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Thermal and fire retardant properties of polyurea

Summary — The thermal and fire retardant properties of polyurea, formed by the polyaddition reaction of a modified diisocyanate with an oligomeric diamine, have been studied using thermogravimetric analysis and cone calorimetry as the principal tools. Approximately forty different conventional fire retardant additives including halogens (chlorine and bromine), phosphorus (nearly all oxidation states), mineral fillers, melamine compounds and intumescent additives were used at constant loading of 15 wt. % for all samples (except mineral fillers, 30 wt. %) and evaluated in polyurea. The thermal properties (onset, maximum degradation temperature and char residue) of filled polyurea samples are compared with the control sample. The fire retarded polyurea samples have been screened on the basis of the percentage reduction of peak heat release rate and smoke evolution.

Keywords: polyurea, fire retardant additives, thermal properties, fire retardancy, cone calorimetry.

WŁAŚCIWOŚCI TERMICZNE I OGNIOODPORNE POLIMOCZNIKA

Streszczenie — Metodami analizy termograwimetrycznej oraz kalorymetrii stożkowej oceniano właściwości termiczne i odporność na palenie, otrzymanego w reakcji poliaddycji modyfikowanych diizocyjanianów z oligomerycznymi aminami, polimocznika z dodatkiem środków uniepalniających. W charakterze antypirenów stosowano ok. 40 różnych tradycyjnych uniepalniaczy: zawierające halogeny (chlor lub brom) bądź fosfor (na wszystkich stopniach utlenienia), napełniacze mineralne, układy z udziałem melaminy oraz środki pęczniejące w podwyższonej temperaturze (w warunkach pożaru), dodając je do polimocznika w stałej ilości 15 % mas. (z wyjątkiem napełniaczy mineralnych — 30 % mas.). Wyznaczano temperaturę początku rozkładu termicznego ($T_{10\ \%}$), maksymalną temperaturę degradacji ($T_{maks.}$) oraz stałą pozostałość w temp. 700 °C, otrzymanych próbek samego polimocznika i polimocznika z dodatkami. Uniepalnienie materiałów oceniano na podstawie procentowego zmniejszenia piku szybkości wydzialania ciepła oraz ilości wydzielanego dymu.

Słowa kluczowe: polimocznik, dodatki opóźniające palenie, właściwości termiczne, uniepalniacze, kalorymetria stożkowa.

INTRODUCTION

In the early 1980's, polyureas (PU) were first developed for automotive fascia applications, like bumpers, cowlings, side panels, dashboards, *etc*., due to their high strength and impact resistance. It is very fast reacting and utilizes an expansive reaction injection molding (RIM) process to make automotive body parts. Recently sprayable polyureas have been formulated to provide coatings, sealants and caulking products that exhibit superior performance characteristics compared to traditional protective materials, such as polyesters, epoxies, polyurethanes, vinyl esters and paints [1]. For example, polyurethane generally utilizes a catalyst to promote proper curing, which leads to problems such as moisture and temperature sensitivity. The reactive nature of polyurea does not require a catalytic process. At cryogenic condition, epoxies cannot be obtained because of the lengthy curing process, whereas polyurea can be a good candidate, even at -20 °C [2]. Furthermore, being free of volatile organic compounds (VOC), PU is popular as a more sustainable, environmentally friendly alternative to traditional solvent-based coating. The PU coating is derived from the reaction product of a diisocyanate and a diamine. PU is quite resistant to a broad range of corrosives, and cured products exhibit excellent adhesion and abrasion resistance [3]. Despite their many qualities, the efficacy of PUs is limited in many applications due to relatively easily flammability and release of toxic smoke while burning. Fire retardants (FRs) must be added to PU to reduce flam-

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mability. In a previous study, the effect of about twelve different commercial FR additives were evaluated in PU using cone calorimetry [4]. According to this study, a few additives, including ammonium polyphosphate (APP), melamine polyphosphate (MPP), a phosphonate (Fyrol PMP) and decabromodiphenyl oxide (Deca) with Sb_2O_3, were found to exhibit some fire retardant activity with PU. This study further examines the effect of additional FR additives on the flammability of PU. Moreover, the effect of the various classes of FR additives on the thermal properties of PU have also been studied; there are very few reports on the thermal stability of PU filled with FR additives [5, 6]. Thermal analysis provides a vital link between thermal degradation and the fire retardant properties of polymeric materials. Awad *et al.* reported the effect of nanofillers like MWCNT (Multi-Wall Carbon Nanotube) and vinyl POSS with conventional FR additives utilized in PU [7]. The main objective of this work is to identify effective fire retardant additives (greater reduction of peak *HRR* and smoke) for PU from the screening of different classes of conventional FR additives.

EXPERIMENTAL

Materials

Poly(tetramethyleneoxide-di-*p*-aminobenzoate) (Versalink P1000, AEW = 600 g/mol eq) and polycarbodiimide modified diphenyl methane diisocyanate (Isonate 143L, NCO content = 29.2) were obtained from Air Products and Dow Chemical Company, respectively. Table 1 shows the different classes of fire retardant additives (chemical and trade name and their designation) used in this study and their sources. The anti-dripping agents, polytetrafluroethylene (PTFE) and graphite powder of particle size 1—2 μm were acquired from Aldrich Chemical Company. All chemicals were used as received.

Samples preparation

The fire retardant polyurea samples were prepared in a beaker by mixing the FR additives in the diamine oligomer; a homogeneous mixture was obtained by using a high speed mechanical stirrer. Then, isocyanate was added to the beaker with vigorous stirring for 30 s, and the resultant mixture was poured into an aluminum mold. The amount of diisocyanate required for the reaction with diamine was calculated from the equivalent weight of diamine. For the completion of the reaction, excess isocyanate (1.05 isocyanate index) was used. The PU samples were cured at room temperature for 12 h, and then were kept in an oven at 80 °C for 24 h to complete the curing.

Methods of testing

— The onset (10 % weight loss temperature), maximum degradation temperature (T_{max}) and char residue at 700 °C were determined by simultaneous TG and differential scanning calorimetry (DSC), SDT Q600, TA Instruments, under nitrogen (gas flow of 100 cm^3/min) at a heating rate of 20 °C/min over the temperature range of 50—800 °C. Typical sample weights of 5—10 mg were employed. All samples were run at least in duplicate and the average values are recorded. The instrument is reproducible to ± 2 °C and ± 0.2 wt. %.

— The flammability was evaluated using the cone calorimeter (Atlas Cone 2, USA) as per ASTM E 1354 at an external heat flux of 50 kW/m^2. The specimen size for the cone calorimeter experiments were 100 × 100 × 6 (mm^3). Reported values are the average of three measurements on each sample. The day-to-day reproducibility of the cone calorimetry is usually considered to be about ± 10 %.

RESULTS AND DISCUSSION

Effect of curing condition

Polyurea shows outstanding performance characteristics, extremely fast cure, good impact, thermal shock and abrasion resistance, water repellency and good adhesive properties. In general, the properties of PU depend upon the extent of curing or crosslinking between diisocyanate and di/or polyamine. Because of the very fast reaction (<60 s) of PU without catalyst at room temperature, it is difficult to control or monitor the reaction profile. In this section, the influence of curing conditions, room temperature (RT) cure (up to 30 days) and elevated temperature (ET) cure (80 °C/24 h) on the thermal and fire retardant properties are discussed. The RT cured samples showed inferior thermal stability (onset 335 °C and T_{max} = 426 °C) compared to elevated temperature cured sample (onset 346 °C and T_{max} = 433 °C). This may indicate that an incomplete reaction takes place during RT curing and additional curing proceeds at elevated temperature, which is confirmed by DSC analysis as shown in Fig. 1. The heat of cure (exotherm) is used to determine the percent cure of the PU material. The broad exothermic peak is the characteristic of heat evolved during PU reaction (0 day/uncured sample), which becomes increasingly smaller during RT curing. The elevated temperature curing (post cure) shows no curing exothermic peak indicates that the PU sample was completely cured by the heating process.

The cone calorimeter is extensively used to evaluate the flammability of polymeric materials. Results correlate with those obtained from large-scale fire tests and can be used to predict the combustion behavior of PU in real fire situation. The various fire retardant parameters, ignition time (t_{ign}), peak heat release rate (P_{HRR}, kW/m^2), total heat released (*THR*, MJ/m^2), average mass loss rate (*AMLR*, g/$m^2 \cdot$ s), average specific extinction area (*ASEA*, m^2/kg), *etc.*, are obtained from the cone calorimeter. Among these the most important parameter is the peak *HRR*, because it is responsible for the flashover condition in a real fire situation.

Table 1. List of different flame retardants used in this study

FR designation	Flame retardant chemicals	Sources
D-Plus	dechlorane plus 25	Laurel Industries
Deca	decabromo diphenyl oxide (Saytex 102E)	Albemarle
EBPBP	ethane 1,2-bis(pentabromophenyl) (Saytex 8010)	Albemarle
EBTBPI	ethylene bis-tetrabromo phthalimide (Saytex BT93)	Albemarle
TBBA	tetrabromo bisphenol A (Saytex CP2000)	Albemarle
DBNPG	dibromo neopentyl glycol (FR522)	Dead Sea Bromine group
TBNPA	tribromo neopentyl alcohol (FR513)	Dead Sea Bromine group
Sb_2O_3	antimony trioxide	Laurel Industries
TPP	triphenyl phosphate (Reofos TPP)	Chemtura
EDAP	ethylene diamine phosphate (Antiblaze NK)	Albemarle
RDP	resorcinol diphosphate (Reofos RDP)	Chemtura
BADP	bisphenol A diphosphate (Reofos BADP)	Chemtura
RP	red phosphorus (Exolit RP6520)	Clariant
TPPO	triphenyl phosphine oxide	Aldrich
NHP	Reofos NHP (structure proprietary)	Chemtura
TDPGP	tris(dipropylene glycol)phosphite (Doverphos 72)	Dover Chemicals
TPP	triphenyl phosphite (Doverphos 10)	Dover Chemicals
ABPAP	alkyl (C_{12}—C_{15}) bisphenol A phosphite (Doverphos 613)	Dover Chemicals
BDCPPDP	bis(2,4-dicumylphenyl)pentaerythritol diphosphite (Doverphos S-9228)	Dover Chemicals
DMMP	dimethyl methyl phosphonate (Antiblaze DMMP)	Albemarle
A-N	cyclic oligomeric phosphonate (Antiblaze N)	Albemarle
PMP	poly(*m*-phenylene methyl phosphonate (Fyrol PMP)	Supresta
OP 1230, OP 1314, OP 1311(LV)	aluminum salt of diethylphosphinic acid (Exolit OP)	Clariant
DOPO	9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide	Krems Chemie
APP P/30, P/42, 3118F	ammonium polyphosphate (Phoschek P/30, Phoschek P/42 and Budit 3118F)	Astaris and Budenheim
A-100	tris-2-chloroethyl phosphate (Antiblaze 100)	Albemarle
A-80	tris monochloroisopropyl phosphate (Antiblaze 80)	Albemarle
A-205	chloroalkyl phosphate (Antiblaze 205)	Albemarle
A-78	chloroalkyl phosphonate (Antiblaze 78)	Albemarle
ATH	aluminum hydroxide (Martinal OL-107/LE)	Albemarle
MDH	magnesium hydroxide (Magnifin H7C)	Albemarle
ZB	zinc borate (Firebrake ZB fine)	Firebrake ZB
Melamine	melamine	AlfaAesar
MPP	melamine polyphosphate (Melapur 200-70)	Ciba Specialty Chemicals
MC	melamine cyanurate (Budit 315)	Budenheim
EG160-50, EG160-80, EG220-50, EG220-80	expandable graphite	Graf-Tech

Table 2. Cone calorimetric data for PU with different cure reaction

Sample	t_{ign} s	P_{HRR} kW/m^2	*THR* MJ/m^2	*AMLR* g/m^2·s	*ASEA* m^2/kg
Polyurea — RT cure	14 ± 1	2261 ± 269	214 ± 5	18 ± 1	433 ± 34
Polyurea — ET cure	12 ± 4	1854 ± 65	160 ± 7	44 ± 5	452 ± 18

Table 2 displays the cone data of polyurea cured under the two different curing conditions and their corresponding heat release curves are shown in Fig. 2. From the table, there is not much change in time to ignition and smoke development (*ASEA*) of the samples, but a vast difference in the peak *HRR* and *THR* is observed between these two different curing protocols. This indicates that the extent of curing could play a major role in the release of heat during combustion. There is a significant difference in mass loss rate which is frequently said to be the reason for a change in the P_{HRR}. It is also noted that the RT cured sample drips more, compared to the elevated temperature cured sample.

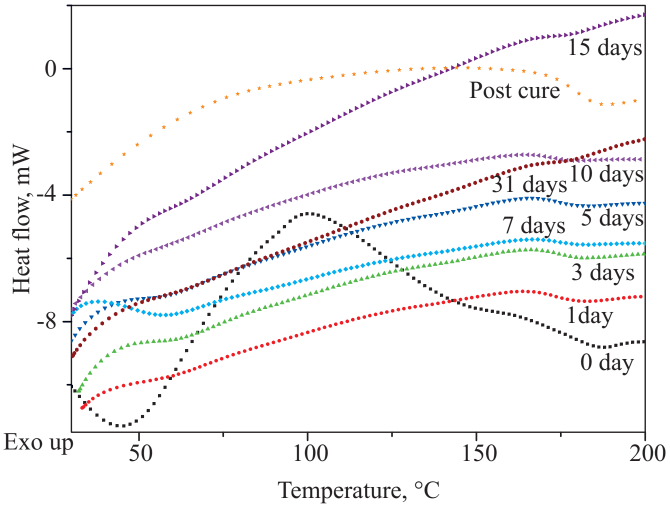

Fig. 1. DSC analysis of the extent of curing of PU

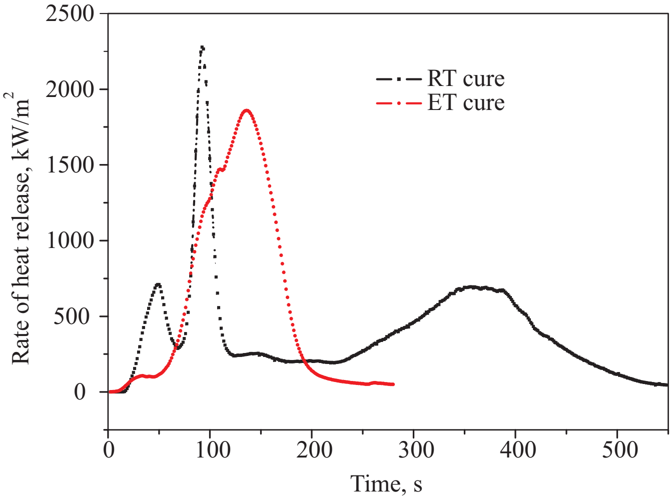

Fig. 2. Heat release curves of PU with two different curing conditions

Effect of anti-dripping agent

Polyurea shows flaming drips during the cone experiment; such dripping may improve or degrade the performance of PU. For example, sometimes dripping can remove material from the heat source and avoid further flame spread or fire growth. On the other hand, the dripping may be toward the heat source, leading to a worsened fire condition. Flaming drips also will result in an unclassified result in the UL-94 protocol. Generally, the addition of very small amounts of finely divided polytetrafluoroethylene (PTFE) or graphite powder may reduce dripping due to a rheological effect. Table 3 shows the effect of PTFE and graphite powder on the thermal properties of neat as well as APP-filled PU. The thermal stability of PU is slightly increased with the addition of anti-dripping agents, but there is no change in T_{max} and char yield. Comparable results are obtained with APP-filled PU, as shown in Table 3.

T a b l e 3. Effect of anti-dripping agent + APP on the thermal properties of polyurea

Sample	$T_{10\,\%}$ °C	T_{max} °C	Char at 700 °C, %
PU	346	433	7.1
PU + 0.5 % PTFE	352	431	7.3
PU + 0.5 % graphite	353	432	7.1
PU + 15 % APP (P/42)	303	380	14.1
PU + 15 % APP + 0.5 % PTFE	307	385	14.1
PU + 15 % APP (3118F)	318	408	13.3
PU + 15 % APP + 0.5 % graphite	326	407	12.3

Fig. 3 shows that the effect of anti-dripping agents on the heat release rate of PU at 50 kW/m^2 and the corresponding data is shown in Table 4. A characteristic feature of neat PU is a small shoulder followed by a large peak. As shown in the figure, the small peak becomes more pronounced upon the addition of the anti-dripping agents; whereas a broad peak stretched in time is obtained upon the addition of APP. PTFE and graphite are somewhat ineffective in promoting anti-dripping behavior. Interestingly, there is a decrease in P_{HRR} and THR of PU as a consequence of the decrease in mass loss rate. Nano-sized fillers can serve as effective anti-dripping agent as well as having a fire retardant effect and provide increased char formation and char strength. The amount of smoke (specific extinction area) slightly increased with the addition of anti-dripping agents. Similar results were also observed with the APP filled PU samples (Table 4).

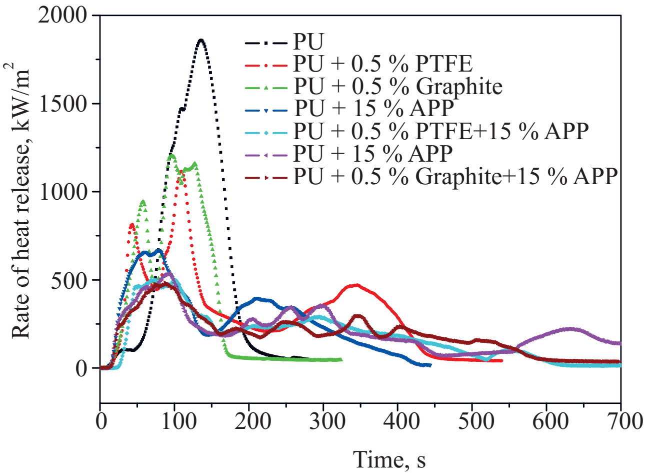

Fig. 3. Heat release curves of PU + anti-dripping agents + APP

Effect of halogenated flame retardant additives

The most widely used halogenated fire retardants are bromine and chlorine compound which may be either reactive compounds that are incorporated into the polymer

T a b l e 4. Cone calorimetric data for PU + anti-dripping agent + APP

Sample	t_{ign}, s	P_{HRR}, kW/m^2 (% reduction)	*THR* MJ/m^2	*AMLR* g/m^2 · s	*ASEA* m^2/kg
PU	12 ± 4	1854 ± 65	160 ± 7	44 ± 5	452 ± 18
PU + 0.5 % PTFE	14 ± 1	1450 ± 126 (22)	132 ± 13	18 ± 1	493 ± 26
PU + 0.5 % graphite	11 ± 2	1187 ± 186 (36)	152 ± 4	22 ± 4	519 ± 35
PU + 15 % APP (P42)	12 ± 1	720 ± 37 (61)	137 ± 10	15 ± 1	500 ± 40
PU + 15 % APP + 0.5 % PTFE	11 ± 1	553 ± 43 (70)	119 ± 12	12 ± 2	585 ± 290
PU + 15 % APP (3118F)	12 ± 2	581 ± 78 (69)	141 ± 1	11 ± 1	467 ± 22
PU + 15 % APP + 0.5 % graphite	10 ± 1	536 ± 99 (71)	130 ± 4	9 ± 1	641 ± 121

or additives. The fire retardant activity of halogenated compounds is often dramatically increased when they are used in combination with antimony trioxide. This synergistic effect is most probably due to the formation of volatile antimony halogen compounds, which act as efficient flame inhibitors in the gas phase. In this study, six (three reactive and three additive) brominated FRs and one additive chlorinated FR are used in combination with antimony oxide at a ratio of 4:1 at constant loading of 15 % by weight. Fig. 4 shows the thermal analysis of PU filled with different halogenated FRs.

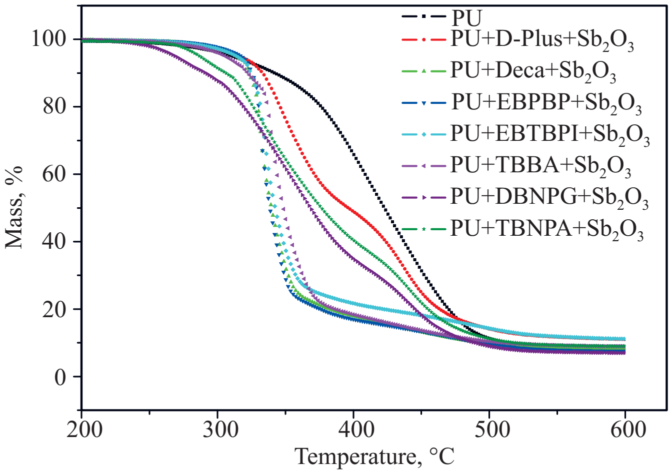

Fig. 4. TGA of polyurea filled with halogenated FR + Sb_2O_3 (4:1)

The thermal stability of PU decreases upon the addition of halogenated FRs for both chlorine and bromine. The decrease in thermal stability is less significant for chlorine compared to bromine compounds. Moreover, the chlorinated-filled PU shows slow degradation with two stages and also retained more char residue at higher temperature, compared to brominated FR. In the case of brominated FRs, the reactive aliphatic brominated FRs (DBNPG and TBNPA) filled PU showed poor thermal stability among the other brominated FRs. But, those samples showed the slow degradation with higher T_{max} as compared to the control sample (Table 5). It was found that the ethylene bis-tetrabromo phthalimide (EBTBPI) filled sample shows more char residue at higher temperature than that of control sample. This may be due to the slow degradation of EBTBPI which also retained more char (26 % at 600 °C) at higher temperature.

T a b l e 5. Effect of halogenated FR additives on the thermal properties of polyurea

Sample	$T_{10\%}$ °C	T_{max} °C	Char at 700 °C, %
PU	346	433	7.1
PU + 12 % D-plus + 3 % Sb_2O_3	333	437	10.6
PU + 12 % Deca + 3 % Sb_2O_3	323	333	7.9
PU + 12 % EBPBP + 3 % Sb_2O_3	325	332	7.0
PU + 12 % EBTBPI + 3 % Sb_2O_3	324	335	10.6
PU + 12 % TBBA + 3 % Sb_2O_3	322	340	8.4
PU + 12 % DBNPG + 3 % Sb_2O_3	291	442	6.5
PU + 12 % TBNPA + 3 % Sb_2O_3	306	444	8.2

The effect of different halogenated FRs on the heat release rate of PU samples is shown in Fig. 5. On the addition of halogenated FRs, a smaller amount of heat is released and moreover, it is found that the heat releases earlier in multiple steps, compared to the control sample.

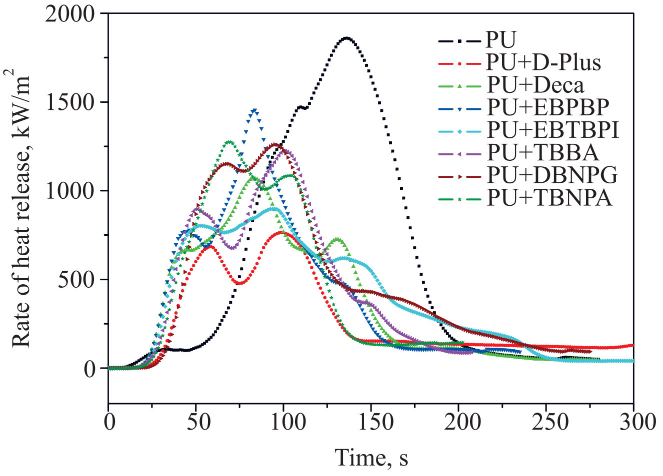

Fig. 5. Heat release curves of PU filled with halogenated FR + Sb_2O_3 (4:1)

T a b l e 6. Cone calorimetric data for PU filled with halogenated additives

Sample	t_{ign}, s	P_{HRR}, kW/m^2 (% reduction)	THR MJ/m^2	$AMLR$ g/m^2 · s	$ASEA$ m^2/kg
PU	12 ± 4	1854 ± 65	160 ± 7	44 ± 5	452 ± 18
PU + 12 % D-plus + 3 % Sb_2O_3	21 ± 2	805 ± 142 (57)	79 ± 10	14 ± 1	5658 ± 195
PU + 12 % Deca + 3 % Sb_2O_3	17 ± 1	1124 ± 142 (39)	101 ± 2	44 ± 4	3867 ± 298
PU + 12 % EBPBP + 3 % Sb_2O_3	18 ± 1	1466 ± 2 (21)	98 ± 5	44 ± 1	3185 ± 674
PU + 12 % EBTBPI + 3 % Sb_2O_3	19 ± 2	920 ± 39 (50)	112 ± 1	29 ± 2	2958 ± 882
PU + 12 % TBBA + 3 % Sb_2O_3	18 ± 1	1149 ± 79 (38)	95 ± 17	24 ± 4	1847 ± 220
PU + 12 % DBNPG + 3 % Sb_2O_3	24 ± 3	1265 ± 35 (32)	127 ± 7	32 ± 1	699 ± 150
PU + 12 % TBNPA + 3 % Sb_2O_3	20 ± 3	1279 ± 26 (31)	108 ± 10	44 ± 3	593 ± 30

The cone data is represented in Table 6. Interestingly, the time to ignition of PU increases with the addition of halogenated FRs.

The dechlorane plus filled sample releases a smaller amount of heat (both P_{HRR} and THR) as well as lower mass loss rate compared to brominated and control sample. But, more smoke is released from the chlorine-containing-filled PU. The halogen-containing samples release more smoke, compared to the control sample. Amongst the brominated FRs, ethylene bis-tetrabromo phthalimide (EBTBPI) performs best in terms of reduction in P_{HRR}; this probably due to the greater thermal stability of EBTBPI (onset 463 °C). The reactive brominated FRs releases less smoke during burning, compared to the other halogenated FR additives. Overall, halogenated-filled PU show a longer time to ignition, reduced THR and higher smoke evolution, compared to the control sample.

Effect of phosphorus based flame retardants

Phosphorus-based fire retardants are most commonly used for oxygen containing polymers. These are reactive and/or additive, organic or inorganic compounds with a variety of structures (phosphate, phosphite, phosphonate, phosphinate, *etc.*) and different oxidation states (V, III, 0, *etc.*). The performance of a particular phosphorus compound depends strongly on the nature of the polymeric materials. The phosphorus fire retardants have been used for a wide range of materials and different applications. In this study, nearly all varieties of commercially available phosphorus fire retardants was used at the constant loading of 15 % by weight in the polyurea system. The effect of different phosphate FR additives on the thermal degradation of PU under nitrogen atmosphere is shown in Fig. 6. There is no significant change in the degradation pattern of PU with the addition of phosphates. It was found that there is an increase in thermal stability of PU with the addition of BADP and RP compared to the other phosphates and the control sample. This is due to the greater thermal stability of BADP (onset 432 °C) and RP (onset 368 °C). RDP- and EDAP-filled PU degrade very rapidly around 400 °C and subsequently there is little weight loss until 800 °C. The effect of phosphates on the thermal properties of PU is shown in Table 7. The onset temperature of PU significantly increases with the addition of BADP, compared to the other phosphates and the control sample. There is no significant change in T_{max} of PU with the addition of phosphates except EDAP, RDP and BADP. Interestingly, these additives maintain a greater amount of char at higher temperature

T a b l e 7. Effect of phosphorus compounds on the thermal properties of polyurea

Sample	$T_{10\,\%}$, °C	T_{max}, °C	Char at 700 °C, %
PU	346	433	7.1
PU + 15 % TPP	325	433	5.9
PU + 15 % EDAP	318	410	10.9
PU + 15 % RDP	344	394	9.6
PU + 15 % BADP	362	423	11.8
PU + 15 % RP	348	432	6.8
PU + 15 % TPPO	324	433	5.6
PU + 15 % NHP	322	430	3.9
PU + 15 % TDPGP	280	429	6.5
PU + 15 % TPP	253	387	13.4
PU + 15 % ABPAP	306	373	10.0
PU + 15 % BDCPPDP	318	372	11.6
PU + 10 % DMMP	292	416	6.5
PU + 15 % A-N	325	380	9.9
PU + 15 % PMP	316	373	10.7
PU + 15 % OP 1230	353	431	10.5
PU + 15 % OP 1314	366	421	10.5
PU + 15 % OP 1311(LV)	349	421	11.1
PU + 15 % DOPO	333	377	6.9
PU + 15 % APP (P/30)	299	382	13.2
PU + 15 % APP (P42)	303	380	14.1
PU + 15 % APP (3118F)	318	408	13.3
PU + 15 % TCEP	277	409	9.0
PU + 15 % TMCP	297	409	8.6
PU + 15 % A-205	314	412	8.8
PU + 15 % A-78	278	412	10.1

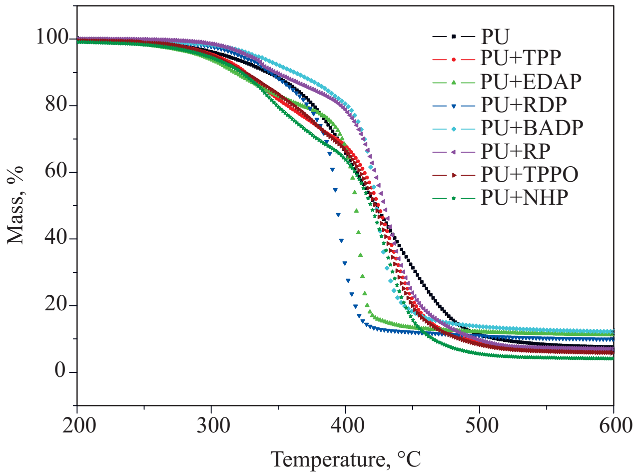

Fig. 6. TGA of polyurea filled with organophosphate FR additives

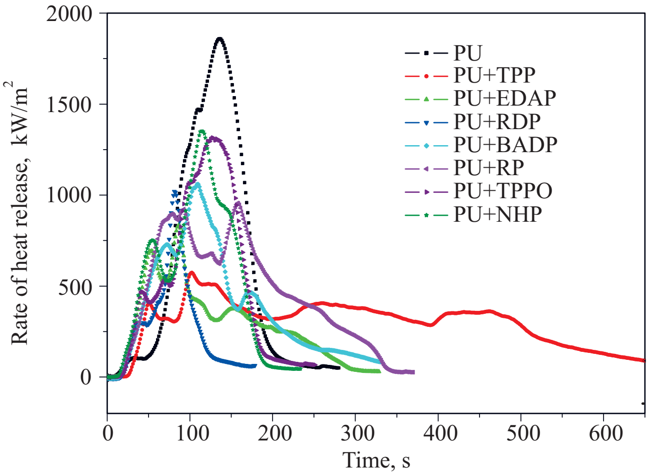

Fig. 7. Heat release curves of PU filled with phosphates

when compared to the control sample and also other phosphates, which provide lower char residues compared to the control sample. It may be that these additives do not interact during combustion and are gas-phase effective fire retardants.

Fig. 7 shows the heat release rate of PU filled with organophosphate FR additives at a constant loading of 15 % by weight. The phosphate-filled PU releases lower amount of heat and follows multiple path ways. The TPP-filled sample shows a prolonged burning behavior while the RDP-filled PU burns for a short time, compared

Table 8. Cone calorimetric data for PU filled with different phosphorus compounds

Sample	t_{ign}, s	P_{HRR}, kW/m^2 (% reduction)	THR MJ/m^2	$AMLR$ g/m^2 · s	$ASEA$ m^2/kg
PU	12 ± 4	1854 ± 65	160 ± 7	44 ± 5	452 ± 18
PU + 15 % TPP	18 ± 3	637 ± 149 (66)	169 ± 23	15 ± 1	632 ± 11
PU + 15 % EDAP	16 ± 2	691 ± 151 (63)	72 ± 31	13 ± 2	434 ± 74
PU + 15 % RDP	16 ± 5	1222 ± 354 (34)	88 ± 37	18 ± 8	656 ± 18
PU + 15 % BADP	17 ± 2	1104 ± 150 (40)	103 ± 22	23 ± 2	677 ± 203
PU + 15 % RP	15 ± 1	964 ± 12 (48)	131 ± 8	25 ± 2	976 ± 43
PU + 15 % TPPO	16 ± 1	1324 ± 23 (29)	130 ± 9	24 ± 3	999 ± 31
PU + 15 % NHP	14 ± 2	1386 ± 146 (25)	162 ± 21	18 ± 2	874 ± 40
PU + 15 % TDPGP	13 ± 2	1146 ± 306 (38)	125 ± 33	22 ± 1	633 ± 24
PU + 15 % TPP	7 ± 1	1255 ± 63 (32)	116 ± 19	29 ± 11	525 ± 36
PU + 15 % ABPAP	10 ± 2	1318 ± 131 (29)	143 ± 27	23 ± 8	444 ± 24
PU + 15 % BDCPPDP	8 ± 2	1212 ± 44 (35)	184 ± 5	24 ± 1	635 ± 19
PU + 10 % DMMP	14 ± 3	993 ± 25 (46)	112 ± 4	28 ± 3	515 ± 43
PU + 15 % A-N	18 ± 2	1315 ± 379 (29)	131 ± 18	18 ± 1	886 ± 233
PU + 15 % PMP	13 ± 2	1137 ± 134 (39)	130 ± 6	27 ± 2	957 ± 518
PU + 15 % OP 1230	16 ± 4	872 ± 157 (53)	122 ± 4	14 ± 2	706 ± 29
PU + 15 % OP 1314	14 ± 2	527 ± 34 (72)	102 ± 6	15 ± 2	488 ± 309
PU + 15 % OP 1311(LV)	16 ± 1	554 ± 30 (70)	108 ± 8	17 ± 3	792 ± 18
PU + 15 % DOPO	20 ± 1	2671 ± 294 (-)	143 ± 13	24 ± 13	670 ± 59
PU + 15 % APP (P/30)	14 ± 1	833 ± 100 (55)	142 ± 11	18 ± 1	487 ± 15
PU + 15 % APP (P42)	12 ± 1	720 ± 37 (61)	137 ± 10	15 ± 1	500 ± 40
PU + 15 % APP (3118F)	12 ± 2	581 ± 78 (69)	141 ± 1	11 ± 1	467 ± 22
PU + 15 % TCEP	13 ± 1	725 ± 10 (61)	120 ± 4	21 ± 2	673 ± 35
PU + 15 % TMCP	11 ± 1	764 ± 101 (59)	155 ± 4	21 ± 1	686 ± 14
PU + 15 % A-205	15 ± 2	775 ± 13 (58)	110 ± 8	24 ± 2	808 ± 127
PU + 15 % A-78	13 ± 1	635 ± 40 (66)	111 ± 2	21 ± 2	685 ± 28

to the control sample. The entire cone data for phosphate-filled PU is presented in Table 8. There is not a considerable change in time to ignition of PU upon the addition of phosphates. TPP- and EDAP-filled samples show a remarkable reduction of P_{HRR}, compared to the other phosphates; considerable *THR* reduction was observed in the case of EDAP-, RDP- and BADP-filled samples. This may be due to a higher amount of char residue (as shown in the TGA section), which effectively acts to block heat transfer. The mass loss rate of PU decreases significantly with the addition of phosphates while the evolution of smoke increases.

Fig. 8 shows the thermogravimetric analysis of PU filled with organophosites. The thermal stability of PU decreases upon the addition of phosphites. PU filled with an aliphatic phosphite [TDPGP — tris(dipropylene glycol)phosphate] has poor initial thermal stability but rather slow degradation at higher temperature, with good thermal stability between about 350—470 °C, compared to other phosphites. At high temperature, the TDPGP-filled sample has almost completely volatilized and leaves little char residue compared to the control sample as well as other phosphites. The data in Table 7 confirms the decrease in thermal stability (onset and maximum degradation temperature) of PU filled with phosphites.

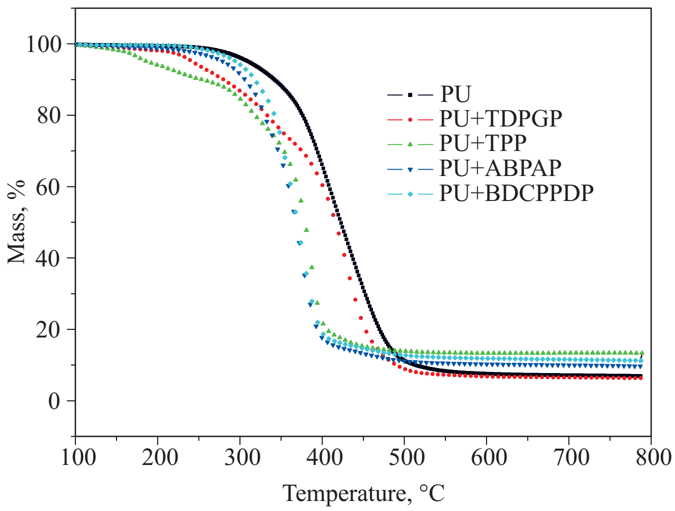

Fig. 8. TGA of polyurea filled with organophosphite additives

Fig. 9 shows the effect of phosphites on the heat release rates of PU sample with respect to time. As compared to the control sample, the phosphite-filled PU shows early heat release as well as multiple steps of heat release. TDPGP-filled PU shows less heat released compared to other phosphites and in addition, the time to P_{HRR} is similar to that of the control. TPP-filled PU burns quicker compared to the other phosphites and the control sample. Table 8 demonstrates the effect of different organophosphites on PU. The time to ignition decreases with the addition of phosphites as a result of low thermal stability of phosphites (170—300 °C), which is well below that of the control (346 °C). Compared to the phosphates, the phosphite-filled samples showed inferior ignition time as well as poor fire retardant properties in PU. This may be due to lower thermal stability of organophosphites compared to the PU. The amount of smoke also increases upon the addition of phosphites.

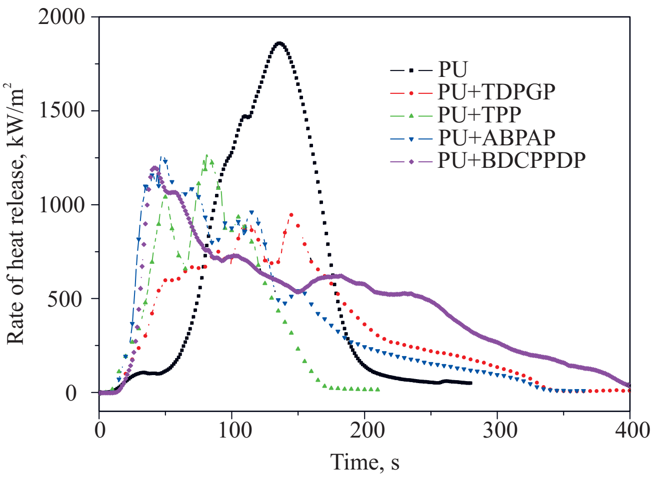

Fig. 9. Heat release curves of PU filled with phosphites

Three different phosphonates were employed in this study, linear (dimethyl methyl phosphonate, DMMP), cyclic (cyclic oligomeric phosphonate, Antiblaze N), and polymeric [poly(*m*-phenylene methyl phosphonate), Fyrol PMP]. DMMP is a low viscosity liquid, which causes plasticization of PU. Because of this, only 10 % DMMP by weight was incorporated into PU; above this loading the material is unsuitable, probably caused by a decrease in crosslinking reaction. The effect of these additives on the thermal stability of PU is shown in Fig. 10 and Table 7. The thermal stability of PU decreases with the addition of phosphonates. The DMMP-filled PU shows poor initial thermal stability compared to the other phos-

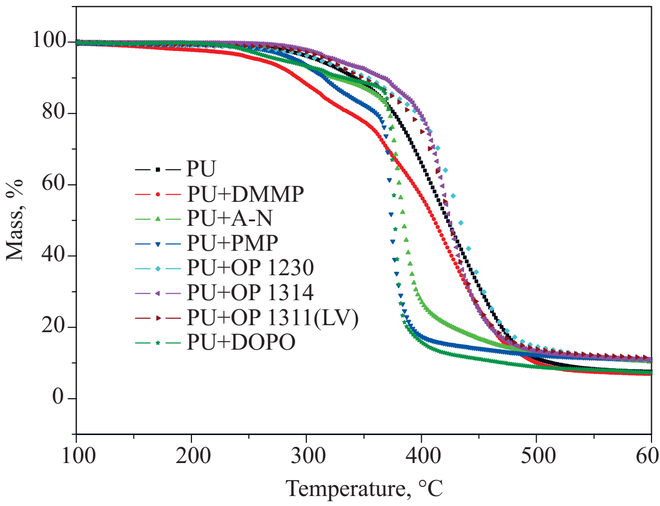

Fig. 10. TGA of polyurea filled with phosphonates and phosphinates

phonates. However, this material is more thermally stable in the range of 380—475 °C and then volatilizes significantly compared to other phosphonates. The Fyrol PMP-filled sample shows greater char residue at high temperature compared to the other phosphonates and the control sample.

The effect of phosphonates on the heat release rate and all of the cone date are collected in Fig. 11 and Table 8. The phosphonate-filled samples show earlier heat release rates with a more pronounced split peak compared to the control sample. In the first stage, the Fyrol PMP-filled sample releases more heat, whereas the cyclic oligomeric phosphonate (Antiblaze N) liberates a greater amount of heat in the second stage. There is no change in time to ignition of PU with the addition of phosphonates. The DMMP-filled sample shows better reduction in P_{HRR} compared to the other phosphonates, as shown in Table 8. This may be due to the formation of thermally stable char between 380 °C to 475 °C (as shown in Fig. 10), which could play a critical role in the fire retardation of PU. A large amount of smoke is released upon the addition of phosphonates to PU.

Fig. 10 displays the TGA of PU filled with phosphinates, aluminum salt of organic phosphinate and 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO). There are two different form of aluminum phosphinates used in this study, neat aluminum diethylphosphinate (OP 1230) and synergistic blend of phosphinates, melamine phosphate with aluminum diethylphosphinate [OP 1314 and OP 1311(LV)]. DOPO contains a monofunctional reactive group, which can react with the isocyanate during the preparation of PU. The thermal stability, as well as the amount of char at high temperature, improves upon the addition of aluminum diethylphosphinate compared to the DOPO-filled and the control PUs. DOPO does not contribute to char formation and the thermal stability is not improved, suggesting that DOPO is a vapor phase active material in PU. The thermal analysis data for phosphinate-filled PU is collected in Table 7. Aluminum diethylphosphinate-filled PU shows better thermal stability (both onset and T_{max}) and char formation compared to DOPO-filled PU. This is likely due to the higher thermal stability and slow degradation of aluminum phosphinates (435—480 °C) compared to DOPO (285 °C) and the control sample (346 °C). Further, the synergistic blend (OP 1314) filled-PU shows a higher onset temperature than does the pristine aluminum diethylphosphinate (OP 1230), but a higher T_{max} is observed with the pristine phosphinate-filled sample, which closely matches with the control sample.

The heat release rate curves with respect to time and the cone calorimetric data of phosphinate-filled PU samples are collected in Fig. 11 and Table 8. The DOPO-filled sample releases a greater amount of heat compared to aluminum diethylphosphinates and the control sample and the filled samples begin to lose heat before the control sample. The synergistic blend shows a lower P_{HRR} compared to the pristine aluminum diethylphosphinate. The times to ignition of filled-PU are slightly higher than those of the control. DOPO-filled PU shows inferior fire retardant properties with much higher heat released compared to the control. This may be due the absence of an interaction with PU and/or its degradation products and the loss of DOPO during burning as a result poor thermal stability (as shown in Fig. 10) and the absence of a contribution to char formation. In addition, the crosslink density of DOPO-filled PU may deteriorate due to acidic cracking of the urea bonds at higher temperature [8] as well as disparity in reaction rates of DOPO and the diamine with diisocyanate during preparation of PU. DOPO-filled PU shows higher *THR* and *AMLR* compared to aluminum phosphinate salts. Phosphinate-filled PU releases more smoke during burning compared to the control. The blend of melamine phosphate with the aluminum diethylphosphinate salt (OP 1314) shows enhanced reduction in P_{HRR} compared to phosphorus-based fire retardants in the other oxidation states of phosphorus.

Ammonium polyphosphate (APP) is a well-known intumescent fire retardant for polyurethane and polyurea systems. The decomposition of APP leads to polyphosphoric acids, ammonia and polyphosphates. The polyphosphoric acid (acid source) reacts with char sources (PU) to form polyphosphate esters, which leads to further dehydration (with evolution of water) to form a foamed char on the surface of the sample during burning. The intumescent (foamed) char prevents mass as well as heat transfer and further degradation of the polymer. In this study, three different forms of APP were used, crystalline form I (P/30), crystalline form II (P/42) and formaldehyde coated APP (3118F) at the constant loading of 15 wt. %. Fig. 12 displays the thermal degradation of PU filled with the three different APP. The coated APP shows better thermal stability compared to the uncoated (forms I and II) APP-filled PU. At the high temperature, the char residues of all three APP-filled samples are similar. Table 7 provides the onset temperature, T_{max} and char residue at 700 °C of all three APP-filled PUs. There is a decrease in onset as well as T_{max} temperature of APP-filled PU. The decrease in thermal stability of APP-filled PU is due to the formation of polyphosphoric acid, a strong Lewis acid catalyst, which accelerates the decomposition of PU, thereby decreasing the thermal stability of PU.

Fig. 13 shows the heat release rate of PU filled with different forms of APP at the constant loading (15 wt. %). It is found that the heat is released earlier with less time to peak *HRR* in the case of APP filled samples regardless of the nature of APP, compared to the control sample. Also, coated APP filled sample shows lower peak *HRR* with prolonged burning behavior compared to types I and II APP filled sample. This may be due to the increased thermal stability of the coated APP filled sample between 300—450 °C (shown in Fig. 12) and moreover, it shows excellent compatibly with PU starting materials (espe-

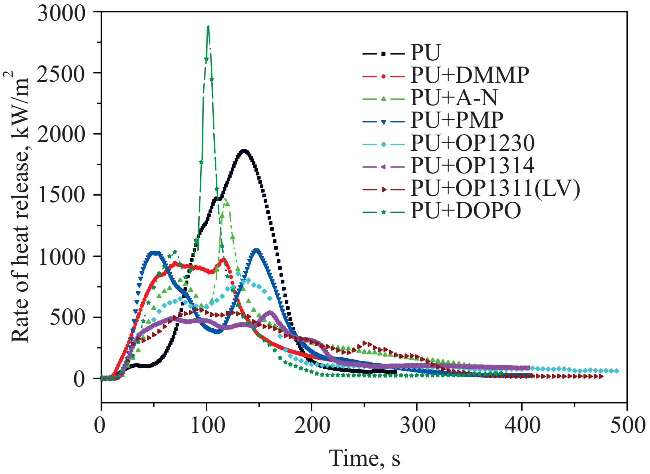

Fig. 11. Heat release curves of PU filled with phosphonates and phosphinates

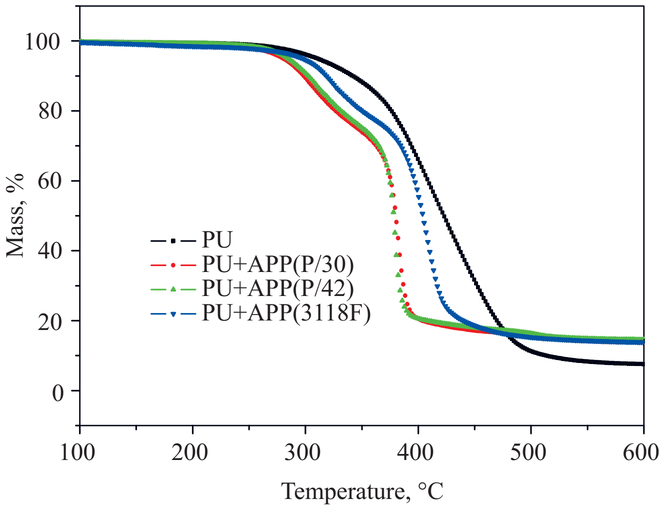

Fig. 12. TGA of polyurea filled with ammonium polyphosphate

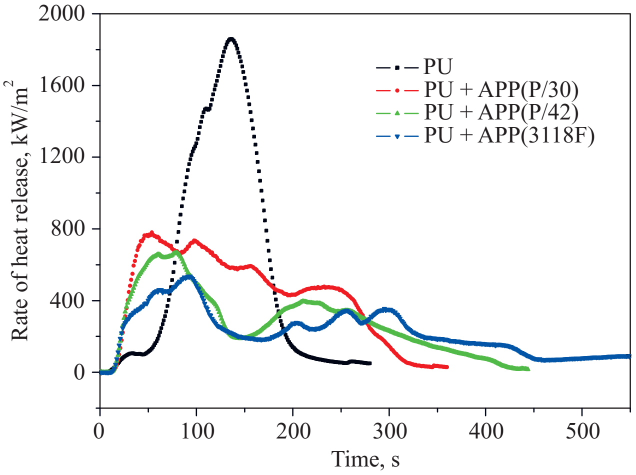

Fig. 13. Heat release curves of PU filled with ammonium polyphosphate

cially diamine), probably because of the formaldehyde coating on the APP. On the whole, APP filled sample releases less amount of heat with longer burning time. The other cone calorimetric data of PU filled with APP are presented in Table 8. There is not a significant change in ignition time of APP-filled PU. The coated APP-filled PU exhibits a larger reduction of P_{HRR} than that of uncoated APP and the *THR* and *AMLR* of PU decrease with the addition of APP but smoke slightly increases.

Replacing halogens with phosphorus in fire retardants provides benefits, including high fire retardant efficiency, lower production of corrosive and toxic gases in flames and less environmental pollution. In this study, three chloroalkyl phosphates (varying amounts of chlorine and phosphorus), Antiblaze TCEP (Cl = 36 %, P = 10.6 %), Antiblaze TMCP (Cl = 33 %, P = 9.4 %), Antiblaze 205 (Cl = 32 %, P = 7.6 %) and one chloroalkyl phosphonate (Antiblaze 78, Cl = 34 %, P = 12 %), fire retardants was used at the constant loading of 15 % by weight. Fig. 14 and Table 7 show the thermal properties of PU filled with chloroalkyl phosphate and phosphonate.

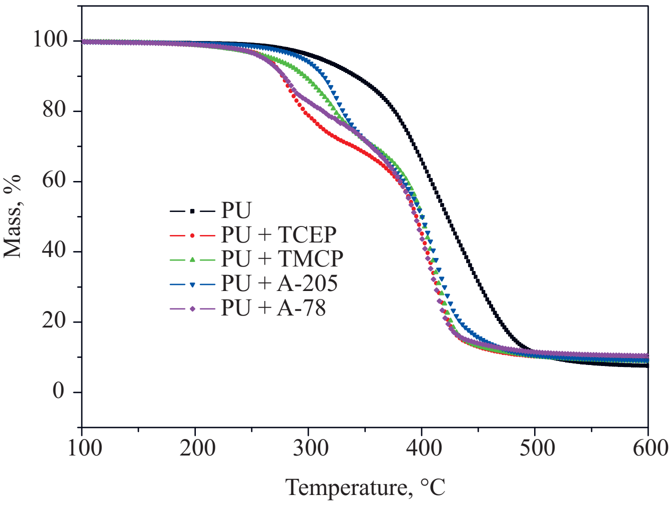

Fig. 14. TGA of polyurea filled with chloroalkyl phosphates

The thermal stability of PU decreases when chloroalkyl phosphate or phosphonate are added, but the amount of char increases. The onset temperature of Antiblaze 205-filled PU is slightly higher than that of the other chloroalkyl phosphate- and phosphonate-filled sample, which may be attributed to the lower amount of phosphorus (7.6 %) in Antiblaze 205. The chloroalkyl phosphonate (Antiblaze 78) filled-PU shows slightly higher amount of char residue compared to chloroalkyl phosphate filled sample. This may be due to the larger amount of phosphorus (12 %). Thermal stability appears to be sensitive to the percentage of phosphorus in chloroalkyl phosphorus fire retardants is sensitive to thermal stability as well as amount of char formation in PU system.

Fig. 15 shows the heat release rate of chloroalkyl phosphate- and phosphonate-filled PUs and their corresponding cone data are collected in Table 8. The main peak of

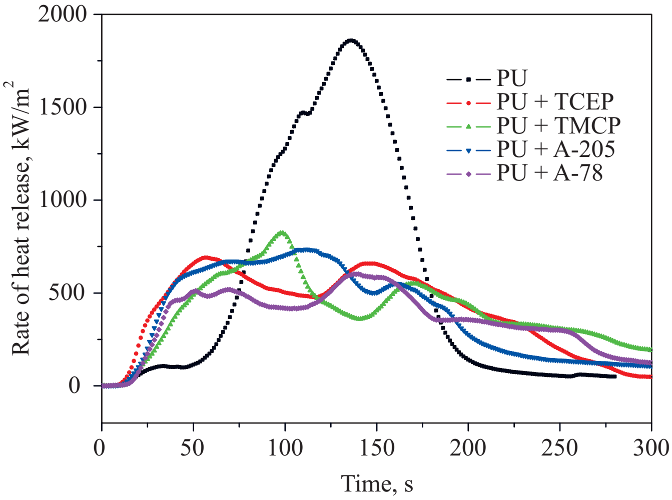

Fig. 15. Heat release curves of PU filled with chloroalkyl phosphates

heat release commences earlier in the filled PUs and there are multiple steps in the release of heat. All of the cone parameters appear to be relatively the same for the three chloroalkyl phosphates and the phosphonate. It is worth mentioning that the combination of chlorine and phosphorus (chloroalkyl phosphates) filled-PU shows better fire retardant efficiency and releases a smaller amount of smoke during burning, compared to halogen-filled PU (either bromine or chlorine) combined with antimony oxide (as shown in Table 6).

Effect of mineral fillers

Mineral fillers have advantages as fire retardants — they are inexpensive, readily available, non-toxic and environmentally friendly. Three different mineral fillers, aluminum trihydroxide (ATH), magnesium hydroxide (MDH) and zinc borate (ZB), are used at the constant loading of 30 wt. %. In general, the required amount of mineral fillers is quite high (>60 wt. %) for effective fire retardancy of polymeric materials, because these materials function by removing the heat from the polymer by the endothermic decomposition of the mineral. High loadings have a detrimental effect on the mechanical properties and may be difficult to process as a result of increased viscosity. Thus, in this study 30 wt. % of mineral fillers is used for convenience in sample preparation.

Table 9. Effect of mineral fillers on the thermal properties of polyurea

Sample	$T_{10\,\%}$, °C	T_{max}, °C	Char at 700 °C, %
PU	346	433	7.1
PU + 30 % ATH	301	425	21.5
PU + 30 % MDH	364	431	25.2
PU + 30 % ZB	355	427	29.2

Fig. 16 displays the TGA curves mineral-filled PUs while the TGA data is shown in Table 9. The thermal stability of ATH-filled PU is lower compared to the other mineral fillers and the control sample. In addition, ATH-filled PU exhibits two discrete degradation steps. This may be due to the higher thermal stability of MDH (373 °C) and ZB (425 °C) compared to ATH (276 °C) and the control PU (346 °C). The addition of mineral fillers leads to more char residue retained at higher temperature, as expected. The amount of char is higher for ZB-filled PU; the experimental amount of is in good agreement with that expected from the degradation of the minerals.

Fig. 17 shows the heat release rate of mineral-filled PU and the corresponding cone data are presented in Table 10. The heat release rate curve is separated into two peaks in the case of filled PU and all three minerals behave similarly; the *THR* is reduced which is likely due to a reduced amount of polymer. All three offers reduced smoke and

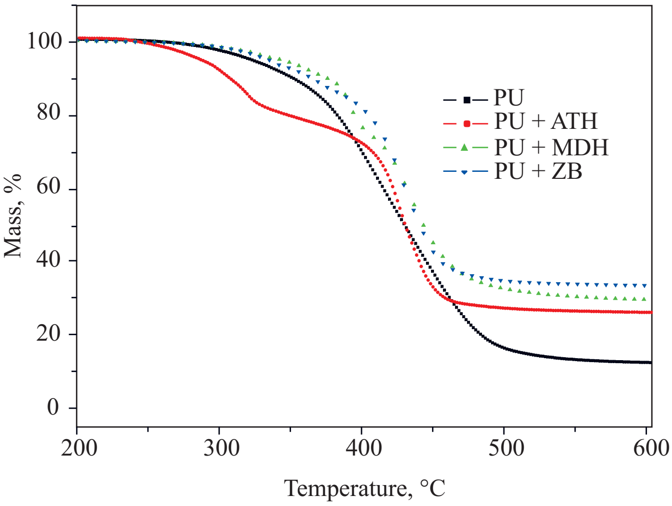

Fig. 16. TGA of polyurea filled with mineral fillers

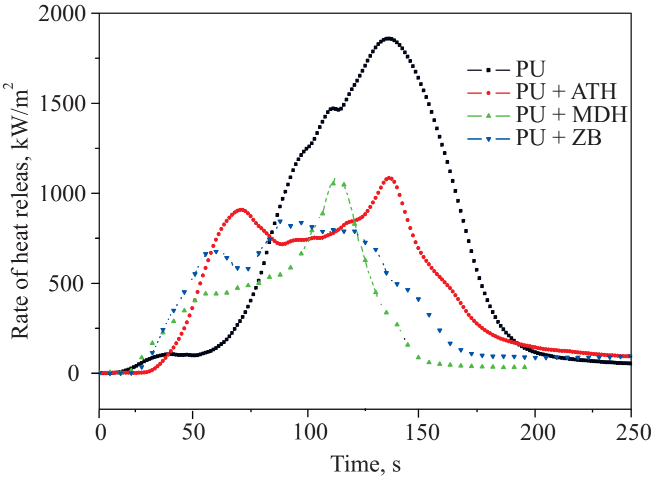

Fig. 17. Heat release curves of PU filled mineral additives

Table 10. Cone calorimetric data for PU filled with mineral fillers

Sample	t_{ign}, s	P_{HRR}, kW/m^2 (% reduction)	*THR* MJ/m^2	*AMLR* g/m^2 · s	*ASEA* m^2/kg
PU	12 ± 4	1854 ± 65	160 ± 7	44 ± 5	452 ± 18
PU + 30 % ATH	22 ± 3	1016 ± 68 (45)	113 ± 6	16 ± 3	182 ± 93
PU + 30 % MDH	21 ± 4	968 ± 23 (48)	101 ± 35	21 ± 9	284 ± 56
PU + 30 % ZB	16 ± 3	902 ± 136 (51)	121 ± 5	9 ± 1	288 ± 26

reduced mass loss rate, with ZB showing the lowest mass loss rate and the largest reduction in P_{HRR}.

Effect of melamine and its derivatives

Melamine and its derivatives are a small but growing family of fire retardants that are considered to be environmentally friendly. The main advantages are that these are low toxicity solids, which, in a fire, will give a low amount of smoke and not evolve toxic gases. Three commercially available melamine compounds, melamine, melamine polyphosphate (MPP) and melamine cyanurate (MC), are used at the constant loading of 15 wt. %.

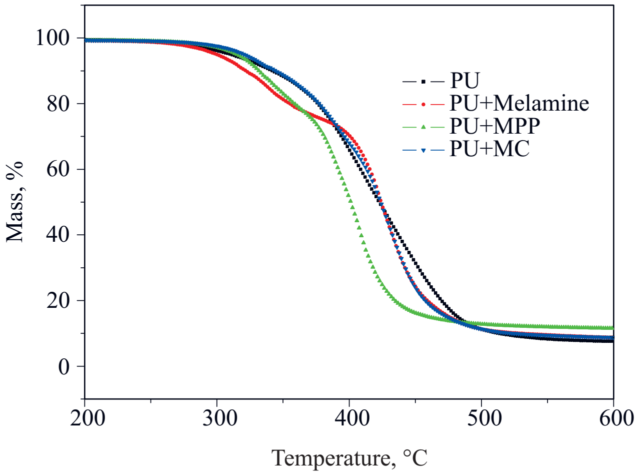

Fig. 18. TGA of polyurea filled with melamine compounds

Fig. 18 shows the TGA curves and melamine-filled PU and the data is collected in Table 11. The thermal stability of melamine- and MPP-filled PU is decreased compared to the control. This is due to the lower thermal stability of melamine (314 °C) and phosphorus present in MPP. However, the MPP-filled PU retains more char residue at high temperature. For MC-filled PU, there is no significant change in either $T_{10\,\%}$ or T_{max}.

Table 11. Effect of melamine additives on the thermal properties of polyurea

Sample	$T_{10\,\%}$, °C	T_{max}, °C	Char at 700 °C, %
PU	346	433	7.1
PU + 15 % melamine	322	424	8.2
PU + 15 % MPP	332	408	11.2
PU + 15 % MC	344	429	8.3

The heat release rate curves of melamine-filled PUs are displayed in Fig. 19 and the data are collected in Table 12. For both melamine- and MC-filled PUs, a two-step heat release is seen but with MPP-filled PU, these steps are less distinct but the heat release continues for a long

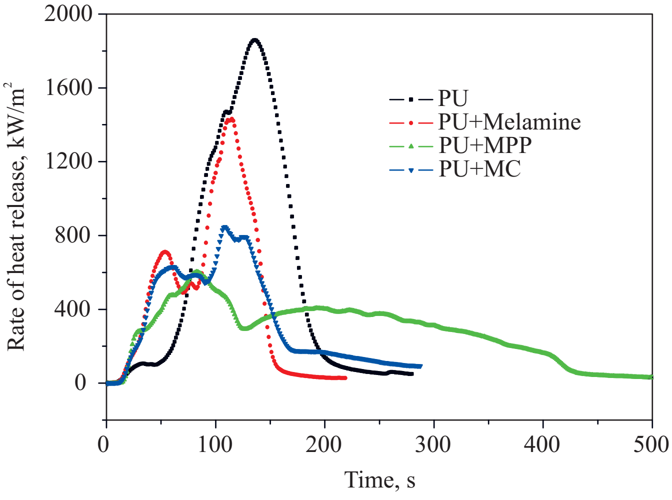

Fig. 19. Heat release curves of PU filled melamine compounds

Table 12. Cone calorimetric data for PU filled with melamine compounds

Sample	t_{ign}, s	P_{HRR}, kW/m^2 (% reduction)	*THR* MJ/m^2	*AMLR* g/m^2 · s	*ASEA* m^2/kg
PU	12 ± 4	1854 ± 65	160 ± 7	44 ± 5	452 ± 18
PU + 15 % melamine	12 ± 2	1163 ± 310 (37)	83 ± 17	29 ± 8	400 ± 212
PU + 15 % MPP	13 ± 2	480 ± 117 (74)	124 ± 24	14 ± 3	1326 ± 380
PU + 15 % MC	12 ± 1	846 ± 48 (54)	96 ± 8	22 ± 6	298 ± 161

time. MPP-filled PU also exhibits the greatest reduction in P_{HRR}, 74 %, but also the greatest amount of smoke. This may be attributed to the presence of both phosphorus and nitrogen in this material and the greater amount of char produced, as seen in Fig. 18.

Effect of intumescent additives

Intumescence involves the formation of a foamed char on the surface of the materials during burning, and this foam is a heat insulator. In general, intumescent fire retardants (IFR) contain a mixture of a carbon source (carbonific) to build up char, an acid source to dehydrate the carbonific and a gas source (spumific) that decomposes to generate blowing gases to foam the char. The classical IFR system is a combination of pentaerythritol, ammonium polyphosphate (APP), and melamine. Expandable graphite (EG) is also well-known as an IFR additive used for polymeric materials. Some parameters to consider for the selection of EG for a particular polymer are: onset temperature, particle size and the expansion volume. The particle size of EG plays an important role in fire retardation of PUF [9, 10]. In this section, EGs with different onset expansion temperatures (160 and 220 °C) and particle sizes (80 and 50 mesh) of EG was utilized.

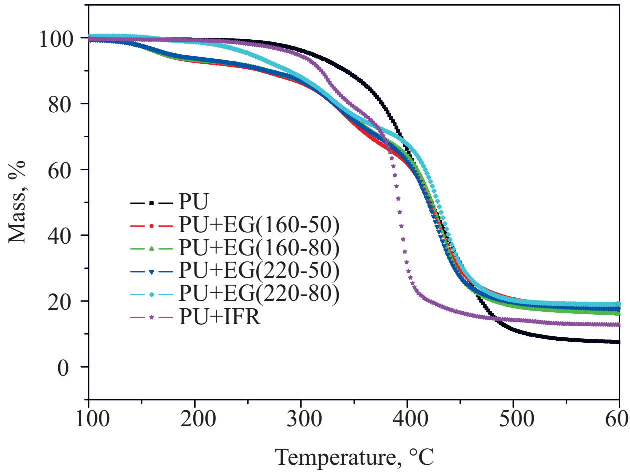

Fig. 20. TGA of polyurea filled with intumescent additives

T a b l e 13. Effect of intumescent additives on the thermal properties of polyurea

Sample	$T_{10\,\%}$, °C	T_{max}, °C	Char at 700 °C, %
PU	346	433	7.1
PU + 15 % EG(160-50)	263	430	17.5
PU + 15 % EG(160-80)	268	431	15.7
PU + 15 % EG(220-50)	269	427	17.2
PU + 15 % EG(220-80)	288	433	19.6
PU + 15 % IFR	319	394	12.4

Fig. 20 shows the TGA curves of EG-filled PU and a classic IFR-filled PU and the data are collected in Table 13. Both the onset of degradation and T_{max} are lower for the filled PUs but more char is obtained. The classic IFR has the highest onset temperature but the lowest value of T_{max}. For EG, it appears that and onset of expansion of 220 °C and a particle size of 80 mesh has the highest temperatures of degradation and the greatest amount of char.

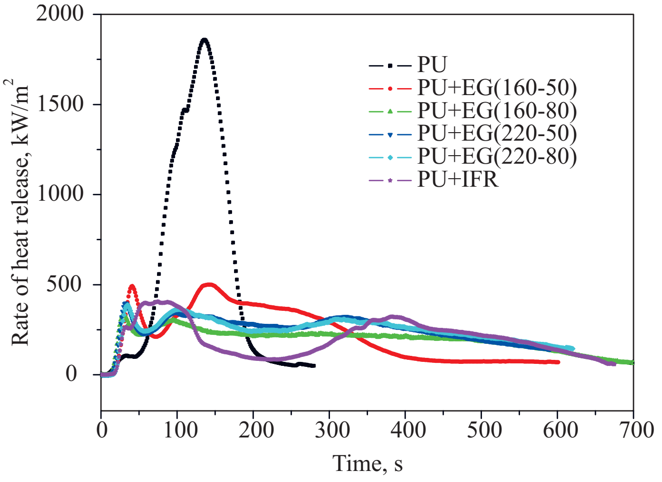

Fig. 21. Heat release curves of PU filled intumescent additives

The heat release rate curves of EG- and IFR-filled PU is shown in Fig. 21 with the data collected in Table 14. There is a quite significant reduction in P_{HRR} for all intumescent systems along with a large reduction in mass loss rate and a small reduction in the total heat released

T a b l e 14. Cone calorimetric data for PU filled with intumescent compounds

Sample	t_{ign}, s	P_{HRR}, kW/m² (% reduction)	*THR* MJ/m²	*AMLR* g/m² · s	*ASEA* m²/kg
PU	12 ± 4	1854 ± 65	160 ± 7	44 ± 5	452 ± 18
PU + 15 % EG(160-50)	14 ± 1	519 ± 31 (72)	130 ± 7	12 ± 1	584 ± 22
PU + 15 % EG(160-80)	11 ± 1	421 ± 95 (77)	130 ± 28	9 ± 1	545 ± 51
PU + 15 % EG(220-50)	12 ± 1	396 ± 10 (79)	121 ± 24	11 ± 2	445 ± 85
PU + 15 % EG(220-80)	14 ± 2	394 ± 24 (79)	129 ± 5	10 ± 1	454 ± 50
PU + 15 % IFR	13 ± 2	456 ± 95 (75)	124 ± 13	10 ± 3	1226 ± 349

with no change in the time to ignition. There does not appear to be any difference between the various grades of EG and EG is comparable with the classic IFR system, except that EG releases much less smoke than does the classic IFR system.

CONCLUSIONS

The objective of this work is to identify the most suitable fire retardant system that can be used for polyurea. The choice will depend on what one hopes to gain from the fire retardant as no additive enhances all properties. If smoke reduction is a major goal, the choice of the fire retardant is likely to be different than if reduction in the peak *HRR* is the primary goal. The major findings are:

— Dechlorane plus showed better fire retardant performance compared to brominated additives; however, it does produce smoke.

— Chloroalkyl phosphates are better fire retardants in polyurea than the halogens.

— Melamine phosphate blended organic phosphinate and intumescent additives are suitable candidate FRs for polyurea.

— Mineral fillers and nitrogen based additives confer release of the lesser amount of smoke compared to other classes of fire retardant additives.

— DOPO provides poor fire retardation in polyurea.

If one were to choose fire retardants from amongst those reported in this work, the best system would contain expandable graphite, perhaps with some ammonium polyphosphate.

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XVII Profesorskie Warsztaty Naukowe „Przetwórstwo Tworzyw Polimerowych"

Bydgoszcz, 23—26 czerwca 2013 r.

Środowisko naukowe **Uniwersytetu Technologiczno-Przyrodniczego w Bydgoszczy** związane z problematyką przetwórstwa tworzyw polimerowych, zaprasza do udziału w ***XVII Profesorskich Warsztatach Naukowych „Przetwórstwo Tworzyw Polimerowych"***, które są kontynuacją Spotkań organizowanych od 1980 roku.

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Program Warsztatów obejmuje omówienie:

- Badania naukowe – obecne uwarunkowania
- Program Rozwoju Przedsiębiorczości do 2020 r. w ramach strategii Innowacyjność i Efektywność Gospodarki
- Kierunki rozwoju metod przetwórstwa materiałów polimerowych
- Rozwój współpracy pomiędzy ośrodkami
- Metody kształcenia w świetle wymagań Krajowych Ram Kwalifikacji
- Stopnie naukowe i tytuł naukowy, nowa lista czasopism

a także prezentację wyników badań przez uczestników Warsztatów w formie krótkich wystąpień ustnych oraz w ramach Sesji plakatowej.

Prezentacje prosimy przesyłać w formie elektronicznej do **10 maja br.** (jako plik tekstowy Word, maksymalnie 2000 słów).

Podobnie jak w poprzednich Profesorskich Warsztatach przewiduje się możliwość publikowania wybranych prac w czasopismach „Polimery" i „Przetwórstwo Tworzyw" (materiały przewidziane do druku powinny być przygotowane zgodnie z wymaganiami redakcji czasopism).

Opłata za uczestnictwo — 900 zł (całkowity koszt pobytu, materiałów konferencyjnych oraz naukowych spotkań towarzyszących, VAT) prosimy wnieść w terminie do 15 maja br. na konto: Bank PEKAO S.A. II O/BYDGOSZCZ: nr 93 1240 3493 1111 0000 4279 1256 z dopiskiem „Warsztaty Profesorskie".

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