Thermal Studies of Polymeric Foams Used in Engineering

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Abstract

Polymeric foams, used in the production of aircraft, are considered in the article. Thermogravimetric analysis and differential scanning calorimetry were used to conduct thermal studies of rigid polyimide foam materials. It was shown, that the process of thermal destruction of these foams had three stages of different intensity: the destruction of rigid segment with the formation of initial components and the emission of volatile elements; the activation of thermo-oxidative processes; the decomposition, accompanied by considerable heat release. Infrared spectroscopy was used to estimate the influence of the content of volatile components on the glass transition temperature of rigid polyimide foams. It was found, that the presence of volatile substances led to a decrease in the glass transition temperature of the foam materials.

Keywords: Foams, Rigid Polyimide Foams, IR Spectroscopy, Thermal Studies, Thermal Destruction.

Introduction

At present, various brands of elastic and rigid gas-filled materials are used in all branches of industry and construction [1-5]. The issue of development of new compositions of polymer foams, which can meet the requirements of lowering their prime costs, reducing toxicity in production, and also the possibility of their operation under different temperature conditions, becomes topical. The use of a large number of initial components during production makes it possible to vary the properties of the resulting polymer foams [2, 4]. For example, the introduction of fillers is widely used for the production of materials with specified technological and operational properties, and for the reduction of their cost. In addition, filling leads to a certain decrease in the combustibility of polymers [6].

As the fillers of polymeric foam materials, traditional disperse and reinforcing fibrous fillers (RFF) can be used [7-8].

The mechanical properties of fibrous polymer composites are determined by reinforcing fibers and filaments (by their types and properties, size and location, that is, the structure of the reinforcing fibrous filler). Fibers, filaments, strings, rovings, slubbings, cables, fabrics, woven fabrics, knitted

fabrics, nonwoven fabrics, paper and other materials are used as reinforcing fibrous fillers.

Using different types of RFF and technological methods of their location in the fiber composite, it is possible to optimize the positioning of reinforcing fibers and filaments in a finished composite or a product on its base, to achieve the most rational variant, where the majority of reinforcing fibers are located in the direction of the main acting mechanical stresses under operating conditions.

Glass-filled polymeric foams make it possible to manufacture large-sized elements with a multi-layer structure, composed of various combinations of solid and porous foam material and short glass fibers, form meeting various functional and aesthetic requirements in different fields of application. Glass-filled polymeric foams are widely used for the production of carcasses, heat-insulating screens in the automotive industry [3, 9-11].

Polymeric foams also find wide application in the production of aircraft. Polymethacrylimide foam materials are the most widely used in the production of laminated materials, which along with high thermal stability, low density and increased mechanical properties, are well combined with resins, that makes them suitable materials for aircraft construction.

It is known, that the main method of production of the polymer foam materials is the foaming of copolymer half-finished product in a mold. The copolymer is synthesized by block copolymerization of acrylonitrile and acrylic acids with simultaneous introduction into the monomer mixture of all components for foaming and adjusting the properties of the future foam material [12, 13].

The world leader in the supply of a wide range of rigid sheet polyimide foams for structural and radio-technical purposes is Evonik (Germany), which has developed various brands of this material under the general name Rohacell.

At present, the structural profiles with filler, made of foam material Rohacell, are successfully used in the designs of aircraft.

An example is the stringer-profiles, filled with foam polyimide material, used for the construction of rear pressure bulkhead of Airbus A340 and A 340-360. The key to the successful introduction of a polyimide foam-filled trapezoidal stringer construction was the ease of mechanical machining and the final

thermoforming of Rohacell. Filled with polyimide foam, trapezoidal profile contributes to the increase in the stability of thin-walled structures, made of carbon fiber reinforced plastic and their resistance to longitudinal bending and axial load. The appliance of Rohacell as a stiffener allows to use one or two layers of CFRP on the walls of the structure and thus to obtain weight gain [14].

In the helicopter industry, high-tech blades with a Rohacell foam core were developed. A high level of mechanical properties of the foam improves the resistance to longitudinal bending of the thinnest U-shaped spars, used for the construction of blades. Due to passive behavior, which is not typical for any other foam, polyimide foam materials withstand the high dynamic loads, to which the main rotor blade is subjected during its operation [14].

Methods

The microstructure analysis was carried out with the microscope Altami MET 3, using Altami Studio software.

Sample 1

Sample 2

Figure 1. Photomicrographs of Cells of Foam Samples of Rohacell Brand (x 200)

Sample 1 is characterized by the presence of larger cells, than sample 2. Consequently, in relation to each other, the sample 1 of rigid polyimide foam is coarsely cellular and the sample 2 is finely porous.

Thermal analysis provides an opportunity to obtain information about the mechanism of materials destruction, chemical changes in the substance and other processes. Applying this method, using the obtained data, it is possible to analyze the thermal decomposition of the foam material.

Thermogravimetric (TG) analysis shows important information about the thermal stability of a substance and its behavior upon the application of heat.

Differential scanning calorimetry (DSC analysis) was established using a differential scanning calorimeter of heat flow "Netzsch DSK 204 F1 Phoenix". The DSC analysis was carried out in a dynamic heating/cooling regime at a rate of 10°C/min in an argon flow at a rate of 50 cm³/min.

The thermal stability of samples was investigated using the thermogravimetric analyzer "Netzsch TG 209 F1 Iris". Heating to 550°C was carried out at a rate of 10K/min under the conditions of constant purging by argon.

The functional composition and the structure of samples were determined using FT-IR spectroscopy "Perkin Elmer Spectrum 100" with ATR crystal ZnSe.

Results and Discussion

It is known, that Rohacell foam materials are characterized by technological parameters of foaming, molding temperature, foam structure, and mechanical properties.

The structure of the rigid polyimide foams under study (Sample 1 and 2) is shown in Figure 1.

In the process of thermal analysis, the changes of the following parameters are defined:

- mass of the test sample in dependence to its heating temperature;
- the rate of the sample mass loss in dependence to its heating temperature.

Based on the analysis of these parameters, it is possible to obtain sufficiently complete information on the kinetics of destruction of the investigated foam material [15].

Initial information about the thermal stability of the material was obtained by analyzing the stages of foams destruction, according to the TG curve (Table 1, Figure 2).

Figure 2. Thermogravimetric Analysis of Rigid Polyimide Foams sSample 1 (curve TGA - 1, curve DTG - 3) and Sample 2 (curve TGA - 2, curve DTG - 4)

From the thermograms of the test samples of rigid polyimide foams (Figure 2), the onset temperature of decomposition (T_o), the loss of mass at the time of reaching the temperature of maximum decomposition

rate (T_{max}), the remaining material at 550°C (Table 1) were determined. As can be seen from Table 1 and Figure 2, the loss of mass of all samples has undergone several stages of different intensity.

Table 1. Results of Thermal Studies of Samples of Rigid Polyimide Foams

Parameter	Sample 1	Sample 2
Glass Transition Temperature, °C	109,2	93,5
Loss of mass up to 300 °C, % mass.	0,9	7,0
T_o of destruction, °C	379,2	376,7
T_{max} of destruction, °C	423,6	411,3
Loss of mass at T_{max} of destruction, % mass.	38,2	38,5
Remaining mass at 550 °C, % mass.	22,7	16,0

Decomposition of the samples under study is three-step. For the samples of rigid polyimide foams, the following stages of thermal destruction process were defined:

-30-300°C - decomposition of polyimide into the primary products and removal of volatile components;

-310-550°C - activation of thermo-oxidative processes and decomposition, accompanied by significant heat release;

-> 550°C –termination of the material destruction.

Analyzing the TG data and the results of their processing (Table 1, Fig. 2), it can be noted, that the first low-temperature stage for the samples under

investigation is characterized by a range of 30-300°C, while sample 2 loses about 7% of mass, and sample 1 - only 0,9% of mass.

The second stage of the process is characterized by an intense destruction in the temperature range of 310-550°C, and significant loss of mass for all samples (38.2-38.5%). This indicates the active processes of thermal destruction and decomposition. Moreover, T_o and T_{max} of decomposition of the sample 2 are lower than the temperatures of the sample 1. This is explained by the acceleration of reactions by the decomposition products, formed at the first stage. Thus, T_o of decomposition of the sample 2 is lower by

2.5°C, and $T_{\max}$ of decomposition is lower by 12.3°C, than the decomposition temperatures of the sample 1. It is known, that the glass transition temperature of copolymers of acrylonitrile and methacrylic acids is characterized by a range of 100-110°C. The glass transition temperature of the test sample 1 is 109.2°C, and the sample 2 is 93.5°C (Table 1). The low glass transition temperature of sample 2 is due to the presence of residual monomers, which act as plasticizers, reducing the glass transition temperature. The investigations, conducted with using FT-IR spectroscopy, as well as the emissions of volatile

components at the first stage of thermal destruction process (up to 7% of mass) of sample 2 (Table 1) confirm this fact.

The composition of foams was determined by the method of "Fourier transform spectroscopy". Peaks, typical for copolymers of acrylonitrile and acrylic acids are present on the IR-spectra (Figure 3) of samples 1 and 2: stretching vibrations of CH_2 of the main chain (1453 cm^{-1}), C-O and C = O groups of aliphatic esters of acrylic acids in the range of 1160 cm^{-1} and 1736-1715 cm^{-1} , respectively, CN groups of acrylonitrile (2238 cm^{-1}).

Figure 3. IR Spectrum of the Test Sample 1

Thus, the thermal decomposition of rigid polyimide foam samples has undergone three stages of different intensity.

Conclusion

Conducted studies showed, that the process of thermal destruction of rigid polyimide foams had undergone three stages. At the first stage, there were the destruction of rigid segment, with formation of initial components and the emission of volatile elements. The sample can contain them up to 7% of mass. This leads to a decrease in the onset temperature of decomposition and the temperature of the maximum decomposition rate. At the second and the third stages, there were the activation of thermo-oxidative processes and decomposition, accompanied by a significant heat release. This fact is explained by the acceleration of thermooxidative reactions by the products, formed at the first stage of thermal decomposition.

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