HIGH CONDUCTIVE GRAPHITE ADDITIVES FOR MAGNESIUM CATALYZED CAST PA6 POLYMER MATRIX

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Abstract At this article we give a brief review about the additives effects for cast polyamide 6 engineering plastics. The natural grade Magnesium catalyzed polyamide 6 has unique mechanical properties. Our target is to keep the mechanical and tribological properties with the development of antistatic and ESD composite version. High conductive very effective to improve the electrical conductivity of magnezium catalized cast PA 6. Only few amount, 0,5% can result good antistatic property for the base matrix. Over 3% of additive the surface resistance of the material – performing 10^7 Ω - can reach the ESD (Electrostatic Dissipative) category.

Key words Polyamide 6, surface resistivity, antistatic behaviour, high conductive graphite additive

1. INTRODUCTION

The spread of plastics in electronic use was quite fast as its insulating characteristics had an invaluable count. By now, with more wide use of plastics a demand rose for such special compounds, which have lower resistance or are antistatic. Plastics considered like conventional ones (insulating plastics) are not able to conduct the charge, therefore they get charged. There are more disadvantages of electrically charged plastics: their surface can get contaminated easily, they can adhere (foils), charges can be taken away by humans that can be observed as a „strike”. Sparks can emerge, which can cause - in special surroundings - explosion or burn. In agricultural point of view this latest effect is not negligible as several times the ambient condition is critical (seeds powder mixed with air, pneumatic transport) in which a spark is enough for explosion (powder explosion). In such fields it is beneficial to use antistatic engineering plastics.

2. ANTISTATIC BEHAVIOUR AND ITS EXAMINATION

To classify the antistatic behaviour the surface resistance and half-period of materials are commonly used. These values are not independent from each other, the relation between them is the discharging process of condensators, which can be characterized with an exponential equation (in more details: [1]). Based on surface resistivity the following categories are used in engineering practice (Table 1) [2, 3, 4] (Kalácska 2007).
Meaning of surface resistance was standardized log time ago. Now the second edition of „IEC 60093 Methods of Test for Volume Resistivity and Surface Resistivity of Solid Electrical Insulating Materials” is valid since 1980 (Figure 1.). For our research the measuring instrument was set with 100V potential for 10^5 - $2{\cdot}10^{11}$ Ω surface resistivity range. That is the investigated range of the cast polyamide 6 versions. The accuracy in this range is ±5 % according to the manufacturer’s data that were controlled, as well.

Table 1. *Classification of materials by surface resistance*

Surface resistance (Ω)	Group
$<10^{-3}$	Electrically conductive range of metals
10^{-2}-10^{0}	Conductive range of natural coal
10^{1}-10^{2}	Electrically shading polymers
10^{3}-10^{5}	Electrically conductive polymers
10^{6}-10^{9}	Continuously conduct the electrical charges (beside little resistance), ESD materials
10^{10}-10^{12}	Polymers having antistatic characteristics (beside high resistance)
$>10^{13}$	Insulating polymers

Fig. 1. *Measuring layout of surface resistivity*

3. SPECIMEN MATERIALS AND PREPARATION

In Germany PA6 was first produced in 1938. This is a polycondensational procedure [3]. Natrium-catalyzed cast PA6 was developed only later, but it did not fulfil the requirements. It was not appropriate for fiber production but it was excellent for block casting. The industrial-scale production technology of magnesium catalysed cast PA6 was worked out by Hungarian researchers in the 1990s. The use of the magnesium catalyzator did not solve the problem of the fiber production, it only modified the characteristics of cast PA6 (better toughness and abrasion resistance). Nowadays the Quattroplast Ltd. produces magnesium catalyzed cast PA6 with a unique production technology in the world. It takes the advantage of ring opening polymerisation [5]. The surface resistance of natural PA6 is 10^{13} Ω (produced with the Hungarian technology).

In plastic industry several additives are used for increasing the volumetric conduction characteristics of the matrix. These materials are [3]: black carbon, graphite, carbon fibre, metal coated graphite, glass fibres, metal coated glassballs. Characteristics change can only be reached by using more additives than a specific concentration. With this, they are able to compose a continual frame in the material. Conventianally more than 30% additive is given to the base matrix to reach electrical conductivity.

One of the additives of material development was high conductive graphite. Graphite is also widely used to decrease surface resistivity [6-9], but the literature is somewhat poor in respect of polyamides. In the case of other polymers (e.g. epoxy resins) surface resistivities in the order of 10^{9} Ω can be achieved. In the case of polyamides graphite additives are also used to improve wear resistance [10-11] and flame resistance [12].

For measuring the surface resistance, the specimen should be prepared, as polyamides are able to absorb humidity, and the absorbed water makes fake the measured results. Casting of test samples took several weeks, so the first samples have time enough to absorb more humidity. To exclude the effect of humidity from measurement, 2 mm of the materials were machined from the surface. The remove the upper 2 mm is sufficient for polyamides because the absorption is in accordance with the law of diffusion (the diffusion speed slows from the surface to the depth of the materials). Beside the measurements in dry conditions, we also made humid condition and standard condition measurements to investigate the potentially best surface conductivity, as well. The humid condition specimens were pre-soaked for 24 hours in 20°C water before the wet measurements. Then we let them dry for 5 minutes on 20°C air before the test. The standard condition specimens were pre-soaked at 20 ºC under 50% relative humidity (RH).

4. RESULTS

Figure 2 shows the effects of high conductive graphite content on surface resistance.

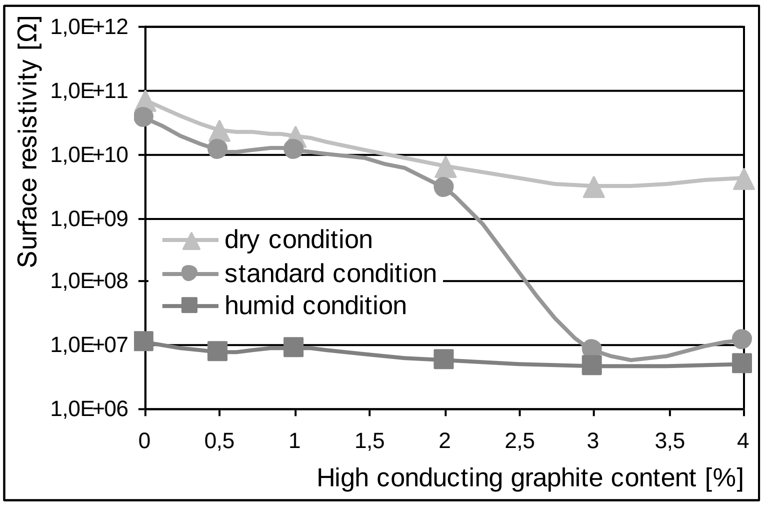

Fig. 2. Effects of high conductive graphite content on surface resistivity

5. EVALUATION

Four important circumstances should be taken into consideration when evaluating the results:
1. The producer delivers semi-finished products (blocks), which is machined by the enduser or customer according to their needs. Therefore the use of coating-like antistatics makes no sense (e.g. by milling the removal of the surface results no antistatic behaviour later).
2. The agricultural circumstances does not mean stable environmental conditions, so the surface resistance of machine parts independently of environmental effect (in worse case despite of it) should stay below 10^9 Ω (the quality limit of the antistatics determined as a target.)
3. During the evaluation it is enough to examine only the surface resistance of specimen: in the agriculture the environment may change, the surface resistance of the cast PA probably follows it with change of magnitudes.
4. The primary (basic) value is the surface resistance measured under dry conditions, as during the use, this is the value which can be provided by the material in the worst environmental circumstances, too (under wet conditions the antistatic characteristics are always better).

In dry condition, with the increasing of the high conductive graphite content, the value of the surface resistance is decreasing, which is in harmony with the literature. It can be stated that in this system, the antistatic effect can be reached also with less additives, there is no need for eg. more than 20% of additive content, as in case of PUR and EP. Only 0,5% additive can decrease the originally electrical insulating base material's surface resistance to antistatic region. At 2% of high conductive graphite content the 10^9 Ω magnitudes can be reached, which means a good antistatic behaviour. After treating the material samples in normal surroundings (50%RH, 23ºC) it can be stated that between 2 - 3% additive content a transition point can be reached, where the distance of additive particles in the matrix decreases to a critical value resulting enhanced transport of electrical charges. Due to that phenomenon over 3% additive (50%RH, 23ºC) the new composite samples perform ESD (Electrostatic dissipative) properties. This means much better behaviour that it was preliminary expected. It can be seen that for the humid conditions the surface resistance of specimen decreases to 10^7 Ω. On the basis of tendency, the sample reaches this magnitude under standard conditions with 3% of high conductive graphite content, so there is no significant difference between the standard and the humid value. These materials are less independent from the environmental effects in case of electrical characteristics. However it should be noticed that the high conductive graphite content rise over a certain limit does not have notable surface resistance change. In case of such surface resistance decrease, the 3-4% graphite content means an ESD polymer compared with the originally insulating PA6.

6. CONCLUSION

High conductive graphite efficiently develops the electrical characteristics in case of magnesium catalyzed cast polyamide 6. Despite of other researchers' earlier experiences, in this system 0,5% of additive was enough for the development of antistatic characteristics (at least 10^{10} magnitude). Only 2% additive material can result good antistatic composite version. PA6 with more than 3% of additives decreases surface resistance in standard condition to 10^7 Ω. This result is better than the expected one reaching the ESD category. The surface resistance values measured under wet conditions are in 10^7 Ω magnitude. With this characteristics they are able to conduct the charges well under standard and wet conditions, too. On the basis of these it can be stated that antistatic and ESD characteristics were managed to reach by magnesium catalyzed polyamide 6 with effective additives.

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