

## Ceramic Sheet Hybrid Kenaf Reinforced Polypropylene Biocomposites

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**ABSTRACT:** Hybrid biocomposites are one of the emerging fields in polymer composites. The purpose of this study is the development and characterization of ceramic sheet (CS) hybrid polypropylene (PP) biocomposites for broadening of the field of potential applications of biocomposites. Hybrid PP biocomposites were manufactured with 20 wt % loadings of kenaf and the addition of a CS (single or double sided) by melting and compression molding. The effects of the CS on the mechanical and thermal properties of the hybrid PP biocomposites were analyzed in terms of tensile, flexural, and impact properties, and inflammability, smoke optical density, and toxicity of the combustion gas. Also, the surface morphology of fractured hybrid PP biocomposites was observed by SEM and AFM. In spite of the brittle properties of the ceramic, the mechanical properties of the hybrid PP biocomposites were improved and, also, the inflammability of the hybrid PP biocomposites with the CS was highly improved. As a result, full impregnation of CSs into the kenaf reinforced biocomposite can contribute to the improvement of both the mechanical properties and the inflammability of biocomposites, resulting in a broadening of the field of potential applications of biocomposites such as aerospace. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 1917–1922, 2013

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### INTRODUCTION

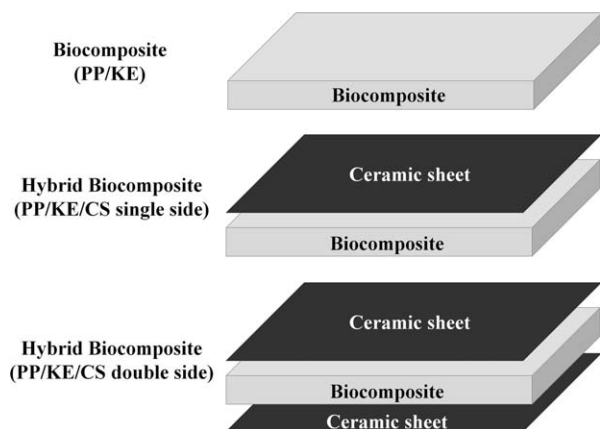
Biocomposites reinforced with natural fibers as an alternative to glass fiber are being extensively studied by many researchers.<sup>1–4</sup> The field of biocomposites is growing in areas in which light weight and strong structures are required, for example, in automobile interior and exterior materials and in the building construction industry; this field is reaching the stage of the commercialization of products.<sup>4–6</sup> In recent years, studies have been carried out actively all over the world in order to utilize eco-friendly biocomposites as various types of high functional materials.<sup>7</sup>

Though the number of potential applications of biocomposites has been broadening, according to the developing progress of biocomposites, the application of biocomposites has been mostly restricted to fields that typically require high thermal stability, such as aerospace materials, due to the low thermal stability of both natural fibers and polymers. Therefore, chemical or mechanical processing occurs to overcome this problem.<sup>5,8,9</sup> In general, most organic/inorganic flame retardants used to improve the inflammability of polymer composites, however, may cause many problems in terms of the environment, because the halogen and phosphorus materials release toxic gas, including gases that are harmful to the human body

and to the environment when the material burns; also, these materials can be a main factor affecting the decrease of the mechanical properties.<sup>10–14</sup> Therefore, nano-composites reinforced with organic/inorganic non-flammable fillers, typically clays, were developed. However, there were several disadvantages, the most important one of them is the non-uniform dispersion of nano-clay in the polymer matrix.<sup>15–18</sup> Therefore, the development of biocomposites that have inflammability and good mechanical properties while uniform characteristic through the biocomposites is required.

Ceramic materials have characteristics of low thermal conductivity, resistance to thermal and physical degradation at high temperatures, high tensile strength and elastic modulus, and potential application to a variety industries; the serious disadvantage of such materials is that they have tendency to brittleness. Ceramic materials have used fibers to compensate for this brittleness, and ceramic fibers either alone or in combination with other fibers have been used as reinforcements for composites with polymers.<sup>19</sup> However, studies of CS hybrid biocomposites have not been reported.

This study is based on biocomposites hybrid with CS to improve the flammability uniformly; the sheets consist of integrated biocomposites; we studied the development of hybrid



**Figure 1.** Schematic configuration of CS hybrid biocomposites.

biocomposites of excellent flammability and mechanical properties, which also led to the possibility of broadening the potential field of applications into such areas as aerospace.

## EXPERIMENTAL

### Materials

Polypropylene (PP) fiber was supplied from Kolon Glotech Co., Korea. PP with an average length and tenacity of 76 mm and 3 g/denier, respectively, were chopped for improved dispersion. The specific gravity and the melting point were 0.91 g/cm<sup>3</sup> and

160–165°C, respectively. The kenaf (*Hibiscus cannabinus L.*) fiber (KE) derived from the outer fibrous bark is also known as bast fiber. KE with an average density and filament diameter of about 1.45 g/cm<sup>3</sup> and generally in the range of 14–48 μm, respectively, was supplied from Bangladesh. The ceramic fiber with content of Al<sub>2</sub>SiO<sub>3</sub> was supplied from KCC Co., Korea. The fiber length and diameter were average 3 μm and below 300 μm, respectively.

### Fabrication of the Ceramic Sheet

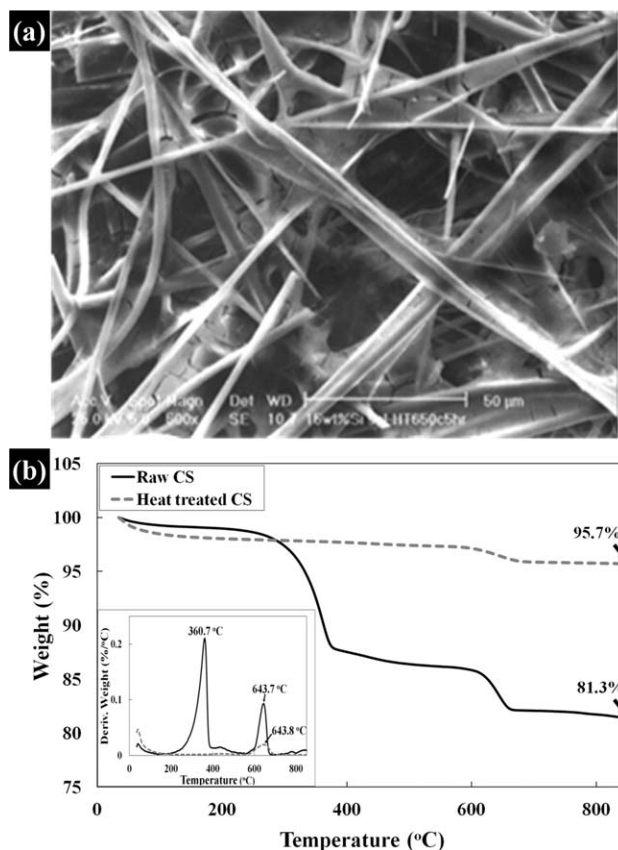
Ceramic sheet (CS) was manufactured with wet forming process. Thickness and tensile strength of ceramic sheet were average 0.2 mm and 3.92 MPa, respectively.<sup>20</sup>

### Fabrication of the PP/KE/CS Biocomposites

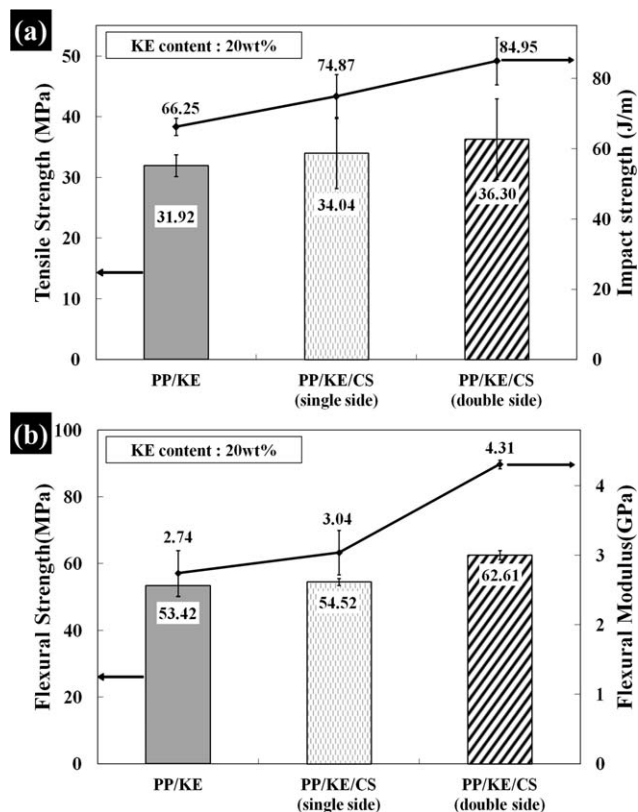
KE was dried at 100°C for 2 h in a convection oven and then chopped 10 mm before mixing with PP. Prior to the fabrication of hybrid biocomposites, CS was heat treated at 550°C for 5 h in a furnace for removal of the organic binder. PP/KE/CS biocomposites was fabricated with 20% by weight of KE and addition of CS for single and double side for ends of PP/KE mixture by a compression molding technique. Figure 1 shows the schematic configuration of CS hybrid biocomposites. The molding compounds were heated to 175°C for 30 min. The pressure of 6.89 MPa applied to the compounds at 175°C and maintained for 10 min, then cooled down to room temperature by circulating cold water.

### Characterization

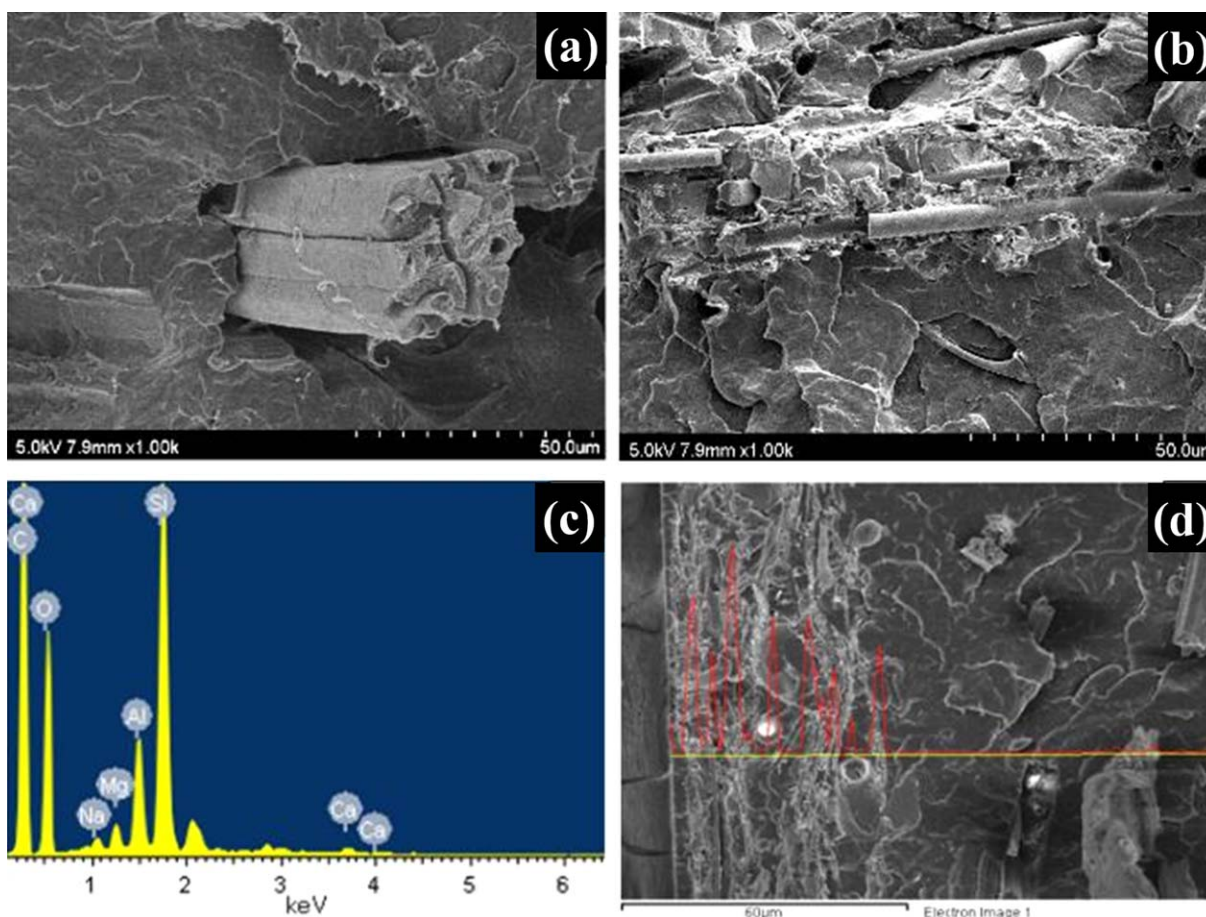
The thermal behavior of the CS was analyzed using a thermogravimetric analyzer (TGA Q 500, TA Instruments). The ~50 mg



**Figure 2.** (a) Morphology observation and (b) thermal properties of ceramic sheet.



**Figure 3.** (a) Tensile and impact strength and (b) flexural properties of PP/KE/CS hybrid biocomposites.



**Figure 4.** SEM images of the (a) PP/KE biocomposite, (b) PP/KE/CS hybrid biocomposites, (c) EDX spectrum of PP/KE/CS hybrid biocomposites, and (d) Silicon distribution map of PP/KE/CS hybrid biocomposites. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

of a sample was heated up to 850°C at the heating rate of 10°C/min under the N<sub>2</sub> atmosphere.

The mechanical properties of the KE/PP/CS hybrid biocomposite were evaluated by tensile strength, I-zod impact strength and flexural test. The tensile test was performed by using a Universal Testing Machine (UTM, Tinius Olsen, H-50K-S T, Redhill, UK) at a crosshead speed of 10 mm/min according to ASTM D 638. The specimens were dog-bone shape in a size of 3.18 mm (width), 63.66 mm (length), and 3.00 mm (thickness). The impact test (notched) was performed by using an I-zod Pendulum Impact Tester (Tinius Olsen, Model IT 504, Redhill, UK) according to ASTM D 256. The specimens were notched by an automatic specimen notcher (Model-899, Tinius Olsen, Redhill, UK). The specimen dimension was 12.5 mm × 63.5 mm × 5.0 mm. The flexural test (three-point loading) was determined using a Universal Testing Machine (UTM, Tinius Olsen, H-50K-S T, Redhill, UK) at a crosshead speed of 1 mm/min and loading span-to-depth ratio at 16, according to ASTM D 790. The specimen dimension was 50 mm × 25 mm × 2 mm.

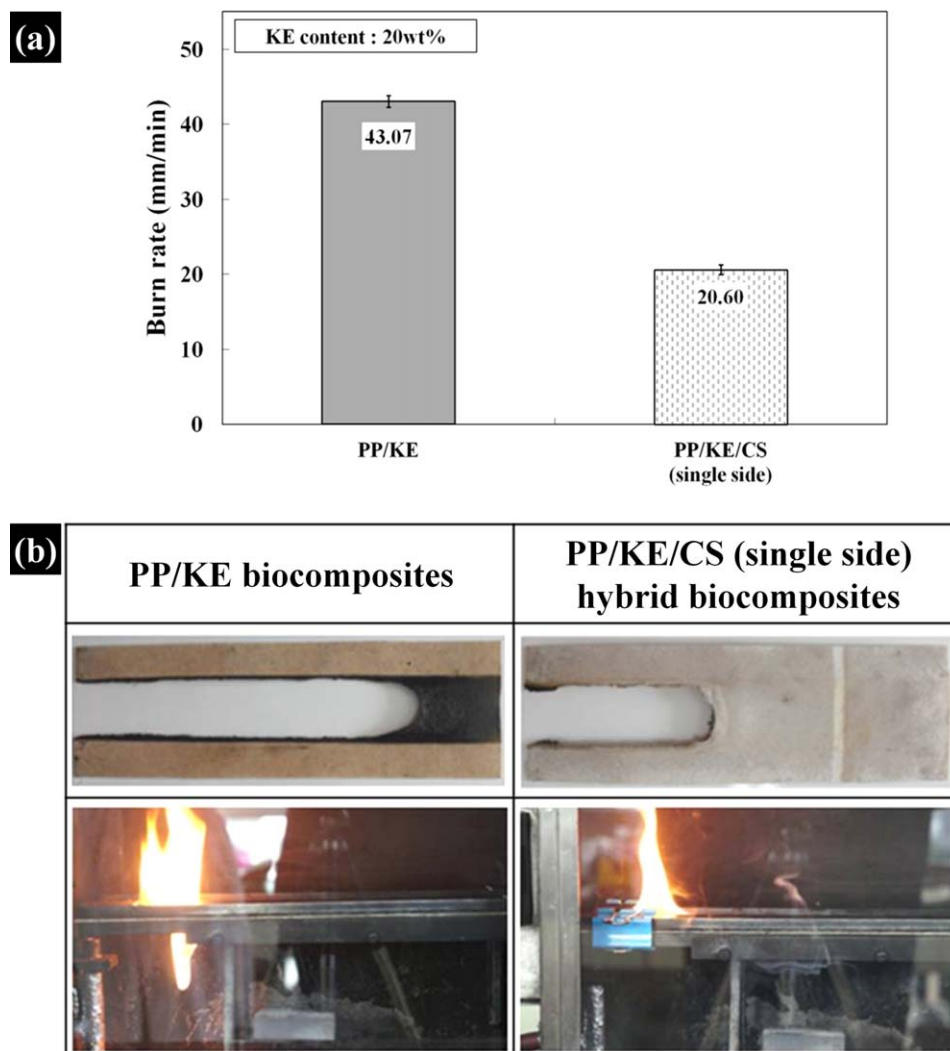
The surface morphology of the CS and the fractured surfaces of hybrid biocomposites were characterized by Scanning Electron

Microscope (SEM, Hitachi). This instrument was equipped with an energy dispersive X-ray spectrometer (EDX) which was used to investigate the compositional variation of ceramic hybrid biocomposites. Prior to the measurement, the specimens were coated with Au in order to prevent electrical discharge. The acceleration voltage used was 15–25 kV.

Flammability behavior of the ceramic hybrid biocomposites was investigated by horizontality burning test (FMVSS 302), density of smoke (ISO 5659-2), and toxicity of gas test (BS6853 Annex B.2-Area based test method). The burning rate is calculated according to the formula:

$$B=60\left(\frac{D}{T}\right) \quad (1)$$

where *B* is the burning rate (mm/min); *D* is the length the flame travels (mm); and *T* is the time (s) for the flame to travel *D*. The optical density test is a measure of the amount of smoke produced per unit area when a material is exposed to flame. These specimens were subjected to a heat flux of 25 kW/m<sup>2</sup> during 5 min. The toxicity test of gas is generally performed during optical density test, and measurement of toxic fumes



**Figure 5.** (a) Burning properties and (b) burning test samples of PP/KE biocomposite and PP/KE/CS hybrid biocomposites. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

starts at the previously determined time to reach 85% of density of smoke. The average concentration for each toxic gas is used to calculate the  $R$  value as follows:

$$r_x = \frac{c_x}{f_x}, \quad R = \sum r \quad (2)$$

where  $c_x$  is the emission of the  $x$ th species in the appropriate units,  $f_x$  is the reference value for the  $x$ th species, and  $r_x$  is the individual index for the  $x$ th species. The specimen dimensions of horizontality burning test and optical density test, toxicity test of gas were  $320 \text{ mm} \times 100 \text{ mm}$  and  $80 \text{ mm} \times 80 \text{ mm}$ , respectively, and the thickness for all specimen was 1 mm. All specimens were measured in condition at  $21^\circ\text{C}$  for 24 h under a relative humidity of 50%.

## RESULTS AND DISCUSSION

### TGA Analysis of Ceramic Sheet

Figure 2(a) shows the surface morphology of the CS. In Figure 2(a), the CS can be expected to have stronger and wider bonding with polymers and natural fibers due to the three-

dimensional arrangement after the removal of the organic binder. Figure 2(b) shows the thermal properties of raw CS and heat treated CS. The weight loss started below  $100^\circ\text{C}$ . It is a mass loss equivalent of moisture that evaporated into the air. Over  $200^\circ\text{C}$ , the decomposition peak of raw CS occurred in the temperature range of 220 and  $380^\circ\text{C}$  and is attributed to the thermal decomposition of the organic binder.<sup>20</sup> The decomposition peak of raw CS and heat treated CS occurred at  $600\text{--}670^\circ\text{C}$  is attributed to sepiolite (Mg–OH group)<sup>21,22</sup> in the CS. The residue of raw CS and heat treated CS were 81.3 and 95.7% at  $850^\circ\text{C}$ , respectively. This result demonstrates the high thermal stability characteristic of the heat treated CS.

### Mechanical Properties of Hybrid Biocomposites

The tensile and impact strength and flexural properties of the PP/KE/CS hybrid biocomposites are shown in Figure 3. In Figure 3(a), when one sheet of CS was added to the biocomposites, the tensile and impact strength of the hybrid biocomposites showed average increases of 6.7 and 13.2%, respectively,

**Table I.** The Specific Optical Smoke Density of PP/KE/CS Hybrid Biocomposites

Test item	PP/KE	PP/KE/CS (single side)
$D_s$ max <sup>a</sup>	241.7	126.6
Time to $D_s$ max (s)	180	210
Time to 85% $D_s$ max (s)	90	180

<sup>a</sup> $D_s$  max: Maximum specific optical density.

compared to the base value of PP/KE biocomposites without CS. Therefore, the tensile and notched I-zod impact strength of the hybrid biocomposites was higher than those of PP/KE biocomposites; the highest value was present at the double side of the CS. It can be explained that CS was fully impregnated into the biocomposites and became an effective complement despite the very brittle characteristic of CS.

In Figure 3(b), the flexural strength and modulus of CS hybrid biocomposites showed an increase of a maximum of 17.2 and 57.3% with the CS for both ends, compared to the PP/KE biocomposites without the CS. These results are similar to the results for tensile and impact strength; flexural properties are also improved for the same reason.

#### Surface Morphology Observation of Hybrid Biocomposites

Figure 4 shows the morphology and atomic distribution of the fractured surfaces of PP/KE biocomposites and PP/KE/CS hybrid biocomposites. In Figure 4(a,b), we can see the network formed inside the PP/KE biocomposites and the PP/KE/CS hybrid biocomposites, which shows good interfacial adhesion between the KE, the PP matrix, and the CS. Also, Figure 4(b) shows that CS was fully impregnated into the PP/KE biocomposites out of recognition of the boundary surface between the CS and the biocomposites. The atomic percentages of carbon (65.24%), oxygen (27.08%), sodium (0.21%), magnesium (0.39%), aluminum (1.50%), silicon (5.45%), and calcium (0.13%) elements resulting from the CS surface are identified

in Figure 4(c). Figure 4(d) shows the silicon distribution on the fractured surfaces of the CS hybrid biocomposites.

#### Flammability of Hybrid Biocomposites

The flammability behavior of hybrid PP biocomposites is characterized as shown in Figure 5, and in Tables I and II. In Figure 5(a), the burning rate of PP/KE biocomposites and PP/KE/CS (single side) hybrid biocomposites showed values of 43.07 and 20.60 mm/min, respectively. These values were found in the FMVSS 302 test according to pass standards of the value being under 102 mm/min. CS hybrid biocomposites showed a burning rate of 52.17%, which was markedly lower than that of biocomposites without CS. Figure 5(b) shows flames during the test and damage on the length of the specimens of hybrid PP biocomposites after the test. Biocomposites without CS burnt easily and can be seen to be flowing with flames, whereas the CS hybrid biocomposites maintained their sheet structure. The improvement of hybrid biocomposites is attributed to the CS-integrated biocomposite structure, which has a full impregnation of CS into the biocomposites, as can be seen in the SEM observations. The CS primarily faces the flame and does not burn before the burning of the PP and KE, accumulating on the surface by forming a barrier outside of the heat, blocking oxygen.<sup>23</sup> Therefore, it can be expected to obstruct burning while maintaining the structure of composites.

Another important variable is whether or not there is any emission of smoke and toxic gases during burning. The density of smoke test is quantified by measuring the specific optical smoke density ( $D_s$ ) of the materials; Tables I and II show the  $D_s$  max and time to  $D_s$  max of ceramic hybrid biocomposites and the gas toxicity of the CS hybrid biocomposites during the density of smoke test. The  $D_s$  max values of the PP/KE biocomposites and the PP/KE/CS (single side) hybrid biocomposites were 241.7 and 126.6, respectively, and therefore the density of smoke value of the CS hybrid biocomposites was significantly decreased, 47.62%, compared to that of the biocomposites without the CS. Also, the time to  $D_s$  max and 85%  $D_s$  max of the CS hybrid biocomposites were increased 16.67 and 100% compared to those values of the biocomposites without CS. The gas

**Table II.** The Toxicity Test of Burning Gas During the Combustion of PP/KE/CS Hybrid Biocomposites

Gas	Detection limit (g/m <sup>2</sup> )	Reference values <sup>a</sup> (g/m <sup>2</sup> )	KE/PP			KE/PP/CS (single side)		
			Av. (g/m <sup>2</sup> )	$r_x^b$	$R^b$	Av. (g/m <sup>2</sup> )	$r_x$	$R$
CO <sub>2</sub>	50	14,000	2947.7	0.211	0.41	1737.0	0.124	0.27
CO	1.0	280	23.1	0.083	—	20.8	0.074	—
HF	0.1	4.9	—	—	—	—	—	—
HCl	0.1	15	—	—	—	—	—	—
HBr	0.1	20	—	—	—	—	—	—
HCN	0.5	11	—	—	—	—	—	—
NO <sub>x</sub>	0.3	7.6	0.9	0.116	—	0.6	0.072	—
SO <sub>2</sub>	2.5	53	—	—	—	—	—	—

<sup>a</sup>Reference values: IDLH (Immediately Dangerous to Life or Health) value; <sup>b</sup> $r_x$ : The individual index for x species; <sup>c</sup> $R$ : The weighted summation index of toxic fume.

—: not detected

toxicity of the CS hybrid biocomposites during burn was decreased 34.15% compared to that of the biocomposites. In Table II, HF, HCl, HBr, HCN, and SO<sub>2</sub> were not detected for all samples, and CO<sub>2</sub>, CO, and NO<sub>x</sub> were detected at values of 1737, 20.8, and 0.6 g/m<sup>2</sup>, respectively, in the CS hybrid biocomposites; however, these values represent improvements of 41.1, 9.9, and 33.3%, respectively, compared to the original values of the sample without CS. It can be explained there is a prevention of heat and oxygen by barrier coating effect of CS.

## CONCLUSION

In this study, CS integrated natural reinforced PP biocomposites have been successfully fabricated with single and double side CS and their mechanical and flammability properties have been investigated. The mechanical properties of CS hybrid biocomposites were increased with the addition of a CS. Also, CS effects delay ignition and prevent flame spread and heat penetration; therefore, the flammability, optical density, and gas toxicity of CS hybrid biocomposites were improved by the presence of an integrated structure between CS and the biocomposites; this improvement was due to the full impregnation of CS into the biocomposites. CS can contribute to the improvement of both the mechanical properties and the flammability of biocomposites, resulting in a broadening of the potential field of applications of biocomposites to such areas as aerospace.

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