

Introduction Due to the ever increasing demands of engineering industries of new techniques to polymeric materials, including created on the base of aliphatic polyamides, an urgent task of improving performance properties of these polymers, including high heat and heat resistance, resistance to thermal-oxidative and aggressive media and adhesion characteristics to various substrates remains actual. Physical properties of aliphatic polyamides are mainly conditioned by strong intermolecular interactions at the expense of hydrogen bonds that are formed between the amide groups of neighboring macromolecules. In the preparation of polyamides it is necessary to enter regulators (stabilizers) of molecular weight, in this case acetic, adipic acids (as the cheapest and most available) and amines, salts of monocarboxylic acids and monoamines or N- alkyl amides of monocarboxylic acids are used [1]. Polyamides as well as other polymers are polydispersed. In the polymer composition there are large macromolecules and low molecular weight amides with a small number of elementary units in the molecules (oligomers). They contain terminal amino groups and carboxyl groups. Furthermore, the oligomers of amides may also exist in a cyclic form. The mechanism of their formation is still not clear. However, it is experimentally proved that in the absence of water cyclic oligomers are not capable of polymerization, but they are easily converted into a polyamide in the presence of water. In this regard, the use of additives that at processing of polyamides may release small amounts of moisture can be very useful for improving the performance properties of materials, products and coatings based on polyamides. One of the effective ways of targeted regulation of properties of commercially available polyamides is their chemical modification by polyfunctional reactive compounds [2-5]. Presence in the macromolecules of polyamides reactive carboxyl, amide and aminogroups which are capable to react with monomeric and oligomeric polyfunctional modifiers enables the production of materials having the properties of crosslinked polymers. Thus, it was found that imido compounds, in particular N, N'- bis- maleimides are effective modifiers of many polymers, also including polyamides [6]. Information about the use of N, N'- bis maleinamido acids as the modifiers in their synthesis of intermediates in the scientific literature were not found. Main part The aim of this work is to study and research the compositions based on polyamide 6 (PA-6), industrially produced by JSC «Grodnoazot» (Grodno, Belarus) (OST 6-06-09-93), intermediate product in the synthesis of modified -N, N'- metaphenylene bis maleineimide (FBMI) -N, N'- bis-maleamido metaphenylenediamine (FBMAK) The modifying reagent was injected into the PA-6 at doses of 5-10 wt. %. FBMAK choice, as previously FBMI [6], due to their high reactivity associated with the content of the reactant molecules of double bonds that can be disclosed under thermal or photographic processing to form a spatial crosslinked polymer structure [6]. Physical and mechanical properties of PA-6 are shown in Table 1. Receiving of FBMAK was performed by reaction of equimolar amounts of metaphenylenediamine with maleic anhydride at 20-25°C by gradual addition to a solution of diamine in a minimum amount of solvent - dimethylformamide

stoichiometric amounts of maleic anhydride. To obtain the corresponding bis-maleinimide, the second step (imidization) of bis-amidoacid by heating it in a mixture of acetic anhydride and sodium acetate in the ratio 2.5 : 0.5 moles per mole of bis - amidoacid at 70-90°C was performed. Upon completion of imidization (about 2.5 hours of heating) FBMI was isolated and recrystallized from a mixture of ethyl and n- propyl alcohol , in the ratio 1 : 1. It should be noted that the yield of the intermediate product - FBMAK - in the first synthesis step is 85-90% while the final product after imidization (FBMI) is only 50-60 %. Table 1 - Physical and mechanical properties of PA- 6

name	Norm	on the highest quality category
Color	From white color to light yellow color	
Number of point inclusions per 100 g of product units	Not more than 8	
Size of crumbs	msm, 1,5-4,0	
Moisture content, %	0,03-2,00	
Relative viscosity, dl / g	2,20-3,50	
Mass fraction of extractables , %	1,0-3,0	
Melting point, °C	214-220	

The melting point of the synthesized N, N'- metaphenylen-bis-maleinimide was 203°C, which corresponded to the literature data [7]. FBMAK when heated in the process of determining the melting point and becomes FBMI and the melting point of this compound is not clearly fixed. Receiving of FBMAK and FBMI is performed according to scheme 1. It is important to note that the perspective of use of polyamide 6 FBMAK as a modifier component instead of FBMI allows to exclude out of the process of synthesizing FBMI the step of high-cost chemical cyclodehydration (imidization) of FBMAK, moreover, the loss of the product during its conversion to the bis - imide of the final step of synthesis is eliminated, and during imidizing process extracted water promotes destruction of cyclic structures in the system of the polyamide. Scheme 1 To study the structure of polyamide- 6, the processes occurring in the polymer system , as well as assessing the completeness of spending FBMAK reactive groups by reacting with amine and amide functional groups of PA-6 during formation of three-dimensional structure when heated samples was performed IR spectroscopic study using FTIR spectrometer Nicolet 7101 (USA) in the range of 4000-300 cm<sup>-1</sup>(resolution 1 cm<sup>-1</sup>) [8]. Furthermore, the possibility of formation of intermolecular cross-linking was confirmed by electron paramagnetic resonance (EPR) [9-10]. EPR spectra are recorded using the modified RE -1306 spectrometer with computer software. The heating process of polyamide compositions of modified FBMAK was carried out in the cavity of the spectrometer in the temperature range 20-250° C. Before recording the spectra the samples were cooled to room temperature. MnO containing ions of Mn was used as an external standard [9] nitroxyl radicals.were used as markers. For example, evidence of more efficient structuring system in polyamide compositions containing as builders FBMAK compared with FBMI is that the time of correlation of stable nitroxyl radicals introduced into FBMAK modified PA-6, increased from 23•10<sup>-10</sup>s (source unmodified P6) to 50•10<sup>-10</sup> s with polyamide -6, modified by 5 wt % FBMAK. For PA-6, modified with the same amount of MFBI correlation time of nitroxide was significantly shorter period from 40•10<sup>-10</sup> s. Comparative analysis of the IR absorption spectra obtained in an airless environment of PA-6 compositions and FBMAK different composition (5-10 wt. %

FBMAK builder) in the polymer melt, followed by heating of the samples at 150-210° C showed that for the modified polymer systems absorbance decrease of absorption bands in the 1647 , characteristic of the amide groups is observed. It appears that at the process of chemical modification of PA-6 by bis- amidoacid, as well as modifying it by its corresponding bis- imide reactions, resulting in an increase in the molecular weight of PA-6 take place. It occurs as by the interaction of the carboxyl groups of the bis- amidoacid modifier with amine-terminated polyamide groups (scheme 2) and by the formation of interchain crosslinks (scheme 3) by opening the double bonds formed during the heat treatment at 150-200°C samples of polyamide compositions. This does not prevent homopolymerization of FBMI and that is due to the ability of the double bonds in FBMI to be activated by adjacent carbonyl groups of the imide cycle and disclosed by reacting with compounds containing labile hydrogen atom. These processes all together result in a change of the supramolecular structure of the PA-6, causing the improvement of mechanical, thermal and adhesive properties of the polymer [6]. In practical use of FBMI their thermochemical characteristics can have essential significance. In this connection it is necessary and appropriate to examine the thermochemical characteristics of a number of different structures of BMI by differential scanning calorimetry. DSC curves (Figure) of all studied BMI taken in the temperature range of 20-400°C at a rate of temperature rise of 10°C / min are clearly played two peaks endothermic the melting process of BMI and exothermic corresponding to the process of disclosure of the double bonds. The position of the peaks in the respective process on the temperature scale depends on the chemical structure of compounds. According to the value of enthalpy disclosure of double bonds, studied compounds in their thermochemical characteristics and probably related to reactivity in the reactions occurring with the opening of the double bonds are not significantly different. In this connection, the use of aliphatic polyamides FBMAK, FBMI is justified as modifying component. This component (MFBI), and accordingly MFBAK as its intermediate are produced in industrial conditions and are widely used for the production of a large range of heat-resistant composite materials. They are used to improve the adhesion of the cord to rubber mass in the manufacture of various kinds of tires for the automotive industry. Effectiveness of modifying action of FBMAK in thermo-oxidative degradation processes of PA-6 compositions was evaluated on samples of three types: model modified FBMAK powder compositions, films, molded samples. Scheme 2 Scheme 3 Model modified powder compositions of PA-6 were prepared for the rapid analysis of possible stabilizing action FBMAK to the polymeric matrix. They were prepared as follows: PA-6 unstabilized granules were placed in a mixer, where nitrogen was supplied to provide oxygen free environment. The temperature was raised to 240°C and a stirrer was switched on. With continuous stirring, the calculated amount of FBMAK was injected into the polymer melt. The mixture was being stirred for 5 min. Then it was poured into a mold and cooled. After curing, the sample was removed from the mold and crushed at a cryogenic

temperature (after soaking for 10 min in liquid nitrogen at  $-180^{\circ}\text{C}$ ) to a fine powder. Investigation of the thermal stability was carried out by differential thermal and thermogravimetric analysis. The sample weight was 10 mg, a heating rate in the range of  $20\text{-}500^{\circ}\text{C}$  was  $5^{\circ}\text{C} / \text{min}$ . The activation energy of thermal oxidative degradation of the polymer Ed was calculated from the Broido method [11-13] according to dynamic thermogravimetry obtained by thermo-setting - module TA-400 of the Mettler Toledo company (Switzerland) in the temperature range  $330\text{-}400^{\circ}\text{C}$ . Instrument calibration was performed on indium standard. Laboratory samples of the polyamide films of 15-20 microns thick were cast from solutions of PA -6 with formic acid. To obtain solutions a sample of the polymer (2 g) with a relative viscosity of 2.8 (determining in a solution of concentrated sulfuric acid) was dissolved in 28 ml of formic acid at room temperature. After that the estimated quantity of FBMAK was injected into the solution and mixed thoroughly. Then degreased and dried on glass plates by pouring through a nozzle with an adjustable gap the layer of film-forming composition was deposited. The glass plates were placed horizontally in a vacuum drying oven, where at a residual pressure of 2 mm Hg. Art. and a temperature not above  $30^{\circ}\text{C}$  for 4.5 h the solvent was removed. Formed on a glass substrate polyamide film was removed and subjected to research. Fig. 1 - DSC curves of BMI: 1 - N,N'- diphenylmethane-bis-maleinimide; 2 - N,N'- diphenyloxide bis-maleinimide; 3 - N,N'- m-phenylene-bis-maleinimide (FBMI)

Samples were also prepared by injection molding as follows: FBMAK modifier in an amount of 5-10 wt. % by weight of PA-6 was applied to the polymer granules without the heat stabilizer with a relative viscosity of 2.8 by dusting. Powdered pellets were peppered through the hopper to the injection molding machine, where they were melted. From the molten mass bilateral blades with working part  $50 \times 10 \times 3 \text{ mm}$  were cast. Experimental samples one day after their manufacture were placed in a heat chamber with a free circulation of air. They were maintained at  $150^{\circ}\text{C}$  for predetermined time (30-210 hours). Determination of the breaking strength of the samples was performed by stretching according to GOST 112-80 using the tensile testing machine T 2020 DS 10 SH (Alpha Technologies UK, USA) at room temperature and velocity of the gripper 100 mm / min. Judging by the results of measurements of the tensile strength of the samples given in Table. 2 generated in the step of heat treating of polyamide compositions meshwork of aliphatic polyamide-6 at the expense of the reactive groups of FBMAK (content in the composition of 5-10 wt.%) and functional groups of PA-6 predetermines the higher rates of heat resistance (temperature of thermo-oxidative degradation increases by  $10\text{-}15^{\circ}\text{C}$ ) and deformation-strength properties (tensile strength increases by almost 10 MPa at initial modified samples, amounting 64,0-68,0 MPa) as compared to the unmodified polyamide 6 (59.0 MPa) and is comparable with PA-6 modified by the bis-maleinimide (FBMI). Importantly, FBMAK as well as FBMI, provides a thermally stabilizing effect on polyamide-6 at various temperature and time of exposure of samples of polymer compositions. Calculation of the activation energy of thermal oxidative degradation of the samples

(Ed) also indicates the formation of crosslinks in a matrix structure of polyamide 6 at the expense of additives of MFBAM and MFBI, increasing depending on the modifier content of FBMAK from 135 to 148 kJ / mol. Table 2 - Tensile strength of PA-6 and modified by MFBI MFBAK samples of PA-6 after thermal oxidation in air at 150° C for 30-210 h

Material	Td, °C	Ed, kJ / mol	30 initial	30 after thermal oxidation in air for, h	60	90	120	150	180	210
PA-6	59,0	50,0	49,0	41,0	35,5	30,5	23,0	18,6	275	120
PA-6+ 5 wt. % FBMAK	64,0	66,5	64,0	61,4	61,0	61,5	61,0	60,0	285	135
PA-6 + 10 wt. % FBMAK	68,0	69,0	69,5	62,4	62,0	63,4	63,0	61,0	290	148
PA-6 + 5 wt. %FBMI [6]	63,4	64,6	63,0	62,6	62,0	62,0	61,4	60,7	287	141

As seen from Table 2 polyamide 6 modified with bis maleamidoacid has not only improved strength characteristics as compared with the original PA-6, but it is also more resistant to high temperature and time fields. Conclusion Thus, the use of bis-aminoacid (FBMAK) as a builder in the system of aliphatic polyamide-6 improves strength properties and thermal characteristics of a polymeric material based on PA -6 virtually in the same range as the previously used for the same purpose FBMI [6].