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Investigations of Fire Retardant Properties of Polypropylene-Clay-Nanocomposites

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Summary: Polypropylene-clay nanocomposites were prepared by compounding using a masterbatch technology. The burning behaviour of the nanocomposites was tested. The nanocomposites show fire retardant effects. The effects were discussed by microscopy investigations of the ash and by rheological behaviour of the composites.

Introduction

The development of polymer-clay nanocomposites is one of the most popular research topics in material sciences of the present time. Natural layered silicates such as montmorillonite, the main fraction of the clay mineral bentonite are commonly used for several purposes and are commercial available in lots of different types. Synthetic clays are also used for the development of nanocomposites. Besides an interesting mechanical behaviour nanocomposites have also potentials in gas barrier applications and fire retardant applications. The high aspect ratio of approximately 100 – 1000 (edge length in ratio to the thickness of the layers) of completely exfoliated layers promises a high influence on the properties of polymers filled with such materials. Polypropylene-clay nanocomposites have a lower step of exfoliation than nanocomposites of hydrophilic polymers like polyamide. This is one of the reasons, that the effect of the clay filling on the mechanical behaviour of polypropylene nanocomposites is not in the same range like in case of polyamide [1-3].

Preparation of the Nanocomposites

Two different clay minerals were used for preparing nanocomposites. The one is a natural clay (EXM), mined and refined by Suedchemie, Germany. The other one is a synthetic clay (Somasif), made by Co-Op Chemical, Japan. Both clay minerals were surface modified in order to achieve compatibility to the polymer matrix. Thus quarternary ammonium salts are required to exchange the sodium ions connecting the

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layers each other and so to make easier the exfoliation. The modified clays were incorporated in a polypropylene grafted with maleic anhydride (PP-g-MA) on a tightly intermeshing co-rotating twin screw extruder (Werner & Pfleiderer) with a screw diameter of 30 mm and a relatively length of 41 L/D. A masterbatch technology was used to prepare the nanocomposites. In the first step the modified clay was added to the PP-g-MA with a loading of 50 wt.-%. In a second step this masterbatch was incorporated in different loadings in a polypropylene homopolymer using the same extruder. The platelet thickness was in the range of 20 nm.

Testing Results and Discussion

All inorganic fillers, also without endothermic effects, exhibit a flame retardant effect in polymer composites. In case of inert inorganic fillers (like talc) a high amount of filler is necessary for reducing the flammability of the composite. The Table 1 show the results of a Limiting Oxygen Index Test (LOI) with a LOI-Tester made by Raczek Scientific Instruments.

Filler type	Clay loading Wt-%	LOI-Index	remarks
unfilled	0	17.8	melt flow from the top
natural clay	2.5	18.6	melt flow from the top
natural clay	5	18.8	no melt flow from the top , melt zone visible, compact residue
natural clay	7.5	19.0	no melt flow from the top, small melt zone visible, compact residue
natural clay	10	19.2	no melt flow from the top, no melt zone visible, compact residue, residue tips very late from the top
synthetic clay	5	19.2	no melt flow from the top, no melt zone visible, compact residue, residue doesn't tip from the top
talc	5	18.0	melt flow from the top
talc	10	18.1	melt flow from the top
talc	40	20.2	no melt flow from the top, no melt zone visible, compact residue, residue doesn't tip from the top

Table 1. Limiting Oxygen Index (LOI) according ASTM D 2863-87

Rothon [4] published results by *Case* and *Jackson* showing, that the reciprocal of the oxygen index can be directly related to the filler loading for reactive and inert fillers. He showed the applicability of the developed equations (details and explanation please see [4]) for coarse fillers with diameters > 10 μm. The figure 1 shows the expected linearity of the dependence on the oxygen index degree from the filler loading and the small effectiveness of this inert filler. Nanocomposites with natural clay are much more effective at the same loading and the highest degree of the LOI we found in case of synthetic filler.

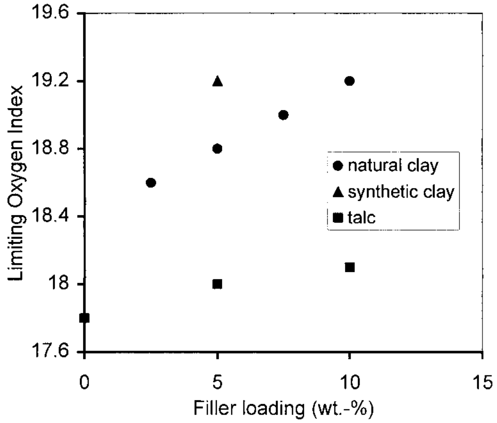

Figure 1. Limiting oxygen index of composites with different inert fillers

There is no reason, that in case of the same polymer matrix the composition of the gaseous products, the initial temperature and the temperature which the gaseous products and solid filler residues exit from the combustion cycle are significant different. The heat capacity of the fillers is similar. The most important differences between the composites are in the filler scale and in the aspect ratio of the fillers.

The figure 2 shows a combustion residue of a natural clay filled nanocomposite and the figure 3 of a synthetic clay filled nanocomposite. The SEM's were made by a low voltage scanning microscope DSM 982 GEMENI Carl Zeiss.

The filler scales in relation to the platelet thicknesses are in both cases similar but the aspect ratios are different. The aspect ratio of the synthetic clay platelets is more than twice in relation to the natural clay platelets. The natural clay forms a more porous ash than the synthetic clay. Talc filled composites form a combustion residue with an essential higher porosity caused by higher platelet scale of the talc.

It would appear, looking at he LOI-tests in consideration of the combustion residue investigations, that the compact combustion residue of the nanocomposits resulted in an effective covering of the burnt parts of the sample. Nevertheless the flame can spread to the sample sides if the top is covered with ash in case of LOI-tests because the sample burns from the top downwards. The effect of coverage is limited in such situation.

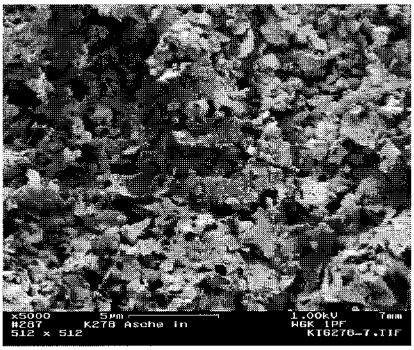

Figure 2. Combustion residue of PP-Nanocomposite with natural clay

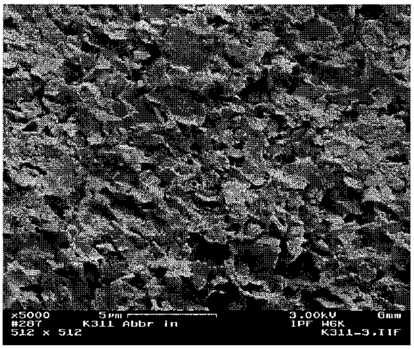

Figure 3. Combustion residue of PP-Nanocomposite with synthetic clay

The vertical burn test UL 94 (Horicontal Vertical Flame Chamber made by Atlas Electric Devices) simulate a more realistic situation. A sample of the test material is held vertically in air and ignited from the bottom with a gas burner. According the standard the materials are characterised by only few ratings. The polypropylene-clay-nanocomposits without additional flame retardants didn't achieve any classification. Nevertheless their burning behaviour is very interesting in such conditions. An important role play burning drops in case of spreading flames in buildings.

The time from the ignition of the sample to the occurrence of the first burning drops was measured for polypropylene-clay-nanocomposits with different clay loadings. The figure 4 shows the strong increase of this time with an increase of filler loading in case of natural filler.

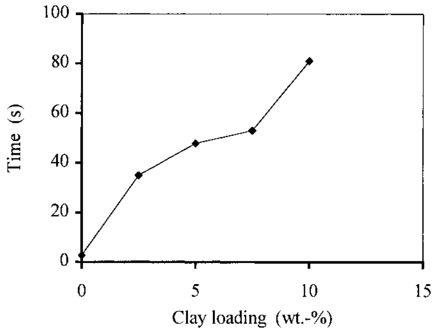

Figure 4. Time from taking off the gas flame from the sample to the dripping of first burning parts

The figure 5 shows the increase of the viscosity level of polypropylene-clay nanocomposites with an increase of filler loading even at low loading rates. This effect corresponds with the dependence of time from the ignition of the sample to the occurrence of the first burning drops on the filler loading.

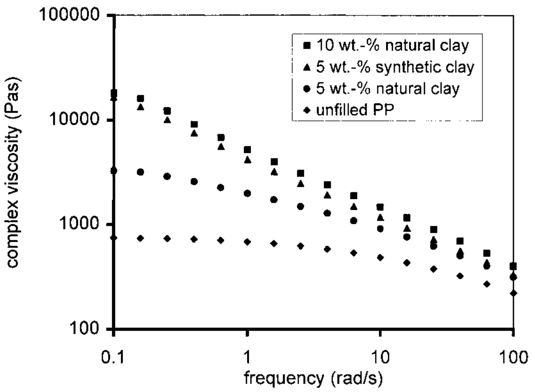

Figure 5. Increase of viscosity in case of filling with different layered silicates (T=220°C)

However the viscosity level of the composites couldn't be the only reason for the observed effect. Different composite types with the same viscosity level have a different behaviour at the vertical burning test. Polypropylene nanocomposites with a loading of 5 wt.-% synthetic clay and 10 wt.-% natural clay have a similar viscosity levels (fig. 5).

During the burning process the sample with natural clay showed an elongation with tears from the sides and in the end big burning pieces fell down. The burning process was very intensive. The sample with synthetic clay burned on the sample surface from the bottom to the top and in the end the flame gone out by itself. The flame was less intensive in relation to natural clay filled composites and the sample showed no elongation and no any dripping parts were observed. The burnt sample was covered with a ash shell of nearly 1 mm. The inner part was a white porous material with low mechanical level. However the rest strength of the material was enough to hinder the dripping.

It would appear, that the high viscosity together with the covering of the sample with a compact ash results in the shown effect in case of synthetic filler.

Conclusions and Outlook

The forming of compact ash on the surface by burning nanocomposites is an inherent effect of such materials. Only this effect is not enough to get fireretardant materials but it can be an useful addition which give the possibility to reduce the loading of fireretardants in composite materials.

The increase of the viscosity is also a positive effect in relation to the burning behaviour. However the possibility to use this effect is limited because it is necessary to take into account the worse processing behaviour. To control the viscosity increase of polymer-clay nanocomposites is an unsolved problem. The level of exfoliation of the clay is lower in case of PP-matrix than e.g. in case of PA-matrix and so the problem is not so actual.

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