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CHAPTER 4

THERMODYNAMIC ASSESSMENT OF THE POSSIBILITY OF USING POLYMERIC MATERIALS IN PROMISING LAUNCH VEHICLES

ABSTRACT

One of the ways to reduce the cost of space launches for the operational launch of constellations of satellites into the Earth's orbit is the creation of targeted launch vehicles based on light and ultralight class rockets. The solution to this problem lies, among other things, in the area of development and application of new structural materials. The presented work considers the possibility of using polymers on the one hand as a structural material for creating the hulls of launch vehicles, and on the other hand as solid fuel for rocket engines. Research is related to the development of a new type of ultralight launch vehicles: combustible or autophage launch vehicles. A short historical excursion into the problem of creating polymer launch vehicles is given. The authors summarized the experience of their own research on the use of polymer materials for the creation of combustible rockets. The thermophysical and mechanical characteristics of various types of polymers were analyzed from the point of view of the possibility of their use as structural materials for the hulls of ultralight missile carriers.

The results of theoretical and experimental studies of thermal destruction of polymer materials under aerodynamic heating conditions are presented. It is shown that polymer materials, in particular polyethylene, under certain conditions, can be used to make fuel tanks for solid-fuel rockets that use a new principle of burning the structure during flight.

The development of such launch vehicles and the commercialization of scientific research in this area will allow domestic companies in the aerospace industry to occupy a niche in the market for launching small satellites.

KEYWORDS

Combustible rockets, polymer bodies, polymer fuel, aerodynamic heating, thermodynamic analysis.

Today, there is a situation where the needs and possibilities of manufacturing small satellites several times exceed the possibilities of their launch [1]. The issue of reducing the cost of putting small satellites into orbit is urgent. The specific cost (USD/kg of payload) of launching such satellites by special small LVs is several times higher than that of large LVs and can reach tens, and sometimes even hundreds of thousands of dollars. for 1 kg of payload due to the scale factor. The absolute cost of launching modern small LV exceeds 10 million USD, which is not always acceptable for the main potential users of small satellites. The main means of delivering small satellites to LEO are still heavy rocket carriers designed to transport payloads weighing thousands of kilograms. Such an approach does not always meet modern requirements, in particular from the point of view of prompt delivery of cargo, and launch vehicles have a high price. The analysis of existing and prospective launch vehicles shows that there is now a tendency to enter the market of new light and ultra-light launch vehicles [2].

However, these small launch vehicles have the same complexity as large launch vehicles and require significant development costs, resulting in a high unit price. Thus, to meet the start-up needs, it is necessary to significantly reduce the specific output cost (in the case of using small LVs – the start-up cost, which is also determined by the specific cost of outputting the maximum payload).

Therefore, a new paradigm for the development of space launch systems is emerging, which requires a clear economic justification. Transportation costs should be lower than existing systems, and development costs should be minimized using modern design principles [3, 4].

In general, from a technical point of view, the problem of developing new means that could reduce the specific cost comprehensively in all 4 directions indicated above is relevant. Such TSSs should have low sensitivity to the scale factor, i.e. should be efficient for launching small payloads. A review of the current state of development, which was conducted by NASA experts [5], shows that the demand for small and cheap TSS has a constant tendency to increase in the coming years. At the same time, it is not excluded that the increase in the number of launches may contribute to the interest in the use of heavy LVs.

But today, launching a satellite using a specially designed launch vehicle is very expensive. Most often, satellites are transported as joint cargo by large LVs, which do not always allow saving money. In addition, finding a joint launch opportunity is difficult, and coordinating it with the microsatellite operator's schedule is even more difficult. The costs associated with a co-launch increase as it waits. It should also be noted that a small satellite often needs its own special orbit, different from the orbit of the main payload of the common LV.

Therefore, the growing needs on the one hand, and fierce competition on the other, force the developers of aerospace equipment to look for new technical solutions.

One of the ways to reduce the cost of launches is the use of new construction materials, which makes it possible to advance in all the mentioned directions at the same time. As such materials, it is suggested to consider polymers, in particular polyethylene, polypropylene, etc. Polymers are used in rocket technology as part of composite materials of individual structural elements or thermal protection [6]. The properties of polymers: low cost, low weight, low thermal conductivity, as well as high energy characteristics, create the basis for their use as the main structural material for creating the missile body. At the same time, the polymer shell itself can be used as a solid fuel [7].

Although there are currently no known realized projects of rockets with combustion or discrete ejection of the tank shell, there are numerous proposals from the time of the pioneers of rocket technology to the present day.

The idea of using structural elements as fuel has been known for a long time. In 1929, Yurii Kondratiuk proposed to reduce the influence of the mass of the structure on the energy characteristics of the rocket. According to the idea, after the multi-stage rocket reaches the state of the Earth's satellite in outer space, it is necessary to disassemble the spent stages. These stages were proposed to be remelted with the help of "some additional devices" and used as fuel for interplanetary flights [8]. He also proposed the use of solid fuel (hydrogen), which is first gasified before being fed into the engine, and then fed using injectors.

The theoretical and practical development in this field was made by Friedrich Zander, who was a supporter of burning not only purely rocket structures (for example, suspended tanks), but also aviation elements intended for the atmospheric part of the flight – wings, motors, propellers, etc. [9]. He formulated the basic requirements for metals from which it is possible to make combustible elements. The use of plastics with a metal filler as materials for such elements was also proposed. In addition, Friedrich Zander was the first to propose the idea of a rocket plane that should burn itself. He outlined the main units necessary for melting and supplying solid fuel – this is a "melting boiler" with a "furnace"; an injector that feeds the melt into the combustion chamber with the help of a gaseous oxidizer; heated pipelines for transporting molten fuel, etc. Friedrich Zander conducted numerous experiments on the manufacture and testing of light alloys for flammability [10].

It should be noted that Friedrich Zander and Yurii Kondratiuk considered the structural elements considered only as an auxiliary component to the main liquid fuel. The opinion about the expediency of burning spent rocket parts is also present in the well-known work of Ary Sternfeld [11], although the author did not provide specific proposals for its implementation.

Walter Hohmann proposed a spaceship project that resembled a high-rise architectural structure and was to be built entirely of solid fuel [12]. Therefore, such a ship had to constantly shrink during the flight. The generator of its body is an exponential curve, and combustion could only occur from the end. Thanks to this, the flight should take place with constant acceleration. The disadvantage of this scheme is the lack of a combustion chamber, which would not allow to achieve the required specific impulse.

The above-mentioned works were rather theoretical reflections of the pioneers of cosmonautics. Real proposals for this kind of rocket technology appeared in the second half of the 20th century in the form of patents.

It is clear that the creation of a rocket with a burnt shell of a fuel tank requires the development of a new type of engine and other original units. The task of discarding the tank shells as they are emptied of fuel seems easier, since it can be solved based on the use of rocket engines that already exist. The logical development of the concept of a transport space system with disposable fuel tanks and reusable engine installations and other expensive elements seems to be the idea of discarding fuel tanks in parts, as they are emptied of fuel. This approach theoretically makes it possible to reduce the energy costs for accelerating those parts of the tanks, the fuel from which has already been spent. There are known patents for proposals for such rockets that continuously eject fuel tanks [13, 14].

The idea of burning spent LV elements also attracted the attention of designers. In one of the projects, it is proposed to use the engine torch to burn the emptied parts of the tank shell and to use elastic elements to supply fuel to the engine. Pyrotechnic means were used to discretely throw off the stabilizers [15].

The patent [16] claims a rocket with the combustion of a fuel tank shell consisting of solid fuel. The authors of another patent [17] proposed to burn the composite shell of the fuel tank with flares of rocket engines and using injectors for air supply. The authors called their rocket autophagic.

The authors [17] suggested using autophage launch vehicles for the purpose of cleaning the outer space. At the same time, the use of autophage launch vehicles has a number of advantages, including the absence of a dry tank, which occupies approximately half of the total dry mass of a modern launch vehicle. According to the authors [17], such a rocket can be developed as extremely cost-effective for picosatellites or as a vehicle for launching space debris removal devices into orbit.

The work [18] presents the design and results of experimental studies of a solid-fuel autophage rocket engine with forced fuel supply to the combustion chamber, similar to a liquid engine. An engine of this design (**Fig. 4.1**) can be considered as a suitable solution for use on small spaceships, when conventional fuel storage and supply systems become unacceptably heavy and/or expensive for the following reasons.

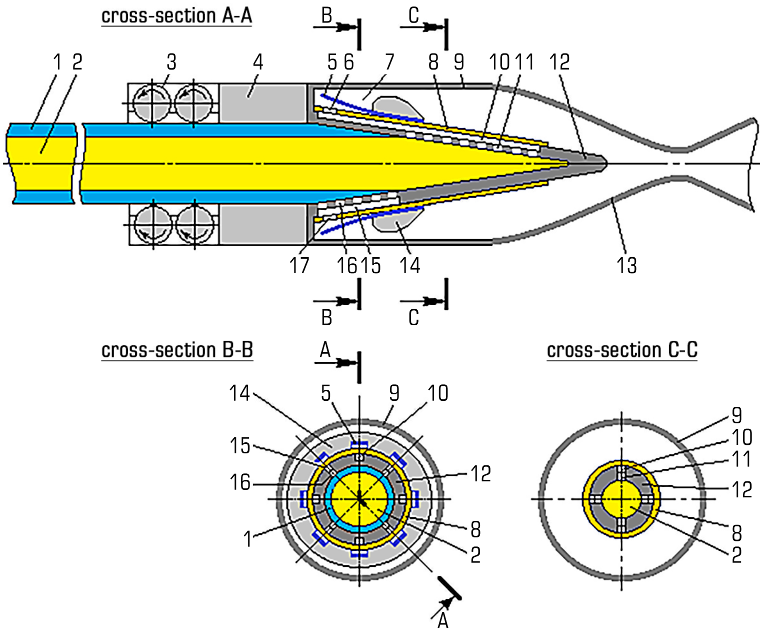
First, the polymer fuel charge forms a tubular structure that serves as a reservoir for the oxidizer. Therefore, there are no special designs and mass losses for fuel storage.

Second, fuel delivery devices in autophage engines can be lighter than modern pressure or pump delivery systems. This is achieved by pulsating combustion. The drive rod is fed into the engine by a small pressure between pulses when the chamber pressure is at a minimum. It is similar to the well-known air impulse engines. Feeding can be done, for example, by means of feed mechanism wheels driven by small electric motors, while the expected chamber pressure between pulses is several hundreds of kPa.

The third reason is safe handling of practically separated solid fuel components: solid polymer fuel (such as polypropylene or ethylene) and solid oxidizer (such as ammonium perchlorate) are not mixed before entering the combustion chamber.

During the engine operation, with the help of the supply mechanism, the fuel rod enters the evaporator through the obturator to convert it into gases. Separated streams of oxidizer and fuel gas pass through collection holes, channels, nozzles and dampers into the combustion chamber. During combustion, the evaporator heats up and gasifies the next portion of fuel. The valves interrupt combustion to facilitate delivery at times when the pressure in the combustion chamber drops.

Compared to modern pressure or turbopump power systems, the masses of forced power systems for autophage pulse engines are acceptable for small spacecraft [19–21], but are clearly too heavy for launch vehicles. At the same time, the concept of burned fuel tanks is promising for launch vehicles, which has been waiting for the development of new technologies for several decades. Therefore, the study of an alternative way of powering the autophage engine is a subject of considerable interest.



1 – solid polymer fuel pipe;
2 – solid oxidizer;
3 – feed mechanism;
4 – obturator;
5 – butterfly valve;
6 – gasified oxidizer injector;
7 – mixing zone;
8 – heat exchange cover;
9 – combustion chamber;
10 – oxidizer collection channel;
11 – hole for collecting oxidizer;
12 – evaporator;
13 – nozzle;
14 – valve holder;
15 – fuel collection channel;
16 – holes for collecting fuel;
17 – gasified fuel nozzle

Fig. 4.1 A variant of the autophage engine with forced feeding

It is impossible to manufacture structural elements from modern fuels – both liquid and solid – therefore one of the tasks of implementing the idea of a burnt rocket is the selection of materials that would combine sufficient strength, manufacturability and processing with high heat-generating capacity, low temperature and heat of fusion or sublimation etc. According to the authors [22], it is possible to use materials proposed for hybrid engines, namely: metals, metal hydrides, and solid hydrocarbons, for the tank shells of burnt rockets.

Metals have long been widely used as rocket fuel [23, 24]. For example, adding powdered metals to liquid fuel increases its heat-generating capacity, since metal combustion products have lower formation enthalpies than hydrocarbon combustion products (**Table 4.1**) [22].

Table 4.1 Enthalpy of the formation of some combustion products

Fuel	**Product of combustion, phase**	**Enthalpy of formation (ΔH°298), kJ/kg**
C	CO_2, gas	–8 941
H	H_2O, gas	–13 423
Mg	MgO, condensate	–14 924
Al	Al_2O_3, condensate	–16 435
B	B_2O_3, condensate	–18 293
Li	Li_2O, condensate	–20 008
Be	BeO, condensate	–24 365

Thanks to this, the heat-generating capacity of the fuel increases, that is, the difference between the enthalpies of 1 kg of fuel $\left(\Delta H^0_{298}\right)$ and 1 kg of combustion products at the exit from the nozzle $\left(\Delta H^{ex}_{\Sigma}\right)$, and, accordingly, the speed of combustion products outflow from the nozzle (w) increases according to the following ratio:

$$w = \sqrt{2\left(H^0_{298} - H^{ex}_{\Sigma}\right)}.$$

However, burning only metals is not advisable, since the high heat-generating capacity leads to high temperatures in the combustion chamber and, as a result, to an unacceptably high energy consumption of combustion products for their dissociation.

The highest values of the most important characteristic of rocket fuel – the specific impulse of thrust (I_{spec}) are achieved if hydrogen is present in the fuel in addition to metal and oxidizer.

At the same time, the oxidant is spent on stoichiometric burning of the metal, and hydrogen is added to achieve the maximum specific impulse [22]. Interest in such compounds as beryllium hydride, aluminum hydrides, borohydrides, etc. is explained by the decrease in molecular weight and, accordingly, the increase in the mass heat capacity of combustion products due to the increase in the amount of light hydrogen in them. It is likely that some hydrides can be made into a tank shell and fed to the combustion chamber after melting or gasification due to thermal destruction. But, according to the authors, first of all, it is necessary to study the mechanical and physical characteristics of potential materials.

The most available and appropriate materials today can be solid hydrocarbon polymers, such as, for example, polyethylene, polypropylene, polystyrene, etc. Their chemical composition is close to the composition of typical hydrocarbon fuel, they are strong enough to make structural elements from them, they melt and gasify easily, which simplifies the installation of supply systems.

Liquids common in rocket technology such as nitrogen tetroxide and hydrogen peroxide can be used as oxidants. By far, the best non-toxic oxidant is liquid oxygen. However, almost all hydrocarbon polymers have a glass transition temperature much higher than the freezing point of liquid oxygen (–222.65 °C), therefore, their field of application is limited only to oxidants with high boiling points. It is known that high-strength ultra-high-molecular low-pressure polyethylene (for example, brands 21506-000 with a molecular weight above 10^6) can be used in a wide range of operating temperatures: from –200 to 130 °C [22]. In addition, ultrahigh molecular weight polyethylene has fairly high strength characteristics, a low coefficient of friction, high resistance to aggressive environments, and high impact toughness [25–28].

An additional argument in favor of the choice of hydrocarbon polymers is the possibility of using them together with powdered metal-containing fillers, which will allow both to avoid the problems associated with the use of metal or hydride tanks, and to improve the energy characteristics of the fuel. It is known that in some solid fuels the aluminum powder content is 15–20 % (by mass), which allows to increase the consumption by 10–15 % [22]. But the use of metals in liquid fuels is complicated by the problems of its storage and supply to the combustion chamber.

The introduction of nanodisperse fillers leads to a change in the structure of the polymer matrix, and therefore to a significant improvement in operational properties. Nanosized particles of the modifier are evenly distributed in the mass of the polymer and ensure its structuring due to the active surface of the nanoparticles. It has been established that the introduction of 2 % (wt.) aluminum-containing filler to ultrahigh molecular weight polyethylene leads to an increase in tensile strength by up to 30 %, wear resistance by an order of magnitude while maintaining relative elongation during stretching and reducing the coefficient of friction and temperature in the contact zone. At the same time, filler particles behave as artificial nuclei of structuring, which contributes to the formation of a more organized and ordered supramolecular structure [22, 29–32].

Combustible rockets, in which a metal-containing powdered filler is introduced into the polymer base during the production of the tank shell, will solve the problem of storing metal-containing fuels. In addition, the polymer base, firstly, will protect hygroscopic and highly reactive hydrides from environmental influences; secondly, the high viscosity of the molten polymer will prevent the fuel stratification in the melting chamber and supply lines (if part of the polymer is not gasified, but only melted in order to supply the fuel in the form of a suspension or colloidal solution) [22].

Thus, solid hydrocarbon polymers are a promising material for the manufacture of rocket shells. Special attention should be paid to ultra-high molecular weight polyethylene due to its high energy efficiency, environmental safety and sufficient strength for tank shell constructions.

From the theory of solid rocket fuels, it is known that to increase I_{spec} it is advisable to add such metals as Li, Be, Mg, Al in the form of simple substances or as part of compounds to solid hydrocarbon fuel. It can be assumed that in the engine chamber they are immediately completely oxidized with the formation of oxides Li_2O, BeO, MgO, Al_2O_3. For these oxides, sublimation or evaporation reactions with the formation of gas of the same chemical composition as the original substance, or with decomposition into monoatomic gases in the temperature range of rocket engines, are characterized by very low values of equilibrium constants, that is, very low saturated vapor pressures. Therefore, it is assumed that the above-mentioned oxides, after their formation, almost immediately completely pass into the condensed state and remain in it throughout the process in the combustion chamber and nozzle. For this reason, any reactions involving Li, Be, Mg, Al or their compounds were not taken into account, excluding complete oxidation and condensation, since it was considered that the transition of these substances into a gaseous state is necessary for the reaction to proceed.

It can be assumed that the oxides Li_2O, BeO, MgO, Al_2O_3 are in a condensed state in the form of simple substances without the formation of solutions, that is, if the combustion products contain oxides of several metals, then each of them forms a separate phase.

The authors [22] carried out I_{spec} calculations for two types of fuels – cryogenic and high-boiling – in which polyethylene was chosen as fuel, and oxygen and hydrogen peroxide were chosen as oxidants. The ratio of components was assumed to be stoichiometric. The pressure in the combustion chamber and at the nozzle section was 25.3 and 0.02 MPa, respectively. As fillers, in addition to the above metals, their hydrides were considered: LiH, MgH_2, $LiAlH_4$, $Mg(AlH_4)_2$. Under the conditions of speed and temperature equilibrium of heterogeneous combustion products, I_{spec} values were calculated, shown in the Figure as a I_{spec} dependence on the mass fraction of the filler in the fuel (η). For the convenience of determining the increase in the specific impulse I_{spec}, a percentage scale is given.

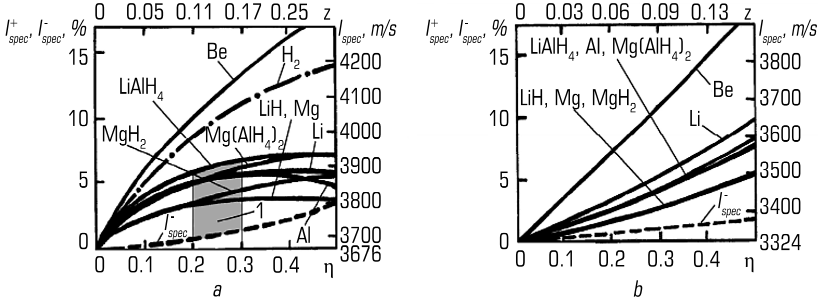


Fig. 4.2 The theoretical specific thrust impulse I_{spec}, its increase I^+_{spec} and decrease I^-_{spec} vs. the filler (η) and condensate mass content (z) in combustion products: *a* – for polyethylene – oxygen propellant; *b* – for polyethylene – hydrogen peroxide (98 %) propellant; 1 – max ($I^+_{spec} - I^-_{spec}$) area

From the given dependence, it is obvious that the fillers have a significant effect on the I_{spec}. The authors of [22] assume that a combustible rocket can be implemented with a filler content of

$\eta \approx 0.2$–0.3 (at such and lower values, the delivery system will still have satisfactory characteristics, and with a higher filler content of η it will be unacceptably complicated), then the given increase in the value of I_{spec} by 5–7 % in the first case and by 3–5 % in the second case is noteworthy, since each additional percentage of I_{spec} will correspond to approximately 4–6 % payload gain in low Earth orbit.

At the same time, it should be noted that the use of thermoplastic polymers as structural materials requires an assessment of thermal and heat resistance in conditions of thermal loads due to aerodynamic heating. It is known that the problem of thermal destruction of traditional structural materials (metals) during launch and passing through the atmosphere is not critical today. At the same time, the strength characteristics of polymers depend significantly on temperature, which requires careful study of the processes of thermal degradation of the material in the atmospheric area.

4.1 EXPERIMENTAL STUDIES OF THERMODYNAMIC PROCESSES DURING THE THERMAL DESTRUCTION OF POLYMERIC MATERIALS

4.1.1 ANALYSIS OF THE PHYSICOCHEMICAL PROPERTIES OF POLYMERIC MATERIALS AS STRUCTURAL MATERIALS OF ULTRALIGHT LV

It is known that the use of polymers of petrochemical origin as fuel is possible due to the high calorific value of such substances [33]. Currently, many technologies have been developed to convert polymers, in particular polyethylene, both low and high density, into liquid fuel [34]. The liquid fuel obtained in this way is quite suitable, for example, for use as diesel fuel [35].

The use of high-density polyethylene as one of the fuel components for hybrid rocket engines is considered in works [36, 37]. The paper [38] analyzed the environmental aspects of polymer fuels when used in rocket engines. The possibility of using polyethylene as rocket fuel or a component of rocket fuel is shown in particular in works [39, 40]. The peculiarity of using polyethylene as a solid rocket fuel is the need for gasification before burning in the combustion chamber. For this, a special gasification chamber is provided in the design of the corresponding engine, the temperature of which reaches 450–550 °C [40]. Gasification of both fuel and oxidizer occurs under the influence of high temperatures. The efficiency of the engine depends on the course of thermodynamic processes in the working chambers of the engine, which requires appropriate research. The study of the physical picture of the processes that occur during the gasification of solid polyethylene under the influence of high temperatures, and the quantitative determination of the thermal effects that occur during the thermal destruction of polyethylene are important for building a mathematical model and determining the optimal parameters of the engine on polymer fuel.

On the other hand, the results of such research are of interest for assessing the possibility of using polyethylene as a structural material for launch vehicle bodies. It should be noted that during the LV launch in the atmosphere there is aerodynamic heating of the surface, which is not a significant problem in the ascending section when using traditional structural materials for the manufacture of bodie (aluminum alloys). In the case of using polymers as structural materials, the stability of the LV polymer body will be determined by the heat resistance of the corresponding material. Therefore, it is necessary to evaluate the effect of thermal loads on the LV lateral surface.

Among plastics produced in the world, polyethylene (PE) and materials based on it account for approximately 35 % [41]. PE is one of the largest polymers by volume of production (84 million tons/year). The great demand for polyethylene is explained by the combination of a fairly low cost, a large volume of production enterprises, a diverse field of its use, and the variability of possible physical properties. The physical properties of polyethylene can be influenced by changing its density, structure, molecular weight, molecular weight distribution, etc. Accordingly, the field of use of polyethylene is very wide – from low-molecular adhesives, films with a thickness of 3–5 microns to high-strength pipes with a diameter of up to 1500 mm. Fibers with a modulus of elasticity up to 250 GPa are also obtained on the PE basis [41].

Traditional for industry are high pressure polyethylene (LDPE), low pressure polyethylene (HDPE) and medium pressure polyethylene (MDPE). Depending on the properties and purpose, different brands of polyethylene are produced, which differ in the degree of branching of the chain, degree of crystallinity, density and other indicators.

A feature of high-pressure polyethylene (LDPE) is the branching of the polymer chain, which is the reason for the formation of a loose, partially crystalline structure, and therefore a decrease in the density of the polymer and its physical and mechanical characteristics.

Low-pressure polyethylene (HDPE) is characterized by a linear structure and belongs to polymers capable of crystallization. The content of the crystalline phase of HDPE reaches 80 %. Density and other characteristics for HDPE are significantly higher than for LDPE. In terms of deformation-strength properties, HDPE is close to structural plastics. The introduction of reinforcing fibrous fillers into HDPE allows the use of this material for the manufacture of products of responsible purpose [41].

In addition to the main polyethylenes, ultra-high molecular weight polyethylene (UHMWPE), linear low-density polyethylene, high molecular weight high density polyethylene and a number of other brands are also produced [41]. Ultra-high molecular weight polyethylene (UHMWPE) is a linear polyethylene with a molecular weight in the range of 3,000,000 to 6,000,000, widely used in body armor, automotive, and aerospace industries [42, 43].

One of the most widespread and versatile polymers is polypropylene (PP), which due to its properties belongs to construction materials and is used for the production of structural products, pressure pipes, rigid films, household products, etc. PP, like HDPE, belongs to polymers capable of crystallization. The content of the crystalline phase is 73–75 %. PE, PP belong to non-polar polymers, they dissolve only at elevated temperatures in strong solvents (chlorinated, aromatic hydrocarbons), resistant to the action of acids and alkalis [41].

The main physical and mechanical properties of thermoplastic polymers, which are important from the point of view of the problem, are considered in [44].

To assess the practical suitability of polymeric materials, their mechanical properties are of primary importance. The physical and mechanical properties of PE and PP depend on the molecular weight of polymers, the structure of polymer chains, and their flexibility. At the same time, the properties of polyethylenes can differ significantly depending on the parameters of their production process and the selected catalytic system [41]. If the polymerization of ethylene takes place in the presence of radical initiators under conditions of high pressure and temperature, LDPE with a large number of side chains is obtained. HDPE, which is obtained by coordination-ion polymerization in the presence of Ziegler-Natta catalysts, has fewer side chains, its macromolecules are linear. This difference accounts for the higher density, strength and rigidity of HDPE, but at the same time it somewhat limits its use in cases where increased flexibility and impact toughness are required. An increase in impact strength and flexibility is achieved by introducing short side chains to macromolecules, which is possible due to the copolymerization of ethylene with other olefins.

The highest mechanical characteristics are typical for polymers of a linear structure. The strength of branched polymers depends on the degree and type of branching, and the physical and mechanical properties of network polymers depend on the number of intermolecular chemical bonds (crosslinks). With an increase in intermolecular bonds, the hardness and modulus of elasticity increase, and the relative deformation decreases [45].

The most important mechanical parameters from the point of view of the practical application of polymer materials are the modulus of elasticity, relative elongation and tensile strength. The main physical and mechanical properties of polyethylene and polypropylene are listed in **Table 4.2** [46].

The authors [47] investigated the physical and mechanical properties of pure PP (with a degree of crystallinity of 51 %) and HDPE (with a degree of crystallinity of 68 %), which demonstrated that the strength and modulus of elasticity of PP are higher than HDPE. The authors explain this by the fact that PP has a CH_3 group bound to the carbon atom, which prevents chain rotation and makes the material stronger, but inflexible. Compression, bending tests have shown that PP exhibits higher resistance to compressive forces than HDPE. The disadvantage of PP compared to HDPE is less resistance to dynamic loading. The presence of a crystalline phase allows polyethylene to maintain its mechanical strength in a wide range of temperatures.

The authors of [41, 46] note that at elevated temperatures there is a significant difference in the behavior of LDPE and HDPE. At a temperature of –60 °C, the tensile stress for HDPE is 1.25 times higher, and at 100 °C, it is approximately 4 times higher. Up to 20 °C, the relative elongation for LDPE is higher than for HDPE, but when the temperature rises above 40 °C, a decrease in relative elongation with increasing temperature is observed, unlike HDPE. The yield strength, modulus of elasticity, density of PE are determined by its composition. The difference in the value of the modulus of elasticity during bending for LDPE, HDPE increases with increasing temperature. Heat resistance increases with increasing degree of crystallinity in the series LDPE < MDPE < HDPE.

Table 4.2 Physical and mechanical properties of polyethylene and polypropylene

Physico-mechanical properties	LDPE	HDPE	UHMWPE	PE-X	PP	PP (iso)	PP (syndio)
Crystallinity, %	28.8–60	60–90	41.2–91.1	22–41	3.2–67	29–75	25–63
Density at 20 °C, kg/m^3	915–929	940–965	930–940	900–1010	840–1330	900–910	880–930
Tensile strength, MPa	10–31.8	13–51	21–50.2	9–26	26–32	30	15.2–25.2
Tensile modulus, MPa	130–348	500–1100	680–860	–	1700	825	483
Tensile stress at yield, MPa	10.8–14.1	21.4–31	17–41	–	31–35.2	33–36	–
Elongation, %	130–780	250–1200	250–600	350–600	10–140	90–500	250–300
Tensile yield strain, %	–	8.7–15	11–20	–	7–12	10–12	10–11
Flexural strength, MPa	7.5	–	20–26.5	–	41	38.9	–
Flexural modulus, MPa	230–495	750–1600	440–1340	–	1240–1600	1150–1570	345
Elastic modulus, MPa	–	700–1000	700–800	–	–	2357–3450	–
Young's modulus, MPa	–	800–1005	1800–3300	–	1200–2000	–	–
Compressive strength, MPa	–	20	23	–	40	–	–

The mechanical properties of polypropylene are determined by its structure. The atactic fraction has the properties of amorphous liquid polymers, the isotactic fraction has the properties of highly crystalline polymers. Industrial polypropylene consists mainly of isotactic macromolecules, which is why its high mechanical characteristics are determined.

Thermophysical and thermal properties

Similar to mechanical properties, the ability of polymer materials to undergo temperature deformation is determined by the chemical structure, physical organization of polymers, morphology of their supramolecular structure, type of intermolecular bonds, etc. Research has established that the lower the physical and mechanical properties of thermoplastic, the more sensitive it is to temperature changes. For example, PP loses approximately 25 % of its standard bending strength when heated to 80 °C, and HDPE at 60 °C loses half of its initial strength [41, 46].

The chemical structure of the molecules determines the values of the softening and melting temperatures, the rate of transition from the crystalline state to the amorphous state. HDPE softens under load at 70–75 °C and melts at 128 °C. LDPE, which has a lower degree of crystallinity, softens at 65 °C and melts at 105–110 °C. Changing the chemical structure of polyolefin by replacing one hydrogen atom with a CH_3 group (PP) leads to an increase in softening and melting temperatures.

In order to determine the practical value of polymeric materials, it is necessary to know their thermophysical characteristics. The physical structure of the polymer significantly affects the coefficient of thermal expansion. When amorphous polymers are heated, the volume of the material increases in proportion to the temperature, but the speed of this process is determined by the physical state of the object. When a certain temperature is reached, thermal expansion increases. For crystalline polymers, at the temperature of crystallization, there is a jump-like increase in the rate of thermal expansion at a higher temperature. During the heating of partially crystallized polymers, the features of the amorphous and crystalline components are successively revealed [41, 46]. Temperature characteristics are given in **Table 4.3** [46].

The transfer of thermal energy by the polymer occurs due to the thermal fluctuations of the kinetic fragments of macromolecules. Therefore, the thermal conductivity of amorphous and partially crystalline thermoplastics changes differently depending on the temperature. For amorphous thermoplastics, when approaching the glass transition temperature, the value of the thermal conductivity coefficient increases slightly due to the increase in the vibrational activity of fragments of macromolecules. With a further increase in temperature, their thermal conductivity decreases due to a sharp increase in kinetic volume, activation of low-frequency oscillations of large fragments. For partially crystalline polymers, an increase in temperature is accompanied by a weakening of the intermolecular interaction due to an increase in the distance between neighboring macromolecules. A significant part of the thermal energy is spent on structural changes, which is the reason for the decrease in the coefficient of thermal conductivity. For example, after melting and transition of PE into an amorphous state, its thermal conductivity increases [41, 46].

The distribution of heat by the mass of the heated polymer depends on the activity of the kinetic fragments of the macrochains. Therefore, for example, the transition from a glassy physical state to a highly elastic one is accompanied by an increase in the amplitude and frequency of oscillatory and rotational movements and an increase in heat capacity. For partially crystalline polymers, the increase in heat capacity is associated with melting temperatures. For LDPE, the amplitude of the heat capacity peak, depending on the temperature, is at 105–110 °C. In general, when transitioning from a highly elastic to a viscous state, the heat capacity of polymers increases [41, 46].

The authors [47] note that PP exhibits higher thermal properties than HDPE. PP also exhibits higher thermal dimensional stability than HDPE, as PP has stronger inter-macromolecular interactions than HDPE. The coefficient of thermal expansion of HDPE is higher than that of PP due to stronger intermolecular interactions.

UHMWPE has high mechanical properties, for example, the yield strength of UHMWPE (Dyneema) is 2.4 GPa, but the specific gravity is very low at 0.97, which is the reason for the high strength-to-weight ratio of this grade of UHMWPE compared to carbon steel. One of the important disadvantages of UHMWPE is poor temperature stability due to the weak bonding between UHMWPE molecules. When a certain temperature is reached, a local thermal excitation occurs at the bonds between molecules, which causes the bonds to break and the long chain to break into short parts [48]. According to the authors of this work, the melting point of UHMWPE (Dyneema) is in the range of 130–136 °C, and the working temperature is about 80–100 °C. However, the authors of [42] stated that the physical and mechanical properties of UHMWPE-based products depend on the parameters of pressing during their manufacture, namely the temperature and compression pressure, cooling rate, etc.

Table 4.3 Thermophysical and thermal properties of polyethylene and polypropylene

Thermophysical properties	**LDPE**	**HDPE**	**UHMWPE**	**PE-X**	**PP**	**PP (iso)**	**PP (syndio)**
Melting temperature, °C	105–115	125–135	133–140	110	120–176	157–171	117–156
Glass transition temperature, °C	–103 to –133	–118 to –133	–110	–	–8 to –51	–10	–15 to +3
Brittleness temperature, °C	–34 to –60	–20 to –76	–70 to –84	-76	–	–	–
Long term service temperature, °C	70	–50 to +82	82	130	–	–	–
Decomposition temperature, °C	–	>250	–	255–285	328	240	260
Thermal conductivity (melt), W/(m·K)	0.55	0.52–0.55	0.39–0.42	–	0.17–0.22	0.12–0.22	–
Specific heat capacity, J/(K kg)	–	2100–2900	1840–2010	–	–	2500–3400	–
Vicat temperature VST/A/50, °C	76–109	122–129	126	–	138–155	150–155	111
Ignition temperature, °C	340–343	340–343	340–343	–	>200	>200	>200
Autoignition temperature, °C	350	350	350	260–320	570	570	570
Heat of combustion, J/g	47740	47740	47740	–	45800	45800	45800
Volatile products of combustion	CO, CO_2, aldehydes, benzene	CO, CO_2, aldehydes, benzene	CO, CO_2, aldehydes, benzene	CO, CO_2, aldehydes, NOx	CO, CO_2, soot	CO, CO_2, soot	CO, CO_2, soot

In work [42], the thermal decomposition of UHMWPE samples produced by pressing from UHMWPE powder with a density of 940 kg/m^3 from the Sigma company was investigated using thermogravimetric analysis in the temperature range of 50–600 °C at a heating rate of 5 °C/min in a nitrogen environment Sigma-Aldrich Co (USA). It was established that the UHMWPE sample produced at a compression temperature of 100 °C and a pressure of 10 MPa remains stable in the temperature range of 50–216 °C, no loss of sample mass is observed. The maximum thermal decomposition is observed in the range of 216–526 °C.

The authors [49, 50] investigated the effect of temperature on mechanical parameters for Marlex 5003 polyethylene with a density of 965 kg/m^3 and polypropylene with a density of 909 kg/m^3. The study was carried out at an increase in temperature from 21 to 117 °C for polyethylene and from 22 to 143 °C for polypropylene under conditions of uniaxial tension up to the yield point. Using the methods of differential scanning calorimetry (DSC), it was determined that the melting point of HDPE is 140 °C, and the melting point of PP is 164 °C. For both polymers, it was established that the dependence of the change in yield strength on temperature is almost linear (**Fig. 4.3**) [49, 50].

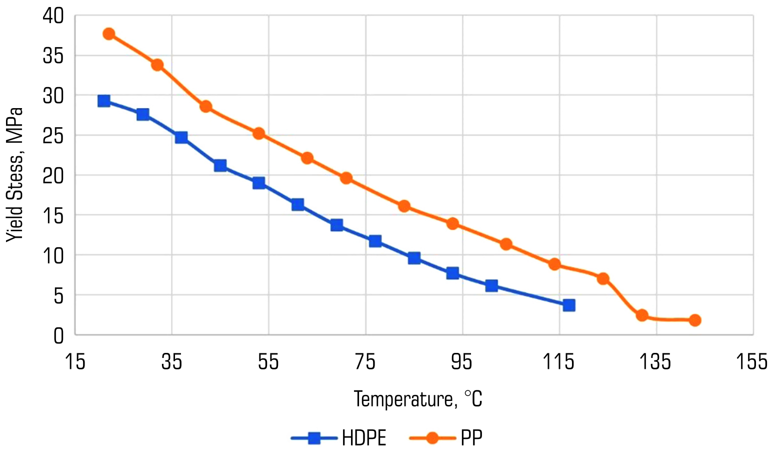


Fig. 4.3 Dependence of yield strength on temperature for HDPE, PP [49, 50]

When the temperature increases from 20 °C to 143 °C, a gradual decrease in the yield point for HDPE is observed by 88 %, for PP – by 95 %. The results of the study by the authors [49, 50] on the change of the Young's modulus under the same conditions demonstrate a decrease in the value of the Young's modulus by 95–97 % for both HDPE and PP (**Fig. 4.4**).

In addition to the polymer materials discussed above, structured (cross-linked) polyethylene PE-X can also be a rather interesting object of future research. According to the standard [51], pipes made of structured (cross-linked) polyethylene PE-X with a degree of cross-linking of at least 60 % are able to withstand a maximum operating temperature of 90 °C from one to ten years (depending on the thickness of the pipes and stress in the pipe walls), and the maximum temperature of short-term exposure is 100 °C for 100 hours. The peculiarity of PE-X is that the structure of polyethylene changes in such a way that the polymer chains are connected to each other by chemical bonds in a three-dimensional network. At the same time, the new structure prevents the melting of the polymer before the destruction of the cross-linked structure. The density of PE-X used to make the pipes is 900–970 kg/m^3, the relative elongation of the pipes at break at 23 °C is not less than 250 %, the tensile strength after heating at 100 °C is not less than 9 MPa, and the strength when stretched at 23 °C – not less than 19 MPa. The change in the length of the pipes after heating is no more than 3 %.

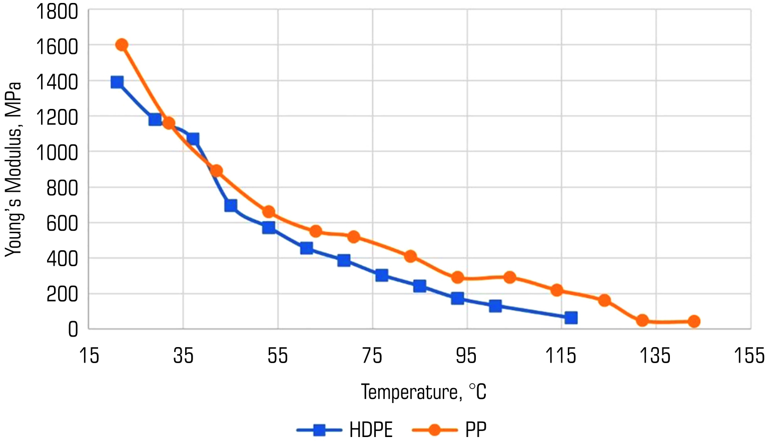


Fig. 4.4 Dependence of Young's modulus on temperature for HDPE, PP [49, 50]

However, when choosing a polymer as a structural material, one should focus not only on physical-mechanical and thermal properties, but also on the technology of manufacturing the product and the possibility of modifying the material. The authors [52] found that the injection molding technology leads to a significantly higher HDPE service life compared to blow molding or pressing. This is believed to be due to higher crystallinity and molecular orientation when injection molding is used.

When choosing materials for traditional LV bodies, they proceed from the need to reduce the mass of the "dry" structure, as well as technological requirements, corrosion resistance, cost, availability of materials, etc. But the main criterion, based on the principles of system design, is the criterion of the minimum weight of the structure. But for burned rockets, the mass of the structure is not passive, it is simultaneously the mass of fuel consumed during the operation of the rocket engine.

Thus, on the basis of the initial review of the literature on the complex of physical, mechanical and thermal properties of polyolefins, UHMWPE, PE-X, PP can be singled out as promising basic alternative construction materials for the manufacture of shells of autophage missiles. At the same time, the need for an experimental study of the physical and mechanical properties of the selected polymers, taking into account the conditions of their further operation, is mandatory.

4.1.2 METHODOLOGY OF EXPERIMENTAL STUDIES OF THERMODYNAMIC PROCESSES DURING THE THERMAL DESTRUCTION OF POLYMER MATERIALS BY METHODS OF THERMAL ANALYSIS

Experimental studies of thermodynamic processes of thermodynamic processes are based on thermal analysis. Thermal analysis (TA) is a method of studying physicochemical and thermodynamic phenomena occurring in a substance under conditions of controlled heating of the external environment. This method allows to qualitatively and quantitatively study the processes of phase transformations, determine temperatures and thermal effects of phase transformations. Methods of thermal analysis are presented in detail, for example, in [53].

Thermal analysis methods were used for the research: differential thermal analysis (DTA), thermogravimetric (TG), differential thermogravimetric analysis (DTG), differential scanning calorimetry (DSC). Thermogravimetric analysis (TG) allows to determine the change in the mass of the sample under investigation during heating. DTA is based on measuring the temperature difference between the substance under investigation and an inert standard using a differential thermocouple. This makes it possible to detect thermal effects in the substance under investigation. The DSC method allows to measure changes in heat flow from temperature and directly determine the change in energy (enthalpy) in the process. The methods of thermogravimetric analysis allow to determine the change in mass during heating, and the DTG curve to determine the temperature of chemical reactions.

The schematic diagram of the simplest thermoanalytical device, which is used in almost all variants of thermal analysis, is shown in **Fig. 4.5**.

The thermal analyzer consists of high-precision scales with crucibles (usually platinum), which are placed in the chamber of a small electric furnace. A control thermocouple is located in the immediate vicinity of the sample, which measures the temperature with high accuracy. The furnace chamber may be filled with an inert gas to prevent oxidation or other undesirable reactions. The system is managed, and data processing is carried out by specialized software.

In this work, the experiments were performed on the basis of the center for collective use of scientific equipment "Innovative technologies in the rocket and space industry" at Oles Honchar Dnipro National University (Dnipro, Ukraine). A high-precision STA 6000 analyzer was used for the experiments, which allows simultaneous thermogravimetric, differential thermal analysis and differential scanning calorimetry. The device is equipped with a SaTurnA sensor, the compact heating furnace is characterized by an improved temperature control system, measurement accuracy and rapid cooling. The general view of the analyzer is presented in **Fig. 4.6**. The device analyzes solid samples in the form of powder, crystals or granules. The object of the study were samples of high-density polyethylene, low-density polyethylene, and polypropylene, which were placed in the crucible of the analyzer in **Fig. 4.7**.

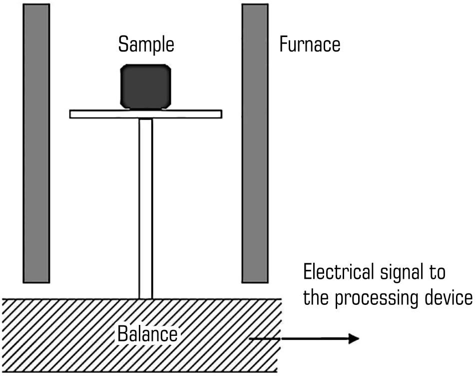


Fig. 4.5 Scheme of a thermoanalytical device

Fig. 4.6 General view of the STA-6000 analyzer

Heating took place at a constant rate in a neutral medium (argon). In the course of the experiment, thermograms were constructed on which DTA, TG, DSC curves were reflected. The nature of the curves reflects the processes occurring in polyethylene during its heating. Visualization of such curves is a thermogram. The obtained curves are processed with the help of specialized software, which allows to determine the thermal effects of the relevant processes, temperatures that correspond to structural transformations and reflect changes in the mass of the investigated samples during heating.

Fig. 4.7 Experimental sample

Methodologically, experimental research consists of the following successive stages:

– preparation of a sample of the substance under investigation: grinding, determination of initial parameters;

– preparation of the analyzer for work: zeroing of parameters, programming of research parameters: heating rate, temperature range, installation of the sample in the crucible in the furnace;

– conducting an experiment;

– processing of experimental thermograms obtained as a result of the experiment: determination of temperatures corresponding to transformations in the material, parameters of mass loss, thermal effects of phase transformations.

Conclusions about physical phenomena and their quantitative characteristics are made on the basis of the analysis of curves on thermograms, for example, **Fig. 4.8** schematically shows a typical view of TG and DSC curves.

Analysis of these curves allows determining the main parameters of thermodynamic processes. Temperature is plotted on the abscissa axis, and mass loss or heat flows are plotted on the ordinate axis. The TG curve usually has an initial section where the change in mass is insignificant and it is most often associated with the release of residual solvent or water from the sample, as well as a second (or more) section that is due to the thermal destruction of the sample under study.

The presence of peaks on the DSC curve indicates the effects of heat release or absorption, which is associated with phase transformations inside the material. The area of the figure bounded by the peak (**Fig. 4.8**) determines the thermal effect of this transformation.

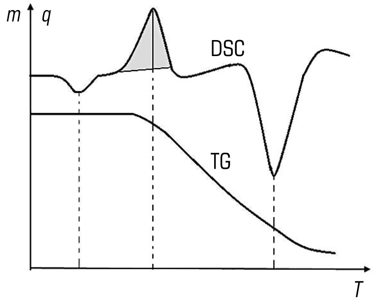


Fig. 4.8 Schematic view of TA curves

4.1.3 RESEARCH RESULTS OF THERMODYNAMIC PROCESSES OF DESTRUCTION OF POLYMERIC MATERIALS DURING HEATING

According to the methodology described above, research was carried out on the following materials: high molecular weight polyethylene, low molecular weight polyethylene, white polypropylene and gray polypropylene.

The research was conducted under the following conditions: at the beginning of the experiment, the furnace temperature was kept constant at 30 °C for 3–5 minutes, then the temperature was varied in the range from 30 °C to 600 °C at a rate of 10 °C/min. The system was filled with argon, which excluded the possibility of accidental oxidation of the materials under study. As a result of the experiments, the thermograms presented in **Fig. 4.9–4.12**.

Fig. 4.9 shows a thermogram obtained during heating of high molecular weight polyethylene.

The data in **Fig. 4.9** show that for polyethylene structural changes in the material began at a temperature of 136 °C (409 K). The thermogravimetric curve shows that the active mass loss of the sample began at a temperature of 251 °C (524 K). At a temperature of 500 °C (773 K), almost complete gasification of polyethylene took place, the rate of mass loss was 0.075 mg/°C.

Fig. 4.10 shows the thermogram obtained during the heating of polyethylene of low molecular weight polyethylene.

The data in **Fig. 4.10** show that the structural changes in the sample of low molecular weight polyethylene began at a temperature of 108 °C (381 K), which is 28 °C lower than the temperature value in the previous case. At the same time, the mass loss of low molecular weight polyethylene begins at a temperature of 229 °C (502 K), which is 20 °C lower than for the previous sample. At a temperature of 498 °C (771 K), the mass loss was 97 % of the initial one, and at 593 °C (866 K), complete gasification of the sample occurred. The rate of mass loss was 0.098 mg/°C.

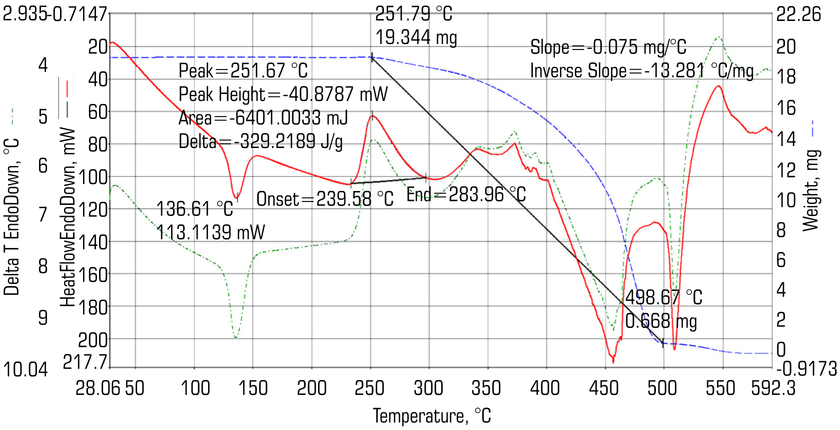


Fig. 4.9 Example of a thermogram for heating a sample of high molecular weight polyethylene

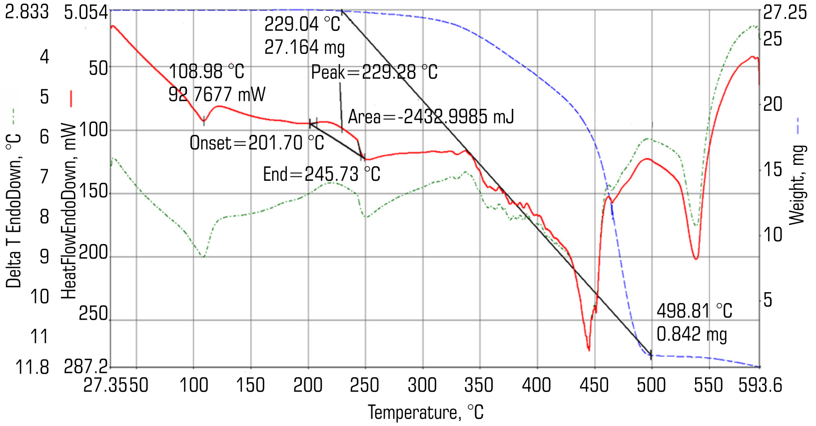


Fig. 4.10 Example of a thermogram for heating a sample of low molecular weight polyethylene

A comparison of two samples of polyethylene shows that from the point of view of using this polymer as a structural material for LV bodies, preference should be given to high molecular weight polyethylene, as it has greater heat resistance. It should be noted that, as was shown above, high molecular weight polyethylene also has higher strength and wear resistance.

Fig. 4.11 shows a thermogram obtained during heating of gray polypropylene.

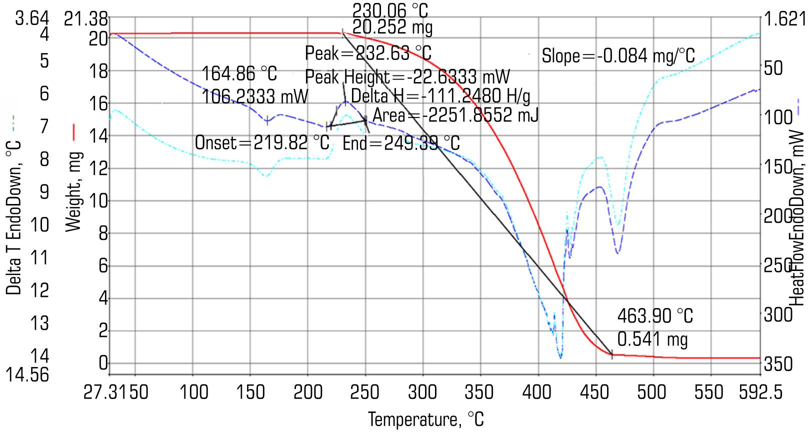


Fig. 4.11 An example of a thermogram for heating a polypropylene sample

For the considered sample of gray propylene, structural changes begin at a temperature of 164 °C (437 K), mass loss begins at a temperature of 230 °C (503 K), at a temperature of 463 °C (775 K), almost complete gasification of the sample occurred, the rate of mass loss was 0.084 mg/°C.

Fig. 4.12 presents the thermogram obtained during the heating of white polypropylene.

As can be seen from the data in **Fig. 4.12**, structural changes in the white polypropylene sample began at a temperature of 131 °C (408 K), mass loss began at a temperature of 258 °C (531 K), at a temperature of 500 °C (773 K), the sample lost 97 % of its mass, complete gasification occurred at 594 °C (867 K), the rate of mass loss was 0.112 mg/°C.

So, the results of experimental studies of selected samples of gray and white polypropylene show that polypropylene has greater heat resistance than polyethylene. In the considered case, white propylene showed better results in terms of heat resistance, while white propylene had higher values in terms of heat resistance, but also a higher rate of decomposition than the other samples.

Based on the obtained results, high molecular weight polyethylene and polypropylene (white) can be recommended for practical use as a structural material under the condition of heat resistance. According to the DTA curves, the thermal effect of thermal destruction was determined as the area of the figures described by the peaks of the heat flow curves. So, based on the results of the experiments and the data of p. 4.1.1, the initial data (**Table 4.4**) were determined for further use during the mathematical modeling of heat and mass transfer processes both in engines and in the conditions of interaction of the polymer shell of the LV body with the high-speed flow of oncoming gas.

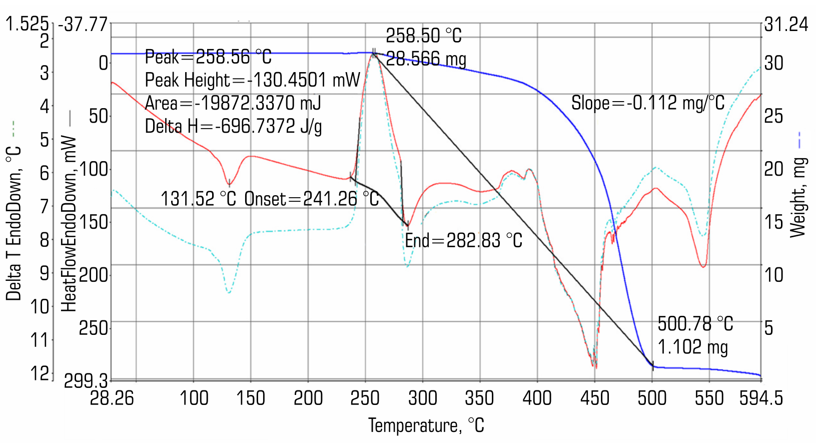


Fig. 4.12 An example of a thermogram for heating a sample of white polypropylene

Table 4.4 Research results

Material	**High molecular weight polyethylene**	**Polypropylene**
Density ρ, kg/m^3	930	920
Thermal conductivity coefficient λ, W/(m·K)	0.335	0.12
Heat capacity s, J/(kg·K)	1.94·10^3	2.5·10^3
Melting point, K	502	531
Full gasification point, K	866	867
The rate of mass loss during heating, mg/°C	0.098	0.112
Total thermal effect of thermal destruction, J/kg	7 173·10^3	3 380·10^3

4.2 ANALYTICAL STUDY OF THE DESTRUCTION RATE OF THERMOPLASTIC POLYMERS UNDER THE INFLUENCE OF HIGH-SPEED GAS FLOWS

4.2.1 PHYSICAL MODELS OF THERMAL DESTRUCTION OF THERMOPLASTIC MATERIALS UNDER THE INFLUENCE OF HIGH-TEMPERATURE AND HIGH-SPEED GAS FLOW

Polymers are high-molecular chemical compounds, the macromolecules of which are formed from a set of monomer units.

Polymer molecules are characterized by a large molecular mass, from several thousand to several million atomic mass units.

The dynamics of the destruction of polymers under thermal and dynamic influence mainly depends on their structure. Polymers with a linear structure do not lose their plastic properties when heated to the melting point, they are called thermoplastics. With a further increase in temperature, they melt, then the macromolecule chain gradually disintegrates into separate links. Due to the fact that the molecular weight of the final products is many times less than the weight of the polymer, these products are in the gas phase at the decomposition temperature.

Given the problem of using polymers as a fuel and the main structural material for the bodies of ultra-light LVs, the most important characteristics are thermal and heat resistance. Heat resistance characterizes the upper limit of the temperature range in which the polymer material can bear mechanical loads without changing its shape. Loss of heat resistance is caused by physical processes (transition of glassy polymers into a highly elastic state or melting of crystalline polymers). Thermal resistance characterizes the upper limit of working temperatures in those cases when the performance of the polymer is determined by resistance to chemical transformations (usually to the destruction of polymers in inert or oxidizing environments).

Recently, polymer materials have begun to be used quite actively in aerospace engineering along with traditional materials – metals. Mainly, polymers are used as part of new composite materials [54]. Polymer composites are used as structural materials for the creation of stabilizers, elements of jet engines, turbine blades, as well as in thermal protection systems, that is, elements that are of critical importance for the functioning of aerospace technology. Consequently, the issues of stability and strength of polymers, which are fundamental characteristics of solids, have attracted the attention of many researchers. These issues become especially important if polymer materials are used in conditions of high temperatures and interaction with high-speed flows of chemically active gases.

The problem of the destruction of materials from a theoretical point of view is quite complex and significantly non-linear. It is known [55] that there are three types of polymer failure: brittle, quasi-brittle, and non-brittle. Each type of destruction takes place in a certain temperature range. Models and approaches to the study of the mechanics of brittle and quasi-brittle failure of polymeric materials are considered in works [56, 57]. It should be noted that today, the theoretical foundations of the mechanics of the destruction of polymeric materials are based on the theory of thermal fluctuation destruction, in which the temperature factor plays a leading role.

Under the conditions of operation of polymeric LVs, the main mechanisms of destruction of polymeric materials will be thermal degradation, destruction, and melting of the material mass. Thus, in the future, it is not possible to consider the processes of brittle and quasi-brittle destruction, given their secondary nature under the conditions of thermal loads in the combustion chamber of the polymeric LV engine or aerodynamic heating of the body. For LVs and spacecraft, the processes of thermal degradation occur under the influence of atmospheric oxygen, thermal loads are accompanied by the introduction of material mass. As a result of such influences, there is mass transfer from the surface and a change in the physical and mechanical properties of materials and erosion (reduction in durability) of the material.

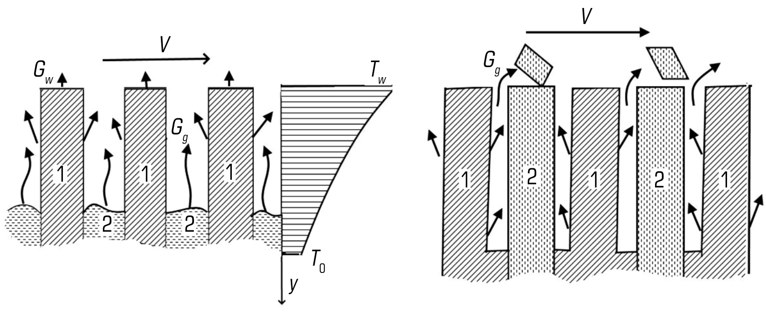
Depending on the level of thermal and gas dynamic loads, several options for applying thermoplastic materials are implemented. At relatively high heat fluxes and low tangential stresses, mass transfer occurs mainly due to thermal decomposition of the material. At high heat fluxes and minor tangential stresses, mass transfer is caused by both thermochemical processes and material erosion. At high heat fluxes and high tangential stresses, thermal decomposition does not occur, since the temperature on the surface does not reach the value of the destruction temperature. The process of destruction, in this case, is caused only by erosion of the material. However, the specific values of the parameters determining one or another failure mode may differ for different thermoplastics.

The failure patterns that occur in practice depend on the scheme of use of the thermoplastic material. In the case of using polymer fillers in composite elements of thermal protection, the destruction process occurs as a result of physical and chemical transformations under the influence of convection and radiation heat flows brought to the surface, diffusion flows of chemically active components, as well as under the influence of gravity and friction. In this case, there is a certain self-regulation of the process – a change in the mass flow rate of the material under the condition of a change in the heat load. The destruction processes are accompanied by phase and chemical transformations. **Fig. 4.13** presents examples of schemes for applying the mass of a composite heat-insulating material with a polymer filler, which can be set depending on the level of heat load and the high-speed pressure of the gas flow.

Fig. 4.13, *a* shows a model of quasi-stationary destruction, when the polymer filler, which has a low temperature of thermal decomposition, is removed at the same speed as the refractory frame. At the same time, the front of the polymer filler is located at a certain depth from the surface of the coating, that is, in the region of lower temperatures.

Fig. 4.13, *b* shows the case when the filler has a sufficiently high thermal resistance and will be mechanically destroyed and carried away by the gas flow due to the influence of high-speed pressure. Such a case is more characteristic of organic sublimating materials.

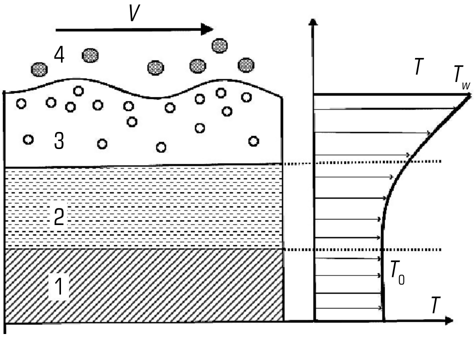
In the case of making LV bodies from polymer materials, the destruction process occurs according to the model presented in **Fig. 4.14**.



1 – a component that forms a frame; 2 – filler (bond)

a *b*

Fig. 4.13 Schemes of destruction of a heat-protective coating with a polymer filler: *a* – a filler with high thermal resistance; *b* – a filler with low thermal resistance



1 – starting material;
2 – softened material;
3 – zone of thermal destruction;
4 – introduction of melt droplets

Fig. 4.14 Scheme of destruction of polymer material

Unlike sublimating materials, the transition to a gaseous state in thermoplastics does not occur on the surface, but in a layer of material of a certain thickness bordering the surface (zone 1 and 2 in **Fig. 4.14**). In zone 2, the softening of the material occurs, and in zone 3, the process of thermal destruction takes place. At high temperatures, a melt film can form directly on the surface and even waves can be formed, as shown in [58]. Such a film is very thin and is worn away in the form of drops 4 by a gas flow. In most cases, during the decomposition of polymers, the solid phase immediately turns into a gaseous state.

Therefore, a zone is formed in the middle of the material where it is necessary to take into account the absorption of heat due to the breaking of chemical bonds in the process of thermal destruction. It should also be taken into account that part of the thermal energy is spent on heating the material to the corresponding destruction temperature. In zone 1 (**Fig. 4.14**), the temperature is low enough and thermal destruction processes do not occur.

The considered physical model of thermal destruction of polymer materials is the basis for building a mathematical model and determining the rate of destruction and mass removal.

In the conditions of the practical use of thermoplastic materials for the manufacture of polymer LV bodies, the phenomenon of polymer aging should be taken into account. This process depends on the flow of heat, oxygen, sunlight, ionizing radiation and has a significant impact on thermodynamic characteristics [59]. Aging of polymer systems is accompanied by the following thermodynamic processes:

– the formation of a surface layer, which has the value of surface tension, adsorption capacity, chemical potential and activation energy, the energy at which chemical transformations in the structure of the polymer begin, which differ from the main mass of the material;

– adsorption of moisture, gases and change in thermodynamic characteristics of the surface;

– diffusion of low molecular weight substances into the volume of the polymer;

– influence of the stress-strain state of the surface layer;

– the influence of a complex of climatic factors: temperature, which increases the total energy of the polymer and increases the mobility of macromolecule links in it, breaks low-energy bonds, and creates new spatial bonds; humidity, which affects thermodynamic and mechanical characteristics, plasticizes and reduces strength.

All these phenomena affect the thermodynamic characteristics of the surface and the ability of the surface to adsorb and enter into chemical interaction with atmospheric liquids and gases, create prerequisites for premature destruction of materials. Therefore, the introduction into practice of the use of polymer casings for LVs, which at the same time are combustible, requires the definition and development of regulations regarding the conditions of storage and operation of polymer casings.

4.2.2 DEVELOPMENT OF A METHOD FOR DETERMINING THE SPEED OF THERMAL DESTRUCTION OF THERMOPLASTIC MATERIALS UNDER THE INFLUENCE OF HIGH-TEMPERATURE AND HIGH-SPEED GAS FLOW

Let’s determine the quantitative characteristics of the process of destruction of thermoplastic material under the influence of a high-temperature gas flow in accordance with the physical model adopted above. Let’s suppose that the destruction process occurs without the formation of a melt film on the surface, and the solid phase of the polymer passes immediately to the gas phase, which is carried by the oncoming gas stream. Let’s analyze the process of removal of thermoplastic material from the LV surface as a result of thermal influence from the standpoint of energy balance. The total thermal effect of destruction consists of the heat required to heat the material to the temperature of loss of heat resistance and the heat of sublimation

$$H = c_S(T_p - T_0) + \Delta Q, \tag{4.1}$$

where the values included in (4.1) are defined in clause 1 of this paper.

Let's assume that the entire mass of the polymer that is gasified during heating will be entrained by the oncoming gas flow, so the rate of mass loss will be equal to the entrained mass rate. For polymers, the rate of thermal destruction is generally determined by the kinetics of the decomposition process. The equation describing the decomposition rate has the form [60]:

$$-\frac{d\rho}{d\tau} = Kf(\rho), \tag{4.2}$$

where ρ – density; t – time; K – reaction rate constant that depends on temperature, $f(\rho)$ – function that K – characterizes the mechanism of decomposition of a substance and is usually given by the dependence $f(\rho)=\rho^n$, n – order of the reaction. The reaction rate constant is determined by the Arrhenius law:

$$K = B\exp\left(-\frac{E}{RT}\right), \tag{4.3}$$

where B – pre-exponential factor; E – activation energy; R – gas constant; T – temperature. So, taking into account (4.3), the expression (4.2) takes the form:

$$g = -\frac{d\rho}{d\tau} = B\exp\left(-\frac{E}{RT}\right)\rho. \tag{4.4}$$

If to assume the one-dimensionality of the heat propagation process in the material layer, the weak dependence of thermal conductivity on temperature. constant filling of cavities with melt formed as a result of thermal destruction in the thickness of the layer, then in the quasi-stationary mode the equation of heat transfer in the material has the form:

$$\lambda\frac{d^2T}{dy^2} + \rho c u_\infty \frac{dT}{dy} - q_v = 0, \tag{4.5}$$

where u_∞ – linear rate of mass removal, λ – thermal conductivity $q_v = B\Delta Q\rho\exp\left(-E/RT\right)$. Taking into account that the rate of destruction is determined by the law (4.4), let's determine the linear rate of mass loss is defined as:

$$u_\infty = \frac{G_\Sigma}{\rho} = \frac{\int_0^h g\,dy}{\rho} = \int^h B\exp\left(-\frac{E}{RT}\right)dy, \tag{4.6}$$

where G_Σ – mass flow rate, h – thickness of the material layer.

The first term of equation (4.5) describes the transfer of heat due to thermal conductivity, the second term of heat absorption due to heat capacity, the third term of heat absorption due to thermal destruction of the material. Knowing the temperature distribution, it is possible to calculate the rate of mass introduction, respectively, the rate of destruction according to the formula (4.6).

Equation (4.5) does not have an analytical solution in the presented form. If to assume that the second term of equation (4.1) can be neglected, then equation (4.5) can be written in the form:

$$\lambda \frac{d^2T}{dy^2} - B\Delta Q\rho \exp(-\frac{E}{RT}) = 0. \tag{4.7}$$

In the case when a sufficiently thick flat layer of polymer material is considered, which decomposes at the surface temperature $T\infty$, then the boundary conditions should be added to equation (4.7)

$$T\big|_{y=0} = T_\infty, \quad T\big|_{y\to\infty} \to T_0. \tag{4.8}$$

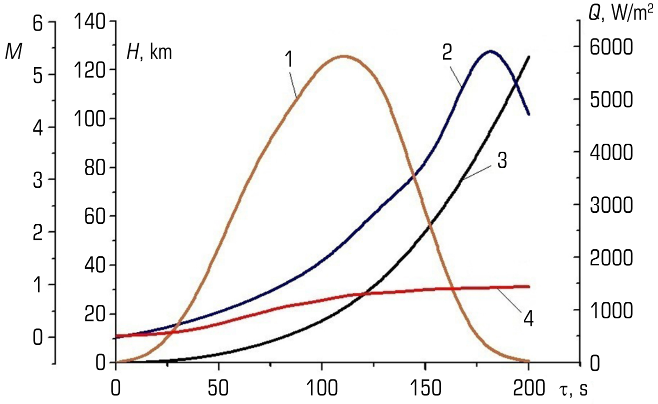
For the problem (4.7)–(4.8) in [61], a solution was obtained, according to which an approximate formula was proposed for calculating the mass rate of removal of polymer material from a unit area of a flat surface:

$$G_\Sigma = \frac{\sqrt{B\rho\lambda \frac{R}{E} \exp\left(-\frac{E}{RT_\infty}\right) T_\infty}}{\sqrt{H - \frac{1}{2}\Delta Q}}. \tag{4.9}$$

Expression (4.9) makes it possible to estimate the contribution of the mass of the polymer material during thermal destruction for the quasi-stationary regime. At the same time, during the LV passage of the atmospheric section of the trajectory, the thermal load conditions change significantly. In work [62], theoretical calculations of the trajectories of a rocket with a polyethylene body and thermal loads during passage through the lower layers of the atmosphere were performed. Let's evaluate the heat loads on the side surface of the LV polymer body according to the data [62], the methodology [63] and the parameters of the standard atmosphere [64].

Fig. 4.15 shows how the flight parameters change: altitude 3, Mach number 2, heat flow due to aerodynamic heating 1, as well as heat flow due to solar radiation 4 [65] in the atmospheric section of the flight of a polymer rocket with a diameter of 0.3 m and an initial overload of 1, 2.

As can be seen from **Fig. 4.15**, the maximum heat loads correspond to the height range of 20...60 km. Under the influence of intense heat flows, thermoplastic materials, including polyethylene and polypropylene can heat up, which leads to a decrease in strength characteristics and possible deformation of the body. When polymer shells are heated, a number of homogeneous and heterogeneous chemical reactions and phase transformations can begin, which are accompanied by heat absorption and mass loss. Therefore, in mathematical modeling, additional terms in the energy equation describing processes of volumetric heat absorption should be taken into account.



1 – heat flow due to aerodynamic heating; 2 – Mach number;
3 – height; 4 – heat flow due to solar radiation

Fig. 4.15 Flight parameters of a polymer rocket in the atmospheric section accepted for calculation

The mathematical model of non-stationary heat transfer in the hull shell during movement on the atmospheric part of the trajectory in a one-dimensional formulation has the form:

$$c\rho\frac{\partial T}{\partial \tau}=\frac{1}{r}\frac{d}{dr}\left(\lambda r\frac{dT}{dr}\right)-q_v(r),\quad \tau>0,\ R_1\le r\le R_2, \tag{4.10}$$

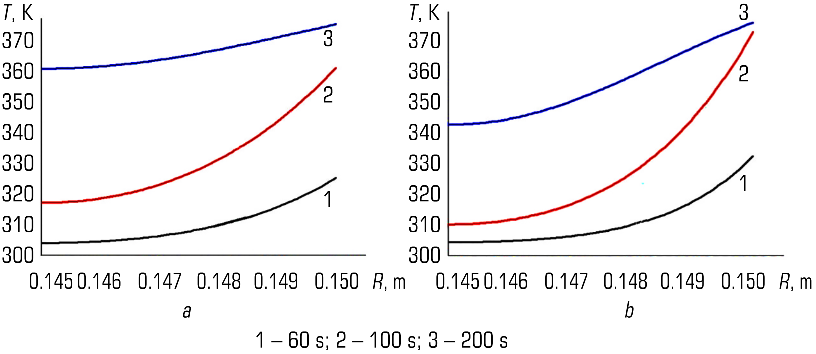
$$T\big|_{t=0}=T_0, \tag{4.11}$$

$$\left.\frac{\partial T}{\partial r}\right|_{r=R_1}=0,\quad \lambda\left.\frac{\partial T}{\partial r}\right|_{r=R_2}=-q(\tau), \tag{4.12}$$

where T_0 – initial temperature of the wall; R_1, R_2 – inner and outer radii of the body shell; c – heat capacity.

The source term in (4.10) is defined as in (4.5), and the right-hand sides of the second equality (4.12) are determined according to the heat flow function presented in **Fig. 4.15**.

Problem (4.10)–(4.12) was solved numerically. **Fig. 4.16, *a*** shows the results of calculating the temperature fields in the polyethylene cylindrical wall of the body during the LV movement along the trajectory described by the data in **Fig. 4.15**. The results of a similar calculation for a polypropylene wall are shown in **Fig. 4.16, *b***.



a

b

1 – 60 s; 2 – 100 s; 3 – 200 s

Fig. 4.16 Temperature distribution at different time points in: *a* – polyethylene shell; *b* – polypropylene shell

As can be seen from **Fig. 4.16**, the outer surface of the walls made of polypropylene heats up during flight in the atmosphere a little more than that of polyethylene. This is due to the lower thermal conductivity of polypropylene than polyethylene. The temperature of the outer surface of the case at the moment of time after 200 s (altitude 125.3 km) is 375 K for polyethylene and 419 K for polypropylene. Therefore, for both materials, the surface temperature remains lower than the temperature at which thermal destruction begins.

If the heat flows are large enough, and the zone of thermal destruction degenerates into a thin layer, then the destruction process will occur only on the surface of the material. It is possible to estimate mass transfer using the ratio used to estimate the process of ablation of materials [66]:

$$G_\Sigma = {}^{q_s}\!\big/_{H}. \tag{4.13}$$

In the case of the combustion process of polymer fuel, it is necessary to take into account the chemical interaction of the polymer surface with the gas flow. For this, it is necessary to take into account the additional heat flow due to the burning of the oxidizer, therefore:

$$q_\Sigma = q_s + G_o \Delta Q_{comb},$$

where G_o – mass flow of the oxidant per unit area, ΔQ_{comb} – heat of combustion of the polymer. The oxidant flow to the polymer surface due to diffusion is equal to

$$G_0 = \beta(C_{o\infty} - C_{ow}),$$

where β – mass transfer coefficient, C_o – oxidant concentration. Heat flow according to the Newton-Richmann law:

$$q_s = (\alpha / c_p)(I_\infty - I_w),$$

where α – heat exchange coefficient, I – enthalpy. If it is supposed that $C_{ow} = 0$, and taking into account the principle of analogy between heat and mass transfer there is $\beta = \alpha / c_p$, then (4.13) it is possible to write

$$G_\Sigma = \frac{q_w}{H}\left(1 + \frac{C_{o\infty}\Delta Q_{comb}}{I_\infty - I_w}\right). \tag{4.14}$$

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interest in relation to this research, whether financial, personal, authorship or otherwise, that could affect the research and its results presented in this paper.

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