Synthesis of modified amino-aldehyde oligo (poly)mers and study of their thermal stability

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Abstract. In the article are discussed the relevance of obtaining amino aldehyde oligomers and the study of their basic physicochemical properties and determines that the synthesis conditions and the ratio of the starting components play an important role on the properties and structure of the synthesized amino aldehyde oligomers. Using the Differential thermal analysis (DTA) method, it was proved that the modification of the urea-formaldehyde oligomer with acrylic acid helps to increase the thermal oxidative degradation of the resulting products. In this case, the modifier - acrylic acid strongly chemically binds with amino aldehyde oligomers, which leads to an increase in the heat resistance of the samples.

1. Introduction
Today, polymeric materials obtained on the basis of amino aldehyde oligomers are very widely used in various industries due to their high physicomechanical, heat and electrophysical, and satisfactory technological properties - heat resistance, adhesion, availability and relatively low cost of raw materials, as well as ease of synthesis polymers are widely used. By changing and regulating the composition of amino aldehyde oligomers, it is possible to obtain polymer materials that satisfy the requirements of various industries [1,2].

One of the important requirements is the thermal stability of materials, which can be solved by synthesizing and using oligoester acrylates containing various thermostable fragments and by introducing reactive crosslinking additives into the compositions [3,4].

The preparation of binders based on thermosetting resins, such as carborane-containing phenol-formaldehyde polymer, is characterized in that in order to improve the thermophysical properties, it additionally contains a resol-type phenol-formaldehyde polymer in an amount of 2-50 weight. % [5].

To prepare esterified urea-formaldehyde resins, usually 2 mol of formaldehyde per 1 mol of urea is taken and the first stage of the process is carried out in a slightly alkaline medium. After the addition of butyl alcohol and acidification, esterification begins and further condensation occurs. After reaching the required degree of esterification and condensation, the solution is neutralized, then water and excess solvent are distilled off. Finished resins are always available in the form of solutions (usually up to 50% concentration) in butyl alcohol or a mixture of butyl alcohol with xylene [6,7].

Of great importance is the ratio between the degree of condensation and the degree of esterification. It is determined by the quantitative ratio between the reactants, the temperature and the reaction time, as well as the nature and amount of the acid catalyst. The amount of bound butyl alcohol usually ranges from 0.5 to 1 mol per 1 mol of urea [8,9].
2. Research methods
Differential thermal analysis is a research method consisting in heating or cooling a sample at a certain rate and recording the time dependence of the temperature difference between the test sample and the reference sample (reference), which does not undergo any changes in the considered temperature range.

The method is used to register phase transformations in a sample and study their parameters.

DTA is the most common thermal analysis method due to the wide range of information it receives. An inert substance with values of heat capacity and thermal conductivity close to the investigated substance is used as a reference sample, which does not undergo any structural and phase changes in the investigated temperature range. Thus, the temperature difference between them arising during the simultaneous heating or cooling of the test and reference samples is due to endothermic or exothermic transformations or reactions in the test sample. Differential thermal analysis allows you to establish:

- presence or absence of phase transformations;
- temperature of the beginning and end of any process accompanied by a change in the energy balance in the system;
- the nature of the course of the process in time;
- displacement of one effect or another under the influence of external factors (pressure, change in the composition of the environment).

The method is used to study drugs, food and biological products, organic and inorganic substances. The following values can be measured: glass transition temperature, crystallization temperature, melting point and sublimation temperature [10,11].

3. Results and discussion
The synthesis of urea-formaldehyde oligomers, the most widely used at present, is as follows: in some cases, the reaction is carried out at the boiling point of the reaction mixture. Upon receipt of unlimited water-soluble urea-formaldehyde resins, it was proposed to increase the temperature of the reaction mass in the alkaline medium to 102°C [12]. In France, Nobel Hoechst Chimie recommends acid condensation at the boiling point of the reaction mixture [12]. It is possible to significantly increase the temperature during the reaction under pressure. For example, at pH = 7-8 and a pressure of 0.4 MPa, the interaction of urea with formaldehyde at 140°C takes 10 minutes.

To elucidate the temperature, range of the effective use of the synthesized modified urea-formaldehyde oligomer, thermal oxidative degradation was studied under dynamic thermo gravimetric conditions [13].

In this regard, obtaining new modified amino-aldehyde oligomers and studying their thermal stability was of no small importance.

In the table 1 showns the name of the starting components and experimental options for obtaining amino aldehyde oligomers. The synthesis was carried out at the natural reaction temperature. Urea and urotropin were dissolved in water at a temperature of 20-30°C. Acrylic (sulfuric) acid was poured into the solution in small portions, preventing the temperature of the reaction mixture from rising from 55-60°C. In I-II variants, viscous oligomers formed. In III – IV variants, homogeneous viscous flowing oligomers. This indicates that between the oligomer and acrylic acid, a substantially different condensation product is formed in physical condition.

| Name of components | Experiment options and component consumption, in parts by weight |
|--------------------|---------------------------------------------------------------|
|                    | I     | II    | III   | IV    |
| Urea-99.8          | 100   | 100   | 100   | 100   |
| Urotropin-99.4     | 50    | 40    | 50    | 40    |
| Crotonic aldehyde - 98.2 | -     | 10    | -     | 10    |
| Acrylic acid –98.2 | -     | -     | 7     | 7     |
| Sulphuric acid –100| 35    | 35    | 28    | 28    |
Modified oligomers (III – IV versions of the experiment) are products of liquid-viscous consistency from yellow to brown, readily soluble in acetone, ethanol, tetrahydrofuran and dioxane. To obtain comparative data under identical conditions, urea-formaldehyde oligomers in the absence of acrylic acid were synthesized and studied (I – II experimental variants).

To clarify the temperature range of the effective use of the modified aminoaldehyde oligomers synthesized by us, we studied the thermal oxidative degradation under dynamic thermogravimetry. The data of thermal analysis of the obtained samples were determined to have a complex stepwise character. The destructive processes that occur during this can conditionally be divided into five stages.

In table 2 the indicators of thermal oxidative degradation during dynamic thermogravimetry of unmodified and modified amino aldehyde oligomers are presented.

| Indicators                                      | Prototypes | I  | II | III | IV |
|------------------------------------------------|------------|----|----|-----|----|
| Half-life, min                                  |            | 37 | 42 | 43  | 46 |
| The beginning of destruction, °C                |            | 182| 203| 212 | 224|
| Half-life, melting °C                           |            | 210| 240| 269 | 282|
| The temperature of the volatilization of gaseous substances, °C | | 290| 310| 382 | 476|
| Expansion temperature, °C                       |            | 437| 463| 513 | 580|
| Destruction end, °C                             |            | 642| 644| 657 | 675|

The first stage of destruction begins with 182 °C, evaporation of free gaseous moisture depending on the composition and structure of the samples and lasts up to 224 °C. The second most intense stage of destruction, in which the mass of the sample is lost by melting, begins at a temperature of 210 °C and ends at 282 °C, and the third stage is the volatilization of various gaseous components, which corresponds to a temperature range of 290-476 °C. In the fourth interval, the samples gradually begin to swell, the beginning of which corresponds to 437 °C and ends within 580 °C. The temperature at which almost all samples pass into ash corresponds to the end of the destruction at 642 - 675 °C.

From the obtained data it was determined that the temperature of the beginning of the destruction of the urea-formaldehyde-crotonic aldehyde oligomer modified with acrylic acid is significantly higher than those of unmodified oligomers obtained under similar conditions.

It is well known that to study the nature of the porous structure of materials, including leather, it is advisable to use various methods of the thermographic method [14].

According to the results of studies, the obtained derivatogram curves have a number of characteristic inflection points. To characterize the moisture content in porous skin at the indicated points, temperature (T) curves and decomposition of aminoaldehyde polymers in the skin structure were used. Based on them, the temperature range of destruction at each site of the process was determined.

In figure 1 showns the curves of temperature (T), differential thermal analysis (DTA) and thermogravimetry with respect to the derivative (TGP) of the studied skin samples.

From the graphical differentiation schemes, we can conclude that the initial portion of the derivatogram is characterized by a linear increase in temperature. It can be assumed that during this period, in the temperature range from 20 to 80°C, the immobilized gaseous components and partially water are removed from the samples.

In the temperature range of 80-110°C for 40 minutes the free moisture gets wet. Moreover, there is a shift of the curves towards high temperatures, depending on the processed samples.

Further desorption of the moisture contained in the micro capillaries occurs as the temperature rises, which manifests itself in the thermo gram as an inflection and this process ends at a temperature of 120°

| Water | 300 | 300 | 300 | 300 |
|-------|-----|-----|-----|-----|
| Total | 485 | 485 | 485 | 485 |
C. From the curves it can be assumed that, with increasing temperature, the amine aldehyde polymers melt in the skin structure in the temperature range 125-160°C.

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![Derivatograms of skin samples](image)

**Figure 1.** Derivatograms of skin samples, 1 - skin not treated with aminoaldehyde oligomers; processed: 2 - I; 3 - II, 4 - III; 5 - IV prototypes.

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For a 3-5 sample, the leathers treated with a urea formaldehyde-crotonaldehyde oligomer significantly increased the melting temperature of the polymers, the beginning for a 5-sample filled with a urea-formaldehyde - crotonic aldehyde oligomer with a modified acrylic acid - up to 110°C, a 4-carbamide-formaldehyde oligomer with a modified acrylic acid - to 105 acrylic acid.

It is known that moisture in micro capillaries of the skin is removed in the temperature range 120-150°C. Its content in the skin is determined by the nature of deposition and fixing of oligomers in the structure of the dermis. It also depends on the degree of fullness of the surface of structural elements. Thus, we can conclude that the modification of the urea-formaldehyde - crotonaldehyde oligomer with acrylic acid also contributes to an increase in the thermo oxidative degradation of the resulting products, that the modifier - acrylic acid is strongly chemically bound to amino aldehyde oligomers which leads to heat resistance of the samples.

The above is confirmed by the fact that filling micro capillaries of the skin with amino aldehyde oligomers reduces the number of pores in the skin. This is obviously due to the fact that with a noticeably large number of oligomers, which can be deposited in the interstructural spaces of the fibers.

As a result of additional filling of macro pores with particles of the amino aldehyde polymer after filling, they are apparently associated with the presence of amino aldehyde oligomers in the fibrous structure.
4. Conclusion
A result of thermographic studies of the process of skin degradation at elevated temperatures, treated with various amino aldehyde oligo (poly) measures, it was found that the bulk of the moisture in the watered skin is in macro- and microcapillaries. So it would be advisable to carry out the filling at the indicated levels of the structure of the samples. For this purpose, it is necessary to use such amine aldehyde oligomers for filling, which are well fixed in the skin and will give it full properties, as well as those deposited in the macropores of the skin.

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