Development of new PA6 composites

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Abstract

Among the large number of engineering polymers the cast polyamide 6 material has special attention in the field of semi-finished structural materials (rods, plates, tubes) due to good mechanical and tribological properties. According to the industrial needs the development of different special properties like greater abrasive resistance, ESD characteristics, better flame-proofing or increased toughness is vital. To identify these properties on different polymer composites (based on PA6), we have carried out more than 2800 standard tensile, flexural, Charpy-impact and Shore-D hardness test, we have produced SEM pictures and we have determined surface resistivity, abrasive tribological properties and carried out flammability tests. As a result of this the optimal quantities of additives: 3wt% graphite, 3wt% conductive graphite, 1wt% conductive carbon black, and 10wt% and 15w% softening material.

Keywords

polyamide 6, mechanical properties, tribological properties, electric behaviour, effect of different additives

1. Introduction

Plastics are used in more and more wide range since their appearance. Due to recent developments, they are not only used in inferior fields like packaging, but are also used as load carrying mechanical parts.

One of the most often used engineering plastic is the polyamide 6 (PA6) because of its quite good mechanical (strength, hardness, toughness, damping) and tribological (sliding, wearing resistance) characteristics [1]. Due to this, it is also used as bearing bushes, wearing laths, different pulleys, gears etc...

During a former Hungarian research, the industrial product technology of magnesium catalyzed cast PA6 semi-finished products (rods, plates) was worked out. This method has several benefits contrary to the commonly used natrium catalyzed product. The magnesium catalyzed PA6 has a more homogeneous structure with a higher crystallizing factor, and has less remaining monomer content. The impact strength is higher and the abrasion wear resistance is better than the natrium (sodium) catalyzed PA6 [2, 3].

The use of tougher cast polyamide 6 materials is especially advisable on those areas where the working environment differs from usual. For example the agricultural machinery, where the agricultural works are often accompanied with extreme conditions, the impacts should be beared by the applied materials. Essential property is the abrasive wear resistance, where the possible improvement is typically responsible for increasing of part's lifetime (e.g. protecting cover, chute) [4-6]. The use of antistatic or fire-resistant plastics is crucial under danger of explosion (grain silos, transport system of fertilizers).

Using of improved polymer machine parts is important both from agrotechnical and environmental protection point of view. These parts play important role at the reduction of weight- fuel consumption- and the emission of harmful materials of agricultural machines, at the reduction of soil compression and for the ground water balance.

The aim of the research is the further improvement and examination of magnesium catalyzed cast PA6 composite semi-finished products, which enables the wider range of use in agricultural systems. The following improvement areas were determined accordingly:

– improved toughness
– improved abrasive wear resistance
– antistatics characteristics
– improved fire resistance.

The targeted features should be reached without significant change of the original mechanical properties of the natural base material. In that case the range of use can be increased (universality), which may cause a real market advantage.

The improved material characteristics can be reached with different additives, because of the below points are among the aims of the research:

– determining which additives are efficient for influencing the characteristics
– detailed examination on the effects with the selected additives depending on their quantity used in the base matrix
– complex evaluation of the recipes and their qualifications on the basis of ambitions – material characteristics.

2. Material and Method

For material development the magnesium catalyzed cast polyamide 6 (PA6) was chosen. By using the pre-research results of composite production (where 39 additives were examined), a research plan was made. The aim was to get to know the exact effects of the selected additives. During the selection of the additives the mechanical and special characteristics, the easy adaptability to the industrial casting technology (the basis of practical use of the research) and the contradictions in the literature and the personal experiences were taken into consideration. The selected additives are shown in Table 1.

Table 1. Additives selected for research plan

Additives	*Content [%]*				
Softening material	10	15	20	25	
MoS_2	2	3			
Graphite	1.5	2	2.5	3	3.5
Montmorillonite	0.5	1	3	6	
Conductive graphite	0.5	1	2	3	4
Conductive carbon black	0.5	1	1.5	2	2.5

The following examinations were made on new, composite sample materials:

- Tensile-test (MSZ EN ISO 527)
- Flexural-test (MSZ EN ISO 178)
- Charpy impact-test (MSZ EN ISO 179)
- Hardness-test (MSZ EN ISO 868)
- SEM microscopic examination on broken surface of impact-test
- Abrasive tribological test (DIN 50322)
- Surface resistivity measurement (IEC 60093)
- Plastics flammability test (UL-94)

3. Results

In this chapter the measured results are summarised, and the effects of additives are evaluated.

Montmorillonite additive

The montmorillonite was selected, because several articles wrote about its use as fire resistant additive in case of polyamides. These articles did not take into consideration that the polyamide 6 under real flaming circumstances burns with dropping, therefore the montmorrilonite's decreasing effect for burn intensity does not predominate (Table 2).

Table 2. Burning characteristics of samples containing montmorillonite

Montmorillonite content [%]	Group sign	Comment
0	HB	Drops every 2 seconds
0.5	HB	Drops every 2 seconds
1	HB	Drops every 2 seconds, 16.4 mm/min
3	HB	Drops every 2 seconds, 16 mm/min
6	HB	Drops rarely, 14.8 mm/min

On the basis of the measured results, it is stated that the montmorrilonite content spoils the fire resistant characteristics of pure material, therefore the additive did not achieve its aim. From the surface resistivity measurements it also can be determined that montmorrilonite results higher surface resistivity for the sample, so it does not help to reach better antistatic behavior. The only improvement was in the abrasion resistance of 6% sample, which results 33% lifetime increase compared to the base material. At this additive quantity, depending on the weighting, mechanical characteristics decrease with 3-9%. On the basis of reached results, the production of new market product containing montmorrilonite is rejected.

Softening material

The first aim of using softening materials is to change the mechanical characteristics, mainly to increase the impact strength of material. During casting, it became clear that the 25% additive content is more than what the base material can take up, therefore visible segregation arose. The mechanical characteristics of this sample (eg. Young's modulus, tensile strength…) significantly decreased, moreover, at burning test it showed weak characteristics. In case of 20% additive content the microscopic examinations proved (typical fracture surface) the assumption drawn from mechanical characteristics, that the two-phased system already appears at this additive content (Figure 1).

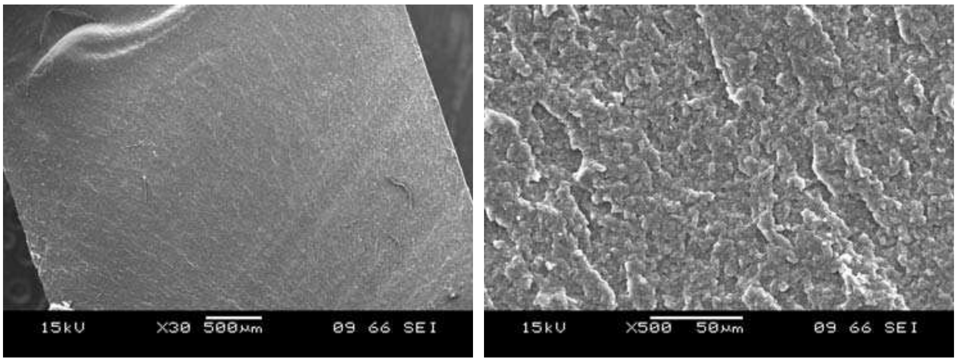

Figure 1. 30× and 500× enlarged SEM picture of 20% softening material

At 15% additive content, 3 times higher impact strength could be reached (Figure 2). Together with this the Young's modulus (with 40%) and the tensile strength (with 50%) decreased. It also could be noticed that the surface resistivity decreased to 10^{10} Ω, so a system with good antistatic characteristics was produced. Due to the decrease of Young's modulus, the abrasive wear intensity doubled. Its general use in abrasive tribological systems is not recommended, but due to its Shore-D hardness decrease (12%) it could be good in such tribological systems, where the particle embedding capability of the surface has a fundamental importance.

In case of 10% additive, the characteristics of sample change similar as in case of 15% additives, but these changes are smaller. In case of the 10% additive, the sample's characteristics are closer to the pure material characteristics. Its impact strength is 70% higher, but its tensile strength decreased with 13%. Antistatic characteristic was not improved by the 10% additive, and the abrasive wear intensity was also raised by 33%. The burning characteristics declined both in case of 10 and 15% additive.

On the basis of the result, the new market product containing softening material can be produced. In case of 10% additive, one should count with better impact strength but worse abrasive wear resistance and burn characteristics. In case of 15% additive, a much better impact strength and antistatic characteristics are obtained, but other mechanical, burn and abrasive tribological properties are worse.

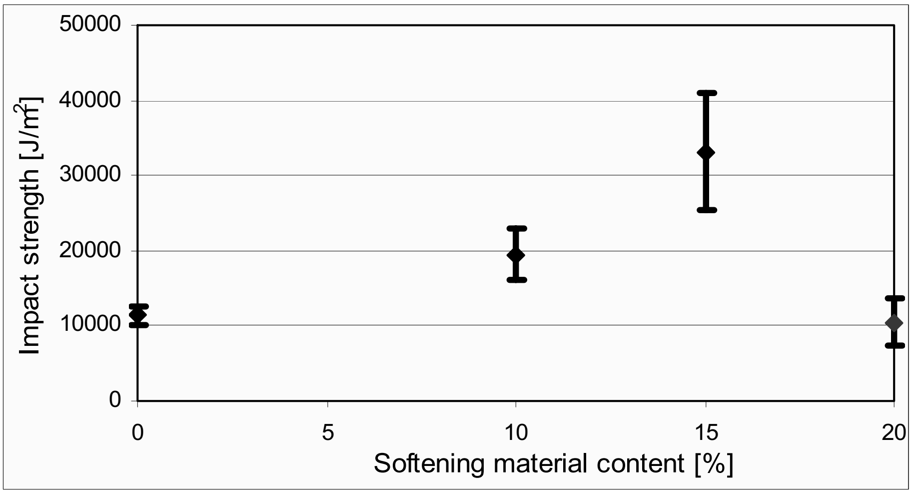

Figure 2. The specific impact strength of samples containing softening materials

Graphite additive

Graphite was chosen because it improves the tribological and electrical characteristics. According to this, the abrasive wear intensity decreases with 25%. (Figure 3). The electrical characteristics are improved by the increase of additive content. In case of 2.5% graphite content, a cast polyamide 6 was produced having good antistatic properties. By adding further additive the upper limit of ESD characteristic can be reached (surface resistivity with a order of magnitude more than 10^9 Ω). The tensile strength decreased with 10-15%, the impact strength decrases with 15-25%, but the Young's modulus of flexure increases with 5-15%. This means at the summarized mechanical characteristics a decrease of 5-8%. The graphite additive beyond the improvement of electric and tribological characteristics, it improved the fire resistance as well, namely the originally HB rated cast polyamide 6, these materials obtained the V-2 rating, which is higher by one step.

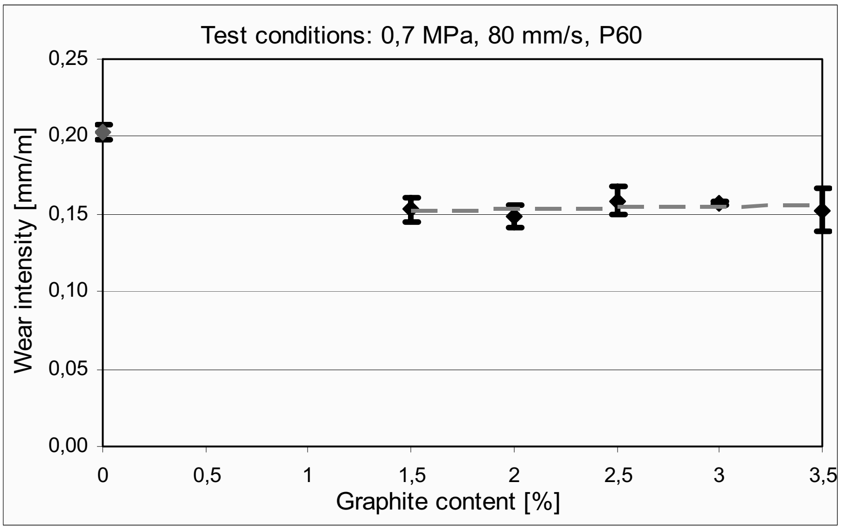

Figure 3. Abrasive wear intensity of samples containing graphite

On the basis of the examinations, in case of 3% adding, ESD characteristics, improved abrasive wear resistance and fire resistance is obtained, whilst the mechanical characteristics decrease is restrained. Due to the improved characteristics, this product is considered to be a successful development.

Conductive graphite additive

The conductive graphite was selected as it showed quite good electric characteristics during pre-tests. According to my examinations, the 3% and 4% sample in normal and wet state has a very low surface resistivity (10^7 Ω magnitude), therefore these materials belong to the ESD group. In dry condition their surface resistance a little bit bigger (10^9 Ω magnitude), so, in this case they also have ESD characteristics.

The conductive graphite does not change significantly the tribological characteristics, so in practical point of view it does not cause better abrasive wear resistance. According to the flammability test, in case of little additive content (0.5-1%) it improves, in case of bigger additive content it does not worsen the burning resistance characteristics. Comparing to the graphite, the tensile strength of the samples is reduced in a smaller volume (5-10%) and beside the Young’s modulus of flexure, the Young’s modulus of tensile also improves (5-10%) (Figure 4). Therefore in the summarized mechanical characteristics only 2-6% decrease occurs. Due to the outstanding electric characteristics reached, the sample containing 3% conductive graphite is also considered to be a successful development.

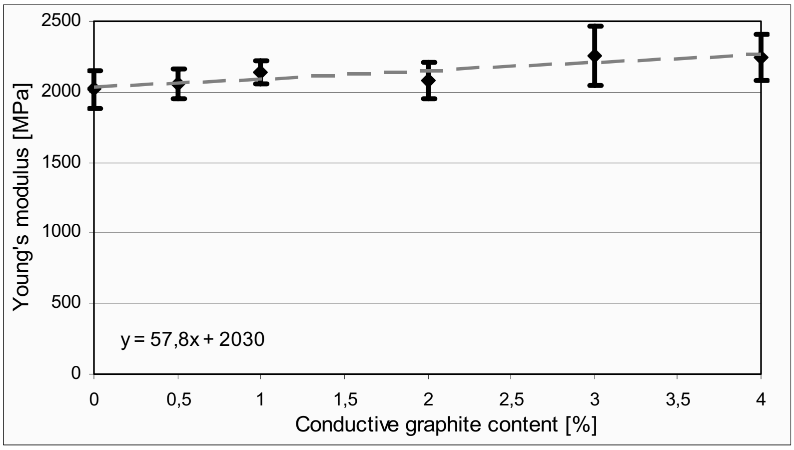

Figure 4. The Young's modulus of conductive graphite

Conductive carbon black additive

The conductive carbon black was selected also due to the improvement of electric characteristics. 1% additive is enough to receive a material with ESD characteristics in normal and wet state (Figure 5).

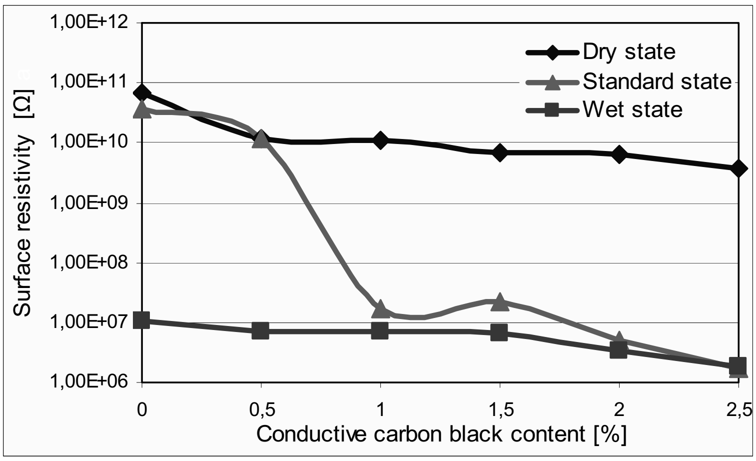

Figure 5. Surface resustance of samples containing conductive carbon.

This is advantageous also, because in case of 1% additive, the mechanical characteristics rarely change (0-1%). The Young's modulus of the sample increased (6-7%), while its impact strength decreased (10%). The tribological characteristics were not modified significantly by this additive – just like as it at conductive graphite. The fire resistance however got worse within category HB, these samples do not burn out by themselves. On the basis of the excellent electric characteristics and the low proportion mechanical change of characteristics reached with a minimal additive, the development having 1% carbon is considered to be successful.

Molybdenum-disulfide additive

The molybdenum-disulfide was selected as it improves tribological characteristics by a little proportion of additive as well. However in abrasive environment, there was no sign of significantly improved wear resistance, therefore it do not fulfill its prime goal. According to the tests, it has no significant effect on electric characteristics as well. The Young's moduluses increased by 10-10%, but the impact strength decreased with 20%. On the basis of the flammability tests, the material can be ranked to the V-2 category. According to the test system set, the adding of molybdenum-disulfide is not practical as graphite makes better characteristics.

4. Conclusions

As a result of the successful material development process, we have chosen 5 receipts, which enables the magnesium catalyzed polyamide 6 for agricultural machinery use:

- 3% graphite,
- 3% conductive graphite,
- 1% conductive carbon black,
- 10% softening material,
- 15% softening material.

Based on the results of the research, the production and sales of magnesium catalyzed polyamide 6 containing graphite and conductive carbon black started.

5. Summary

Based on the survey of technical literature we have identified 35 additives used at injection molding and at natrium (sodium) catalyzed cast polyamide 6 to change certain characteristic. These materials would be suitable to reach the following goals mainly characterizing agricultural engineering practice:

- better tribological properties – greater abrasive resistance,
- improved electrical properties – antistatic or ESD characteristics
- better flame-proofing,
- improved mechanical properties – increased toughness,

The main task was to select the efficient additives and work out the procedure (for example dispersing) needed to carry out the preliminary tests together with the production-developing company with the additives selected. We have selected from these those additives which are capable to produce suitable composites with magnesium catalyzed cast polyamide 6 base material. Based on preliminary tests We have identified six additives to be used efficiently (softening material, molybdenum-disulfide, graphite, montmorillonite, conductive graphite and carbon black).

We have worked out a complex material-testing and evaluation system according to as an aim set. Based on the system it can be determined whether an additive results suitable structural material for industrial requirements. We have set up an experimental plan being familiar with technical literature, the additives selected and the experimental system, which is suitable to determine the optical quantity of additives selected. We have machined out standard specimens from the cast composite box as a next step. Then we have carried out more than 2800 standard tensile, flexural, Charpy-impact and Shore-D hardness test, we have produced SEM pictures and we have determined surface resistivity, abrasive tribological properties and carried out flammability tests.

We have elaborated the measurement results by statistical methods then (for example: Young's tensile modulus, formation in the function of the softening material content) which were unknown previously in case of using magnesium catalyzed, cast polyamide 6. Parallel with this we have also discovered the causes of changes following the effects of additives.

We have evaluated the effects of certain additives taking into account more aspect based on the experimental system worked out. As a result of this we have determined the optimal quantities of additives in experimental circumstances given, which are the following: 3wt% graphite, 3 wt% conductive graphite, 1wt% conductive carbon black, and 10 wt% and 15w% softening material.

References

1. Bruyne D.: ERTA Engineering Plastics. 3P Engineering Workshop. Seminar booklet. Tielt, Belgium (1998).
2. DOCAMID (PA-Polyamide) properties http://www.quattroplast.hu/files/file/B_kategoria.pdf
3. Kohan M.I: Nylon plastics handbook. Hanser Publishers, 1995
4. Zsidai L., De Baets P., Samyn P., Kalacska G., Van Peteghem A. P., Van Parys F.: The tribological behaviour of engineering plastics during sliding friction investigated with small-scale specimens. Wear, 253 (5-6), p. 673-688 (2002).
5. Van De Velde F., De Baets P.: The friction and wear behaviour of polyamide 6 sliding against steel at low velocity under very high contact pressures. Wear, 209 (1-2), p.106-114 (1997).
6. Mergler Y.J., Huis in 't Veld A.J.: Micro-abrasive wear of semi-crystalline polymers. Tribology and Interface Engineering Series, 41, p.165-173 (2003).