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Hybrid Composites: amalgamation of proteins with polymeric phenols as a multifunctional material for Leather Processing.

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Abstract

In recent years blending various proteins waste resulted in the development of new hybrid composites displaying innovative functionalities with superior physico – chemical properties. One of the options being explored in this work is the suitable modification of collagen hydrolysate (waste from leather industry), along with degraded black liquor from paper and pulp industry. In detail, the preparation of hybrid composites from collagen hydrolysates and degraded black liquor of different pH (14 and 7) was made through simple process. The characteristic features of composites were thoroughly investigated by Fourier transform infrared spectroscopy (FTIR), Malvern Zeta sizer and Scanning electron microscope (SEM). The multi functionality of the hybrid composites provided opportunity to utilize this composite as a retanning agent in leather processing. The composites also exhibited enhanced functional properties as well as improved dyeing thus making it as a better retanning agent. The composites treated leather shows good softness, improved belly filling, and high strength, with uniform dyeing. Hence, the potential use of multifunctional hybrid composite has gained more importance in economic processing.

Index Keywords: Collagen hydrolysate, Black liquor, Leather retanning, Dyeing, Economic process, Hybrid composites.

Introduction

Nowadays, a great deal of research has been devoted to the design and fabrication of hybrid polymeric composite material with tailored physical and chemical properties [1]. By-product recovery is becoming a challenge for sustainable growth[2,3]. The proper modification and utilisation of various waste needs to be encourage for low environmental pollution[4]. Composite is considered to be any multi- phase material system that exhibits a combination of properties that makes the composite superior to each of the individuals[5]. The design of bio-based composites is an interesting strategy for lowering the environmental impact of the composites industries while maintaining economic competitiveness[6]. Amongst all the by-products, collagen hydrolysate, which is obtained from the waste generated at different stages of leather processing act as crucial material for hybrid preparation[7]. The hydrolysed product obtained from collagen, as collagen hydrolysate made up of various amino acids with different functional groups[8]. Collagen containing leather trimmings waste emerged as a resource with a significant potential to be employed as a raw material for the preparation of gelatin[9], collagen films[10], production of energy by biomethanation[11], composite films[12] and finally as a syntan for leather processing[13]. Collagen hydrolysate was not to be suitable for direct application as retanning agent due to its poor interaction and filling in nature[14]. Despite the limitations stated above, it has been currently used in diverse fields, including food[15], pharmaceuticals[16], and biomedical[17,18]. In order to obtain collagen hydrolysate from tannery waste, a hydrolysis was processed by the addition of acid[19], alkali[20] or enzymes[21] . The alkaline treatment is more suitable than the others to obtain hydrolysates with suitable properties. To address the limitation of improper filling, further modifications of collagen hydrolysate as composite was designed. To augment the physical property of the collagen hydrolysate, it is essential for further modification with high molecular weight polymeric materials. But, up to now, only a small part of skin waste was utilized for further processing, and most of them were disposed as waste[22]. Therefore, the exploration of new approaches of reusing skin waste is a significant work in view of both full utilization of biomass resource and alleviation of environmental impact. The quest for the fabrication of multifunctional materials with interesting morphologies and tailored properties is the key driving force for the development of hybrid composite material[23]. In this concern usage of polymeric black liquor from paper and pulp industry will act as a key role for modification of collagen hydrolysate for composite. The complex aqueous nature of black liquor constitutes both organic and inorganic materials[24]. The organic materials were from wood or fibrous plants (lignin,

polysaccharides and resinous compounds of a low molar mass) and inorganic compounds (mainly soluble salt ions)[25,26]. As reported by Marcelo[27], Frederick[28] the black liquor containing lignin and polysaccharide macromolecule conformation is directly related to the pH environment.

The physical properties of the black liquor were entirely dependent on the chemical composition of the black liquor at different pH conditions. Among various functional groups in black liquor, phenolic and aliphatic hydroxyl groups are the most abundant reactive sites responsible for more number of hydrogen bonding with collagen of leather matrices[29] .The black liquor which consists of large polymeric materials[30, 31] can able to give fullness properties, like polymeric complexes of vegetable tannins[32]. The collagen hydrolysate along with the polymeric material with additional functional property will act as a hybrid composite with multifunctional property[33] and can be utilized as syntan for leather processing[34]. Until now, more work has been done to investigate the retanning property of collagen hydrolysate with and without modification[35]. However, there are relatively few studies on the retanning property of collagen hydrolysate –black liquor composite, as well as their effects on the final leather properties. In this work hybrid composite was made from collagen hydrolysate and black liquor at different pH of 7 and 14. We expect that this composite material will exhibit superior properties[36], which is not observed in the individual component. To investigate the effect of this composite on the final leather properties, this composite was utilised as a retanning agent during the post tanning process. The results reveal that as prepared composites exhibit enhanced functional properties as well as improved dyeing, to the end it can be served as an ideal material for better retanning. Similarly the composite retanned leather shows good softness, improved belly filling and high strength with uniform dyeing.

Materials

Trimming waste was collected from the tannery for preparation of collagen hydrolysate, raw degraded black liquor was gifted from paper and pulp industry, commercial wet blue was chosen as a raw material for retanning trials, sodium hydroxide was purchased from Hi-media, chemicals used for processing were of commercial grade, and the analysis of spent liquor were made through using analytical grade chemicals.

Experimental section

Preparation of collagen hydrolysate

The collagen hydrolysate was prepared by simple alkaline treatment by using various concentrations of alkali to optimize the required material. Trimming was treated with various concentrations of NaOH in reflux process at 90˚C for 5 hours. After the completion of the reaction, the solutions were filtered through Whatman No.1 filter paper to separate unhydrolysed residue from collagen hydrolysate solution. The clear filtered solution was taken for further analysis. For this, 100 g of trimming (dry weight) was added to 100 mL of sodium hydroxide solution varying from 0.5M- 5M concentration and heated at 90˚C for 5 hours.

Acidification of black liquor – black liquor Preparation at various pH

Concentrated black liquor in aqueous media obtained through conventional Kraft process contains 60% degraded black liquor and 40% inorganic (commercial paper and pulp industry). The pH of the black liquor obtained initially was 14. The various inorganic present were sodium carbonate, sodium sulphate, sodium sulphide, magnesium sulphates, silica, sodium hydroxide, calcium hydroxide, etc. Initially the highly alkaline concentrated black liquor was neutralized by adding continuous drop of sulphuric acid to reach the pH 7 under constant stirring. Black liquor at pH 14 and pH 7 were taken for composites preparation with organic of 60% and 40% respectively. The molecular weight of the black liquor at pH14 was 6 KDa and after acidification the molecular weight was reduced to 1.2 KDa.

Preparation of hybrid composites

Hybrid composites were prepared by blending the waste probably lignin containing black liquor and collagen hydrolysate in 1:1 ratio based on the percentage organics through the simple route. Initially collagen hydrolysate was placed magnetically stirred 250 ml two

neck reactor immersed in a water bath, where temperature was maintained about 40˚C. The reaction was carried out in a water medium. The one neck was fitted with a dropping funnel containing the black liquor and the other neck was sealed with a glass stopper. The black liquor at pH 7 was then added dropwise until a brown colour solution was formed and the mixture was stirred for 4 h at 40˚C. The composite prepared by using black liquor at pH 7 was mentioned as a composite 1 for further. Similarly the same process was carried out for black liquor at pH 14 (composite 2). After the preparation of composite the product was taken for spray dried to make into powder.

Appraisal of using hybrid composites in leather processing

To evaluate the prepared composites in retanning process, the shaved wet blue (chrome tanned leather) of thickness 1.1 mm was chosen as a raw material for further processing. The shaved wet blue was loaded into the drum along with 100% water based on shaved weight. Drum was rotated for 10 min and then drains the water. After that the neutralisation was carried out by adding the mixture of 0.5 % sodium formate, 1% sodium bicarbonate and 30% water into the drum. The pH of the wet blue was adjusted to 5 by controlled addition of bicarbonate in a three instalment at an interval of 10 min. This is followed by rotation of the drum for 30 min to get complete pH distribution over the entire leather substrate and the water was drained out. For matched pair comparison the above mentioned leather was cut into the two halves along the backbone, in which a right half was chosen as an experimental and the left half was taken as a control. For control the retanning was done with 10% offer of direct black liquor 7 or black liquor 14 or conventional syntan. Similarly for experimental the corresponding cut piece was loaded with 10% offer of composite 1 or composite 2. After retanning the conventional dyeing, fatliquoring and fixing of chemicals was followed by using standard procedure to make crust leather. Finally the crust leathers were set twice, hooked to dry and staked.

Instrumental Methods

The hydrodynamic diameter of particles in solution was determined using Dynamic Light Scattering (DLS) with high performance particle sizer (Zetasizer Nano series, Malvern) at 25˚C .This instrument operates at 4 mW He-Ne laser power, scattering angle of 175˚C and wavelength of 633 nm. The obtained particle size was an average of five separate measurements, and the measurement uncertainty is indicated as standard deviation.The functionality of the composites was studied using FTIR spectrum. The spectrum of the

sample was recorded on ABB MB3000 Fourier transform infra-red (FTIR) spectrometer. All spectral analysis were performed with the resolution of 4 cm^{-1} and recorded at 45˚incident angle using calcium fluoride crystal plate in the region 4000 to 6000 cm^{-1}. The nature of crust leather prepared from hybrid composites were analysed in detail. The surface morphology of the crust leather and the composites were investigated by scanning electron micrographs (SEM with a Hitachi-SU6600 operating at 15.0 kV). The strength properties of the crust leather (tensile and tear) was performed by INSTRON universal testing machine. The organoleptic properties like softness, fullness, grain smoothness, grain tightness, and general appearances by hand and visual examination. Three experienced tanners rated the leathers on a scale of 0-10 points for each functional property, where higher points indicate better property. The tanners evaluated the dyeing characteristics viz., uniformity of dye, shade intensity L*, a*, b*, c*, h* differential dyeing for both experimental and control crust leathers. The porosity of the leather was measured by using PMI capillary flow porometer. The softness of the leather samples was analysed by ST 300 softness tester. All UV-Vis absorption Spectra of samples were recorded on a Perkin Elmer Lamba 35 spectrophotometer.

Results and discussion

The protein hybrid composite was prepared through simple route by utilising the solid residues obtained as a by-product of leather and paper-pulp industry. The morphology and functionality of prepared hybrid composites were investigated by using various techniques like SEM, DLS, and FTIR. Owing to the presence of more functional group it is conceivable that hybrid composite will act as a retanning agent in leather processing. The final properties of the composites treated leathers were analysed and results are compared with control leather. The functionality of hybrid composite and their influence on final leather properties were thoroughly investigated and were presented below.

Dynamic Light Scattering Measurement

The hydrodynamic diameter of the particles was accurately measured by Malvern Zetasizer. The size distribution graph of the collagen hydrolysate prepared from different percentage of alkali was shown in the Fig. 1 .The hydrodynamic diameter of the collagen hydrolysate reveals that the particles are distributed in various sizes depending upon the concentration of alkali. In case of concentration of 0.5 M (Fig. 1a) and 1.5 M (Fig. 1b) NaOH the particles are distributed in higher range with larger particle size because of the improper hydrolysis by

insufficient concentration of alkali. The optimal concentration of 2.5 M (Fig. 1c) shows the narrow distribution of particle size which can easily penetrate into the leather substrate during retanning process. The higher concentration of 5M NaOH (Fig. 1d) increased the high degree of hydrolysis leads to very smaller size particles with broad distribution. From the measurement of particle size a concentration of 2.5 M is optimal for collagen hydrolysate preparation. So collagen hydrolysate preparation by 2.5 M NaOH was considered as an optimal sample for next stage of composites preparation.

Before the analysis of composite, size measurement of another ingredient of black liquor at different pH is important to know the influence of polyphenols in average particle size of the composite. The black liquor of pH 14 and acidified black liquor of pH 7 was analysed for particle size distribution. The size measurement reveals that the particles are distributed in average range of 250 nm in case of pH 7 and larger particle size of 600 nm in case of pH 14 as shown in the Fig. 2 a and b respectively. The variation in the size may be attributing to the presence of lager size phenolic compounds get break down into smaller size because of its acid addition. Further the particle size of the hybrid composite showed the narrow range of size in wide distribution. The particles were covered in the range of 100 – 1000 nm which was much suitable for filling nature of retanning agent. The particle size is made into fit for leather processing because of its narrow size through composite preparation.

Scanning Electron Microscope

The high magnification SEM image (Fig. 3) of the black liquor showed that obtained sample consists of uniform spherical spheres with an average diameter of 7.5 μm. The surface topography of the sample shown in the Fig. 3a reveals that the surface of the hollow sphere is coarse in texture. The magnified SEM image of broken hollow sphere is shown in the Fig. 3b which indicates the hollow structure of the obtained sphere with inner crystalline material loosely deposited on the surface. The clustered multiple porous structure of the sphere shown in the Fig. 3 (c and d) implies applications of the hollow sphere with average size distribution as retanning agent because of easier penetration of small molecules into the porous leather substrate[37, 38].

Further the comparison of topography of composites as well as individuals have been investigated. The morphology of spray dried black liquor at different pH was dominant by spherical particles with average diameter of about 10-20 μm, and some broken spheres could also be observed from the image (Fig. 4 (a and b)), confirming the existence of hollow

interior inside the spheres. The key advantage of spherical particle shape lies in imparting unique benefits to composites[39]. Furthermore, they have greater dimensional stability which helps in uniform distribution of particles over the substrate. The overall SEM image of spray dried powder of black liquor shows the relatively smooth surface with porous structure. Similarly Fig. 4 (c and d) display the structure of spray dried powder of collagen hydrolysate. In addition, it is also observed that the hygroscopic nature of collagen hydrolysate showed undefined arrangement and shape of the particles. The morphology of prepared composites was shown in the Fig. 4 (e, f, g and h) and it displayed clustered particles built over the polymerised matrix. It should be noted that composite composed of densely packed hollow spherical particles randomly distributed in the porous matrix. However, both the composites do not display much difference on their structural morphology. In general the porous material as substrate modifiers facilitates the more uptake of chemicals used in the processing. Therefore, highly ordered structures are desirable for practical leather processing application as a retanning agent.

FTIR Analysis

In order to investigate the functionality with interaction between the Collagen hydrolysate and the polymeric black liquor, FTIR analysis was carried out. The FTIR spectrum is presented in the Fig. 5. The characteristic absorption bands of pure collagen hydrolysate and their corresponding composite are shown in the Fig. 5a. For Collagen hydrolysate, the characteristic NH stretching of amide A appeared at 3,600 cm^{-1}, N–H stretching of amide B appeared at 2919cm^{-1}, the absorption band at 1,662 cm^{-1}(amide I, C=O stretching), 1,563 cm^{-1}(amide II, N–H bending and C–N stretching) and 933 cm^{-1} (amide III, CN stretching and N–H bending) for hydrolysate[40, 41]. However the characteristics absorption band of collagen hydrolysate as a composites appeared at 1600 cm^{-1},1480 cm^{-1}, 1099 cm^{-1} in Composite 1 and at 1584 cm^{-1}, 1407 cm^{-1}, 1114 cm^{-1} in composite 2. It can be inferred that the shifting in the amide bonds confirms the mutual interaction between the collagen hydrolysate and black liquor. The shift in the characteristic absorption band at 2922 cm^{-1} in composite 1and 2973 cm^{-1} in composite 2 confirms the hydrophobic interaction between the protein hydrolysate and black liquor.

For pure black liquor (Fig. 5b) the absorption bands at 1605 cm^{-1} and 1517 cm^{-1} were characteristic of aromatic phenyl ring vibration of polymeric macromolecules. 3455 cm^{-1} stretching vibrations of alcoholic and phenolic OH groups involved in hydrogen bonding.

The small protrusion at 1644 cm^{-1} which is indicative of stretching vibrations of C=O bond at β location and in COOH group. The absorption band at 1116 cm^{-1} deformation vibrations of C-H bonds in associated with aromatic rings. Compared to black liquor at pH 7 (acidified black liquor) there is a difference in the characteristic band of composite 1shown in Fig. 5c indicates the appearance of interaction between the polymeric black liquor and Collagen hydrolysate. The characteristic band at 1570 cm^{-1},1440 cm^{-1},1096 cm^{-1},3432 cm^{-1} shifted to 1600 cm^{-1},1480 cm^{-1},1099 cm^{-1},2922 cm^{-1} . These demonstrate that C=O, phenolic hydrogen bonds from black liquor responsible for interaction with collagen hydrolysate.

For black liquor alone (pure black liquor) system it shows the characteristics peak at 1099 cm^{-1},1370 cm^{-1},1500 cm^{-1} shifted to 1114 cm^{-1},1407 cm^{-1},1584 cm^{-1} in case of composite 2 Fig. 5d. The absorption peaks at 1600 cm^{-1}, 1184 cm^{-1} also get disappeared. These demonstrated the hydrogen bonding interaction between the phenolic polymeric macromolecules with protein rich hydrolysate.

Likewise the characteristic band of composites reveals that the protein part of collagen hydrolysate was rich in glycine, proline, hydroxyproline, glutamic acid and alanine[19]. Similarly the black liquor which was rich in more aromatic polymeric components[25, 42], could leads to many intermolecular hydrogen bonds between the OH of the black liquor and the NH_2, COOH and O=C-N-H groups in the collagen hydrolysate. The synergetic and modifying effect of collagen hydrolysate could be due to the hydrogen bonding interaction between the oxygen containing groups (C=O) in black liquor and (N-H) nitrogen containing groups in collagen hydrolysate. The composites are well characterised for the presence of functionality and size range which is suitable for leather retanning application. The presence of more hydroxyl group will help for large number of hydrogen bonding and the protein functionality will lead for protein - protein interactions.

From the whole, observations conclude that the high functional with average size of the composites are in fine distribution. The superior property of the composite open the way for utilise as a retanning agent. In leather processing instead of commercial syntan the composites were used as retanning agents and its properties are evaluated in detail. The black liquor alone does not have much interaction with the protein substrate, to improve its interaction behaviour the composite has made from collagen hydrolysate as a hybrid composite. The multifunctional properties like perfect size distribution for filling and broad range of available functional groups in the composite may have a chance to address the

problem of commercial syntan with filling alone. Herein the attempt has been made to utilize this composite as filler cum retanning agent in leather processing. The composite was applied in the retanning stage of leather processing, the characteristics of the leather was analysed by various technique presented below.

Scanning Electron Microscope of Crust Leather

The Scanning Electron microscope is an effective tool to analysis the morphology, surface topography like orientation of grain, surface smoothness of the material[43]. In nature leather texture shows variation in structural orientation depends upon the chemicals input while processing[44]. Here the hybrid composites were used as filler for chrome tanned leather to fill up the voids space between the fiber bundles during post tanning process. The Scanning electron microscope of the crust leather prepared by using conventional syntan as a control leathers and hybrid composite1 and 2 as an experimental leathers showing the grain surface at a magnification of 200X are presented in the Fig. 6 (a), (c) and (e) respectively. It has been clearly seen that the grain surface of the experimental leather displays the more uniform surface with closed pores by deposition of hybrid composite. These demonstrate the even filling of voids space by hybrid composites. The close inspection of the grain surface of control leathers reveal that the surface with uneven surface morphology with fine deposition of small foreign particles which is not visible in the experimental leathers. Control leathers showed less filling than the experimental leathers due to the poor exhaustion of syntans by reversible interaction with the collagen fibres. On the other hand the experimental leathers exhibit more smoothed surface by the fine deposition of composite over the surface. The hybrid composites contain highly charged amino acid side chains, which can undergo protein-protein interaction leading to effective filling rather than deposition. The cross sectional image (Fig. 6 (d) and (f)) confirms the compactly organised fibre bundles and positive morphological alterations induced by the irreversible composite interaction. The strength properties of the fibres can be understood from the structural arrangement and packing of the fibre matrix. The highly packed structure of the experimental leathers showed high strength properties compared to voids containing control leathers. From the cross sectional image (Fig. 6 (d) and (f)) it can be seen clearly that fibres are coagulated by composite reinforcement tends to increase the strength property. While in the case of control leather (Fig. 6 (b)) it shows voids space by improper filling. We can assert that the structural modification detectable by SEM indicate high compact fibre bundles, smoothened surface,

and uniform filling over the entire surface of skin matrix, when treated with the hybrid composites.

Air Permeability and Porosity

Further the filling nature of composites was studied by compared permeability measurement of leather substrate with and without treatment. The permeability is the one of the most precious physical property of the leather which may greatly affects the breathability and the comfortable feelings of leather goods[45, 46]. The presence of plenty capillaries among the collagen fibrils with rich hydrophilic groups endow leather with high water vapour permeability[47]. The permeability alteration induced by process modulation may favour or unfavour to end use. The chemical usage may modulate the permeability during the process[48]. The permeability of leather may calculate from the flow rate of dry sample and pore size distribution from difference in the wet and dry path for air passage which depends upon the flow rate. The amount of water passes through the porous nature of the leather. Here the amount was measured through the difference in flow rate. The permeability indirectly relates the ability of the composite to evenly fill the voids present in the leather substrate. The permeability of the leather greatly reduced after treatment with the composite at the same without damage to the end use shown in the Fig. 7. Thus it effectively proves the filling nature of the composite. The traditional problem lies in collagen hydrolysate of poor filling was overcome by preparation of composite from waste. Similarly the pore size distribution of composite treated leathers are compared with control leathers, and the results shown in the Fig. 8 reveals that the positive modulation in the pore size. The decreases in the number of larger pores (shown in the Fig. 8b and 8d) in case of composite treated leather indicate the effective filling of the leather substrate while compared to control leathers (shown in the Fig. 8a and 8c).

Strength Characteristics

The tensile strength property means the resistivity of the fibres against the force input[49]. If the fibres are strongly coagulated each other the resistivity against the force is higher and on the other hand, if the fibres tends to break easily which is indirectly meant for less force resistivity[50]. Here to investigate the strength property of the leather affected by hybrid composites. The tensile property of composite as well as control leathers is analysed and shown in the Fig. 9. The black liquor treated leather shows less strength property because of poor coating over the surface. After adding the additional functional sites by collagen

hydrolysate uptake of chemicals were improved and showed high strength property. Which is attributed to the reason that more interacted composite sitting over the surface leads to high strength. From the graph it was inferred that for the composites treatment, there was an increase of strength. While in the case of black liquor alone it does not show much difference in their strength property when compared with standard requirements. The strength property of the as prepared composite treated leathers was enhanced by synergetic effect of phenolic and protein portion present in the composite. The tear strength is perhaps analogous to "toughness" in materials[51, 52]. The tear strength of hybrid composite treated leathers is likely to be higher than found in the control leathers. The reason for high tear value could be due to the high compactness established by hybrid composite. In general less crosslinking mechanism of collagen hydrolysate impute to the poor strength property. Herein the presence of polyphenols act as a mediator to enhance the uptake of hybrid composite which will greatly support compact fibre orientation leads to high strength property.

Colour Measurement

Surface colour photograph of the crust leather prepared from composite syntan. The Fig. 10(a and c) represents the surface colour (gran side) of the dyed crust leather prepared by using the different hybrid composites (composite1 and composite 2). Similarly the lighter shade was obtained for black liquors (acidified and pure) treated leathers (Fig. 10 (b and d)).From the Fig. 10 it is clearly shown that the presence of composite with multifunctional side group act as an additive for the development of darker dye shade.

Here the percentage of dye offer has varied to know the effect of composite in dyeing process. As per visualization the composite presence makes the leather darker with high exhaustion as shown in the Fig. 11.

The effects of complexation of composite with dyes are further investigated by varying the percentage dye offer from 1 to 3% during the dyeing process. The surface colour of the leather treated with different dye percentage was shown in the Fig. 11 that's also showed the good shades without any negative impact on surface dyeing with minimum percentage of dye. Herein, the additional functional sites provided by the composites enhance the dye uptake even at low percentage of dye compared to conventional syntans. As the whole dyeing property of the leather get improved because of using this composite in leather colouring stage. The hybrid composites act as an additive for development of dye shade by providing additional functional sites. As a part of it colour coordinates are measured to

further confirm the darker shade surface[53] by L*, a*, b* measurements tabulated below in the table 1. The higher the hue value, higher the surface shade, as per the above discussion higher hue value obtained for hybrid composites treated leather. Similarly the L*, a*, b* value assigned as a darker shade in case of leather made from hybrid composite 1, while compared with lighter shades control leathers. Finally, the registered higher hue value and L*, a*, b* measurements on the surface further proven the positive impact of hybrid composites over the dyeing.

Higher the rate of physical absorption, higher the rate to leach out so it is necessary to have less leaching of dyes over a period of time. The amount of unbound dyes leaching from the leather was calculated by using maximum absorbance of dye in UV Visible spectroscopy[54]. Interestingly, there is no substantial amount of leaching was observed. The percentage and values of dye exhaustion were shown in the Fig. 12. It is seen from the Fig. 12, the presence of composite improved the uptake of dye as compared to control and black liquor alone (pH 7 and pH 14)

The minimum leaching in case of hybrid composite treated leather may be attributed to the reduced repulsion between the equal functional group of the protein (leather substrate) and hybrid composite. Even though the repulsive force aroused between the proteins, they hold together physically through absorption. At that stage the uses of anionic dye will attracted to both of them equally and thus reducing their repulsion, as a net result uptake of dye gets increased.

Organoleptic Properties

The prepared composite treated substrate showed enhanced property can be attributed to the suitable size range and more outer reactive functional group[34, 55]. The organoleptic properties of the leather substrate are measured by the experienced tanners and the values are plotted as a graph shown in the Fig. 13. As expected the high value of property were registered for composite treated leather with the good softness and grain smoothness even at lower quantity of the hybrid composite. The porous structure revealed from SEM image of the hybrid composite responsible for increases in smoothness of the grain with less uneven deposition over the entire surface of the leather. The softness measurement of both control and experimental leathers are tabulated in the table 2. The value reveals that the more softness value was registered for the composite 1 treated leather when compared to control leathers. The presence of lower molecular weight compounds in the composite 1 show uniform surface

coating leads to more softness property. Herein leather treated with composite is considerably softer with enhanced organoleptic properties.

Conclusions

Hybrid composite was prepared from by-product of leather and paper pulp industry through simple route. Positively, the characterised composite also exhibited multifunctional property of having additional sites for dyeing and filling nature in porous materials. As a result, the multifunctional property obtained act as an efficient syntan with filling property rather than filling alone. The hybrid composite properties were greatly improved compared each individual. It is noteworthy that the composites treated leathers showed high softness and fullness as that of the individual treated leathers, whereas the tensile strength property of experimental leathers was high as compared with the control leathers. However the addition of composite in leather retanning stage resulted in improved uniform uptake of dye with minimum dye percentage. The present study indicated that by-product like collagen hydrolysate and black liquor is a promising material for the preparation of high functionality material for industrial application like leather retanning agent, filler and dye enhancers. It is also expected that as prepared composite will utilise the solid residues of two different wastes with less pollution to the environment.

References

1. G. J. A. A. Soler-Illia and O. Azzaroni, *Chem. Soc. Rev.,*, 2011, 40, 1107-1150.
2. H. Chen, W. Wang, J. C. Martin, A. J. Oliphant, P. A. Doerr, J. F. Xu, K. M. DeBorn, C. Chen and L. Sun, *ACS Sustainable Chem. Eng.*, 2012, 1, 254-259.
3. A. Idris, R. Vijayaraghavan, A. F. Patti and D. R. MacFarlane, *ACS Sustainable Chem. Eng.*, 2014, 2, 1888-1894.
4. M. Balakrishnan, V. S. Batra, J. S. J. Hargreaves and I. D. Pulford, *Green Chem.*, 2011, 13, 16-24.
5. D. Ponnamma, K. K. Sadasivuni, Y. Grohens, Q. Guo and S. Thomas, *J. Mater. Chem. C*, 2014, 2, 8446-8485.
6. R. L. Quirino, T. F. Garrison and M. R. Kessler, *Green Chem.*, 2014, 16, 1700-1715.
7. M. Catalina, J. Cot, A. M. Balu, J. C. Serrano-Ruiz and R. Luque, *Green Chem.*, 2012, 14, 308-312.
8. T. D. Kroner, W. Tabroff and J. J. McGarr, *J. Am. Chem. Soc.*, 1955, 77, 3356-3359.
9. E. M. Brown, M. M. Taylor and W. N. Marmer, *J. Am. Leather Chem. Assoc.*, 1996, 91, 270-276.
10. C. K. Liu, N. P. Latona and M. M. Taylor, *J. Am. Leather Chem. Assoc.*, 2014, 109, 35-40.
11. D. Q. Lima, L. C. A. Oliveira, A. R. R. Bastos, G. S. Carvalho, J. G. S. M. Marques, J. G. Carvalho and G. A. de Souza, *Applied and Environmental Soil Science*, 2010, 2010, 7.
12. A. Anumary, P. Thanikaivelan, M. Ashokkumar, R. Kumar, P. K. Sehgal and B. Chandrasekaran, *Soft Mater.*, 2013, 11, 181-194.
13. C. Mu, W. Lin, M. Zhang and Q. Zhu, *Waste Manag*, 2003, 23, 835-843.

14. I. G. I.chakarska, k. Idakieva,s. Todinova, g.apostolov, *J. Soc. Leather Technol. Chem.*, 2007, 92, 81-84.
15. S. Walrand, E. Chiotelli, F. Noirt, S. Mwewa and T. Lassel, *J. Agric. Food. Chem.*, 2008, 56, 7790-7795.
16. R. W. Moskowitz, *Semin Arthritis Rheum*, 2000, 30, 87-99.
17. V. Serpooshan, M. Zhao, S. A. Metzler, K. Wei, P. B. Shah, A. Wang, M. Mahmoudi, A. V. Malkovskiy, J. Rajadas, M. J. Butte, D. Bernstein and P. Ruiz-Lozano, *Biomaterials*, 2013, 34, 9048-9055.
18. M. F. Desimone, C. Hélary, I. B. Rietveld, I. Bataille, G. Mosser, M.-M. Giraud-Guille, J. Livage and T. Coradin, *Acta Biomaterialia*, 2010, 6, 3998-4004.
19. T. D. Kroner, W. Tabroff and J. J. McGarr, *J. Am. Chem. Soc.*, 1953, 75, 4084-4086.
20. Y. Taga, M. Kusubata, K. Ogawa-Goto and S. Hattori, *J. Proteome Res.*, 2014, 13, 3671-3678.
21. Y.-l. Chi, Q.-x. Zhang, X.-p. Liao, J. Zhou and B. Shi, *Ind. Eng. Chem. Res.*, 2014, 53, 8501-8508.
22. J. Kanagaraj, K. C. Velappan, N. K. C. Babu and S. Sadulla, *J. Sci. Ind. Res.*, 2006, 65, 541-548.
23. U. G. K. Wegst, H. Bai, E. Saiz, A. P. Tomsia and R. O. Ritchie, *Nat Mater*, 2014, advance online publication.
24. X. L. Sun, X. H. Zhao, Y. G. Zu, W. G. Li and Y. L. Ge, *Energ. Fuel*, 2014, 28, 3957-3963.
25. S. Gouveia, C. Fernandez-Costas, M. A. Sanroman and D. Moldes, *Bioresour. Technol.*, 2013, 131, 288-294.
26. Z. L. Zhu, M. M. Sun, C. G. Su, H. M. Zhao, X. M. Ma, Z. D. Zhu, X. L. Shi and K. F. Gu, *Bioresour. Technol.*, 2013, 128, 229-234.
27. M. Cardoso, É. D. de Oliveira and M. L. Passos, *Fuel*, 2009, 88, 756-763.
28. G. T. Frederick WJ. In: Adams TN, Hupa M, Lisa K, Jones AK, Tran H, and editors., *New York: TAPPI Press*, 1997, 381.
29. G. Gea, M. B. Murillo and J. Arauzo, *Ind. Eng. Chem. Res.*, 2002, 41, 4714-4721.
30. S. Nanayakkara, A. F. Patti and K. Saito, *ACS Sustainable Chem. Eng.*, 2014, 2, 2159-2164.
31. B. Lochab, S. Shukla and I. K. Varma, *RSC Adv.*, 2014, 4, 21712-21752.
32. Y. L. Chi, S. N. Lv, Q. He, X. P. Liao, W. H. Zhang and B. Shi, *J. Soc. Leather Technol. Chem.*, 2011, 95, 209-214.
33. S. Yang, J.-L. Wen, T.-Q. Yuan and R.-C. Sun, *RSC Adv.*, 2014, 4, 57996-58004.
34. K. J. Sreeram, S. Saravanabhavan, J. R. Rao and B. U. Nair, *Ind. Eng. Chem. Res.*, 2004, 43, 5310-5317.
35. C. J. Tang Keyong, Wang Jintao, Wang Zhongtai *J. Soc. Leather Technol. Chem.*, 2008, 92, 23-29.
36. T. Saito, J. H. Perkins, D. C. Jackson, N. E. Trammel, M. A. Hunt and A. K. Naskar, *RSC Adv.,* 2013, 3, 21832-21840.
37. M. Sathish, J. Raghava Rao and N. N. Fathima, *J. Appl. Polym. Sci.*,2014, 131, n/a-n/a.
38. M. Swerdlow and R. R. Stromberg, *J. Res. Natl. Bur. Stand.*, 1955, 54, 83.
39. S. Wan, F. Guo, L. Shi, Y. Peng, X. Liu, Y. Zhang and Y. Qian, *J. Mater. Chem.*, 2004, 14, 2489-2491.
40. K. J. Payne and A. Veis, *Biopolymers*, 1988, 27, 1749-1760.
41. H. Imanieh and H. Aghahosseini, *Syst Synth Biol*, 2013, 7, 175-184.
42. R. J. Stoklosa, J. Velez, S. Kelkar, C. M. Saffron, M. C. Thies and D. B. Hodge, *Green Chem.*, 2013, 15, 2904-2912.
43. S. Rades, V.-D. Hodoroaba, T. Salge, T. Wirth, M. P. Lobera, R. H. Labrador, K. Natte, T. Behnke, T. Gross and W. E. S. Unger, *RSC Adv.,* 2014, 4, 49577-49587.
44. M. M. Basil-Jones, R. L. Edmonds, T. F. Allsop, S. M. Cooper, G. Holmes, G. E. Norris, D. J. Cookson, N. Kirby and R. G. Haverkamp, *J. Agric. Food. Chem.*,2010, 58, 5286-5291.

45. K. Tang, F. Wang, J. Liu, P. Jia and J. Liu, *Rev. Adv. Mater. Sci*, 2013, 33, 373-382.
46. R. R. Stromberg, *J. Res. Natl. Bur. Stand.*, 1955, 54, 73-81.
47. J. A. Wilson and G. O. Lines, *Ind. Eng. Chem. Res.*, 1925, 17, 570-573.
48. S. N. Jaisankar, S. Ramalingam, H. Subramani, R. Mohan, P. Saravanan, D. Samanta and A. B. Mandal, *Ind. Eng. Chem. Res.*, 2012, 52, 1379-1387.
49. K. H. Sizeland, M. M. Basil-Jones, R. L. Edmonds, S. M. Cooper, N. Kirby, A. Hawley and R. G. Haverkamp, *J. Agric. Food. Chem.*, 2013, 61, 887-892.
50. M. M. Basil-Jones, R. L. Edmonds, S. M. Cooper and R. G. Haverkamp, *J. Agric. Food. Chem.*, 2011, 59, 9972-9979.
51. C. Wang, *Macromolecules*, 2001, 34, 9006-9014.
52. M. M. Basil-Jones, R. L. Edmonds, S. M. Cooper, N. Kirby, A. Hawley and R. G. Haverkamp, *J. Agric. Food. Chem.*, 2013, 61, 12327-12332.
53. S. P. Radhika, K. J. Sreeram and B. Unni Nair, *ACS Sustainable Chem. Eng.*, 2014, 2, 1251-1256.
54. S. V. Kanth, R. Venba, B. Madhan, N. K. Chandrababu and S. Sadulla, *Dyes and Pigments*, 2008, 76, 338-347.
55. S. Saravanabhavan, P. Thanikaivelan, J. R. Rao, B. U. Nair and T. Ramasami, *Environ. Sci. Technol.*, 2003, 38, 871-879.

Figure Captions

Figure 1 The hydrodynamic diameter of the collagen hydrolysate obtained by using various molar of NaOH concentration a) 0.5 M, b) 1.5 M, c) 2.5 M. d) 5 M.

Figure 2 The hydrodynamic diameter of the prepared a) composite 1(acidified black liquor 7 + collagen hydrolysate) and b) Composite 2 (black liquor 14 + collagen hydrolysate).

Figure 3 High magnification SEM image of the (a) hollow sphere, (b) broken hollow sphere, and Low magnification SEM images showing the details of (c) surface morphology of the spray dried acidified black liquor, and (d) clustered structure of acidified black liquor.

Figure 4 SEM image of the surface morphology of (a) and (b) represent the acidified black liquor (spray dried powdered), (c) and (d) represents the Collagen Hydrolysate, (e) and (f) represent the composite 1, and (g) and (h) represents the composite 2.

Figure 5 The FTIR spectra of the a) Collagen hydrolysate, b) Black liquor (pure and acidified), c) Composite 1 and d) Composite 2.

Figure 6 The Scanning Electron Microscopic image showing the details of grain surface of (a) Control leather, (c) Composite1 treated leather, (e) Composite2 treated leather. Then (b), (d), and (f) are their corresponding cross sectional image.

Figure 7 The change in the permeability of the leather treated with both acidified black liquors and composites.

Figure 8 The pore size distribution of the leather treated with a) acidified black liquor (BL7), b) Composite 1, c) Pure black liquor (BL14), and d) Composite 2.

Figure 9 The strength property of the composites treated leather compared with control leather.

Figure 10 The surface colour of the dyed crust leather prepared in the presence of a) Composite1, b) acidified black liquor, c) Composite 2, and d) Pure black liquor.

Figure 11 Variation in the surface colour of the leather treated with different percentage of dye in the presence of A) Conventional syntan, B) Composite 1 C) Composite 2.

Figure 12 The percentage exhaustion of the dye in presence of hybrid composites and their corresponding individuals.

Figure 13 The organoleptic properties of the composites treated leather compared with control leathers.

Table 1 The colour coordinates of the experimental dyed crust leather compared with controls leathers.

Table 2 The softness measurement value of both experimental and control leathers

Figure 1

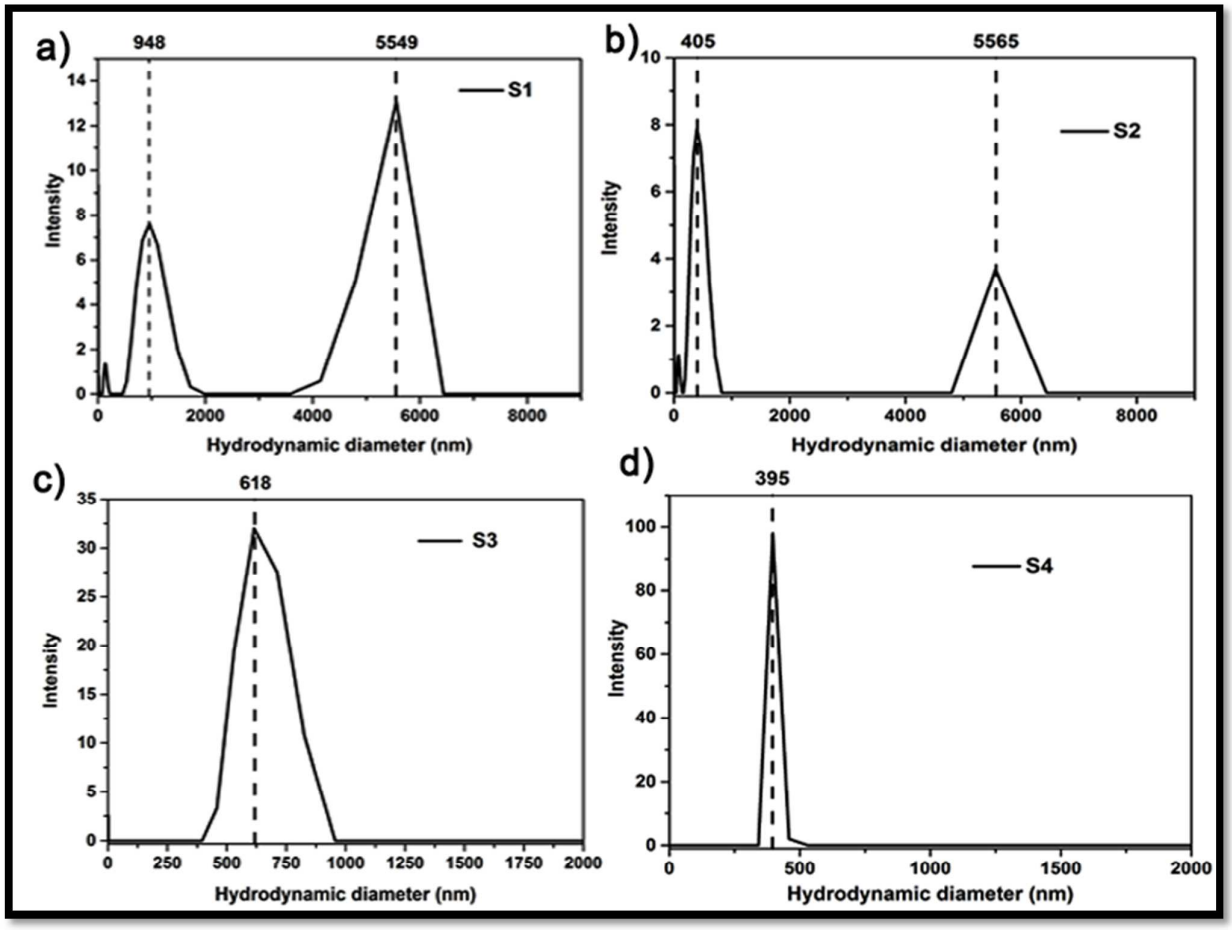
a)
948
5549
S1
Intensity
Hydrodynamic diameter (nm)
b)
405
5565
S2
Intensity
Hydrodynamic diameter (nm)
c)
618
S3
Intensity
Hydrodynamic diameter (nm)
d)
395
S4
Intensity
Hydrodynamic diameter (nm)

Figure 2

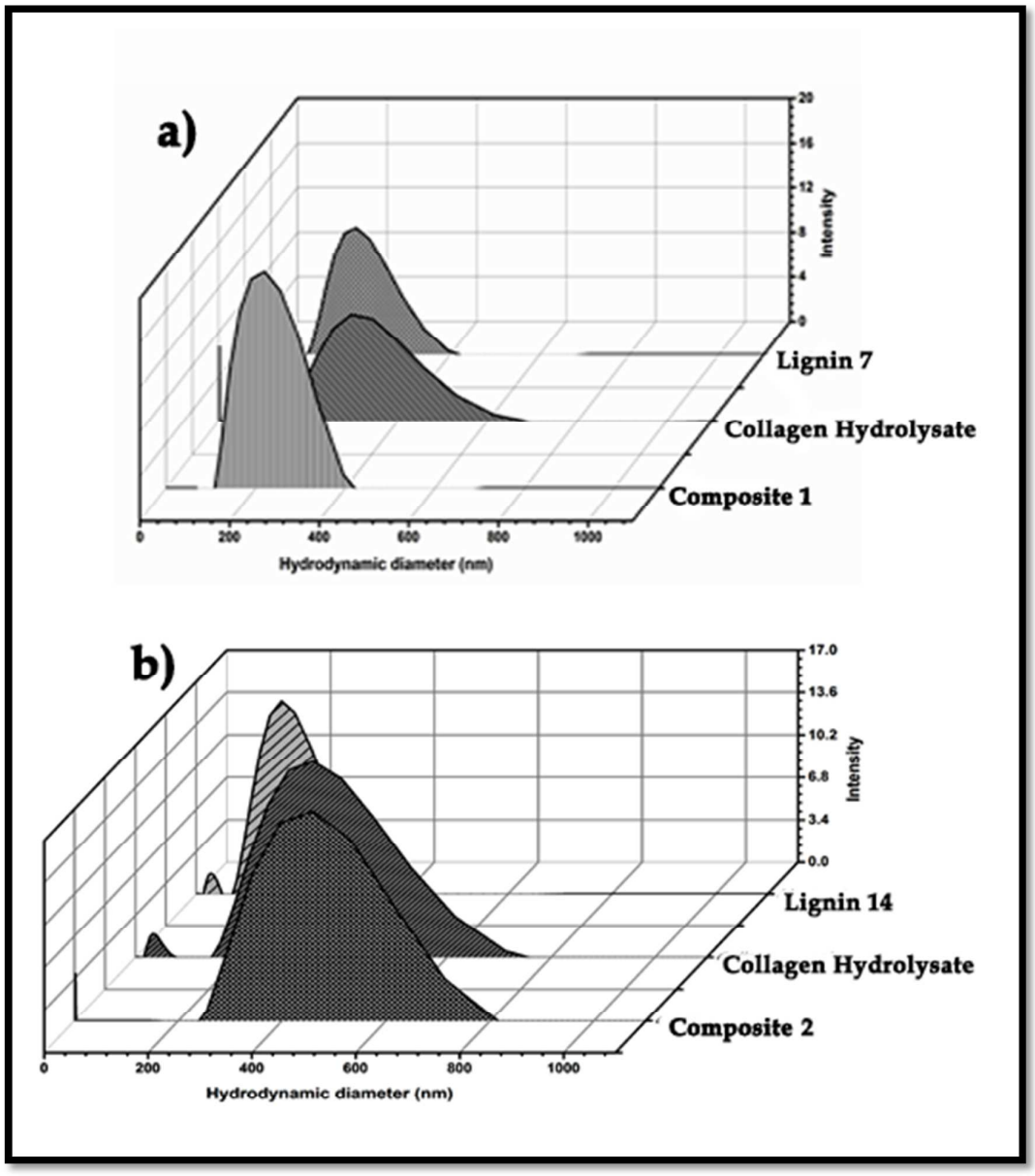
a)
Intensity
Lignin 7
Collagen Hydrolysate
Composite 1
Hydrodynamic diameter (nm)
b)
Intensity
Lignin 14
Collagen Hydrolysate
Composite 2
Hydrodynamic diameter (nm)

Figure 3

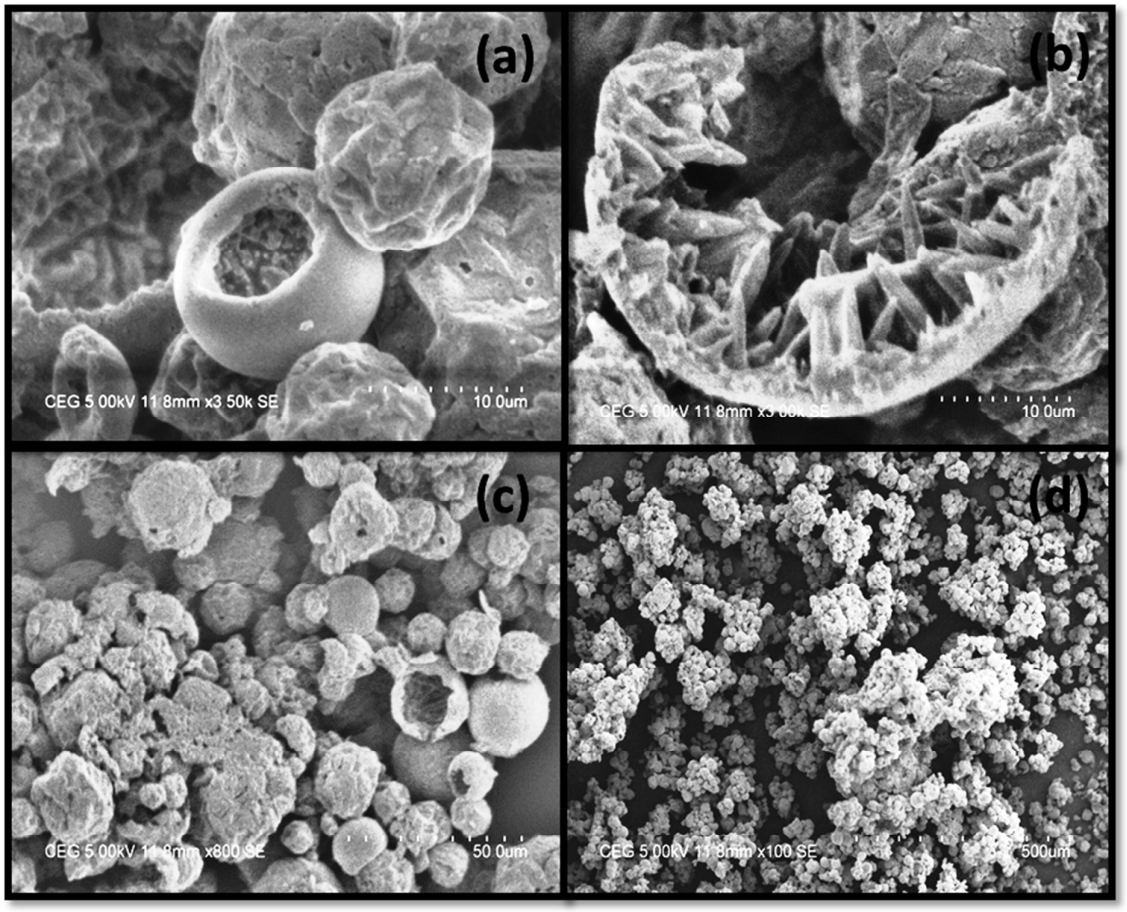

Figure 4

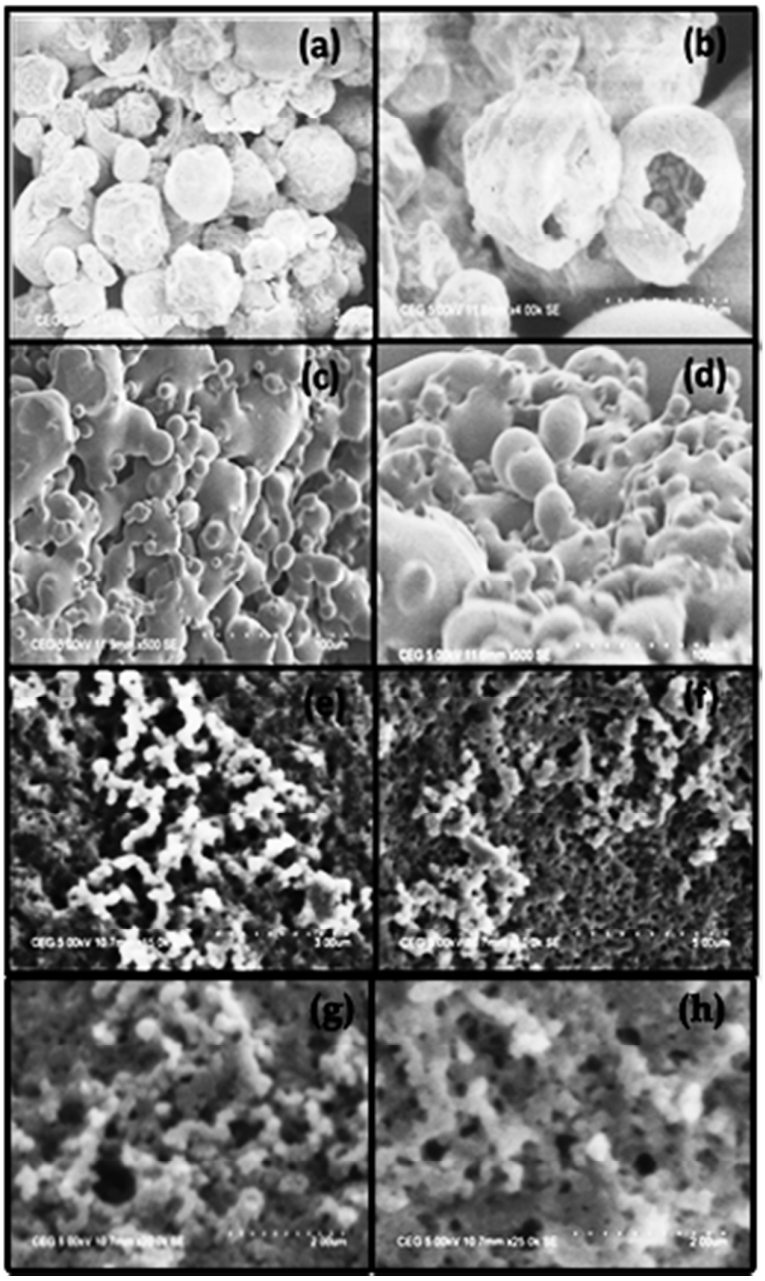

Figure 5

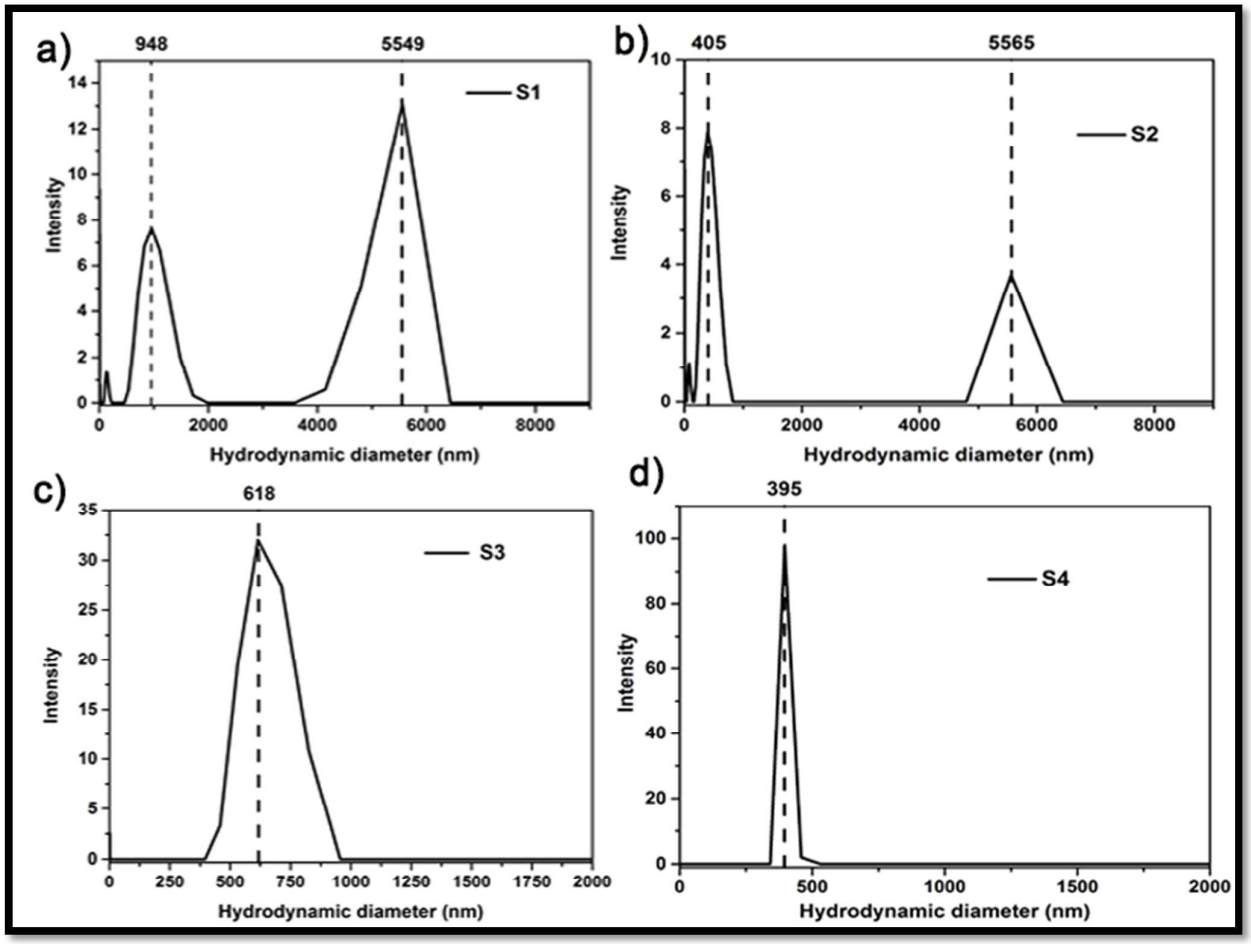
a)
948
5549
S1
Intensity
Hydrodynamic diameter (nm)
b)
405
5565
S2
Intensity
Hydrodynamic diameter (nm)
c)
618
S3
Intensity
Hydrodynamic diameter (nm)
d)
395
S4
Intensity
Hydrodynamic diameter (nm)

Figure 6

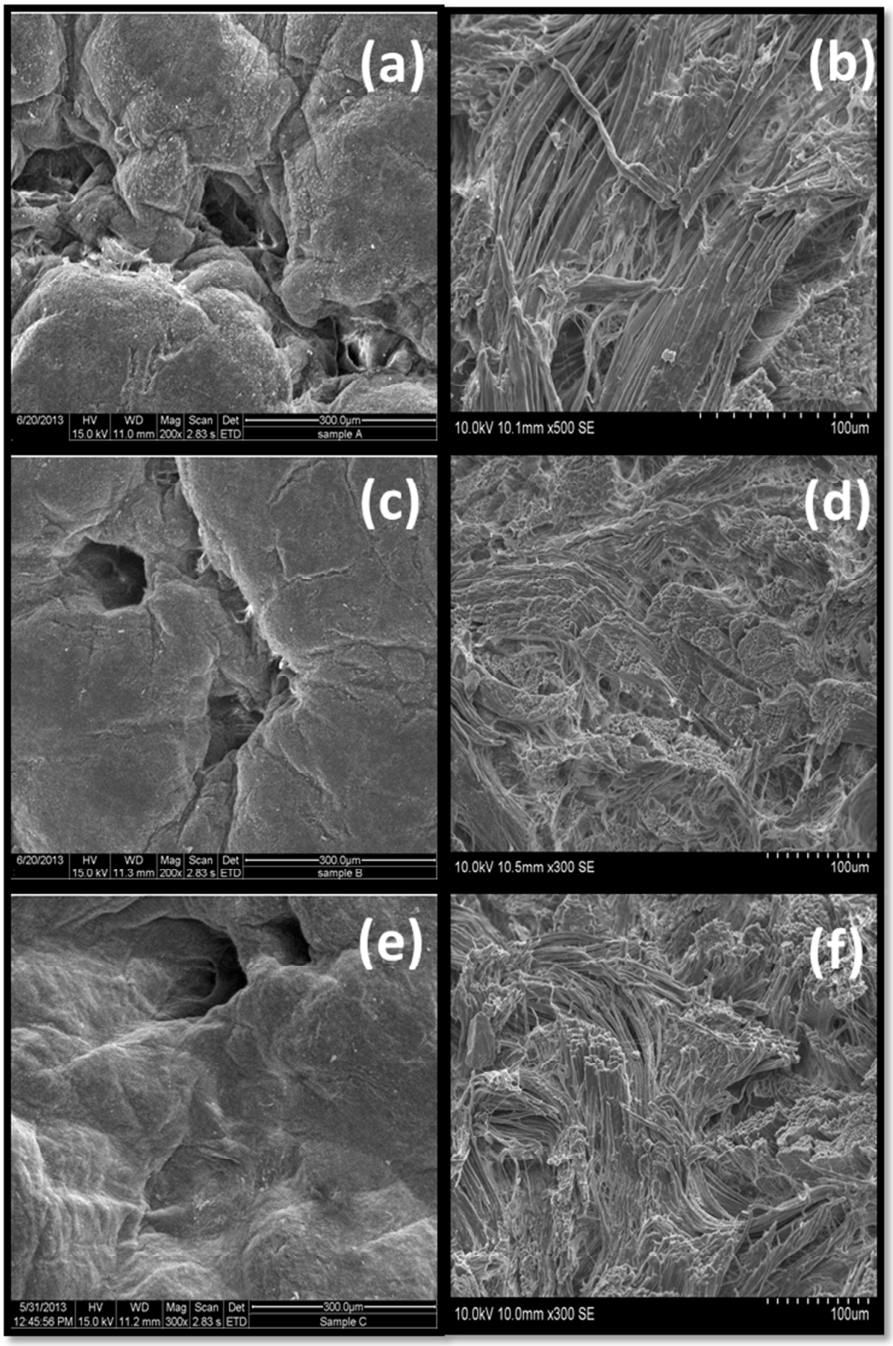
(a)
6/20/2013 HV 15.0 kV WD 11.0 mm Mag 200x Scan 2.83 s Det ETD 300.0µm sample A
(b)
10.0kV 10.1mm x500 SE 100um
(c)
6/20/2013 HV 15.0 kV WD 11.3 mm Mag 200x Scan 2.83 s Det ETD 300.0µm sample B
(d)
10.0kV 10.5mm x300 SE 100um
(e)
5/31/2013 12:45:56 PM HV 15.0 kV WD 11.2 mm Mag 300x Scan 2.83 s Det ETD 300.0µm Sample C
(f)
10.0kV 10.0mm x300 SE 100um

Figure 7

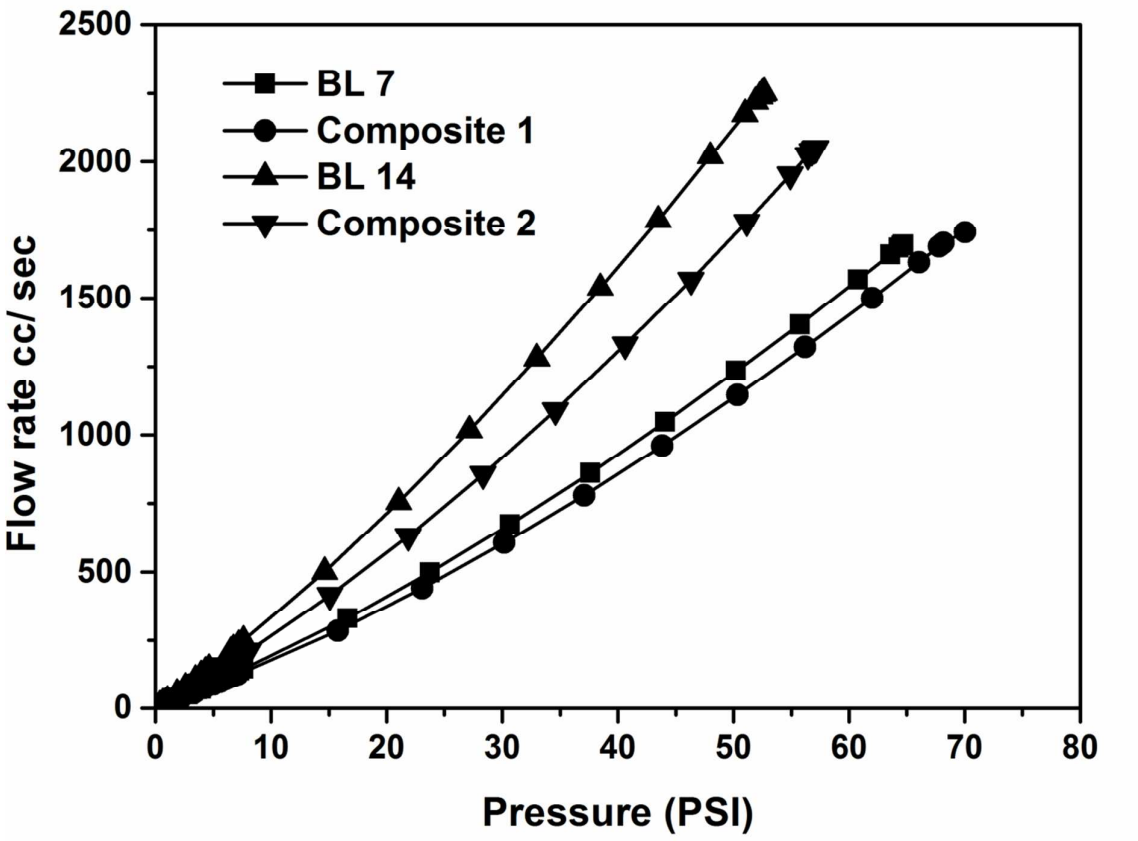
BL 7
Composite 1
BL 14
Composite 2
Flow rate cc/ sec
Pressure (PSI)
0
500
1000
1500
2000
2500
0
10
20
30
40
50
60
70
80

Figure 8

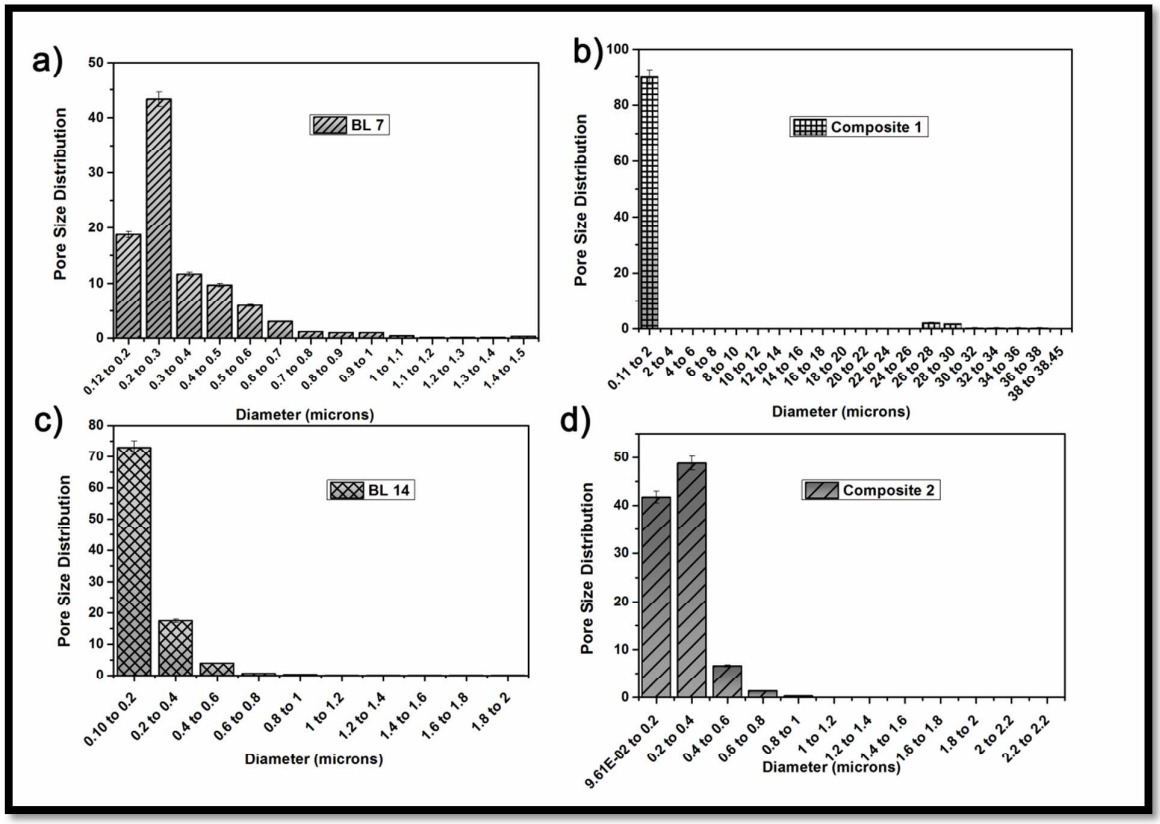
a)
Pore Size Distribution
BL 7
0.12 to 0.2
0.2 to 0.3
0.3 to 0.4
0.4 to 0.5
0.5 to 0.6
0.6 to 0.7
0.7 to 0.8
0.8 to 0.9
0.9 to 1
1 to 1.1
1.1 to 1.2
1.2 to 1.3
1.3 to 1.4
1.4 to 1.5
Diameter (microns)
b)
Pore Size Distribution
Composite 1
0.11 to 2
2 to 4
4 to 6
6 to 8
8 to 10
10 to 12
12 to 14
14 to 16
16 to 18
18 to 20
20 to 22
22 to 24
24 to 26
26 to 28
28 to 30
30 to 32
32 to 34
34 to 36
36 to 38
38 to 38.45
Diameter (microns)
c)
Pore Size Distribution
BL 14
0.10 to 0.2
0.2 to 0.4
0.4 to 0.6
0.6 to 0.8
0.8 to 1
1 to 1.2
1.2 to 1.4
1.4 to 1.6
1.6 to 1.8
1.8 to 2
Diameter (microns)
d)
Pore Size Distribution
Composite 2
9.61E-02 to 0.2
0.2 to 0.4
0.4 to 0.6
0.6 to 0.8
0.8 to 1
1 to 1.2
1.2 to 1.4
1.4 to 1.6
1.6 to 1.8
1.8 to 2
2 to 2.2
2.2 to 2.2
Diameter (microns)

Figure 9

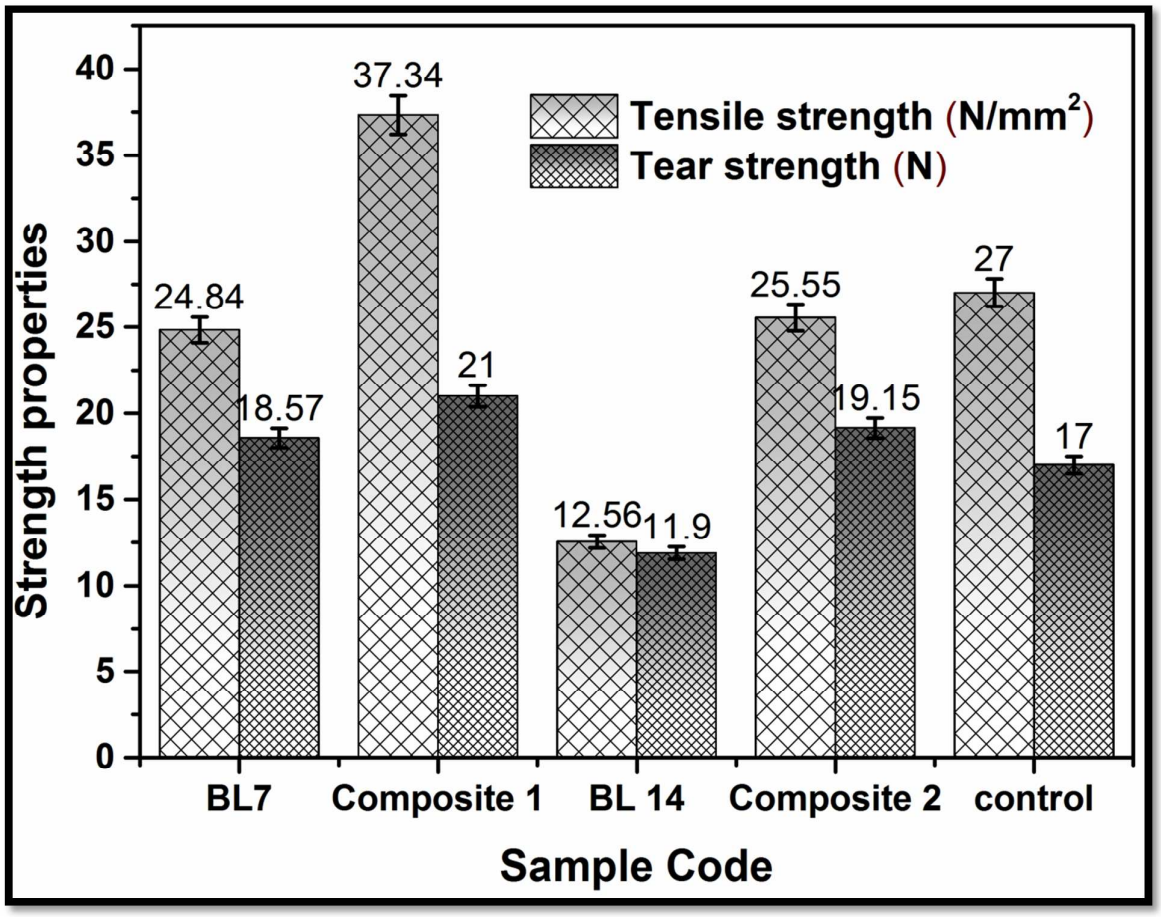
Strength properties
Sample Code
Tensile strength (N/mm²)
Tear strength (N)
0
5
10
15
20
25
30
35
40
24.84
18.57
37.34
21
12.56
11.9
25.55
19.15
27
17
BL7
Composite 1
BL 14
Composite 2
control

Figure 10

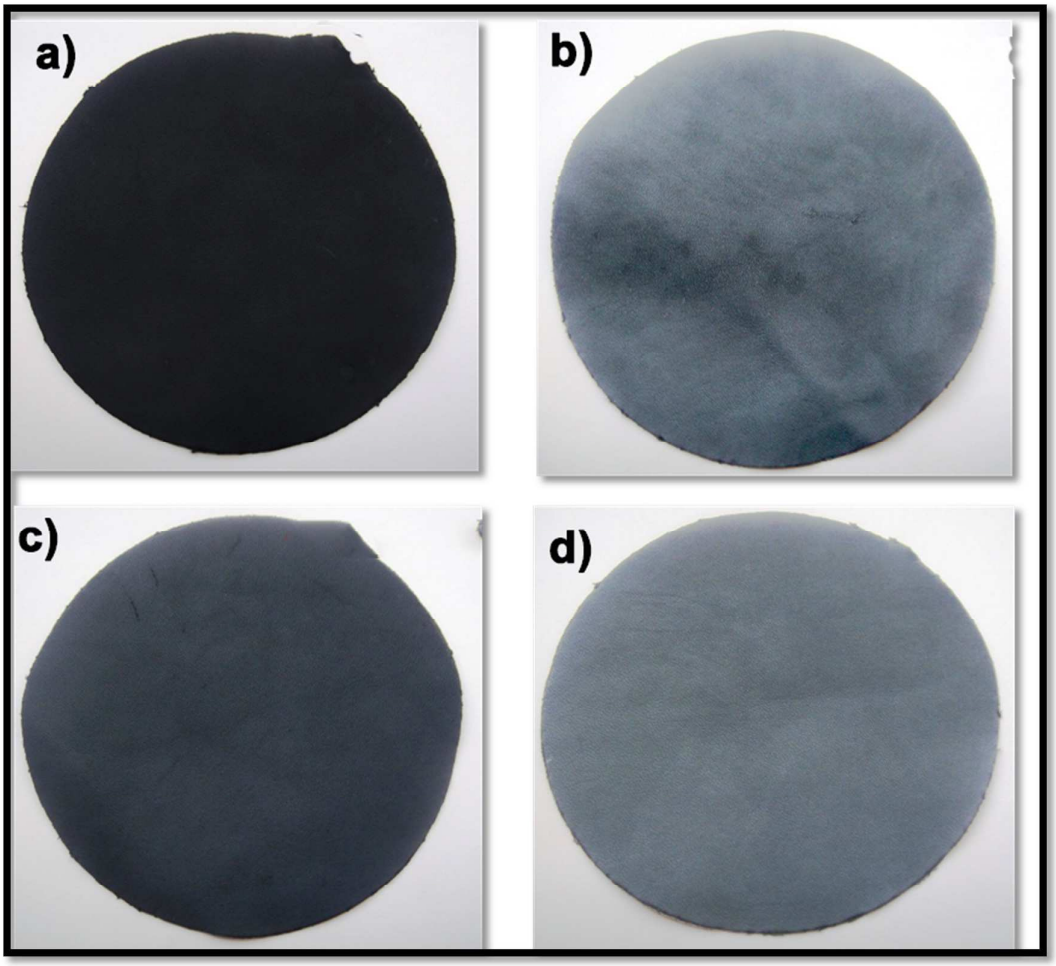

Figure 11

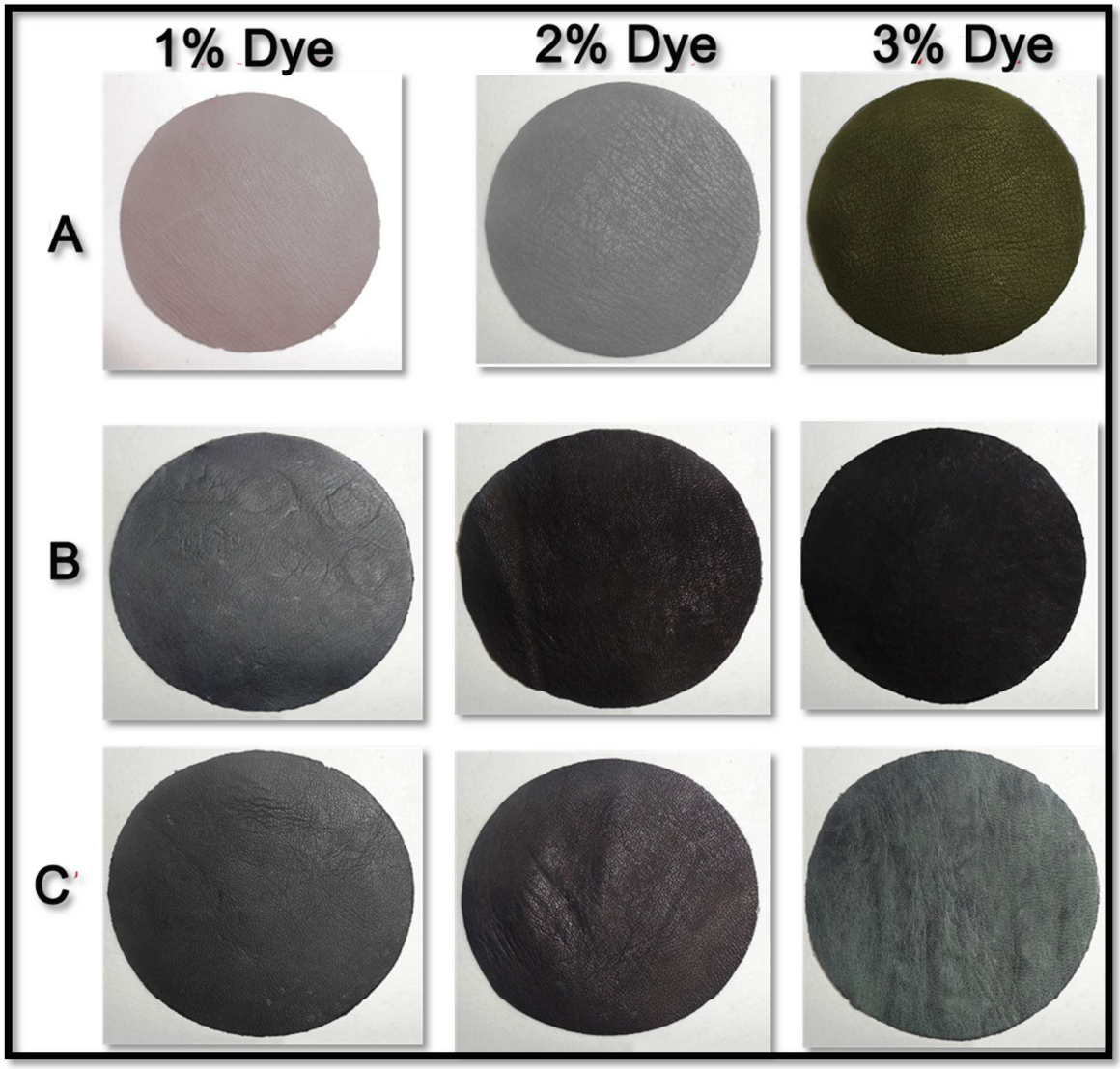

Figure 12

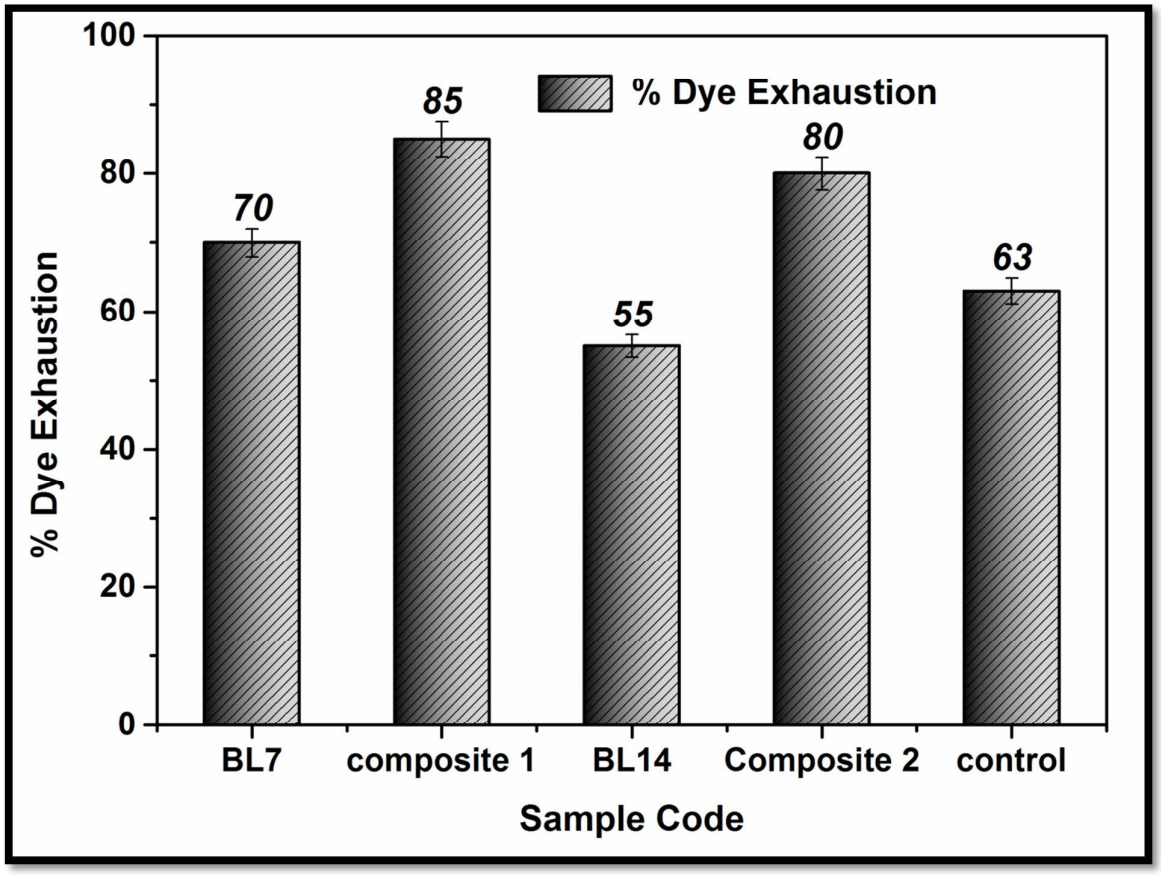
100
80
60
40
20
0
% Dye Exhaustion
% Dye Exhaustion
70
85
55
80
63
BL7
composite 1
BL14
Composite 2
control
Sample Code

Figure 13

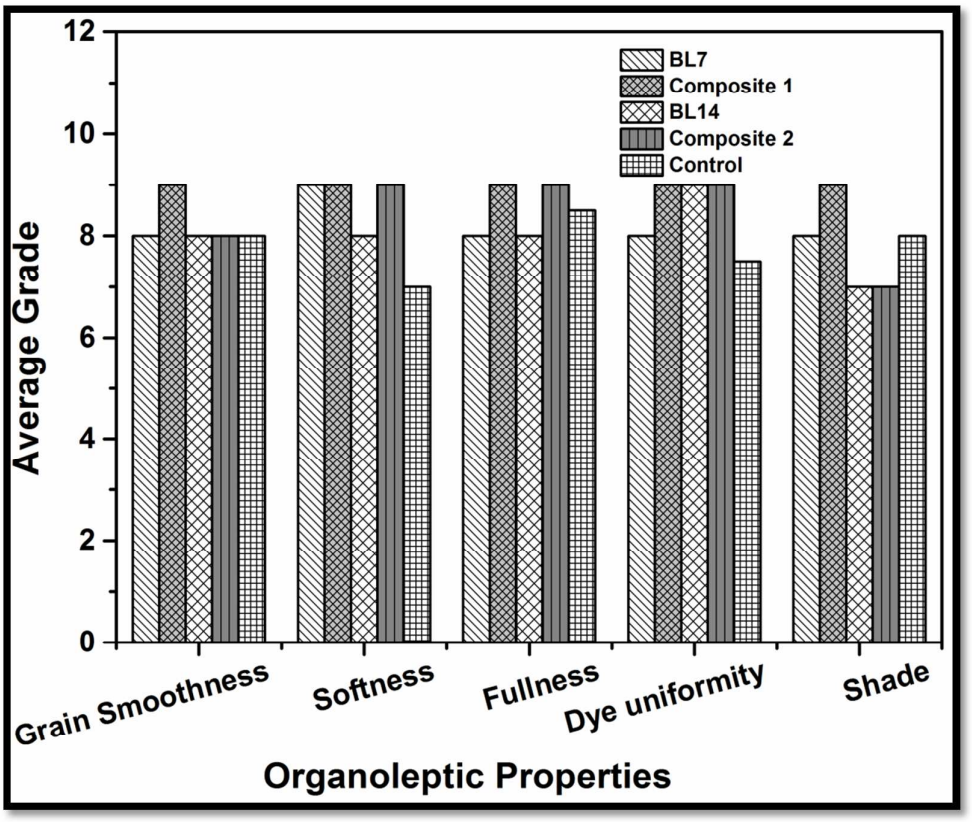
12
10
8
6
4
2
0
Average Grade
BL7
Composite 1
BL14
Composite 2
Control
Grain Smoothness
Softness
Fullness
Dye uniformity
Shade
Organoleptic Properties

Table 1

Samples	L*	a *	b *	C *	h *
Control	40.658	-1.687	-2.386	3.926	220.05
BL 7	41.076	-2.001	-3.572	4.094	240.718
Composite 1	43.853	-1.713	-2.621	4.231	256.810
BL 14	39.528	-1.963	-4.035	3.8039	191.419
Composite 2	41.4408	-2.610	-2.775	4.110	246.736

Table 2

Samples	Softness
Control	4.56± 0.3
BL 7	5.8±0.6
Composite 1	6±0.4
BL 14	4.3±0.2
Composite 2	4.7±0.8