Fire retardation of polystyrene/clay nanocomposites: Initial study on synergy effect

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Abstract

Polystyrene and its copolymers are a group of polymers with a wide field of applications. A big disadvantage amongst many of them is their high flammability. Previous research showed that one of the possibilities to reduce this negative property is to synergize conventional fire retardants and other types of fillers. Recent research showed that there is a synergy effect in composites with clays. This initial study is focused not only on the evaluation of synergy with modified or unmodified layered clay nanofillers but with wide variety of other fillers e.g. clay nanotubes, melamine or magnesium hydroxide. All results are compared to pure polymer and polymer with conventional fire retardants. The samples were prepared in laboratory Brabender Plasti-Corder kneader and analyzed by X-ray diffraction. Flammability was the most important evaluated property; moreover, mechanical properties were observed.

Key words: fire retardation, synergy, clay, nanocomposite, polystyrene

Introduction

Polystyrene is a commodity plastic manufactured on a very large scale. The brittleness of polystyrene considerably limits its use in engineering and high-performance products. The toughness of polystyrene can be improved by copolymerization or blending with a butadiene elastomer or other rubberlike polymer (the rubber should be present as a separate dispersed phase). This polymer is known as high-impact polystyrene (HIPS) [1]. The biggest applications for HIPS are in television and computer cabinets [2], electronic instruments and building materials [3]. HIPS as well as polystyrene has the big disadvantage, which is their high flammability, therefore flame retardation is required in most of products made of these polymers.

Flame retardants can act several possible ways to provide the increased fire resistance e.g. by reducing the rate of burning or flame spread, raising the ignition temperature, and reducing

smoke generation [4]. The two principle modes of action for flame retardants are based on gas-phase and condensed-phase activity [4]. For gas-phase activity, the flame retardant produces an active species in the vapour or gas-phase that impacts the burning/combustion process. An example of gas-phase activity is a molecule such as hexabromocyclododecane (HBCD) that can degrade with simultaneous production of HBr in the gas phase [5-7]. Condensed-phase activity comprises action in the solid or melt phase of the polymer in order to impact or reduce the burning process. The most important condensed-phase mechanism is the formation of a char layer that serves as a barrier to heat and mass flow. Another example of condensed activity is fire retardant interaction with the base polymer in order to evocate increased polymer degradation and melt flow during the burning process [4,8].

Many phosphorous-based fire retardants such as triphenyl phosphate (TPP) are thought to provide both char forming condensed-phase as well as gas-phase activity [8].

Many fire retardants are used nowadays, but in the near future some of them will be prohibited (bromine-based fire retardants) because of their negative influence on the environment or human health. Therefore significant research activity has been recently directed to the development of styrene/clay nanocomposite materials [9,10] with enhanced flame-retardant properties [11-18]. The clay nanocomposites are materials which have attracted great interest in recent years, because they often exhibit remarkable improvement in materials properties. One of them is the increased resistance for heat and flame [16,18,19]. The flame-retardant mechanism of the nanocomposites involves the formation of a carbonaceous char layer on the surface of the burning material due to the presence of clay particles that act as an insulating barrier [4,18,20]. The extent of this layer depends on various factors e.g. the concentration or compatibility of the particles with the polymer [21]. The most important factor is the dispersion of nanofilers in the polymer matrix – the structure of nanocomposite material. There are two structurally different types of clay nanocomposites – the intercalated structure, where the individual polymer chains are sandwiched between silicate layers (chains are in the interlayer of clay platelets); and the delaminated or exfoliated structure, where the silica is exfoliated and produces 'a sea of polymer with rafts of silicate'. The exfoliated structure is the one which obtains the biggest betterment of properties. [16,19,20,22,23].

Recent research showed that there is a synergy effect between conventional fire retardant (e.g. HBCD, triphenyl phosphate, red phosphorus) and clays [16,20,24-29] or other fillers (e.g. magnesium hydroxide) [16,28,30-32] on fire retardation.

In this article, the initial comparative study of synergy is carried out on commercial HIPS with conventional fire retardant TPP. As a second additional ingredient, a wide variety of other fillers was chosen: melamine, magnesium hydroxide, magnesium carbonate hydroxide hydrate, powdered siloxane, organosilicate nanotubes Halloysite NT and organically modified clays Nanofil 5 and Nanofil SE3010. All results are equated to pure HIPS and HIPS with conventional bromine-based fire retardants tetrabromobisphenol A and HBCD.

Experimental

Materials and preparation

Commercial high-impact polystyrene (HIPS) KRASTEN ® 552M from SYNTHOS Kralupy a.s. (The Czech Republic) was used as a polymer matrix. The following fillers were used: magnesium hydroxide Duhor C-043/S (MgOH) from Duslo Šala (The Slovak Republic); powdered siloxane Dow Corning® 4-7081 (Siloxane) from Dow Corning (USA); organically modified clay nanofillers Nanofil 5 and Nanofil SE3010 from Südchemie (Germany); magnesium carbonate hydroxide hydrate (MCH), triphenyl phosphate (TPP), hexabromocyclododecane (HBCD), tetrabromobisphenol A (TBBP-A), melamine and organosilicate nanotubes Halloysite NT from the Aldrich Chemical Company.

Table 1 shows the composition of prepared samples. Pure HIPS and the first three samples only with fire retardant were used for equation of results.

The compounds were prepared by kneading in laboratory Brabender Plasti-Corder mixing bowls for 10 min. The temperature was 180 °C and the rotational speed 30 min^{-1}. The specimens were prepared by compression moulding at the temperature 190 °C for 3min.

Instrumentations

X-ray diffraction (XRD) measurements were performed using PANalytical X´Pert PRO diffracto-meter with a Cu tube source ($\lambda = 0.1540$ nm) operated at 1.2 kW. The scans were taken from 4 to 28 º2θ.

Pictures of transmission electron microscopy (TEM) were taken by JEM 200CX machine. Temperature of sample and knife (Leica cryo-ultramicroton) was -70 °C and -45 °C respectively.

Mechanical properties under tension were measured on the servo hydraulic INSTRON 8870 machine. Modulus, tensile stress at break and extension were examined.

Fire tests were carried out in the digester by 6 cm high flame of gas burner. The specimens of 100x10x1 mm dimensions were put into the flame for 5 s. The tests results are decrease in weight, burning time and dripping.

Limiting oxygen index (LOI) was measured according to norm ČSN ISO 4589-2 using Ceast – oxygen index device. Flame was ignited on the upper surface (method A).

Results and Discussion

Morphology (XRD and TEM)

XRD spectra were taken only for pure HIPS, nanofillers powders and specimens with nanofillers; all the spectra are shown in Figure 1. XRD spectra of powder samples were measured by a measuring technique different from that used for other materials. Peaks around 5 and 7 º2θ, which represent the structure of nanocomposites (intercalated/exfoliated), are visible only in scan of HIPS/TPP/Nanofil SE3010 samples, but the peaks of HIPS/TPP/Nanofil 5 samples disappeared, which suggest that Nanofil 5 perhaps has exfoliated structure in its matrix, but Nanofil SE3010 has only intercalated structure. This was confirmed by TEM pictures. They show better dispersion of clay particles in polymer matrix in the case of Nanofil 5 (Figure 2B) than Nanofil SE3010 (Figure 2A). Halloysite NT shows peaks at different places, which is due to the dissimilar type of particle shape. The relation between the spectrum and the structure of this composite is not clear. The TEM image (Figure 2(c)) showing an aggregate of filler suggests that the dispersion of filler in polymer matrix is not optimal.

Mechanical properties

The obtained results from mechanical properties under tension tests are summarized in Figure 3. The zero base line represents pure HIPS. The specimens of TBBP-A-containing compound could not be prepared for this measurement. The values of tensile stress at break show that the strength significantly decreased for all samples except the composites HIPS/TPP/Nanofil 5. The modulus is moderately higher for some samples, Nanofil 5 samples have approximately the same values as pure HIPS, but most of composites have decreased values; this means that stiffness of these materials is lower. The elongation at break falls down more than about 60 % which advert to the higher brittleness of composites compared to the pure polymer.

Fire tests and limiting oxygen index

The results of fire tests are summarized in Table 2. The burning time means time necessary for the spontaneous flame extinction or to 100 % burning out of specimens. Only one composite approves synergy – HIPS/TPP/Nanofil 5 which has better fire retardation than the sample only with TPP. Its results are comparable with bromine-based fire retardant TBBP-A. Specimens of Nanofil 5 do not burn after removal from fire and have appropriate decrease of weight. This very good result of fire retardation was proven by LOI measurement. The LOI value of HIPS/TPP/Nanofil 5 is higher than in the case of samples only with fire retardant TPP and even with TBBP-A . These results suggest that the nanocomposite with TPP and Nanofil 5 is a possibility to achieve the fire-retardation properties without using bromine-based fire retardants.

Good fire retardation properties also have composites with MgOH and melamine, which are comparable with TPP. These composites with improvement slightly dripped only directly in flame. The rest of all composites dripped relatively heavily. The composites with MCH and Siloxane have the worst results. The both lose 100 % of their weight, but after threefold longer time than pure HIPS, which is rather a small improvement.

Conclusions

Synergy effect does occure for the composite HIPS with conventional fire retardant TPP and layered clay nanofiller Nanofil 5. The results from fire tests and LOI measurements suggest that this nanocomposite has an auspicious opportunity to become an alternative to conventional bromine-based fire retardants. As demonstrated in the XRD spectrum and TEM image, this composite perhaps has exfoliated structure that might give the improvement in fire retardation and the increase of tensile stress at break.

Further research will be focused on the determination of opportune loading of TPP and Nanofil 5 to reach the best fire retardation with the lowest loading of additives.

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Table 1. Composition of prepared compounds.

	Conventional fire retardant – its loading [%]	Other filler in 5 % loading (abbreviation)
Samples for comparison	Pure HIPS - matrix	−
	HBCD - 15	−
	TBBP-A - 15	−
	TPP - 15	−
Samples with conventional retardant and other filler	TPP - 10	Melamine
		Commercially modified clay Nanofil 5
		Commercially modified clay Nanofil SE3010
		Clay nanotubes Halloysite NT
		Magnesium carbonate hydroxide hydrate (MCH)
		Powdered siloxane Dow Corning (Siloxane)
		Magnesium hydroxide Duhor (MgOH)

Table 2. Values or evaluation of fire retardation properties.

| Sample (filler)	Decrease of weight [%]	Burning time [s]	Limiting oxygen index
Pure HIPS	100.0 ± 0.9	20.06 ± 2.13	19.5
HIPS/HBCD	18.3 ± 2.4	67.56 ± 3.02	21.5
HIPS/TBBP-A	22.6 ± 1.5	0.00 ± 0.09	21.5
HIPS/TPP	24.3 ± 1.7	2.13 ± 0.36	21.5
HIPS/TPP/Melamine	20.3 ± 1.5	2.25 ± 0.19	21.0
HIPS/TPP/Nanofil 5	21.1 ± 1.2	0.00 ± 0.07	22.0
HIPS/TPP/Nanofil SE3010	56.6 ± 2.1	40.65 ± 2.23	20.0
HIPS/TPP/Halloysite NT	56.9 ± 4.2	105.12 ± 5.13	20.0
HIPS/TPP/MCH	100.0 ± 0.7	75.29 ± 3.12	20.0
HIPS/TPP/Siloxane	100.0 ± 0.6	65.46 ± 2.56	20.0
HIPS/TPP/MgOH	29.3 ± 1.3	2.84 ± 0.45	21.0
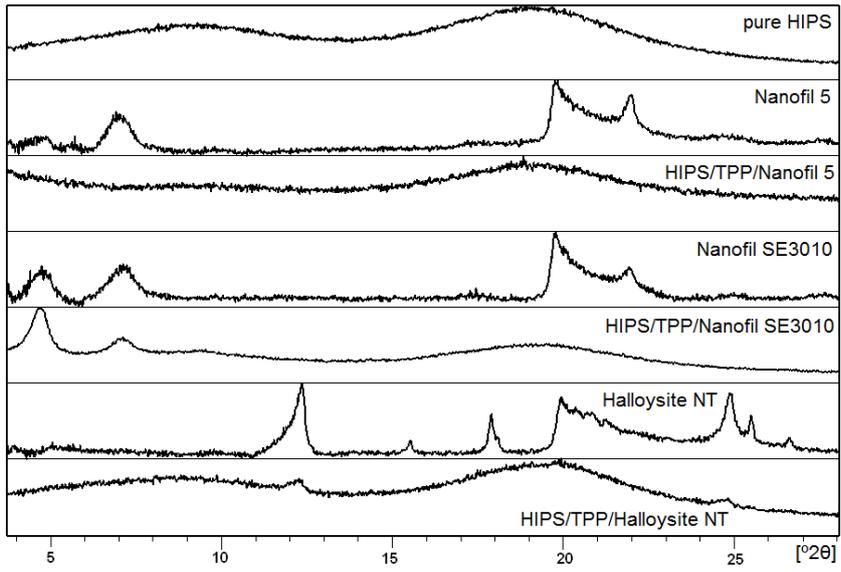
Figure 1. XRD spectra of pure nanofillers and composites with nanofillers.
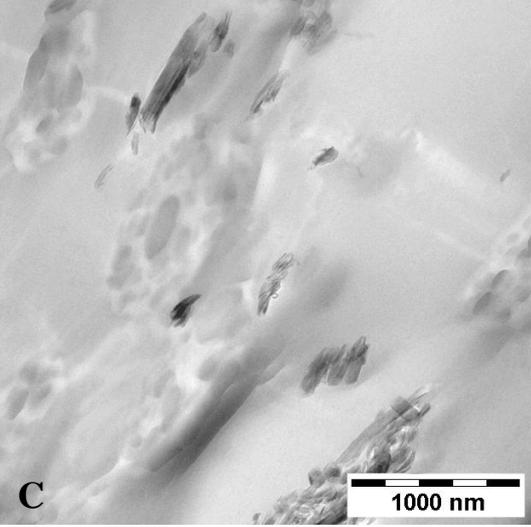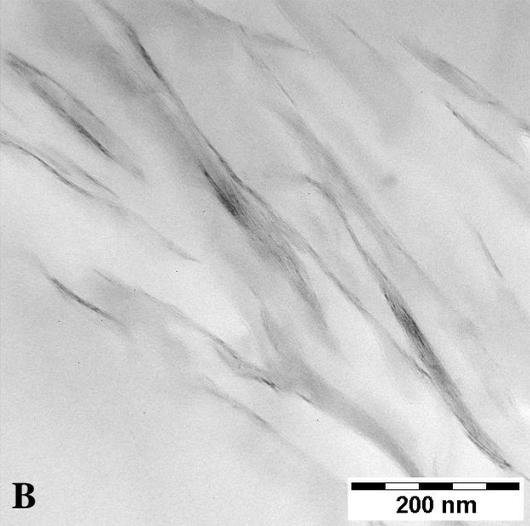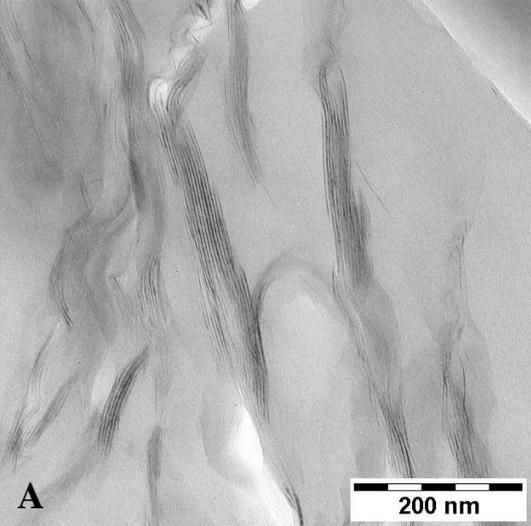
Figure 2. TME pictures of samples with TPP + Nanofil SE3010 (A), TPP + Nanofil 5 (B) and TPP + Halloysite NT (C).
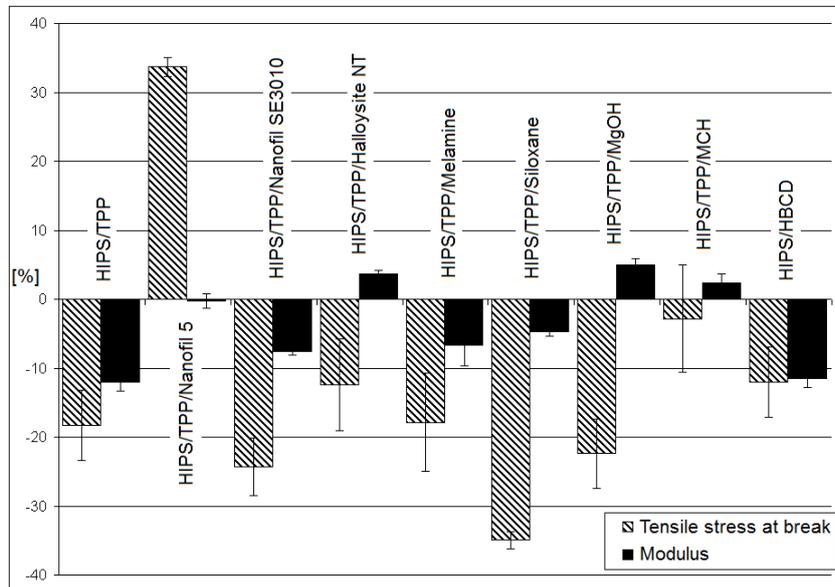

Figure 3. Comparison of tensile stress at break and modulus.