

Cone Calorimeter Study of Inorganic Salts as Flame Retardants in Polyurethane Adhesive with Limestone Filler

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ABSTRACT: A cone calorimeter was used to test inorganic water-releasing and low-melting compounds as flame retardants in polyurethane adhesive samples. Sodium metasilicate pentahydrate, potassium carbonate mixed with silica gel, sodium hydrogen carbonate, calcium oxalate monohydrate, zinc and magnesium chloride mixed with potassium chloride, aluminium and magnesium hydroxides, ammonium polyphosphate (APP), sodium and potassium phosphates were tested. These additives were used to partially (10–20%) replace the limestone used as a filler in the adhesive. Thermo-

gravimetric analysis was used to study decomposition and melting of the inorganic compounds. The results showed that sodium metasilicate monohydrate formed a protective layer of sodium silicate on the sample surface, significantly delaying the time to ignition. Addition of APP resulted in the lowest overall heat release rate curve. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 1793–1800, 2012

Key words: polyurethane adhesive; flame retardants; cone calorimeter; heat release rate; time to ignition; fire testing

INTRODUCTION

Flame retardants can be active in several different ways, physically and/or chemically, in the condensed phase and/or in the gas phase.^{1–3} Endothermic degradation, dilution of fuel, intumescent shield formation, gas phase dilution, and radical quenching can be mentioned as examples of how flame retardant mechanisms. A flame retardant does not necessarily function in every material even if it works in one. Usually, a potential flame retardant needs to be experimentally tested in the specific application to ascertain its efficiency.

Halogens, especially bromides, have been used as flame retardants for decades due to their low cost and high efficiency.^{4,5} They have been used in many forms of polyhalogenated compounds, which have been shown to bioaccumulate in the human body and potentially be toxic.⁶ Recently, new regulations have banned the use of some polyhalogenated compounds for flame retarding purposes.⁷ The halogens formed and released during the combustion process, are corrosive and highly toxic.

Polyurethane (PUR) is one of the most common plastics due to its many varieties.⁸ The density of PUR can vary from 6 to 1200 kg/m³, and the stiffness varies from soft and flexible to very rigid. The two main ingredients in PUR production are polyalcohol (polyol), containing two or more hydroxyl groups, and isocyanate (–N=C=O). The result of the addition reaction between an alcohol group and an isocyanate group is the urethane linkage (–NH–COO–). PUR adhesives contain relatively large amounts of filler substances, which are added to improve the properties of the glue. Typical filler materials are dolomite and limestone.

The industrial two-component PUR adhesive studied in this work is used in construction and shipbuilding industries. The fire properties of this type of adhesive are restricted by regulations, and need to fulfil testing criterias, such as IMO FTPC.⁹ Therefore, there is an interest in lowering the heat release, without affecting other properties of the adhesive. Depending on legislation and the end use of the products, different types of flame retardants are used in PUR.^{10–12} Phosphorous, halogen, melamine, metal hydroxide containing compounds, to mention a few, have been commonly used to flame retard PUR. Phosphates are well known to increase char formation. In a study by Mequanint *et al.*¹³ the activation energy of PUR is lowered by increased phosphorous content. Ammonium polyphosphate (APP) acts an effective flame retardant in PUR by

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TABLE I
Inorganic Salts Tested for Flame Retarding Effects in PUR Adhesive Samples

| Flame retardant salt | Chemical formula | Manufacturer and product |
|--|---|--------------------------------|
| Sodium metasilicate pentahydrate | $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ | Fluka 71746 |
| Potassium carbonate/silica gel – 40/60 wt % | $\text{K}_2\text{CO}_3/\text{SiO}_2$ gel | J.T.Baker 0204 |
| Sodium hydrogen carbonate | NaHCO_3 | Merck 6329 |
| Calcium oxalate monohydrate | $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ | Fluka 21201 |
| Zinc chloride/potassium chloride – 55/45 mole % | ZnCl_2/KCl | Sigma Aldrich 31650/Merck 4936 |
| Magnesium chloride/potassium chloride – 30/70 mole % | MgCl_2/KCl | Sigma Aldrich M8266/Merck 4936 |
| Aluminium trihydroxide | $\text{Al}(\text{OH})_3$ | n/a, provided by Kiilto Oy |
| Magnesium dihydroxide | $\text{Mg}(\text{OH})_2$ | n/a, provided by Kiilto Oy |
| Ammonium polyphosphate | $[\text{NH}_4\text{PO}_3]_n$ | Clariant Exolit AP 422 |
| Sodium dihydrogen phosphate monohydrate | $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ | J.T.Baker 0303 |
| Potassium dihydrogen phosphate | KH_2PO_4 | Merck 4873 |
| Potassium hydrogen phosphate trihydrate | $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$ | Merck 5099 |

increasing the char formation.¹⁴ It is commonly used especially in PUR foams.

Chattopadhyay and Webster¹⁵ recently published an extensive review on thermal stability and flame retardancy of PURs. They concluded that when choosing suitable PUR raw materials and flame retardants, a proper selection and evaluation process depending on the use is needed. When a polymeric material is exposed to heat, the polymer chains start to break down to shorter units, which will ignite.¹⁶ The stepwise decomposition of PUR was studied already 30 years ago.¹⁷ PURs with different structures show different thermal stabilities.¹⁸

The aim of this work was to improve the flame retardancy of PUR adhesive samples with limestone filler, by exchanging part of the limestone to inorganic salts. Special focus was put on time to ignition and peak heat release rate (pHRR). The samples were fire tested in a cone calorimeter. The approach when choosing the potential flame retardants was that the salts all have low melting points and/or water release in common. The water release may originate from bound crystal water or form as a decomposition product. Melting and water vapour formation are endothermic processes, which consume energy, and the released water acts as an incombustible diluting agent when mixed with the other volatilized compounds. To maintain comparability, most flame retardants were used at a 20 wt % load. However, to test some of the effects, experiments with other loads were performed as well.

EXPERIMENTAL

Inorganic salts as flame retardants

The inorganic salts tested for flame retarding effects in the PUR adhesive samples are listed in Table I.

PUR adhesive sample preparation

Castor oil (OH-functionality 3, M_w 933 g/mol, Alberdingk Boley, Germany), inorganic filler (grain size

<30 μm , average 14 μm , Imerys, France), triethylenediamine catalyst (Sigma Aldrich, St. Louis, MO), zeolite powder moisture scavenger (Sigma Aldrich, St. Louis, MO) and 4,4'-diphenylmethane diisocyanate (PMDI, average NCO-functionality 2.7, M_w 366 g/mol, Huntsman, Orlando, FL) hardener were used as the main ingredients to manufacture the PUR adhesive samples. The oil and PMDI content was always kept constant in all samples, whereas part of the inorganic filler was substituted to other materials, to test their flame retarding effects in the PUR adhesive. The part exchanged was calculated based on all the components excluding the PMDI. This way the organic fraction stayed unchanged, making the results comparable. The recipe is shown in Table II. Castor oil, inorganic filler, including the tested salts, moisture scavenger, and catalyst were mixed and mechanically stirred in a disposable 200-mL plastic cup using a Heidolph RZR 2051 equipped with a three-bladed stainless steel impeller at 2000 rpm for \sim 5 min, until a smooth and homogenous paste was formed, after which PMDI was added (1 : 5 by weight) and mixed by hand to start the curing process.¹⁹ The paste was then poured into Teflon moulds to form \sim 4 mm thick 10 cm \times 10 cm samples, and left to cure overnight. The manufacturing and curing processes took place at room temperature.

Apparatus

Thermogravimetric analysis (TGA) was used to evidence the thermal decomposition of the inorganic salts, prior to cone calorimeter sample preparation, by using a TA Instruments SDT Q600 device. All experiments were performed in N_2 atmosphere using a Pt-crucible. The heating rate was 10°C/min in most cases. However, for practical reasons, 3°C/min was used for sodium metasilicate, 5°C/min for APP, and 20°C/min for the phosphates, oxalate and carbonate. To our experience, variations within this range do not significantly affect the results. The

TABLE II
PUR Adhesive Sample Recipe, Excluding Hardener (wt %)

| | Castor oil | Inorganic filler | Flame retardant | H ₂ O scavenger | Catalyst |
|--|------------|------------------|-----------------|----------------------------|----------|
| Blank | 35 | 63 | 0 | 2 | 0.02 |
| Na ₂ SiO ₃ · 5H ₂ O | 35 | 43 | 20 | 2 | 0.02 |
| K ₂ CO ₃ /SiO ₂ gel | 35 | 43 | 20 | 2 | 0.02 |
| NaHCO ₃ | 35 | 43 | 20 | 2 | 0.02 |
| CaC ₂ O ₄ · H ₂ O | 35 | 43 | 20 | 2 | 0.02 |
| ZnCl ₂ /KCl | 35 | 53 | 10 | 2 | 0.02 |
| MgCl ₂ /KCl | 35 | 53 | 10 | 2 | 0.02 |
| Al(OH) ₃ | 35 | 43 | 20 | 2 | 0.02 |
| Mg(OH) ₂ | 35 | 43 | 20 | 2 | 0.02 |
| [NH ₄ PO ₃] _n | 35 | 43 | 20 | 2 | 0.02 |
| NaH ₂ PO ₄ · H ₂ O | 35 | 43 | 20 | 2 | 0.02 |
| KH ₂ PO ₄ | 35 | 43 | 20 | 2 | 0.02 |
| K ₂ HPO ₄ · 3H ₂ O | 35 | 43 | 20 | 2 | 0.02 |

maximum temperature was 1200°C, but in many cases the experiments were interrupted earlier, when decomposition had occurred according to theory.

An FTT dual cone calorimeter was used to fire test the samples. The cone calorimeter is the most common bench-scale apparatus used for flammability testing of materials.^{20–23} The method is based on the relationship between the oxygen consumed during combustion and the released heat.^{24–26} The cone calorimeter calibrations and settings were carried out according to standard instructions.^{27–31} The PUR adhesive samples were weighed and wrapped in aluminium foil. Only the top surface of the sample should be exposed to the radiation from the conical heater. The sides of the aluminium foil were made 2–3 cm high, to avoid overflow and leakage during the experiment.

A 60-mm distance between the bottom plate of the cone and the sample surface was used due to the swelling behavior of the PUR adhesive samples. The irradiation was set to 50 kW/m². All samples were manufactured and tested in duplicates. In addition, at least one blank sample with limestone was run every testing day to assure the reproducibility of the results. A total of 12 blank samples were tested. Based on these test results, the error is assumed to be within ±10% for our cone calorimeter, and duplicate tests were considered sufficient. Because of the intumescent behavior, testing was carried out without the edge frame that is meant to be used with samples that have a tendency to burn along the edges.

RESULTS AND DISCUSSION

In this work, the main focus was on heat release rate, especially the peak value, and on time to ignition. A higher heat release rate corresponds to a

greater fire.^{20,21} The swelling behavior was approximately similar for all samples tested.

It was shown that the PUR adhesive samples with limestone filler decompose in three consecutive steps when heated: first the isocyanate followed by the polyol, and finally the inorganic part. The two first-mentioned steps take place between 200 and 500°C. This information provides us with the temperature range of interest.

The main filler used in all PUR adhesive samples was also studied. The TGA results in Figure 1 indicate that the inorganic filler used consisted of pure CaCO₃. When heated, limestone releases CO₂ to form CaO. This reaction, however, takes place when the temperature is roughly 750–800°C — depending on conditions.^{31–35} These temperatures are too high for flame retarding effects when the sample starts to decompose.

Flame retardant characterisation

TGA experiments were carried out for all the additive compounds of interest, to assess their decomposition and melting behavior. The results are shown in Figure 2.

Silicates and carbonates

Sodium metasilicate pentahydrate, Na₂SiO₃ · 5H₂O, also known as waterglass, melts—or forms an aqueous solution—at 72.2°C, which gradually releases its water, forming a solid anhydrous sodium metasilicate. Theoretically, 43 wt % of the Na₂SiO₃ · 5H₂O is water. The TGA thermogram showed that the five crystal water molecules are released over a wide temperature range from below 100°C up to around 250°C in three steps. The resulting solid anhydrous sodium metasilicate melts at 1088°C.

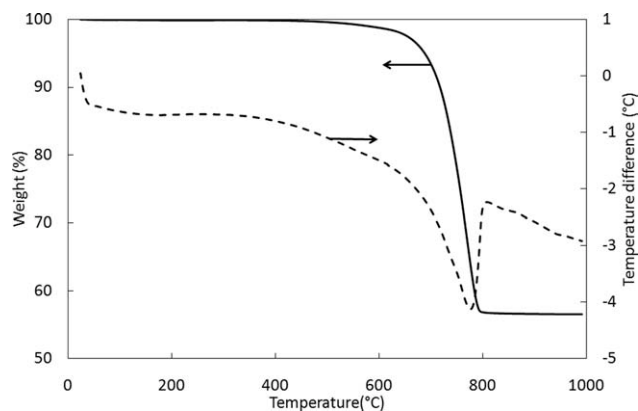
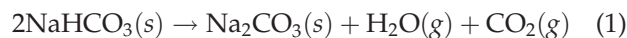


Figure 1 Thermal analysis (TGA/DTA) of the main inorganic filler at 10°C/min in N₂ atmosphere.

Potassium carbonate, K₂CO₃, and silica, SiO₂, are major ingredients in glass. Low-melting glasses as flame retardants have previously been successfully tested for other polymeric materials.^{36,37} The lowest temperature at which a melt will exist in the binary K₂O-SiO₂ system is around 700°C.³⁸ A thermogravimetric experiment of a K₂CO₃/silica gel mixture confirmed the melting. The TGA thermogram showed that thermal decomposition of sodium

hydrogen carbonate, NaHCO₃, according to reaction (1), mainly takes place between 100 and 200°C. Depending on heating rate and particle size, decomposition can take place between 100 and 270°C.^{39–42} NaHCO₃ acts as a flame retardant in two ways: endothermic decomposition, and release of both H₂O and CO₂ gases. At higher temperatures the formed Na₂CO₃ decomposes further to Na₂O by release of CO₂. This reaction was not part of this study.



The thermal decomposition of calcium oxalate monohydrate, CaC₂O₄ · H₂O, is shown in Figure 2. Calcium oxalate decomposes through three separate reactions: release of water (100–200°C), release of carbon monoxide (400–525°C), and release of carbon dioxide (600–780°C).^{43,44} As shown in reactions (2) and (3), one intermediate product is CaCO₃, which also was used as the main filler in the PUR adhesive.

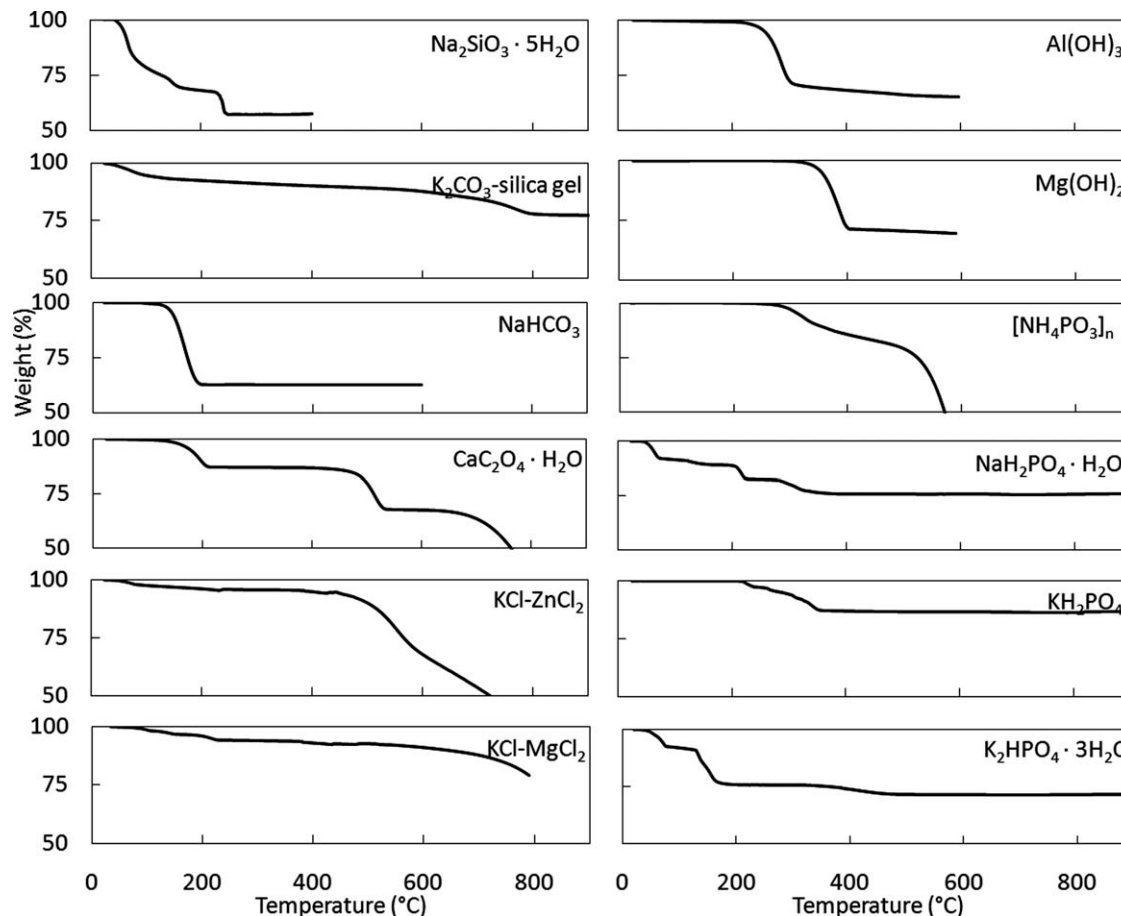
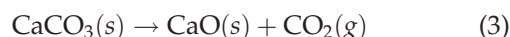
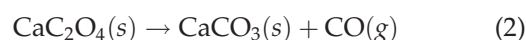


Figure 2 Results from TGA of the inorganic salts tested for flame retarding effects in PUR adhesive.

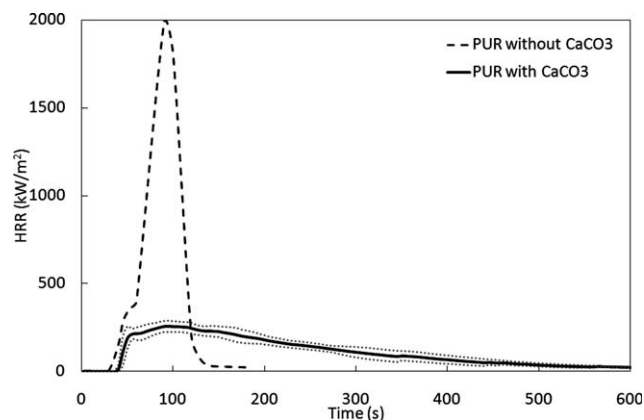


Figure 3 Heat release rate curves for PUR adhesive samples. The dotted lines show the standard deviation around the average curve.

Chlorides

To study the role and mechanism of low-melting salts as flame retardants in the PUR adhesive, chlorides were chosen as well-known compounds with low melting points, knowing that they themselves may not be practically applicable. Chlorides are highly hygroscopic and toxic, and therefore as such not suitable as flame retardants. However, due to the interesting melting temperatures, chlorides were included in this study. Pure zinc chloride, ZnCl_2 , melts at 292°C and potassium chloride, KCl , at 790°C . A 55 mole % ZnCl_2 mixture with KCl gives a melting point of 230°C .⁴⁵ Pure magnesium chloride, MgCl_2 , melts at 714°C . 30 mole-% MgCl_2 mixed with KCl gives a melting point of the salt mixture of 423°C .⁴⁵ The salt mixtures were prepared and tested experimentally with Thermogravimetric Analysis (TGA)/Differential Thermal Analysis (DTA).

Hydroxides

Aluminium trihydroxide, $\text{Al}(\text{OH})_3$, ATH, starts to release water at around 200°C and continues up to 550°C .⁴⁶ The formed non-flammable aluminium oxide and the endothermic release of water vapour create an unfavourable environment for combustion at the surface of the material, thus cooling and slowing down the burning. 35 wt % of the ATH was released as water. Magnesium dihydroxide, $\text{Mg}(\text{OH})_2$, MDH, decomposes in a similar way as ATH.⁴⁷ MDH releases water between 300 and 400°C . 31 wt % of the MDH was released as water. The differences between the decomposition temperatures of ATH and MDH are shown in Figure 2.

Phosphates

APP, $[\text{NH}_4\text{PO}_3]_n$, is the most important nitrogen-phosphorous containing flame retardant.⁴⁸ APP is an

inorganic salt of polyphosphoric acid and ammonia. When heated, ammonia is released from APP from around 200°C . APP decomposes in three steps.^{49–52} After the heating cycle, the TGA experiment left 10 wt % of residue. The intumescent thermally insulating layer is formed by a reaction between the polymer and phosphoric acid, which leads to carbonisation.⁵³ The released gaseous ammonia helps the formation of the intumescent layer by swelling the melted polymer.⁴⁹

When heated, sodium dihydrogen phosphate monohydrate, $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$, releases its crystal water from room temperature to roughly 200°C . Further decomposition of NaH_2PO_4 forms NaPO_3 , and releases H_2O in two steps between 200 and 400°C . By analogy, potassium dihydrogen phosphate, KH_2PO_4 , decomposes by releasing H_2O between 200 and 400°C to form KPO_3 . The differences are shown in Figure 2.

Potassium hydrogen phosphate trihydrate, $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$, decomposes at temperatures above 300°C releasing 0.5 mole of H_2O , and forming 0.5 mole of potassium pyrophosphate, $\text{K}_4\text{P}_2\text{O}_7$, seen as a small step in the weight curve. The crystal water released is observed as two steps at temperatures below 200°C .

Fire testing

Twelve blank PUR adhesive samples with limestone filler were tested between the samples containing the potential flame retarding inorganic salts. The average pHRR for the blank samples with limestone was 266 kW/m^2 , and the average time to ignition was 40 s. An average HRR curve with standard deviation limits is shown in Figure 3. The standard deviation was calculated based on the number of burning samples, and plotted as dotted lines in the figure. For comparison, a HRR curve of a PUR

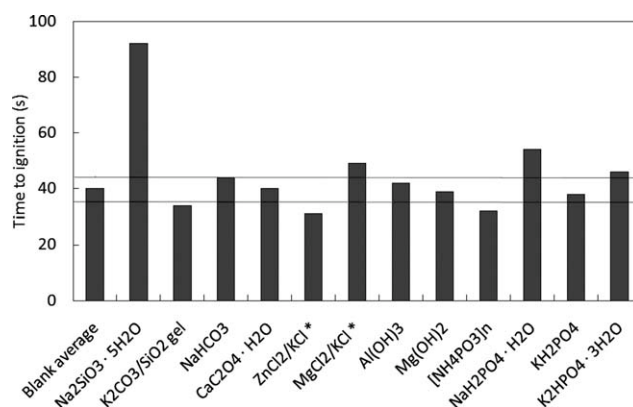


Figure 4 Time to ignition results from cone calorimeter experiments with PUR adhesive samples. Average values from duplicate tests. 20% load. The dotted lines show the standard deviation around the average value of time to ignition of the blank samples.* 10% load.

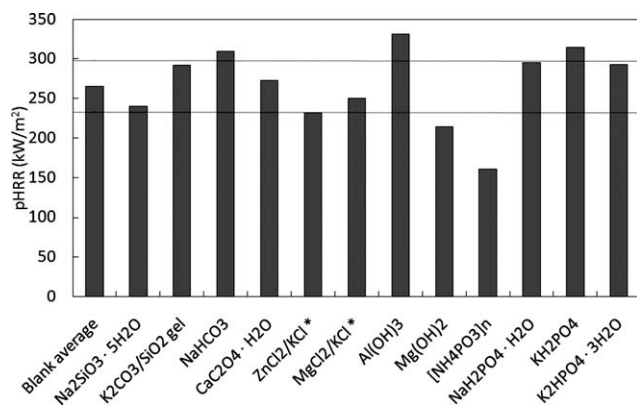


Figure 5 pHRR results from cone calorimeter experiments with PUR adhesive experiments. Average values from duplicate tests. 20% load. The dotted lines show the standard deviation around the average value of pHRR of the blank samples. *10% load.

adhesive sample without limestone is plotted as a dashed line. This result showed that limestone has a key flame retarding effect in the PUR adhesive.

Figures 4 and 5 summarize the cone calorimeter results for the salt containing PUR adhesive samples regarding time to ignition and pHRR, respectively. By far the longest delay in time to ignition was achieved by using sodium metasilicate pentahydrate. Sodium hydrogen phosphate monohydrate also improved the results. The rest of the experiments resulted in times within the standard deviation of the blank samples with limestone, and therefore no improvement could be identified. The greatest reduction in pHRR was achieved by using APP. MDH also reduced the pHRR considerably. Most of the other results were found within the limits of the standard deviation of the blank samples with limestone, and could not be recognized as significant changes.

A major improvement in the delay in time to ignition was made by using the solid waterglass gran-

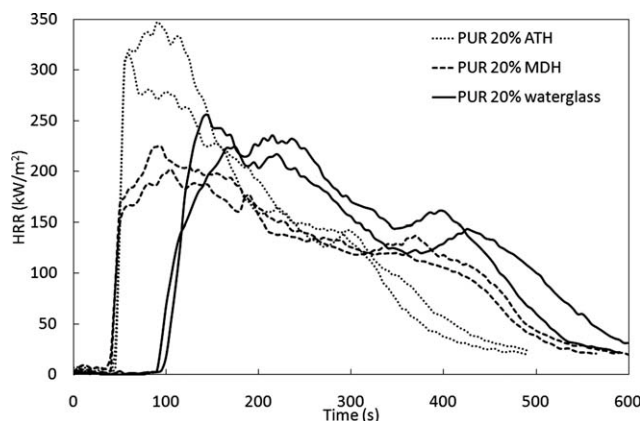


Figure 6 Cone calorimeter results of sodium metasilicate pentahydrate (waterglass), ATH, and MDH containing PUR adhesive samples.

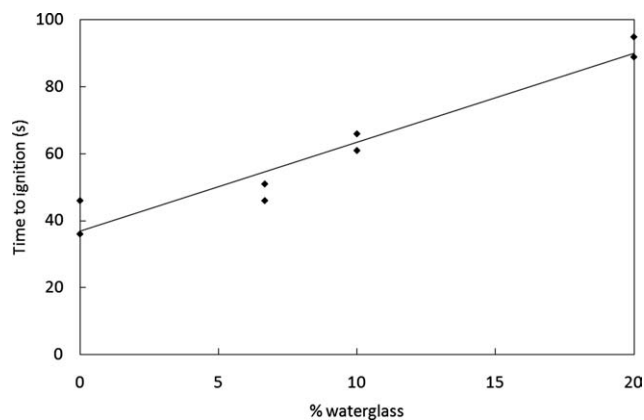


Figure 7 Load effect on time to ignition for the sodium metasilicate pentahydrate containing PUR adhesive samples.

ules, as shown in Figure 6. When the load was 20%, the samples ignited just before 100 s after the start of the experiment. A 10% load made the samples ignite after 60 s. Figure 7 shows that the delay increased linearly with added amount of waterglass. Before the sample ignited in the cone calorimeter experiment, when the sample was heated, spherical particles formed on the sample surface. SEM/EDXA analysis showed that the spheres were very porous and consisted of sodium silicate. A SEM image of a porous particle is shown in Figure 8. These particles seemed to create a protective and insulating layer on the surface, reducing the radiation reaching the sample surface and delaying ignition. The porosity of the particles probably originates from the crystal water molecules, which were shown to be released during a wide temperature interval, and hereby acting as a blowing agent for the sodium silicate.

When comparing the cone calorimeter results of the tested hydroxide containing samples shown in

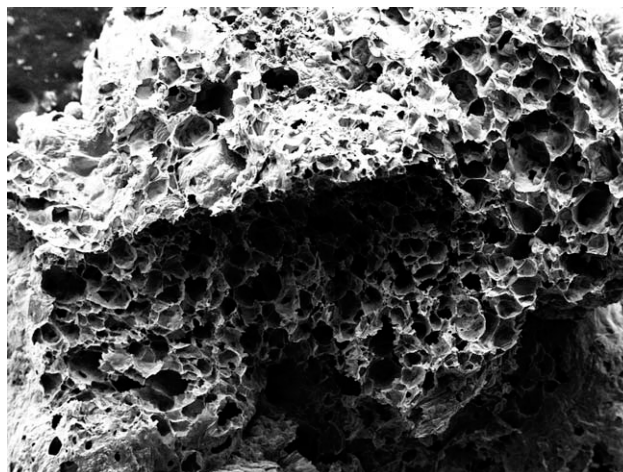


Figure 8 SEM image of a porous sphere formed on the surface of the sodium metasilicate pentahydrate containing PUR adhesive sample. 30x magnification.

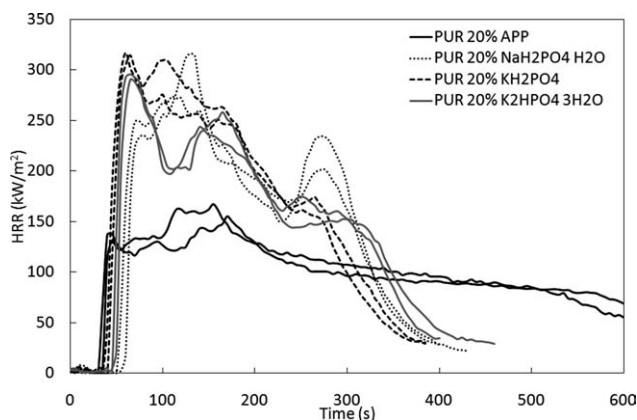


Figure 9 Cone calorimeter results of the phosphate containing PUR adhesive samples.

Figure 6, MDH had a significantly better effect than ATH in the PUR adhesive. The 20% load of ATH seemed to have only minor or no effect, while MDH decreased the peak values for the heat release rate by roughly 50 kW/m². Time to ignition was not affected by any of the hydroxides.

Figure 9 shows the HRR curves of the tested phosphate containing PUR adhesive samples. The APP addition decreased the pHRR value to 161 kW/m², which was the best result in this test series. The burning time on the other hand was longer than for the other tested phosphates. The cone calorimeter results for the other tested phosphates did not differ significantly from the blank samples with limestone. The only major difference was the improvement in time to ignition for the sodium dihydrogen phosphate monohydrate containing samples.

A more extensive presentation of the cone calorimeter results is shown in Table III. It can be noted that the remaining mass of the blank samples match

that of the limestone filler. This would indicate that there was no char residue. The alkali phosphate containing samples showed a mass loss close to the one of the blank samples. However, keeping in mind that the samples contained 20% less limestone filler, a greater mass loss due to decomposition could be expected in these cases, as the TGA study indicated that the phosphates are likely to decompose during the cone calorimeter experiment. As the mass loss could not be seen in the cone calorimeter results, this would indicate char formation. The remaining samples left a residue lower than the blank ones, indicating thermal decomposition of the inorganic salts. Neither for the total heat release, nor for the mean effective heat of combustion significant changes could be observed. Nevertheless, the results indicated that the total heat release of the alkali phosphate containing samples may be slightly lower than of the blank samples. Consequently, the possible char formation used to explain the mass loss is plausible. In addition, the measurements showed that the alkali phosphates and the sodium metasilicate increased the smoke production.

CONCLUSIONS

The flame retardancy of selected inorganic salts in PUR adhesive samples with limestone filler was tested by means of a cone calorimeter. TGA was used to assess decomposition and melting of the mixtures and compounds tested for flame retarding effects.

Limestone released CO₂ between 600 and 800°C. This temperature range is too high for the limestone decomposition products to interact with the combustion properties in the early stage of a fire. However, some of the samples containing inorganic salts

TABLE III
Cone Calorimeter Results. Average Values From Duplicate Tests. 20% Load

| | Time to ignition (s) | Peak HRR (kW/m ²) | Mass lost (%) | Total heat release (MJ/m ²) | Mean Effective Heat of Combustion (MJ/kg) | Total smoke release (m ² /m ²) |
|--|----------------------|-------------------------------|---------------|---|---|---|
| Blank average ^b | 40 | 266 | 46 | 65 | 23 | 1378 |
| Na ₂ SiO ₃ · 5H ₂ O | 92 | 240 | 50 | 71 | 23 | 1625 |
| K ₂ CO ₃ /SiO ₂ gel | 34 | 292 | 48 | 64 | 24 | 1414 |
| NaHCO ₃ | 44 | 310 | 55 | 62 | 22 | 1513 |
| CaC ₂ O ₄ · H ₂ O | 40 | 273 | 51 | 69 | 25 | 1265 |
| ZnCl ₂ /KCl ^a | 31 | 232 | 50 | 60 | 22 | 1455 |
| MgCl ₂ /KCl ^a | 49 | 250 | 54 | 63 | 20 | n/a |
| Al(OH) ₃ | 42 | 331 | 51 | 66 | 24 | 1297 |
| Mg(OH) ₂ | 39 | 214 | 49 | 65 | 25 | 1263 |
| [NH ₄ PO ₃] _n | 32 | 161 | 51 | 68 | 24 | 1253 |
| NaH ₂ PO ₄ · H ₂ O | 54 | 295 | 47 | 60 | 23 | 2023 |
| KH ₂ PO ₄ | 38 | 315 | 47 | 62 | 25 | 1648 |
| K ₂ HPO ₄ · 3H ₂ O | 46 | 293 | 49 | 62 | 23 | 1548 |

^a 10% load.

^b 12 tests.

resulted in higher pHRR than the blank samples containing only limestone. This indicates that the limestone not only acts as a filler but also as a flame retardant, as it reduces the pHRR more than several of the tested inorganic salts, which produces incom-bustible species at lower temperatures do. Neither the H₂O- and CO₂-releasing, nor the low-melting flame retardants were found to significantly improve the cone calorimeter results of PUR adhesive directly. No major effects were seen, except when using MDH. Indirectly, however, an effect of H₂O acting as a blowing agent for sodium silicate was found. The protective layer of porous sodium silicate on the surface, combined with release of water over a wide temperature range, resulted in the longest delay in time to ignition when using sodium metasilicate pentahydrate. Sodium dihydrogen phosphate monohydrate also delayed ignition to some extent. The lowest overall HRR curve was achieved by exchanging 20% of the limestone to APP. A MDH exchange also improved the fire performance of the PUR adhesive significantly.

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