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Water absorption of thermoplastic matrix composites with polyamide 6

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Abstract
This paper describes the process of drying of thermoplastic composites warp knows polyamide 6, an engineering polymer material. The results of absorption measurements of pure and polyamide 6 reinforced with cut glass fiber. Composite for injection molding processing conditioned in conditions similar to those prevailing in industrial warehouses and exposed to direct contact with water. Both, in one and in the second case of modified natural polyamide 6 cut glass fiber polymer material reduces the susceptibility to moisture absorption. Being the most important for the moisture content in the material has the first 10 hours of exposure of granules to various weather conditions.

Introduction

Thermoplastics due to their advantageous properties are widely used in the technique and in the production of consumer products. The requirements for the quality are increasing. Therefore, it is important to know the characteristics of a good plastic material and the possibilities and limitations resulting from them. Associated with thermoplastics absorption phenomenon has both negative and positive meaning. One possible use of this phenomenon are superabsorbent materials that are used in many fields such as medicine [1] and construction [2] and they are now developing rapidly.

The problem of the absorption capacity is also related to a number of problems both in the use of thermoplastics and their processing. In the case of injection molding, which is currently the predominant method of processing thermoplastics, including increasingly used in engineering thermoplastics, there are many ways to reduce or eliminate adverse effects on the absorbency of processing, such as storing and drying the correct inputs. Another way of influencing the size of the phenomenon of absorption materials is to modify the various fillers.

Sorption is a phenomenon of the surface (adsorption) or by volume (absorption) to take the plastic vapors, gases or liquids. The phenomenon of physical adsorption is a surface binding substances and is based on the interaction of short-range intermolecular. Chemical adsorption is to create a chemical bond between the sorbent and sorbate. As a result of adsorption forces in the unimolecular layer adsorption of the adsorbate is formed [3]. Since the physical sorption absorbed particles do not form chemical bonds with the sorbent may be removed in the drying process [3, 4]. With the concept of absorption is necessary to clarify the meaning of terms such as moisture related material, absorption, absorption and hygroscopicity. Absorption, and adsorption are terms often used interchangeably. However, it should be noted that the adsorption may refer to the absorption by the material, both liquids and vapors and gases, whereas absorption refers to the absorption of liquids. Hygroscopicity is the tendency of material to absorb water [4, 5]. However, the material moisture content refers to the percentage of water contained in it.

For this reason, almost the crystalline phase does not absorb moisture, it is assumed that the water absorption is proportional to the contribution of the amorphous structure. This assumption suggests the method of determining participation in the plastic crystalline phase or post-assessment allows for water absorption in the material partially crystalline. However, to determine these values need to know the boundary conditions, and in particular, absorption material in a completely amorphous and crystalline phase involving the maximum [5]. The absorption materials are also affected by the type and proportion of fillers in the plastic, which can cause an increase (organic fillers such as wood flour, cellulose fibers), or decrease in absorption or may not have a material effect on the absorption of [4, 5].

Impact on the absorption properties of polymeric materials

Group of thermoplastics is the most widely used group of modern materials and thermoplastics are used as construction materials for the machinery and equipment [6].

The phenomenon of absorption of thermoplastic characteristics affect their exploitation. The absorption of liquid by the plastic, mainly water, can cause changes in their mechanical properties such as elasticity, tensile strength, impact strength [7]. The absorption of the substance may also lead to changes in mass and dimensions of the products caused by the swelling, and the stress caused by this can lead to damage to the element or the entire structure. Dimensional stability is particularly important in the implementation and operation of components with narrow tolerances, shape and position. The improvement of the dimensional stability of the hydrophilic materials is affected by adding an extender type, such as glass fiber [4, 8, 9].

Absorption phenomenon is particularly detrimental to the plastic products, which in contact with the substances absorbed is long (pipes, container, tank), due to a transfer of the absorbed liquid to the inside of the element. The wet material is also more permeable to gases. For moist PA6 CO2 permeability is three times greater than for PA6 dried. As a result, changes cannot be stored in the properties of products, such as taste, odor. The presence of moisture in the material structure is also influenced by the deterioration of the thermal insulation and dielectric properties [3].

Methods for determining the absorbency of materials based on measuring the change in weight, and the linear dimensions of the mechanical properties of the sample. Absorbence measurements is applicable to all polymers and porous solid. In the method of determining the boiling water absorption is not applicable materials, which at 100°C are seen to change shape. For measuring the absorption liquid is used, such as distilled water and oil.

The absorption and the presence of moisture in the polymer structure is one of the factors causing aging of the material. In industrial environments, the air contained in the aggressive factors as oxides of sulfur, carbon and nitrogen oxides formed in conjunction with moisture, strong organic acids. Long-term effects of water and aqueous solutions of acid and alkaline hydrolysis work. As a result of the aging process is changed appearance material (by sandblasting, exfoliation of the surface) and mechanical properties, thermal, optical, electrical, physical and chemical [8, 10].

Water absorption is significant also a factor in the use of the polyamide-du. The presence of moisture has a major influence on the properties of the material. Dried polyamide is fragile and low impact, and has high tensile strength and flexural strength. Increasing moisture content increases the impact resistance and flexibility, and loss of strength (Fig. 7), in that the modulus of elasticity. Therefore, the results of strength tests of administration is important to provide information about the moisture content of the polyamide structure [8].

Effect of absorption on polymer processing

Plastic water absorption is an important aspect in the process of thermoplastic processing, in particular in an injection molding process. In injection molding, extrusion, and other materials are used in the form of pellets, regrind or scrap recycled. Polymeric materials absorb in these forms are more or less moisture [11]. Hydrophobic materials such as PS, PE, PP, PVC water absorb minimally and appearing in the process of injecting water comes mainly from moisture condensing on the surface of the granules [12]. Partially crystalline plastics, such as technical POM, PA, PET, PBT have properties superior to amorphous materials [12], however, due to hygrophilic properties may take up water to the inside of the structure [11].

During the processing of plastic materials humidity level may not exceed the limit values. If the injection molding process is used wet granulation, the plasticization stage, the reaction occurs in water. Hydrolysis leads to structural changes in the material (degradation) and the result of the deterioration of the mechanical properties, particularly toughness and resistance [12].

The presence of excessive moisture will reduce the viscosity of the plastic, which is the cause of many processing problems [13]. Moisture in the material also affects the appearance of the part.

Such defects can easily be seen because of their extensive nature. [14] They come in a clear, oblong, dull streaks on the surface of the molding, KOTRA is always oriented in the direction of flow of plasticized material. The cause of the formation is the presence of phase plasticizing or injection of water vapor bubbles, which are apart at the surface of the molding and formed into elongated ribbons for fast material. Other visual defects are wrinkle the surface corrugation [13]. Visual defects moldings, due to the high demands on the surface of the finished products, disqualify them further use [11].

The use of moist granules by PMMA injection causes the matured parts with poor surface quality and the POM injection also leads to a raid in shape. In the case of PET and PBT materials can lead to shorter-chain molecules present in the hydrolytic decomposition. This results in a significant deterioration in the mechanical properties of the material. For example, when the moisture content in PBT at 0.1% (0.04% limit) the tensile strength is reduced by 12% compared to the optimal, but the impact strength decreases by 25%. The deterioration of the mechanical properties of the granules as a result of moisture is also strong in the case of PA or TPE (thermoplastic elastomers) and less in the case of other plastics [14, 15]. Effect of moisture on the processing conditions and properties to work out-sec is presented in table 1.

A special case for the processing of plastic materials are phenolic compounds. The presence of water in the material during processing, particularly during the injection, improves the flowability of the material and facilitates the process of processing. At the same time the evaporation of water during the drying molding makes it a significant contraction. Therefore, the amount of water must be adjusted to allow easy processing and phenolic plastics for molding to obtain a satisfactory properties [16].

In order to achieve the process of injecting high-quality finished products should be used-core preventive measures or carry out the drying process of wet granulation. Preventive measures must be adequate storage materials:

- use of bags with a special layer of aluminum to limit the penetration of moisture to the inside;
- start to sealing the packaging;
- storage regrind, ingots and scrap in closed containers;
- use of closed hoppers.

Preventive measures can significantly reduce moisture content material, but due to the highly hygroscopic properties of some materials is often necessary to carry out the drying process [11].

Experiment

The study used three polymeric materials of nylon 6 in the form of a granulation. Polyamide produced by Polimarky SA was used in three typestries:

1) VIRGIN-PA6 polyamide 6 with no additives as fillers. Manufactured in a translucent pellet. Granulate properties consistent or similar to the reported in the literature.
2) RESTRAMID PA6 20GF – polyamide 6 with a filler in the form of a glass fiber in an amount of 20%. Partially crystalline material in granular form.
3) RESTRAMID PA6 35GF – polyamide 6 with a filler in the form of a glass fiber in an amount of 35%. Produced in granular form. Partially crystalline material.

Preparation of the samples. On a laboratory scale weighed about 20 gram portions of the pellets for each type of granules and the length of time of exposure to moisture. Weighed, placed in a container, one part was quenched with distilled water at 20°C, so that the whole granules was immersed in water. The remaining samples were left in a high relative humidity about 70–80% and a temperature of about 5°C. These conditions largely correspond

Table 1. Effect of humidity on the material processing conditions and properties of the molded [11, 12]

Material	Injection process	Presence of plastic moulding	Mechanical characteristics
PA	The presence of bubbles in the stream of injected plastic or plastic moulding	– The presence of streaks in the direction of material flow – Increased bead	Deterioration of impact strength and mechanical strength
POM	– The presence of bubbles in the stream of plastic moulded – A raid on a form	The possibility of streaks on the finished item	No effect
PET PBT	No effect	No effect	Significant deterioration in impact strength and durability
TEEE	No effect	Increased bead	Deterioration of impact strength and mechanical strength

to existing conditions at industrial buildings (excluding the summer period, in which the air temperature is usually higher), on which the pellets are stored and subjected processed. All of the sample containers placed in the pellet was exposed to water, both air and in direct contact, for a specified time: 0.5 h, 1 h, 2 h, 4 h, 10 h, 24 h, 48 h, 168 h.

After a fixed time of exposure, the samples were thoroughly dried pellets of filter paper in such a way that the granule remains dry to the touch. This procedure allowed the reduction of the measurement error in the case of granules kept in water. In this way, the drying was measured only the content of water absorbed by the material.

Measurement of moisture content. Humidity measurement performed on wagosu granule blender WPS-50SX. The measurement was performed at 120°C. The drying time was variable dependent on the amount of water in the material. The measurement is continued to determine the mass of material constant. At the end of the drying process the information recorded with a mass of wet granulation and drying, the percentage of moisture content and drying time, which was used to determine the rate of moisture by putting pellets. Donating speed-ing moisture quotient amount of water evaporated during drying to its length, is a measure of the efficiency of drying.

Results

Polyamide granules undergo immersed in distilled water at 20°C the amount of water absorbed vary according to their kinds. The output was the amount of moisture they contain material upon receipt from the manufacturer.

The greatest amount of water absorbed pure polyamide 6th after 7 days of immersion in water, the moisture content in the granules was 4.8%, about half of the theoretical values of the plastic water saturation of approximately 9–10% [8]. The presence of the filler significantly reduced absorption granules. The moisture content of the granules PA6 20GF after 7 days immersion was less than half than in pure PA6 (2.29%) and granules PA6 35GF more than three times less (1.49%), which is presented in figure 1.

The samples conditioned at a temperature of 5°C, 70–80% relative humidity at the start of the test contained the same initial moisture content of the sample as to be immersed in water. Polyamide granules exposed to moisture in the air atmospheric moisture absorbed different. Measurements have shown (Fig. 2) that in the pure PA6 after 7 days of exposure to moisture, water was 2.83%. Due to the addition of glass fiber moisture content of the granules PA6 and PA6 35GF 20GF was relatively smaller (PA6 20GF – 25% less, and PA6 35GF – 60% less moisture than pure PA6).

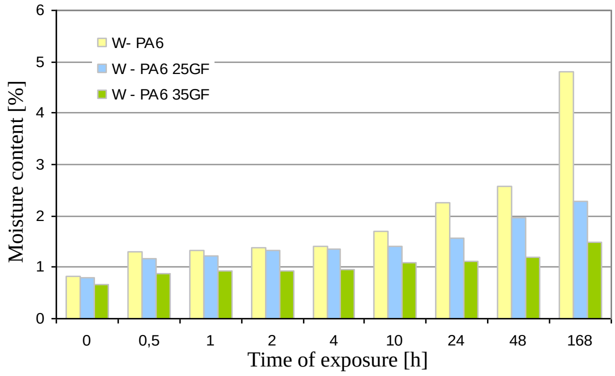

Fig. 1. The moisture content of granule of pure PA6 and PA6 with glass fiber according to the time of exposure to the time length of waters immersion

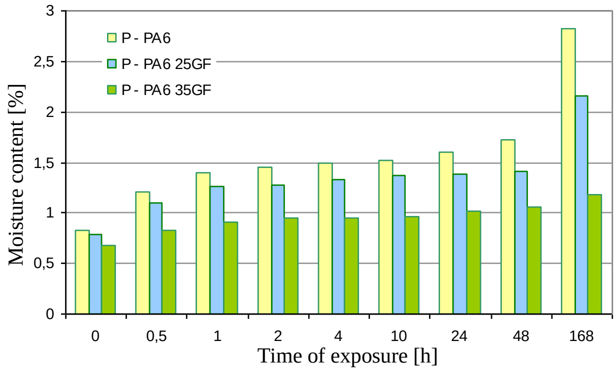

Fig. 2. The moisture content of granule of pure PA6 and PA6 with glass fiber according to the time of exposure to the atmospheric air

For each type of granules, both immersed in the water and exposed to the atmosphere rapid increase of water content in the material in the first hour followed absorption which is shown in figure 3 (in order to distinguish the samples soaked in water, the following curves are marked with W, while the air in the air means P). For example, after 1 hour, the moisture content of pure PA6 soaked in water was 1.32%, which is 58.5% moisture absorption after 24 h and 27.5% moisture content, after one week immersion in water. The granulate moisture content of PA6 35GF after 1 h of absorption was 0.93%, and therefore the moisture content of 62.5% after one week of absorption.

Smaller differences occurred when the moisture absorbent granules from the air. The moisture content in the PA6 after 1 hour was 1.4%, which was 49.5% of the quantity of water in the material after a week. The water content in the pellets PA6 35GF after 1 hour was 0.9%, and so much as 76% percent of water content absorbed after 7 days.

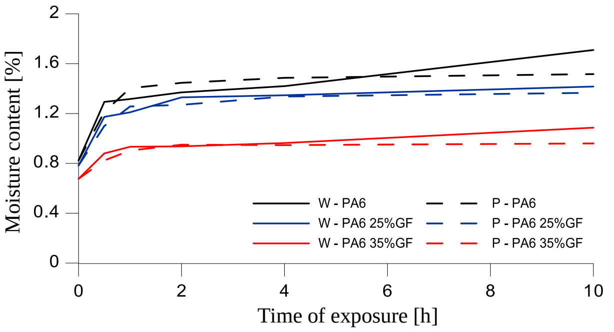

Fig. 3. The amount of moisture absorbed by the granules in the 10 hours test

In figures 3 and 4 depicting the process of water absorption by the granules are visible at some deviations from the trend of increasing the amount of moisture in the granules. This is particularly evident for the first 2 h period of the study (Fig. 3) and for PA6 due to absorption in the 24 h as a result of absorption for PA6 20GF after 48 h (Fig. 4). This may be due to heterogeneity of respondents granules.

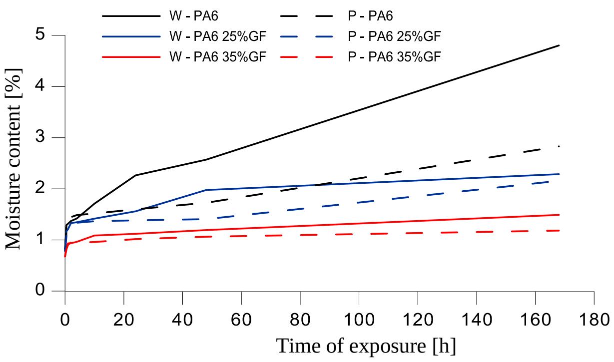

Fig. 4. The amount of moisture absorbed by the granules in the 7 days test

From the graphs shown in figure 3, both as figure 4 shows that adding 35% fiberglass significantly reduced absorption particularly in relation to pure polyamide and the process of absorption during the first 10 h runs almost linearly. The addition of PA6 20% glass fiber reduced the absorption to a lesser extent. Cost increase the moisture content of granules PA6 20GF placed in water and air, and soaked in water PA6 are close to each other. Line increase the moisture content in the pellets PA6 moczonym in water is the most reward-womb of the others and has the strongest upward trend.

From the graph shown in figure 4 can be seen that the increase in moisture content is higher in the long term test. The exception is the line on the chart corresponding to the PA6 25GF W, which indicates progress to stabilize the moisture content of the granules.

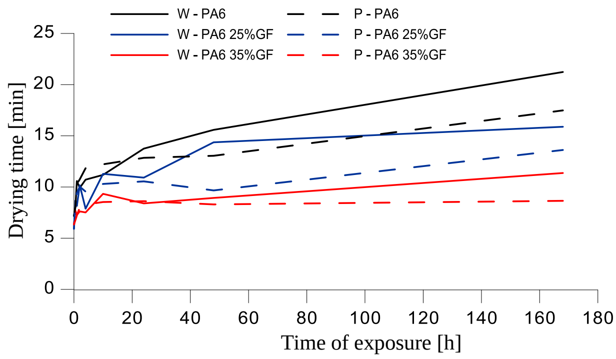

Fig. 5. Average drying time of granule depending on the exposure time

Minor differences between the water content in the pellets after 1 h and 7 days, in the granules between absorbing moisture in the air due to the lower concentration of moisture in the environment. After a certain period, and the absorption of water reaches a certain level of moisture absorption by the pellets approaches the equilibrium state. In the case of granules lats soaked in water the concentration of the absorbed (water) in the environment is much higher and thus the faster moisture absorption. Clearly visible is the comparative charts absorption granules immersed in water interne out in air (Fig. 5 and 6). In the first 4 h difference between

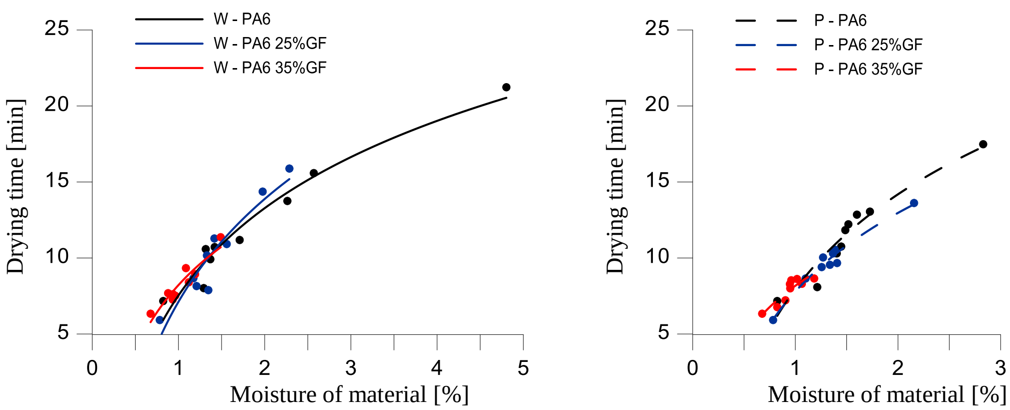

Fig. 6. Average drying time of granule depending on the amount of moisture content, a) exposure to water, b) exposure to air

the rate of uptake-nanny are insignificant. However, at longer times the difference is noticeable, and shows that the sample immersed in water faster moisture absorption.

Time of drying moist granules increases with increasing moisture content of the granules. For example, the average drying time for moist granulation samples weighing 5 g of PA6 and the average moisture content of 0.82% was 7 minutes 17 seconds, while the average drying time for moist granules PA6 samples weighing 5 g and an average moisture content of 4.8% was 21 minutes 23 seconds. Average granule drying times are shown in figures 5 and 6.

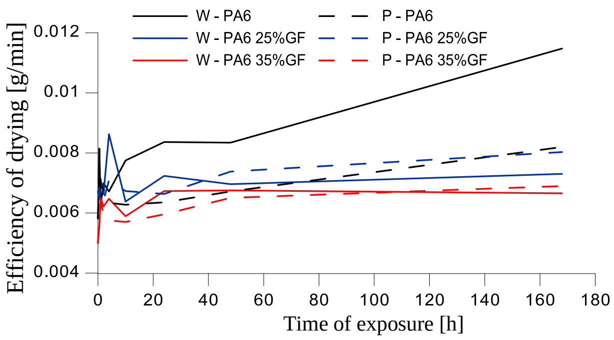

Fig. 7. Average efficiency of drying the granulate according to the exposure time

The rate of moisture it (Figs 7 and 8) of the granules in the drying process was relatively constant at an average of 0.006–0.008 g/min, which gave from 0.11 to 0.16 percent of moisture per minute. Only in the case of PA6 granules immersed in water for 7 days (4.8% moisture content) the rate of moisture it was significantly higher-strength and amounted 0.011 g/min (about 0.23 percent moisture per minute). Result of the drying rate of the granulate containing 4.8% indicates the impact on the speed of this phenomenon is the difference in concentration of the agent, in this case water, between the environment and the material.

From these data also show that the presence of an additive in the form of glass fiber has a negligible effect on the speed of the granulate moisture donation. Rendering the speed of moisture in the pellets according to the type of the granules was conditioned: PA6 – 0.007 g/min, PA6 20GF – 0.007 g/min, PA6 35GF – 0.006 g/min. For pellets soaked in water: PA6 – 0.008 g/min, PA6 20GF – 0.007 g/min, PA6 35GF – 0.006 g/min.

Conclusions

Moisture granules for processing, it will need to dry, which increases the production process and increases the cost of production and causes heat aging plastic. Reducing the moisture content of granules during processing can be achieved by appropriate measures, such as sealing the packaging and containers for granulation, drying in a drying apparatus and the introduction of the injection molding process in the drying hopper.

The research described in the above refer absorbent granules work polyamide 6 in most industrial environments granules absorb moisture from the air, in extreme cases, such as flooding absorb moisture through contact of liquid. The study focused on the absorption of moisture from the air at 5°C and 70–80% relative humidity largely correspond to the conditions prevailing for industrial buildings. However, the results of tests made on samples immersed in water allowed to obtain a comparative scale phenomena in a variety of environments. Based on the results it can be seen that the phenomenon of absorption materials can be significantly reduced by the modification. One way is to add the modified filler in the form of glass fibers. Modification of glass fiber reduces absorption of granules, even several times. During the study period, addition of 20% glass fiber resulted in approximately 2-fold, and 35% of the approximately 3-fold decrease in absorption for pellets soaked in water. The addition

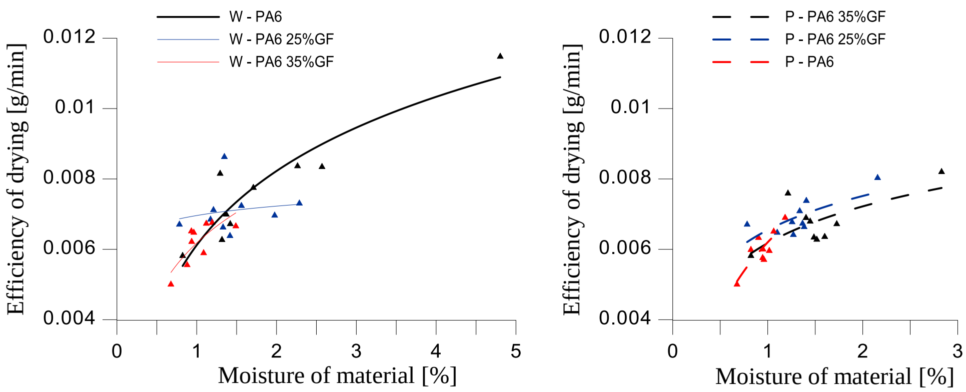

Fig. 8. The average efficiency of drying the granulate material according to the moisture content, a) exposure to water, b) exposure to air

of air conditioning raw fibers caused a 20% decrease in absorption of about 1/4 and the addition of 35% fiber by 1/2. Decrease in absorption is due to negligible water absorption of glass fibers, which filling material, reduce the volume of the moisture-receptive.

The moisture absorption is the fastest in the dry granules. This is due to the desire to achieve a balance between the amount of moisture in the material and its environment. Similarly dries quickly in the case of granules, in which the concentration of moisture absorbed is much higher compared to the concentration of moisture in the environment. The drying process is a wet sample, the longer the greater the moisture content of the granules. For pellets containing 4.8% was 21 minutes 23 seconds. In industrial environments, where the drying is subjected to a large number of granules, large moisture will result in time-consuming drying process.

Absorption air polyamide granules depends on the environmental conditions (temperature and humidity). Also reaches a value lower than the water absorption, especially with a long exposure time, because of the limit to the steady-state moisture in the material and the environment. The use of modified processing raw fiber glass allows you to limit the negative impact of the water. This allows to shorten the drying process due to the lower absorption, and thus saving energy. In addition, the properties of articles made of plastic-modified, although also are reduced when exposed to moisture, they still have better mechanical properties than the unmodified material.

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