Effect of Thermal Aging on the Mechanical and Barrier Properties of an e-PTFE/Nomex® Moisture Membrane Used in Firefighters' Protective Suits

Rachid El Aidani, Patricia I. Dolez, Toan Vu-Khanh

École de technologie supérieure, Montréal, Canada

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ABSTRACT: Moisture membranes play a key role in high performance protective clothing by preventing outside water to get in while allowing the human body to perspire properly. However, these membranes are confronted to high environmental constraints, in particular within firefighters' protective clothing. The resulting aging effect may lead to modifications of their performances, for example their mechanical or barrier properties. In this study, the thermal aging of an e-PTFE/Nomex® moisture membrane was carried out at five temperatures between 190 and 320°C. The effect of aging on the mechanical performance was assessed by tensile tests and trapezoid tear strength measurements. Variation in the moisture membrane water vapor permeability due to aging was also studied. Large modifications in the membrane mechanical properties as a result of thermal aging were recorded. It was associated in part with a degradation of the Nomex® fibers. The membrane water vapor permeability was observed to decrease with aging time below 220°C while values larger than those corresponding to the unaged material were measured above that temperature. This was possibly related to the occurrence of two competing phenomena relative to water vapor permeability: closure of pores in the e-PTFE laminate and creation of cracks and holes. These results show that the aging of the moisture membrane must be considered carefully while estimating the service life of protective clothing. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 3101–3110, 2011

Key words: thermal aging; moisture membrane; water vapor permeability; tensile properties; trapezoid tear strength

INTRODUCTION

During their lifetime, materials used in protective clothing age under the action of various environmental and operation aggressors (temperature, light, moisture, etc...). These factors constitute a severe limitation to the use of protective materials. The consequences of the degradation of these materials' functional properties are high, not only in terms of economical costs, but also in terms of safety. Indeed, the loss in performance may not always be easily detected unless it has reached an extreme level.[1] It is thus of primary importance to understand the mechanisms behind these aging processes and to characterize their effects.

Moisture membranes are an essential element in protective clothing against heat and flame due to their double role in preventing water penetration while allowing water vapor perspiration to exit.[2] Microporous moisture barriers are generally made of expanded polytetrafluroethylene (e-PTFE) laminated on an aramid fabric. The principle under the membrane breathable function is the enormous difference in size between water vapor molecules (~ 0.4 nm in diameter) and water droplets which usually exceed 100 μm in diameter and are thus larger than the membrane pores.[3]

Exposure of protective materials to different environments during their use (heat, light, water, chemicals, etc...) has been reported to affect their properties. However, even if the water barrier is the most heat sensitive layer in protective clothing,[4] very few studies have looked at the consequences of thermal aging on their performance. Rossi and Zimmerli studied the effect of short exposures to radiant heat (10 kW/m^2) and convective heat (180 and 250°C) on the water vapor permeability and watertightness of several breathable membranes and coatings used in the firefighters' protective clothing.[4] They generally observed a decrease in moisture barriers' water vapor permeability as a result of heat exposure. In some cases, large reductions in water vapor permeability occurred before any change could be detected by the naked eye. The consequence of heat exposure on watertightness was much more limited. Day et al.

Correspondence to: P. I. Dolez (patricia.dolez@etsmtl.ca).
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tested three types of moisture membranes and reported no decrease in tearing strength after thermal aging treatments of 24 h at 180°C and 1 h at 220°C.[5] They even measured an increase for some of them. In the case of neoprene-coated Nomex®, it was attributed crosslinking reactions. Only limited effects of thermal aging on the dimensional stability, weight, and flame resistance of the three types of moisture barrier were recorded.

Some works can also be found in the literature regarding the aging behavior and mechanisms of the two components of the studied moisture membrane taken individually, aramid fibers, and PTFE film. Thermal aging of Nomex® has been shown to lead to a reduction both in modulus and in breaking stress and strain of the fabric.[6] The change in the polymer mechanical strength as a result of thermal aging has generally been associated with the chemical degradation of the network chains.[7] In the case of Nomex®, the decrease in mechanical properties may be attributed in part to a phenomenon of chain scission involving the rupture of hydrogen bonds in the structure of the fibers.[8] A reduction in Nomex® fiber crystallinity measured by X-ray has also been reported as a result of thermal aging.[6] For its part, PTFE has been shown to experience an increase in crystallinity both when thermally aged below its melting temperature of 327°C[9] and as a result of argon ion implantation.[10]

In this article, the effect of accelerated thermal aging on the mechanical and barrier properties of a moisture membrane made of e-PTFE laminated on a Nomex® fabric is reported. More precisely, the consequences of thermal aging were evaluated through tensile and tear tests as well as water vapor permeability measurements. Complementary scanning electron microscopy analysis was also performed.

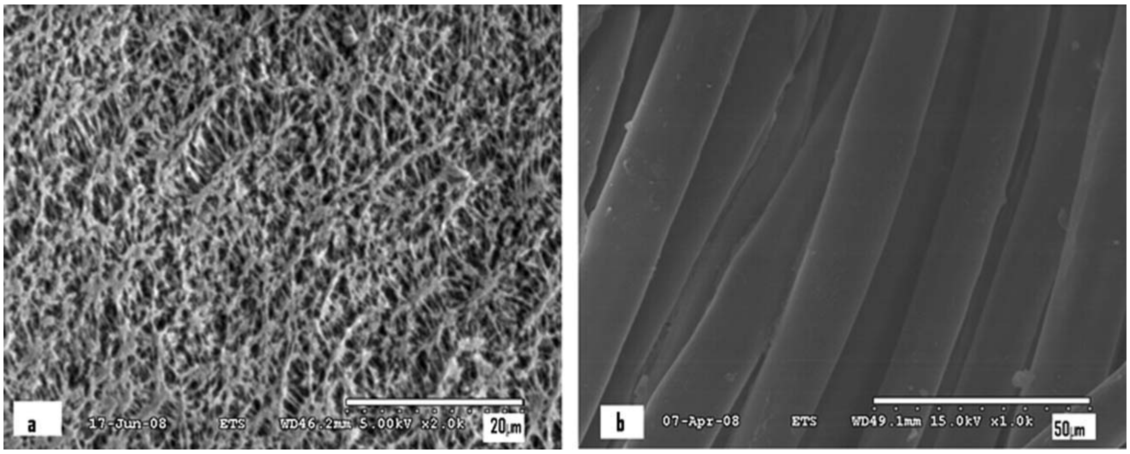

Figure 1 Scanning electron microscopy pictures of the e-PTFE side (a) and Nomex® fabric side (b) of the moisture membrane.

EXPERIMENTAL

Materials

The studied moisture barrier is composed of an enhanced bi-component e-PTFE membrane laminated on a Nomex® IIIa woven fabric. This material is sold under the brand name Crosstech® Fabric by W. L. Gore and Associates (Maryland, USA) and has been provided by Innotex® Inc (Québec, Canada). The average pore size in the e-PTFE membrane is 1 μm [Fig. 1(a)] and the yarn diameter for the Nomex® fabric is 15 μm [Fig. 1(b)]. For comparison purposes, tests were also performed on a plain Nomex® fabric with comparable properties.

Thermal aging treatments

The accelerated aging treatments were performed in a convectional electrical oven. Samples were kept for selected durations in the oven in a hanging position and with a distance of at least 4 cm from each other and from the oven walls. The aging program temperatures of 190, 220, 275, 300, and 320°C were selected considering the tabulated continuous operating temperatures of respectively, 260 and 200°C for e-PTFE and Nomex®[11] as well as the 100–300°C standard conditions reported for firefights in operation.[12] Aging durations ranged from 1 to 1056 h.

Water vapor permeability measurements

Water vapor (WV) permeability of the membrane was measured using a MOCON PERMATRAN-W Model 101 K. This apparatus can evaluate the transmission rate of water vapor through membranes in the range of 500–100,000 cm^3/(m^2 24 h). The sample size is 5 × 5 cm^2. Tests were carried out at a

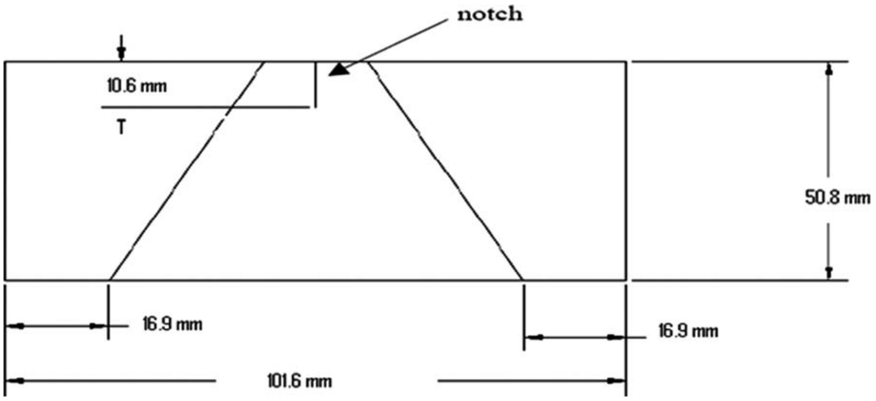

Figure 2 Geometry of the tear test sample.

temperature of 23°C and at a humidity level of 60%. Three replicates were measured for each condition.

Mechanical testing

Tensile properties were measured on 15 × 10 mm^2 rectangular specimens. Measurements were performed with an Alliance 2000 (MTS) universal testing machine equipped with 1000*N* load cell and operated at a cross-head speed of 300 mm/min according to the ASTM D5035 standard test method.[13] The modulus was determined from the initial slope of the stress–strain curve. The tensile strength was also calculated. For each condition, five replicates were measured.

Tear strength was also assessed since it has been reported to be more sensitive to heat aging than tensile strength in a study involving various laminate-type fabrics.[14] A sample similar to the ASTM D 5587 standard test method[15] but with slightly scaled-down dimensions was used. An isosceles trapezoid was drawn on 50.8 × 101.6 mm rectangular samples to mark the position of the grips (see Fig. 2) and a notch was cut in its smallest side. Samples were fixed in the grips of the Alliance 2000 test machine by clamping it along the oblique marks, leaving the side opposite to the notch wavy. Grips were pulled apart at a rate of 200 mm/min until the sample was completely torn apart. Tear strength is obtained from the maximum value of the force. For each condition, five replicates were measured.

Surface morphology

Scanning electron microscopy (SEM) (Hitachi S570 model) was used to investigate potential changes in the sample external morphology due to thermal aging. Observations were made on both sides of the membrane, i.e., on the e-PTFE laminate and on the Nomex® fabric. Prior to analysis, samples were coated according to the standard technique with a thin layer of gold to limit the charging effect.

RESULTS AND DISCUSSION

Effect of thermal aging on the membrane water vapor permeability

The results of the measurement of the membrane water vapor permeability are displayed in Figure 3 as a function of the aging time for four aging temperatures: 190, 220, 275, and 320°C. They are expressed in terms of variation relatively to the unaged membrane. Coefficients of variation for individual data points are between 1 and 10% for $T_{\text{aging}} \leq 220°\text{C}$ and 15–80% for $T_{\text{aging}} \geq 275°\text{C}$. In the case of aging at 190°C, the permeability was observed to decrease with aging time, retaining only about 30% of its initial value after 24 days of exposure. Even if the test method differs from what is used in firefighter protective equipment standards,[16] it is highly possible that a reduction in water vapor permeability of that extent will lower the membrane

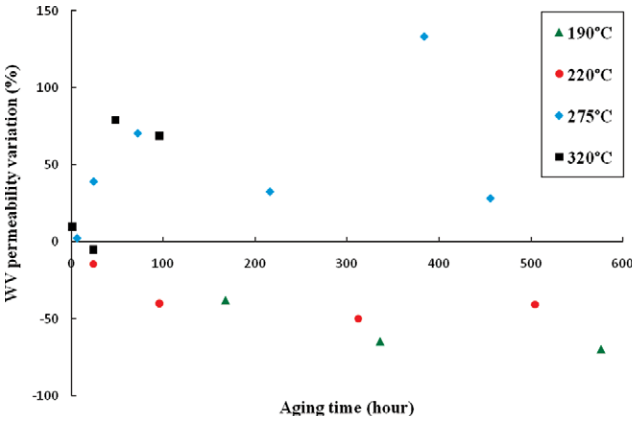

Figure 3 Relative variation of the water vapor permeability of the e-PTFE/Nomex® membrane as a function of aging time at four aging temperatures (190, 220, 275, and 320°C). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

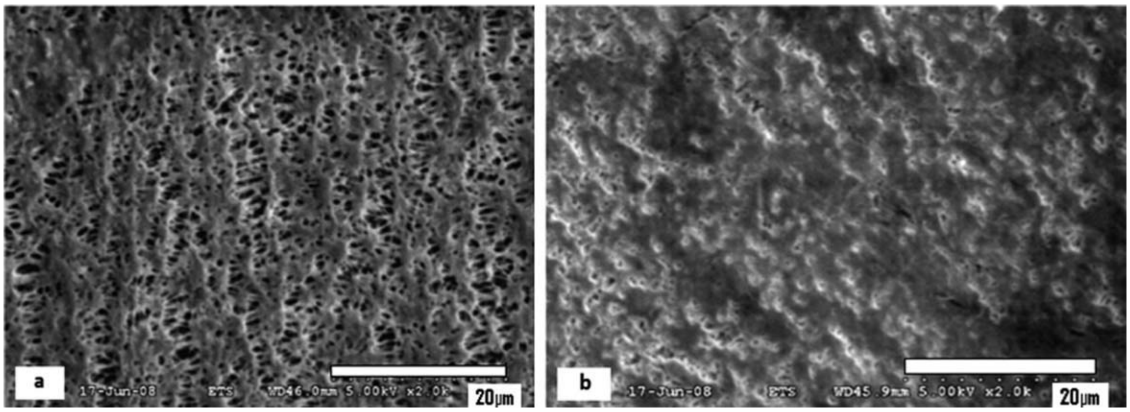

Figure 4 Scanning electron microscopy pictures of the e-PTFE laminate side of samples aged at 190°C during 7 days (a) and 24 days (b).

performance below the standard requirement for firefighter suit moisture membranes.[17]

Aging at 220°C produced a similar reduction effect in the membrane water vapor permeability. However, if the initial decrease rate seems to be higher with aging at 220°C than at 190°C, the two sets of data cross each other after about 10–12 days of aging. A plateau and even a slight further increase can be observed for the 220°C water vapor permeability values.

A totally opposite behavior can be observed in the case of the two highest aging temperatures, 275 and 320°C, which are situated above the tabulated value of 260°C for e-PTFE continuous operating temperature.[11] For these temperatures, a large and rapid increase in the sample water vapor permeability was observed as a result of aging, with a much larger scatter in the data points. Even if water vapor transmission rate is only defined as a lower limit criterion in firefighter protective equipment standards,[17] such high values of moisture membrane permeability might also be a problem.

To understand this phenomenon, the e-PTFE side of the membrane was analyzed by SEM. Figure 4 displays typical examples of pictures obtained for samples aged at a temperature of 190°C for 7 and 24 days. By comparison with Figure 1(a), which corresponds to the surface of an unaged sample, a progressive closure of e-PTFE laminate pores with aging time can be observed. Such phenomenon of pore closure in the e-PFTE laminate has already been reported in the case of microporous moisture barriers exposed to radiant heat.[4] Therefore, the observed decrease in water vapor permeability as a result of aging at 190 and 220°C can be attributed to a gradual reduction in pore size and number in the moisture membrane. Since these aging temperatures are situated above the 120°C glass transition temperature of PTFE, the larger chain mobility in the polymer network may allow a modification in the material morphology leading to a progressive closure of the pores. This hypothesis is supported by the reduction in sample dimension which was observed as a result of the aging treatments.

In the case of samples aged at temperatures above 260°C, SEM pictures revealed the formation of cracks and holes in the e-PTFE laminate in addition to pore closure (see Fig. 5). The size of these cracks seems to increase with aging time. These large breaches in the moisture barrier integrity explain the

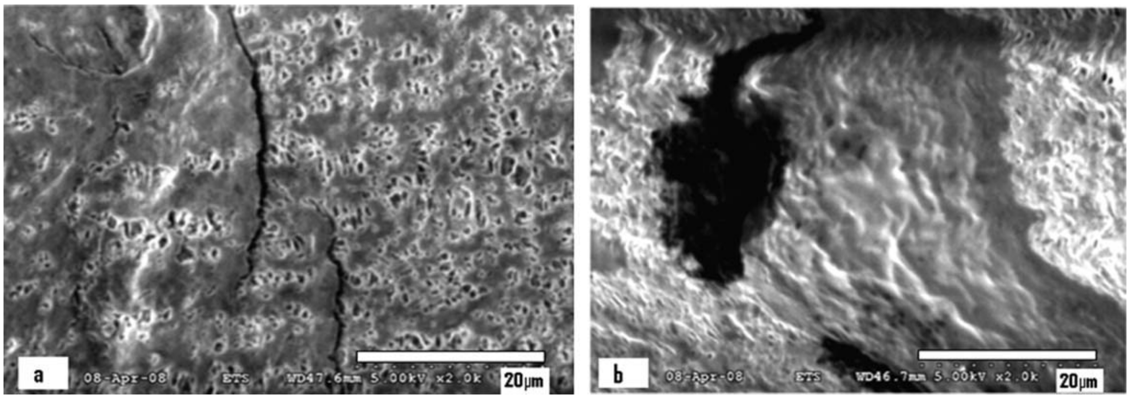

Figure 5 SEM pictures of the e-PTFE side of the membrane aged at 275°C during (a) 9 days and (b) 16 days.

increase in water vapor permeability recorded for aging treatments at temperatures of 275 and 320°C. The formation of these defects might be due to stress build-up resulting from a nonuniform reduction in pore size across the sample. It can also be observed in Figure 3 that the increase in the water vapor permeability of samples exposed to these temperatures begins after very short aging times, i.e., less that 1 h. In the course of their service life, firefighters' protective suits may experience this serious type of damage and the corresponding reduction in performance, either as a result of a single high temperature exposure or more probably due to the combined effect of successive events.

Finally, the presence of a plateau slightly inching upward in the 220°C water vapor permeability data (see Fig. 3) may indicate the occurrence of the two competing phenomena relative to water vapor permeability—pore closure and hole/crack formation—at that aging temperature. If pore closure controls the membrane water vapor permeability for the first 100 h of aging, hole/crack formation may be at the origin of the upward curvature of the data points at the longest aging times. This could also explain why water vapor permeability values corresponding to the longest aging times at 190°C are situated below than those recorded with aging at 220°C. Degradation in the e-PTFE laminate thus appears to occur even for temperatures below the continuous operating temperature of 260°C reported for e-PTFE.

It is worth noting that neither pore closure nor crack formation can be detected with the naked eye. Since visual inspection is generally the only available technique to fire services for assessing the condition of their protective equipment, this raises large concerns regarding the safety of firefighters.

Effect of thermal aging on the membrane tensile properties

Figure 6 presents an example of stress–strain curves obtained for different aging times at 320°C. Data for an unaged sample are also included. Stress–strain curves are observed to display a two-stage behavior. By analogy with what Serwatka et al. have proposed for textile yarns,[18] the initial part of the stress–strain curve may be associated with a rearrangement and a pretensioning of the yarns and of the fibers within them. The second part of the curve is due to the elastic deformation of the yarns. Rupture occurred before any significant plastic deformation of the yarns.

As seen in Figure 6, longer aging times induced a reduction in the fabric initial modulus and maximum stress as well as an increase in the elongation at break. In addition, the relative proportion of the initial rearrangement/pretensioning part in the stress–strain curves increased with the aging time. On the other hand, for exposures of up to 48 h, the slope of the elastic part of the stress–strain curves did not seem to be strongly affected by aging.

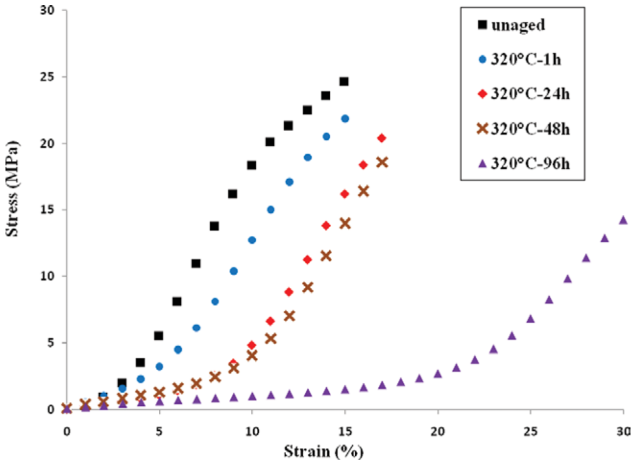

Figure 6 Stress–strain behavior of the e-PTFE/Nomex® membrane for an unaged sample and after different aging times at 320°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

This behavior may be linked in part to the manufacturing process of Nomex® fibers which includes a stretching step where polymer chains are aligned along the fiber direction to improve the product mechanical properties.[19] During thermal aging, the polymer chains may tend to relax from their aligned configuration to a more random orientation, which lowers the fiber mechanical properties.[20] This effect may explain in part the observed reduction of the fabric initial modulus with aging time.

As a result, during the first phase of the tensile test, which corresponds to the pretensioning of the yarns, the pulling force exerted on polymer chains in fibers parallel to the pulling direction produces a realignment of their orientation. Since the amount of deformation necessary to realign the polymer chains depends on the level of randomization generated during the aging treatment, the initial pretensioning stage should increase with aging time as is observed in Figure 6.

Once the pretensioning of the sample has been achieved, i.e., during the elastic deformation phase, no major modification of the corresponding modulus should be observed if the polymer chains involved in the tensile deformation of the fabric have been completely realigned by the pretensioning stage. Such behavior appears to characterize the shorter aging treatments performed at 320°C, i.e., with aging durations of up to 48 h. On the other hand, a decrease in the second modulus as well as a change in the elongation at break can be seen in Figure 6 for the 96 h aging treatment.

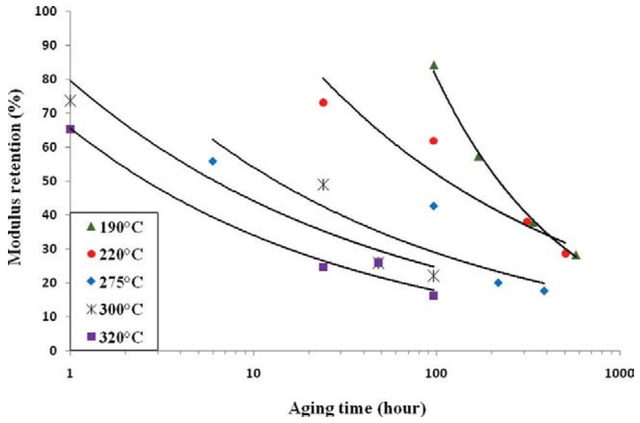

Figure 7 Tensile modulus retention as a function of aging time for five aging temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The variation in the initial modulus, tensile strength, and elongation at break as a function of aging time was recorded for five aging temperatures (190, 220, 275, 300, and 320°C). The corresponding curves are displayed respectively, in Figures 7–9. A decrease in the initial modulus and tensile strength as a function of the aging time and temperature is observed. In particular, the modulus reached less than 30% of its initial value after 576 h at 190°C, a temperature lower than the 200°C and 260°C service temperatures of Nomex® and e-PTFE.[11] The reduction in tensile strength as a result of thermal aging is more limited however still very substantial. In the case of the elongation at break, the observed increase remained smaller than 40% except for the 96 h-320°C aging treatment for which the value of the elongation at break almost doubled.

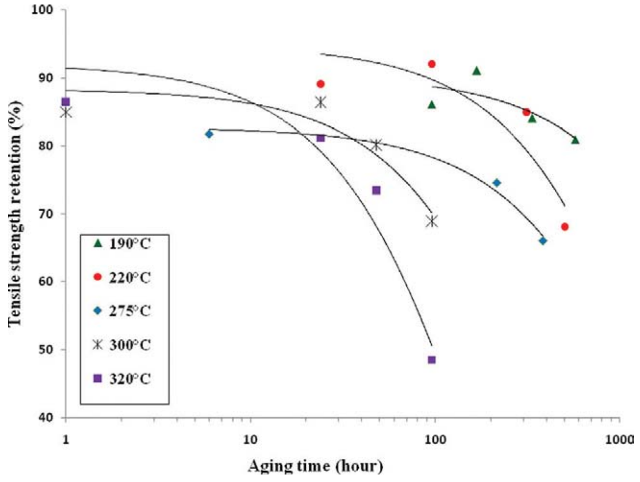

Figure 8 Tensile strength retention as a function of aging time for five aging temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

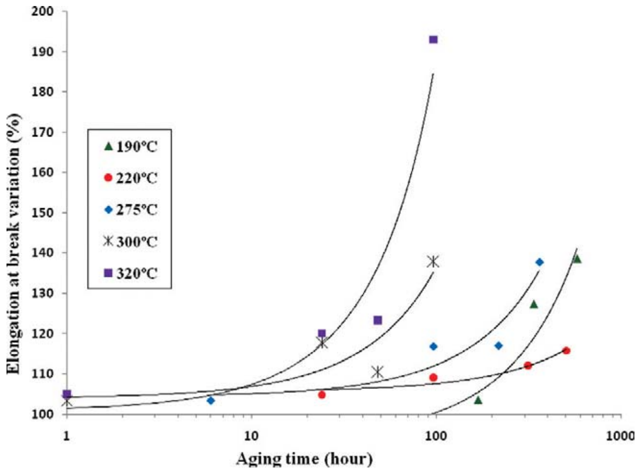

Figure 9 Variation of the elongation at break as a function of aging time for five aging temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

A strong effect of thermal aging on the e-PTFE/Nomex® moisture membrane tensile properties is thus observed as a result of the various aging treatments. A similar decrease in modulus had already been reported by Jain and Vijayan for Nomex® fibers aged at 300, 350 and 400°C.[6] In the case of the elongation at break, they also observed a reduction with aging time and temperature, i.e., the opposite behavior to what is obtained here. However, the shape of the force-extension curves corresponding to their Nomex® fibers lacked the pretensioning phase observed with the e-PTFE/Nomex® moisture membrane. The difference in the effect of thermal aging on the elongation at break between the two sets of data may thus be attributed to the variation of the strength of the polymer chain alignment in the fibers as well as eventually the presence of a woven structure and a laminated e-PTFE layer.

The change in e-PTFE laminate morphology (pore closure and crack formation) already observed (see section Effect of thermal aging on the membrane water vapor permeability) is also accompanied by a reduction in mechanical performance of the membrane. In addition, a SEM analysis of the surface of the Nomex® side of the membrane was performed to look for additional signs of material deterioration. Results are shown in Figure 10 for aged samples. While unaged Nomex® fibers display a very smooth surface [see Fig. 1(b)], the presence of fissures and peel-offs [see Fig. 10(a)] as well as extraneous deposits [see Fig. 10(b)] can be observed at the surface of aged fibers. Such features were observed at all aging temperatures, their quantity and magnitude depending on the aging conditions. The presence of these peel-offs and deposits indicates that a deterioration is induced in the Nomex® fibers by the thermal aging treatments. Such types of observations have

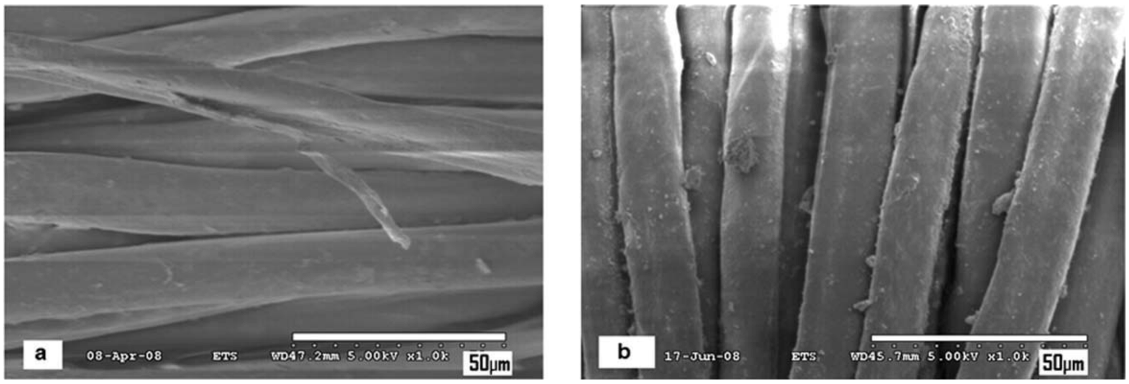

Figure 10 SEM pictures of the Nomex® side of aged membrane samples: (a) showing fissures and peel-offs (aged at 275°C during 216 h), (b) showing extraneous deposits (aged at 320°C during 24 h).

also been reported by Jain and Vijayan for thermally aged Nomex® fibers.[6]

Effect of thermal aging on the membrane tear strength

The effect of thermal aging on the tearing behavior of the e-PTFE/Nomex® moisture membrane was also studied. Figure 11 presents examples of tearing force-displacement curves obtained for different aging times at 320°C. Data for an unaged sample are also included. A reduction of the tear strength for increasing aging times is observed while no effect on the tearing distance is recorded.

The variation of the tear strength retention with aging time for five aging temperatures (190, 220, 275, 300, and 320°C) is displayed in Figure 12. A decrease in tear strength as a function of aging time and temperature is observed. The loss in tear strength appears far less stringent than what was observed for the initial modulus (see Fig. 7), which was associated with a randomization of polymer chain orientation during thermal aging. On the other hand, it is much closer still quite larger than the scale of reduction observed in tensile strength. Indeed it has been shown that that the tear strength of fabrics in the trapezoid configuration can be related to the breaking characteristics of the material.[21] The discrepancy between tearing and tensile strength loss level due to aging may be attributed in part to the fact that the model of[21] assumes a linear force elongation shape and thus neglects the initial crimp removal.[22]

For comparison purposes, some tear strength measurements were also performed on a plain Nomex® fabric. The results in terms of tear strength retention as a function of aging time and temperature are displayed in Figure 13. Values of tear strength retention for plain Nomex® appear to be slightly lower than those corresponding to the e-PTFE/Nomex® membrane. Coating materials have been reported to restrict the slippage of textile yarns during tearing.[2] This effect may thus be attributed to

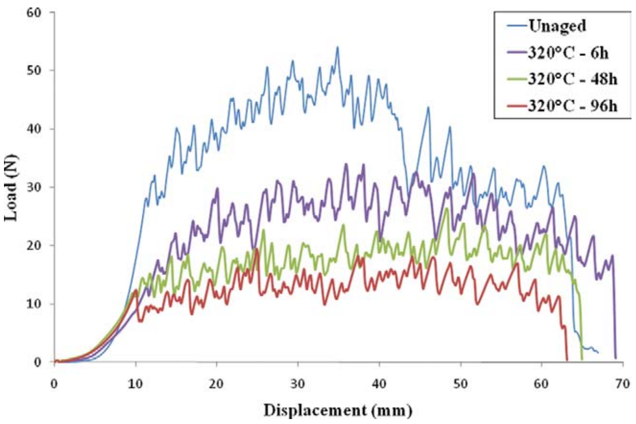

Figure 11 Examples of tearing force-displacement curves for the unaged e-PTFE/Nomex® membrane as well as after different aging times at 320°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

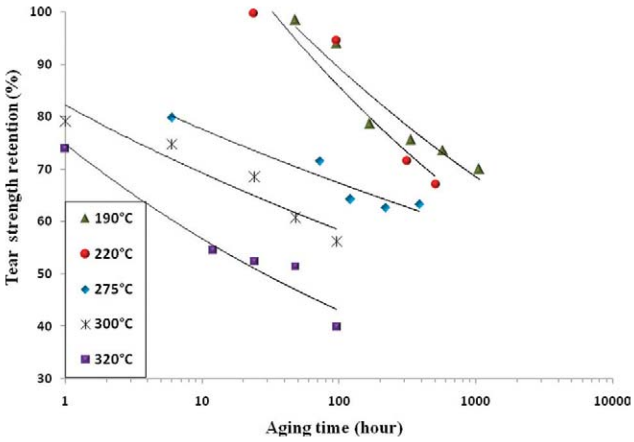

Figure 12 Effect of aging time on tear strength retention of the e-PTFE/Nomex® membrane at five aging temperatures (190, 220, 275, 300, and 320°C). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

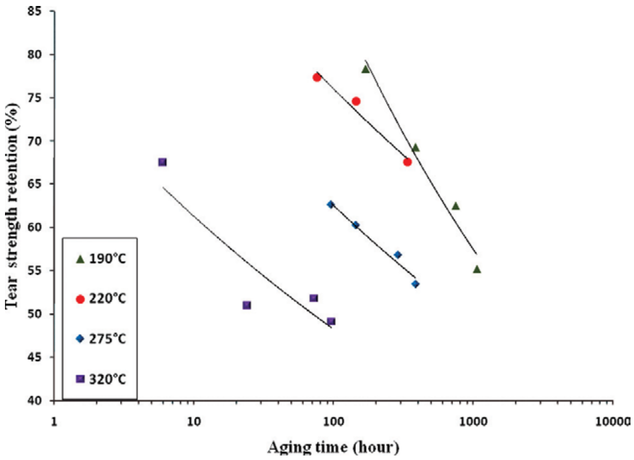

Figure 13 Effect of aging time on tear strength retention of a Nomex® fabric at four aging temperatures (190, 220, 275, and 320°C). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the contribution of the e-PTFE laminate, which has a higher service temperature than Nomex®,[11] to the tear strength of the membrane.

Therefore, thermal aging, even at a level lower than the lowest of the continuous operating temperatures of the two moisture membrane components, appears to have a strong effect on the material tear resistance. In addition, as the damage produced on the material is most probably cumulative, the moisture membrane may reach a high level of degradation over the course of its service life as a result of successive short term exposures to severe conditions or to longer term exposures to more mild temperatures. Therefore, even if no direct comparison with requirements included in firefighter's protective equipment standards can be made due to the difference in the methods used, it is possible that the level of performance displayed by the protective clothing becomes lower than the 22*N* criterion specified for moisture membranes in the NFPA 1971 standard due to service thermal aging for example.[23]

Aging kinetics

An important aspect in the study of the aging behavior of materials is the possibility to predict their thermal life, which can be defined as the time to reach a certain amount of damage. In the case of protective equipment, this concept can be associated with a safety limit for the user. While polymer thermal aging generally involves complex combinations of chemical reactions, research has shown that the whole degradation process can often be approximated with a single effective activation energy.[7] According to the Arrhenius model, the temperature dependence of the rate of a chemical reaction is proportional to exp $(-E_a/RT)$, where E_a is the effective activation energy of the reaction, R is the ideal gas constant, and T is the temperature. As a result, the thermal life of the polymer t_c can be written as:

$$t_c = t_0 . \exp(E_a/RT) \tag{1}$$

TABLE I
Thermal Lives Corresponding to a 60% e-PTFE/Nomex® Membrane Modulus Retention for Five Aging Temperatures (190, 220, 275, 300, and 320°C)

Aging temperature (°C)	Thermal life corresponding to 60% modulus retention (h)
190	161.7
220	62.5
275	6.9
300	3.0
320	1.4

The Arrhenius model has been shown to describe successfully the aging behavior of a large number of materials,[7] even in the case of multicomponent systems.[24]

Thermal life values for the membrane initial tensile modulus have been computed for each aging temperature using 60% modulus retention as the failure criterion. They are displayed in Table I. These values of thermal life were then used to produce an Arrhenius plot shown in Figure 14 by plotting the logarithm of the thermal lives as a function of the reciprocal of the aging temperatures according to eq. (1). A very good agreement with the Arrhenius model can be seen from the high value of the correlation coefficient corresponding to a linear fit. This indicates that the effect of thermal aging on the e-PTFE/Nomex® membrane initial tensile modulus can be described by a constant effective activation

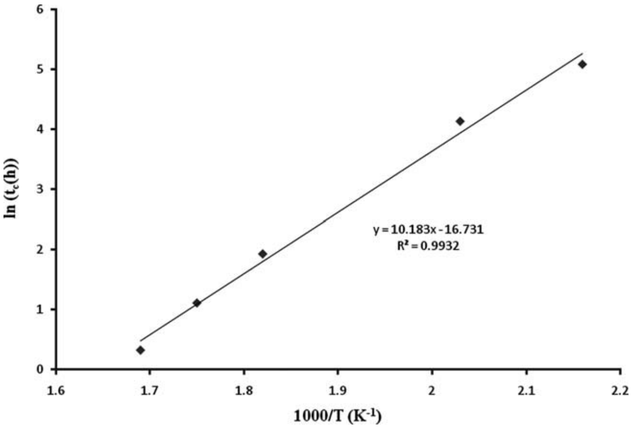

Figure 14 Arrhenius plot of the calculated thermal lives corresponding to a 60% tensile modulus retention of the e-PTFE/Nomex® membrane at five aging temperatures (190, 220, 275, 300, and 320°C)

energy between 190 and 320°C. A value of activation energy of 85 kJ/mol was obtained.

The same exercise was carried out for the two other tensile properties measured on the moisture membrane, i.e., tensile strength and elongation at break. For each of them, the criterion used in the calculated thermal life approach was adjusted to the level of property variation resulting from the thermal aging. It was set to 80% for tensile strength and 120% for elongation at break. In both cases, a very good agreement was obtained with the Arrhenius model. Values of activation energies were equal to 54 kJ/mol in the case of tensile strength and 76 kJ/mol for elongation at break. The Arrhenius model thus appears as a valuable tool to analyze and predict the effect of thermal aging on the tensile properties of the e-PTFE/Nomex® moisture membrane.

A comparison was made between the aging behavior of the e-PTFE/Nomex® moisture membrane and that of a Kevlar®/PBI fabric used as the outer layer in firefighter suits, for which the effective activation energy corresponding to tensile strength has been measured to be in the range of 107–137 kJ/mol.[25] This value is much higher than what has been obtained here for the membrane tensile strength. The e-PTFE/Nomex® moisture membrane thus appears to be much more sensitive to thermal aging. This result is in agreement with the previous claim by Rossi and Zimmerli that the moisture membrane is the most heat sensitive layer in protective clothing.[4] This situation may raise serious problems since its core position in the firefighter suit superimposed-layers configuration makes the early detection of these already difficult-to-see signs of degradation even more improbable.

The applicability of the Arrhenius model to the study of the effect of thermal aging on the membrane tear resistance was also investigated. However, in that case, the computation of the Arrhenius plot for thermal life values corresponding to a 60% property retention criterion did not appear to provide any straight line as can be seen in Figure 15. The absence of agreement of the tear strength data with the Arrhenius model was observed as well with the Nomex® fabric. This indicates that, in the range of temperatures between 190°C and 320°C, the effect of aging on the tearing properties of the Nomex® fabric and e-PTFE/Nomex® moisture membrane involves several processes which cannot be described by a unique activation energy. This behavior might be associated with the complex nature of the tearing process, which includes a friction contribution generated by the slippage motion of the fabric longitudinal yarns on the transverse ones at the edge of the tearing zone.[26] Since a modification of the surface of Nomex® fibers was observed during thermal aging (see Fig. 10), a variation of the interfiber friction coefficient with aging time and temperature may occur, leading to the non-Arrhenius behavior observed here for the effect of thermal aging on the tearing strength of the Nomex® fabric and e-PTFE/Nomex® moisture membrane.

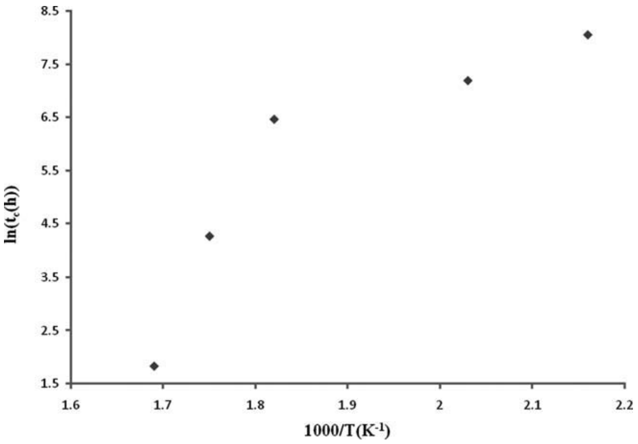

Figure 15 Arrhenius plot for the thermally aged e-PTFE/Nomex® membrane using a 60% tear strength retention criterion (five aging temperatures: 190, 220, 275, 300, and 320°C).

CONCLUSIONS

This study has looked at the effect of thermal aging on the mechanical resistance of an e-PTFE/Nomex® moisture membrane used in firefighters' protective clothing. Thermal treatments were carried out in a convectional oven at aging temperatures between 190 and 320°C. The effect of aging on the membrane mechanical performance was evaluated through tensile and tearing measurements. Large modifications in the mechanical performance of the laminate were recorded and attributed to a deterioration of the membrane components. In particular, SEM observation of the surface of the Nomex® fibers revealed the presence of fissures and peel-offs as well as extraneous deposits as a result of aging. The effect of thermal aging on the tensile properties of the e-PTFE/Nomex® moisture membrane was successfully described using the Arrhenius model.

Measurements involving the membrane water vapor permeability showed the existence of two opposite behaviors depending on the aging temperature. For aging temperatures situated at 220°C and below, the water vapor permeability decreased with aging time. On the opposite, the permeability was larger than the value corresponding to the unaged material for aging treatments performed at temperatures equal or higher than 275°C. This was related to the occurrence of two competing phenomena relative to water vapor permeability observed in the e-PTFE laminate: closure of pores starting at low temperature and creation of cracks and holes at high temperatures and/or long exposure times.

These results show that the aging of moisture membranes must be considered carefully while estimating the service life of protective clothing of firefighters. In particular, modifications in the material mechanical and barrier properties have been shown to occur at aging temperatures lower that the tabulated continuous operating temperatures of the two moisture membrane components. This situation is even more troublesome that the signs of this early degradation of the membrane — pore closure or crack and hole formation in the e-PTFE laminate, fissures, peel-offs and extraneous deposits on the surface of the Nomex® fibers — cannot be easily detected by the naked eye, which currently generally represents the only evaluation method available to firefighters for assessing the condition of their protective equipment.

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References

1. Rossi, R. M.; Bolli, W.; Stampfli, R. Proceedings of the 3rd European Conference on Protective Clothing and Nokobetef 8, Gdynia, Poland, 10-12 Mai, 2006.
2. Keighley, J. H. J Indus Text 1985, 15, 89.
3. Lomax, G. R. J Indus Text 1985, 15, 40.
4. Rossi, R. M.; Zimmerli, T. In Performance of Protective Clothing: 6th volume, ASTM STP 1273; Stull, J O.; Schwope, A. D., Eds.; American Society for Testing and Materials, WestConshocken, PA, 1997.
5. Day, M.; Cooney, J. D.; Suprunchuk, T. Text Res J 1988, 58, 141.
6. Jain, A.; Vijayan, K. Bull Mater Sci 2002, 25, 341.
7. Verdu, J. In Techniques de l'ingénieur, traité plastiques et composites, AM 3151; Techniques de l'Ingénieur: Paris, 2002.
8. Villar-Rodil, S.; Martinez-Alonso, A.; Tascon, J. M. D. J Anal Appl Pyrolysis 2001, 58-59, 105.
9. Jain, A.; Vijayan, K. Polym Eng Sci 2007, 47, 1724.
10. Jizhong, Z.; Qinglan, W.; Xiaojun, Y.; Ping, Z.; Hengde, L. Mater Lett 2001, 48, 362.
11. Bourbigot, S.; Flambard, X. Fire Mater 2002, 26, 155.
12. Rossi, R. Ergonomics 2003, 46, 1017.
13. American Society for Testing and Materials, Standard test method for breaking force and elongation of textile fabrics (strip method); ASTM International: WestConshocken, PA, 1995.
14. An, S. K. J Soc Fiber Sci Technol Jpn (Sen'i Gakkaishi) 1999, 55, 464.
15. American Society for Testing and Materials, Standard test method for tearing strength of nonwoven fabrics by the trapezoid procedure; ASTM International: WestConshocken, PA, 1995.
16. Canadian General Standard Board, Textile Test Methods - Resistance of Materials to Water Vapour Diffusion CAN/CGSB-4.2 n 49-99, Ottawa, Canada, 1999.
17. Canadian General Standard Board, Firefighters' Protective Clothing for Protection Against Heat and Flame CAN/CGSB-155.1-2001, Ottawa, Canada, 2001.
18. Serwatka, A.; Bruniaux, P.; Frydrych, I. Fibres Text Eastern Eur 2006, 14, 30.
19. Needles, H. L. Textile Fibers, Dyes, Finishes, and Processes—A concise Guide, Noyes Publications: Park Ridge, New Jersey, 1986.
20. Bresee, R. R. J Am Inst Conserv 1986, 25, 39.
21. Caiyuan, C.; Dhingra, R.; Postle, R. J China Text Univ 1991, 8, 1.
22. Steele, R.; Gruntfest, I. J. Text Res J 1957, 27, 307.
23. National Fire Protection Association, Standard on protective ensembles for structural fire fighting and proximity fire fighting NFPA 1971, Qincy, MA, 2006.
24. Baer, N. S.; Indictor, N. In Preservation of Paper and Textiles of Historic and Artistic Value; Williams, J. C., Ed.; American Chem Society, Washington DC, 1978, p336.
25. Arrieta, C.; David, E.; Dolez, P.; Vu-Khanh, T. J Appl Polym Sci 2010, 115, 3031.
26. Witkowskaand, B.; Frydrych, I. Text Res J 2008, 78, 510.