World Academy of Science, Engineering and Technology
International Journal of Chemical and Molecular Engineering
Vol:9, No:9, 2015

Influence of Hydrolytic Degradation on Properties of Moisture Membranes Used in Fire-Protective Clothing

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Abstract**—**This study intends to show the influence of the hydrolytic degradation on the properties of the e-PTFE/NOMEX® membranes used in fire-protective clothing. The modification of water vapour permeability, morphology and chemical structure was examined by MOCON Permatran, electron microscopy scanning (SEM), and ATR-FTIR, respectively. A decrease in permeability to water vapour of the aged samples was observed following closure of transpiration pores. Analysis of fiber morphology indicates the appearance of defects at the fibers surface with the presence of micro cavities. ATR-FTIR analysis reveals the presence of a new absorption band attributed to carboxylic acid terminal groups generated during the amide bond hydrolysis.

Keywords**—**Hydrolytic ageing, moisture membrane; water vapor permeability, morphology.

I. Introduction

During their service lifetime, materials used in protective clothing are undergoing various environmental and operation aggressors (temperature, light, moisture, etc. . .). These factors constitute a severe limitation to the use of protective materials (Fig. 1) [1], [2].

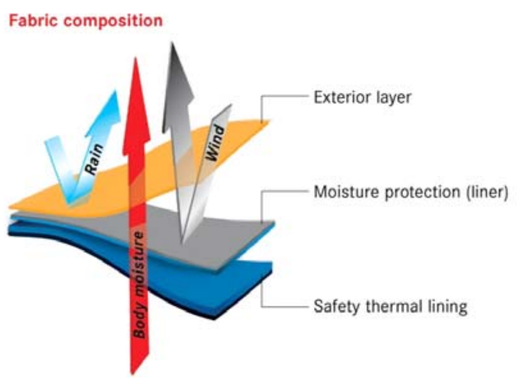

Fig. 1 Fabric composition of fire-protective clothing

Burns caused by water vapor or steam are among the possible burns that can suffer from a fire. These are caused by the transfer of relative large amounts of energy when the evaporated moisture is concentrated on the surface of the human skin. Lawson [3] discussed about how firefighters may unexpectedly suffer from these burns even outside the envelope of a flame. Fire-protective clothing usually contains a moisture barrier membrane to prevent outside water from soaking through the garment. This membrane helps keep the firefighter dry and they are often made of microporous materials which will prevent water from reaching the skin but will allow the water vapor. This helps also to reduce heat stress and the likelihood of steam-related burns. Different researchers have been investigated the transfer of moisture in protective clothing. Zimmerli [4] studied the influence of humidity on heat transfer in fire-protective gloves and protective clothing [5] under dangerous conditions, including the importance of moisture. He has also developed a test method to measure the protection and thermal comfort of protection clothing for firefighters and other applications by using a specially designed cylinder that simulates a sweating torso [6]. Veghte examined the effects of moisture on the protection of fire-protective gloves [7]. Makinen compared the effects of various types of underwear on moisture transfer in the fire-protective clothing and the performance of this garment [8]. In this paper, the effect of humidity on the e-PTFE/Nomex® membrane properties is investigated by assessing its influence on permeability to water vapor, morphology and the evolution of the chemical structure throughout the aging process is also followed by ATR-FTIR analysis.

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II. Experimental

A. Materials

The materials used in our work consists of an expanded PTFE membrane laminated on Nomex® III fabric. This material is marketed under the brand name Crosstech® by WL Gore & Associates (Maryland, USA) and was graciously provided by Innotex Inc. (Quebec, Canada). The expanded PTFE has large enough pores to allow water vapor to pass, but too small to liquids transfer. This also allows the transfer of heat, thus reducing heat stress while providing protection against outside liquids. The average e-PTFE membrane pore size is 1 µm (Fig. 2 (a)) and the diameter of the Nomex® fabric thread is 15 µm (Fig. 2 (b)). To prevent contaminants from compromising the performance of the PTFE-membrane, an additional membrane made of PU is employed to protect the PTFE surface.

B. Hydrolytic Aging Program

In order to reproduce conditions close to those experienced by the membrane in fire protective clothing in operation, the samples were placed in a BURNSCO BTH-1.3p humidity chamber equipped with a PID relative humidity controller of a

± 5% RH accuracy. Three temperatures were chosen 50, 70, and 80°C, and at each temperature, different humidity levels were selected ranging between 60 and 100% relative humidity for periods ranging from 1 to 600 hours. Distilled water was used for aging treatments to ensure the environment remained neutral.

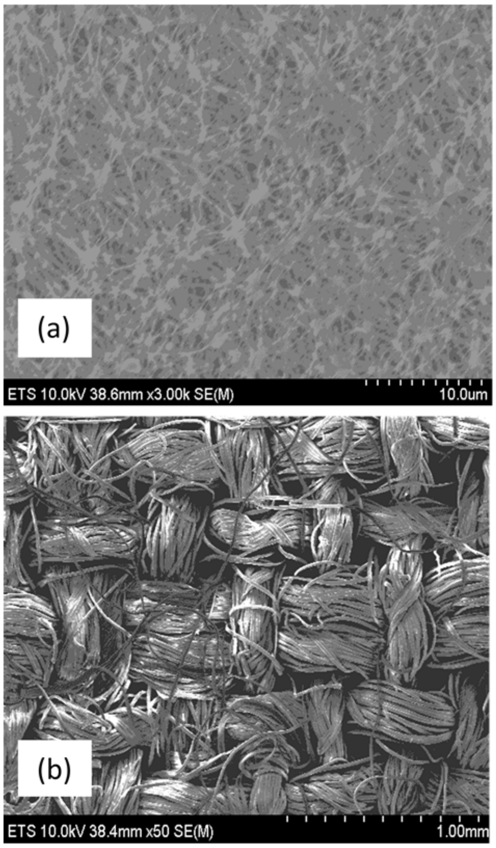

Fig. 2 SEM images of the two membrane components e-PTFE (a) Nomex® (b)

C. Water Vapor Permeability

Measurements of permeability to water vapor were carried out on the MOCON Permatran W-Model 101K. The round sample with dimension of 50 × 50 mm was prepared for measuring the rate of transmission (TR) of the water vapor through the membranes. The test temperature is controlled at 23°C ± 2°C and the humidity percent is fixed at 60%.

D. Infrared Spectroscopy Analysis (FT-IR)

The evolution of molecular structure of the e-PTFE/Nomex® membranes during the hydrolytic aging has been followed by using ATR-FTIR. The analysis of unaged and aged samples was performed using a Thermo Nicolet spectrometer equipped with a mono-reflexion ATR accessory. This instrument allowed the analysis of the membrane surface with a depth of penetration of 3-5 µm. The spectra were collected between 650 to 4000 cm^{-1}, by accumulating 128 scans at 4 cm^{-1} resolution.

E. Scanning Electron Microscopy (SEM)

Scanning electron microscopy model Hitachi S570 was used to investigate of potential changes of external morphology of analyzed samples due to hydrolytic aging process. Observations were made on both sides of the membrane meaning on the e-PTFE laminate and on the Nomex® fabric.

III. Results and Discussion

Water Vapour Permeability

Fig. 3 shows the results of water vapor permeability of the e PTFE/Nomex® membrane as a function of hydrolytic aging exposure time at 80% RH and 80°C. Results show that water vapor permeability decreased about 30% compared to its initial value after 456 hours of aging.

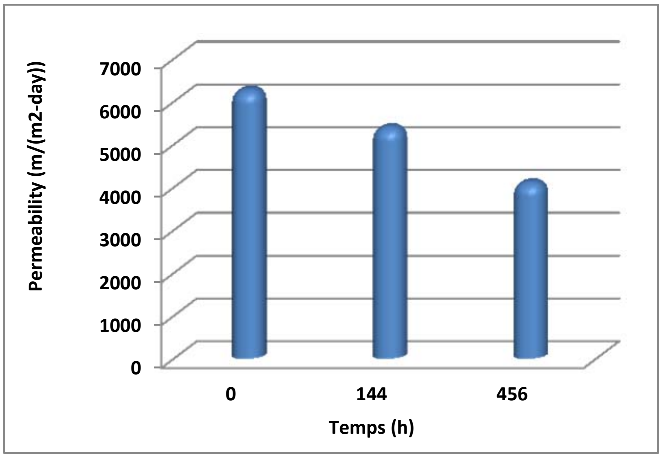

Fig. 3 Effect of hydrolytic aging on water vapor permeability at 80%RH and 80°C

It was previously observed that water vapor permeability decreased due to the closure of transpiration pores [1], [2]. To investigate this phenomenon, the e-PTFE membrane surface was analyzed by SEM. Fig. 4 shows the SEM images of unaged and aged samples at 80% RH and 80°C for 144 and 456 hours. Comparing to the non-aged sample images, the gradual closure of the e-PTFE pores can be clearly observed. The decreased permeability to water vapor due to hydrolytic aging can therefore be attributed to the gradual reduction of the size and the number of pores of the e-PTFE layer. The layer polyurethane is used to reduce the effects of contamination having considering the sensitivity to moisture [9], [10]; it is therefore possible that degradation of the PU can also contribute to the closure of transpiration pores.

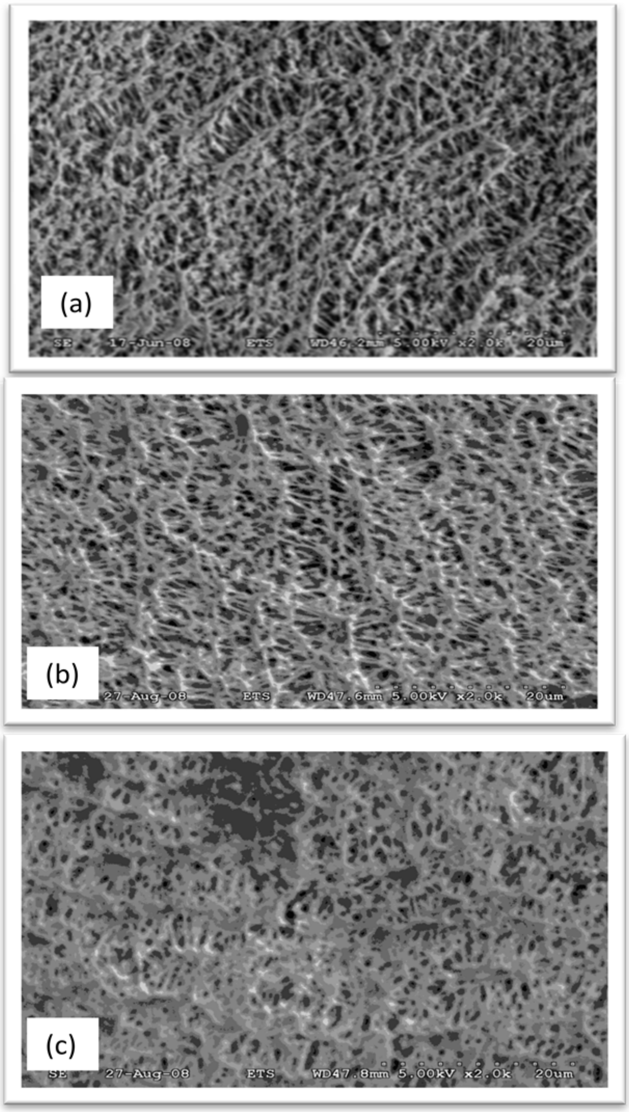

Fig. 4 SEM images of non-aged sample (a); aged samples at 80% RH-80°C for 144 hours (b); and 456 hours (c) of the e-PTFE

ATR- FTIR Chemical Composition

FTIR-ATR spectra of the amide function in Nomex®, is presented in Fig. 5. This degradation mechanism induced divisions of strings at the C-N bond of the amide function, which binding lead to the formation of acid functions and amines in the end of the chain [11], [12]. To confirm the presence of the hydrolysis phenomenon, we followed the evolution of the chemical structure of Nomex® fibre samples, aged and non-aged FTIR-ATR. A comparison of the non-aged Nomex® spectra and those aged 60% RH-80˚C for 192 and 240 hours is shown in Fig. 5.

Fig. 5 shows a new absorption band in the carbonyl region (1725 cm^{-1}). This band corresponds to the formation of the same end group formed during photochemical aging [8]. In a high humidity environment, the group carbonyl (-COOH) can be deeper transfer when the amide bonds are hydrolyzed under the action of an acid catalyst [13]-[15]. The proposed degradation mechanism shown in Fig. 6, this mechanism is in good agreement with the literature [13]-[16]. For each chain scission break following, a group of carboxylic acid and an amine group are created. Contrary to carboxylic acid terminal groups, which are clearly observable in the carbonyl area of the aged samples spectra, the bands corresponding to the amino groups are similar to existing bands, which makes them difficult to distinguish in the spectra.

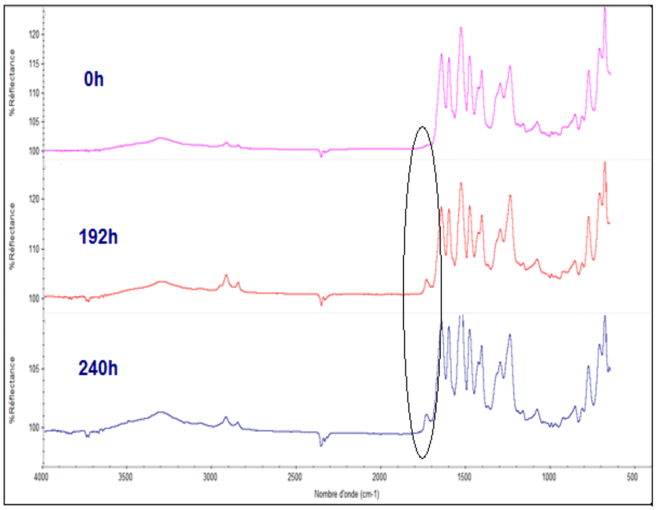

Fig. 5 FTIR-ATR spectra evolution of Nomex® fibers during hydrolytic aging (HR 60% 80°C)

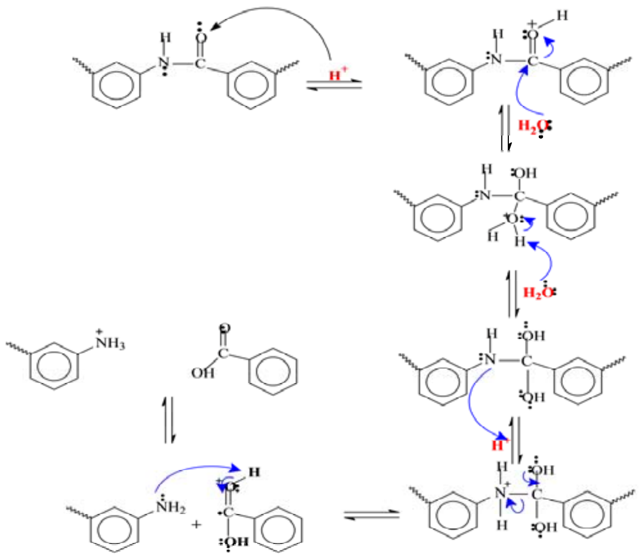

Fig. 6 Hydrolysis mechanism catalyzed by an acid of the amide bond in Nomex®

EDS analyses performed on fabric samples exhibit traces of sulphur as shown in Fig. 7. This may be due to the use of solvent during the polymerization process of Nomex® [11]. Traces observed in Fig. 7 are probably the remains of solvent of the acid used for the treatment of fibres. These traces of sulphuric acid are then acted as a catalyst for the hydrolysis reaction.

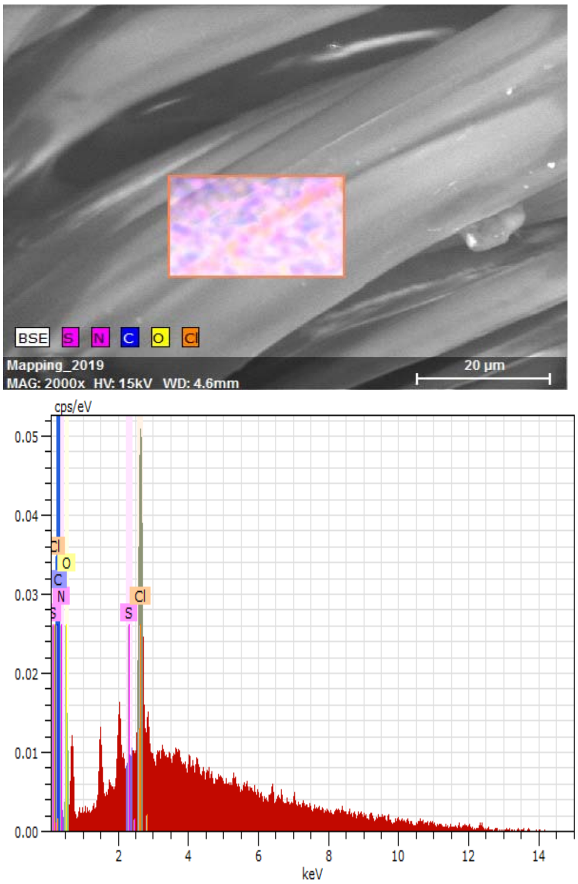

Fig. 7 EDS basic analysis of Nomex® threads

SEM Morphology Analysis

Fig. 8 shows SEM images of non-aged (a) and aged fibers Nomex® at 100% HR at 50°C for 120 (b) and 653 hrs (c). After 120 hrs of hydrolytic aging, the defects at the fibers surface appear in the form of cavities as well as fibrils. After 652 hours, initial morphology of the fibers completely changed with the presence of the surface peels on fibers.

IV. Conclusion

The purpose of this article is to study the influence of moisture on different properties of an e-PTFE/Nomex® membrane. A decrease in water vapor permeability in hydrolytic aging can be linked to the gradual closure of pores in the e-PTFE layer as shown on SEM images. ATR-FTIR analysis of the molecular structure showed the appearance of a new IR absorption band assigned to the carboxylic acid group. A reaction mechanism describing this process has also been proposed. These results provide a better understanding of the phenomena occurring during the hydrolytic ageing of the membrane. They also provide tools to help improve the safety of fire-protective clothing.

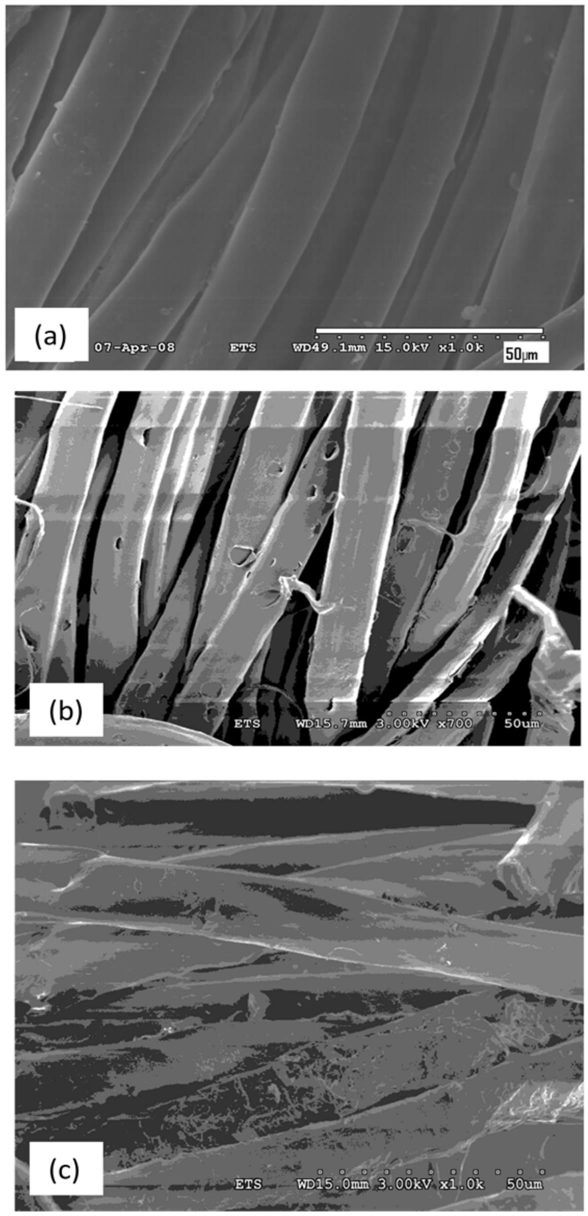

Fig. 8 SEM images of non-aged (a); aged at 100%RH-50°C for 120 hours (b); and 653 hours (c) of Nomex®

Acknowledgment

The authors thank Innotex, for providing the materials used in the study. We are also very grateful to Dr. Mélina Hamdine from the Ecole Polytechnique de Montreal for her help with the water vapor permeability measurements.

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