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Surface Modification of Fabrics for Improved Flash-Fire Resistance Using Atmospheric Pressure

Plasma

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ABSTRACT

Improving flash fire resistance of otherwise flame resistant fabrics is a recognised challenge within the civil emergency and defence communities. Simulation of the flash fire condition using cone calorimetry has demonstrated the effectiveness of atmospheric plasma treatments in which either a functionalised nanoclay, a polysiloxane (poly(hexamethyldisiloxane)) or both are deposited on to plasma-activated fibre surfaces. Textile substrates comprised flame retardant (Proban®) cotton and a poly (meta-aramid) (Nomex®). Results show that the generated surface layer has a measurable effect on fabric ignition and burning characteristics when exposed in a cone calorimeter at heat flux levels up to 70 kW/m². Reductions in peak heat release (PHRR) values are observed for all substrates especially for argon/clay and argon/clay/polysiloxane, plasma-treated samples, with reductions of over 50% being observed for Proban® cotton and smaller reductions ($\leq 20\%$) for Nomex® fabrics. Both scanning electron microscopic and cone calorimetric studies show that these properties are retained after a simulated washing process including the argon/clay plasma-treated Proban® and Nomex® fabrics in which no potentially binding polysiloxane was present. This suggests that plasma-activated fibre surfaces in the presence of a functionalised clay enables relatively strong binding forces to be generated.

The results provide further evidence in addition to our earlier reported studies, that atmospheric plasma treatment of fabric surfaces in the presence of a nanoclay produces an inorganic coating that confers reduced flammability at the high heat fluxes used suggesting increased resistance to flash fire ignition.

Keywords: Atmospheric-pressure plasma, flash-fire resistance, nanoclay, polysiloxane, flame retardant fabrics, cotton, poly(meta-aramid)

INTRODUCTION

The majority of battlefield fire hazards are in the vicinity of a fire-level with an incident heat flux ranging from 20 to 100 kW/m². Typical so-called flash-fires generated from improvised explosive devices (IED) have heat fluxes of the order of 75-100 kW/m² incident upon the target for up to 3 s [1]. Military clothing with moderate levels of flame retardancy, while shielding the wearer from heat radiation, can ignite under such flash-fire conditions causing burn injuries even when the underlying garments have some level of flame retardancy. It is therefore necessary to provide flash-fire resistance to underlying garments including protective clothing for up to 3- 8s. Because of the hazards posed by thermoplastic fibre-containing fabrics in terms of shrinkage and melting when exposed to heat, such fabrics are never used in military applications. However, flame retardant varieties of non-thermoplastic fibres and blends are preferred. Generally, the flame retardancy of such fabrics is achieved by applying flame retardant finishes using textile finishing and coating methods to conventional fibres (eg cotton and wool) , the use of inherently flame retardant fibres and blends (eg flame retardant viscose and meta- and para-aramids) or a combination of both [2]. However, these flame retardant fabrics are often designed to pass conventional textile flammability tests where fabrics must resist ignition to small igniting sources applied in typically vertical orientations for times up to 12 seconds [3]. Unless these fabrics comprise fibres possessing extremely high levels of flame retardancy which are typified by the all-aromatic or carbonised groups of so-called high performance heat and fire resistant fibres [4], they cannot sustain the high fluxes associated with flash fires for more than a second or two. Consequently, if there were a means of increasing the underlying textile flame resistance to one commensurate with flash fire incidence, this would find considerable application where such risks are high. Currently, there is no technology or treatment available which can apply flash-fire-resistant behaviour to the surfaces of textiles without adding undue weight and cost to the underlying substrate such as a fire resistant coating, for example. The introduction of a heat reflective, fire resistant and preferably nanoceramic surface

treatment could offer such a solution and with this in mind, plasma treatment offers such possibility of selective modification of the surface while keeping the bulk characteristics unchanged. Furthermore, a given plasma treatment has the potential to be applied to a range of fabrics comprising different fibre types, yarn and fabric structures and levels of underlying or inherent flame retardancy. Plasma processes are of also of particular interest in textile finishing treatments in that they offer the means of fibre and fabric surface modification without the use of water and bulk chemicals consumed in conventional wet processes. Moreover, a plasma coating might be expected to be more durable than other thin surface coatings such as traditionally applied and sprayed-on finishes because the coating is chemically bonded to the treated fabric [5].

Basic objectives during the application of any textile surface treatment is the removal of the inherently loosely-bonded surface contamination followed by the introduction of stable functionalities that provide required nucleation and chemical bonding sites for the subsequent deposition of any outer layer or coating [6] and the advantage of a plasma treatment is that it offers the combination of surface cleaning, activation, deposition, grafting and cross-linking [5].

Plasma treatments of textiles are not new and have been reported and reviewed considerably elsewhere although the bulk of published work refers to the use of vacuum or low pressure plasma where interactive intermediates may have longer effective lifetimes thereby enabling higher levels of bonding to activated fibre surfaces [7, 8]. Attempts to improve the flame resistance of underlying fabrics by plasma treatments has recently been reviewed by Horrocks [9] and in the main reported research uses low pressure plasma which are effectively promoting graft polymerisation of potentially flame retarding comonomers on to the fibre substrate surfaces. While high levels of grafting are often achieved with values as high as almost 40 wt% being reported on cotton for example with accompanying high levels of flame retardancy, which as determined by limiting oxygen index yield values approaching 30 vol% [10-12], the resulting grafts have poor durability. This is most likely a consequence of both high levels of

ungrafted surface polymer being present coupled with an absence of ordered physical structure within the grafted surface layer.

Of particular relevance to this paper is the recently reported plasma deposition of silicon-based films to improve the flame retardancy of underlying polymer surfaces in which normal and nanocomposite polyamide 6 films were activated by a cold nitrogen plasma and then transferred to a reactor containing 1,1,3,3-tetramethyldisiloxane (TMDS) vapour in an oxygen carrier gas for 20 minutes [13]. This remote plasma-assisted polymerization is similar to that used by Tsafack et al. above [10-12] except that the monomer is in the vapour phase prior to polymeric deposition. Thermogravimetry showed that the thermal stability in air of deposited coatings as the increasingly oxygenated polysiloxane coating transformed to a silica-based structure at about 800°C. This gives the opportunity for a thermal barrier effect coupled with a moderate increase in flame retardancy of a coated polyamide 6 film and a surprising increase in the flame resistance of the nanocomposite polyamide 6 films and LOI >45 vol%. The presence of the nanoclay at 2 wt% appears to have synergized the formation of silica from the plasma-generated coating and the thermal barrier efficiency of the coated nanocomposite films was demonstrated by reductions peak heat release rates (PHRR) by cone calorimetry of up to 25%. A subsequent paper [14] demonstrated that on scaling up and enabling larger and more consistently coated samples to be produced that the film thicknesses, previously about 48µm obtained in the earlier and smaller reactor, reduced to only 1.5µm thickness and yet yielded film LOI values as high as 48 vol%. Again, reductions in PHRR values were observed and analysis of residues demonstrated that the coated nanocomposite film had transformed to a silica-like structure and it is this that creates the thermal shielding effect.

Such plasmas, however, do not lend themselves to commercial processing where open-widths of fabrics are typically processed at relatively high throughputs. More recently, atmospheric pressure plasmas which operate at standard atmospheric pressure (~ 100 kPa) have become available and not surprisingly are creating considerable interest in the textile finishing academic and commercial sectors [8].

The major disadvantage of atmospheric pressure plasma is that the properties of plasma are more difficult to control than low-pressure plasmas because an unknown quantity of air, mixed with the carrier and the treatment gases, may induce complex interactions, which may influence the effectiveness of the treatment [15]. While atmospheric pressure plasmas are capable of treating fabrics on one or both sides at a time, low pressure plasma still generates better penetration [16] although commercially less feasible.

This work extends our initial studies [17] which showed that the combination of microwave-generated, atmospheric-pressure cold plasma and functionalised nanoclay, in the presence and absence of a silicon-containing monomer, offers a means of conferring ceramic nanolayers on the surfaces of a range of textile materials to yield a thermal barrier to a high level of short term fire protection.

Hexamethyldisiloxane (HMDSO) was used because its plasma polymerisation has been widely reported in the literature [18-24] and that the resulting polyenr barrier and flame retardant properties are documented [25-29]. Furthermore, the chemical content and physical properties of resulting SiO_x films can be controlled by monitoring plasma process parameters including the selection of appropriate carrier gases. Plasma modified fabrics have been characterised for their surface morphology as well as simulated flash-fire resistance both before and after laboratory durability treatments.

EXPERIMENTAL

Materials

Fabrics: Commercial woven samples of Proban®-treated, flame retardant cotton (300 g/m²) and meta-aramid (Nomex®); 200 g/m²) fabrics were selected as textile substrates for nanoparticulate treatments using atmospheric plasma because of their wide usage in protective and military clothing applications.

Nanoclay: Based on our previous experience [30], a commercial clay Cloisite Na⁺ montmorillonite, Na-MMT (Southern clay Products, USA) was functionalised with a quaternary phosphonium salt (vinyl triphenyl phosphonium bromide). The salt was dissolved in distilled water and gently agitated to obtain a homogeneous 0.1 M solution, to which 50g of Na-MMT was added and stirred for 6 h at room temperature. The resulting mixture was filtered and washed repeatedly with hot water (60°C) until free of excess organic modifier (tested with AgNO₃ solution). The exchange process was repeated for another 48 h and the resulting clay was collected by filtration, washed, finally dried in a vacuum oven (40°C, 24 h) and then ground into a fine powder.

To remove any unexchanged or excess organic modifier and anion exchanged product (sodium bromide/chloride), the clay was first extracted with ethanol and then with tetrahydrofuran using routine soxhlet extraction procedures for 4 hours. The organo-modified clay was dried under high vacuum for 18 hours at 120°C.

Monomer: Hexamethyldisiloxane (HMDSO), C₆H₁₈OSi₂ of synthetic grade with 98% purity and specific gravity of 0.76 (supplied by Sigma-Aldrich, UK) was used as the monomer.

Gas: Argon gas (99.99% purity) with a flow rate of 20 l/min was used to initiate and generate the plasma at atmospheric pressure before introducing the monomer to the system. Ar gas was chosen due to its ease in ionisation at atmospheric pressure and moreover, for plasma polymerisation of HMDSO, studies [20] have shown that the degree of fragmentation is fairly high when Ar is used as a carrier gas.

Plasma equipment and process

Atmospheric pressure, non-equilibrium cold plasma experiments were carried out using the atmospheric plasma apparatus shown in Figure 1. It consists of a Surfatron Microwave cavity into which a plasma

containment quartz tube was placed. This was connected to the microwave generator operating at 2.45 GHz frequency with a power output of 60 W. The argon plasma was ignited using a copper wire and, once ignited, the plasma was self-balancing and had a very low reflected power (RP) component. For plasma treatments when HMDSO monomer was present, the argon gas was bubbled through HMDSO monomer which is in liquid form at room temperature under atmospheric pressure. 75 x 75 mm fabric samples were treated with atmospheric argon plasmas for 15 min, maintaining a constant distance of 10 mm between the tip of quartz tube containing plasma flame and the sample surface and the gas flow rate constant at 20 l/min.

A two-step plasma process was carried out to produce final functionalised nanoparticulate plasma coatings on to the fabric surface. The first step comprised a non-polymer-forming Ar plasma treatment for activation and roughening at the nano- and micro-levels of the fibre surfaces. This was followed by dusting the fabric sample with functionalised nanoclay and a subsequent cross-linking of the surface using Ar- plasma or Ar-HMDSO plasma.

This deposition of flame retardant coating on the surface of the fabric was monitored gravimetrically:

Degree of grafting (%) = $(w_g - w_o) \times 100 / w_o$, where, w_o and w_g are the weights of the fabric samples before and after surface treatments.

Washing Treatment

An accelerated laboratory-based washing procedure [31] was carried out to assess the durability of plasma treated fabrics. Samples were placed in a 1500 ml liquid solution, containing 0.5% w/v tribasic sodium phosphate and 0.1% v/v Triton X-100. Samples were kept in solution at 40 °C for 1 h with continuous stirring. Samples were removed from solution after 1 h, rinsed with distilled water and allowed to dry overnight at room temperature.

Characterisation

Microscopy

The surface characteristics of plasma-treated cotton fabrics were studied using scanning electron (Cambridge Stereoscan 200 SEM) and optical microscopy (Nikon Labophot 2 optical microscope with image capture by a JVC TK-C1381 colour video camera) where appropriate.

Assessment of Flash-fire resistance

To assess the flash-fire resistance of textile materials, the ASTM F 1930 requires exposure of fully dressed manikin to the heat flux of 84 kW/m² for 3s. To simulate flash-fire conditions, a cone calorimeter (Fire Testing Technology Ltd., UK) was used to assess ignition resistance of plasma treated fabrics. 75 x75 mm samples were exposed to incident heat flux and auto-ignition times were recorded for all the samples which were tested in triplicate. In these experiments the spark ignition was not switched in accordance with the ISO 5660 standard since in these studies, we consider that ignition should be initiated by the effects of heat flux alone. According to ISO 5660 standard, the spark ignition usually ignites volatile species from the sample and is representative of forced ignition scenario. Significant burning parameters measured were time-to-ignition (TTI), peak heat release rate (PHRR) and the time at which PHRR occurs (TTP). Cone calorimeter heater fluxes up to 70 kW/m² were used since initial experiments on Nomex® fabrics before plasma treatment required a heat flux of at least 60 kW/m² to enable them to ignite before plasma treatment [17]. After plasma treatment in the presence of HMDSO, clay or both agents, fabrics became non-ignitable. However, while Proban®-treated cotton fabrics were still reported to ignite at heat fluxes as low as 35 kW/m² with and without plasma treatment, in this work the use of 70 kW/m² heat flux enables both fabric behaviours to be examined since untreated and treated Nomex® fabrics ignite reproducibly after plasma treatments.

RESULTS AND DISCUSSION

Percent weight changes due to plasma treatments

Average of percentage weight changes for different plasma treatments, before and after washing treatment are given in Table 1. Fabrics exposed to Ar-plasma for up to 15 min lose mass in the range of 0.53 to 0.86 wt%, attributed to ablation of material. Plasma treated samples subjected to washing treatment show further weight losses in the range of 1.5- 9 wt%.

Results in Table 1 show small weight gains for all fabrics samples which although not substantial, indicate increase in deposition of siloxane polymer and/or clay as high as about 3% for Proban®-treated cotton and 5 wt% for the Nomex® fabric after adjusting for initial weight losses following respective argon-only treatments. It is well known that during plasma polymerisation or plasma enhanced chemical vapour deposition (PECVD) processes, a competition between polymer formation (deposition of material) and ablation (removal of material) occurs [16]. Smaller weight gains in case of Ar-HMDSO treated fabrics could be due to greater rate of ablation than deposition of the HMDSO polymer.

Moreover, as soon as a plasma is created, the gas phase is no longer the vapour of original monomer, but becomes a complex mixture of the original monomer, ionised and/or excited species of the monomer and fragments thereof and of ablated species from the substrate. Further percentage weight losses due to simulated washing of Ar-HMDSO-treated fabrics suggest that the polymer which is not chemically adhered to the fabric surface is lost during the washing procedure. Percentage weight losses due to washing procedure are very similar (2-2.5 wt%) for all the fabrics studied under this plasma condition. Nanoclay-coated (Ar-Clay-Ar) fabric samples show slight increases in weight which appear not to be simply proportional to the amount of nanoclay added to the sample. It is probable that the excess clay that was not physicochemically bonded to the fabric surface was physically removed by the plasma flame. Thus only a fraction of the initial nanoclay on the fabric surface after plasma treatment is

assumed to remain and be physicochemically bonded to the fabric surface. Plasma polymerisation of nanoclay-coated Proban® and aramid fabrics (Ar-Clay-Ar-HMDSO samples) show slightly higher increases in weight compared with respective Ar-clay-Ar-treated samples. Percentage weight loss of Ar-Clay-Ar- and Ar-Clay-Ar-HMDSO-coated samples after washing treatment are similarly less for Proban® - treated cotton as compared to Nomex® suggesting poorer clay/polysiloxane adhesion to the meta-aramid surfaces.

Surface Morphology

Figure 2 shows SEM micrographs of Proban®-treated cotton and Nomex fabrics exposed to Ar-plasma for 15 min and the effects of surface ablation are clearly seen.

Figures 3(a) and 3(b) shows the thickness of surface layer developed through columnar growth of the deposited polymerised HMDSO on Proban® - treated cotton and Nomex fabrics respectively.

Examination of SEM micrographs in Figures 3(c) and 3(d) for washed Ar-HMDSO-treated Proban® and Nomex® samples undoubtedly show evidence of the presence of most probably retained HMDSO polymer.

Presence of nanoclay on the surface of modified fabrics before and after washing is clearly seen in Figures 4(a)-(d) for Ar-Clay-Ar samples. The amounts of clay remaining deposited on Nomex® fabric (Figure 4(d)) appear to be higher compared to Proban®-treated (Figure 4(c)). A similar behaviour is seen for the Ar-Clay-Ar-HMDSO-treated samples in Figures 5(a)-(d) with significant loss of clay occurring after washing. In the case of Ar-Clay-Ar samples, it is probable that the reduced numbers of clay particles after washing both fabrics are physicochemically adhered to fibre surfaces as a consequence of plasma excitation. However, the Ar-Clay-Ar-HMDSO treated fabrics (Figures 5(c) and (d)) appear to show little evidence of polysiloxane suggesting that most is lost after simulated washing treatment although mass losses are similar for these and respective washed Ar-Clay-Ar-treated samples. This unexpected result could be due to the fact that the polysiloxane layer is formed on the clay particles as

opposed to fibre surface and so polymerised HMDSO is not chemically attached directly to the fibre surface; hence it is easily washed off.

Flash-fire resistance of modified fabrics

For Proban®-treated cotton samples, it can be seen from Figures 6(a) and (b) that when exposed to 70 kW/m² heat flux, the samples ignite almost instantaneously and burn for no longer than 15-20s. This fast ignition is partly a consequence of the reduced decomposition temperature with respect to pure cotton that the organophosphorus-based Proban® chemistry confers and hence volatilisation occurs sooner. However, under the same heat flux conditions, the heat flux of this fabric is less than that of pure cotton as reported earlier [17] thereby demonstrating that although ignition may be fast, the flame retardant effect is still present. Comparison of PHRR data in Table 2 shows the values for Proban® cotton to be similar to those for Nomex® fabrics. Because the ignition of Proban® cotton is so fast, timing HRR output accurately from t=0 s is impossible to achieve using the current cone calorimeter arrangement which has a time resolution of 1 s. However, with this proviso, it is evident that no significant changes in ignition times are apparent for all the Proban®-treated cotton samples tested (see Table 2) and under 70 kW/m² heat flux, they ignite at about 3s giving peak heat release rates of 113 kW/m² at 4s. TTI values increase slightly to as high as 7s following plasma treatment although PHRR values for Ar- (110 kW/m²) and Ar-HMDSO (112 kW/m²)- treated samples are also unchanged while TTP values have slightly increased in case of Ar-HMDSO Proban®-treated cotton (TTP= 8s). Thus it may be concluded that the effects of Ar- and Ar-HMDSO plasma on Proban®-treated cotton samples are not as clearly evident in this study as was the case in our previous work at 35 kW/m² [17]. Inclusion of nanoclay in the surface modification of Proban®-treated cotton certainly reduces the PHRR value for Ar-Clay-Ar treated sample to 52 kW/m², a factor of about 50%, however. Of significance is the observation that the Ar-Clay-Ar-HMDSO- treated sample does not ignite at all and the low intensity heat release curve in

Figure 6(a) reflects this. Thus, at very high heat fluxes, it is possible that the nanoclay presence is essential to enhance flame retardant properties of already flame retarded cotton. Our earlier reported results [17] undertaken at 35 kW/m^2 showed that within the error of cone calorimetric data, a significant reduction in PHRR of about 20% was observed for this same Ar-Clay-HMDSO-treated sample although no shifts in TTI were observed and only the Ar-Clay-treated sample showed a significant increase in TTP. There is clear evidence here, therefore, that the nanoclay/polysiloxane treatments may in fact be more effective under higher heat fluxes than lower ones.

Comparing the effects of simulated washing on surface treatments for Proban®-treated cotton in Table 2, it can be noted that although TTI values are essentially unaltered in all the samples, there are noticeable changes in PHRR of the washed samples. That for Ar- treated sample after washing has slightly increased to 131 kW/m^2 when compared to the value of 110 kW/m^2 for the unwashed Ar-treated sample, although within the accepted $\pm 10\%$ error associated with cone calorimetric measurements, these values could be considered to be the same. However, the PHRR value (112 kW/m^2) for Ar-HMDSO- treated Proban®-treated cotton shows a significant reduction (95 kW/m^2) after washing. This could arise from pick up of sodium phosphate species from the washing treatment and similar results with respect to slight increases in limiting oxygen index have been reported following washing of normal Proban® cotton fabrics in tripolyphosphate-based detergents [32]. Moreover, the SEM micrographs in Figure 3 suggest that the polysiloxane deposits appear as a coherent coating on the surface of Proban®-treated cotton fibres after washing. The nanoclay-containing surface treatments show dissimilar trends after washing treatment in that the Ar-Clay-Ar Proban® cotton now does not ignite and appears to be more fire resistant whereas the Ar-Clay-Ar-HMDSO sample ignites at 8s giving PHRR of 107 kW/m^2 . The Ar-Clay-Ar samples, on the other hand, show presence of clay even after the washing treatment in Figures 4(a) and (c), hence providing evidence for the flame retardant effect. Figures 5(a) and (c) for Ar-Clay-Ar-HMDSO samples respectively before and after washing show less distinct clay presence although surface polysiloxane is also apparent.

The full heat release curves for Nomex® fabrics at 70 kW/m² are shown in Figures 7(a) and (b). When exposed to 70 kW/m² heat flux, untreated Nomex® fabric ignites at 9s giving PHRR = 119 kW/m² at 14s. Ar-plasma treated Nomex® fabric ignited at 8s, giving a similar peak at 10s also with PHRR=119 kW/m². The Ar-HMDSO plasma treatment of Nomex® fabric does not show significant reduction in PHRR (113 kW/m²) and this is in agreement with the flame retardant Proban® cotton in that once ignited, the polysiloxane layer alone does not provide any thermal barrier effect. Figure 7(a) and Table 2 suggest that clay alone (Ar-Clay-Ar samples) shows a slightly suppressed HRR curve with PHRR = 109 kW/m² and the Ar-Clay-Ar HMDSO sample HRR curve intensity is further reduced (PHRR = 99 kW/m²). These results are similar to those previously reported [17] which show that after Ar-clay-Ar and Ar-Clay-Ar HMDSO plasma treatments, Nomex® fabric which normally ignites under 60 kW/m² no longer ignites. In fact, in this same work, the presence of polysiloxane alone rendered the Nomex ignition resistant.

After subjecting samples to a simulated wash, Figure 7(b) and Table 2 shows that within error, very little changes occur to the overall relative sample behaviours except that the suggested reductions in PHRR values following argon plasma treatment in the presence of HMDSO, clay or both are further evident. These results concur with the SEM micrographs for Ar-HMDSO samples in Figures 3(b) and (d), for Ar-Clay-Ar samples in 4(b) and (d) and for Ar-Clay-Ar-HMDSO samples in Figures 5(b) and (d) which show the presence of relevant surface deposits after washing.

CONCLUSIONS

The application of a surface layer comprising a polysiloxane, clay or combination of the two, has a significant effect upon the burning characteristics of various already flame retardant textile substrates, such as flame retarded (Proban®) –treated cotton and meta-aramid (Nomex®) at higher (70 kW/m²) heat flux values. There is a tendency for times-to-ignition and times-to-peak to increase although the effect is small except for Ar-Clay-Ar-HMDSO-treated samples . However, reductions in PHRR values

are evident for both substrates especially for Ar-Clay-Ar- and Ar-Clay-Ar-HMDSO-plasma-treated samples with reductions of over 50% being observed for Proban® cotton and smaller reductions (\leq 20%) for similarly treated Nomex® fabrics. Both scanning electron microscope and cone calorimetric studies show that these properties are retained after a simulated washing process indicating that the surface plasma coatings have achieved some level of durability. Although this durability is less convincing on Proban® cotton, for both substrates even the Ar-Clay-Ar-treated fabrics demonstrate good levels of durability in terms of retention of reduced burning behaviour. This suggests that plasma-activated fibre surfaces in the presence of a functionalised clay enable relatively strong binding forces to be generated.

In conclusion, this paper provides further evidence in addition to our earlier reported studies, that plasma treatment of fabric surfaces in the presence of a nanoclay may produce an inorganic or even nanoceramic coating having reduced flammability at the high heat fluxes used, which could be indicative of increased resistance to flash fire ignition. Clearly further work is required which will include use of clays with functionalities that improve fibre surface bonding, other silicon-containing polymers and changed plasma atmosphere conditions. Furthermore, experimental scaling up will be essential to enable larger scale trials to be undertaken.

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Table 1: Percentage weight changes in plasma-modified samples

Plasma treatment	Proban® cotton		Nomex® aramid	
	U	W	U	W
Ar- : Fabric exposed to Ar-plasma for 15 min	-0.53	-0.99	- 0.86	- 2.6
Ar-HMDSO- : Fabric exposed to Ar-HMDSO-plasma for 15 min	+ 1.0	-2.0	+ 1.5	- 2.5
Ar-Clay-Ar- : Fabric exposed to Ar-plasma for 15 min followed by dusting the fabric surface with functionalised clay and subsequent exposure to Ar-plasma for 15 min.	+ 2.0	- 2.5	+4.3	-4.0
Ar-Clay-Ar-HMDSO- : Fabric exposed to Ar-plasma for 15 min followed by dusting the fabric surface with functionalised clay and subsequent exposure to ArHMDSO- plasma for 15 min.	+ 3.0	- 1.0	+ 5.1	-4.0

Note: U denotes unwashed, W denotes after washing

Table 2: Cone calorimetry data for Proban® cotton and Nomex® fabrics.

Samples	Cone Calorimetric data					
	Before washing			After washing		
	TTL, s	TTP, s	PHRR, kW/m ²	TTL, s	TTP, s	PHRR, kW/m ²
Proban® –treated cotton (70 kW/m²)						
Untreated Proban® –treated cotton	3	4	113	3	4	100
Ar- Proban® –treated cotton	4	4	110	4	4	131
Ar- HMDSO Proban® –treated cotton	5	8	112	5	6	95
Ar-Clay-Ar Proban® –treated cotton	4	4	52	NI	*	*
Ar-Clay-Ar-HMDSO Proban® –treated cotton	7	8	*	7	11	107
Nomex® (70 kW/m²)						
Untreated Nomex®	9	12	119	9	12	111
Ar- Nomex®	8	10	119	10	10	114
Ar-HMDSO Nomex®	9	12	113	11	12	107
Ar-Clay-Ar Nomex®	9	12	109	11	12	107
Ar-Clay-Ar-HMDSO Nomex®	12	16	99	12	14	80
Note: NI = no ignition, * no data recorded						

Figures

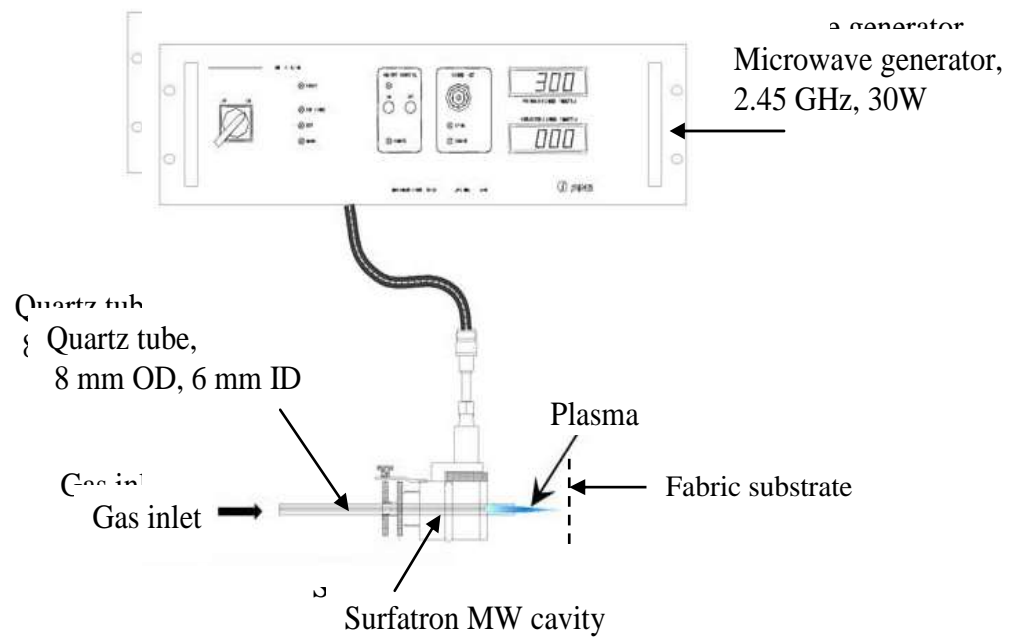


Figure 1: Experimental set-up for atmospheric-pressure cold plasma deposition.

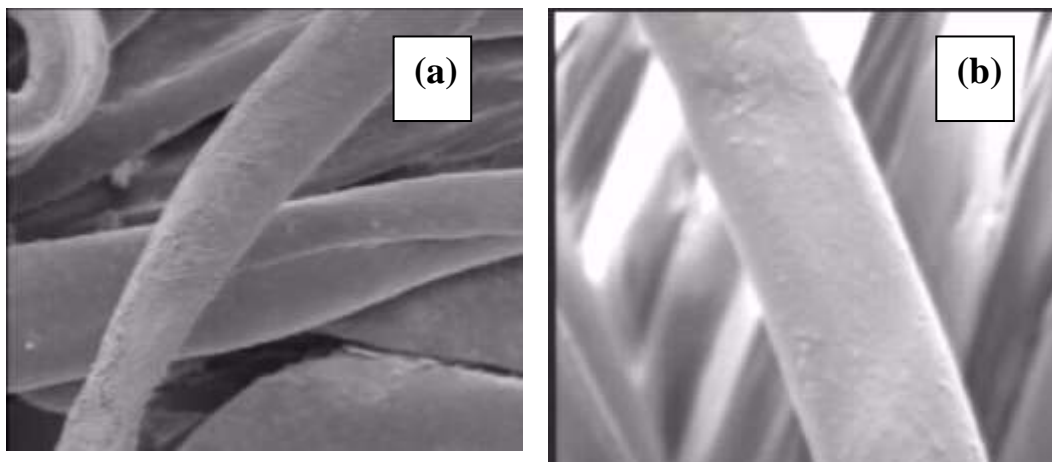


Figure 2: Argon (Ar) plasma- treated: (a) Proban® treated cotton and (b) Nomex® samples before and after washing

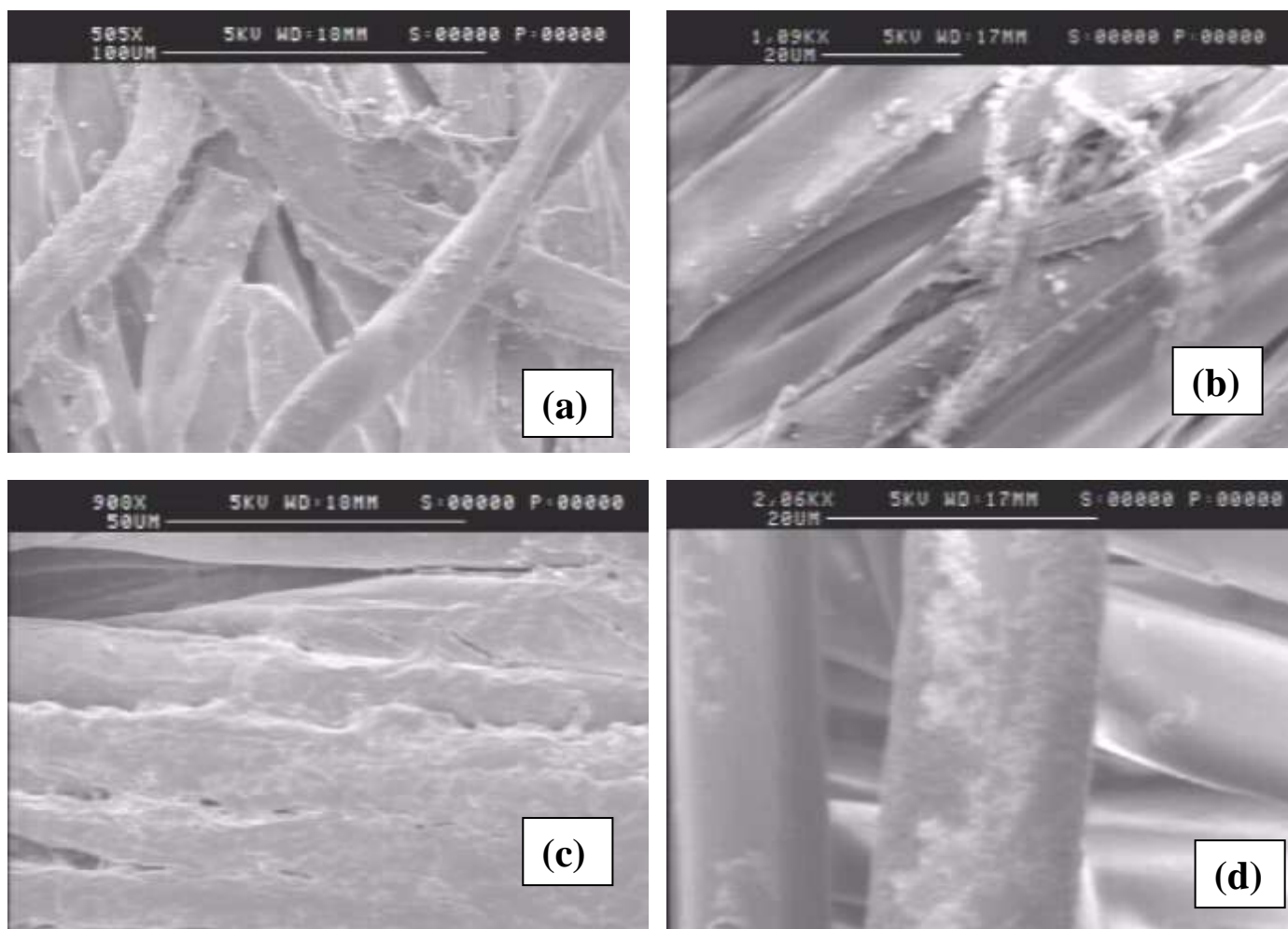
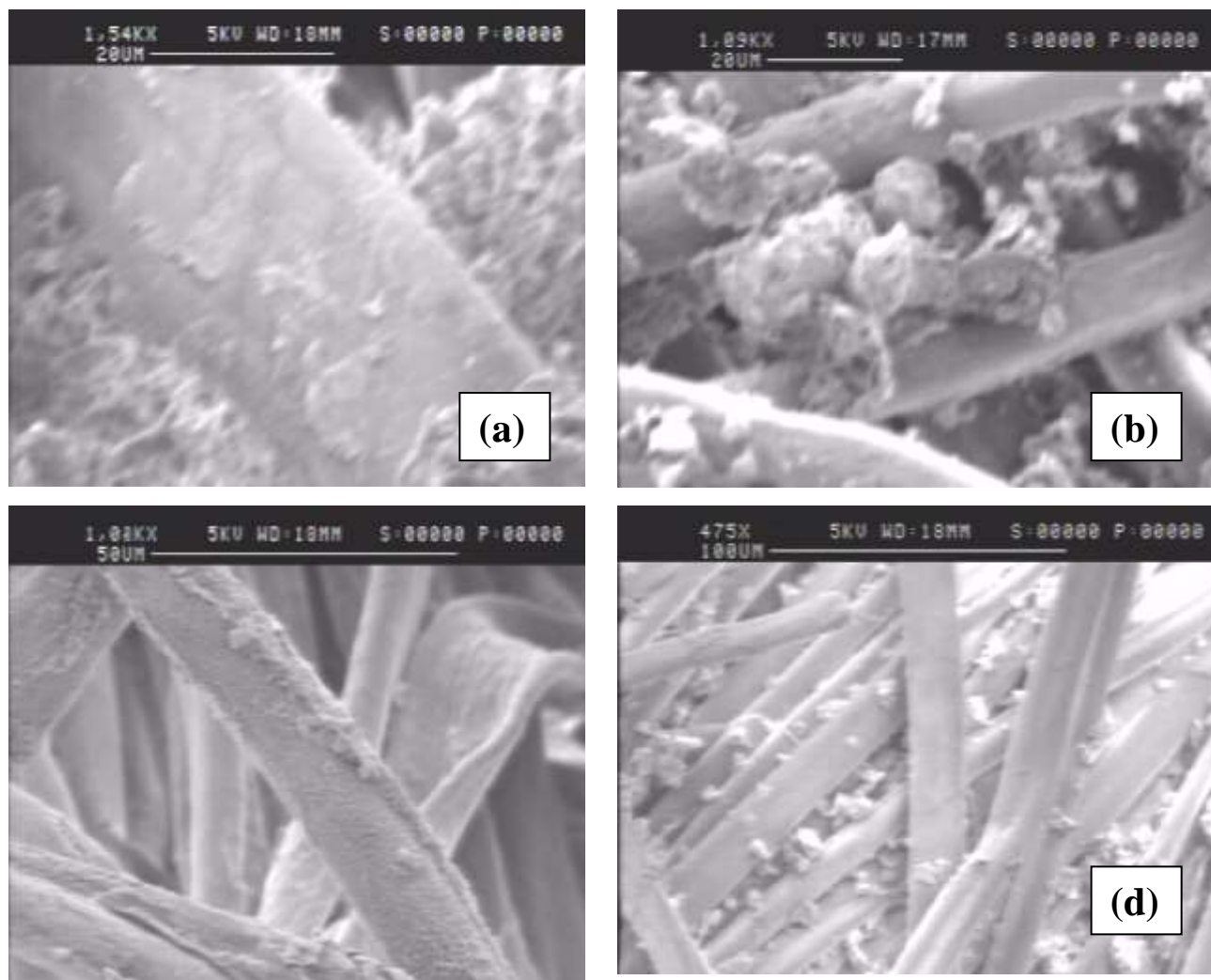


Figure 3 : Ar-HMDSO treated samples before and after washing (a) Ar-HMDSO-Proban® cotton(unwashed), (b) Ar-HMDSO- Nomex® (unwashed), (c) Ar-HMDSO- Proban® cotton (washed) and (d) Ar-HMDSO- Nomex® (washed).

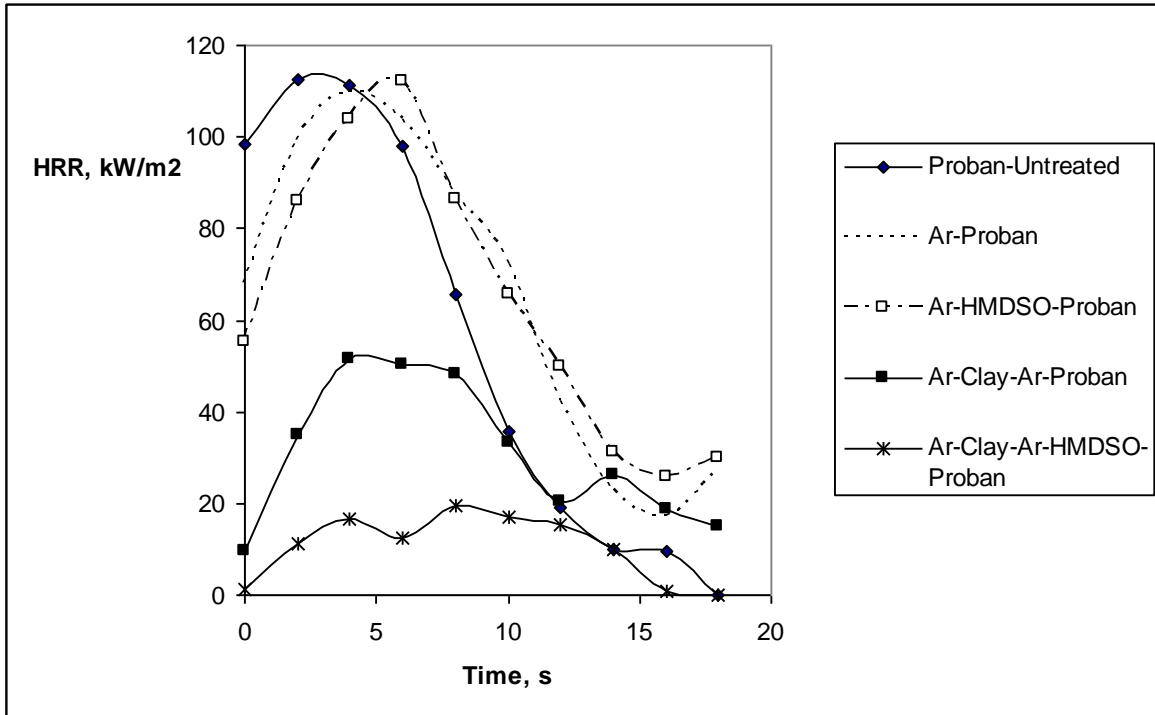


Figure 4: Ar-Clay-Ar treated samples before and after washing (a) Ar-Clay-Ar-Proban® cotton (unwashed), (b) Ar-Clay-Ar-Nomex® (unwashed), (c) Ar-Clay-Ar-Proban® cotton (washed) and (d) Ar-Clay-Ar-Nomex® (washed).

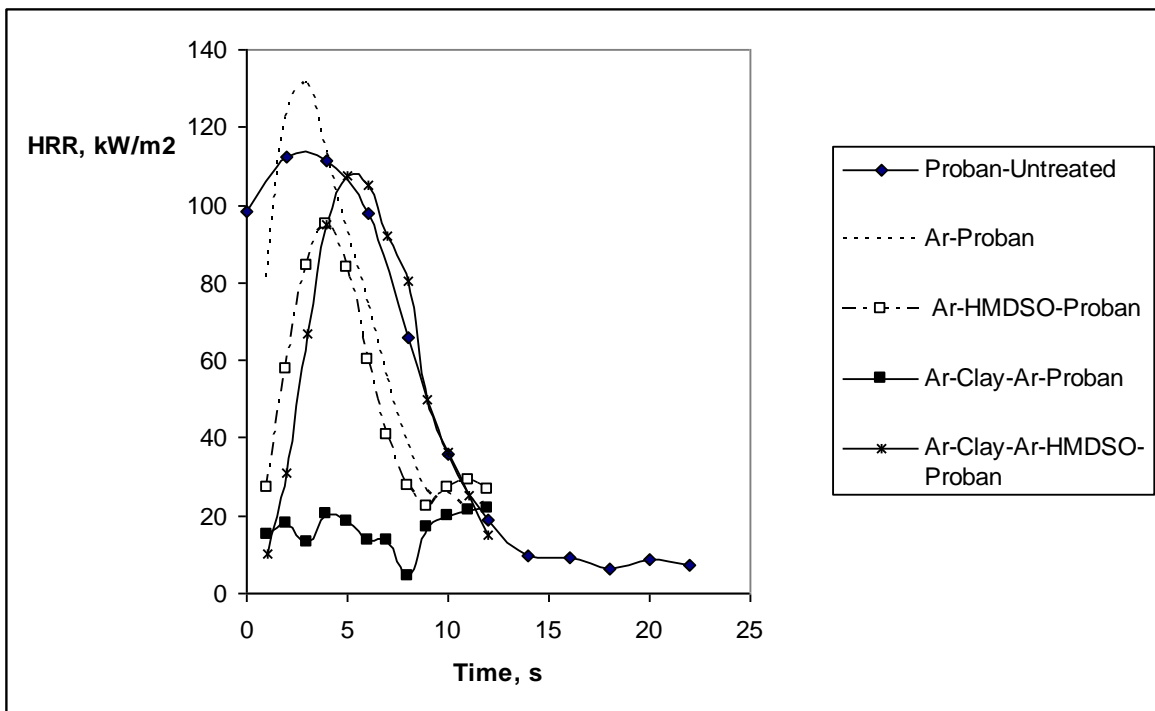


(c)

Figure 5: Ar-Clay-Ar-HMDSO treated samples before and after washing (a) Ar-Clay-Ar-HMDSO-Proban® cotton (unwashed), (b) Ar-Clay-Ar-HMDSO-Nomex® (unwashed), (c) Ar-Clay-Ar-HMDSO-Proban® cotton (washed) and (d) Ar-Clay-Ar-HMDSO-Nomex® (washed).

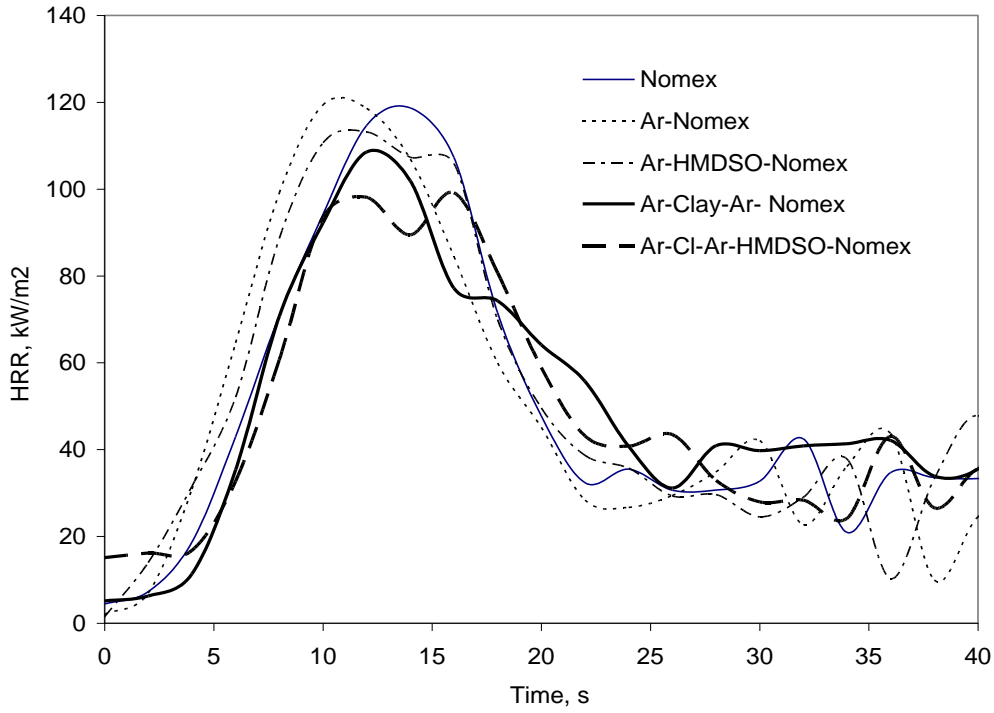


(a) Unwashed

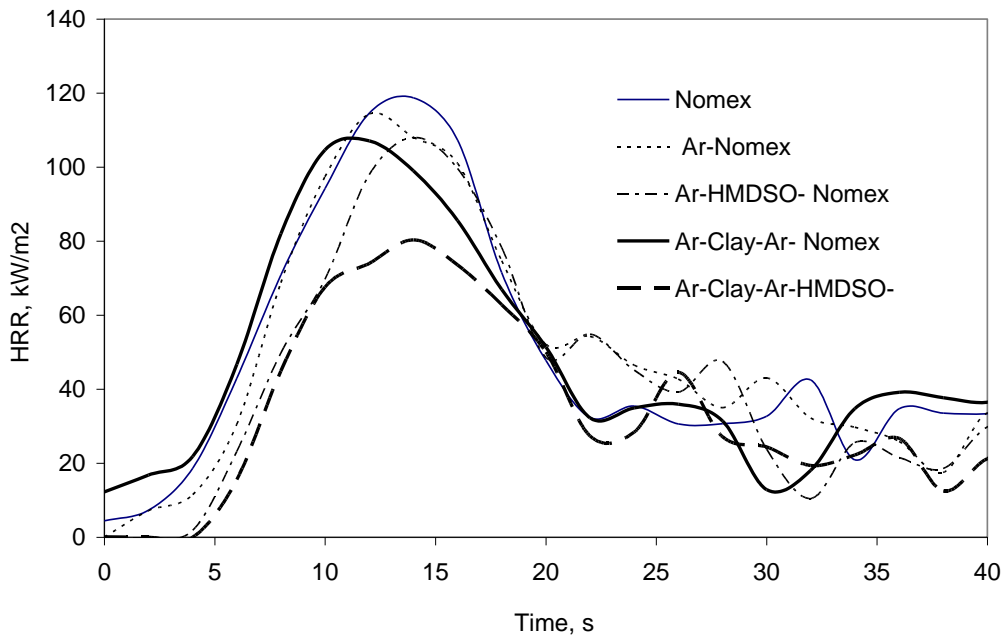


(b) Simulated washed

Figure 6: Heat release rate curves for plasma-treated Proban®- treated cotton fabrics: (a) before and (b) after washing treatment at 70 kW/m² heat flux in cone calorimeter



(a) Unwashed



(b) Simulated washed

Figure 7: Heat release rate curves for plasma-treated Nomex cotton fabrics: (a) before and (b) after washing treatment at 70 kW/m^2 heat flux in cone calorimeter.