Thermal Properties and Flame Retardance of Al(OH)$_3$/Polypropylene Composites Modified by Polypropylene Grafting with Acrylic Acid

KANCHENG MAI,[1,2] ZHENGJUN LI,[1] YUXIN QIU,[1] HANMIN ZENG[2]

[1] Materials Science Institute, School of Chemistry and Chemical Engineering, Zhongshan University, Guangzhou, 510275, People's Republic of China

[2] Key Laboratory of Polymeric Composites and Functional Materials, The Ministry of Education, Zhongshan University, Guangzhou, 510275, People's Republic of China

ABSTRACT: The effect of polypropylene grafting with acrylic acid, PP-*g*-AA (FPP), on crystallization and melting behavior, thermal degradation, and limiting oxygen index of Al(OH)$_3$/PP composites were investigated. The results indicated that crystallization temperature of PP shifted to high temperature with increasing content of Al(OH)$_3$ because of the interfacial heterogeneous nucleation of Al(OH)$_3$ and further increased by the addition of FPP and with increasing FPP content because of the improvement of the dispersion of Al(OH)$_3$ in PP matrix and the increase in the nucleating sites of Al(OH)$_3$. With adding Al(OH)$_3$ and increasing the content of Al(OH)$_3$, limiting oxygen index values of composites increased and further improved by adding FPP. This is attributed to the presence of an interfacial interaction between FPP and Al(OH)$_3$. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 2679–2686, 2001

Key words: polypropylene; functionalized polypropylene; Al(OH)$_3$; crystallization and melting behavior; thermal degradation; limiting oxygen index

INTRODUCTION

Polypropylene (PP) materials for mechanical purposes have been widely studied.[1–5] However, the usefulness of PP can be limited by its high flammability. The flammability of PP is a serious problem in practical applications. To solve this problem, the main approach is to use a flame retardant (FR), which is blended into PP to decrease the flammability. Reducing the inherent flammability of PP is normally achieved either by incorporating fire-retardant additives, such as brominated compounds in combination with antimony trioxide synergists, or by using intumescent formulations based on phosphorous-containing materials.[6] However, certain hydrated inorganic compounds such as metal hydroxide, in particular aluminum hydroxide, Al(OH)$_3$, and magnesium hydroxide, Mg(OH)$_2$, offer an attractive alternative because they are acid and halogen free; and in addition to inhibiting polymer ignition, they function as effective smoke suppressants.[7] Therefore, they are of increasing interest as FRs. They decompose endothermically and release water of crystallization thus withdrawing heat from the

Table I   DSC Results of Al(OH)$_3$/PP Composites Modified by FPP

| Code	FPP	G (%)	Al(OH)$_3$/FPP/PP	T_c (°C)	T_{co} (°C)	T_m (°C)	T_{mo} (°C)	X_c %
0	No		0 : 0 : 100	116.7	120.5	161.9	157.9	50.5
1	No		20 : 0 : 80	118.1	121.8	162.8	159.1	49.5
2	No		40 : 0 : 60	121.6	124.3	162.8	159.5	44.8
3	No		60 : 0 : 40	124.4	127.3	163.9	159.7	47.1
4	FPP1	0.15	0 : 5 : 95	118.0	121.8	163.5	158.4	45.8
5	FPP1	0.15	20 : 5 : 75	119.0	122.3	162.4	158.4	47.9
6	FPP1	0.15	40 : 5 : 55	125.4	128.1	163.0	156.8	45.6
7	FPP1	0.15	60 : 5 : 35	125.4	128.4	163.5	158.4	44.3
8	FPP1	0.15	60 : 2.5 : 37.5	126.3	129.7	164.2	158.6	43.0
9	FPP2	0.23	60 : 5 : 35	127.0	130.3	163.7	157.3	45.1
10	FPP3	0.30	60 : 5 : 95	128.2	131.5	164.5	156.0	48.5
11	FPP4	0.56	0 : 5 : 95	120.1	123.4	162.7	158.8	46.4
12	FPP4	0.56	20 : 5 : 75	123.0	126.3	164.3	160.2	47.9
13	FPP4	0.56	40 : 5 : 55	129.3	133.2	165.2	154.4	46.8
14	FPP4	0.56	60 : 5 : 35	128.8	132.1	164.2	154.9	44.1
15	FPP4	0.56	60 : 2.5 : 37.5	127.9	131.2	164.4	156.5	44.6

$\Delta H_f = 207.15$ J/g.[53]

polymer substrate. However, to be effective, high filler loadings are necessary, typically in excess of 60% by weight (37% by volume) when used in PP, resulting in a significant loss in composite toughness.[8]

Generally, there is a lack of adhesion between PP and Al(OH)$_3$ because of large surface energy differences, necessitating the application of modifiers onto the filler surface to enhance interaction at this interface, or through chemical functionalization of the polymer to generate sites for reaction with the filler surface.[9,10] In common with other mineral filler, improvements in impact strength can be obtained by treatment of the filler; for example, using silane or titanate surface modifiers.[11] Surface treatment of Al(OH)$_3$, with fatty acid, fatty acid derivations, functionalized polymer, and organosilicon compounds, can ease their incorporation into thermoplastic melts, such as PP.[12,13] Liauw et al.[12] found at filler levels below those required for effective flame retardation, a dicarboxylic acid anhydride treated filler gave the composite with the best mechanical properties. At higher filler levels, i.e., more than 50% by weight, the composites based on Al(OH)$_3$ coated with the strong coupling agent silane afforded the best properties. A maleinized polybutadiene treated Al(OH)$_3$ gave a composite with improved properties relative to the dicarboxylic acid anhydride treated Al(OH)$_3$.

Grafting copolymerization is an effective technique for the modification of the compatibility of the immiscible polymer blends and the interfacial adhesion in polymeric composites.[14–36] It works because of the enhanced polymer-filler interfacial adhesion and the improved filler dispersion in the matrix. The improvements in flame retardance and mechanical properties of PP/FR blends by acrylic acid (AA) graft copolymerization have been reported by Chiang and Hu.[36] The PP was blended together with the FR additive, tri(2,3-dibromopropyl)isocyanurate for flammability reduction. Antimony trioxide was selected as a synergistic agent. It was found that, although the flammability of the PP/FR blends was reduced by the addition of the FR, the tensile and impact strengths were also decreased. For PP-g-AA/FR blends, the limiting oxygen index, the temperature of crystallization peak, tensile strength, impact strength, and Young's modulus all increased because of AA grafting modification. In the PP composites containing Mg(OH)$_2$ fire retardant filler, improvements in flame retardance and mechanical properties of PP composites have been observed by the addition of functionalized polymers.[34,37–40]

Although the effect of the filler surface treated by coupling agents with low molecular weight on physical and mechanical properties of Al(OH)$_3$/PP composites have been investigated,[41–45] few studies on the surface treatment of Al(OH)$_3$ by a macromolecular coupling agent, functionalized polymer, were reported in the Al(OH)$_3$/PP composites. In our laboratory, PP functionalized with AA was
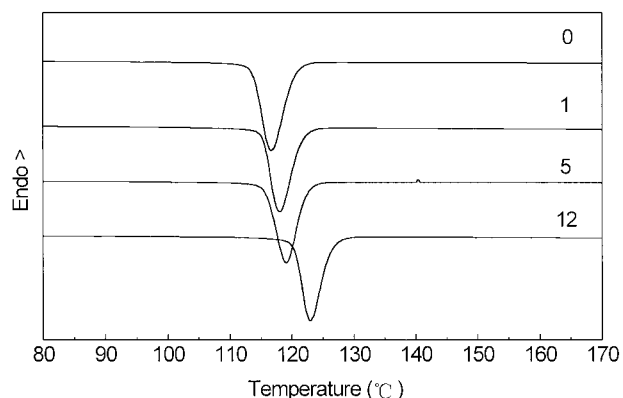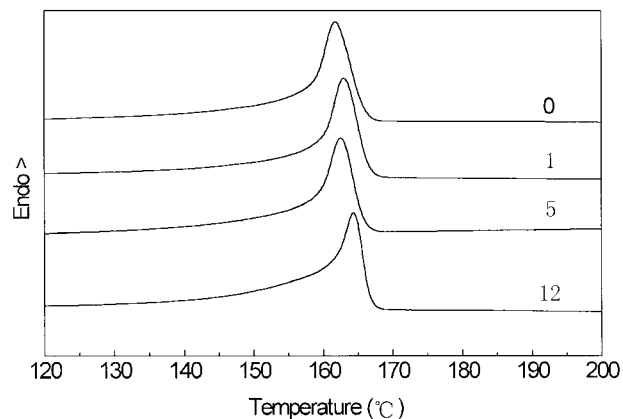
Figure 1 DSC cooling curves of Al(OH)$_3$/FPP/PP(20:5:75) composites.

prepared by melting extrusion, and the effect of PP-*g*-AA (FPP) on structure, physical and mechanical properties of Al(OH)$_3$/PP composites were investigated.[46] In this article, the FPP with different grafting rates were blended with PP and Al(OH)$_3$. The effects and properties of Al(OH)$_3$/PP composites with FPP modification are reported and discussed with regard to the investigation of flame retardance, crystallization and melting behavior, and processability.
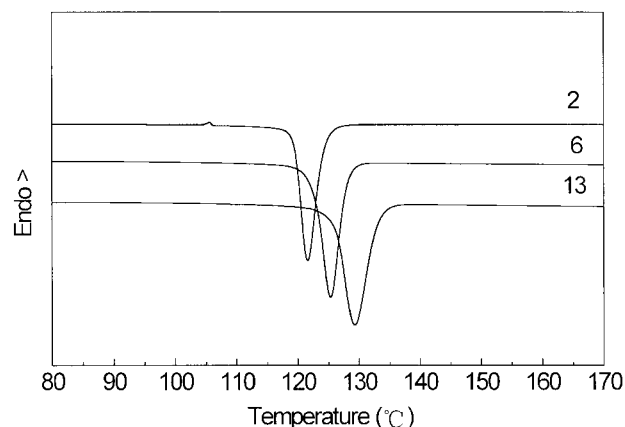
EXPERIMENTAL

Materials

PP, powdered F401, was a commercial product of Guangzhou Petrochemical Co., China. Pelletized PP, 1600, was obtained from Beijing Yanshan Petrochemical Co., China. Chemical-grade AA
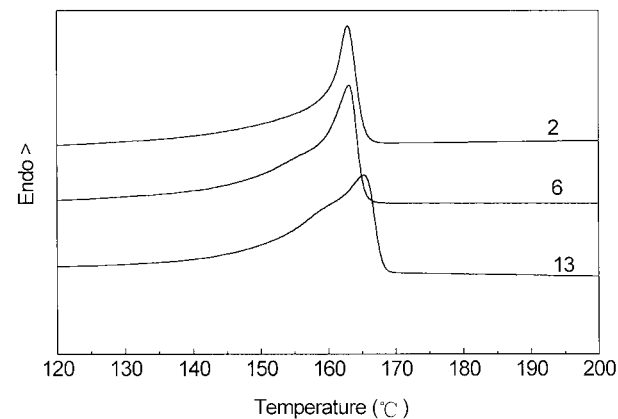

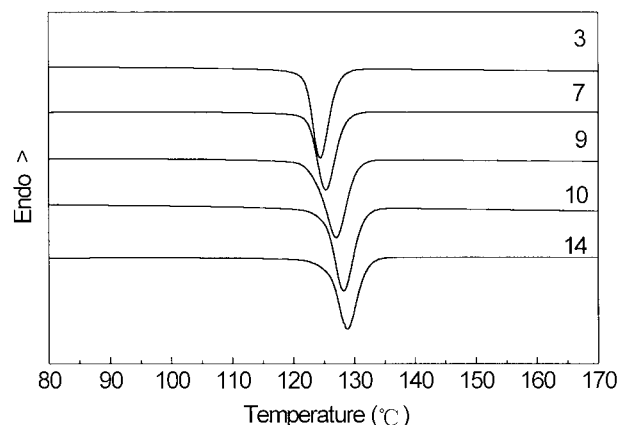**Figure 3** DSC cooling curves of Al(OH)$_3$/FPP/PP(40:5:55) composites.

was purchased from Fushan Chemical Factory, Guangdong, China, and used without further purification. Chemical-grade dicumyl peroxide (DCP), used as an initiator for the AA grafting reaction, was a commercial product of Shanghai Chemical Reagent Factory, China. Al(OH)$_3$ was obtained from Shandong Aluminum Co., China. The solvent, acetone, was obtained from Guangzhou Chemical Reagent Factory.

Preparation of Samples

DCP and AA were dissolved in acetone, totally blended with powdered PP and Al(OH)$_3$ in a GH-10 high-speed mixing machine. After the solvent, acetone, had completely evaporated, the mixture of AA and DCP was coated on the surface of the powdered PP and Al(OH)$_3$, and was then extruded by a SHJ-53 twin screw extruder at a

Figure 2 DSC heating curves of Al(OH)$_3$/FPP/PP(20:5:75) composites.

Figure 4 DSC heating curves of Al(OH)$_3$/FPP/PP(40:5:55) composites.

Figure 5 DSC cooling curves of Al(OH)$_3$/FPP/PP(60:5:35) composites.

temperature of 185–190°C, with the screw speed set at 60 rpm. The extruded products, Al(OH)$_3$/FPP/PP composites, were frozen in-line in a water bath, dried, and granulated to <3 mm.

Preparation of Test Specimens

The pelletized Al(OH)$_3$/FPP/PP composites were dried at a temperature of 90°C for 4 h before injection molding and were injection molded into test specimens by using a CJ150 ME-NC injection molding machine, set with barrel temperature profile ranging from 190 to 210°C. The shape and size of the test specimens were described elsewhere.[47]

Characterization of Structure and Properties

Melting and crystallization of the samples were studied by differential scanning calorimetry (DSC) using a Perkin-Elmer DSC-7 (USA) in a nitrogen atmosphere with 10°C/min heating and cooling. The samples were heated from 30 to 220°C, and held at that temperature for 3 min. The nonisothermal crystallization process was recorded from 220 to 50°C, followed by heating from 50 to 210°C for the second heating run. The crystallization and melting parameters were obtained from the cooling and reheating scans. The transition temperature and heat of crystallization and fusion were calibrated using an indium standard.

Thermal degradation of the samples was investigated with a Shimazu TGA-50 thermogravimetric analyzer (Japan). Thermogravimetric analysis (TGA) was performed at a heating rate of 20°C/min and a nitrogen flow rate of 33 mL/min. Through the above analyses, the pyrolysis peak

temperature (T_{pm}), the temperature of 5 wt % weight loss ($T_{5\%}$), and the weight loss at different temperatures were obtained.

The limiting oxygen index was measured in accordance with ASTM D 2683-70. The sample consisting of a bar 6-mm wide, 3-mm thick, and 150-mm length, was placed vertically at the center of a glass chimney 75 mm in diameter with a height of 450 mm. A mixture of oxygen and nitrogen of known composition was passed through the chimney at a rate of about 10 L/min.

RESULTS AND DISCUSSION

Effect on Crystallization and Melting Behavior of Al(OH)$_3$/PP Composites

The DSC results of Al(OH)$_3$/PP and Al(OH)$_3$/FPP/PP composites modified by FPP are presented in Table I. From the results in Table I, it can be seen that the crystallization of PP is affected by the addition of FPP with different grafting rates ($G\%$).[46] For the unfilled polymer, homogeneous nucleation occurs, with the formation of low-temperature crystallites commencing at 120.5°C. For the PP filled with Al(OH)$_3$, heterogeneous nucleation occurs on the surface of Al(OH)$_3$, forming higher-temperature crystallites. The onset crystallization temperature (T_{co}) and temperature of crystallization peak (T_c), onset melting temperature (T_{mo}), and temperature of melting peak (T_m) are slightly higher than that of unfilled PP, and increase with increasing the Al(OH)$_3$ content, indicating a higher nucleating ability, but degree of crystallization is reduced. Some fillers act as a nucleating agent of PP, for
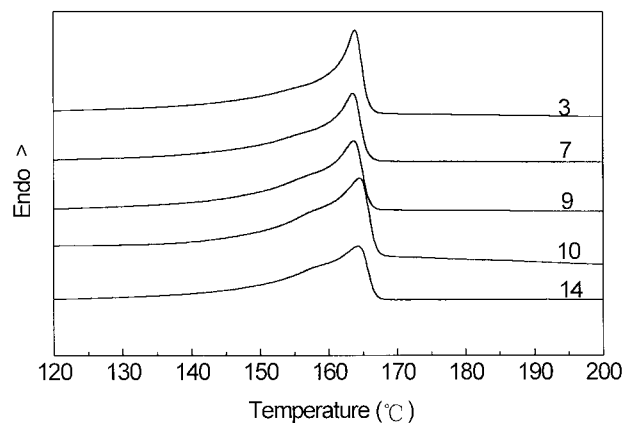
Figure 6 DSC heating curves of Al(OH)$_3$/FPP/PP(60:5:35) composites.

Table II   Thermogravimetric Analysis of FPP/PP Samples

FPP	FPP/PP	$T_{5\%}$ (°C)	T_{pm2} (°C)	Weight Loss (wt %)			
				350°C	450°C	500°C	600°C
—	0 : 100	394.3	468.6	0.9	34.4	99.7	99.8
FPP1	5 : 95	416.5	472.2	0.4	21.1	99.7	99.8
FPP4	5 : 95	399.3	474.3	0.9	29.3	99.6	99.7

example talc, where loadings as low as 0.5% by weight are effective.[48,49] However, the Al(OH)$_3$ is a weak nucleating agent and only produces a significant effect at high loadings.[50,51] Such concentration-dependent nucleation is considered to arise when only a small fraction of the filler particles have the required surface feature[50,51] and/or when melt stress concentration occurs at the filler surface.[50]

The DSC cooling and heating curves of Al(OH)$_3$/PP composites containing 5% FPP and 20% Al(OH)$_3$ by weight are shown in Figures 1 and 2, respectively. Because of the low filler content, the addition of FPP with low grafting rate had not influenced the crystallization and melting behavior of the composites. The FPP with a high grafting rate resulted in a further increase in the crystallization and melting temperature. Compared with the unfilled Al(OH)$_3$/PP composite, the change of the shape of melting peak was observed. These experimental results indicated that in the Al(OH)$_3$/PP composite, the heterogeneous nucleation of Al(OH)$_3$ was weak because of the incompatibility and larger surface energy difference of PP and Al(OH)$_3$. The addition of FPP with a high grafting rate into PP resulted in an increase in the polarity and surface energy of PP, leading to the enhanced interfacial interaction and adhesion between PP and Al(OH)$_3$ and the increased heterogeneous nucleating sites. How-

ever, the addition of FPP with low melt viscosity improved the flow properties of the PP melt and the filler dispersion, which also resulted in an increased heterogeneous nucleation of PP crystallization. As a result, the crystallization temperature of PP in the Al(OH)$_3$/PP composite further increased by the addition of FPP.

Figures 3 and 4 are DSC cooling and heating curves of Al(OH)$_3$/PP and Al(OH)$_3$/PP composites modified by 5% FPP containing 40% Al(OH)$_3$. It was found that an increase in the filler content, the T_{co}, T_c, and T_m were further increased, but the degree of crystallization was reduced. The addition of FPP resulted in a significant effect on the crystallization and melting behavior. The peak of crystallization and melting shifted to high temperature and the T_c increased with increasing the grafting rate of FPP. The T_c of the Al(OH)$_3$/FPP/PP composite was higher than that of the unmodified Al(OH)$_3$/PP composite. However, the degree of crystallization slightly increased with increasing the grafting rate of FPP. Compared with the shape of the melting peak of unfilled PP and the Al(OH)$_3$/PP composite, the width of the crystallization peak and the width at half height of the crystallization peak of Al(OH)$_3$/FPP/PP composites increased with increasing the grafting rate of FPP. This suggests that FPP has influenced the crystalline size distribution, leading to the different melting behavior.

Table III   Thermogravimetric Analysis of Al(OH)$_3$/PP Composites

Al(OH)$_3$/PP Composites	$T_{5\%}$ (°C)	T_{pm1} (°C)	T_{pm2} (°C)	Weight Loss (wt %)			
				350°C	400°C	500°C	600°C
0 : 100	394.3	—	468.6	0.9	6.4	99.7	99.8
100 : 0	265.1	301.8	—	19.9	29.4	32.2	33.5
20 : 80	311.9	311.9	485.0	7.5	9.2	80.3	81.9
40 : 60	315.4	313.4	484.6	7.5	20.7	81.0	82.5
60 : 40	302.5	328.6	488.4	15.6	17.1	58.1	61.9

Table IV   Thermogravimetric Analysis of Al(OH)$_3$/PP Composites Modified by FPP

FPP	Al(OH)$_3$/FPP/PP	$T_{5\%}$ (°C)	T_{pm1} (°C)	T_{pm2} (°C)	Weight Loss (wt %)			
					350°C	400°C	500°C	600°C
—	100 : 0 : 0	265.1	301.8	—	19.9	29.4	32.2	33.5
—	20 : 0 : 80	311.9	311.9	485.0	7.5	9.2	80.3	81.9
FPP1	20 : 5 : 75	312.0	315.1	484.1	8.2	9.7	79.3	81.0
FPP4	20 : 5 : 75	348.3	309.7	483.5	5.2	7.6	88.2	89.3
—	40 : 0 : 60	315.4	313.4	484.6	7.5	20.7	81.0	82.5
FPP1	40 : 5 : 55	306.9	326.2	483.9	11.3	21.4	70.8	72.7
FPP4	40 : 5 : 55	305.1	327.2	484.6	13.0	21.9	67.1	69.4
—	60 : 0 : 40	302.5	328.6	488.4	15.6	17.1	58.1	61.9
FPP1	60 : 5 : 35	302.0	330.9	487.5	16.6	18.3	56.4	59.9
FPP2	60 : 5 : 35	305.9	330.8	487.1	15.0	16.8	60.3	63.7
FPP3	60 : 5 : 35	304.8	332.3	489.2	16.4	18.3	55.5	59.5
FPP4	60 : 5 : 35	299.7	327.8	485.8	23.2	16.9	55.8	59.1
—	60 : 0 : 40	302.5	328.6	488.4	15.6	17.1	58.2	61.9
FPP4	60 : 2.5 : 37.5	299.5	328.8	485.5	16.9	18.7	56.0	58.9
FPP4	60 : 5 : 35	299.7	327.8	485.8	23.2	16.9	55.8	59.1
—	60 : 0 : 40	302.5	328.6	488.4	15.6	17.1	58.1	61.9
FPP1	60 : 2.5 : 37.5	299.1	328.2	485.4	17.6	19.5	54.7	57.8
FPP1	60 : 5 : 35	302.0	330.9	487.5	16.6	18.3	56.4	60.0

For the composites containing 60% Al(OH)$_3$, the addition of FPP and an increase in the grafting rate of FPP resulted in a more significant effect on the crystallization and melting behavior of Al(OH)$_3$/PP composites. The DSC curves are shown in Figures 5 and 6. The higher Al(OH)$_3$ content resulted in an increased heterogeneous nucleating ability, leading to a further increase in the T_c, T_m, and the width of peak. The above results indicated that the crystallization and melting behavior depended on the grafting rate of FPP. The higher the grafting rate, the more the polarity of PP, the stronger the interfacial interaction between PP and Al(OH)$_3$, the higher the heterogeneous nucleation.

However, surface modification of filler with fatty acid generally reduces the nucleation ability of the filler.[50,51] Silanes have been shown to have a variable effect on the nucleation behavior of filler. Generally, untreated glass is often found to be a poor nucleating agent for PP, but silane-treated glass flakes give a nucleating effect, provided the silane is applied by a dry blending method.[52]

Effect on Thermal Degradation Behavior of Al(OH)$_3$/PP Composites

The TGA results of PP and FPP/PP blends are presented in Table II. It was found that the temperature of 5% weight loss ($T_{5\%}$) and the pyrolysis peak temperature (T_{pm}) of FPP/PP blends were higher than that of the PP. The weight loss of 450°C was lower than that of the PP. This suggests that grafting AA onto PP improves the thermal stability of PP. Chiang and Hu[36] found that the initial pyrolysis temperature of PP-g-AA is higher that of the PP and suggested that a reasonable explanation is that of an interchain steric hindrance caused by the AA side chain.

For the Al(OH)$_3$/PP composites, the TGA results are shown in Table III and two pyrolysis peaks were observed. T_{pm1} and T_{pm2} were the temperature of degradation of Al(OH)$_3$ and PP matrix, respectively. Because the pyrolysis peak temperature and $T_{5\%}$ of Al(OH)$_3$ were lower than

Table V   Limiting Oxygen Index of Al(OH)$_3$/PP Composites Modified by FPP

Al(OH)$_3$/PP	None	FPP1	FPP2	FPP3	FPP4
0 : 100	18.0	18.0	—	—	18.0
20 : 80	20.2	20.4	—	—	20.6
40 : 60	22.6	23.2	—	—	23.3
60 : 40	24.1	26.1	27.0	27.2	27.4

FPP, 5 wt %.

that of PP, the addition of Al(OH)$_3$ resulted in a decrease in the T$_{5\%}$ and an increase in the weight loss at 350–400°C. However, the T$_{5\%}$ and T_{pm} of Al(OH)$_3$ in the composites were higher than that of Al(OH)$_3$ because of the effect of Al(OH)$_3$ encapsulated by the PP matrix. It was found that the T_{pm2} of composites was higher than that of the PP. This suggested that Al(OH)$_3$ offers an effect against flammability of the PP like the other FR does by raising the thermal resistance of the matrix.

The TGA results of Al(OH)$_3$/PP composites modified by FPP with different contents and grafting rates are shown in Table IV. For the composite containing the Al(OH)$_3$ content of 20% by weight, the addition of FPP resulted in an increase in the $T_{5\%}$ and T_{pm1}, and weight loss at 350–400°C was significantly reduced. The $T_{5\%}$ of the Al(OH)$_3$/FPP4/PP composite was 36°C higher than that of the unmodified Al(OH)$_3$/PP composite. It is suggested that for the low filler content, the addition of FPP resulted in improved filler dispersion in the matrix and enhanced interfacial interaction between the filler and PP, leading to a decreased weight loss of Al(OH)$_3$.

For the composite containing the Al(OH)$_3$ content of 40%, the T_{pm1} of the Al(OH)$_3$/FPP/PP composite was further increased and the $T_{5\%}$ was further reduced by the addition of FPP. In the Al(OH)$_3$/FPP/PP composite containing the filler content of 60% by weight, the thermal degradation behavior of composites mainly depended on the nature of Al(OH)$_3$ and was little affected by the content and the grafting rate of FPP. In the composite containing different Al(OH)$_3$ contents, the content and the grafting rate of FPP had not influenced the T_{pm2} of Al(OH)$_3$/FPP/PP composites.

Effect on Flame Retardance of Al(OH)$_3$/PP Composites

The limiting oxygen index values of Al(OH)$_3$/PP and Al(OH)$_3$/PP composites modified by FPP with different grafting rates are presented in Table V. It can be seen that the addition of Al(OH)$_3$ and increased Al(OH)$_3$ content resulted in increased limiting oxygen index form 18.0 of PP to 24.1 for Al(OH)$_3$/PP composite containing 60% by weight. Although the limiting oxygen index of PP was not affected by FPP with different grafting rates, the limiting oxygen index of Al(OH)$_3$/PP composites increased with the addition of FPP and increasing the grafting rate of FPP. For the Al(OH)$_3$/FPP/PP

composites containing the FPP4 content of 5% by weight, the limiting oxygen index of 27.4 was obtained. The improvement in the flame retardance is attributed to the filler dispersion in the PP matrix because of the addition of FPP. However, the enhanced interfacial interaction between FPP and Al(OH)$_3$ because of improved filler dispersion, which increases with increasing the grafting rate of FPP, offers another effect on the flame retardance.

CONCLUSIONS

Al(OH)$_3$/PP composites modified by PP grafting with AA were prepared. The effect of FPP on crystallization and melting behavior, thermal degradation, and limiting oxygen index of Al(OH)$_3$/PP composites were investigated. Although the addition of FPP with a low grafting rate had not influenced the crystallization and melting behavior of PP in the composites, the FPP with a high grafting rate resulted in an increase in the crystallization and melting temperature of PP. The heterogeneous nucleation of Al(OH)$_3$ was weak because of the incompatibility and larger surface energy difference of PP and Al(OH)$_3$. The addition of FPP with a high grafting rate into PP resulted in an increase in the polarity and surface energy of PP, leading to the enhanced interfacial interaction between PP and Al(OH)$_3$ and the increased heterogeneous nucleating sites. The addition of FPP increases the thermal stability of Al(OH)$_3$/PP composites. The addition of Al(OH)$_3$ and an increase in the Al(OH)$_3$ content resulted in an increased limiting oxygen index. The limiting oxygen index of Al(OH)$_3$/PP composites further increased with the addition of FPP and an increase in the grafting rate of FPP.

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