

CAST POLYAMIDE 6 POLYMER COMPOSITES FOR AGRICULTURAL MACHINE APPLICATIONS

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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 chemical properties and easy for composite production. In the agricultural machinery we can find more often engineering plastics and the possible applications could be extended with special features of any basic polymer grade. At our research project we selected the magnesium catalytic cast polyamide 6 natural polymer matrix as basic grade and targeted some new composites of that according to the agricultural needs. We prepared some pilot samples and evaluated them for further developments.

1. INTRODUCTION

In the agricultural applications of structural materials show some typical environment for machine elements. Very often improved abrasion resistance is needed due to high dust content of the surroundings. In slideways and transport systems of crops and grains the antistatic surface is important to avoid static charge and explosion. Further step is when the antistatic behaviour is not enough and fire-retardant or fire-safe polymer is required. Finally we decided to develop some new composite versions of magnesium catalytic cast polyamide 6:

- improved tribology grade having abrasion resistance
- antistatic composite version
- improved fire-resistant version

The magnesium catalytic cast polyamide 6 has a traditional production process in Hungary, so we could launch the research project on the basis of the present chemical plant and laboratory. The new chemical processes for the targeted composites were developed by the industrial partner, Quattroplast Ltd.

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 [6]. 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 [4, 13,16].

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 $10^{12} \Omega$. Such materials are [6] 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 [3]. 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 [8, 11]. Among carbon derivatives, foam graphite, pitch and carbon nanotubes are also used [7, 12]. The latter is also distributed in a master mixture for a targeted area of use [10].

Increasing the burn resistance of plastics is a fundamental goal for which the following additives are widely used [9]: 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 [2, 5, 15]. Moreover, montmorillonite significantly reduces the expansion of composite even more than on order of magnitude in comparison with the base materials [1]. 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. Examination of Mechanical properties

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 to 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.

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/m²). 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 $83/79 \approx 1,05$). 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. All in all, we could select by testing mechanical properties 5 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.

3.1 Examination of tribological properties

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 [14, 17]. 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: $0,55/0,467 \approx 1,18$).

It is apparent that the samples satisfying the requirements are only four 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.

3.2 Examination of electrical properties

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 1.)

Table 1. Antistatic samples

Codes of samples	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 graphite content helped the distribution in the base material. Depending on the treatment 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.

3.3 Burning properties, fire behaviour

The cast natural polyamide 6 is easy to burn just like most of the polymers, since they have many carbon and hydrogen atoms. Following the literature the montmorillonite mineral was often found to be suitable to spoil the burning process of some polymers. We also produced montmorillonite composite samples and tested them according to the standard methods. Oxygen index testing and UL-94 burning examination were applied. The results showed a little improvement (1-1.5%) in the Oxygen Index tests comparing to the pure PA6. That means that the burning of montmorillonite composite needed 1.5% more oxygen to keep burning comparing to the natural cast polyamide 6. But during UL-94 tests the effect of the additive was not obvious. The plastic unfortunately was burning during dropping down (Figure 1) with natural and composite samples as well.

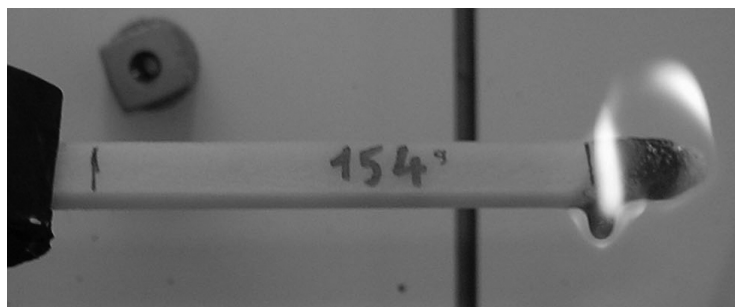


Fig. 1. Burning of montmorillonite composite samples during UL-94 test

Finally we concluded that montmorillonite composite needed more oxygen, but the form and method of burning and dropping does not let state better ranking (UL-94) of the composite. Another point came to highlight as influencing factor together with montmorillonite. That is water absorption. Due to “amide” group of molecular structure, all the polyamide types have more or less water absorption capability. The absorbed water content can also influence the burning behaviour, thus we made some control of water absorption of the different test samples.

3.4 Water absorption properties

Water absorption of different polyamide 6 samples
[Surface: A=4560 mm² (127%), B=3600 mm² (100%)]

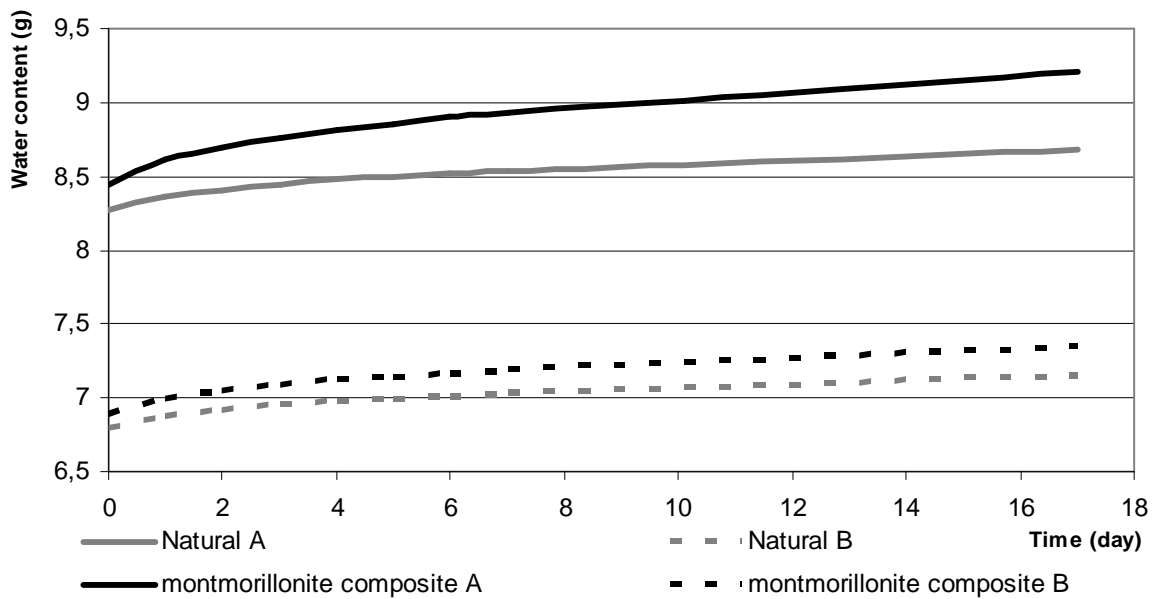


Fig 2. Water absorption of different polyamide 6 samples

During the water absorption tests we applied natural and motmorillonite composite polyamide 6 having 1% montmorillonite samples. The duration was 17 days soaking the samples in 20°C water. After 17 days the natural samples had 5% and the composite ones 7% mass increase in average (fig.2.). The increase of weight accompanied with the change of dimensions of samples, too. Regarding the possible agricultural applications of natural and composite polyamide 6, beside the fire behaviour the water absorption also have to be clarified.

4. CONCLUSION

Based on the first control measurements with the pilot samples we could define a further research plan for a given target additives to achieve better abrasive resistance, lower surface resistivity (antistatic or Esd property) and better fire resistance (table 2.).

Table 2. Further composite developing project

	Phase 1.	Phase 2.	Phase 3.	Phase 4.
	Additive	Additive	Additive	Additive
Impact strength	TA-52 (polyether)			
Elongation and tribological properties	MoS ₂			
Tribological property	PTFE			
Surface resistivity and tribological properties	grafit	Carbon nanotubes	EP-120 (dispertent)	Carbon nanotubes
Fire resistance	Montmorillonite			

According to the measured material properties we can state that

- To improve the mechanical properties of the magnesium catalytic natural cast polyamide 6 with additives, the TA-52 polyether and MoS₂ is suitable.
- Regarding the abrasive wear resistance as essential tribological property in the agricultural environment, MoS₂, PTFE, carbon nanotube and graphite can be applied as additives in different combination and selection.
- Better fire resistance may achieve with montmorillonite additive with a combination of graphite

The carbon nanotube/graphite systems are difficult to produce due to the strongly differing particles and properties. Evenly dispersed system in the liquid caprolactame, which is the monomer state of the cast polyamide 6, is rather complicated chemical engineering task. The carbon nanotube/graphite systems are promising in the field of tribological improvements and antistatic applications, too, so huge research effort is addressed for that chemical engineering stage of the technology.

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