

Processing Conditions of Expandable Graphite in PP and PA Matrix and their Performance

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Polypropylene (PP) and polyamide (PA) polymers are used in different situations where they provide a flame retarding effect to meet safety standards. The expandable graphite as an additive for polymer materials has a good flame retardant effect and it does not harm the environment. The processing of this additive is presented for those two different polymers. Compounds with proportions of 10, 20, 30% of this additive were prepared in order to investigate the processability and flame retarding effect of PP and PA samples. The results show that the process conditions differ greatly between the polymers used in higher proportions. The improvement of the flame retarding effect was observed for both polymer compounds with expandable graphite. The plastics flammability standard UL 94 V0 could be achieved for the PP compound in all additive proportions and for the PA compounds only above 20%. The processing of the PP compound with co-rotating twin-screw extruder and an injection moulding machine takes place works well and provides a good homogenous mixture. The PA compound could not be processed at a higher additive content by the extruder. Special screw configuration is necessary to process this polymer compound. Also the flame retardant effect was inferior to the PP compound. The mechanical properties of the compounds decrease with the increasing additive content, particularly the impact strength of the samples.

Keywords: Polypropylene (PP), polyamide (PA), flame retardant effect

Polypropylene (PP) and polyamide (PA) polymers are widely used in different applications because of their technical properties, such as strength and strain, as well as their economical advantages [1]. At the same time producers and consumers likewise require that these materials and the end-products are flame retardant without losing their original properties in a too great extend. However, as both materials are mineral oil-based they have a natural propensity to burn well and consequently offer only a very insufficient protection against fire. Therefore, the virgin materials can not be used for a wide range of applications that have to meet the as UL 94 standard – the internationally accepted prescription for test for flammability of plastic materials for parts in devices and appliance.

Various types of flame retardants can be used to inhibit or delay the spread of fire by suppressing the chemical reactions in the flame or by the formation of a protective layer on the surface of a plastics [2]. These can be reactive or additive flame retardants based on organohalogen and organophosphorus compounds, or mineral flame retardants, which are typically additives [1-3]. The new regulations regarding the toxicity of plastic products and hazardous gas emissions limit the choice of flame retardant additives.

In light of this, this paper seeks to describe how the introduction of expandable graphite as an additive to both polymers changes their technical properties and their processability in standard extrusion and injection moulding equipment and to what extend flame retardant effects can be achieved.

Expandable graphite was chosen for this investigation because as a carbon product it does not harm the environment so it meets current regulations concerning toxicity [3, 4]. Different processing methods are used to produce expandable graphite from natural mineral graphite, with the unique property of abruptly expanding by many times its volume when it is exposed to heat [3, 5]. The most important benefit of this additive as a halogenfree

flame retardant is that it slows or stops the spread of fire and counteracts the spread of toxic gases, while a high efficiency can be achieved by low input quantities [3, 5]. It is also easy to apply: flakes of this material can simply be added to the plastic for extrusion or injection moulding, where also the processing at higher additive content is possible due to the lubricant property of graphite [3].

Investigation

Materials and Machinery

The following polymers were used for the preparation of the compound and samples:

- Homo-Polypropylene (PPH 9069) (Producer TOTAL, with the density 0.905 g/cm³, Tensile E-Modulus 1600 MPa and melting point 165°C);

- Polyamid (PA 66) (Producer Solvay Engineering Plastics, with the density 1.14 g/cm³, Tensile E-Modulus 3100 MPa (dry) and melting point 263°C).

The expandable graphite in the form of flakes provided by the company Georg H. Luh GmbH (www.luh.de) served as additive. The additive can be activated at a temperature above 230°C, at which the flakes of expandable graphite can increase their volume up to 375 times, and thus providing a flame retardant effect by absorbing the oxygen from the environment (fire) [4-6]. If the ignition source is removed from the samples the flames quickly extinguish because of the inert properties of the graphite and the huge expansion of this additive [4, 6].

The processing machine used for the preparation of the compounds is co-rotating twin-screw extruder KraussMaffei Berstorff (ZE250Ax45DUTXi) and for injection moulding of the samples Type A (ISO 3167) Injection moulding machine: KraussMaffei 130t (KM PolySet CXL – 130 750/380).

Processing Conditions

Samples of the two polymers with a proportion of 0%, 10%, 20% and 40% of expandable graphite were prepared were prepared in extrusion processes to ensure the same

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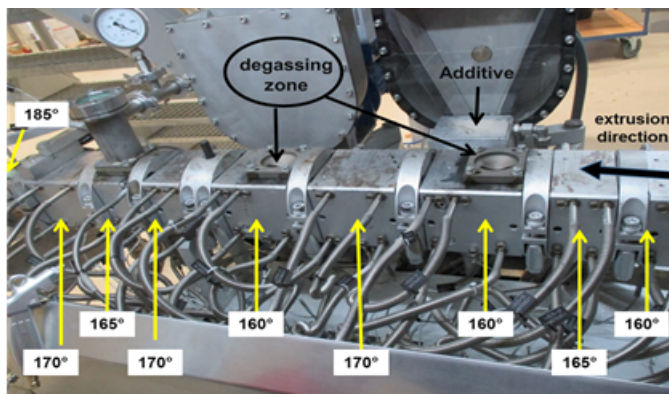


Fig. 1. Temperature profile for different zone of the extruder for PPH

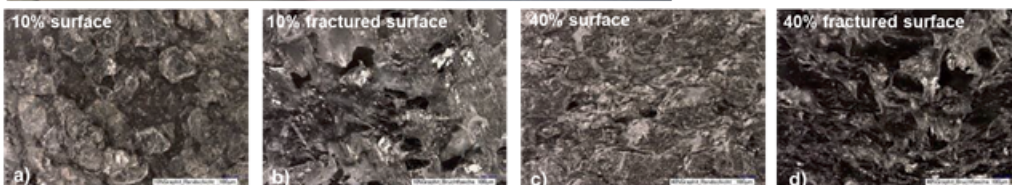


Fig. 2. PPH granulate with 10 % (a, b) and 40 % (c, d) expandable graphite and different surfaces

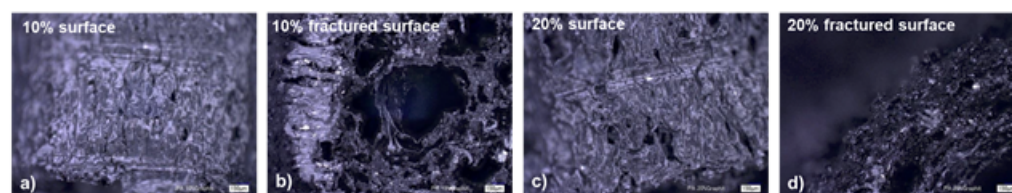


Fig. 3. PA granulate with 10 % (upper row) and 20 % (down row) of expandable graphite and different surface

quality of the polymer before injection, and dried. No other additives or fillers were added during to the process. The compounds were injection-moulded and tested for their mechanical and flammability properties. Between each compounding and injection moulding process of the prepared material, the machines were cleaned to avoid contamination of the prepared materials or samples.

The additive was introduced to the polymer matrix by a gravimetric dosing system, positioned close to a degassing zone to avoid the thermal damage (activation) of the graphite due to the high friction (temperature) in the cylinder. The temperature profile of the extruder cylinder zone, figure 2, was taken from the processing information of the polymer.

To avoid the activation of the expandable graphite the processing temperature of the compound for both polymer matrixes (PP & PA) should be below 230°C. If this effect starts during the processing of the compounds and the sample preparation, the flame retardant effect on the samples could be minimized. The measured temperature on the compounded PPH material, which came out of the mould, was 170°C. The compounded material was cooled off in a water bath and pelletized. The processing of the PPH polymer with a proportion of 10, 20 and 30 % of expandable graphite went without any problems and the distribution of the graphite flakes was homogenous for all contents, figure 3. The expected lubricant effect of the expandable graphite was also observed, because the

process parameters (temperature, pressure) of the extrusion at varying contents of additives did not change significantly. The next figure presents microscopic pictures of the granulate surface and the granulate fractured surface, where the graphite flakes are visible.

For all three PPH compounds one can see that the graphite flakes are closed in the polymer matrix and the increasing amount of additive is also visible. In comparison to the extrusion of the PPH compound the extrusion of the PA with expandable graphite was rather difficult. The processing parameters were set according to the technical data sheet of the material. The temperature profile of the extruder cylinder was kept as low as possible to avoid the activation of the expandable graphite in PA matrix, which have a higher processing temperature than the PPH. The measured temperature of the compound at output from the mould was 220°C. One reason of the difficulty of the processing of PA is its lower wall-adhering properties, which can be a disadvantage for a twin-screw extruder even at a higher graphite content, which increases the lubrication effect. Compounds with a proportion of 10% and 20% of the graphite could be prepared, but at 40% additive content the melted plastic strands produced by the extruder break and the granulating of the compound was impossible. The next figure shows the microscopic structure for 10% and 20% additive content and the different surfaces of the granulates.

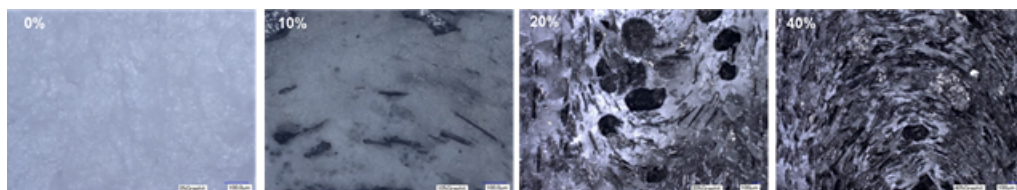


Fig. 4. Microscopy of the fracture surface of PP samples with different graphite content

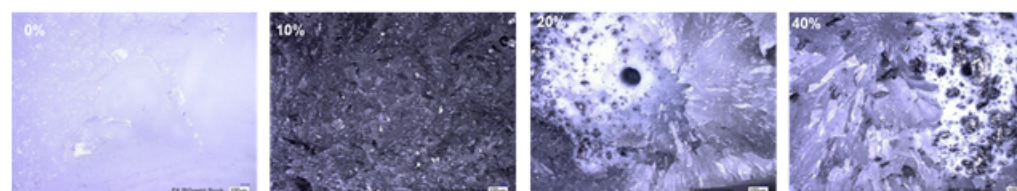


Fig. 5. Microscopy of the fracture surface of PA samples with different graphite contents

After pelletizing the compounds, the plastic granulates (PPH & PA) had to be dried because of the water absorption properties of the graphite flakes. The drying of the plastic granulates took place after 48 h of waiting but immediately before the manufacturing of the samples.

To provide some samples with 40% of additive, PA granulate material with expandable graphite was mixed in a bag and added directly in the hopper of the injection moulding machine.

The injection moulding of the samples Typ A (ISO 3167) for PPH with different expandable graphite went without any difficulties. The process parameter of melt pressure for the granulates with different graphite content changes minimally, from 660 bar at PP-H with 0%, to 675 bar at 10%, to 700 bar at 20% and to 710 bar at 40%. The good lubrication properties of the graphite provide this effect in the processing of the material. The figure 4 shows microscopic pictures of the fractured surface of the samples with different additive percentage.

The geometry of the expandable graphite flakes can be observed, also that the distribution is homogeneous and in the melt flow direction of the sample. The distribution is circular from the middle of the sample.

The injections moulding of the PA compound with different graphite contents for manufacturing tensile testing samples was difficult compared with the processing of the PP compounds. Whereas for the virgin PA materials an injection time of 3.5 sec was necessary, the PA with 10% of expandable graphite required 6.4 sec. The back pressure was reduced and the screw speed increased. For a better processing of the PA compound the plastification unit of the injection machine should be adapted (screw, injection volume, etc.). The figure 5 presents microscopic pictures of the fractured surface of PA samples after injection moulding.

For the samples with PA compounds only at a proportion of 10% of expandable graphite a relatively good homogeneity was achieved. At 20% and 40% of expandable graphite a separation between the PA matrix and additive can be observed. The samples with 40% of expandable graphite, for which the plastic and the additive were mixed directly in the hopper of the injection moulding machine, the distribution of the graphite flakes is very inhomogeneous and some of them show damage of the shape. The reason for such a degeneration are most likely the hard processing conditions.

Testing results

The prepared samples of PPH and PA were tested in the tensile testing machine and pendulum impact tester. For a good reproducibility five samples for each compound were tested and the results are presented in the next diagrams.

The tensile testing results show that for PPH samples the tensile stress decreases when the additive concentration increases. This decrease is almost linear and at 40% of graphite the value of the tensile stress is 29% lower than for the virgin material. The tensile stress results for the PA samples show a different trend. The standard deviation is much higher than for PPH samples, which may be an indication that the material of the samples was not homogeneous, due to the problems when processing the PA compound with the extruder and injection moulding machine. If the maximum and minimum results of the PA sample are not considered, a linear behaviour of the tensile stress results can be observed. The following picture shows the elongation at the break of the PPH and PA samples with different additive concentrations.

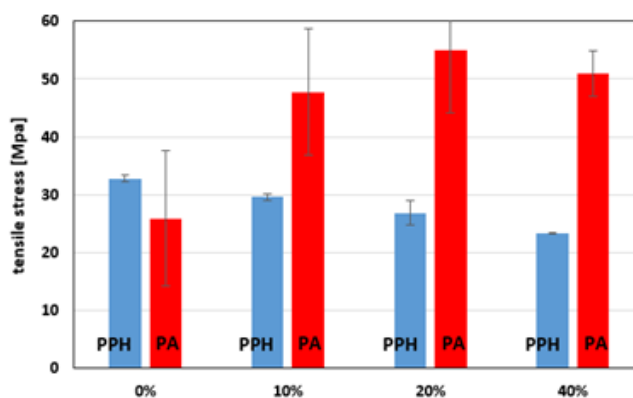


Fig. 6. Tensile stress of PPH and PA samples at different concentrations of expandable graphite

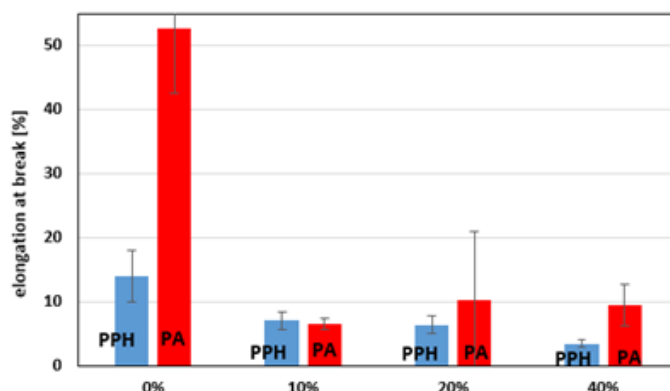


Fig. 7. Elongation of PPH and PA samples at different concentrations of expandable graphite

The PPH samples show a linear decreasing of the values, which was expected because the material starts to be brittle at higher additive concentrations. The elongation decreases with PPH samples with 10% graphite at approx. 50% and by 40% graphite at 75%. The expandable graphite substantially reduces the elongation of the samples, which may be very important for certain applications. At the next concentration of 20% and 40% the differences in elongation is smaller. The results form PA samples show again a higher standard deviation and also a considerable decrease of approx. 70% of the elongation value compared to the results of the original material with samples of 10% graphite. The next figure presents the results of the impact testing with a pendulum impact tester.

The results of the impact testing show for the PPH samples a decrease of the impact strength with an increasing graphite concentration. The difference between the virgin material and a compound with a proportion of 10% of expandable graphite is very high for both materials, e.g. PPH samples lose 75% of the impact strength. The PA samples of the virgin material have the higher impact strength, so that the 4J energy of the pendulum hammer is not sufficient to break them. In the diagram the results for these samples are labelled with *n.b.* (no break). At PA samples a high standard deviation can be noticed but also a nonlinear behaviour when the increasing the additive concentration.

Fire test

The expandable graphite in polymer matrixes has a flame retardant effect when the heat is high enough so the additive is activated. The UL 94 standard is widely used by different laboratories to determine a material's tendency to either extinguish or spread the flame once the specimen has been ignited [7]. The commonly used classification

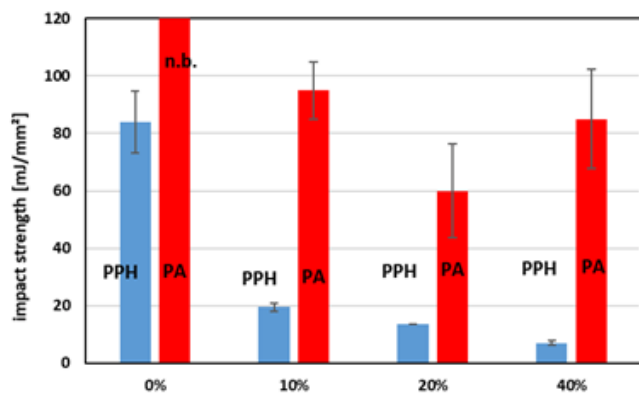


Fig. 8. Impact test results of PPH and PA samples at different concentrations of expandable graphite (n.b. - the samples do not break)

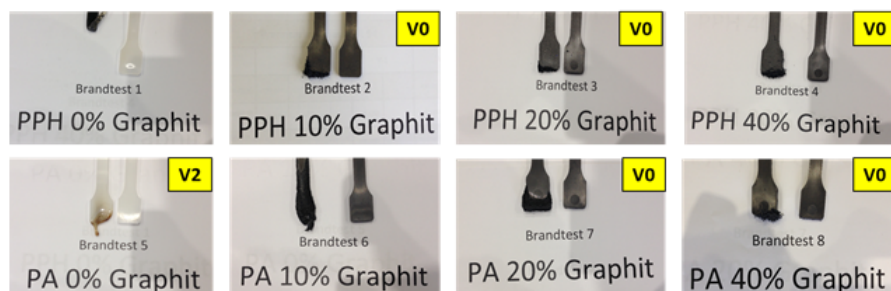


Fig. 9. Results of the flammability tests according to UL 94 for the PPH and PA samples

for a vertical specimen is V2, V1 and V0, categories, which are defined as follows:

V2 - if burning stops within 30 s and dripping of flaming particles is allowed;

V1 - if burning stops within 30 s and dripping of flaming particles is allowed as long as they are not inflamed;

V0 - burning stops within 10 s and dripping of flaming particles is allowed as long as they are not inflamed.

The best classification is V0 which is requirement for different plastic parts in applications as airplane construction, railways or insulators for consumer electronic products. The prepared PPH and PA samples were tested in a test bench according to UL 94 and under laboratory conditions. The results of the flammability tests are summarized in the figure 9.

The unfilled PPH polymer cannot achieve any UL94 standard, but by mixing expandable graphite even with a proportion of only 10% the requirements for standard V0 could be met. It is quite likely that V0 can also be achieved at a lower concentration.

The PA virgin material achieved only V2 classification and at 10% graphite the preconditions for V2 were no longer fulfilled. This effect could not be explained, but it is another indication of an insufficient homogeneity of the compound. At a proportion above 20% of expandable graphite the PA samples achieve also the V0 classification.

Conclusions

Polypropylene (PPH) and Polyamide (PA) polymers were prepared with different amounts of expandable graphite and tested for their mechanical and flame retardant properties. The compounding and injection moulding of the PPH samples was possible with the standard configuration of the machines. A good dispersion of the graphite flakes was observed, which could be correlated with the mechanical properties of the prepared samples.

The processing of the PA with expandable graphite was very difficult and the results of the mechanical tests could not be correlated with the added additive amount. A better

processing of the PA with expandable graphite should be possible when using a special screw configuration for the twin-screw extruder, which would allow a better distribution of the graphite flakes in the polymer matrix, without damaging the flake shape. The mechanical properties of the prepared samples changed with the increasing amount of the expandable graphite. The strength properties under impact load changes dramatically for the PPH. The samples lose 75% of their impact strength at a proportion of 10% of graphite. The testing results of the PA samples could not be characterised because of the high discrepancy between mechanical properties and amount of additive. However, adding expandable graphite to PPH and PA polymers can improve the flame retarding effect. For PPH the standard V0 was achieved even at a lower additive content.

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