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# Flame Retardant Properties of Polymer Composites of Urea Complex of Magnesium and Vermiculite

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**Abstract.** Polymeric materials are increasingly used in several applications. However, their relatively high flammability presents a danger to people and property. Their use therefore requires that they are made more resistant to both the initiation and propagation of fires.

In the present work we evaluate, by cone calorimeter tests, the efficiency of urea complex of magnesium and vermiculite (urea- vermiculite) as a stand-alone flame retardant in polyurethane (PU) resin and flexible polyvinyl chloride (PVC).

Flexible PVC cone calorimeter tests proceeded without a visible flame following an initial short-lived ignition which degenerated into a bulk pyrolysis, in combination with a surface glowing-combustion event. Urea-vermiculite formed an exfoliated protective barrier layer which allowed thermal stabilisation of the condensed phase. The simultaneous release of halogen species by the PVC and the action of the exfoliated barrier layer prevented the formation of a flammable air-fuel mixture. The addition of urea-vermiculite lowered the peak heat release rate (pHRR) and the total heat released (THR) significantly.

In PU composites the urea-vermiculite was unable to form a cohesive protective barrier layer. The poor compatibility between the molten PU and the exfoliated flakes also led to the consumption of the underlying PU. Nevertheless, the addition of urea-vermiculite lowered significantly the pHRR of PU composites.

In general, cone calorimetry results revealed that urea-vermiculite allowed thermal stabilization of the condensed phase at high temperatures but had little influence in the vapour phase behaviour. The amount of released urea's degradation products (non-flammable vapours) was not enough to dilute the flammable vapours' mixture. Thereby when used with PVC, which releases halogen flame poison, it showed great fire performance.

**Keywords:** Urea-vermiculite, Flame Retardancy, Polyurethane, Polyvinyl Chloride, Cone Calorimeter.

## 1. INTRODUCTION

Polymer composites are extensively used in various areas due to their relatively low cost and the broad range of properties that can be attained<sup>1</sup>. Fully exfoliated composites have been claimed, but some studies have shown that delamination and dispersion of individual clay layers is still a challenge<sup>1,2</sup>.

Flame-barrier compositions have been proposed that rely on vermiculite's expansion properties<sup>3</sup>. Vermiculite can impart fire resistance to polymers, provided the exfoliation temperature can take place at temperatures just below the volatilisation of the polymer.

Current methods for the protection of materials from fire risk are based on engineering approaches, the use of inherently low flammable polymers and flame retardant (FR) additive materials<sup>4</sup>. According to Dufton<sup>5</sup>, an effective FR material has to be able to impede or reduce heat supply to below the critical levels required for flame stability. This prerequisite can be accomplished by: i) limiting the heat and mass transfer between the solid and gas phases; ii) scavenging of the free radicals in the gas phase; and iii) creating a heat sink. Existing FR materials in polymers are generally based on halogenated additives and antimony trioxide (as synergist), inorganic fillers, melamine derivatives and phosphate-based materials<sup>6</sup>. To be effective, a FR material has to supply the flame inhibitor in the same temperature range as the decomposing polymer<sup>5</sup>. This criterion complies with the "right place at the right time" theory.

The categorisation of FR materials is somewhat inconsistent due to the multiplicity of polymer processing techniques and, on the other hand, to the fact that the very same FR material can exhibit different FR mechanisms. Nevertheless, all types of FR materials can be classified according to the mode of action (physical or chemical) or the means of incorporation into the polymer matrix (additive, reactive and coatings).

Halogenated chemical FR act essentially in the vapour phase as flame poison stopping the chain reactions and therefore the combustion of the molten polymer<sup>4,7</sup>. Although economically and technically very effective, halogen-based FRs also produce obscuring, toxic and corrosive smoke, and are a source of various environmental concerns<sup>4,5,7,8</sup>. Some phosphorous compounds can be either vapour phase and/or condensed phase FR, depending on their chemical structure and their interaction with the molten polymer matrix<sup>4,6</sup>. The most important organic nitrogen-based FR is melamine (and its derivatives) and ammonium polyphosphate is the most important inorganic additive<sup>9</sup>. Well-dispersed nanoparticles are known to enhance the thermal stability and some studies have shown that nanoparticles have to be used in combination with other FR additives in order to meet some required fire performance levels<sup>6,10</sup>. Intumescent systems provide radiation shielding and thermal insulation by forming a heat-induced swollen multi-layer barrier<sup>5,6</sup>. Mineral fillers can delay the time to ignition ( $t_{\text{ign}}$ ), slow the initial heat release rate (HRR), lower the smoke production rate (SPR) and reduce overall toxic gas emissions. However, in general, they have a limited fire performance window and cannot reduce the total heat release rate (tHR) if enough constant external heat is applied. To be effective, high loadings are needed and such loading levels may impair the processability and the mechanical properties of the polymeric material<sup>4,6,11</sup>. According to Horrocks and Price<sup>12</sup>, char-forming agents seem to be the best choice and the way forward in developing effective fire-resistant composites.

Flexible PU foams are highly flammable and are the main and most combustible components of upholstered furniture and mattresses. Nevertheless, rigid PU foams are among the best heat-insulating materials and one of the most used in the building industry<sup>13</sup>. Flame-retarded thermoplastic polyurethane is used in wire and cable applications with aluminium hydroxide and magnesium hydroxide as fire-retardant additives. The use of mica and zinc borate is also reported in the literature. The latter is a synergist for aluminium or magnesium hydroxides<sup>13</sup>.

Polyvinyl chloride (PVC) is a very versatile polymer used in diverse applications, including flooring, rigid pipes, flexible hoses, conveyor belting, and wire and cable insulation. Neat PVC features a relatively high chlorine content of 56.7 wt.%. However, the conventional plasticisers used in the manufacture of flexible PVC detract from this outstanding fire resistance. Thus FR and smoke-suppressant (SS) additives must be incorporated in order to meet product test specifications such as the oxygen index, HRR, smoke evolution, or the extent of burning<sup>14</sup>. Plasticised PVC is flexible and offers versatile applications from semi-rigid to very soft materials; it is also cost-effective<sup>15,16</sup>.

A key property of urea-vermiculite is its tendency to exfoliate when heated to high temperatures in a worm-like manner to form expanded material with a low density. Urea-vermiculite can be compared to expandable graphite. A disadvantage of graphite-based FRs is the black colour and electrical conductivity they impart to the material. Hence the utility of urea-modified vermiculite was investigated as a FR for PVC and PU composites.

## 2. EXPERIMENTAL

### 2.1. Materials and methods

Detailed preparation of urea-vermiculite followed the procedure reported elsewhere<sup>17</sup>.

The ultra-low-viscosity liquid urethanes (Smooth-Cast© 300) were used as received from Smooth-On. TPC Paste Resin Co, Ltd supplied the PVC emulsion grade PG680. Reofos 50, a synthetic isopropylated triaryl phosphate ester plasticiser, was supplied by Chemtura.

TGA experiments were performed on a Mettler Toledo A851 TGA/SDTA instrument. The combustion behaviour was assessed according to the ISO 5660-1 standard procedure in a Dual Cone Calorimeter (Fire Testing Technology (UK) Ltd). The sheets (100 mm × 100 mm × 3 mm) were placed on aluminium foil and exposed to an external heat flux of 35 kW m<sup>-2</sup>. The time to ignition was manually set from the computers keyboard. The HRR, its pHRR and MLR were obtained directly from the FTT “ConeCalc” software.

### 2.2. Preparation of the urea-vermiculite PU composites

Part A and Part B (100A:90B, wt.) were mixed thoroughly together with urea-vermiculite and then poured into the mould. The white sheets were fully cured by pressing them at room temperature and 5 MPa for 10 min. A (Universal Mold) release agent was applied to the metallic plates to facilitate demoulding.

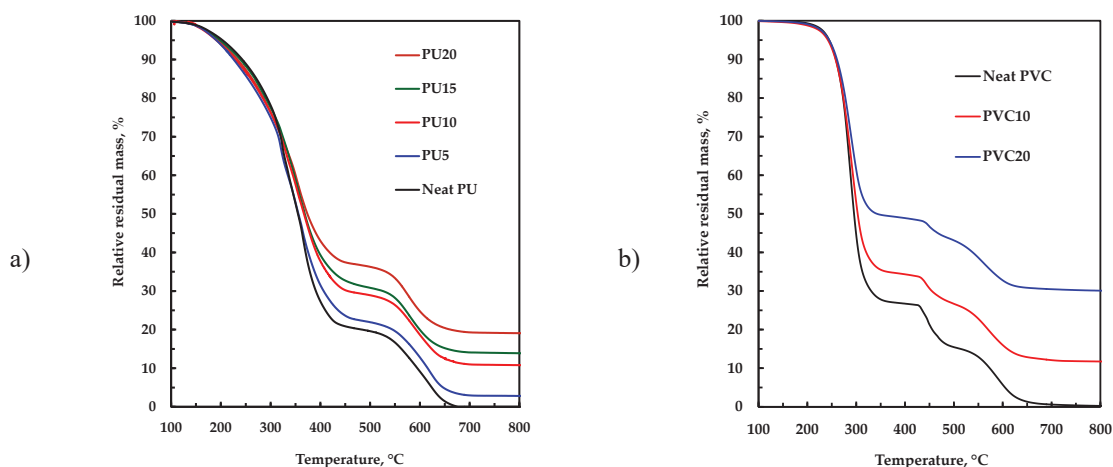
### 2.3. Preparation of the urea-vermiculite PVC composites

The urea-vermiculite/PVC compounds were prepared using the plastisol route. PVC powder (100 g), Reofos 50 (60 g) and an adequate amount of urea-vermiculite were thoroughly mixed together in a high shear mixer for 10 minutes<sup>16</sup>. The paste mixture was immediately poured into a mould and heated for 10 minutes in a convection oven set at 120 °C. Thereafter the sheets were cured at 150 °C and 5 MPa in a hot press for 5 minutes. The mass ratio of PVC and the plasticizer (1000 parts per 60) was kept constant for all samples.

## 3. RESULTS AND DISCUSSION

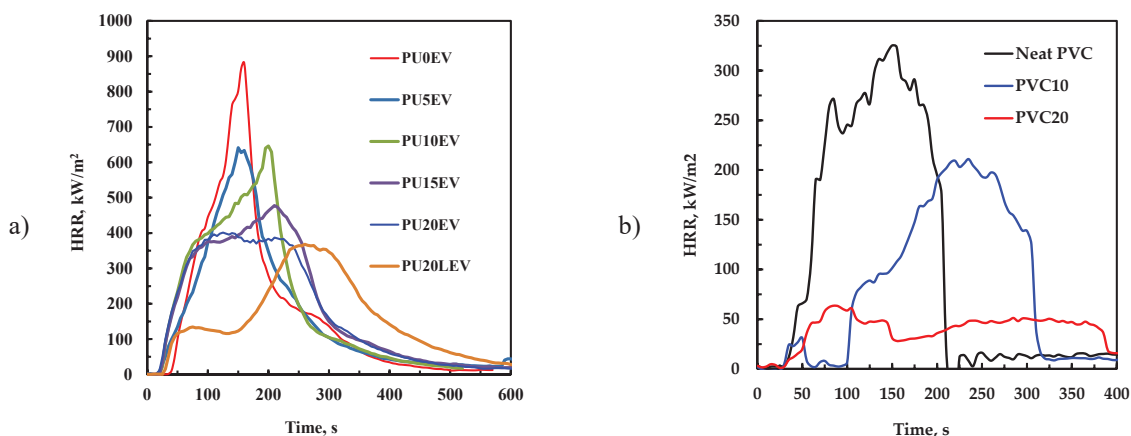
All PU compositions exhibited two thermal decomposition steps. The neat PU volatilised completely, before 700 °C, but the composites still retained a residue even at 800 °C (Fig. 1a)).

PVC thermograms (Fig. 1b) show three degradation steps. The first two steps are related to PVC's dehydrochlorination and to the degradation of the plasticiser<sup>16,18</sup>. The last thermal event corresponds to the degradation of the oxidised PVC<sup>16,19</sup>. For the PVC compound and for the urea-vermiculite composites the maximum degradation rate was observed during the first step at  $T_{max} = 289 \pm 2$  °C. The typical urea-vermiculite thermal degradation steps were overlapped by those from the PVC and could not be clearly observed. The amount of the residual mass, in the composites, corresponded to more than the urea-vermiculite added and raised with the increment of the quantity of the filler.



**Figure 1.** Thermal degradation plots of a) PU and b) PVC with their composites with urea-vermiculite, in air.

Fig. 2a) compares the HRR for PU composites with that of their PU reference polymer. The data in Table 1 summarise the cone calorimeter results. The HRR curves for the neat PU exhibited the shape characteristic of thermally thin samples<sup>20</sup>.



**Figure 2.** Cone calorimeter average peak HRR for a) PU and b) PVC composites with urea-vermiculite

Compared with the neat PU, the pHRR of the composites was greatly reduced while the tHR was almost not affected. As expected, the  $t_{ign}$  was negatively affected, due to the clay-catalysed polymer decomposition<sup>8,10,11</sup>. However, when the filler was concentrated at the top of one of the sides (sample denoted 20T), subjected directly

to the cone heat flux, the composite showed better fire performance. The tHR was still high due to fact that the composite had two burning stages: the first one retarded by the filler and second one corresponding to the underlying material.

**Table 1.** Flammability data summary of PU composites

Property, Units	Urea-vermiculite, wt.%					
	0	5	10	15	20	20T
Time to ignition ( $t_{ign}$ ), s	40 ± 2	25 ± 2	24 ± 1	26 ± 1	22 ± 4	28 ± 2
Time to flameout, s	521 ± 33	527 ± 98	563 ± 53	517 ± 9	538 ± 8	798 ± 102
Peak heat release rate (pHRR), kW m <sup>-2</sup>	900 ± 5	779 ± 115	483 ± 20	647 ± 96	433 ± 29	377 ± 13
Total heat release (tHR), MJ m <sup>-2</sup>	104 ± 1	107 ± 17	112 ± 4	107 ± 1	107 ± 3	98 ± 1
MAHRE (kW m <sup>-2</sup> )	374 ± 9	399 ± 32	371 ± 11	332 ± 7	312 ± 7	203 ± 4
pHRR/ $t_{ign}$ , kW m <sup>-2</sup> s <sup>-1</sup>	23 ± 1	31 ± 6	25 ± 3	20 ± 1	20 ± 2	14 ± 1

Fig. 3 a) shows the appearance of the 10 wt.% composite's residue char after the cone calorimeter test. This image also indicates clearly that the urea-vermiculite flakes could not bond properly to the PU matrix. This lack of bonding between PU char and the exfoliated flakes allowed the consumption of the exposed polymer as well as the underlying material. Some flakes were even swept away from the pyrolysis zone while exfoliating.



**Figure 3.** a) Image of 10 wt.% PU composite char residue after cone calorimeter test. Images of char residue of 10 wt.% urea-vermiculite/PVC after cone calorimeter tests: b) just after flameout and still smoking, and c) after complete extinction of flame and smoke.

The urea-vermiculite/PU composites featured lower CO, CO<sub>2</sub> and smoke production rates owing to the reduction in the rate of mass loss. The observed trends mirror those observed for the HRR almost perfectly.

The urea-vermiculite/PVC cone calorimeter results are summarised in Table 2. Representative HRR curves obtained from the cone calorimeter tests are presented in Fig. 2 b). All the neat PVC compound samples ignited and flamed briefly and produced a large amount of smoke. This gave rise to the sharp peak in the HRR at short times. From Fig. 3 b) and c), showing the PVC samples on the cone calorimeter sample holder after flameout, it can be seen that the PVC composites continued releasing smoke even after flameout. A considerably expanded residue was observed due to the action of the urea-vermiculite filler. This latter fact is consistent with the TGA findings. The HRR curves for the neat plasticised PVC compound exhibited the shape characteristic of thermally thin samples<sup>20</sup>.

**Table 2.** Flammability data summary of PVC composites

Property, Units	Urea vermiculite, wt.%		
	0	10	20
Time to ignition ( $t_{ign}$ ), S	35 ± 3	33 ± 6	59 ± 6
Time to flameout, S	146 ± 59	174 ± 143	122 ± 27
Peak heat release rate (pHRR), kW m <sup>-2</sup>	325 ± 11	229 ± 16	60 ± 23
Total heat release (tHR), MJ m <sup>-2</sup>	55 ± 11	42 ± 14	7 ± 2
pHRR/ $t_{ign}$ , kW m <sup>-2</sup> s <sup>-1</sup>	9.3 ± 0.8	7.1 ± 0.9	1.5 ± 0.9

The HRR curves for the samples containing urea-vermiculite were a bit more complex. Most of them ignited briefly, almost flamed out and then reignited. The subsequent abrupt reignition was due to the increase in the amount of flammable volatiles because of the continued pyrolysis and smoking while not burning. On the other hand, the halogen entering the vapour phase also contributed to a “flame poisoning effect”, i.e. the reaction and termination of oxygen-based chain branching, free radical reactions occurring in the flame<sup>15,21</sup>. The profuse smoke evolution suggests that the composite samples were pyrolysed while at the same time a glowing combustion

occurred at the surface. The urea-vermiculite composites featured lower CO, CO<sub>2</sub> and SPRs. Their trends were identical to those observed for the HRR. The lower “fire performance index” ( $PI = p\text{HRR}/t_{\text{ign}}$ ) of the composite containing 20 wt.% of urea-vermiculite is a clear indication of better cone calorimetry performance.

The expansion of the urea-vermiculite formed a low-density layer of ‘worm-like’ structures which provided a protective barrier at the polymer surface. This limited heat transfer to the substrate and thus slowed down the rate of thermal degradation. On the other hand, the release of the HCl by the decomposing PVC apparently also prevented flaming combustion during the latter part of the cone calorimeter tests. This can be attributed to a dilution effect on the air–fuel mixture in the gas phase. However, the halogen entering the gas phase also contributed to a “flame poisoning effect”, i.e. the slowing down of the free radical chain reactions occurring in the flame<sup>22</sup>. In combination, these two effects explain why the cone calorimeter test proceeded without a visible flame following an initial short-lived ignition. It degenerated into a bulk pyrolysis experiment in combination with a surface glowing-combustion event.

#### 4. CONCLUSIONS

The cone calorimeter results revealed that the fire performance of urea-vermiculite in PU composites is greatly affected by the distribution of the FR additive along the vertical direction of incidence of the heat flux. The addition of 20 wt.% urea-vermiculite lowered the pHRR. The urea-vermiculite formed an exfoliated but non-cohesive protective barrier layer on top of the PU composites. However, after all the urea-vermiculite had expanded, the loose flakes offered efficient protection only at high loadings.

Urea-vermiculite / PVC cone calorimeter tests proceeded without a visible flame following an initial short-lived ignition which degenerated into a bulk pyrolysis experiment in combination with a surface glowing-combustion event. These results revealed that addition of 20 wt.% urea-vermiculite lowered the pHRR and the tHR. The urea-vermiculite forms an exfoliated protective barrier layer. In addition, the simultaneous release of halogen species by the polymer matrix and the exfoliating vermiculite prevents the formation of a flammable air–fuel mixture. The cone calorimetry results also showed that urea-vermiculite allowed thermal stabilisation of the condensed phase at high temperatures, but had little influence on the vapour phase behaviour.

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