Synergistic Effect of Supported Nickel Catalyst with Intumescent Flame-Retardants on Flame Retardancy and Thermal Stability of Polypropylene

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ABSTRACT: Supported nickel catalyst (Ni-Cat) was used as a catalyst to improve the flame retardancy of intumescent flame-retardants (IFR) systems based on ammonium polyphosphate and pentaerythritol (PETOL) in polypropylene (PP) matrix. Limited oxygen index (LOI), UL-94 rating, and thermogravimetric analysis were used to characterize the flame retardancy and thermal stability of the PP systems, and field emission scanning electron microscopy (FE-SEM) and Fourier transformed infrared spectroscopy (FTIR) were used to analyze the microstructure and composition of the chars formed during measuring LOI value and after combustion at 800°C. The catalytic effect of Ni-Cat was shown in an increase of LOI, a change in the char microstructure, and improvement of the thermal stability in the PP systems, which result from the synergistic effect of Ni-Cat and IFR. The results from FE-SEM and FTIR spectra of the char can explain how this synergistic effect happened. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 5988–5993, 2006

Key words: polypropylene; supported nickel catalyst; intumescent; flame retardancy

INTRODUCTION

Polymers are widely used in a variety of applications, such as in transportation, construction, electrical/electronic appliances, and in general household materials. However, the flammability of most polymers is one of the main problems limiting their wider application in several areas. Up to now there are already various methods of improving flame retardancy of polymers as required in many applications for safety consideration. However, to some degree, these methods are limited with respect to environment requirement and performance of polymers.[1] In the quest for effective and satisfactory flame retardants, recently much research has been focused on intumescent flame-retardants (IFR). IFR systems are designed to swell and form a porous carbonaceous char layer on the surface of the materials that act as a barrier for hot air and pyrolysis products fuelling the fire. The IFR based on combination of ammonium polyphosphate (APP) with pentaerythritol (PETOL) has demonstrated good flame retardant property in polyolefin matrices, especially when used in further combination with other additives that lead to improved fire retardance.[2] The use of synergistic agents not only produces more efficient flame retardancy, but also makes it possible to reduce the amount of the IFR. It has been found that divalent metal compounds and their derivatives have good synergistic effect with the IFR.[3] In a previous report, we demonstrated that nickel formate had a synergistic effect on flame retardancy in polypropylene (PP) matrix containing APP/PETOL mixture.[4] Similar effects were found by Le Bras and coworkers, when adding 1.5 wt % of zeolite 4A into an intumescent formulation (APP and PETOL applied to terpolymer of ethylene/butylacrylate/maleic anhydride EBM, LRAM3.5).[5–10] Antonov et al. also reported a maximum increase in limited oxygen index (LOI) from 26 to 32 unit upon adding 0.05 wt % of nanoparticles of elementary Cu with a diameter of < 200 nm.[11]

In this report, supported nickel catalyst (Ni-Cat) as a synergistic agent was used to improve flame retardancy of APP/PETOL mixture in PP matrix, which exhibits a distinct synergistic effect with APP and PETOL. Morphologies of the chars obtained from the sample during measuring LOI value and the pyrolytic char at about 800°C were examined by means of field emission scanning electron microscopy (FE-SEM). Fourier transformed infrared spectroscopy (FTIR) was used to identify the composition of the char obtained from the sample during measuring LOI value, which can

TABLE I
Effect of Ni-Cat on UL-94 Rating of PP-IFR Systems
(APP/PETOL = 2/1 by weight)

Sample	IFR (wt %)	Ni-Cat (wt %)	UL-94 rating
PP-IFR0	0	0	Not rating
PP-IFR1	20	0	V2
PP-IFR2	19.5	0.5	V0
PP-IFR3	19	1	V0
PP-IFR4	18	2	V2
PP-IFR5	17	3	Not rating
PP-IFR6	15	5	Not rating

explain how this synergistic effect happened. The flame retardant properties and thermal stability of the materials were evaluated by UL-94 standard, LOI, and TGA, and a fundamental analysis for the mechanism of char formation was studied.

EXPERIMENTAL

Materials and sample preparation

Polypropylene (PP, MW = 3×10^5) used in this study was a commercially available extrusion-grade powder with 0.8 g/min of melt flow index from Panjin Chemical Co. Ammonium polyphosphate (APP) was supplied by Zhenjiang Xingxing Flame-retardant Co., Jiangsu. Pentaerythritol (PETOL) was bought from Shanghai Chemical Reagent Corp., Shanghai, and supported nickel catalyst (Ni-Cat, supported on silica- alumina, Ni content ~66%) was obtained from Alfa Aesar. The components of the designed formulations were mixed in a Brabender mixer with 100 rpm for 10 min at 190°C.

Characterization

The limited oxygen index (LOI) was measured on a JF-3 oxygen index meter (Jiangning, China) with sheet dimensions of 130 mm ×6.5 mm ×3 mm, according to ISO4589-1984. The UL-94 rating was rated according to the UL-94 (ANSI/ASTM D 635-77) standard. Thermogravimetric analysis (TGA) was carried out under air at a heating rate of 20°C/min by means of a PerkinElmer TGA 7 thermal analyzer. The samples of intumescent char were taken after burning the PP/APP/PETOL mixture in a crucible at 800°C under air and from sample when measuring LOI value. The char surface was observed by means of field emission scanning electron microscopy (FE-SEM, XL303SEM). The char composition was pelletized with KBr and characterized by FTIR spectrometer (BRUKER Vertex 70 FTIR).

RESULTS AND DISCUSSION

LOI and UL-94 analysis

Table I lists the composition of the PP mixtures and their UL-94 rating. It could be seen that when PP did not contain any of the IFR, it had no rating by the UL-94 standard. To achieve V2 rating, the PP should contain 20 wt % of APP/PETOL = 2/1 (by weight) mixture. However, the addition of even small amounts (0.5 wt %) of Ni-Cat into the PP/APP/PETOL mixture (PP-IFR) could stop the dripping observed in the PP matrix containing only the same amount of the IFR, and raised its rating from V2 to V0. A similar phenomenon can be seen in the LOI increase when adding a little Ni-Cat into PP-IFR systems.

The effect of the content of Ni-Cat on the flame retardancy of PP-IFR system was investigated. Figure 1 shows that the addition of Ni-Cat into the PP matrix containing APP/PETOL results in a significant increase in the LOI values. The LOI values increase with the amount of the Ni-Cat at first until the maximum is reached. The highest LOI value in these experiments was 33.4 obtained at 0.5–1 wt % of Ni-Cat. But the LOI begins to decrease because of further increase in the content of the Ni-Cat. The results clearly signified a synergistic effect between Ni-Cat and the IFR system, and there is an optimal content of the Ni-Cat in this system for obtaining the best flame retardancy of PP.

Thermal stability

Figure 2 presents TGA curves of the PP-IFR systems with varying contents of the Ni-Cat. It can be seen that pure PP began to decompose at about 270°C under N_2. When the temperature was increased further, the weight loss increased rapidly until all the PP was exhausted at about 500°C, and no residue remained. The PP-IFR systems have similar TGA behavior under this experimental condition. But we
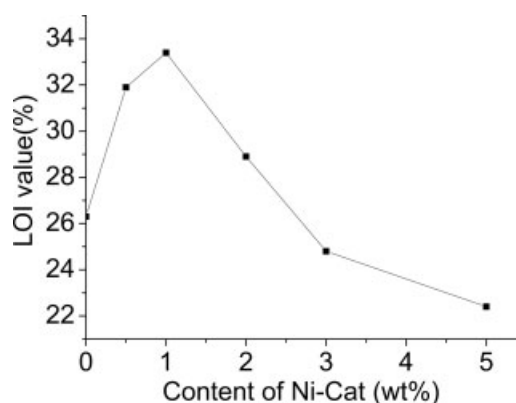

Figure 1 Effect of the content of the Ni-Cat on the LOI of PP-IFR systems (PP/IFR/Ni-Cat = 80/20-X/X; IFR: APP/PETOL = 2/1, by weight).
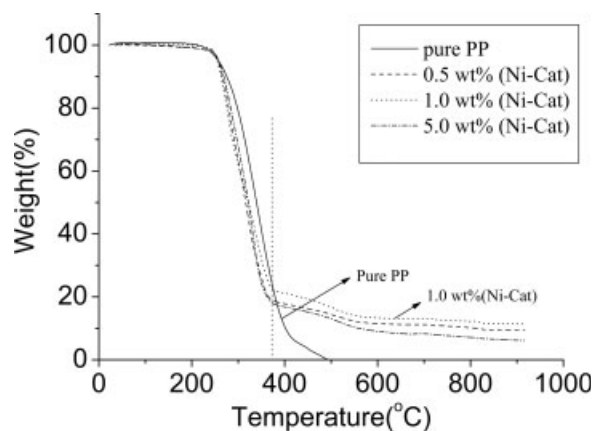
Figure 2 Effect of the content of the Ni-Cat on the thermal stability of PP-IFR systems (PP/IFR/Ni-Cat = 80/20-X/X; IFR: APP/PETOL = 2/1, by weight) measured by TGA under N_2.

can see that higher amounts of the residue were obtained for the PP-IFR system than for pure PP at temperature ranging from 370 to 700°C. The melting zone of PP is about 170–250°C. Between 250 and 370°C, the development of intumescence occurs. Above 370°C, the intumescent coating degrades.[12] From Figure 2 it can be seen that the percentage of weight loss before 370°C for PP-IFR3 is almost 78 wt %, which is lower than those of other samples. At above 370°C, the degradation is still very slow. This implies that when the Ni-Cat was added into the PP-IFR system by 1 wt %, the highest amount of residue was obtained in the PP-IFR system. The above results demonstrate that an appropriate content of Ni-Cat can promote the formation of a carbonaceous material in the PP/APP/PETOL systems, and thus the flame retardancy of PP is improved.

Figure 3 shows the derivative TG curve ((d(TG)/dT) denoted by DTG) as a function of temperature, obtained from the TGA. It can be seen clearly that the PP matrix decomposition process was influenced by the addition of IFR and Ni-Cat. For the PP-IFR containing Ni-Cat, the DTG peak centered at about 272°C, corresponding to a weight loss of almost 18%. This could be mainly attributed to the phosphorylation of PETOL by the polyphosphate with the release of water and ammonia, which finally leads to the formation of intumescent char. At the same time, the PP matrix started to degrade. The weight loss in the second step was the degradation of the intumescent char accompanied by the degradation of PP.[13] It is easy to see that when 1.0 wt % of Ni-Cat was added into PP-IFR systems, the first degradation peak became weak and the second peak shift to higher temperature. This phenomenon might be attributed to the formation of more stable char on the surface of PP. Further increasing content of Ni-Cat led to the reverse effect on degradation of PP.

Analysis of the morphology of the residual char

To further investigate effect of the Ni-Cat on the char formation of PP-IFR during combustion, the morphologies of the chars obtained from the sample after the flame extinguished during measuring LOI value and the pyrolytic char at about 800°C were examined by FE-SEM (Fig. 4). From Figure 4(a1, a2), which came from the samples without the Ni-Cat, it can be seen that the residue of the PP-IFR system has a good char structure, to some degree, which can serve as a barrier to O_2 supply and the pyrolytic gas. However, a lot of flaw can be seen on the surface of the residual char, especially the pyrolytic char at high temperature in Figure 4 (b1, b2), which may be a main reason making the flame-retardants performance of PP-IFR decrease. In Figure 4(c1, c2), which are the images of the surface of the residual char from the PP-IFR system containing 1.0 wt % of the Ni-Cat, the char structure changes a lot. The surface layer is a stable and integrated char structure that plays an important role in improving flame retardancy. Even at high temperature, the surface char structure in Figure 4(d1, d2) could not be destroyed. On the contrary, the chars in Figure 4(e1, e2) and 4(f1, f2), which belong to the PP-IFR system containing 5 wt % of the Ni-Cat, were loose and nonintegrated. Obviously, the PP-IFR system was destroyed and the char formed under this condition could not serve as a good barrier. Based on these results, it is not difficult to understand the results of LOI and TGA for PP-IFR systems containing the Ni-Cat.

Analysis of the char composition by FTIR

To further analyze how the Ni-Cat affects the formation of intumescent char, FTIR spectroscopy was used to analyze the char composition of PP-IFR1, PP-IFR3, and PP-IFR6 in which the content of the Ni-Cat was different. The chars were collected after the flame
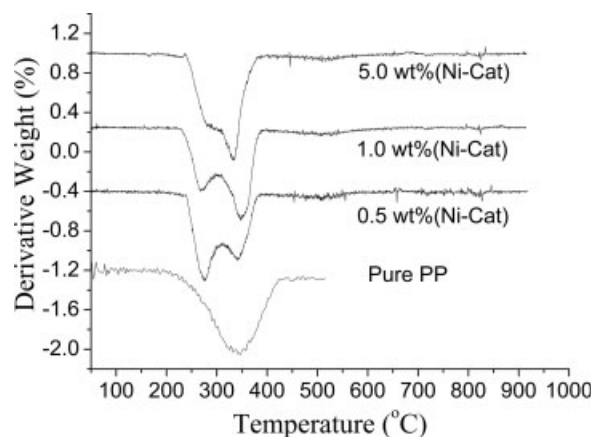

Figure 3 DTG curves of PP-IFR systems containing different contents of the Ni-Cat (PP/IFR/Ni-Cat = 80/20-X/X; IFR: APP/PETOL = 2/1, by weight).
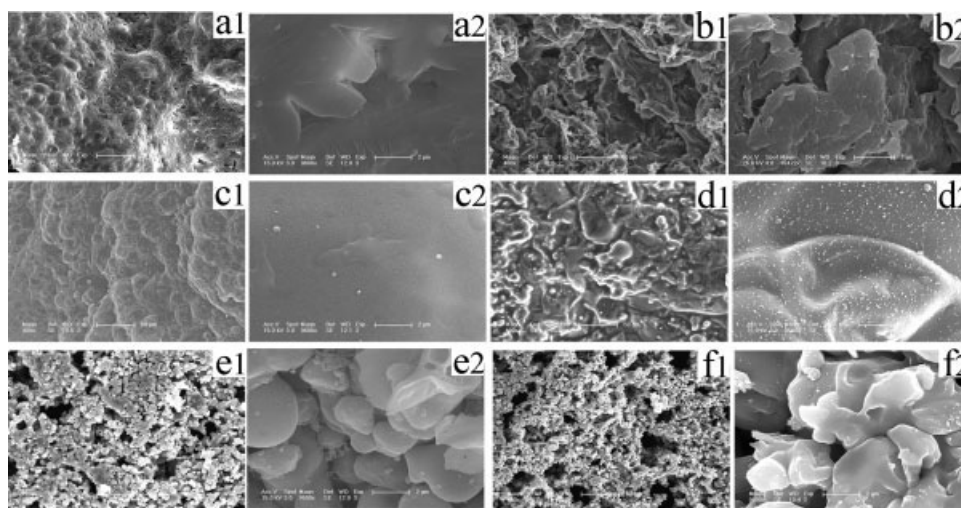
Figure 4 Scanning electron micrographs of the char structure formed after extinguishing when measuring LOI value and after combustion at 800°C. (a1), (a2), (b1), and (b2): PP-IFR1; (c1), (c2), (d1), and (d2): PP-IFR3; (e1), (e2), (f1), and (f2): PP-IFR6.

extinguished at LOI value of 26.3, 33.4, and 22.4 respectively, in accordance with the sample's LOI value, and so the char composition can represent the real composition of intumescent char formed from PP-IFR1, PP-IFR3, and PP-IFR6. The char of PP-IFR1 without Ni-Cat was collected at the LOI value of 26.3. From Figure 5, it can be seen that aliphatic groups exist in the char, which is characterized by the peak at 2952, 2919, 2868, 2839, 1460, and 1378 cm^{-1} attributed to absorption peaks from $\upsilon_{as}CH_3$, $\upsilon_{as}CH_2$, υ_sCH_3, υ_sCH_2, $\delta\,CH_2$, and $\delta\,CH_3$, resulting from the incompletely burned hydrogen–carbon compound, as reported in the literature.[13] The broad absorption peak at 1150–1300 cm^{-1} can be assigned to the P—O—C bands in the phosphocarbonaceous complexes and the P=O bonds in the phosphate complexes, as reported in the literature.[14] It indicates that PP-IFR systems without Ni-Cat can form a good char structure, which can effectively protect the PP matrix below the char layer during combustion. The char of PP-IFR3 with 1.0 wt % Ni-Cat collected at LOI value of 33.4. From Figure 5, we can see that all characteristic absorption peaks of the aliphatic groups and P—O—C absorption peak exist under higher O_2 concentration, which demonstrates that the formed char of PP-IFR3 is more stable than that of PP-IFR1 to serve as a protecting barrier for PP matrix. At the same time, we can see that the characteristic absorption peak at 1272 cm^{-1} related to P=O double bond stretching and the characteristic peak of 1455 cm^{-1} related to NH_4 became apparent when compared with those of the PP-IFR1, which maybe be attributed to the crosslinking of APP at some degree catalyzed by Ni-Cat, and therefore more APP will be available for phosphorylation and char formation. Finally, we detected the char composition of PP-IFR6 with 5 wt % Ni-Cat at the LOI value of 22.4, which is lower than that of PP-IFR1

without Ni-Cat. From Figure 5, it can be seen that the aliphatic groups were also included in the char composition. However, the intensity of some characteristic absorption peaks of aliphatic groups became weak; even the peak of 1378 cm^{-1} almost disappears. At the same time, the characteristic absorption peaks of P—O—C bonds disappear and the intensity of P=O (υ P=O) and P—O (υ P—O) peaks at 1272 and 1048 cm^{-1} increase a lot. Combined with the SEM image in Figure 4, we can conclude that the intumescent char coating could not be formed when 5 wt % of Ni-Cat was added into the system, and this flame retardancy for PP only is attributed to the decomposition of APP.

Mechanism consideration

Recently, the mechanism of improved flame retardancy for IFR systems has been explored. Up to now, the most
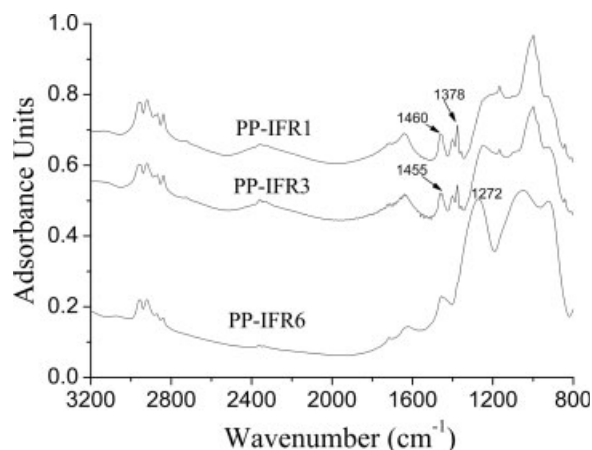

Figure 5 FTIR spectra of the char layer formed after extinguishing when measuring LOI value for PP-IFR1, PP-IFR3, PP-IFR6.

dominant view thinks that during combustion, the APP, as the acid source, first breaks down to form polyphosphate, and then the PETOL is phosphorylated by the polyphosphate with the release of water and ammonia, the phosphate ester is thermally decomposed to form double bonds during pyrolysis, which finally leads to formation of intumescent char (Reaction 1 in Scheme 1).[15] However in this work, via adding the Ni-Cat into the PP-IFR systems, the approach of char formation was changed. A possible reaction mechanism may be that the Ni-Cat can catalyze APP to crosslink and form a three-dimensional network with the release
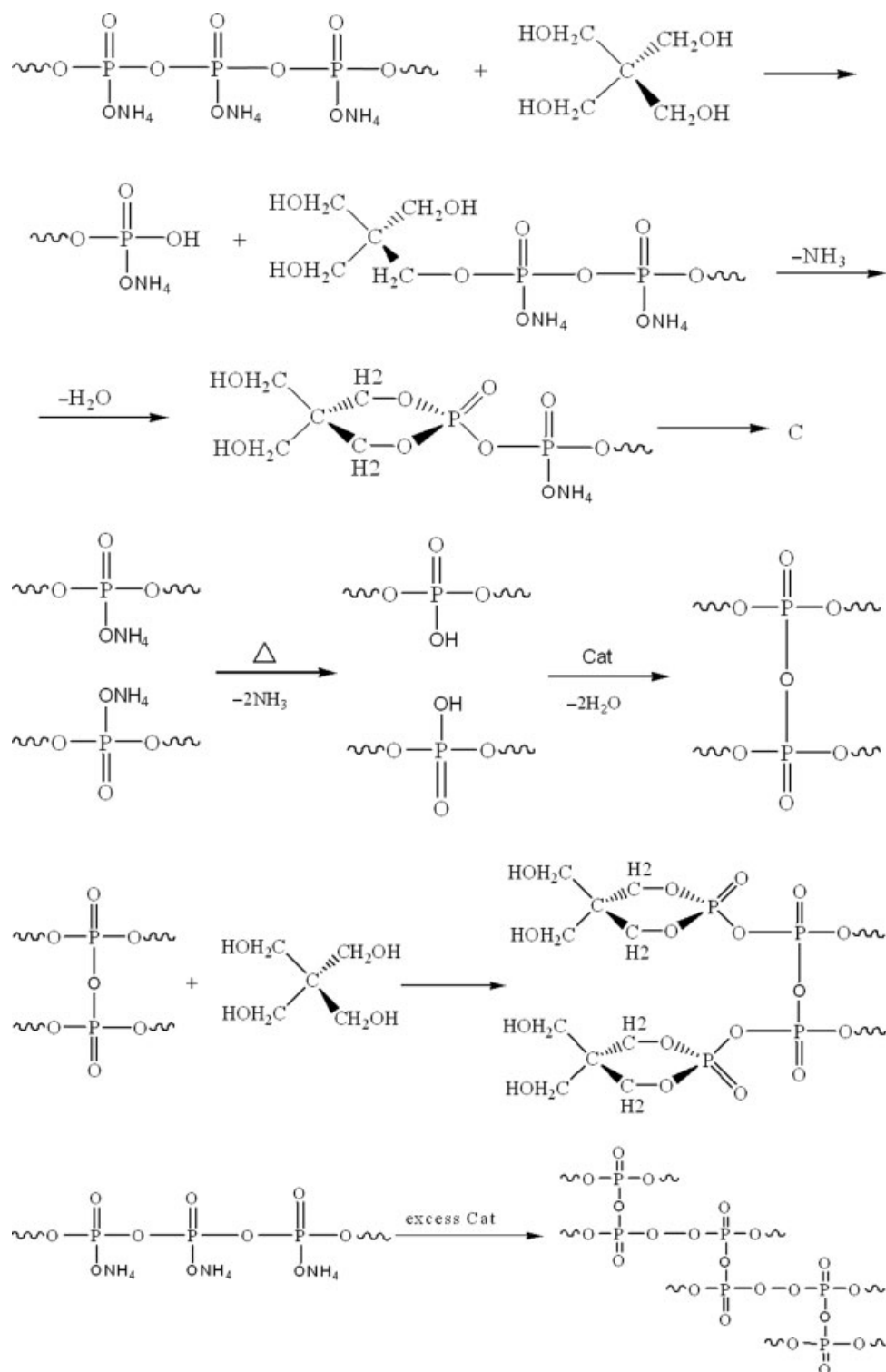
Scheme 1 Possible reaction mechanisms of char formation during combustion of PP/IFR/Ni-Cat systems.

of water and ammonia (Reaction 2 in Scheme 1). As we know, this kind of structure will stabilize the APP and decrease the volatility of the phosphorus, and therefore more APP will be available for phosphorylation and char formation, subsequently resulting in a more integrated char structure.[16] Furthermore, the char structure prevents the inside pyrolytic product into the flame zone and that of the O_2 into the inner of the polymers. But when the content of the Ni-Cat is too high, the excessive crosslinking of APP makes the chain of APP lose its flexibility and turn rigid and unreactive (Reaction 3 in Scheme 1). They form lumps of APP gel that do not participate in the formation process of intumescent char, which has been mentioned in some other literature.[16] In addition, they disrupt the homogeneity of the char structure and render it ineffective as barrier.

CONCLUSIONS

In summary, we have found that the combination of the Ni-Cat with IFR system based on APP and PETOL exhibited an evident synergistic effect in the flame retardancy of PP. The LOI value of PP-IFR systems increases from 26.3 to 33.4 unit and raises UL-94 rating from V2 to V0 via adding Ni-Cat. The synergistic effect on the flame retardancy of PP can be obtained at an optimum content of Ni-Cat. The FE-SEM image and FTIR spectra of the residual chars can further explain that an appropriate content of the Ni-Cat in IFR system can make more APP available for phosphorylation and char formation, and subsequently result in a more integrated char structure. We believe that the above-mentioned results will be helpful to understand some other synergistic effects in the IFR systems.

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