

Atmospheric Pressure Plasma Grafting of a Vinyl-Quaternary Compound to Nonwoven Polypropylene and Cotton

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ABSTRACT

Nonwoven polypropylene and cotton fabrics are grafted to a vinyl quaternary compound using atmospheric-pressure plasma. Two different atmospheric plasma devices are used -the NCAPS (North Carolina Atmospheric Plasma System), a dielectric barrier discharge device created by North Carolina State University, and a plasma device from APJeT[®] Inc. The addition of additives such as Mohr's salt, potassium persulfate, and diacrylates are assessed to see if graft yield can be increased. Acid dye tests, SEM, and XPS reveal successful grafting of the vinyl quaternary compound. A combination of all four additives is found to yield the highest graft yields and greatest uniformity.

INTRODUCTION

After weaving, knitting, or nonwoven formation, most fabrics are subjected to some form of finishing. Finishes are surface treatments that add desirable properties such as softness, color, water repellency, water absorption, or fire retardancy. Fabric finishing is typically accomplished by padding aqueous chemistry onto a fabric and then curing in an oven. Plasma treatment offers an alternative and successful method for achieving a functional finish [1,2]. Unlike conventional processes, plasma can induce the reaction between the fabric and the finish without the need for a heated oven or immersion in an aqueous chemical bath [3,4,5,6] or aqueous system. Thus, plasma processing has the potential to reduce water and energy consumption, thereby reducing the environmental fingerprint of industrial textile processing.

Cold plasma consists of electrons, ions, excited atoms and molecules, neutral gas species, and UV radiation that occur at low temperatures [7]. Historically, plasma treatment was carried out in high vacuum, low-pressure devices [4,5,8,9,10]. Vacuum plasma treatment allows particles to achieve large mean free paths and results in very energetic ions and electrons capable of rapid and extreme surface modification

and highly successful grafting. However, low-pressure devices are most suitable for batch processing and require long processing times, and therefore integration into a continuous industrial manufacturing process was not achievable.

The development of atmospheric-pressure plasma by Yokoyama and associates in the early 1990's greatly expanded the opportunities for textile processing applications [11]. Unlike low-pressure plasma devices, atmospheric-pressure devices operate at ambient conditions, eliminating the need for long pump-down times and allowing for a continuous process. Atmospheric-pressure plasmas differ significantly from low-pressure plasmas, in that they are more highly collisional and dominated by neutral-neutral collisions and electron-neutral collisions. Additionally, mean free paths are shorter and active species less energetic. Despite these differences, similar results can be obtained for fabric processing if gas type, power, and frequency are modified to accommodate the change in density [12].

For chemical grafting by plasma, vinyl monomers are most commonly selected due their ability to polymerize and to react with free radicals produced by the plasma. In many cases, the substrate and monomer are first treated with plasma and then placed into an aqueous solution and heated to induce grafting [8,9,10,13,14,15]. Although highly successful, this method of grafting does not reduce water consumption or eliminate the need for external heat. This method is also not scalable to industry, where textile finishing requires continuous processing and fast speeds.

Newer approaches to plasma polymerization focus on direct application of the monomer to the fabric without any need for an immersion bath with long periods of heating [3,4,16,17] These methods involve spraying, padding, or evaporation and deposition of the vinyl monomer in sequence with plasma

treatment and represent a viable approach that can be adopted by the industrial textile industry as a replacement for conventional methods of fabric finishing.

However, this new approach to plasma grafting typically requires long durations of plasma exposure or multiple passes under the plasma to achieve sufficient graft yield. To address and understand this problem, this paper investigates the use of additives, such as Mohr's salt, potassium persulfate, and diacrylate to increase the graft-yield of a vinyl monomer treated in atmospheric-pressure plasma without use of submersion baths or heat. Addition of Mohr's salt and potassium persulfate has been shown to increase graft yield during reaction kettle plasma grafting [18,19] and during conventional polymerization reactions [20,21,22,23]. This research seeks to determine if these compounds can also improve the graft-yield when combined with the monomer mix and grafted directly to the fabric by the plasma without use of heat or water baths.

3-Acrylamidopropyl)trimethylammonium chloride

3-Acrylamidopropyl)trimethylammonium chloride was selected as the "active" monomer for these experiments due to the presence of a quaternary ammonium group. Quaternary ammonium groups readily react with acid dye and the amount of acid dye molecules can be quantified by UV spectroscopy. This allows for a quantitative comparison of the amount of grafted monomer at each experimental condition.

3-Acrylamidopropyl)trimethylammonium chloride has additional benefits as a polymeric coating. When grafted to cotton, the resulting fabric has antimicrobial activity to *S. Aureus* and *E. Coli* [24].

Mohr's Salt

In previous studies of vacuum and atmospheric-pressure plasma-aided graft polymerization in which a substrate was first exposed to plasma and then reacted with monomer in a heated shaker bath, addition of Mohr's salt, $(\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O})$ has been shown to successfully decrease the formation of homopolymers that compete with the grafting reaction and thereby increase graft yield [10,13,25]. The method of action of Mohr's salt is illustrated in *Figure 3*. Initially, plasma treatment results in formation of free radicals on substrates, e.g. polypropylene [26] and cellulose [27]. Upon exposure to air either simultaneous to or following atmospheric-pressure plasma processing, these radicals react with oxygen to generate unstable

peroxy radicals [28]. Next, the peroxy radicals split into hydroxyl radicals that become mobile in solution (*Figure 1*). The hydroxyl radicals combine with the monomer, inducing homopolymerization without grafting to the polymeric substrate (*Figure 2*). Mohr's salt reacts with the hydroxyl groups to effectively reduce homopolymerization (*Figure 3*), thereby increasing potential for grafting reactions between the substrate and monomer (*Figure 4*).



FIGURE 1. Scission of hydroxyl radicals from the polymer (polypropylene) backbone.

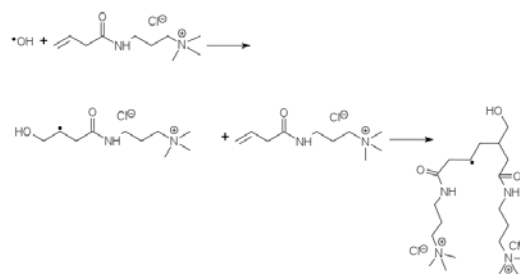


FIGURE 2: Homopolymerization.



FIGURE 3: Deactivation of hydroxyl radicals by Mohr's salt.

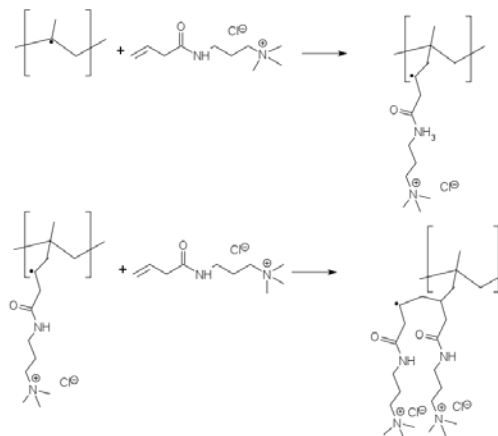


FIGURE 4: Polymerization on the polymer backbone

Potassium Persulfate

Potassium persulfate is a common thermal dissociation initiator used in conventional polymerization reactions. Optimally, the atmospheric plasma grafting process will occur at ambient temperature and will require no additional application

of thermal energy. Although the degree of polymerization of a monomer using potassium persulfate increases with elevated temperature, a conversion rate of 20% has been observed in reactions performed at room temperature [29]. In addition, electrode warming has been shown to increase ambient temperature for the NCAPS plasma system used in this research.

The effect of potassium persulfate in a plasma system and in a grafting process has not been reported. However, considering the effects of its use in standard chemical processing, it can be expected to actively influence grafting in one of three ways:

- 1) Increase homopolymerization
- 2) Reduce the inhibitory affect of the HEMQ, thereby increasing grafting
- 3) Increase grafting due to entanglement if a diacrylate is included. Entanglements are formed by the 3D polymerization of the diacrylate.

Diacrylate

Diacrylate compounds contain two polymerizable vinyl groups, and are therefore able to react with multiple monomer units. As a result, when a diacrylate is included in a monomer solution, chain crosslinking is likely to occur. The crosslinked polymer might potentially entangle or even envelop polymer chains on the surface of the substrate, creating a permanent, albeit non-covalent link. If chains are sufficiently entangled or linked around the substrate, it could increase durability to laundering and resistance to Soxhlet extraction and it might behave similarly to a covalently-bound, grafted polymer. Therefore, the effect of including a diacrylate in a plasma grafting is of interest.

EXPERIMENTAL

Fabric

The samples included nonwoven polypropylene, and bleached and scoured cotton from Test Fabrics Inc. (West Pitston, PA, USA). Nonwoven polypropylene was provided by NCRC (Nonwovens Cooperative Research Center) and was produced by cold calendared with a weight of 60grams/m². Samples were cut into 10 cm x 15 cm swatches, and are labeled with a Tex Pen.

Chemicals

The selected monomer is (3-Acrylamidopropyl) trimethylammonium chloride (3ATAC) (TCI America (Portland, OR, USA). It consists of 74-76% chemical in water stabilized with 100 ppm MEHQ.

The selected diacrylate is 1,6-hexanediol diacrylate (Sigma Aldrich) at 80%, stabilized with 100ppm MEHQ.

Potassium persulfate was also purchased from Sigma Aldrich at 99+% A.C.S. Reagents.

Mohr's salt, ammonium iron (II) sulfate hexahydrate, was obtained at 99% A.C.S. reagent grade from Sigma Aldrich.

Plasma Device

Plasma treatment was performed on two devices. The first was an APJeT[®] system, model APPR 300-13. This device measures 14" by 38" with metal electrodes and a gap spacing of .0910 cm. The system delivers helium or 1% oxygenated helium to the gap and is powered by a RF-matching network. The lower electrode, a grounded moving plate was adjusted to treat the samples for the desired exposure time.

Atmospheric-pressure plasma treatment was also performed on the NCAPS (North Carolina Atmospheric Plasma System) device, a capacitively-coupled, dielectric barrier discharge device operated (*Figure 5*). The device consists of two 60x60cm parallel copper electrodes with adjustable gap spacing covered in Lexan[®] dielectric material. The input power to the electrodes is approximately 4.8kW, supplied by eight Pyramid 15V direct current power supplies coupled and two step-up transformers 180 degrees out of phase. Peak voltage and peak current to the electrodes are 8,000V and 0.01A, respectively.

The system is monitored in real time by a custom LabView[®] program that displays and stores data including peak-to-peak and RMS voltage, current, gas flow rates, and internal temperature. The hardware used to monitor voltage and current consist of a capacitively coupled, compensated high-voltage probe and a Pearson current-monitoring coil. Temperature measurements are taken by an Omega Teflon coated thermo-couple moderated by a mV/ °F or a V/°C analog-to-digital converter. The program provides the real-time data to solve for electron-number density and electron temperature.

To generate the discharge, helium gas is introduced at 10.00L/min into a batch cell. The batch cell encompasses the electrodes and has a height of 3.8cm. In the center of the batch cell is a porous nylon mesh on which batch samples can be placed to

receive plasma exposure on the upper and lower sides. The batch cell is used for this application due to the small size of the samples, but larger samples or rolls of fabric can be run continuously through the device on fabric rollers. Helium gas is used as a seed gas to initiate the discharge due to its low ionization potential, however, small fractions of other gases including oxygen, CF₄, C₃F₆, CO₂, CH₄, etc. could also be introduced into the helium stream and ionized by collisional processes. Only oxygen was used for these experiments.

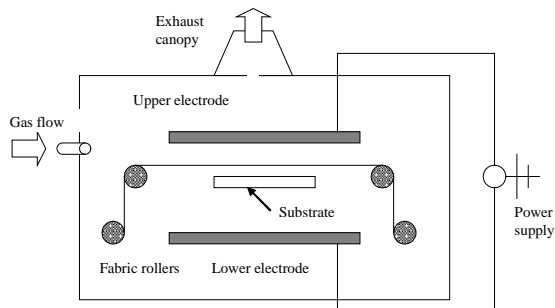


FIGURE 5. Inner plasma chamber and optional cell

Solutions

Aqueous solutions were prepared with one or more additives according to concentrations referred to in literature: 0.01M potassium persulfate (P), [13] 0.345mM Mohr's salt (M), [10,13,25] 1:10 moles diacrylate (D):3ATAC (Q). The chemicals combined with 3ATAC to produce a final dry add-on of 3% 3ATAC on the weight of the fabric with 100% wet pickup. Three percent was chosen as a maximum desired concentration and represented an expected excess of chemical graft yield. As such, the quantity of 3ATAC should not be a limiting factor in the grafting process.

TABLE I. Monomer solutions for plasma grafting 3ATAC to polyester and cotton.

Solution Combinations
Q
QD
QM
QP
QDM
QDP
QDMP

PROCEDURE

Plasma Treatments

Samples were treated using the APJeT[®] machine or the NCAPS device. Device treatments were selected based on differences in electron number density (greater for APJeT[®] than NCAPS). For the APJeT[®] device, the moving stage was adjusted to 25 seconds of plasma exposure and the samples were placed on the stage and passed through the plasma. Plasma gas consisted of 99% helium/1% oxygen plasma and the electrode gap space was fixed at 0.090cm. Alternately, samples were treated in the NCAPS device for two minutes using 99% helium/1% oxygen plasma. Four samples were treated for each experimental condition.

Immediately following plasma treatment, samples were painted with the chosen solution to an add-on of about 100%. Samples were then air-dried and re-exposed to the same plasma device at the same conditions and duration.

To examine the effect of solvent on grafting, an additional set of samples was prepared for the NCAPS device for which the painted sample was not allowed to dry before re-exposure to the plasma. Processing limitations prohibited introduction of water solvent into the APJeT[®] device and so wet processing was restricted to the NCAPS device.

It was hypothesized that solvent might inhibit contact between chemical and plasma-activated substrate or reduce plasma activation of the chemical, reducing graft yield.

Samples were then Soxhlet extracted in water for 12 hours, rinsed, dried, reconditioned at 20±5°C and 65% humidity for 24 hours and reweighed.

CHARACTERIZATION TECHNIQUES

Laundering

Samples were laundered following the AATCC Test Method 61-1993 Colorfastness to Laundering: Accelerated.³⁰ Samples were cut into 2"x6" strips and placed in individual metal canisters with 50 stainless steel balls and 150mL of wash liquor. The wash liquor consisted of a 2% AATCC detergent and the canisters were tumbled in an Atlas Model LHT Launder-Ometer for 45 minutes at 120°F to simulate 5-10 home launderings. Once the wash cycle was complete, samples were removed, rinsed with water to remove excess detergent, and air-dried.

Change in Mass

Each sample was weighed after conditioning for 24 hours at 65% humidity and 20±5°C before (W_0) plasma and chemical exposure and after Soxhlet extraction (W_f) using an Explorer microbalance with an accuracy of ±1000 micrograms. The percent weight change, see Eq. (1), was then plotted versus the exposure time for plasma treatment.

$$\text{Weight Change (\%)} = 100 \left(\frac{W_f - W_0}{W_0} \right) \quad (1)$$

Contact Angle

Contact angle was measured using a Model A-100 Rame-Hart, Inc goniometer. Sampling was conducted in ambient conditions at room temperature and standard humidity. Each sample was tested at five locations with a 6µL of deionized water drop. Samples were tested simultaneously to eliminate any ageing effects.

Scanning Electron Microscopy

All samples were sputter-coated with gold on a SC 760 Mini Sputter Coater from Quorum Technologies for 45 seconds and examined in a Phenom Scanning Electron Microscope (FEI Company).

XPS (X-ray Photoelectron Spectroscopy)

A Riber XPS (12kV, 14mA, and spot size of 1mm) was used to characterize surface modifications of selected samples. The resolution of the XPS device was 0.3-4eV with an acceptance solid angle of 6% of 2π .

Quaternary Dye Testing

Colorimetric assessment of fabrics dyed with acid dyes was used to confirm the presence of grafted 3ATAC. Four samples from each experimental set were dyed simultaneously and the dye bath water reserved for analysis by UV Spectroscopy.

To ascertain the quantity of 3ATAC on the dyed nonwoven polypropylene fabrics, K/S values were taken with a spectrophotometer. To obtain a more accurate standard deviation and average, the spectrophotometer was placed on the uniformly and nonuniformly dyed portions of each sample set.

Neither the nonwoven polypropylene nor the cotton contains positive groups capable of reacting with acid dye. Therefore, fabric staining is indicative of successful grafting.

CI Acid Blue 9 dye was selected for the acid dyeing and was prepared at 0.304g/L in deionized water. Portions of samples were cut using a template into 3.7" x 3.7" squares. Four squares were selected per treatment condition and immersed in 20mL of room-temperature dye solution for 40 minutes (past exhaustion). Samples were then rinsed thoroughly in warm water and air-dried. The dye bath water was reserved for each sample set.

Quaternary Dye Testing

To evaluate the acid dyeing of the 3ATAC-grafted polypropylene, dye bath water was evaluated using UV Spectroscopy. UV spectroscopy was conducted on a Care 3E UV-Visible spectrophotometer using Varian Scan Software.

A scan of the CI Acid Blue 9 solution was taken from 200nm to 800nm to determine key absorption peaks (Figure 6). A single absorption peak was identified at 629nm.

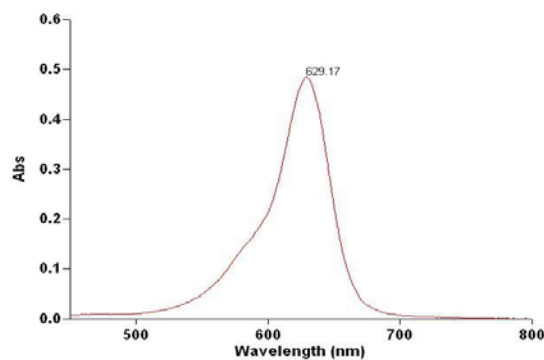


FIGURE 6. Acid blue 9 dye absorption peak.

Three standards of known dye concentration were used to generate a calibration curve for dye with and without acid. Dye absorption is directly proportional to concentration, as expressed by Beer's Law [31].

A linear curve fitted to the calibration data for the dye produced the linear relationship $\text{Abs} = 96.190 \cdot \text{Conc}$, with a correlation coefficient of 0.999 as shown in Figure 7.

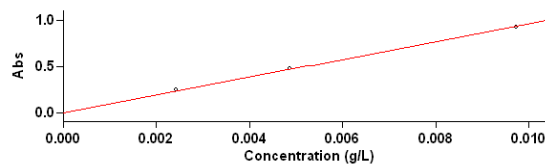


FIGURE 7. Acid blue 9 dye calibration curve.

X-Rite Spectrophotometer

The dyeability of the samples was evaluated by obtaining the coefficient (K/S) values for each sample using a X-Rite Spectrophotometer.³² GretagMacbeth Color iControl software was employed. Three to four samples from each experimental set were evaluated to generate a standard deviation.

RESULTS AND DISCUSSION

Change in Mass

The change in mass was assessed to determine the percent grafting of the 3ATAC compound. The combination of chemicals used for each grafting solution is identified as:

Control-untreated fabric

AP- fabric treated by APJET device

NCAPS-fabric treated by NCAPS device

Q-Quaternary monomer, 3ATAC

D-Diacrylate

M-Mohr's salt

P-Potassium persulfate

d-exposure to plasma after drying of solution

w-exposure to plasma while solvent is present

Control and plasma treatment data for polypropylene (Figure 8a) indicates little change in mass for samples exposed only to plasma or chemicals. Samples exposed to the chemical and to the APJET plasma device, however, (Figure 8b, 8c, & 8d), indicate up to 0.5% add-on, with highest yields for solutions containing the diacrylate and either Mohr's salt, potassium persulfate, or both.

Use of the NCAPS device on dry chemicals also showed high yields with the diacrylate and either Mohr's salt, potassium persulfate, or both. However, samples treated with only the monomer and diacrylate showed the greatest add-ons of over 1%. For the samples treated on the NCAPS while wet, the highest yield on the NCAPS occurred when all chemicals were present.

In all cases, the use of additives increased grafting over yield achieved by pure monomer, suggesting their presence can improve grafting of monomer on the nonwoven polypropylene substrates.

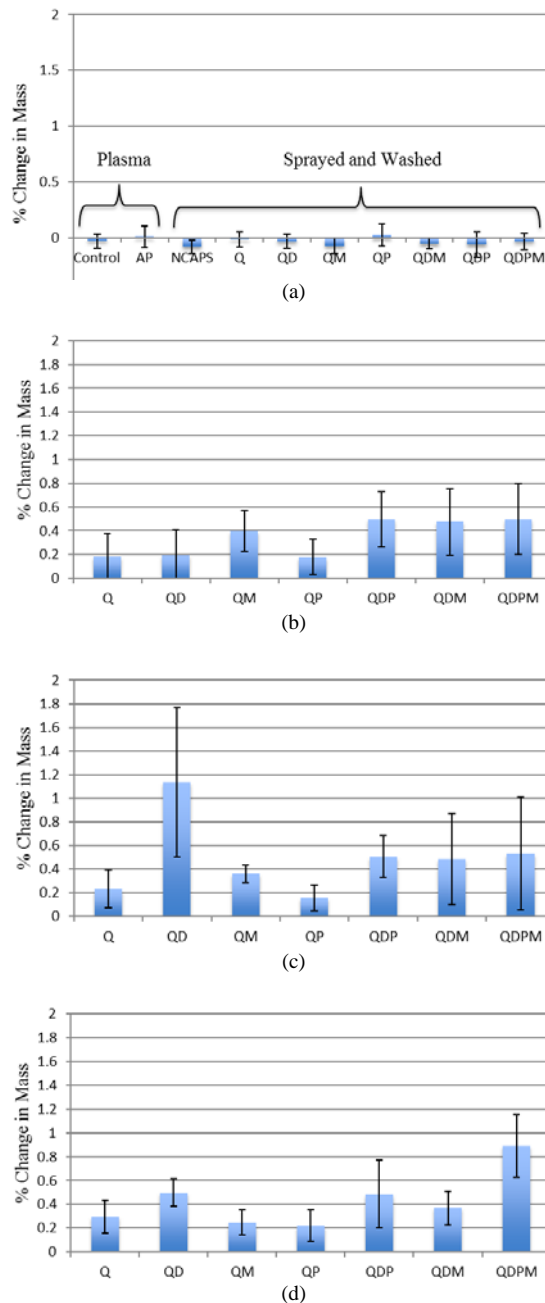


FIGURE 8. Grafting of 3ATAC to polypropylene fabric (a) without plasma treatment, (b) on the APJeT® device, (c) on the NCAPS device after solution was dried on fabric, and (d) on the NCAPS device without drying solution.

Cotton fabric is highly hydrophilic and therefore significantly influenced by humidity conditions. Despite the use of controlled rooms, the percent mass data was inconsistent and not considered a valid indication of grafting.

Contact Angle

Contact angle of the grafted polypropylene was obtained to determine presence of 3ATAC and surface functionalities created by plasma processing. Untreated polypropylene contains only carbon and hydrogen and is therefore hydrophobic, with contact angles greater than 90°. Plasma processing creates hydrophilic oxygen functional groups including hydroxyls, carboxylic acids, and peroxides that reduce the contact angle [33,34]. Successful grafting of the 3ATAC monomer was expected to introduce a positive charge to the surface of the polypropylene, increasing hydrophilicity and decreasing contact angle.

The control and APJeT® sample still possess a high contact angle of over 90° as shown in Figure 9. In contrast, treatment on the NCAPS reduced contact angle to around 70°. Samples treated on the NCAPS with 3ATAC and additives have a similar contact angle to the sample treated only with plasma on the NCAPS. All samples treated on APJeT® with 3ATAC and additives displayed lower contact angles than a control sample or a sample exposed to the APJeT®, but no chemicals, indicating presence of the 3ATAC.

Samples grafted with the quaternary and diacrylate, or quaternary, diacrylate, and potassium persulfate show the lowest overall contact angles, indicating greatest presence of quaternary compound.

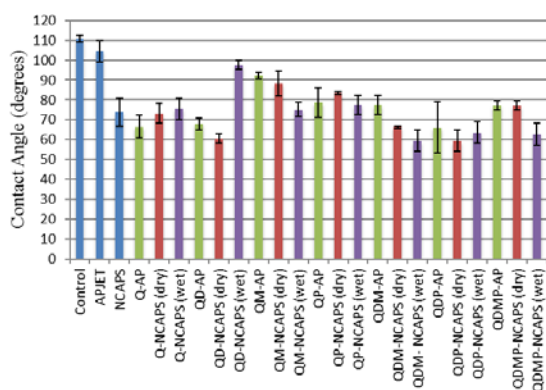


FIGURE 9. Contact angle of grafted 3ATAC on polypropylene.

Quaternary Dye Testing-Visual Assessment

A picture of dyed nonwoven polypropylene samples is shown in Figure 10. The rows represent the control, different plasma devices, and samples painted with chemical, but not plasma-treated. The columns represent the various chemical combinations used in grafting. Only one sample is shown per experimental condition, and this sample represents the sample with the greatest presence of dye. Significant variation in uniformity of dye was observed for both cotton and nonwoven polypropylene samples.

For the polypropylene samples, all samples treated only with plasma or with chemical but no plasma (top row) show no coloration and therefore no 3ATAC presence. Samples treated in the APJET device showed indication of 3ATAC grafting when the monomer was combined with diacrylate and potassium persulfate (QDP) or diacrylate, potassium persulfate, and Mohr's salt (QDPM). Samples treated on the NCAPS and exposed dry dyed for those same chemical combinations as well as with only the 3ATAC and diacrylate (QD) indicate grafting. NCAPS samples exposed wet showed little change in coloration regardless of chemical combination. Across the board, the presence of a diacrylate was significant in increasing grafting of 3ATAC regardless of device or additional additives. After laundering, no samples showed indications of dyeing, indicating removal of the quaternary or impediment by the anionic detergent.

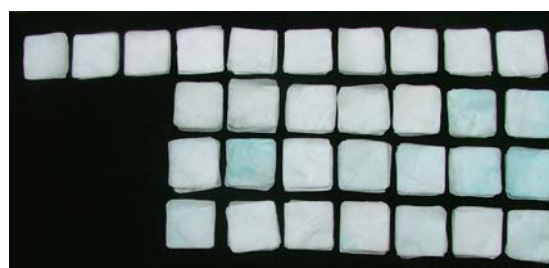


FIGURE 10. Quaternary dyeing of 3ATAC on nonwoven polypropylene
 1st Row: Control, APJET, NCAPS, Q, QD, QM, QP, QDM, QDP, QDMP
 2nd Row (all treated on APJET): Q, QD, QM, QP, QDM, QDP, QDMP
 3rd Row (all treated on NCAPS, dry): Q, QD, QM, QP, QDM, QDP, QDMP
 4th Row (all treated on NCAPS, wet): Q, QD, QM, QP, QDM, QDP, QDMP

Cotton samples exposed to the acid dye exhibited considerably better grafting than polypropylene (Figure 11). All dry samples treated with APJeT® or NCAPS and any combination of chemical show significant color change indicating successful grafting of the quaternary compound. Samples treated wet on NCAPS, excluding the pure 3ATAC sample (Q), show little grafting without addition of a diacrylate.

As with the nonwoven polypropylene samples, samples laundered using the AATCC standard exhibited no ability to dye. This could be a result of poor durability, but is most likely due to interference by the anionic component of the AATCC detergent with the quaternary ammonium group.



FIGURE 11. Quaternary dyeing of 3ATAC on cotton.
 1st Row: Control, APJET, NCAPS, Q, QD, QM, QP, QDM, QDP, QDMP
 2nd Row (all treated on APJET): Q, QD, QM, QP, QDM, QDP, QDMP
 3rd Row (all treated on NCAPS, dry): Q, QD, QM, QP, QDM, QDP, QDMP
 4th Row (all treated on NCAPS, wet): Q, QD, QM, QP, QDM, QDP, QDMP

Overall, two trends are clear. First, diacrylate presence significantly increases the ability of a sample to graft. Secondly, polypropylene samples plasma treated while wet generally exhibit reduced grafting ability.

Both polypropylene and cotton display inconsistent coverage of the grafted quaternary compound. The non-uniform, patchy appearance of the grafting is examined might be attributed to non-uniform coverage by the airbrush during chemical application or to preferential plasma effect in amorphous regions [8].

Dye Uniformity

Dye uniformity of the grafted samples was rated for each experimental condition in Table II. For each of the four samples, every uniformly-dyed sample was assigned one point. If one or more samples exhibited uniform dyeing on at least 50%, it was assigned 0.5 points. Depth of shade was not considered, only uniformity of dye.

Dye uniformity of the cotton samples was best for samples treated dry on the NCAPS device. In addition, the best uniformity was obtained for all devices with or without solvent when 3ATAC was combined with the potassium persulfate, diacrylate, and Mohr's salt (QDMP).

TABLE II. Dye uniformity of cotton grafted with 3ATAC.

ID	Device	Uniformity Rating
Q	AP	0.5
	NCAPS dry	3.0
	NCAPS wet	4.0
QD	AP	2.5
	NCAPS dry	4.0
	NCAPS wet	2.0
QM	AP	2.5
	NCAPS dry	3.0
	NCAPS wet	0.0
QP	AP	2.0
	NCAPS dry	1.0
	NCAPS wet	0.5
QDP	AP	3.0
	NCAPS dry	4.0
	NCAPS wet	4.0
QDM	AP	1.5
	NCAPS dry	3.0
	NCAPS wet	2.0
QDPM	AP	4.0
	NCAPS dry	4.0
	NCAPS wet	4.0

Uniformity of shade was far more difficult to quantify for the nonwoven polypropylene fabric (Table III). Due to the translucent character of the fabric, visual assessment of uniformity was difficult.

Overwhelmingly, presence of the diacrylate or Mohr's salt increased uniformity of dye for the polypropylene samples. Potassium persulfate was ineffective when combined solely with 3ATAC, but increased graft uniformity when used in conjunction with Mohr's salt and diacrylate (QDMP) over uniformity achieved without it (QDM).

TABLE III. Dye uniformity of polypropylene grafted with 3ATAC.

ID	Device	Uniformity Rating ng
Q	AP	1
	NCAPS dry	0
	NCAPS wet	0
QD	AP	3
	NCAPS dry	4
	NCAPS wet	1.5
QM	AP	0
	NCAPS dry	3
	NCAPS wet	0
QP	AP	0
	NCAPS dry	0
	NCAPS wet	0
QDP	AP	3
	NCAPS dry	3.5
	NCAPS wet	0.5
QDM	AP	1
	NCAPS dry	1.5
	NCAPS wet	4
QDPM	AP	3
	NCAPS dry	4
	NCAPS wet	0.5

Quaternary Dye Testing- Spectrophotometry

The K/S values obtained for the polypropylene fabric are shown in Figure 12. The highest K/S values were obtained with addition of diacrylate on the NCAPS dry (QD) or on the NCAPS dry with the addition of all additives (QDMP). Unlike the cotton fabric in Figure 13, the standard deviation of the K/S values for the polypropylene is much smaller, indicating superior uniformity of grafting.

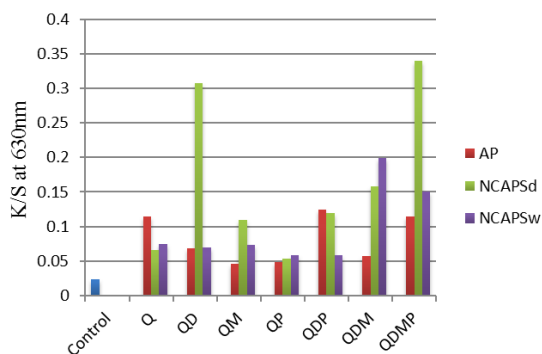


FIGURE 12. K/S Values for polypropylene grafted with 3ATAC.

Cotton samples exhibited K/S values significantly higher than the polypropylene (Figure 13). High K/S values were observed for samples treated with only the 3ATAC (Q), but increases in grafting were achieved when Mohr’s salt was included with the 3ATAC (QM) for samples treated on the NCAPS(d) or APJeT® device.

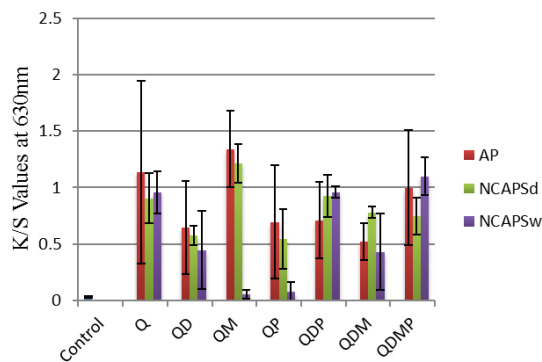


FIGURE 13. Spectrophotometry of cotton grafted with 3ATAC.

Quaternary Dye Testing-UV Spectroscopy

The grams of dye absorbed by each experimental set are graphed in Figures 14 & 15 for the cotton and polypropylene fabrics. Dye absorption should be proportional to the quantity of 3ATAC present, where greater quantities of dye absorbed indicate more grafting.

The polypropylene samples illustrate some clear trends. Addition of diacrylate and Mohr’s salt (QDM) increased dye uptake significantly, from 0.005g to 0.02g, a factor of 4. Addition of a combination of all additives was clearly the most successful, however, increasing grams absorbed to 0.035, almost doubling the uptake when potassium persulfate was added (QDMP).

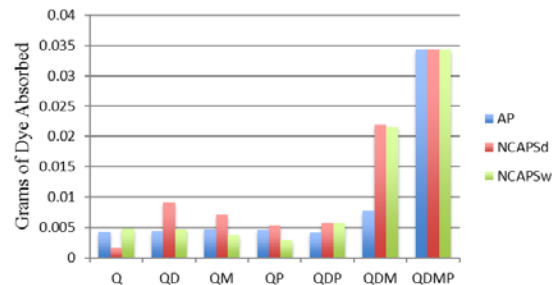


FIGURE 14. Dye absorption of polypropylene grafted with 3ATAC.

Data indicates that for the cotton, the NCAPS device was more successful at grafting than the APJET device. The solution containing the 3ATAC, potassium persulfate, Mohr's salt, and diacrylate (QDMP) was also the most successful combination of additives for grafting on the NCAPS wet or dry.

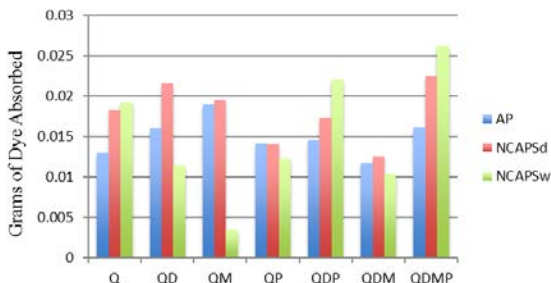


FIGURE 15. Dye absorption of cotton grafted with 3ATAC.

XPS (X-ray Photoelectron Spectroscopy)

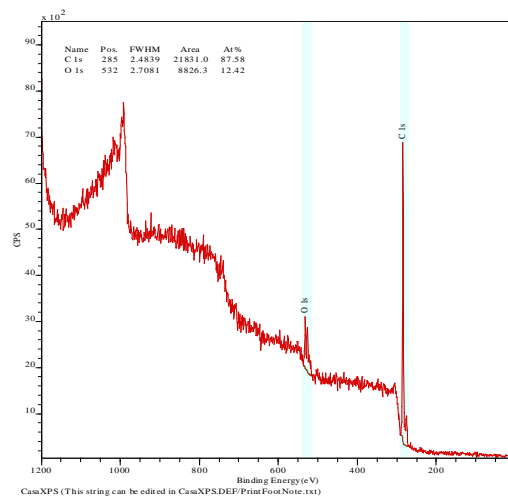
XPS was performed on cotton and polypropylene controls, on plasma-treated samples, and on samples QDMP NCAPS (dry) as shown in *Figures 16 and 17*. *Tables IV and V* illustrate the relative intensities of the elements observed on the surface of the cotton and polypropylene samples.

Polypropylene fabric exhibited only carbon and oxygen surface elements. Exposure to atmospheric-pressure plasma increased in oxygen content by about 2%, indicating the generation of oxygen-functional groups by the plasma. Since XPS was conducted months after initial treatment of polymers, it is likely that some ageing affects had occurred and that more oxygen functional groups were present immediately after plasma exposure [35].

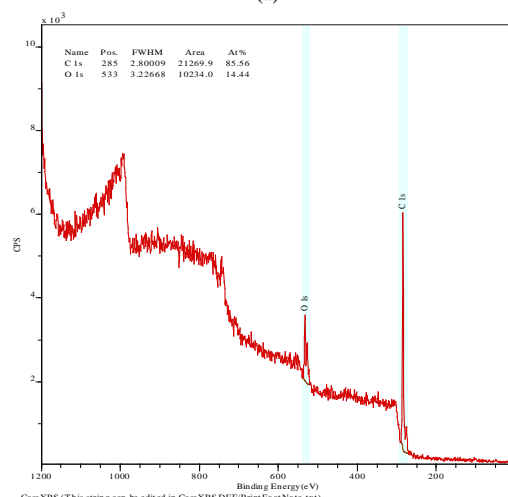
After treatment with the QDMP, the carbon to oxygen ratios were 4% higher than for the plasma treated sample. Nitrogen was also observed on the surface of the polypropylene. Presence of the nitrogen and the increased oxygen content can be attributed to the presence of the grafted QDMP.

TABLE IV. Relative intensities of chemical composition of polypropylene fabric treated with atmospheric plasma and HTCC

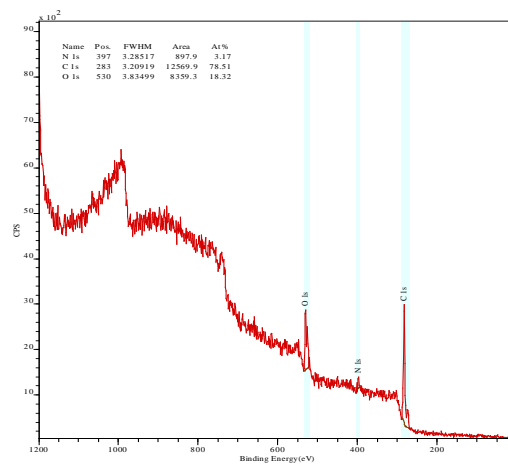
Treatment	C _{1s}	O _{1s}	N _{1s}
Control	87.58	12.42	----
NCAPS	85.56	14.44	----
QDMP NCAPS (dry)	78.51	18.32	3.17



(a)



(b)



(c)

FIGURE 16. XPS of (a) polypropylene (b) plasma treated polypropylene (c) QDMP NCAPS (dry).

The surface composition of the cotton samples exhibited changes similar to the polypropylene. Control cotton samples contained a carbon to oxygen ratio of 1.8:1, and plasma treatment increased the oxygen content by 5%, indicating the generation of new oxygen functionalities.

Samples grafted with the QDMP compound and plasma further slightly modified the surface content observed by XPS. After grafting of the QDMP onto the cotton, an increase in nitrogen is observed. Nitrogen content is indicative of the QDMP chemical, indicating successful grafting by the plasma.

TABLE V. Relative intensities of chemical composition of cotton fabric treated with atmospheric plasma and QDMP NCAPS (dry)

Treatment	C _{1s}	O _{1s}	N _{1s}
Control	64.09	35.91	----
NCAPS	59.96	40.04	----
QDMP NCAPS (dry)	64.42	34.94	0.64

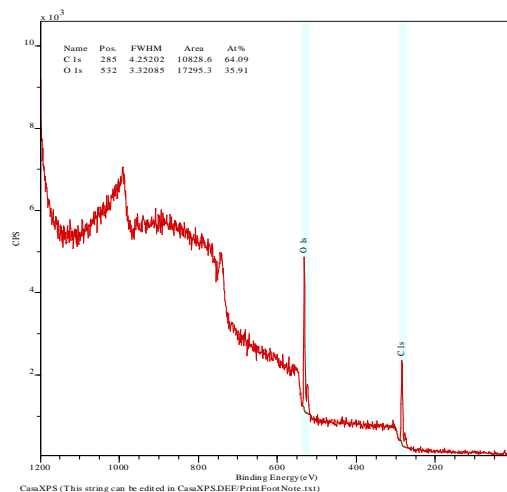
Scanning Electron Microscopy

A scanning electron microscope was used to examine the surface of the grafted cotton and polypropylene fabric. Images of a control and a plasma treated sample were also taken.

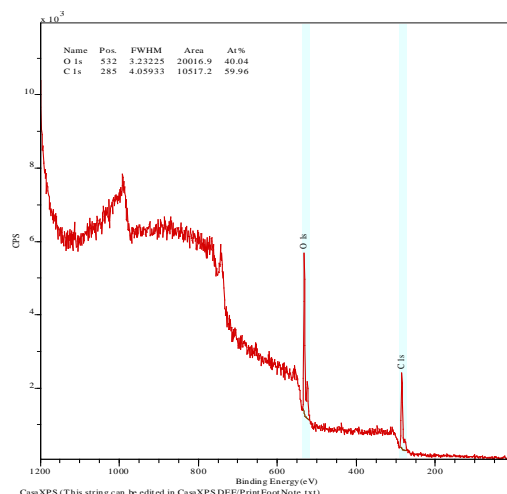
The polypropylene nonwoven is thermally bonded and consists of fibrous regions interspersed with regions where fibers we melted together under pressure. Both areas were examined at several magnifications.

For the cotton samples, there was no notable difference between the control and the plasma treated sample, but the presence of 3ATAC is clearly visible as tiny, globular particles on the cotton fabric treated dry on the NCAPS device (Figure 18). Similar, although less prevalent particles can be observed on the QDMP sample grafted using the APJeT® device (Figures 19 and 20).

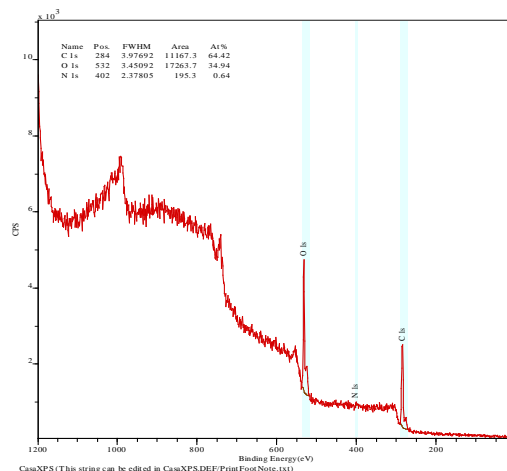
The polypropylene sample grafted with QDMP dry on the NCAPS was also examined by SEM (Figure 21). It was selected due the large quantity of grafting and good dye uniformity. The control polypropylene fabric was relatively smooth with some globular regions indicating the presence of residue, which might include oils, surfactants, and other processing-aids used in production.



(a)



(b)



(c)

FIGURE 17. XPS of (a) cotton (b) plasma treated cotton (c) QDMP NCAPS (dry) and plasma treated cotton.

The sample treated with four minutes of plasma on the NCAPS device is similar in appearance to the control. However, in general, it appeared to contain slightly less chemical residue, which can be attributed to etching in the plasma that effectively cleans the surface [36].

Grafting of the 3ATAC onto the polypropylene sample was visually evident and manifested as tiny visible clumps, similar in appearance to those observed on the cotton samples. The distribution of polymerized 3ATAC was relatively uniform, indicating good and consistent plasma conditions.

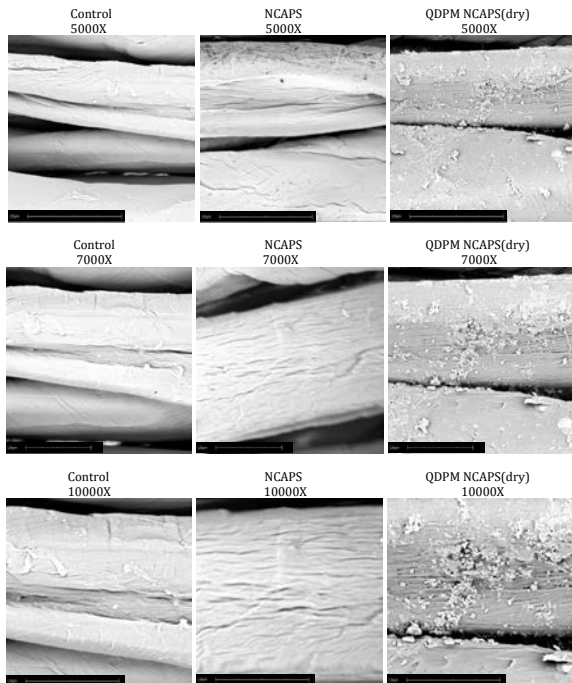


FIGURE 18. Cotton fabric grafted on NCAPS (dry) to QDPM examined by scanning electron microscopy.

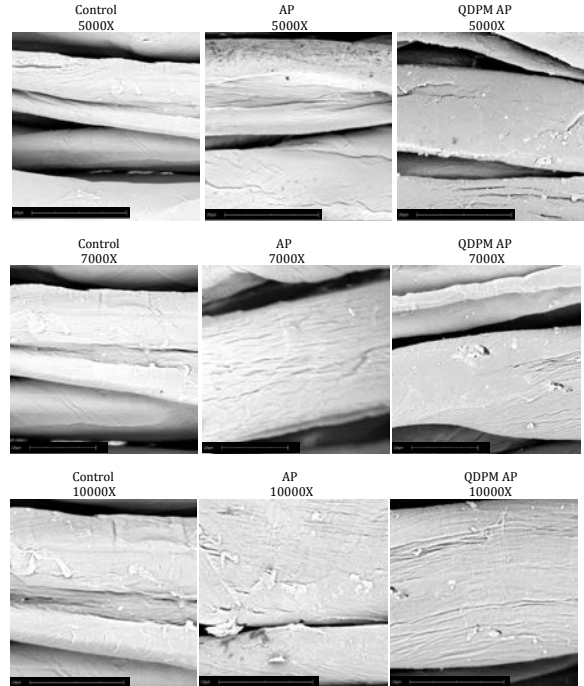


FIGURE 19. Cotton fabric grafted on AP to QDPM examined by scanning electron microscopy.

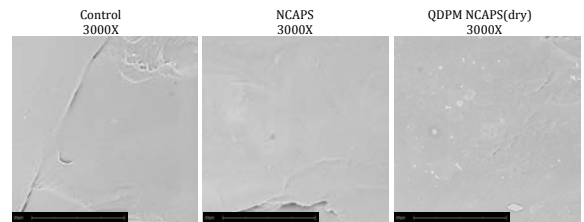


FIGURE 20. Polypropylene fabric grafted with QPMP to NCAPS (dry) examined by scanning electron microscopy melted portion.

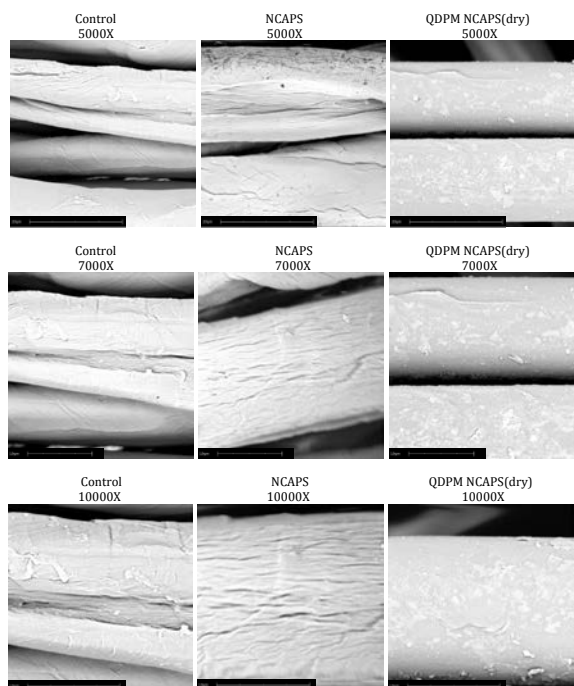


FIGURE 21. Polypropylene fabric grafted with QPMP to NCAPS (dry) examined by scanning electron microscopy fiber portion.

CONCLUSION

Direct grafting of 3ATAC to polypropylene and cotton using atmospheric-pressure plasma and without need for heat or wet solvent baths proved successful and was confirmed by acid dye tests and scanning electron microscopy. Grafting was successful on both the NCAPS dielectric barrier discharge plasma device and the APJeT[®] plasma device. Presence of solvent did not significantly alter grafting of the cotton, but inhibited grafting of polypropylene, perhaps due to the hydrophilic nature of the solvent and hydrophobic nature of the polypropylene. The addition of diacrylate and Mohr's salt improved the grafting of the 3ATAC monomer (QP), and a combination of all investigated additives, diacrylate, potassium persulfate, and Mohr's salt (QDMP) appear to have achieved the highest graft yields.

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