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Investigation of UV resistance in polyurethane foam.

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ABSTRACT

The effect of UV radiation on the thermal stability of polyurethane foam was evaluated. The methods of thermal analysis and IR spectroscopy were used to evaluate the degree of UV degradation of polyurethane foam. The degradation of polyurethane foam is accompanied by breaking of a weak bond and formation of alcohol, ether, olefin. The results of IR spectroscopy indicate the start of degradation processes in the UV exposed samples of PU foam. The thermogravimetric analysis was used to investigate the thermal properties of UV irradiated PU foam. It was established that the UV exposed PU foam composites started decomposing at a lower temperature than the reference material. It was shown how UV radiation affected the thermal stability of the test composites. The paper confirmed the possible mechanism of PU foam degradation. The DSC method was used to evaluate the PU foam resistance to oxidative attack, that is indicative of the material operating life.

Keywords: polyurethane foam, thermal stability, UV radiation, thermal analysis, IR spectroscopy, thermo-oxidative degradation.

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INTRODUCTION

Polyurethane (PU) foam is one of the most effective building insulation materials [1-3]. While in use, building products made of PU foam (thermal insulation panels, etc.) are subjected to various environmental impacts such as changes in temperature, humidity, solar radiation, etc. Solar radiation affects the durability of PU foam materials and products, and degrades the original stress-strain and heat transfer properties, leading to early failure of PU foam products. The solar radiation resistance of the material can be evaluated by the UV resistance. The relationship between changes in polyurethane foam composition and properties, and UV exposure time was determined.

In the experimental investigation, the two-component PU foam (Izolan 210-7 system) was used as basic components of the urethane forming mixture [4].

The effect of UV radiation on the PU foam samples was evaluated using the test facility with 1000 W tubular mercury vapour lamp as a UV radiation source. The former Soviet Union was divided into 12 climatic zones according to the standard GOST 16350-80, Climate of the USSR. Regionalizing and statistical parameters of climatic factors for technical purposes [5]. In case of product operation in the temperate climate conditions, climatic area II5 (temperate) shall be applied. The total solar radiation dose (300-400 nm) is 148.10 MJ/m^2 (including annular losses). The radiant flux is 128 W. With regard for the distance to the test samples (250 mm), the hold time under the 1000 W tubular mercury vapour lamp (equivalent to 1 year) is 20 hours and 5 minutes.

The samples were subjected to UV radiation over a period of 550 hours and 606 hours, and then analyzed.

The thermal stability of the samples was studied using Netzsch thermogravimetric analyzer TG 209 F1 Iris. The samples were heated up to 550 °C with a rate of 10 *K*/min under continuous argon purge.

The oxidation onset temperature (OOT) and oxidative induction time (OIT) were recorded with Netzsch differential scanning calorimeter DSC 204 F1 Phoenix. The OIT was determined by heating the samples up to the test temperature with a rate of 10 *K*/min under continuous argon purge. After the test temperature (230 °C) was reached the inert gas supply was stopped, air supply (50 ml/min) and DSC signal recording were started. The OOT was determined by heating the samples with a rate of 10 *K*/min. After the test temperature (150 °C) was reached the inert gas supply was stopped and air purge (50 ml/min) was started.

The functional composition and structure of the samples were investigated using PerkinElmer Spectrum 100 FTIR spectrometer with ZnSe ATR crystal.

DISCUSSION

A thermal analysis provides the sufficient information on the degradation mechanism of materials, substance chemical transformations and other processes accompanied by loss in substance mass, endothermic and exothermic reactions. This method uses the findings for analysis of PU foam thermal decomposition.

A thermogravimetric analysis reveals the critical information on thermal stability of a substance and its behavior during heating.

A thermal analysis shows the changes in:

- mass of a test sample depending on its heating temperature;
- loss rate of the sample mass depending on its heating temperature.

The analysis of these parameters can give the sufficient information on degradation kinetics of test material [6].

The initial information about the effects of preliminary UV exposure was obtained from the analysis of the material degradation stages with the thermogravimetric curve (Fig. 1).

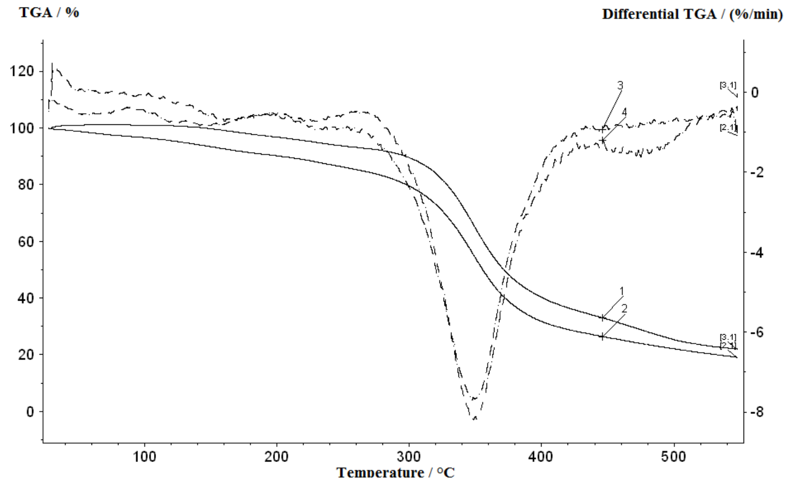

Figure 1: Thermogravimetric analysis of the reference PU foam (TGA curve - 1, differential TGA curve - 3) and PU foam samples after 606-hour UV exposure (TGA curve - 2, differential TGA curve - 4)

The thermograms of the reference PU foam (sample 1), PU foam after 550-hour (sample 2) and after 606-hour UV exposure (sample 3) (Table 1, Fig. 1) revealed the onset temperatures of the samples, temperatures indicative of 5 % mass loss, mass loss (Δm) at a temperature of maximum decomposition rate (T_{max}), amount of the material residue at 550 °C, maximum decomposition rate (Table 1). As can be seen in Table 1 and Fig. 1, the mass loss of all the samples goes through a number of stages of varying intensity.

The rate of TGA curves is similar for all the samples. The paper [6] has established that PU foam samples decompose in three stages. The decomposition of all the test PU foam samples also passes through three stages. However, if PU foam composites are subjected to UV radiation they have lower onset temperature than the reference material. The PU foam was found to go through the following stages when exposed to UV radiation:

- 30-260 °C: polyurethane breakdown into isocyanate and polyalcohol, and removal of highly volatile components;

- 270-550 °C: intensification of thermal oxidation processes and decomposition, with release of large amounts of heat;

- >550 °C: end of material degradation.

RESULTS

Table 1 - Thermal degradation of test PU foam samples

Sample	Onset temperature (T_o), °C	T at 5 % mass loss, °C	T_{max}, °C	Maximum decomposition rate, mg/min	Mass loss at T_{max}	Residual mass at 550 °C, %
1	150	228	350	0.1	32.9	22.0
2	30	142	347	0.2	41.6	20.3
3	30	127	347	0.2	43.2	19.0

Based on the analysis of TGA data and data processing results (Table 1, Fig. 1), it may be noted that for PU foam low-temperature stage I features 150-260 °C, and for UV irradiated samples 2 and 3 it practically starts at 30 °C due to the already present processes of polyurethane breakdown into isocyanate and polyalcohol. With that, samples 2 and 3 suffer almost 12-14% mass loss, and PU foam sample – only 7%.

The second stage shows the rapid decomposition in a temperature range of 270 to 550 °C, significant mass loss for all the samples (up to 43 %) with maximum rate of 0.2 mg/min at 347 °C. It indicates the vigorous processes of thermal degradation and decomposition. Besides, samples 2 and 3 have two times higher decomposition rate than sample 1 due to acceleration of these reactions with thermal degradation products.

Therefore, when exposed to UV radiation, PU foam composites have lower decomposition temperature than the reference material. So that, at the first stage the decomposition rate of UV irradiated PU foam is two times higher, and thermal degradation starts at 30 °C instead of 150 °C in comparison with standard PU foam sample.

Stability of the samples in oxidizing atmosphere was evaluated by oxidative induction time and temperature. PU foam resistance to oxidative attack is one of the most critical parameters for a material, as it has to withstand the destructive effect of oxygen and thermal stress during operation [7]. It is known that the DSC method can be used to evaluate the stability of PU foam during storage and operation. The comparison of the oxidation in the reference PU foam samples (sample 1) and the PU foam samples after 550-hour (sample 2) and 606-hour UV exposure (sample 3) (Table 2, Fig. 2) showed that the oxidation reaction started at 230 °C after 87.7 minutes in sample 1, and after 63.1 minutes, 61.4 minutes in samples 2 and 3, respectively. It is evident that sample 1 has significantly higher oxidation stability than the UV irradiated samples of PU foam. It attests to the fact that the later the degradation starts the higher oxidation stability the sample has, and the higher operating life the material has. Thus, after 550-hour UV exposure, the stress-strain performance of PU foam samples degrades, and their operating life decreases.

Table 2 - Oxidative induction time and temperature of test PU foam samples

Sample	Oxidation onset temperature, °C	Oxidative induction time at 230°C, min
1	250	87.7
2	244	63.1
3	244	61.4

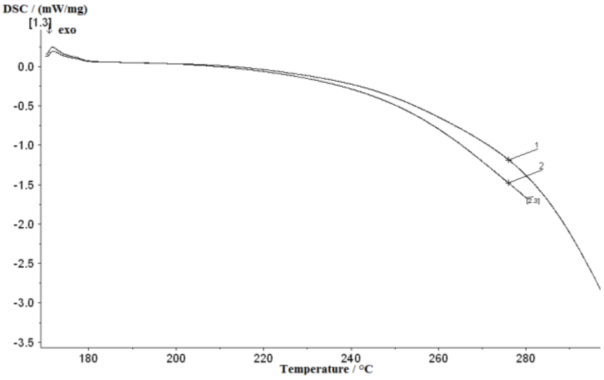

Figure 2: OOT for the samples of reference PU foam (1) and PU foam after 550-hour UV exposure (2)

The paper [8] shows that oxidation reaction forms peroxide radicals when interacting with molecular oxygen in response to heating. Then these peroxide radicals turn to hydroperoxides due to hydrogen abstraction from the chain. The breakdown of hydroperoxides into alkoxide and hydroxyl radicals is a reaction with significant activation energy. That’s why, at a higher temperature the reaction rate increases, besides, in this case it is accelerated by UV radiation.

As the oxidation onset temperature is 150 °C for the reference sample, and 144 °C for UV irradiated samples it can be assumed that in samples 2 and 3 peroxide radicals are formed in air at the UV radiation stage. The investigation of the oxidation reaction shows that additional peroxide radicals are formed in samples 2 and 3 at a higher temperature. As a result, the oxidation reaction in samples 2 and 3 has higher rate than in the reference PU foam (sample 1) (Table 2, Fig. 2).

Infrared molecular spectroscopy is the most practical method for investigation of the functional composition and structure of PU foam. IR spectra give the ability to detect oxygen (hydroxyl, carbonyl, carboxyl, ether), nitrogen functional groups; aliphatic and aromatic hydrocarbon moieties in substances. The deficiency of IR spectroscopy is limited differentiation of substances with similar compositions [6].

In all the spectra of the test PU foam samples we observed the bands of 2926 cm^{-1}, 2854 cm^{-1} (related to stretching vibrations of CH_2, CH_3-groups) and bands of 1460 cm^{-1}, 1375 cm^{-1} (related to bending vibrations of these groups) (Fig. 3) [8].

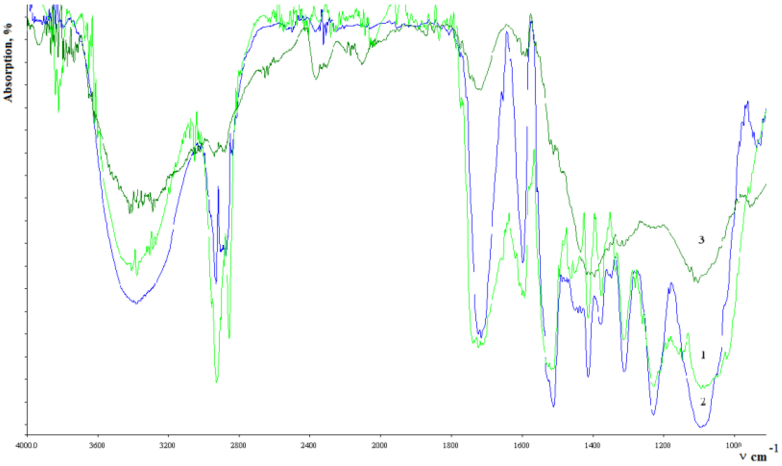

Figure 3: IR spectra of the reference PU foam (1), PU foam after 606-hour UV radiation (2), PU foam sample after the oxidation reaction at 230 °C (3)

It can be seen in the spectrum of the reference PU foam that it is polyether-based as a band of 1080-1090 cm^{-1} is observed in the spectra (related to C-O-C linkage of polyether). The spectra of the UV irradiated samples retain the bands inherent to polyurethanes: bands in a region of 1720 cm^{-1} related to absorption of C=O urethane group, bands in regions of 1590 cm^{-1} and 1515 cm^{-1} related to absorption of N-H groups (Amide I, Amide II), and a band in the region of 1100 cm^{-1} – C-O-C of polyether (Fig. 3) [9].

In the spectra of samples 2 and 3 the band intensity and contour are different in ranges of 3200-3600 cm^{-1} and 1100 cm^{-1}. It indicates the formation of new C-O-C linkages and OH groups. There is a new, more intense band in a range of 910-920 cm^{-1}, which is indicative of bending vibrations of H-C=C-H groups (Fig. 3).

The spectra of the thermo-oxidative degradation products contain the bands indicative of the formation of carbon structures in ranges of 1400 cm^{-1} and 1100 cm^{-1}. Bands of 1720 cm^{-1} and 1590 cm^{-1} inherent to urethane groups lose their intensity. It indicates the band decrease and vigorous nitrogen evolution in the samples. In addition, the band inherent to double bonds is observed in a range of 910-920 cm^{-1} (Fig. 3) [9].

The findings are consistent with the results of the investigation in the review [6]. It established that the first stage of polyurethane degradation is breaking of the weakest C-NH bond. The band in a region of 1510 cm^{-1} is practically not seen in the spectra of thermo-oxidative degradation products as opposed to the reference PU foam. The degradation mechanism specified in the review is described with four types of the reaction (Fig. 4).

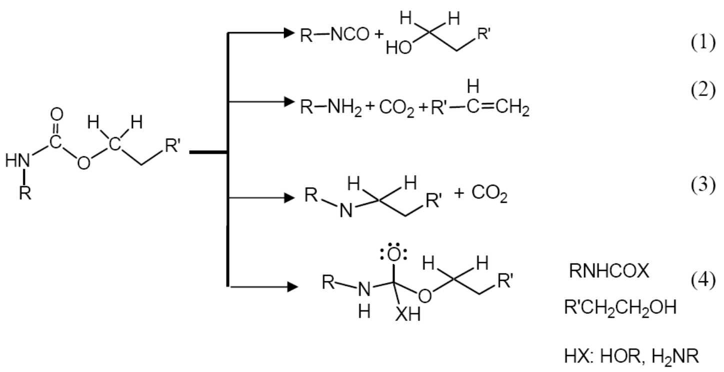

Figure 4: Degradation mechanism of urethane segment

Hence, at a temperature of thermo-oxidative degradation of 230 °C the degradation process is most likely to run in PU foam based on polyether and aromatic diisocyanate by reaction mechanism 1 and 2 (Fig. 4).

CONCLUSION

The investigation showed that thermal degradation of PU foam passes through three stages. At the first stage a hard segment breaks down, and isocyanate, alcohol, olefin are formed. Besides, for UV exposed PU foam the rate at the first stage is two times higher, and thermal degradation starts at 30 °C instead of 150 °C as compared with standard PU foam sample. The findings are consistent with IR spectroscopy data. The first degradation stage of UV radiated PU foam is breaking of the weakest C-NH bond, and formation of alcohol, ether and olefin. The values of oxidative induction time were found with DSC method to predict the operating life for PU foam products. After 550-hour UV radiation (equal to 27 years of operation) the material starts to degrade at temperatures as low as the room temperature. The possible mechanism of PU foam thermo-oxidative breakdown reaction was confirmed.

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