MECHANISM OF DESTRUCTION OF SEMITRANSPARENT POLYMERS BY A RADIANT HEAT FLUX

Yu. A. Buevich, O. K. Egorov, and M. I. Yakushin

We describe experiments on the destruction of some polymers in the air plasma of an electrodeless high-frequency discharge in conditions where the radiant heat flux is comparable with or exceeds the convective heat flux. Two different mechanisms of destruction are discussed.

An analysis of the behavior of various thermoplastics under the combined action of convective and radiant heat fluxes in a jet of high-enthalpy gas is of considerable interest for several applications of modern technology.

The experiments were conducted on a high-temperature gasdynamic apparatus in which the gas was heated by a high frequency electrodeless discharge by the method described in [1]. The diameter of the working part of the jet was 35 mm and its mean velocity was 20 m/sec. The working gas was air at atmospheric pressure. The mean enthalpy of the gas was determined by the balance method from the measured power supplied to the discharge and the air flow rate. The temperature of the jet was measured spectrometrically and was also calculated from the known mean enthalpy. Both methods gave values of 10,000-11,000° K for T in the working part of the jet.

The total heat flux to the front surface of the investigated specimens was 1-1.2 kW/cm^2 in the described experiments. The flux measured by a copper flow-type calorimeter with a polished surface, which slightly exceeded the convective heat flux, was only 0.4-0.5 kW/cm^2. The radiant heat flux (the thickness of the emitting layer of the plasma was 180 mm) was measured by a radiation thermocouple provided with a special system for drawing inert gas (argon) through the light guide. This prevented absorption of ultraviolet radiation in the light guide and also, in conjunction with water cooling, provided protection for the thermocouple. The radiant flux was also determined from the increase in heat flux to the flow-type calorimeter when the reflecting system of the apparatus was changed so that there was no scattering of radiant energy to the surroundings (in this way we managed to increase the heat flux to the copper calorimeter by approximately 50%), and also from the flux to the same calorimeter when its surface was covered by a vacuum-evaporated thin aluminum film, which reflects better in the ultraviolet region of the spectrum. All these experiments indicated that the radiant flux was 60-70% of the total heat flux to the front surface of the specimens.

We investigated cylindrical specimens of diameter 12-30 mm of two types: with a flat end face and with a spherical nose of the same radius as the cylindrical part of the specimen. The convective heat flux to the front surface of specimens of the second type was, depending on the specimen diameter, 1.5-2.5 times greater than the specimens of the first type (the figures given above refer to specimens with a flat front face). This correlates well with published empirical relations (see [2, 3], for instance). Alteration of the shape of the nose of the specimens had practically no effect on the radiant heat flux.* Some time after the start of the experiment with specimens of the first type their shape became similar to specimens of the second type, as was revealed by visual examination and by the similar rates of ablation.

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*Similar results were reported in N. A. Anfimov and V. P. Shari's paper "Calculation of a flow of radiating gas in a shock layer," at the Third All-Union Conference on Theoretical and Applied Mechanics, Moscow, 1968.

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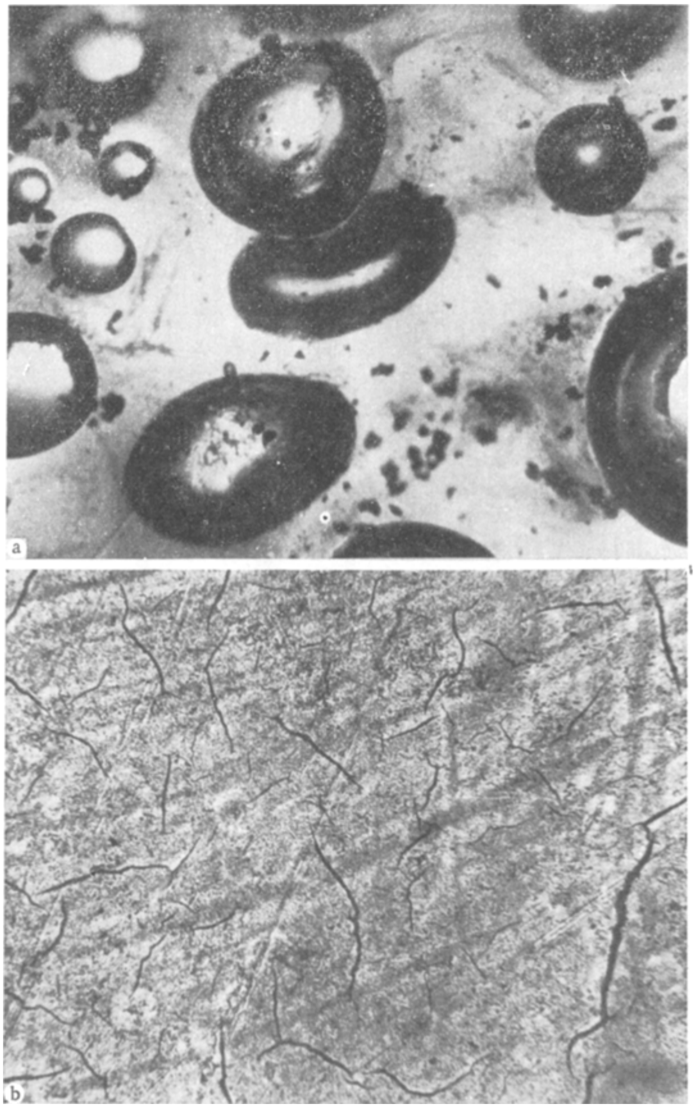

Fig. 1 a, b

The course of the destruction process was recorded simultaneously by two cine cameras: One of them (1 frame/sec, scale 1:1) was used for subsequent determination of the rate of ablation, and the second (96 frames/sec, scale 2:1) was used for a detailed analysis of the destruction of the nose of the specimen. We used infrared films sensitized in narrow spectral ranges (Agfa-Infrarapid 750, etc.) and DS-5 color film.

The surfaces of the specimens, after the tests, were examined under the microscope and photographed at a magnification of 8-12, which enabled us to distinguish the most interesting regions on the specimens, from the interior and surface of which thin film-type sections were cut. These thin sections were examined in transmitted light and photographed on a Nu universal microscope at a magnification of 50-250 X.

The results of the experiments indicated two different types of destruction of polymers in a plasma jet. The first type of destruction, which is characteristic of organic glass and polystyrene, for instance, involves rapid pyrolysis and the release of gaseous products throughout the heated material and at its surface, which leads to the formation of bubbles throughout the specimen. A photograph of part of the front surface of a polystyrene specimen after subjection to the plasma jet is shown in Fig. 1, a. The figure clearly shows the surface bubbles, which can have a diameter of up to 0.5 mm or more. The formation of bubbles is accompanied by the release of solid pyrolysis products, primarily carbon, on their walls and combustion of these products. The carbon coating is also clearly seen in Fig. 1, a. A similar picture of

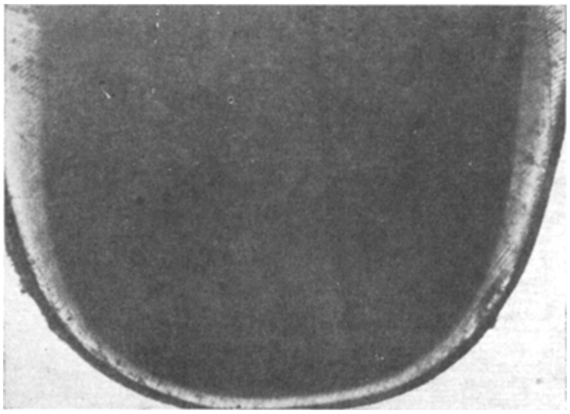

Fig. 2

destruction is observed in organic glass, in which bubble formation is even more pronounced and the bubbles themselves are a little larger. There is no doubt that the main mechanism of such destruction and bubble formation consists in decomposition of the initial material due to the energy of thermal fluctuations, irrespective of the mode of heat supply – radiant or convective. In fact, bubbles are formed on the front surface, where the radiant heat flux plays the main role, and also on the side surface where the convective or molecular flux predominates.

The second mechanism of destruction is characteristic of Teflon, polyethylene, polypropylene, and several other complex materials based on these polymers. Thermal decomposition of these materials leads to the formation of a thin layer with increased carbon content on their surface (see [1], for instance, where a very simple explanation of this effect was given). The thickness of this layer is greatest on the side of polyethylene and polypropylene specimens, where it attains a few tens of microns, and is least on the surface of Teflon specimens. Carbon does not appear at all on the front surface of Teflon specimens. The front surface of Teflon specimens, however, becomes covered with a network of fine cracks with a length of hundreds of microns and a thickness of 10 μ or less (Fig. 1 b). The walls of the cracks, which are 0.1-0.3 mm deep, are also coated with a carbon film. Such cracks are not found on the side surface.

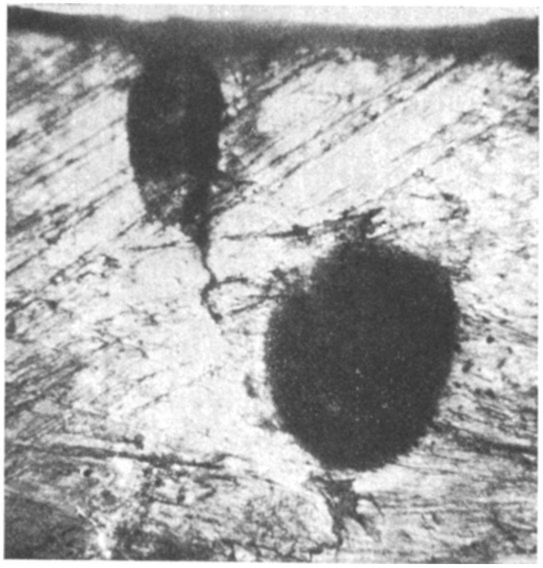

Fig. 3

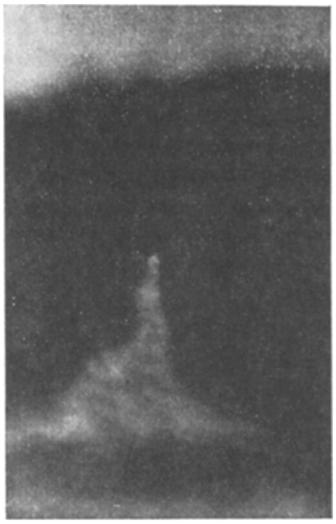

Fig. 4

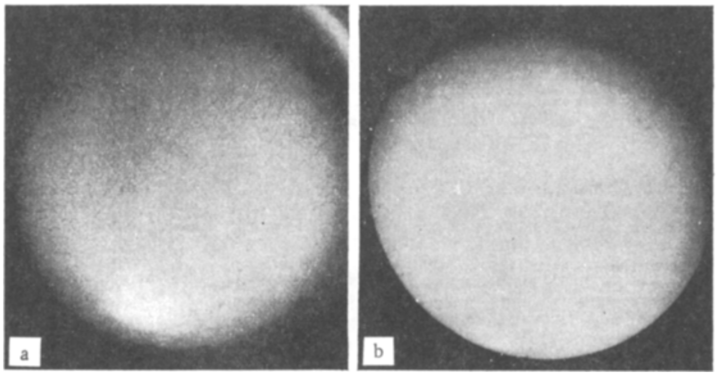

Fig. 5

The bulk properties of polymers which undergo destruction of the second type are practically unaltered. Directly under the carbon layer, however, there is a thin layer of polymer in which the bulk properties are significantly altered. A photograph in transmitted light of a film-type section cut from a Teflon specimen is shown in Fig. 2. The external dark ring in Fig. 2 is the carbon layer (on the side surface) and also the end face of the section photographed at an acute angle. The figure shows that under the carbon layer there is a layer which is much more transparent than the original polymer. The thickness of this layer at the front surface is 0.3 mm, and near the side surface it reaches 1.5-2 mm. This layer is presumably due to thermal destruction of the polymer at the level of quasicrystalline formations and at the molecular level, and there is a very distinct destruction front. The thinness of the destruction layer at the front surface is evidently due to the greater ablation at this part of the surface. Destruction layers of the same type, but more like the original material in their optical properties, were observed in specimens of other polymers subjected to plasma action.

An analysis of thin sections cut from the destruction layer of Teflon showed that on the side surface this layer was very homogeneous. The absence of any cavities or bubbles filled with gaseous pyrolysis products and the absence of cracks indicated that the energy of thermal fluctuations is not sufficient for breakage of intramolecular bonds in the polymer, i.e., for pyrolysis proper, and hence, the destruction and ablation of Teflon (and also of polyethylene and several other polymers) are effected by a purely heterogeneous mechanism in correspondence with the experimental data of [4] and the theory of [1].

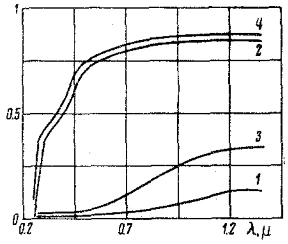

Fig. 6

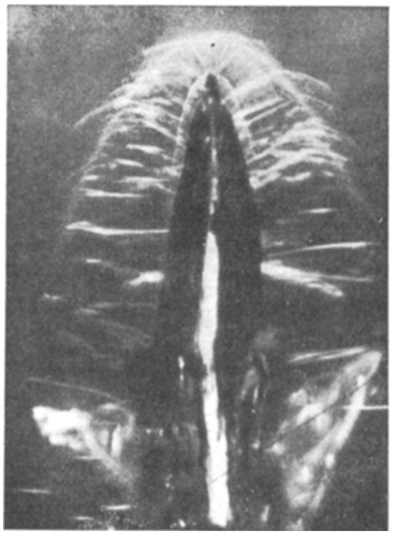

Fig. 7

On the other hand, in the regions of destruction layer adjoining the front surface there are numerous cavities filled with gases and connected with one another and with the external surface of the layer by a system of fine cracks (see photograph of section in Fig. 3). The density of these cavities and cracks decreases rapidly on passage from the front to the side surface; the maximum number of cavities is observed in the region of the destruction layer close to its inner boundary with the unaltered material, but the cracks do not pass through this boundary. The formation of such cavities close to the front surface and their absence from the side surface were characteristic of the other investigated polymers (see, for instance, the photograph of the bubble in the destruction layer of polyethylene in [1]). In polymers in which a film of melted material is formed on the surface, cracks are found only in the carbon layer, and not in the destruction layer. As an example, Fig. 4 shows a photograph of such a crack in polyethylene; the thickness of the carbon layer in Fig. 4 is approximately 50 μ.

The cine films showed that these cracks are formed in the ablation process and are not in any way due to cooling of the tested specimen. Hence, the appearance of cracks can obviously be attributed to the splitting effect of heated gases at high pressures in the cavities. (In polyethylene specimens cracks are also observed in the carbon layer on the side surface. This is due to the high thermal diffusivity of this layer and heterogeneous decomposition and gas formation at the boundary of the carbon layer and the destruction layer.) A similar mechanism was suggested in [5], where the destruction of transparent polymers by a laser beam was analyzed. This explanation of crack formation was confirmed by color cinematography of Teflon specimens immediately after the discharge was switched off. Frames illustrating cooling specimens showed random bursts of incandescent gas from the cracks; these bursts lasted hundredths of a second and occurred in a period of approximately 0.1 sec after the discharge was switched off. Cracks on the front surface of the specimens play an important role in the ablation of the destroyed material, since they facilitate its mechanical destruction – the chipping off of pieces of material and their removal by the encircling flow. This reduces the main practical characteristic of heat-shielding material – its effective enthalpy. This chipping-off process was observed repeatedly on cine films of ablation of different materials, including Teflon and polyethylene.

The total thickness of the carbon and destruction layers in the case of combined action of radiant and convective heat fluxes is, thus, significantly greater than the thickness of the layer of significant temperature drop due to the effect of a convective heat flux alone on these materials. This latter layer is hundredths of a millimeter thick [4]. This indicates that the actual temperature gradients in the surface region in the considered case are less than the gradients measured in [4]. This can be attributed to the increase in effective thermal diffusivitity in the material due to absorption of radiant energy within the semitransparent material and not directly on its surface. The question of the interaction of the surface layer of a transparent body with radiation has been theoretically examined in connection with ablation problems in [6, 7], for instance, where it was shown that such absorption can lead even to a change in the sign of the temperature gradient.

The effect of the radiant flux in the considered experiments, however, does not consist merely of an increase in the effective thermal diffusivity. The results of these experiments clearly indicate that the presence of the radiant flux significantly alters the mechanism of destruction in comparison with situations where there is only a convective heat flux. In fact, it follows from the foregoing that thermal fluctuations by themselves cannot cause decomposition within Teflon or polyethylene. On the other hand, the energies

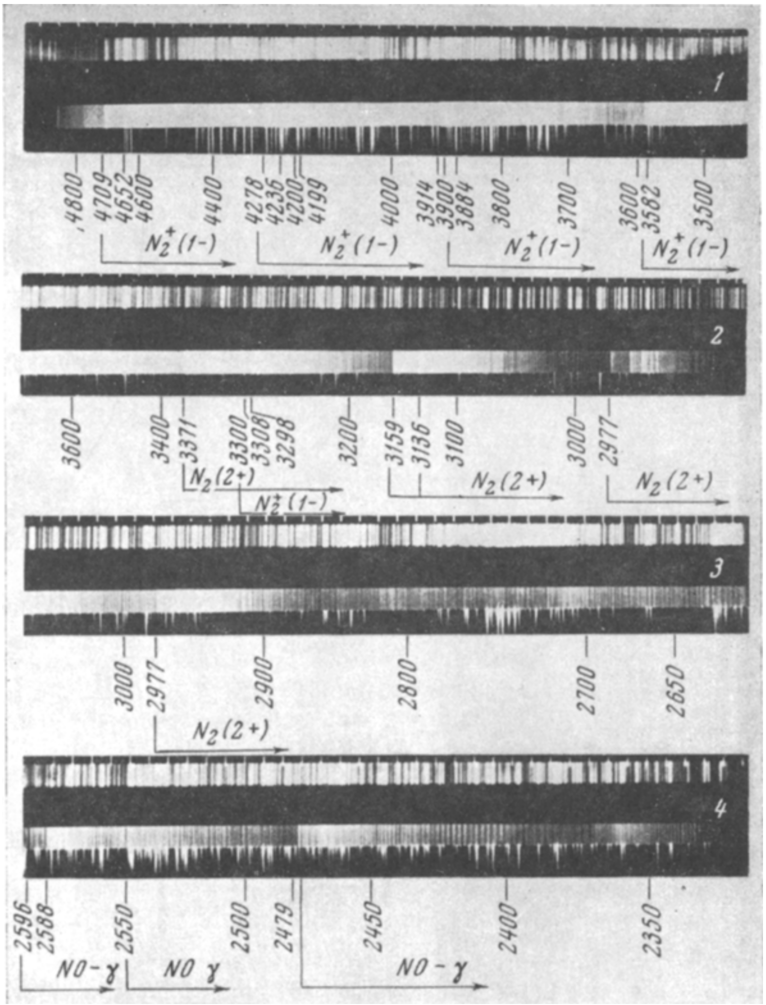

Fig. 8

of the ultraviolet quanta emitted by the plasma are quite sufficient for the breakage of several chemical bonds in the polymer and the release of gaseous products, which form cavities and cracks. Hence, it is natural to assume that the appearance of cavities and the formation of cracks are due to the radiant component of the total heat flux. Direct experimental evidence of this assumption is given in Fig. 5, which shows the front surfaces of Teflon specimens after exposure to the same total heat flux on the apparatus described above (a) and an electric-arc heater (b), where the radiant flux was only about 5% of the total flux. As distinct from the specimen in Fig. 5 a, the specimen in Fig. 5b shows no cracks. Careful microscopic examination of thin sections also confirmed the absence of cavities and cracks in the destruction layer of a specimen subjected to the action of a convective heat flux alone.

Spectral curves showing the fraction of radiant energy transmitted by 0.3-mm-thick films of Teflon (curve 1) and polyethylene (curve 2) at 20° C are illustrated in Fig. 6. With increase in temperature the optical properties of these polymers change considerably and they become more transparent. For instance, when a Teflon film was heated to ~400° C it became much clearer and very transparent, but on cooling it became cloudy again. The transmission curve of such a film heated to 400° C and then cooled in natural conditions is also shown in Fig. 6 (curve 3). For comparison the same figure shows the transmission curve of a polyethylene film heated to 100°C and then cooled naturally (curve 4). Unfortunately, owing to the lack of suitable apparatus, the transmission curves of hot polymer films could not be obtained. The available data, however, suggest that such curves, particularly in the short-wave part of the spectrum, must lie well above the curves in Fig. 6, which were obtained on SF-4 and Perkin-Elmer 402 spectrometers. We note that the reduction in ultraviolet absorption with temperature increase would explain why the maximum number of cavities is formed near the destruction front.

On the Lund-100 apparatus we simultaneously conducted experiments on burning holes in polymers with an infrared Laser beam ($\lambda = 10.5\ \mu$) focused on the surface of the specimen. In every case we found a distinct destruction layer. There were no gaseous cavities or cracks, however, in polymers which were destroyed by the second mechanism in the plasma jet. This is obviously due to the fact that the energy of the thermal fluctuations and the energy of the infrared quanta are not sufficient for the breakage of chemical bonds in these materials. On the other hand, in the case of burning holes in organic glass (Fig. 7) and polystyrene, where the thermal perturbations or the infrared quanta are sufficient for initiation of decomposition, the destruction layer shows a system of microcavities, similar in many respects to the corresponding cavities formed by ablation, and fine cracks passing through some of these cavities. An analysis of thin sections showed that these cracks are irregular channels. These channels subsequently become large disklike cracks, which can also be seen in Fig. 7. In destruction by a laser beam the previous mechanism, involving absorption of radiant energy in a relatively transparent destruction layer and especially on the destruction front, is significant.

The reported mechanism of bulk destruction of thermoplastics by a radiant flux is of importance for applications. Hence, an investigation of this mechanism itself and the spectral composition of the plasma and optical properties of the boundary layer of heated transparent materials is of definite interest. The spectrum of the air plasma used, obtained on ISP-30 spectrographs, is shown in Fig. 8. The most important series of lines are indicated at the edges of the spectrum.

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