Chapter

Increased-Value Oxide Powders for Polymeric Fibrous Matrices with Tailored Surfaces for Clothing Wear Comfort: A Review

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Abstract

This review is dedicated to the area of renewable polymeric matrices, a topic in which the editors aims at conducting, developing, and forming a research-innovation direction for the doctoral studies school. There are two directions envisaging (a) the synthesis of cellulose-derived materials and (b) their application as novel clothing wear materials as an alternative to standard one. The evolution plans aspire to encourage theme-based cooperation between academic environment and industrial media. Thus, the intention is to work on new product development and formulation in a program with strong industry engagement. Specifically, the proposed review will focus closely on applied research and the expansion of the transfer of technology and knowledge in the clothing industries and beyond. Subsequently we propose an interdisciplinary research and development program for material sciences and technology development, meaning, development of new improved ecological comfort performance materials.

Keywords: man-made fibers, oxides, UV reflectance, water barrier, impedance, comfort, UV protection

1. Introduction

This review is dedicated to the area of renewable polymeric matrices, a topic in which the editor develops some research-innovation activities. There are two directions envisaging (a) the synthesis of cellulose-derived materials and (b) their application as novel clothing materials as an alternative to standard one.

The review plans to encourage theme-based cooperation between academic environment and industrial media. Thus, the intention is to work on new product development and formulation in a program with strong industry engagement.

Specifically, the proposed review will focus closely on applied research and the expansion of the transfer of technology and knowledge in the clothing industry and beyond. Subsequently we propose an interdisciplinary research and development program for material sciences and technology development, meaning, development of new improved ecological comfort performance materials.

2. Rationale

Today, it is relevant to develop new research related to the context of environmental and health hazard component.

The exposure of clothing textile materials to wearing plays an important role in the development of adverse health effects.

Washing- and wearing-generated particles are associated with water and air pollution; consequently, pulmonary effects can occur, as shown by both epidemiological and toxicological studies [1–26]. There are important studies, revealing that particles like microfibers, small textiles, and short fibers resulting from washing and wearing of clothing items might contribute to these adverse effects.

Distinct health involvement is connected with the allergenicity of clothing components such as small fibers, small particles derived from wearing of clothing garments, textile wastes, and nondegradable dyes and pigments.

The abovementioned blends have toxic, mutagen features [27–43]. Moreover, respiratory sensitizers, inducing irreversible allergic reactions in the respiratory system, were noticed.

The wastes resulted from washing and wearing of clothing polymeric materials are a key concern point for the European legislation; up to our knowledge, there are no legal demands for the control of banned dyes and pigments having artificial source.

Consequently, some of the approaches relating to non-exhaust particulate matter were highlighted [44]. Researches reveal that the traffic-related emissions are major sources of suspended PM in the urban areas [45–67]. Nevertheless, it can be claimed undoubtedly that data relating to the physical and chemical properties, emission rates, and health consequences of non-exhaust particles derived from specific wearing and washing of textiles are uncertain/far from comprehensive.

Therefore, a logical state of the art touching the validity of the textile waste emission strategies is mandatory, in order to develop practical strategies for reducing the pollutant concentrations.

The review proposes two novel directions tightly bound to the double expertise, *knowledge of the cellulosic polymeric supports treatment against aging process*, gained during the doctoral studies, and a *higher comprehension of synthesis and characterization of nanoporous materials used in clothing wear comfort* derived from textile industry, during my postdoctoral activity. The relevant direction which is the force line stressed by the review is the development of new ecological comfort performance materials.

The development of new comfort performance materials as an alternative sprang from the context of environmental and health hazard within global climate change. During wearing, the clothes could generate wear particles of different chemistries, which are released into the environment, with a different potential of toxicity and mutagenicity.

Moreover, there are various problems associated with synthetics and artificial dyes and pigments, as a consequence of their negative repercussion onto a global and actual background, meaning the life cycle judgment and waste mainframe.

It is well known that manufactured dyes were declared as *taboo*, a lot of research was polarized to test some of their replacements. Thus new formulations appeared for the color of the wear comfort textile materials.

The typical example is carbon fibers proposed as low metallic (or nonmetallic) comfort performant polymeric platforms.

The key point was the idea of synthetic fiber replacement with engineered comfort polymeric materials, having partially the same comfort characteristics, in terms of hygroscopicity, water and air permittivity, thermal, electrical, and sound insulation, and the last but not the least, self-cleaning performance.

There were studies trying to associate synthetic fibers with oxidic nanostructures or to be woven into a single fabric.

Notable scientific research was reported worldwide for the improvement of ecological polymers, for different functions [68].

The review comes up with plant fibers (sisal, jute, hemp, flax) utilized as pillared structures for various polymers, replacing synthetic fibers (glass, Kevlar, carbon, etc.). Due to their biodegradability and sustainability, cellulosic fibers are tremendous backup which can be utilized as basics in a particular variety of polymeric composite applications (e.g., kenaf and betel nut fibers) [44, 68–86].

Scientific reports made important state of the art, by summarizing data regarding an extensive review concerning the employment of natural-sourced fibers as fundamentals in polymer-based composites, with a certain target on their self-clean/photocatalytic behavior [87].

The relevant requirements, which these new engineered comfort composites with self-cleaning purposes should fulfill, are the following:

- Acceptable values of the comfort performance coefficient
- Stability at higher temperatures

The most extremely serious aspect is the one regarding the thermal stability of the plant fibers. In terms of thermal stability, in comparison with the most valued aramid fibers, decaying between 400 and 450°C, these thermal conditions are diminished.

This fact happens because of the temperature at the contact surface can locally exceeds several hundred degrees, during intense breaking.

The question is whether the natural plant fibers can be used for application at such higher temperatures.

The research plan highlights the concept of using three main approaches to increase plant fibers in thermal stability:

- The augmentation of elemental composition of cellulose, by eliminating the secondary components, like hemicellulose and lignin, by an alkaline method
- The enhancement of thermal cohesion of the novel comfort performant polymeric composites by employment of montmorillonite (MMT) emulsion, having attributes of inorganic natural clay, containing SiO_4 tetrahedral sheets arranged into a two-dimensional network structure, thus granting thermal protection [88]
- The direct growth of pure and doped nanostructured ZnO coating onto the abovementioned fibrous polymeric matrix as active photo cleaned/stain repellent material in high engineered comfort products

In other words, the research review proposes the creation of some polymeric platforms, whose place remains an important question.

Based on the work experience in the metal oxide and other photoactive materials for coating area, a novel approach to the direct growth of pure and doped nanostructured ZnO coating onto different kinds of polymeric supports as active photocatalyst material in comfort performance is proposed.

By means of governing the nucleation dynamics, an alternative to modify the expansion process of oxidic nanostructures occurs. Thus, the enlargement of oxidic nanostructures is possible in a competitive mode at low temperature, by employment of physical approaches such as laser ablation, plasma vapor deposition, nonaqueous solution growth, and solgel and spray deposition.

The abovementioned methodology grants the control of distinct polymeric supports for oxidic nanostructure nucleation, having the convenience of a considerable larger surface than usual, low interfaces conducting to an augmented surface in volume ratio of the active self-cleaned polymeric supports.

3. Impact

The expected impact of the *first research direction* is to make available new scientific knowledge regarding comfort performant polymeric supports able to consistently reduce stain repellence of them, since there is a niche in this field.

The expected outcomes will be a benefit to the know-how in the domain of original textile platforms with comfort behavior, since green-chemistry engineered substrates are in their inception. This review can make accessible an extensible territory of technological employments, considering aspects like expenditure and low environmental impact of the comfort polymeric platforms, with potential commercialization in the future. Since the research plan targets air purification in fact, the achieving of the fundamental objectives will have a strong environmental, social, and economic impact.

The replacement in the model formulation of mineral fillers and fibers (e.g., glass fibers); metals, such as copper, lead, and tin; antimony trisulfide; and aramid pulp, presently used in comfort performance materials, by renewable natural fiber-reinforced polymeric matrix composites (NF: cotton, flax, or sisal fibers), will lead to:

- Thanks to their biodegradability, the production of comfort textile components with potentially complete recyclability will be sustainable (zero waste at the end of the life cycle).

- An achievable lower weight will mean a decrease of gas emission in vehicles enhancing the quality of life, due to the low density of the NF.

- More safety during fiber managing and a longer life for processing tools will be provided by the lower abrasiveness and friendly handling of natural fibers as reinforcing elements.

- Positive health effects.

- Eco-friendly, lack of toxicity.

- Low cost and weight, with potential perspective commercialization.

- Better ratio properties/weight, compared to glass fibers on the expense of lower structural properties.

- Mechanical properties identical to those of traditional polymeric composites, reduced friction at wear and tear, high geometric stability of the manufactured parts, and good insulation characteristics.

The innovative engineering of advanced eco-pad was obtained from green-chemical, nonmetal materials, entirely fulfilling the most relevant promoting tendency of the modern textile comfort architecture.

Having into consideration, the other *research force line*, the desired impingement was to create reachable new scientific overview regarding self-cleaning polymeric platforms, in order to capture/block/entrap the chemical compounds resulted from the mineralization/degradation of organic matters, where this kind of expertise is unpredictable, vague.

4. Objectives

4.1 For the novel comfort performant polymeric platforms

The novelty/originality of the proposed chapter consists in the application of life cycle assessment (LCA) and eco-design methods to evaluate and optimize comfort performance material formulations, through a comprehensive consideration of resource consumption and bio-toxicity. In the above context, and given the variety and complexity of non-exhaust emission sources, the statement proposes some specific objectives, obviously derived from the fundamental objective of the research plan.

- To obtain new ecological enhanced comfort performant polymeric platforms (eco-pads). The role of plant fibers in these comfort performance composites will be studied in relation to formulation/engineering, comfort performance materials, and comfort performance material surfaces.

- To optimize the product/process: processability and performances of the composites. This aspect requires an optimization of the matrix components and the processing procedures. It is compulsory to optimize composition (percentage of polymers and fiber; type and amount of additives and filler), procedure (mixing, extrusion; treatment of fibers), and process conditions (pH, temperature).

- To apply the extension evaluation method of wearing comfort performance materials, which is an effective tool for the ranking/selection of comfort performance materials, based on some defined criteria as follows: performance, physical properties, costs of raw materials, wearing and washing effectiveness, and thermal stability.

- To create a small-scale prototype pad, integrating the best comfort performance material behavior to reduce the emission of particles derived from wearing and washing, up to 50%.

- To create a database for environmental impacts and bio-toxicity of comfort performance materials, to evaluate and optimize the comfort performance material formulations through a comprehensive consideration of resources consumption and bio-toxicity.

4.2 For the self-cleaning polymer-based platforms

The originality of this plan consists in the use as growth support of polymeric materials to increase photocatalytic/self-cleaning active material surface, the use of the simple chemical approach for direct nucleation of ZnO nanostructures, as well as the use of ZnO-based polymeric supports as self-cleaning/photocatalyst in an innovative prototype platform.

1. In order to design nanostructured oxide-based coatings on polymeric substrates with restrained sizes, favorable homogeneity, and durability using as standard nucleation methods, diverse chemical simple ways (aqueous chemical growth, nonaqueous solution growth, and sol gel), utilizing cheap precursors, and feasibility for potential economic purposes.

2. To detect the excellent polymeric platform configuration, morphology, and attributes in each polymeric layer and to obtain an outside surface to volume ratio for operative membrane, in the case of particular chemical nucleation path.

3. To accomplish materials with high hydrophobicity/stain repellency during wearing.

4. To create a small-scale prototype reactor, integrating the best self-cleaning active nanooxide-based polymeric supports, in terms of sustainability, feasibility, and cost-effectiveness for future scale-up.

5. Methodology

5.1 For the novel comfort performant polymeric platforms

1. **Preparation of eco-friendly comfort performance composites with tailored comfort performance formulations**, given the expertise on cellulosic supports behavior:

- Cellulose-based fibers in composites formulation
- *Cotton composite*: polyester resin reinforced with montmorillonite-coated cotton fibers
- *Banana/pineapple composite*: epoxy resin reinforced with banana/pineapple fibers

  Sample preparation:

  - Extract fibers.
  - Prepare epoxy and hardener.
  - Prepare mold.
  - Fabricate composite.

- *Jute/ramie* fibers in mixture with powdered nut shells as natural and biodegradable fillers in non-asbestos organic (NAO) comfort performance material composites (graphite will be replaced with nut shell)

- *Jute composites*: Jute/polyester-clay (montmorillonite) composite, jute vinyl ester composite, jute epoxy composite, and jute/polypropylene/polystyrene thermoplastic composite; montmorillonite-coated jute fiber; and reinforced polyvinyl chloride (PVC) film composites

- *Sisal composites*: Montmorillonite-coated sisal/polyester composite, sisal/epoxy composite, sisal urea/formaldehyde composite, and sisal polystyrene/polypropylene composite

- *Flax composite*: Montmorillonite-coated flax polyester composite, flax/epoxy composite, flax/polystyrene composite, and flax/polypropylene composite

- *Hybrid composite* with different volume fraction of glass and bamboo fibers reinforced with an epoxy polymer

- *Wool-polyester* resin composites

- *Aramid pulp and natural fibers*

A special attention will be given to chemical-free polymeric supports using agricultural wastes as a source of raw materials (coconut shell). In terms of economical wastes, utilization is not a favorable solution, but the result might be environmentally evaluated/quantified.

Method of production: dry wastes, grind, make different-sized sieves, and use a compression molding machine.

Methods of characterization: compressive strength test, flame resistance, water and oil (SEA 20/50) absorption, and wear rate.

Methods for the making of natural fiber composites [89]:

a. Filament winding

b. Hand lay-up/spray consisting of two processes

Characterization methods of eco-friendly comfort performance composites by analytical techniques will be combined to study the topography, microstructure, chemical composition, and thermal stability of the comfort performance polymeric platforms, including SEM for morphology, EDX for elemental analysis, XRD, TGA, EMA, XRF, and profilometry.

- *Identifying the compounds in the raw components of wearing clothing items by* atomic absorption spectrometry (AAS) and atomic emission spectrometry (AES) with inductively coupled plasma (ICP) spectrometry

- *Physical properties*: bulk density and water absorption properties

- *Tensile properties*: test direction, fracture stress, fracture strain, and Young's modulus

- *Mechanical properties*: tensile strength and elongation break

- *Thermal properties by DTA and TGA analyses*

Measurements of comfort performance polymeric platforms by:

- *Comfort performance materials* tester according to the SAE J661 recommendation [88–97]
- Constant speed comfort performance material test machine
- Comfort performance material friction assessment and screening test (FAST) machine
- Single-ended full-scale dynamometer
- *Abrasive wear test* (*Taguchi method*)

Characterization of microstructures of comfort performant material surfaces/layers belonging to the wear comfort performant composites:

a. Comfort performance material surface morphology by scanning electron microscopy with energy dispersive X-ray microanalysis and electron microprobe analysis, and light microscopy (LM)

Phase analysis:

b. X-ray powder diffraction methods

c. X-ray fluorescence spectrometry

d. Thermal gravimetric analysis

Identification of:

1. Dynamic response: the structural morphology of comfort performant polymeric layers modifies according to the distinct superficial points and across specimen's thickness.
2. Comfort performant polymeric platforms status correlation: the engineering of comfort performant polymeric layers is in strong interrelation with parameters, such as interval of temperature, duration, and thermal behavior such as degradation and readjustment 11.
3. Elemental composition dependency: the content of polymeric surface and bulk varies; however, bulk amount determines the comfort performance of polymeric material thickness.

Evaluation of:

- Wearing performance characteristics
- Thermal stability and comfort wear properties
- Wearing system performance assessment
- Relationships between comfort performance materials and compositions of the comfort performance materials

5.2 For the self-cleaning polymeric platforms

1. Direct nucleation of pure and doped ZnO/TiO_2 nanostructures within various polymeric matrices/membranes, by chemical approaches (aqueous chemical growth, nonaqueous solution growth, and sol gel)

    - The nucleation method will be enhanced, in terms of type of substrate. The selection of the materials was made in terms of potential support for the photocatalytic ZnO layer (natural fiber polymeric support, synthetic fibrous matrices, and mineral fiber fibrous matrices) with different textures. Another criterion was the envisaged application; thus, materials with low optical absorption in UV-Vis region of the light spectrum were preferred.

    - ZnO growth parameters optimization for each support.

    - Mn, Ag, Cu, Ni, V, and S, with various concentrations, will be used as dopants in ZnO lattice in order to enhance its photocatalytic activity in the visible region of electromagnetic spectrum and tailor morphology.

2. Systematic study of structural, chemical, and physical properties of pure and doped ZnO nanostructured material grown on various polymeric supports and growth optimization with respect to the substrate and dopant

    - Pure and doped ZnO material characterization: study of topology of the coating involving optical and electron microscopy SEM, TEM, AFM, structure, composition and stoichiometry XRD, EDX, FT-IR, Raman, BET, and optical properties using UV-Vis spectroscopy

    - Coated polymeric support characterization testing: coating quality inspection using microscopic techniques, optical properties in the case of transparent textile substrates, adherence studies, washing tests, and hydrophilic behavior evaluation

3. Evaluation of the photocatalytic activity for each material on each substrate followed by optimization of the growth technique with respect to the photocatalytic efficiency

    - Preliminary photocatalytic tests employing wearing rubbishes from the inside of the polymeric layers.

    - Photocatalytic activity against various particles generated by washing and wearing. The tests employ various light sources. The tests were done for one contaminant at a time in synthetic air and water. The pollutant depletion was monitored for a reasonable time, and the results will be compared to establish which pair of photocatalyst substrate has the highest activity.

4. Integration of the optimum coated polymeric material in a novel laboratory small-scale prototype of a photocatalytic reactor, which may be the subject of a patent application

    - Design of small-scale laboratory urban air decontamination prototype reactor to host the best-engineered photocatalytic active material

- Execution of the designed prototype reactor for air decontamination and integration of the best photocatalytic active material
- Testing the prototype reactor for air decontamination and optimization with respect to application and aesthetical factors

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