Leather Sensors: Summit of Technological Excellence

Kalarical Janardhanan Sreeram[1], Vairapperumal Tamilmani[1], Sri Parasara Radhika[1], M Vedhanayakam Kabil[1], Selvam Sangeetha[1], Rathinam Aravindhan[2], Jonnalagadda Raghava Rao[1], Balachandran Unni Nair[1]

[1]Chemical Laboratory, CSIR-Central Leather Research Institute, Adyar, Chennai 600 020
[2]Leather Process Technology Division, CSIR-Central Leather Research Institute, Adyar, Chennai 600 020

Abstract

Leather is today a worldwide mark of performance. Common man is seeking technology support for identifying sudden changes in environment - easiest means of identification being 'color'. A color change reversible or irreversible, brought about by stimuli is classified as chromism. Major concerns in the near future include sudden or unexpected release or exposure to UV radiation, such as through ozone layer depletion, toxic or dangerous gases such as hydrogen, such as from a fuel cell and presence of solvents beyond permissible limits in industrial atmosphere. All these changes are detectable through changes in color and are known as UV-photo, gaso- and solvatochromism respectively. The ability to synthesize nanoparticles has kindled the application of chromism in day-to-day products. We report facile hydrothermal/sol-gel synthesis of three nano-sized compounds, in each of the three categories for potential applications in leather. As a UV-photo material, a rare earth carbonate (Ce/Eu) doped with terbium was synthesized. This compound provided a green or red luminescence under UV source. Mixed oxide of $PdO\text{-}TiO_2$ was synthesized by sol-gel technique. The oxide turns from light brown to dark grey when exposed to hydrogen gas. Synthesized iron(II) doped chromium(III) isocyanate complex demonstrated negative solvatochromism (such as pink, yellow and colorless in acetone, acetonitrile and water, respectively). It is expected that the use of such X-chromic materials as color component in leather finishing, would provide the user a visually monitorable change to his/her environment.

Keywords: Sensors, nanoparticles, chromism, leather finishing, doped systems; sol-gel synthesis

Introduction

Intelligent textiles, which can adopt according to customer preferences is slowly gaining prominence. One such is the chameleon fibre based textile that can change their color according to an external environmental condition. In general chemistry terms, this property is referred to as chromism, which can be classified according to the stimuli as photochromism (light induced), solvato chromism (solvent induced) or gasochromism (gas induced). To date, the most important commercially exploited ones are photo, thermo, electro, iono and solvatochromism. The advent of nanotechnology and our ability to synthesize doped nanoparticles has resulted in other forms such as gasochromism also to be exploited commercially.

Chromism dates back to several years. Solvatochromism, for instance was known since 1878. Predominantly based on the dyes used, the change in color is attributed to the difference in solvation energies of ground and excited states of the dye molecule as the solvent varied. However, since 1990 the applications of chromism has enhanced significantly. Classical example is the use of solvent dye markers for visual identification of fuel oil fractions, polymer characterization and as biological probes.

This paper narrows down to a feasibility analysis of employing chromism as feature of intelligent or smart leathers. The analysis will be restricted to photo, solvato and gaso chromism.

Photochromism: A survey of the literature indicates that a significantly large number of compounds which display photochromism fall under five major classes of compounds, viz., spiropyrans, specifically spiroindolinobenzopyrans, spironaphthoxazines, naphthopyrans, fulgides and diarylethenes. The chromophore, in most instances, seems to be employed as a dye rather than as a pigment, which makes the process of application in leather significantly challenging as dyed leathers are often finished using pigments.

Solvatochromism: Even in the case of solvatochromism, the chromophore in the presence of a solvent gets involved in certain electronic transitions, resulting in the change of color. Here again, the challenge to the leather researcher is to ensure that such a change is brought about through dye solutions or pigments employed in finishing. The selection process would be limited by the solubility of the binder etc. and its effect on the charge transitions responsible for change of color.

Gasochromism: Mankind in recent years and more so in the future would be subjected to exposure of several harmful gases. Compared to instruments, simple sensors, such as a leather jacket, which would undergo a change in color on exposure to such gases would be ideal. This paper narrows down to deploying hydrogen sensors on leather as this gas is steadily progressing to be an energy provider in automobile fuel cells. A safety mechanism on the leather which would report an accidental release of hydrogen from the fuel cell through a change in color has been envisaged in this work. Among the various types, of semiconductor sensors exhibit high sensitivity, fast response, long-term stability and potential for integration in hydrogen sensing performance. There are reports on the possible application of mixed oxides of Pd as a possible hydrogen sensor. Such oxides would posses a characteristic color, which make them an ideal candidate to be explored as a pigment in leather finishing.

This paper reports select examples of application of photo, solvato and gasochromic materials with potential applications in leather finishing. The changes in the color observed in the compound as well as on leather upon their application along with finishing chemicals is also reported. Though not conclusive, this paper thus opens up a new area of research where leather could now be looked up on as a sensor rather than just a fashion accessory.

Experimental Procedures

Synthesis of iron(II) doped chromium(III) isocyanate complex involves two steps

Synthesis of $K_3[Cr(NCS)_6]$

The reaction scheme is presented

$$KNCS + 6\ KCr(SO_4)_2 .12H_2O \longrightarrow K_3[Cr(NCS)_6].4H_2O + 2K_2SO_4$$

500 mg of $KCr(SO_4)_2.12H_2O$and 584 mg of KCNS was dissolved in 5 ml of distilled water. The solution was stirred under heating (50-60 ˚C) at 450 RPM for 2 h. The resultant product was dried to flakes by heating on a hot plate. The obtained flakes was dissolved in ethanol, so as to obtain $K_3[Cr(NCS)_6]$ in solution and the byproduct, potassium sulfate was removed as an insoluble precipitate. Ethanol was removed from the product by evaporation at 60 ˚C.

Synthesis of $[FeL_8][Cr(NCS)_6]$

1 M equivalence of $K_3[Cr(NCS)_6]$ obtained was dissolved in 2 mL of distilled water and 8 M equivalence of caprolactam (dissolved in 2 mL of distilled water) was added and stirred for 1min. pH of the solution was adjusted to 4-6 using 1M of acid or alkali. To this solution 1 M equivalence of $FeCl_2$ dissolved in 1.5 mL of distilled water was added slowly and stirring continued for 5 min or till a semi-solid product was obtained. The product was subsequently dried to powder form by treating in a hot air oven at 80 ºC.

Synthesis of terbium doped Cerium carbonate

Ce $(NO_3)_3.6H_20$ (0.039g) and $TbCl_3.6H_2O$ (0.0037 g) were added to a glass beaker containing deionized water and β-cyclo-dextrin (0.02g). The mixture was stirred at room temperature for 30 min until a clear solution was obtained. Na_2CO_3 (0.3mmol) was then added to the reaction mixture, during which the clear solution immediately turned turbid. The mixture was then stirred for another 3h, during which time a white precipitate formed. In a similar way terbium doped europium carbonate was also synthesized using europium oxide instead of cerium nitrate. The solid was collected by centrifugation, washed successively with deionized water and ethanol several times, and dried in air.

Synthesis of PdO-TiO_2 nanocomposites

Titanium (IV) butoxide was dissolved in isopropyl alcohol and this solution was allowed to stir for 30 minutes. Subsequently, 0.2 mL of concentrated nitric acid was added and stirred for further 10 minutes. A mixture of palladium chloride in isopropyl alcohol, raised to pH~ 10 by the addition of ammonium hydroxide was added gradually to titanium butoxide solution. Stirring was continued for 60 minutes. To this, 1 mL of deionized water was added drop wise so as to start the hydrolysis of the mixture and left to stir for 36 hrs. which resulted in the formation of gel. The solvent was removed and samples allowed to dry in an air oven at 60 °C. The dried product was calcined in furnace at 500 °C for 1 hour at the rate of 5°C/min which resulted in the formation of PdO-TiO_2 nanocomposites.

Particle size was measured using a Zetasizer Nano ZS using the principle of dynamic light scattering (DLS).

Results and discussion

Solvatochromism: The synthesized iron(II) doped chromium(III) isocyanate complex in different solvents such as water and DMSO exhibited color change from colorless to yellow and intensity size distribution was predominantly in the range of 100 – 200 nm in water and 200 – 500 nm in DMSO.

Photochromism: The small mean particle size observed for terbium doped europium (241nm) as compared to (462 nm) for terbium doped cerium as measured by DLS indicates that this size is thermodynamically more stable or that the ratio between the nucleation rate and the growth rate is larger for europium doped material compared to terbium doped cerium carbonates. Reduction in size also shows an enhancement in optical properties. Obviously, terbium doped europium results in intense luminescence.

Gasochromism: The synthesized PdO-TiO_2 nanocomposites when subjected to hydrogen gas changed color form brown to black, indicating their ability to serve as a sensor.

Applications on Leather: The synthesized products were evaluated for their application as a pigment in leather finishing. For this the retention of chromism observed at the native state, even in the presence of binder and other formulations conventionally employed in leather finishing was evaluated. A combination of soft acrylic resin binder and cationic polyurethane binder and the synthesized products in 1:1 ratio was optimized. The mixture was then subjected to ball milling for 4 hours at a speed of 700 rpm in order to achieve fine dispersion. The dispersion was then sprayed onto the leather through conventional methods.

Demonstration of solvatochromism: Application of solvatochromism was found to range from that of a solvent sensor to fashion oriented product, wherein designs could be generated on finished leather through selected area treatment with solvent of interest. For instance when the finish formulation containing iron(II) doped chromium(III) isocyanate complex was coated on the leather, the leather which was initially brown in color changed to yellow in areas exposed to DMSO (Figure 1).

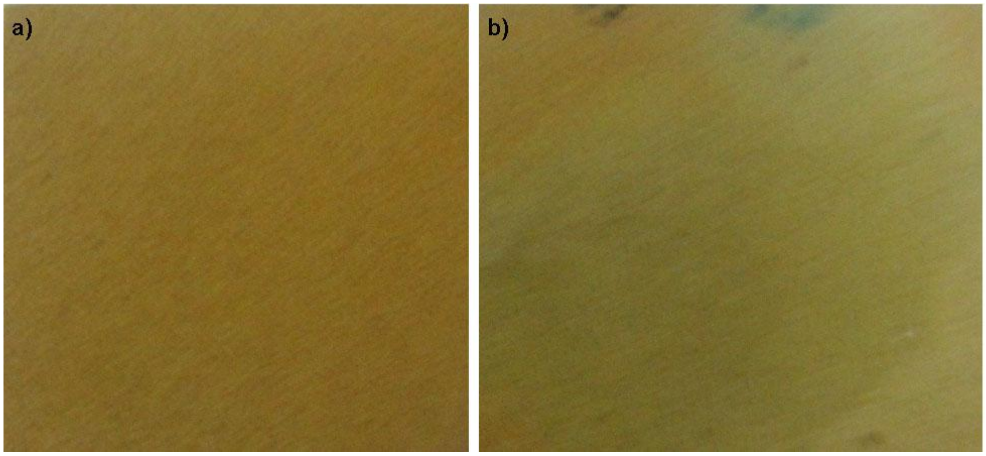

Fig 1. a) Leathers finsihed using formulation containing iron(II) doped chromium(III) isocyanate complex b) on exposure to DMSO

Demonstration of photochromism: The studies were carried on undyed crust. The color of the finished leathers (cerium and europium doped terbium carbonate pigment) appeared white in the visible light (Fig 2a-b), which on exposure to UV light at 254nm, shifted to fluorescent green and red respectively (Fig 2c-d).

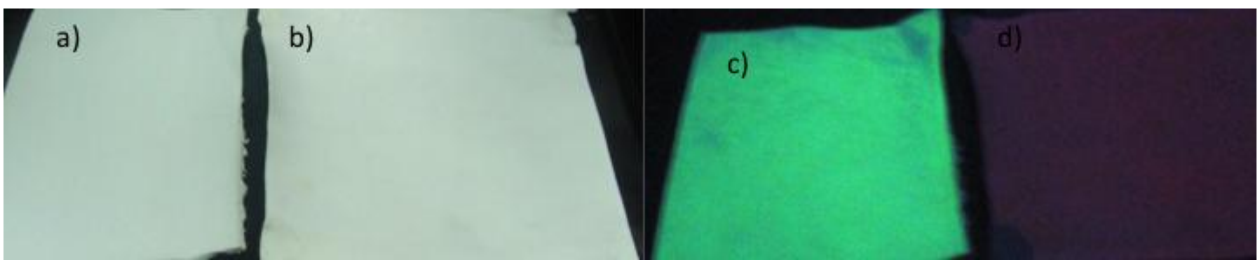

Fig 2. White crust leather finished with a) cerium terbium carbonate under visible light, b) europium terbium carbonate under visible light, c) cerium terbium carbonate under UV light @ 254 nm and d) europium terbium carbonate under UV light @ 254 nm.

Demonstration of gasochromism: Leathers finished with formulation containing the synthesized PdO-TiO_2 nanocomposite was exposed to hydrogen gas for 10 minutes. A color change from brown to intense black was observed (Fig 3).

Fig 3. Leather finished using formulation containing PdO-TiO_2 nanocomposite before (left image) and after exposure to hydrogen gas (right image).

Conclusion

This paper demonstrates the potential application of materials demonstration chromism as a pigment in leather finishing, through appropriate screening of formulation chemicals. This adds a new dimension to applications of leather, such as those in wearable sensor applications or transformation of the same into value added products such as intelligent leathers, which can change color according to customer preferences. Though only miniscule of the possibilities is demonstrated here, the enormity of the materials that demonstrate chromism available opens up a new avenue for leather.

Acknowledgement

The authors that the Council of Scientific and Industrial Research, New Delhi for funding the research program under XII Plan suprainstitutional project – S&T Revolution in Leather with a Green Touch. The authors VT and SPR thank the Department of Science and Technology, New Delhi for their research fellowships through the INSPIRE and WOS-A schemes. Authors remain indebted to Mr. RC Jayakumar for the assistance rendered in leather finishing.