

# Development of a Biodegradable Rice Straw-g-poly(methylmethacrylate)/Sodium Silicate Composite Flame Retardant

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Received 4 August 2008; accepted 8 December 2008

DOI 10.1002/app.30064

Published online 13 May 2009 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Natural fiber composites have been prepared by grafting hydrophobic monomer methyl methacrylate (MMA) onto chemically modified rice straw (RS) using complex initiating system [CuSO<sub>4</sub>/glycine/ammonium persulfate (APS)] in an aqueous medium with and without the additive, sodium silicate (SS). The chemically modified RS, RS-g-PMMA, and RS-g-PMMA/SS composite have been characterized by FT-IR, and their morphology was studied by scanning electron microscopy (SEM). The thermal behavior

and tensile properties of the samples have been studied, and the flame retardant properties have also been evaluated by limiting oxygen index (LOI) test and cone calorimetry. The biodegradation and water absorbency have been carried out for its ecofriendly nature and better commercialization. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 3710–3715, 2009

**Key words:** rice straw; poly(methyl methacrylate); sodium silicate; flame retardant; biodegradation

## INTRODUCTION

Rice straw (RS) is a low cost, multicellular, lignocellulosic fiber mainly produced in the developing countries, especially in India and south Asia, which is used as an animal food and for burning purpose.<sup>1,2</sup> During burning, the RS produces harmful environmental implications through global addition of carbon dioxide and other gases contributing to the green house effect. Because of its low cost and easy availability, it is mainly used in construction and transporting industries, but its use has been hampered because of its high flammable nature. Increasing their flame-retardancy properties can increase the utilization of these substances.

In our previous work, we have prepared grafted sample of various vinyl monomers on the backbone of jute<sup>3–5</sup> and pineapple leaf fibers (PALF)<sup>6</sup> and studied their mechanical properties, water absorbency, etc. There are a few articles on RS<sup>7,8</sup> grafted materials, where the mechanical, water absorbency, crystallography properties, etc. have been studied along with their compost applications.<sup>9,10</sup> There are a few articles on flame retardancy of natural fibers or cellulose,<sup>11–13</sup> but the report on flame retardancy of RS is limited.<sup>14</sup>

In this study, we have prepared a new flame retardant (RS-g-PMMA)/SS composite by using sodium sili-

cate (SS) additive, and the material was characterized by infrared (IR), scanning electron microscopy (SEM), thermogravimetric analysis (TGA), limiting oxygen index (LOI), and cone calorimetry along with its studies on water absorbency and biodegradability.

## EXPERIMENTAL

### Materials

Methyl methacrylate (MMA) monomer from CDH India was purified as per literature.<sup>15</sup> Ammonium persulfate (APS), glycine, Cu(II)SO<sub>4</sub>, methanol, and benzene were from E. Merck, India. SS was a solid granular sample (CAS 1344-098, Batch No.-2023BB H<sub>2</sub>O-1) gift from PQ Corp. (Maastricht, the Netherlands). All reagents were used after purification by standard techniques. A local product RS was cut into 3–4 cm and then extracted by a mixture of methanol and benzene (1 : 1) for 6 h to remove waxes and resins. The residual materials were air-dried till a constant mass was obtained. The dried materials were bleached with sodium chlorite (3%) solution for 24 h at 35°C to remove the lignin content. Then, it was washed with 3–4 times in double distilled water. It was dried in a vacuum-evaporated oven at 50°C for 12 h to find out RS.

### Method of preparation

The graft copolymerization reaction of RS and MMA with CuSO<sub>4</sub>, glycine, and APS were carried out in a

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constant-shaking bath at temperature 45°C, with an accuracy of 0.1°C under oxygen-free nitrogen atmosphere in water medium containing required amount of SS (10% w/v). The RS was first soaked with appropriate quantities of monomer MMA, and other reagents were taken in a reaction vessel and deaerated by oxygen-free N<sub>2</sub> gas. The known quantities of APS were injected through after thermal equilibrium as described in detail elsewhere.<sup>4,6</sup> After 3 h, the reaction was arrested by the addition of ammonium ferrous sulfate solution in ice-cold water to consume unreacted APS. Then, the grafted composites were washed in deionised water for 2–3 times to remove the excess SS and other water soluble substances present and were also washed in benzene for 2–3 times to remove the homopolymer PMMA, and the composite was dried in air till a constant mass.

### Characterization

The samples of RS, RS-g-MMA, and (RS-g-MMA)/SS composite in the form of KBr pellets were recorded in the Perkin Elmer model Paragon-500 Fourier transform infrared spectrometer.

The surface morphology of the samples was observed with a JEOL, Ltd. (Japan) model 5200 SEM after coating it with gold at different magnifications.

TGA was conducted with a Shimadzu DTA-500 system. It was carried out in air from room temperature, gradually raised to 550°C at a heating rate of 10°C/min.

### Flame retardancy

The flame retardancy of the composites was assessed by LOI test according to ASTM D 2863, apparatus from Fire Instrument Research Equipment Ltd. with a digital read out of oxygen concentration to +0.1%. The dimension of the compression mold sample is (100 × 6.5 × 3) mm. The LOI value corresponds to the minimum concentration of oxygen in the mixture of oxygen/nitrogen necessary to burn the sample during 3 min or over a length of 80 mm.

The cone calorimetry is one of the effective methods for studying the flammability of fire retardant polymers.<sup>16</sup> Fire retardant properties measured by the cone calorimeter, such as heat release rate (HRR) peak, and smoke and carbon monoxide yield are vital to the evaluation of fire safety materials.<sup>17</sup> The horizontal orientation using a Stanton Red croft Cone Calorimeter<sup>18</sup> in accordance with the procedure outlined in AS/NZS 3837 : 1998, which was based on ISO 5660-1 : 1993, with dimensions 100 × 100 × 4 mm<sup>3</sup> at an external heat flux<sup>19</sup> 35 kW/m<sup>2</sup>. The peak HRR is known to be an important factor in predicting fire hazard. Comparisons were made between the HRRs of neat polymers and polymer/clay hybrids, when

exposed to a 35-kW/m<sup>2</sup>, a multilayered silicate heat flux, as measured by cone calorimeter.

### Tensile strength

The tensile properties of the RS, RS-g-PMMA, and (RS-g-PMMA)/SS composite were determined by measuring stiffness at break (tensile strength) following the methods of Haque and Habiduddowla<sup>20</sup> and others.<sup>21,22</sup> The stiffness at break was determined from the value of tenacity and elongation at break by using the following relationship:

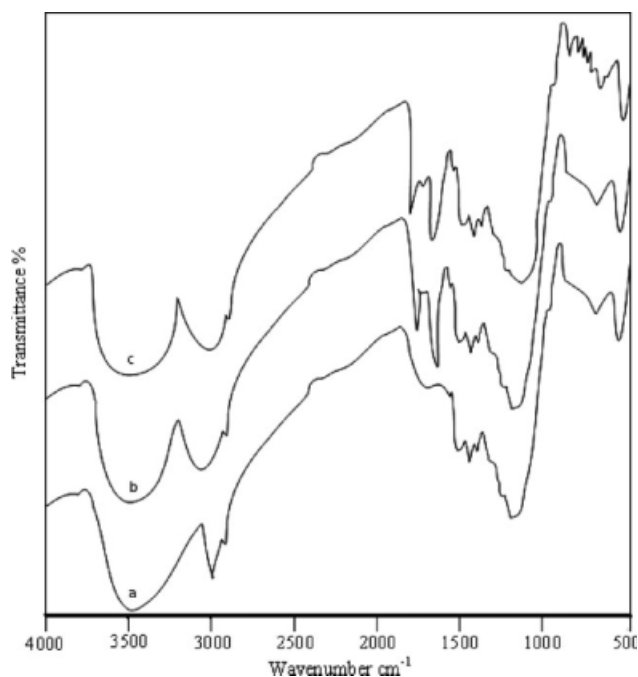
Stiffness at break

$$= (\text{Tenacity at break/elongation at break}) \times 100.$$

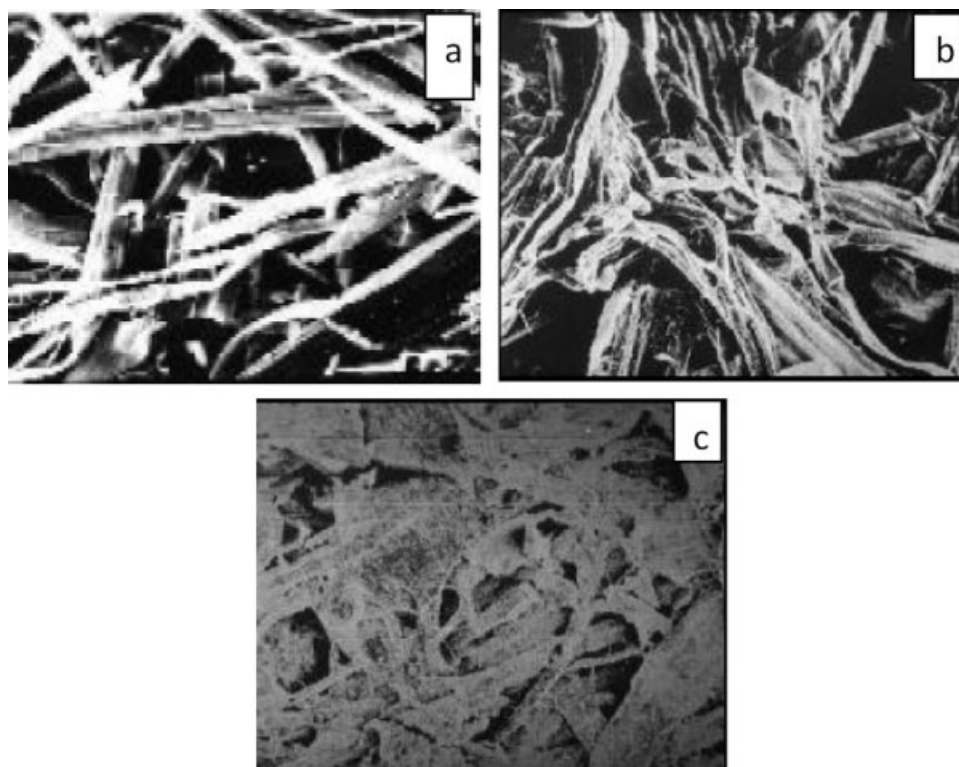
The tenacity was expressed as g/den. After the samples were conditioned, they were combed, and fiber aggregates of uniform length were taken. Their weight and length were determined, and their mechanical properties were measured by means of Dutrons tensile tester, Brand-20 Kgf capacity.

### Water absorbency

The water absorbency<sup>23</sup> ( $W_{\text{abs}}$ ) of the RS, RS-g-PMMA, and (RS-g-PMMA)/SS composite was determined by immersing the dry samples ( $W_0 = 1$  g each) in deionized water at room temperature for 24 h. After the required time period, the samples were drained for 30 min for the elimination of excess non-absorbed water, and the weight of the swollen



**Figure 1** FTIR of (a) RS, (b) RS-g-PMMA and (c) (RS-g-PMMA)/SS (10% w/v) composite.



**Figure 2** Photograph of SEM of (a) RS, (b) RS-g-PMMA and (c) (RS-g-PMMA)/SS (10% w/v) composite.

samples ( $W_s$ ) was recorded. The water absorbency was calculated using the following equation:

$$Q(\text{gH}_2\text{O/g sample}) = [(W_s - W_0)/W_0]$$

### Biodegradation by activated sludge

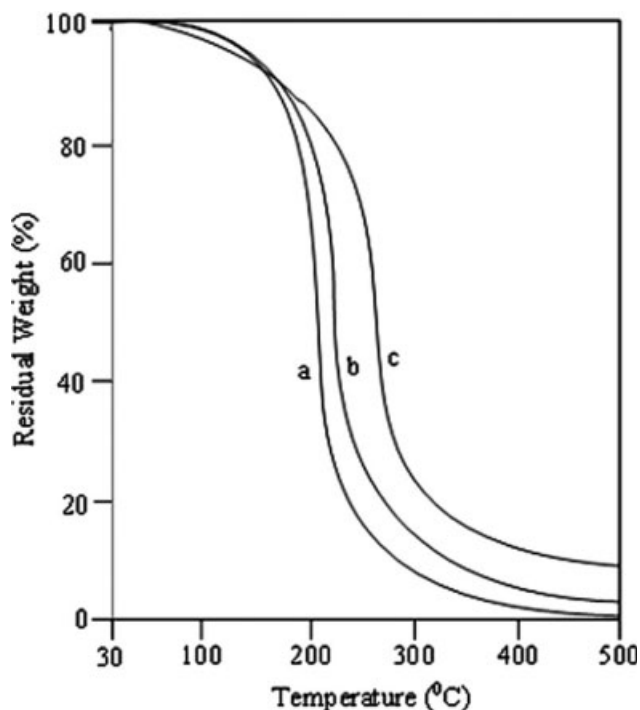
Biodegradation of RS, RS-g-PMMA, and (RS-g-PMMA)/SS composite was studied under sludge water at different conditions. A series of above-mentioned samples (0.1 g) were immersed in the supernatant of standard activated sludge and were incubated at 40°C. On the day of testing, the activated sludge was collected from a waste dump area, centrifuged, and the supernatant liquid was taken for detailed study.

## RESULTS AND DISCUSSION

### Infrared spectra (FT-IR)

According to the literature, the lignin content decreases with bleaching the RS. Graft copolymerization of natural fiber increases with a decrease in the lignin content.<sup>24</sup> Figure 1 shows the graft copolymerization of MMA on the backbone of RS. In the case of bleached RS, there is a peak at 3300–3400  $\text{cm}^{-1}$  due to hydrogen bonded —OH vibration. The sharp band at 1590  $\text{cm}^{-1}$  indicates the aromatic rings. When com-

pared to RS, in the case of RS-g-PMMA, the new peak obtained at 1755  $\text{cm}^{-1}$  is the stretching vibration of carbonyl group present in MMA [Fig. 1(b)]. From



**Figure 3** TGA of (a) RS, (b) RS-g-PMMA and (c) (RS-g-PMMA)/SS (10% w/v) composite.

TABLE I  
Cone Calorimetric Data and LOI Values of RS, RS-g-PMMA, and (RS-g-PMMA)/SS (10% w/v) Composite

Samples	Cone calorimetric data							LOI
	TTI (s)	PHRR (kW/m <sup>2</sup> )	AvRHR (kW/m <sup>2</sup> )	THR (MJ/m <sup>2</sup> )	MLR (g/s)	AvCO (kg/kg)	PSEA (m <sup>2</sup> /k)	
RS	64	554 ± 12	156 ± 5	21 ± 2	0.045	3.4	154	18.8
RS-g-PMMA	69	543 ± 12	163 ± 5	24 ± 2	0.043	3.7	189	20.4
(RS-g-PMMA)/SS (10% w/v)	55	423 ± 12	148 ± 5	17 ± 2	0.036	3.9	172	24.8

Figure 1(c), a very strong peak is obtained at 1100 to 1400 cm<sup>-1</sup> for (RS-g-PMMA)/SS due to Si—O—Si stretching.

### Scanning electron microscopy

The surface morphologies of RS-g-PMMA and (RS-g-PMMA)/SS composite are shown in Figure 2. On grafting with MMA, the surface morphology of RS is changed as shown in Figure 2(b). Figure 2(c) shows the presence of SS embedded on the surface of the RS. On addition of SS to a crosslinked sample, i.e. (RS-g-PMMA)/SS, the porosity increases, and as a result, the composite sample is compelled to carry more water than the RS-g-PMMA copolymer.

### Thermogravimetry analysis

The thermal behaviors of the RS, RS-g-PMMA copolymer, and (RS-g-PMMA)/SS composite were studied by comparing their thermogram curves as shown in Figure 3. The temperature of decomposition ( $T_D$ ) is very much influenced by the addition of SS. From the curves, the  $T_D$  was found to be 205°C for RS-g-PMMA and 250°C for the (RS-g-PMMA)/SS composite. Residual mass for RS-g-PMMA and (RS-g-PMMA)/SS composite was found to be 9% and 15%, respectively. Thus,  $T_D$  values and residual mass indicates that on addition of SS, the (RS-g-PMMA)/SS composite becomes somewhat resistant to thermal action.

### Flame retardancy

LOI is a popular research measurement to evaluate fire extinction. The errors associated with LOI measurements generally are ±0.2%, and the results reported in Table I are the average of three to five determinations. A large increase in LOI is seen for the presence of SS<sup>25</sup> with only 5%, but as the amount of SS increases the LOI leaves out and the value is relatively constant above 15%.

The evidence for protective, effective effect of layered silicate has on the composite obtained by cone calorimeter. The cone calorimeter instrument provides a method for measuring the amount of heat or energy released from a material during combustion.

Other parameters that are measured simultaneously include smoke, carbon monoxide generation, ignition behavior, mass loss, etc.

Rate of HRR is one of the most important parameters associated with the flammability and combustion of materials. The samples that have low value of HRR are better fire retardant than those with high HRR value. From Figure 4 and Table I, it was found that the HRR value of RS or RS-g-PMMA was more than RS-g-PMMA/SS composite. The flammability properties of a solid phase flame retardant can be the result of formation of charred residue with silicate layer present in it. Because of the formation of char residue, layered silicate acted as a protective barrier by reducing the heat and mass transfer between the flame and the samples. In our previous article<sup>26,27</sup> we proved that the HRR was normally lowered because of the presence of SS such as clay, which was explained by Gilman et al.<sup>28</sup> and others.<sup>29,30</sup>

From Figure 4 and Table I, the time to ignition (TTI) value of (RS-g-PMMA)/SS composite was lower than the others because the first decomposition of silicate

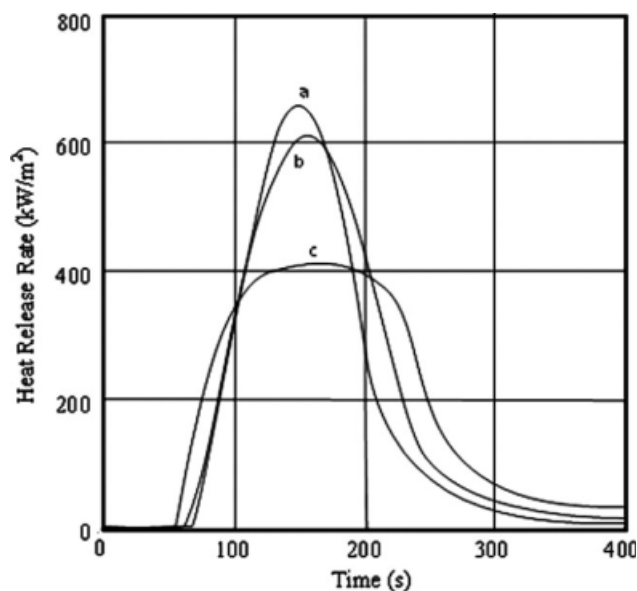


Figure 4 Heat release rate curve of (a) RS, (b) RS-g-PMMA and (c) (RS-g-PMMA)/SS (10% w/v) composite.

**TABLE II**  
**Tensile Strength of RS, RS-g-PMMA, and (RS-g-PMMA)/SS (10% w/v) Composite**

Sample	Elongation at break (BL %)	Tenacity (g/den)	Tensile strength (N/m <sup>2</sup> )	Tensile strength after 28 days (N/m <sup>2</sup> )	Strength retain (%)
RS	28.8	0.087	37.8	5.6	14.81
RS-g-PMMA	40.4	0.426	48.7	7.1	14.45
(RS-g-PMMA)/SS (10% w/v)	38.5	0.389	45.7	6.4	14.00

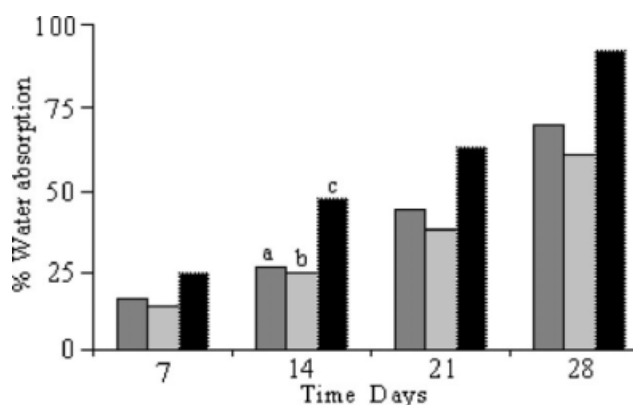
formed a charred residue like clay on sample. Further, the flame retardancy of polymer is explained by mass loss rate (MLR) value. The flame retardancy of polymers is mainly dependent on HRR value. But HRR mainly depends on the MLR, i.e., the substance having lower MLR have lower HRR. From Table I, it is found that the (RS-g-PMMA)/SS has low MLR than others. The decrease of MLR during combustion in cone calorimeter is due to the formation of charred residue on samples, which is coincided with data of Lee et al.<sup>31</sup>

The tensile properties of RS, RS-g-PMMA, and RS-g-PMMA/SS composite are given in Table II. The results show that RS has the lowest tensile strength than other samples. The tensile strength of fibers mainly depends on the presence of lignin and binding materials, and the substances having less lignin and binding materials have lower tensile strength. Presently, in RS, the lignin and binding materials are removed by alkali treatment; hence, the tensile strength is decreased. From Table II, the tensile strength of RS-g-PMMA copolymer is more because of the grafting of PMMA onto the back bone of RS. The presence of SS in (RS-g-PMMA)/SS composite is the cause of the decrease in its tensile strength than that of RS-g-PMMA, which was explained by us in our previous article.<sup>5</sup>

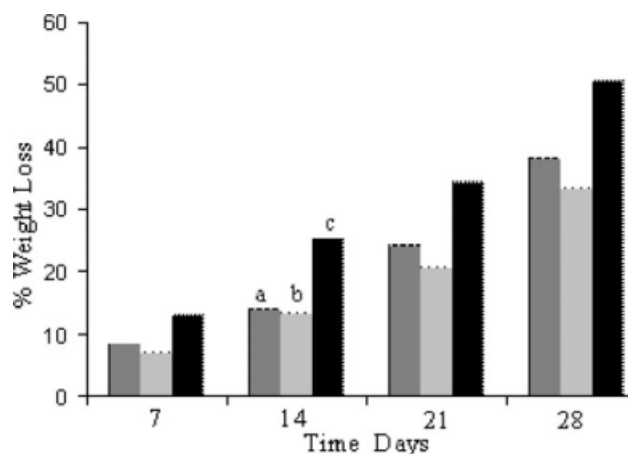
Figure 5 shows the absorption of various samples in deionized water. It is found that the water absorption of RS is low because of the absence of lignin and binding materials. But the water absorption of RS-g-

PMMA shows low value when compared to RS because of the increasing hydrophobic nature by grafting of hydrophobic PMMA onto the backbone of RS. The water absorption of (RS-g-PMMA)/SS composite is increased with increasing hydrophilicity because of the presence of hydrophilic SS. The water absorption also depends upon the porosity, i.e., the substance having more porosity has more water absorbency. Addition of SS facilitates more water absorption and increases the porosity of the composite.

Figure 6 shows the biodegradation of RS, RS-g-PMMA copolymer, and (RS-g-PMMA)/SS by activated sludge water with their water uptake capacity. The presence of microorganisms in sludge water is the cause of biodegradation of the samples. The biodegradation of RS is low because of the absence of lignin and binding materials. Addition of hydrophobic PMMA onto the backbone of RS causes further decrease in the biodegradation of RS-g-PMMA copolymer than the RS. But the biodegradation of (RS-g-PMMA)/SS composite is increased with addition of hydrophilic SS because of the presence of dispersed silicate layers with large ratio in the composite matrix, which forces the microorganism diffusing in the bulk of the matrix through more tortuous path. All these data are also in agreement with the decrease in tensile strength after 28 days in activated sludge water (Table II).



**Figure 5** Water absorption of (a) RS, (b) RS-g-PMMA and (c) (RS-g-PMMA)/SS (10% w/v) composite.



**Figure 6** Biodegradation of (a) RS, (b) RS-g-PMMA and (c) (RS-g-PMMA)/SS (10% w/v) composite.

## CONCLUSIONS

Natural fiber-based composite was prepared from RS through grafting with MMA monomer and SS. The resulting composite was characterized by IR, TGA, SEM, and tensile properties. The observed IR peaks indicate the inclusion of silicate onto the RS-g-PMMA forming a composite. TGA and tensile strength data reveal that, on addition of SS, the composite becomes resistant to thermal action, but is not as strong as the samples without silicate. The LOI and cone calorimetric values show the composite with SS is more flame retardant than the virgin fiber and the copolymer. The porous nature of the RS and the grafted composite with silicate showed higher water absorption as well as biodegradation in active sludge water. They may find use in industries as flame retardant, tough and durable materials.

Ramakanta Samal highly acknowledges to Council of Scientific and Industrial Research, New Delhi, India, for providing the financial assistance in the form of NET JRF.

## References

1. Samar, S.; Malik, R. K.; Mangat, R.; Singh, S.; Ram, M. *Indian J Agronomy* 1999, 44, 361.
2. Diaz, L. F.; Sarvage, G. M.; Egerth, L. L.; Golueke, C. G. *Composting & Recycling Municipal Solid Waste*; Lewis Publishers: Boca Raton, 1998.
3. Sahoo, P. K.; Rana, P. K.; Debsarkar, N. L.; Sahoo, A.; Swain, S. K. *J Polym Sci Part A* 2003, 41, 2696.
4. Sahoo, P. K.; Swain, S. K.; Debsarkar, N. L. *J Appl Polym Sci* 2002, 83, 1963.
5. Sahoo, P. K.; Mohapatra, R.; Sahoo, A.; Debsarkar, N. L.; Swain, S. K. *Int J Polym Anal Charact* 2005, 10, 153.
6. Sahoo, P. K.; Sahoo, G. C.; Mohapatra, R. *Indian J Fiber Text Res* 2005, 30, 157.
7. Lim, S. K.; Cho, K. M.; Tasaka, S.; Inagaki, N. *Macromol Mater Eng* 2001, 286, 187.
8. Kamel, S. *Polym Adv Technol* 2004, 15, 612.
9. Zayed, G.; Abdel-Motaal, H. *Bioresour Technol* 2005, 96, 929-035.
10. Singh, R. D.; Yadav, D. V. *Agric Wastes* 1996, 18, 247.
11. Kozłowski, R.; Mieleniak, B.; Muzyczek, M.; Kubacki, A. *Flame retardant nonwovens on the basis of natural fibers – production and application*. Presented at the Proceedings of the 4th International Wood and Natural Fiber Composites Symposium; Kassel, Germany, April 2002.
12. Horrocks, A. R.; Kandala, B. K. *Flame retardant cellulose textiles*. Presented at the 6th European Meeting in Fire Retardant Polymeric Materials; Lille, France, 1997.
13. Tian, G.; Kolawole, G. O.; Tian, G. L.; Sinclair, F. L. In *Phosphorous Availability, Uptake and Cycling in Tropical Agroforestry*; Buresh, R. J., Ed.; Wiley: New York, 1999; Vol. 9, pp. 40–42.
14. Perks, B. *Chem World* 2004, 1, 7.
15. Sahoo, P. K.; Mahapatra, R. *Eur Polym J* 2003, 39, 1838.
16. Scudamore, M. J.; Briggs, P. J.; Prager, F. H. *Fire Mater* 1991, 15, 61.
17. Wickstrom, U.; Goransson, U. *Heat Release in Fires*; Elsevier: London, 1992.
18. Redfern, J. P. *J Therm Anal* 1989, 6, 1861.
19. Recommendation for the use of the cone calorimeter, STD.BSI.DD246-ENGL; 1999.
20. Haque, M. M.; Habiduddowla, M. *J Sci Res* 1980, 15, 64.
21. Odian, G. *Principle of Polymerization*, 3rd ed; Wiley: New York, 1991.
22. Jang, B. Z. *Advanced Polymer Composites: Principles and Application*, ASM International: Materials Park, OH, 1994.
23. Raju, K. M.; Raju, M. P. *Polym Int* 2001, 50, 946.
24. Kubuta, H.; Ogiwara, Y. *J Appl Polym Sci* 1969, 13, 1569.
25. Wang, Z.; Hu, Y.; Gui, Z.; Zong, R. *Polym Test* 2003, 22, 533.
26. Samal, R.; Rana, P. K.; Mishra, G. P.; Sahoo, P. K. *Polym Comp* 2008, 29, 173.
27. Sahoo, P. K.; Samal, R.; Swain, S. K.; Rana, P. K. *Euro Polym J* 2008, 44, 3522.
28. Gilman, J. W.; Kashiwagi, T. *Polymer-Clay Nanocomposites*; Pinnavaia, T. J., Beall, G. W., Eds.; Wiley: New York, 2000; Vol. 193.
29. Gilman, J. W.; Kashiwagi, T.; Giannelis, E. P.; Manias, E.; Lomakin, S.; Lichtenhan, J. D.; Jones, P. *Fire Retardancy of Polymer*; Le Bras, M., Camino, G., Bourbigot, S., Delobel, R., Eds.; The Royal Society of Chemistry: Cambridge, 1998.
30. Babrauskas, V.; Peacock, R. *Fire Saf J* 1992, 19, 255.