Flame retardancy of thermoplastic polyurethane nanocomposites

Nanocomposites are a new class of polymer systems. Modified layered silicates (organoclays) are dispersed at a nm-level within a polymer matrix with new extraordinary properties. Thermo-oxidative stability and peak of heat release rates for thermoplastic polyurethane nanocomposites are improved by organoclays. Organoclays together with classical flame retardants for TPU are a highly flame retardant system.

1. Introduction

Once a fire starts in a room containing flammable materials, it can heat up and ignite additional combustible materials. As a consequence the rate at which the fire progresses now speeds up because more and more heat is released and a progressive increase of the room temperature is observed. The radiant heat and also the temperature can rise to such an extent that all materials within the room will be ignited resulting in an extremely high rate of fire spread. This point in time is called „flashover" leading to a fully developed fire. Escape from the room then will be nearly impossible and the spread of the fire to other rooms is very likely. When a fire goes to flashover, every polymer will release roughly 20 % of its weight as carbon monoxide resulting in highly toxic smoke. Therefore most people die in large fires and 90 % of fire deaths are the result of fires becoming too large with release of lethal smoke [1-2].

Each year about 5000 people are killed by fires in Europe and more than 4000 people in the USA. The direct property losses by fires are roughly 0,2 % of the gross domestic product and the total costs of fires are around 1 % of the gross domestic product [3]. Therefore it is important to develop well designed flame retardant materials.

* Dr. Günter Beyer
gbeyer@euregio.net

Kabelwerk Eupen AG, Eupen, Belgium

Polymers are used in more and more fields of applications and specific mechanical, thermal and electrical properties are required. One further important property is the flame retardant behaviour of polymers, which can be fulfilled traditionally by the following routes:

- Use of intrinsically flame retardant polymers like PVC or fluoropolymers

- Use of flame retardants like alumina trihydrate, magnesium hydroxide, organic brominated compounds, phosphorus compounds or intumescent systems to prevent the burning of polymers like EVA, PE, PP, PA, TPU and other polymers

A new class of materials, called nanocomposites, is also used as a flame retardant system. Nanocomposites are of interest as a simple and cost-effective method to enhance polymer properties by the addition of a small amount (5 weight-%) of a properly designed organoclay to the polymer, leading to the creation of composites with the filler distributed in the polymer matrix at the nanometer level. Depending on the nature of the organoclay distribution within the matrix, the morphology of nanocomposites can evolve from the intercalated structure with a regular alternation of organoclays and polymer monolayers to the exfoliated (delaminated) structure with organoclays randomly and homogeneously distributed within the polymer matrix.

The easiest and technically most attractive way to produce these types of materials is kneading the polymer in the molten state with a modified layered silicate such as montmorillonite. The native Na^+ interlayer cation within the silicate layers has been exchanged by a bulky quaternary alkylammonium cation. This modified layered silicate is now called an organoclay and much more compatible with the polymer matrix.

Highly interesting properties exhibited by polymer-layered silicate nanocomposites concern their increased thermal stability and also their ability to promote flame retardancy at very low filling levels. The formation of a thermal insulating and low permeability char to volatile combustion products caused by a fire is responsible for these improved properties [4-7]. The low filler contents in nanocomposites which provide a drastic improvement in thermal stability are highly attractive for the industry because flame retardant end-products can be made cheaper and easier to process.

Thermoplastic polyurethanes (TPU) are polymers with properties designed for their end applications. The properties are high tensile strength and flexibility, high abrasion resistance and tear strength. However virgin TPUs have only moderate thermal stability and low flame retardancy.

This study explores the use of organoclays as flame retardants for TPUs.

2. Experimental, processing and characterisation

Dimethyl-distearyl-ammonium exchanged montmorillonite (organoclay 1) was used as an organoclay.

Polyether based TPUs including a virgin non-flame retardant TPU and a traditional flame retardant TPU containing a phosphate ester (as reported by the supplier) were used.

Compounding was done by a twin roll mill at 160°C.

Informations on TPU-nanocomposite morphology were recieved from X-ray diffraction (XRD). Intercalated silicate sheets were observed for the virgin TPU melt-compounded with 5 phr organoclay 1.

The cone calorimeter experiments were carried out at 35 kW/m² heat flux with horizontal orientation of the samples (plates with 100 mm x 100 mm x 3 mm) according to ASTM E 1354. The reported data were the average of 3 measurements for each sample with a standard uncertainty of the measured heat release rates of ± 5 %.

Thermogravimetric analyses (TGA) were performed by utilizing a TGA 7 from Perkin-Elmer under air flow at 20°C/min heating rate.

3. Results

3.1 Thermal stability by TGA for TPUs

Thermal stabilities of TPUs were studied by TGA in air. For the virgin TPU and the same TPU intercalated with 5 phr of organoclay 1 mass losses at the same temperature up to 350 °C are only marginally higher for the nanocomposites. At same temperatures higher than 350 °C the mass losses are significantly lower for the nanocomposite than for the virgin TPU indicating an improved stabilization **(figure 1).**

3.2 Flammability properties

From an engineering point of view, it is important to know what hazards within a fire must be prevented and only then optimum strategies for measurements and improvements can be developed. Extensive research at NIST (National Institute for Standards and Technology, USA) led to the important conclusion which allows a significant simplification of the problem for hazards in fires: The heat release rate, in particular the peak heat release rate, is the single most important parameter in a fire and can be viewed as the "driving force" of the fire [8]. Therefore, today the universal choice of an engineering test for flame retardant polymers is the cone calorimeter. The measuring principle is the oxygen depletion with a relationship between the mass of oxygen consumed from the air and the amount of heat released.

The flame retardant properties of the TPUs and TPU nanocomposites were determined using cone calorimetry under a heat flux of 35 kW/m². The reduction for the peak of heat release rate was 44 % for a TPU nanocomposite with 5 phr organoclay 1 compared to the corresponding virgin TPU **(figure 2).** Time to ignition was lowered for the nanocomposite; this may be related to the Hofmann-elimination reaction of the quaternary anmmonium compound within the organoclay 1 [9].

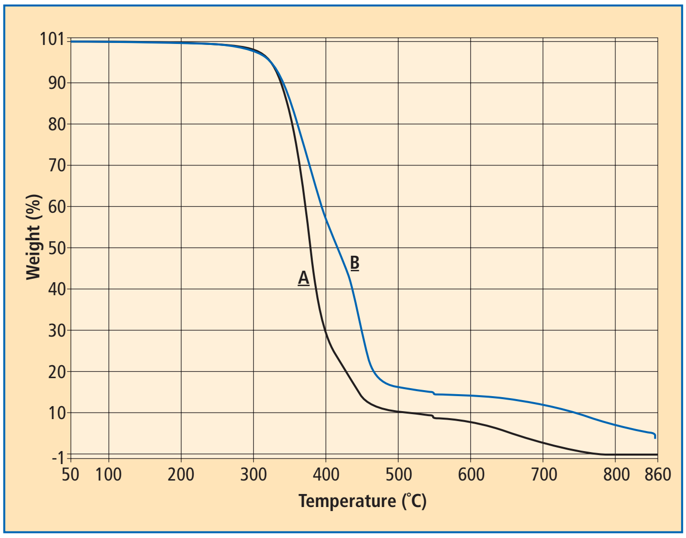

Fig. 1: *Thermogravimetric analysis in air of various TPU based materials:*
A: *unfilled TPU;*
B: *TPU + 5 phr organoclay 1*

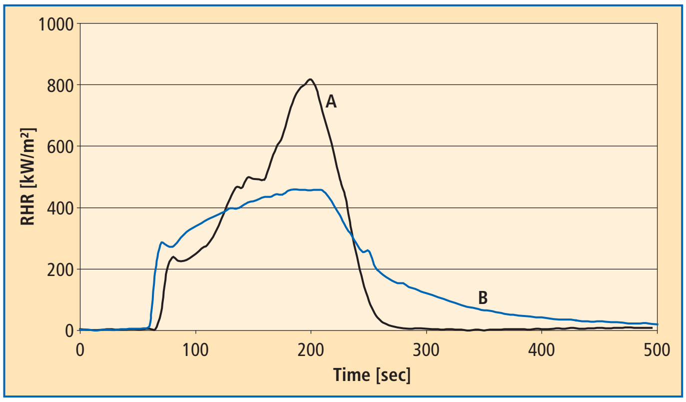

Fig. 2: *Rate of heat release vs. time measured by cone calorimeter (heat flux: 35 kW/m²) for various TPU based materials:*
A: *unfilled TPU, red curve;*
B: *TPU + 5 phr organoclay 1, blue curve*

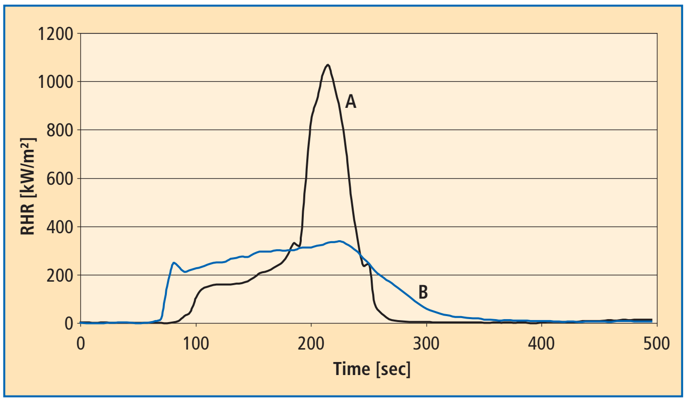

Fig. 3: *Rate of heat release vs. time measured by cone calorimeter (heat flux: 35 kW/m²) for various TPU based materials:*
A: *FR-TPU with phosphate ester, black curve;*
B: *FR-TPU with phosphate ester + 5 weight-% of organoclay 1, blue curve*

A TPU with a liquid phosphate ester as classical flame retardant showed a reduction of 70 % for the peak of heat release rate, if only 5 weight-% organoclay 1 were added; again, the time to ignition was lowered **(figure 3).**

The fire peformance index (FPI), which is the ratio between the time to ignition and the peak heat release rate, is often used to characterize the flame retardancy of materials [10]. The FPI is important because it relates to the „time to flashover" and indicates the time available to escape in a full-scale fire. Therefore it may be considered as the best individual indicator of overall fire hazards. The higher the FPI value, the better is the flame retardancy of a material. The FPI values are higher for TPUs with the organoclay 1 **(table 1).**

Finally, organoclay-containing TPUs do not generate burning droplets (UL 94 vertical procedure) [11], a characteristic feature that furthermore limits the propagation of a fire.

4. Summary

TPU nanocomposites with organoclays can be synthesized easily with virgin and also classical flame retardant TPUs. A reduction up to 70 % for the peak of heat release and also a non-dripping behaviour of burning polymer was observed.

5. Acknowledgement

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6. References

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Material	***Fire Performance Index***
Virgin TPU (no organoclay)	*0,073*
TPU with 5 phr organoclay 1	*0,130*
FR-TPU with phosphate ester (no organoclay)	*0,071*
FR-TPU with phosphate ester and 5 weight-% organoclay 1	*0,199*

Tab. 1: *Fire performance index of TPUs*