Surface Modified Aluminium Hydroxide in Flame Retarded Noise Damping Sheets

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Summary: Flame retarded polyethylene compounds were prepared using a series of aluminium hydroxide of different particle size applying a milling processes and special precipitation technologies. The processability and flame retardant efficiency of the flame retarded systems were compared. The effects of various surface modifications were analysed in case of one selected type of aluminium hydroxide. A silicone terminated reactive surfactant promoted not only the processability but also the flame retardant efficiency. Noise damping sheets were prepared by simultaneous application of aluminium hydroxide and barium sulphate in an elastomer blend matrix. V0 flame retardant grade could be achieved this way accompanied with improvement in the acoustic properties and maintenance of the mechanical properties.

Keywords: aluminium hydroxide; flame retardancy; noise damping; surface modification

Introduction

Metal hydroxides are used for a long time in huge quantities as flame-retardant additives because of their minimal smoke emission and corrosivity. Still a continuous development exists in this field. New surface modification methods[1,2] for improving the compatibility and processability, and new production technologies for modifying the morphology are reported in the literature, for example bulk manufacturing of synthetic hydrotalcite,[3] application of new milling and precipitation technologies for influencing the size distribution[4] and application of synergists such as expandable graphite,[5] boroxo-siloxane,[3] zinc-borate,[6] lignin[7] and compound like zinc hydroxyl stannate[8] for increasing the efficiency of the additives. The main application field of the metal hydroxide containing elastomeric compounds is the preparation of flame retardant cable insulation with high loading of additive. Changes in compounding techniques and formulation technology as well as the use of processing aids and modification of the metal hydrate are needed for incorporating these flame retardants into polyethylene matrix to form better products.[9]

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In this work the processability and flame retardancy of polyethylene compounds containing variously prepared aluminium hydroxide of different particle sizes are compared. The influence of different surface treatments on the processability and flame retardance are also discussed, as well as the noise damping acoustic character of barium hydroxide/aluminium hydroxide filler-containing compounds.

Experimental

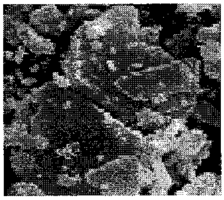
The materials used in the experiments are as follows: medium density polyethylene (PE): Tipelin K 341 94 (TVK, Hungary); thermoplastic elastomer blend (TEB): PEMÜBLEND (PEMÜ, Hungary); aluminium hydroxide of various grades (ATH): Alolt types (MAL Corp. Hungary), the average particle sizes and the SEM pictures of the particles are shown in Figure 1; surface treating agents: various derivatives of stearic acid of low cationic activity (LIS), of medium cationic activity (MIS), of high cationic activity (HIS), of non-ionic character (NIS) and silicone-containing reactive surfactant (RS) (The agents were prepared in the laboratory); barium sulphate $BaSO_4$ (Barite, Merck).

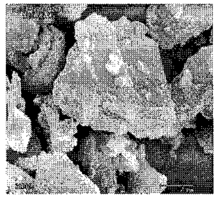
The PE-based compounds, containing 60 % ATH, were homogenised in the mixing chamber of a Brabender Plasti-Corder (PL2000 type, Brabender) equipment for 12 min at 170°C with rotor speed 50 rpm. Sheets (100 x 100 x 3 mm) were prepared by compression moulding in a Collin P200E press at 170°C and a pressure of 3 MPa. The surface modifying additives were applied in 0.1%, related to the amount of the ATH.

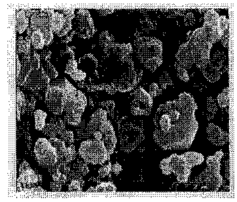
The reference noise damping compound consisted of 64.3% Barite in PEMÜBLEND. The flame retardant noise damping compounds were prepared by gradual replacement of Barite by ATH.

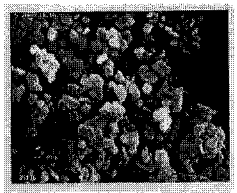
The bending loss factor was measured on a small, narrow band with bending wave excitation.[10] The applied sizes of samples, length: 300 mm, width: 20 mm, thickness: 0.68 mm, cover the most important acoustic frequency range. The samples were excited by an electrodynamics exciter. The samples were fixed to the exciter by a thin layer of adhesive.

The flammability properties were characterized by limited oxygen index (LOI) and UL 94 tests. Mechanical properties were characterized by determination of tensile strength and elongation at break, applying Instron 1195 testing machine.


ATH 5 μm


ATH 3 μm


ATH 1.5 μm


ATH 1.4μm

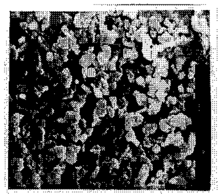

ATH 1.1μm

Fig. 1. SEM micrographs of various $Al(OH)_3$ types produced by MAL Corp. Hungary.

Results and Discussion

Effect of Particle Diameter on the Processability and Flammability

The average diameter of the various grades of ATH used for the test varies in the range of 1.1 to 5 μm. The decrease of filler diameter generally increases the melt viscosity of the polymer compound, which increases the mixing torque of melt during polymer compounding. Consequently, very small filler diameter is not favourable for the processing. Regarding the flame retardant properties, however, the smaller diameters are favourable. This antagonistic impact is reflected in Figures 2 and 3. Figure 2 shows the diagram of the steady state kneading torques of the PE compounds containing 60% of various grades of ATH. A dynamic increase in the processing torque can be observed with decreasing particle size, getting very high below 1.5 μm.

Figure 3 shows the LOI and UL 94 flammability characteristics of PE compounds containing 60% of various grades of ATH. No strict correlation can be observed between the particle size and the flammability, which can be explained by the uncompletedispersion of the small size ATH. However, as a general trend, compounds with smaller particles have better FR characteristics. The best flame retardancy could be achieved by the application of ATH having an average diameter of 1.5 μm.Thus ATH of 1.5 μm was applied for the further works.

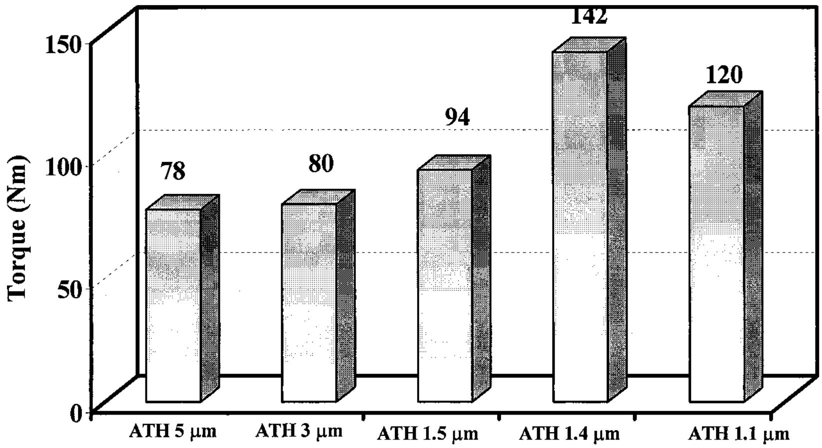


Fig. 2. Processing torque of PE compounds containing 60% of various grades of ATH.

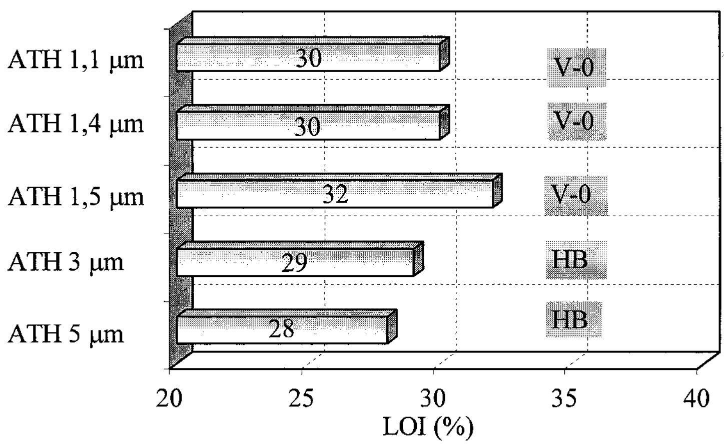


Fig. 3. Flammability of PE compounds containing 60% of various grades of ATH.

Surface Modification of ATH

A series of stearic acid derivatives, of different ionic activity, that is of low-, medium- and high cationic activity (LIS, MIS, HIS), and of non-ionic character (NIS) and silicone containing reactive surfactant (RS) were applied for surface modification of the ATH. The influence of the various modifying agents on the mixing torque can be seen in the Figure 4. The additives in general reduce the mixing torque considerably. The most favourable effect is produced by the additives LIS and RS.

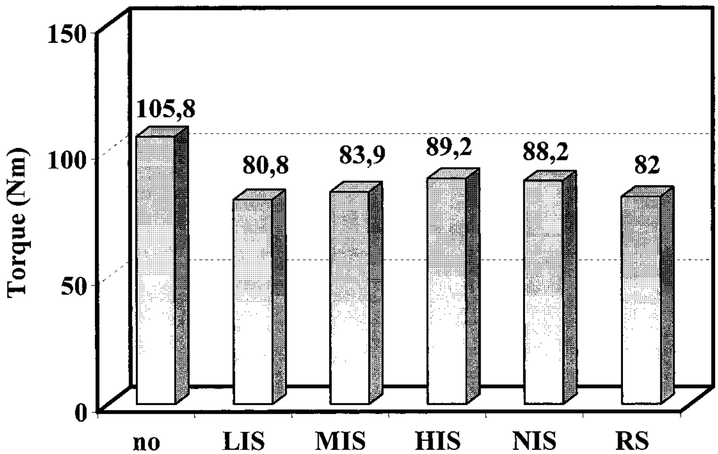


Fig. 4. The equilibrium mixing torque of ATH-PE compounds containing different surface modifiers.

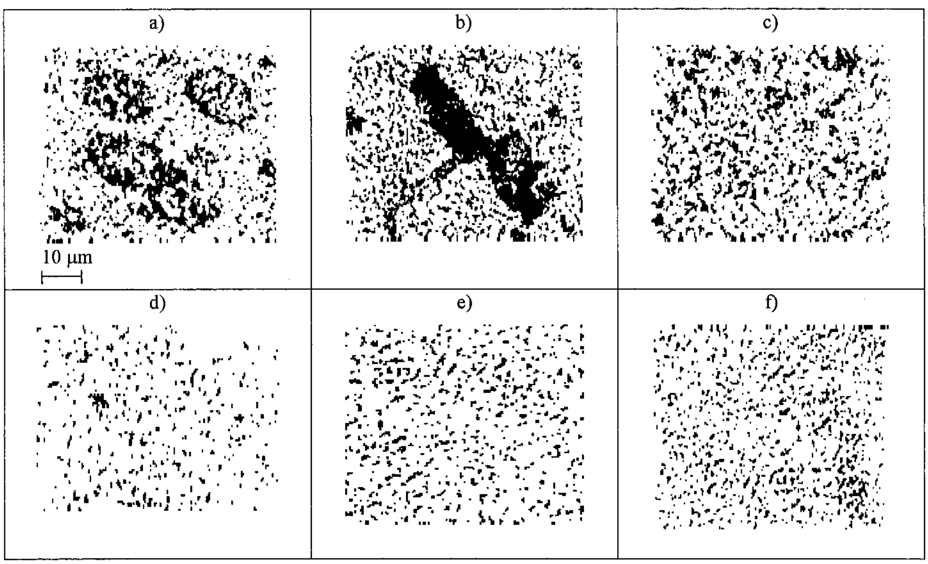


Fig. 5. Influence of various surface modifying additives on the distribution of ATH in PE compounds a) no modification, b) LIS, c) MIS, d) HIS, e) NIS, f) RS

The effect of the additives on the distribution of ATH is demonstrated by the optical microscopic picture of the thin film of the compounds in Figure 5 (enlargement: 100X). Concerning the homogenization effect of the additives, substantial differences can be observed. Without surface modification, picture “**a**” in Figure 5, the ATH is not distributed homogenously, a part of them agglomerates in globular islets. The additive of low ionic activity, picture “**b**” in Figure 5, does not improve the distribution, only the shape of the agglomerates change. The homogeneity is improved by the use of MIS and HIS additives (pictures “**c**“ and “**d**” in Figure 5). The best distributions, however, could be achieved by application of NIS and RS additives (pictures “**e**“ and “**f**” in Figure 5). Based on the favourable effects of the additives on the mixing torque and mainly on the homogeneity of the compounds, in the further experiments NIS was applied as surface modifying agent.

Noise Damping Properties

The floor assembly and some of the walls in public transport vehicles are prepared using a special sandwich structure, having a noise absorbing interlayer. This interlayer is a polymer compound consisting in general of a thermoplastic elastomer blend (TEB) and of barium sulphate (Barite). In spite of the high loading of Barite, above 60%, the compound is flammable. A flame retardant noise damping compound was formulated by partial substitution of Barite by ATH.

The influence of gradual substitution of Barite on the physical properties of the noise absorbing compound is illustrated in the Figure 6. Increase of the ATH content, on the expense of the Barite content, favourably influences the strength and the modulus. However, above a certain ATH content the elongation at break is reduced considerably. The specific density (a factor effecting the noise absorption) was reduced gradually with the increasing share of ATH.

The acoustic properties, that is the bending loss factor of the compounds consisting of TEB as matrix and a mixture of Barite/ATH in various weight ratios, can be seen in Figure 7. This series demonstrates the influence of the ATH contents on the acoustic properties. It can be observed that the trend of transfer damping in the low frequency range (up to 100 Hz) is slightly reduced in the presence of the ATH, while in the high frequency range (above 600 Hz), all of the compounds show a similar acoustic character. In the frequency range from 110 Hz to 700 Hz, however, the compound in which 66.6% of the Barite have been replaced by ATH, shows a better noise damping than the reference compound, containing only Barite. Thus, the partial replacement of Barite may result in improved acoustic character, in spite of the reduction of the specific density. The only question is whether the applied amount of ATH is satisfactory for achieving the necessary flame retardancy.

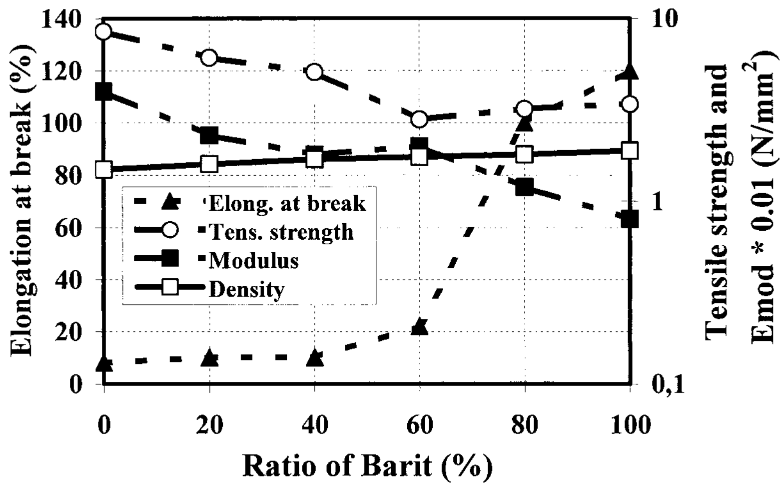


Fig. 6. Physical properties of noise damping compounds containing 64.3% additives (Barite+ATH) plotted against weight ratio of Barite.

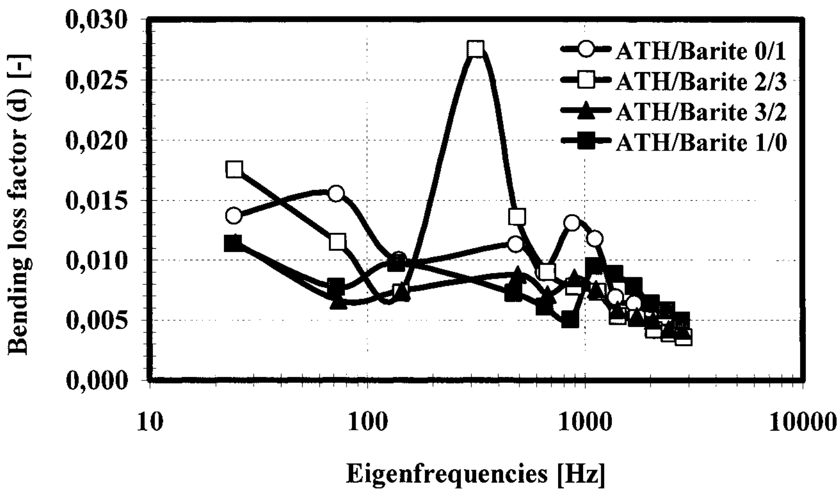


Fig. 7. Bending loss factor of different TEB containing 64.3% (Barite+ATH) additives (for bending wave excitation).

Figure 8 shows the LOI and UL 94 flammability properties of the compounds containing ATH/Barite in various weight ratios. As is seen, that the gradual replacement of Barite by ATH increases the flame retardant character. Above the ATH/Barite weight ratio of 3/2 the compounds achieves the self extinguishing V0 UL 94 flammability level, and the LOI also achieves or exceeds the 30% value as a sign of good flame retardancy. Based on Figures 7 and 8 it can be concluded, that a partial or a total substitution of Barite by ATH in the noise damping compound, having a TEB matrix, provides an improved flame retardant character. Simultaneously, at a particular ATH/Barite weight ratio, it also improves the sound absorbing character.

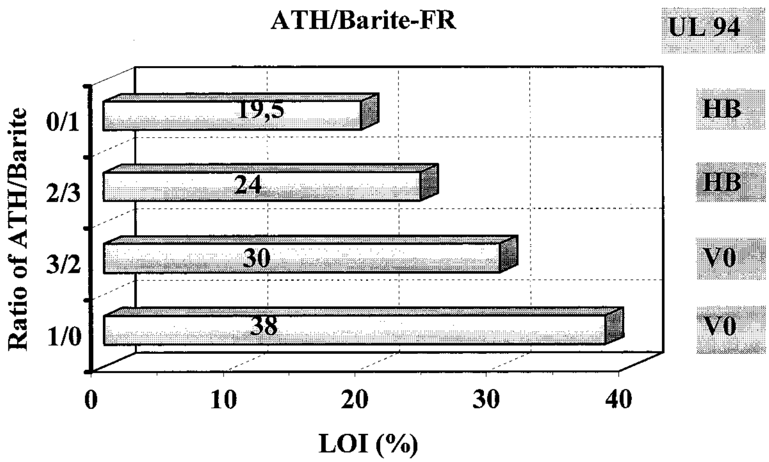


Fig. 8. Flammability of noise damping compounds containing ATH/Barite in various weight ratios.

Conclusion

In the 5 to 1.1 μm diameter range the decrease in the particle size of ATH, increases the mixing torque necessary for the preparation of the PE compounds. No direct correlation exists between the particle size and flame retardant effect of ATH. The best flame retardancy was obtained when the ATH of 1.5 μm particle size was applied. The application of stearic acid derivatives of different cationic activity, non-ionic and reactive silicon derivatives (especially the last two mentioned) considerably reduces the mixing torque necessary for compounding and improves the dispersion of ATH. A partial substitution of barium sulphate by aluminium hydroxide in the thermoplastic elastomer blend compounds provides a flame retardant character and improves the noise damping.

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