

팽창성 난연 고분자 복합체 코팅에 대한 알루미나 삼수화물의 효과

Riyazuddin · Tentu Nageswara Rao · Imad Hussain · S. N. Khan* · 구본흔[†]

창원대학교 신소재공학부, *압둘 왈리 칸 대학교 물리학과

(2019년 5월 5일 접수, 2019년 6월 18일 수정, 2019년 8월 18일 채택)

Effect of Alumina Trihydrate on Intumescent Flame Retardant Polymer Composite Coatings

Riyazuddin, Tentu Nageswara Rao, Imad Hussain, S. N. Khan*, and Bon Heun Koo[†]

School of Materials Science and Engineering, Changwon National University, Changwon, Gyeongnam 51140, Korea

*Department of Physics, Abdul Wali Khan University Mardan, Pakistan

(Received May 5, 2019; Revised June 18, 2019; Accepted August 18, 2019)

초록: 탄화 발포제(CFA) 폴리머는 친핵체 치환 반응을 통해 합성되며 팽창성 난연제(IFR) 코팅제에 사용된다. CFA 구조는 푸리에 변환 적외선 분광법(FTIR) 및 원소 분석으로 분석하였다. IFR 시스템은 암모늄 폴리 포스페이트(APP) 및 발포제(CFA)로 구성된다. APP 및 CFA는 2:1 비율로 고정하였고 ATH 양을 바꿔가며 에폭시 수지에 첨가된 IFR 코팅제를 제조하였다. TGA 분석 결과는 800 °C에서 alumina trihydrate(ATH)의 첨가가 코팅의 열분해 잔류물(char)의 비율을 크게 증가시켰다. UL-94V 시험 결과는 코팅제에 ATH를 첨가하여 V-0 등급을 얻었음을 나타낸다. 콘칼로리미터 실험 결과는 코팅의 최대 열 방출 속도(PHRR)와 전체 열 방출(THR)이 ATH 첨가 양의 증가에 따라 현저히 감소한 것으로 확인된다. 에폭시/IFR에 ATH를 포함시키면 코팅 후에 열 안정성 및 난연성 거동이 향상되었다.

Abstract: A charring-foaming agent (CFA) polymer was synthesized via a nucleophile substitution reaction and used in intumescent flame retardant (IFR) coating preparations. The CFA structure was characterized by Fourier transform infrared spectroscopy (FTIR) and elemental analysis. The IFR system was composed of the ammonium polyphosphate (APP) and a foaming agent (CFA). APP and CFA were fixed at 2:1 ratio and different amount of alumina trihydrate (ATH) are loaded into an epoxy resin to prepare IFR coating compositions. The TGA results showed that the addition of ATH greatly increased the char residue percentage of the coatings at 800 °C. The UL-94V data indicated that the V-0 ratings were obtained with the addition of ATH into coatings. The cone calorimeter data showed that the peak heat release rates (PHRR) and total heat releases (THR) of the coatings remarkably decreased with the increase of ATH loading. The incorporation of ATH into epoxy/IFR enhanced the thermal stability and incombustible behavior of the coating system.

Keywords: intumescent flame retardants, foaming agent, alumina trihydrate, epoxy coating.

Introduction

People have been choosing wood as raw material for home appliances such as tables, windows, doors due to its emergence (color, texture, low weight, etc.).¹ Wood-based products have been largely used in different fields such as commercial, residential buildings also.^{2,3} Many countries have been utilizing wood-based products for commercial buildings and timber

constructions.⁴⁻⁶ Even though it is having attractive properties, the usage of wood is getting limitation in some fields due to its intrinsic flammability. To make wood as the safest raw material, we need to increase the flame retardancy of it.

Three methods are available to increase the flame retardance of wood products; (I) chemical impregnation methods,⁷⁻¹⁰ (II) flame retardant with adhesion,^{11,12} and the last (III) one is flame-retardant coatings.¹³⁻¹⁷ The first and second methods are not recommended because they can show an adverse effect on wood mechanical properties. Some flame retardant coatings contain halogens which can increase the flame retardance of wood but they generate a huge amount of smoke and car-

[†]To whom correspondence should be addressed.
bhkoo@changwon.ac.kr, ORCID[®]0000-0003-2867-056X
©2019 The Polymer Society of Korea. All rights reserved.

cinogenic gases like dibenzofurans at burning. So the usage of halogen contained FR system causes the environment pollution.¹⁸ To overcome these problems so many trials were performed to prepare environment-friendly coatings.

From the past few years, a new flame retardant coating system using intumescence flame retardant (IFR) has been developed and recognized as environmentally friendly. IFR system majorly consists of three compounds such as (1) an acid source, (2) carbon source, and (3) blowing agent.¹⁹ To prepare IFR systems ammonium polyphosphate (APP), pentaerythritol (PER), and melamine (MEL) have been used as the acid source, carbonizing agent, and blowing agent respectively. While burning, IFR (APP+PER+MEL) components involved in a dehydration reaction to form a double bond (C=N) contained poor protective char with a foam structure which blocks fire spread. The PER carbon source does not bring that much of satisfactory results as it is a small molecule. PER is hygroscopic, so atmospheric moisture can easily attack it and the IFR system is corrosive. To solve this problem, researchers made great trials to develop a polymer which shows both charring and foaming agent (CFA) properties. Some researchers made a different kind of CFA polymers from 1, 3, 5-triazine as a starting molecule and their efficiencies were well evaluated.²⁰ It is already reported that CFA polymers containing tertiary nitrogen in their structure had shown good thermal stability.²¹ New IFR systems have been found with CFA combination. The synergistic actions of some molecules like zeolite^{22,23} and some transition metal oxides^{24,25} have been examined.

In the present study, a very cheap, readily available, and eco-friendly chemical compound alumina trihydrate (ATH) was selected to examine the synergism in epoxy/IFR based coatings. ATH undergo thermal decomposition at around 180 °C to form a protective dense layer (Al_2O_3) and liberates water into the flame zone. Previous studies reported^{26,27} that ATH showed a significant enhancement of flame retardance of polypropylene, polyethylene, etc. In the present study, ATH was added to IFR coating which contained both APP and CFA molecules. The effect of ATH with IFR was investigated with the limited oxygen index (LOI), UL-94V, thermogravimetric analysis (TGA), and cone calorimetric test.

Experimental

Materials. Epoxy resin (ED-20 grade- medium viscosity) and triethylenetetramine hardener were procured from Struers Company (Japan). Commercial APP (crystalline form II,

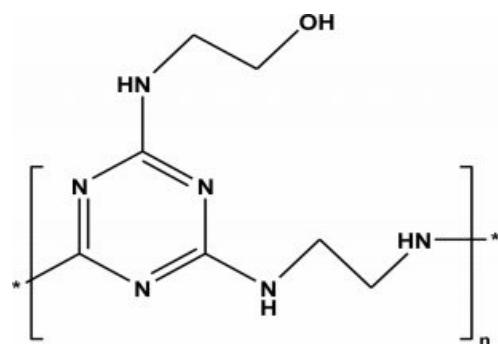


Figure 1. Chemical structure of CFA polymer.

20 µm particle size) was obtained from HELM Korea Ltd. Ethanolamine (AR, 99.8%), ethylenediamine (AR, 99.8%), cyanuric chloride (99%), and alumina trihydrate were purchased from Sigma Aldrich. Acetone (AR, 99%), NaOH pellets, and ethanol (AR-98%) were obtained from Samchun Chemical Company.

Preparation of CFA. The cyanuric chloride, ethanolamine, and ethylenediamine were used to prepare a thermally stable CFA polymer and its structure is represented in Figure 1.

In the first step, 1000 mL of acetone and 1 mol of cyanuric chloride were taken into a three-necked flask equipped with a magnetic stirrer, reflux condenser, and a thermometer. One mol of ethanolamine and 1 mol of NaOH pellets were dissolved in distilled water to make homogenous mixture solution and it was added to the flask by maintaining the reaction temperature at below 10 °C for 3 h using ice and NaCl mixture.

In the second step, 0.5 mol of ethylenediamine and 1 mol of NaOH were dissolved in water and this homogenous aqueous solution was added into the above solution and the reaction temperature was increased to 50-60 °C and maintained for 4 h. In the last step, a mixture solution of NaOH (1 M) and ethylenediamine (0.5 M) were added slowly throughout 2 h to the above reaction solution. The reaction temperature was maintained at 75 °C for 6 h. After the completion of the reaction, it was cooled to room temperature, the obtained white precipitate was filtered and washed with ethanol for three times to remove unreacted reactants. Then, the product was kept in an oven at 120 °C for 4 h to remove the existed solvents. Finally, 94% yield was obtained.^{28,29}

Preparation of Coatings. To prepare coating samples, epoxy (binder), APP, and CFA were used as an IFR system and $\text{Al}(\text{OH})_3$ as a synergistic agent. The ratio of APP to CFA was set at 2:1 w/w ratio and the loading content of $\text{Al}(\text{OH})_3$ was varied. For the preparation of coatings, APP, CFA, and alu-

Table 1. Compositions of the Coating Samples

Sample	Epoxy (%)	APP (%)	CFA (%)	ATH (%)
1	100	0	0	0
2	70	20	10	0
3	68	20	10	2
4	66	20	10	4
5	64	20	10	6

minum tri-hydroxide were mixed in a dispersion mixer for 3 h. Then this mixture was mixed in a solution of resin and hardener (2:1) w/w ratio and applied on the plywood pieces of different dimensions for analysis purpose. The coatings were applied on plywood with a paint brush at room temperature for two times with 3 h intervals. After, the plywood sheets were dried at room temperature for two days in the ventilated condition. The thickness of the coating on plywood was measured to 1.5 ± 0.2 mm by an Elcometer (model A456, USA). The compositions of the coating are shown in Table 1.

Characterization Methods. A Nicolet spectrophotometer (model 4700, USA) was used to perform an FTIR analysis of the samples. The samples were scanned in the range of 500 to 4500 cm^{-1} . A Carlo Erba (model 1106, Italy) elemental analyzer was employed for the elemental analysis of the samples.

Limited oxygen index test was performed using an HC-2C oxygen index instrument (JF-3, China). The coatings were applied on $130\text{ mm} \times 6.5\text{ mm} \times 3.2\text{ mm}$ sized plywood sheets and analyzed according to ASTM D2863 standard procedure.

UL-94V experiment was conducted on the CZF-2 instrument (China) according to ASTM D3801 standard procedure. The plywood pieces of $130\text{ mm} \times 13\text{ mm} \times 3.2\text{ mm}$ dimension were coated with IFR coatings and dried. The 5 specimens of coated plywood pieces were ignited twice for 10 s, then the burning times were measured for each sample to give UL-94V rating.

For thermal gravimetric analysis, the weight of each sample was between 4 and 6 mg. This study was conducted on SDT Q-600 (TA instrument, USA) under the nitrogen flow of 20 mL/min . The temperature range was 30 to 800°C with a heating rate of $10^\circ\text{C}/\text{min}$. The combustion behavior of the samples was carried out by a cone calorimeter (fire testing technology, UK). For this test, $100\text{ mm} \times 100\text{ mm} \times 3\text{ mm}$ sized plywood sheets were coated at all sides with coating samples and dried for two days. Then, these plywood sheets were horizontally laid on the sample holder of the cone calorimeter device. A 35 kW/m^2 external heat flux was exposed on to the coated plywood sheets.

Results and Discussion

Characterization of CFA. FTIR Analysis of CFA: Figure 2 represents the FTIR spectrum of the CFA polymer. The peaks at 3435 and 3230 cm^{-1} are for $\nu_{\text{N-H}}$ and $\nu_{\text{O-H}}$ symmetric stretching vibrations respectively. The two peaks of 2930 and 2849 cm^{-1} are assigned to C-H vibration in $\text{CH}_2\text{-CH}_2$ group. The absorption peaks at 1578 and 1362 cm^{-1} are appeared due to the $\text{C}=\text{N}$ vibrations in triazine ring. The other main peaks at 1161 and 1055 cm^{-1} are for $\nu_{\text{C-N}}$ and $\nu_{\text{C-O}}$ respectively. The peak at 808 cm^{-1} has appeared for $\nu_{\text{N-H}}$ mode vibration. Also, this spectrum is not showing a peak at 850 cm^{-1} which preferentially corresponds to C-Cl bond stretching. The absence of absorption peak at 850 cm^{-1} suggests that all the three chlorine atoms are removed from triazine ring. All of the above peaks confirm that targeted CFA polymer is formed successfully.

Elemental Analysis. Table 2 shows the elemental analysis data of the prepared CFA polymer. From this data, it can be seen that both calculated and measured values are the same. From the above results, it can be concluded that the targeted CFA polymer is synthesized successfully.

Thermal Degradation Pattern of CFA. TGA is a well-known technique for the evaluation of thermal stability and thermal degradation pattern of a compound. The thermograms (TGA and DTG) of CFA under nitrogen atmosphere are shown

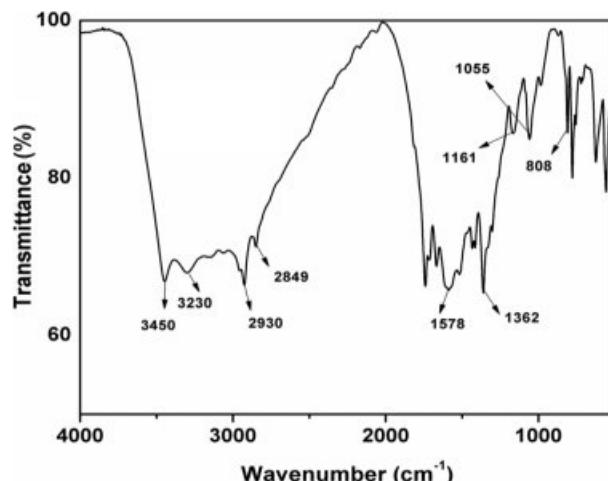


Fig 2. FTIR spectrum of CFA polymer.

Table 2. Elemental Analysis of the CFA Polymer

Sample	C	N	O	H
CFA (Calculated %)	42.86	42.85	8.17	6.12
CFA (Measured %)	42.85	42.87	8.18	6.10

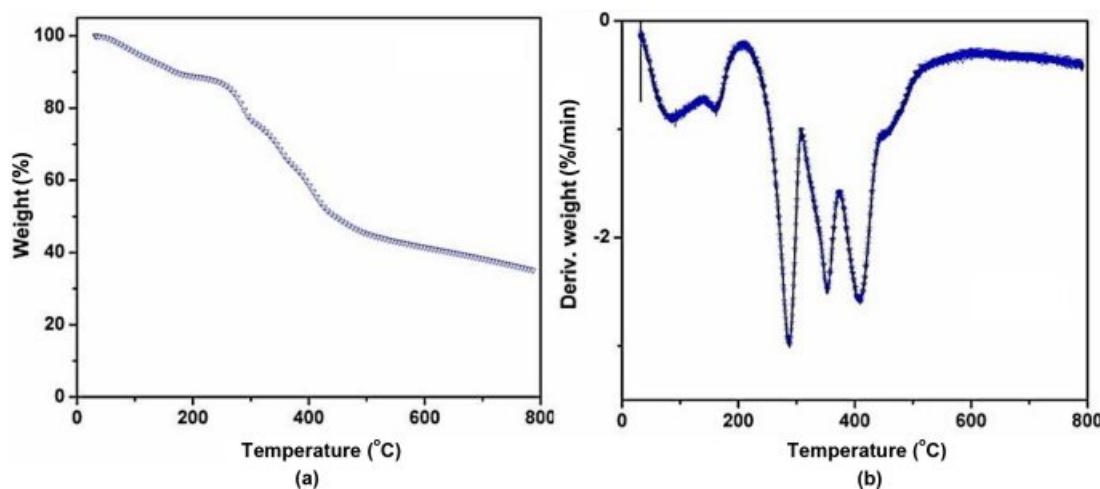


Figure 3. (a) TGA of CFA polymer; (b) DTG of CFA polymer.

Table 3. Thermogravimetric Data of CFA Polymer

Sample	Char residue (wt%)	
	700 °C	800 °C
CFA	38.25	34.96

in Figure 3 and Table 3. From these data, it can be observed that CFA is thermally stable at a higher temperature. The char residue percentage of the CFA at 700 °C and 800 °C are 38.25 and 34.96% respectively. The CFA polymer initially showed thermal degradation at around 70 °C due to the evaporation of solvent residue (acetone and water). It is also seen that CFA shows three major steps of thermal degradation at temperature ranges of 260 to 310 °C, 315 to 375 °C, and from 380 to 440 °C respectively. The degradation of CFA both at 260 to 310 °C and 315 to 375 °C temperatures may be due to the dehydration and the loss of ammonia from the CFA molecule. The weight loss of CFA at third degradation stage (380 to 440 °C) is due to the breakage of macromolecular backbone structure which results in the release of ammonia and finally forms a char layer. This indicates that the prepared CFA acts as a charring and foaming agent at high temperatures.

Flame Retardancy of the Coatings. To evaluate the flame retardancy of the coatings, the LOI and UL-94V tests were conducted. The effect of Al(OH)₃ on epoxy/IFR coating system is represented in Table 4. The data shows that pristine epoxy coating is very flammable. The addition of IFR (APP+CFA) to the epoxy is greatly increased the LOI value from 25.2 to 27.6% and meets the V-0 rating in UL-94V test. It is insisted that APP involves in thermal degradation and produces acids such as meta-phosphoric acid and pyro-phosphoric

Table 4. Flame-Retardancy Results of the Coatings

Sample	LOI	UL-94V
Pure epoxy	25.2	Not rated
Epoxy/IFR	27.6	V-0
Epoxy/IFR/ATH-2%	28.2	V-0
Epoxy/IFR/ATH-4%	30.7	V-0
Epoxy/IFR/ATH-6%	32.4	V-0
Epoxy/IFR/ATH-8%	18.7	V-2
Epoxy/IFR/ATH-10%	19.5	V-2

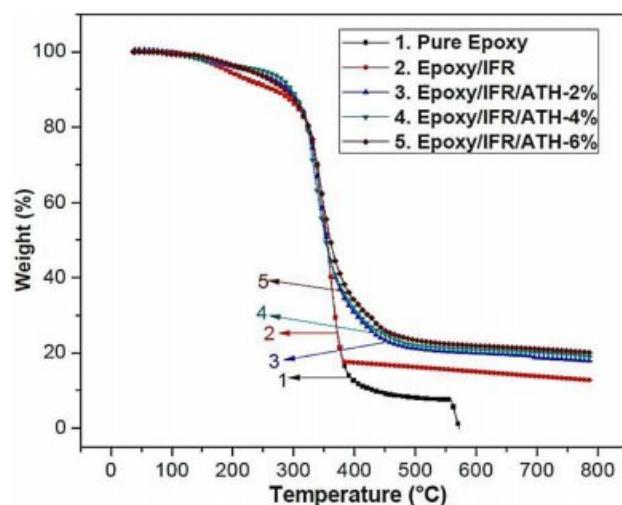
acid which can effectively react with CFA and result in the formation of a carbon-phosphor char. This char can restrict the transfer of both oxygen and heat, so flame will stop easily. The CFA preferentially involves in dehydration reaction as it belongs to poly-hydroxyl containing triazine polymer. Table 4 also shows that the LOI values effectively increase for epoxy/IFR/ATH coatings and V-0 rating is accomplished for those. The addition of ATH at 6% greatly improved the LOI value to 32.4%. It may be due to the catalytic action of ATH on the condensation reaction between APP and CFA. The coatings which contain the ATH content more than 8% are unable to increase the LOI value and can not reach the V-0 rating. The reason may be due to that, high (more than 8%) loading of ATH can result in incompatibility and consequently destroys the char layer.

Thermogravimetric Analysis of Coatings. Thermal decomposition pattern and thermal stability results of the coating samples of epoxy/IFR, epoxy/IFR/ATH-2%, epoxy/IFR/ATH-4%, and epoxy/IFR/ATH-6% are shown in Table 5 and Figure 4. The pure epoxy coating sample is gently flammable

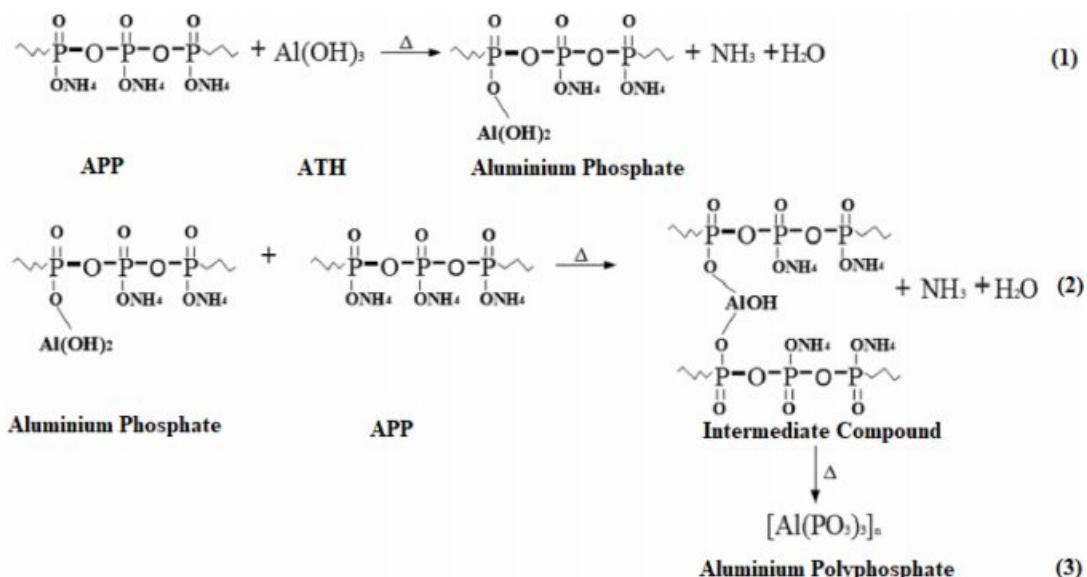
Table 5. Thermo-gravimetric Results of the Coatings

Sample	Char residue (%)	
	At 600 °C	At 800 °C
Pure epoxy	0.0	0.0
Epoxy/IFR	14.70	12.78
Epoxy/IFR/ATH-2%	19.62	17.93
Epoxy/IFR/ATH-4%	21.44	18.60
Epoxy/IFR/ATH-6%	22.35	20.20

and non-rated in UL-94V test. From the figure, it is seen that all coatings are showing the same thermal degradation pattern with two main stages. At the first stage (around 220 °C) of degradation, all the coating samples have shown a similar pattern due to the partial melting of the IFR material. All the coating samples are showing major decomposition at the second stage in the temperature range of 250 to 520 °C. At this stage, the coating samples result in a great weight loss. While coating samples are crossing 250 °C, at first the APP involves in decomposition and generates the water and ammonia gas, and at last, it can be converted into acids such as meta-phosphoric and pyro-phosphoric acids. These acids effectively act as a dehydrating agent and remove the water from the CFA polymer. Figure 1 shows that CFA is a poly-hydroxyl triazine type polymer, so it can easily cause the dehydration process. This dehydration reaction of APP and CFA results in the formation of phosphor-carbonaceous protective char. One highlighting fact is that CFA is also having an abundant amount of nitrogen,

**Figure 4.** TGA curves of the coating compositions.

so it also involves in the releasing of ammonia with APP at around 300 °C. As the ammonia releases, the protective char will become intumescent and so significantly stops the burning process. From Figure 4, it can be seen that over 520 °C temperature, epoxy/IFR coating has shown a greater amount of weight loss than ATH contained coatings. The char residue percentages of the epoxy/IFR, epoxy/IFR/ATH-2%, epoxy/IFR/ATH-4%, and epoxy/IFR/ATH-6% at 800 °C are 12.78, 17.93, 18.60, and 20.20% respectively. It confirms that the addition of ATH remarkably increases the char residue percentage. It may be due to two reasons; the first one is due to that the ATH makes decomposition very complicated. A

**Figure 5.** A scheme of a chemical reaction between APP and ATH.

scheme of the chemical reaction between APP and ATH was shown in Figure 5.^{26,27} As ATH undergoes thermal decomposition at 180–220 °C, it releases water and forms a dense Al₂O₃ char. The second reason may be that during decomposition process ATH forms cross-linkages with IFR system.

Cone Calorimeter Analysis. The combustion behavior of coating samples is evaluated by a cone calorimeter as it can give a complete profile of flame parameters of a material.

Figure 6 and Table 6 show the heat release rate curves of the coating materials. From this figure, it can be seen that pure epoxy coating material is highly flammable. It is burnt very quickly with the releasing of the huge amount of heat 179.5 kW m⁻² within the short time of 52 s. The epoxy/IFR coating has shown much lower heat release rate peak than pure epoxy coating. The addition of the IFR system significantly decreased the PHRR value of the coating from 179.5 to 119.6 kW m⁻². In addition to this, the incorporation of ATH at 2, 4, and 6% into the coating system, a great decrease in the PHRR value than epoxy/IFR coating is obtained. From Figure 6, it can also be observed that ATH effectively delay the burning process by decreasing PHRR value. As compared to pure

epoxy coating, the PHRR values are reduced by 34% for epoxy/IFR, 45% for epoxy/IFR/ATH-2%, 51% for epoxy/IFR/ATH-4%, and 57% for epoxy/IFR/ATH-6%. The decrease in PHRR value concludes that the addition of ATH shows a synergistic action with IFR to increase the incombustible properties of the coating material.

It may be due to the formation of a char layer by the synergism of IFR and ATH. This char prevents the transfer of both heat and oxygen in between matrix inside part and outside part (flame zone). There is a clear difference between the PHRR curves of the epoxy/IFR and epoxy/IFR/ATH coatings. During the combustion process of epoxy/IFR coating, APP and CFA involve in a condensation reaction to produce a protective char. In the case of combustion of epoxy/IFR/ATH coatings, ATH involves in the formation of Al₂O₃ dense protective layer with releasing water and it can form cross-linkages with IFR system to produce a thick char.

The total heat release rate (THR) values of the coating materials are presented in Figure 7 and Table 6. This data shows that pure epoxy coating has the highest THR value than others. Due to the addition of the IFR system into the coatings, the THR value is reduced from 7.5 to 6 MJ m⁻² (20% reduction). In addition to this, when the ATH is added to the coating composition at 2 to 6% the THR values effectively decreased from 7.5 to 4.6, 4.2, and 3.4 MJ m⁻² respectively. It means that 2 to 6% addition of ATH decreased the THR of the coatings by 39, 44, and 55% respectively. It is suggested that ATH can strengthen the char and also form a dense Al₂O₃ protective layer which prevents the flow of heat. Finally, it results in

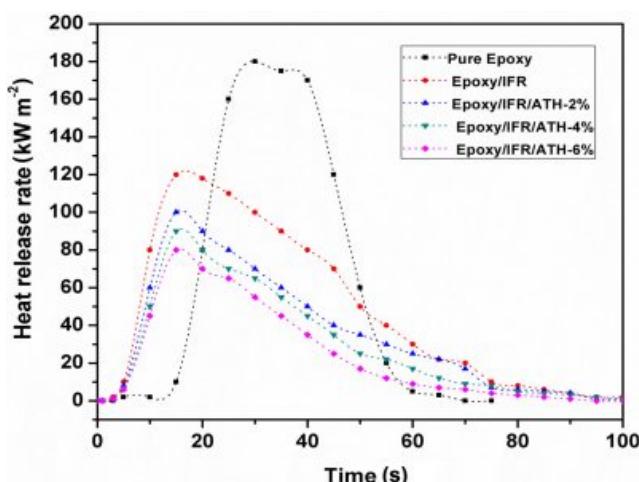


Figure 6. Heat release rate curves of the coatings applied on plywood sheets.

Table 6. Cone-calorimetric Results of the Coatings

Sample	PHRR (kW m ⁻²)	THR (MJ m ⁻²)
Pure epoxy	179.5	7.5
Epoxy/IFR	119.6	6.0
Epoxy/IFR/ATH-2%	100.0	4.6
Epoxy/IFR/ATH-4%	89.0	4.2
Epoxy/IFR/ATH-6%	78.0	3.4

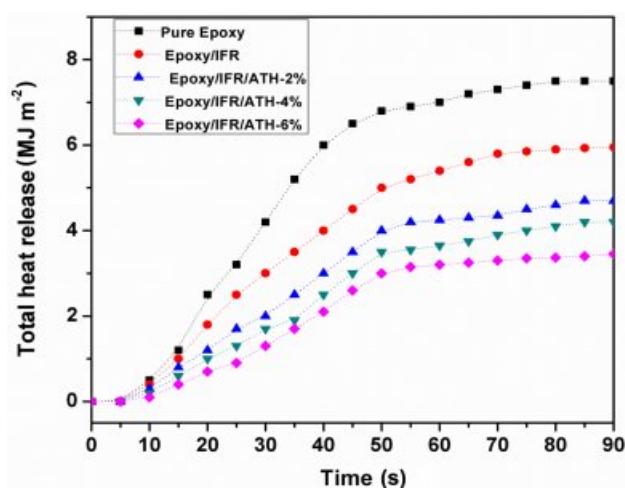


Figure 7. Total heat release curves of the coatings applied on plywood sheets.

slowing down the burning process and decreases the heat release from the sample.

Conclusions

In this work, a charring-foaming agent was synthesized successfully and its structure was characterized by FTIR and elemental analysis. The APP and CFA are used in epoxy/IFR coating. The ATH was added at different amount into the coating system and its effects were investigated by LOI, UL-94V, TGA, and cone calorimeter. The 2 to 6 wt% loading of ATH into coating system resulted in a great influence on increasing the thermal stability at high temperatures. The cone calorimeter data confirmed that ATH acts as a synergistic agent and can effectively decrease the peak heat release rate. The LOI and UL-94V results indicated that incorporation of ATH remarkably increased the LOI values with V-0 ratings.

Acknowledgment: This work was supported by the National Research Foundation of Korea Grant funded by the Korea government (No. 2018R1A6A1A03024509).

References

- M. Nikolic, J. M. Lawther, and A. R. Sanadi, *J. Coat. Technol. Res.*, **12**, 445 (2015).
- A. Temiz, S. Akbas, I. Aydin, and C. Demirkir, *Wood Sci. Technol.*, **50**, 179 (2016)
- Z. Candan, N. Ayrilmis, and T. Dundar, *Wood Res.*, **57**, 651 (2012).
- K. Cheung, "Multi-storey wood frame construction in North America", in *Proceedings of the World Conference on Timber Engineering*, Riva del Garda, Italy, June 20-24, 2010.
- A. Ceccotti, C. Sandhaas, M. Okabe, M. Yasumura, C. Minowa, and N. Kawai, *Eng. Struct. Dyn.*, **42**, 2003 (2013).
- J. W. G. Van De Huilen, A. Ceccotti, Z. Y. Xia, and M. J. He, *Procedia Eng.*, **14**, 1621 (2011).
- R. X. Cheng and Q. W. Wang, *J. Adhes. Sci. Technol.*, **25**, 1715 (2011).
- E. Terzi, S. N. Kartal, R. H. White, K. Shinoda, and Y. Imamura, *Eur. J. Wood Prod.*, **69**, 41 (2011).
- H. A. Kol, G. Ozbay, L. Kose, and S. Kurt, *Bio. Resour.*, **5**, 70 (2010).
- N. Ayrilmis, Z. Candan, and R. White, *Holz als Roh-und Werkstoff*, **65**, 449 (2007).
- W. Wang, Z. Zhang, H. Chen, S. F. Zhang, and J. Z. Li, *Constr. Build. Mater.*, **79**, 337 (2015).
- W. Wang, W. Zhang, S. F. Zhang, and J. Z. Li, *Constr. Build. Mater.*, **65**, 151 (2014).
- C. S. Chou, S. H. Lin, and C. I. Wang, *Adv. Powder Technol.*, **20**, 169 (2009).
- C. S. Chuang, K. C. Tsai, M. K. Wang, C. C. Ou, C. H. Ko, and I. L. Shiau, *Wood Sci. Technol.*, **42**, 593 (2008).
- F. P. Liu and W. M. Zhu, U.S. Patent 5,968,669 (1999).
- M. K. Yalinkilic, W. Y. Su, Y. Imamyra, M. Takahashi, Z. Demirci, and A. C. Yalinkilic, *Holz als Roh-und Werkstoff*, **56**, 347 (1998).
- H. Ellis, U.S. Patent 5,130,184 (1992).
- N. Ferre-Huguet, M. Nadal, M. Schuhmacher, and J. L. Domingo, *Environ. Sci. Technol.*, **40**, 61 (2006).
- W. U. Qiang and Q. U. Baojun, *Polym. Degrad. Stab.*, **74**, 255 (2001).
- C. M. Feng, Y. Zhang, S. W. Liu, Z. G. Chi, and J. R. Xu, *J. Appl. Polym. Sci.*, **123**, 3208 (2012).
- J. F. Dai and B. Li, *J. Appl. Polym. Sci.*, **116**, 2157 (2010).
- H. Demir, X. E. Arkis, and S. Ulku, *Polym. Degrad. Stab.*, **89**, 478 (2005).
- S. Bourbigot, M. Le Bras, R. Delobel, P. Breant, and J. M. Tremillon, *Polym. Degrad. Stab.*, **54**, 275 (1996).
- L. R. M. Estevao, M. Le Bras, R. Delobel, and R. S. V. Nascimento, *Polym. Degrad. Stab.*, **88**, 444 (2015).
- L. I. U. Yuan and Q. I. Wang, *Polym. Degrad. Stab.*, **91**, 2513 (2006).
- M. Fuzail, G. Shah, and J. Anwar, *Iran. Polym. J.*, **19**, 47 (2010).
- N. Wang, D. Xiang, P. Mo, and Y. Lu, *Adv. Mater. Res.*, **652**, 485 (2013).
- Y. Wang, M. J. Xu, and B. Li, *Polym. Degrad. Stab.*, **131**, 20 (2016).
- Y. Li, B. Li, J. Dai, H. Jia, and S. Gao, *Polym. Degrad. Stab.*, **93**, 9 (2008).