

Determination of Thermal Properties and Fire Retardant Ability of Philippine Bamboo as Natural Thermal Insulation

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Abstract

This study investigated the thermal characteristics for organic thermal insulation materials developed from single-layer particleboard from bamboo-waste and analyzed concerning fire retardant ability. The Differential Scanning Calorimetry conducted the precise heat capacity extent (DSC), Pyrolysis Combustion Flow Calorimeter and Scanning Electron Microscope (SEM) are utilized to characterize the materials. The exothermal value was observed in all of the DSC curves with a high middle part content up to an average of 13.65 mW. Beyond that consideration, the bottom and top part specimen are two comparable value with smaller exothermic peaks appeared. SEM of unidirectional fiber causes the bamboo to have strength in the direction of bamboo fibers. Cellulose for middle part had the highest quantity of carbon. Interfacial adhesion using epoxy resin ($C_{21}H_{25}C_{105}$) of the material is effectively enhanced after the surface modification of the fiber. Pyrolysis assessment reveals that the primary stage at 68-89°C is the exothermic dehydration of the biomass with the release of water and low-molecular-weight gases like CO and CO₂. Thermal analysis shows that the increment of heat distortion temperature can reach 341°C, and the thermal stability is significantly improved. Conclusively, Philippine bamboo as green composites materials does not only have quality thermal and mechanical properties but also have a good flame retardant ability.

Keywords: Green composite, epoxy resin, thermal characterization, flame retardant

1. INTRODUCTION

Nowadays, industries are trying to divert attention toward lignocellulosic-based natural fibers as composite materials for reinforcement. Natural fibers, such as flax, cordenka, hemp, jute, ramie, kenaf, bamboo, caraura, and sisal, have been engaged as a reinforcement to provide green composites with sustainable properties like cellulose, hemicelluloses, and lignin (Jacob and Thomas, 2008; Justiz-Smith et al., 2008; Mantia and Morreale, 2011) as three essential components of crude biomass. Considering this thermoplastic as materials reinforced with natural fibers, this have been pull to much attention in research and development substituting glass fibers and some

manufactured materials in industrial fields in lately come into existence (Wambua et al., 2003; Colom et al., 2000; Araujo et al., 2003; Li et al., 2013). The fallout of those elements varies depending on the harvesting area and agricultural conditions (Bilba et al., 2007). Lignin contains amorphous polyphenolic macromolecules, whereas, Cellulose and hemicelluloses to be made up of polysaccharides (i.e., three kinds of phenylpropanes) (Muensri et al., 2011). Literature work on bamboo and bamboo composites have been reported (Jain et al., 1992; Jain et al., 1993). It is an environmentally performing material attribute adequate absorption properties. Assessment of bamboo through life cycle assessment (LCA) is presented to resolve the environmental implication of bamboo as a source for construction material and other applications. The results of this interpretation show that, in some implementations, bamboo has marked by a high “factor 20” environmental impact, a 20 times less load on the environment than compared to some alternatives (Van der Lugt et al. 2006). Wood and bamboo have renown in the green engineering technology industry recently because of their environmentally promising characteristics: a natural process can replace them, biodegradable, confine carbon from the atmosphere, low in combined energy, and providing less pollution in development than concrete or steel (Falk 2009 and Mahdavi et al. 2011). Bamboo is a green material that can substitute to wood for reasons that, bamboo can be crop in 3–4 years from the time of plantation as compared to timber which takes decades (Lakkad & Patel 1980 and Amada et al. 1997). Compared with other similar composite building materials, strength-to-specific gravity ratio, bamboo is much stronger and has a higher value than that of common hardwood, softwood and even metals such as aluminum alloy, cast iron, and structural steel (Mahdavi et al. 2011).

Bamboo has high strength fibers, this engages a critical function in economic and cultural tropical areas worldwide, in which, one of the existing flowering plants and available forest resources. Utilization of natural fibers in biocomposites has a lot of advantages, to name a few; economic, low density, mechanical properties and availability from renewable resources. However, the thermal sharpness at a high temperature of combined processes and the flammability of those fibers, and low compatibility with hydrophobic polymer matrices could end the use of the resembling biocomposites. A

lot of research papers provides breakthrough of the fiber matrix compatibility that has generated (Xie et al., 2010; Bourmaud et al., 2009; Belgacem and Gandini, 2005; Faruk et al., 2012), thermal stability and the fire behavior enhancement has limited data. (Hapuarachchi and Peijs, 2010) Flame retardant of multi-walled carbon nanotubes and sepiolite nanoclays could drop the progress in a biocomposite based on polylactic acid (PLA) and hemp. A system based on PLA declined the peak of heat release rate (pHRR) significantly due to the integration of flame retardant, and lower when natural fibers were added.

In this study, parts of Philippine bamboo will be compared to four different natural fibers (cellulose, hemp, flax and sugar cane) as literature that has been used as a support of a polybutylene succinate thermoplastic matrix (PBS). This work intends to study the thermal stability and the fire behavior of the *Dendrocalamus asper* as mentioned above this bamboo as natural fibers and their corresponding bamboo biocomposites. This paper will mainly focus on bamboo-based biocomposites and the impact of fiber content. Finally, ammonium polyphosphate will be incorporated in bamboo-based

biocomposite to study char formation and fire retardant properties.

2. MATERIALS AND METHODS

2.1 Materials

Three-year-old Giant Bamboo (*Dendrocalamus asper*) was harvested from Mandaue City, Province of Cebu in the Philippines. Portions cut up to 3.0 m from the basal part that will be used for the assessment. The bamboo was manually cut into a specified length of 300 mm and was split longitudinally at the top, a middle and bottom portion of the bamboo. During the submersion of specimens, 5 for each bamboo parts were immersed in salt water to protect bamboo against insect attack for seven (7) days cycles as traditional preservation. A set up was performed using traditional treatment to show up the specimens to wetting and drying cycle; the bamboo specimens were removed from the water and were stacked vertically in air-drying for one (1) week (Amatosa and Loretero 2017).

Table 1.

Macroscopic characteristics of Giant bamboo (*Dendrocalamus asper*)

Macroscopic Characteristics	Unit	a	Literature b	c	Philippine Bamboo *
Culm length	m	20-30	18-23	-	20-30
Internode length	cm	20-25	35	14-45	30-35
Internode Diameter	cm	8-20	9-13	1.2-9.3	8-18
Culm wall Thickness	mm	11-20	10-14	4-30	6-13

*Present study

^aDransfield and Widjaja. 1995.

^bOthman et al. 1995.

^cPakhkeree. 1997.

2.2 Experiment

2.2.1 Scanning Electron Machine (SEM) Analysis. The surface morphology of the Philippine bamboo by a Hitachi SEM (Model TM300, Hitachi Co. Ltd., Japan) at an acceleration voltage of 15 kV.

2.2.2 Differential Scanning Colorimetry (DSC) Analysis. DSC analysis of the Philippine bamboo waste was performed using a thermal analyzer (Mettler DSC 25 module). All of the measurements were made under an N₂ flow (150 mL/min), keeping a constant heating rate of 10 °C/min and the samples of 5 – 10 mg were encapsulated using an aluminum crucible with a pinhole.

2.2.3 X-ray Diffraction (XRD) Analysis. Crystalline structures of bamboo and liquefied bamboo analyzed by an Ultima III X-ray Diffractometer (Rigaku Co. Ltd., Japan). Ni-filtered Cu K α radiation ($\lambda = 0.1542$ nm) generated at a voltage

of 40kV and a current of 40 mA used. Intensities in the range from 10 \circ to 40 \circ with 4 \circ /min scan speed set for total X-ray Diffraction (XRD) analysis experiment. The crystalline height 200 (h₂₀₀) and amorphous height (h_{am}) was used to calculate the crystalline index (CI) by following equation (1).

$$\text{Crystalline index (CI)} (\%) = ((h_{200} - h_{am}) / h_{200}) \times 100 \quad (1)$$

3. RESULTS AND DISCUSSION

This paper analyzed the treated Philippine bamboo species for thermal properties and fire retardant within one week and air-dried for another week if could influence the mechanical properties of the specimen specifically compressive and bending strength together with the other data of the laminated composite.

Table 2.

The chemical composition of the different natural fibers

Fiber	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Ash (%)
^a Cellulose	100	0	0	0
^{a,b} Flax	80	13	2	1
^{a,b} Hemp	70-77	17.9-22.4	3.7-5.7	0.8
^{a,c} Sugar cane	32-34	27-32	19-24	1.5-5
^{d,e} Rice husk	24.3	24.3	14.3	15.3
^{f,g} Corn cob	43.2-50.5	31.0	14.6-15.0	2.2
^{e,f} Barley straw	31.0-45.0	24.0-29.0	14.0-15.0	3-7
Bamboo (*Present study)				
Top	60.97		63.31	
Middle	71.68		62.63	1-2.3
Bottom	64.11		62.45	

*Present study

^aYao et al. 2008.

^bKozlowski and Wladyka 2008.

^cBledzki et al. 1996.

^dBlasi et al. 1999

^eRowell et al. 1996

^fSun 2010

^gDemirbas 2004

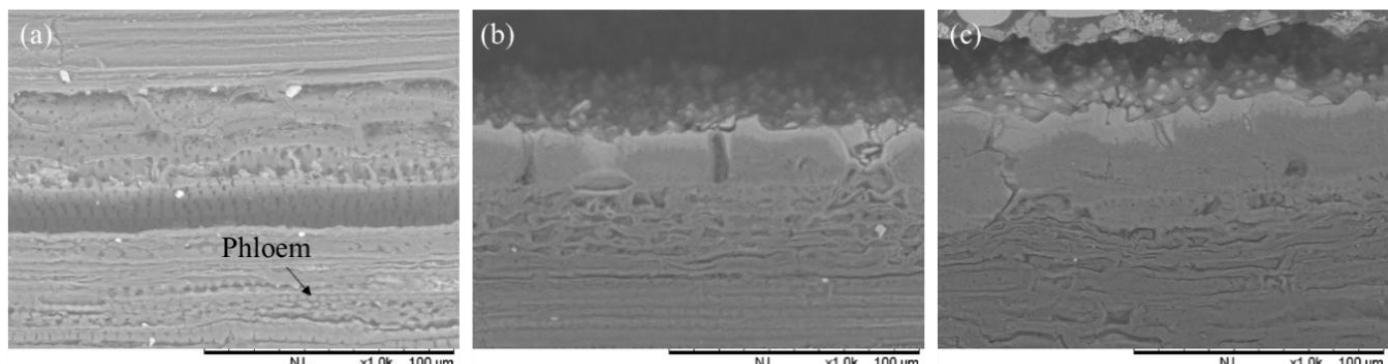


Figure 1. Typical longitudinal cross-sectional SEM image of Philippine bamboo culm, showing phloem on (a) bottom, (b) middle, and (c) top part

The present study was analyzed and compared to different crop by-product: Flax, Hemp, Sugarcane, rice husk, corn cob, and barley straw. Table 2 summarizes their chemical composition according to the values documented in the related literature.

Natural thermal insulations were crafted with the above organic materials. The formulations in Table 2, were optimized in previous work (Palumbo et al., 2014) arrange to obtain appropriate composites. Table 2 also shows the corresponding materials of bulk densities. Since the thermal conductivity values are similar in all cases, the thickness of (17-20 mm) of composite required to reach a given thermal resistance is likely the same in some organic composite cases. Therefore, insulations made with bamboo comparable with Hemp, which

has the highest value of cellulose, will have the high thermal ability.

The bamboo cell walls mainly conform of cellulose, which is constructed from polysaccharide chains arranged into amorphous and crystalline regions. Bamboo trees generally have lignin and cellulose. Lignin in Philippine bamboo is a cube-shaped matrix and visible pores, while cellulose in bamboo is fiber. In Figure 1, Philippine bamboo indicates the direction of the grain. The direction of the grain shows that the bamboo has a similar fiber direction. The direction of this unidirectional fiber causes the bamboo to have strength in the direction of bamboo fibers. In this experiment, the center position for cellulose had the highest quantity of carbon.

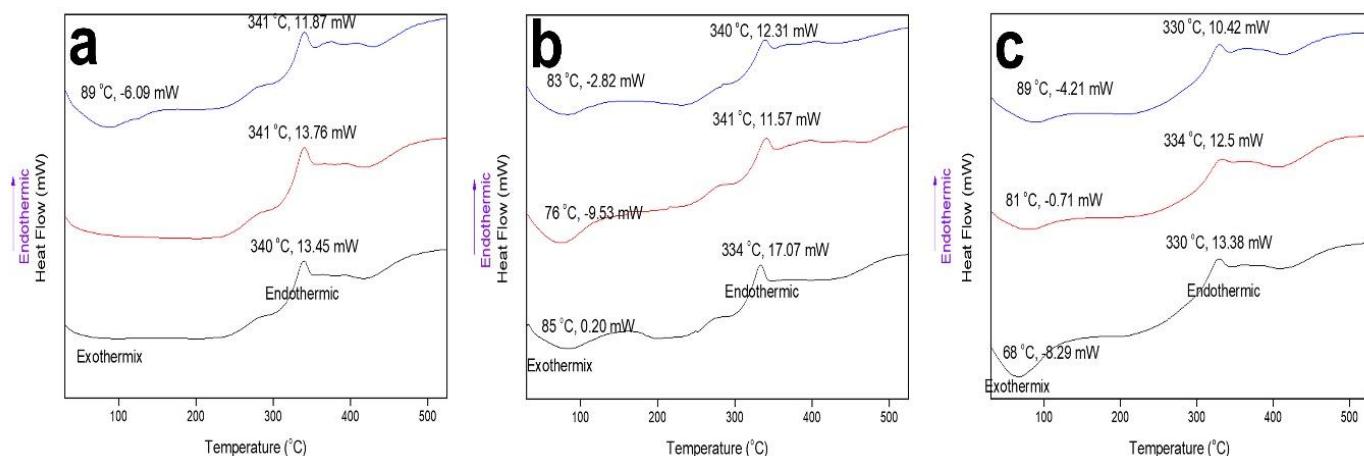


Figure 2. DSC curves of Philippine bamboo on (a) bottom, (b) middle, and (c) top part

Analysis using Differential scanning calorimetry (DSC) performed on the different portions (bottom, middle and top) of giant bamboo are shown in Figures 2a, 2b, and 2c. Comparing the three graphs in Figures 2, an endothermic and exothermic event for giant bamboo fiber is observable in the all position. These events were displayed through a result of exothermic and endothermic peaks. For the examined giant bamboo, parts have broad endothermic peaks could be observed in the temperature range of 30 to 135°C.

Negative displacement occurred when heat concentration by the bamboo fibers direct to the evaporation of free water position within cellulose. The transition temperature of unbound or open water in a natural mixture of the compound is the same measurement to pure water, while it is higher than bound water (Nakamura et al., 1981). From Fig. 2, it can be noticed that in the endotherm, the endothermic peak of bottom giant bamboo fig. 2a (89 °C) is the highest and that of bottom giant bamboo fig.2c (68 °C) is the lowest similar to others. Thus, bottom giant bamboo number 3 probably has the highest lignocellulose content which means endothermic reactions indicated that the depolymerization of cellulose molecules of bamboo required higher temperatures due to their higher stabilities. The endothermic peak of bottom giant bamboo fig. 2a has a higher temperature 82.82°C compared with (Zakikhani et al. 2016).

The observation involved bottom giant bamboo figures 2a, 2b and 2c portions that exhibited an exothermic peak at 330, 334, and 330 °C, respectively, which was indicative of the charging process and resulted in little residual material. The exothermic events in these parts might be connected to breakage of cellulose chains in a crystalline region (highly ordered) of their microfibrils (Yang et al., 2007). From Figure 2 it can be seen that giant in the middle has the endothermic peak in the range 76 to 85°C. The endothermic has a peak in the range 334-341°C. While in Figure 3, only giant in the top number 3 that has an endothermic peak, 89 °C. The endothermic has a peak in the range 340-341°C.

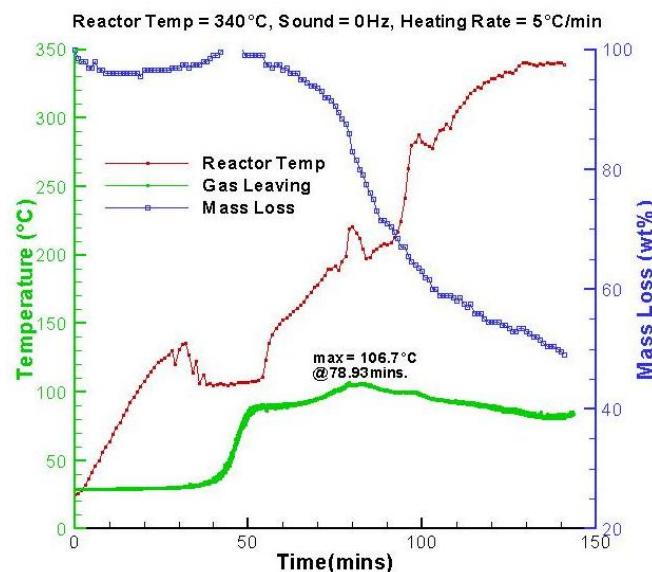


Figure 3. Curves of Philippine bamboo in Temperature vs. Time vs. Mass loss

The significant mass loss was noticed in figure 3 at around 300°C — the same as the work of (Sun et al., 2015) on pyrolysis. This stage, according to them, is attributed primarily to the decomposition into volatiles. Moreover, the mass loss at 20-280°C was mostly due to the successive evaporation of the volatile hydrocarbon and the low-molecular-weight hydrocarbons at 280-400°C; 400 and 500°C mass loss due to a composition of thermal cracking and medium-molecular-weight hydrocarbons (Ali et al., 2013).

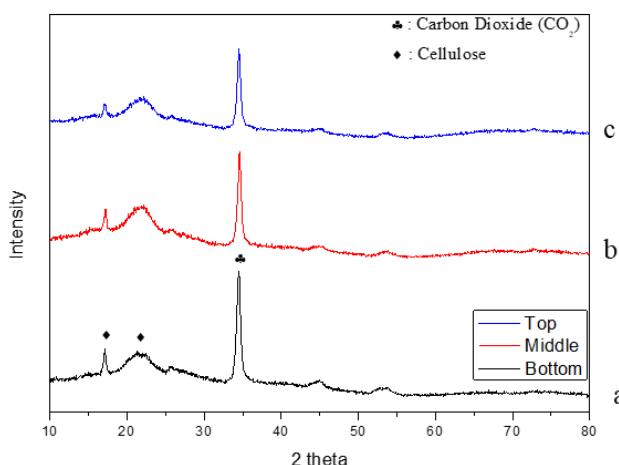


Figure 4. XRD of Philippine bamboo on (a) bottom, (b) middle, and (c) top part

Figure 4 shows the results of XRD diffraction. The effects of XRD diffraction of Philippine bamboo before treatment have the same peak with all positions. At the peak of about 17° and 22° with a cellulose structure that matches the JCPDS card number 50-2184 with the orientation of cellulose crystals. The

highest peak of the three positions is at 2 theta around 35° according to the JCPDS number 73-2058 card; it is known that there are carbon dioxide compounds. The highest peak in position 2 theta is owned by bamboo Philippine in the bottom position.

Different laboratory tests were conducted for mechanical properties of *Dendrocalamus asper* bamboo for laminated bamboo composite (LBC) specimens to provide a direct comparison with some commercial composite products. Samples were produced by prescribe dimensions was performed according to ASTM D143 (ASTM 1999). Due to the higher value of properties by sea-water treated bamboo, this was utilized to produce LBCs for evaluation. This size of the specimen and test procedure was selected to be consistent with other LBL to establish similarities of strong values and to prevent the contrast of configuration result between size and load. Flatten specimens were tested in the horizontal lamination (joist) orientation. All tests were performed using a 600 kN capacity universal testing machine. A continuous compression load with a load rate of 0.6 mm/min was applied and distributed equally to 5% of the sample thickness up to deformation until it reached and the stress at that point is calculated. The relative humidity of the specimen is 8% - 12% average for moisture content were placed in the laboratory with ambient temperature.

Table 3.

Comparison of mechanical strength properties of LBCs *Dendrocalamus asper* with another similar composite

Materials	Density	Compressive		Tension		Shear	Bending	
		ρ_{mean} kg/m ³	f_{\parallel} (MPa)	f_{\perp} (MPa)	f_{\parallel} (MPa)	f_{\perp} (MPa)	f_{mean} (MPa)	
Laminated Bamboo*	1,022.24		27.47	1.97	-----	1.49	52.59	
C24 – EN 338 ^a	420		21.00	-----	32.00	4	24.00	
GL 24h-EN 14080-06 ^b	420		24.00	-----	14.00	3.5	24.00	
Norway spruce ^{c,d}	----		44.00 ^h	-----	19.50	6	48.00	
Glue laminated spruce ^e	450		32.00	-----	-----	-----	50.00	
Thermally modified beech ^f	580		48.70 ^h	-----	14.00	-----	31.00	
Caramelized bamboo ⁱ	686		77.00	22.00	90.00	2.00	16	77 – 83
Sitka spruce ^{j,k}	383		36.00	-----	59.00	-----	9	67.00
Douglas-fir LVL ^{l,m}	520		57.00	-----	49.00	-----	11	68.00
Sheathing-grade Plywood ⁿ	----		20.7-34.5	-----	10.3-27.6	-----	-----	20.7-48.3
Sheathing-grade OSB ⁿ	----		10.3-17.2	-----	6.9-10.3	-----	-----	20.7-27.6
Normal laminated wood ⁿ	----		44.10	-----	153.10	-----	-----	140.60
Low density cement-wood ⁿ	----		0.69-5.5	-----	0.69-4.1	-----	-----	1.7-5.5
Wood-Polypropylene ⁿ	----		38.3-72.4	-----	28.5-52.3	-----	-----	-----

*Present study

^aCEN (2009)

^bCEN (2013)

^cSteiger and Arnold (2009)

^dJenkel et al. (2015)

^eDe Lorenzis et al. (2005)

^fWidmann et al. (2012)

^gTest not conducted in accordance with EN 408 (CEN, 2012)

^hExperimental mean

ⁱSharma et al. (2015)

^jLavers (2002)

^kKretschmann DE (2010)

^lKretschmann et al. (1993)

^mClouston et al. (2002)

ⁿForest Products Laboratory. (1999).

Presenting from this research work of table 3, the mean strength values results of these tests are provided for the proposed LBCs. This table also shows the flexural properties of LBL with those published from the Wood Handbook (1999) with the consistency of specimens of 10% moisture content made using Method 3 (Lee et al. 1998). The flexural strength is most comparable data to some CEN standards and other softwood and hardwood structural composites. LBCs specimens may

share partly to the observed differences of the samples; flexural properties exhibit an inclination to increment with a decrease in moisture content for clear wood (Bergman et al. 2010). Data analysis indicates that mechanical properties of LBCs of Dendrocalamus asper are better than other structural composite materials and even comparable to one of the hardest and most durable woods such as the teak wood.

Table 4.

Specific Data for Energy Transfer

Blower	Heating Rate (°C/min)	Reactor Temperature (°C)	Experiment Duration (min)	Weight (grams)			Percent from Total (%)			Energy Transfer of Cooling Air (kJ)
				Char	Tar	Char	Tar	Gas		
35	3	340	141	522	296	52.20	29.60	18.20	134.578	

The pyrolysis procedure can be divided, from a thermal standpoint, into stages, according to (Basu 2013). At the drying stage (~100°C), free moisture and some unbound water are released. This explains the discovery of temperature due to the available moisture released by the feedstock (Dendrocalamus asper). The initial stage at 100-300°C is the exothermic dehydration of the biomass to allow water and early-molecular-weight gases like CO and CO₂. The intermediate stage which occurs at 200-600°C is the primary pyrolysis where most of the vapor or precursor to bio-oil is produced. This explains the continued rise of the temperature because of the presence of gases aside from the moisture.

Moreover, from the work of (Siengchum et al. 2013) on pyrolysis of coconut biomass, CO₂ was produced as the temperature reached 150°C. The formation of CO, CH₄, and H₂ followed that of CO₂ as the temperature continued to increase. The composition of CO₂ and CO reached the maximum at a temperature equal to 300°C. It has been explained that the pyrolysis of cellulose produces between 300 and 400°C of CO₂ and CO (Yang et al., 2007).

4. CONCLUSION

Laminated bamboo composite from Dendrocalamus asper bamboo, a native from the organic materials from the Philippines has properties showing the better performance to some other natural fibers (cellulose, hemp, flax, and sugar cane). In this study, the importance of water and low-molecular-weight gases like CO and CO₂ in the natural fibers biocomposites as low flammable compound has been highlighted. In most cases, this char layer leads to reduction because of the limitation of mass and thermal assign, but it has been shown that a lesser fiber content is required to form a fire protective layer. However, further research much is given attention in characterization and standardization is needed before acceptance in the marketplace of LBC as natural thermal insulation materials.

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