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Developing fiber and mineral based composite materials from paper manufacturing by-products

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Abstract. Developing valuable materials from the by-products of paper industry can help to address some environmental and economic issues associated with traditional synthetic composites. Particularly, the management of paper mill sludge (PMS) waste remains an economic and environmental challenge for the pulp and paper industry. 11 million tons of PMS is generated annually in Europe from the waste water treatment (WWT) process of paper mills. PMS is mostly used in low value applications. However, PMS contains fibers and minerals with physio-chemical properties that exhibit a high potential to substitute some conventional materials in other industries. The research presented in this paper aims to explore new directions for further investigation on PMS material applications by reviewing the literature on PMS materials and subsequently characterizing sludge from 6 different mills. The study shows the technical feasibility, opportunities and technological readiness of fiber and mineral based composites obtained from PMS, such as; cementitious products, polymer reinforcement and fiberboards.

Keywords: Paper mill sludge, Waste recovery, Sustainable materials, Cellulose

1 Introduction

It is expected that by 2020 over 60% of paper products will be recycled to aid the reduction of environmental impacts caused by the pulp and paper industry. However, the waste water treatment process of recycled paper mills produces a solid waste by-product in large quantities known as paper mill sludge [1]. Paper mills are pressured by stringent environmental legislations, limited landfill space and taxation costs of £82.60/ton of waste [2]. Moreover, the environmental impact of 1 ton of PMS in landfill releases 2.69 tons of CO_2 and 0.24 tons of Methane [3]. Over the years, the industry has investigated valorization options to manage PMS. The most common adopted means is energy recovery and agricultural land spreading.

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PMS is recovered for energy by incineration which still generates 50% PMS waste ash. The use of PMS on agricultural land helps in improving soil nutrition and condition, the PH of the soil is also ameliorated by the $CaCO_3$ in the paper sludge. Paper sludge is rich in carbon though lacking in nitrogen and phosphorus, thus fertilizers are still required to satisfy total plant requirement [4]. These applications are a critical stepping stone away from landfill however there remains scope to optimize valorization. According to the circular economy principles; to fully valorize waste, its maximum value must be extracted before considering energy recover or soil restoration [5].

2 Characteristic of paper mill sludge waste

PMS comprises of cellulose fibers (A) and mineral fillers (B), shown in figure 1. The prime constituents of natural cellulose fibers are: cellulose; hemicellulose and lignin. However, during the processing of cellulose fibers into paper form, lignin is almost completely removed.

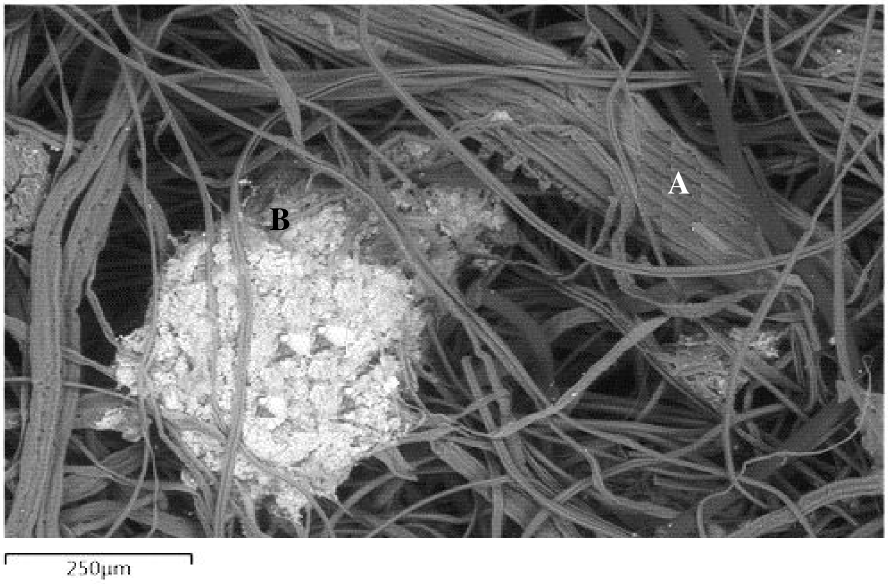

Fig. 1. SEM micrograph of PMS showing minerals enclosed with cellulose fibers at 100 x

Cellulose exhibits a crystalline structure with amorphous-like regions of hemicellulose, providing structure and strength to plant cell walls. These crystals are in nanoscale also known as cellulose nanocrystals (CN) or nanoparticles. The chains of hydrogen bonds allow cellulose to obtain an orderly molecular stacking, thus rendering cellulose suitable for reinforcing materials [6]. Cellulose nanocrystals possess mechanical properties similar to engineering materials. They have similar elastic modulus (150GPa) as carbon fiber and a tensile strength of 7.5 GPa, which is higher than steel wire and Kevlar-49 fibers [7]. Lignin is an amorphous polymer also present in plant cell wall, the removal of lignin is required before producing Nano cellulose materials. This process is highly energy intensive, whereas in paper production lignin is already dissolved during the pulping process. This suggests PMS as an option for processing cellulose materials as it contains less lignin. Advances in cellulose materials research reveal its desirable properties such as high tensile strength and light weight [6]. This implies that PMS may contain some untapped resources for material applications. Therefore, a future perspective is necessary to explore innovative value adding solutions to improve the use of this byproduct.

A biological process breaks down the organic matter to generate secondary sludge, containing a higher content of minerals, proteins, microorganisms and cellulose fibers. Some paper mills combine both processes for ease of dewatering. Mills using recycled paper produce deinking sludge that primarily consists of high inorganics, ink and paper coating materials. The combination of these wastes consists of organics and inorganics as seen in figure 2. The organics content of the sludge is from the woody fibers contained in the pulp. The fibers have a crystalline structure with amorphous-like regions of hemicellulose. Lignin acts as a strengthening agent in the plant cell wall. Extractives are non-structural parts of wood such as fats and waxes. Lignin and extractives in PMS are present in very small traces (<2%) as they are mostly dissolved during pulping process. The inorganic minerals contained in PMS form compounds such as aluminum oxide (Al_2O_3), silicon dioxide (SiO_2), iron oxide (Fe_2O_3), calcium (Ca) and magnesium oxide (MgO) which are common chemicals present in Portland cement [8]. The general characteristics of PMS are identified based on content of; ash, cellulose, chemical composition, fiber length, extractives, lignin and particle size. The contents depend on the paper mill operations, WWT and final paper product. The amount of these constituents also determines the overall properties of its end product. Thus it is of much significance to quantify these PMS contents in order to understand the mechanical properties of PMS based materials

2.1 Analysis of PMS from different paper mills

Most studies have reported on PMS based materials obtained from one mill to develop specific materials applications [9-11], this lacks a thorough investigation of the PMS potentials. Table 1 shows the characterization of PMS obtained from 6 different mills for an in depth study of their possible material applications. PMS was oven dried at 105°C for 24 hours to reduce moisture content below 3%. Ash refers to the inorganic matter consisting of chemicals and minerals used in the paper. Ash content was determined based on TAPPI[1] 211 methods for ash in wood, pulp, paper and paperboard [12].

[1] Technical Association of Pulp and Paper Industry

The sludge is ignited in a furnace at 525ºC, volatile organic compounds are burnt off to leave the inorganics. Based on the ash analysis, the data table presents two groups of sludge types; low ash sludge (LAS) < 30% of ash (mill 6, mill 5 and mill 1) and high ash sludge (HAS) > 30% ash (mill 3, mill 2 and mill 4). This gives an approximate indication of the ratio of cellulose fiber content to mineral content. Elemental oxides such as calcium oxide CaO and silicon di oxide SiO2 were identified with ESEM chemical analysis. The HASs show a higher percentage of CaO compared to LASs. The LASs contain more SiO, this indicates they have a higher organic content as a result of silicon dioxide being a natural compound commonly found in biomass.

Table 1. Characteristics of PMS from 6 paper mills

Mill Code	Mill 1	Mill 2	Mill 3	Mill 4	Mill 5	Mill 6
Feedstock	Virgin fibers, Coffee cups	Office paper	Office paper	Office paper	Virgin fibers	Virgin fibers, Fine PE[2]
Color	Black	Grey	Grey	Grey	White	Brown
Ash (%)	25	54	66	70	4	7
Cellulose (%)	47.40	30.70	17.49	11.89	81.61	77.20
Extractives (%)	17.11	15.23	16.51	18.11	14.39	15.80
Ca	35.5	55	52.8	52.4	7.8	16.1
SiO_2	20.7	5.3	4.1	5.2	46.5	34.9

Cellulose was determined with 17.5% NaOH solution [13]. Extractives appear soluble in acetone which can be determined in accordance with the TAPPI 204 solvent extraction of wood and pulp method [14]. The classification of fiber lengths was carried out based on TAPPI 203 standard using a Bauer McNett classifier. PMS was diluted in water and evenly dispersed using a pulp disintegrator at 3000 rpm. The analysis gives the weighted average fiber lengths for the following mesh screen sizes; 14(1.19 mm), 28(0.595 mm), 48(0.297 mm) and 65 (0.149 mm) as reported in figure 2. Fines are contents < 0.149 which contain both minerals and tiny fibers. The mill 6 sludge shows a high fiber content of 81% of ≥1.19mm fibers and 14% fines. Sludge from mill 2, mill 1, mill 5 show an even distribution of different fiber lengths and fines. Mill 5 sludge contains mainly cellulose fibers between 1.19-0.595 mm with 20% fines. Sludge's from mill 3 and mill 4contain mainly fines (86.22% and 87.10%) respectively.

[2] Polyethylene

3 Material applications from paper mill sludge and their mechanical properties

The literature on PMS materials covers two groups; fiber applications and mineral applications. The technological readiness for these applications range from analytical concepts (TRL 3) to commissioning (TRL 8) as illustrated in figure 2 below.

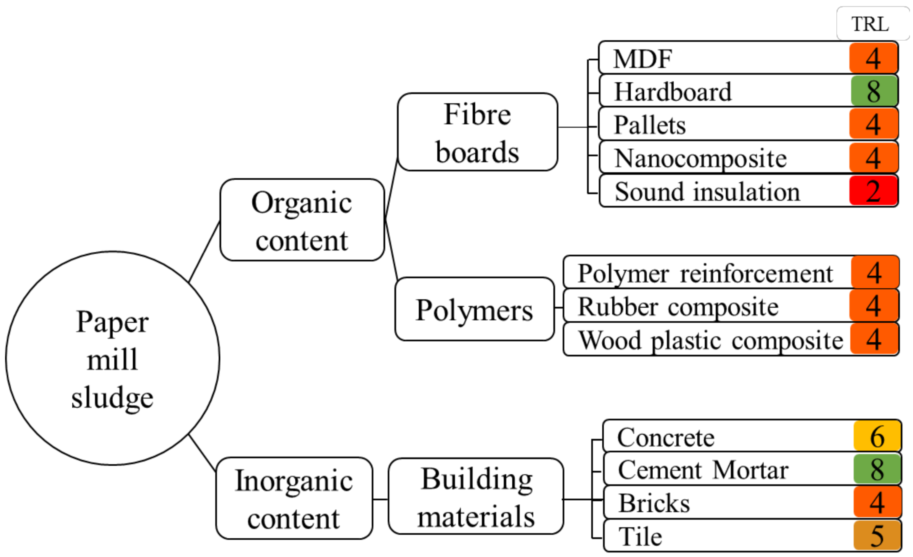

Fig. 2. Material applications from paper mill sludge

It is possible to choose suitable material applications of PMS depending on their characteristics by referring to table 1 and figure 2. Sludge from mill 1, 2 and 5 which contain a mixture of both fiber and fillers are suitable for board materials such as hardboard and medium density fiberboard (MDF). The high fiber percentage of mill 5 sludge and it being free from impurities renders a possibility for processing nanocellulose. Mill 6 sludge which contains 81% of fibers with similar lengths, is suitable for board applications requiring loads. To form fiber matrix for MDF and pallets. Sludge from mill 3 and 4 which show high inorganic content and contain more calcium have the ability to derive pozzolanic properties when reacted with water, for applications such as concrete, cement, mortar and bricks.

3.1 Mineral based PMS materials

Minerals from PMS are chemically compatible with traditional materials used to produce cement and concrete. Hollow concrete blocks were substituted with 50% PMS which met Thailand standards (TIS109-2517) for non-load bearing [15]. Cement in concrete can be replaced with up to 10% of PMS which met EU standards for indoor or outdoor plaster, though increase in PMS decreases compressive strength [16]. The lightweight property of PMS ash is attractive for the production of aggregates for cement mortars and plaster blends. PMS ash and Expanded Polystyrene (EPS) was mixed to make lightweight mortar with insulation properties, although the thermal conductivity and compression strength of mortar reduced by 50% and 20% respectively compared to control mortar. The PMS/EPS mortar met EU standards [17]. Hydrophobic coatings can be used in applications such as self-cleaning surfaces and applications for water repellence in concrete. PMS was dry milled for eight hours with stearic acid to create a super-hydrophobic powder which maintained a water contact angle of approximately 153^{o} [18]. 12.5% cellulose fibers were used as a substituted in brittle gypsum board which successfully improved the boards impact strength and modulus of rupture. PMS tiles were produce on a pilot scale. PMS was bonded with Methylene diphenyl di-isocyanate (MDI) and Polyurethane (PU) then hot pressed to produce ceramic tiles. The tile was bonded with MDI and PU was used as a surface finish.

3.2 Fiber based PMS materials

Fiber board materials.

Particle board or fiber board is typically manufactured by binding wood fibers together to form MDF. PMS was used to develop MDF using urea formaldehyde (UF) and methylene-diphenyl di-isocyanate (MDI) as binding agents. The characteristic of the paper sludge used contained; (27.76%) Ash, (20.83%) cellulose, (17.41%) Lignin and (6.37%) extractives. UF bonded samples and MDI bonded samples with the following ratios of PMS to wood fibers (0:100, 15:85, 30:70 and 45:55) were produced by hot pressing formed fiber mats [6]. They were tested for bending strength, sheer strength, water absorption and thickness swelling (TS). The bending strength of the boards ranged from 7Mpa to 18 MPa, EN standards 312-2 minimum requirement for bending strength in boards is 12 MPa. The 3 layer 15:85 UF bonded sample fully satisfied the requirements set for EN standards for general uses. However, the mechanical properties of the other boards decreased as PMS content increased.

The major problem affecting the other samples were as a result of inorganic material content (ash content) and water absorption. The addition of wax, had no effect on improving the thickness swelling of the boards. However, a study showed that ultrasonic wave processing combined with an alkali treatment of cellulose fibers, improved the water absorption of the fibers by 50%, this also had an effect on increasing the surface area of the cellulose fibers [19] PMS with the following characteristics; ash 19.50% and cellulose content 62.7% was mixed with 100% virgin spruce pine fibers (SPF) at different ratios bonded with UF resin [20]. The elastic modulus and modulus of rupture for the virgin SPF was 2250 MPa and 28 MPa respectively. The PMS/SPF board of ratio 3:7 showed elastic and rupture modulus of 2000 MPa and 24 MPa respectively, the fiber board was tested to meet ANSI A208.2-2002 MDF standard for interior applications. Urea-formaldehyde (UF) is a common binding agent used in the particle board industry which leads to formaldehyde emissions. A major environmental advantage of PMS in fiber boards is the reduction of formaldehyde (HCHO). Addition of secondary sludge (SS) for particle board production showed a reduction of HCHO by an average of 48% the effect occurs due to the proteins contained in SS which react with the formaldehyde [21].

Paper mill reject fibers were used for partial replacement of virgin wood fibers in hardboards. The optimal fiber content to maintain the mechanical properties was at 10% and has been used to manufacture commercial building boards in the Netherlands. However, the facility was later shut down. Natural fiber from kapok, cotton, milkweed and basalt fibers have been studied for sound insulation panels [22,23] which improved sound reduction. PMS fibers could be used in a similar study to determine their acoustic properties.

Wood plastic composite.

Wood Plastic Composites (WPC) are environmental friendly options used in non-structural building components such as roof tiles, fencing, decking [10]. PMS was used as a reinforcement with Maleic anhydride-grafted polypropylene (MAPE) for PMS-WPC [24]. The materials were extruded, milled and injection molded to form test specimens. The composite was proven to have a higher young's modulus although lower tensile strength and deformation at break. The mechanical properties showed that it is feasible to substitute conventional mineral fillers in PP composites with PMS for composites in low mechanical applications such as panels, furniture and fencing. PMS-PP composites were compared against polypropylene co-polymer material currently being used in a commercial fence. 10%wt of PMS showed no effect on the mechanical properties, though when Wood fiber was replaced with 50%wt of sludge the flexural strength and young modulus decreased and the impact strength increased. The inorganic contents in the PMS is said to have affected the flexural strength of the composite as the fibers were enclosed in $CaCO_3$. Increase in cellulose fibers has a positive effect on the flexural and tensile strength, although a negative impact on Thickness Swelling (TS) and water absorption. The WPC composites were not limited by the ash content as the ash may have played the role of mineral fillers typically used in plastic composites. The fibrillation of the fibers will cause a better interlocking with the polymer. The study concluded PMS could play a role in substituting wood flour used in WPC as a reinforcing fiber.

Pallets.

Pallets used in the transportation of goods are made from materials such as wood, plastic and metal. Lightweight pallets have been found to be beneficial for logistics operations. PMS was mixed with wood particles using UF as a binder and hardened with NH_4CL and cold pressed to form pallets. The characteristics of the sludge used was 27.76% ash, 20.83% cellulose and 6.37% extractives. The PMS pallet met European standards of minimum requirements for green pallet manufacturing, when 10wt% PMS is used. The water absorption property of the pallet was not significantly affected by 10%wt paper sludge thus no thickness swelling was observed. Inorganic materials such as kaolin clay and calcium carbonate resulted in weaker adhesion between the PMS and wood particles [25]. Understanding variables such as particle size and inorganic content which affect the pallets mechanical properties will improve research on PMS for pallets. Pallets could also be manufactured from PMS-WPC and compared against standards for green pallets.

Polymer reinforcement and rubber composites.

Cellulose fibers have been investigated in recent studies as a reinforcement to improve the mechanical properties of polymers. PMS fibers and Polyamide (PA) were extruded and injection molded into thin parts to develop a biodegradable thermoplastic composite. The average modulus of the samples was higher than the control samples and had good moisture resistance. This lead to further investigations of cellulose fibers reinforced in rubber. Typically, toxic materials such as Carbon black (CB) and silica are used as fillers in rubber composites. These fillers were partially replaced with short cellulose fibers from PMS to produce a hybrid rubber composite. Two samples, PMS carbon black and PMS silica were tested for fatigue, tensile properties and curing [26] The PMS/CB rubber composite samples had a better fatigue life and loading capacity than PMS/Silica rubber composite. Though the PMS/CB had lower curing and tensile properties than the control samples. Micro Crystalline Cellulose (MCC) was used as partial replacement of the silica fillers in rubber composite with up to 18% of silica replaced showing no effect on the mechanical properties of the rubber. In some cases, (5% MCC) the tensile strength of the rubber increased. The use of MCC also reduced the energy consumption of the process [27]. Thus the production of MCC from PMS could be of interest to be used as a filler in rubber composites

Nanocomposites.

Nanocellulose are ideal materials for reinforcement in biopolymer composites materials as a result of their high aspect ratio, high stiffness and low density [28,29]. Nano cellulose was obtained from PMS using high pressure defibrillation by steam exploding the fibers at 138kPa and chemical purification process with NaOH and acetic acid. The nanofibrils were successfully separated to uniform diameter below <20nm.The nanofibrils also preserved the original crystalline cellulose structure. The fibers were used in preparation of polyurethane (PU) nanocellulose composites which showed increase in mechanical properties after an addition of 4wt% of cellulose. The PU nanocellulose composite exhibited 45.6MPa tensile strength and a modulus of 152.63 MPa, ordinary PU specimen tested was at 17.5MPa and 37.5MPa respectively, this represents over 50% increase in mechanical properties [30]. Nano cellulose composite derived from PMS cellulose will be essential for lightweight materials. The nanofibers were bundles of cellulose fibers with 5 to 30 nanometers in width; this method of obtaining PMS nanofibers could be essential for improving applications of PMS.

4 Conclusions

Paper mill sludge shows a high potential for valorization into material applications. However, it is of no doubt that these applications require further research to meet technical standards for use in commercial products. The major issue with sludge in concrete is its effect on compressive strength and water absorption above 10%. Fiber board applications of PMS are generally affected by the increasing thickness swelling caused by water absorption, poor internal bonding between the fibers and inorganic content which results in low tensile and flexural strength. Further research into obtaining nanofibers from PMS for use in PMS board applications will improve their mechanical strength. Thermogravimetric analysis is required to study the effects of the hot press on the behavior of PMS fiber board composite due to the thermal decomposition of cellulose. Hydrophobic powder generated from PMS could be used to reduce the water absorption of the boards and concrete mixes. The type of resin used also has an effect on the properties of the PMS fiber composite which requires further investigation. PMS and recent biodegradable polymers such as Poly-lactic acid (PLA) or Polybutylene succinate could be investigated to form biodegradable fiber boards. Overall the research requires a holistic study on various sludge compositions used in multiple applications to assess how the material properties are affected by different variables. These considerations will assist the continuing development of recycling options for a range of sludge compositions.

References

1. Likon, M., Saarela, J.: The conversion of paper mill sludge into absorbent for oil spill sanitation - the life cycle assessment. Macromol Symp 320:50–56. (2012)
2. HM Revenue and Customs.: A general guide to landfill tax. (2015).
3. Likon, M., Cernec, F., Svegl, F., et al.: Papermill industrial waste as a sustainable source for high efficiency absorbent production. Waste Manag 31:1350–6. (2011)
4. Nemati, M., Caron, J., Gallichand, J.: Using Paper De-inking Sludge to Maintain Soil Structural Form Field Measurements. Soil Sci 64:275–285. (2000)
5. Ellen MacArthur Foundation:. Towards the circular economy vol.1: Available from: http://www.ellenmacarthurfoundation. org/publications/towards-the-circular-economy-vol-1-an-economic-and-business-rationalefor-an-accelerated-transition (2013)
6. Eichhorn SJ, Dufresne A, Aranguren M, et al (2010) Review: current international research into cellulose nanofibres and nanocomposites. J Mater Sci.
7. George J, S N S (2015) Cellulose nanocrystals: synthesis, functional properties, and applications. Nanotechnol Sci Appl Volume 8:45. doi: 10.2147/NSA.S64386
8. Bajpai, P.: Management of Pulp and Paper Mill Waste. Spring, Switzerland (2014)
9. Taramian, A., Doosthoseini, K., Mirshokraii, S.A., Faezipour, M.: Particleboard manufacturing: an innovative way to recycle paper sludge. Waste Manag 27:1739–46. (2007)

10. Huang, H.B., Du, H.H., Wang, W.H., Shi, J.Y.: Characteristics of Paper Mill Sludge-Wood Fiber-High-Density Polyethylene Composites. Polym Polym Compos 16:101–113. doi: 10.1002/pc (2012)
11. Davis E, Shaler SM, Goodbell B.: The incorporation of paper deinking sludge into fiberboard. For Prod Ind 53:46–54 (2003)
12. TAPPI T. : 211 om-02; Ash in wood, pulp, paper and paperboard: combustion at 525 C. TAPPI test methods 2005:3–6 (2004)
13. Rabemanolontsoa, H., Ayada, S., Saka, S.: Quantitative method applicable for various biomass species to determine their chemical composition. Biomass and Bioenergy 35:4630–4635 (2011)
14. Tappi .: TAPPI Slovent Extractives of wood and pulp (T204cm-97). Tappi 7–10 (2007)
15. Kaosol, T.: Reuse water treatment sludge for hollow concrete block manufacture. Energy Res J 1:131 (2010)
16. Nazar A.M., Abas N.F., Mydin M.A.: Study on the Utilization of Paper Mill Sludge as Partial Cement Replacement in Concrete. (2014)
17. Ferrándiz-Mas, V., Bond, T., García-Alcocel, E., Cheeseman, C.R.: Lightweight mortars containing expanded polystyrene and paper sludge ash. Constr Build Mater (2014)
18. Wong, H.S., Barakat, R., Alhilali, A., et al.: Hydrophobic concrete using waste paper sludge ash. Cem Concr Res (2015)
19. Guo, X., Jiang, Z., Li, H., Li, W.: Production of recycled cellulose fibers from waste paper via ultrasonic wave processing. J Appl Polym Sci 132 (2015)
20. Geng, X., Zhang, S.Y., Deng, J.: Characteristics of Paper Mill Sludge and Its Utilization for the Manufacture of Medium Density Fiberboard. Wood Fiber Sci 39:345–351 (2007)
21. Xing, S., Riedl, B., Deng, J., et al.: Potential of pulp and paper secondary sludge as co-adhesive and formaldehyde scavenger for particleboard manufacturing. Eur J Wood Wood (2013)
22. Ganesan, P., Karthik, T.: Development of acoustic nonwoven materials from kapok and milkweed fibres. J Text Inst 5000:1–6 (2015)
23. Moretti, E., Belloni, E., Agosti, F.: Innovative mineral fiber insulation panels for buildings: Thermal and acoustic characterization. Appl Energy 169:421–432. (2016)
24. Soucy, J., Koubaa, A., Migneault, S., Riedl, B. : The potential of paper mill sludge for wood-plastic composites. Ind Crops Prod 54:248–256 (2014)
25. Kim, S., Kim, H.J, Park, J. C.: Application of recycled paper sludge and biomass materials in manufacture of green composite pallet. Resour Conserv Recycl 53:674–679 (2009)
26. Ismail, H., Rusli, A., Azura, A.R., Ahmad, Z.: The Effect of Partial Replacement of Paper Sludge by Commercial Fillers on Natural Rubber Composites. J Reinf Plast Compos 27:1877–1891 (2008)
27. Bai,W., Li, K.: Partial replacement of silica with microcrystalline cellulose in rubber composites. Compos Part A Appl Sci Manuf 40:1597–1605 (2009)
28. Moon, R.J., Martini,A., Nairn,J., et al.: (2011) Cellulose nanomaterials review: structure, properties and nanocomposites. Chem Soc Rev. doi: 10.1039/c0cs00108b
29. Potulski D,C., De Muniz G,B., Klock, U., De Andrade A,S.: Green composites from sustainable cellulose nanofibril. Sci For Sci 40:345–351 (2014)
30. Leao A. L., Cherian, B.M., Narine, S., Sain, M.: Applications for Nanocellulose in Polyolefins-Based Composites. Polym Nanocomposites Based Inorg Org Nanomater 215–228 (2012)