Roles of anion of polyoxometalate-based Ionic liquids in properties of intumescent flame retardant polypropylene

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1. Experimental

1.1 Preparation of PILs

1-Butyl 3-methylimidazolium chloride ([BMIm]Cl) IL was synthesized by stirring1:1 molar ratio of MIm and [BMIm]Cl at 80ºC for 24 h in nitrogen atmosphere. After recrystallization from ethyl acetate, the intermediate product was obtained. Then 0.47 g of [BMIm]Cl and 2.88 g of PWA were dissolved in deionized water, respectively, and mixed together under constant stirring for 12 h. Then a white precipitate was formed. The product was filtered and washed for several times with deionized water until chloride-free ($AgNO_3$ aqueous test). Finally, the obtained PIL1was dried overnight at 80 ºC in oven. For PIL2 and PIL3, the process were

similar to PIL1and the weight of [BMIm]Cl and POM were 0.47g/1.82g and 0.47g/3.84g, respectively.

2. Results and discussion

2.1 LOI and UL-94 tests

The flame retardant properties of PP/IFR/PIL2 composites at the whole content of flame retardants 13.5 wt% and 20 wt% are shown in Table S1. It is found that with the addition of PIL2 in the range of 0.1 % to 1.0 %, all the samples of PP/IFR composites show an increase in LOI value. When 0.1% of PIL2 is added into the whole content of flame retardants 13.5 % system, the LOI value goes up clearly to 25.2 from 22.5 for PP/IFR. According to Table S1, when the PILs increase gradually, the LOI value of the samples was increased before the addition is 0.5 % and then decreased. Similar trend is also recognized of the whole content flame retardants 20.0 % system. However, all PP composites fail in the UL-94 V0 tests except PP9. More or less of catalyst cannot increase the flame retardant properties. Only an optimum content can increase the flame retardant properties, so it confirmed the conclusion once again.

2.2 TG-IR of IFR/PILs

Fig. S1 shows the evolved gas phase from the thermal decomposition of IFR/PILs. The overall IR spectra for IFR/PILs and IFR are similar. Some small molecular gaseous species, such as CO_2, CO, H_2O, NH_3, $H_2C{=}NH$, C_5H_4, are easily identified by their characteristic transmittance: CO_2 at 2357, 668 cm^{-1}, CO at 2285 and 2181 cm^{-1}, NH_3 at 964, 929 cm^{-1}; H_2O at 3500-3600 cm^{-1}; C_5H_4 at 3333 cm^{-1}; $H_2C{=}NH$ at 1629

cm^{-1}.

Table S1 Flame retardant properties of PP/IFR/PIL2 composites at the whole content of flame retardants 13.5 wt% and 20 wt%.

Samples	PP (wt %)	IFR (wt %)	Catalyst (wt %)	LOI (vol %)	UL-94	Melt Dripping	t_1+t_2
PP22	86.5	13.5	0	22.5	NC	Y	/
PP23	86.5	13.4	0.1 PIL2	25.2	NC	Y	2+/
PP24	86.5	13.25	0.25 PIL2	25.9	NC	Y	0+/
PP25	86.5	13.0	0.5 PIL2	26.7	NC	Y	2+/
PP26	86.5	12.5	1.0 PIL2	25.4	NC	Y	4+/
PP27	80	20	0	24.5	NC	Y	0+/
PP28	80	19.9	0.1 PIL2	28.2	NC	Y	0+/
PP29	80	19.75	0.25 PIL2	28.0	V-1	N/N	0+14
PP30	80	19.5	0.5 PIL2	30.2	V-0	N/N	0+3
PP31	80	19	1.0 PIL2	30.1	V-1	N/N	0+30

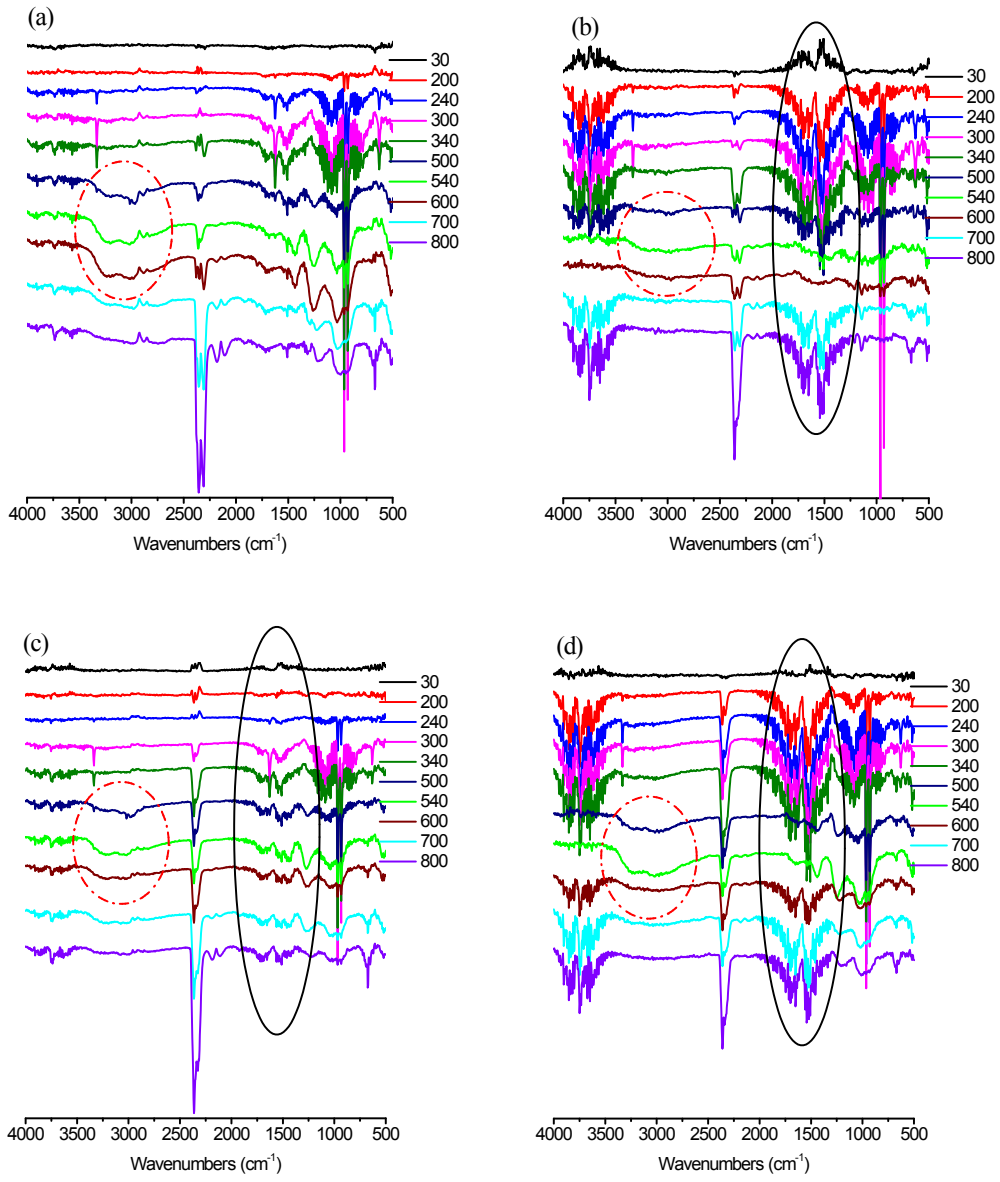

Fig. S1 FTIR spectra of pyrolysis products for (a) IFR , (b) IFR/PIL1, (c) IFR/PIL2 and (d) IFR/PIL3 at different temperatures.