

금속-인계 친환경 난연제를 적용한 Poly(1,4-cyclohexylene dimethylene terephthalate)의 난연성 향상 연구

안해연 · 강수정 · Hai Vothi · 이평찬* · 김진환[†]

성균관대학교 고분자공학과, *자동차부품연구원 자동차소재융합시스템 연구본부
(2016년 3월 16일 접수, 2016년 4월 27일 수정, 2016년 4월 28일 채택)

Halogen Free Metal Phosphinate for Flame Retardancy Enhancement of Poly(1,4-cyclohexylene dimethylene terephthalate)

Haiyan An, Soo-Jung Kang, Hai Vothi, Pyoung-Chan Lee*, and Jinhwan Kim[†]

Department of Polymer Science and Engineering, Sungkyunkwan University, Suwon, Gyeonggi-do 16419, Korea

*Automotive Materials Convergence & System R&D Division, Korea Automotive Technology Institute,
Cheonan, Chungnam-do 31214, Korea

(Received March 27, 2016; Revised March 30, 2016; Accepted April 7, 2016)

초록: Poly(1,4-cyclohexylene dimethylene terephthalate) (PCT)의 열분해와 PCT와 AlPi 혼합물의 난연성 연구를 위해 난연제로는 알루미늄 포스피네이트(AlPi)를 사용하였고, 열중량분석기와 FTIR를 이용하여 다양한 조성의 열분해 현상과 화학적 분석을 하였다. AlPi는 주로 기상형태로 난연성을 나타내었고, 적은 범위에서 고체상 응축으로 난연성에 기여하였다. AlPi를 적용한 혼합물에서 UL-94 시험법에 의한 난연성 평가에서 V-0를 얻었고, 콘 칼로리미터 실험에서 열방출량이 눈에 띄게 감소하였음을 확인할 수 있었다.

Abstract: The thermal decomposition and flame inhibition behaviors of poly(1,4-cyclohexylene dimethylene terephthalate) (PCT) with aluminum phosphinate as flame retardant were investigated. The thermal decomposition behaviors of various formulations were studied using thermogravimetric analysis, and chemical analysis was carried out for the residues using FTIR. We found that the action of AlPi was based mainly on the flame inhibition effect in the gas-phase and showed only a limited contribution from the condensed-phase mode of action through the formation of aluminum phosphate in the solid state. A UL-94 V-0 rating was achieved by using a PCT formulation containing 11 phr of AlPi, and a noticeable reduction in the cone calorimeter experiment was observed in this sample.

Keywords: flame retardant, poly(1,4-cyclohexylene dimethylene terephthalate), aluminum phosphinate, decomposition pathway.

Introduction

Aromatic polyesters such as poly(ethylene terephthalate) (PET) and poly(1,4-butylene terephthalate) (PBT) are made by reacting terephthalic acid with an aliphatic diol. These materials are widely used as engineering plastics in electrical and electronic applications because of their good heat and solvent resistance and their excellent processability. Recently,

another type of aromatic polyester, poly(1,4-cyclohexylene dimethylene terephthalate) (PCT), has received much attention as an engineering plastic because it has higher heat resistance and hygrothermal stability than PET and PBT. The crystalline melting temperatures (T_m) of PBT, PET, and PCT, as determined by differential scanning calorimetry (DSC), were found to be 227, 243, and 289 °C, respectively. PCT has the highest T_m and is suitable for high-temperature electrical and electronic applications. For example, the high T_m and excellent hygrothermal stability of PCT resulting from its inherent cycloaliphatic structural unit render it useful as a material for LED reflectors (the molded part of LED devices assembled in

[†]To whom correspondence should be addressed.
E-mail: jhkim@skku.edu

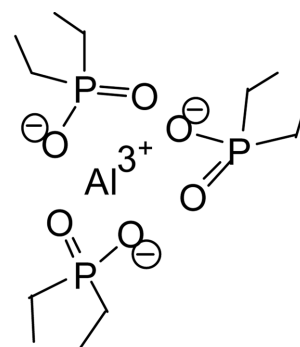
©2016 The Polymer Society of Korea. All rights reserved.

LED TVs and high power lighting fixtures).^{1,2}

Flame retardancy is essential when PCT is used in electrical and electronic applications. However, there are no reports in the literature on this subject. Only two partially relevant investigations can be found in the literature. Bostic *et al.* applied tris(2,3-dibromopropyl) phosphate and triphenyl phosphate flame retardants (FRs) to a series of PCT fabrics.³ They concluded that char formation in fabrics treated with FRs was affected by competing scaffolding and inhibition effects, and that the percentage of phosphorus remaining on the fabrics affected their flame retardancy. In a patent registered by Branscome,⁴ a combination of poly(dibromophenylene oxide) and antimony oxide was employed as a FR system for flame retardant reinforced PCT. However, it is now well known that halogen containing compounds cause environmental problems.⁵ A great deal of works has been conducted to develop environmentally friendly FRs that can replace halogen compounds. Among the many FRs developed so far, phosphorus-based FRs are considered the most promising.⁶⁻¹⁰ The two investigations mentioned above employed halogen FRs. Therefore, there is a great need to develop halogen-free FRs that can be used with PCT, especially in the LED industry, which is growing very rapidly. This is the main theme of the present work.

Very limited numbers of organo-phosphorus FRs can be utilized for improving the fire retardant behavior of engineering plastics that are processable at elevated temperatures. As noted in the previous comparison of T_m , PCT is processed at much higher temperatures than PET and PBT. Thus, many of the well-known organo-phosphorus compounds cannot be employed as FRs for PCT because of their relatively low decomposition temperatures.¹⁰⁻¹² In contrast, metal phosphinates may be suitable for this purpose because their decomposition temperatures are very high.¹³ Among the various metal phosphinates, aluminum diethylphosphinate (AlPi) has been the most intensively investigated for fire retardancy.¹⁴⁻¹⁶ Although its effectiveness as a FR in glass-fiber reinforced PBT and polyamide is well established,^{14,16,17} its use in PCT has not been investigated.

In the present work, we investigated the pyrolysis and fire behaviors of PCT when employing AlPi as a flame retardant (FR). The chemical structure of AlPi is given in Figure 1. The fire behavior of PBT was also investigated for comparison. The flame retarding performances of various formulations were examined mainly by means of the Underwriters Laboratories (UL-94) test, cone calorimetry, and thermogravimetric analysis



Aluminium diethylphosphinate
(AlPi)

Figure 1. Chemical structure of AlPi.

(TGA). Decomposition pathways were also postulated by interpreting the experimental results.

Experimental

Materials. PCT (Puratan®) with an intrinsic viscosity (IV) of 0.65 was provided by the SK Chemical Company, Korea. PBT (VB-5150G) was supplied by Cheil Industries, Korea. AlPi (Exolit OP1240) was purchased from Clariant, Germany. All the polymers and additives were dried overnight in a vacuum oven at 60 °C before mixing the designated formulation.

Sample Preparation. Mixtures of PCT and AlPi at various designated compositions were processed in a Haake Poly Drive mixer at 60 rpm and at 290 °C for 7 min. A processing temperature of 235 °C was employed for the PBT mixtures. Four different compositions were prepared of PCT+AlPi mixtures, and four compositions were prepared of PBT+AlPi mixtures for comparison.

Thermogravimetric Analysis. Thermogravimetric analysis (TGA) was carried out using a TA Q50 thermogravimetric analyzer on samples of 7-10 mg under a nitrogen atmosphere at a heating rate of 10 °C/min.

Differential scanning calorimetry (DSC) was carried out using a TA Q20 on about 10 mg samples under a nitrogen atmosphere at a heating rate of 10 °C/min.

UL-94 Measurement. Fire retardancy performance was evaluated according to the testing procedure of FMVSS 302/ZSO 3975 with test specimen bars 127 mm long, 13.0 mm wide, and 3.2 mm thick.

Cone Calorimetry. Fire risk was determined in terms of

heat release rate (HRR) and total heat release (THR) by using a cone calorimeter (Fire Test Technology, East Grinstead, UK) according to ISO 5660. Specimen plates 100 mm long, 100 mm wide and 3 mm thick were placed in aluminum trays. The samples were irradiated at 50 kW/m². Each material was tested at least twice.

Spectroscopic Analysis with FTIR for Residue Collected after Combustion. Char residues collected after combustion in a furnace (Barnstead Thermolyne Furnace 1300) at designated temperatures were analyzed by using an FTIR spectrometer (Bruker IFS-66/S). Spectra with an optical resolution of 0.1 cm⁻¹ were taken for the specimens prepared by using KBr pellets.

Results and Discussion

Thermal Decomposition Behaviors of PCT+AlPi Mixtures. Figure 2 shows TGA results for PCT and its mixture with AlPi from 30 to 600 °C under a nitrogen atmosphere. The TGA data shown in Figure 2 are summarized in Table 1. PBT and its mixtures with AlPi were also tested for comparison. Both PCT and PBT decomposed in a sharp, single decomposition step. The decomposition of PCT took place between 375 and 435 °C, and about 98 wt% of the total mass was lost, leaving only 2 wt% of solid charred residue at 600 °C. As addressed by other researchers,^{13–16} PBT also showed a sharp, single decomposition in the temperature range between 350 and 425 °C. PBT lost about 94 wt% of its total mass, leaving only 6 wt%

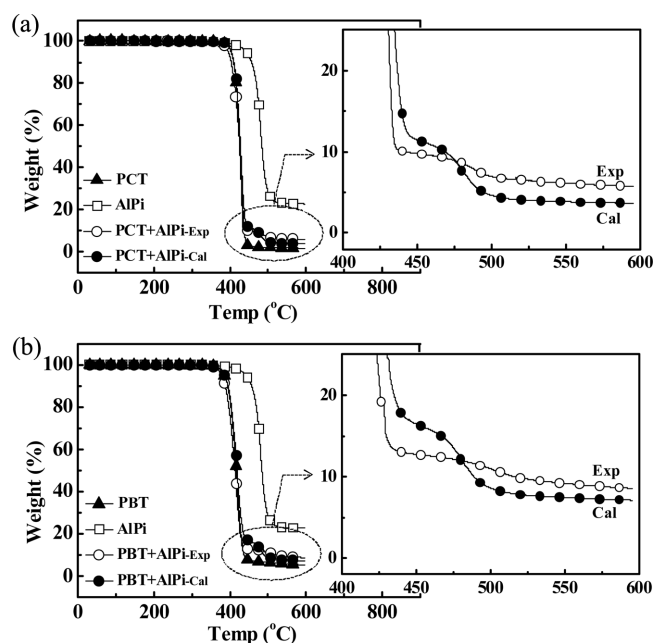


Figure 2. TGA results at heating rate of 10 °C/min under N₂ for (a) neat PCT and AlPi, and PCT+AlPi(11 phr) mixture; (b) neat PBT and AlPi, and PBT+AlPi(12 phr) mixture. Exp is the data obtained experimentally and Cal is the data calculated by adopting the additive rule.

of solid charred residue at 600 °C. These results revealed that PCT and PBT have similar decomposition behaviors and can be considered moderately charrrable polymers. The decomposition of neat AlPi proceeded in a single decomposition step at temperatures between 400 and 520 °C, which is much higher

Table 1. Summary of TGA and UL-94 Test Results for Various PCT+AlPi and PBT+AlPi Mixtures

Sample	Composition (wt)		TGA results (under N ₂)			UL-94 results		
	Polymer	AlPi	T _{2%} (°C)	Residue (wt%) at 600 °C	ΔResidue ^a (wt%) at 600 °C	Dripping	T _{ig} (s/s)	Rating
PCT	100	0	392	1.59	-	Yes	8/12	V-2
PCT+AlPi ₁	100	9.0	381	4.42	2.83	Yes	2/4	V-2
PCT+AlPi ₂	100	10.5	382	4.81	3.22	Yes	1/0	V-2
PCT+AlPi ₃	100	11.0	383	5.78	4.19	Yes ^b	2/2	V-0
PCT+AlPi ₄	100	11.5	383	6.09	4.50	Yes ^b	0/0	V-0
PBT	100	0	373	5.29	-	Yes	3/7	V-2
PBT+AlPi ₁	100	10.5	366	6.94	1.65	Yes	2/6	V-2
PBT+AlPi ₂	100	11.0	363	7.15	1.86	Yes	2/3	V-2
PBT+AlPi ₃	100	11.5	363	7.41	2.12	Yes	2/2	V-2
PBT+AlPi ₄	100	12.0	366	8.60	3.31	Yes ^b	2/3	V-0

^aΔResidue (wt%) = Residue (wt%) of polyester+AlPi mixture – Residue (wt%) of neat polyester. ^bNo burn to the clamp.

than the decomposition temperature ranges of PCT and PBT. AlPi lost about 78 wt% of its total mass, leaving around 22 wt% of solid residue at 600 °C.

When AlPi was added to PCT or PBT, the decomposition of the resulting mixture became complex. The PCT+AlPi mixture decomposed in two steps. The first step (Step A) was observed at lower temperatures between 380 and 435 °C. We believe this step is related to the decompositions of the two constituents of PCT and AlPi. No interaction between PCT and AlPi was expected during this decomposition step. Braun *et al.* reported that diethyl phosphonic acid is the main decomposition product at these temperatures.¹³ If there is no interaction between the products decomposed from PCT and AlPi, the masses of the residues calculated by adopting the additive rule should be equal to those observed experimentally. Or, if the presence of AlPi promotes the decomposition of PCT, the experimentally observed values should be lower. The results presented in Figure 2(a) and Table 1 clearly demonstrate that the decomposition of PCT was accelerated in Step A when AlPi was added. The experimentally observed masses of the residues were lower than the calculated values, and the decomposition temperature ($T_{2\%}$) decreased by about 10 °C.

However, the situation changed adversely in the second step (Step B) of decomposition, which took place at higher temperatures between 435 and 510 °C. It has been well established that the decomposition of AlPi alone at this temperature range is characterized mainly by ethene release and that the addition of AlPi to PBT changes the main decomposition process of PBT slightly through polymer-additive interactions, leaving an increased amount of residue.¹³ The TGA results shown in Figure 2 clearly indicate that the masses of residues did not decrease as much as predicted for the case where no interaction occurred between the polymer and the AlPi. Instead, greater amounts of charred residue were observed experimentally in the case of both PCT and PBT.

We concluded from the thermogravimetric analysis results that the addition of AlPi slightly changed the main decomposition of PCT and PBT. Furthermore, the interaction between the polyester and the added AlPi contributed to the increased residue amount observed in Step B of the two step decomposition process.

Decomposition Model and Residue Analysis for PCT+AlPi Mixture. Even though very similar decomposition behaviors were observed for both PCT+AlPi and PBT+AlPi mixtures, it is worth noting that the final amount of remaining charred residue was slightly greater for the PCT+AlPi mixture

than for the PBT+AlPi mixture. Table 1 summarizes the amounts of residues at 600 °C determined for various AlPi containing mixtures. In the table, $\Delta\text{Residue}$ represents the difference in residue amount between the AlPi containing mixture and neat PCT at a given temperature. The $\Delta\text{Residue}$ value increased with increasing AlPi amount, indicating that the interaction between AlPi and polyester was enhanced with increasing AlPi content. Moreover, this effect was much more profound for the PCT+AlPi mixture than for the PBT+AlPi mixture, suggesting that there were more interactions between AlPi and the polymer in the PCT+AlPi mixture. It is well established that the main mode of flame retardancy observed for a metal phosphinate is based on the gas phase mechanism.¹³ If the interaction of AlPi with the polyester contributes to flame inhibition, then the residue that remains after combustion would result from the condensed phase action. Based on the experimental results mentioned above, we concluded that the decomposition of the PCT+AlPi mixture proceeded in the lower temperature range by means of the gas phase process in Step A. This was followed by the residue formation process at elevated temperatures in Step B. During Step B, the enhanced contribution from condensed phase action was possible for both PCT+AlPi and PBT+AlPi mixtures, although the effect was more profound for the former.

A decomposition model was constructed for the PCT+AlPi mixture, and this model is presented in Figure 3. Most of the decomposition pathways were adopted from the work of Braun *et al.*¹³ (in which PBT and the PBT+AlPi mixture were employed) and from the work of Yu *et al.*¹⁸ (in which the decomposition pathway of neat PCT was investigated). During the pyrolysis of PCT+AlPi mixture, most of the PCT decomposed through an intramolecular proton transfer, generating benzoic acid, 1,4-bis(methylene)-cyclohexane, and 4-methylene cyclohexanemethanol (MCH), and leaving no residue. A minor portion of decomposed PCT left a variety of phosphorus containing residues through the interaction of benzoic acid and 4-methylene cyclohexyl carboxylic acid, both pyrolyzed from PCT with phosphonate anions pyrolyzed from AlPi. Only the formation of aluminum phosphate was considered in the model. The formation of aluminum phosphate from the interaction with 4-methylene cyclohexyl carboxylic acid, shown on the right side of Figure 3, is believed to be responsible for the greater $\Delta\text{Residue}$ amount observed for PCT+AlPi mixtures relative to PBT+AlPi mixtures.

The postulated decomposition model presented above can be verified by analyzing the chemical nature of residues collected

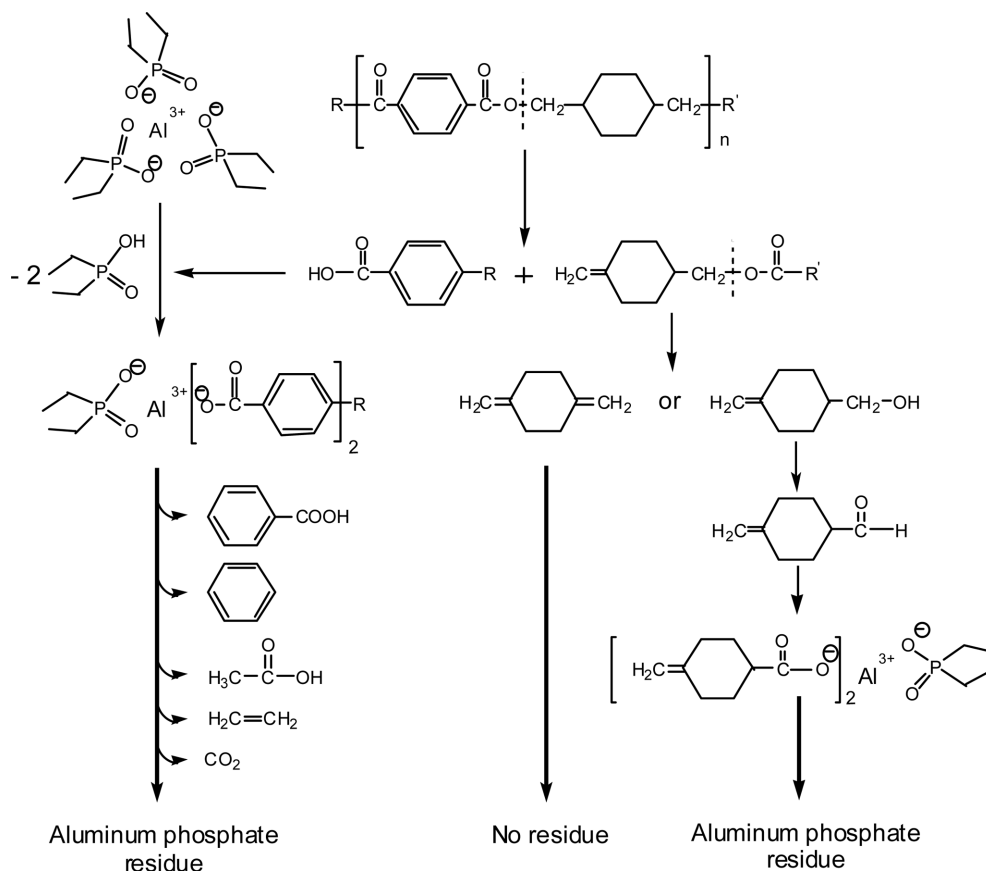


Figure 3. Main decomposition pathway of PCT and its interaction with AlPi.

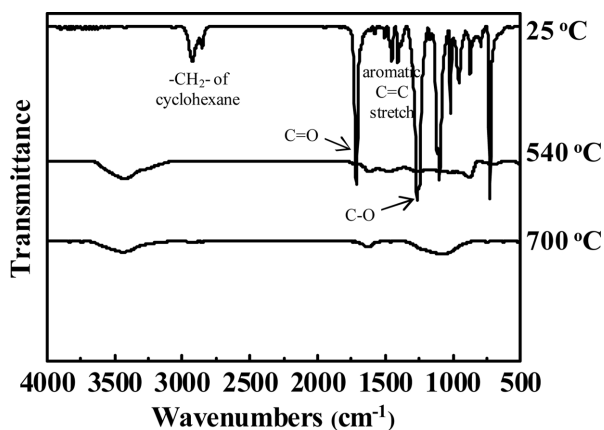


Figure 4. FTIR spectra of PCT before combustion and its charred residues obtained after combustion at 540 and 700 °C.

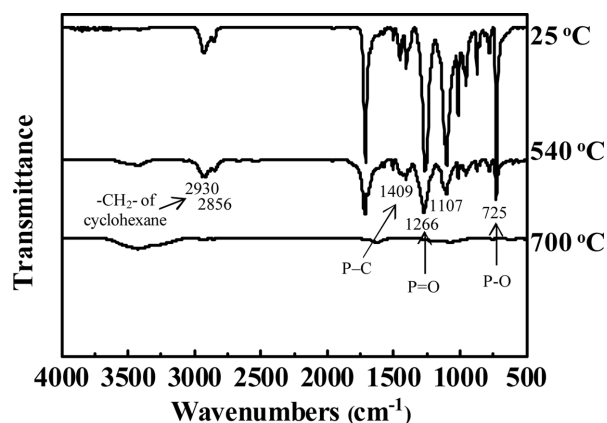


Figure 5. FTIR spectra of PCT+AlPi(9 phr) before combustion and its charred residues obtained after combustion at 540 and 700 °C.

after combustion at specific temperatures. The temperatures were selected by considering the thermogravimetric analysis results shown in Figure 2. The FTIR spectra of neat PCT and PCT+AlPi mixtures are given in Figure 4 and 5. In Figure 4, all characteristic peaks of neat PCT observed at 25 °C became

much broader and even disappeared at 540 °C, indicating that most PCT decomposed at this temperature and left carbonaceous residues. It should be noted that the characteristic peaks of $\text{-CH}_2\text{-}$ in the cyclohexane appearing at 2930 and 2856 cm^{-1} diminished at 540 °C and disappeared completely at

700 °C. This finding strongly implies that PCT decomposed and vaporized below 540 °C, as evidenced by the thermogravimetric results shown in Figure 2. In contrast, these characteristic peaks were well preserved in the spectra of the PCT+AlPi mixture combusted at 540 °C. This implies that a considerable amount of the cyclohexane species remained in the residues as suggested in the decomposition model presented in Figure 3.

Flammability and Ignitability of PCT+AlPi Mixtures. Flammability was evaluated according to the UL-94 test method, and ignitability was determined using a cone calorimeter at an irradiation of 50 kW/m². The results are presented in Table 1 and Figure 6. The results for PBT+AlPi mixtures are also given in Table 1 for comparison. UL-94 V-2 ratings were obtained for both neat PCT and PBT. Considering that no rating is obtained for highly flammable polymers such as polyolefins and styrenics, neat PCT and PBT can be classified as moderately flammable polymers. When AlPi was added to

PCT and PBT, a V-0 rating was achieved. The amounts of AlPi used to achieve the V-0 rating were 11 and 12 phr for PCT and PBT, respectively. Even though the difference was only 1 phr, this difference might be related to the different Δ Residue values, which were discussed in the previous section. The enhanced contribution from condensed phase action is a plausible explanation for the difference in performance between the PCT+AlPi and PBT+AlPi mixtures, although the gas phase action was dominant in both cases.

The heat release rate (HRR) and total heat release (THR) from the cone calorimeter test were determined, and the results are shown in Figure 6. After ignition, both neat PCT and the PCT+AlPi mixture showed a sharp peak in HRR (PHRR) followed by a second smaller, broader peak. When AlPi was incorporated into PCT, the PHRR was reduced by 11.4% (from 598 to 490 kW/m²), and the THR decreased by 18.2 % (from 88 to 72 MJ/m²). The time to ignition (t_{ig}) was only slightly improved (from 54 to 63 s) by the inclusion of AlPi. Based on the above experimental results, we concluded that the flammability and ignitability of PCT were inhibited due to the addition of AlPi.

Conclusions

The thermal decomposition and flame inhibition behaviors of various mixtures of flame retarded PCT were investigated, and AlPi was employed as a main FR. The thermal degradation behaviors were investigated by means of TGA and chemical analysis of charred residue collected after combustion using FTIR. These results were used to construct a proposed decomposition pathway. We found that the action of AlPi was based mainly on the flame inhibition effect in the gas-phase with only a very limited contribution from the condensed-phase mode of action through the formation of aluminum phosphate in the solid state. The flammability was determined by UL-94 tests, and the fire behavior was measured using a cone calorimeter. A UL-94 V-0 rating was achieved by adding 11 phr of AlPi to PCT; this also yielded a noticeable reduction in the HRR and THR observed in the cone calorimeter experiment.

Acknowledgements: This work was supported by the Korean government through a grant funded by the Ministry of Trade, Industry & Energy (10040860) and through the R&D Program of the Ministry of Science, ICT & Future Planning (Grant number: 2013M3C8A3075845).

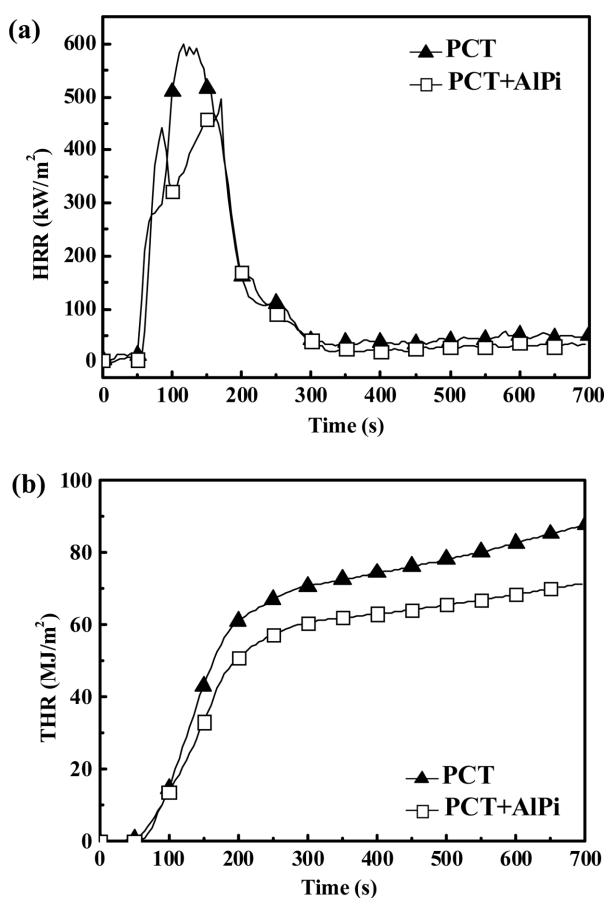


Figure 6. (a) Heat release rate (HRR); (b) total heat release (THR) at an external heat flux of 50 kW/m² (solid triangles = PCT, and open squares = PCT+AlPi (13 phr)).

References

1. G. Topoulos, WO 033129 A2 (2007).
2. B. Lu, US Patent 0262925 A1 (2012).
3. J. E. Bostic, K. N. Yeh, and R. H. Barker, *J. Appl. Polym. Sci.*, **17**, 471 (1973).
4. L. W. Branscome, US Patent 4837254 (1989).
5. G. E. Zaikov and S. M. Lomakin, *J. Vinyl. Addit. Techn.*, **5**, 12 (1999).
6. S. V. Levchik, D. A. Bright, G. R. Alessio, and S. Dashevsky, *J. Vinyl. Addit. Techn.*, **7**, 98 (2001).
7. S. Y. Lu and I. Hamerton, *Prog. Polym. Sci.*, **27**, 1661 (2002).
8. S. V. Levchik, and E. D. Weil, *Polym. Int.*, **53**, 1901 (2004).
9. S. V. Levchik and E. D. Weil, *Polym. Int.*, **54**, 981 (2005).
10. S. V. Levchik and E. D. Weil, *J. Fire. Sci.*, **24**, 345 (2006).
11. B. N. Jang and C. A. Wilkie, *Thermochim. Acta.*, **433**, 1 (2005).
12. C. Nguyen and J. Kim, *Polym. Degrad. Stab.*, **93**, 1037 (2008).
13. U. Braun, H. Bahr, H. Sturm, and B. Scharrel, *Polym. Adv. Tech.*, **19**, 680 (2008).
14. E. Gallo, U. Braun, B. Scharrel, P. Russo, and D. Acierno, *Polym. Degrad. Stab.*, **94**, 1245 (2009).
15. S. Brehme, B. Scharrel, J. Goebbels, O. Fischer, D. Pospiech, Y. Bykov, and M. Döring, *Polym. Degrad. Stab.*, **96**, 875 (2011).
16. E. Gallo, B. Scharrel, U. Braun, P. Russo, and D. Acierno, *Polym. Adv. Tech.*, **22**, 2382 (2011).
17. T. Köppl, S. Brehme, F. Wolff-fabris, V. Altstädt, B. Scharrel, and M. Döring, *J. Appl. Polym. Sci.*, **124**, 9 (2012).
18. A. F. Yu and X. Huang, *J. Appl. Polym. Sci.*, **101**, 2793 (2006).