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Simple Method for Grafting of Glycidyl Methacrylate onto Nylon-6 Nonwoven Fabrics for Ion Exchange Applications

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Abstract: ***In this work an affective and generally applicable method for grafting of glycidyl methacrylate (GMA) onto Nylon-6 nonwoven fabrics for ion exchange applications has been developed. The method consists of the creation of dimethylalkylbenzyl ammonoium chloride (DMABAC) in alkaline medium in Nylon-6 textile fabrics followed by treatment the fabrics in a solution containing $K_2S_2O_8$ at room temperature, followed by thoroughly washing with cold water and drying at room temperature. The so-obtained Nylon-6 fabrics were introduced in an aqueous solution of GMA, and copper sulphate. Grafting of GMA was accomplished under required temperature and duration with high rate and almost without homopolymer formation. Factors affecting the yield of grafted polyglycidyl methacrylate (PGMA) were studied. The overall activation energy of the graft copolymrization reaction was found to be 66.7 $KJ.mol^{-1}$. Characterization of grafted Nylon-6 nonwoven fabrics was carried out through Scanning Electron Microscopy (SEM), and Fourier Transform Infrared spectra (FTIR). The availability of aminated Nylon-6 nonwoven fabrics grafted with PGMA as polymer adsorbent for removal Cu^{+2}, Pb^{+2}, Cr^{+6}, and Ag^{+1} ions from its solutions was investigated. The influence of various adsorption parameters on the degree of extraction (R %) and adsorption capacity (SC mg/g) was studied.***

Keywords: Nylon-6 Nonwoven Fabrics, DMABAC, Grafting, SEM, FTIR, Degree of extraction (R %), Adsorption Capacity (SC mg/g)

1. Introduction

Nylon-6 fibers are one of the most important synthetic fibers used in textile industry. However, their surface properties need to be modified to make them suitable for a number of other uses. Recently, the scientific literature has revealed a growing interest in modifying their properties, and consequently, expanding their applications. The preparation of ion exchangers based on Nylon-6 textile materials is one of the new fields which gained a great interest in the last years. A great number of such fibers were developed by grafting Nylon-6 with different vinyl monomers such as methyl vinyl pyridine (MVP), glycidyl methacrylate (GMA), Syrene (ST), acrylonitrile (AN), and methacrylic acid (MAA) **[1-5]**. However, technical and economical constrains remain important factors in the search for the so-called best available technology not including excessive cost. The chemical modification of Nylon-6 fibers via grafting with vinyl monomers could be applicable on industrial scale, only when the grafting process proceeds with high rate and without homopolymer formation. Shalaby et al **[6]** reported that these limitations could be fulfilled only when Nylon-6 contains function groups which are capable of formation of a complex with the initiator on the fibers. Further decomposition of the obtained complex leads to the formation of free radicals on the fibers. This is paving the way for direct grafting of vinyl monomers almost without the formation of homopolymer. In our previous investigations **[7-10]** the graft copolymerization of each of dimethylaminioethyl methacrylate (DMAEMA) **[7]**, hydroxyethyl methacrylate (HEMA) **[8]**, glycidyl methacrylaye (GMA) **[9]** and acrylamide (Am) **[10]** onto Nylon-6 fibers containing polydiallyldimethyl ammonium chloride (PDADMAC), in the presence of $K_2S_2O_8 - Cu^{+2}$ as redox initiating system was carried out with high rate and almost without hompolymer formation. It is important to mention that this method in spite of the fact that it directly provides the creation of the quaternary ammonium groups within polyamide macromolecule, it suffers from a number of drawbacks that prevent its application because of: (1) salt used in this method is costly and unpopular and (2) the fixation of such salt within nylon-6 fabrics requires a lengthy complicated set of steps.

It is well known that glycidyl methacrylate (GMA is one of the most important vinyl monomers used in preparation of ion exchangers based on Nylon-6 textile materials. For this reason it is highly needed to develop a simple and effective method for implementation of common quaternary ammonium salts in Nylon-6 fabrics before grafting with GMA.

Based on the above mentioned the objective of the present work is to study the grafting of GMA onto modified Nylon-6 nonwoven fabrics containing chemically bonded dimethylalkylbenzyl ammonium chloride (DMABAC) instead of modified fabrics containing thermally grafted polydiallyldimethyl ammonium chloride (PDADMAC) in the presence of $K_2S_2O_8 - Cu^{+2}$ as aredox initiating system. This helps to clarify the role of the chemical structure of quaternary ammonium salt (QAS) and the method of its creation in Nylon-6 macromolecule on the rate of grating reaction. Characterization of the grafted fabrics was examined throughout SEM, and FTIR spectroscopy. In addition, sorption properties of grafted with PGMA Nylon-6 nonwoven fabrics were investigated.

2. Experimental Work

2.1 Materials

Nylon-6 nonwoven fabrics used throughout this study were kindly supplied by Egyptex Co. Dimethylalkylbenzyl ammonium chloride (DMABAC) used in this work was in the form of 50% aqueous solution, and was kindly supplied by NIIPAV, Volgodonck, Russia. Glycidyl methacrylate (GMA) of pure grade was freed from the inhibitor by distillation. $K_2S_2O_8$ and $CuSO_4.5H_2O$ were of pure grade chemicals. Sodium thiosulphate ($Na_2S_2O_3$), starch, methyl ethyl ketone and Potassium iodide (KI) used were analytical grade chemicals.

Methods

Fixation of DMABAC on Nonwoven Nylon-6 Fabrics

Preparation of Nylon-6 nonwoven fabrics containing DMABAC was carried out according to the method described by Shalaby et al **[11].**

Grafting Process

Nylon-6 nonwoven fabrics containing DMABAC was grafted with GMA according to the method described by Shalaby et al **[11].**

Adsorption Procedure

Dried samples (0.1 g each) of reactive nonwoven fabrics were added into 100 cm^3 Erenmeyer flask containing 30 cm^3 of each metal ion solution (100 ppm) and adjusted to desired pH. The mixture solution was stirred at 25°C. After filtration of the solution, the ion concentration of the filtrates was analyzed with atomic adsorption spectrophotometer. The degree of extraction (R, %), and sorption capacity (SC, mg/g) were calculated as follows:

$$R = \frac{C_0 - C_i}{C_0} \quad X\,100$$

$$SC = \frac{(C_0 - C_i)\,V}{m}$$

Where C_0 is the initial concentration of investigated metal ions in the solution, g/liter; C_i is the concentration of investigated metal ions in the solution at the time of measurement, g/liter; V is the volume of solution, ml; m is the mass of the sorbent, g.

Analysis

SEM

A JEOL-Model JSM T20 scanning electron microscope (SEM) operating at 19 kV was used to obtain photomicrographs of fibers surfaces.

FT-IR

The chemical structure was determined using the Fourier transformation infrared (FT-IR) spectrometer, model NEXUS 670, NICOLET USA. The measurements were carried in spectral range from 4000 cm^{-1} to 500 cm^{-1}. Reflection percentage measurement technique was applied (R %) to all investigated samples.

Potassium persulfate concentration

Potassium persulfate concentration in solution and in the dried Nylon - 6 nonwoven fabrics was measured according to the method described by Jenkins **[12].**

3. Results and Discussion

Grafting with vinyl monomers as a method for chemical modification of Nylon-6 fibers for preparation of ion exchangers, could be used on industrial scale only when grafting reaction proceeds with high rate and without homopolymer formation. These requirements could be fulfilled only when Nylon-6 macromolecules contains function groups which are capable of formation of a complex with the initiator on the fibers. The decomposition of such complex leads to the formation of free radicals on the fibers which directly initiate grafting without homopolymer formation. Hahan, et al **[13]** have declared that quaternary ammonium groups (QAG) can form complex with peroxides. Steaming from this Shalaby, et al [6] have developed a method for creation of polydiallyldimethyl ammonium chloride (PDADMAC) in Nylon-6 fibers and have grafted these modified fibers with GMA **[9]** in the presence of $K_2S_2O_8$ – Cu^{+2} as redox initiating system with high rate and almost without homopolymer formation. However, in spite of the fact that this method directly provides the creation of such QAS in chemical structure of Nylon-6 fibers it susters, in addition to high cost and unpopularity of the salt, from lengthily and complicated set of steps.

In the present investigations, we report on the effect of the chemical structure of the QAS and the method of its creation in Nylon-6 nonwoven fabrics and on simplification of implementation of QAG in polyamide macromolecule. To achieve this, the grafting of GMA was carried out on modified Nylon-6 nonwoven fabrics containing chemically bonded DMABAC in alkaline medium by using exhaustion technique **[11]** instead of those containing PDADMAC in the form of grafted chains. It was found that, grafting reaction did not take place when Nylon -6 /GMA/Cu^{+2}/H_2O or Nylon-6/GMA/$K_2S_2O_8$/Cu^{+2}/H_2O systems were applied irrespective of any reaction conditions used. Under these conditions a great amount of homopolymer was formed with the latter system. It was found, on the other hand, that, the graft yield increased significantly when DMABAC was chemically bonded to Nylon-6 nonwoven fabric prior to grafting reaction. The increase in weight was still existing even after several extractions of the nonwoven fabrics with methyl ethyl ketone (MEK), which is the solvent of PGMA. The increase in weight is, mainly, due to inclusion of PGMA within Nylon-6 nonwoven fabrics. Such incorporation is believed to be grafting by vinyl addition to Nylon-6 radicals formed during polymerization process. The mechanism of such incorporation is similar to that indicated in our previous paper **[9].**

Given below are the different factors that affect grafting Nylon-6 nonwoven fabrics containing chemically bonded DMABAC with GMA.

Cupric ion concentration

The effect of incorporation of various concentrations of $CuSO_4.5H_2O$ on the graft yield of PGMA on Nylon-6 nonwoven fabrics was studied (Table 1). It was observed that $K_2S_2O_8$ can induce grafting of GMA onto Nylon-6 nonwoven fabrics containing DMABAC even in the absence of Cu^{2+} ion. Nevertheless, the rate of reaction is slow (graft yield is 14.5 % compared with 10 % in case of Nylon-6 nonwoven fabrics untreated) and some amount of homopolymer is formed. The presence of Cu^{2+} ion in the initiating system affects the grafting reaction. An increase in the graft yield could be achieved when Cu^{2+} ion was included in the system. The enhancement in the extent of grafting was dependent on Cu^{2+} ion concentration. The graft yield increased gradually with increasing Cu^{2+} ion concentration and reached 130% at [Cu^{2+}] of 1.5 x 10^{-3} mol/l compared with 213.8% at the same concentration of cupric ions in case of Ntlon-6 fibers containing PDADMAC. Thereafter, the graft yield falls down. The mode of increasing the graft yield with increasing Cu$^{+\ 2}$ concentrations in the reaction medium is similar to that in case of grafting modified Nylom-6 fibers containing grafted PDADMAC and can be explained in the same manner **[9]**. Table 2 also shows that increasing the reaction time causes a significant increase in the graft yield. It was found that 30 minute is required for attaining the maximum graft yield regardless of cupric ion concentration used.

Table 1: Effect of [$CuSO_4.H_2O$] and [GMA] on the Percent Polyglycidyl Methacrytlate (PGMA) Add On

Reaction Conditions	Graft Yield %
$^{(a)}$ [$CuSO_4.5H_2O$], mol/l ×10^{-3}	
0.00	14.5
0.50	35.0
1.00	100.0
1.50	130.1
2.00	98.1
2.50	55.9
3.00	45.9
3.50	30.9
4.00	28.7
$^{(b)}$ [GMA], mol/l ×10^{-1}	
0.175	35.0
0.350	66.0
0.700	110.0
1.050	130.1
1.400	98.4
1.750	70.4
2.100	60.4
2.450	60.8
2.800	55.9

Reaction Conditions:
^{a}[GMA], 1.05×10^{-1} mol/l; [$K_2S_2O_8$], 1.96×10^{-4} mol/l; [DMABAC], 4.79×10^{-4} mol/100gr Nonwoven Fabric; Temperature, 85°C; Duration, 60 min; M :L, 1:100.
^{b}[$CuSO_4.5H_2O$], 1.5×10^{-3} mol/l; [$K_2S_2O_8$], 1.96×10^{-4} mol/l; [DMABAC], 4.79×10^{-4} mol/100gr Nonwoven Fabric; Temperature, 85°C; Duration, 60 min; M :L, 1:100.

GMA concentration

The effect of GMA concentration on polymer add-on was investigated within the range from 0.175×10^{-1} to 2.8×10^{-1} mol/l (Table 2). It was found that the polymer add-on is directly related to GMA concentration up to 1.05 mol/l. The increase of monomer concentration above this value is accompanied with a substantial reduction in grafted PGM. That is, concentration of 1.05 mol/l constitutes the optimal concentration for achieving maximum polymer add-on. It was observed that increasing the reaction time is accompanied with a significant increase in the polymer add-on, irrespective of the GMA concentration used in the reaction medium (Table 2). The best indicator for emphasizing the importance of creation DMABAC rather than PDADMAC in polyamide-6 macromolecule prior grafting reaction is the follow up the effect of GMA concentration on the graft yield. It has been found that, the grafting reaction onto Nylon-6 fibers containing PDADMAC proceeds but with low yield (8.0%, 12.0% and 20%) after 10, 20 and 30 minutes respectively **[9]** in the presence of 0.75×10^{-1}mol/l of GMA. At the same time and under the same conditions, a concentration of 0.70×10^{-1}mol/l of GMA is quite sufficient to attain a graft yields of 27.0%, 50.6% and 68.6% after 10, 20, and 30 minute respectively (Table 2).

Potassium Persulphate Concentration

The effect of reaction time on degree and rate of grafting was studied at constant GMA concentration, for Nylon-6 nonwoven fabrics containing DMABAC over a range of 1.033xl0^{-4} to 1.966x10^{-4} mol/l $K_2S_2O_8$. It was found that, the graft yield increases with increasing the reaction time for all the studied concentrations. However, at longer reaction time the degree of grafting levels off. Moreover, the graft yield and Rp increase as the $K_2S_2O_8$cocentrations increase (Table 2). The character of increasing the graft yield with increasing [$K_2S_2O_8$] in the reaction medium is in full agreement with that in case of grafting Nylon-6 fibers containing PDADMAC and can be explained in the same manner [9]. Based on the results listed in previous work **[9]** a graft yield of 99.0% could be attained on Nylon-6 containing PDADMAC when the reaction proceed for 30 minute in the presence of 2.404x10^{-4} mol/l $K_2S_2O_8$ in the reaction medium. At the same time and under the same conditions a concentration of 1.966x10^{-4} mol/l $K_2S_2O_8$ is sufficient to attain higher (105.0%) graft yield on Nylon-6 nonwoven fabric containing DMABAC (Table 2).

Polymerization Temperature

The graft copolymerization reaction of GMA on Nylon-6 nonwoven fabrics was carried out under four temperatures between 70°C and 85°C. It is clear (Table 2) that, the percentage of grafted PGMA and the rate of grafting (Rp) increase with increasing temperature. This is in agreement with previously mentioned grafting of GMA onto Nylon-6 fibers containing PDADMAC and can be interpreted in the same manner as indicated in **[9].** Based on the data given in Table (2) the activation energy was calculated and it was found to be 66.7 KJ/mol. This compared with 134.7 KJ/mol in case of using Nylon-6 fibers containing PDADMAC.

Characterization of Treated Nylon-6 fibers

FTIR spectrum

Figure 1 shows the FTIR spectra of Nylon-6 nonwoven fabrics before [Fig. 1(A)] and after [Fig. 1(B)] treatment with DMABAC. On the basis of the obtained spectra, one can conclude the following:

- The FTIR spectrum of regular Nylon-6 fabrics shows absorptions at 1662–1531, 3071.1, and 2920–2852 cm^{-1}, which are typical to those of >C=O in CONH, NH_2, N—H and C—H stretching respectively.
- The spectrum of grafted Nylon-6 with PGMA [Fig.1(C and D)] shows an additional absorption band at 1727.9 cm^{-1} that can be attributed to >C=O in GMA.

Table 2: Effect of [$CuSO_4.5H_2O$], [$K_2S_2O_8$], [GMA], and Temperature on the Extent and Rate of Grafting (Rp)

Reaction Conditions		Reaction Time (sec.)							
		300		600		1200		1800	
[$CuSO_4.5H_2O$], (mol/l) [a]		G.Y* (%) (1)	Rp** (mol/l.sec) (2)	G.Y* (%) (3)	Rp** (mol/l.sec) (4)	G.Y* (%) (5)	Rp** (mol/l.sec) (6)	G.Y* (%) (7)	Rp** (mol/l.sec) (8)
0.2×10^{-3}		3.2	3.75×10^{-6}	12.2	1.44×10^{-5}	14.7	1.72×10^{-5}	21.5	2.52×10^{-5}
0.5×10^{-3}		9.7	1.14×10^{-5}	23.0	2.69×10^{-5}	30.6	3.59×10^{-5}	35.8	4.19×10^{-5}
0.7×10^{-3}		15.8	1.85×10^{-5}	25.4	2.97×10^{-5}	55.9	6.55×10^{-5}	75.7	8.87×10^{-5}
1.0×10^{-3}		20.1	2.36×10^{-5}	35.3	4.14×10^{-5}	80.4	9.43×10^{-5}	105	12.3×10^{-5}
[$K_2S_2O_8$], (mol/l) [b]									
1.033×10^{-4}		9.7	1.14×10^{-5}	24.3	2.85×10^{-5}	42.6	4.99×10^{-5}	56.8	6.66×10^{-5}
1.56×10^{-4}		12.4	1.45×10^{-5}	30.4	3.56×10^{-5}	56.0	6.57×10^{-5}	73.6	8.63×10^{-5}
1.78×10^{-4}		15.6	1.83×10^{-5}	32.1	3.76×10^{-5}	69.0	8.10×10^{-5}	87.3	1.02×10^{-4}
1.96×10^{-4}		20.1	2.36×10^{-5}	35.3	4.14×10^{-5}	80.4	9.43×10^{-5}	105	1.23×10^{-4}
[GMA], (mol/l) [c]									
0.175×10^{-1}		4.3	5.04×10^{-6}	7.30	8.56×10^{-6}	17.4	2.04×10^{-5}	26.5	3.11×10^{-5}
0.35×10^{-1}		7.2	8.44×10^{-6}	13.0	1.52×10^{-5}	31.2	3.66×10^{-5}	38.5	4.51×10^{-5}
0.70×10^{-1}		12.4	1.45×10^{-5}	27.0	3.16×10^{-5}	50.6	5.93×10^{-5}	68.5	8.03×10^{-5}
1.05×10^{-1}		20.1	2.36×10^{-5}	35.3	4.14×10^{-5}	80.4	9.43×10^{-5}	105	1.23×10^{-4}
Temperature (^0C) [d]	1000/T								
70	2.91	5.6	6.57×10^{-6}	13.4	1.57×10^{-5}	22.6	2.65×10^{-5}	26.3	3.10×10^{-5}
75	2.87	10.4	1.22×10^{-5}	18.3	2.14×10^{-5}	42.4	4.97×10^{-5}	52.7	6.18×10^{-5}
80	2.83	14.3	1.68×10^{-5}	26.2	3.10×10^{-5}	58.5	6.88×10^{-5}	76.8	9.0×10^{-5}
85	2.79	20.1	2.36×10^{-5}	35.3	4.14×10^{-5}	80.4	9.43×10^{-5}	105	1.23×10^{-4}

Grafting Conditions:

[a] [GMA], 1.05×10^{-1} mol/l; [$K_2S_2O_8$], 1.96×10^{-4} mol/l; [DMABAC], 4.79×10^{-4} mol/100gr Nonwoven Fabric; Temperature, 85°C; M :L, 1:100.

[b] [GMA], 1.05×10^{-1} mol/l; [$CuSO_4.5H_2O$], 1.50×10^{-3} mol/l; [DMABAC], 4.79×10^{-4} mol/100gr Nonwoven Fabric; Temperature, 85°C; M :L, 1:100.

[c] [$CuSO_4.5H_2O$], 1.50×10^{-3} mol/l; [$K_2S_2O_8$], 1.96×10^{-4} mol/l; [DMABAC], 4.79×10^{-4} mol/100gr Nonwoven Fabric; Temperature, 85°C; M :L, 1:100.

[d] [GMA], 1.05×10^{-1} mol/l; [$K_2S_2O_8$], 1.96×10^{-4} mol/l; [$CuSO_4.5H_2O$], 1.50×10^{-3} mol/l; [DMABAC], 4.79×10^{-4} mol/100gr Nonwoven Fabric; M:L, 1:100.

* G.Y, Graft Yield * * Rp, Rate of Grafting

The presence of this band verifies that the grafting of GMA to Nylon-6 fibers has occurred as expected.

- The absorption corresponding to N—H group at 3071.1 cm^{-1} has gradually weakened with the increase of grafting. This leads to the suggestion that the grafting reaction happened on the nitrogen atoms of amide groups (CONH) inNylon-6 macromolecules.

The fabric topography

Figure 2 presents scanning electron micrographs corresponding to Nylon-6 nonwoven fabrics treated with DMABAC and grafted by PGMA. It is seen from the SEM results that, regular Nylon-6 surface has a smooth and relatively homogeneous appearance [Fig.2 (A)]. After treatment with DMABAC, Nylon-6 surface has gained a roughness [Fig.2 (B)]. The grafting with PGMA led to formation of a layer on the surface of all investigated samples [Fig.2 (C and D)]. The density of this layer increases gradually with increasing the graft level from 40 to 80.0%.

Sorption Properties of Nylon-6 Nonwoven Fabrics Grafted with PGMA

The sorption properties and factors affecting sorption of several metal ions (Cu^{+2}, Pb^{+2}, Cr^{+6}, and Ag^{+}) with Nylon-6 nonwoven fabrics containing DMABAC and grafted with GMA were investigated. To do this, Nylon-6 nonwoven sorbent was initially prepared by polymer –analogous transformation under the action of aqueous amine. Diethylamine was used for amination of nonwoven fabrics grafted with GMA fabrics. This treatment enhances their adsorption availability. It allows obtaining complexing fiber sorbents since its functional groups are not only capable of ionization but also have electron- donor properties. For this reason, when such sorbents come into contact with transition metal ions with vacant orbital metals are sorbed as a result of a donor acceptor reaction **[14].**

Dried samples (0.1g each) of Nylon-6 nonwoven fabrics containing DMABAC grafted with PGMA and aminated with aqueous diethylamine were added into 100 cm^3 flasks containing 30 cm^3 of each metal ion solution having constant concentration and adjusted to desired pH. The mixture solution was stirred under desired temperature for the desired duration. Then the solution was filtered and the ion concentration of the filtrates was analyzed. Finally, the degree of extraction (R %) and sorption capacity (SC mg/g) were calculated. The effect of adsorption conditions on both (R %) and SC (mg/g) of studied metal ions with reactive Nylon-6 nonwoven fabrics was investigated (Table 3)

Effect of Time

Based on the data listed in Table 3 the following can be concluded:

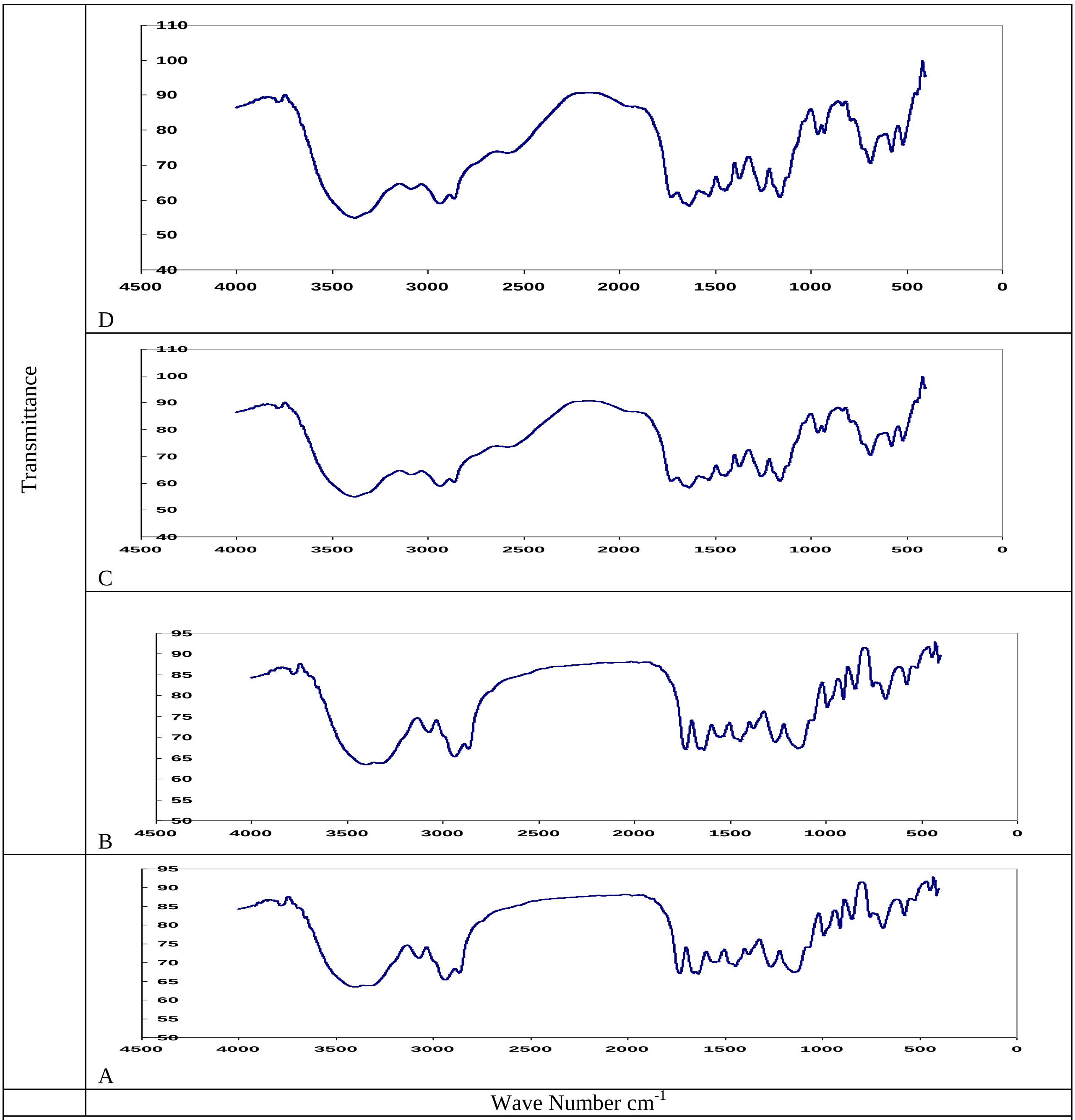

Figure (1): Infra Red Spectroscopy For Nylon-6 Nonwoven Fabrics Treated with DMABAC and Grafted With PGMA

[A] Nylon-6
[B] Nylon-6 – DMABAC
[C] Nylon-6-DMABAC - gr.- PGMA (40%)
[D] Nylon-6- DMABAC gr.- PGMA (80%)

1. It was found that, at a short adsorption time (10min.) there is a significant increase in values of both R% (64.6, 59.5 and 55.3) and SC (4.1, 10.9, and 5.94 mg/g) in case of sorption of Cu^{+2}, Pb^{+2}, and Cr^{+6} respectively. Further increase in the adsorption time has a little effect on the aforementioned properties.
2. The reactive Nylon-6 nonwoven fabrics has a higher sorption capacity (SC) for Pb^{+2} (11.6 mg/g) and Cr^{+6} (6.64 mg/g) ions than Cu^{+2} (4.63 mg/g) and Ag^{+} (1.46 mg/g) ions.
3. The adsorption equilibrium of the reaction nonwoven fabrics for the investigated ions were reached at 20-30 minute.

Effect of pH

Data which illustrate the effect of pH values on the adsorption of studied ions (Table 3) reveled that Cu^{+2}, Pb^{+2}, and Cr^{+6} are adsorbed poorly on the reactive nonwoven

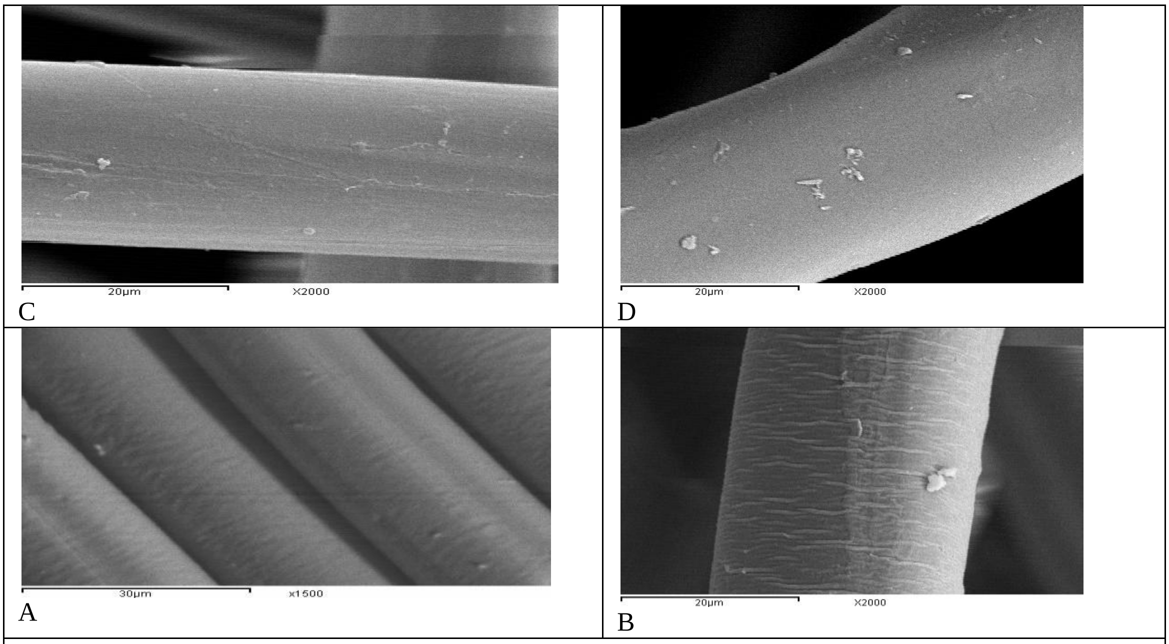

Figure (2): Scanning Electron Micrograph For Nylon-6 Nonwoven Fabrics Treated with DMABAC and Grafted With PGMA (X2000)
[A] Nylon-6
[B] Nylon-6 – DMABAC
[C] Nylon-6- DMABAC- gr.- PGMA (40%)
[D] Nylon-6- DMABAC- gr.- PGMA (80%)

fabrics at pH which is lower than pH 4. The adsorption increased significantly with the increase of pH in the range from 4 to 6, reaching values of 4.63, 11.63, and 6.64 mg/g, respectively. At low pH values, the high hydrogen ion concentrations at the interface repel positively charged metal ions and prevent their approach to the fiber surface [15]. At pH 6, the adsorbed amount of pb^{+2} (11.63 mg/g) and Cr^{+6} (6.64 mg/g) ions are more than that of the Cu^{+2}, and Ag^{+} ions. This proves the way for selective adsorption of pb^{+2} and Cr^{+6} ions from a mixture, containing pb^{+2}, Cr^{+6}, Cu^{+2}and Ag^{+} ions, by carefully adjusting the pH values and other adsorption conditions.

Effect of Graft Yield

The effect of graft yield on the adsorption amount of ions have been studied by performing adsorption experiments using reactive nonwoven fabrics having graft yield in the range 20-90%. The obtained results are listed in Table 3. It is obvious that, the adsorption amounts of Cu^{+2} , pb^{+2}, and Cr^{+6} ions increased with the increase of graft yield, then level off after 80 % graft yield, reaching 4.63, 11.63, 6.64 and 1.46 mg/g of Cu^{+2} , pb^{+2}, Cr^{+6} and Ag^{+} ions, respectively. These increases in adsorption can be attributed to the existence of multifunctional groups, which are grafted onto fiber. Therefore, more interactions with the ions take place. The leveling off of adsorption amount after a certain graft yield is due to the densely packed structure of Nylon-6 nonwoven fabrics which acts as a barrier after a certain value of grafting and impedes diffusion of ions into polymer backbone.

Effect of initial Ion Concentration

Table 3 shows the relationship between initial concentration of metal ions and the adsorption amount. It is clear from the data that, the adsorption amount of metal ions increased with increasing initial ion concentration then reached a plateau value at higher concentration. This is attributed to that the chelating sites of the reactive fiber become saturated when the metal ion concentration is reached 200 ppm.

Effect of Temperature

The effect of the temperature on the adsorption amount of ions onto reactive nonwoven fabrics was studied within the range 25^{o}C – 80^{o}C. The results are shown in Table 3. It is seen from these data that, the increase of temperature from 25°C up to 60°C practically did not affect the sorption of Ag but caused a little increase in the sorped amount of Cu^{+2} (from 4.63 to 5.30 mg/g). At the same time and under the same conditions the sorption capacity of both Pb^{+2} and Cr^{+6} ions increased (from 11.63 to 12.9 and from 6.64 to 7.54 mg/g respectively). However, further increase in the adsorption temperature has a little effect on the aforementioned property. The increase in adsorption capacity of reactive nonwoven fabrics with temperature may be caused by the enhancement of the swilling ability of the sorbent.

It is clear from the results of studying the effect of different factors on the degree of extraction and sorption capacity for each of the investigated ions that:

1. The proper temperature for carrying out adsorption process is 25°C. In spite of the fact that the increase in this temperature above25°C leads to an increase in sorption

properties this increase is not equivalent to the energy consumption needed to increase the temperature.

Table 3: Effect of Adsorption conditions on the Degree of extraction (R %), and Adsorption Capacity (SC, mg/g)of Metal Ions with Nylon-6 Nonwoven Fabrics Treated with DMABAC and Grafted with PGMA

(a) Adsorption Time (min.)	Metal Ions							
	Cu^{+2}		Pb^{+2}		Cr^{+6}		Ag^{+}	
	R%	SC, mg/g	R%	SC, mg/g	R%	SC, mg/g	R%	SC, mg/g
10	64.6	4.10	59.5	10.9	55.3	5.94	5.61	1.10
20	68.1	4.32	61.3	11.2	58.2	6.25	5.91	1.14
30	73.0	4.63	63.5	11.6	61.8	6.60	7.57	1.40
60	73.0	4.63	63.5	11.6	61.8	6.64	7.60	1.46
120	73.7	4.68	63.6	11.6	61.9	6.65	7.63	1.47
(b) Adsorption pH	Cu^{+2}		Pb^{+2}		Cr^{+6}		Ag^{+}	
	R%	SC, mg/g	R%	SC, mg/g	R%	SC, mg/g	R%	SC, mg/g
3	16.9	1.07	7.10	1.30	9.13	0.89	5.70	1.10
4	19.7	1.26	11.8	2.16	13.2	1.42	5.95	1.15
5	36.9	2.34	28.9	5.30	30.5	3.28	5.95	1.15
6	73.0	4.63	63.5	11.63	61.5	6.64	7.60	1.46
(c) Adsorption Temperature (°C)	Cu^{+2}		Pb^{+2}		Cr^{+6}		Ag^{+}	
	R%	SC, mg/g	R%	SC, mg/g	R%	SC, mg/g	R%	SC, mg/g
25	72.9	4.63	63.5	11.63	61.8	6.64	7.56	1.46
40	78.0	4.95	65.7	12.03	68.0	7.31	7.90	1.52
60	83.5	5.30	70.7	12.90	70.2	7.54	8.55	1.65
80	87.1	5.53	72.3	13.24	73.0	7.84	9.20	1.77
(d) Initial Concentration (ppm)	Cu^{+2}		Pb^{+2}		Cr^{+6}		Ag^{+}	
	R%	SC, mg/g	R%	SC, mg/g	R%	SC, mg/g	R%	SC, mg/g
20	29.5	1.87	23.8	4.35	22.4	2.41	2.02	0.39
40	49.0	3.11	54.5	9.98	43.8	4.71	2.75	0.53
100	73.0	4.63	63.6	11.63	61.8	6.64	7.60	1.46
200	73.6	4.76	63.7	11.70	62.2	6.68	7.73	1.49
(e) Graft Yield %	Cu^{+2}		Pb^{+2}		Cr^{+6}		Ag^{+}	
	R%	SC, mg/g	R%	SC, mg/g	R%	SC, mg/g	R%	SC, mg/g
21	36.2	2.29	38.9	7.12	42.8	4.60	3.90	0.76
42	56.5	3.58	46.5	8.51	49.3	5.30	5.70	1.10
66	64.5	4.10	55.2	10.10	57.3	6.20	6.70	1.30
80	70.0	4.41	60.0	11.20	59.9	6.46	7.20	1.39
90	73.0	4.63	63.5	11.63	61.8	6.64	7.60	1.46

Adsorption Conditions:

(a) Initial Concentration of Salts, 100 ppm; Adsorption pH, 6; Adsorption Temperature, 25°C, Graft Yield, 90 %; [DMABAC], 4.79×10^{-4} mol/100 gr Nonwoven Fabric.

(b) Initial Concentration of Salts, 100 ppm; Adsorption Time, 60 min.; Adsorption Temperature, 25°C; Graft Yield, 90 %; [DMABAC], 4.79×10^{-4} mol/100gr Nonwoven Fabric.

(c) Initial Concentration of Salts, 100ppm; Adsorption pH, 6; Adsorption Time, 60 min.; Graft Yield, 90 %; [DMABAC], 4.79×10^{-4} mol/100 gr Nonwoven Fabric.

(d) Adsorption pH, 6; Adsorption Time, 60 min.; Adsorption Temperature, 25°C; Graft Yield, 90 %; [DMABAC], 4.79×10^{-4} mol/100 gr Nonwoven Fabric.

(e) Initial Concentration of Salts, 100ppm; Adsorption pH, 6; Adsorption Temperature, 25°C; [DMABAC], 4.79×10^{-4} mol/100 gr Nonwoven Fabric.

2. The adsorption equilibrium for the reactive Nylon-6 nonwoven fabrics in case of the investigated ions takes place after 30 minutes from the beginning of sorption process. In addition, the maximum values of the sorption properties have been attained at pH equal to 6.
3. The sorption properties of Nylon-6 nonwoven fabrics are directly related to the polymer add – on up to 80% PGMA. The increase in the amount of grafted polymer on nonwoven fabrics above 80% did not, practically, affect the sorption values. It is important to mention that creation of a very small amount of DMABAC into Nylon-6 fabrics (4.79×10^{-4} mol/100gr nonwoven fabric) before grafting provides reaching maximum graft yield (130 %). This graft yield is almost double the amount of grafted PGMA needed for obtaining maximum adsorption properties of the fabrics. This, in turn, means that, the maximum graft yield (213 %) **[9]** obtained after creation of 0.5-1.0 % PDADMAC into Nylon-6 nonwoven fabrics followed by its grafting with GMA is not required if these modified fabrics will be applied for extraction of metals from its aqueous solutions.
4. Table (4) illustrates the feasibility of the developed method for grafting GMA onto Nylon-6 nonwoven fabrics. Based on the data listed in this table, one can conclude that, it is more effective for grafting GMA onto Nylon-6 nonwoven fabric using $K_2S_2O_8$ – Cu^{+2} as initiating system to use fabrics containing chemically bonded DMABAC rather than fabrics containing

PDNABAC. This approach provides attaining the optimal PGMA (80-90 %) for achieving maximum sorption capacity for pb^{+2}, Cr^{+6}, and Cu^{+2} within a shorter sorption time, less monomer (GMA), $K_2S_2O_8$, $CuSO_4.5H_2O$ and QAS concentrations.

Table 4: The Feasibility of Creation of DMABAC Instead of PDADMAC into Nylon-6 Nonwoven Fabrics for Grafting GMA

No.	Fabrics	Graft Yield %	Grafting Conditions						
			[GMA] (mol/l)	[$CuSO_4.5H_2O$] (mol/l)	[$K_2S_2O_8$] (mol/l)	QAS mol/100 gr Fabric		Temperature (°C)	Duration (min.)
						[DMABAC]	[PDADMAC]		
1	Nylon-6 Nonwoven Containing DMABAC and Grafted with PGMA	80.0	1.05×10^{-1}	1.0×10^{-3}	1.97×10^{-4}	4.79×10^{-4}	-	85	20
2	Nylon-6 Nonwoven Containing PDADMAC and Grafted with PGMA	80.0	3.02×10^{-1}	1.5×10^{-3}	2.96×10^{-4}	-	1.5×10^{-3}	85	40

4. Conclusions

1. An effective and generally applicable method for grafting of glycidyl methacrylate onto Nylon-6 nonwoven fabrics for ion exchange applications has been developed. This method is based on creation of a small amount of dimethylalkylbenzyl ammonium chloride instead of polydiallyldimethyl ammonium chloride into Nylon-6 nonwoven fabrics before grafting followed by grafting GMA using $K_2S_2O_8$ – Cu^{+2} as initiating system. It was found that this approach provides proceeding the grafting reaction with high rate and almost without homopolymer formation. Moreover, this developed method paves the way for attaining the optimal percent of grafted polyglycidyl methacrylate (80 %) for achieving maximum sorption capacity for pb^{+2}, Cr^{+6}, and Cu^{+2}. This occurs within a shorter time, and less monomer (GMA), $K_2S_2O_8$, $CuSO_4.5H_2O$ and quaternary ammonium salt concentrations.
2. The sorption properties and factors affecting sorption of the investigated metal ions (pb^{+2}, Cr^{+6}, Cu^{+2}, and Ag^{+1}) with Nylon-6 nonwoven fabrics containing DMABAC, PGMA and aminated with diethylamine were investigated.

References

[1] T. V. Druzhnina, L. A. Nazarina, and K. V. Kardash, Sorption – Active Modified Chemical Fibers, Fiber Chemistry, Vol.32, No. 6, 407 (2002).

[2] T. V. Druzhinina, and L. A. Nazarina, Khim Volokna, No. 4, 8-16, (1999). Chem Abst. 132: No.19, 252345 S (2000).

[3] T.V. Druzhinina and M. A.Struganova, Fabrication of Polycaproamide Chemisorption Fiber with Hydrazide Groups, Fiber Chemistry,Vol. 33, No. 1, 33 (2001).

[4] L. V. Gulina, G. A. Gabrielyan, and L. S. Galbraikh, USSR Inventors Certificate No.1578239 (1990).

[5] N. V. Smirnova, G. A. Gabrielyan, and L. S. Galbraikh, USSR Inventors Certificate No.1726481 (1991).

[6] S. E. Shalaby and N. G. Al-Balakocy, A Simple Efficient and Generally Applicable method For Imparting Polyester and Polyester/Cotton Fabrics Antimicrobial Activity Egypt. Pat. No. 23507 (2006).

[7] S. E. Shalaby, N. H. Abdella, and A. M. Rabie, Chemical Modification of Polyamide -6 Fibers, Containing Chemically Bonded Quaternary Ammonium Groups, with 2-Dimethylaminoethyl-methacrylate,1st International Conference of Textile Research Division, National Research Centre, Cairo, Egypt, March 2-4, (2004).

[8] S. E. Shalaby, N. G. Al-Balakocy, S. M. Abo El-Ola, Surface Modification of Nylon-6 Fibers for Medical Applications, J Appl Polym Sci, 104, 3788 (2007).

[9] S. E. Shalaby, N. G.Al-Balakocy, and S. M.Abo El-Ola, Graft Copolymerization of Glycidylmethacrylate onto Modified Nylon-6 Fibers, J Appl Polym Sci, 99, 613 (2006).

[10] N. G. Al-Balakocy, Ph D thesis, Ain –Shams University, Faculty of Science, Cairo, Egypt (2002).

[11] S. E.Shalaby, N. G. Al-Balakocy, O. M. Abel-Fatah, , and A. M. El-Shafei, Antimicrobial Finishing of Regular and Modified Nylon-6 Fabrics, J Appl Polym Sci, 110, 738-746 (2008).

[12] A. D. Jenkins, Polymer Science-Analytical Science Hand - book, Vols. I and II, North-Holland, Amsterdam (1972).

[13] M. C. Hahn, , W. Jaeger, C. H. Wandrey, and G. Reinnisch, The Kinetics of the Radical Polymerization of Diallyl dimethyl Ammonium Chloride. IV. Mechanism of Start and Termination Reaction with Persulfate as Initiator, Acta Polym .,35 , 5, 350 (1984).

[14] T. V. Druzhinina, L. M. Smolenskya, and A. M. Struganova, Sorption of Heavy Metals from Model Solutions with Amine-Containing Chemisorption Polyamide, Fiber Russian Journal of Applied Chemistry, Vol.76, No.12, 1925 (2003).

[15] M. Yigituglu, M. Eros, R. Coskun, O. Sanli, and H. Unal, Adsorption of copper (II), Cobalt (II), and Iron (III) Ions from Aqueous Solutions on Polyethylene Terephthalate Fibers, J Appl Polym Sci, 68, No. 12, 1935 (1998).