Green Synthesis of Monodispersed Iron Oxide Nanoparticles for Leather Finishing

by

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Abstract

Industries worldwide, including leather, have had to phase out pigments based on lead, chromium(VI), cadmium etc. due to the toxicity associated with these transition metal ions. Coupled to this phase out is also a need to enhance the functional properties of the otherwise safe pigments, with low use, so as to avoid wastage. In this direction, the use of nano-pigments is slowly coming into vogue. This paper explores the advantages of replacing an otherwise popular brown pigment – the hematite (α-Fe_2O_3) with nanosized oxides in leather finishing. Any synthesis methodology for nanoparticles is sustainable only when green methods are employed for their synthesis. This work takes adequate care in employing an environmentally friendly methodology based on biocompatible polysaccharide – starch as a template. The advantages of this method, such as the monodisperse character of the oxide, low particle size, ability of the carbon residue from the template to aid easy homogenization of the pigment to the finish formulation have resulted in excellent covering of surface, improved levelness, no overloading of grain, excellent physical properties and ageing resistance.

Introduction

Pigment provides protection against rain, dirt, wear, UV radiation etc., in addition to covering the natural blemishes in the skin. It has been recognized that the cutting value of leather increases on account of pigments as they end up producing even shades. Leather finishing industry is facing challenges of replacing pigments containing metal ions such as nickel, chromium, lead and cobalt etc.[1] There is also a growing need to develop eco-benign processes for synthesis of pigments without toxic chemicals. Introduction of nanoparticles to the leather finishing sounds interesting and would play an important part in leather manufacture.[2]

Nanotechnology offers tremendous opportunity. Even though, there are pigment-free finishes for leather, a reasonable amount of pigment is being used in leather finishing.[3] Biological methods of nano pigment synthesis using microorganisms, fungi, plants or plant extracts and polysaccharides have been suggested as possible ecofriendly alternatives to chemical and physical methods.[4] The high surface energy of these particles makes them extremely reactive, and most systems undergo aggregation without protection or passivation of their surfaces.

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Several leading researchers have suggested bio-derived methods employing renewable material such as starch as reducing and passivation agents in the synthesis of nanoparticles. Through our concerted efforts methodologies to synthesize α-Fe_2O_3 nanoparticles by calcination method on polysaccharide template such as starch has been standardized.[5,6] The nanoparticles of α-Fe_2O_3 synthesized on starch templates are chemically stable, biocompatible and biodegradable.[6] The preparation of nanoparticles has been evaluated from a green chemistry perspective and the choice of the solvent medium used for the synthesis has been water, alongside an environmentally benign stabilizing agent starch. In a separate communication, the advantage of using starch over other polysaccharides such as alginate and chitosan has been highlighted. This includes a narrow particle size distribution and low polydispersity index. The mechanism of nanoparticle formation has been suggested to be one of Fe ion inclusion within the mesoporous framework of starch, resulting in a spatial separation of the ions prior to calcination.[7]

EXPERIMENTAL

Materials and Methods

All chemicals were procured from Sigma-Aldrich and used without any further purification. The source of iron for this study was confined to ferrous sulfate ($FeSO_4.7H_2O$) (Cat.No. F7002) and starch (Cat. No. 85642) was chosen as the polysaccharide template for evaluation. MilliQ water with a conductivity of 18Ω was used throughout. High temperature calcination reactions in 98% alumina crucibles were employed to synthesis iron oxide nanoparticles preferably as α-Fe_2O_3. For the preparation of molar solutions, the molecular mass of the polysaccharide-starch was determined through intrinsic viscosity measurements. Leather finishing chemicals used in this study are of commercial grade. The commercial pigment used in the study had a solid content of 25 to 27%.

Synthesis of α-Fe_2O_3 Nanoparticles

A stock solution of 0.2 mM starch was prepared. To 50 mL of the stock solution, requisite weight of ferrous sulfate was added under vigorous stirring to obtain a Polysaccharide:Fe mole ratio of 1:500, 1:1000, 1:1500, and 1:2000. Stirring was continued for 30 min to ensure complete complexation of the metal ion with the polysaccharide. The complex thus obtained was subjected to a two stage heat treatment, wherein a slow heating up to 100°C, ensured the removal of free water and the formation of a film of the complex, which was treated at high temperature (1000°C). The product was cooled to ambient conditions in the furnace itself and taken for characterization and application studies without any further processing.

Characterization of the Synthesized Nanoparticles

Powder XRD studies were carried out on a Rigaku, Miniflex (II) Desktop X-ray diffractometer and the diffraction patterns were recorded using CuKα (λ=1.5406Å), 30kV, 15mA with a scan speed of 4°C/min; step size of 0.05°. Morphology of products was analyzed by scanning electron microscopy (FEI Quanta 200 FEG High resolution Scanning Electron Microscope). Reflectance measurements of the synthesized samples were recorded with Perkin-Elmer Lambda 35 spectrophotometer.

Application Trials

The nanoparticles synthesized in this work were used as pigments in a conventional leather finish formulation, as such (Table I). For comparison purpose, an industrial grade iron oxide pigment having 25-27% of solid content was employed. Two controls with 40 parts pigment (same as nanopigment) and 80 parts pigment were developed. Comparison was made in terms of color coordinates.

TABLE I
Finishing formulation employed for iron oxide nanoparticles for leather finishing.

Base Coat		
Polyurethane binder	100 parts	
Penetrator	5 parts	
Water	50 parts	Apply Two cross coats and dry
Season Coat		
Pigment	40 parts	
Resin binder	80 parts	
Protein binder	10 parts	
Wax emulsion	10 parts	
Penetrator	10 parts	
Water	500 parts	Apply Four cross coats, dry
Top coat		
Lacquer emulsion	100 parts	
Water	50 parts	Apply Two cross coats, dry
The dried leathers were plain plated @ 60 bar, 80°C for 1 Sec		

RESULTS AND DISCUSSION

Unified green chemistry approach to the overall process of nanoparticle synthesis is extremely important. Only limited numbers of green chemistry approaches are reported. Most of the synthetic methods reported to date rely heavily on organic solvents.[8] This is mainly due to the advantage gained from hydrophobicity of the capping agents used in ensuring an aggregation free system. The polysaccharide template synthesis, especially starch as a template, for the synthesis of α-Fe_2O_3 nanoparticles was interesting. The extensive number of hydroxyl groups present in starch can, in the present case, facilitate the complexation of iron ions to the molecular matrix.[9]

The morphology of the synthesized α-Fe_2O_3 nanoparticles was measured using FESEM. The FESEM image (Figure 1) clearly showed the synthesized α-Fe_2O_3 nanoparticles to be spherical with particle size of around 48±5nm. The nanoparticles synthesized on starch template showed good uniformity and monodispersity. The starch template, through its hydroxyl groups, provides spatial separation of iron centre, adequate nucleation and growth and prevented the aggregation of the nanoparticles. The particles produced are stable and comparable in size and polydispersity to those produced using typical methods. The combination of solvent (water) and renewable reactant (starch) presents a wide range of possibilities for the further development of green nanoparticle synthesis. The low particle size/size distribution with starch template may be due to the presence of large number of hydroxyl groups present in the structure of starch which keeps the metal ion centers spatially separated and ultimately helps to form uniform spherical shaped α-Fe_2O_3 nanoparticles.

The crystallinity and phase identification of the synthesized α-Fe_2O_3 nanoparticles were carried out using XRD. Figure 2 shows the XRD pattern of the synthesized α-Fe_2O_3 nanoparticle on starch template. The XRD peaks clearly show good crystallinity and matched well with that of standard hematite (JCPDS 33066). No or very few impurity peaks were observed. The diffraction peaks could be indexed to rhombohedra structure of α-Fe_2O_3 (Space group: *R-3c*), which are in good agreement with literature results (JCPDS 33-0664). The crystallite size was found to be 31±3nm using the Debye–Scherrer formula.[10] Differences in crystal size obtained by Debye-Scherer approximation and FESEM analysis could be attributed to the fact that the Scherer formula only provides the lower limit on mean crystalline size.

Each color in the CIELAB color space has a unique location defined by its Cartesian co-ordinates with respect to the axes L, a* and b* where L is the degree of lightness and covered a range from white (100) to black (0) along a gray scale, a* is the degree of redness and greenness and b* is the degree of yellowness and blueness.[11] L, a*, b*, parameters of α-Fe_2O_3 nanoparticles on starch template was found to be 38.24, 20.74 and 24.33, respectively. This shows that the α-Fe_2O_3 nanoparticles are reddish brown in color.[12]

From TGA measurements, the weight percentage of iron oxide in the residue was determined as 5.4% by the Peniche method,[7] given by the formula, $\frac{R_q}{\Delta W_q} x\Delta W_m + M = R$, where Rq is the residue (wt %) at 800°C of the polysaccharide alone, ΔW_q and ΔW_m are weight-loss percentages for the starting polysaccharide and the iron-polysaccharide composite in the interval of initial and ending decomposition temperature respectively, M is the weight percentage of α-Fe_2O_3 in the polysaccharide and R is the residue at 800°C (in wt %) for the α-Fe_2O_3-polysaccharide.

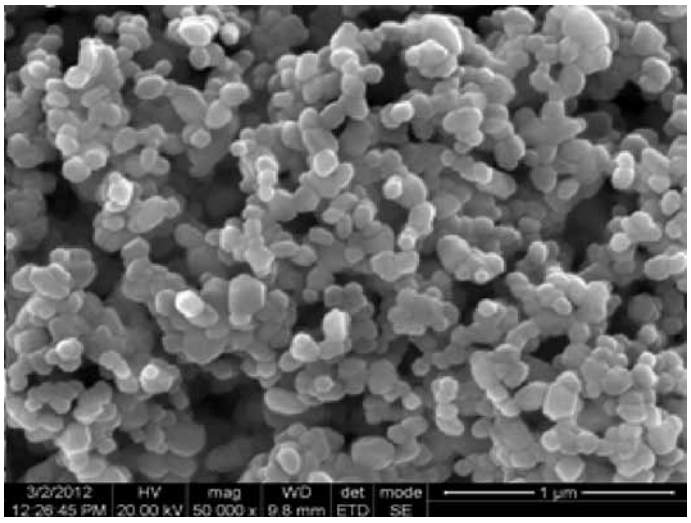

Figure 1. FESEM images of the synthesized α-Fe_2O_3 nanoparticles.

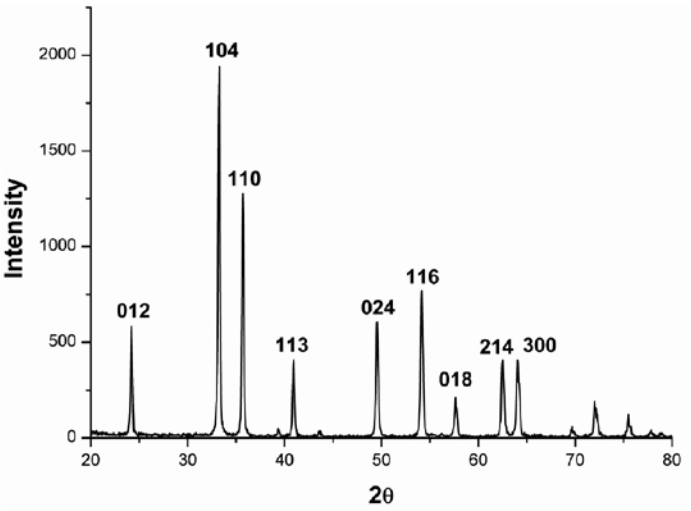

Figure 2. XRD pattern of the synthesized iron oxide nanoparticle on starch template.

A decrease in the iron oxide content with starch template indicates the enhancement in spatial distribution of the samples during complexation process and thus in the size and size distribution of the iron oxide nanoparticles generated. The increase in residue weight% of iron-polysaccharide complex, which was much higher than the stoichiometric weight of α-Fe_2O_3 expected, indicating that the residual carbon from the polysaccharide contributed to the weight of the total residue.

The synthesized iron oxide nanoparticles when used as pigments in finishing of leather exhibited a good compatibility to the medium. Excellent covering of surface and improved levelness, no overloading of grain, excellent physical properties, ageing resistance and miscibility with water were observed. Due to the high surface to volume ratio of α-Fe_2O_3 nanoparticles, only small quantities of the α-Fe_2O_3 nanoparticles were required compared to the conventional pigments. However, pigment particle size, size distribution and shape plays an important role in the rheology of the coating formulation. Both low shear and high shear viscosities are influenced by the particle size. Further, monodisperse particles, such as that of ours, produce higher viscosity than polydispersed systems.[13] It thus becomes imperative to adjust the finish formulation to meet the demands of such particle usage. For this, for the same formulation, the pigment quantity was varied. Leathers finished with nanopigment (40 parts) had a closer match to that with 80 parts of commercial pigment in terms of color values (Table II), indicating that only lesser quantity of pigment is required for the same covering when nanopigments are employed. Figure 3 shows the leather finished using the synthesized α-Fe_2O_3 nanoparticle pigment, in comparison with that employing 80 parts of pigment. The resulting leather showed better covering and uniform color throughout leathers. The wet and dry fastness of the finished leather showed a grey scale rating of 4/5. The film adhesion test results showed that the film formed was strong. The leathers passed the perspiration resistance test as well.

CONCLUSIONS

Nano colorants of α-Fe_2O_3 nanoparticles are the new class of materials that receive great attention both in academy and in industry. They have been utilized as replacement for traditional to toxic chemicals such as chromium, lead and cadmium. Green method of synthesis has been used to prepare the new class of α-Fe_2O_3 nanocolorants. Nano pigments of α-Fe_2O_3 were synthesized with a size of 48±5nm. α-Fe_2O_3 nanoparticles exhibited a good compatibility to the medium,excellent covering of surface and improved levelness, no overloading of grain, excellent physical properties, ageing resistance and miscibility with water were observed.

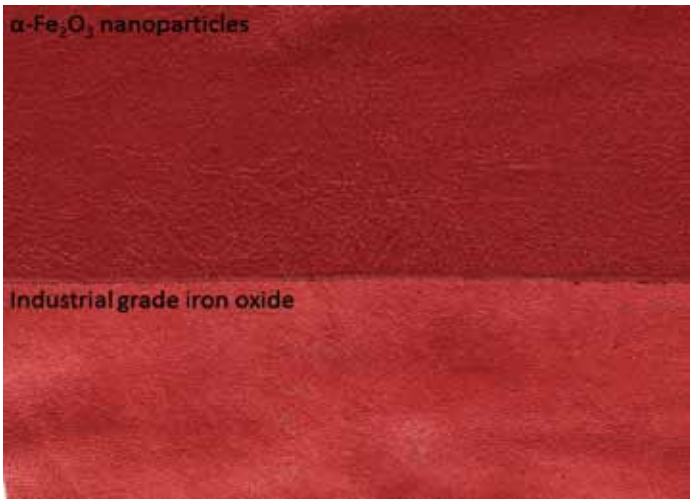

Figure 3. Photograph of leather finished with α-Fe_2O_3 nanoparticles.

TABLE II
Color coordinates for leathers finished with α-Fe_2O_3 nanoparticles and industrial grade iron oxide pigment.

Finish Method	L	a*	b*	DE
α-Fe_2O_3 nanoparticles (40 parts)	33.9	19.6	20.1	-
Industrial grade pigment (40 parts)	42.4	19.4	10.3	12.97
Industrial grade pigment (80 parts)	36.8	20.0	13.2	7.5

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