

Absorbent for Metal Ions and Dyestuffs Based on Modified Polyethylene-coated-Polypropylene Non-Woven Fabric

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ABSTRACT: A modified polyethylene coated polypropylene (PE-coated-PP) non-woven fabric was prepared by surface coating with a constant layer of thickness (25 μm) of a mixture of an aqueous solution of carboxymethyl cellulose (CMC) and different concentrations of acrylic acid (AAc). Radiation curing of the coated layer was accomplished by electron beam irradiation with a constant dose of 30 kGy. The value of coating percent was calculated in terms of difference in weight. Properties related to hydrophilicity, such as swelling and water uptake %, were investigated by difference in weight of dry and wet samples after several washing cycles. Weight loss, before and after several washing cycles, was monitored. The effect of AAc concentration on the weight loss % of the modified fabric was studied. Moreover, the swelling in different solvents, dilute acid and base, was investigated. The structure of the modified fabric was characterized by Fourier transform infrared spectroscopy and scanning electron microscope in order to examine the compatibility between the coated layer and fabric. Mechanical properties in terms of tensile strength and elongation at break were studied. The efficiency of the uptake of this modified fabric toward basic, reactive dyes, and metal ions such as Cu^{2+} , Ni^{2+} , and Co^{2+} was measured by UV spectrophotometer and energy dispersive X-ray. The results obtained show good efficiency of these modified fabrics toward heavy metal ions and dyes. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

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INTRODUCTION

Sorption and permeability of water and water vapor to improve the comfort and wear properties of textiles can be enhanced by increasing the hydrophilic nature of synthetic fabrics. Several methods have been used for introduction of some hydrophilic monomers to different polymer materials, such as the grafting of vinyl monomers to textile for producing fibers with hydrophilic properties.¹ Another alternate method in practice is the coating of natural or synthetic fibers with coated layer containing hydrophilic group.² Crosslinking of these coated layers can be carried out by chemical methods or by electron beam curing.³ The advantage of electron beam curing over the chemical method is that it does not contain solvent and has no need of temperature.⁴

One of the important polymers used in this technique is carboxymethyl cellulose (CMC). Like other natural polymers, CMC is also a degradable polymer under irradiation but can be crosslinked to form hydrogel under suitable

irradiating conditions, which has been reported by Pengfei et al.⁵

Also, polyethylene coated polypropylene (PE-coated-PP), as a synthetic non-woven fabric, is considered as an industrial important fabrics used in this technique. Increasing hydrophilicity of this fabric has been accomplished by grafting, or surface coating, with suitable hydrophilic ingredient.

PE-coated-PP was modified by radiation-induced graft copolymerization of binary mixtures of 2-hydroxyethyl methacrylate (HEMA) and glycidyl methacrylate (GMA). This modified fabric was used for removal of dyes from dye wastes.⁶

Moreover, the electron beam radiation grafting of GMA on PE-coated-PP was studied. It was found that the grafted substrate possess high efficiency toward the absorption of heavy metal ions such as Cu, Pb, Ca, from waste water.⁷

Modified textile fabrics such as Nylon-6, polyester woven, and knitted fabrics were surface coated with aqueous solution of

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CMC and acrylic acid (AAc). This study leads to obtain modified textile fabrics which can be used for the purpose of removal of some heavy metals such as Cu and Cr.⁸

In the present study, electron beam irradiation has been used for preparing PE-coated-PP fabrics possessing good hydrophilic property by using a coating solution consisting of aqueous CMC and different concentration of AAc. Hydrophilic property was determined in terms of water uptake (%) while the compatibility between the coated layer and the fabrics was examined by Fourier transform infrared spectroscopy (FTIR) spectroscopy and scanning electron microscope (SEM). Mechanical properties in terms of tensile strength and elongation at break were measured. The efficiency of the modified fabric for uptaking metal ions such as Cu²⁺, Ni²⁺, and Co²⁺ and different dyestuffs such as basic and reactive dyes from wastewater were measured by UV-visible spectrophotometer.

EXPERIMENTAL

Materials

PE-coated-PP non-woven fabric, thickness 13 μm , was provided by Kurashiki Textile MFG, Osaka, Japan. A laboratory grade AAc (CH₂=CH-COOH) monomer with purity 99% from Merck (Germany) was used as received. A sodium salt of CMC (C₆H₇O₂(OH)₂OCH₂COONa)_n in the form of granules was supplied by El-Nasr Pharmaceutical Chemical-Prolabo (Egypt). Three metal salts were used throughout this work namely, copper sulfate (CuSO₄), cobalt sulfate (CoSO₄), and nickel sulfate (NiSO₄) and were purchased from El-Nasr Co. for chemical Industries, Egypt. Two dye stuffs belonging to different classes were used throughout this work. These dyes are: Sandocryle Blue (basic dye) and Remazol Golden Orange (reactive dye). The basic and reactive dyes were supplied by Hoechst, Germany.

Coating Preparation and Irradiation

A known weight of sodium salt of CMC granules (3 g) was dissolved in 100 mL of distilled water. The coating solution was first prepared by dissolving different concentration of AAc (2, 4, 6, 8, and 10%) in aqueous solution of CMC with continuous stirring. This solution was then coated on PE-coated-PP non-woven fabric with a floating knife coater forming a coated layer of constant thickness of 25 μm . The surface coated fabrics were exposed to accelerated electrons using the electron beam accelerator of 1.5 MeV and 25 kW made by High Voltage Engineering, USA, at National Center for Radiation Research and Technology, Cairo, Egypt. The required dose was obtained by adjusting the electron beam energy parameters and conveyor speed. The dose being used was 30 kGy.⁹ The coating percent of modified fabric was calculated according to eq. (1)

$$\text{Coating percent (\%)} = [(W_2 - W_1)/W_1] \times 100 \quad (1)$$

where W_1 is the weight of uncoated fabric, and W_2 is the weight of modified fabric after several washing.

Washing Cycle Measurements

Washing cycle measurements were carried out by weighing the dry coated sample (W_1) then immersing it in water bath at

40°C for 10 min and then it was dried in a vacuum oven. This process is repeated for three washing cycles until constant weight (W_2). Finally, the weight loss was calculated by the following equation,

$$\text{Weight loss (\%)} = [(W_1 - W_2)/W_1] \times 100 \quad (2)$$

Swelling Behavior in Water, Different Solvents, Acids, and Alkalis

A known weight of the modified fabric was soaked in bidistilled water and different solvents (benzene, acetone, dimethylformamide, and methanol) for 24 h at room temperature. The swelled modified fabric was then removed and blotted on filter paper to remove the excess of water or solvent on the surface. The swelling (%) was calculated according to the following equation:

$$\text{Swelling (\%)} = [(W_2 - W_1)/W_1] \times 100 \quad (3)$$

where, W_1 is the weight of the dry modified fabric and W_2 is the weight of the swelled modified fabric.

Water Uptake (%)

A known weight of the modified fabric was soaked in bidistilled water for different time intervals at room temperature, the sample was then removed and blotted on filter paper to remove the excess water. The water uptake (%) was calculated using the following equation:

$$\text{Water uptake (\%)} = [(W_2 - W_1)/W_1] \times 100 \quad (4)$$

where W_1 is the weight of the dry modified fabric where as W_2 is the weight of modified fabric after being immersed in water and blotted.

Determination of Metal Uptake (%)

An attempt was made to use the modified fabrics for the removal of some heavy metals such as Cu²⁺, Ni²⁺, and Co²⁺ from waste water. Different metal salt solutions (CuSO₄, NiSO₄, and CoSO₄) of known concentration (500 ppm) were first prepared. A sample of known weight (0.5 mg) of the modified fabric was then immersed in these solutions for different time intervals ranging from 1 h to 24 h. The residual metal solution was measured by UV spectrophotometer. The metal uptake (%) was carried out in a batch process and determined using 10 mL of metal ions solution as following equation¹⁰:

$$\text{Metal uptake (\%)} = [(C_0 - C_1)/C_0] \times 100 \quad (5)$$

where C_0 and C_1 are the initial and residual concentrations of metal ions solution (ppm), respectively.

Dye Sorption Measurements

The dye sorption of basic and reactive dyes by modified fabric was carried out by a general procedure based on the measurements of the absorption of the dye solution. Standard curves were first constructed representing a relation between different known concentrations from basic and reactive dye and the corresponding absorption which was measured at wavelengths of 660 and 384 nm, respectively. The different expressions governing these relations were calculated as follows¹¹:

$$\text{Light absorption} = 0.223 \times \text{basicdye concentration (mg/L)} \quad (6)$$

$$\text{Light absorption} = 0.028 \times \text{reactive dye concentration (mg/L)} \quad (7)$$

In this procedure, the dye solution was prepared as follows: a known concentration from each dye under investigation (20 mg/L) was first dissolved in boiled water. Thereafter, a constant weight of the sample was then immersed in different dye solutions (10 mL) and the dye uptake was determined by measuring the light absorption of the residual dye solution. The dye sorption by samples was determined according to the following equation:

$$\text{Dye uptake (\%)} = \frac{\text{Dye concentration of sample/initial dye concentration} \times 100}{\text{Dye concentration of sample/initial dye concentration} \times 100} \quad (8)$$

Mechanical Properties

Mechanical tests including break stress and strain were performed at room temperature using an Instron machine (Model No. 1195) at a crosshead speed of 5 mm/min. Modified samples were cut (dog-bone shape) to initial dimensions of 40 mm length and 4 mm width. The recorded value for each mechanical parameter is the average of five measurements.

IR Spectroscopic Analysis

FTIR spectrophotometer model Mattson 100, made by Unicam, (UK) was used for FTIR measurements over the range 500–4000 cm^{-1} .

Scanning Electron Microscopy

The surface morphology of the PE-coated-PP before and after surface coating was examined by SEM fixed with energy dispersive X-ray (EDX) unit (JEOL, Tokyo, Japan).

UV-Visible Spectroscopy

UV-vis Pye Unicam spectrophotometer Type Sp 8-200 was used to determine C_1 and C_0 . All spectrophotometer measurements were carried out at room temperature (25°C).

RESULTS AND DISCUSSIONS

Effect of AAc Concentration on Coating Percent

The effect of AAc concentration on the coating (%) of modified fabric resulting from the presence of the coated layer consisting of CMC and different concentration of AAc has been studied. The results obtained are illustrated in Figure 1. From these results, it was found that generally the coating (%) of modified fabric increases with increasing AAc concentration. This increase may be attributed due to the presence of crosslinkable polyelectrolyte polyacrylic acid (PAAc) and radiation degradable CMC as well as their radicals, formed during irradiation, which are available for eventual interaction with the fabrics. Moreover, the presence of the bulky functional groups CH_2COOH of both CMC and AAc monomer affords attractive sites for further chemical reaction. After irradiation, the cellulose structure may open up, thereby increasing the diffusion of AAc monomer in

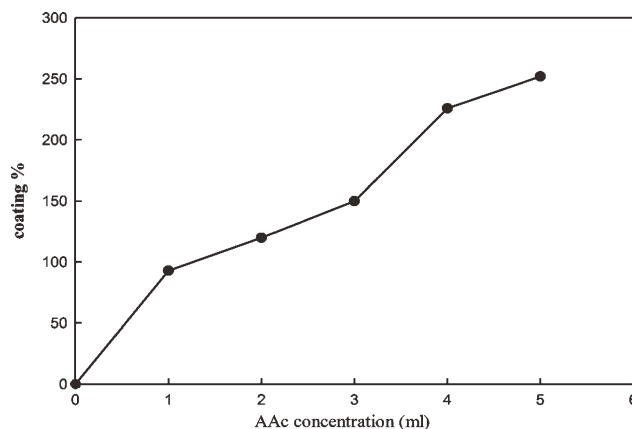


Figure 1. The effect of AAc concentration on coating (%) of PE-coated-PP coated with a layer of CMC and AAc irradiated at 30 kGy.

CMC, which enhances the diffusion of the coated layer on PE-coated-PP fabric.

Durability of Coated Layers Toward Washing Cycles

It is important to study the effect of several washing cycles on the durability of modified fabric at different AAc concentrations. This was carried out by subjecting modified fabric to three washing cycles. The results obtained are shown in Table I and illustrated in Figure 2. These results indicate that there is a stability of the coated layer toward washing cycles at all AAc concentrations under investigation.

Table I shows that the value of coating (%) of modified fabrics subjected to three washing cycles is still high and not markedly affected by washing. It would be then expected that the durability and stability of the coated layer of the modified fabric used in this work are may be due to:

1. The possible stable and strong chemical linkage through the strong hydrogen bond group, namely OH groups of PAAc and CMC with the fabrics.
2. The solubility parameters of the PE/PP (7.9–8.4) (cal/cm^3)^{1/2}, CMC (11.4) (cal/cm^3)^{1/2}, and finally PAAc of 12 (cal/cm^3)^{1/2} are close enough indicating a possible compatibility between this fabric and the ingredients of the coated layer.¹²

Swelling (%) in Water and Different Organic Solvents

The swelling (%) of modified fabrics in water and different organic solvents was carried out by immersing modified fabrics in different solvents for 24 h. The results are shown in Table II. From these results, it can be observed that modified fabrics have a high tendency to swell in DMF, methanol, and water. The swelling (%) in water and different solvents has the

Table I. Effect of Monomer Concentration and Washing on Coating (%)

Concentration of AAc monomer %	Initial coating % (W_1)	Final coating % (W_2)	Weight loss %
1.9	93	76	18.3
3.8	120	91	24
5.6	150	115	23
7.6	226	160	28
9.6	254	192	24

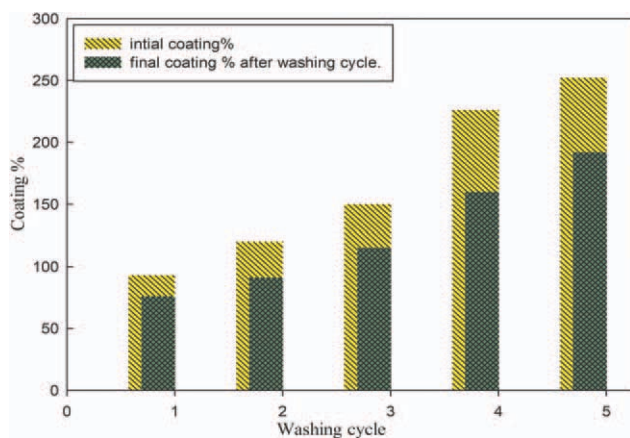


Figure 2. Effect of washing cycle on coating (%) of PE-coated-PP coated with a layer of CMC and AAc irradiated at 30 kGy. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

following order: Water > DMF > Methanol > Acetone > Benzene. The less swelling in benzene may be due to non-polarity of the solvent. The high swelling in DMF may be due to the presence of PAAc which has a high tendency to swell in DMF.

The Swelling (%) of Modified PE-coated-PP Fabrics in Acids and Alkalis

The swelling (%) of modified fabrics was studied by immersing the fabrics in 0.1N sodium hydroxide and hydrochloric acid for 2 h. The results obtained are shown in Table III. The immersion in NaOH results in high swelling (%) due to the conversion of carboxylic acid group into strong electrolytic groups. On the other hand, the swelling in dilute acid is low due to the presence of AAc in the coated layer.

Water Uptake (%) of Modified PE-coated-PP Fabrics

The variation of water uptake (%) of the unmodified and modified fabrics with different AAc concentrations as a function of immersion time was measured and the results obtained are shown in Figure 3. As expected, unmodified fabric as hydrophobic material shows a very low water uptake (%) value. It was observed that there is a sudden increase in water uptake (%) after 1 h of immersion for all AAc concentration under investigation. Moreover, increase in immersion time up to 5 h is accompanied with increase in water uptake (%) for all AAc concentration. This increase is attributed to the possible chemical linkage of side chains of PAAc and eventually CMC with the fabric. By increasing immersion time up to 24 h there is a leveling off for all AAc concentration, which indicate that after a

Table II. Swelling (%) of Modified PE-co-PP Fabric in Organic Solvents After 24 h

Solvent	Swelling (%)
Benzene	12.1
DMF	169.8
Methanol	128.7
Acetone	50.5
Water	1046

Table III. The Swelling (%) of Modified PP-co-PE in Acid and Alkali After Immersion Time Equal to 2 h

Swelling (%)	
HCl (0.1N)	NaOH (0.1N)
85.6	1190

certain time all the voids in the polymer are filled with water which leads to water super saturation. It is noteworthy to observe that most of the water sorption occurs in the amorphous regions of semicrystalline fibers.

Mechanical Properties

The tensile strength (TS) and elongation at break ($E\%$) of unmodified and modified fabric with different coating (%) were measured. The results are shown in Figures 4 and 5. As shown in these figures, tensile strength increases while elongation decreases with an increase in the coating (%). Moreover, from these figures it was also found that the tensile strength of unmodified fabric equal to 108 kg/mm, while the tensile strength of the modified fabrics having coating (%) (76%) increases sharply to 140 kg/mm. After that, tensile strength increases with increasing coating (%). The higher increase of tensile strength may be due to an increase in crosslinking density as the coating (%) increases. While elongation (%) decreases due to the fact that elongation is inversely proportional to tensile strength.

Infrared Measurements

IR measurements of unmodified and modified fabrics was carried out in order to confirm the occurrence of the coating process. The results observed are given in Figure 6. In the spectrum of unmodified fabrics there are bands at 2915, 1463, and 719 cm^{-1} , responsible for deformation vibrations of CH- groups⁹ as shown in Figure 6(a). Figure 6(b) shows IR spectrum of modified fabric in which there was new bands around 1700 cm^{-1} due to C=O absorption characteristic of the COOH group. The OH stretching vibration gives rise to absorption at 3250–3300

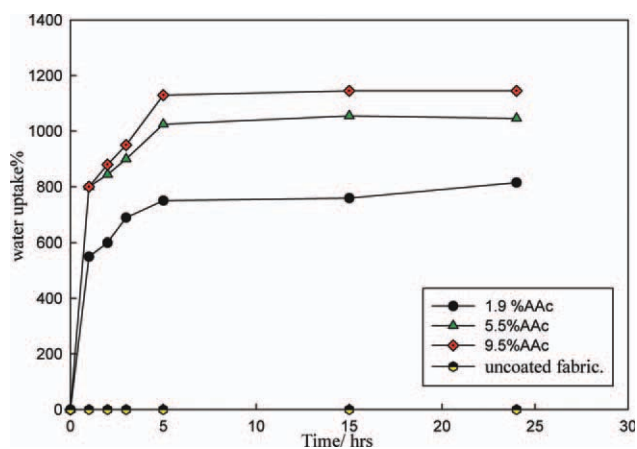


Figure 3. Effect of immersion time (h) on water uptake (%) of modified PE-coated-PP with different AAc concentration. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

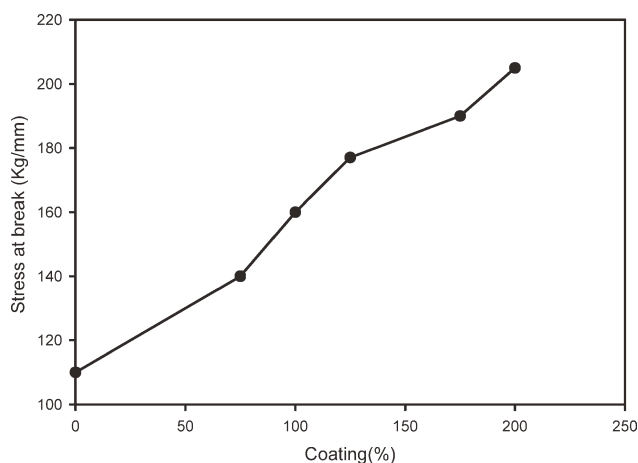


Figure 4. Effect of coating (%) on the stress at break of the modified PE-coated-PP fabric.

cm^{-1} to the left of the aliphatic $-\text{CH}$ bands ($2800\text{--}3000\text{ cm}^{-1}$). The presence of these new bands in the spectra confirm the coating process.

Structural Morphology of Unmodified and Modified Fabrics

SEM technique was used to investigate the surface morphology of unmodified and modified fabric. The microphotographs are shown in Figure 7. Unmodified fabrics were clear and distinctly separated from each other. After modifying, there is a clear change in dimension of fabrics, resulting to their closeness, compactness of the fabric structure as seen in Figure 7(A,B). This behavior may be affiliated with the relative covering of the fabrics with chemically linked PAAc and CMC. The results obtained from SEM offer further confirmation to previously discussed results obtained by water uptake (%) and coating (%).

Sorption of Heavy Metal Ions by Modified Fabric

The metal uptake (%) was determined by UV/VIS spectrophotometer analysis based on measuring the absorption of the different color solutions of the different metal ions before and after metal uptake process. The sample was immersed for

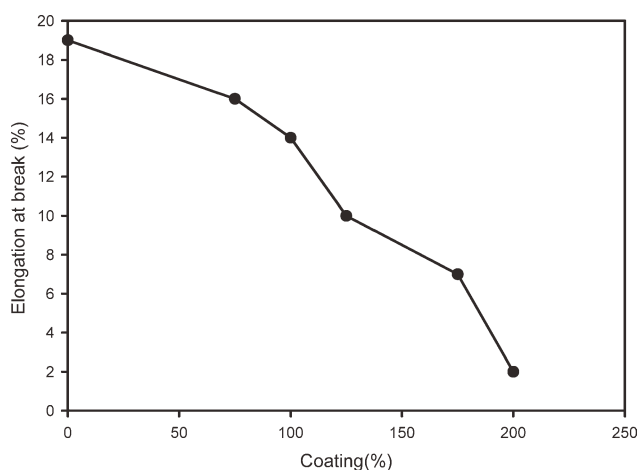


Figure 5. Effect of coating (%) on the elongation at break of the modified PE-coated-PP fabric.

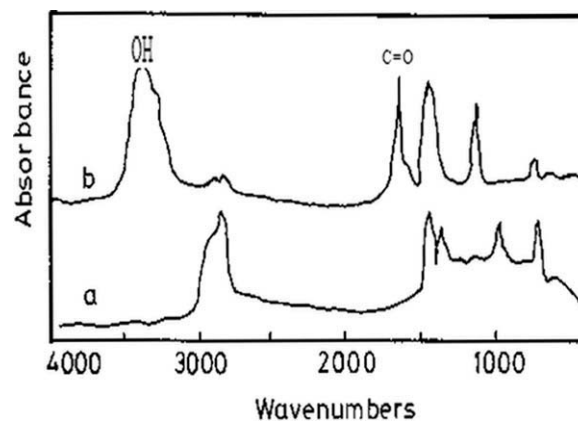


Figure 6. IR spectra of unmodified and modified PE-coated-PP fabric: (a) unmodified PE-coated-PP fabric, (b) modified PE-coated-PP fabric.

different time intervals in the different color solutions of each metal ion. The results obtained are shown in Figure 8. From these results, it can be seen that the metal uptake (%) (expressed in ppm) increases with time to reach a certain limiting value, which is called the maximum metal uptake capacity. The maximum uptake (%) is reached at a constant immersion time for all metal ions, equal to 24 h. The results obtained show that the modified fabric has a tendency toward metal ions according to the following order $\text{Ni} > \text{Co} > \text{Cu}$. These results can be explained by taking into consideration:

1. The diffusibility of such metals through the pores of the modified fabric and stability of chelating structure formed between metal ions and the coated layer of modified fabric.
2. Atomic size, atomic radii, and valence of metal ions.
3. The affinity of coated layer on polymer toward such metal ions may be also attributed to the presence of carboxylic acid groups which are strong chemically bonded to metal ions.

The SEM was used to detect the topography of the surface of modified fabric after recovery of different metal ions such as Cu, Ni, and Co. The obtained results are shown in Figure 9. It

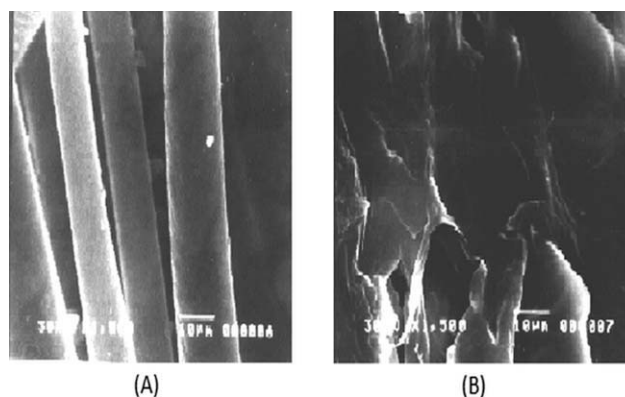


Figure 7. SEM micrographs of the cross-section of PE-coated-PP before and after electron beam coating with CMC and AAC. A: unmodified fabric, B: modified fabric.

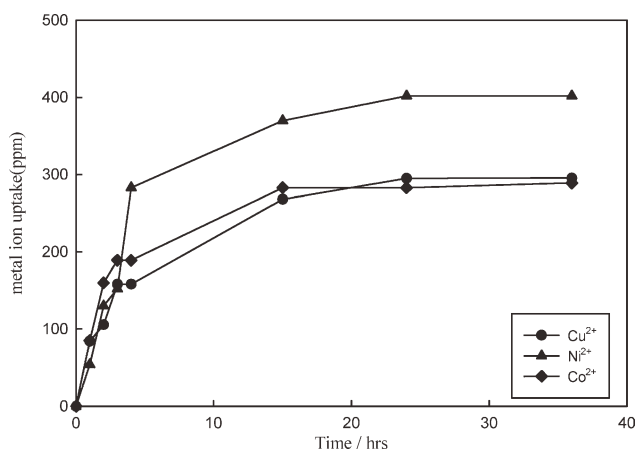


Figure 8. Metal ions uptake (%) of modified PE-coated-PP at different immersion time.

can be seen that the modified fabric differs from the parent one. The topography of the surface of the modified fabric shows that all metal ions form complexes with the carboxylic acid groups and/or metal salt inside the coated layer and not just physically adsorbed onto the surface. Also, a metallic luster appeared in the polymer loaded with different metal ions.¹³

Selectivity of the Modified Fabric Toward a Mixture of Metal Salts

The selectivity of the modified fabric toward the recovery of different metal ions was studied using EDX. Thus, the sample was immersed in a feed solution mixture of three metal ions with concentration (500 ppm) for 24 h. The amounts of metal ion uptake toward one metal ion rather than other in a mixture of different ions (Cu^{2+} , Ni^{2+} , and Co^{2+}) were studied. The results are shown in Figure 10. From these results it was observed that the selectivity toward metals ions is in the following order: $\text{Cu}^{2+} > \text{Ni}^{2+} > \text{Co}^{2+}$

Removing of Dye Waste

In the present work, the modified fabric is used to remove basic and reactive dyes from waste waters. The dye sorption of the different dyes by the modified fabric, as a function of immersion time, was investigated by using UV spectrophotometric analysis. The results obtained are shown in Figures 11 and 12. From these figures it can be observed that the dye sorption—time trend by the modified fabric differs from one dye to another. As general behavior, the dye sorption was found to increase with increasing time of immersion. Also, the level of coloration of all the modified fabrics dyed with basic and reactive dyes is significantly enhanced. The enhancement in the degree of coloration is attributed mainly to the fact that PAAC

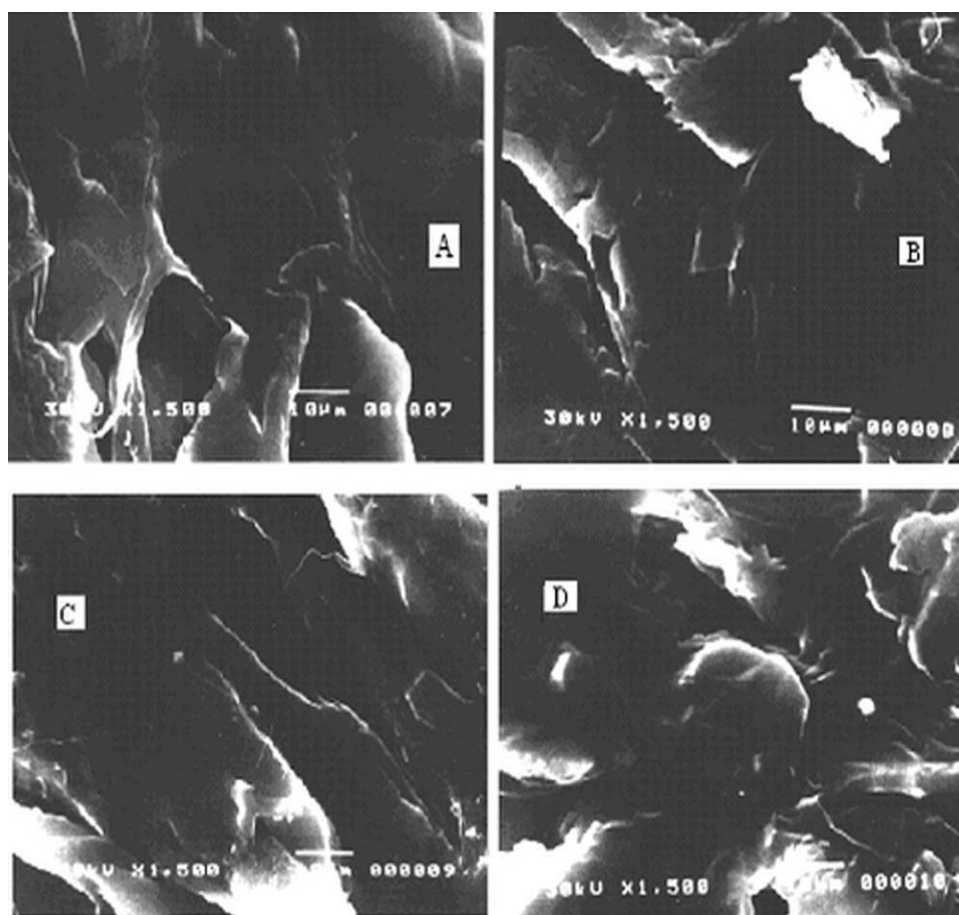


Figure 9. SEM micrographs of modified PE-coated-PP fabric after recovery with metal ions. A: modified fabric, B: modified fabric loaded with Cu, C: modified fabric loaded with Ni, and D: modified fabric loaded with Co.

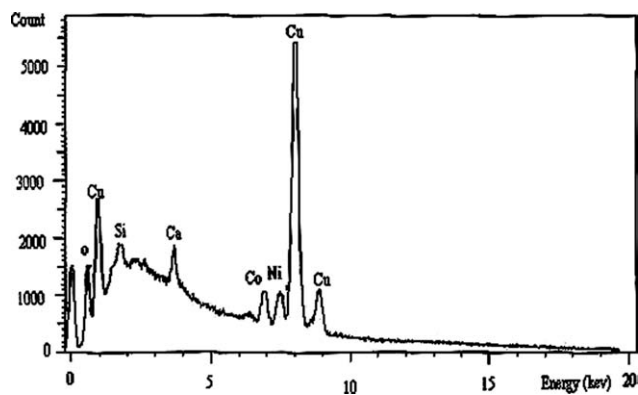


Figure 10. Energy dispersed X-ray spectrum of modified PE-coated-PP fabric loaded with different metal ions such as Cu, Ni, and Co.

is completely ionized in dilute solution. PAAc, chemically bonded to the substrate fabric, may then exist as polyion, namely polycarboxylate anion in the dyeing solution and perform as sites of negatively charged group necessary for interaction with positively charged counter part of basic dye molecule. On the other hand, the data obtained corresponding to reactive dye (Figure 12) shows a lower affinity than that of the basic dye (Figure 11). The reactive dye used is of the halogen substitution type and it would be expected that its labile chlorine atoms react with the already existing hydroxyl groups of the cellulose structure.¹⁰

CONCLUSION

An attempt has been made for modifying hydrophilic properties of PE-coated-PP non-woven fabric by using water-soluble biodegradable polymer produced from CMC together with AAC monomer. Hydrophilicity of modified fabric was examined in terms of water uptake (%). It was found that there is an improvement in the water uptake (%) of the modified fabric compared to that of the unmodified. Also, FTIR and SEM confirm the occurrence of complete adhesion between the fabric and the coated layer. Tensile strength increases with increasing

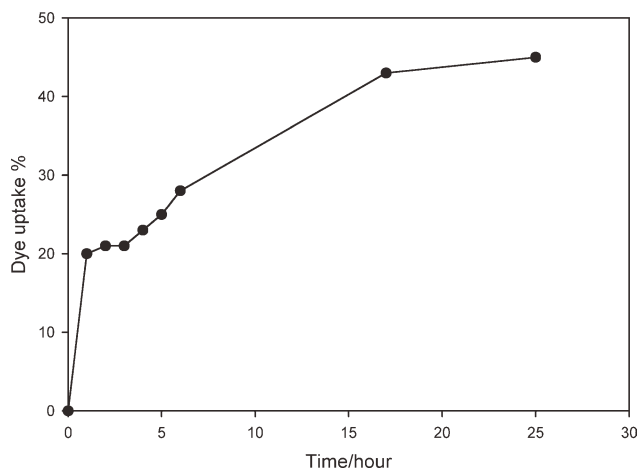


Figure 11. Dye uptake of basic dye by modified PE-coated-PP fabric at different immersion time at room temperature.

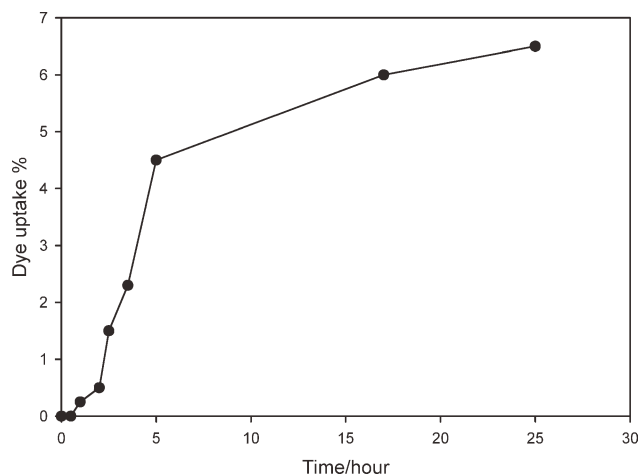


Figure 12. Dye uptake of reactive dye by modified PE-coated-PP fabric at different immersion time at room temperature.

coating (%) while elongation decreases. The performance of the modified fabric toward metal ions and dye waste was evaluated by determining the removal of Cu(II), Co(II), and Ni(II) ions from aqueous solutions. It was found that the modified fabric show a marked efficiency toward these metal ions. Also, the results obtained showed that the highest percentage of dye sorption was found in the case of basic dye and the lowest one in the case of reactive dye.

REFERENCES

1. Ibrahim, M. S.; El Salmawi, K. M.; Ibrahim, S. M. *Appl. Surf. Sci.* **2005**, *241*, 309.
2. Shaoyu, W.; Kang, E. T.; Neoh, K. G. *Macromolecules* **1999**, *32*, 186.
3. Stannet, V. T. *Radiat. Phys. Chem.* **1990**, *35*, 82.
4. Morshedian, M.; Bagheri, R.; Mirzataberi, M.; Moghadam, M. M.Sc., Thesis, IPP press, Iran, **2004**.
5. Pengfei, L.; Maolin, Z.; Jilan, W. *Internet. Symp. Radiat. Technol. Emerg. Ind. Appl. (IAEA)*, **2000**, *43*, 176.
6. El-Salmawi, K. M.; Ibrahim, S. M. *Polym. Plast. Technol. Eng.* **2005**, *44*, 1.
7. Shoji, A.; Kenichi, S.; Akio, K.; Takano, S. *Anal. Sci.* **2001**, *17*, 89.
8. Ibrahim, S. M. *Appl. Polym. Sci.* **2010**, *117*, 3098.
9. Ibrahim, S. M.; El-Salmawi, K. M.; El-Naggar, A. A. *Appl. Polym. Sci.* **2006**, *102*, 3240.
10. Nizam El-Din, H. M.; Ibrahim, M. S. *Conf. Nucl. Sci. Appl.* **2000**, *1*, 179.
11. El-Salmawi, K. M.; Abu Zaid, M. M.; Ibrahim, S. M.; El-Naggar, A. M.; Zahran, A. H. *J. Appl. Polym. Sci.* **2001**, *82*, 136.
12. Rudin, A. *The Elements of Polymer Science and Engineering*; Academic Press: New York, **1982**.
13. El-Naggar, A. A. M.Sc. Thesis, Ain Shams University, **2002**.