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Flame Retardancies of Novel Organo-Phosphorus Flame Retardants Based on DOPO Derivatives When Applied to ABS

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Abstract: A series of novel organo-phosphorus flame retardants (FR) derived from 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) have been synthesized in order to investigate their flame retarding performances for acrylonitrile-butadiene-styrene copolymer (ABS). The success of synthesis was confirmed by ^{1}H and ^{31}P NMR. The flame retardancy performances evaluated by UL-94V test revealed that V-0 ratings are achieved when 27.5-30.0 wt% of FRs are added to the ABS/FR mixtures. The most dominating factors affecting the flame retardancy of phosphorus containing FR are the phosphorus (P) content in the mixture and the chemical structure of FR incorporated. It was found that 4.86-5.05 wt% P in the formulation is required to exhibit self-extinguishing ability when phosphinate or phophonate FRs are employed. On the other hand, no rating is obtained for phosphate type FR containing mixture even though higher amount of P, that is, 5.07 wt% is present in the mixture, indicating that oxidation state of the phosphorus element in FR is very important in governing the flame retardancy. The modes of actions of FRs in terms of gas versus condensed phase are also discussed. Thermogravimetric analysis (TGA) results showed that the FR containing compounds possess inferior thermal stability compared to neat ABS at the beginning of decomposition, suggesting that the thermal degradation of ABS is accelerated by the presence of FR at earlier stage of degradation and then hindered by the char formed at later stage of degradation.

Keywords: 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO), organo-phosphorus, flame retardant, acrylonitrile-butadiene-styrene copolymer (ABS), flame retardancy mechanism.

Introduction

Nowadays, various polymeric materials are being used in ever more areas and, in some applications, are required to be utilized under conditions demanding more environmental concerns. However, fire hazards associated with the uses of these polymeric materials, which cause the loss of life and property, are of particular concerns among government regulatory bodies, consumers, and manufacturers alike.[1-3] The use of flame retardants to reduce the combustibility of polymer and the resulting reduction of smoke or toxic fume production become a pivotal part of the development and application of new materials based on polymers. The well-known flame retardants (FRs) which are known to be very effective regarding to flame retardancy only are halogen-containing compounds, for examples, decabromodiphenyl oxide, tetrabromobisphenol, and *etc*. However, the methods to improve the flame-retarding property by employing halogen-containing compounds lead to environmental concerns. Therefore, organo-phosphorus compounds which are halogen-free have been accepted as one of the most promising candidates that can replace the halogen based FRs.[4-11] Among various organo-phosphorus FRs, the ring structured FRs based on 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) have been studied in most extensive manner.[12-16] They are found to generate less toxic gases and corrosive smoke. However, these studies mainly focused on modifying the epoxy backbone structure by incorporating them in an attempt to improve thermal and flame retarding properties. Furthermore, the derivatives of DOPO employed contains relatively low phosphorus (P) content inherently (14.33 wt% on the P element basis) so they cannot pass UL-94 test, which is a most commonly employed test method to evaluate the flame retardancy of non-charrable and highly flammable polymers such as acrylonitrile-butadiene-styrene copolymer (ABS) and polyolefins for the applications to electronics and electric devices.

ABS has a good balance among various physical properties such as processability, toughness and chemical resistance, and impact resistance through the balance of composition of co-monomer units and excellent appearance of its molded products. Therefore, it is widely used in many applications such as appliances and consumer electronics, automobiles,

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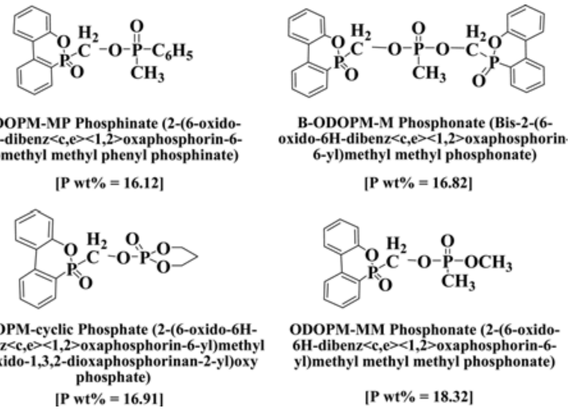


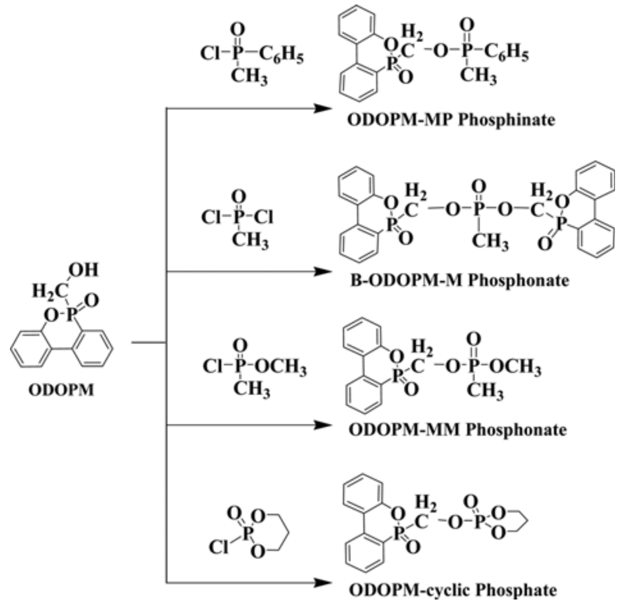
Figure 1. Chemical structures and abbreviations of synthesized FRs.

tools, toys, and so on. Definitely, for ABS to be used for such applications, the impartment of flame retardance is a must. In this study, a series of novel organo-phosphorus FRs were synthesized from DOPO in an attempt to obtain higher P content compared to DOPO. Furthermore, synthesized FRs are expected to leave greater amounts of charred residues. From that aspect, meaningful contribution from condensed mode of retardancy action is expected. Three different novel FRs, phosphinate, phosphonate, and phosphate, are employed in this study. They have almost the same P content but are different in chemical structures. Therefore, it is expected that they are very adequate to investigate the effect of P content as well as the influence of the oxidation state of the phosphorus on the fire retardancies of ABS/FR mixtures. The chemical structures and abbreviation of synthesized FRs are presented in Figure 1.

Experimental

Materials. Paraformaldehyde, dimethyl methylphosphonate, phosphorus oxychloride, methanol, dichlorophenylphosphine, 1,3-propandiol, and methyl iodide of reagent grades were purchased from Aldrich. Xylene, thionyl chloride, methylene chloride, pyridine, acetonitrile, hexane, methanol, chloroform, triethylamine, and diethyl ether were purchased from Samchun Chemical Company, Korea. 9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) was purchased from Tokyo Chemical Industry Co., Ltd., Japan. Acrylonitrile-Butadiene-Styrene copolymer (ABS) of a commercial grade was provided by the Cheil Industries, Korea. 2-(6-Oxido-6H-dibenz <c,e><1,2> oxaphosphorin-6-yl) methanol (ODOPM), 2-chloro-1,3,2-dioxaphosphorinane 2-oxide, methylphosphonic dichloride, methyl methylphosphonochloridate, and phenyl methyl phosphinyl chloride as the starting materials for synthesizing the target FRs were prepared in our laboratory as described below.

2-(6-Oxido-6H-dibenz <c,e><1,2> oxaphosphorin-6-yl) methanol (ODOPM) was prepared by reacting DOPO with paraformaldehyde following the procedure reported in the literature.[15]



Scheme I. Synthesis scheme for four different organo-phosphorus FRs employed in this study.

2-Chloro-1,3,2-dioxaphosphorinane 2-oxide was synthesized by reacting phosphorus oxychloride with 1,3-propanediol as described in the literatures.[17,18]

Methylphosphonic dichloride, methyl methylphosphonochloridate, and phenyl methyl phosphinyl chloride were prepared by adapting the synthesis methods mentioned in our previous work.[19]

Synthesis of Organo-Phosphorus Flame Retardants (FRs). Four different novel organo-phosphorus FRs shown in Figure 1 were synthesized according to the synthesis scheme presented in Scheme I.

ODOPM-MP Phosphinate, B-ODOPM-M Phosphonate, ODOPM-MM Phosphonate, and ODOPM-cyclic Phosphate were synthesized by reacting ODOPM and phenyl methyl phosphinyl chloride, methylphosphonic dichloride, methyl methylphosphonochloridate, and 2-chloro-1,3,2-dioxaphosphorinane 2-oxide, respectively. The products in high purity were obtained. ^{1}H and ^{31}P NMR were employed to prove the success of synthesis and the results are given in Figure 2 and summarized in Table I.

Measurements and Sample Preparation.

Spectroscopic Analysis: ^{1}H and ^{31}P NMR were performed on a Varian Unity Inova 500NB spectrometer by using $CDCl_3$ and DMSO-d_6 as solvents and tetramethylsilane (TMS) as a reference. The chemical shift of ^{31}P NMR spectra are relative to the external standard of 85% H_3PO_4.

Thermogravimetric Analysis: TGA was performed on 2 to 10 mg samples under nitrogen and air atmospheres at a heating rate of 5, 10, 20, and 40 °C/min using a TGA 2050 thermogravimetric analyzer.

Sample Preparation for UL-94 Test: Mixture of a syn-

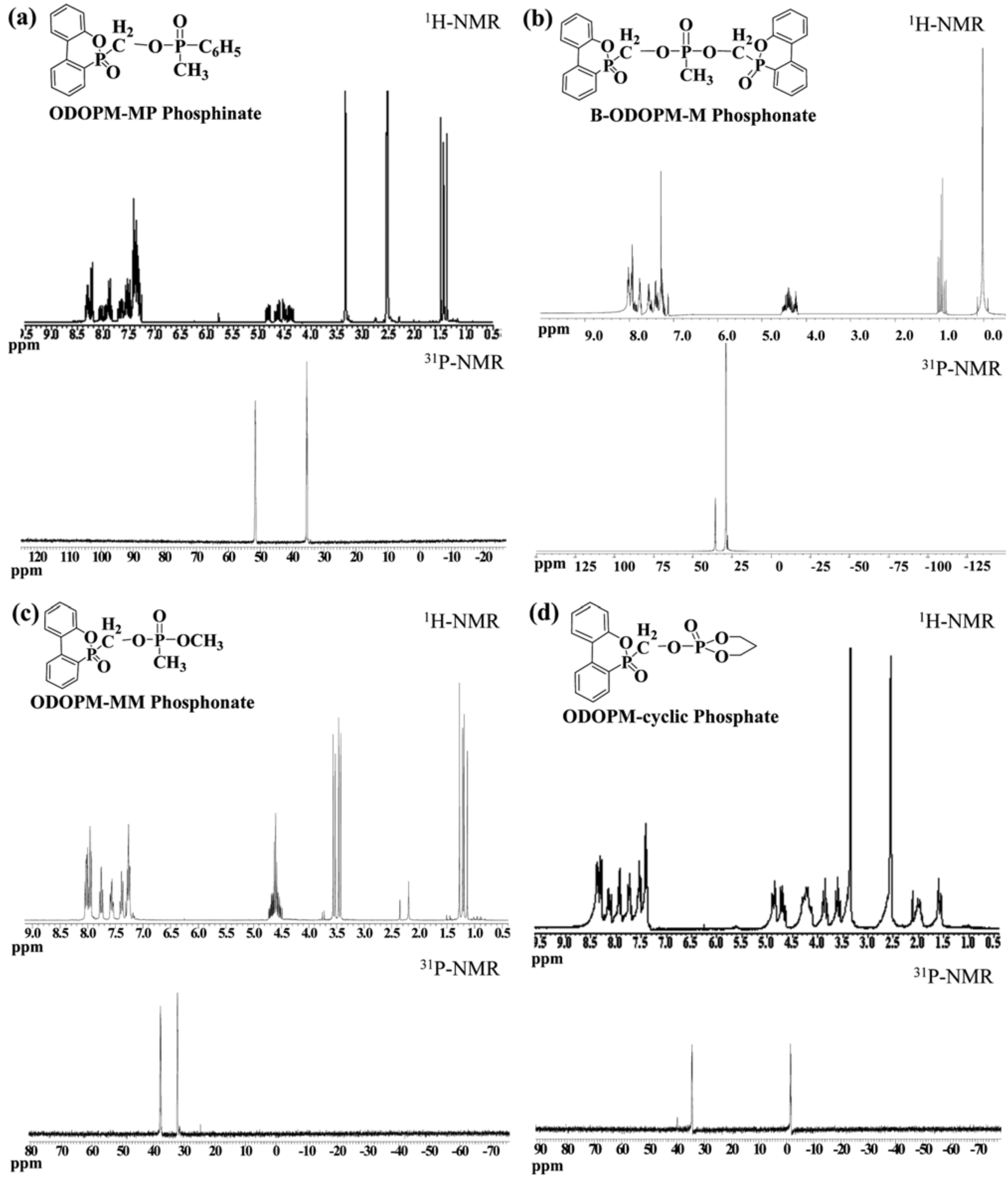


Figure 2. ^{1}H and ^{31}P NMR spectra of ODOPM-MP phosphinate (a), B-ODOPM-M phosphonate (b), ODOPM-MM phosphonate (c), and ODOPM-cyclic phosphate (d).

thesized flame retardant with ABS at the designated composition was processed in a Haake PolyDrive mixer with 60 rpm for 7 min at 230 °C. The compounded mixtures were compression molded at 220 °C for 7 min in a 30 ton press to obtain test bars.

UL-94 Measurement: Fire retardancy performance was evaluated according to the testing procedure of FMVSS 302/

Table I. The Chemical Shifts and Splitting Patterns of NMR Spectra for the Compounds Employed in this Study

FR	^{1}H NMR	^{31}P NMR
ODOPM	7.22-8.25 (m, 8H), 5.59 (t, 1H), 4.02-4.28 (m, 2H)	39.90 (s)
ODOPM-MP Phosphinate	7.30-8.35 (m, 13H), 4.34-4.88 (m, 2H), 1.38-1.49 (q, 3H)	35.35 (s), 51.52 (s)
B-ODOPM-M Phosphonate	7.18-8.10 (m, 16H), 4.19-4.55 (m, 4H), 0.84-1.04 (m, 3H)	35.71 (s), 28.89 (s)
ODOPM-MM Phosphonate	7.24-8.08 (m, 8H), 4.50-4.72 (m, 2H), 3.42-3.58 (q, 3H), 1.12-1.28 (q, 3H)	32.09 (s), 37.58 (s)
ODOPM-Cyclic Phosphate	7.40-8.40 (m, 8H), 4.62-4.92 (m, 2H), 4.11-4.35 (m, 2H), 3.80-3.90 (m, 1H), 3.55-3.65 (m, 1H), 1.92-2.08 (m, 1H), 1.52-1.64 (m, 1H)	34.38 (s), -1.63 (s)

ZSO 3975 with test specimen bars of 127 mm in length, 12.7 mm in width, and about 3.2 mm in thickness.

Results and Discussion

Flame Retardancy and Mode of Action. Lorenzetti *et al.*[20] studied the effect of P oxidation state on the gas and/or solid phase action of flame retarded polyurethane foams. The results showed that phosphorus flame retardants showing decomposition/volatilization at temperatures lower than those of neat polymer act in the gas phase irrespective of their valency. It was also reported that the relative predominance of different mechanisms depends on the chemical structure of the polymer.[21] In this study, three different FRs, ODOPM-MP phosphinate, B-ODOPM-M phosphonate, and ODOPM-cyclic phosphate whose P contents are almost the same but differs in the P oxidation state are employed. One more FR, ODOPM-MM phosphonate, is employed to investigate the effect of P content. All FRs are applied to ABS, which is non-charrable polymer, to minimize the contribution of condensed mode of action.

It was reported that, with increasing the oxidation state of the phosphorus, additional charring is observed and the release of phosphorus-containing volatiles diminishes whereas the flame inhibition decreases.[20,22,23] The relative amount of phosphorus-containing volatiles escaped from combusting medium was reported to be abundant in an order: phosphate < phosphonate < phosphinate, indicating that gas phase action increases with decreasing the oxidation state of the phosphorus. Our results shown in Figure 3(a) are exactly agreed with those assertions. Even though very large amount of charred residue are observed for ODOPM-cyclic phosphate, almost no residues are noticeable for other FRs.

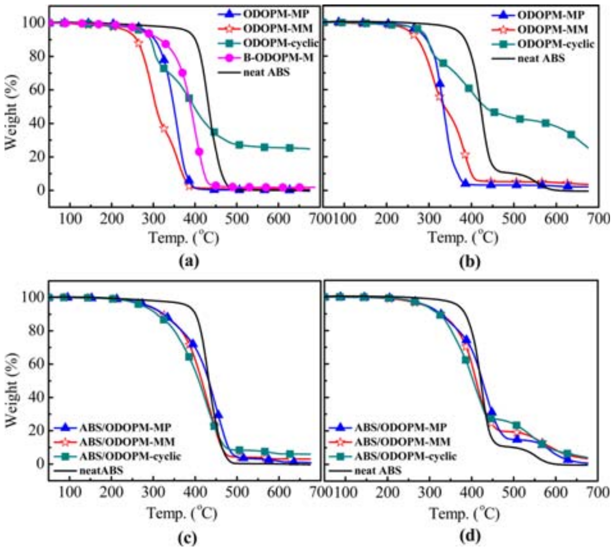


Figure 3. TGA thermograms of neat ABS, pure FRs, and the 70/30 (wt/wt) ABS/FR mixtures under nitrogen (a, c) and air (b, d).

Now, these FRs were incorporated into ABS and their flame retardancies were evaluated. The minimum amount of FR loading to give UL-94 V-0 rating was determined for each ABS/FR mixture and the results are presented in Table II. No rating is recorded for ODOPM-cyclic phosphate containing mixture although 30 wt% FR loading can obtain V-0 rating in case of ODOPM-MP phosphinate and B-ODOPM-M phosphonate containing mixtures. The P content in the mixture is 16.12 and 16.82 wt% for ODOPM-MP phosphinate and B-ODOPM-M phosphonate containing mixtures, respectively, while this value is 16.93 wt% for ODOPM-cyclic phosphate containing mixture. The P content of ODOPM-cyclic phosphate is the greatest among three FRs. In other words, ODOPM-MP phosphinate and B-ODOPM-M phosphonate exhibit more outstanding flame retarding performance even though the amount of P content is the greatest for the

Table II. UL-94 Results for the Mixtures of ABS with Various Organo-Phosphorus FRs

FR	wt% of P in FR	ABS/FR (wt/wt)	UL-94	%P in the Mixture at a Given FR Loading
ODOPM-MP Phosphinate	16.12	70.0 / 30.0	V-0	4.86
B-ODOPM-M Phosphonate	16.82	70.0 / 30.0	V-0	5.05
ODOPM-Cyclic Phosphate	16.91	70.0 / 30.0	No rating	5.07
ODOPM-MM Phosphonate	18.32	72.5 / 27.5	V-0	5.03

mixture containing ODOPM-cyclic phosphate. ODOPM-MM phosphonate gives V-0 rating at 27.5 wt% loading while B-ODOPM-M phosphonate does the same rating at 30 wt% loading, indicating that lower amount of FR loading is needed to obtain the same flame retardancy for the former FRs if the P oxidation state is identical. Therefore, it can be concluded from these results that the flame retarding effect of a FR is strongly dependent on not only the P content of FR incorporated but also the chemical structure of FR.

The modes of action of DOPO flame retandancy were studied extensively and discussed thoroughly in numerous literatures.[14,22,24-27] DOPO releases the stable dibenzofuran under thermal decomposition and then, phosphorus-containing PO radical is formed. Schafer *et al.*[14] studied the properties of flame-retardant epoxy resins based on DOPO and reported that the significant amounts of PO radicals are released from the DOPO-containing epoxy. The PO radicals which are the active species during the combustion process interact with H and OH radicals existing in the gaseous phase of the fire. Moreover, Braun *et al.*[22] reported in their comparable evaluation of epoxy resins containing different phosphorus compounds that the flame inhibition effect decreases with increasing oxidation and vanishes for phosphate, which is in very good agreement with our results. In the meanwhile, ABS is non-charrable polymer and is very difficult to achieve effective flame retardancy by the use of condensed phase working FR.[5,6,19] The charring effect should be the strongest for phosphate among three phosphorus species employed in this study as clearly seen from the TGA results presented in Figure 3. Lower mass loss and higher residual mass are observed for both phosphate FR itself and the FR containing ABS mixture over all temperature. Therefore, it is concluded that the superior flame retardancy of phosphinate and phosphonate to phosphate is mainly resulted from the gas phase mode of action and very little contribution from the condensed phase mode of action is expected for the ABS/FR mixture. The char layer formed during the degradation of ODOPM-cyclic phosphate containing ABS is not enough to play an efficient insulating protective layer which prevents the transfer of combustible gases to the surface of the compound.

It is worthy to note in Table II that V-0 ratings are obtained for the mixtures containing 4.86-5.05 wt% P in the formulation. It was found from our previous study that at least 4 wt% of P content is needed to achieve UL-94 V-0 rating for the mixtures of non-charrable polymers such as ABS and EVA with various organo-phosphorus compounds.[28] The results found in this study are in good agreements with our previous study.

Thermal Degradation Behaviors. The TGA results for neat ODOPM-MP phosphinate, ODOPM-MM phosphonate, and ODOPM-cyclic phosphate, and their mixtures with ABS are shown in Figure 3. It can be seen that the ABS/FR mixtures under nitrogen display a major mass loss *via* a single-step decomposition of approximately 90-95 wt% between 250 and 480 °C (Figure 3(c)). In air environment, more complicated degradation behaviors are observed (Figure 3(d)). A major mass loss (approximately 70-85 wt%) at 240-450 °C is followed by the continued mass decrease at a reduced rate at 450-550 °C. The degradation of the second step is believed to be related to the residual char formation during oxidative degradation. The continued mass loss above 550 °C belongs to furthermore degradation of the char layer (Table III). In addition, TGA results clearly show that the mixtures containing FR possesses less thermal stability than neat ABS at the early stage of decomposition, indicating that phosphorus containing volatiles are evaporated into the flame zone. It is worthy to note that, at the first stage of oxidative degradation under both nitrogen and air atmospheres, the decomposition takes place at lower temperatures for phosphate containing mixture. On the contrary, ABS/ODOPM-cyclic phosphate mixture leaves slightly higher residual char compared to ABS/ODOPM-MM phosphonate and ABS/ODOPM-MP phosphinate mixtures. These results again imply that the phosphate evaporates at lower temperatures and leaves higher charred residue at higher temperatures but contributes less to the flame retardancy, meaning that the main flame retardancy is governed by the gas phase action of mode rather than the condensed action of mode. The same observation has been found for the epoxy resins containing different types of organo-phosphorus compounds.[22]

In order to understand more clearly the effect of FR addi-

Table III. Summary of Thermal Stability Parameters for the TGA Results Presented in Figures 3 and 4

Samples	T_{onset} (°C)		T_{10} (°C)		Residue at 500 °C (%)		Residue at 650 °C (%)	
	N_2	Air	N_2	Air	N_2	Air	N_2	Air
Neat ABS	**355**	**350**	**402**	**384**	**0.3**	**10.0**	**0.0**	**0.0**
ODOPM-MP Phosphinate	255	252	304	292	0.4	3.2	0.2	2.3
ODOPM-MM Phosphonate	211	230	263	275	0.8	5.5	0.8	3.9
ODOPM-Cyclic Phosphate	250	260	294	293	28.1	43.2	25.3	30.5
70/30 ABS/ODOPM-MP Phosphinate	256	239	324	325	4.1	14.9	0.9	1.6
70/30 ABS/ODOPM-MM Phosphonate	250	240	323	326	4.2	19.3	3.2	4.3
70/30 ABS/ODOPM-Cyclic Phosphate	247	252	309	322	8.5	24.2	6.1	5.4

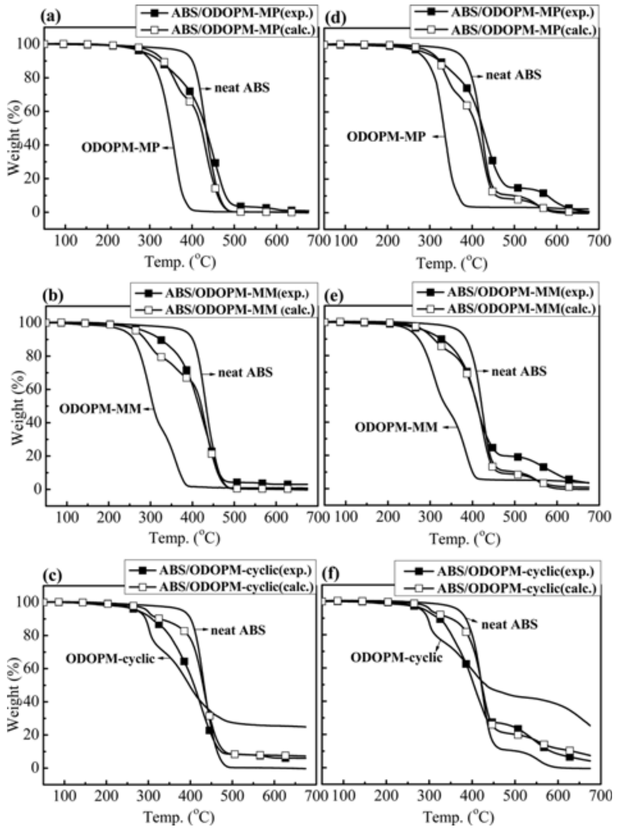


Figure 4. Comparison between experimentally determined TGA results and calculated values by adapting the additive rule for the 70/30 (wt/wt) ABS/FR mixtures under nitrogen (a, b, c) and air (d, e, f).

tion on the thermal degradation behaviors, experimentally observed TGA data are compared with TGA values calculated by adopting an additive rule. The calculated data was composed by combining the TGA data of the components comprising of the mixture.[29-31] The results obtained are presented in Figure 4. The amounts of charred residues experimentally observed are higher than those values calculated for both phosphinate and phosphonate containing mixtures all over the temperatures whilst the opposite results are observed at lower degradation temperatures for phosphate containing mixture. This again indicates that the condensed mode of action from DOPO based FRs contributes very scarcely to the flame inhibition of non-charrable ABS.

The kinetic parameters of thermal degradation can be used to evaluate the thermal stability. The activation energy (E) is calculated using dynamic TGA experiments measured at various heating rates by adopting the modified Ozawa's method as follows.[32,33]

$$\frac{d(\log r)}{d(1/T)} = -0.4567\frac{E}{R}$$

where r is the heating rate, T corresponds to the temperature giving the same heat loss at different heating rate, E is the activation energy of the decomposition reaction, and R is the gas constant. According to above equation, the activation energy can then be determined from the plot of log r *vs.* $1/T$ at a given mass loss. TGA experiments at four different heat rates of 5, 10, 20, and 40 ºC/min were carried out and the experimental results and the kinetic parameters obtained therein are given in Figure 5 and summarized in Table IV. It is found that the E values of ABS/FR mixtures are lower than that of neat ABS at low mass loss and higher at high mass loss. This suggests that the thermal degradation of ABS is accelerated by the presence of FR at earlier stage of degradation and then hindered by the char formed at later stage of degradation.

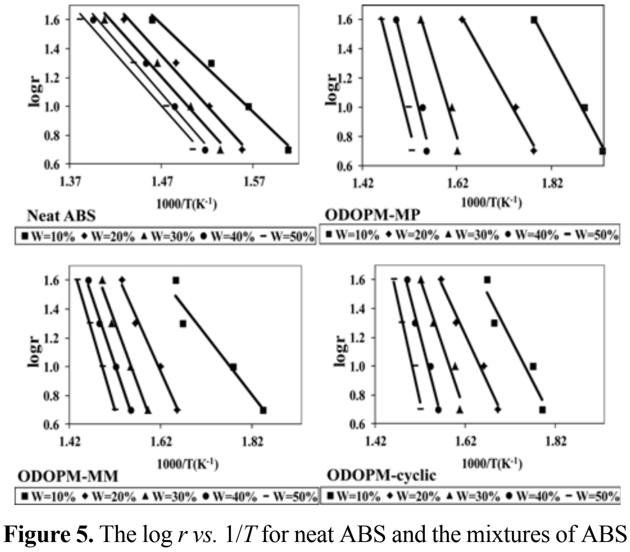


Figure 5. The log r *vs.* $1/T$ for neat ABS and the mixtures of ABS with three different FRs at various mass losses (W: mass loss).

Table IV. Calculated *E* for Neat ABS and Various ABS/FR Mixtures at Different Heating Rates Under Air

Mass Loss	Activation Energy (kJ/mol) of Various 70/30 ABS/FR Mixtures			
	ODOPM-MP Phosphinate	ODOPM-MM Phosphonate	ODOPM-Cyclic Phosphate	**Neat ABS**
0.1	110.3	74.6	110.2	**111.3**
0.2	105.5	129.4	123.1	**127.2**
0.3	193.6	157.1	170.8	**129.1**
0.4	231.9	172.3	218.4	**134.2**
0.5	231.2	197.1	262.9	**131.3**

Conclusions

A series of novel organo-phosphorus flame retardants (FR) derived from DOPO have been synthesized in an attempt to obtain higher P content compared to DOPO and investigate their flame retarding performances for ABS. It was found that 27.5-30.0 wt% of FRs are needed to achieve UL-94V V-0 ratings for the ABS/FR mixtures and 4.86-5.05 wt% P in the formulation is required to exhibit self-extinguishing ability when phosphinate or phophonate FRs are employed. On the other hand, no rating is obtained for phosphate type FR containing mixture even though higher amount of P, that is, 5.07 wt% is present in the mixture, indicating that oxidation state of the phosphorus element in FR is very important in governing the flame retardancy. From these results, it is concluded that, for ABS, that P content of FR is one of the most important factors governing the effectiveness of flame retardancy and phosphinate and phosphonate FRs exhibit more outstanding performance as flame retardant than phosphate FR, indicating that condensed mode of retardancy action from phosphate contributes very little to the combustion of highly flammable and non-charrable polymer such as ABS. It becomes clear that ABS is very difficult to be flame retarded by employing a condensed phase working FR and effective retardancy is achieved by employing a gas phase working FR.

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