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CAST POLYAMIDE 6 POLYMER COMPOSITES FOR SPECIAL APPLICATION

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Abstract*: In the first part of the article, those international publications will be reviewed which will help us in selecting the additives that are worth using in the designated directions of development. In the second part of the article, our own method by which these samples can be selected will be presented. This method will use specific values due to the comparability of individual values. Taking all boundary products into account, an establishment will be made that only four samples are worth further researching for the development of tribology properties. In the third part of the article, the summing of early experimental results are presented.*

1. INTRODUCTION

As a basis of material development, we have chosen a plastic used in several areas of industry. The selected material is magnesium catalyzed polyamide 6 (PA6). One basic principle of the development process is that we can only produce such plastics of special properties, which can satisfy market-based special requirements, as well. Thus, the direction of development turned towards agricultural needs. In this area, a characteristic challenge against materials is a better wear resistance, which signifies better lifetimes, so one of the areas of development is creation of plastics with better tribology properties. In the course of movement and storage of various cereals, dust can be formed which can create an explosive medium, thus antistatic plastics are in demand, as well. Plastics with combustion inhibition can be used in that agricultural area where due to flammability, the use of highly fireproof materials is necessary. General application can be achieved by improvement of mechanical properties, e. g. by the addition of carbon nanotubes.

In the article, we have presented additives that can be used for achieving special properties and in the second part, the method used for selecting samples.

2. ADDITIVES

The following materials are generally used for improvement of the tribology properties: graphite, silicon dioxide, polytetrafluoro-ethylene, polyethylene, molybdenum disulfide, lead, oils, mineral oils, phosphates, calcium silicate (calcium metasilicate), waxes, metal powders, silicone (Kalácska 2003). Polyamides have a very low friction coefficient when applied with lubricants, just even better than PTFE (the well-known name of which is Teflon). Under dry conditions, when during sliding and sticking, strong surface adhesion may be manifest, the value of the friction coefficient can be really high. In order to ensure operating safety, additives are necessary which reduce the friction coefficient under dry circumstances, as well. Molybdenum disulfide (MoS_2), and PTFE has long been used as such an additive in plastic industry. Graphite and MoS_2 are solid lubricants the use of which reduces solidity and resistance (Jaklewicz 2004, Rusu 2007, Xu 2007).

In the plastic industry, numerous additives are used for increasing the electron-conducting capability of the base matrix. Antistatic characteristics are present when the surface resistance is under 10^{12} Ω. Such materials are (Kalácska 2003) pitch, graphite, carbon filaments, powders and conductive flakes, disks, filament, metal coated graphite and glass filament, metal coated glass beads. If these materials are used, the change of properties is only achieved if the concentration of the additive is higher than a certain value, because in this case, they can form a secondary, continuous conducting structure in the material. Another method of avoiding charging is the use of an antistatic material (Gächter et al 1989). The additive is mixed to the base matrix in this case, as well, which provides long-term protection against electrostatic charge, but the polymer will not become conducting. Various graphite powders can be used relatively easily and successfully, but even these additives worsen mechanic properties (Novák 2004, Piddubnyi 2005). Among carbon derivatives, foam graphite, pitch and carbon nanotubes are also used (Li 2005, Potschke 2007). The latter is also distributed in a master mixture for a targeted area of use (Pásztor 2006).

Increasing the burn resistance of plastics is a fundamental goal for which the following additives are widely used (Pál 2006): chromium compounds, brominated compounds, materials containing crystal water, aluminum hydroxide, magnesium hydroxide, materials forming a coke-like foamy layer. Due to the phase-out of halogenic compounds, more and more new additives are emerging on the market. One such new material of combustion resistance is montmorillonite, as a result of which, heat formation at combustion undergoes a significant change.

It is apparent that as a result of montmorillonite, the intensity of combustion is significantly reduced and combustion itself is prolonged over time. Another important property from the aspect of combustion is that it prevents dripping, which reduces significantly the chance of spreading of the fire (Dong 2006, Jang 2006, Song 2004). Moreover, montmorillonite significantly reduces the expansion of composite even more than on order of magnitude in comparison with the base materials (Chow 2007). Apart from montmorillonite, other additives can also be used for the prevention of combustion, which further reduce the intensity of combustion.

The structure of carbon nanotubes is highly characteristics, it is a graphite layer with the thickness of a single atom, rolled to a perfect cylinder.

One problem is posed by the fact that carbon nanotubes have a high tendency for aggregation, thus in the polymer base matrix, they are embedded in groups as a result of which, their excellent mechanical properties are not manifest, and they also form locations that accumulated tension. Thus, for this additive, the problem of distribution is increasingly present.

3. MATERIAL SELECTION

After performing the first casting series, more than 100 different samples were available to us. As a first step of selection, a significant part of the samples could be excluded because those precipitations were also visible to the naked eye which showed the lack of success of additive building. We performed the following tests on the remaining 52 sample types: tensile test, Charpy impact test, tribology tests, electric tests.

From the aspect of material development, it is important to be able select those samples among the many types of additive buildings with which it is worth continuing the process. Basic evaluation will be performed according to mechanical properties because due to this fact, we will be able to concentrate on additives, which do not significantly deteriorate the properties of our generally accepted technical plastic, but is capable of improving some special properties. Thus, promising samples can be selected according to the following considerations: samples with the greatest tensile strength; samples with the greatest elongation at break; samples with the greatest impact strength; samples with proportionately good mechanical properties.

By testing the first three categories, those additives can be mainly identified which increase the special mechanical property on the basis we are making our selection. However, this method cannot be used in our case, because the objective is to preserve the generally good mechanical property of the base material. The tensile strength of plastics can be smaller than metals by one order of magnitude, but their elongation at break can be greater by even two orders of magnitude than the value characteristics of metals. Under such proportion, it is furthermore characteristic of plastics that in the case of a small increase of their tensile strength, their elongation is significantly reduced but even a significant change of the specific impact strength causes a significant change of the other mechanical properties. The imbalance between traditional proportions would prevent universal usability in particular.

3.1 EXAMINATION OF MECHANICAL PROPERTIES

The mechanical properties of the natural base material (without additives) are targeted for further development (tensile strength: 79 MPa, elongation at break: 26%, impact strength (Charpy): 4870 J/m^2)

For the evaluation of mechanical properties, we have used specific numbers, which mean the following: we divided the measurement results of experimental samples by the respective property of the base sample (e. g. the tensile strength of a sample is 83 MPa, the specific tensile strength is 105%, because 83/79≈1,05). We have included the calculated specific tensile strength specific elongation at break and specific impact strength values in a decreasing order in tables, and above a designated limit, we assessed the samples as good.

Testing and ordering individual specific mechanical properties will not bring any usable result because some prominent values are accompanied by a significant reduction of the other properties. Thus, we have introduced specific multiplication, which represents the product of specific values (for example, a sample has the specific tensile strength of 105%, the specific breaking expansion is 50% and the specific impact strength is 152%, in this case, the value of the specific product is 80%). Using this value, we can characterize the experimental materials from all of their mechanical properties. In accordance with literature sources, we have also experienced that additive utilization results in a deterioration of mechanical properties. In the case of specific multiplications, this meant that 70% of the resulting specific sample values was under 40%. We draw the limit of selection at this 40%. This means that out of 52 samples, only 15 samples had such mechanical properties, which could be deemed as acceptable. In practice, this means that the reduction of mechanical properties of the selected samples due to the application of additives is acceptable and the three characteristic properties changed in such a way that they compensated for each other with regard to the order of magnitude. Due to this selection, we only had to search for extra low values in the case of these fifteen samples. This was needed in order not to use in the future such additives as a result of which for example the tensile strength is very good, however tension reduced dramatically, because this would greatly reduce universal usability from the aspect of mechanical properties.

Upon testing the issue of proportionality, an important factor is what property is being developed, but this only exerts a secondary influence on the respective value. Therefore, for mechanical properties, we specified such general minimum values for which if they are exceeded by the experimental material, they remain generally usable technical plastics. Minimal values were as follows: specific tensile strength: minimum 70%, specific elongation at break: minimum 45% and specific impact strength values: minimum 90%. On the basis of this, we could further reduce the 15 samples with good specific multiplication values to 9 types of samples. All in all, we could select by testing mechanical properties 9 samples out of the 52, for which mechanical properties are generally favorable and therefore, they can be used in everyday practice in many locations along with having other special properties.

3.2 TRIBOTESTING AND EVALUATION

A second part of the elaborated selection method is that the samples are selected according to their special properties. In order to present this, we have used the direction of improving tribology properties. On the basis of the results of tribology properties, we are familiar with the characteristic value of friction coefficients in the sample, as well as wear and friction heat generation. Our primary goal in the case of this direction of material development is to reduce the value of the friction coefficient and not to spoil the wear resistance in a forced run (without lubrication). Therefore, we primarily took into account this factor upon selection.

For tribotesting we applied pin-on-disc laboratory measurements. The method and the typical obtained curves are published more times elsewhere (Samyn 2007, Zsidai 2002).

For the purpose of better operability, we also worked with a specific friction coefficient value, but in this case, we derived it differently, since in this case, a minimum value is the objective. A specific friction coefficient is the quotient of the characteristic friction coefficient of basic samples (0.55) and the characteristic friction coefficient of the tested sample (e. g. the value of the friction coefficient for the sample no. 60 is 0.467, in this case, the specific friction coefficient is identical to the value of the following fraction: 0,55/0,467≈1,18).

We determined the lower limit of the success of additive application in an improvement of properties of 10%, which means that the additive application for samples of specific friction coefficients not smaller than 110% can be regarded as successful. For this series of measurements, this represented 14 samples. The next step of selection is to check the mechanical properties of the good friction samples. For this, we have created a Table 1.

Table 1. Specific mechanical results of good tribo composites

Good Friction samples no.	Specific Friction coefficient	Specific tensile Strength	Specific Elongation at break	Specific Impact strength	Resulting Specific product
71	217% (•)	71%	10%	42%	3%
68	200% (•)	76%	13%	173% (•)	16%
79	199% (•)	87%	47%	102% (•)	42% (•)
30	175% (•)	70%	537% (•)	107% (•)	404% (•)
17/2a	154% (•)	119% (•)	27%	143% (•)	45% (•)
22	153% (•)	10%	26%	51%	1%
10/1	147% (•)	56%	6%	82%	3%
12	139% (•)	61%	6%	90%	3%
14	135% (•)	79%	9%	92%	6%
34	126% (•)	73%	198% (•)	104% (•)	151% (•)
10/2	122% (•)	71%	8%	63%	4%
11/4	120% (•)	81%	19%	84%	13%
60	118% (•)	105% (•)	50%	152% (•)	80% (•)
16	110% (•)	98% (•)	12%	89%	11%

• selected sample according to a given property

It is apparent that the samples satisfying the previous requirements are No 30, 34, 60 and 79 since the other samples were not prominent from the aspect of a specific product, or their specific mechanical properties did not reach the minimum value selected. Thus, due to selections presented earlier, it can be established that in order to improve tribology properties, the formulation of the above four samples should be perfected.

4. SUMMARY OF EARLY EXPERIMENTAL RESULTS

On the basis of the pre-experiments it can be stated that the main direction of the tribological material development is worth to going on with MoS_2 and the carbon nanotubes. By using MoS_2 additive, the value of friction coefficient decreased from 0.55 to 0.31. This 75% improvement is a considerable result and proves that the MoS_2 solid lubricants can act as a friction modifier in the cast PA6 matrix. In case of adding the specially treated carbon nanotube the friction coefficient became 50% of the original’s (0.55→0.28). In this case the contact temperature was lower during the test, too. One of the reasons of this could be that the heat conduction of carbon nanotubes can reach 6600W/mK. Because of this feature the temperature on the contact surface remains relatively low, and the disadvantageous temperature rise of sliding contact can not happen. Finally the measured friction coefficient and the wear remained lower.

For reaching antistatic characteristics the carbon nanotubes made by different methods are proper. The needed amount of additives are very low, in every case the volume is below 0.1%. Independently from the treatment of carbon nanotubes the antistatic characteristic was reached in every case. (Table 2.)

Table 2. Antistatical samples

Sample codes	Content of carbon nanotube (%)	Content of graphit (%)	Surface resistance ($10^9\ \Omega$)
91	0,05%	1,00%	87,00
98	0,05%	1,00%	0,07
105	0,05%	1,00%	0,09
131	0,05%	1,00%	0,7
116	0,05%	2,00%	3,60

The graphit content helped the distribution in the base material. Depending on the treatement of carbon nanotube, the surface resistance could change with 4 orders of magnitude. Further experiments are needed with carbon nanotube used in the sample No. 105, because in this version the mechanical characteristics were more favourable.

Montmorrillonit additive was used for combustion obstruction. The measurement results showed a little improvement in the Oxygen Index tests. During UL-94 tests the effect of additve was not obvious. The plastic was burning during dropping down.

5. CONCLUSION

In the first part of the article, we reviewed those international publications which help us in selecting the additives that are worth using in the designated directions of development. After experimental casting and performance of mechanical and other special tests, those samples should be selected with which work should be continued and their formulations should be refined.

In the second part of the article, we have presented our own method by which these samples can be selected. This method uses specific values due to the comparability of individual values. We selected various boundary conditions from the fundamental objectives of material developments. Such were for example that the value of the specific product could not be lower than 40%. Taking all boundary products into account, we established that only four samples are worth of further research for the development of tribology properties. Thus, the advantages of selection are as follows: several types of properties can be compared, specific values are descriptive, by the introduction of boundary conditions, we can exclude non-marketable directions, quick and easy expandability.

On the basis of pre-experiments it is defined that the magnesium catalyzing PA6 can be improved for agricultural engineering use. It has revised tribological characteristics, and it is appropriate for producing antisatic composits.

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