

# Properties of POSS-Filled Polypropylene: Comparison of Physical Blending and Reactive Blending

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**ABSTRACT:** Polypropylene (PP)/octavinyl polyhedral oligomeric silsesquioxane (OvPOSS) composites were prepared by physical blending or reactive blending methods. The comparison of the PP/OvPOSS composites prepared by these two methods was investigated by mechanical tests, thermogravimetric analysis, and cone calorimeter. The graft ratio of OvPOSS to PP chain increased with increasing OvPOSS and dicumyl peroxide content for the reactive blending composites. The reactive blending com-

posites had better mechanical properties, thermal stability than physical blending composites. The peak of the heat release rate and mass loss rate of PP/OvPOSS had also decreased, indicating better flame retardancy of PP/OvPOSS composites. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 3745–3751, 2008

**Key words:** polypropylene; polyhedral oligomeric silsesquioxane; reactive processing

## INTRODUCTION

Polyhedral oligomeric silsesquioxane (POSS)/polymer composites have generated much interest recently, both from the academic and industrial points of view. POSS is completely defined molecule of nanoscale dimensions that may be functionalized with reactive groups suitable for the synthesis of new organic–inorganic hybrids, hence providing the opportunity to design and build materials with extremely well-defined dimensions possessing nanophase behavior.<sup>1</sup> POSS was incorporated into polymers by copolymerization, grafting, or melt blending. The incorporation of POSS or its derivatives into polymers can lead to some dramatically improved properties, such as the increase in heat distortion temperature, oxidation resistance, surface hardening, and improved mechanical properties, as well as reductions in flammability, heat evolution, and viscosity during processing, etc.<sup>2</sup>

POSS has been widely introduced into polymers by copolymerization or blending. The morphology, crystallization behavior, mechanical properties,

thermal properties, and surface properties of polypropylene (PP)/POSS composites have been widely studied.<sup>3–14</sup> For PP/POSS composites, good dispersion of POSS is obtained particularly at low loadings of POSS functionalized with long organic chains.<sup>10</sup> The addition of octamethyl POSS into PP increased the Young's modulus and decreased the yield strength, whereas the Young's modulus and yield strength both decreased when octaisobutyl or octaisooctyl POSS was added to PP.<sup>11</sup> The incorporation of metal-functionalized POSS into PP could improve the thermal stability and considerably reduce the heat release rate (HRR) of PP.<sup>12,13</sup> The surface energy and relative coefficient of friction also reduced when octaisobutyl POSS was added to PP.<sup>14</sup>

POSS-containing hybrid polymers reported in most literature are made from one-pot copolymerization method or by melt blending, whereas little reports focused on direct graft copolymerization of POSS to polymers chains.<sup>15,16</sup> Reactive blending is proved to be a key technology in the polymer industry and regarded as an efficient method for the continuous polymerization of monomers and for the chemical modification of existing polymers in the absence of solvents. In this article, octavinyl POSS (OvPOSS) was successfully grafted to isotactic PP chains by reactive blending of PP and POSS in the presence of dicumyl peroxide (DCP). Compared with the physical blending PP/OvPOSS composites, reactive blending composites had better mechanical and thermal properties.

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## EXPERIMENTAL

### Materials

PP, F401 was produced by Liaoning Panjin Petrochemical Co., Ltd., China, with a melt flow index (MFI) of 2.3 g/10 min (230°C, 2.16 kg). OvPOSS, OL1160 was produced by Hybrid Plastic Co., USA. DCP was produced by Shanghai Gaoqiao Petroleum Co., China.

### Samples preparation

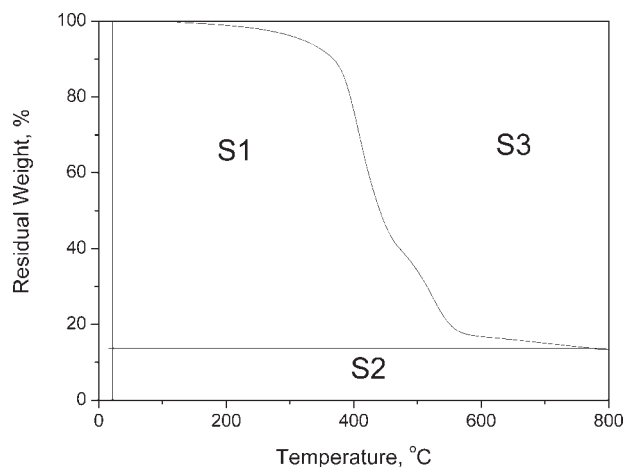
PP and OvPOSS were dried at 70°C under vacuum for about 12 h. PP, OvPOSS, and DCP were reactively blended in the mixing chamber of a Haake Rheometer RC90 at 180°C and 60 rpm for 8 min. The composites obtained were compression molded under a press at 190°C for 20 min, then cold pressed to get samples for testing. Physical blending composites of PP/OvPOSS (0 wt % DCP) were also underwent similar processes for comparison.

### The graft ratio of POSS and gel determination

The reactive blending composites were cut into small pieces, weighed and packed with filter paper, respectively and then were Soxhlet extracted in boiling acetone for 72 h, dried and weighed to determine the grafted OvPOSS content in the composite. The samples were further Soxhlet extracted in boiling xylene for 48 h, dried, and weighed to determine gel content. No gel was observed for all the samples. The reactive blending composites were resolved in refluxing xylene, precipitated, and washed by acetone, the precipitate was resolved and reprecipitated at least three times and dried at 80°C for 12 h and thought as OvPOSS-grafted PP (OvPOSS-g-PP). The grafted product was proved by the Fourier transform infrared spectroscopy and the Si element content analysis by inductively coupled plasma-atomic emission spectrometry which will be published elsewhere in the future.

### Measurements of mechanical properties

The tensile properties were measured using a Instron 4465 Tester according to ASTM D638, and at least three specimens were measured to calculate the average value for every sample. Notched Izod impact strength was tested using a Ray-Ran Universal Pendulum Impact Tester with the pendulum speed of 3.5 m/s according to ASTM D256, and seven specimens were measured to calculate the average value for every sample. Flexural properties were measured using the Instron 4465 Tester and a three-point-loading rig, and the central head was loaded on the specimen at a speed of 1.7 mm/min



**Figure 1** Schematic representation of  $S_1$ ,  $S_2$ , and  $S_3$  for  $A^*$  and  $K^*$ .

according to ASTM D790, at least three specimens were measured to calculate the average value for every sample.

### Thermogravimetric analysis (TGA)

The thermogravimetry was carried out in a Perkin-Elmer TGA7 (USA). The samples were scanned from 30 to 800°C at a heating rate of 20°C/min under a nitrogen flow of 20 mL/min. The integral procedure decomposition temperature (IPDT), which is usually used to evaluate the thermal stability of materials, was calculated from the following equation<sup>17</sup>:

$$\text{IPDT}(\text{°C}) = A^*K^*(T_f - T_i) + T_i \quad (1)$$

where  $A^*$  is the area ratio of total experimental curve defined by the total TGA thermogram,  $K^*$  the coefficient of  $A^*$ ,  $T_i$  the initial experimental temperature, and  $T_f$  the final experimental temperature. A representation of  $S_1$ ,  $S_2$ , and  $S_3$  for calculating  $A^*$  [ $A^* = (S_1 + S_2)/(S_1 + S_2 + S_3)$ ] and  $K^*$  [ $K^* = (S_1 + S_2)/S_1$ ] is shown in Figure 1.

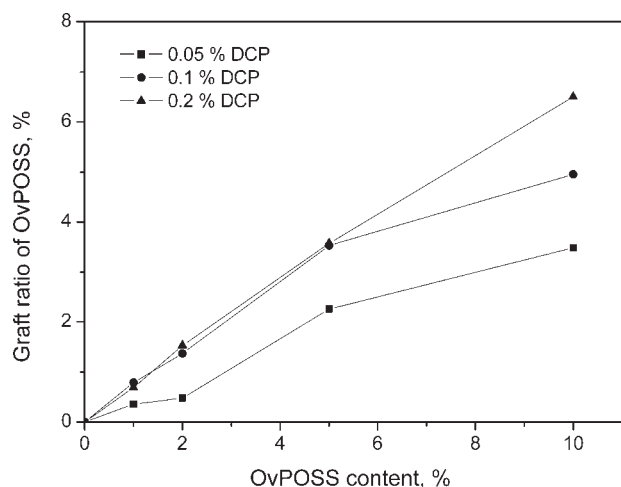
### Cone calorimeter tests

The flammability properties of the composites were conducted with the FTT standard cone calorimeter (Fire Testing Technology Limited, UK) under a heat flux of 50 kW/m<sup>2</sup> according to ISO 5660-1 standard. The surface area of the samples was 80 × 80 × 4 mm<sup>3</sup>.

## RESULTS AND DISCUSSION

### The graft ratio of OvPOSS

The graft ratio of OvPOSS to PP (the weight ratio of OvPOSS grafted to PP) was determined by Soxhlet



**Figure 2** The graft ratio of OvPOSS versus DCP content.

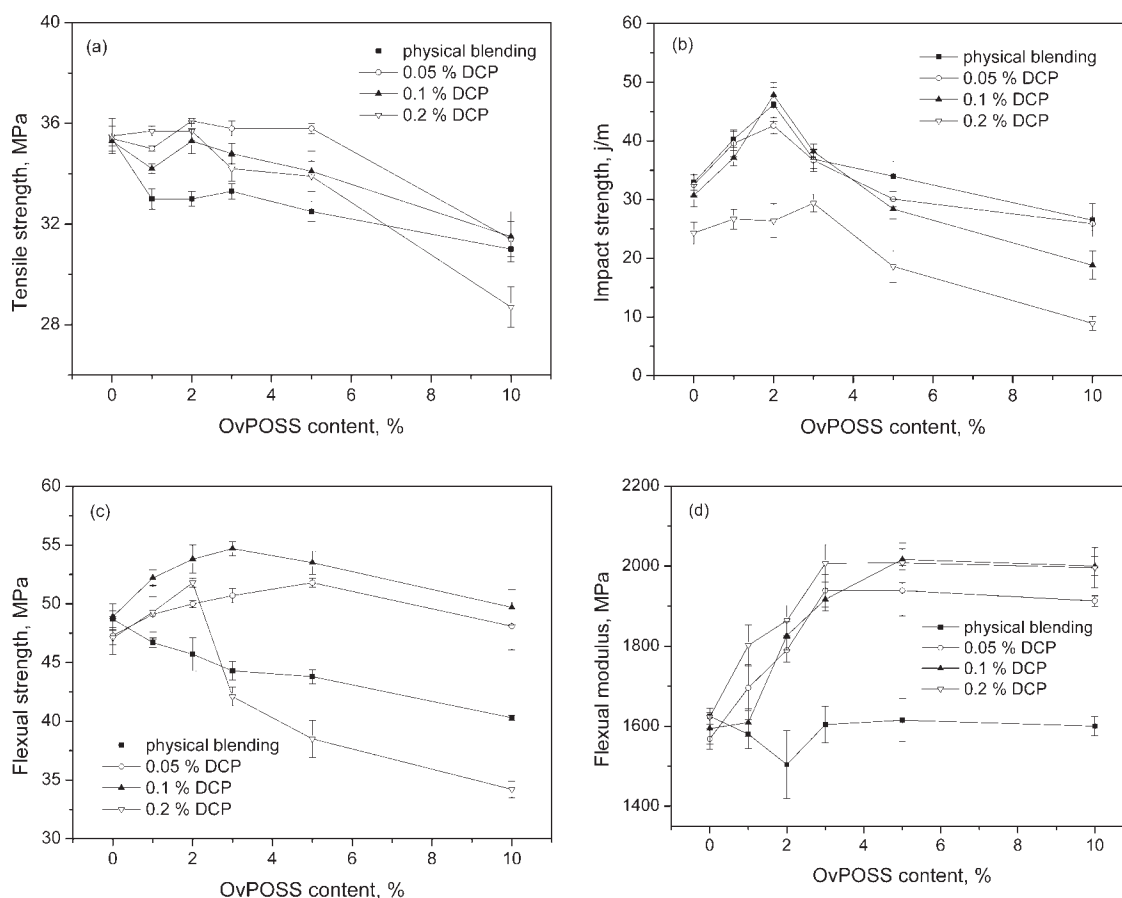
extraction. It is clearly seen that the graft ratio increases with increasing OvPOSS and DCP content (Fig. 2), and the graft ratio reached 3.5% when 5% OvPOSS and 0.1% DCP was added, which indicated nearly 70% OvPOSS was grafted to PP chains. Although the graft ratio changes slightly when DCP content was higher than 0.1% at low OvPOSS content (>5%). In general, the grafted PP exhibits lower

tensile strength and stiffness, worse thermal stability, and crystallizability than the unmodified PP due to the chain scission and degradation under peroxide.<sup>18</sup> Lower DCP content is favorable to attain suitable graft ratio and balanced properties for the reactive blending.

The reactive blending composites were Soxhlet extracted in boiling xylene for 48 h, whereas no gel was observed for all the samples, which indicated the crosslink network was neglectable or quite weak in the composites. In principle, network structure should be formed during the graft of PP and OvPOSS. There was no observed gel probably due to the spatial hindrance. It has also been reported that the network is much weaker during the copolymerization of styrene or methyl methacrylate and OvPOSS<sup>19,20</sup> initiated by the azobis(isobutyronitrile) because of strong spatial hindrance from the bulky POSS, which leads to its lower polymerization activity.<sup>21,22</sup>

### Mechanical properties

The mechanical properties of the PP/OvPOSS composites are shown in Figure 3. The tensile yield



**Figure 3** The mechanical properties of PP/OvPOSS composites: (a) tensile strength, (b) impact strength, (c) flexural strength, and (d) flexural modulus.

strength of physical blending composites decreased when POSS was added, whereas the tensile strength of the reactive blending composites changed little at lower POSS content. Baldi et al.<sup>11</sup> reported that the tensile yield strength of PP increased when octamethyl POSS was added to PP, but decreased when octaisobutyl or octaisooctyl POSS was added. It is suggested that POSS molecules behave as particles having a siliceous hard core surrounded by a hydrocarbon soft shell, which limit the stress transfer from the matrix to the core in dependence on the strength of the alkyl groups.<sup>11</sup> The alkyl group strength of vinyl is between methyl and isobutyl, so the tensile strength of PP/OvPOSS composites would be between that of PP added octamethyl POSS and PP added octaisobutyl POSS.

The notched Izod impact strength of PP/OvPOSS increased with increasing OvPOSS content at lower OvPOSS content (>3%), whereas the impact strength decreased dramatically with increasing POSS content due to the poor compatibility of OvPOSS and PP and the aggregate of OvPOSS at higher OvPOSS content. Although the reactive blending composites with 0.2% DCP content had lower impact strength than others due to the serious degradation of PP when superabundant DCP (0.2%) was added. The flexural strength of physical blending composites decreased with increasing OvPOSS content, whereas reactive blending composites increased at low POSS content (less than 3%). Then the impact strength of PP/OvPOSS with 0.1% DCP was higher than others. The flexural modulus of physical blending composites decreased slightly at low OvPOSS content (less than 2%) and slightly increased with further increasing OvPOSS content. Although the flexural modulus of reactive blending composites increased with OvPOSS or DCP content.

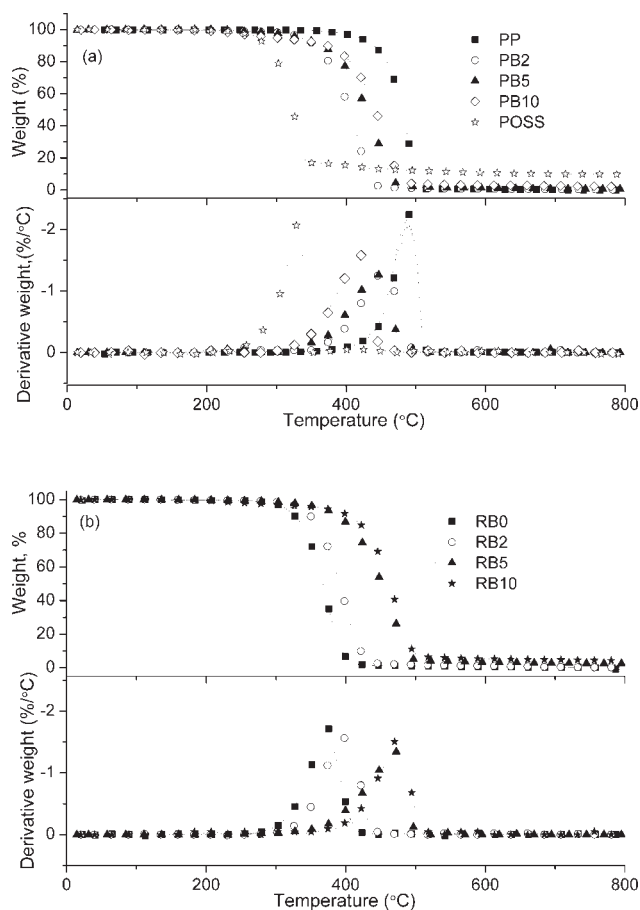
The observed phenomena can be explained by several effects: (1) The reinforcement effect of nano-OvPOSS particles could increase both the impact and flexural strength. Although at higher OvPOSS content, OvPOSS is incompatible and begins to agglomerate and crystallize which would decrease the mechanical properties of PP matrix. This is consistent with some nano-particles-filled polymers.<sup>23</sup> (2) The crystalline transformation of PP. It is well known that PP with  $\beta$ -form crystalline has lower stiffness and higher impact strength than that with  $\alpha$ -form.<sup>24-26</sup> The physical blending composites exhibit the  $\beta$ -monoclinic structure according to wide angle X-ray diffraction. At lower POSS content, the relative proportion of the  $\beta$ -form increased rapidly with increasing POSS content (>2%), whereas it was nearly kept constant with further increasing POSS content. But the  $\beta$ -form crystal disappeared when DCP was added (The crystalline transformation has been certificated and will be published elsewhere.).

For the physical blending composites, crystalline transformation of PP was predominant due to the increase of impact strength and the decrease of flexural strength at low OvPOSS content. (3) The degradation of PP with DCP. The reactive blending PP/OvPOSS composites have much higher MFI than physical blending composites because the molecular weight of PP decreased dramatically due to the  $\beta$  scission.<sup>27</sup> The mechanical properties of PP would deteriorate seriously when superabundant DCP was added. The reactive blending composites had highest impact strength, flexural strength, and modulus compared with physical blending composites and PP. It is supposed that the reinforcement effect of OvPOSS is predominant and can compensate the degradation effect at low POSS content and DCP content. Although the lowest impact strength and highest flexural modulus for the reactive blending composites when 0.2% DCP was added indicate both the degradation effect and reinforcement effect of OvPOSS is predominant. The mechanical properties decreased at high POSS content due to the poor compatibility of PP with OvPOSS. In conclusion, reactive blending composites have better balanced mechanical properties than physical blending composites at low POSS content, and the optimal DCP content is 0.1%. The impact strength and flexural modulus of PP filled with 2% POSS and 0.1% DCP is about 50% and 20% higher than pure PP, respectively. Here, the reactive blending and physical blending composites are referred as RBx and PBx, respectively, and the number  $x$  reflects the weight content of OvPOSS.

### Thermal stability

The influence of OvPOSS on the thermal behavior of the PP matrix is evaluated by means of TGA analyses. The TGA analyses of PP/OvPOSS composites are shown in Figure 4. The initial decomposition temperature ( $T_d$ ) is determined with the temperature of 5 wt % weight loss of the sample. The maximum weight loss temperature ( $T_{max}$ ) is taken from the peak values of the differential thermogravimetric curves (DTG). All the TGA curves displayed one-step degradation mechanism, and all the values of  $T_d$  and  $T_{max}$  were lower than PP because that of OvPOSS were significantly lower than PP. The values of  $T_d$  decreased with increasing OvPOSS content due to the poor thermal stability of OvPOSS, whereas  $T_{max}$  values increased with OvPOSS content for the physical blending composites (Table I). Although for the reactive blending, all the values of  $T_d$  and  $T_{max}$  increased with increasing OvPOSS content and are significantly higher than reactive blending composites at higher OvPOSS content (higher than 2%). The changes of IPDT were consistent with





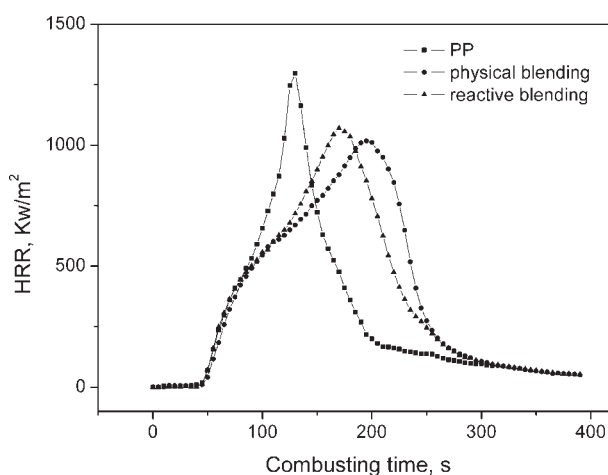
**Figure 4** TGA and DTG curves and in nitrogen of PP/POSS composites: (a) physical blending composites and (b) reactive blending composites.

that of  $T_{max}$ . The degradation pathways of POSS derivatives clearly show a competition between two possible mechanisms, namely evaporation and degradation.<sup>12</sup> It is supposed that the OvPOSS would undergo polymerization of vinyl group competition with evaporation, scission, and chemical crosslinking reaction.<sup>13,28,29</sup> It is supposed that the free radicals produced by the scission/evaporation of OvPOSS would strongly affect the degradation and decrease the  $T_d$  of PP, whereas the superficial layer produced by the degradation of OvPOSS could act as a physical barrier, limiting the gas, and heat flux transport at the interface. The barrier effect would compensate and overlap the degradation effect of OvPOSS and improve the degradation temperature of PP at high OvPOSS content. For the reactive blending composites, evaporation of OvPOSS could be effectively restricted due to the OvPOSS particles were grafted to PP chains; at the same time, the barrier effect would increase the degradation temperature of PP of the reactive blending composites. So, the reactive blending composites had better thermal stability than physical blending composites. The char yield of PP/OvPOSS composites was higher than the calculated value and

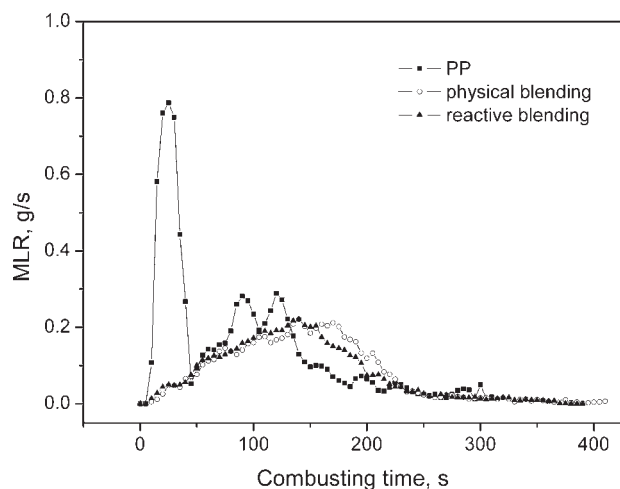
increased with the increase of OvPOSS content. The char yield of reactive blending composites was higher than physical blending due to the strong interaction of PP and grafted OvPOSS. Such superficial layer could be a good thermal barrier when generated on the surface during the PP matrix combustion process and improve the thermal stability and flame retardancy of PP matrix.

### Flame retardancy

The flame-retardant properties of the PP/OvPOSS composites were studied with a cone calorimeter. Samples were characterized by the HRR, the peak of the heat release rate (pHRR), the time to ignition (TTI), and mass loss rate (MLR) in the test. It has been claimed that the HRR of a polymer is the most important property predicting hazard in a fire situation, based on the assumption that HRR is a measure of the intensity of burning.<sup>30</sup> At an OvPOSS loading of 5%, the reduction in pHRR is around 18 and 22% for the reactive blending and the physical blending composites, respectively (Fig. 5). This is similar to polyurethane/POSS nanocomposites<sup>31</sup> and clay-filled PP.<sup>32,33</sup> The change of the TTI is small, whereas the time of flame out became longer for the PP/OvPOSS composites which means the composites combust longer time with smaller HRR, this is profitable for the flame retardancy of PP. For the reactive blending composites, the HRR value is slightly higher than the physical blending composites, indicating it had worse flame retardancy properties than physical blending composites due to the degradation under DCP. The MLR curves of PP and PP/POSS are shown in Figure 6, the MLR values of PP/OvPOSS composites are also lower than PP. This is consistent with the change of HRR due to the



**Figure 5** Comparison of the HRR plots of PP and PP/OvPOSS composites.



**Figure 6** Comparison of the MLR plots of PP and PP/OvPOSS composites.

slower combustion and lower HRR of PP/OvPOSS composites.

## CONCLUSIONS

The PP/OvPOSS composites were prepared by physical blending and reactive blending methods, and the mechanical, thermal properties, and flame retardancy were studied. The graft ratio of OvPOSS to PP chain increased with increasing OvPOSS and DCP content for the reactive blending composites. The reactive blending composites have better balanced mechanical properties than physical blending composites at low POSS content, and the optimal DCP content is 0.1%. At low OvPOSS content (>3%), the physical blending composites have higher impact strength and lower tensile and flexural strength than PP, whereas the reactive blending composites have higher tensile, flexural, and impact strength than PP at low POSS and DCP content. The impact strength and flexural modulus of PP filled

**TABLE I**  
The Thermal Stability Parameters of PP and PP/OvPOSS Composites

Sample	$T_d$ (°C)	$T_{max}$ (°C)	Char yield (%)	IPDT (°C)
PP	418	490	0	474
OvPOSS	270	332	10.8	559
PB2	337	427	0.35	388
PB5	335	447	0.79	436
PB10	297	452	2.29	473
RB0	313	376	0	365
RB2	335	400	0.26	396
RB5	365	477	2.53	493
RB10	367	473	4.28	536

with 2% POSS and 0.1% DCP are about 50% and 20% higher than pure PP, respectively. All the values of  $T_d$  and  $T_{max}$  of PP/OvPOSS composites were lower than PP because that of OvPOSS were significantly lower than PP. The values of  $T_d$  decreased with increasing OvPOSS content due to the poor stability of OvPOSS, whereas  $T_{max}$  values increased with OvPOSS content for the physical blending composites. Although for the reactive blending, all the values of  $T_d$  and  $T_{max}$  increased with increasing OvPOSS content and are significantly higher than reactive blending composites at higher OvPOSS content (higher than 2%). The changes of IPDT were consistent with that of  $T_{max}$ . The PP/OvPOSS composites have higher char yield, lower the pHRR and MLR, indicating better flame retardancy of PP/OvPOSS composites.

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