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A Novel Application of Ionic Liquid in Improvement of The Felting Resistance of Wool

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THE EFFECT of treatment of wool using two different ionic liquids namely 1-ethyl -3-methyl imidazolium acetate (EMIA), and 1-butyl -3-methyl imidazolium chloride (BMIC), on the felting resistance of wool was studied. The effect of treatment temperature and treatment time on the yellowing index, tenacity, and elongation at break of the treated wool fibres, was examined. Elemental analysis elucidated a remarkable reduction in sulphur content of the treated wool, which is mainly present in the wool scales. Scanning electron microscopy confirmed partial removal of wool scales under the effect of ionic liquid.

Keywords: Wool fibre, Ionic liquid, Imidazolium salts and Anti-felting.

Felting of wool is due to its scaly surface that point away from the fibre root and overlap like tiles on a roof. The protruding scale edges result in differential friction between the with-scale and against-scale direction, which under some conditions results in irreversible migration of individual fibres toward their root-ends(1). The most common shrink-proofing treatment (chlorine-Hercosett) still uses chlorine, which pollutes effluents with adsorbable organo halogens (AOX) by-products(2).

Recent research has been directed toward environmental aspects of the shrink-resist treatment of wool, particularly the reduction or elimination of organochlorine compounds in effluents. Modifications of wool surface morphology were conducted either by chemical degradation of the wool scales or by deposition of polymer on the scales (3-5). A wide range of enzymatic treatments are being studied as an ecological and economical way (6-14). Moreover, low temperature plasma was regarded as an environmentally friendly process to achieve the effect of an anti-felt finishing in wool(14-18).

The ionic liquid (IL) refers to organic or inorganic ionic salts whose melting points are relatively low, have non-measureable vapour pressure, limited flammability, and high thermal stability(19). The ionic liquid consists mainly of an organic cation, such as 1-alkyl-3-methylimidazolium, 1-alkyl pyridinium, or 1-methyl-1-alkyl pyrrolidinium and counter-ions such as halides, acetate, ethyl sulphate, tetraflouro borate, and hexaflouro phosphate…, etc.

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Recent publication has shown the possibility of dissolution different materials in ionic liquids including cellulose and wool, for different industrial purposes[21, 22]. Moreover, ionic liquids which have good solubility for wool keratin were employed to treat the wool fiber for improving its dyeability[21-23].

Previous work in our labs showed that, improvement on the dyeability of wool fiber treated by ionic liquid is due to partial descaling of wool[24]. In this study, the effect of treatment of wool fiber using two different ionic liquids on improving its antifelting properties was assessed.

Experimental

Materials

Scoured Australian merino wool tops were supplied from Misr Company for Spinning and Weaving, El-Mehalla El-Kobra, Egypt. The properties of these wool tops are summarized in Table 1.

TABLE 1. Properties of the used wool fibers.

Property	Value
Mean fibre diameter	19.6 micron
Fibre strength	11.5 cN/tex
Alkali solubility	15.2%
Urea-bisulphite solubility (%)	46.5%
Yellowing index	33.41

Chemicals

1-Butyl-3-methyl imidazolium chloride (BMIC) was purchased from Merck, Steinheim, Germany and 1- Ethyl-3-methyl imidazolium acetate (EMIA) was purchased from Io-li-tec, Denzlingen, Germany. Egyptol PLM nonionic detergent based on nonyl phenol ethoxylate was supplied from Starch and Brewer's Company, Alexandria, Egypt. All other chemicals are of laboratory grade chemicals.

Methods

Scouring

Wool tops were scoured in a bath containing 1 g/l Egyptol PLM for 30 min at 60 °C. The fibre was then rinsed thoroughly with running water, squeezed, and finally air-dried at ambient temperature.

Treatment with ionic liquid

The scoured wool fibre was immersed for two minutes in aqueous or non-aqueous solution containing 5 % w/w of BMIC or EMIA in water or in 1-propanol. The samples were mangle-squeezed to a pick up of 80 % and so the ionic liquid content is 4% on the weight of the fibre (owf).

Drying

The treated wool samples were dried and left for different periods (10-60 min) at various temperatures; (100–120) °C in case of EIMA, and 120°C & 130°C in case of BMIC to remove residual water or organic solvent. After drying and heating, the samples were washed with water for several times and air-dried before being subjected to the felting test. The washing water containing ionic liquids was filtered to remove any residual fibers, and the residual ionic liquid was recovered by distillation under vacuum.

Analyses

Felting test

The Aachener three-dimensional shaking machine was used to produce felt balls according to IWTO 20-69 test method[25].

Yellowness index

The yellowness index of wool fibre was measured using Ultra Scan PRO, Standards Box, S/n: USP 1229, Hunter Lab. Yellowness index (YI) was determined using ASTM method (E 313) according to the following equation:

$$YI_{(E\ 313)} = 100\ [1- (0.847\ Z/Y)]$$

where Y and Z are the first numerical scale offered to quantify colour.

Elemental analysis

The amount of carbon, nitrogen, hydrogen, and sulphur, in the untreated and selected treated wool fibers were assessed using Elementary CHNS Analyser, Model Vario EL III, Germany.

Mechanical properties

The mechanical properties of the bundle untreated and the ionic liquid treated wool fibers were measured using INSTRON- assembled in USA, Load cell 100 N.

Scanning Electron Microscopy

The untreated as well as the treated wool fabrics were mounted on aluminium stubs sputter coated with gold in an S150A sputter (Edward, UK), and examined by JEOL (JXA-840A) Electron Probe Microanalyzer (Japan).

Results and Discussion

The effect of treatment of wool fibres using ionic liquids (ILs); namely 1-ethyl-3-methyl imidazolium acetate (EMIA) and 1-butyl-3-methyl imidazolium chloride (BMIC) on their felting resistance was monitored. Water or 1-propanol was used as a diluent for the used ILs to decrease the consumption of the used ILs and to minimize any deterioration that might take place to the substrate under the influence of the pure ionic liquid.

The Aachener three-dimensional shaking machine was used to produce felt balls according to IWTO 20-69 test method. The diameter of the formed felt balls was taken as a measure of the degree of felting; as the felting resistance increases the diameter of the felt ball increases.

Treatment with 1-ethyl-3-methyl imidazolium acetate (EMIA)

Effect of diluents

The effect of treatment of wool fiber with 5% (w/w) EMIA/propanol or EMIA/water and drying at 120 °C for different intervals on the felting resistance was studied and tabulated in Table 2.

TABLE 2. Effect of treatment of wool fibre with 5% (w/w) EMIA in propanol or water at 120 °C for different times on its felting resistance.

Diluting agent	Treatment Time (min)	Felt ball diameter (cm)
Water	10	2.95
	20	2.88
	30	2.79
	40	2.81
	50	3.07
	60	3
Propanol	10	3.73
	20	3.8
	30	3.71
	40	3.8
	50	3.8
	60	3.81

Results in Table 2 showed that, at the same drying time and temperature the diameter of the felting balls of the wool fibers treated with EMIA/propanol are greater than those of the fibers treated with EMIA/water. This may be due to the rapid evaporation of propanol, characterized by lower boiling point than water, leading to early starting the action of ionic liquid and early etching of wool scales.

Effect of treatment conditions

The effect of treatment of wool with EMIA at different conditions, *i.e*. temperature and time were studied.

Results of this investigation, given in Table 3, show that the diameter of the felting balls of the treated fibers is greater than that of the untreated ones. This can be attributed to partial removal of wool scale under the action of the used ionic liquid resulting in a smooth fibre surface and an enhancement of the antifelting property of wool. Kantouch *et al.* have studied the morphological structure of wool fibres treated with EMIA by scanning electron microscopy and confirmed partial de-scaling of the treated fibres[24].

Table 3 clarifies also that at the same drying temperature of the treatment, the felting resistance of the treated wool was improved by increasing the drying time. As the drying temperature increased the felting resistance increased. At 120°C, the felt balls have a relatively deformed ball indicating higher felting resistance of wool.

TABLE 3. Effect of treatment of wool fibre with 5% (w/w) EMIA in propanol at different temperatures for different times on its felting resistance .

Treatment temperature (°C)	Treatment time (min)	Felt ball diameter (cm)
Untreated	-	2.57
100	10	2.61
	20	3.06
	30	3.32
	40	3.31
	50	3.57
	60	3.57
110	10	2.96
	20	3.35
	30	3.46
	40	3.75
	50	3.51
	60	3.78
120	10	3.73
	20	3.8
	30	3.71
	40	3.8
	50	3.8
	60	3.81

The effect of treatment with 1-butyl-3-methyl imidazolium chloride (BIMIC)

The effect of treatment of wool with BIMIC at different temperature (120 - 130 °C) for various periods (10-60 min) on the antifelting behavior is shown in Table 4.

Table 4 shows that, there is a slight increase in the diameter of the felting balls of the BIMIC treated wool fiber as compared with the untreated ones. A maximum of felt ball diameter of 2.9 cm was obtained by treatment with this reagent at 130 °C for 60 min.

The relatively higher effect of 1- Ethyl-3-methyl imidazolium acetate (EMIA) as compared with 1-butyl-3-methyl imidazolium chloride (BMIC) may be due to the relatively small molecular volume of the EMIA compared to the BMIC which results in fast and easy penetration of the EMIA in the voids of wool fiber.

TABLE 4. Effect of treatment of wool fibre with 5% (w/w) BIMIC in propanol at different temperatures for different periods on its felting resistance.

Treatment Temperature (°C)	Treatment Time (min)	Felt Ball Diameter (cm)
Untreated	-	2.57
120	10	2.57
	20	2.58
	30	2.59
	40	2.62
	50	2.62
	60	2.64
130	10	2.57
	20	2.58
	30	2.66
	40	2.69
	50	2.83
	60	2.9

Elemental analysis

Nitrogen, carbon, sulphur, and hydrogen contents of selected treated wool with EMIA or with BIMIC as well as the untreated wool were determined .

Results of this analysis, tabulated in Table 5, show that there is a slight decrease in sulphur content of the BIMIC treated fibers, (3%), as compared with sulphur content of the untreated fiber. On the other hand, the sulphur content of the EMIA treated wool decreased by about 10% as compared to the untreated wool. This decrease in sulphur content can be explained in terms of the partial removal of wool scales, rich in sulphur, under the effect of the ionic liquid EMIA. On the other hand, there is no remarkable change in nitrogen, carbon or hydrogen contents which may indicate that, this treatment has a physical effect and not a chemical one.

TABLE 5. C, H, S, and N contents of wool fiber treated with 5% EMIA & BIMIC.

Sample	N%	C%	S%	H%
Blank	14.9	44.9	3.0	10.2
BIMIC at 120°C for 60 min	15.1	44.8	3.0	10.2
BIMIC at 140°C for 60 min	14.9	44.4	2.9	11.4
BIMIC at 150°C for 50 min	15.0	45.1	2.9	10.4
EMIA at 100°C for 60 min	15.0	44.7	2.9	11.2
EMIA at 110°C for 60 min	15.0	44.9	2.7	10.2
EMIA at 120°C for 20 min	15.1	45.1	2.7	11.0

Yellowning index

The effect of treatment of wool fibers with the two ionic liquids EMIA and BIMIC at different temperatures for several intervals on the yellowness of the fiber was studied and the results are tabulated in Tables 6 and 7.

TABLE 6. The effect of treatment of wool fiber with 5% EMIA in propanol on the yellowness of the fiber

Treatment Temperature (°C)	Treatment Time (min)	Yellowness
Untreated	-	33.94
100	10	33.5
	20	35.16
	30	35.3
	40	35.52
	50	36.43
	60	37.46
110	10	30.57
	20	33.68
	30	36.82
	40	37.1
	50	35.62
	60	34.86
120	10	27.43
	20	36.33
	30	36.55
	40	37.79
	50	38.09
	60	38.03

TABLE 7. The effect of treatment of wool fiber with 5% BIMIC in propanol on the yellowness of the fiber

Treatment Temperature (°C)	Treatment Time (min)	Yellowness
Untreated	-	33.94
120	10	34.81
	20	35.31
	30	36.43
	40	37.09
	50	37.65
	60	40.25
130	10	37.72
	20	38.98
	30	39.62
	40	41.84
	50	42.50
	60	43.87

Table 6 clarifies that the treatment of wool fiber with the ionic liquid 1-ethyl-3-methyl imidazolium acetate (EMIA) has a very slight effect on the yellowness of the treated fiber as compared to the untreated wool.

On the other hand, data of Table 7 show that, the treatment of wool fiber with the ionic liquid 1-butyl -3-methyl imidazolium chloride (BMIC) results in remarkable yellowing of wool that increases on increasing the treatment temperatures.

Mechanical properties

The mechanical properties of the ILs-treated as well as the untreated wool fibres were examind, and the data are tabulated in Tables 8 and 9.

TABLE 8. Tensile strength and strain at break of the treated wool fiber with 5% EMIA in propanol at different temperatures for various intervals.

Treatment		Tensile strength (g/den)	Strain at break (%)
Temperature (°C)	**Time (min)**		
Untreated	--	0.024	42.53
100	10	0.020	41.11
	20	0.0161	38.29
	30	0.0149	35.82
	40	0.0135	32.61
	50	0.0134	29.00
	60	0.013	26.11
110	10	0.0185	48.00
	20	0.0132	32.22
	30	0.0122	31.67
	40	0.0111	27.23
	50	0.0092	22.22
	60	0.0086	19.44
120	10	0.0165	30.05
	20	0.0093	22.78
	30	0.0092	20.26
	40	0.0089	18.53
	50	0.0078	17.22
	60	0.0069	17.01

Data of the table clarify that, the tenacity of the trerated fibres decreases as a function of the treatment time and temperature. An acceptable felting resistance was imparted to wool fibres upon treatment with EMIA at 100 °C for 20 min at which the less in tensile strength was 20 %. Further study would be carried out to decrease the loss of tensile properties of the treatd fibre to a minimum value.

On the other hand, limited loss in tensile strength of the treated fibres was encountred upon treatment with BMIC; a result which is in harmony with the felting resistance data in Table 4.

Similar results have been recorded for the loss of elongation at break of the treated wool fibres.

TABLE 9. Tensile strength and strain at break of the treated wool fiber with 5% BIMIC in propanol at different temperatures for various intervals.

Treatment		Tensile strength (g/den)	Strain at break (%)
Temperature (°C)	Time (min)		
Untreated		0.024	42.53
120	10	0.026	41.23
	20	0.025	40.03
	30	0.024	40
	40	0.0239	38.8
	50	0.0226	38.09
	60	0.0195	37.78
130	10	0.0258	41.92
	20	0.0239	40.0
	30	0.0232	39.91
	40	0.0197	37.88
	50	0.0183	37.00
	60	0.0180	35.96

Scanning Electron Microscopy

The scanning electron micrographs of untreated as well as wool fiber treated with either EMIA or BMIC are shown in Fig. 1–3.

These Figures show that the morphological structure of wool has been significantly modified as a result of pre-treatment with the said ionic liquids.

Whereas Fig. 1 shows the normal scaly structure of wool fibres, Fig. 3 reveals that there is removal and deterioration in the scales on the fibre surface; under the effect of EMIA, resulting in an improvement of the anti-felting propeties of wool fiber. Figure 2 shows only slight deterioration in wool scales after treated with BMIC

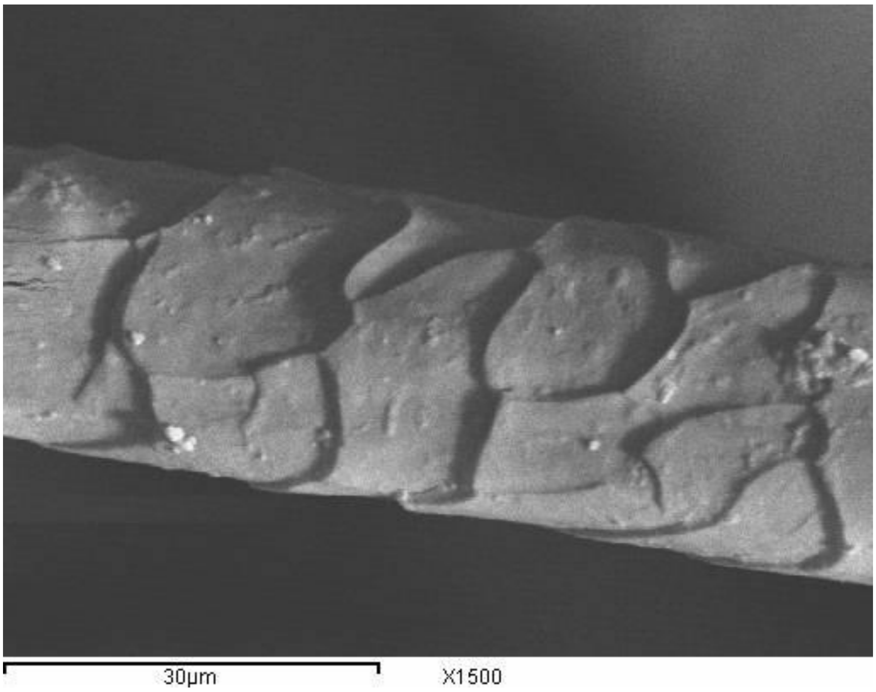

Fig. 1. SEM of untreated wool fibers

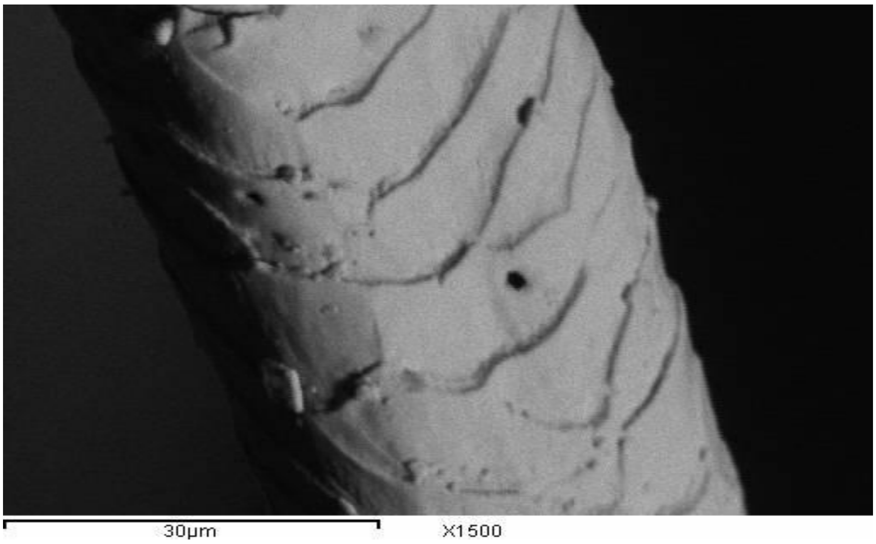

Fig. 2. SEM of wool fibre treated with 5% BIMIC and dried at 130°C for 50 min.

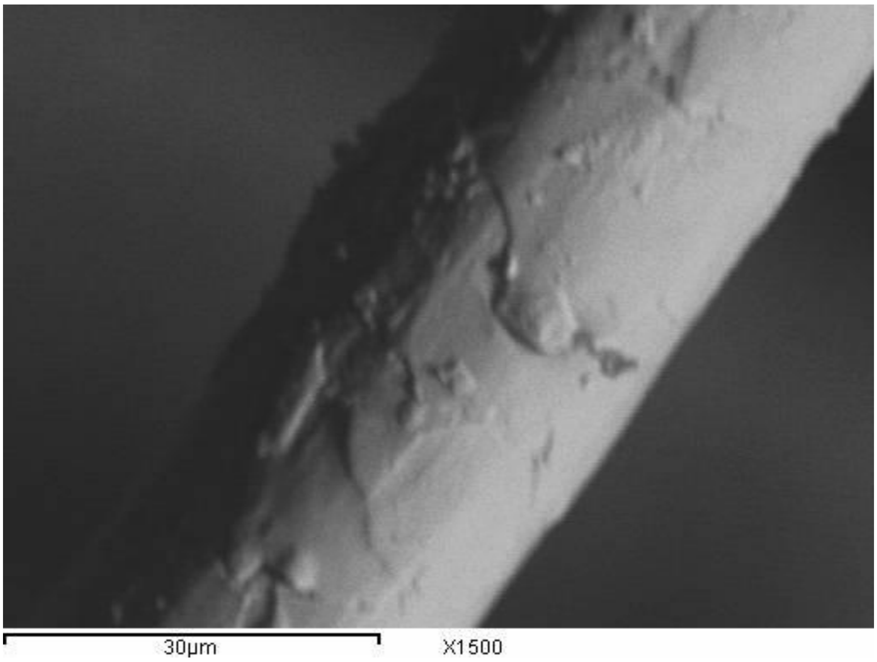

Fig. 3. SEM of wool fibre treated with 5% EMIA and dried at 120°C for 20 min .

Conclusion

The treatment of wool fiber using 1-ethyl -3-methyl imidazolium acetate (EMIA) has relatively high improvement in the antifelting properties. Elemental analysis shows that this treatment reduces the sulphur content of the treated fibers due to removal of wool scales, rich in sulphur, under the action of the ionic liquid EMIA. Yellwoness of the EMIA treated wool fiber is slightly increased by this treatment. Scanning electron micrographs reveals that there is removal and deterioration in the scales on the wool fibre surface; under the action of EMIA, that resulted in improvement of its anti-felting properties.

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26. **IWTO Test Method**, 20-69

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إستخدام جديد للسائل الأيونى لتحسين مقاومة الصوف ضد التلبد

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تم دراسة تأثير معالجة الصوف بإستخدام نوعين من السوائل الأيونية هى:-
١- إيثيل-٣ - ميثيل إميدازوليم أسيتات (EMIA) ، ١- بيوتايل -٣ - ميثيل إميدازوليم كلوريد (BMIC) على مقاومة الصوف للتلبد.

وقد تم دراسة تأثير درجة الحرارة وزمن المعالجة على مدى تأثر الصوف مثل درجة اصفراره و قوة الشد والاستطالة عند القطع.

وقد أظهر تحليل العناصر فى الصوف حدوث إنخفاض ملحوظ فى نسبة الكبريت بالصوف المعالج على العلم بأن الكبريت يعد العنصر الاساسى الذى يكثر تواجده فى حراشيف الصوف.

كما أكدت الدراسة بالميكرسكوب الألكترونى حدوث إزالة جزئية لحراشيف الصوف تحت تأثير السائل الأيونى.