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Effects of Heat Treatment on the Mechanical and Thermal Performance of Fabric Used in Firefighter Protective Clothing

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Abstract
With excellent thermal stability and resistance, X-fiper® fabric has been applied in firefighter protective clothing. In this paper, X-fiper® fabric was subjected to heat treatment at 6.5 kW/m² and 9.7 kW/m² for durations between 0 to 30 min. Effects of the heat intensity and exposure duration on mechanical properties, thermal protective performance, surface morphology, and structural properties were studied and analysed. The results showed that the intensity of heat flux had significant effects on the tensile strength, elongation at break, and tear strength. The tear strength of X-fiper® fabric was less than 100 N after 5-minute's exposure at 300 °C. The thermal protective performance, however, did not change considerably. From the scanning electron microscope (SEM) analysis, specimens showed grooves, peel-offs and deposits as a result of heat treatment. The results observed by SEM and FTIR-Raman spectroscopy revealed the mechanisms of changes in mechanical properties and thermal protection.

Key words: *heat treatment, X-fiper® fabric, thermal protective performance, mechanical properties.*

Introduction

Aramid fabrics, with excellent thermal stability and resistance to ignition, have been widely applied in firefighter protective clothing designed to protect firefighters and ensure their safety. In general, firefighter protective clothing is a three-layer system which consists of an outer shell, moisture barrier, and thermal liner. In recent decades, considerable progress has been made in evaluating and predicting the thermal protective performance of new firefighter protective clothing [1 - 7]. These researches mainly focused on the effects of fibre types, fabric thickness, air gaps, moisture and the heat source on the thermal protective performance and modeling of heat and moisture transfer through firefighter protective clothing.

In general, performance of firefighter protective clothing deteriorates with time. During its lifetime, various environments such as heat, sunlight, and moisture affect the material properties, especially for the outer layer fabric. The consequence of degradation of functional properties is high, not only in terms of economical cost but also in terms of safety. Therefore it was important to know how environmental conditions affect the performance of fabrics over time. There are some publications describing the impact of simulated environmental conditions on fabrics. Day et al [8] conducted research on the effects of fabric type on degradation after thermal and light exposures. The effect of thermal exposure on thermal shrinkage was dependent on the fabric. Some fabrics such as flame resistant wool were shown to be more susceptible to thermal shrinkage in short thermal exposures at higher temperatures than longer duration exposures at lower temperatures. Jain, et al [9] investigated the impact of thermal ageing on Nomex fibre. Thermal aging has been shown to lead to a reduction in breaking stress and strain. Mäkinen [10] studied the effects of wear and laundering on the properties of FR wool, aramid, FR viscose blend and FR cotton fabrics. The flame resistance, mass per unit area, thickness, tensile strength, and tear strength of the fabrics were tested. The results showed that wear and 3 - 4 launderings changed the materials to the same extent as 50 in the laboratory. Meanwhile some researchers investigated the effect of ultraviolet irradiation. Davis et al [11] studied the effect of ultraviolet radiation on the mechanical performance of polyaramid and polybenzimidazole firefighter protective clothing fabrics. The results showed that mechanical properties of the samples decreased significantly due to ultraviolet aging.

Table 1. *Parameters of X-fiper® fabric.*

Material	Weave	Thickness, mm	Weight, g/m²
93% X-fiper® meta-aramid, 5% para-aramid, 2% P-140	twill	0.33	210

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The goal of this research was to identify the effects of heat treatment on X-fiper® fabric used for the outer shell of firefighter protective clothing and to determine to what extent the fabric was damaged. The fabric was exposed to radiant heat fluxes, as the outer shell is the first line of defense against the abrasive and sharp physical hazards common to a fire scene. In this study, the consequences of heat treatment were evaluated through tensile and tear properties as well as thermal protective performance. In order to study the changes on a microscopic scale, the surface morphology and FTIR-Raman spectroscopy of the fabrics treated were also discussed.

Experimental

Material

Commercial high-performance fabric used for the outer shell of firefighter protective clothing was studied. The X-fiper® fabric was produced by SRO Inc., China, made of a 93/5/2% fibre blend of X-fiper® meta-aramid, para-aramid and P-140 (antistatic fibre). ***Table 1*** shows more information about the sample.

Heat treatment

The exposure conditions faced by fire fighters were classified into three categories depending on the temperatures and heat flux: routine (< 1.68 kW/m^2, up to 60 °C), hazardous (1.68 - 12.6 kW/m^2, up to 300 °C), and emergency (12.6 - 21 kW/m^2, above 300 °C) [12]. In this study the specimens were exposed to radiant heat flux values of 6.5 and 9.7 kW/m^2 to simulate the actual conditions of firefighter protective clothing and accelerate aging. The surface temperature of X-fiper® fabric exposed to a heat flux of 6.5 kW/m^2 was 250 °C. For the 9.7 kW/m^2 exposure, the surface temperature was about 300 °C. The duration of thermal exposure was set as 5, 10, 20, 30 min. The heat treatments were performed by means of a quartz tube. The temperatures were measured by a virtual instrument (National Instruments, USA) and heat flux by a copper radiometer on the fabric's surface.

Mechanical testing

Before and after thermal exposure, mechanical properties of the fabrics including the tensile strength, percentage of elongation at break, and tear strength were measured. Tensile properties evaluated using an Instron 3365 test machine (Instron Inc, USA) according to the ASTM D5035 strip method [13]. Fabrics were conducted in both the warp and fill directions. In addition, the tear property was also important for evaluating the performance of the outer shell fabric used for firefighter protective clothing. The tear strength was assessed as described in ASTM D5587 [14]. The tear strength specimens were 75 × 150 mm with a single 25 mm tear introduced at one end. The tear strength was calculated using the average of the five highest load points of the load-extension curves. The coefficient of variation of the results was less than 5%.

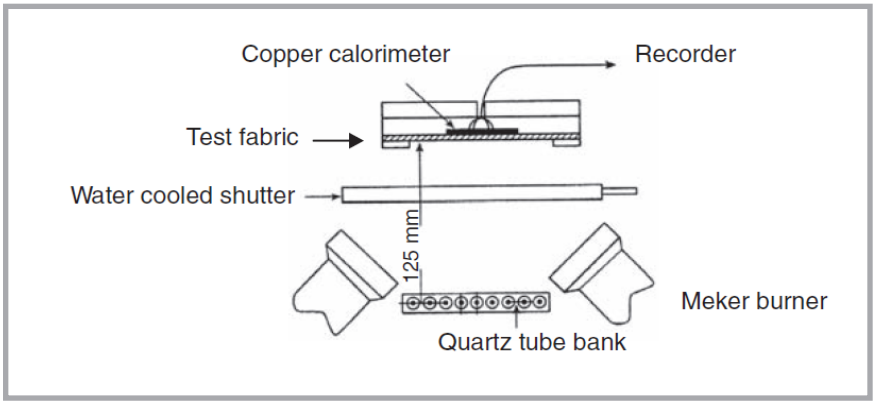

Figure 1. *Scheme of CSI-206 TPP tester.*

Thermal protective performance

The thermal protective performance of the specimens was evaluated by a CSI-206 (Custom Scientific Instrument Inc., USA) tester in this study. A TPP tester was the most versatile laboratory instrument available for examining the thermal protection of the fabrics based on the NFPA1971 test standard [15]. This tester used a combined flame and radiant source in time-controlled exposures to measure the thermal protective index (***Figure 1***).

The TPP rating was defined as the total exposure energy causing the test fabric to transfer a sufficient amount of heat to result in a 2nd degree burn injury, which was calculated as follows:

$$\text{TPP rating} = F \times T \qquad (1)$$

where, F - incident heat flux in kW/m^2; T - time to burn in s.

In this study, the specimen was 15 × 15 cm and exposed sample area 100 cm^2. At least three samples of each fabric were tested.

Scanning electron microscopy

To examine the physical effects of heat treatment on the fabric surfaces, the morphologies of untreated and heat treated fabrics were observed with JSM-5600LV scanning electron microscope (JEOL Co. Ltd., Japan). All the samples were sputtered with gold.

FTIR-Raman spectroscopy

FTIR-Raman spectroscopy was a common technique used for the detection of chemical changes of fabrics. The FTIR-Raman spectrum was obtained using Nicolet Nexus 670 FTIR-Raman spectroscopy (Nicolet Thermo, USA) in this study. As Raman was similar to infrared spectroscopy, the vibrational spectroscopy technique was used so that each spectral line could be ascribed to a specific vibration mode of a molecule.

Results and discussion

Tensile properties

The variation in the tensile strength of the warp and fill directions as a function of the heat flux and duration of exposure is recorded in ***Figure 2.a*** (see page 76). The results showed that the tensile strength of the warp direction was higher than that of the fill direction. After exposure to a radiant heat flux of 6.5 kW/m^2 for periods of 5 min to 30 min, the tensile strength was not reduced but increased slightly with the heat treatment. This behaviour may be linked to the rearrangement of fibres with heat treatment at 250 °C [16], which improved the tensile strength of the blend fabric.

The data in ***Figure 2.a*** show that the tensile strength decreased rapidly after exposure to 9.7 kW/m^2 heat flux. After a 20-minute exposure to 9.7 kW/m^2 heat radiation, it experienced a 24% de-

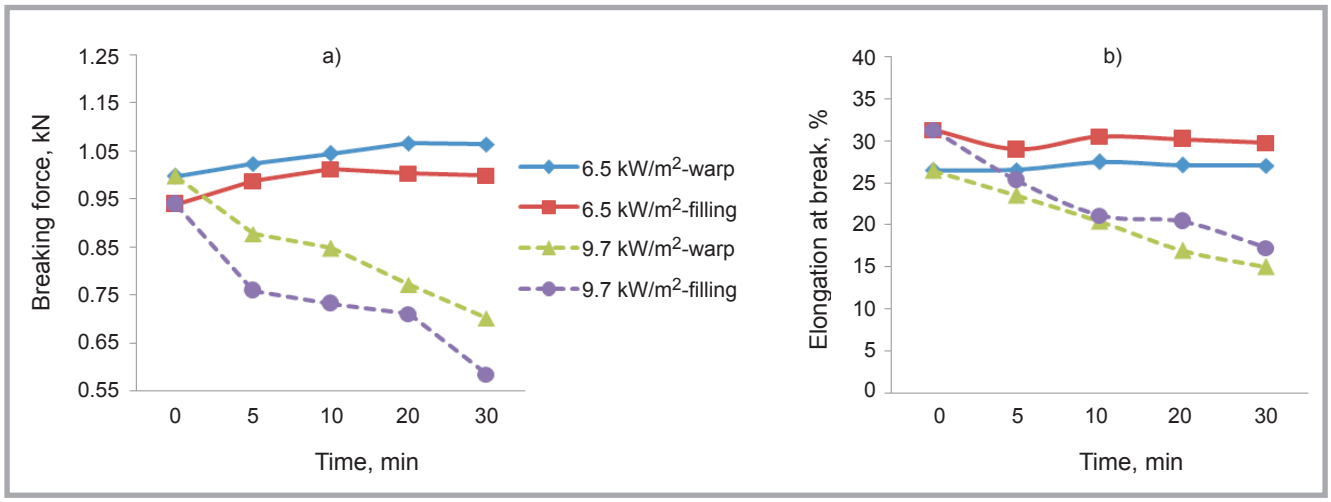

Figure 2. *Variation in: a) tensile strength and b) elongation at break as a function of heat flux and time.*

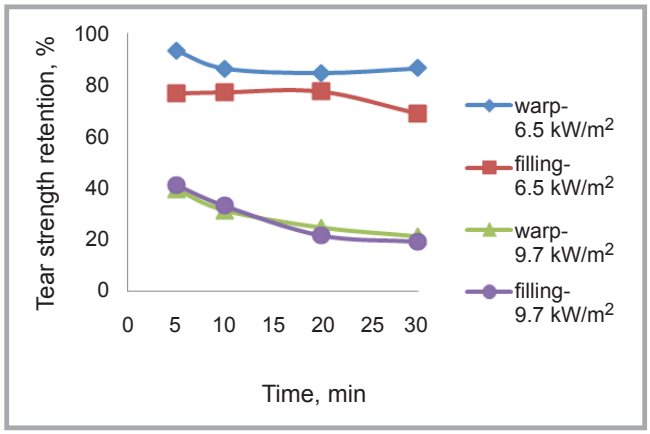

Figure 3. *Variation in the tear strength retention as a function of heat flux and time.*

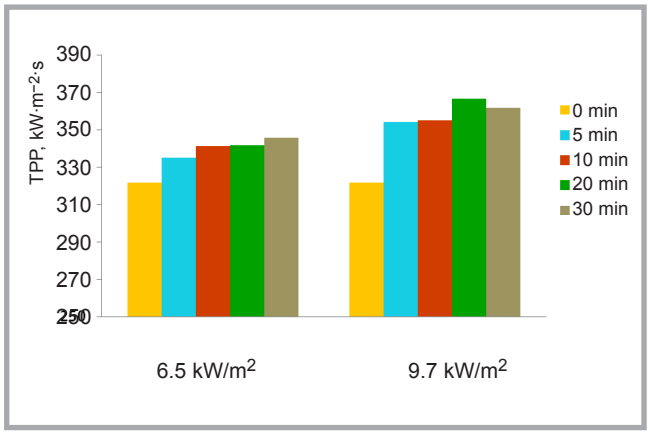

Figure 4. *TPP ratings of heat treated fabrics as a function of time and heat intensity.*

crease in tensile strength on average. The fabrics treated still passed the requirements of NFPA 1971[15]. When they were exposed to 9.7 kW/m^2 radiation for 30 minutes, however, the tensile strength of the warp and fill directions were 702 N and 585 N, respectively. The value of the tensile strength in the fill direction was lower than the minimum value (623 N) required in NPFA1971. It may be assumed that a higher heat flux led to the breaking of polymer chains at a molecular level and resulted in a drop in fabric tensile strength. Changes in the microscopic structure are discussed in more detail later in the paper.

Figure 2.b presents changes in the elongation at break as a function of the heat flux and time, with the results being similar to the tensile strength. The fabrics exposed to 6.5 kW/m^2 radiation did not show any significant variation in the elongation at break either. However, after exposure to 9.7 kW/m^2 heat flux, the elongation at break tended to decrease with an increase in the exposure duration. Substantial drops were observed after 30 minutes of exposure to 9.7 kW/m^2. For instance, the initial value of the elongation at break in the fill direction was 28.45% and that of 30-minute treated fabric was only 9.67%.

These results indicated that a higher heat flux of 9.7 kW/m^2 caused a severe decrease in the tensile properties. The breaking strength and elongation at break decreased with an increase in the exposure duration. Therefore an analysis of variance was conducted to investigate the effect of heat treatment on tensile properties. The results showed that the effect of heat intensity on the tensile strength and elongation at break was significant ($p < 0.05$). As the duration of exposure was short in this paper, the effect was not significant.

Tear strength

The effect of heat treatment on the tearing behaviour of the fabrics was also studied. The initial tear strengths of the warp and fill directions were 127 N and 133 N, respectively. To be able to compare the heat treated behaviour of the fabrics, the results were converted into a tear strength retention percentage. A comparison of the curves for 6.5 kW/m^2 and 9.7 kW /m^2 exposures is depicted in ***Figure 3***, indicating that there was a reduction in tear strength for all samples after thermal treatment. With a 5-minute heat exposure to 6.5 kW/m^2, the tear strength retention of the warp and fill directions were 93.1% and 76.6%, respectively. The tear strength retention of the warp direction was 86.4% after heat exposure for 30 minutes and that of fill direction - 68.9%. It revealed that the tear strength retention of the warp direction was better than that of the fill direction.

For a 9.7 kW/m^2 exposure, however, it was observed that the tear strength retention of the outer shell fabric decreased sharply with the exposure time (***Figure 3***), the reason for which was that

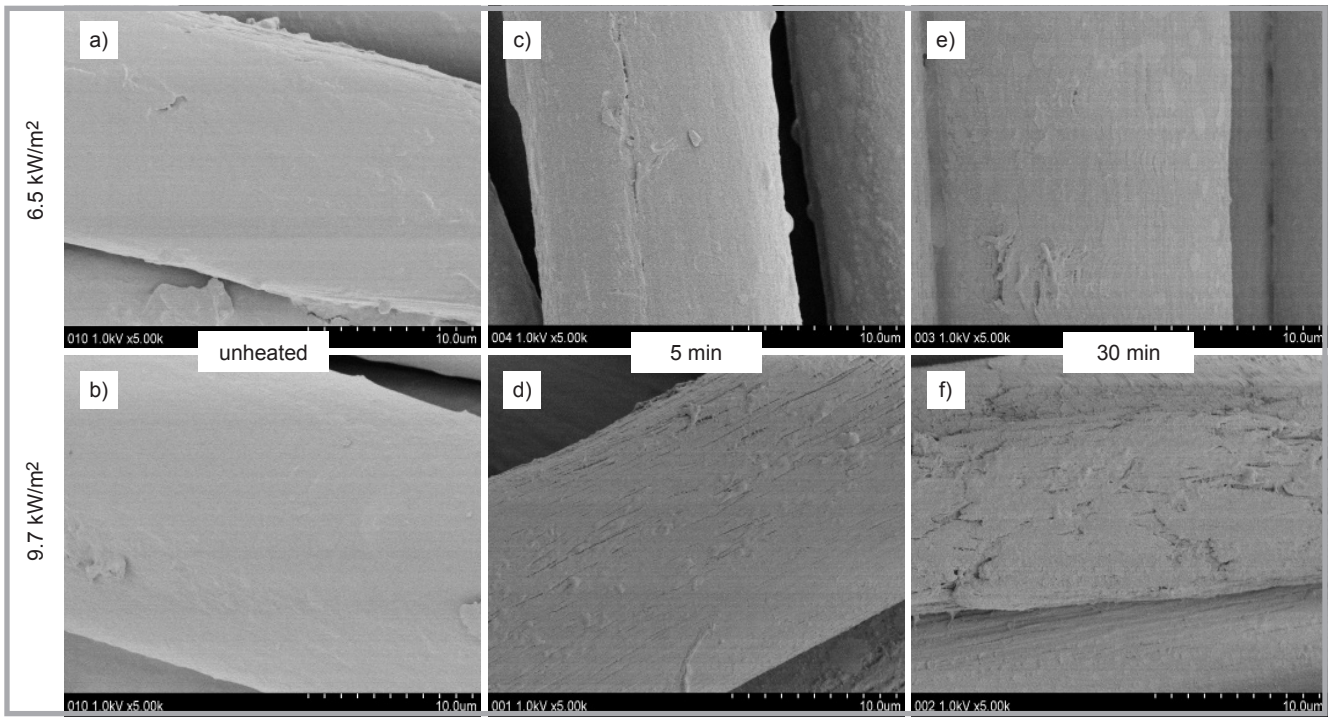

Figure 5. *SEM photographs of fabrics: before a), b); after c) 5 min, e) 30 min, exposure to 6.5 kW/m² and after d) 5 min, f) 30 min exposure to 9.7kW/m².*

the surface temperature (300 °C) was higher than the Tg of meta-aramid fibre (270 °C)[17]. For the first 5-minute exposure, the tear strength retention of the warp and fill directions dropped to 39.5% and 41.2%. Values of the tear strength were 50.2 N and 54.7 N, respectively, which were lower than the minimum value (100 N) required in NPFA1971 after a 5-minute exposure [15]. Furthermore after 30 minutes of exposure to 9.7 kW/m², the warp tear strength retained by the X-fiper® fabric was only 21% i.e. to a value of 27 N. In the case of the fill direction, the tear strength retained was 19% i.e. to a value of 25 N. Therefore it was dangerous for firemen with X-fiper® fabric to work for more than 5 minutes at the extreme condition of 300 °C. The results of variance analysis also showed that the heat intensity had a significant effect on the tear strength ($p < 0.05$).

Effect of heat exposure on TPP

The results of TPP ratings are displayed in ***Figure 4*** as a function of the exposure duration and heat intensity. Data for unheated samples are also included. It could be observed that there was a slight change in the level of heat protection for all samples after 6.5 kW/m² thermal treatment in this study, attributed to an increase in fabric thickness due to thermal shrinkage. It was thought that the fabric treated contained more air spaces, which increased the TPP rating. In addition, for the same duration of thermal exposure, the samples exposed to 9.7 kW/m² showed better thermal protection than those exposed to 6.5 kW/m². This was because the samples were partially charred after exposure to 9.7 kW/m² heat flux, which could, in general, have a positive influence on heat protection. However, as the charred material became brittle, it could no longer be used in practice.

Scanning electron microscopic analysis

The changes in the mechanical properties and thermal performance were probably caused by variations in the physical or chemical structure of the fibres. To obtain a better understanding of the modification caused by heat radiation, surface morphologies were evaluated by scanning electron microscope (SEM). ***Figure 5*** illustrates the surface characteristics of treated fabrics exposed to different heat fluxes. ***Figure 5.a - 5.b*** present micrographs depicting the surface characteristics of unheated X-fiper® fabric. ***Figure 5.c - 5.d*** illustrates the surface structures of fabrics which were exposed for 5 minutes. While unheated fabrics displayed a very smooth surface, the presence of fissures and grooves could be observed on the surface of fabric exposed to heat for 5 minutes. ***Figure 5.e - 5.f*** was from fabrics exposed for 30 minutes. The results showed that there was more severe surface damage to fabric exposed to 9.7 kW/m². ***Figure 5.f*** shows large quantities of extraneous deposits and fissures. These morphological changes were accompanied with a decrease in the tear and tensile strength of the specimens, which indicated a good correlation between these properties.

FTIR-Raman analysis

The revolution of mechanical properties and modification of morphology at macro or micro levels is often related to structural changes. FTIR-Raman spectral analysis was performed to investigate the effect of heat treatment on the structures. Absorbance bands for untreated X-fiper® fabric are shown in ***Figure 6*** (see page 78). The peaks attributed to the X-fiper® function were 3304, 1647, 1530, and 1298 cm^{-1}. The peak at 3304 cm^{-1} was the stretching vibration of the N-H bond. The peak at 1647 cm^{-1} was the stretching vibration of Amide I (amide C=O). The peak at 1530 cm^{-1} was the N-H deformation and C-N stretching coupled modes of Amide II. The peak at 1298 cm^{-1} was the aromatic C-N stretching vibration. These spectra were typical of those obtained from FTIR microscopy for meta-aramid fibre, and were consistent with results published in literature [18].

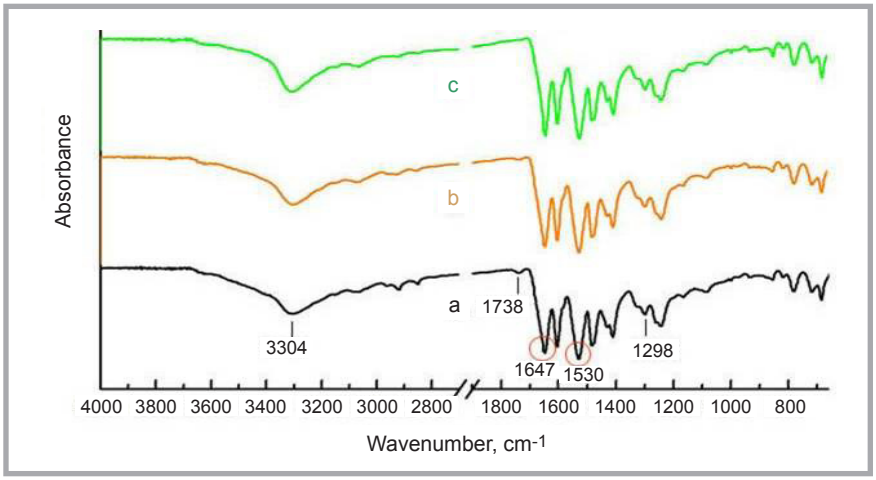

Figure 6. *FTIR-Raman spectra of X-fiper® fabric before and after heat treatment (30 min); a) unheated, b) 6.5 kW/m², and c) 9.7 kW/m².*

A comparison of the spectra of unheated and heated fabrics which were exposed to 6.5 kW/m² and 9.7 kW/m² for 30 minutes is also shown in ***Figure 6***. The peak intensity of heated X-fiper® fabric did not change because the decomposition temperature of meta-aramid fibre was higher than 300 °C. But Raman peaks of 1738 cm^{-1}, 2880 cm^{-1} and 2928 cm^{-1} disappeared gradually after exposure for 30 minutes. In this study these peaks were assigned to the water repellant coating, as the outer shell fabric was treated with it. Waterproof treatment was required for the outer shell fabric of firefighter protective clothing in NFPA 1971. After 30 minutes of 9.7 kW/m² heat exposure, these peaks were not observed due to the melting and peeling off of the water repellant coatings, suggesting that the coating was sufficiently degraded. This phenomenon was in accordance with the previous observation of deposits by SEM, indicating that these fabrics were in danger because of not complying with the waterproof requirement after exposure to 9.7 kW/m² heat flux for 30 minutes.

Conclusions

This study investigated the effects of heat treatment on the mechanical properties and thermal protective performance of X-fiper® fabric used in firefighter protective clothing. The results of variance analysis showed that the heat intensity had significant effects on the tensile strength, elongation at break, and tear strength in this study. Mechanical properties of the treated fabrics decreased greatly after exposure at 9.7 kW/m², which may be a threat to firefighters working more than 5 minutes at the extreme condition of 300 °C as the tear strength was lower than the minimum value required in NFPA1971 after 5-minute's exposure. Therefore the tear strength of X-fiper® fabric should be improved. TPP ratings of the samples, however, exhibited no considerable changes after heat treatment. The results observed by SEM and FTIR-Raman spectroscopy indicated a good correlation between these properties.

To ensure the safety of firefighters, it was necessary to evaluate the thermal protective performance as well as mechanical properties during the useful life of protective clothing. Meanwhile more work was required to improve the mechanical properties of X-fiper® fabric and study the effects of other environmental factors on performance.

Acknowledgement

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