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Development of thermostable polymers for repair of gas production complex equipment

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Abstract

Polymer materials with high temperature resistance have been developed to repair the equipment of the gas production complex. For their formation, epoxy dian oligomer DER-331, hardener triethylenetetramine TETA and multi-functional filler oxytetracycline with a dispersion of 5–10 μm at a content of q = 0.50–2.50 pts.wt. (per 100 pts.wt. of epoxy oligomer DER-331) were used. The thermal transformations of the developed polymers were studied by thermogravimetric analysis method (TGA) using the derivatograph Thermoscan-2. It is shown, that polymer materials containing the filler oxytetracycline ($C_{22}H_{24}N_2O_9$) at q = 1.00–1.50 pts.wt. are characterized by the following parameters: the maximum of the initial mass loss temperature T_0 = 608.9–609.5 K, the final mass loss temperature T_{final} = 740.0–743.9 K, relative mass loss ε_{rel} = 66.7–67.3. Complex assessment of thermal parameters using TGA-curves allows to ascertain the possibility of their use for the formation of coatings or adhesive materials up to a temperature of 609.5 K without changing their properties.

Keywords: dispersible filler, hardener triethylenetetramine, heat resistance, oligomer DER-331.

Today, a significant problem of the gas production complex is the restoration of damaged sections of pipelines. To solve this issue, adhesive materials based on reactive plastic polymers are used [1–3]. At the same time, for the formation of adhesive materials, low-molecular epoxy resins are used as a binder, in particular: ED-16, ED-20, ED-22 and their analogues. Their approval is carried out with the help of diethylenetriamine (DETA), triethylenetetraamine (TETA), polyethylene polyamine (PEPA), which allows to improve a set of properties, in particular, adhesive and cohesive strength [4–8]. Additional strengthening of such polymers is achieved by physical and chemical modification of the binder, which increases the service life of the equipment of the gas production complex at variable temperatures [9–13]. However, for filled polymer materials during the heating process the release of free radicals, which suspend the combustion process, is characteristic. At the same time, toxic substances (HBr, HCl), which negatively affect both working personnel and the environment as a whole, are released [14]. In this way, the study of the process of heat resistance allows to make conclusions about the rationality of using polymer materials in conditions of temperature changes, including an extreme rise in temperature. Therefore, when forming multifunctional polymers, it is important to ensure their thermal stability, which will allow the operation of new materials in different climatic conditions and temperature modes.

The purpose of the work is to determine the optimal content of dispersed filler in the epoxy binder when forming coatings with increased heat resistance indicators.

Materials and methodology of research

Epoxy oligomer DER-331 (CAS No. 25085-99-8) was used to form epoxy composite materials. Hardener triethylenetetramine TETA (CAS No. 112-24-3) was used to crosslink the epoxy composition.

Dispersed (5–10 μm) oxytetracycline ($C_{22}H_{24}N_2O_9$) was used as a filler. The additive is characterized by a wide range of properties, in particular biocidal properties. Oxytetracycline by its nature is a lipophilic substance and can easily penetrate through the cell membrane of bacterial microorganisms, which in turn leads to inhibition of the development of their population. Therefore, determining the rational content of such an additive will improve both the thermophysical characteristics of coatings and resistance to fouling. This, in turn, will allow to expand the scope of use of such polymers.

The coating formation technology was carried out in the defined sequence specified in the work [15].

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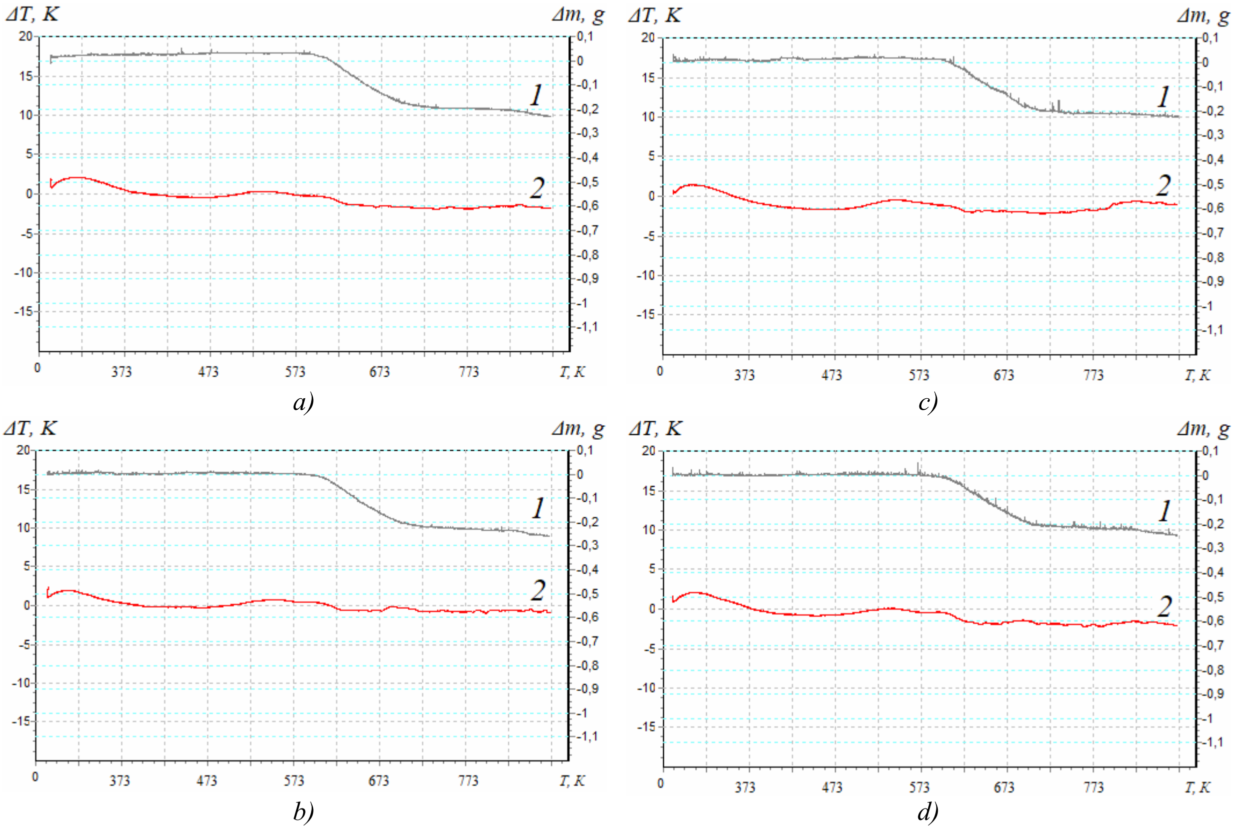

a – matrix (without filler); b – 0.50 pts.wt.; c – 1.00 pts.wt.; d – 2.00 pts.wt.

Figure 1 – Mass loss of polymer material filled with oxytetracycline with an interval of ΔT = 10 K in the temperature range T = 573–873 K

To study the effect of dispersed filler for the thermal transformation of composites, the method of thermogravimetric analysis (TGA) was used, using the derivatograph "Thermoscan-2". The research was conducted in the temperature range T = 298–873 K, using quartz crucibles for samples with a volume of V = 0.5 cm^3. During the study, the rate of temperature rise was υ = 5 K/min, while Al_2O_3 (m = 0.5 g) was used as a reference substance, the weighted test sample was m = 0.3 g. The temperature determination error was $\Delta T = \pm 1$ K. The accuracy of thermal effects determination was – 3 J/h. The accuracy of change in sample weight determination was Δm = 0.02 g.

Research results and their discussion

Studying the behavior of materials at elevated temperatures is an important aspect in the operation of polymer coatings. To study the thermal resistance of such coatings, thermogravimetric analysis (TGA) is carried out, which allows to evaluate the change in the mass of materials during heating, as well as to study the stages of thermal destruction, which are indicators of resistance to the influence of elevated temperatures. The thermal stability of reactive plastic polymer materials was studied in the temperature range T = 303–873 K. Therefore, according to the previous works [16, 17] by TGA-curves (Fig. 1), which are parallel to the ordinate axis, the mass loss of materials during increase in temperature (Table 1) was determined. The initial section of the TGA-curves (Fig. 1, *a–d*) characterizes the temperature interval at which structural transformations do not occur during heating. However, the presented graphs (Fig. 1, *a–d*) clearly show the deviation of the curve (from the horizontal straight segment), which is accompanied by the mass loss of the studied materials, that is, the moment of the beginning of the developed composites destruction. Based on the research results, it was established that there is no mass loss for polymer materials in the temperature range T = 303.0–589.1 K (Fig. 1, Table 1). At the same time, the lowest value of the temperature of the initial mass loss (T_0) is characterized by the epoxy matrix (unfilled polymer) – 589.3 K, which is associated with a significant amount of the sol fraction in the volume of the polymer. That is, such materials are characterized by the lowest heat resistance. Whereas, the beginning of the destructive processes of filled polymers occur at higher temperatures (Table 1), which indicates a change in the structure, and, therefore, a change in the thermophysical properties of the polymer.

It is shown (Table 1), that the introduction of dispersed filler up to q = 1.00–1.50 pts.wt. provides a linear increase in the value of the initial mass loss temperature. Exceeding the above-mentioned content of the additive in the epoxy binder ensures the reverse trend – a linear decrease in the initial temperature of mass loss (to the value of the matrix – T_0 = 585–589 K). It was believed that the shift of the initial mass loss

Table 1 – Heat resistance of composites filled with oxytetracycline

Oxytetracycline content q, pts.wt.	T_0, K	T_5, K	T_{10}, K	T_{20}, K	T_{final}, K	ε_{rel}, %
0	589.1	607.5	618.4	623.5	695.6	73.3
0.50	592.3	609.4	617.3	631.0	737.0	73.0
1.00	609.5	618.1	626.3	636.9	743.9	67.3
1.50	608.9	617.2	624.2	635.0	740.7	66.7
2.00	585.6	608.0	617.1	630.3	703.0	65.3
2.50	600.5	611.3	619.5	632.5	707.7	65.3

Note: T_0 – is the initial mass loss temperature (the beginning of the material destruction);
T_5, T_{10}, T_{20} – mass loss temperature (5 , 10 and 20 %);
T_{final} – final mass loss temperature (completion of material destruction);
ε_{rel} – relative mass loss.

temperature by 19.9 K to the high temperatures zone, with the optimal filler content (q = 1.00 pts.wt.), indicates a decrease in the oscillatory movements of polymer segments and macrochains due to the compaction of the structural net. At the same time, the analysis of the study results of the mass loss temperature at -5, 10 and 20 % allows to state the correlation of the study results. At the same time, although the final mass loss temperature does not carry practical information, that is, at such temperature range, the developed polymers do not work, but the maximum values of the final mass loss temperature T_{final} = 740.7–743.9 K and the minimum values of the relative mass loss ε_{rel} = 66.7–67.3 %, polymers are characterized, containing q = 1.00–1.50 pts.wt. of oxytetracycline.

Conclusions

By TGA methods it was established, that materials containing oxytetracycline with a content of q = 1.00–1.50 pts.wt. per 100 pts.wt. of epoxy oligomer DER-331 and 10 pts.wt. of triethylenetetramine TETA hardener, in the temperature range T = 589.1–743.9 K, lose mass in the range of ε_{rel} = 66.7–67.3 %. The obtained research results allow to state that such materials are characterized by improved heat resistance and are suitable for the formation of coatings or adhesive materials capable to work up to a temperature of 609.5 K without changing their properties.

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Розроблення термостабільних полімерів для ремонту устаткування газовидобувного комплексу

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Для ремонту устаткування газовидобувного комплексу розроблено полімерні матеріали з високими показниками термостійкості. Для їх формування використано епоксидний діановий олігомер марки DER-331, твердник триетилентетрамін ТЕТА і багатофункціональний наповнювач окситетрациклін дисперсністю 5–10 мкм за вмісту q = 0.50–2.50 мас.ч. (на 100 мас.ч. епоксидного олігомеру DER-331). Термічні перетворення розроблених полімерів досліджували методом термогравіметричного аналізу (ТГА) із використанням дериватографа «Thermoscan-2». Показано, що полімерні матеріали із вмістом наповнювача окситетрациклін ($C_{22}H_{24}N_2O_9$) при q = 1.00–1.50 мас.ч. характеризуються такими параметрами: максимальне значення температури початку втрати маси T_0 = 608.9–609.5 K, кінцева температура втрати маси T_{final} = 740.0–743.9 K, відносна втрата маси ε_{rel} = 66.7–67.3. Комплексна оцінка термічних параметрів за допомогою ТГА-кривих дозволяє констатувати можливість їх використання для формування покриттів або клейових матеріалів до температури 609.5 K без зміни своїх властивостей.

Ключові слова: дисперсний наповнювач, олігомер DER-331, твердник триетилентетрамін, термостійкість.