The thermo-oxidative stability of thermoplastic polyurethane nanocomposites was improved by organoclays. The nanocomposites were synthesised by simple means using virgin and also conventional flame-retardant TPs. A 70% reduction in the peak heat release rate and no dripping of the burning polymer were observed. PVC containing organoclays showed rapid HCl release through an accelerated chain stripping reaction of the polymer, catalysed by the quaternary ammonium compound in the organoclays, resulting in severe discoloration. Synthesis routes based on EVA or TPU masterbatches of organoclays substantially reduced the darkening of PVC compounds. Cone calorimeter experiments showed no significant improvement in the flame retardancy properties of PVC filled with organoclays.

1. INTRODUCTION

If a fire breaks out in a room containing flammable materials, the room can heat up further, causing other combustible materials to ignite. So the rate at which the fire spreads increases as more and more heat is released. This leads to a progressive rise in room temperature. The radiation heat and the temperature too can increase to such an extent that all the materials in the room ignite, resulting in an extremely rapid rate of propagation of the fire. Known as flashover, this is the moment when the fire becomes a full-blown blaze. Escaping from the room is almost impossible. The fire is very likely to spread to other rooms. Once a fire reaches flashover, every polymer releases up to 20% of its mass as carbon monoxide, leading to highly toxic smoke. 90% of deaths in fires occur as a result of fires which spread too vigorously, releasing deadly dense smoke [1-2].

Every year some 5000 people are killed in fires in Europe and more than 4000 in the USA. The direct loss of property caused by fires amounts to about 0.2% of gross domestic product, and the total cost due to fires is around 1% of GDP [3]. That is why it is important to develop flame-retardant materials.

Polymer applications are growing all the time, and specific mechanical, thermal and electrical properties are required. Another important property of polymers is their flame retardancy, which conventionally can be achieved in the following ways:

- use of PVC or fluoropolymers with intrinsic flame-retardant properties
- use of flame-retardant substances such as aluminium hydroxide (ATH), magnesium hydroxide, organic brominated compounds or intumescent systems to prevent the combustion of polymers such as EVA, PE, PP, PA and others.

Nanocomposites have attracted interest as a simple and cost-effective method of improving the properties of polymers. A small amount (approx. 5 percent by weight) of a type of filler known as an organoclay is added to the polymer and distributed in the polymer matrix at a nanometric level. Depending on the way in which the organoclay is distributed in the polymer matrix, the morphology of the nanocomposites can vary from an intercalated structure with regularly alternating organoclays and polymer monolayers to an exfoliated (delaminated) structure, in which the organoclays are distributed randomly and uniformly in the polymer matrix.

The simplest and technologically the most attractive way of producing this class of materials is to blend the molten polymer with a modified, laminar silicate such
as montmorillonite, in which the naturally occurring Na+ cations within the silicate layers have been replaced by bulky quaternary alkyl ammonium cations. This modified, laminar silicate known as an organoclay is much more compatible with the polymer matrix.

Nanocomposites consisting of polymer and laminar silicate offer interesting properties in terms of increased thermal stability and flame retardancy with very low organoclay contents. These improved properties are due to the formation of a thermally insulating, non-permeable crust for volatile, combustible polymer decomposition products caused by the fire [4-6]. The fact that dramatic improvements can be obtained in thermal stability with only small amounts of filler in the nanocomposites is of great interest to industry, since it means that flame-retardant end products can be produced more cheaply and more easily.

A ratio of 65 percent by weight of ATH and 35 percent by weight of a polymer matrix such as EVA, which can absorb a high filler content, is commonly used for flame-resistant, halogen-free cable sheathing [7]. It has been demonstrated that a mixture of conventional fillers such as aluminium hydroxide (ATH) or magnesium hydroxide (MDH) and organoclays can be used to obtain a better flame-retardant effect [8]. The vast improvements in flame resistance achieved through the use of organoclays have also opened up the possibility of reducing the high ATH content that is needed in EVA. The reduction in the total amount of these fillers has led to improvements in the mechanical and rheological properties of EVA-based nanocomposites.

Flexible PVC (containing plasticisers) has been used for many years in the cable industry for insulation and sheathing. These compounds have excellent mechanical and electrical properties, and PVC tolerates a broad range of functional additives. Flame-resistant PVC compounds commonly contain additives such as antimony oxide and zinc borate; their flame retardancy can also be improved by replacing phthalate plasticisers with less flammable phosphate esters.

A few publications describe PVC nanocomposites. Intercalated PVC nanocomposites and also in some cases mixed intercalated/exfoliated PVC nanocomposites with organoclays were produced by blending in the polymer melt [9, 10, 11]. Discoloration was observed during processing, which increased with the organoclay content. It was assumed that the main reason for this discoloration is the decomposition of the quaternary ammonium compound in the organoclay and the subsequent catalytic effects on the dehydrochlorination of PVC. Other authors reported on PVC blends obtained by dispersing nanorange organoclays in the melt [12-18].

A masterbatch method for PVC was useful in improving the dispersion of organoclays in PVC. Part exfoliated/part intercalated structures were found for organoclays in PVC [19, 20]. Adding EVA to PVC produced an exfoliated structure. An intercalated structure was observed when PVC was mixed directly with organoclays; polycaprolactone was first filled with organoclays and then dispersed in PVC [21].

Thermoplastic polyurethanes (TPU) are polymers whose properties are tailored to their intended application. These properties are high tensile strength and flexibility, high abrasion resistance and high tear propagation strength. However, pure TPUs have only moderate thermal stability and a low flame-retardant effect. A polyether-based TPU was mixed with an organoclay in a co-rotating twin-screw extruder, giving rise to exfoliation [22]. The same structure has also been observed by other authors [23, 24].

The study below analyses the use of organoclays as flame retardants for TPU and plasticised PVC.

### 2. EXPERIMENTAL

#### 2.1 Preparation of Specimens

The organoclays used were dimethyl distearyl ammonium-substituted montmorillonite (organoclay 1), dodecyl ammonium-substituted montmorillonite (organoclay 2), methyl dodecyl bis-(2-hydroxyethyl) ammonium-substituted montmorillonite (organoclay 3) and 12-carboxydocetyl ammonium-substituted montmorillonite (organoclay 4).

Polyether-based TPUs, including an unfilled and hence non-flame-resistant TPU as well as a conventional flame-resistant TPU containing a phosphate ester (according to the supplier), were used.

A PVC blend with a constant ratio of PVC, diisodecyl phthalate as plasticiser, calcium carbonate as filler, antimony trioxide and zinc borate as flame-retardant substances and a calcium-zinc stabiliser system were used. Organoclays 1 to 4 were used in this formulation by substituting 5 phr of calcium carbonate in the same amount. All ingredients were premixed before being blended in the melt; this method of synthesis is known as direct blending.

EVA Escorene UL00328 from Exxon with a VA content of 28 percent by weight and the polyether-based TPU (88 Shore A) Estane 58887 from Noveon were used as polymers to synthesise the organoclay masterbatches.

The mixtures were prepared in a rolling mill at 180°C. Test sheets for the experiments were produced in a laboratory press with a pressing time of 10 minutes at 180°C and 250 bar.

#### 2.2 Tests

X-ray diffraction (XRD) using a Siemens D 5000 diffractometer fitted with a Cu-Kα radiation source
(λ = 0.15406 nm) was used to check the formation of a TPU nanocomposite. The XRD values were recorded between 1.5 and 15° in 0.04° intervals.

Cone calorimeter flame retardancy tests were performed at a heat flux of 35 kW/m² with the specimens in a horizontal arrangement (sheets measuring 100 x 100 x 3 mm) corresponding to ASTM E 1354. The stated values were averages from three measurements on each specimen with a standard uncertainty for the measured heat release and the times to ignition of the flammable gases of ± 5%.

Thermogravimetric analysis (TGA, no repetition) to analyse the thermo-oxidative behaviour took place in air at a heating-up rate of 20°C/min.

3. RESULTS

3.1 Morphology of the TPU Nanocomposite

A pure, non-flame-retardant TPU was mixed with organoclay 1 in a rolling mill. X-ray diffraction was used to characterise the structure of the TPU nanocomposite. Changing the angle resulted in a change in the layer spacing in the organoclay. The shift in the XRD signal for organoclay 1 from 3.19 nm (Figure 1, curve A) to 3.46 nm after incorporation into the TPU (Figure 1, curve B) revealed the formation of intercalated structures.

3.2 Determining the Thermal Stability of TPU by TGA Analysis

The thermal stabilities of various TPUs were measured in air using TGA. For pure TPU and TPU intercalated with 5 phr of organoclay 1, mass losses at identical temperatures up to 350°C were only very slightly higher for the nanocomposite. By contrast, at identical temperatures over 350°C mass losses for the nanocomposite were markedly lower than for pure TPU, indicating that the nanocomposite has a better thermal stability (Figure 2).

3.3 HCl Release from PVC Through Organoclays

The colours of blends of PVC with 5 phr of organoclays 1 to 4 darkened during processing. This phenomenon was most marked with organoclays 1 and 2; these PVC specimens turned black. Clearly a rapid dehydrochlorination of the PVC occurred. The time to the start of HCl evolution was measured from the colour change of an indicator paper at 200°C in a small glass tube in accordance with IEC 60811-3-2 (Table 1).

Only organoclay 4 demonstrated an acceptable slight reduction in the time to HCl evolution. A possible explanation for this could be the presence of the carboxyl group in organoclay 4. This group could lower the pH in comparison to organoclays 1 to 3, leading to a slower reaction rate for dehydrochlorination.

One possibility for preventing hydrochloric acid release by PVC is the use of EVA or TPU masterbatches with organoclays. Both polymers are known to be highly compatible with the PVC matrix and are used as polymeric plasticisers. Both polymers also easily form nanocomposites with organoclay 1 [8, 22].

To prepare the organoclay masterbatch, 30 parts of organoclay 1 or 4 were mixed with 70 parts of EVA or TPU in a rolling mill. These masterbatches were then incorporated into the flexible PVC compound in the rolling mill; the organoclay content was 7.4 phr (resin: PVC + EVA or PVC + TPU). The times for HCl release at 200°C in accordance with IEC 60811-3-2 are summarised in Table 2.
In comparison to the directly blended versions, both masterbatch methods with organoclay 1 showed improvements in the times for release of HCl; both values were still very low, however. The masterbatch methods for organoclay 4 produced only slight reductions in the times for HCl release as compared with PVC blends with virgin EVA or TPU. All six of the compounds listed in Table 2 were used for further tests with a cone calorimeter.

### Table 1. Time for HCl release by flexible PVC compounds with 5 phr organoclay, produced by direct blending

<table>
<thead>
<tr>
<th>Material</th>
<th>Time for HCl release (IEC 60811-3-2)</th>
<th>Colour effect due to organoclay</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC compound (no organoclay)</td>
<td>118 minutes</td>
<td>-</td>
</tr>
<tr>
<td>PVC compound with organoclay 1 (direct blending)</td>
<td>&lt; 3 minutes</td>
<td>black</td>
</tr>
<tr>
<td>PVC compound with organoclay 2 (direct blending)</td>
<td>25 minutes</td>
<td>very brown</td>
</tr>
<tr>
<td>PVC compound with organoclay 3 (direct blending)</td>
<td>44 minutes</td>
<td>pale brown</td>
</tr>
<tr>
<td>PVC compound with organoclay 4 (direct blending)</td>
<td>97 minutes</td>
<td>almost no discoloration</td>
</tr>
</tbody>
</table>

### Table 2. Time for HCl release by flexible PVC compounds with 7.4 phr organoclay, produced by the masterbatch method

<table>
<thead>
<tr>
<th>Material</th>
<th>Time for HCl release (IEC 60811-3-2)</th>
<th>Colour effect due to organoclay</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC compound with EVA (no organoclay)</td>
<td>114 minutes</td>
<td>-</td>
</tr>
<tr>
<td>PVC with organoclay 1 (via EVA masterbatch)</td>
<td>15 minutes</td>
<td>very brown</td>
</tr>
<tr>
<td>PVC with organoclay 4 (via EVA masterbatch)</td>
<td>102 minutes</td>
<td>slight discoloration</td>
</tr>
<tr>
<td>PVC with TPU (no organoclay)</td>
<td>97 minutes</td>
<td>-</td>
</tr>
<tr>
<td>PVC with organoclay 1 (via TPU masterbatch)</td>
<td>18 minutes</td>
<td>very yellow</td>
</tr>
<tr>
<td>PVC with organoclay 4 (via TPU masterbatch)</td>
<td>92 minutes</td>
<td>no discoloration</td>
</tr>
</tbody>
</table>

### 3.4 Flammability

From an engineering perspective, it is important to know the risks to be guarded against in a fire. Only then can optimum strategies for measurements and improvements be developed. Extensive research at the NIST (National Institute for Standards and Technology, USA) has led to the following important conclusion for reducing risk in fires: heat release, and particularly the
peak heat release rate, is the single most important parameter in a fire and can be considered to be the “driving force” [25]. That is why the cone calorimeter is now the standard choice for an engineering test of flame-retardant polymers. The measuring principle is based on the correlation between oxygen loss and heat release.

3.4.1 TPU

The flame-retardant properties of the TPU nanocomposite were determined using a cone calorimeter at a heat flux of 35 kW/m². The drop in the peak heat release rate for a TPU nanocomposite with 5 phr of organoclay 1 was 44% compared with the corresponding pure TPU (Figure 3). The time to ignition of the flammable gases was somewhat reduced for the nanocomposite, however; this can be attributed to the early Hofmann elimination reaction of the quaternary ammonium compound in organoclay 1 [26, 27].

A TPU containing a liquid phosphate ester as a conventional flame retardant showed a 70% drop in the peak heat release rate with an addition of just 5 percent by weight of organoclay; the time to ignition also fell (Figure 4).

The fire performance index (FPI) is a parameter that is commonly used to characterise the flame-retardant effect of materials [28, 29]. This empirical value is calculated as the ratio of the time to ignition and the peak heat release rate. The FPI is important because it correlates to the time to flashover and indicates the time available to escape from a fully developed fire; this has been demonstrated by experiments involving simulated fires in aircraft cabins [30]. It can therefore be regarded as an indicator for all types of fire risk. The higher the FPI value, the better the flame-retardant effect of a material. The FPI values were in all cases higher for TPUs with organoclay 1 (Table 3).

<table>
<thead>
<tr>
<th>Material</th>
<th>Fire performance index</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unfilled TPU</td>
<td>0.073</td>
</tr>
<tr>
<td>TPU with 5 phr organoclay 1</td>
<td>0.130</td>
</tr>
<tr>
<td>FR-TPU with phosphate ester [no organoclay]</td>
<td>0.071</td>
</tr>
<tr>
<td>FR-TPU with phosphate ester and 5 wt.% organoclay 1</td>
<td>0.199</td>
</tr>
</tbody>
</table>

Table 3. Fire performance index for TPU

Figure 3. Heat release versus time, measured with a cone calorimeter (heat flux 35 kW/m²) for various TPU-based materials

Figure 4. Heat release versus time, measured with a cone calorimeter (heat flux 35 kW/m²) for various TPU-based materials
Finally it should be noted that TPUs with organoclay 1 produced no flaming droplets (UL 94, vertical method), a characteristic feature which further limits the spread of a fire. This is important for the classification of the new Euro ratings within the CPD regulations, which determine the fire resistance ratings in Europe.

3.4.2 PVC

The flame-retardant properties of various PVC compounds with and without organoclays (Table 2) were measured with a cone calorimeter at a heat flux of 35 kW/m².

In the synthesis routes with EVA or TPU masterbatches (Figure 5 and 6), an early peak heat release rate was found in all cases for organoclay 1, which can be attributed to the Hofmann elimination reaction of the quaternary ammonium compound for the organoclay [26, 27]. Organoclay 4 did not exhibit this early peak; although a Hofmann elimination is possible, it clearly did not contribute to an early peak heat release rate. This explanation was also supported by the fact that organoclay 1 had a higher loss of mass than organoclay 4 at identical temperatures (Table 4) under the thermo-oxidative conditions of the TGA analysis.

**Table 4.** Loss of mass at various temperatures for organoclays 1 and 4; TGA in air, heating-up rate 20°C/min

<table>
<thead>
<tr>
<th>Material</th>
<th>Temperature</th>
<th>Loss of mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organoclay 1</td>
<td>180°C</td>
<td>0.5%</td>
</tr>
<tr>
<td>Organoclay 4</td>
<td>180°C</td>
<td>0.5%</td>
</tr>
<tr>
<td>Organoclay 1</td>
<td>300°C</td>
<td>5%</td>
</tr>
<tr>
<td>Organoclay 4</td>
<td>300°C</td>
<td>3%</td>
</tr>
<tr>
<td>Organoclay 1</td>
<td>350°C</td>
<td>16%</td>
</tr>
<tr>
<td>Organoclay 4</td>
<td>350°C</td>
<td>6%</td>
</tr>
<tr>
<td>Organoclay 1</td>
<td>500°C</td>
<td>25%</td>
</tr>
<tr>
<td>Organoclay 4</td>
<td>500°C</td>
<td>12%</td>
</tr>
</tbody>
</table>
The cone calorimeter graphs for organoclay 4 were no better than the corresponding graphs for the PVC-EVA and PVC-TPU compounds without organoclays (Figure 5 and 6).

Further research is therefore needed in order to produce organoclay-filled engineering PVC compounds with improved flame-retardant properties.

4. CONCLUSIONS

TPU nanocomposites with modified, laminar silicates can be produced by simple means with both virgin and conventional flame-retardant TPUs. A 70% reduction in the peak heat release rate and no dripping of the burning polymer are observed.

In the case of PVC combined with modified, laminar silicates, HCl release is observed, leading to severe discoloration. A masterbatch method with EVA or TPU can almost eliminate this undesirable reaction. Reductions in the peak heat release rate were only marginal, however, and there was no improvement in flame-retardant properties.

5. ACKNOWLEDGMENTS

The author wishes to thank the management of Kabelwerk Eupen AG for permission to publish these findings. His thanks go also to Dr M. Alexandre from the University of Mons in Belgium for the XRD analyses.

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