Manuscript Details

Manuscript number	POC_2018_462
Title	Graft polymerization of wool fibre for improved functionality
Article type	Review Article

Abstract

Internal deposition of specific monomers into the wool structure can alter its physiochemical properties, such as, improving thermal and mechanical stability, or improving the chemical resistance. Wool has a number of functional pendant groups e.g., thiol, amino and hydroxyl with the ability to form bonds with various vinyl monomers. There are number of irradiation and chemical based methods for the initiation of the grafting including metal and non-metal ion oxidisers and hydroperoxides. In this review, the techniques that are available for the internal deposition of the different monomers into the wool structure were reviewed with a focus on the properties of the grafted wool, such as, the thermal stability and the chemical and mechanical properties. The major grafting mechanisms are summarized and the effect of important parameters on the grafting reaction are discussed. These include time, temperature, pH and the concentration of grafting initiators and the monomers.

Keywords	wool grafting; monomers; polymerisation; reaction initiators
Corresponding Author	Amin Shavandi
Corresponding Author's Institution	University of Otago
Order of Authors	Amin Shavandi, Azam Ali
Suggested reviewers	Esmat Jalalvandi, Xungai Wang, Sudip Ray

Submission Files Included in this PDF

File Name [File Type]

Cover_Letter_Decemeber_01_06_2018.doc [Cover Letter]

Wool modifcation 08.docx [Manuscript File]

To view all the submission files, including those not included in the PDF, click on the manuscript title on your EVISE Homepage, then click 'Download zip file'.

Research Data Related to this Submission

There are no linked research data sets for this submission. The following reason is given:
No data was used for the research described in the article

University of Otago
PO Box 56
Dunedin 9054
New Zealand

Professor **Dean Webster**

North Dakota State University, Fargo, North Dakota, USA.

Editor-in-Chief, Progress in Organic Coatings

Sub: Submission of the review article titled "Graft polymerization of wool fibre for improved functionality" for publication in Progress in Organic Coatings

Dear Professor **Webster**

It is my pleasure to submit our review article titled, **"Graft polymerization of wool fibre for improved functionality"** for publishing in your well-reputed journal, Progress in Organic Coatings.

In natural polymers, wool, is one of the most commonly used fibre for incorporation into the synthetic polymers. The grafting process can add specific additional properties to the natural fibre without eliminating the intrinsic properties it has. This review focuses on the techniques that are available for the internal deposition of the different monomers into the wool structure. It focus on the properties of the grafted wool, such as, the thermal stability and the chemical and mechanical properties. The major grafting mechanisms aresummarized and the effect of important parameters on the grafting reaction are discussed.

This work has enormous scientific values, and is expected to draw strong attentions of materials, biomedical and mechanical engineers, professors and researchers working in the relevant fields.

I hope you will find our paper apt enough to be published in your journal, and will take necessary steps for publication of this paper.

With best regards

Amin Shavandi, Ph.D.
Bioengineering Research Team, Centre for Bioengineering and Nanomedicine,
Department of Food Science, University of Otago, Dunedin 9054, New Zealand
Email:amin.shavandi@otago.ac.nz

Graft polymerization of wool fibre for improved functionality

Amin Shavandi* [1], Azam Ali [1]

[1]Bioengineering Research Team, Centre for Bioengineering and Nanomedicine, Department of Food Science, University of Otago, Dunedin 9054, New Zealand.

Corresponding author email: Amin.shavandi@otago.ac.nz

Azam .Ali@otago.ac.nz

Abstract

Internal deposition of specific monomers into the wool structure can alter its physiochemical properties, such as, improving thermal and mechanical stability, or improving the chemical resistance. Wool has a number of functional pendant groups e.g., thiol, amino and hydroxyl with the ability to form bonds with various vinyl monomers. There are number of irradiation and chemical based methods for the initiation of the grafting including metal and non-metal ion oxidisers and hydroperoxides. In this review, the techniques that are available for the internal deposition of the different monomers into the wool structure were reviewed with a focus on the properties of the grafted wool, such as, the thermal stability and the chemical and mechanical properties. The major grafting mechanisms are summarized and the effect of important parameters on the grafting reaction are discussed. These include time, temperature, pH and the concentration of grafting initiators and the monomers.

Keywords: wool grafting; monomers; polymerisation; reaction initiators

Table of Contents

1   Introduction

Natural fibres, such as, wool have not been used to their full potential. There has been a growing interest for the production of new composite materials to replace the synthetic fibres with natural fibres, such as, wool. In addition to the obvious environmental benefits of these works, natural fibres are loaded with interesting properties that can lead to the generation of new products with improved mechanical and physiochemical properties. The potential of cellulose, for example, has been widely investigated for the production of polymer composites with various properties (Gürdağ and Sarmad 2013). Synthetic polymer reinforced composite usually showed higher mechanical properties compared to the base synthetic polymer materials. Examples are glass or Carbone fibre reinforced thermoplastic materials which have good mechanical properties (Mohammed, Ansari et al. 2015). The application of abundant and low-cost natural fibres in the production and development of new composite materials can also help to reduce the environmental concern regarding the disposal of these by-product fibres. Waste wool and poultry feathers are durable and chemically resistance materials that can stand the harsh environmental condition. Keratin as the base chemical structure of these materials has self-arrangement helical structures which provide the essential functional properties, such as, chemical, physical and mechanical properties (Martínez-Hernández, Velasco-Santos et al. 2007). Various synthetic polymers have been used as the base polymer for the addition of fibre. Some of the most commonly used polymers include polypropylene, polyethylene, polystyrene, and other thermoplastic materials. In natural polymers, wood fibres, silk, kenaf, rice and corn starch, pineapple leaf, henequen fibres and sago are the most commonly used fibres for incorporation into the synthetic polymers (Kubo and Kadla 2005, Yu 2009).

1.1   Importance of grafting

Polymer grafting is a common technique to increase the compatibility of the natural polymers with the synthetic polymers. Natural fibres are inexpensive, low density and biodegradable, have good mechanical and thermal properties, and do not have abrasive properties. Nevertheless, natural fibres suffer from some drawbacks, for example, hydrophilicity and low thermal stability. This makes them incompatible with hydrophobic synthetic polymers and limits their wide industrial applications. In addition, Natural fibers tend to form and agglomerate during processing and have a finite length (Martínez-Hernández, Velasco-Santos et al. 2007). Since they have hydrophilic surface properties this also imparts a lack of good adhesion to base polymers which consequently results in a loss of strength. To overcome this issue, various surface modification techniques, such as, alkali treatment, silane treatment, isocyanate, plasma, and peroxide treatment have been proposed and tried (Mitra and Saha 2008, Supri, Tan et al. 2011). The aim of the grafting process is to add specific additional properties to the natural fibre without eliminating the intrinsic properties it has (Martínez-Hernández Ana, Velasco-Santos et al. 2003). Using polymer grafting, it is possible to diversify and increase the application of the naturally abundant fibres, such as, wool. It is also possible to impart additional properties to the wool fibre by introducing other synthetic or natural polymer into the wool polypeptide chain without

suppressing the original characteristics it has (Martínez-Hernández Ana, Velasco-Santos et al. 2003). This introduction of polymers into the internal structure of wool can improve its properties including the tensile properties, hygroscopicity, chemical resistance, thermal stability and the durability it has (Martínez-Hernández Ana, Velasco-Santos et al. 2003). The surface modification of the natural fibres via grafting has become an interesting technique to improve the naturally poor characteristic of the natural fibres. In addition, to improving the compatibility of the natural fibres with synthetic fibres through grafting, some other characteristics including dimensional stability, yellowing, repellence of oil and water and fibre resistance to rubbing can also improve using the grafting method (Archanamoni and Saikia 2000, Tsukada, Md. Majibur Rahman Khan et al. 2011). The internal deposition of different polymers into wool may change the tensile properties, felt abrasion, shrinkage, hygroscopicity, durability, bacterial, chemical and pilling resistance and thermal stability it has (Giri and Samal 1991, Sarac 1999). This work presents an updated review of the various physical and chemical methods of grafting onto wool fibres.

2   Process of grafting and different grafting techniques

The fundamentals of grafting onto wool is based on the formation of the radicals onto wool and the polymerization of the monomers on the selected fibres. These free radical sites can be produced through hydrogen abstraction from the thiol, amino or hydroxyl groups of the wool. The generation of the free radicals on the surface can be conducted using physical or chemical methods, such as, the redox system, high-energy irradiation, or low energy irradiation in the presence of a sensitizer. The use of powerful oxidizing agents, such as, through the use of ceric ions is another method, which directly attacks the functional groups of the wool (Tsukada, Md. Majibur Rahman Khan et al. 2011).

Free radical sites can also be achieved using copper (II) complexes which form through complexation of bis (acetonyl-acetonato) copper (II) with tri chloroacetic acid or ammonium tri chloroacetate (Hebeish and Bendak 1974). Free radicals can also form on the wool backbone using permanganate and periodate under a so-called catalytic influence (Hebeish and Bendak 1974).

Chemical and radiation methods have been major grafting techniques that have been tried with varying degree of success (Table 1). In any event, unwanted simultaneous homopolymer formation during the reaction can have an adverse effect on the purification of the graft. Therefore, it is important to choose a proper initiating method for the graft copolymerization that leads to selective grafting.

Given that high-energy radiation can cause the degradation of the polymer backbone, chemical methods have been preferred over radiation-induced grafting. The oxidation-reduction method has been documented as an efficient chemical method for grafting which can selectively generate grafting sites on the wool polypeptide backbone and therefore it has a low incidence of homopolymerization (Table 2) (Martínez-Hernández Ana, Velasco-Santos et al. 2003).

Using oxidation-reduction technique, the side reactions are minimum and the process is carried out under a mild condition. More importantly using the oxidation-reduction method, selective initiation

sites are generated on the polypeptide backbone (Misra and Sood 1982). The thiol groups on the cysteine amino acids followed by the NH and OH groups are the preferred reactive sites for the grafting sites (Misra and Sood 1982).

2.1   Microwave and gamma rays radiation

The polymerization reaction can be activated using the microwave (MW) or gamma-ray radiation (Xu, Bao et al. 1998). Using irradiation, various vinyl monomers have been grafted (Xu, Bao et al. 1998) to a diverse range of natural and synthetic polymers, such as, cellulose (Kubo and Kadla 2005, Yu 2009). However, little attention has been paid to applying MW or gamma-ray radiation for the grafting of the monomer onto the wool.

Comparing the microwave heating with the conventional heating for the grafting of the monomer on to wool, Xu et al, (Xu, Bao et al. 1998), reported a higher yield of grafting using the MW (35%) compared to the normal heating (25%). This phenomenon can be due to the uniform distribution of heat using the microwave. The microwave intensity of the 260-400 Watt was also reported as the optimum powder, and the unwanted homo polymerization was observed at the higher intensities (Xu, Bao et al. 1998). In addition, using the MW the monomer and the catalyst are heated at the same time. The temperature of the solution increases more rapidly using MW compared to the conventional heating which can also improve the grafting process. Burke et al. (Burke, Kenny et al. 1962), showed that the fibre weight increased by 27% after using the trapped radicals in the irradiated wool to graft acetonitrile.

 The amount of polymerization is related to the dose of irradiation (Burke, Kenny et al., 1962). Styrene and acrylonitrile grafted to the wool using the irradiation method. The authors found that swelling agents, such as, water and methanol are necessary for the grafting process, which enable the diffusion of the monomer in the active centres of the wool created by the irradiation process. In this regard, water was more effective than methanol and a maximum of 200% styrene grafting and 60% poly acrylonitrile grafting were achieved while 6.1% water was used at the 5 MRads irradiation dose. The better performance of the water can be due to the higher hydrogen bonding capacity of the water molecules which can facilitate the diffusion process of the monomer (Stannett, Araki et al. 1965). The grafted wool fibre showed hydrophobic properties and a considerable decrease in relation to the water drainage of the modified wool fibres (Williams, Stannett et al. 1966).

2.2   The role of thiourea in the grafting reaction

Thiourea and N-substituted thiourea can be used as redox components for the initiation of the aqueous vinyl polymerization. These reducing agents and hydrogen peroxide as an oxidant agent have been used for the initiation of the aqueous polymerization of the acrylonitrile (Hebeish and Bendak 1974).

Thiourea has also been used with other oxidant agents, such as, ferric chloride (Fe^{3+}), ethylene dibiguanide complex salts of tri positive silver (Ag^{3+}), hydrogen peroxide and persulfate for the

initiation of the aqueous polymerization of methyl methacrylate. The named redox systems have been reported to be effective for initiating the vinyl polymerization (Hebeish and Bendak 1974).

In an early study, the graft copolymerization of the methyl methacrylate (MMA) onto the wool fibres using V^{5+}-thiourea redox system was reported (Hebeish and Bendak 1974). The grafting yield was significantly higher (50%) in the presence of thiourea compared to the absence of thiourea. The authors also reported a direct relationship between the concentration of thiourea and the yield of the monomer grafting, and 0.0075M was reported as the optimum concentration for the thiourea, while higher concentrations were found to be detrimental.

2.3 The role of ceric ions

Ceric ion as a redox initiator has been widely used in the graft copolymerization of the vinyl monomers onto cellulose, poly vinyl alcohol and starch (Hebeish and Mehta 1968). Given that wool is a natural protein, it has different functional groups, such as, sulfhydryl, hydroxyl, amino, imino, and disulphide linkages and it can be considered as a material that has a high potential for the grafting of vinyl monomers using ceric ion. Ceric ion can also form complexes with groups, such as, OH, NH_2, SH, COOH, SS and imino, all of which are present in wool. If the ceric ion is present, NH_2 and OH provide active sites for grafting. All of these groups can also enter into a redox reaction with ceric ions. The complexes that form can then decompose and will result in macro radicals on the backbone of the wool (W·) where the vinyl monomers can be grafted (Misra, Sood et al. 1982).

Misra and Chandel (Misra and Chandel 1977) grafted poly methyl acrylate onto wool using a ceric ion initiator in the presence of nitric acid at various concentrations. The degree of grafting was dependent upon the temperature, acid concentration, monomer and ceric concentration. A reaction temperature of 45°C was reported to be suitable for grafting, and a higher temperature resulted in a sticky wool, while the sample processed at 45°C retained the natural white colour of the wool sample.

Grafting increased with increasing the ceric concentrations and a maximum grafting of 270% was achieved in the presence of 9mmol/L ceric ion and 0.18 mol/L nitric acid after a three hours reaction at 45°C (Arai, Shimizu et al. 1973). A similar trend has been reported for starch, however, since the increase in the grafting of wool is higher than in starch, because wool has different functional groups, which facilitates the complex formation with ceric ions, and therefore, a greater grafting was observed for wool compared to cellulose and starch. It is worth noting that ceric ion alone is not capable of effecting graft copolymerization, and grafting only occurs while the nitric acid is also present. In another study, Arai et al., grafted vinyl monomers onto wool using the $K_2S_2O_8$-Br- system (Arai, Shimizu et al., 1973). Formation of a considerable amount of homopolymer was observed during the grafting of poly (methyl methacrylate) onto wool in the presence of ceric ion (Kantouch, Abdel-Fattah et al., 1972).

2.4 Effect of mineral acids and salts in grafting

The presence of acid can help with the scission of wool disulphide bonds which leads to the production of more available thiol groups and consequently higher grafting is predictable. The production of new radical centres upon chain scission was observed by William and Stanett who studied the grafting of ethyl acrylate onto wool in water (Williams and Stannett 1968). In low acid concentrations, the fast thiol – disulphide bond interaction, prevents the disulphide bond scission.

Given the role of acid ions and pyridine, grafting does not occur in the absence of either pyridine or acid. The maximum grafting of 38% was observed at the reaction temperature of 60°C and a decrease in grafting occurred at a higher temperature probably due to the accelerated termination process (Chandel and Misra 1977). The catalysing effect of mineral acid for the grafting process has also been reported by other researchers (Kenyon and Garnett 1973, Garnett and Kenyon 1977) using benzoyl peroxide as an initiator, Chandel et al., grafted polystyrene onto the wool. A mixture of acidic acid-pyridine was also used as a pH modifier. The concentration of acetic acid, pyridine, the monomer, BPO, and temperature of reaction were reported as important for the grafting reaction. It has been also observed that, the percentage of grafting increases with the increase in the acid concentration from 0.5 to 1 M and it increases at a higher acid concentration (Chandel and Misra 1977). Acid is required during the grafting process using metallic ions. Varying the concentration of perchloric acid from 0.2 to 0.8M, while the percentage of grafting initially increased as the acid concentration is increased to 0.5M, it decreased at higher acid concentrations. In high acid concentrations, the acid anion can form a complex with the monochromate ion and by reducing its oxidising power it will result in a reduction in the grafting yield. Similar to previous studies, the higher temperature had a positive effect on the grafting yield as the temperature increased up to 55°C (Nayak, Lenka et al. 1979, Nayak, Lenka et al. 1980). In parallel to the previously reported studies on the importance of acid addition, Garnett et al. (Mitra and Saha 2008), indicated that addition of 0.2N H_2SO_4 can lead to a tenfold increase in grafting. The acid concentration also plays an important role in the grafting process and the rate of oxyanion reaction depends on the acid concentration. It was reported by Nayak et al. (Nayak, Lenka et al. 1980), that along with increasing the acid concentration up to 0.15 mole/l, the grafting yield increases. The presence of nitric was also found to promote the grafting, however, the exact role of nitric acid is not clear (Sood, Singha et al. 1983). Nitric acid can catalyse the process of copolymerization. The low concentration of nitric acid can swell the wool fibre and promote the accessibility of the functional groups for grafting. However, at a high concentration, it can oxidise the initiator, such as, Iron(II) acetylacetonate and $FeII(acac)_2$, into Fe^{3+} and therefore terminate the grafting process (Misra and Rawat 1984). The reactivity of the mineral acid also has effects on the yield of the grafting. In this regard, H_2SO_4 has the highest reactivity, followed by $HClO_4$ and HNO_3.

The presence of certain salts, such as, KCl, NaF, Na_2SO_4, $MgSO_4$ can also increase the yield of grafting. Salt crystals can catalyse the propagation step and increase the efficiency of grafting. Nayak et al.,

observed an increase in the grafting yield with increasing the $CuSO_4$ concentration up to 0.39M, which can be due to the role of Cu^{2+} in the formation of wool macro radicals and the creation of a free radical's species. However, a further increase in the salt concertation reduced the grafting probably due to its role as a free radical scavenger and therefore terminated the free radicals in the solution. The nature of hydrolysis using either acid or alkalis are due to the catalysis of the water either by acid hydrogen or alkali hydroxyl ion. Wool keratin has ampholytes and contains both acidic and basic groups, therefore, it uses strong acids, such as, hydrochloric acid which at a low pH of 1 can lead to swelling and to the dissolution of the protein (Elangovan and Saccubai 1992).

3   The role of grafting reaction initiators

3.1.1   *Metal chelating ions*

Metal ions, such as, quinquevalent vanadium ion (V^{5+}) can suppress the homopolymerization and reduce the formation of homopolymer during the grafting of the vinyl monomer onto wool. Increasing the concentration of the V5+ initiator from 0.005 to 0.02 M can also lead to the progressive increase of the grafting. In addition to V^{5+} (Nayak, Lenka et al. 1978), and V^{5+} redox system (Nayak, Lenka et al. 1978), hexavalent chromium was also investigated for the initiation of the graft copolymerization of methyl methacrylate onto the wool fibres. With the increase in the concentration of Cr(VI) from 0.005 to 0.035 M the rate of grafting increased from below 10% to above 25%.

In a system containing perchloric acid and MMA, Cr (VI) in reaction with the wool form macro radical, can react with a vinyl monomer and form graft copolymer on the fibre backbone. The initial increase in grafting yield can be due to the presence of Cu^{2+} ions near the wool which favours the grafting (Nayak, Lenka et al. 1979).

3.1.2   *Benzoyl peroxide (BPO)*

It has been reported that if BPO is used as an initiator in the graft copolymerization of the cellulose and the starch, the reaction was seldom selective and it has had limited success, due to the formation of a considerable amount of homopolymer (Gürdağ and Sarmad 2013).

However, in the case of wool, it is different, as it has a number of functional groups which permit the formation of a large number of active sites on the polymeric backbone. Therefore, the homopolymer formation in the case of the wool is not to the extent to prevent the grafting onto the wool.

The maximum grafting of 38% achieved using 0.005mole/L of BPO as the initiator. By using a higher BPO concentration, the percentage of grafting decreases which can be due to the chain transfer with the solvents, cage recombination, chain transfer with monomer or formation of homopolymer because of the growing radical related to the monomer (Gürdağ and Sarmad 2013).

Wool is a polymer made of amide units, this polyamide structure has many functional groups, which are embedded in its rigid structure and therefore are not readily accessible for grafting. Given this close structure, wool pre-treatment is required for successful grafting. Pre-treated wool can swell which makes the inner functional groups available to the surface where the reaction is commenced. BPO alone

was reported to be ineffective in initiating the graft polymerization reaction, and the presence of hydrogen ions was helpful for the initiation of the grafting (Abdel-Fattah, Shalaby et al. 1977).

3.1.3 *Peroxydiphosphate and peroxydisulfate*

Peroxydiphosphate was also used as an initiator for the copolymerization of the MMA onto the wool (Nayak, Lenka et al. 1980). It was observed that by increasing the peroxydiphosphate concentration up to 80×10^{-4} Mole/L, the grafting yield increases while with a further increase the yield of grafting drops. While increasing the peroxydiphosphate concentration, the radicals, such as, $H_2PO\cdot$, $OH\cdot$, and $HPO\cdot$ increase which can interact with the wool backbone and give rise to free radicals at several sites. This process initiates grafting and therefore increases the grafting yield.

The Higher increase of the oxidant concentration can terminate the grafted chain and the oxidant can react with the growing free radicals and increase the oxidation product. Additionally, there is a possibility of the formation of homopolymer which could have a negative impact on the rate of grafting. In another study, Nayak et al. (Nayak, Lenka et al. 1980), used peroxydisulfate catalysed by silver ions to graft methyl methacrylate onto wool fibers. Peroxydisulfate, while coupled with monovalent silver ion, is reported as a better initiator compared to peroxydisulfite alone, as the Ag^{2+} produced during the reaction is a powerful initiator. Parameters, such as, monomer concentration, peroxydisulfate ion, thiourea, the temperature and the solvent were reported to be important on the rate and yield of grafting, and in all cases, the grafting yield increased to a certain point with an increase in the mentioned parameters.

In terms of the interaction of the wool along with the effect of the polymers on its water adsorption ability, Leeder et al. (Leeder, Pratt et al. 1967), observed that the polymerization of the polyacrylamide and poly acrylic acid resulted in increased water uptakes. This could be due to the hydrophilic nature of these polymers. Wool has amino, hydroxyl, carboxyl and guanidine groups which have reactive hydrogen atoms and are able to react with reagents, such as, acid chloride, acid anhydride, and isocyanates. Electrostatic forces along with hydrogen and disulphide bonds held together the amino acid chains of the wool molecule. These compact and complex structures usually stop the penetration of large molecules and only a few small molecules can penetrate. Using vanadyl acetyl acetonate, methyl methacrylate grafted onto wool fibre, the authors (Leeder, Pratt et al. 1967), recorded a higher yield of grafting at a higher temperature of up to 55°C. This higher grafting can be due to the easier formation of the acetylacetonate radicals along with increased solubility and enhanced diffusion rate of the monomers.

Fructose is another good reducing agent, which can produce free radicals in the solution. Nayak et al., in another study evaluated the graft copolymerization of methyl methacrylate onto wool using the peroxydiphosphate-fructose redox system (Samal, Sahu et al. 1984). There was a significant increase in grafting that was obtained by increasing the fructose concentration of up to 7.5×10^{-4} mol/L. In addition, the higher monomer concentration was also beneficial for grafting, and increasing the monomer concentration up to 65.72×10^{-2} mol/L increased the yield of the grafting.

3.1.4   Role of styrene in copolymerization

Using the ionising radiation technique, styrene can be successfully grafted onto wool with little homopolymerization. For this purpose, the styrene needs to be dissolved in a swelling solvent, such as, methanol (Dilli, Garnett et al. 1972). Nevertheless, this technique is not applicable to other monomers, particularly acrylates, because the high amount of copolymer formation occurs and prevents the successful wool grafting. Garnett et al. showed that if styrene is used as one of the monomers in the mixture, then it is possible to achieve wool grafting using a simultaneous irradiation method (Garnett and Kenyon 1977). Therefore, incorporation of styrene, for example, with ethyl acrylate results in a successful grafting with a minimum formation of unwanted homopolymer. In addition, at high ratios of ethyl acrylate/styrene of 5 to 1 (w/w), the graft was mainly (87%) consisting of ethyl acrylate (Garnett and Kenyon 1977). If styrene is not present in the mixture, the homopolymerization of ethyl acrylate would be dominant or virtually no copolymerization can occur (acrylonitrile). Homopolymer formation on the wool backbone during the grafting process is a major drawback that is very difficult to remove using normal solvent extraction techniques.

3.1.5   Bromide salts

Bromide salts have fibre swelling properties, in particular, bromide salts of ammonium or proteinaceous materials, such as, wool, gelatine, and silk can easily adsorb alkali metals. In this regard, Li^+ salts result in the highest wool fibre hydration and swelling properties followed by Na^+ and K^+ salts (Negishi, Arai et al. 1965). Dissolving a small amount of persulfate in a concentrated solution of bromide salts, such as, LiBr result in the liberation of Br^2. In order to dissolve water-insoluble vinyl monomers, in a solution containing bromide and persulfate, the addition of a solvent compatible with the salt solution and the redox system is required. Negishi et al., performed a series of preliminary studies and diethylene glycol monobutyl ether was selected as the optimum solubilizing agent. Even though sodium and ammonium bromide were found to be efficient for the polymer grafting, the low water solubility of these salts compared to LiBr is the main limitation for their application in the grafting. Comparing LiBr, LiCl and LiI, LiBr showed a significantly better grafting yield (Negishi, Arai et al. 1965).

Looking into the end group incorporated into the polymer, and evaluating the amino acid composition of the grafted polymer and the kinetic of the grafting reaction, Arai et al. suggested that the polymer was grafted onto the wool fibre through covalent bonds. These bonds formed with the protein chains through some amino acid residues, such as, cysteine and tyrosine. Using an initiating system of LiBr–potassium persulfate or benzoyl peroxide methanol, grafting sites selectively occurred to be on a low sulphur protein chain. The maximum number of grafting sites were reported to be approximately two moles per low sulphur protein molecule with 48kDa molecular weight (Arai and Hagiwara 1980). The wool fibre structure does not denaturize chemically during the grafting process. During grafting, wool is physically modified and acquires specific properties so the proteins can interact with the polymer chains. Regardless of the amount of the polymer that might deposit on the wool fibre, the concentration of the disulphide groups remained unchanged in the fibre.

4 Effect of various parameters on the grafting process

4.1 Effect of reaction time and temperature on grafting

Graft copolymerization of different monomers onto wool has been studied at various temperatures (room temperature up to 80°C) for less than an hour up to more than 18 hours (Tsukada, Shiozaki et al. 1997, Anbarasan, Kalaignan et al. 1999, Monier, Nawar et al. 2010, Ranjbar-Mohammadi, Arami et al. 2010). It has been widely reported that the yield and the efficiency of the grafting have increased by increasing the reaction temperature. This improvement in the percentage of grafting can be due to activation of the backbone of the wool where the grafting sites are generated. Higher temperature also increase the rate of monomer diffusion and mobility into the wool matrix where the grafting sites are present (Giri, Nanda et al. 1989). The swellability of the fibre also increases by increasing the temperature, increase the monomer solubility, improve the rate of initiation and the propagation of the graft (Kantouch, Abdel-Fattah et al. 1972). In spite of the very high temperature of 80°C recommended by some studies (Hebeish and Bendak 1974), a temperature of around 50°C has been widely reported as the optimum grafting temperature (Nayak, Lenka et al. 1978, Nayak, Lenka et al. 1979, Nayak, Lenka et al. 1981). Besides, the high temperature of above 60°C can result in faster homopolymerization compared to copolymerization which is not desired (Liouni, Touloupis et al. 1992).

While the reaction of grafting normally initiates instantly and without any delay, on prolonging the reaction time this process becomes slower.

Due to the advancement of the grafting, the concentration of both monomer and initiator decreases, and consequently the number of available sites on the wool fibre backbone drops as the grafting proceeds. Therefore, it is necessary to increase the contact time to promote the possibility of further grafting. In addition, the grafted polymer on the fibre surface might act as a barrier and prevent the diffusion of the monomer and initiator inside the fibre and therefore prevent the grafting progress (Kantouch, Abdel-Fattah et al. 1972).

4.2 Effect of type of monomer and its concentration on grafting

In addition to the methyl methacrylate, the grafting of the other monomers, such as, ethyl acrylate and methyl methacrylate on to the wool were also evaluated by the authors and the reduction in the grafting was observed by the increase in the size of the monomers (Nayak, Lenka et al. 1978, Nayak, Lenka et al. 1978, Nayak, Lenka et al. 1980).

Therefore, methyl acrylate with the smallest monomer showed the highest grafting and reactivities followed by ethyl acrylate, then methyl methacrylate and finally n-butyl acrylate (Nayak, Lenka et al., 1978, Nayak, Lenka et al. 1978, Nayak, Lenka et al. 1980). Thus, with the increase in the monomer size, the diffusion of monomer to the available sites on the fibre reduces and the grafting yield decreases. Changing the monomer concentration from 5 to 11% and keeping all other reagents constant, the graft percentage increased by increasing the monomer concentration to above 100 after four hours reaction

time. The higher monomer concentration is favoured for the complexation of the wool along with the monomer. In addition, the higher monomer concentration results in a solution with higher viscosity and forms a gel, which can hinder the termination of the grafting reaction by the coupling of the growing polymer chains. The formed gel also results in the swelling of the wool which facilitates the diffusion of the monomer into the wool's backbone and active sites for grafting. The grafting percentage also increased with the increase in the wool content from 0.1 to 0.6 g. This trend indicates that the polymerization of the MMA takes place on the wool matrix (Nayak, Lenka et al. 1978). The formation of a charge transfer complex between oxidant and monomer at high monomer concentration might increase the grafting. The other reason could be gel formation due to the high viscosity of the medium that improves the diffusion of the monomer into the wool backbone. This gelling effect also causes the swelling of the wool fibre, which enhances the diffusion of the monomer to the active sites of the wool backbone and the growing chain. There are also some species that are generated or are present during the copolymerization reaction which are acting as efficient radical scavengers. Therefore, at a higher monomer concentration, the monomer dominates the media and is able to better capture the wool radicals compared to the radical scavenger species. Depending on the type of monomer, the rate of grafting can be variable. Monomers with bulky side chains result in a low yield in terms of grafting because the bigger monomers have a lower capability of diffusion compared to the active sites on the fiber (Liouni, Touloupis et al. 1992). Wool grafted with a low (32-36%) percentage of the polymer showed similar or lower tensile properties compared to the control wool, while samples with a 270% uptake of polyethyl acrylate were reported to be very elastic with a complete immediate recovery from the extension of up to 230% (Williams and Stannett 1968). The grafting of different monomers on wool, such as, MA, MMA, EA, AA, butyl acrylate (BA), styrene (St) and vinyl acetate (Vac) have been evaluated (Misra, Sood et al. 1982). While a mixture of monomers VA and MA is used for grafting on the wool, a lower percent of grafting (90%) is observed compared to the grafting of MA alone (271%), therefore, the presence of VA can have a negative effect on the grafting of MA. Vinyl acetate is a weak monomer for grafting with poor reactivity. This could be due to the high tendency of VA to undergo a monomer transfer reaction. Therefore, the monomer is wasted in the side chain reactions (Misra, Sood et al. 1982). Misra et al., reported MMA with the highest reactivity, followed by EA, BA, MA, and VA (Misra, Sharma et al. 1982). MMA is more reactive compared to EMA as well, this higher grafting ability of MMA can be due to its higher polymerization ability, therefore, MMA is able to produce more grafted polymeric chain and generate more active sites on wool fibre compared to EMA (Misra and Rawat 1984). Elangovan and Saccubai observed that grafting at a low percentage of up to 15% does not provide resistance or protection for the wool fibre against acid solubility. In fact, the degradation and wearing of the fibre might enhance the acid dissolution. However, as the percentage of grafting increased, the grafted fibres were resistant to the acid solubility and polymer chain backbone and the free amino acid side chains were protected against hydrolysis condition (Elangovan and Saccubai 1992).

In many studies, the methyl methacrylate monomer has been widely used for grafting on to the wool fibre however little work has been performed concerning the addition of wool to the poly methyl meth acrylate (PMMA) polymer. PMMA has a wide application, nevertheless, the polymer is rigid and so the addition of the keratin fibre can help to improve its mechanical properties.

With the use of 2,2-azobis(isobutyronitrile) (AIBN) as a reaction initiator, up to 5% of the keratin fibre was grafted on to PMMA. Given the hydrophobicity of the keratin fibre a good fibre polymer interaction and distribution of the fibre within the polymer structure was observed and the viscoelasticity and the thermal properties of the keratin grafted PMMA was higher than the control PMMA (Martínez-Hernández, Velasco-Santos et al. 2007).

4.3   Grafting of antibacterial agents onto wool

The production of antibacterial wool through grafting antibacterial materials e.g., silver onto wool has been evaluated by some studies (Wang, Hou et al. 2007, Ranjbar-Mohammadi, Arami et al. 2010). Using plasma treatment, Wang et al., activated the surface of the wool fibre followed by grafting Ag-loaded nano-SiO_2. The antibacterial agent concentration of the treatment suspension increased from 0.05g/50ml to 0.5g/50ml in this study. The Nano silver particles dispersed well on the surface of the wool fibres as the particle concentration increased up to 0.25g/50ml and in the higher concentration the particle became agglomerated on the surface, which could be due to the high surface energy of the particles.

The grafted wool showed the antibacterial efficiency of more than 80% for the tested *E.coli* and *S.aureous* (Wang, Hou et al. 2007). In another study (Xu, Niu et al. 2007), Ag loaded silver nanoparticles were grafted on to the wool fibre through the photo grafting method. In this study, the wool fibres were exposed to ultraviolet light before impregnating in the antibacterial solution under UV irradiation. Molecular valence was suggested as the attachment method of the antibacterial layer on the fibre surface. A homogeneous distribution of the particles was observed on the surface of the fibre and the measured content of the Nano particles on the fibre surface was 0.69 wt.% which was twice as high as mentioned earlier in the report by Wang et al. and the material showed a good antibacterial activity even after 30 washing times.

Chitosan also grafted on to wool using succinic anhydride which showed antibacterial and anti-felting properties (Ranjbar-Mohammadi, Arami et al. 2010). The acylation of the wool samples was performed in DMSO and DMF. Although both solvents are dipolar aprotic with a moderate hydrogen bonding tendency, a higher wool weight was observed for the samples treated with DMSO compared to DMF. This better performance of DMSO can be due to the higher dielectric constant and the dipolar moment of DMSO compared to DMF (Ranjbar-Mohammadi, Arami et al. 2010). Having a higher dielectric constant can also reduce the electrostatic attractive forces within the wool fibre and promote the penetration and diffusion of solvent into the fibre (Koenig 1977) and with an improved resistance to

alkali, acids and an oxidizing condition were reported for the acylated wool fibres (Koenig 1977). Depending on the properties of the fibre, such as, steric and morphological properties, different anhydrides were used for the fibre acylation. Anhydrides with bulkier side chains will result in a slower reaction and the presence of electronegative groups can promote the rate of reaction (Ranjbar-Mohammadi, Arami et al. 2010). Up to 3% of chitosan grafted onto wool and a maximum weight gain value of 8.5% was observed for the chitosan-grafted samples at a reaction pH of seven.

After grafting chitosan onto wool using succinic acid as a crosslinker, the same research group tried to reduce the time and efficiency of the process using the ultrasonic power for grafting chitosan on acylated wool (Ranjbar-Mohammadi, Hajir Bahrami et al. 2013). A 10% weight gain due to chitosan grafting was obtained during 1h, which was significantly faster than an 18 hour reaction time that was recorded in their previous study to obtain a 8.5% weight gain. Chitosan grafted wool showed antibacterial properties with a higher moisture gain and lower shrinkage compared to the control wool. Anbarasan grafted polyaniline onto the wool fibre and compared the electro conductivity of the pure wool (0.0012 ohm^{-1} cm^{-1}) and the grafted polymer (120 ohm $^{-1}$ cm^{-1}) (Anbarasan, Kalaignan et al. 1999).

Transglutaminases enzymes can cross-link proteins and increase their stability by forming covalent bonds between glutamyl and lysyl residues. TGases were used to graft functional compounds or proteins into wool fibres and therefore, changes the functionality of the wool fibre and generates the new potential for its applications. Cortez et al., grafted silk sericin protein onto the wool fibre using TGases. In this reaction, the silk protein was mainly attached to the wool cuticle and to a lower degree cortex was involved in this grafting process. An improved softness, shrink resistance and fibre strength was observed for the silk grafted wool samples (Cortez, Anghieri et al. 2007).

4.4 Effect of wool treatment and reaction reagents in grafting

The physical or chemical modification of the wool has an effect on its grafting ability. Reduction, esterification, and trinitrophenylation can change the behaviour of wool during grafting. Nayak et al. reported the reduced wool as the most reactive material, followed by unmodified wool, esterified wool, and trinitrophenylated wool. Wool treated with thioglycolic acid is reduced and has more available thiol groups (-SH), due to the breakage of disulphide bonds (-S-S-) in cysteine molecules. Therefore, a higher graft yield can be obtained using the reduced wool. Nevertheless, other treatments, such as, acetylation and trinitrophenylation reduce the grafting ability of the wool. These modifications block the amino hydroxyl and thiol groups on the wool and therefore, the grafting decreases due to the lack of free radicals on the wool backbone (Nayak, Lenka et al. 1978, Nayak, Lenka et al. 1979). Acetylation and trinitrophenylation also reduce the swelling ability of the wool fibre and can prevent the adsorption of MMA molecules. Given that the swelling property of the wool has an important effect on the yield of grafting, therefore, the solvent used for the reaction is important. Nayak et al. (Nayak, Lenka et al. 1978), reported that a higher grafting yield was achieved using formic acid as the solvent compared to

dimethylformamide and tetrahydrofuran. The better effectiveness of formic acid compared to dimethylformamide, ethanol, n-propanol, and tert-butanol also reported (Nayak, Lenka et al. 1979).

The physical structure of the fibre is important on graft copolymerization. Additionally, the conformation of the fibres is of importance, especially, the availability of thiol groups is favourable for the grafting of the vinyl monomers onto the wool (Chandel and Misra 1977).

The reduced wool showed the highest rate of grafting followed by oxidised wool, untreated wool, cross-linked wool and finally trinitrophenylted wool. The higher grafting percentage of reduced wool might be due to the reduction of the cysteine disulphide bond of the wool and the increase in the number of thiol groups (-SH) which act as the active centres for grafting. The abstraction of the hydrogen from the thiol groups by initiating radicals is easier compared to the abstraction of hydrogen from the amino and hydroxyl groups in the wool molecule (Nayak, Lenka et al. 1980). The selection of the most suitable solvent for the grafting polymerization of MMA onto wool fibre is of importance, and various solvents can be used for this purpose. Nayak et al., found dioxin to be the optimum solvent for the grafting, following by acetone, methanol, hexane and chloroform. The effectiveness of the solvent depends on the ability it has to cause the wool to swell and its miscibility with the monomer. The activation of the wool and the termination of the graft chain radical both contribute to the other important roles of the wool (Nayak, Lenka et al. 1980). The chemical modification of the wool was achieved effectively with the use of hot pyridine (Nayak, Lenka et al. 1980). However, other organic liquids can facilitate the internal modification of the wool. Reagents, such as, Dimethyl sulfoxide, dimethylformamide (DMF), 1- methyl-2-pyrrolidinone and 4-butyrolact were used effectively for the modification of the wool and for the grafting of different polymers on to wool. Compared to pyridine, these liquids are less toxic, do not have an offensive odour, are less expensive and have a lower vapour pressure which allows chemical modification at a temperature higher than 90°C with a lower danger of toxic gases and explosion (Koenig 1977).

The main role of the reaction reagent is to provide an electro donating medium. In this regard, solvents, such as, DMF, tetrahydrofuran (THF) and dioxane with a 70-110 cm^{-1} electron donating power are suitable (Yoshikuni, Saito et al., 1980). Despite the availability of a number of reagents for the chemical modification of wool, DMF has often been often used as the medium of choice to achieve a rapid reaction and the desired reaction. Although Dimethyl sulfoxide is the most reactive of the reagents for the modification of wool with low toxicity, it can penetrate the skin and there is the possibility of carrying the dissolved chemicals with it to the skin (Koenig 1977). Given the structure of the wool fibres, the penetration of large molecules is prevented, therefore, the reagent medium should have a low molecular weight in order to penetrate into the wool and modify it. In addition, the reagent should not have hydrogen atoms, which can react with acylation agents. Having said that, some common swelling agents, such as, water, ethanol and formic acid are deemed to be inappropriate. The polarity of the medium is also of importance. A medium with high polarity can reduce the electrostatic attractive forces within the wool molecules. Therefore, a high dielectric constant can promote the medium in penetrating

the keratin structure. A proper reagent medium should have the ability to swell the wool, for this reason, a reagent medium with a low molecular weight and high polarity can help to promote the swelling of wool and the rate of wool modification reaction can be controlled with the rate of swelling.

Having a high boiling point is also important for the solvent, because if the reagent is volatile, therefore, it would not be possible to get a temperature high enough to break the salt linkages, hydrogen bonds and other noncovalent forces that restrict the penetration of the reagent.

Chemical treatment, such as, formylation, acetylation, and trintrophenylation blocks active radical sites on the wool and makes them inaccessible for the grafting reaction. These modifications also reduce the capacity of the wool to swell and therefore reduce the capacity of the wool as it relates to the adsorption of the monomer (Samal, Sahu et al. 1984).

Different reducing agents, such as, alcohols, thiols, ketones or acids have been used along with various oxidizing metal ions with variable charges including Mn, Ce, V, Co, Cr and Fe. Using potassium permanganate for the polymerization of acrylamide, acrylonitrile, vinyl acetate and methyl methacrylate Manganese dioxide is produced as a result of the reaction between the monomer and the permanganate. The produced manganese oxide reacts with reducing agents and generate Mn (III) ions, which are very reactive and consequently react with the reducing agent and produce free radicals in the aqueous medium. Different acids, such as, tartaric, citric, malic and lactic can be used to produce free radicals to initiate the grafting polymerization (Martínez-Hernández Ana, Velasco-Santos et al. 2003).

If wool is treated with thioglycolic acid (TGA), the reduced wool swells which facilitates a radical attack on the wool structure. Even though, the reduction of the wool does not necessarily result in a better grafting yield and prolonged treatment with TGA at high concentration does not promote grafting but also TGA remains in a wool structure which acts as a chain transfer agent (Misra, Mehta et al. 1980). While other techniques, such as, sulfation and oxidation reduce the thiol groups. Sulfation and oxidation, oxidise cysteine along with serine, threonine, and tyrosine residues. For this reason, the reduction has been widely reported as the preferred method of wool modification for grafting (Niezette, Geurts et al. 1981). Graft copolymerization onto reduced wool is significantly higher than other named modification techniques (Negishi, Arai et al., 1967) and graft copolymerisation increases significantly by the reduction of the disulphide bonds to thiol groups (Negishi, Arai et al., 1967). The degree of wool reduction also has effects on the molecular weight of the grafted polymer.

Niezette and co-workers compared different wool modification methods for grafting methyl methacrylate. Large differences were observed between the reduced wool and the samples treated with other techniques. A poor grafting tendency was observed for acetylated wool, while oxidised, sulphated and S-carboxymethylated wool samples recorded a lower grafting compared to the natural wool. The improved swelling properties of the wool fibre because of the treatment techniques were deemed to be of low importance for grafting. Nevertheless, the importance of amino groups was significant and S-amino ethylated samples showed the second best grafting yield after reduced wool (Niezette, Geurts et

al., 1981). Treatment of wool with potassium cyanide resulted in the conversion of disulphide to lanthionine bonds and the content of thiol groups also increased during this process.

If wool is treated with TGA, the acid attacks the intermediate filament (IF) and the matrix proteins in the hydrophobic region of the keratin and result in the decrease of SS groups and their conversion into cysteic acid and cysteine groups by splitting the SS bonds. L-cysteine, on the other hand, disrupts the SS cross-links associated with the non-helical segments of IF (Ogawa, Fujii et al. 2008).

Similar to TGA, tributyl phosphate (TBP) reduces the intramolecular and mechanically ineffective SS linkages of the wool fibre in the hydrophobic regions (Naito and Arai 1996). Disulphide bonds are composed of covalent cross-links which form a 3-dimensional network structure with high crosslink density. The SS bonds can be classified in two groups of intermolecular linkage group comprised of SS1 (35%) and SS2 (18%) and an intramolecular group of SS3 (47%). It is reported that SS1 and SS2 are located in the microfibril and matrix. The SS2 is more hydrophilic and accessible to water and the SS1 linkage situated within the more hydrophobic part of the matrix. Given that the hydrophilic monomer solubilizes in the aqueous solution, achieving a high yield of grafting is difficult. In an aqueous medium, radicals diffuse into the aqueous phase and so formation of homopolymer in the reaction media is preferable to grafting. In this case, the reduction of SS bonds to the SH bonds help to obtain a high polymer-grafting yield. The location of the disulphide bonds is another issue for achieving a high yield grafting. It has been reported that the pre-treatment of the wool with silane reagent of 3-mercaptopropyl tri-methoxysilane increases the yield of grafting. This grafting enhancement can be due to the introduction of SH groups and to initiate the radicals for the formation of the grafted polymer. By doing so, the rate of grafting reaction accelerated through two reactions. First, the reaction of the silane agent with the wool fibre and second, the formation of the radicals from the introduced SH groups. Using the MPMSi silane agents, the authors proposed this reagent reacts with OH and COOH groups of wool peptides (Kamshi and Arai 1996).

5   Effect of grafting on physicochemical properties of wool

In spite of the large number of tests carried out on the graft copolymerization onto the wool, copolymerized wool found little commercial attention or large scale application. One reason for this pause can be the complex and relatively difficult process of copolymerization on an industrial scale. Additionally, grafted wool showed little improvement in properties, which limits commercial investment.

While the grafted wool normally has improved mechanical properties, the main advantages that can make it commercially interesting would be the improved chemical properties, such as, chemical setting, improved thermal stability and dye fixation. Nevertheless, the success of the wool grafting process largely depends on the degree of improvement in the properties of the wool in relation to the economic feasibility of the copolymerization process. Grafting reduces the alkali solubility of the wool samples.

The grafted chain plays a barrier role for the diffusion of the solubilising agent, therefore, the polypeptide chain of the wool along with the salt and disulphide linkage that remains unbroken.

It has been reported that the thermal stability of the grafted wool remained relatively unchanged compared to the wool that had not been modified in most of the cases. The wool grafted poly sodium acrylate showed a slower rate of contraction and a slightly higher melting point, while the wool containing divinyl benzene had a lower thermal stability as a result of the rupture and break down of the disulphide bonds (Watt 1970). Looking into the mechanical properties of the grafted wool, Watt et al. (Watt 1970), reported higher torsional moduli for the grafted wool. In particular, the samples grafted with polydivinylbenzene introduce additional cross-linking into the wool structure. The elongation at break, tenacity and tensile modulus increased with the increase of the graft percent. This enhancement can be attributed to the formation of internal cross-linking of the wool fibre backbone as a result of the grafting of the MMA onto the wool fibres (Giri and Samal 1991).

Shrinkage, pilling resistance, abrasion, chemical resistance, thermal stability, hygroscopicity and the dying properties of wool can change after grafting. Different kind of polymers have been tried for grafting onto the wool, in particular, vinyl monomers, methacrylic esters and epoxide (Xu, Bao et al. 1998).

Depending on the degree of grafting, grafted wool might become mechanically weaker. Given that the fibre is subjected to high temperature and extreme acidic condition for a prolonged time, the peptide bond might be damaged and result in a reduction in the tensile strength of the sample. Owing to this harsh condition, the impairment in the tensile strength is expected. However, loading the fibre with the polymer can bring strength to the fibre (Giri and Samal 1991, Elangovan and Saccubai 1992). The polymer can fill the voids within the fibre. In addition, the reaction between the polymer and the functional groups of the fibre can also increase the strength of the fibre. During thermal analysis of the wool fibre, at about 180°C the generation of gases including H_2O, CO_2, NH_3, H_2S occurs as a result of the breakdown of peptide and disulphide bonds and result in the pyrolysis of the fibre. Disordering, degradation, and melting of keratin start at around 200°C. Tsukada et al. (Tsukada, Shiozaki et al. 1997), showed that by increasing the percent of benzyl methacrylate grafting, the endothermic peak related to alpha keratin degraded and shifted to the higher temperature of 240°C and the rate of degradation becomes slower. Samples grafted with 180% benzyl methacrylate only lost 10% of the weight when heated up to 300°C, while the control samples lost more than 35% when heated to the same degree (Tsukada, Shiozaki et al. 1997).
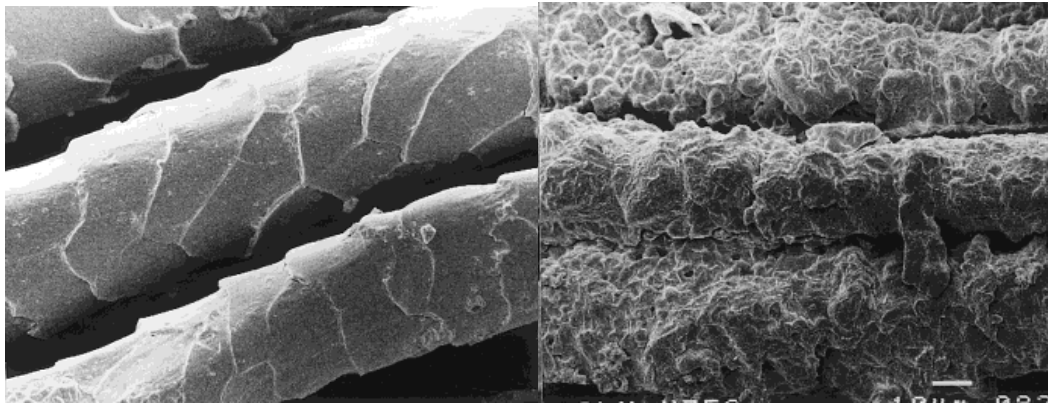
Figure 1. Untreated wool fibre and fibre treated with 180% of benzyl methacrylate (Tsukada, Shiozaki et al. 1997)

No difference in the moisture uptake of the grafted wool was also reported (Watt 1970). These findings suggest that the grafting of the wool has no effect on the moisture holding capacity of the wool. Nevertheless, wool samples modified with hydrophilic polyacrylamide or poly acrylic acid showed higher moisture adsorption compared to the control wool (Leeder, Pratt et al. 1967). Wool samples grafted with polystyrene also showed a lower diffusion of water compared to the control samples (Armstrong and Stannett 1966). Similarly, a decrease in water retention and in the moisture holding capacity of the wool was observed with an increase in the percent of grafting (Giri and Samal 1991). Given the hydrophobic nature of benzyl methacrylate, grafting wool with benzyl methacrylate resulted in a drastic reduction in moisture gain. Grafting with a hydrophobic polymer can mask the groups responsible for binding water or can play a role providing a barrier to block the diffusion of moisture. The presence of polymer can also interfere with the adsorption of moisture. The polymer grafting process can affect the alpha and beta crystallinity of the wool fibre. The onset of alpha keratin melting and thermal degradation increased after grafting and grafting with hydrophobic polymers was reduced by half the amount of alpha crystalline (Arai and Ishikawara 1982). This decrease in alpha form was significantly lower when hydrophilic polymer was used for grafting. It is noteworthy that the amount of beta form was not correlated with the changes in the amount of alpha form (Arai, Negishi et al. 1973).

6   Grafting mechanism

Free radical formation is fundamental to the grafting process onto wool. Reactions, such as, hydrogen abstraction from thiol, amino and hydroxyl groups of the wool result in the generation of the free radicals. Given that wool has different pendant functional groups, such as, OH, NH_2, SH, COOH, SS and imino, these free radicals can attach to the active sites of the wool fibre and produce grafting. However, these free radicals may also initiate the homopolymerization of the monomer in the media. Therefore, the selection of the grafting reaction initiator is of importance.

Some transitional metals can reduce the homopolymer formation during the grafting process. Quinquevalent vanadium (V5+) is one of the most effective metal ions which can effectively reduce the homopolymerization (Nayak, Lenka et al., 1978).
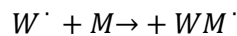
6.1.1 Metal ion redox systems

In a system comprised of metal ions (e.g. V^{5+}), wool and monomer, such as, MMA, an intermediate complex can be formed between metal ion and wool, which can, later on, dissociate and result in macro radicals of the wool. (eq 1)

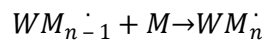$$WH + V^{+5} \rightleftharpoons complex \rightarrow W^{\cdot} + V^{4+} + H^{+} \qquad \text{(eq 1)}$$

The formed free radical on the wool then acts as an active site for the initiation of the grafting reaction, which is followed by the addition of the monomer that propagates in a conventional manner. (eq 2)

Initiation
$$W^{\cdot} + M \rightarrow + WM^{\cdot}$$

Propagation $\quad MW^{\cdot} + M \rightarrow + WM_1^{\cdot}$

$$WM_{n-1}^{\cdot} + M \rightarrow WM_n^{\cdot}$$

Termination

$$WM_n^{\cdot} + V^{+5} \rightarrow WM_{n+1} + H^{+} + V^{4+}$$
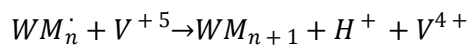
V^{5+} can also react with wool radicals and result in the production of the different oxidation products

$$W^{\cdot} + V^{5+} \rightarrow wool\ oxidation\ products + H^{+} + V^{4+}$$

The grafting reactions using other metal ions, such as, chromium (VI) are also similar to the equation 2 (Nayak, Lenka et al. 1979).

6.1.2 Metal ion-thiourea redox systems

In these redox systems, thiourea is sometimes used as the cocatalyst. Systems, such as, Fe^{3+}-thiourea, hydrogen peroxide-thiourea, Cr^{6+} or V^{5+}-thiourea have been examined for grafting monomers onto the wool structure.

In all thiourea containing systems, isothiourea, a thiol existing in tautomeric form is the redox component.

H_2N ... S → H_2N^+ ... SH ↔ H_2N ... $\overset{+}{S}H$

H_2N^+ ... SH + Cr^{6+} → H_2N^+ ... $S^{\cdot}$ + H^+ + Cr^{5+}

$$\left(R^{\cdot} \right)$$

H_2N^+ ... $S^{\cdot}$ + WH → $W^{\cdot}$ + H_2N^+ ... SH
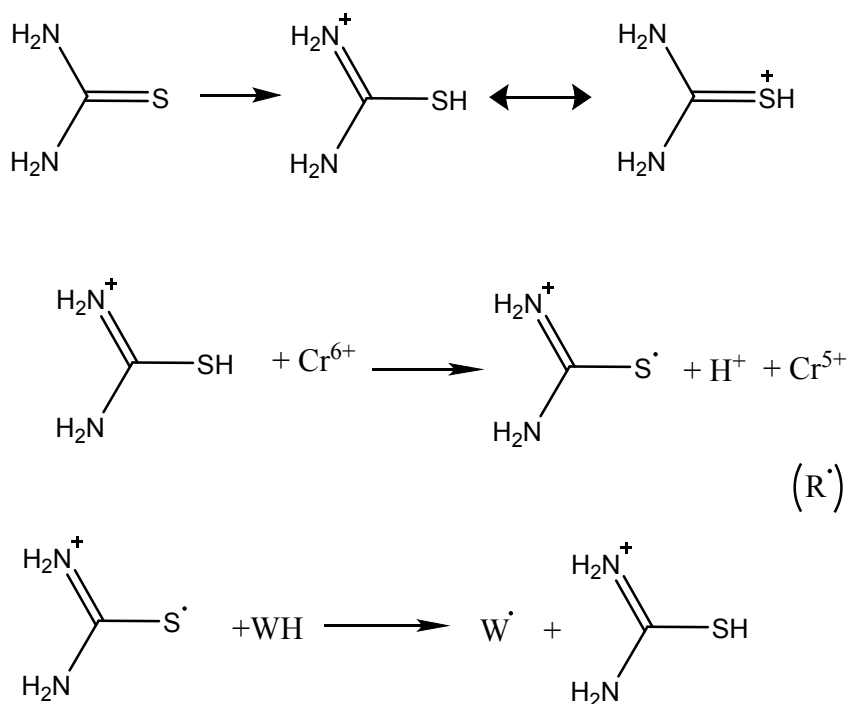
The isothiocarbamido radicals (R·) then abstract hydrogen from amino, thiol, or carboxyl groups in wool macro radicals, which initiate graft copolymerization (Hebeish, Abdel-Fattah et al. 1974, Hebeish and Bendak 1974, Nayak, Lenka et al. 1979).
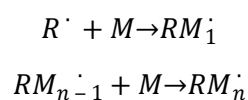
Therefore, polymerization onto wool can be initiated either by hydroxyl radicals, isothiocarbamido radical or both (Hebeish and Bendak 1974).

These isothiocarbamido radicals can also react with the monomer radicals and initiate homopolymerization (Nayak, Lenka et al., 1979).

$$R^{\cdot} + M \rightarrow RM_1^{\cdot}$$
$$RM_{n-1}^{\cdot} + M \rightarrow RM_n^{\cdot}$$

Given the complexity of the grafting reaction process, there is a number of variables that can affect the process and yield of the grafting. Using a reduced wool for the reaction with higher susceptibility to grafting under the action of thiourea can increase the grafting yield. In addition, the initiator efficiency for the generation of the macro radicals on wool is also important. Monomer solution and its diffuse ability on to the fibre structure, monomer adsorption on fibre, degree of homopolymerization in the solution, the potential of monomer to capture wool macro radicals and initiate copolymerization/propagation are other important parameters in the grafting reaction process (Hebeish and Bendak 1974).

6.1.3 *Metal ion-Thiourea-peroxydisulfate*

The polymerization of certain vinyl monomers can be initiated by peroxydisulfate ion. The peroxydisulfate ion can be coupled with metal ions, such as, monovalent silver ion for the purpose of generating a better reaction initiator.

The following reaction scheme might possibly occur:

$$S_2O_8^{-2} + Ag^+ \rightarrow SO_4^- + Ag^{2+} + SO_4^-.$$

$$SO_4^-. + Ag^+ \rightarrow Ag^{2+} + SO_4^{2-}$$

$$SO_4^-. + H_2O \rightarrow SO_4^- + \cdot OH + H^+$$
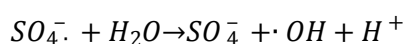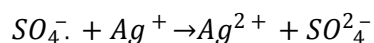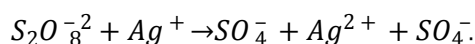
In the presence of thiourea

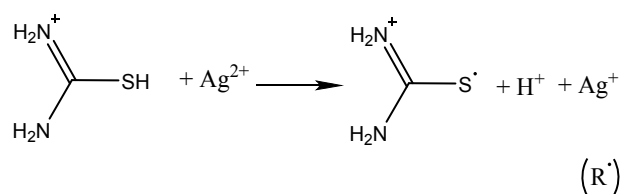The generated R·, HO· and SO4· can interact with the functional groups present in the wool backbone and generate macro radicals which can later react with monomer thorough initiation, propagation and termination reactions that have been described earlier and result in grafting (Nayak, Lenka et al. 1980). During the grafting process, the backbone of the base polymer, in this case, the wool remained intact while new groups and properties were added to the side chain of the polymer without changing the main properties. Grafted polymer might have higher thermal properties, hygroscopicity, antistatic properties, viscoelasticity, antibacterial, improve dye ability, soil resistance and many other properties which can increase the commercial value of the polymer fibre. Several reactions are involved in the grafting process. The first monomer needs to be solubilised in the reaction medium and diffuse in the fibre medium, then the monomer is adsorbed on the fibre and forms a complex with the wool molecules to enhance the reactivity of the monomer, followed by propagation and formation of graft on the fibre and enhancement of the activation of monomer. Temperature has a positive effect on all of these reactions and therefore, grafting yield improves with increasing temperature to a certain limit (Nayak, Lenka et al., 1980).

Thiol groups (-SH) play a definite role during the grafting of the MMA onto the wool by providing sites for grafting (Sood, Singha et al. 1983). Misra et al., studied the role of –SH and –SS groups in wool grafting. Thiol groups present on the cysteine aminoacids have been reported as the preferred sites for

grafting monomers by some researchers (Tsukada, Shiozaki et al. 1997, Sarac 1999, Martínez-Hernández Ana, Velasco-Santos et al. 2003).

The progress and development of the grafting process are depending on the presence of thiol groups in the wool fibre samples. Given the importance of thiol groups, the modification of wool fibres has to be performed in a way to increase the thiol groups. Using the reduction techniques, the thiol groups are increased as a result of a reduction in the cysteine bonds. The type of monomer and the selected condition for the grafting process determine the location of the graft chain and the interaction between the polypeptide chain of the wool fibre (Arai and Ishikawara 1982). Alpha crystalline fraction of the wool is comprised of two sections, one is very stable and suitable for grafting while the other section is unstable for grafting. Microscopic studies revealed that graft chains go into a weak aggregated region of micro fibrils (Arai and Ishikawara 1982). The unstable region is about half of the total alpha crystalline section and has a region with fewer side crosslinks.

7 Other wool modification methods

7.1 Acylation and acetylation

The successful grafting of the polymers on the wool surface depends on the characteristics of the surface. The surface properties and surface modification are important factors for the deposition of polymer on the wool surface. Chemical modification can introduce new physiochemical properties to the wool. The wool with improved functional properties can be used for the development of new products to meet the market demand. Grafting of monomers onto the wool has been the most common technique for the modification of the wool, as discussed in the previous sections. Nevertheless, usually large amount of monomers need to be grafted on the wool in order to impart a desirable effect. Apart from grafting, wool surface modification with some chemical agents can also result in a wool product with new and improved functional properties without damaging the wool structure, which does not require loading a large amount of polymer on the wool.

Acid anhydrides and epoxides have been widely used for wool surface modification. Wool fibres were first treated with di- and trifunctional epoxides by Tanaka and Shizaki, who reported on the enhanced shrink resistance and crease recovery for expoxide treated wool (Tanaka and Shiozaki 1982, Freddi, Tsukada et al. 1999). The authors reported on the reaction between the epoxide and the hydroxyl groups of tyrosine. In another study, a weight gain of up to 18% and acyl content of 140 mol/105g were obtained when the wool samples were treated wool with succinic, glutaric and itaconic anhydrides for 2 hours at 65°C (Tanaka and Shiozaki 1982). Functional groups on the wool surface, such as hydroxyl, phenol, and amine are the most important groups involved with the reaction. The crystalline structure, elongation at break and tensile properties of the wool samples remained unchanged after acylation (Tanaka and Shiozaki 1982). The high affinity of the acylated wool for cationic dye was reported as the remarkable change in the wool samples. This change can be due to the introduction of the extra acidic group in the fibre.

Acylation can improve the molecular motion within the wool polymer chain by interfering with the inter and intramolecular hydrogen bonds within the wool structure in both the amorphous and alpha crystalline region resulting in decreasing the glass transition temperature. Nucleophiles which are present in the side chains of some aminoacids, such as, amino, a guanidyl, hydroxyl, imidazole, phenolic, free sulfhydryl groups and carboxyl are the reactive sites for the dibasic acid anhydrides (Freddi, Innocenti et al. 2003). The alpha crystalline of the wool has two regions of high and low cross-linked structure. Freddi et al. (Freddi, Tsukada et al. 1999), suggested that the anhydride molecules diffuse and penetrate into the less cross-linked structure and by reacting with the reactive sites result in structural changes and the local disordering of the keratin chain. The reaction of the anhydride molecules changes the thermal stability of the α helix region. The appearance of an endothermic peak at 213-220°C in the DSC graph of wool samples treated with succinic or glutaric anhydride confirm the

destabilization of the α helix (Tsukada, Shiozaki et al. 1990, Freddi, Tsukada et al. 1999, Arai, Freddi et al. 2001).

The appearance of an endothermic peak in the range of 220°C is related to the melting of α helical structure of the microfibrillar proteins, while beta crystalline microfibrillar melts in the range of 250 – 270°C (Sakabe, Miyamoto et al. 1982).

In another study, silk and wool were acylated with acid anhydrides; dodecenyl succinic anhydride (DDSA) and octadeceny lsuccinic anhydride (ODSA), using DMF or DMSO as the solvent. The endothermic peak related to the melting of the α helix observed at 232°C which become broader in the treated wool samples. In addition, a shoulder also appeared at a lower temperature indicating the presence of α helices with lower thermal stability. The alteration of the inter and intramolecular region of the amorphous alpha helix was reported to be responsible for improving the molecular motion of the non-hydrogen bond section (Arai, Freddi et al. 2001).

The bimodal melting peak at around 230-240°C can be described by the helix/matrix hypothesis. According to this hypothesis, the low-temperature peak denoted to the melting of the alpha helices in the intermediate filaments and the peak at higher temperature indicate the degradation of the matrix where the filaments are embedded. In another hypothesis known as ortho/para, the low and high-temperature peaks denoted to the melting of alpha-helical structure in the ortho and paracortical cells, respectively (Spei and Holzem 1987, Wortmann and Deutz 1998, Freddi, Innocenti et al. 2003). In support of the later theory, specific and distinct melting peaks reported for isolated ortho and para cortical cells. Given the heterogeneous structure of wool, which is composed of a hierarchical complex structure, it is not easy to correlate the overall recorded thermal changes to a specific fraction of the polymer (Freddi, Innocenti et al. 2003).

In spite of the destabilising effect of acylation on the structure of the α helix, the reaction of wool with epoxide make it more thermally stable (Tanaka and Shiozaki 1982, Tsukada, Nagura et al. 1991). Tanaka et al (Tanaka and Shiozaki 1982) reacted wool samples with 1, 3-bis (2, 3-epoxy-1-propoxy) benzene. The authors reported that hydroxyl groups of amino acids, such as, histidine, lysine, arginine, serine, tyrosine, cystine, aspartic and glutamic acids react with the epoxides.

Wool samples treated with isocyanates and di isocyanates and the following reaction between the amine and hydroxyl groups of the wool and the isocyanate compound suggest the following:

$$Wool - OH + R - NCO \rightarrow Wool - O - CO - NH - R$$

$$Wool - NH2 + R - NCO \rightarrow Wool - NH - CO - NH - R$$
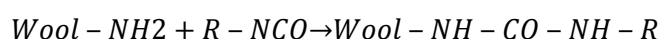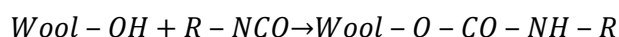
R is the side chain group of the isocyanate.

Comparing the DMF and DMSO solvents for the reaction of isocyanates with wool, a significant extent of fibre swelling was observed when DMSO was used as the solvent. The remarkable ability of the DMSO for the swelling of the protein fibres enhances the diffusion and penetration of the reactant into

the fibre matrix. Having said that, a faster reaction of anhydrides and isocyanate is expected using dipolar aprotic solvents, such as, DMSO. DMSO is a dipolar aprotic solvent frequently used for the reaction of isocyanates, as well as acid anhydrides, with protein fibres. DMSO has the ability to induce a remarkable extent of fibre swelling.

7.2 Plasma treatment

Plasma treatment using a gaseous discharge is a relatively inexpensive and safe surface treatment technique. Plasma is used for cleaning the surfaces or to help the deposition of polymers onto the surface. Given the simple operation procedure and being free from chemicals, plasma has attracted wide application which can replace the conventional wet chemicals techniques. Concerning protein-based materials, plasma treatment enhances the functionality of the surface by generating active radicals through the oxidation of the protein. Given that the plasma only impacts on the surface, the bulk characteristic of the wool materials was not damaged and remained intact. The oxidation of the wool surface by the plasma treatment results in the removal of the hydrophobic lipid layer from the surface. In addition, plasma oxidises the disulphide bonds on the surface and consequently, the surface area of the wool increased. The formation of functional groups on the surface improves the ability to bond various polymers/coating on the wool surface (Höcker 2002). Canal et al. (Canal, Gaboriau et al. 2009), deposited antibacterial polymer on the wool surface for a wound dressing application, after applying the plasma treatment. Given the availability of various plasma treatment techniques, it is not easy to compare the reported results from different studies and compare the outcomes of different research groups. Nevertheless, an improvement in the hydrophilic ability and surface oxidation are usually reported after the plasma treatment (Meade, Caldwell et al., 2008). Improving the hydrophilicity of the wool material can be desirable, enhancing the dye ability and wettability of the fibre and enhancing the comfort of the final product. It is also possible to deposit hydrophilic polymers, such as, acrylic acid on the surface of plasma treated fibre (Kutlu, Aksit et al. 2,010). Increased dye ability and colour intensity were also observed while the plasma treatment is combined with chitosan coating (Ristić, Jovančić et al., 2010). Corona discharge and hydrogen peroxide (HP) treatment can increase the wettability of the wool. The scale of wool fibre breaks after the treatment and therefore, the surface properties of the wool change and the treated wool shows better interaction with water (Wang, Zhao et al., 2015). Comparing the HP and corona discharge treatment for the surface modification of the wool, a higher surface temperature and longer drying process were reported for HP treated wool sample due to the improved moisture holding ability of the wool samples. Corona discharge and HP can also combine. Part of the wool scales etched after the corona discharge which consequently peeled off after the HP treatment resulting in the improved hydrophilicity of the treated-wool fibre. Variation of treatment voltage and a number of treatment passage were also effective in improving the hydrophilic properties of the wool fibres (Wang, Cao et al., 2009). Plasma treatment of cashmere wool followed by coating with fluorocarbon resin (FCR) studied by Zanini et al., in order to produce hydro and oleo repellent fibre. A

uniform coverage of FCR on the plasma-treated-wool fibres was obtained compared to the non-treated sample (Zanini, Freti et al., 2016). Similar uniform coating results were reported while chitosan was used as the coating agent for wool (Shahidi, Ghoranneviss et al., 2015). Chitosan treatment of wool fibre after plasma treatment was also reported to be beneficial improving the dying and shrink proofing properties of the wool fibre (Şahan, Demir et al., 2016). The gas uses for plasma treatment can have an effect on the surface properties of the treated wool. Nitrogen has been reported as the most effective gas improving the dye ability of the wool using acid dyes. Followed by a mixture of nitrogen /oxygen and, oxygen and argon. the authors indicated that nitrogen gas introduces new NH_2 group onto the wool surface and therefore, enhances the wool dying ability (El-Zawahry, Ibrahim et al. 2006). In another study, oxygen was found to be the most effective gas for wool plasma treatment to enhance the moisture adsorption ability of the wool. This is followed by oxygen, argon, and nitrogen. Part of this discrepancy in the result might be related to the various treatment conditions, such as, the treatment time and voltage (Jeon, Hwang et al., 2015). The effect of using oxygen as the plasma treatment gas on the surface morphology and the physiochemical properties of wool was studied by Barani and Calvimontes. Using oxygen plasma the wool samples were treated at the various time of 2.5 and 5 minutes, the roughness of the surface increased while the scale edges also became sharper due to the etching effect of the plasma treatment. The removal of the surface lipid and the oxidation of the cysteine in the exo cuticle was observed for the plasma-treated wool samples. The authors suggested that the alpha crystalline structure of the wool disrupted and the amorphous region transformed to the beta structure (Barani and Calvimontes 2014).

8   Conclusion

Grafting of monomers into the wool has been the most common technique for the modification of the wool. Polymer grafting can change and improve the physical and chemical properties of the wool. The wool with improved functional properties can be used for the development of new products to meet the market demand. Grafting offers wool processors a wider scope to diversify their products depending on the demand from the consumer.

References

Abdel-Fattah, S. H., S. E. Shalaby, E. A. Allam and A. Hebeish (1977). "Benzoyl peroxide-induced graft polymerization of 2-methyl-5-vinylpyridine onto polyester/wool blend." Journal of Applied Polymer Science **21**(12): 3355-3365.

Anbarasan, R., G. P. Kalaignan, T. Vasudevan and A. Gopalan (1999). "Characterization of Chemical Grafting of Polyaniline onto Wool Fiber." International Journal of Polymer Analysis and Characterization **5**(3): 247-256.

Arai, K. and K. Hagiwara (1980). "Grafting onto wool: 9. Alpha and beta forms in keratin-polymer system." International Journal of Biological Macromolecules **2**(6): 355-360.

Arai, K. and M. Ishikawara (1982). "Structure-dynamic mechanical properties relationship of the grafted wools." Sen-i gakkaishi: 60-70.

Arai, K., M. Negishi and T. Okabe (1968). "Infrared spectroscopy of graft polymers separated from graft copolymers of wool and silk with methyl methacrylate." Journal of Applied Polymer Science **12**(12): 2585-2596.

Arai, K., M. Negishi, T. Suda and S. Arai (1973). "Grafting onto wool. III. Relationship between alpha- and beta-forms in wool keratin of grafted fibers." Journal of Applied Polymer Science **17**(2): 483-502.

Arai, K., M. Shimizu and M. Shimada (1973). "Grafting onto wool. IV. Interaction of polymer radicals in the viscous media of wool fibers." Journal of Polymer Science: Polymer Chemistry Edition **11**(12): 3271-3281.

Arai, T., G. Freddi, R. Innocenti, D. L. Kaplan and M. Tsukada (2001). "Acylation of silk and wool with acid anhydrides and preparation of water-repellent fibers." Journal of Applied Polymer Science **82**(11): 2832-2841.

Archanamoni, D. and C. N. Saikia (2000). "Graft copolymerization of methylmethacrylate onto non-mulberry silk-Antheraea assama using potassium permanganate-oxalic acid redox system." Bioresource Technology **74**(3): 213-216.

Armstrong, A. A. and V. Stannett (1966). "Temperature effects during the sorption and desorption of water vapor in high polymers. I. Fibers with particular reference to wool." Die Makromolekulare Chemie **90**(1): 145-160.

Barani, H. and A. Calvimontes (2014). "Effects of Oxygen Plasma Treatment on the Physical and Chemical Properties of Wool Fiber Surface." Plasma Chemistry and Plasma Processing **34**(6): 1291-1302.

Burke, M., P. Kenny and C. H. Nicholls (1962). "28—FREE RADICALS IN γ-IRRADIATED WOOL : A ESTIMATION AND RÔLE IN POLYMERIZATION OF ACRYLONITRILE." Journal of the Textile Institute Transactions **53**(8): T370-T378.

Canal, C., F. Gaboriau, S. Villeger, U. Cvelbar and A. Ricard (2009). "Studies on antibacterial dressings obtained by fluorinated post-discharge plasma." International Journal of Pharmaceutics **367**(1–2): 155-161.

Chandel, P. S. and B. N. Misra (1977). "Grafting onto wool. II. BPO-initiated grafting of polystyrene." Journal of Polymer Science: Polymer Chemistry Edition **15**(7): 1549-1554.

Cortez, J., A. Anghieri, P. L. R. Bonner, M. Griffin and G. Freddi (2007). "Transglutaminase mediated grafting of silk proteins onto wool fabrics leading to improved physical and mechanical properties." Enzyme and Microbial Technology **40**(7): 1698-1704.

Dilli, S., J. L. Garnett, R. S. Kenyon, E. C. Martin, D. H. Phuoc, Y. Yen and J. D. Leeder (1972). "Radiation-Induced Reactions with Cellulose. XI. Comparison of Cellulose with Wool and Polyethylene as Trunk Polymers in Copolymerization." Journal of Macromolecular Science: Part A - Chemistry **6**(4): 719-744.

El-Zawahry, M. M., N. A. Ibrahim and M. A. Eid (2006). "The Impact of Nitrogen Plasma Treatment upon the Physical-Chemical and Dyeing Properties of Wool Fabric." Polymer-Plastics Technology and Engineering **45**(10): 1123-1132.

Elangovan, V. J. and S. Saccubai (1992). "Chemical and mechanical properties of methyl methacrylate-grafted wool fiber." Journal of Applied Polymer Science **44**(12): 2179-2183.

Freddi, G., R. Innocenti, T. Arai, H. Shiozaki and M. Tsukada (2003). "Physical properties of wool fibers modified with isocyanate compounds." Journal of Applied Polymer Science **89**(5): 1390-1396.

Freddi, G., M. Tsukada and H. Shiozaki (1999). "Chemical modification of wool fibers with acid anhydrides." Journal of Applied Polymer Science **71**(10): 1573-1579.

Garnett, J. L. and R. S. Kenyon (1977). "Acid effects in the styrene comonomer technique for radiation grafting to wool." Journal of Polymer Science: Polymer Letters Edition **15**(7): 421-425.

Giri, G., C. N. Nanda and R. K. Samal (1989). "Graft Copolymerization onto Wool Fibers: Graft Copolymerization of Acrylic Acid onto Wool Fibers Initiated by Quinquivalent Vanadium." Polym J **21**(11): 883-893.

Giri, G. and R. K. Samal (1991). "Grafting onto wool fibers: Graft copolymerization of methyl methacrylate onto wool fibers initiated by KHSO5/Fe(III) couple." Journal of Applied Polymer Science **42**(8): 2371-2375.

Gürdağ, G. and S. Sarmad (2013). Cellulose Graft Copolymers: Synthesis, Properties, and Applications. Polysaccharide Based Graft Copolymers. S. Kalia and M. W. Sabaa. Berlin, Heidelberg, Springer Berlin Heidelberg**:** 15-57.

Hebeish, A., S. H. Abdel-Fattah and A. Bendak (1974). "Redox-initiated vinyl graft copolymerisation onto wool with thiourea as the reductant. II. Fe3+-thiourea co-catalyst induced graft copolymerisation of methyl methacrylate on wool and modified wool fibres." Die Angewandte Makromolekulare Chemie **37**(1): 11-25.

Hebeish, A. and A. Bendak (1974). "Redox-initiated vinyl graft polymerization onto wool with thiourea as the reductant. I. Grafting of methyl methacrylate with the hydrogen peroxide–thiourea catalyst system." Journal of Applied Polymer Science **18**(5): 1305-1317.

Hebeish, A. and P. C. Mehta (1968). "Cerium-initiated grafting of acrylonitrile onto cellulosic materials." Journal of Applied Polymer Science **12**(7): 1625-1647.

Höcker, H. (2002). Plasma treatment of textile fibers. Pure and Applied Chemistry. **74:** 423.

Jeon, S.-H., K.-H. Hwang, J. S. Lee, J.-H. Boo and S. H. Yun (2015). "Plasma treatments of wool fiber surface for microfluidic applications." Materials Research Bulletin **69**: 65-70.

Kamshi, Y. and K. Arai (1996). "Graft Polymerization onto Wool Pretreated with a Mercaptosilane." Textile Research Journal **66**(8): 529-532.

Kantouch, A.-a., S. Abdel-Fattah and A. Hebeish (1972). "Manganese(IV)-Initiated Graftcopolymerization of Methyl Methacrylate on Wool Fibers." Polym J **3**(6): 675-680.

Kantouch, A., A. Hebeish and A. Bendak (1972). "Graft Copolymerization of Methyl Methacrylate on Wool by Periodate Ions." Textile Research Journal 42(1): 7-9.

Kenyon, R. S. and J. L. Garnett (1973). "Acid catalyzed grafting of monomers to wool." Journal of Polymer Science: Polymer Letters Edition 11(10): 651-654.

Koenig, N. H. (1977). "Chemical modification of wool in aprotic swelling media." Journal of Applied Polymer Science 21(2): 455-465.

Kubo, S. and J. F. Kadla (2005). "Lignin-based Carbon Fibers: Effect of Synthetic Polymer Blending on Fiber Properties." Journal of Polymers and the Environment 13(2): 97-105.

Kutlu, B., A. Aksit and M. Mutlu (2010). "Surface modification of textiles by glow discharge technique: Part II: Low frequency plasma treatment of wool fabrics with acrylic acid." Journal of Applied Polymer Science 116(3): 1545-1551.

Leeder, J. D., A. J. Pratt and I. C. Watt (1967). "Wool–polymer systems: Effect of vinyl polymers on water absorption." Journal of Applied Polymer Science 11(9): 1649-1659.

Liouni, M., C. Touloupis, N. Hadjichristidis, S. Karvounis and E. Varriano-Marston (1992). "Graft copolymerization of methacrylates onto wool fibers." Journal of Applied Polymer Science 45(12): 2199-2205.

Martínez-Hernández, A. L., C. Velasco-Santos, M. de-Icaza and V. M. Castaño (2007). "Dynamical–mechanical and thermal analysis of polymeric composites reinforced with keratin biofibers from chicken feathers." Composites Part B: Engineering 38(3): 405-410.

Martínez-Hernández Ana, L., C. Velasco-Santos, d. Icaza Miguel and M. Castaño Victor (2003). Grafting of methyl methacrylate onto natural keratin. e-Polymers. 3: 209.

Meade, S. J., J. P. Caldwell, A. J. Hancock, K. Coyle, J. M. Dyer and W. G. Bryson (2008). "Covalent Modification of the Wool Fiber Surface: The Attachment and Durability of Model Surface Treatments." Textile Research Journal 78(12): 1087-1097.

Misra, B. N. and P. S. Chandel (1977). "Grafting onto wool. I. Ceric ion-initiated grafting of poly(methyl acrylate) onto wool." Journal of Polymer Science: Polymer Chemistry Edition 15(7): 1545-1548.

Misra, B. N. and P. S. Chandel (1980). "Grafting onto wool. IV. Effect of amines upon ceric ion-initiated grafting of poly(methyl acrylate)." Journal of Polymer Science: Polymer Chemistry Edition 18(4): 1171-1176.

Misra, B. N., P. S. Chandel and R. Dogra (1978). "Grafting onto wool. III. Graft copolymerization of poly(vinyl acetate) by use of fenton's reagent as initiator." Journal of Polymer Science: Polymer Chemistry Edition 16(8): 1801-1805.

Misra, B. N., R. Dogra, I. K. Mehta and K. D. Gill (1981). "Grafting onto wool. XI. Graft copolymerization of poly(vinyl acetate) and poly(methyl acrylate) onto reduced wool in presence of potassium persulfate–ferrous ammonium sulfate (KPS—FAS) system as redox initiator." Journal of Applied Polymer Science 26(11): 3789-3796.

Misra, B. N., I. Kaur and R. Dogra (1979). "Grafting onto wool. VI. Effect of amines in ceric ion-initiated grafting of poly(vinyl acetate)." Journal of Applied Polymer Science 24(7): 1595-1602.

Misra, B. N., I. Kaur and R. K. Sharma (1981). "Grafting onto wool." Polymer Bulletin 4(11): 635-640.

Misra, B. N. and I. K. Mehta (1980). "Grafting onto wool. VIII. Graft copolymerization of methyl methacrylate (MMA) by use of Ce4+ -amine system as redox initiator." Journal of Polymer Science: Polymer Chemistry Edition 18(6): 1911-1916.

Misra, B. N., I. K. Mehta and R. Dogra (1980). "Grafting onto wool. VII. Ceric ion-initiated graft copolymerization of vinyl monomers. Comparison of monomer reactivities." Journal of Applied Polymer Science 25(2): 235-241.

Misra, B. N., I. K. Mehta and D. S. Sood (1980). "Grafting onto Wool. IX. Graft Copolymerization of Vinyl Monomers by Use of Vanadium Oxyacetylacetonate as Initiator." Journal of Macromolecular Science: Part A - Chemistry 14(8): 1255-1268.

Misra, B. N. and B. R. Rawat (1984). "Grafting onto Wool. XXIV. Graft Copolymerization of Methyl Methacrylate and Ethyl Methacrylate by Use of Ferric Acetylacetonate as Initiator: Comparison of Monomer Reactivities." Journal of Macromolecular Science: Part A - Chemistry 21(4): 495-508.

Misra, B. N., R. K. Sharma and I. K. Mehta (1982). "Grafting onto Wool. XV. Graft Copolymerization of MA and MM A by Use of Mn(acac)3 as Initiator." Journal of Macromolecular Science: Part A - Chemistry 17(3): 489-500.

Misra, B. N. and D. S. Sood (1982). "Grafting onto wool. XVI. Graft copolymerization of vinyl monomers by use of TBHP–FAS as redox initiator." Journal of Applied Polymer Science 27(7): 2417-2425.

Misra, B. N., D. S. Sood and I. K. Mehta (1982). "Grafting onto WooJ. XIX. Graft Copolymerization of Mixed Vinyl Monomers by Use of Ceric Ammonium Nitrate as Redox Initiator." Journal of Macromolecular Science: Part A - Chemistry 18(2): 209-218.

Mitra, S. K. and A. A. Saha (2008). Surface Modification, Methods. Encyclopedia of Microfluidics and Nanofluidics. D. Li. Boston, MA, Springer US: 1933-1939.

Mohammed, L., M. N. M. Ansari, G. Pua, M. Jawaid and M. S. Islam (2015). "A Review on Natural Fiber Reinforced Polymer Composite and Its Applications." International Journal of Polymer Science 2015: 15.

Monier, M., D. M. Ayad and A. A. Sarhan (2010). "Adsorption of Cu(II), Hg(II), and Ni(II) ions by modified natural wool chelating fibers." J Hazard Mater 176(1-3): 348-355.

Monier, M., N. Nawar and D. A. Abdel-Latif (2010). "Preparation and characterization of chelating fibers based on natural wool for removal of Hg(II), Cu(II) and Co(II) metal ions from aqueous solutions." Journal of Hazardous Materials 184(1–3): 118-125.

Naito, S. and K. Arai (1996). "Type and location of SS linkages in human hair and their relation to fiber properties in water." Journal of Applied Polymer Science 61(12): 2113-2118.

Nayak, P. L., S. Lenka and M. K. Mishra (1980). "Grafting vinyl monomers onto wool fibers. V. Graft copolymerization of methyl methacrylate onto wool using peroxydiphosphate as initiator." Journal of Applied Polymer Science 25(1): 63-75.

Nayak, P. L., S. Lenka and M. K. Mishra (1981). "Grafting Vinyl Monomers onto Wool Fibers. VII. Graft Copolymerization of Methyl Methacrylate onto Wool Using Peroxydiphosphate-Thiourea Redox System." Journal of Macromolecular Science: Part A - Chemistry 16(4): 843-857.

Nayak, P. L., S. Lenka and M. K. Mishra (1981). "Grafting vinyl monomers onto wool fibers. VIII. Graft copolymerization of methyl methacrylate onto wool using peroxydiphosphate–fructose redox system." Journal of Applied Polymer Science **26**(2): 733-740.

Nayak, P. L., S. Lenka and N. C. Pati (1978). "Grafting vinyl monomers onto wool fibers II. Graft copolymerization of methylmethacrylate onto wool by quinquevalent vanadium ion." Die Angewandte Makromolekulare Chemie **71**(1): 189-199.

Nayak, P. L., S. Lenka and N. C. Pati (1978). "Grafting vinyl monomers onto wool fibers. I. Graft copolymerization of methyl methacrylate onto wool using V5+–thiourea redox system." Journal of Applied Polymer Science **22**(11): 3301-3309.

Nayak, P. L., S. Lenka and N. C. Pati (1979). "Grafting vinyl monomers onto wool fibers. III. Graft copolymerization of methyl methacrylate onto wool using hexavalent chromium ion." Journal of Polymer Science: Polymer Chemistry Edition **17**(11): 3425-3434.

Nayak, P. L., S. Lenka and N. C. Pati (1980). "Grafting vinyl monomers onto wool fibers IV. Graft copolymerization of methyl methacrylate onto wool using peroxydisulfate catalysed by silver ions." Die Angewandte Makromolekulare Chemie **85**(1): 15-28.

Nayak, P. L., N. C. Pati and G. Panda (1981). "Grafting Vinyl Monomers onto Wool Fibers. VI. Graft Copolymerization of Methyl Methacrylate onto Wool Using Tetravalent Manganese-Oxalic Acid Redox System." Journal of Macromolecular Science: Part A - Chemistry **16**(4): 829-842.

Negishi, M., K. Arai and S. Okada (1967). "Graft copolymerization of vinyl monomers in wool fibers." Journal of Applied Polymer Science **11**(1): 115-126.

Negishi, M., K. Arai and S. Okada (1967). "Kinetics of graft copolymerization of methyl methacrylate in wool fibers." Journal of Applied Polymer Science **11**(12): 2427-2441.

Negishi, M., K. Arai, S. Okada and I. Nagakura (1965). "New method for graft polymerization of vinyl monomers in wool fibers." Journal of Applied Polymer Science **9**(10): 3465-3470.

Niezette, J., R. Geurts and R. Erilli (1981). "Graft polymerization of methyl methacrylate onto chemically modified wools using LiBr–K2S2O8 redox system as initiator." Journal of Applied Polymer Science **26**(4): 1073-1083.

Ogawa, S., K. Fujii, K. Kaneyama and K. Arai (2008). "Action of Thioglycolic Acid and L-Cysteine to Disulfide Cross-Links in Hair Fibers during Permanent Waving Treatment." 繊維学会誌 **64**(6): 137-144.

Ranjbar-Mohammadi, M., M. Arami, H. Bahrami, F. Mazaheri and N. M. Mahmoodi (2010). "Grafting of chitosan as a biopolymer onto wool fabric using anhydride bridge and its antibacterial property." Colloids and Surfaces B: Biointerfaces **76**(2): 397-403.

Ranjbar-Mohammadi, M., S. Hajir Bahrami and M. Arami (2013). "Eco-friendly grafting of natural biopolymer chitosan onto acylated wool fabrics using ultrasonic and study its properties." Journal of Applied Polymer Science **129**(2): 707-713.

Ristić, N., P. Jovančić, C. Canal and D. Jocić (2010). "Influence of corona discharge and chitosan surface treatment on dyeing properties of wool." Journal of Applied Polymer Science **117**(5): 2487-2496.

Şahan, G., A. Demir and Y. Gökçe (2016). "Improving certain properties of wool fibers by applying chitosan nanoparticles and atmospheric plasma treatment." Fibers and Polymers **17**(7): 1007-1012.

Sakabe, H., T. Miyamoto and H. Inagaki (1982). "DIFFERENTIAL THERMAL ANALYSIS OF COMPONENT PROTEINS FROM WOOL." Sen'i Gakkaishi **38**(12): T517-T522.

Samal, S., G. Sahu and P. L. Nayak (1984). "Grafting vinyl monomers onto silk fibers: Graft copolymerization of methyl methacrylate onto silk using acetylacetonate Mn(III) complex." Journal of Applied Polymer Science **29**(11): 3283-3293.

Samal, S., G. Sahu and P. L. Nayak (1984). "Grafting vinyl monomers onto wool fibers: Graft copolymerization of methyl methacrylate onto wool fibers using vanadyl acetyl acetonate complex." Journal of Applied Polymer Science **29**(6): 2007-2015.

Sarac, A. S. (1999). "Redox polymerization." Progress in Polymer Science **24**(8): 1149-1204.

Shahidi, S., M. Ghoranneviss and S. Dalalsharifi (2015). "Preparation of multifunctional wool fabric using chitosan after plasma treatment." The Journal of The Textile Institute **106**(10): 1127-1134.

Sharma, R. K. and B. N. Misra (1983). "Grafting onto Wool. XVIII. Graft Copolymerization of Methyl Methacrylate onto Wool Fiber in the Presence of Tertiary Butyl Hydroperoxide-Mineral Acid as Initiator." Journal of Macromolecular Science: Part A - Chemistry **20**(2): 225-235.

Sood, D. S. and B. N. Misra (1984). "Grafting onto Wool. XXVI. Graft Copolymerization of Vinyl Monomers by Use of Cr(acac)3-TBHP as Initiator." Journal of Macromolecular Science: Part A - Chemistry **21**(10): 1267-1279.

Sood, D. S., A. S. Singha and B. N. Misra (1983). "Grafting onto Wool. XXI. Graft Copolymerization of Methyl Methacrylate onto Reduced Wool by Use of Manganese Acetylacetonate as Initiator." Journal of Macromolecular Science: Part A - Chemistry **20**(2): 237-245.

Spei, M. and R. Holzem (1987). "Thermoanalytical investigations of extended and annealed keratins." Colloid and Polymer Science **265**(11): 965-970.

Stannett, V., K. Araki, J. A. Gervasi and S. W. McLeskey (1965). "Radiation grafting of vinyl monomers to wool. Part I." Journal of Polymer Science Part A: General Papers **3**(11): 3763-3779.

Supri, A. G., S. J. Tan, H. Ismail and P. L. Teh (2011). "Effect of Poly(methyl Methacrylate) Modified Water Hyacinth Fiber on Properties of Low Density Polyethylene/Natural Rubber/Water Hyacinth Fiber Composites." Polymer-Plastics Technology and Engineering **50**(9): 898-906.

Tanaka, Y. and H. Shiozaki (1982). "ADDITION REACTION OF MULTIFUNCTIONAL EPOXIDES WITH WOOL KERATIN." Sen'i Gakkaishi **38**(11): T491-T499.

Tsukada, M., Md. Majibur Rahman Khan, T. Tanaka and H. Morikawa (2011). "Thermal characteristics and physical properties of silk fabrics grafted with phosphorous flame retardant agents." Textile Research Journal **81**(15): 1541-1548.

Tsukada, M., M. Nagura, H. Ishikawa and H. Shiozaki (1991). "Structural characteristics of silk fibers treated with epoxides." Journal of Applied Polymer Science **43**(4): 643-649.

Tsukada, M., H. Shiozaki, G. Freddi and J. S. Crighton (1997). "Graft copolymerization of benzyl methacrylate onto wool fibers." Journal of Applied Polymer Science **64**(2): 343-350.

Tsukada, M., H. Shiozaki and A. Konda (1990). "Physical properties of wool keratin yarn modified with dibasic acid anhydrides." Journal of Applied Polymer Science **41**(5-6): 1213-1223.

Wang, S., W. Hou, L. Wei, H. Jia, X. Liu and B. Xu (2007). "Antibacterial activity of nano-SiO2 antibacterial agent grafted on wool surface." Surface and Coatings Technology **202**(3): 460-465.

Wang, X., G. Cao and W. Xu (2009). "Improving the hydrophilic properties of wool fabrics via corona discharge and hydrogen peroxide treatment." Journal of Applied Polymer Science **112**(4): 1959-1966.

Wang, X., Y. Zhao, W. Li and H. Wang (2015). "Effect of surface modifications on the thermal and moisture behavior of wool fabric." Applied Surface Science **342**: 101-105.

Watt, I. C. (1970). "Properties of Some Wool Keratin Copolymers." Journal of Macromolecular Science: Part A - Chemistry **4**(5): 1079-1089.

Williams, J. L. and V. Stannett (1968). "High-Yield Pre-Irradiation Grafting to Wool Leading to Highly Elastic Fibers." Textile Research Journal **38**(10): 1065-1066.

Williams, J. L., V. Stannett and A. A. Armstrong (1966). "Studies of the chemical modifications of wool and their effects on the wool–water relationship. Part II. Wool-water relationships of modified and unmodified wool." Journal of Applied Polymer Science **10**(9): 1229-1245.

Wortmann, F. J. and H. Deutz (1998). "Thermal analysis of ortho- and para-cortical cells isolated from wool fibers." Journal of Applied Polymer Science **68**(12): 1991-1995.

Xu, B., M. Niu, L. Wei, W. Hou and X. Liu (2007). "The structural analysis of biomacromolecule wool fiber with Ag-loading SiO2 nano-antibacterial agent by UV radiation." Journal of Photochemistry and Photobiology A: Chemistry **188**(1): 98-105.

Xu, W., J. Bao, J. Zhang and M. Shi (1998). "Microwave irradiation graft copolymerization of hydroxyethyl methacrylate onto wool fabrics." Journal of Applied Polymer Science **70**(12): 2343-2347.

Yoshikuni, M., K. Saito and K. Kojima (1980). "Graft polymerization of methyl methacrylate onto wool initiated by ferric acetylacetonate/dichloroacetic acid system." Journal of Applied Polymer Science **25**(9): 1991-2000.

Yu, L. (2009). Biodegradable Polymer Blends and Composites from Renewable Resources, Wiley.

Zanini, S., S. Freti, A. Citterio and C. Riccardi (2016). "Characterization of hydro- and oleo-repellent pure cashmere and wool/nylon textiles obtained by atmospheric pressure plasma pre-treatment and coating with a fluorocarbon resin." Surface and Coatings Technology **292**: 155-160.

Table 1. A summary of polymer grafting onto wool fiber.

Grafting reaction initiator	Initiator concentration (M)	Thiourea concentration (M)	Monomer concentration (methyl Acrylate) (M)	Optimum temperature (°C)	Optimum time (hr)	Acid concentration (M H_2SO_4)	Optimum substrate	Optimum Amount of wool (gr)	Inorganic salt/surfactant	Grafting yield (%)	Ref
V^{5+}-Thiourea redox system	□	0.0025-0.015 Optimum 0.0075	0.2347	45	1	0.75 H_2SO_4	Reduced wool	0.1-0.6	□	□	(Nayak, Lenka et al. 1978)
Quinquevalent Vanadium Ion V^{5+}	V^{5+}, 0.005 to 0.02	□	1.03 (11%)	55	4	1 H_2SO_4	Reduced wool	□	□	□	(Nayak, Lenka et al. 1978)
Hexavalent chromium ion	0.005-0.035	□	0.657	55	4	0.5 perchloric	Unmodified wool		$CuSO_4$ 0.03	□	(Nayak, Lenka et al. 1979)
Peroxydisulfate Catalysed by Silver ions	0.002	0.015	0.8	40	4	□	□	□	0.01 M 0.02 $CuSO_4$	□	(Nayak, Lenka et al. 1980)
Peroxydiphosphate	0.008	0.00025	1.03	55	6	0.15 H_2SO_4	Reduced wool	□	□	□	(Nayak, Lenka et al. 1980)
Tetravalent Manganese-Oxalic Acid Redox	Oxalic acid 0.015	□	□	□	□	□	□	□	□	□	(Nayak, Pati et al. 1981)
Peroxydiphosphate-Thiourea Redox	Peroxydiphosphate 0.008	□	□	□	□	□	□	□	□	□	(Nayak, Lenka et al. 1981)
Peroxydiphosphate-Fructose Redox	0.00075 fructose 0.012 peroxydiphosphate	□	0.657	55	6	0.5 H_2SO_4	Reduced wool	□	□	□	(Nayak, Lenka et al. 1981)
ceric ion as redox initiator	9 mM ceric ammonium nitrate	□	□	45	3	0.19 HNO_3	□	1:300	□	□	(Misra and Chandel 1977)
Polystyrene						□	□			□	
benzoyl peroxide (BPO) as initiator acetic acid-pyridine as a pH modifier	BPO 0.005 Pyridine 0.2160	□	Styrene 0.1450	60	3	0.29 acetic acid	□	1:300	□	38	(Chandel and Misra 1977)
Fenton's reagent as redox initiator	H_2O_2 /Fe^{+2}: 1.43 H_2O_2: 0.086 Ferrous ammonium sulfate (FAS): 0.006	□	Poly (viny acetate) 0.35	45	3	□	□	1:300	□	65	(Misra, Chandel et al. 1978)
Ceric ammonium nitrate in the presence of triethylamine, diethylamine, nbutylamine, triethanolamine, and N,N-dimethylaniline	9 mM ceric ammonium nitrate	0.023 triethylamine	0.184	45	3	0.16 H_2SO_4	□	□	□	**147**	(Misra and Chandel 1980)
Ceric ammonium nitrate in the presence of amines	0.0015 CAN	□	Poly (viny acetate) 0.16	45	2.5	0.09 HNO_3	□	1:200	□	32.26	(Misra, Kaur et al. 1979)
Ceric ammonium nitrate	0.0075 CAN	□	0.23	55	3	0.14 HNO_3	□	1:200	□	55.61	(Misra, Mehta et al. 1980)
Ce^{4+}-Amine diethylamine (DEA), dipropylamine (DPA), triethylamine (TEA), triethanol amine, and pyridine.	0.0075 CAN	□	0.14	55	3	0.14 HNO_3	□	1:200	□	40.40	(Misra and Mehta 1980)
Manganese acetylacetonate	[Mn(acac)3] 0.00852 M	□	0.23	65	3	HNO_3: 0.08	Reduced wool	1:200	□	57	(Sood, Singha et al. 1983)
Manganese acetylacetonate	[Mn(acac)3] 0.0088 M	□	MMA 0.23	65	3	HNO_3: 0.24	□	1:200	□	MMA 82.5 MA 27.5	(Misra, Sharma et al. 1982)
Tertiary butyl hydroxide.Mineral acid H2SO4, HNO3, HClO4	TBHP: 0.049	□	MMA 0.23	70 75	3	$HClO_4$: 0.12	□	1:200	□	$HCLO_4$:15 8	(Sharma and Misra 1983)

Grafting reaction initiator	Initiator concentration (M)	Thiourea concentration (M)	Monomer concentration (methyl Acrylate) (M)	Optimum temperature (°C)	Optimum time (hr)	Acid concentration (M H_2SO_4)	Optimum substrate	Optimum Amount of wool (gr)	Inorganic salt/surfactant	Grafting yield (%)	Ref
						HNO_3: 0.24 H_2SO_4: 0.028				HNO_3:139	
Chromium acetonate-tertiary butyl hydroperoxide (Cr(acac)3-TBHP)	Cr(acac)3: 0.00587 0.0060 0.0078 TBHP:0.025 0.1 0.0787	☐	MMA:0.32 MA:0.38 EA:0.32	55 65	3	HNO_3: 0.16-0.24	☐	1:200	☐	MMA:119.8 MA: 56 EA: 41.9	(Sood and Misra 1984)
Ferric acetyl acetonate	Fe (acac)3 =0.0028 0.0049	☐	MMA: 0.25 EMA: 0.15	65	3	HNO_3: 0.16 And 0.24	☐	1:200	☐	MMA:152.2 EMA:114	(Misra and Rawat 1984)
Fe3+-thiourea	0.95 Fe^{3+} (g/100gwool)	0.4	*552* mmole 10-1	60	2	0.8 N HNO_3	☐	1:100	☐	268.4	(Hebeish, Abdel-Fattah et al. 1974)
Peroxide-Thiourea Catalyst	H_2O_2: 12	4 mM	1104 mM	80	2	pH 2	☐	1:50	0.8 mM $CuSO_4$	60	(Hebeish and Bendak 1974)
Periodate ions	15mM	☐	Monomer 4%	60	2	pH 4	☐	1:50	☐	☐	(Kantouch, Hebeish et al. 1972)
Quinquivalent vanadium	V^{5+}: 0.025	☐	Acrylic acid:1.46M	55	6	☐	Defatted wool	0.2 g	☐	193.7%	(Giri, Nanda et al. 1989)
Potassium permanganate (Manganese IV)	$KmNO_4$: 4mM	☐	6% methyl methacrylate	70	2	HNO_3 pH=1	Reduced wool	1:100	☐	180% if the wool treated with thioglycolic acid	(Kantouch, Abdel-Fattah et al. 1972)
Vanadyl Acetyl Acetonate	0.000087	☐	0.5634	55	4	$HClO_4$ 0.012	Reduced wool	1:100	☐	120	(Samal, Sahu et al. 1984)
(KHS06) /Fe(111) system	$KHSO_5$ = 0.0195 Fe (iii) = 0.00012	☐	0.46	40	4	formic acid 50%	☐	☐	$FeCl_3$	210.8	(Giri and Samal 1991)
ammonium peroxydisulphate	3% on BzMA weight	☐	(BzMA) 35-200% on wool weight	80	1.1	Formic acid (3ml/L)	Defatted wool	1:15	☐	180	(Tsukada, Shiozaki et al. 1997)
K2S2O8 or K2S2O8-LiBr redox system as initiator	0.5-0.6 for $K_2S_2O_8$ and 0.55-0.7 for $K_2S_2O_8$-LiBr system	☐	butyl (BuMA), decyl (DeMA), and octadecyl methacrylate (ODeMA) 0.75	50	5 h for $K_2S_2O_8$-LiBr 96 h for $K_2S_2O_8$	☐	Reduced wool	☐	☐	200	(Liouni, Touloupis et al. 1992)
microwave irradiation in the presence of catalyst (NH4)2S2O8	$(NH_4)_2S_2O_8$: 0.05%	☐	Hydroxyethyl methacrylate 4%	MW intensity 400 W	1	☐	Defatted wool	3:100	☐	35	(Xu, Bao et al. 1998)
ferric acetyl acetonate/ dichloroacetic acid	Fe(acac)s, 0.02; dichloroacetic acid : 0.08	☐	MMA, 3.12	60	2	☐	Defatted wool	0.5: 30	☐	20	(Yoshikuni, Saito et al. 1980)
Ceric ammonium nitrate as redox initiator	CAN 0.0089	☐	Mixed vinyl 0.72 monomer and methyl acrylate 0.18	45	3	HNO_3: 0.16	Purified wool	1:300	☐	90	(Misra, Sood et al. 1982)

Grafting reaction initiator	Initiator concentration (M)	Thiourea concentration (M)	Monomer concentration (methyl Acrylate) (M)	Optimum temperature (°C)	Optimum time (hr)	Acid concentration (M H_2SO_4)	Optimum substrate	Optimum Amount of wool (gr)	Inorganic salt/surfactant	Grafting yield (%)	Ref
$KMnO_4$ /malic acid redox system	$KMNO_4$: 0.006 Malic acid:0.01	□	0.85	50	4	H_2SO_4:0.15	Feather keratin fibre	1:150	□	□	(Martínez-Hernández Ana, Velasco-Santos et al. 2003)
$KMnO_4$ and oxalic acid	10 ml of 2mmol $KMnO_4$ 10 ml 4mmol oxalic acid	□	acrylonitrile (AN) 0.12 mol	Room temp	1	□	Purified wool (1% sulphuric, 1% NaOH)	1:50	hydroquinone solution (10 ml, 3% (w/w)) to terminate the reaction	160	(Monier, Nawar et al. 2010)
potassium persulphate and Mohr's salt redox initiator	10 ml of 2mmol potassium persulphate 10 ml 2mmol Mohr's salt	□	Ethyl acrylate (EA): 0.12 mol	Room temp	1	□	Purified wool (1% sulphuric, 1% NaOH)	1:50	10ml, 3% hydroquinone	156	(Monier, Ayad et al. 2010)
LiBr-K2S2O8 Redox	$K_2S_2O_4$: 0.2% LiBr: 27.5%	□	MMA 5%	30	1	□	Reduced wool	1:100	□	600 in presence of –SH: 630μmol/g wool	(Niezette, Geurts et al. 1981)
potassium peroxydisulfate (PDS)	PDS : 0.01 mol/L	□	Polyaniline 0.3	45	0.5	□	□	0.2 g	□	95	(Anbarasan, Kalaignan et al. 1999)
Tgases	100g/ml mTGase	□	Sericine: up to 5g/ml	40	1	□	□	1:20	□	□	(Cortez, Anghieri et al. 2007)
Acylation of wool Grafting of chitosan	40g/L succinic anhydride in DMSO Chitosan up to 3%	□	□	50	18	□	□	1:20	□	□	(Ranjbar-Mohammadi, Arami et al. 2010)
Acylation of wool Grafting of chitosan	40g/L succinic anhydride in DMSO Chitosan up to 3%	□	□	65	1	□	□	1:20	□	10	(Ranjbar-Mohammadi, Hajir Bahrami et al. 2013)
LiBr –ammonium LiBr- Potassium persulfate	$K_2S_2O_8$: 0.2% LiBr: 27.5%	□	MMA 5% by weight	30	3	□	□	1:100	□	215	(Negishi, Arai et al. 1967)
LiBr-K2S2O8 Redox	LiBr: 22.5% $K_2S_2O_8$: 0.2% BC:	□	MMA 2%	30	5	□	□	1:100	□	111	(Negishi, Arai et al. 1965)
LiBr-$K_2S_2O_8$	$K_2S_2O_8$: 0.2%	□	MMA 2%	30	3	□	□	□	□	□	(Arai, Negishi et al. 1968)
LiBr-$K_2S_2O_8$	LiBr: 27.5 g $K_2S_2O_8$: 0.2 g Butyl carbitol: 22.5 g	□	5g MMA or MA or EA	30 for MMA 40 for MA and EA	3	□	Reduced, carboxymethylated	1:100	□	109	(Arai and Ishikawara 1982)
potassium peroxidsulfate (KPS) and 3-mercaptopropyl tri-methoxysilane (MPMSi).	KPS: 0.2%	□	2-hydroxyethyl methacrylate (HEMA) 3%	50	1	□	Silanized wool	1:20	□	98	(Kamshi and Arai 1996)
NH4Br K2S2O8 system	NH4Br: 15 g $K_2S_2O_8$: 0.3g BC: 40 g		MMA: 5g	40	24	□	reduced	1:100	□	57	(Arai and Hagiwara 1980)
LiBr K2S2O8 system	LiBr: 27.5 g $K_2S_2O_8$: 0.2g BC: 22.5 g		MMA: 5g	40	5	□	reduced	1:100	□	82	(Arai and Hagiwara 1980)

Table 2. A summary of chemical strategies has used for modification of wool before grafting reaction.

Wool Modification technique	pH	Time	Sample content (gr)	Temperature (°C)	Liquor ratio	Treatment solution	wash	Thiol and disulphide group	Ref
Reduction	4.7	24	1	30	□	TGA 100 ml	Ethanol: water 200m: 200 ml	□	(Liouni, Touloupis et al. 1992)
Reduction	5	26	0.5-1	30	100:1	TGA aqueous solution	0.01N hydrochloric acid then water (1L)	□	(Negishi, Arai et al. 1967)
Reduction	4.8	24	0.5	30	100:1	TGA 0.28-0.5N, 50 ml	Ethanol : water then water	□	(Negishi, Arai et al. 1967)
Reduction	4.8	24	1	30	100:1	TGA 0.516N, 100 ml	Water, ethanol, water	31.0 mole thiol groups/10^5 g wool	(Arai, Negishi et al. 1968)
Reduction	□	20 min 24h	□	25	50:1	First: 0.042 M sodium sulphide Second: 0.01 N HCl	Water, condition for 3days at 65% RH		(Arai, Negishi et al. 1968)
Reduction	8	24 24	□	20	□	Frist: TBP, Tri-n-butyl phosphine 0.0484 mmol Second) CH_3I (0.5 g)	water	25.7 and 331 μmol/g wool	(Arai and Hagiwara 1980)
S-β-carboxymethylated wool	8	5	□	20	1:00	ICH_2COOH (0.2g) n-propanol (25ml) borate phosphate buffer (2ml)	With same buffer, water	8 μmol/g thiol 390 μmol/g disulphide	(Arai and Ishikawara 1982)
Reduced and S-β-carboxymethylated	6	10 24	0.5	20	□	1) TGA: 0.1N AN(0.5g), n-propanol (25ml) borate phosphate (25ml)	water	35 thiol 87 disulphide	(Arai and Ishikawara 1982).
Reduced and methylated	8	24	0.5	20	□	TBP (0.0484 mmole), n-propanol (50ml) buffer (50ml)	water	28 thiol 331 disulphide	(Arai and Ishikawara 1982)
Silanized wool	□	1h	□	30-50	1:20	3-mercaptopropyl tri-methoxysilane (MPMSi) 5% in isopropyl alcohol.1-2%	Water at 40°C	□	(Kamshi and Arai 1996)
Reduction	□	24	1	□	□	$NaHSO_3$ 1%	Water and methanol	□	(Misra, Dogra et al. 1981)
Reduction	□	48	1	□	□	TGA 0.5% solution	Water and methanol	□	(Misra, Kaur et al. 1981)
Reduction	□	24	□	30	1:100	TGA 0.2N solution	□		(Hebeish, Abdel-Fattah et al. 1974)
Esterification	□	6	□	65	1:50	Anhydride methanol in presence of HCL (0.1N)	□	□	(Hebeish, Abdel-Fattah et al. 1974)
Dinitrophenylated	□	Several days	□	Room temp		l-fluoro-2.4-dinitrobenzene in ethanolic solution	□	□	(Hebeish, Abdel-Fattah et al. 1974)