely in materials processing technology. The majority of applications of CVD polymerization involve applying solid thin-film coatings to surfaces, but they are also used to produce high-purity bulk materials and powders, as well as fabricating composite materials via infiltration techniques. The applications of thin films produced by CVD polymerization include sensors for detection of toxic

gases,¹⁵ for making electroluminescent materials,⁷ synthesis of carbon nanotubes,¹⁶ light-emitting devices,¹⁷ microcapsules,¹⁸ etc.

CVD polymerization can be classified into three types, being plasma, oxidative, and initiated CVD polymerization. In plasma polymerization, gaseous monomers are activated and polymerized by plasma which forms a highly cross-linked polymeric coating.^{6,19} In oxidative CVD polymerization, monomers are injected into a reaction chamber where it comes in contact with oxidative agents (usually oxidant is impregnated into substrate), and forms polymer thorough step-growth polymerization. The growth of chain proceeds by the addition of new monomer molecule to the active chain ends.²⁰ The most investigated monomers in the oxidative CVD polymerization process are pyrrole,²¹ aniline,²² thiophene,^{23,24} and 3,4-ethylenedioxythiophene.^{25,26} They are usually polymerized by oxidation polymerization process, which usually takes place at cold to room temperatures. On the other hand, there are vinyl monomers, such as hydroxyethyl methacrylate,²⁷ glycidyl methacrylate,⁴ 4-vinylpyridine,²⁸ and alkyl acrylates²⁹ that are usually polymerized by an initiated CVD polymerization. In this method, a gaseous mixture of monomers and free-radical initiators are separately injected at moderately low pressure (e.g., 1 Torr)

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into a vacuum chamber where they come in contact with red-hot wire filaments. The initiators are broken down into free radicals and initiate free radical polymerization of vinyl monomers at the vapor phase, and polymers are deposited on a target-substrate. Initiated CVD polymerization was initially studied by Okui et al. in Japan during the last part of the last century^{30,31} and early part of this decade was extensively investigated by Gleason et al. in the USA.^{3–6} It was observed that when a vinyl monomer was evaporated in the presence of a red-hot filament, a thin film of polyvinyl polymer was deposited on the substrate and in the same way they prepared thin films of several polymers.^{30–33}

PMMA is a very popular commodity polymer which has very high clarity, UV resistance, and hydrophobicity.³⁴ One of the main disadvantages of wool fabrics is that the light fastness of dyed fabrics can be poor as the dyes are decomposed by UV radiation present in sunlight. It is anticipated that if wool fabrics are coated with a thin film of PMMA, it may help to increase light fastness of dyed wool fibers. Moreover, the surface of wool fiber is hydrophobic because of the presence of polyethylene-like long chain thioesters.³⁵ Oxidative and pulsed plasma-based CVD polymerization processes have been investigated previously to improve the surface electro-conductivity and adhesion of wool fibers respectively.^{36,37} In the pulsed plasma process, wool fibers were treated with hexamethyldisiloxane, which introduced silanol groups onto wool fiber surfaces.

The aim of this current work is to identify whether it is possible to form thin film of PMMA on wool fabric surface by a simple technique. The initiators impregnated into wool fabric samples were activated by heat to initiate polymerization of MMA vapor when the vapor comes in contact with fiber surface. The developed technique is quite different from the traditional iCVD polymerization. Here, instead of red-hot filament, we used chemical initiators to initiate polymerization of vaporized MMA at the boiling temperature of MMA (100 °C). In traditional iCVD, polymerization of a monomer takes place at vapor state before it comes in contact with the substrate; therefore no grafting with the substrate occurs. In this present method, MMA is polymerized on the surface of fiber and therefore there is possibility of formation of grafting between the fiber and the polymer. The grafting of acrylates onto wool fiber by free-radical polymerization has been investigated before by several researchers,^{38,39} but the work presented here is quite different from the published works. The initiators were selected on the basis of their half-life of decomposition at the boiling temperature of MMA. At that temperature, the initiators are broken down into radicals by heat and initiate free radical polymerization.

2. EXPERIMENTAL SECTION

2.1. Materials. A wool fabric of 210 g/m² having 34 ends/cm and 24 picks/cm was purchased from South Canterbury Textiles Ltd., New Zealand, and was used for all experiments. The wool fabric samples were chlorinated with 1% on the weight of wool (oww) dichloroisocyanuric acid according to the method (without the treatment with sodium sulfite) published in literatures to remove surface-bound lipids and also to make the fiber surfaces of wool smooth by removing scales.^{40,41}

Methyl methacrylate (MMA) was purchased from Sigma-Aldrich Chemicals (U.S.A.), and was purified by vacuum distillation. Dicumyl peroxide (DCP) was purchased from Elf-Atochem (France). Potassium peroxydisulphate (PPS) and *tert*-butyl peroxide (TBP) were purchased from Sigma-Aldrich Chemicals (U.S.A.). Teric GN, a nonionic surfactant, was supplied by ICI (U.K.). Delatin POE, a

dispersing agent, and Albegal FFA, an antifoaming agent, were supplied by BASF Chemicals (Germany). Sandozin MRN, a nonionic wetting agent, was purchased from Clariant Chemicals (Switzerland). Terasil Red 3BL, a disperse dye, was purchased from Huntsman Chemicals (U.S.A.).

2.2. CVD Polymerization Method. Figure 1 shows schematic diagram of the CVD polymerization apparatus used in these

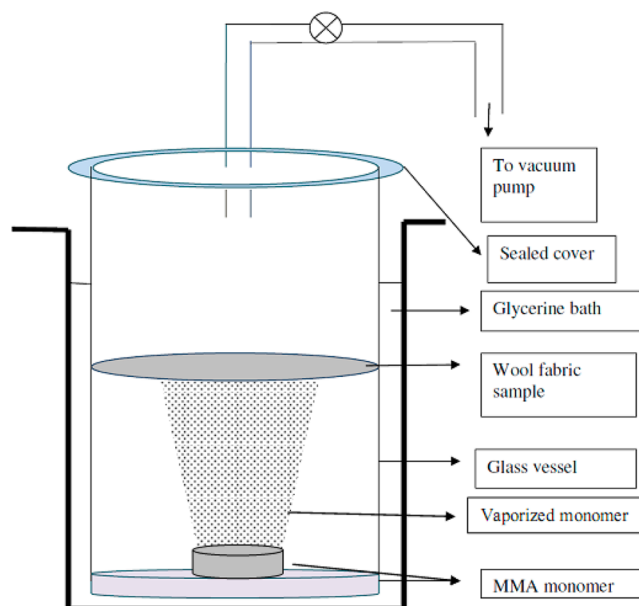


Figure 1. Schematic diagram of apparatus used for CVD polymerization of MMA onto wool fabrics.

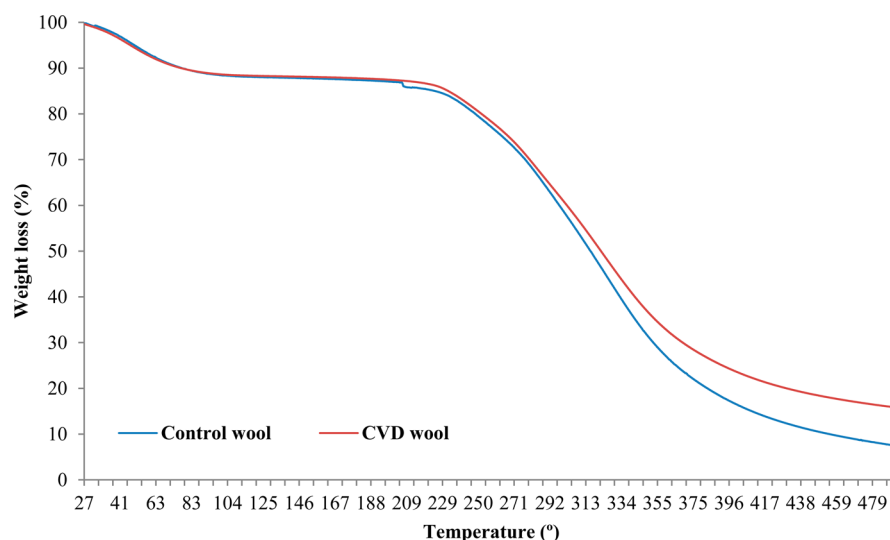
experiments, which is quite simple in construction. The main apparatus is made of a glass jar with a sealable glass lid and a suitable adapter with glass tubing, which is connected to a vacuum pump by rubber tubing. Initially, the wool fabric was padded with water-based or solvent-based solution of an initiator and then dried at normal temperature for few minutes under fume hood. A circular 100 mm diameter ring was made using stainless steel wire and the samples on which vapor deposition of monomer were to be carried out were attached to it. Then a flat glass vessel with MMA monomer (0.2 g) was placed inside the CVD polymerization apparatus and the fabric attached to the ring was placed inside, 5 cm above the monomer vessel as shown in Figure 1. Then the top of the glass jar was vacuum sealed and the CVD polymerization apparatus was then placed in a glycerine bath which was heated to 100 °C. All of the monomer was gradually vaporized, moved upward and deposited on the fabric surface, where it was immediately polymerized after coming in contact with wool fabric surfaces bearing the polymerization initiator. The fabric was then soaked in water (in ethanol in the case of DCP) to remove the initiators. The fabric samples were then dried, and again washed in ethanol to remove unreacted monomer. The dried samples were stored in a sealed polyethylene bag.

2.3. Characterization of the Grafted Wool. Elemental analysis of the untreated and polymer treated wool were carried out on a Carlo-Erba CHNSO elemental Analyzer at the Campbell Micro-analytical Laboratory, University of Otago (New Zealand) after drying them under vacuum for overnight at 80 °C. FTIR-ATR spectra were obtained using a Perkin-Elmer 2000 spectrophotometer and a Zn/Se ATR crystal. The coated surfaces of samples were placed down on the upper side of the crystal. Good fiber to crystal contact was ensured by applying 50 N pressure using a calibrated torque wrench.

The contact angle was measured in dynamic mode by using a KSV CAM 100 Contact Angle Measurement Apparatus.⁴² For each sample, contact angle was measured at four places and the average contact angle was reported. For each sample, the first measurement was taken 30 s after placing the drop of water and then at 20 s intervals until 90 s,

Table 1. Elemental Analysis of Control Wool Fabric and Wool Fabric Vapor Coated with PMMA by Using Different Initiators

initiators used	carbon %	hydrogen %	nitrogen %	sulfur %
control wool	50.50 (±0.12)	6.80 (±0.08)	16.50 (±0.07)	3.70 (±0.08)
PPS	49.50 (±0.10)	6.84 (±0.12)	15.73 (±0.09)	3.98 (±0.06)
DCP	48.52 (±0.14)	7.05 (±0.10)	14.55 (±0.12)	3.03 (±0.10)
TBP	50.19 (±0.08)	7.54 (±0.06)	13.15 (±0.07)	2.53 (±0.05)

**Figure 2.** TGA curves of control wool fabric and wool fabric coated with MMA by CVD polymerization.

and the average values are reported here. For the control wool fabric, the contact angle was measured 20 s after dropping the water droplet as it quickly soaked into the specimen.

TGA was carried out in a TA Instrument's DSC/TG Analyzer (Model Q200) from room temperature to 800 °C at a heating rate of 5 °C/min under nitrogen environment. A constant flow of high purity oxygen-free nitrogen gas was fed at a rate of 20 mL/min to the system from a point below the samples to purge air in the pyrolysis zone for avoiding unwanted oxidation of samples during pyrolysis. The thermogravimetric (TG) and differential thermal analysis (DTA) curves were recorded simultaneously along with temperature rise.

2.4. Surface Morphology. The morphology of control and CVD polymerized wool fabrics was examined by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The untreated and PMMA-coated wool fabric surfaces were scanned in a JEOL JSM-6100 scanning electron microscope at 20 kV. Before placing the samples in the SEM chamber, the samples were mounted onto an aluminum stub with carbon tape, and sputter coated with gold for 90 s to prevent charging.

Single fibers from the exposed fabric surfaces were pulled out and the PMMA-coated surfaces of the fiber were scanned under Digital Instruments Dimension 3100 AFM, and cuticle edges were scanned. Contact imaging mode in air was selected to study the scale surfaces at a room temperature of 20 °C. The samples were scanned without any preparative procedure except they were attached to steel discs with double-sided tape.

2.5. Dyeing of CVD Polymerized Wool Fabrics with a Disperse Dye. All dyeings were carried out in an Ahiba Turbomat laboratory dyeing machine using tap water and a materials-to-liquor ratio of 1:30. The dyeing pot was filled with sufficient water, and 0.5 g/L Albigal FFA, 0.5 mL/L Sandozin MRN, and 1 mL/L Delatin POE were added to it. All treated samples were dyed together in one bath to minimize bath to bath variation. A small piece of fabric of the same weight was cut from each treated sample. All the cut samples were then placed together into the dyeing pot and the dyebath pH was adjusted to 4.5–5 with diluted acetic acid. The machine was then run for 10 min at room temperature after which time the required amount of Terasil Red 3BL dye was added to the dyebath. The temperature of

the bath was then raised to 98 °C at 2 °C/minute, and held for 45 min. After completion of dyeing, the dyebath was cooled to 45 °C and the liquor was drained. The samples were then rinsed in cold water, dried, and assessment of color carried out.

2.6. Assessment of Color. The reflectance values (at the appropriate wavelength of maximum absorption for each dyeing) of the dyed samples were measured using a Datacolor Spectraflash 600 reflectance spectrophotometer, interfaced to a personal computer.⁴³ Samples were measured under illuminant D65, using a 10° standard observer with UV component excluded and specular included. The color strength or *K/S* value was calculated by using the Kubelka–Munk equation

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

where *K* is the absorption coefficient of the substrate, *S* is the scattering coefficient of the substrate, and *R* is the reflectance value of the dyed samples at the wavelength of maximum absorption. For each sample, the measurements were made at four positions on the fabric and the average value is reported.

3. RESULTS AND DISCUSSION

3.1. Chemical Compositions of PMMA-Coated Wool.

Chemical compositions of wool fibers coated by the CVD polymerization method using various initiators were determined by elemental analysis and were compared with the chemical compositions of untreated wool in order to reveal any change in chemical composition of wool resulting from CVD polymerization. The chemical composition of wool would be expected to be changed after grafting and coating by PMMA. The results of elemental analysis of various coated wool fabrics are shown in Table 1. As PMMA is composed of C, H, and O, therefore changes in percentage of C and H in the PMMA-modified wool would be marginal as wool fiber is also composed of C, H, N, and S. However, the change in percentage of S would be the indicator of addition of PMMA to

the wool fiber surfaces as percentage of S should be reduced in the case of PMMA-deposited wool fiber as PMMA does not have S in their chemical structure. It can be seen that the control wool was composed of 50.50% carbon, 16.50% nitrogen, 6.80% hydrogen and 3.70% sulfur but their relative quantity was changed in the case of CVD polymerization of PMMA onto wool, with the level of change depending on the initiators used. The maximum change of composition of carbon (C), hydrogen (H), nitrogen (N) and sulfur (S) was observed in the case of TBP initiator as the quantity of H, N and S changed to 7.54, 13.15 and 2.53% respectively. As the PMMA film produced could be very thin, therefore the change in chemical composition between the control and the treated fabrics were small. The change in H, N, and S content of fiber indicates that PMMA was deposited on the treated fabrics. The second best one in terms of initiation of polymerization of MMA was DCP. The performance of PPS as an initiator was the poorest as the half-life of PPS was the lowest of the initiators investigated. The results indicate that an initiator having high half-life of decomposition shows better results than initiators having short half-lives. As the maximum change in chemical composition of wool fabrics was observed in the case of TBP, it can be anticipated that the thickness of coating of PMMA was maximum in the case of TBP.

3.2. Thermogravimetric Analysis (TGA). TGA was carried out to identify whether deposited PMMA onto wool fiber surfaces changes their thermal decomposition behavior. Figure 2 shows the TGA curves of the control wool fabric and also the wool fabric coated with PMMA by CVD polymerization. The thermal curves of untreated and PMMA-coated wool fabrics were quite similar, but the latter showed better thermal stability than the former as the ash content in the case of the PMMA-coated wool fabric was considerably higher than the ash content of the untreated wool fabric. It indicates that grafting of PMMA onto wool (possibly to thiol groups in wool fibers) might reduce the reactivity of thiol groups toward nucleophilic attack on the amide bonds of wool during pyrolysis.

3.3. Contact Angle. Contact angle is a quantitative measure of the wetting of a solid surface by a liquid. It is defined goniometrically as the angle formed by a liquid at the three-phase boundary where a liquid, gas and solid intersect. It is the measure of wettability of a surface, higher contact angle means higher hydrophobicity and lower contact angle means higher hydrophilicity.

Wool fabrics are naturally hydrophobic but the formation of a more-hydrophobic polymer film (such as PMMA) on the surfaces of wool may alter their wettability by increasing hydrophobicity. The optical images of water droplets on the surfaces of the control and the PMMA-coated wool fabrics 5 s after dropping were shown in Figure 3. It can be noticed that in the case of the control wool fabric, the water droplets spread and wetted the surface but in the case of coating with PMMA the droplet was almost spherical in shape and did not spread. In the case of untreated wool fabric, the water droplet was fully absorbed within 30 s but in the case of wool fabric coated with PMMA (using all polymerization initiators) hydrophobicity remain unchanged until the end of the measurement period.

The contact angle of untreated and PMMA-coated wool fabrics by the CVD polymerization method is shown in Figure 4. It can be seen that the average contact angle of untreated wool fabrics is 97.3° but for PPS, the contact angle was increased to 109° . The highest contact angle was shown for

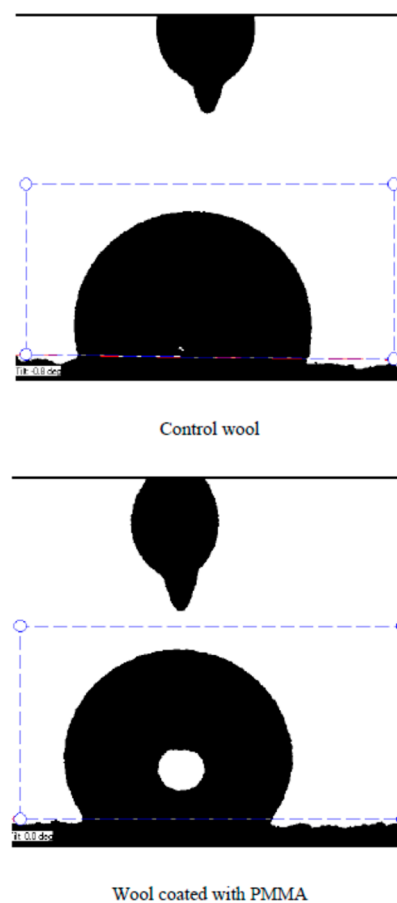


Figure 3. Optical image of water droplet after dropping on the surfaces of the control and the PMMA-coated wool fabric.

TBP which was 117.6° and showed the highest water repellency. The second highest contact angle was shown by PMMA-coated surface polymerized by the DCP. Therefore, the order of hydrophobicity for various initiators were TBP > DCP > PPS. It has been reported that the contact angle of pristine wool is 112° ,⁴² but Molina et al. found that the contact angle of untreated wool was 103° .⁴⁴ As the surface lipids of wool fibers were partially removed by chlorination, wool fabrics used here should show lower contact angle than the untreated wool. Therefore, the contact angle shown by the control wool fabric was not unexpected.

3.4. Assessment of Color. Hydrophobic fibers, such as polyester fibers, are usually dyed with hydrophobic disperse dyes. It is anticipated that the increased hydrophobicity of wool fibers by coating with PMMA would allow them to be dyed with disperse dyes. If the thickness of the coating is high, the absorption of dye by the fiber will be high and the color strength of treated and dyed fabric will be high. Therefore, the higher color strength indicates better polymerization. The color strength of various coated wool fabrics dyed with Terasil Red 3BL dye is tabulated in Table 2. The highest strength of the color (K/S) was produced by the TBP initiator for the 120 min exposure time as the strength of the color was 4.58 but the color strength showed by the control was only 0.25. The results of color strength obtained showed that the color strength of the control wool fabric had the least color strength, which was expected. Wool fibers cannot be dyed with disperse dyes as these nonionic dyes are not absorbed into wool (although the surface of wool is hydrophobic). If some dye molecules are

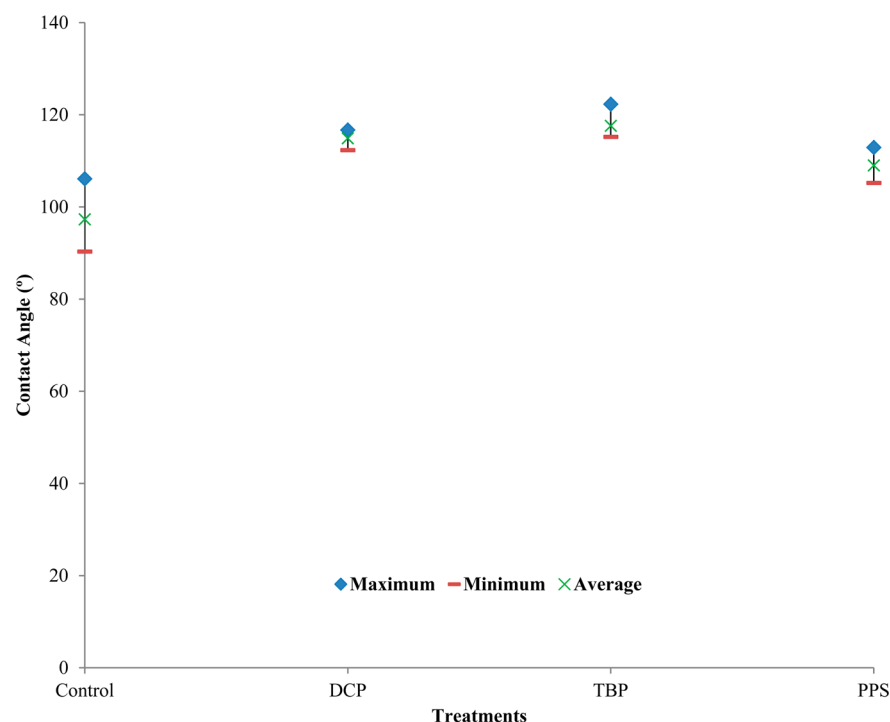


Figure 4. Effect of polymerization initiators used in the CVD polymerization of MMA on the contact angle of wool fabric surfaces.

Table 2. Color Strength of Fabric Samples Dyed with Terasil Red 3BL

sample id	initiators used	reaction time (mins)	color strength
control			0.25 (± 0.03)
1	TBP	30	2.08 (± 0.07)
2	TBP	60	2.25 (± 0.12)
3	TBP	120	4.58 (± 0.15)
4	DCP	30	2.08 (± 0.10)
5	DCP	60	2.19 (± 0.08)
6	DCP	90	2.23 (± 0.11)
7	DCP	120	2.26 (± 0.05)
8	DCP	30	2.00 (± 0.10)
9	PPS	60	2.10 (± 0.07)
10	PPS	90	2.10 (± 0.15)
11	PPS	120	2.14 (± 0.08)

absorbed, they cannot be held inside the fiber because no bonding is possible between wool fibers and disperse dyes. On the other hand, if the fiber has a hydrophobic polymeric coating, then at high temperatures, the coated polymer is swelled and allows disperse dye molecules to enter into the fiber where they are held inside the polymer by hydrophobic–hydrophobic interaction and also by van der Waals force. Table 2 shows that all wool fabric samples coated with PMMA by using various initiators for different times absorbed Terasil Red 3BL dye to levels higher than that of the control wool fabric, and the color strength increased with increasing monomer exposure time. The higher color strength indicated that coatings were progressively becoming thicker with time. The thickest coatings were produced by the TBP initiator as the color strength for 120 min exposure increased to 4.58 and the second best initiator was DCP. PPS showed the poorest performance as the color strength produced by the PMMA coating using PPS was low compared to the color strength showed by the coating produced using TBP and DCP. The

thicker the PMMA film was, the more it absorbed dyes and therefore the color strength increased. The results indicate that PMMA thin film was successfully produced on the surfaces of wool fabrics.

3.5. ATR FT-IR. Figure 5 illustrates the ATR-FTIR spectra of control wool and wool fabrics coated with PMMA polymer. The bands at 1550 and 1600 cm^{-1} represent the characteristic amide ($>\text{C}=\text{O}$) absorption band of wool keratin. The absorption band of atactic homopolymer appears at 750 ($-\text{CH}_2$), 1730 ($>\text{C}=\text{O}$) and near 3000 cm^{-1} ($>\text{CH}_3\text{O}$). It is reported that thiol groups in the wool keratin are the main sites of grafting and therefore the absorption spectrum of C–S–C should appear.⁴⁵ It can be seen that the absorption of C–S–C is present in the range of 600–750 cm^{-1} . The spectral bands at 668 and 741 cm^{-1} can be attributed to C–S–C and indicates the grafting site as expected. The weak band at 899 cm^{-1} ($\text{C}=\text{CH}_2$) indicates that thiols are not the only grafting sites; beta-secession of the keratin macromolecular chain also produces grafting sites.⁴⁵ The IR band at 1730 cm^{-1} can be attributed to carbonyl ($>\text{C}=\text{O}$) groups which is visible for the control wool and also wool coated with PMMA, but the intensity of the band at 1730 cm^{-1} for PMMA-coated wool is much higher than that of control which means that PMMA was covalently bonded to the backbone of wool keratin.⁴⁶ The two new doublet bands at 1140 and 1190 cm^{-1} (not available in control wool) for the PMMA-coated wool correspond to C–O stretching vibrations of ester groups of poly(methyl methacrylate).⁴⁷

3.6. Surface Morphology. SEM is an excellent tool to observe the surface morphology of fibers/fabrics. Wool fibers have characteristic scales that have an important role in protecting wool from damage but cause shrinkage and felting.⁴⁸ Figure 6 shows SEM micrographs of the control and the wool fabrics treated with PMMA using TBP initiator. It was clear that the surface characteristics of wool fabric samples coated with PMMA by CVD polymerization were quite different from the control wool fabric sample. Figure 6a showed that in the case of

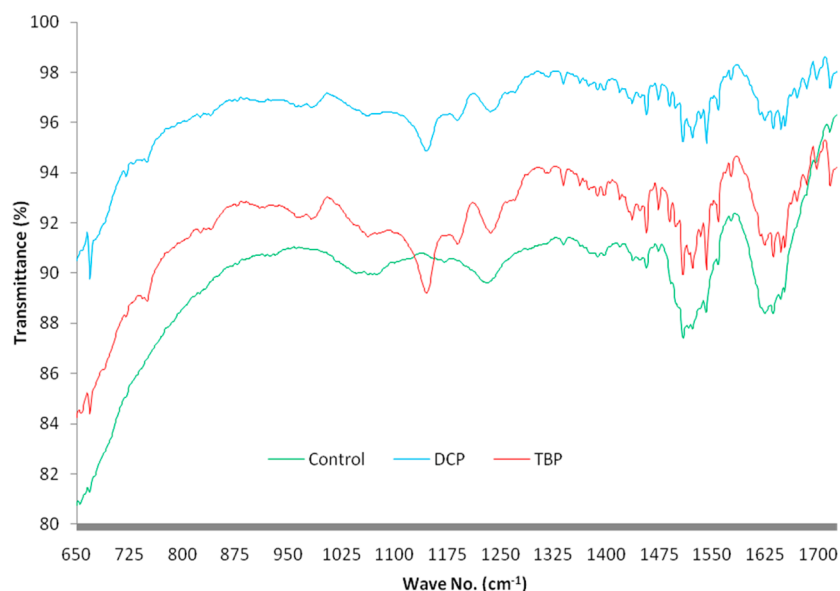


Figure 5. FT-IR spectra of control and wool fabrics coated with PMMA by the CVD polymerization using TBP and DCP initiators.

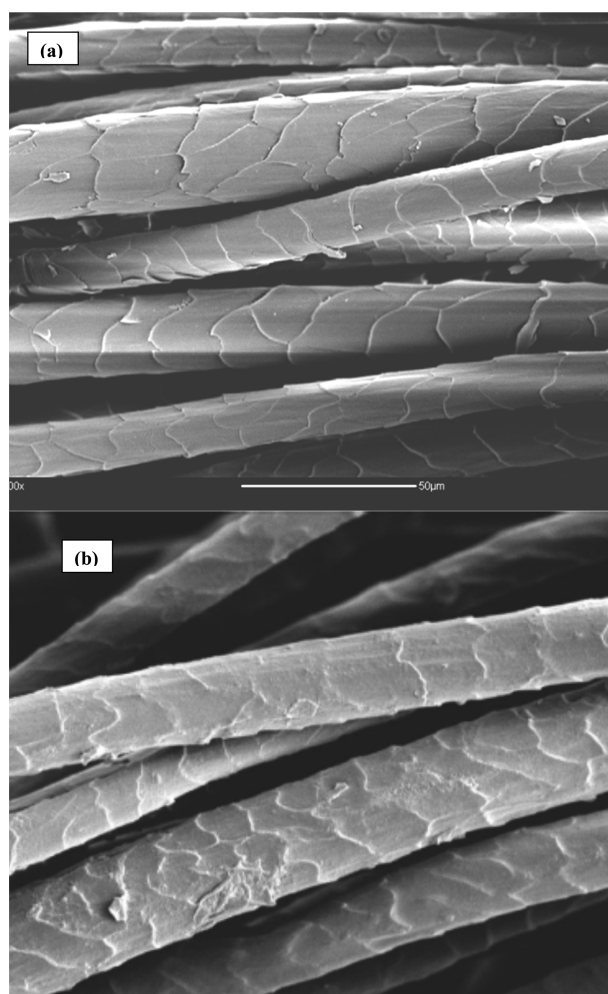


Figure 6. SEM images of control wool fiber and wool fiber coated with PMMA by CVD polymerization using TBP initiator. (a) Control wool fabric and (b) wool fabric coated with PMMA. Both of the images are at the same scale.

control treatment, the typical scaly structure of wool was visible but scale edge was not well-defined in the SEM image as the fabric used here had been chlorinated. The scales were damaged and some fragments were dislodged from the scales but no visible damage in the structure of fibers occurred. Figure 6b showed that in the case of PMMA coated wool fabric sample, the typical scale pattern of the wool fiber surfaces of the control wool fabric was slightly diminished and no structural damage was visible. It is evident that PMMA polymer smoothly coated the surfaces of wool fabrics, but scaly structure is still visible, which indicates that the thickness of the formed PMMA film is quite thin.

3.7. Surface Topography. AFM is an excellent tool to observe the topography of fibers/fabrics, which provides us three-dimensional images of surfaces with both lateral and vertical resolution. Figure 7 shows the topographic images of control and PMMA-coated wool fabrics at scale edge. It is evident that there are significant differences in edge profile between the control and the PMMA-deposited wool fiber surfaces. In the case of the control, the edge of the scale was somewhat perpendicular to the length of the fiber and there were several grooves lengthwise along on the edge of the scale. As the control fabric was chlorinated, damage on the surface of scales is apparent. On the other hand for PMMA-coated fiber, the typical scale structure was not visible and the backfilling of the scale with polymer made the edge not perpendicular to the length but made a curve and no grooves were visible as they were covered by PMMA coating. We measured the thickness of the PMMA coating from the AFM image profile, and calculated that it could be 0.3–1.0 μm . We also tried to measure the thickness of PMMA coating by an ellipsometer but were unsuccessful to measure as no signal was coming from the control and the treated wool fabric surfaces. The analysis of the topographic images confirms the existence of a polymer coating on the surface of wool fiber and is consistent with the SEM images.

4. CONCLUSIONS

We demonstrated that coating of wool fabric surface by CVD polymerization of MMA monomer can be carried out at its

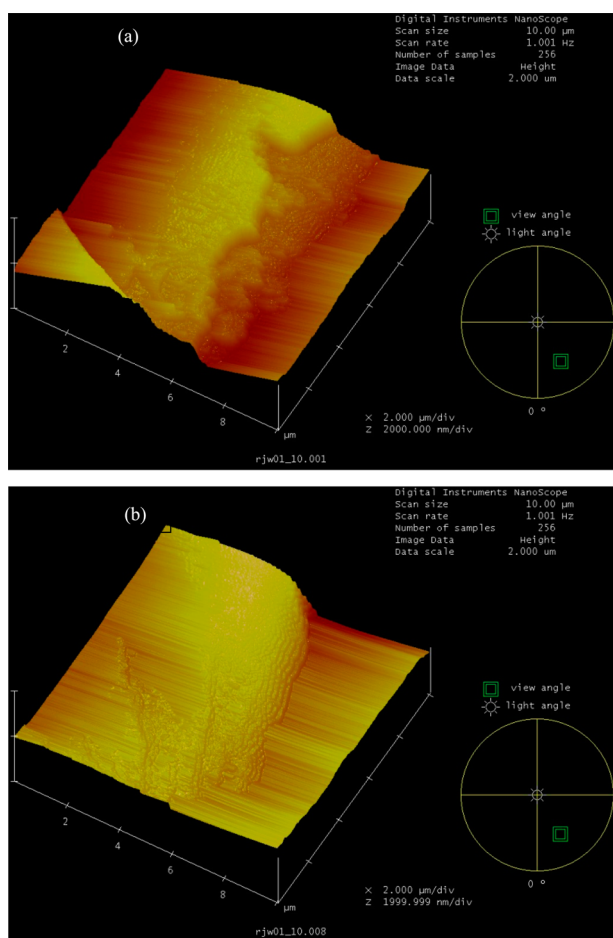


Figure 7. AFM image of cuticle edge of control wool fiber and wool fiber coated with PMMA by CVD polymerization using TBP initiator. (a) Control wool fiber and (b) wool fiber coated with PMMA.

boiling temperature under vacuum. Elemental analysis showed that the chemical composition of wool fibers changed after the deposition of PMMA by the CVD polymerization using different initiators. The color strength of the untreated dyed wool with Terasil Red 3BL was only 0.25 but for the wool fabric exposed to MMA vapor with polymerization initiated by TBP, for 120 min followed by dyeing with Terasil Red 3BL, the color strength increased to 4.58. The treatment with PMMA significantly increased the hydrophobicity of wool fabric surfaces. SEM analysis showed that wool fiber surfaces were smoothly coated with thin films of PMMA and ATR-FTIR spectra confirmed the presence of PMMA on the surfaces of treated wool fabrics. The results obtained by the elemental analysis, contact angle measurement, SEM, AFM, ATR-FTIR and dyeing with a disperse dye indicate successful deposition of PMMA by CVD polymerization.

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Notes

The authors declare no competing financial interest.

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