The prolonged effect of temperature, temperature and moisture, and the brief effect of moisture on the properties of polyamides were investigated in [1, 2]. We found no published data on the effect of moisture on aging of aliphatic polyamides.

The mechanism of action of moisture on polyamide-6 (PA-6), despite the large number of studies of this problem, has not yet been established [1]. Absorption of moisture by polyamide-6 worsens its properties [2] and decreases the glass transition temperature [3, 4]. Moisture is basically sorbed by the amorphous regions of polyamide [2, 4]. The negative effect of moisture is usually reversible [1, 2], but the changes in the properties are irreversible in some cases, and it is thus believed that moisture can act as a physical (plasticizing) or chemical (hydrolyzing) agent [1]. The plasticizing effect of moisture is attributed to breaking of intra- and intermolecular hydrogen bonds in [3-5], but it was shown in [6] that plasticization takes place without breaking of hydrogen bonds. It was also observed in [4] that moisture has an antiplasticizing effect in PA-6 below the glass transition temperature. The effect of moisture on aging of glass-filled PA-6 was investigated in the present study.

Brand PA6-211-DS and PA6-211-DS-K glass-filled polyamides were studied. The samples were prepared by pressure molding. The breaking strength was determined according to GOST 11262-80 on type 2 blades with a clamp movement rate of 25 ± 2.5 mm/min; the breaking bending stress was determined according to GOST 4648-71. The results of the tests were statistically processed according to GOST 14359—69. Before conducting the physical-mechanical tests, the samples were conditioned at 20°C and 65% relative humidity in accordance with GOST 12723—66. Moisture was sorbed by holding the samples in water at 293 K.

As the data from differential scanning calorimetry (DSC) on a Mettler TA 3000 instrument with a temperature elevation rate of 5°C/min show, the sorbed moisture causes changes in both the amorphous (Fig. 1) and crystalline components (Fig. 2). The region of the glass transition \( T_g \) is located in the 45-80°C range in absolutely dry glass-filled PA-6 (sample previously dried at 80-90°C and then held in the measuring cell at 130-150°C until liberation of volatile substances stopped). For moisture absorption equal to 0.5 wt. %, the glass transition region narrows slightly and lies in the 45-65°C temperature range. On subsequent moisture saturation, the height of the glass transition peak in the observed temperature region decreases, an endothermic peak \( T''_g \) appears in the negative temperature region, and its area increases constantly.

With maximum moisture saturation equal to 7 wt. %, the first glass transition region \( T_g \) disappears completely, and the area of the peak of the new region becomes maximum. The presence of two glass transition regions in moistening of PA-6 was also observed previously based on data from low-frequency acoustic measurements of unfilled PA-6 and attributed in [4] to the presence of different levels of supermolecular organization in the amorphous component in the starting polymer: the moisture initially penetrates the unordered regions of the amorphous phase more easily and subsequently enters the depth of the ordered regions, destroying them, due to a decrease in the intermolecular interaction. The data in Fig. 1 indicate that these features are also characteristic of glass-filled PA-6, where it is necessary to assume that the intermolecular hydrogen bonds are totally destroyed in the amorphous component of PA-6 at the time of maximum moisture absorption.

The observed slight "blurring" (relatively wide range) of the glass transition region is most probably due to desorption of moisture during DSC, and it is totally eliminated at 110-120°C (endothermic peak in the 100°C region). An endothermic peak in the region of 0°C corresponding to the melting point of ice appears on the DSC curves of glass-filled polyamides containing more than 5.1 wt. % water. This is probably the cause of the antiplasticizing effect of moisture (water forms a separate phase) at temperatures below the glass transition temperature of PA-6 [4].
Fig. 1. DSC curves of glass-filled PA-6 with a different moisture content: 1) dry; 2) 0.5 wt. %; 3) 2.5; 4) 3.5; 5) 5.1; 6) 7 wt. %. The glass transition regions are indicated by the arrows.

Fig. 2. DSC curves of glass-filled PA-6 with a different moisture content. The legends are the same as in Fig. 1.

The data in Fig. 1 indicate that sorption of moisture causes a significant decrease in the glass transition temperature of glass-filled PA-6, i.e., in these conditions, the sorbed moisture plays the role of a plasticizer. It should be noted that the DSC curves of polyamide with any initial moisture content in the region up to 100°C after remelting (drying) are almost identical to the DSC curve of the initial dry sample. This probably indicates the absence of hydrolytic processes under the effect of moisture in these conditions.

Let us examine the not previously studied effect of moisture on the crystalline component of glass-filled PA-6. Only one melting peak with $T_m = 223.6°C$ is observed for the dry sample (see Fig. 2, Table 1). The onset of melting of crystallizable polymers, including PA-6, is due to melting of the least complete, and the end is due to melting of the most complete crystallites. The total range of melting, $\Delta T_m = T_{c.m.} - T_{b.m.}$ can be considered as the criterion of structural homogeneity of the polymer crystallites, and the range of $\Delta T_1 = T_{m} - T_{b.m.}$ and $\Delta T_2 = T_{c.m.} - T_{m}$ can be considered as the criterion of homogeneity of the least and most complete crystalline formations. Sorption of water causes almost no change in the temperature of the beginning and character of melting. Insignificant moisture absorption (0.5 wt. %) decreases $T_{b.m.}$ to 165°C and causes the appearance of a new melting peak. As the moisture content increases, the position and intensity of the low-temperature melting peaks ($T_{m}^{*}$, $T_{m}'^{*}$) change significantly (see Fig. 2, Table 1).

The above indicates important structural rearrangements in the crystalline component of PA-6 under the effect of sorbed water, characterized by the following common features: formation of mesomorphic crystal structures from the most defective and incomplete crystallites (and not from the amorphous phase, indicated by the slight decrease in $\Delta H$) and their completion, confirmed by the change in $\Delta H$ and the position of the low-temperature melting peaks for samples with a 3.5, 5, and 7 wt. % moisture content. Breaking of hydrogen bonds in PA-6 by the moisture and its being in the highly elastic state cause the rapid occurrence of recrystallization processes; an increase in the fraction $q$ and structural homogeneity of the more complete crystallites, indicated by the increase in $T_m$, decrease in $\Delta T_2$, and increase in the enthalpy of fusion $\Delta H$ of the complete form. It should be noted that there are no low-temperature melting peaks outside of the dependence on the level of moisture absorption on the