Synergistic effects of sepiolite on intumescent flame retardant polypropylene

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Abstract. In this paper, the effects of sepiolite as a synergistic agent on the flame retardancy of intumescent flame retardant polypropylene (PP/IFR) were studied using the limiting oxygen index (LOI), the UL-94 test, thermogravimetric analysis (TGA), laser Raman spectroscopy (LRS), cone calorimeter test (CCT) and scanning electron microscopy (SEM), and the IFR system mainly consisted of the ammonium polyphosphate modified with γ-aminopropyltriethoxysilane coupling agent, melamine and dipentaerythritol. The results from the LOI and UL 94 tests show that sepiolite added to the PP/IFR system has a synergistic flame retardant effects with the IFR system. The TGA results reveal that sepiolite enhances the thermal stability of the PP/IFR composite and increases the char residue formation. The cone calorimeter results indicate that the heat release rate, mass loss rate, total heat release and average specific extinction area of the PP/IFR/sepiolite composite decrease in comparison with the PP/IFR composite. The LRS measurements provide useful information on the carbonaceous microstructures. The morphological structures observed by SEM have demonstrated that sepiolite promote the formation of the reinforced and homogeneous char barrier on the surface of the composites. Simultaneously, the Young's modulus and flexural modulus of the PP/IFR composites are also much better improved with the increase of sepiolite added.

Keywords: *polymer composites, sepiolite, polypropylene, intumescent flame retardant, synergistic effect*

1. Introduction

Polypropylene (PP) is an important commodity plastic and used extensively in many fields, such as housing, transportation, and electrical engineering materials, but its usage is often limited because of its poor flame retardancy (the limiting oxygen index (LOI) is often lower than 18%). Therefore, studies on flame-retardant PP have attracted considerable interest during the last decades. One of the most important ways to improve the fire retardancy of PP is by applying an intumescent flame retardant (IFR) [1–5]. On heating, the IFR additives form a foamed cellular charred layer on the surface of the product, which slows down the heat and mass transfer between the gas and the condensed phase. Moreover, the IFR systems reduce the smoke density and produce little corrosive gas during combustion.

However, the IFR systems are relatively effective at low concentrations but not enough in stringent cases. In order to enhance the flame retardancy, new intumescent flame retardant systems have been developed rapidly [3, 6–8], which has high flame retardant efficiency. In addition, some synergistic agents have also been used to improve further the flame retardant of intumescent flame retardant PP systems, such as nano-$Mn_{0.4}Zn_{0.6}Fe_2O_4$ [9], zeolites [10], montmorillonite [11, 12], silica [13],

alumina [13], silicotungstic acid [14], lanthanum oxide [15, 16], nano-$BaWO_4$ [17], expandable graphite [18], iron powder [19], nanoflaky manganese phosphate [20], phosphotungstic acid [21], hydroxy silicone oil [22], a-ZrP [23], colemanite [24], zinc borate [25], polysilsesquioxane [26], borosiloxane [27] and other metallic compounds [1]. Sepiolite is a family of fibrous hydrated magnesium silicate with the theoretical half unit-cell formula $Si_{12}O_{30}Mg_8(OH)_4$ $(OH_2)_4 \cdot 8H_2O$ characterized by a needle-like morphology [28]. It can have a surface area as high as 200–300 m^2/g, lengths of 0.2–4 µm, a width of 10–30 nm and thickness of 5–10 nm [29]. In a previous study, we found that sepiolite has a good flame retardant synergistic effect with magnesium hydroxide in EVA [30] or PP [31]. However, there are few reports about sepiolite use in IFR polypropylene [32, 33].

In general, the poor water resistance and compatibility with PP matrix of traditional IFR system based on ammonium polyphosphate (APP), melamine and pentaerythritol restrict its application. Demir *et al.* [34] found that surface modification of APP with 3-(trimethoxysilyl)-1-propanethiol coupling agent can improve its water resistance and the compatibility. So, the IFR system based on APP modified with γ-aminopropyltriethoxysilane coupling agent was used as flame retardant in this paper.

The objective of this paper is to study the synergistic effects of sepiolite with the IFR system based on ammonium polyphosphate (IFR) modified with γ-aminopropyltriethoxysilane coupling agents, melamine and dipentaerythritol in PP using the limiting oxygen index (LOI), UL-94 test, thermogravimetric analysis(TGA), cone calorimeter test, Raman spectroscopy, and scanning electron microscopy (SEM). Mechanical properties of the composites have also been tested. More detailed investigations concerning the thermal degradation mechanism of PP/IFR/sepiolite composite are still ongoing by using *in situ* FTIR, TG/FTIR, Py-GC-MS and XPS techniques in the lab.

2. Experimental

2.1. Materials

Polypropylene powder (PP) (PPH-XD-075, melt flow rate: 2.1 g/10 min, 230°C, 2.16 kg), with the particle size 140–240 µm, was purchased from Wuhan Petroleum Chemical Plant, China. The intu-

mescent flame retardant system containing 22±2 wt% P, 18±1 wt% N with an average particle size of 10 µm, which consisted of ammonium polyphosphate modified with γ-aminopropyltriethoxysilane coupling agent (APP), melamine (MN) and dipentaerythritol (DPER) (the mass ratio of APP, MN and DPER is 4:1:1), was purchased from Hangzhou JLS Flame Retardants Chemical Co., Ltd., China. Non-modified Pangel S9 sepiolite was kindly supplied by Tolsa SA (Spain).

2.2. Composites preparation

Prior to mixing and getting the sepiolite dried the sample was heated first at 100°C for 4 h and cooled slowly then to room temperature under vacuum for 16 h. PP matrix composites were firstly prepared by blending of PP, IFR and sepiolite using a high-speed mixer (approximately 1000 r/min). Concentration of fillers was fixed at 25% mass of total amounts of composite. Sepiolite was added with mass fractions of 1, 2, 3 and 4%. Then flame retardant PP composites were extruded by a co-rotating twin-screw extruder (diameter = 20 mm, length/diameter = 36, model: SHJ-20, Lanzhou Tianhua Chemical Engineering and Automation Company, China) at a temperature profile of 130, 150, 180, 190, 200, 205, 200°C, and cutting into pellets using a granulator. The resulting sample bars for testing were prepared by injection moldings (injector: model HBL-1300, Zhejiang Haibo Co., Ltd., China) at a temperature profile of 200, 210 and 215°C.

2.3. Characterization

2.3.1. Limiting oxygen index

Limiting oxygen index (LOI) measurements were carried out using a JF-3 type instrument (Jiangning Analysis Instrument Factory, China) according to GB 2406-80 (ASTM D 2863-77). The samples used for the test were of dimensions 100 mm× 6.5 mm×3 mm.

2.3.2. UL-94 test

The UL-94 vertical test was measured on a CZF-2 type instrument (Jiangning Analysis Instrument Factory, China) with sample dimensions of 127 mm× 12.7 mm×3 mm according to ASTM D 635-77. UL-94 test results are classified by burning ratings

V-0, V-1 or V-2. V-0 rating presents the best flame retardancy of polymeric materials.

2.3.3. Thermogravimetric analysis

Thermogravimetric analysis (TG) was performed on a NETZSCH thermal analyzer (TG 209 F1). Samples weighting about 5.0 mg were heated from room temperature to 700°C at a heating rate of 10°C/min in a dynamic nitrogen atmosphere. The nitrogen flow rate was 50 ml/min.

2.3.4. Cone calorimeter test

Combustion experiments were performed in a cone calorimeter (Fire Testing Technology, UK) at an incident heat flux of 35 kW/m^2 according to ISO 5600. The bottom and edges of each specimen with a dimension of 100 mm×100 mm×4 mm are wrapped with aluminum foil. All samples were run in duplicate and the average value was reported. Various parameters can be measured including time to ignition (TTI), heat release rate (HRR) as a function of time, peak of heat release rate (PHRR), mass loss rate, and so on. The experimental error of data from the cone calorimeter was about 5%.

2.3.5. Raman spectroscopy

The Raman spectra were obtained from a Thermo Fisher Scientific Raman Spectrometer (model DXR) coupled with an OLYMPUS BX51 optical microscope. Excitation wavelengths were 633 nm using a He-Ne laser. The laser power at the sample was kept below 2 mW to avoid degradation problems or peak shifts due to overheating effects. The laser was focused to a 2 μm diameter spot on the sample using a 50× objective lens. The spectral resolution was 2 cm^{-1}. The Raman spectra were collected and recorded using a Peltier cooled charge-coupled device (CCD) detector with an exposure time of 30 s. Data (baseline calibration and integral) were processed by the Software 'OMNIC 8.1', Thermo Fisher Scientific Company, USA.

2.3.6. Scanning electron microscopy

The SEM micrographs of intumescent chars were observed by a JEOL JSM-7401F scanning electron microscopy. The specimens were previously coated with a conductive gold layer.

2.3.7 Mechanical properties testing

The impact strengths were measured with an XJJ-5 Charpy impact tester (Chengde Tester Co., Ltd., China) at 23°C according to GB/T1043. Tensile tests were carried out on an Instron Universal Tester Machine (model 5566) with a crosshead speed of 50 mm/min according to ASTM D 638. The tested parallel samples were 10, the presented results are average data.

3. Results and discussion
3.1. LOI and UL 94 testing

Table 1 presents the changes of LOI values versus sepiolite level for the PP/IFR/sepiolite composites at the total amount of 25 wt% additives kept constant. It is seen that the LOI value of the PP/IFR composite containing 25 wt% IFR increases rapidly to 34.4 from 17.6% of PP, indicating that IFR when used alone can significantly improve flame retardancy of PP. The LOI values of samples (PP0 to PP1) increase to 36.0% with 1.0 wt% loading of sepiolite in the formulation. However, the LOI decreases with further addition of sepiolite. When the loading of sepiolite reached to 4 wt% the LOI value of PP4 decreased to 32.3%. The main reason for this phenomenon may be that, during the combustion process, higher concentration of sepiolite makes the char too rigid and fragile and it increases the heat conductivity.

Table 1. LOI and UL-94 data of PP and its flame retardant composites with different loadings of sepiolite

Sample code	PP [wt%]	IFR [wt%]	SP [wt%]	LOI	UL 94 test	Dripping
PP	100	0	0	17.6	no rating	yes
PP0	75	25	0	34.4	V-1	no
PP1	75	24	1	36.0	V-0	no
PP2	75	23	2	35.8	V-0	no
PP3	75	22	3	35.8	V-1	no
PP4	75	21	4	32.3	V-2	no

UL-94 test results of the PP/IFR composites versus sepiolite loading are given in Table 1. From Table 1, when the loading of sepiolite was kept in between 1 and 2 wt% in IFR, and samples of the PP/IFR composites can pass the V-0 rating. However, further increasing to 3 and 4 wt%, they only pass the V-1 rating and V-2 rating as revealed by samples PP3 and PP4, respectively. These results indicate that an appropriate amount of sepiolite may cause the synergistic effect in the PP/IFR/ Sepiolite composites more efficient.

3.2. Cone calorimeter study

Cone calorimetry is widely used to evaluate fire performance of materials. Various parameters can be obtained from cone calorimetry including the time to ignition (TTI), the heat release rate (HRR), the peak heat release rate (PHRR), the total heat release (THR), average mass loss rate (av-MLR), average specific extinction area (av-SEA) and fire performance index (FPI) (defined as a ratio of TTI/PHRR) [35], and so on. The heat release rate (HRR) is a very important parameter, and can be used to express the intensity of a fire. An effective flame retardant system normally shows a low HRR value.

The heat release rate curves for PP and its flame retardant PP composites are shown in Figure 1 and all of the cone calorimetric data is presented in Table 2. It can be seen that the pristine PP burns very fast after ignition and a sharp HRR peak appears with a PHRR of 662 kW/m². The curve of the PP/IFR composite without sepiolite showed much lower peak heat release rate (PHRR) of 71 kW/m², and two peaks are observed at about 63 and 440 s, respectively. According to a former study [20], the first peak could be due to the development of the intumescent protective structure, and the second peak could be assigned to the degradation of this protective layer. In the IFR system, ammonium polyphosphate is used as the acid
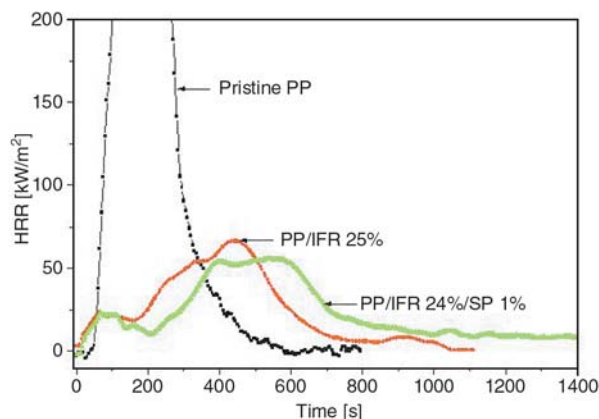

Figure 1. Heat release rate curves for pristine PP, PP/IFR and PP/IFR/SP 1% composites at a heat flux of 35 kW/m²

source; during heating, the poly(phosphoric acid) formed in the degradation of APP provides an acid catalyst for organic reactions [36]. During the heating process of APP, gaseous products (mainly ammonia), make the mixture of the phosphor-carbonaceous residue swollen; this leads to the formation of the intumescent char residue. The PHRR values (see Table 2) for PP/IFR composite with 1% sepiolite was 51 kW/m², which was much lower than that for pristine PP (662 kW/m²) and that for PP/IFR composite (71 kW/m²). It was also noteworthy that the HRR curve for PP/IFR/SP 1% composite exhibited a flattened pattern at 400–600 s, as shown in Figure 1. This was probably because sepiolite enhanced the strength and thermal stability of char layer, prevented the char layer from cracking and promoted the formation of the homogenous and compact intumescent char layer (see the SEM micrographs to be presented later). It was also found that IFR and sepiolite obviously render the ignition time shortened (see Table 2) which is attributed to the char layer formation on the surface of the PP/IFR composites. This is because the char layer prevents heat and oxygen from transferring into the matrix interior [16]. At the initial stage of heating, the surface temperature of the PP/IFR and PP/IFR/SP composites rises quickly due to the char

Table 2. Cone summary results of pristine PP and its flame retardant composites (35 kW/m²)

Sample	TTI [s]	PHRR [kW/m²]	THR [MJ/m²]	av-SEA [m²/kg]	av-MLR [g/s·m²]	FPI [kW/m²·s]
Pristine PP	48	662	83.3	487.8	0.040	0.073
PP/IFR 25%	30	71	32.5	348.2	0.012	0.423
PP/IFR 24%/SP 1%	29	51	30.8	238.9	0.009	0.569

TTI, time to ignition; PHRR, peak heat release rate; THR, total heat release; av-SEA, average specific extinction area; av-MLR, average mass loss rate; FPI, fire performance index
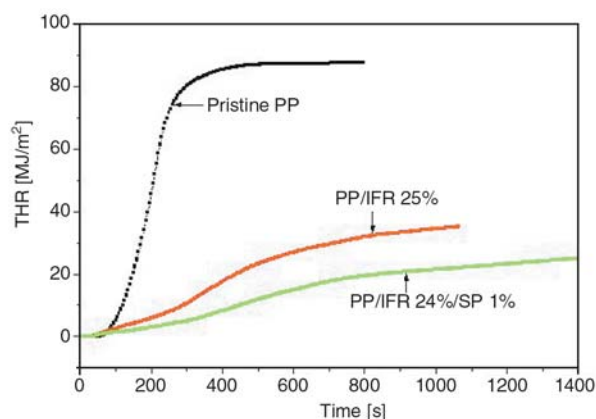
Figure 2. Total heat release (THR) curves for pristine PP, PP/IFR and PP/IFR/SP 1% composites at a heat flux of 35 kW/m²
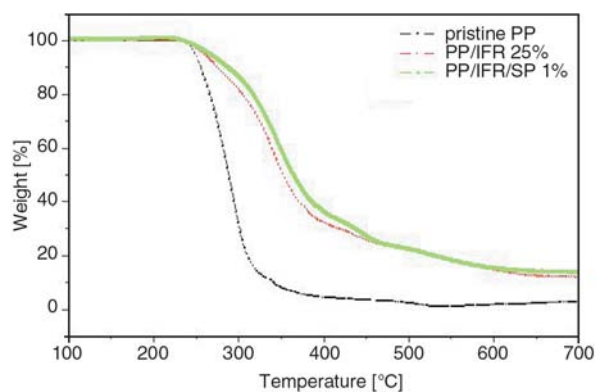

Figure 3. TG curves of pristine PP, PP/IFR and PP/IFR/SP 1% composites in N_2 at a heating rate of 10°C/min

layer formation, this results in fast decomposition of PP on the surface of the composites. Therefore, this makes the ignition time (TTI) shortened.

Figure 2 shows another plot for total heat release (THR) of all samples. Similar conclusion can be drawn that the THR goes down while the flame retardant IFR and IFR/SP were incorporated in. Consequently, it is also suggested that the synergistic effect between IFR and sepiolite is well deserved in the system.

Fire performance index (FPI) is independent of the tested sample thickness and often used to predict whether a material can easily develop drastic combustion after ignition. Therefore, the smaller the FPI value is, the better the fire resistance is. From Table 2, PP/IFR/SP 1% composite has the smallest value of 1.76, indicating that sepiolite can improve the flame retardant efficiency of PP/IFR composite. In addition, it clearly shows that both the smoke emission and average mass loss rate during combustion process are depressed by the incorporation of sepiolite.

3.3. Thermogravimetric analysis

Figures 3 and 4 present TG and DTG curves of pristine PP, PP/IFR, and PP/IFR/SP 1% samples under a flow of N_2, respectively. The 10% mass loss
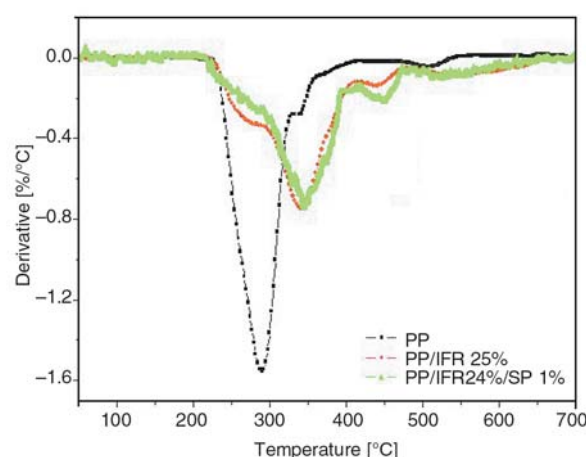

Figure 4. DTG curves of pristine PP, PP/IFR and PP/IFR/SP 1% composites in N_2 at a heating rate of 10°C/min

temperature ($T_{10\%}$), the maximum mass loss temperature (T_{max}), the maximum mass loss rate (R_{max}), and char (or residue) yield values at 700°C are all summarized in Table 3. PP loses the weight in the temperature range 249–350°C, formation a residue of about 2.7% at 700°C. It is clearly seen from Table 3 that the onset temperature (temperature at 10% mass loss, $T_{10\%}$) is increased for all composites, by 23°C for PP/IFR composite and 33°C for PP/IFR/SP 1% composite, respectively. The above results indicate that sepiolite improves the thermal stability of PP/IFR composite. However, this does

Table 3. TGA data of pristine PP, PP/IFR and PP/IFR/SP 1% samples under N_2 at a heating rate of 10°C/min

Sample	$T_{10\%}$ [°C]	T_{max} [°C]	R_{max} [%/min]	Residue yield at 700°C [wt%]
Pristine PP	255	295	1.55	2.7
PP/IFR	278	340	0.75	11.8
PP/IFR/SP 1%	288	347	0.73	13.9

$T_{10\%}$ is the temperature at 10% weight loss; T_{max} is the temperature at which the rate of weight loss reaches a maximum.
R_{max} is the maximum rate of weight loss.

notcorrelate with a decrease of TTI in the cone calorimeter (see Table 2). The fact may be attributed to the existence of sepiolite which may cause the whole process more complicated.

The IFR made a profound effect on the maximum thermal decomposition temperature (T_{max}). It can be seen from Table 3 that with the IFR obviously enhanced T_{max} of PP, which is 295°C for pristine PP, 340°C for the PP/IFR composite and 347°C for the PP/IFR/SP 1% composite, respectively. This fact demonstrated that the char layer formed at higher temperature protected PP from decomposing. The maximum mass loss rate (R_{max}) for PP/IFR composite with and without sepiolite are decreased from 1.55 to 0.75, 0.73%/°C, respectively. It is noteworthy that the char residue of pristine PP and PP/IFR composite are only 2.7 and 11.8 wt% at 700°C, respectively, while that of PP/IFR composite containing 1 wt% sepiolite is 13.9 wt%. This illuminates that sepiolite could promote the char formation of the PP/IFR composites.

3.4. Morphology analysis of the char residue

The morphology of the residual char formed after cone calorimeter testing is investigated by scanning electron microscopy (magnification 500×). Figures 5a and 5b present the SEM photographs of the outer char of the PP/IFR composite and PP/IFR/SP 1% composite, respectively. As shown in Figure 5a, it is observed that the char is loose and

porous, so it cannot provide the good flame shield for the underlying material. Comparing Figure 5b with Figure 5a, it is found that the char of the PP/IFR/SP 1% composite is more homogenous than that of the PP/IFR composite. Moreover, the addition of sepiolite also seems to reinforce the char barrier, keeping it more resistant against the disintegrating effect of the bubbles evolved. So the char layer with improved performance leads to the enhancement of flame retardancy.

3.5. Microstructure characterization of carbonaceous charred layers

Raman spectroscopy has been proven an effective method to investigate the carbonaceous char formed by combustion of polymers [37–39]. Figure 6 shows the Raman spectra of the char residues formed after cone calorimeter testing. The spectra of the char residues with or without sepiolite exhibit two broad bands around 1580 and 1350 cm⁻¹, similar to the graphite-like species [40]. The first band (G peak) may be assigned to the E_{2g} vibrational mode (C–C vibrations). The band at 1350 cm⁻¹ (D peak), the so-called defect band [41], is assigned to the A_{1g} vibrational mode and may be related to the structural organization of the carbonaceous matter. These results provided a positive evidence for the formation of the carbonaceous matter.

Tuinstra and Koening [42] found that the relative intensity ration R of the D peak to the G peak is
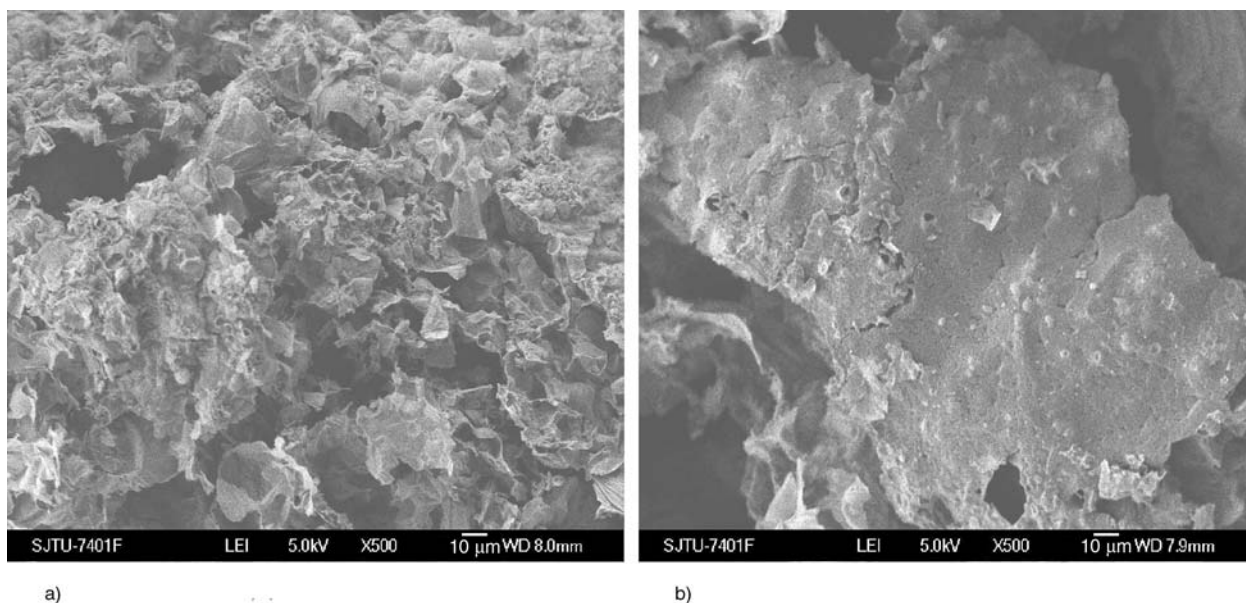

Figure 5. SEM micrographs of PP/IFR char residue with and without sepiolite: (a) PP/IFR composite, 500×; (b) PP/IFR 24%/SP 1% composite, 500×
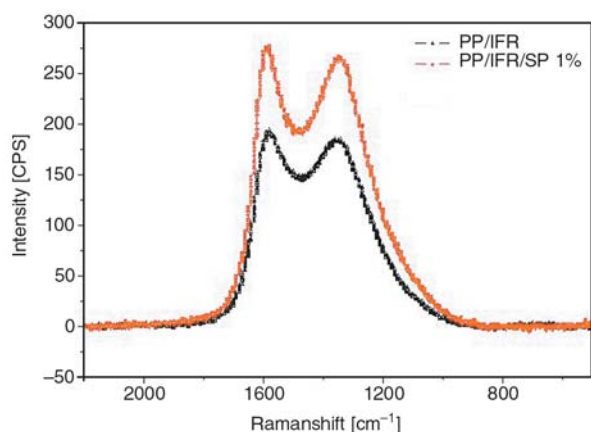
Figure 6. Raman spectra of chars produced during cone calorimeter experiments

inversely proportional to an in-plane microcrystalline size. From Figure 6, the relative intensity ration *R* of the *D* peak to the *G* peak for PP/IFR/SP 1% composite (*R* is about 1.15) is higher than that of PP/IFR composite (*R* is about 1.07). That is to say, the size of carbonaceous microstructures from the PP/IFR/SP 1% composite could be smaller than from the PP/IFR composite. Bourbigot *et al.* [43] believed that the higher protective shield efficiency was related to the smaller size of carbonaceous microstructures. Therefore, it is proposed that sepiolite or its pyrolytic products repress the increase of the carbonaceous micro-domain in size during burning, which leads to formation of more compact charred layers.

3.6. Mechanical properties

The mechanical properties of pristine PP and its flame retardant composites with different loading of sepiolite are listed in Table 4. Taking PP0 as an example, the addition of IFR by great amount into PP matrix reduces the tensile strength, elongation at break and notched Charpy impact strength, but oppositely for the Young's modulus, flexural strength and flexural modulus. An explanation for the reduction in elongation at break may be the for-

mation of microvoids due to debonding of clay fibres from the polymer matrix upon failure. Comparing sample PP0 with the samples PP1, PP3 and PP4, adding sepiolite into PP/IFR system does not influence the tensile strength, flexural strength and elongation at break very much. However, Young's modulus and flexural modulus for the samples PP1, PP3 and PP4 are increased with increasing sepiolite content, probably because the rigid needle-like sepiolite in PP matrix directly enhanced the stiffness of flame retardant composites. At the same time, notched Charpy impact strength at 23°C for the samples PP1, PP3 and PP4 is slightly increased with increasing sepiolite content.

4. Conclusions

Flame-retardant system composed of sepiolite and IFR system (ammonium polyphosphate modified with aminosilane coupling agents and combined with melamine and dipentaerithritol) was processed by melt compounding to flame retard PP resin. The LOI, UL94 test results showed that sepiolite had a significant influence on flame retardancy and LOI value reached 36.0% with loading of 1.0 wt% sepiolite at the total amount of additives kept constant at 25 wt%. Besides, the PP/IFR composites could pass UL 94 V-0 rating with 1–2 wt% sepiolite loading. The TGA results showed that sepiolite enhanced the thermal stability of PP/IFR composite and played a role of promoting the formation of char layer. From the results of cone calorimeter tests, sepiolite had obvious effects on CONE data, such as decreasing the heat release rate (HRR), the total heat release (THR), the average specific extinction area (av-SEA) and the average mass loss rate (av-MLR) during combustion. By the analysis of the morphology and microstructures of char residue by the LRS and SEM, it was revealed that the synergistic effects between sepiolite and IFR on flame retardance was attributed to the improvement in building a reinforced and homogeneous char bar-

Table 4. Mechanical properties of pristine PP and its flame retardant composites

Sample code	PP	PP0	PP1	PP3	PP4
Tensile strength [MPa]	32.4±0.6	29.3±0.4	30.2±0.4	29.8±0.3	29.7±0.6
Elongation at break [%]	32.2±2.1	10.1±0.4	8.8±0.2	9.1±0.4	9.2±0.4
Young's modulus [MPa]	456±37.8	670±80.4	738±83.6	755±38.5	768±37.8
Flexural strength [MPa]	38.9±1.0	44.9±0.5	46.1±0.9	45.4±0.4	45.8±1.0
Flexural modulus [MPa]	1280±47.6	1458±17.8	1540±17.3	1545±17.4	1589±27.6
Notched charpy impact strength 23°C [kJ/m²]	6.1±0.6	2.5±0.3	2.7±0.2	2.8±0.3	3.0±0.3

rier on the surface of the burning composites. In addition, the rigid needlelike sepiolite in PP matrix directly enhanced the stiffness of flame retardant composites and improved the Young's modulus and flexural modulus.

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