USE OF ALUMINUM TRIHYDRATE FILLER TO IMPROVE THE STRENGTH PROPERTIES OF CELLULOSIC PAPER EXPOSED TO HIGH TEMPERATURE TREATMENT

Hua Chen, Kefu Chen, Rendang Yang, Fei Yang,* and Wenhua Gao

Cellulosic paper is thermolabile and its strength properties tend to decrease under high temperature conditions. In this work, the effects of aluminum trihydrate filler on the tensile and burst strength of paper prepared from bleached wood pulps were investigated. The use of aluminum trihydrate maintained the tensile and burst strength of paper sheet dried at 200 °C for 4 hours. Thermogravimetric analysis and differential scanning calorimetry gave the evidence that the maintainance of strength after drying associated with the use of aluminum trihydrate filler is possibly due to the increase in degradation temperature and heat absorption of cellulosic paper. The results regarding Fourier Transform Infrared spectroscopy, and the water retention value (WRV) and crystallinity index of fibers indicated the alleviated degradation of fibers when aluminum trihydrate was incorporated into the paper matrix.

Keywords: Aluminum trihydrate; Flame retardant; Strength properties; Fiber characteristics

*Contact information: State Key Lab of Pulp and Paper Engineering, South China University of Technology, Guangdong Public Laboratory of Paper Technology and Equipment, Guangzhou, China; *Corresponding author: yangfei@scut.edu.cn*

INTRODUCTION

Paper is usually made from plant fibers, which are complex materials composed of an orderly arrangement of cells within a cell wall including varying amounts of cellulose, hemicellulose, lignin, and extractives (Billa et al. 2000; Bertaud and Holmbom 2004; Conrad et al. 2003).

It is well known that the poor thermal stability of paper can be attributed to the degradation of celluloses and hemicelluloses of fibers (Sefain and Nada 1984; Odlyha et al. 1990). However, in practical applications, the suitability of certain paper grades to high temperature conditions is sometimes needed. For example, hot sheets of steel (at the temperature from 190 °C to 200 °C) are separated by interleaving paper during the production process of stainless steel, and the pattern on leather release paper is transferred to artificial or synthetic leather at temperatures from 160 °C to 200 °C, so the thermal stability of the paper at 200 °C is a very important parameter (Yang et al. 2007, 2008).

Great efforts have been made to improve the thermal stability of thermolabile substances, the applications of flame retardants are one of the most effective methods. Compounds used as flame retardants are usually divided into five groups based on their chemical composition: halogen compounds, phosphorous compounds, inorganic hydroxy compounds, nitrogen compounds, metallic oxides, and sulfides (El-Wahab et al. 2010).

Although the use of halogen and phosphorous compounds as flame retardants have been reported by many researchers (Hergenrother et al. 2005; Toldy et al. 2006; Kandola et al. 2010), much attention has been paid to the safety of halogen compounds, as they can discharge toxic gases along with acidic smoke during combustion (Sen et al. 1991), and the use of phosphorous compounds is usually hindered by its exorbitant price and the tendency to generate heavy smoke (Yeh et al. 1998). Thus, in recent years, a more significant amount of research and development efforts have been invested to the applications of inorganic flame retardants, including aluminum trihydrate, magnesium hydroxide, bentonite, borate, antimony oxide, stannate, and inorganic silicate, etc. (Xu and Deng 2006; Brebu et al. 2007; Du et al. 2009; Hamdani et al. 2009). Aluminum trihydrate has experienced increasing consumption owing to its good performances as flame retardant, smoke suppression effects, environment-friendliness, and low cost (Daimatsu et al. 2007; Wang et al. 2010).

In the papermaking industry, the use of fillers and the relevant filler engineering technologies has recently been a very hot topic (Deng et al. 2010; Dong et al. 2008; Hubbe 2004; Koivunen and Paulapuro 2010; Shen et al. 2009a,b,c,d, 2010a,b,c,d,e; Yoon and Deng 2006a,b, 2007; Zhao et al. 2005,2008). Significant benefits associated with the industry can potentially be achieved through innovations in the wet end use of fillers. As reported in the literature, the use of aluminum trihydrate as a filler can confer flame-retardant properties to cellulosic paper, in addition to its contribution to the optical properties (Holik 2006; Ma 2006; Shen et al. 2011). In this work, by applying aluminum trihydrate as a filler at the wet end, the effects of filler addition on the tensile and burst strength of paper (when exposed to treatment at relatively high temperature of 200 ^{o}C for 4 h) were investigated, and the water retention value and crystallinity index of fiber were analyzed.

EXPERIMENTAL

Materials

Northern bleached kraft pulp (NBKP) and bleached *Eucalyptus* kraft pulp (BEKP) were kindly supplied by Tianting Yalun Co. Ltd. (Zhejiang, China). Aluminum trihydrate (96% ISO brightness and 1.57 refractive index) was obtained from Martinswerk (Germany), and its mean diameter was determined to be 1.8 μm using a Laser Diffraction Particle Size Analyzer (MS2000MU, Malvern, Worcestershire, UK). Cationic polyacrylamide with the molecular weight of 8 million, substitution degree of 20% and positive charge of 1.53 meq/g was provided by Hengfeng Chemical Co.Ltd (Zhejiang, China).

Mechanical Refining

Softwood fibers are usually considered to be capable of achieving high sheet strength, while hardwood fibers can result in uniform sheet formation (Ai and Tschirner 2010). In this study, the weight ratio of softwood pulp and hardwood pulp was 85 to 15. The mixed pulp was refined to 40 ^{o}SR using a Valley Beater (ZQS2-23, SUST, Shanxi, China).

Handsheets Preparation and Testing

The refined pulp was diluted to 1.2% consistency with distilled water, then disintegrated in the standard disintegrator at 20,000 revolutions until all fiber bundles were dispersed. Then 400 ppm cationic polyacrylamide was added under stirring at 6000 revolutions followed by aluminum trihydrate, with the addition levels of aluminum trihydrate (at the consistency of 5%) fixed at 1%, 3%, 5%, and 7% (based on oven- dry pulp mass) under stirring at 6000 revolutions. Handsheets with target basis weight of 60g/m^2 were prepared using the Model 1600 Ecno-Space Automatic Sheet Former System (Réalisations Australes Inc., Canada) according to TAPPI T 205, except that the pressure for wet sheet pressing was controlled at 200 kPa, followed by drying at 102°C using a Formax 12" Drum Dryer (Thwing-Albert Instrument, USA). The handsheets were conditioned under controlled environment (temperature of 23±1^{o}C and relative humidity of 50±1 %) before analysis.

The tensile indices, burst indices, and ash contents of handsheets were determined according to the relevant TAPPI Standards. Incidentally, the tensile indices and burst indices were also measured for the handsheets having been thermally treated in an oven at 200°C for 4 hours. The strength properties (tensile and burst indices) of the paper sheets were determined using the L&W CE062 Tensile Strength Tester (Sweden) and L&W CE180 Bursting Strength Tester (Sweden). All samples were tested three times, with standard deviations of about 5%.

Thermal Gravimetric Analysis

Thermal gravimetric analysis (TGA) of the handsheets was conducted using a NETZSCH TG209 Jupiter Thermal Analysis System (TA Instruments, USA) as follows: sample weight about 5mg, heating rate 10 °C min^{-1} from 40 °C to 600 °C, and flow rate of N_2 30 mL min^{-1}.

Differential Scanning Calorimetry Analysis

The Differential scanning calorimetry analysis (DSC) was performed under standard conditions with a flow of extra-pure nitrogen using a DSC Q200 differential scanning calorimeter (TA Instruments, USA). The operating conditions were: temperature range of 0 °C to 350 °C, heating rate of 10 °C min^{-1}, and flow rate of extra pure nitrogen of 30 mL min^{-1}.

Measurement of WRV

The measurement of WRV was conducted following the centrifugation method (Lindström and Söderberg 1986). 1.5 g hansheet samples based on dry weight were soaked with deinozied water for 24 h; subsequently disintegrated in standard disintegrator with 6000 revolutions. Then the stock was centrifugated at 3,000 g for 15 min and then weighed in a pre-weighed weighting bottle, followed by drying in an oven at 105±2 °C for 24 h and re-weighing. WRV was calculated based on the following equation,

$$WRV = \frac{m_1 - m_2}{m_2} \times 100\% \quad (1)$$

where m_1 is the weight of the wet paper mat after centrifugation, and m_2 is the weight of the dry paper mat (in grams).

Fourier Transform Infrared Spectroscopy Analysis and Determination of Crystallinity Index

Fourier transform infrared spectroscopy analysis (FTIR) of the handsheets was carried out in transmission mode using macro techniques (13mmΦ pellet; ca.1.5mg sample with 350mg KBr). The spectra were recorded with a Nexus Vector spectrometer made by Thermo Nicolet (Nexus 670, Thermo Nicolet Company, USA) under the following specifications: Apodization: triangular; Detector: DTGS/KBr; Regulation: 4 cm^{-1};Number of scans: 32.

Crystallinity index was calculated from the relative intensities of the infrared bands (Nelson and O'Connor 1964),

$$N.O'KI = \frac{I_{1372}}{I_{2900}} \times 100\% \quad (2)$$

where I_{1372} represents the intensity (1372 cm^{-1}) of the band belonging to the CH bending vibration, and I_{2900} is the intensity (2900 cm^{-1}) of the band belonging to the CH and CH_2 bending vibrations.

RESULTS AND DISCUSSION

Influence of Aluminum Trihydrate on the Physical Strength of Paper

The influence of aluminum trihydrate on the strength properties of paper is shown in Table 1. With the increase in the amount of aluminum trihydrate (from 1% to 7%), the ash content increased; however, the tensile and burst strength of paper without thermal treatment at 200 °C was somewhat negatively influenced. When the unfilled handsheets were thermally treated at 200 °C for 4 hours, the tensile index and burst index decreased from 99.52 N·m/g to 70.81 N·m/g (decreased by about 30%) and from 6.12 kPa·m^2/g to 3.79 kPa·m^2/g (decreased by about 40%), respectively. Interestingly, although the use of aluminum trihydrate slightly decreased the tensile and burst strength of paper without thermal treatment at 200 °C, the strength properties of the filled paper thermally treated at 200 °C were much superior to those of unfilled paper. Thus, as far as the strength properties of paper are taken into consideration, the use of aluminum trihydrate filler can contribute to the thermal stability of paper. For example, the use of aluminum trihydrate with the amount of 1% improved the tensile strength of thermally treated paper by above 14%, while the tensile strength of paper without thermal treatment was basically unaffected.

Table 1. Influence of ATH on Strength Properties of Paper Sheet

Handsheet Samples	Amount of Aluminum Trihydrate (%)	Ash Content (%)	Tensile Index (N·m/g)		Burst Index (kPa·m²/g)	
			a	b	a	b
Unfilled Handsheets	0	0.2	99.52	70.81	6.12	3.79
Filled Handsheets	1	0.7	98.56	81.11	6.01	4.75
	3	1.8	95.41	86.44	5.93	5.16
	5	2.6	92.23	86.79	5.80	5.28
	7	3.0	90.16	85.74	5.61	5.17

(a): handsheets without thermal treatment; (b): handsheets after exposure to 200 □ for 4 h

Thermal Degradation

The thermogravimetric, DTG, and DSC curves of the unfilled and filled handsheets with 5% aluminum trihydrate are shown in Fig. 1. When the temperature was lower than 350 °C, the weight loss of unfilled handsheets was greater than the filled handsheets. The weight loss peak of unfilled handsheets was 330 °C, and the relevant peak of filled handsheets was 341 °C.

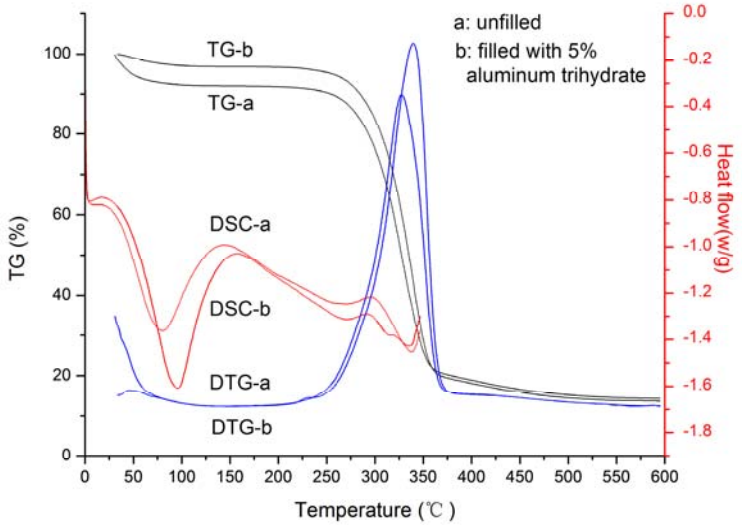

Fig. 1. Thermogravimetric, DTG, and DSC curves of unfilled and filled handsheets: (a): unfilled handsheets; (b): filled handsheets with 5% aluminum trihydrate.

An endothermic peak associated with the loss of absorbed water was observed at about 78°C in DSC-a curve (Schmolz et al. 2000), and the enthalpy change (ΔH) was 143.7 J/g. When aluminum trihydrate was added with the amount of 5%, the temperature of the first endothermic peak was shifted to 95°C, and ΔH was increased to 241.2 J/g, showed some heat was adsorbed by aluminum trihydrate, and the thermal stability of paper was enhanced. Residual lignin in pulp degraded at 270°C induced the endothermic peak at this temperature (Martin et al. 2010). The endothermic peak at 310°C of filled handsheets was attributed to the decomposition of ATH (Klprogge et al. 2002). On the other hand, the endothermic peaks at 335°C for unfilled handsheets and 339°C for filled handsheets are due to the dehydration and depolymerization of cellulose, respectively (Nada and Hassan 2000).

Water Retention Values

In recent years, extensive attention has been given to the research on irreversible changes in cellulose reswelling after drying due to the wide applications of recycled fibers in papermaking industry (Nazhad and Paszner 1994; Diniz et al 2004; Brancato et al 2007; Hubbe et al 2007). The polymer structure change taking place in lignocellulosic materials upon drying or water removal is called 'hornification' (Östlund et al. 2010). WRV has been used to evaluate the degree of hornification upon drying by measuring the change in water sorption behavior (Fernandes et al. 2004). Figure 2 shows the WRVs of unfilled and filled handsheets with or without drying treatment. The WRVs of both unfilled and filled handsheets without drying treatment were 131.09% and 127.19%, respectively. When thermally treated in an oven at 200 °C for 4 hours, the WRV of unfilled handsheets decreased to 55.21% (decreased by 57.88%), and the value of filled handsheets decreased to 69.89% (decreased by 45.05%), possibly indicating the positive role of filler addition in maintaining fiber swelling. The reason for the decreased WRVs of handsheets when thermally treated at 200°C is that thermal treatment increases not only the rate of evaporation but also molecular mobility (Kato and Cameron 1999), resulting in irreversible pore closure in cellulose fibers and the decreased swelling capacity (Häggkvist et al. 1998).

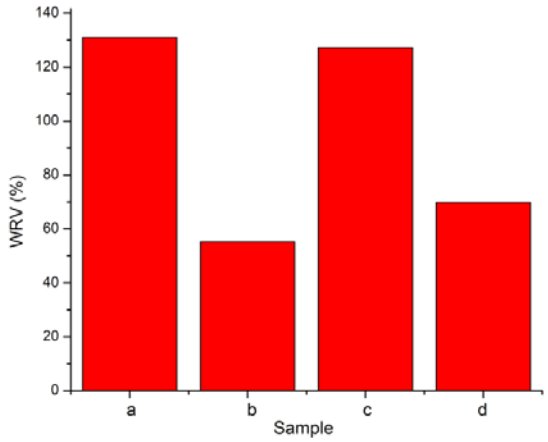

Fig.2. WRVs of different handsheet samples: (a) unfilled handsheets without drying treatment in an oven at 200 °C for 4 hours; (b) unfilled handsheets thermally treated in an oven at 200 °C for 4 hours; (c) filled with 5% aluminum trihydrate handsheets without drying treatment in an oven at 200 °C for 4 hours; (d) filled with 5% aluminum trihydrate handsheets thermally treated in an oven at 200 °C for 4 hours.

Functional Group Analysis and Crystallinity Indices

Figure 3 shows the FTIR spectra of the above mentioned handsheet samples. The 3400 cm^{-1} peak was attributed to hydroxide groups (OH) among the fibers (Meireles et al., 2007). The peak at 2900 cm^{-1} indicates the absorption peak of C-H. The strong band at 1640 cm^{-1} might be assigned to the vibration of absorbed water molecules in the non-crystalline region of cellulose. The bands at 1431, 1374, 1165, 1114, and 1033 cm^{-1} were due to the characteristic bending or stretching vibrations of different groups for lignin and cellulose, and the peak at 898 cm^{-1} might be associated with cellulose P-chains, C-H stretching out of plane of aromatic ring (Chen et al. 2010). In spectra c and d, the peak at

560 cm^{-1} represents the characteristic vibration of Al-O groups (Wang et al. 2008). In spectrum b, relative intensity of peaks of 1660 and 898 cm^{-1} to 3400 cm^{-1} were obviously weaker compared with spectrum a, indicating that the glucose unit of the cellulose chain was significantly degraded. As this obvious difference was not found in spectra c and d, these results showed that the presence of filler particles might alleviate the degradation of cellulosic fibers.

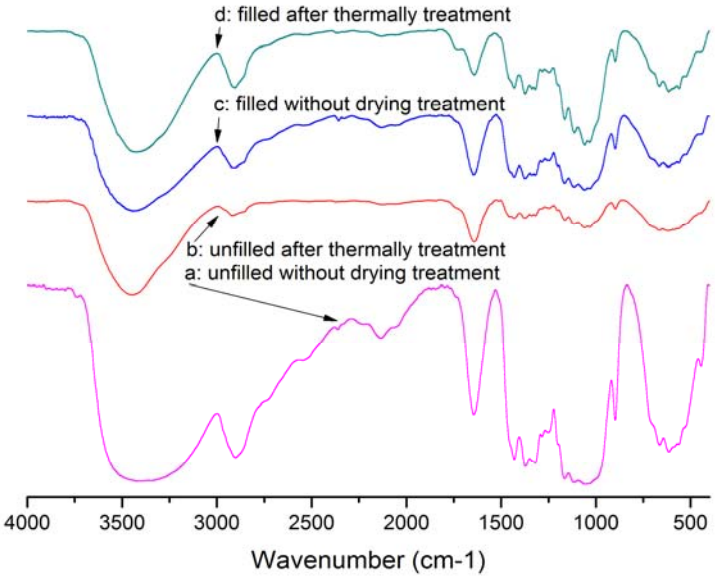

Fig. 3. FTIR spectra of different handsheet samples: (a) unfilled handsheets without drying treatment in an oven at 200 °C for 4 hours; (b) unfilled handsheets thermally treated in an oven at 200 °C for 4 hours; (c) filled with 5% aluminum trihydrate handsheets without drying treatment in an oven at 200 °C for 4 hours; (d) filled with 5% aluminum trihydrate handsheets thermally treated in an oven at 200 °C for 4 hours.

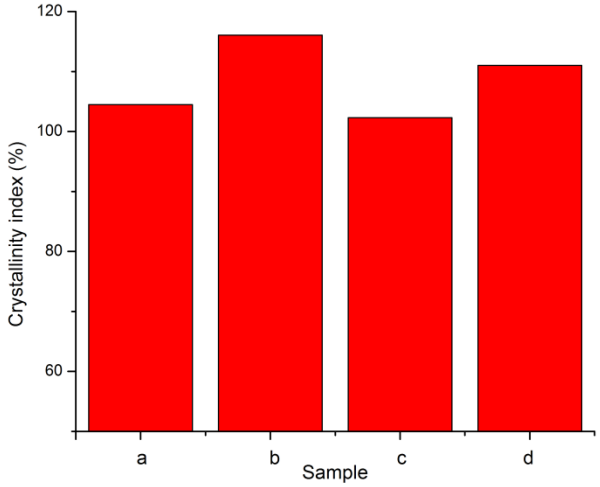

Fig.4. Influence of ATH on crystallinity index of fiber: (a) unfilled handsheets without drying treatment in an oven at 200 °C for 4 hours; (b) unfilled handsheets thermally treated in an oven at 200 °C for 4 hours; (c) filled with 5% aluminum trihydrate handsheets without drying treatment in an oven at 200 °C for 4 hours; (d) filled with 5% aluminum trihydrate handsheets thermally treated in an oven at 200 °C for 4 hours

The crystallinity index of cellulosic fibers is defined as the weight fraction of crystalline cellulose in fibers. The crystallinity indices of different handsheet samples are shown in Fig. 4. For both unfilled and filled handsheets, thermal treatment at 200°C for 4 hours increased the crystallinitity indices (by 11.09% and 7.64%, respectively). It has been reported that the cellulose crystallinity of pulps increased after drying (Rebuzzi and Evtuguin 2006). While this phenomenon is still not very well understood, one possible reason might be associated with co-crystallization: a small fraction of cellulose chains in adjacent crystalline domains are induced to be parallel over a sufficient distance, causing an increase in crystallinity index (Newman 2004). Another possible reason is that amorphous regions in fibers partly crystallize during drying (Karnis 1994). Evidently, the increase in crystallinity index means a decrease in amorphous regions as well as in the capacity for swelling.

CONCLUSIONS

The above studies can be summarized as follows:

1. The use of aluminum trihydrate filler in papermaking was found to be capable of improving the tensile and burst strength of cellulosic paper exposed to treatment at 200 °C for 4 hours, in comparison to un-filled paper samples.
2. Thermogravimetric analysis and differential scanning calorimetry indicated that the use of aluminum trihydrate filler could possibly result in the increase in degradation temperature and heat absorption of cellulosic paper, which might contribute to the maintainance of tensile strength at the relatively high temperature conditions, The alleviation of degradation was also confirmed by the results from Fourier transform infrared spectroscopy, WRV, and the crystallinity index of paper.

ACKNOWLEDGMENTS

The authors would like to acknowledge support from the National Basic Research Program of China (973 Program) (2010CB732205), the Natural Science Foundation (X2QSE5090600) of South China University of Technology for Young Scholar ， Specialized Research Fund (20090172120021) for the Doctoral Program of Higher Education and the Fundamental Research Funds for the Central Universities，SCUT.

REFERENCES CITED

Ai, J., and Tschirner, U. (2010). “Fiber length and pulping characteristics of switchgrass, alfalfa stems, hybrid poplar and willow biomasses,” *Bioresource Technol.* 101, 215-221.

Bertaud, F., and Holmbom, B.(2004). "Chemical composition of earlywood and latewood in Norway spruce heartwood, sapwood and transition zone wood, " *Wood Sci. Technol.*38, 245-256.

Billa, E., Pastou, A., Monties, B., Romero, J., and Koukios, E. G. (2000). "Multivariate chemometric analysis of the fluorescence spectra of eucalyptus wood, " *Ind. Crop. Prod.* 11, 187-196.

Brancato, A., Walsh, F. L., Sabo, R., and Banerjee, S. (2007). "Effect of recycling on the properties of paper surfaces," *Ind. Eng. Chem. Res*. 46, 9103-9106.

Brebu, M., Jakab, E., and Sakata, Y. (2007). "Effect of flame retardants and Sb2O3 synergist on the thermal decomposition of high-impact polystyrene and on its debromination by ammonia treatment," *J. Anal. Appl. Pyrol.* 79, 346-352.

Chen, H. L., Ferrari, C., Angiuli, M., Yao, J., Raspi, C., and Bramanti, E.(2010). "Qualitative and quantitative analysis of wood samples by Fourier transform infrared spectroscopy and multivariate analysis," *Carbohyd. Polym.* 82, 772- 778.

Conrad, M. P.C., Smith,G. D., and Fernlund, G. (2003). "Fracture of solid wood: A review of structure and properties at different length scales," *Wood Fiber Sci.* 35, 570- 584.

Daimatsu, K., Sugimoto, H., Kato, Y., Nakanishi, E., Inomata, K., Amekawa, Y., and Takemura, K. (2007). "Preparation and physical properties of flame retardant acrylic resin containing nano-sized aluminum hydroxide," *Polym. Degrad. Stabil.* 92, 1433-1438.

Deng, Y. L, Jones, P., McLain, L., and Ragauskas, A. J. (2010). "Starch modified fillers for linerboard and paper grades: A prospective review," *Tappi J.* 9(4), 31-36.

Dong, C.X., Song, D. L, Patterson, T., Ragauskas, A., and Deng, Y. L. (2008). "Energy saving in papermaking through filler addition," *Ind. Eng. Chem. Res.* 47, 8430-8435.

Diniz, J. M. B. F., Gil, M. H., and Castro, J. A. A.M. (2004)."Hornification- Its origin and interpretation in wood pulps,"*Wood Sci. Technol.* 37(6), 489-494.

Du, B. X., Guo, Z. H., Song, P. A., Liu, H., Fang, Z. P., and Wu, Y. (2009). "Flame retardant mechanism of organo-bentonite in polypropylene," *Appl. Clay Sci.* 45, 178-184.

El-Wahab, H. A., El-Fattah, M. A., and Gabr, M. Y. (2010). "Preparation and characterization of flame retardant solvent base and emulsion paints," *Prog. Org. Coat.* 69, 272-27.

Fernandes Diniz, J. M. B., Gil, M. H., and Castro, J. A. A. M. (2004). "Hornification—its origin and interpretation in wood pulps," *Wood Sci. Technol.* 37, 489-494.

Häggkvist, M., Li, T. Q., and Ödberg, L. (1998). "Effects of drying and pressing on the pore structure in the cellulose fiber wall studied by ^{1}H and ^{2}H NMR relaxation," *Cellulose* 5, 33-49.

Hamdani, S., Longuet, C., Perrin, D., Lopez-cuesta, J. M., and Ganachaud, F. (2009) "Flame retardancy of silicone-based materials," *Polym. Degrad. Stabil*. 94, 465-495.

Hergenrother, P. M., Thompson, C. M., Jr, J. G. S., Connell, J. W., Hinkley, J. A., Lyon, R. E., and Moulton, R. (2005). "Flame retardant aircraft epoxy resins containing phosphorus," *Polymer* 46, 5021-5024.

Holik, H. Handbook of Paper and Board. John Wiley & Sons Inc., 2006.

Hubbe, M. A. "Filler particle shape vs. paper properties - A review". (*2004). TAPPI Paper Summit - Spring Technical and International Environmental Conference*, p 141-150.

Hubbe, M. A., Venditti, R. A., and Rojas O. J.(2007)."What happens to cellulosic fibers during papermaking and recycling? A review, "*BioRes.* 2(4),739-788.

Kandola, B. K., Biswas, B., Price, D., and Horrocks, A. R. (2010). "Studies on the effect of different levels of toughener and flame retardants on thermal stability of epoxy resin, " *Polym. Degrad. Stabil*. 95, 144-152.

Karnis, A. (1994). "The mechanism of fiber development in mechanical pulping, " *J. Pulp Pap. Sci.* 20(10), 280-288.

Kato, K. L., and Cameron, R. E. (1999). "A review of the relationship between thermally-accelerated ageing of paper and hornification, " *Cellulose* 6(1), 23-40.

Kloprogge, J. T., Ruan, H. D., and Frost, R. L. (2002). "Thermal decomposition of bauxite minerals:infrared emission spectroscopy of gibbsite, boehmite and diaspore, " *J. Mater. Sci.* 37,1121-1129.

Koivunen, K., and Paulapuro, H. (2010). "Papermaking potential of novel structured PCC fillers with enhanced refractive index," *Tappi J.* 9(1), 4-11.

Lindstr**ö**m, T., and Söderberg, G. (1986). "On the mechanism of sizing with alkylketene dimers part 1. Studies on the amount of alkylketene dimer required for sizing different pulps," *Nord. Pulp Paper Res*. 89(1), 26-42.

Ma, H. C. (2006). "Application of a special pigment ATH in special and high quality paper and paper board, " *China Pulp Paper Ind.* 27(2), 51-53.

Martin, A. R., Martins, M. A., da Silva, O. R. R. F., and Mattoso. L. H. C. (2010). "Studies on the thermal properties of sisal fiber and its constituents, "*Thermochimica Acta 506*, 14-19.

Meireles, C. D. S., Filho, G. R., de Assuncao, R. M. N., Zeni, M., and Mello, K. (2007). "Blend compatibility of waste materials-cellulose acetate (from sugarcane bagasse) with polystyrene (from plastic cups): Diffusion of water, FTIR, DSC, TGA, and SEM study, " *J. Appl. Polym. Sci.* 104(2), 909-914.

Nada, A. M. A., and Hassan, M. L. (2000). "Thermal behavior of cellulose and some cellulose derivatives, " *Polym. Degrad. Stabil*. 67, 111-115.

Nazhad, M. M., and Paszner, L.(1994). "Fundamentals of strength loss in recycled paper,"*Tappi J*. 77(9), 171-179.

Nelson, M. L., and O'Connor, R. T.(1964)."Relation of certain infrared bands to cellulose crystallinity and crystal lattice type. Part Ⅱ. A new infrared ratio for estimation of crystallinity in celluloses Ⅰ and Ⅱ, " *J. Appl. Polym. Sci.* 8, 1325-1341.

Newman, R. H. (2004). "Carbon-13 NMR evidence for cocrystallization of cellulose as a mechanism for hornification of bleached kraft pulp, " *Cellulose* 11,45-52.

Odlyha, M., Seeley, N. and Wettasinghe C. S. (1990). "Applications of differential scanning calorimetry and dielectric thermal analysis to the study of paper deterioration, " *Thermochimica Acta* 166(15), 1-16.

Östlund, Å., Tobias, K., Nordstierna, L., and Nydén, M. (2010). "NMR cryoporometry to study the fiber wall structure and the effect of drying, " *Cellulose* 17, 321-328.

Rebuzzi, F. D., and Evtuguin, V.(2006). "Effect of glucuronoxylan on the hornification of Eucalyptus globulus bleached pulps, " *Macromol. Symp.* 232, 121-128.

Schmolz, E., Brüders, N., Daum, R., and Lamprecht, I. (2000). "Thermoanalytical investigations on paper covers of social wasps, " *Thermochimica Acta* 361, 121-129.

Sefain, M. Z, and Nada, A. M. A. (1984). "Thermal behaviour of paper sheets strength, " *Thermochimica Acta* 78(1-3), 211-218.

Sen, A. K., Mukheriee, B., Bhattacharya A.S., Sanghi, L. K., De, P. P., and Bhowmick, K.(1991). "Preparation and characterization of low-halogen and nonhalogen fire-resistant low-smoke (FRLS) cable sheathing compound from blends of functionalized polyolefins and PVC, " *J. Appl. Polym. Sci.* 43(9), 1673-1684.

Shen, J., Song, Z. Q., Qian, X. R., and Liu, W. X. (2009a). "Modification of precipitated calcium carbonate filler using sodium silicate/zinc chloride based modifiers to improve acid-resistance and use of the modified filler in papermaking, " *BioRes.* 4(4), 1498-1519.

Shen, J., Song, Z. Q., Qian, X. R., and Liu, W. X. (2009b). "A preliminary investigation into the use of acid-tolerant precipitated calcium carbonate fillers in papermaking of deinked pulp derived from recycled newspaper, "*BioRes.* 4(3), 1178-1189.

Shen, J., Song, Z. Q., Qian, X. R., and Liu, W. X. (2009c). "Modification of papermaking grade fillers: A brief review, " *BioRes.* 4(3), 1190-1209.

Shen, J.; Song, Z. Q., and Qian, X. R. (2009d). "Investigations on the preparation of starch/sodium oleate/alum modified precipitated calcium carbonate filler and its use in papermaking, " *Appita J.* 62(5), 360-364, 382.

Shen, J.; Song, Z. Q., Qian, X. R., Liu, W. X., and Yang, F. (2010a). "Carboxymethyl cellulose/alum modified precipitated calcium carbonate fillers: Preparation and their use in papermaking, " *Carbohyd. Polym.* 81(3), 545−553.

Shen, J., Song, Z. Q., Qian, X. R., Liu, W. X., and Yang, F. (2010b). "Fillers and the carbon footprint of papermaking, " *BioRes.* 5(4), 2026-2028.

Shen, J., Song, Z. Q., Qian, X. R., Yang, F., and Kong, F. G. (2010c). "Nanofillers for papermaking wet end applications, " *BioRes.* 5(3), 1328-1331.

Shen, J., Song, Z. Q., Qian, X. R., Liu, W. X., and Yang, F. (2010d). "Filler engineering for papermaking: Comparison with fiber engineering and some important research topics, "*BioRes.* 5(2), 510-513.

Shen, J., Song, Z. Q., and Qian, X. R. (2010e). "Possible trends of renewable organic fillers and pigments derived from natural resources for sustainable development of paper industry, " *BioRes.* 5(1), 5-7.

Shen, J., Song, Z. Q., Qian, X. R., and Ni, Y. H., (2011). "A review on use of fillers in cellulosic paper for functional applications, " *Ind. Eng. Chem. Res*. 50, 661-666

Toldy, A., Tóth, N., Anna, P., and Marosi, G. (2006). "Synthesis of phosphorus-based flame retardant systems and their use in an epoxy resin, " *Polym. Degrad. Stabil*. 91, 585-592.

Wang, X., Zheng, S. L., and Zhang, Y.(2008). "Preparation of aluminum hydroxide with dissolution of sodium, "*Chin. J. Process Eng.* 8(1), 72-77.

Wang, Z. Y., Liu, Y., and Wang, Q. (2010). "Flame retardant polyoxymethylene with aluminium hydroxide/melamine/novolac resin synergistic system, " *Polym. Degrad. Stabil*. 95, 1149-1157.

Xu, H., and Deng, X. R. (2006). "Preparation and properties of superfine $Mg(OH)_2$ flame retardant, " *T. Nonferr. Metal. Soc.* 16, 488-492.

Yang, F., Chen, K. F., Yang, R. D., You, P., and Chen, Q. F. (2007). "Manufacture of heat resistant interleaving paper for sheet metal, " *China Pulp Pap.* 26(5), 11-13.

Yang, R. D., Liao, X. S., Yang, F., and Chen, K.F. (2008). "Research and heat- resistant paper used for stainless steel, " *Paper Paper Making* 27(5), 33-35.

Yeh, J. T., Hsieh, S. H., Cheng, Y. C., Yang, M. J., and Chen, K. N.(1998). "Combustion and smoke emission properties of poly(ethylene terephthalate) filled with phosphorous and metallic oxides, " *Polym. Degrad. Stabil*. 61, 399-407.

Yoon, S. Y.and Deng, Y. L. (2006a). "Clay-starch composites and their application in papermaking," *J. Appl. Polym. Sci.* 100, 1032-1038.

Yoon, S. Y.and Deng, Y. L. (2006b). "Starch-fatty complex modified filler for papermaking," *Tappi J.* 5(9), 3-9.

Yoon, S. Y.and Deng, Y. L. (2007). "Experimental and modeling study of the strength properties of clay-starch composite filled papers," *Ind. Eng. Chem. Res.* 46, 4883-4890.

Zhao, Y.L, Hu, Z. S., Ragauskas, A., and Deng, Y. L. (2005). "Improvement of paper properties using starch-modified precipitated calcium carbonate filler," *Tappi J.* 4(2), 3-7.

Zhao, Y.L, Kim, D., White, D., Deng, Y. L, Patterson, T., Jones, P., Turner, E., and Ragauskas, A. J. (2008). "Developing a new paradigm for linerboard fillers," *Tappi J*. 7(3), 3-7.

Article submitted: December 30, 2010; Peer review completed: March 4, 2011; Revised version accepted: April 30, 2011; Published: May 6, 2011.