UNCONVENTIONAL SURFACE TREATMENTS FOR CONFYRING FLAME RETARDANCY TO COTTON, POLYESTER AND THEIR BLENDS

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Within the continuous seeking for novel, more environmentally friendly and performing flame retardant systems for textiles, two main approaches have been developed in the last years, namely sol-gel and layer by layer (LbL) processes.

The sol–gel technique has remarkably proved its exceptional potential regarding the synthesis of new materials with a high degree of homogeneity at molecular level and with extraordinary physico-chemical and thermo-mechanical properties. It is based on a two-step process involving hydrolysis and condensation reactions starting from (semi)metal alkoxides, such as tetraethoxysilane, tetramethoxysilane and titanium tetraisopropoxide. This approach is relatively novel when applied for improving thermal stability, hydrophobicity, antistaticity and flame retardancy of polymeric substrates and textiles. First of all, this technique promotes the formation of (nano)particles aggregates or coatings directly on the polymer substrate or on the textile fabrics. In addition, it can be also exploited for preparing organic-inorganic hybrid nanocomposite coatings, which consist of nanophase separated metal-oxo clusters connected to a continuous organic polymer network via a phase coupling agent, exploiting dual-cure processes.

LbL is a novel method for enhancing flame retardant properties of textiles using multilayered nanoarchitectures. More specifically, it allows obtaining multilayered thin films made of nanosized layers, with a total thickness ranging from submicron to a few millimeters. Nowadays, this technique can be exploited in order to form multimaterial assemblies, avoiding any particular and specific chemical modification of the layer components and thus tailoring the surface interactions to improve physico-chemical properties or fabricating surface-based devices. The technique consists in an alternate immersion of the substrate in oppositely charged polyelectrolyte solutions and/or nanoparticle suspensions, thus creating a structure of positively and negatively charged layers piled up on the substrate surface. Due to the fact that during the multilayer building-up there is electrostatic attraction in between layers, the resulting interactions are very strong; furthermore the process is independent of the substrate size and topology and therefore it can be successfully applied to textiles.

References
INCREASED FIRE RESISTANCE OF CELLULOSE AND CELLULOSE/MODACRYL KNITTED FABRICS

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Abstract:
Textile materials that are more flammable can have their fire resistance drastically improved applying treatments with flame retardant chemicals. It is very important to use flame retardant finishing processes that contain extremely low formaldehyde levels. The ignition and burn factors of fabrics are also affected by weight, weave and knitting of the fabric. Another way to obtain hardly flammable fabrics is mixing the cellulose yarns with certain synthetic yarns that are extremely resistant to flame. In this paper, the FR properties of 100% knitted cellulose materials and their blends with modacryl fibres which were treated with free halogenide hydrox-functional organophosphorus agent and appropriate catalyst were studied. The flame retarding behaviour and the thermal stability of knitted fabrics were evaluated with limited oxygen index (LOI), Microscale Combustion Calorimetry (MCC) and thermal gravimetric analysis (TGA) as well as by the coupled TG-FT-IR technique in order to better understand the decomposition process of the FR-treated cotton and the cotton/modacryl knitted fabrics.

Keywords: cotton, modacryl, blend, free of halogenide hydrox-functional organophosphorus agent, FR properties
NANO/MICRO PARTICULATE FLAME RETARDANT SURFACE TREATMENTS FOR POLYMER COMPOSITES

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Exposure of fibre-reinforced polymeric composites (FRCs) to high temperatures causes the organic resin matrices to soften, undergo thermal degradation and/or ignite, resulting in loss of mechanical integrity of the structure. Conventional methods of flame retarding resins, namely their chemical modification or addition of flame retardant (FR) chemicals, have limited effects in fire protecting conventional (e.g. polyester, epoxy) resins. The most effective technique without affecting composite’s physical and mechanical properties is the use of surface coatings, which can inhibit or reduce the heat transfer from the fire/heat source to the underlying structure. Conventional intumescent coatings provide passive fire protection by slowing down the rate of heat transfer and burning, where most often the polymeric binder used ignites prior to the activation of the intumescent chemicals.

Since the 1990s, nanoparticles, in particular layered silicate nanoclays and carbon nanotubes have been extensively studied in terms of increasing thermal stability and fire retardancy of polymers. The flame retardant effect of those nanoparticles is believed to be due to formation of a thermally insulative layer on the surface of the burning polymer, which slows down the burning process. In this work we have used these nanoparticles in fire retardant surface coatings for glass fibre-reinforced epoxy composites. These nanoparticles act as ceramicizing elements, providing thermal barrier effect and hence resulting in enhanced performance of the fire retardant surface coatings. The methodology adapted involves selection and application of polymerisable fire retardant coatings containing nanoparticles, which can be chemically bound to the organic resin of the laminate. A number of laminates with different surface coatings containing different types of nanoparticles have been prepared. The effectiveness of coatings are studied by exposing composite laminates to different heat fluxes in a cone calorimeter. The residual mechanical strength of the laminates after exposure to heat/fire is also being investigated.
DEVELOPMENT OF THE PERFORMANCE OF FLAME RETARDANT VISCOSE-SILICIC ACID HYBRID FIBERS

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The rising demand for polymers/fibres with high temperature resistance and fire retardant properties as well as the concerns on negative environmental and toxic effects of existing materials have been forcing since 50’s to develop alternative hybrid systems. Basing on the viscose fiber process, a novel cellulose silicic acid hybrid polymer fiber and process was developed during the 90’s and was gaining some success in markets in the beginning of the 00’s. The process represents a wet spinning technique in forming an organic-inorganic flame retardant fiber with advantages of easy and economical manufacture, dimensional stability, low gas emission, very low toxicity and a relatively low price. During processing the hybrid fiber is behaving very much like viscose, and is easy to process for nonwovens by needling and hydroentangling processes. However, due to the porous surface the fiber-to-fiber friction is high and increased amounts of finishing agents are necessary for yarn spinning. Cellulose hybrid fibers with 35% of polysilicic acid contents show a LOI value of 26% and can be further improved by surface modification with aluminium salts up to 30%. At the same time the alkaline sensitivity in the pH range of 7-9 is reduced and the washing resistance is improved up to 20 cycles.

For optimization the polymerization process of silicic acid, the removal of sodium ions should be fast and total during the spinning process in sulphuric acid. In respective conditions, silicic acid is forming nanoparticles of 1-3 nm, which are simultaneously aggregated in order to form chains. The increasing amount of electrolytes in the spinning process increases the formation of colloidal precipitated silica. The introduction of polysilicic acid into cellulose matrix increases the amount of amorphous regions around 50% and no chemical bonds between silicon and carbon are found in hybrid fiber. There might be some possibilities for covalently bonded silicon-cellulose hybrids by applying the principles of silanol grafting with organic silanols. However, a bifunctional precursor as well as reactive with cellulose and with polysilicic acid is needed.

Preliminary studies were carried out for the development of the performance of flame retardant viscose fibers manufactured by hybrid technology. Specified industrial cellulose xanthate solution and water glass were used to prepare films for the optimization of important parameters. Electrolyte concentration, specific mass of the spinning bath, additive concentration, and precipitation temperature were important for obtaining high regeneration degree of silicic acid and sufficient tenacity of the hybrid polymer. The gelation process of water glass alone in regeneration bath is sensitive to changes in concentrations, temperature and additives. Cellulose-silicic acid fiber samples from the industrial production showed a round-shaped cross-section and maximum strength of 2 cN/dtex of hybrid fiber when using a moderate spinning temperature without the aluminate aftertreatment. This can be further improved up to 2.1-2.2 cN/tex by the treatment of dilute sodium aluminate and lubrication surfactants resulting fibers capable for ring spinning processing.
PERMANENT FLAME RETARDANT FINISHING OF TEXTILE MATERIALS BY THE USE OF PHOTO-INDUCED GRAFTING AND CROSS-LINKING REACTIONS

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Photochemical treatments allow a permanent surface modification of synthetic and natural fibers such as polyesters, polyamides, polyolefins or cotton by the irradiating with UV light in the presence of reactive media. These processes are based on a homolytic bond cleavage initiated by the absorption of energetic photons leading to the generation of radicals on the irradiated polymer surfaces. This allows manifold subsequent reactions such as photo oxidations, grafting and cross-linking. In particular, monochromatic excimer UV lamps, allow a selective irradiation taking advantage of substrate and agent specific absorption bands. Using allyl compounds grafting reactions can be achieved by the addition of the surface radicals to the double bond. Depending on further functional groups of the added molecule the surface properties of the treated polymer are adjustable in wide ranges. For example, the hydroxyl groups of photochemically bonded glycerol-1-allylether equip PET with a very high hydrophilicity and the addition of perfluoro-4-methylpent-2-en yields hydrophobic and oleophobic properties due to the immobilization of perfluorinated carbon groups. Using diallylic compounds barrier layers on PET can be achieved, which, e.g., protect the substrate against alkaline hydrolysis. Other investigations aim at the photochemical fixation of proteins or biopolymers on polymer surfaces resulting in highly functionalized synthetic fiber materials for widespread applications in catalysis, medicine, textile industry and food technology.

In addition, we succeeded in the photo-induced coupling of flame retardant agents on various textile materials. Using the monochromatic excimer UV lamps system or broadband UV lamps high amounts of, e.g., vinyl phosphonic acid or allyl polyphosphazenes can be fixed covalently and, therefore, permanently to different textile materials such as cotton, polyester, polyamide and its blends yielding textiles with flame retardant properties. Here, we report the principles of the UV technology and show some results of our latest research projects in the field of photo-induced flame retardant finishing.
NEW DEVELOPMENT IN FLAME RETARDANT FINISHING OF COTTON BLENDS (ABSTRACT)

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Cotton is the most commonly used fibre in apparel whereas cotton blends are widely used in protective clothing. Because cotton is among the most flammable textile fibres, the fire hazards of cotton clothing represent genuine risk to consumers as well as to industrial workers and military personnel. Home furnishing is another area in which cotton’s high flammability presents genuine fire risk, because cotton and cotton blends are also widely used in upholstered furniture, rugs, bedding materials and other home textiles. Little has been achieved to produce flame retardant cotton blends fabrics. The needs for flame retardant finishing technology for cotton blends were undoubtedly recognized [1].

In this paper, we first discuss the flame retardant finishing of the Nomex/cotton (65/35) blend fabric using a hydroxy-functional organophosphorus oligomer as the flame retardant agent, 1,2,3,4-butane tetracarboxylic acid (BTCA) as the bonding agent and triethanol amine (TEA) as the co-reactant [2]. Because cotton is a highly flammable fiber, the Nomex/cotton blend fabric containing more than 20% cotton is not self-extinguishable. Therefore, a durable flame-retardant finishing treatment becomes necessary to make the Nomex/cotton blend flame-resistant if it contains more than 20% cotton fiber [3]. BTCA reacts with HFPO, cotton and TEA to form a BTCA/HFPO/TEA/cotton crosslinked, thus improving laundering resistance of the HFPO on cotton. The Nomex/cotton blend treated with the HFPO/BTCA system showed high flame retardant performance and excellent laundering durability at relatively low add-on levels (<10% fabric weight increase). The treated fabric also showed limited strength loss and little change in hand properties. This flame retardant finishing system is a formaldehyde-free system and odor-free process.

![Scheme 1. HFPO](image)

We also discuss the applications of HFPO to the flame retardant finishing of the nylon-66/cotton (50/50) blend known as batter dress uniform (BDU) fabrics. We found that HFPO can be bound to the nylon fabric in the presence of dimethyloldihydroxyethyleneurea (DMDHEU) by forming a polymeric crosslinked HFPO/DMDHEU network [4]. The HFPO/DMDHEU system was applied to the nylon/cotton BDU fabric. The blend fabric was treated with 32% HFPO and DMDHEU at different concentrations and cured at 165°C for 2 min. The fabric treated using ≥6% DMDHEU passed the vertical burning test after 40 launderings. The char length of the fabric treated with 32% HFPO and 10% DMDHEU (after 40 laundering cycles) reached 81 mm. The data clearly show that DMDHEU concentration plays a critical role in determining the flame retardant performance of the nylon/cotton blend fabric treated with HFPO/DMDHEU. A higher DMDHEU concentration increased the amount of HFPO bound to the treated fabric and it also improved the hydrolysis resistance of the HFPO bound onto the treated fabric probably by forming more stable crosslinked HFPO/DMDHEU polymeric network. The 50/50 nylon/cotton blend BDU fabrics thus treated demonstrated negligible fabric strength loss [5].

References
Intensive development of nanotechnology linked with generation of nanostructures and nanomaterials offers great possibilities of creating modern multifunctional materials. Such materials based on semi-porous surfaces, e.g. textile substrates, can have very wide applications due to the new properties and functions rendered to these substrates such as self-cleaning, anti-bacterial, UV protection, electrical conductivity, friction and wear resistance, pH/thermo-responsive hydrophobicity or hydrophilicity and flame resistance\(^1\). The ultimate impact of nanotechnology in the area of textile and other potential application areas will depend on the type and structure of nano-structured functional agents and their coating process\(^2\).

Concerning flame retardant materials, bromine- and chlorine-containing flame retardants are still used in some products, the need for new alternatives is being driven by a confluence of policy, standards, and pressure from environmental groups. One promising approach is to use nanoclays as flame retardant materials. Flame retardants made with naturally occurring clay called montmorillonite are poised to have a huge influence on future fire safety. Montmorillonite-based nanoclays have been investigating how this clay can help reduce the amount of energy released during fires for more than a decade.

Among established wet-chemical modifications processes, inkjet printing techniques can be used as a novel approach with high efficiency and low cost to deposit functional agents on fabric surfaces. In our studies, multi-functional formulations, containing various functional agents which have high affinity to natural and/or synthetic smooth (foils) and semi-porous (textile materials) are prepared. Differently sized and shaped aluminium hydroxide nanoparticles being artificial nanoclays are used to coat polyester fabrics. A thermogravimetric analysis was used to evaluate water losses as a function of temperature applied and of the type of alumina nanoparticles used. Process parameters of nanoparticles pre-treatment and polyester fabrics post-treatment after application of nanoclays were investigated. The quality of fabrics coating were checked using a scanning electron microscope.

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THE POTENTIAL FOR A NOVEL FLAME RETARDANT POLYAMIDE 6 (PA6) FIBRES BASED ON A NANOCLAY/AMMONIUM SULFAMATE/DIPENTAERYTHRITOL SYSTEM

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Earlier work of Lewin et al [1, 2] showed that high levels of flame retardancy could be conferred on polyamide 6 (PA6) in the presence of small concentrations of ammonium sulphamate (AS) and dipentaerythritol (DP). Bourbigot et al [3] have recently shown that PA6 filaments containing between 3 and 5 wt% AS and 4wt%AS/1.4wt%DP yield coarse filaments (~100 micron dia) may be produced having reduced peak release rate values compared with pure PA6 analogues although no tensile properties were reported. However, ammonium sulphamate starts to thermally decompose and cause degradation of PA6 at temperatures above 250°C and if acceptable fibres are to be produced, this effect must be taken into account and minimised. In this paper, we extend these ideas to consider the feasibility of generating a novel group of flame retardant PA6 fibres having acceptable tensile and related textile properties.

PA6 samples were compounded with similarly low concentrations (2.5% w/w AS and 1%w/w DP) with or without nanoclays and fumed silica present at 1 and 2 %w/w levels. Compounded samples were characterised by X-Ray diffraction (XRD), thermal analysis (DTA/TGA) and FTIR. Flammability properties were measured by UL-94, LOI and cone calorimetry test methods. All PA6 blended samples with or without nanoparticles were found to be V-2 rated according to the UL-94 test classification which differed from the results reported by Lewin et al for similar samples in that V-0 ratings were obtained for clay-free samples. While LOI values were well above those for pure PA6 (20.5-21.9 vol%), LOI increases promoted by the inclusion of AS and DP alone were slightly reduced from 25.0 vol% for bar samples following the addition of all nanoparticles with the functionalised clays showing the largest effect to yield reduced values of 23.8 vol% and less. Introduction of silica, however, had the smallest effect in reducing LOI.

Cone calorimetric results show that while the presence of AS and DP raise peak heat release rate (PHRR) values with respect to PA6 as a consequence of sulphation-enhanced degradation reactions, addition of nanoparticles reduces values to below that for pure PA6. Reductions in PHRR are dependent on clay or silica concentration although differences between clays and silica are within experimental error very similar. While smoke generation is little affected by addition of AS and DP, presence of clays and silica promotes a slight increase.

Trial extrusion into filaments based on the above optimal formulations has been undertaken in spite of the challenge posed by the onset of thermal degradation above 250°C. The preliminary results of this work are also presented.

Nanostructured materials based on pure and doped oxides are of increasing high interest for a large field of high-tech applications. Their properties are strongly dependant on the synthesis route due to defect formation, level and distribute of doping elements as well as purity. Hydrothermal method is a rapid, one-step environmental friendly method proposed for the synthesis of different nanostructured materials [1-3].

The paper presents a review on the current state of the art in the hydrothermal and solvothermal synthesis of pure and doped nanocrystalline oxide powders with potential applications as flame retardants of textiles: ZrO$_2$, TiO$_2$, ZnO, perowskite structured oxides [4], phyllo-siloxides and modified layered oxides such as KMg$_2$FeSi$_4$O$_{12}$ [5]. An important new and original feature of high pressure hydrothermal synthesis is the ability to obtain hybrid inorganic-organic functionalized nanopowders, enhancing the reactivity with textile fibers. The role of temperature and pressure parameters on the thermodynamic and kinetic modeling of the synthesis process is discussed.

The thermal stability and crystallization energy of these different oxide and hybrid nanomaterials using DSC methods is also modeled.

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In this presentation we will present our recent work on developments of new phosphorus-nitrogen based flame retardants for application in polymers. We have synthesized novel derivatives of 9, 10-Dihydro-9-Oxa-10-Phosphaphenantrene-10-oxide (DOPO), incorporated them as additives in various polymers and evaluated them for burning and thermal decomposition behavior. These flame retardants primarily work in gas phase by radical scavenging action and thus suitable for application as bulk additive and coatings for most polymers. By suitable choice of substituents attached to the phosphorus atom we can obtain flame retardant compounds with varying thermal stabilities and solubility in different solvent. Varying thermal and solubility properties of these DOPO based compounds help define their potential applications. The presentation will also cover our recent experience in successful collaboration of not only developing new chemistry in lab scale but it’s up-scaling in industrial scale and pilot-scale production of flame retardant foams from these additives.
Worldwide consumption of flame retardants amounts to around 2 million tons a year. According to a 2012 market study (Townsend), the consumption of flame retardants has grown substantially in the past 4 years, notably in electronics, and will continue to grow at a global annualized rate of 4-5%. Use in plastics accounts for approximately 85% of all flame retardants used with textiles and rubber products accounting for most of the rest. North America consumed the largest volume of flame retardants in 2011 with 28% share. Asia-Pacific is one of the most dominant markets for flame retardant chemicals, accounting for 48.5% of the global volume consumption in 2011. It is the fastest growing region for the flame retardant chemicals market both in terms of production and consumption. Flame retardant chemicals owing to their advanced and better quality characteristics are one of the fastest growing segments of today's plastic additives industry. The shift in product mix toward lower cost non-halogenated flame retardants will be offset by their higher loading levels, with overall sales of flame retardants rising 7.8 percent per annum to $1.2 billion in 2016. Many materials contain quite high levels of flame retardants: cellulose insulation is about 20% flame retardant by weight, plastic television and computer cases are often 10–20%, and polyurethane foam cushioning can be up to 30%. Some materials have very low levels of flame retardants: polystyrene foam insulation is typically 0.5–2.0% HBCD (hexabromocyclododecane) by weight. Environmental problems relating to brominated flame retardants (BFRs) have become a matter of greater concern than ever before, because of the recent marked increase in levels of polybrominated diphenyl ethers (PBDEs) found in human milk in Sweden and North America. The question that arises is whether environmental levels of PBDEs and other BFRs will continue to increase.
In this paper will present a comparison of results obtained using different standards of fire behavior for two different categories of textile. The first one is curtains and vertical oriented textiles tested with the following standards: EN 1101, EN 1102, EN 13773, EN 6940 and EN 6941. The second category is fabrics for apparel in accordance with EN 1103 and EN 14878. Finally we compared the results obtained in the same class.
SUSTAINABLE SOLUTIONS FOR FLAME RETARDANT TEXTILE TREATMENT

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Since many years, ICL-IP, a major producer of chemicals for different applications, is committed to develop more sustainable solutions, namely in our range of flame retardant products. Replacing existing flame retardant solutions for textiles with more sustainable and durable products is one of the major goals of our development work. Quite a few new products have been introduced to the market. Our new solutions TexFRon® 9025, TexFRon® 9020, TexFRon® P, TexFRon® 3000, TexFRon® P+ and TexFRon® 9001 will be presented.

An overview on the application for different fabrics and FR requirements & durability will be provided, ICL-IP’s view on sustainable flame retardants and on actions industry undertakes in the framework of EFRA (the European Flame Retardants Association) in cooperation with customers and downstream customers to avoid emissions during use of flame retardants (VECAP® program), attention to end of life aspects and the development of new products with an improved health and environmental profile.
This paper works with silicone-based compounds added to the bath with conventional flame retardants for improving their initial flame retardancy and for better explanation the burning behaviour of cotton fabric. Our previous results with zeolite in cotton finishing bath suggested that this complex silicone compound may have a considerable influence on cotton flammability. It is known that zeolite contains a high portion of silicone that is close to 70%. Silicone has excellent thermal stability and high heat resistance with very limited release of toxic gases during the thermal decomposition. In this paper polydimethylsiloxan emulsion is used in the bath with conventional flame retardants to improve their properties. Conventional and no toxics ones, as ISO in 2012 started a new work item on the banned/ restricted flame retardants.

Twill weave chemical bleached cotton material (211 g/m2) were treated by pad-dry procedure in Benz Pad-dry system with different conventional compounds. The conventional compounds used for cotton flame retardancy showed expected high flame retardancy in the range of LOI 25 to LOI 29. Addition of polydimethylsiloxan shows the higher these values as higher temperature of full degradation and more residue then conventional compounds. Polydimethylsiloxan is helped to the conventional compounds by reaching high flame retardancy. This paper will modify cotton fibres by implementation of nanozeolite in the mercerisation bath for additional contribution to the flame retardancy of cotton.

For better understanding the surface changes in these treatments the Scanning Electron Microscope was used, for cotton structure changes under the heat conditions thermogravimetric method (TGA) was used.