

Porosity and Opacity of Paper Handsheets Using Lime Mud Waste from HDPE Catalyst Production as a Filler

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Abstract

This research work observed the variation of porosity and opacity of paper handsheets using a high-density polyethylene (HDPE) catalyst waste, a by-product from a HDPE catalyst production, as a filler. Chemically, this waste composition is ceramic based, it was calcium oxide-rich mud. The as-received mud waste was oven-dried and finely ground before applying for papermaking. The dried mud was screened through a series of sieves to get powders of various particle size ranges, i.e. over 80, 80-100, 100-200 and under 200 mesh. The waste powders replaced the conventional and commercial fillers: kaolin clay and ground calcium carbonate (GCC), in the filler to fiber weight ratio of 15:85. Then, fiber pulpstock and filler materials were thoroughly blended in water to make handsheets with a grammage of 65 g/m², without retention aid. Air resistance of the handsheets was examined by Gurley method to define porosity. The work revealed that particle size of the HDPE waste filler altered the air resistance of the handsheets, representing the porosity along the paper thickness. The handsheet papers with HDPE waste fillers contained higher pore content compared with those with conventional kaolin and GCC at the same filler load as well as paper grammage. However, it was noticed that smaller particle size facilitated air penetration compared to the larger one. The HDPE catalyst waste also provided slightly higher opacity relative to the conventional ones, yielding approximately 87-89%; however, this property was slightly sensitive to filler particle sizes. This suggested that the use of HDPE catalyst waste in papermaking offered ink absorption and may affect printing ability.

Keywords: HDPE catalyst waste; porosity; opacity; filler; papermaking

Introduction

In papermaking, filler materials are very important in order to control the whole properties of the papers to serve various specific purposes, for example, strength, brightness, opacity, whiteness

and smoothness, not only for more reasonable production cost. A variation in paper properties strongly depends on filler particle characteristics including chemical composition, particle size, shape and distribution, specific surface area, refractive

index, hardness, color etc. The main role of fillers is to fill up voids between fiber network, meanwhile, porosity and strength still are to be compromised. Filler materials can be obtained from natural mineral sources, such as ground limestone or ground calcium carbonate (GCC), talc, chalk and calcined kaolin. Fillers derived from synthetic sources, like precipitated calcium carbonate (PCC), synthetic gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), synthetic titanium dioxide (TiO_2), amorphous silica (SiO_2), gibbsite (ATH) and precipitated aluminosilicate or chemically structured kaolin, can be also employed [1]. The search for alternative sources of filler materials becomes more challenging to extend paper properties to serve different paper applications. The use of inorganic, non-toxic, solid industrial waste has been recently and globally of interest.

The HDPE catalyst production commonly requires the active additives, so called Ziegler-Natta catalysts, to urge the ethylene polymerization process. The HDPE catalyst production involves several Ti-containing reactants covering titanium tetrachloride (TiCl_4), titanium trichloride (TiCl_3) together with some organoaluminium and organoaluminium chloride compounds to chemically react under low pressure and moderate temperature. After the Ziegler-Natta catalysts are obtained and the catalyst treatments are undergone, the process leaves a solid by-product, a slaked lime, behind. This lime, known as lime mud, is a precipitation of very fine particles mainly containing calcium carbonate or limestone (CaCO_3) as well as calcium oxide (CaO). Such components are of interest in paper making because fine CaCO_3 particles are most commonly used as fillers in papermaking, apart from kaolin clay and chalk. Meanwhile, titanium dioxide (TiO_2) can offer opacity to papers, which may be beneficial to enhance the paper optical and physical properties.

In fact, the lime mud wastes come from petrochemical industries being utilized as fillers or binders in various materials have been studied and reported. Lime mud or lime sludge derived from various origins, which may hold toxicity and be dumped off the landfills in vain, can be technically used in many ways. Industrial lime sludge derived from paper mill was surface treated by stearic acid and applied as reinforced particles in HDPE and other polymeric composites [2,3]. Paper mill lime mud from paper mill industries could be partially substituted in cement-free ultra-high-performance concretes [4] by replacing silica sand and silica powder. It was reported that this lime-rich waste could offer satisfactory mechanical properties. Lime mud from HDPE catalyst containing high TiO_2 and CaO could be employed as an opacifier in mid-fired white and opaque ceramic glazes [5], however, thermal expansion matching between body and glaze was to be carefully considered. As a binder, the eco-friendly cement clinkers made from a mixture of lime mud, wastewater sludge and biomass ash were also introduced [6]. Lime mud collected from chemical recovery in pulp and paper manufacturing process could be used as a paper filler [7]. From the study, lime mud could become a potential source of crude carbonates in coated papers when the alkali-washed and dried lime mud was employed. The mechanical and physical properties of the tested handsheets were equivalent to those made from commercial CaCO_3 fillers. Most studies reviewed that the applications of such wastes could be achieved when the wastes were alkali removed, chemically treated or thermally treated (calcined) before being used.

This research focused on the use of lime mud obtained from HDPE catalyst production as a filler in papermaking. Without washing or chemical treating, the as-received HDPE catalyst lime mud

wastes were oven dried, ground into powders and screened. The powdery wastes of 4 different sizes, ranging from over 80, 80-100, 100-200 and under 200 mesh, were then employed in the prepared paperstocks to form handsheets. The physical properties of the handsheets, i.e. paper porosity and opacity, were observed and compared with two natural, conventional commercial-grade fillers: kaolin clay and ground calcium carbonate (GCC) powders.

Materials and Methods

Material Preparation

There were 2 main ingredients in the paper mixture, i.e. wood fiber and fillers. Commercial bleached hardwood fibers, together with both commercial grade kaolin clay and GCC were derived from SCG Packaging Public Company Limited, Thailand (formerly SCG Thai Paper Public Company Limited). As for the lime mud, the as-received HDPE catalyst production waste, in the form of filtered cake, was also obtained from SCG Chemicals Public Company Limited (Thailand). The lime waste collected from the plant in the form of mud-like paste was oven-dried at 110 °C overnight. The dried paste was hand-ground into powders. The characterization of the HDPE waste material was reported in literatures elsewhere [1,5,9-10]. The finely ground mud waste was then screened through a series of sieves after ASTM E11 [11], the aperture sizes of which were over 80 mesh, 80-100 mesh, 100-200 mesh and under 200 mesh, representing >180 μ m, 150-180 μ m, 75-150 μ m and <75 μ m, respectively. Later, the 4 different particle size ranges were collected and kept in a dry place. Other 2 fillers, i.e. commercial filler-grade kaolin clay and ground calcium carbonate (GCC) were used to prepare the reference papers.

Sample Preparation

To get the paperstock, the hardwood fibers were soaked and disintegrated evenly in water with a stirrer to achieve 350 ml fiber mixture. Then, the filler of 15wt% based on the oven-dried sheet weight was added into the mixture, so the weight fraction of filler to fiber yielded 15:85. Neither cationic and anionic dispersants, retention aids nor other additives were used. After that, the paperstock was carefully fabricated into tested handsheets according to ISO 5269-2 with a grammage of 65 g/m² and a thickness of 0.10 mm, approximately.

Characterization

The characteristics of the filler materials, including specific gravity, phase presence, chemical composition, were observed. Specific gravity was measured using a pycnometer, whereas phase and chemical compositions were analyzed by the means of X-ray diffractometry (XRD) and X-ray fluorescence spectrometry (XRF), respectively. XRD parameters covered the scan angle (2θ) of 10-70° and the scan rate of 0.02 °/point, with CuK _{α} target ($\lambda=1.54060$ Å). The particle size values of the fillers were also reported by a sieve analysis. Chemical composition of the fillers used in this study is shown in Table 1. Meanwhile, the prepared handsheets paper were characterized. The handsheets were later dried and cut into test sheets. Air resistance was examined by Gurley method [12] according to TAPPI T460 standard and reported in the term of time (in seconds). The Gurley method, so called Gurley densometer, is a measurement of air permeability, estimating by time of a 100 ml air travelling in seconds through a 1.0 square inch paper area under the ambient condition. The applied pressure of air is 1.22 kPa. Higher Gurley time indicates the greater resistance of air permeability. Air resistance can inversely reflect the porosity presented along the paper handsheet thickness. Meanwhile, the opacity

of the handsheets was determined according to TAPPI T425 standard. The relationship of porosity, opacity and particle size of the HDPE catalyst waste filler was discussed and reported.

Results and discussion

Raw material characterization

After drying the as-received HDPE catalyst waste mud at 110 °C, the off-white dried waste containing only 20% solid content was left behind. The chemical composition of the dried waste is displayed in Table 1, showing the major elemental constituents of Ti, Ca, Cl and Al along with the small amounts of other attachments. The Ti element was from the Iso-par treatment to deactivate titanium-based compound reactivity using water. High contents of Ca came from the pH neutralization of the HDPE catalyst production by-products using limestone (CaCO_3). Unlike lime muds from other sources, the alkali content could not be detected, thus the alkali washing was not necessary. The possible compounds formed in the waste were in the forms of oxides, chlorides, hydroxides or the combination of them. The X-ray patterns of the dried mud waste confirmed a combination of possible compounds was formed, that is, titanium dioxide (TiO_2), both anatase and rutile phases, calcium aluminium oxide hydroxide hydrate ($3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Ca}(\text{OH})_2\cdot 18\text{H}_2\text{O}$), gibbsite ($\text{Al}(\text{OH})_3$), calcium chloride hydroxide hydrate ($\text{Ca}(\text{OH})_2\cdot\text{CaCl}_2\cdot 2\text{H}_2\text{O}$), as presented in Figure 1. This could be explained that the HDPE catalyst waste contained some structural water. Once the waste was left in an ambient air, the moisture could be slightly reabsorbed. As far as the specific gravity values of the filler powders were concerned, the measured waste powder specific gravity yielded to 2.04 [5,9], while that of typical commercial kaolin clay and GCC were 2.5 and 2.6, respectively

Table 1. Specification of chemical composition of HDPE catalyst waste

Elemental composition	Amount (wt%)
Ti	48.8
Ca	28.8
Cl	10.7
Al	10.6
Mg	0.49
Si	0.25
Fe	0.24
S	0.14
Others (Cu, Zn, Zr etc.)	<0.06

Physical properties of the prepared handsheets are exhibited in Table 2, showing that the grammage values of the papers containing filler content of 15% of the dried sheet weight fell between 63-66 g/m². At the similar filler loading of 15%, the experimental results revealed slightly higher grammage values compared with those containing kaolin clay and GCC even though the specific gravity of the HDPE catalyst waste powder was only 2.04. The higher paper grammage was possibly caused by the difference in particle size. This finding clearly agreed with the study reporting the relationship between thickness index and filler diameter [14]. Relatively, the particle sizes of the introduced HDPE catalyst waste filler were much larger than those of kaolin clay and GCC, thus they can retain and stay among fiber spacing, as seen in Figure 2. During handsheet formation, the hardwood fibers and filler particles were thoroughly blended with water before dewatering onto the screen. Larger particles could stay inside fibrous networks, not go along with white water, leading to higher amounts of particles trapped within the handsheets.

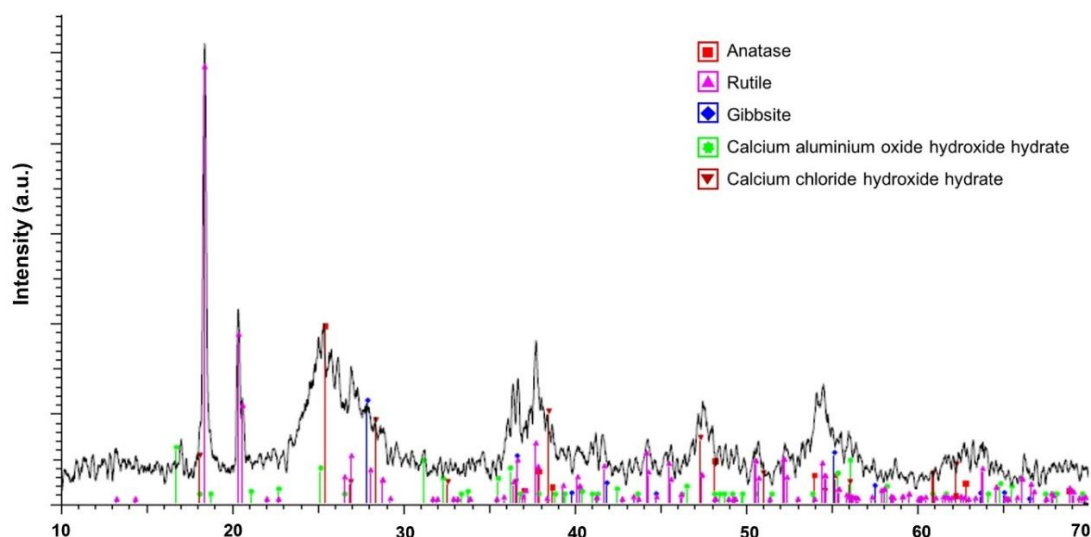


Figure 1. XRD pattern of the dried lime mud waste

Table 2. Physical properties of filler materials and the prepared handsheets with 15% filler

Filler type	Particle size	Grammage (g/m ²)	Thickness (mm)
Fiber (no filler added)	n/a	64.66 ± 0.90	0.095 ± 0.004
Kaolin clay*	2-5 mm, approx.	64.27 ± 0.76	0.090 ± 0.001
GCC*	10 mm, approx.	63.75 ± 0.11	0.097 ± 0.003
HDPE waste, > 80 mesh**	> 180 mm	65.72 ± 0.78	0.136 ± 0.007
HDPE waste, 80-100 mesh**	150-180 mm	64.87 ± 0.48	0.134 ± 0.006
HDPE waste, 100-200 mesh**	75-150 mm	65.32 ± 0.42	0.114 ± 0.004
HDPE waste, < 200 mesh**	< 75 mm	65.86 ± 0.63	0.116 ± 0.005

* Information from MSDS ** Calculated values according to ASTM E11 [11]

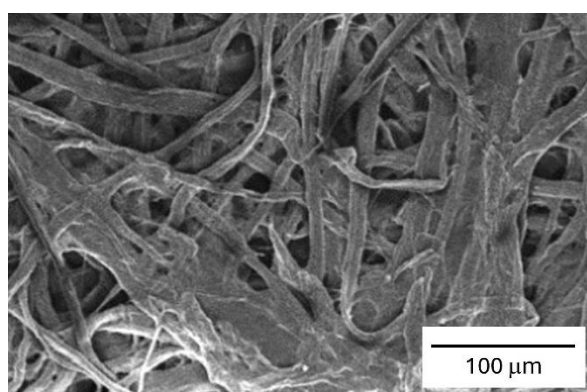


Figure 2. Micrograph of fiber packing in the paper handsheets

A variation in air resistance through the handsheets is displayed in Figure 3, indicating HDPE catalyst waste powders obviously blocked the air penetration at different levels and the time of

air passing through the handsheets related to its particle sizes. By the filler particle sizes and shapes, the air flow ability may vary since the filler particles are located among fiber networks. Larger particles

tended to be trapped, and they extended the pore cavity in the fiber networks. Actually, air resistance can infer to the porosity throughout the paper thickness. The air resistance values, obtained from Gurley method, depend on various factors [12] including void volume among fibers, pore size distribution, pore connectivity and filler characteristics. Fibers and fillers are solid materials; therefore, they do not allow the air to flow through freely. Air can flow through the connected pores. The addition of fillers may result in either pore blockage or enhance air path connectivity. From Figure 3, smaller particles of under #200 (< 75 μm) could possibly embed inside fibers or deposit on fiber surfaces. Without retention aids, some of them went out with white water (the water removed from the handsheet during papermaking) while the rest stayed on the handsheets, creating poor pore bridging or even mildly disrupt fiber-to-fiber bonds. Fine particles tended to agglomerate and generate many small, open and connected pores instead. Meanwhile, slightly larger particles, i.e. #100-200 (75-150 μm) and #80-100 (150-180 μm), the HDPE catalyst waste powders were large enough to fill void between fibers and could block pore entrance. This led to a reduction in pore opening and more dead-end pores could be found, resulting in a gradual increase in air travelling times. As far as the coarse particles were considered, such larger particles could possibly act as a spacer, physically bridge across fibers and lodge between fibers. They turned the fibrous structure from macro- and connected pore-containing structure to narrower pore channels, in other words, sheets have more closed structure. So, it was suggested that coarser particles could facilitate interfiber spacing within the papers [13-14]. Due to strong bridging effects, air took more time to flow through as seen as higher air resistance values. The addition of HDPE catalyst

waste powders with various sizes might not change the pore volume but it did reduce the pore connectivity.

When compared to the conventional fillers, the air flow constraints through the handsheets were higher even though their particle sizes were much smaller. This could be caused by the difference in particle alignment, particle morphology, regularity and uniformity. Practically, both commercial GCC and kaolin clay have massively finer particle sizes than that of the HDPE catalyst waste, as shown in Table 2. Fine particles of GCC can randomly obstruct pore network and affect the structure heterogeneity. Meanwhile, the plate-like particles of kaolin clay can align along the fiber network [1,13], leading to less pore connection. In addition, filler morphology affects dewatering of papers during sheet formation and the needs in sizing chemicals [13]. Unfortunately, no additives were included in the study. It could be concluded that the change in air resistance according to the existence of HDPE catalyst waste was related to its particle sizes. More effective pore blockage was enhanced when larger particle HDPE catalyst waste by disturbing pore connectivity. Finer particles, in turn, were more evenly and less effective at pore blockage. The schematic of filler particles in fiber structures showing fiber packing and pore formation have been illustrated in literature [e.g. 1,15].

Figure 4 displays the effects of filler materials on opacity of the paper handsheets. As far as the opacity of the handsheets according to HDPE catalyst waste addition is concerned, it could be seen that handsheets with the waste powder fillers were opaquer than the other two with kaolin clay and GCC fillers, fibers without fillers ranked lowest opacity. This could be explained in the term of optical property: light scattering. In fibers only handsheets, the light is scattered from fibers and air

cavity which depends on fiber-air bonding structure. The packing in fibers only handsheets shown in Figure 3 suggested the paper is quite dense, leading to high air resistance. Light, therefore, could pass through the fibers and air cavities without any light scattering from filler particles. Meanwhile, the introduction of the filler material changes the light-fiber-air cavity interaction. Kaolin clay provided slightly higher opacity due to its plate-like morphology, the platelet particles allowed scattering efficiency along with pore creation. Blocky GCC powders scattered the light better than kaolin clay because of coarser particle size. Finer particle size of clay compared with GCC exhibited more opacity. Apart from particle morphology and pore formation, refractive index might also come into play [1]. Higher refractive index value is supposed to promote opacity, that is, kaolin refractive index is around 1.55 while that of GCC yields approximately 1.59 and possibly more varied due to particle size distribution.

As for the HDPE catalyst waste addition, the range of particle size employed in the handsheets did govern opacity. The opacity values of HDPE catalyst waste fillers were 87-89%, a bit higher than that of kaolin clay (85.3%) and GCC fillers (86.98%). The obtained opacity values were greater than the

study using treated lime mud (median diameter of 5.3 mm, approximately) from chemical recovery plant in papers which achieved only 78% [7]. In fact, light scattering which governs opacity is controlled by several factors [1] : i.e. (1) particle size of the fillers relative to visible light wavelength (400-700 nm), (2) dispersion and distribution of the particles and pores along fiber network structure and (3) refractive index of the filler and fiber-air and (4) particle shape or aspect ratio [13]. Too coarse particles of over #80 had fewer interfaces and scattered less efficiency than the finer one at the same volume, accompanying with less porosity throughout the sheets. Fine particles tended to offer higher pore content as well as better light scattering according to higher interfacial areas, therefore, slightly higher opacity could be observed [13]. The schematic of fillers agreed with the experimental results of air resistance mentioned above. Due to the waste composition, high content of TiO_2 , in the form of rutile, might show its efficiency as an opacifier, as it does in typical opaque glaze compositions. The residual multiphase composition may increase refractive index heterogeneity. However, the study on refractive index value of the HDPE catalyst waste powder was not yet included herein.

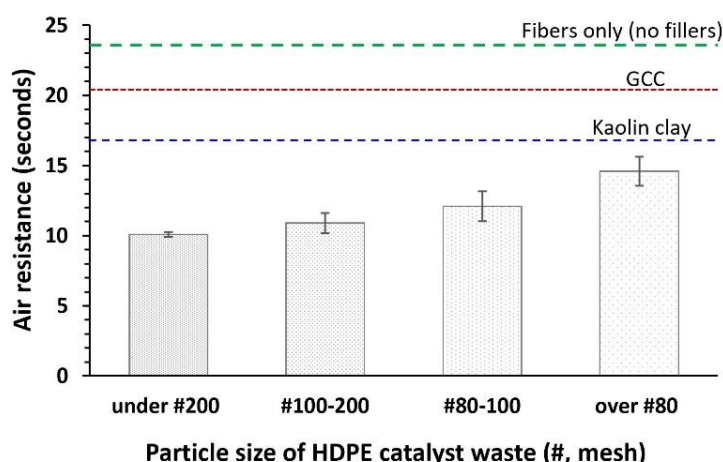


Figure 3. A variation in air resistance through the handsheets as a function of particle size of the HDPE catalyst waste powders

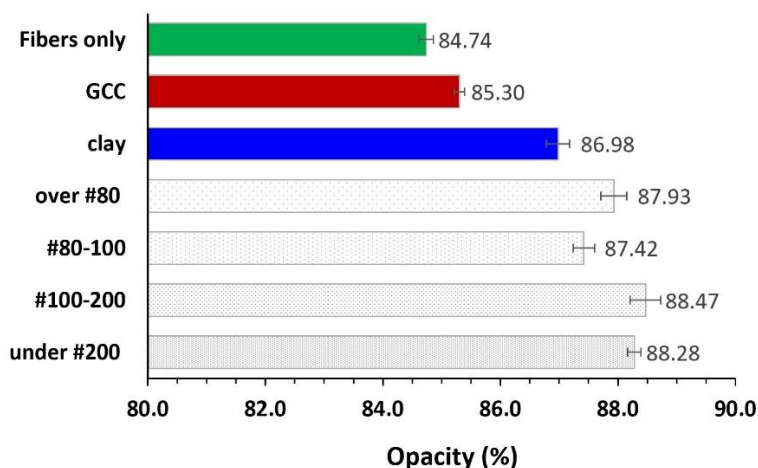


Figure 4. The measured opacity values of the handsheets using different types of powder fillers

Conclusion

The physical and optical properties of the paper handsheets containing the HDPE catalyst waste powders, porosity and opacity, respectively, were investigated and compared with conventional and commercial filler materials: kaolin clay and GCC. The HDPE catalyst waste powder could be employed and could be a potential filler substitute due to it provided opacity, even it exhibited high pore contents along the handsheet thickness. Particle sizes of the HDPE catalyst waste powders controlled both air resistance and opacity. More effective opacity in papers with HDPE catalyst waste powders was observed. Larger particle sizes brought about more porous handsheets but smaller ones favor opaque efficiency. Better performance can be achieved when optimal particle size of HDPE catalyst waste powders could balance both light scattering activity and pore preservation. The future work should cover the finer HDPE catalyst waste powder sizes, at the same levels of commercial clay and GCC. The studies on refractive index, particle shape and distribution of HDPE catalyst waste particles in the fiber network microstructure are strongly recommended.

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