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REVIEW

Recent Developments and Needs in Materials Used for Personal Protective Equipment and Their Testing

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The field of personal protective equipment (PPE) has led to several high technology innovations. Indeed, improved protection against the various possible encountered risks is looked for, in particular at the workplace. This has generated the development of new materials and new manufacturing technologies, as well as the introduction of new applications for existing ones. However, the remaining challenges are numerous. This paper presents some of the new technologies introduced in the field of protective clothing against heat and flames, mechanical risks and chemical aggressors. It also describes new challenges that are currently worked on, in particular the effect of service aging and the need for testing methods that reproduce real-use conditions. Finally, it discusses various existing and potential applications of nanomaterials and smart textiles for PPE.

personal protective equipment protective clothing protective gloves heat resistance mechanical risks protection against chemicals test methods aging

1. INTRODUCTION

The U.S. market for advanced personal protective equipment (PPE) was valued in 2005 at ~2 300 million USD per year [1]. It is expected to reach 3 350 million USD by 2010, with an average annual growth rate (AAGR) of 7.9%. Within that, the textile industry takes a large share, e.g., with the advanced fire protective garments, expected to increase to 628 million USD by 2010, with an AAGR of 12%. In Western Europe, protective clothing and gloves account for ~60% of the total PPE market [2]. Such a vitality of the protective clothing market also translates into the development of new materials and technologies. In addition, the PPE sector has seen the progressive introduction of nanomaterials, taking advantage of their outstanding properties.

PPE includes a wide range of items designed for providing added protection to the human body. It should always come as the last resource, i.e., after engineering, work practice and administrative risk control strategies have been implemented to the greatest extent possible [3, 4]. PPE can be divided into six major categories [3]: eye and face, head, foot and leg, hand and arm, body, and hearing. The types of hazards they can help reduce exposure to are numerous: mechanical, chemical, biological, thermal, electrical, noise, radiations, etc. In addition, most situations generally involve a combination of several types of hazards, thus requiring a multirisk approach [5]. In the absence of appropriate protection, this may eventually lead to the need for superimposed layers of protective clothing, each corresponding to a certain type of risk, with all the drawbacks this implies in terms of loss of dexterity and motion freedom, among others [6]. Indeed, in addition to protection requirements, functionality and comfort must be carefully considered during PPE selection since it

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controls the impact of PPE on task performance and even the wearer's health. Unsatisfactory PPE functionality and comfort may also lead people to decide not to wear necessary PPE.

This paper presents some examples of recent developments and needs in PPE, and in particular in protective clothing, to illustrate that the real conditions in which this equipment will be used must be taken into consideration during the design process. It covers the aspects of materials, characterization of properties and aging behavior. The discussion on materials focuses on three types of risks, heat and flame, mechanical, and chemical, where large effort is currently deployed. It also describes some potential promising applications of nanotechnologies and smart textiles to PPE. In terms of test methods, four areas have been selected: the measurement of the resistance to mechanical risks, chemical aggressors, heat and flame as well as of functionality factors. They are examples showing that results of standard tests do not always correspond to real-use conditions of PPE. Finally, the phenomenon of material aging is appearing more and more as a growing source of concern for PPE, in particular in the case of new synthetic fibers. As a consequence, PPE performance may be reduced below requirements during service life without the user being able to notice it.

2. MATERIALS FOR PROTECTION AGAINST HEAT AND FLAME

Original firefighters' protective clothing against heat and flame used natural materials such as cotton, wool and leather, with possible treatment with fireretardant agents [7]. Over the last 40 years, new synthetic fibers with better thermal, chemical and mechanical resistance have been developed [8]. Their application to firefighters' protective clothing was driven by the improved protection they offer as well as the reduction in physical constraints associated with wearing the bulky suits. Indeed, the thermal burden suffered by firefighters in operation is a major concern. It has been associated with the occurrence of heat strokes, the number one cause of death among firefighters [9]. The current firefighters' protective clothing technology is based on six synthetic fibers, Nomex® (meta-aramide, DuPont), Kevlar® (para-aramide, DuPont), PBI (polybenzimidazole, Performance Products), Basofil® (melamine, Basofil LLC), Zylon® (polyphenylene benzobisoxazole, Toyobo) and PI (polyimide, Inspec Fibres GmbH). Polyurethane and polytetrafluoroethylene (PTFE) are used as the moisture barrier semipermeable coating. In terms of protective gloves, major issues are related to questions of dexterity, comfort and grip in the various environmental conditions encountered by firefighters [10].

New materials and designs have been developed for heat protective clothing. For example, improved thermal insulation can be provided by nonwovens made with thin hollowed fibers[1] and can be made thermo-adaptive with two-way shape memory alloys like nickel-titanium [11]. Better thermoregulation inside the garment is sought with phase change materials [12], either encapsulated [13] or incorporated in a matrix [14]. Other solutions use external power, e.g., for liquid coolant circulation [15] or with Peltier cells embedded in the textile [16]. New-generation waterproof and breathable membranes include W.L. Gore & Associates' Crosstech™ membrane[2], which combines microporous expanded PTFE dispersed in a monolithic element, and Stedfast's Stedair® membrane[3], which is based on laminated layers of various hydrophilic and oleophobic properties. Temperature-dependant permeability to moisture could even be provided by polyurethane-based shape memory polymer [17]. Better comfort is also provided by pulling humidity and sweat away from the surface of the skin, either with hydrophilic linings [18] or by the use of channeled cross-section fibers with reinforced wicking properties[1].

New requirements included in the 2007 version of the NFPA 1971 standards, even if

[1] http://www.thorlo.com
[2] http://www.crosstech.com
[3] http://www.stedfast.com

still optional, deal with the protection against chemical, biological, radiological and nuclear (CBRN) terrorist agents [19]. Indeed, the events of September 11 have created awareness of new types of threats that first responders, among them firefighters, may be subjected to [20]. As a consequence, two projects, funded by the U.S. Department of Homeland Security, have been initiated for the development of firefighter turnout gear providing CBRN protection [21]. In Project HEROES, the traditional moisture barrier is replaced with a selectively permeable membrane and special attention is given to interfaces between components [22]. For its part, the CB.Ready project team [23], led by the Textile Protection and Comfort Center (North Carolina State University), is working with DuPont on the development of a new moisture barrier as well as a new thermal barrier.

3. MATERIALS FOR PROTECTION AGAINST MECHANICAL RISKS

In terms of resistance to cutting, new materials more resistant than Kevlar® have been developed. These high modulus fibers (Spectra® produced by Honeywell (USA) [24] and Dyneema® by DSM (The Netherlands) [25]) are based on ultra high molecular weight polyethylene combined with patented gel spinning processes. They offer a specific strength 40% higher than that of aramid fibers and a large resistance to various aging agents.

With a technology called SuperFabric® based on tiny hard guard plates embedded in a base fabric, HDM (USA) is offering engineering solutions for high resistance to cutting, abrasion and puncture while retaining a good level of flexibility [26]. The possibility of layering is even claimed to produce some level of resistance to puncture with medical needles. Indeed, the problem of resistance of protective gloves to puncture with needles is currently a major issue for several professional sectors such as law enforcement officers. In addition, it is not accounted for by current standards on protection, whose rounded probes are highly different from medical needles as illustrated in Figure 1 [27].

For resistance to impact, a new technology based on intelligent molecules has been developed by d3o™ Lab[4] [28]. It has several potential applications in protective clothing, e.g., for bulletproof vests. At low rate of movement, the molecules simply flow past each other. If subjected to an impact, they instantly lock together, and then unlock when the impact is over. Other new energy absorbing technologies include tridimensional mesh knitted fabrics and deformable pouches filled with elastic capsules immersed in a liquid or grease matrix [29].

4. MATERIALS FOR PROTECTION AGAINST CHEMICALS

The current technology for protection against chemicals, liquids and gases, is based on two

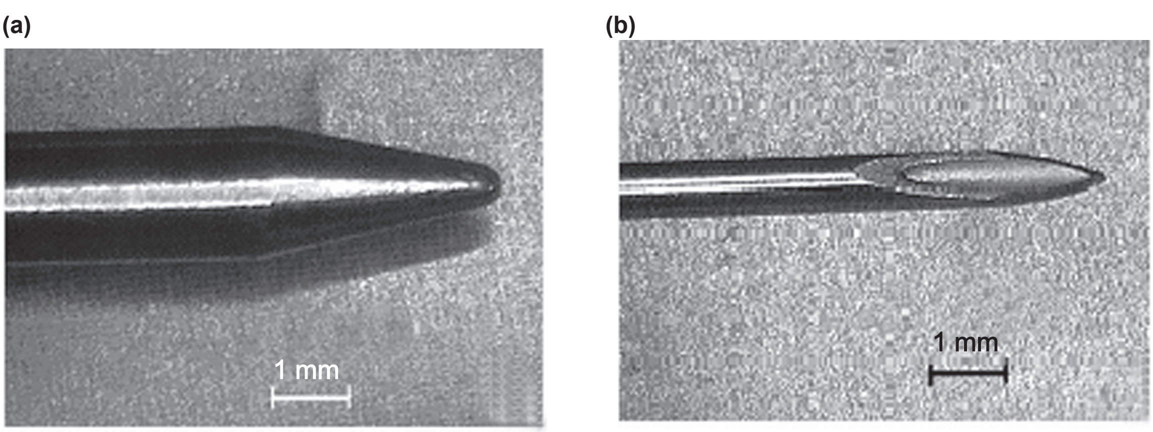

Figure 1. Pictures of (a) the ASTM F1342-05 puncture probe A and (b) a medical needle.

[4] http://www.d3olab.com

approaches [30]. In one of them a full barrier protection is ensured by impermeable film-laminated fabrics, e.g., in fully encapsulated HAZMAT suits. The less constraining solution consists in using semipermeable adsorptive carbon liners that allow vapor and air exchange while blocking liquids. New developments in this area include, e.g., activated carbon sprayed on polyethylene nonwovens for heat stress reduction [31]. Sol-gel derived carbon xerogel coated on cotton and plasma-treated polypropylene fabrics are also proposed for protection against volatile organic compounds [32].

Three new orientations of research for protective clothing against chemicals are currently being investigated [30]: selective blocking of toxic chemicals, chemical destruction of toxic materials that contact the fabric and detection of hazardous agents. Selective permeability is based on the principle of allowing the permeation of water vapor molecules while blocking larger organic ones as illustrated in Figure 2 [33]. Selective permeability membranes are currently developed by some manufacturers, e.g., the Gore™ Chempak® which is based on a chemical protective polymer combined with an expanded PTFE membrane[5]. For the question of self-decontamination, solutions include ultrathin enzyme-containing composite layers deposited on fabrics [34] and electroactive polymer coatings[6]. Finally, conductive polymers, like doped polypyrrole, polythiophene and polyaniline, are being investigated for the detection of toxic chemicals [35]. As an alternative to the measurement of resistivity change induced by chemical agents, some researchers are also looking at optical properties of optic fibers coated with these conductive polymers [36].

5. APPLICATIONS OF NANOTECHNOLOGIES AND SMART TEXTILES

Intense research has been carried out to take advantage of the exceptional properties of different materials because of their nanometric scale, with current and potential applications for PPE. The great expectations associated with nanotechnologies have led, e.g., to the founding of the Institute for Soldier Nanotechnologies[7] in

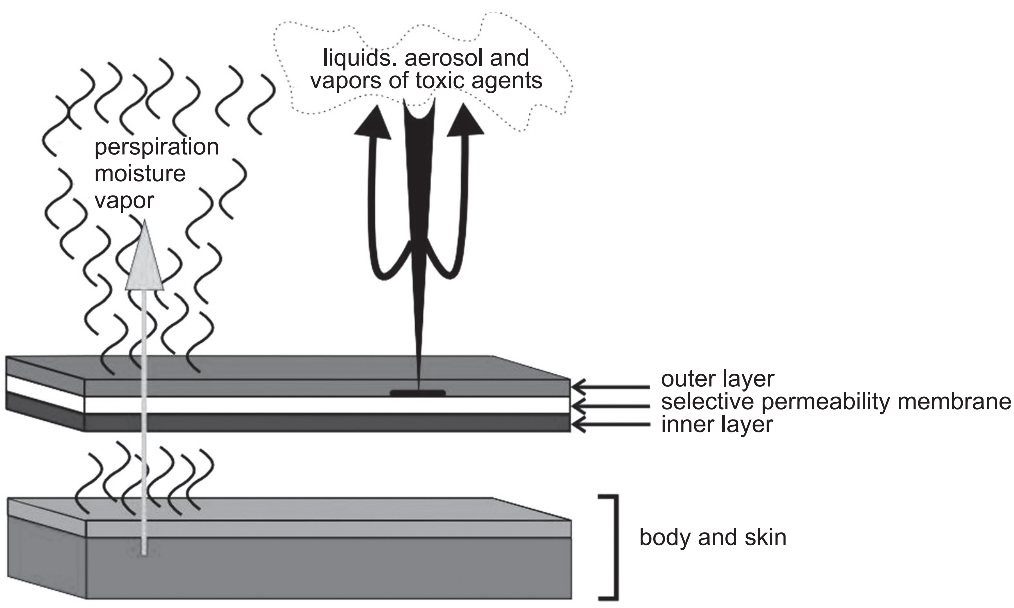

Figure 2. Principle of the selective permeability membrane in 3-layer protective clothing [30].

[5] http://www.goreprotectivefabrics.com
[6] http://www.crosslinkusa.com
[7] http://web.mit.edu/isn

2002 at Massachusetts Institute of Technology. Its ultimate goal deals with creating the 21st century battlesuit combining high-tech capabilities with light weight and comfort.

In terms of potential applications, nanocomposite fibers including nanoparticles or carbon nanotubes have displayed increased electric and mechanical properties [37]. Yarns made of spun carbon nanotubes could be used in bulletproof vests thanks to their large resistance to impact [38]. In addition, they can allow the easy incorporation of actuators and sensors into clothing. The barrier effect of nanomaterials can also be exploited, either in the form of a web of nanofibers for selective filtration as shown in Figure 3 [39] or as nanolayers deposited on fabrics made of natural fibers, providing them with selective transport properties [40, 41].

Another example relates to antimicrobial capabilities imparted to fabrics coated with nanosized silver salt crystals [42]. The resulting product displays a high antibacterial activity while maintaining a wide of range biocidal properties. For increased thermal insulation, the use of nanoporous gels macroencapsulated in viscose-based thin, light-weight nonwovens seems promising [43]. Finally, application of nanoclay-reinforced resin coatings to textiles has been shown to improve flammability resistance [44].

In another field of interest, smart textiles have opened the door to very promising applications for protective clothing. They include being able to sense the wearers' physiological condition [45], their posture and activity [46] and outside environment [47] as well as responsive action [48]. Conductive yarns can be produced by coating with conductive polymers or by embedded conductive fillers like carbon nanotubes [49]. Electrically active structures can then be formed, e.g., through specially patterned knitting [50]. However, numerous challenges remain, in particular with contactless sensors, interconnects, electronic reliability, data and power transmission lines and shielding [51].

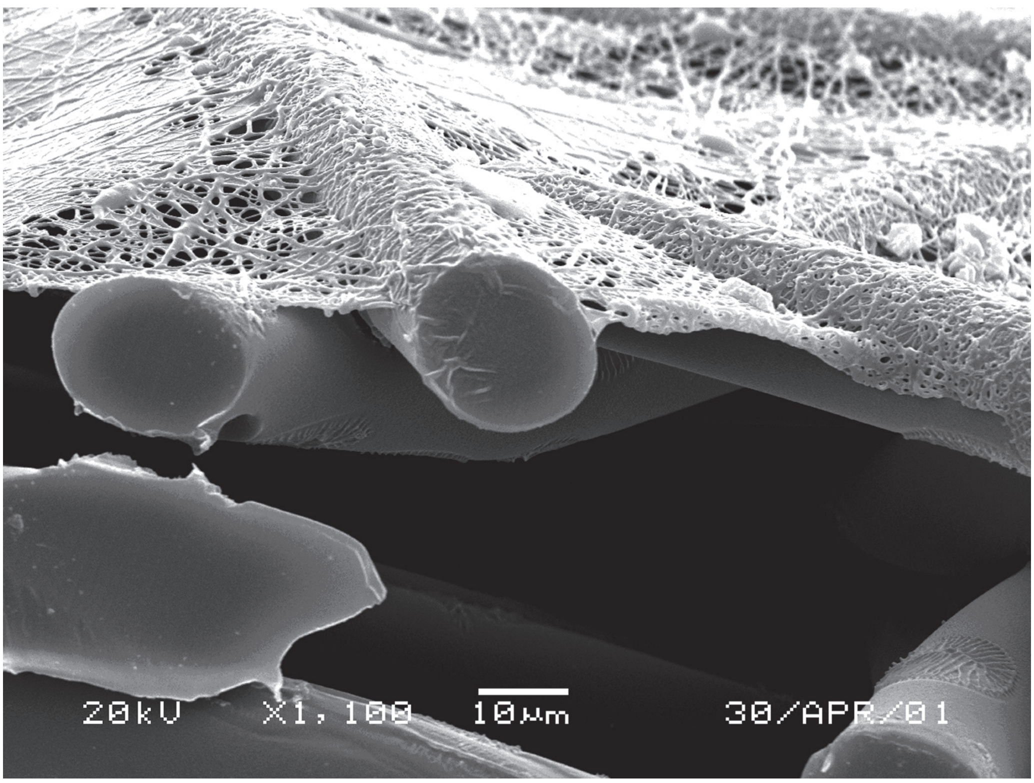

Figure 3. Cross-section view of a nanofiber web electrospun on a polyester spunbond substrate (reproduced with permission, Donaldson [USA], scanning electron microscopy [SEM] image of nanofiber structure from Donaldson website, 2002–2005).

6. CHARACTERIZATION OF PPE PERFORMANCE

With time, increased requirements of workers and organizations in terms of PPE performance have led to the need for more reliable and realistic characterization methods. For example, in the field of resistance to cutting, a new apparatus, the TDM-100, has been developed and proposed as a standard [52, 53], to solve the dulling problem of circular blade devices and the unwanted influence of blade–sample friction observed using the original CPP tester [54]: in this new device, a straight blade is moved across the material at constant speed until the sample is cut through. The measurement is repeated for various levels of the applied vertical load. It has been shown that the friction contribution to cutting, which adds up to the material's intrinsic strength, involves two phenomena [55]: macroscopic friction induced by the gripping of the material on the two sides of the blade and sliding friction taking place at the tip of the blade. The energies lost during cutting respectively on the sides and at the tip of the blade have opposite effects on the cut resistance of materials [56]. For example, the application of a lubricant can produce a reduction in the material gripping frictional force on the sides of the blade which can then lower the resistance of the material to cutting. As shown in Figure 4 for nitrile rubber, a reduction in the blade displacement until sample cut-through is observed for all values of the applied vertical force when the blade sides are lubricated with soapy water. Such effect may have major consequences when mechanical risks occur within a standard work environment, which may involve the presence of various lubricants like oil and grease as well as dust.

The resistance to puncture corresponds to the maximum force recorded when a probe passes through the sample. Here, the main concern deals with the size and shape of that probe, which should simulate realistic mechanical aggressors. For example, it has been shown with elastomers that the puncture force strongly depends both on the probe tip diameter and angle for conical and rounded tip probes [57, 58]. Indeed, they affect the contact surface area between the probe tip and the sample and, consequently, the point at which the failure strain is reached. The latest version of the American Society for Testing and Materials (ASTM) standard offers 1- and 2-mm diameter probes with conical-spherical and spherical tips [59], which is a large improvement compared to former versions of that standard and

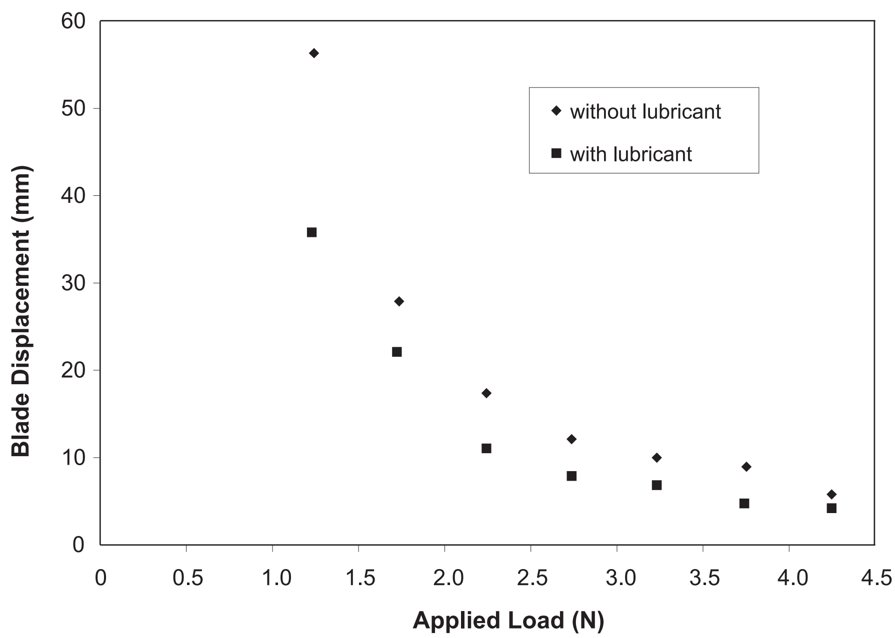

Figure 4. Effect of lubrication with soapy water on the maximum blade displacement used as a measurement of the resistance to cutting for a sheet of 0.61-mm thick nitrile rubber [56].

to other standards. However, medical needles create a largely different behavior, both in terms of puncture mechanism and quantitative results. Indeed, because of its sharp edge, the needle cuts gradually into the material while puncture with rounded probes occurs suddenly when the strain at the probe tip reaches the material's failure value [27]. This is illustrated for neoprene in Figure 5 where force-displacement curves measured respectively in the case of puncture with ASTM probes (Figure 5a) and medical needles (Figure 5b) are provided [60]. One can note in Figure 5 the lower range of force and displacement values involved in the process of puncture with needles. Indeed, large reductions in the measured maximum force have been recorded when puncture is performed with medical needles as compared to standard probes [61], which raises concern about the fact that current standards do not properly characterize the level of protection offered by gloves when medical needles are involved. In addition, the difference in mechanisms between puncture with rounded probes and medical needles is also revealed by a different level of friction contribution to the puncture process. Tests carried out with lubricants have shown that friction plays only a minor role in the case of rounded probes [58] while puncture with medical needles involves cutting and is thus strongly affected by friction [27]. Therefore, like resistance to cutting, resistance to puncture with medical needles may be subjected to some level of interaction with lubrication agents present in a standard work environment. Research is currently underway to study the phenomenon of puncture with medical needles with a special focus on materials used as PPE.

The question of resistance to chemical aggressors is also still under debate. First, current glove regulations generally consider only permeation results, i.e., breakthrough times [62, 63]. They do not take into account the fact that chemicals often also degrade materials. For butyl rubber, e.g., even after complete solvent evaporation, large modifications in the mechanical properties have been recorded [64]. In addition, breakthrough-time data have major weaknesses [65]; in particular, they cannot be related to permissible exposure limits. In a new method proposed by Stull [65], cumulative permeation mass measurements are used, which encompass the various types of interaction between the chemical and the glove, i.e., continuum contact, repeated contacts and splashes. Approximate exposure dermal limits are provided by inhalation toxicity levels since they are more extensively documented. Finally, with the increasing number of chemicals encountered in the workplace, several of them mixtures, systematic testing is not feasible. As a consequence, researchers have been working on prediction models, in particular thermodynamic models based on enthalpies of mixing for mixtures of organic liquids [66].

One last example of protection property for which large limitations have been identified in terms of testing methods concerns the resistance

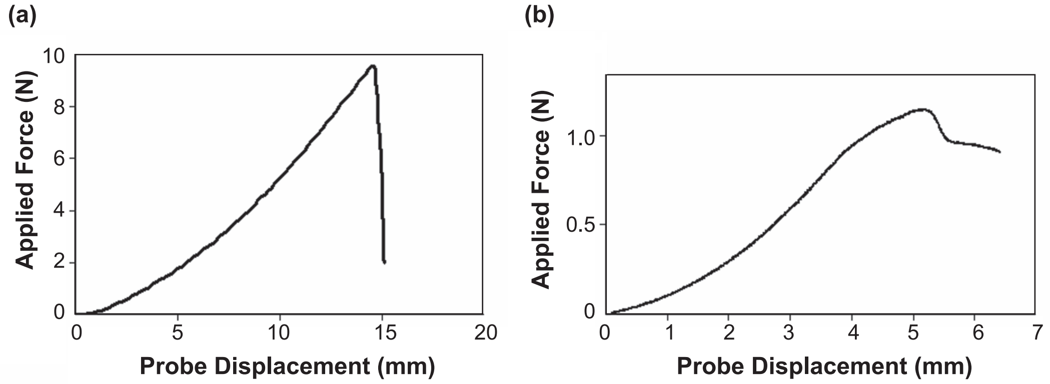

Figure 5. Variation of the applied force as a function of the probe displacement for the puncture of a 0.78-mm thick neoprene sheet with (a) the ASTM F1342-05 probe A and (b) a 25G/3-bevel hypodermic needle [60].

to heat and flame. Development needs include taking into account the real, multihazard work environments, characterizing the performance of the whole ensemble, and allowing product development based on protection, functionality and comfort requirements [67]. However, progress is underway. For instance, thermal protection performance test methods initially neglected the effect of the stored energy that can be released naturally or by compression, and may cause burn injuries even at low heat levels [68]. This has been incorporated in the new ASTM Standards No. F2702-08 [69] and F2703-08 [70] relative to unsteady-state heat transfer and radiant heat performance [71]. For its part, the new Standard No. ISO 11612:2008 [72] includes a section providing guidance for the ergonomic assessment of clothing [73]. Another problem concerns the effect of heat- or flame-generated dimensional change on thermal performance of fabrics. A new test based on a cylindrically-shaped configuration is evaluated for adoption as an International Organization for Standardization (ISO) standard [74]. Researchers have also developed a new test apparatus to allow the measurement of the thermal performance of fabrics that are wet or compressed [75]. Regarding needs relative to the service life assessment, nondestructive test methods are being developed based on color change analysis due to thermal aging, with promising results [76].

However, the selection of PPE should not be solely based on protection properties. Great care must also be put on functionality factors like dexterity, breathability, grip, etc., since they contribute to wearers' comfort and their ability to perform their tasks with a minimal impediment. A study was recently carried out to evaluate the capacity of 12 dexterity tests to discriminate between gloves covering a large range of dexterity [77]. It showed unsatisfactory results when considering individual tests. The authors suggested that a combination of several tests sensitive to different ranges of dexterity may provide a full-range discrimination tool. As an alternative to dexterity tests involving human subjects, research has been carried out to design mechanical test methods that would make it possible to measure glove stiffness and adherence, two properties that have been shown to contribute to dexterity in addition to snugness of fit [78]. A mechanical method has been successfully developed for the characterization of protective glove stiffness; it was validated in comparisons with biomechanical and psychophysical tests involving human subjects [79, 80]. Figure 6a schematizes the principle of this multidirectional mechanical method for glove stiffness measurement. A probe with a

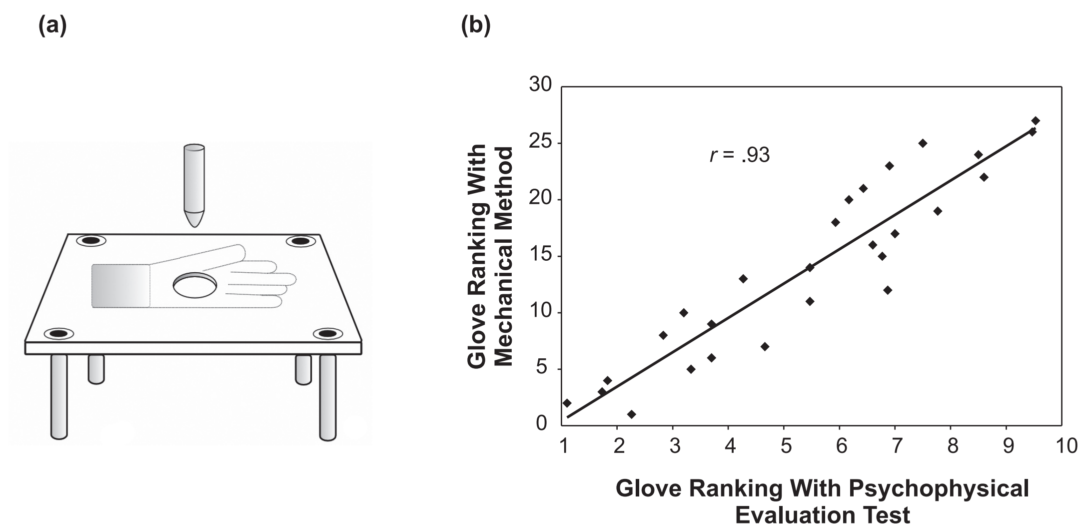

Figure 6. (a) Principle of the multidirectional mechanical test method for the characterization of protective glove stiffness; (b) correlation of the stiffness ranking provided by the multidirectional mechanical method and by a psychophysical evaluation test for 26 protective gloves [80].

spherical-conical head simulating service-life deformation pushes the glove through a hole in a support plate. The stiffness is evaluated in terms of the work corresponding to the initial 10-mm deformation of the sample. Figure 6b illustrates the excellent correlations of the results expressed in terms of ranking obtained with this multidirectional mechanical method for 26 protective gloves with those provided by a psychophysical evaluation test. This method is simple to implement and can be extended to other types of protective clothing. It should allow manufacturers to provide quantitative information on the level of stiffness of their products that a user would really feel when performing his tasks. Concerning adherence, the TDM-100, designed for the measurement of the resistance of PPE to cutting, has been modified to allow the measurement of protective gloves' static and dynamic friction coefficients [81]. The results compared favorably with biomechanical and psychophysical evaluation tests performed on the same gloves.

7. AGING BEHAVIOR

New synthetic fibers have found numerous applications in PPE due to their outstanding performances. However, if the properties of these materials have been thoroughly evaluated when new, very little information is currently available on the way they behave over their entire service lifetime. This worrying situation has been reported, e.g., for firefighters' protective suits [82]. One type of moisture barriers has even been discovered to degrade at an unacceptable rate [83]. In response to the firefighters' community concerns about the residual protection offered by in-service clothing, the National Fire Protection Association has incorporated mandatory ultraviolet radiation aging tests to be performed on moisture barrier materials in the latest version of its requirements for firefighter's protective ensemble [19]. However, moisture barriers do not seem to be the only weak link. Environmental aging tests performed on whole suits have shown large reductions in the shear resistance after short periods [84]. The most worrying point is that reductions of up to 80% in mechanical resistance can occur before any change in the fabric can be detected with the naked eye, which is currently the only evaluation technique available to firefighters [85].

In the field of ballistic protection, a case was reported for the first time in 2003 of a U.S. National Institute of Justice (NIJ)-compliant Zylon®-based body armor failing to prevent the penetration of a bullet [86]. A Pennsylvania police officer wearing the armor sustained serious injuries. A large investigation was launched by the U.S. Department of Justice to evaluate, among others, the performance of used Zylon®-based body armors. It showed that only 4 of the 103 used body armors tested met all the NIJ-requirements for new body armor compliance. A preliminary study of the degradation mechanisms of Zylon® seems to point towards a combination of moisture and light as possible damaging agents. Figure 7 displays the strength retention measured for Zylon® samples subjected to various aging conditions as a function of time. It illustrates that, while the material does not degrade significantly in a hot and dry environment (sealed tube), the presence of humidity, even at a very low level (5% relative humidity), induces a large loss of strength over time. The authors suggest that the degradation of Zylon® by hydrolysis leads in the first stage to a compound similar to Kevlar®, which displays lower tensile properties than Zylon®. The second stage involves a complete breakage of the polymer chain. Another finding is related with the fact that no correlations can be made between the appearance of the armor and its ballistic performance. This raises concern about the false feeling of safety that some degraded body armors may provide to users. A program has been set in the USA to replace Zylon®-based body armors. However, the materials in other available models of body armors, e.g., Spectra®, Twaron® and Dyneema®, have not proved their compliance to NIJ-requirements throughout their warranty period, either. In addition, Zylon® is also used in firefighters' protective suits, which may be subjected to much tougher service conditions.

Finally, even for materials known for much longer, there has been new awareness about

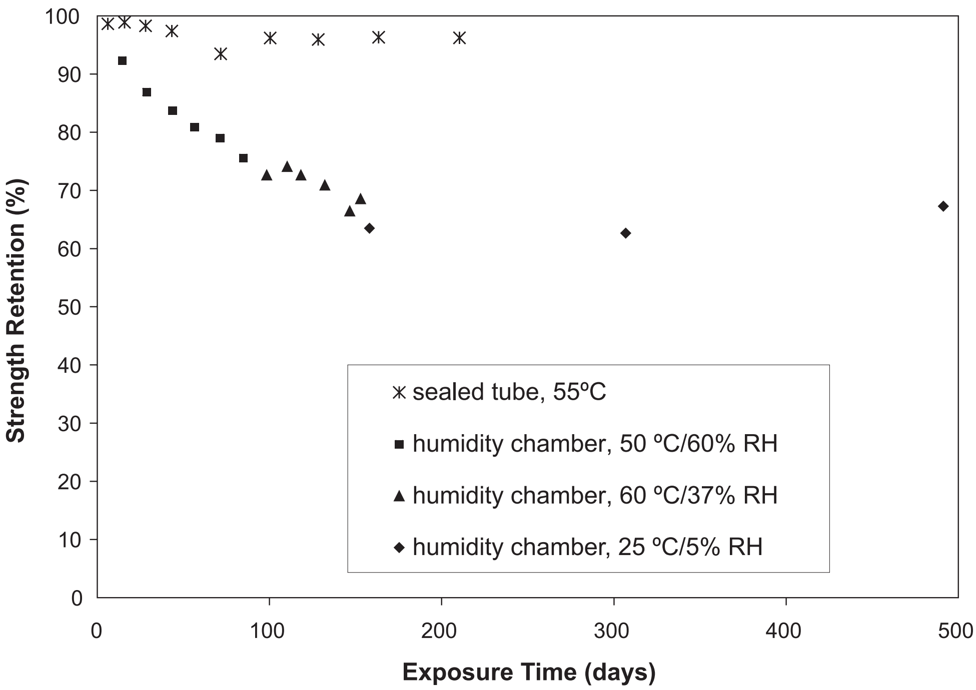

Figure 7. Strength retention of Zylon® yarns when exposed to various levels of relative humidity (RH) and temperature (reproduced from [86]).

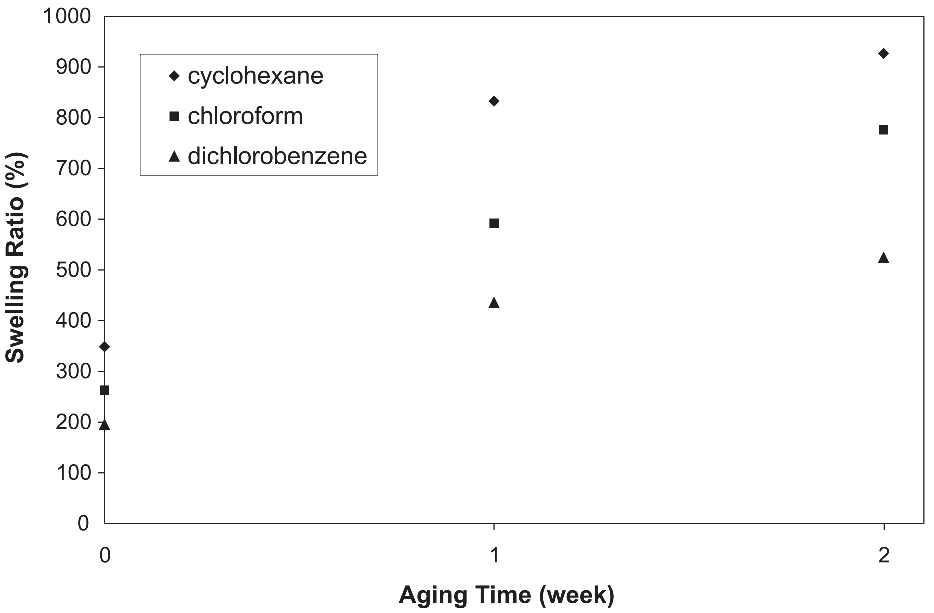

Figure 8. Effect of aging time at 140 ºC on the swelling of butyl rubber by cyclohexane, chloroform and dichlorobenzene [87].

their behavior during service life. For example, a study has shown the devastating effect of thermo-oxidative aging on the swelling behavior and mechanical resistance during swelling of butyl rubber, which is used, among others, in high-performance protective gloves against chemical risks [87]. Figure 8 illustrates how samples subjected to accelerated thermo-oxidative aging display much higher swelling ratios when in contact with cyclohexane, chloroform and dichlorobenzene. This is a concern since PPE may be stored conveniently in a noncontrolled environment, e.g., in war zones, for some time before being possibly used. As a result, even if still considered new, the equipment may not display the level of protection that the user could expect from it. For its part, polypropylene, with widespread applications in numerous fields and in equipment for fall protection in particular, has also demonstrated sensitivity to physicochemical aging [88].

8. CONCLUSION

Decisive progress has been achieved in terms of improvement of PPE, in particular thanks to intensive research in materials science. Examples are provided in this paper of advances recorded in protection against fire, mechanical risks and chemical agents. In addition, nanotechnologies and smart textiles have found several applications in the improvement of PPE. However, major challenges still call for intensified research in all aspects related to textiles, in particular in materials, design and manufacturing as well as in characterization of PPE performance and aging behavior. For example, even if large improvements have been made in characterization of PPE performance, a number of questions remain, in particular regarding the fact that test methods should reproduce real use conditions. Another domain where research is mostly needed is the study of the aging behavior of the materials used in PPE, so that the compliance to safety requirements can be ensured during the whole service life.

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