

The Effects of APP, APP/MMT Nanocomposites on the Thermal Degradation of ABS Resin

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ABSTRACT: The thermal degradation of acrylonitrile-butadiene-styrene (ABS) added ammonia polyphosphate (APP) or APP/montmorillonite (MMT) nanocomposite was studied. The whole degradation progress of ABS could be regarded as the combination of the thermal degradation of polystyrene (PS) and polybutadiene (PB). The PB influences the formation of char while PS influences the maximum mass loss rate and its decomposition temperature. APP or APP/MMT nanocomposite could decrease the maximum mass loss rate and promotes the formation of char. A SiO₂ network was formed on the char surface of the ABS-APP/MMT composite which could improve the strength of the char and flame retardancy of ABS. It was found that when APP/MMT mixture or APP/MMT nanocomposite are added to ABS, NH₃ (the gas product of APP) was buried in the residue and released until full degradation of ABS. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40704.

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INTRODUCTION

Acrylonitrile-butadiene-styrene (ABS) is a widely used thermoplastic material because of its good mechanical properties, chemical resistance, and easy processing characteristics. One of the main drawbacks of ABS is its inherent flammability.^{1,2} To prevent complete combustion of the polymers, flame retardants have been used. Because of the ecological problems caused by traditional halogen flame retardants, increasing attention is focused on halogen-free flame retardants, but halogen-free flame retardant provides much lower flame retardancy.^{3,4} However, intumescent flame retardants (IFR) are preferably used in thermoplastics due to their advantages of low smoke and toxicity.⁵

Recently, phosphorus compounds have demonstrated good ability as flame retardants, and the effect of ammonia polyphosphate (APP) proved to be significant on the thermal decomposition of vinyl polymers and copolymers by increasing considerably the char formation.^{6,7} Levchik⁸ clearly stated in his review article that single phosphorus-based flame retardant is unlikely to give UL-94 V-0 rating (burning stops within 10 s on a vertical specimen; drips of particles allowed as long as they are not inflamed) along with a required set of physical properties for styrene plastics including ABS and high impact

polystyrene (HIPS). A synergistic effect was studied between montmorillonite (MMT) and poly(4,4-diaminodiphenyl methane spirocyclic penmerythritol bisphosphonate) (PDSPB) in ABS nanocomposites.⁹ Moreover, using halogen-free flame to retard ABS is a difficult subject. In order to explore suitable flame retardant to ABS, it is necessary to study further the mechanism of degradation progress of ABS. Thermogravimetric analysis linked to a Fourier transform infrared spectrometer (TGA/FTIR) was used to investigate the initial characterization of the polymer.^{10,11} Masanori and Charles¹² had studied the thermal degradation of ABS terpolymer by TGA/FTIR, and they found that the degradation of ABS may be considered to be essentially the same as that of its constituents. In this article, 30%APP or 30%APP/MMT nanocomposite loading is used to flame retard ABS resin respectively, and the thermal degradation progress was studied by TGA/FTIR as the same with the thermal degradation of ABS resin. Deqi and Rongjie¹³ reported that APP particles disperse in the flame-retarded polymers at micron size, whereas MMT disperses in polymers at nanosize and the MMT layers are completely exfoliated in the APP/MMT particles. Through direct melt intercalation technique, an exfoliated-intercalated ABS/modified-clay nanocomposite can be prepared.¹⁴ We also investigated the effects of APP and

Table I. Data of TGA and DTGA Curves of ABS and Its Constituent Parts

Polymer	T_{onset} (°C)	T_{max} (°C)	W_{max} (%/min)	Residue%/ (800°C)
ABS	388	437	40.6	0
PAN	305	316	14.91	39.43
PS	381	423	58.98	0
PB	382	476	36.47	0

6% wt MMT mixture on the thermal degradation of ABS resin for comparison for effective halogen-free flame retardants of ABS.

EXPERIMENTAL

Materials

ABS, polybutadiene (PB), polystyrene (PS), and polyacrylonitrile (PAN) were obtained from Zhenjiang Qimei Chemical Co., Ltd. APP and APP/MMT nanocomposites were supplied by ZiBo SaiDa Flame Retardant New Materials Co., Ltd. MMT was obtained from Shouguang Zhonglian Jingxi Mengtuoshi Co., Ltd.

Experiment and Characterization

The flame retardant ABS composites with 30% wt APP or APP/MMT nanocomposites were prepared by co-rotating twin-screw plastics extruder at 185–195°C, and produced into sheets by injection moldings at 195–205°C.

TGA was conducted with a Netzsch 209 F1 thermal analyzer under nitrogen atmosphere at a heating rate of 20°C/min from 40°C to 800°C, and TGA and derivative TGA (DTGA) curves were plotted. FTIR was recorded on a Nicolet 6700 IR spectrometer. The spectra were collected at 32 scans with a spectral resolution of 4 cm⁻¹ (attenuated total reflection). To detect gas species, the TGA was coupled with FTIR (TGA-FTIR). The TGA-FTIR experiments were all carried out under nitrogen atmosphere at a heating rate of 20°C/min from 40°C to 800°C.

Scanning electron microscopy (SEM) experiments were performed with a Hitachi S-4800. The char residue was obtained in the muffle oven under air atmosphere.

The X-ray photoelectron spectroscopy (XPS) data were obtained using a PerkinElmer PHI 5300 ESCA system at 250 W (12.5 kV at 20 mA) under a vacuum below 10⁻⁶ Pa.

RESULTS AND DISCUSSION

The Thermal Degradation of ABS

The TGA and DTGA data and curves are shown in Table I and Figure 1, respectively. All of the polymers investigated (PS, PB, PAN, and ABS) degrade in a single step leaving no residue except PAN as shown in Figure 1. The initial decomposing temperature is T_{onset} which means the sample loses the 5% weight; T_{max} is the temperature at maximum weight loss and W_{max} is the maximum weight loss rate.

Compared the degradation of ABS with that of its constituent parts, it is noticed that the degradation of ABS is quite similar to the combination of PB and PS. The T_{onset} of ABS is 388°C

and continues rapidly until about 450°C, and at the same temperature range both PS and PB have degraded completely. While PAN degrades between 305°C and 350°C, it is believed that when PAN is grafted to PB main chain, the structure of PAN is stabilized by the presence of PB.

The evolutions of ABS resin for comparisons with PS, PB, and PAN were studied as shown in Figure 2(a–d). The gas degradation products are collected from 388°C to 480°C. It is discovered that the initial evolution of ABS at 388°C measured is mostly mono-substituted benzene (1558, 1506, and 1456 cm⁻¹ benzene skeleton vibration; 773 and 700 cm⁻¹ benzene mono-substitution, 3072 and 3032 cm⁻¹ aromatic =C–H) from Figure 2(a), and is similar to the initial decomposition of PS. It is confirmed that the PS chain segment of ABS decomposes first. And there is also some aliphatic C–H stretching vibration (2937 cm⁻¹) which is very weak. It is showed that the PB chain segment of ABS decomposes partly; moreover, the peak at 2937 cm⁻¹ become strong at 437°C.

After 437°C PS segment almost degrades completely and PB segment degrades rapidly as shown in Figure 2(c,d). The absorbance peak of aromatics suddenly becomes weaker while the absorbance peak of butadiene becomes very strong. And

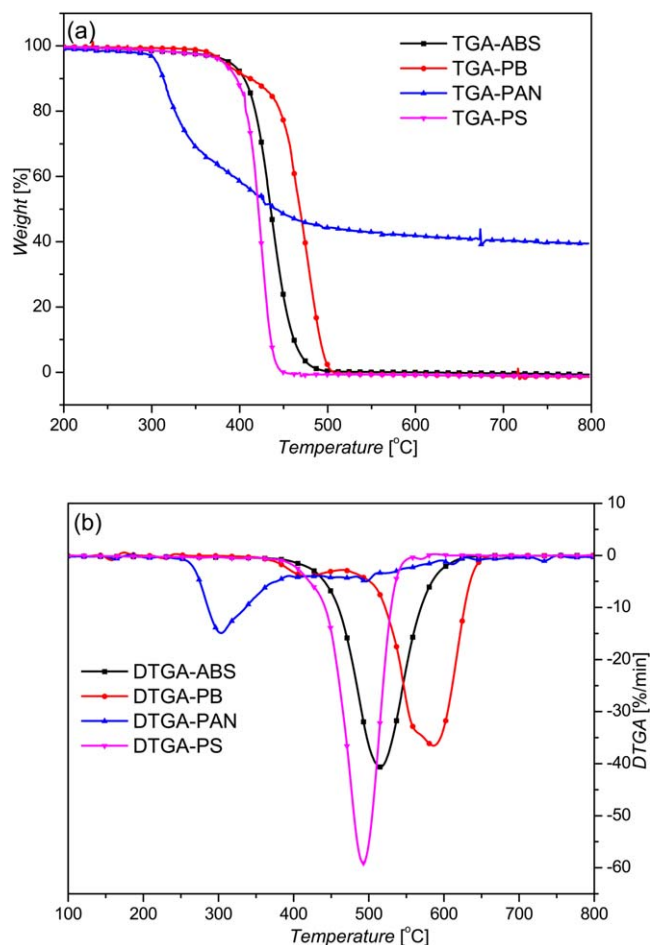


Figure 1. TGA (a) and DTGA (b) curves for ABS and its constituent parts. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

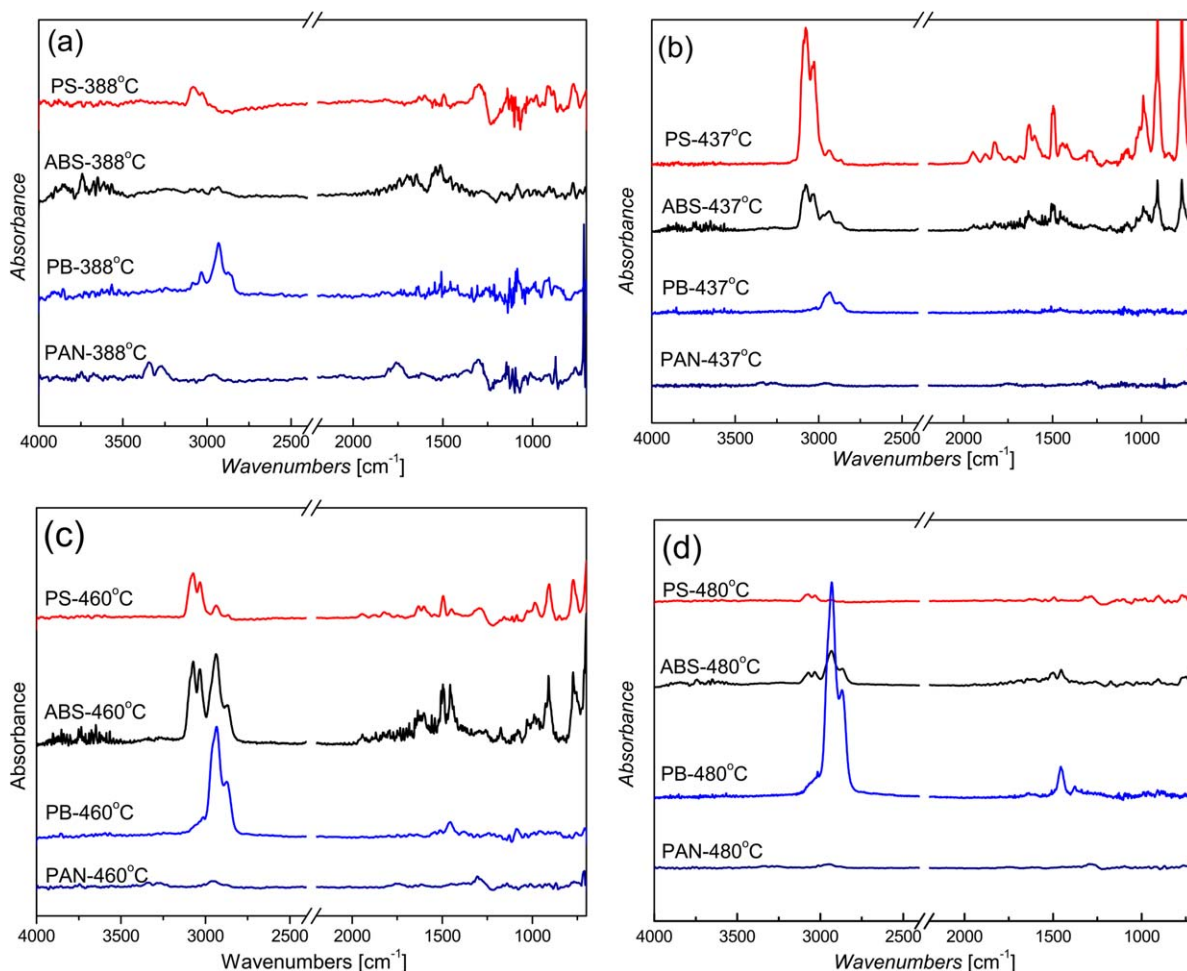


Figure 2. FTIR spectra of the evolutions of ABS and PS, PB and PAN at different temperatures: 388°C (a), 437°C (b), 460°C (c), and 480°C (d). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

RCH=CH₂ out-of-plane bending (989 and 910 cm⁻¹) decreases rapidly while C—H bending vibration (1436 cm⁻¹) grows at 480°C, demonstrating that from 460°C to 480°C the gas products mostly come from the degradation of PB segment.

Meantime there is no obvious evidence from FTIR spectra that PAN degrades before ABS as the same with the TGA and DTGA, the typical absorption peak of PAN was never found clearly in the FTIR spectra during the whole degradation progress of PAN while linear polymerization of nitrile group is the principal reaction and cyclization followed by extended conjugation is the degradation process of PAN.¹⁵

In order to study the products of degradation in the condensed phase, the FTIR of char residue of different temperatures to ABS in muffle oven are studied, as shown in Figure 3. The absorption at 2230 cm⁻¹ indicates the group of cyano in ABS, which exists in the char till the end of the degradation. Besides, the PB remains in the residue till the maximum weight loss temperature at 440°C which corresponds well with the result from the gas production analysis. When ABS degrades completely, the broad absorption less than 1500 cm⁻¹ indicates the formation of a graphite structure which is caused by the polymer combustion. The C=C group is engaged in the formation

of char. Thus, the residue of ABS is mostly influenced by the amount of PB while PS effects on the maximum weight loss temperature of ABS.

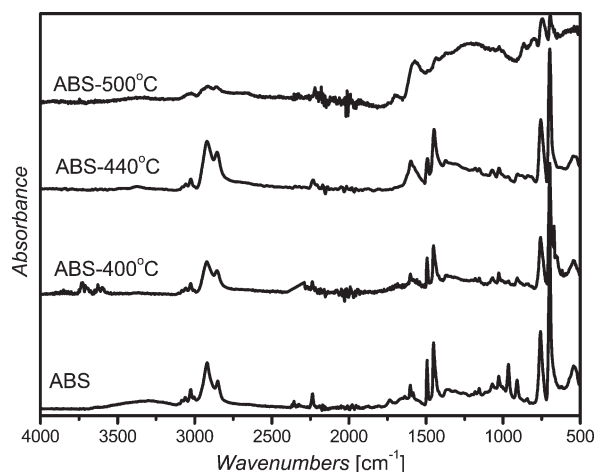


Figure 3. FTIR spectra of the residues of ABS in muffle oven.

Table II. Data of TGA and DTGA Curves of ABS Composites

Polymer	T_{onset} (°C)	T_{max} (°C)		W_{max} (%/min)		Residue%/ (800°C)
		1st step	2nd step	1st step	2nd step	
ABS	388	437		40.6		0
APP	326	320	581	13.1	60.5	20.46
ABS-APP	357	439	587	27.2	4.13	5.56
APP/MMT	311	315	685	12.4	60.06	22.54
ABS-APP/MMT	378	440	680	28.8	2.3	10.8
ABS-APP-MMT	350	438		27.0		19.25

The Degradation of APP, APP/MMT Nanocomposite

Previous literature studied the degradation progress of APP: the elimination of NH_3 into polyphosphoric acid and then crosslinks into P_2O_5 ; the dehydration into ammonium phosphate; and phosphoric acid partly turn into polymetaphosphoric acid and then both eliminate H_2O and then volatilize in the form of P_2O_5 in which stage APP loses its most weight, only remains some high viscosity compounds such as pyrophosphoric acid which dehydrates slowly. APP/MMT nanocomposite has the same degradation process but the

second maximum weight loss temperature is about 100°C higher than APP.^{16,17}

For better flame retardancy, 30 wt % loading of IFR material is necessary to obtain V-0 rating, and this IFR was developed quite a long time ago and has been mentioned in many patents.^{18–21} About 30 wt % APP or APP/MMT nanocomposite was added to ABS respectively and their effects on ABS degradation progress is studied, and the physical mixture of APP and MMT is studied too as a comparison. TGA and DTGA data and curves for ABS-APP and ABS-APP/MMT composites are shown in Table II and Figure 4.

ABS-APP composite degraded early than the pure ABS. APP decomposes and releases NH_3 between 284 and 400°C and experiences an earlier weight loss compared to ABS resin. Besides, the first maximum weight loss rate of ABS-APP composite is 27.23%/min at 439°C while ABS resin is 40.64%/min at 437°C, and the maximum weight loss rate temperatures in the first step are almost the same in the Table II and Figure 4. This result means that APP can decrease weight loss rate and delay the degradation process of ABS.

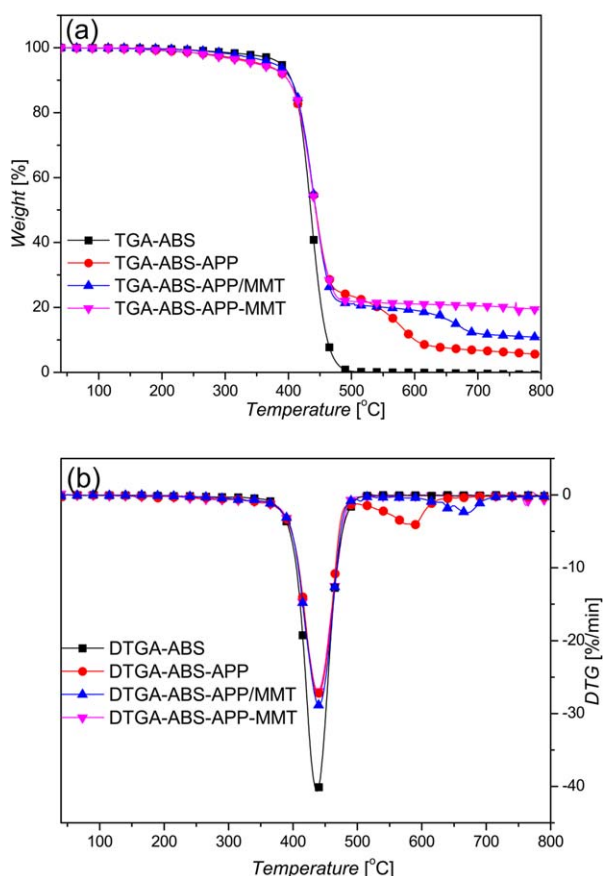


Figure 4. TGA (a) and DTGA (b) curves for ABS, ABS-APP, ABS-APP/MMT, ABS-APP-MMT composite. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

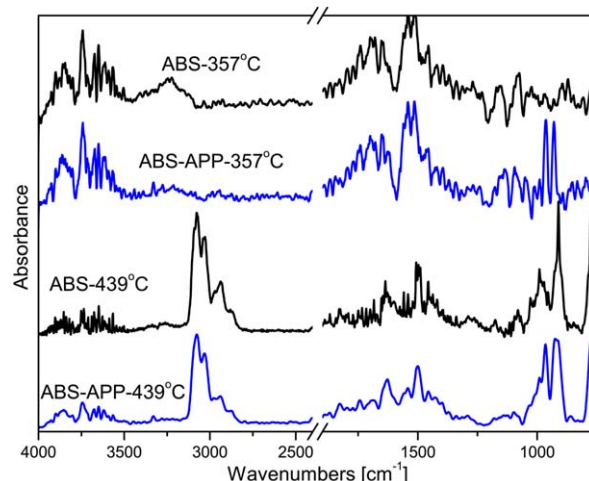


Figure 5. FTIR spectra of the gas degradation products of ABS-APP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

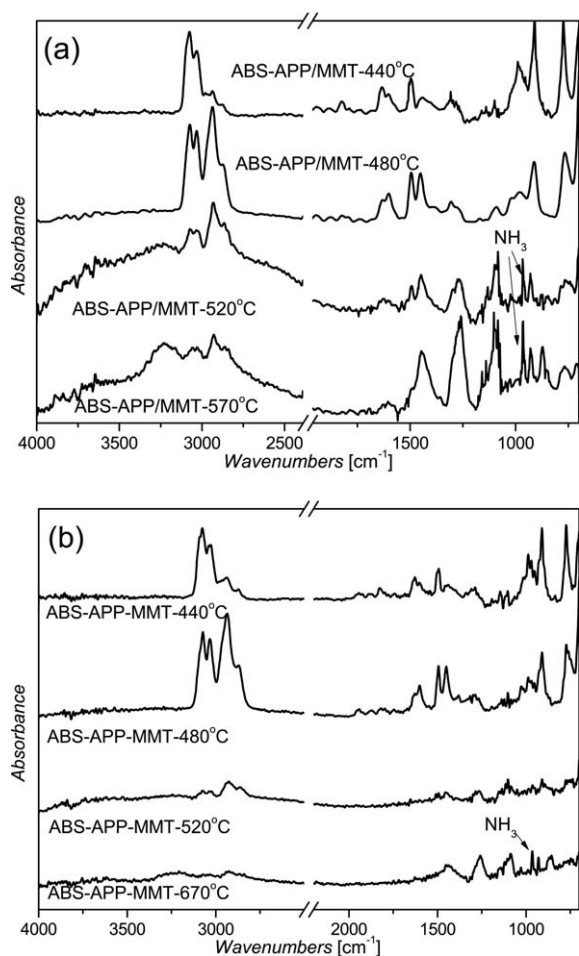


Figure 6. FTIR spectra of the gas degradation products of ABS-APP/MMT (a), ABS-APP/MMT (b).

It is clear to see that two-step degradation is found in ABS-APP and ABS-APP/MMT composites in Figure 4. ABS-APP losses about 75% weight between 350 and 480°C leaving a 5.56% residue. Comparing to the degradation process of APP, it is believed that the second step degradation is caused by the decomposition of APP. As shown in Figure 4, the first degradation step of ABS and ABS-APP/MMT composite is almost the same, and the ABS-APP/MMT is similar to the ABS-APP, which indicates that APP/MMT nanocomposite rarely effect on the initial decomposition temperature of ABS. However, the mixture of APP and MMT has no influence on the temperature on the maximum weight loss of ABS, and promotes the char formation.

A one-step decomposition of ABS-APP/MMT is found from 380 to 500°C under nitrogen leaving about 25% residues. Its initial decomposing temperature is near to the ABS-APP composites. A larger residue proves an enhanced thermal stability due to the barrier action of clay mineral layers.

Results from TGA and DTGA curves show that the combination of MMT with APP can significantly enhance the thermal stability of flame retarded ABS systems and enhance the char formation. It is believed that metal elements react with

O atoms to form M—O bonds which have strong complexation ability to OH and NH_4^+ , that can effectively catalyze dehydration, NH_3 deprivation, and phosphorylation process. These actions could form a more stable crosslink structure. With the decrease of the radius of M—O bond the catalytic effect grows stronger.²²

The FTIR spectra gas degradation products of ABS-APP are shown in Figure 5. There is no evident difference between the pyrolysis gases of ABS-APP composite and ABS resin, except for the NH_3 release. This result means that the loading of APP has no influence on the degradation progress of ABS and it is the same with APP/MMT nanocomposite of APP/MMT. It comes to a conclusion that APP works in the condensation-phase. However, during the degradation of ABS-APP/MMT and ABS-APP/MMT, NH_3 appears until 520°C and at 670°C respectively in Figure 6.

XPS results of the residues are shown in Table III and Figure 7. NH_3 could participate in the formation of char or is just buried behind the char layer, which will be confirmed further by XPS. NH_3 could be inhibited by the char layer and cannot be released. At the same time, NH_3 does not take part in the formation of char.

Apparently, N atom cannot be found neither in the ABS-APP and ABS-APP/MMT composite or the ABS-APP/MMT composite. The Si content in the exterior is more than that in the interior of ABS-APP/MMT. However, Si content in the exterior is equal with that in the interior of ABS-APP/MMT composite. The P content of the ABS-APP/MMT is similar to the ABS-APP/MMT composite, which confirmed that the MMT could migrate to the surface of the char. The MMT is helpful in joining the char formation with APP. This is the reason for the char residue of the later is higher than the former.

The char morphology of different composites obtained from muffle oven at 800°C in 10 min observed by SEM is shown in Figure 8.

SEM results exhibited that a relative continuous and compact char layer formed in the system with the addition of APP, but no perfect compact char layer could form during burning process. Serious holes were observed in the uneven surface indicating the limited flame retardancy of APP. In the micrographs of ABS-APP/MMT, the white webbed spherical regions are SiO_2 particles which could consolidate the char layer. APP/MMT nanocomposite is a better flame retardant than APP. Compared to ABS-APP/MMT, the char structure of ABS-APP/MMT in which MMT is added by physical mixing processes is totally different. A spongy structure which could increase the quantity of micro-vias and thus reduce the thermal conductivity of expansion layer to provide a better insulating effect was observed.

CONCLUSIONS

The thermal degradation of ABS and its constituent parts were studied first, and then the effects of APP, APP/MMT, and APP/MMT were also studied. The whole degradation progress could be regarded as the combination of the thermal degradation of PS

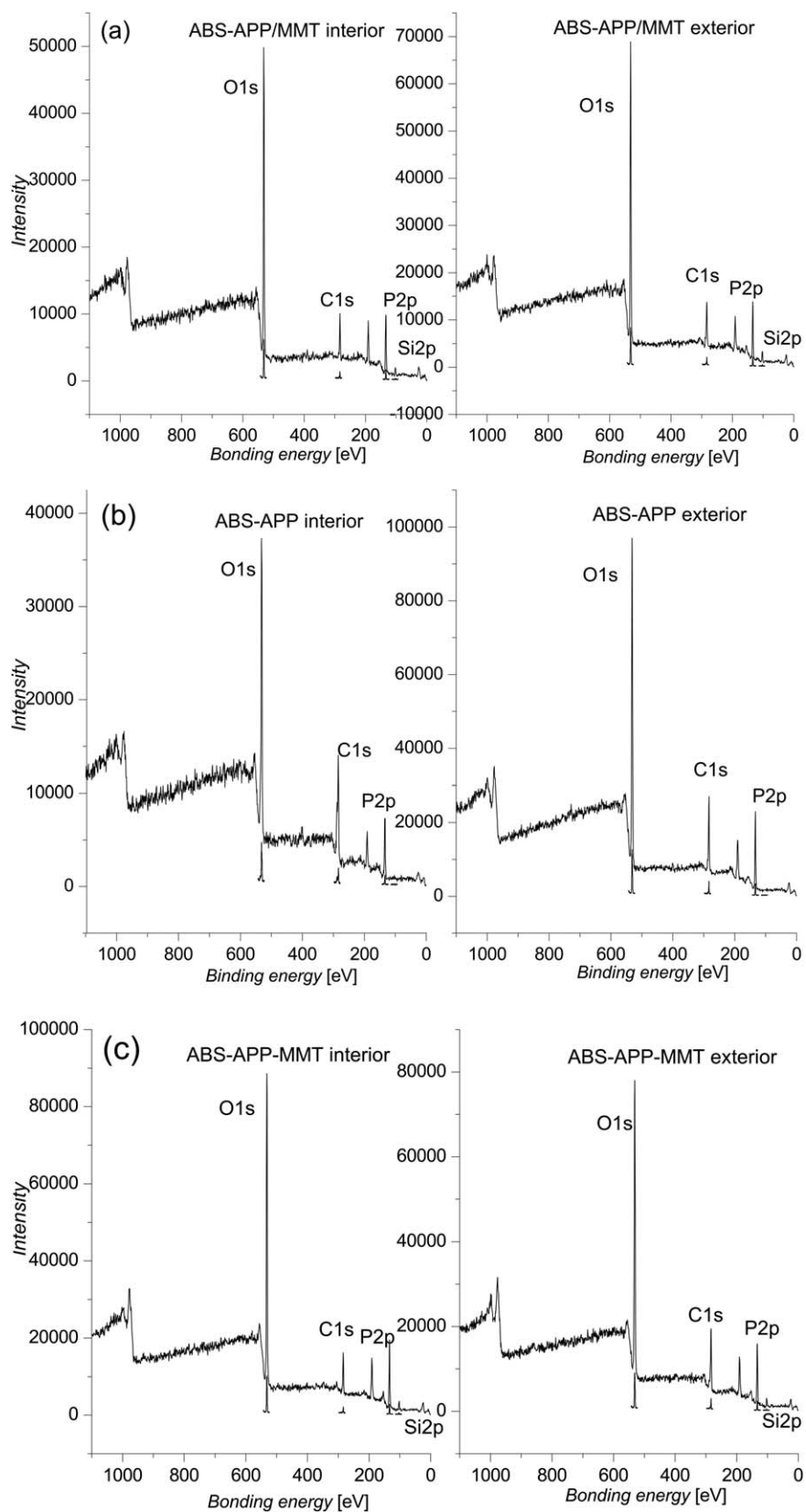
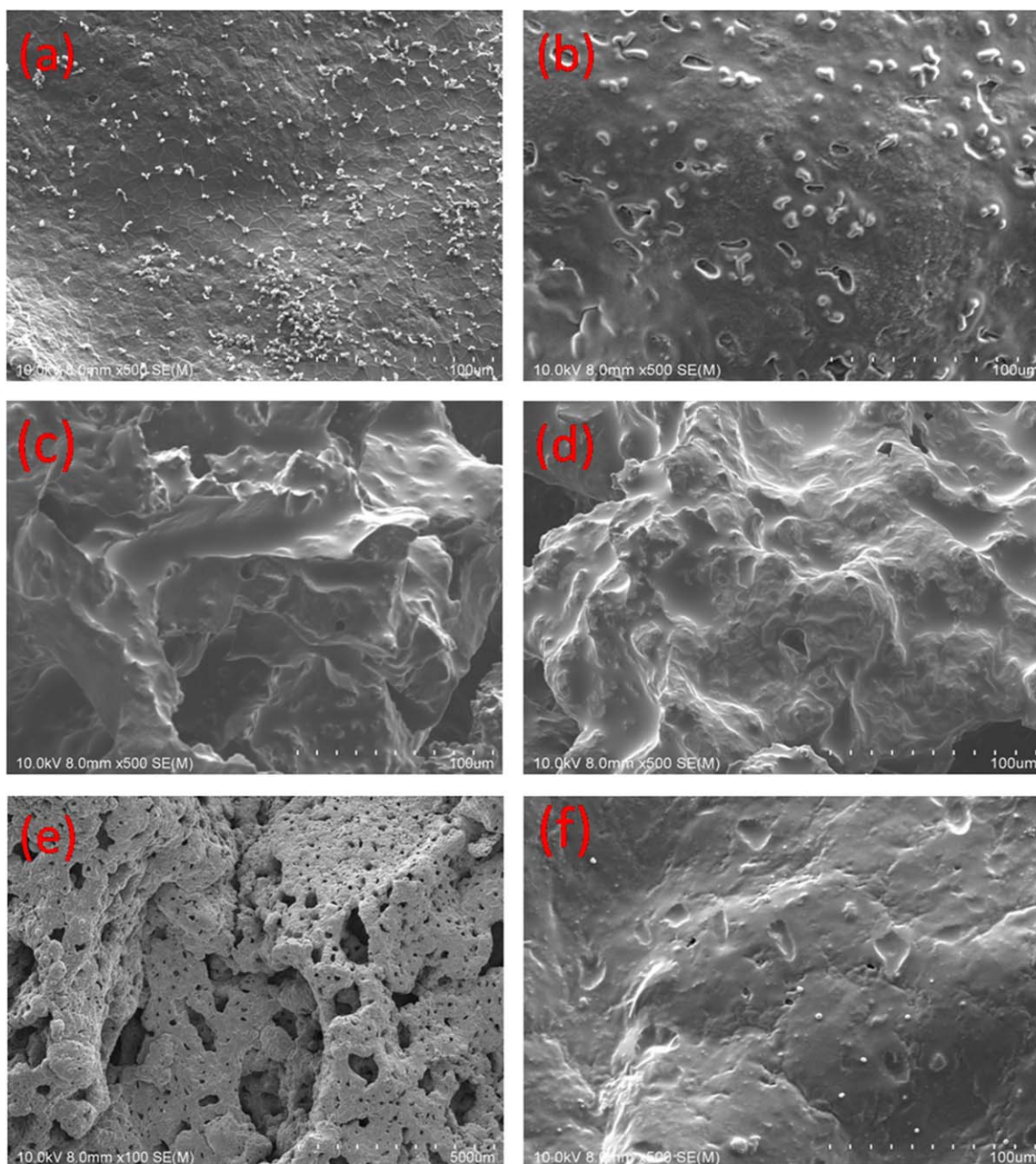


Figure 7. XPS result of ABS-APP/MMT (a), ABS-APP (b), and ABS-APP/MMT (c).

Table III. The Relative Atom Quantities of the Residues of ABS-APP, ABS-APP/MMT

Elements	ABS-APP		ABS-APP/MMT		ABS-APP/MMT	
	Exterior	Interior	Exterior	Interior	Exterior	Interior
C	27.5	42.49	222.23	17.75	26.77	16.97
O	57.46	46.61	60.82	64.38	56.87	64.70
Si	0	0	2.52	1.82	2.08	2.52
P	15.03	10.90	14.43	16.04	14.28	15.80

**Figure 8.** SEM micrographs of the residues: ABS-APP/MMT (a), ABS-APP (b), ABS-APP/MMT (c). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

and PB. The PB influenced the formation of char while PS influenced the maximum weight loss rate and its temperature. APP and APP/MMT have some flame retardancy on ABS and the later proved to be a better flame retardant for ABS. MMT catalyzes the dehydration, NH_3 deprivation, and phosphorylation process, so as to form a more stable crosslinked structure, and flame retardancy is improved when MMT is added by physical mixing processes. The gas evolution of APP (NH_3) is buried in the residue and released after ABS finishes its degradation process.

REFERENCES

- Owen, S. R.; Harper, J. F. *Polym. Degrad. Stab.* **1999**, *64*, 449.
- Joseph, V. R.; Barbara, C. L. *Fire Mater.* **1986**, *10*, 93.
- Lu, S. Y.; Hamerton, I. *Prog. Polym. Sci.* **2002**, *27*, 1661.
- Sergei, V. L.; Edward, D. W. *Polym. Int.* **2005**, *54*, 11.
- Imai, T.; Hamm, S.; Rothenbacher, K. P. *Environ. Sci. Technol.* **2003**, *37*, 652.
- Sergei, V. L.; Edward, D. W. *J. Fire Sci.* **2006**, *24*, 345.
- Zsuzsanna, C.; Marianne, B. *J. Anal. Appl. Pyrol.* **2008**, *81*, 218.
- Levchik, S. V. In Proceedings of the 17th Annual BCC Conference on Recent Advances in Flame Retardancy of Polymeric Materials, Stamford, CT, May 21–24, **2006**.
- Ma, H. Y.; Tong, L. F.; Xu, Z. B. *Appl. Clay Sci.* **2008**, *42*, 238.
- William, J. H.; Paul, T. W. *J. Anal. Appl. Pyrol.* **2007**, *79*, 375.
- Liu, S. M.; Ye, H.; Zhou, Y. S.; He, J. H.; Jiang, Z. *J. Polym. Degrad. Stab.* **2006**, *91*, 1808.
- Masanori, S.; Charles, A. W. *Polym. Degrad. Stab.* **1995**, *47*, 217.
- Deqi, Y.; Rongjie, Y. *Appl. Polym. Sci.* **2010**, *118*, 834.
- Wang, S. F.; Hu, Y.; Song, L.; Wang, Z. Z.; Chen, Z. Y. *Polym. Degrad. Stab.* **2002**, *27*, 423.
- Surianarayanan, M.; Vijayaraghavan, R.; Raghavan, K. V. *J. Polym. Sci.* **1998**, *36*, 2503.
- Camino, G.; Costa, L.; Trossarelli, L. *Polym. Degrad. Stab.* **1984**, *6*, 243.
- Camino, G.; Costa, L.; Trossarelli, L. *Polym. Degrad. Stab.* **1985**, *12*, 203.
- DongQuy, H.; Jinhwan, K.; BokNam, J. *Polym. Degrad. Stab.* **2008**, *93*, 2042.
- Gan, J.; Goodson, A.; Koening, R. A.; Everett, J. P. U.S. Pat. 1,998,013,618 (**1999**).
- Hong, S. H.; Yang, J. H.; Ryu, Y. S. U.S. Pat. 20,060,041,040, (**2006**).
- Hong, S. H.; Yang, J. H.; Ryu, Y. S.; Kim, T. U. U.S. Pat. 7,781,517 (**2010**).
- Lewin, M.; Endo, M. *Polym. Adv. Technol.* **2003**, *4*, 3.