

# Primary Molecular Products of Mechanical Fracture of Polymers

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## Synopsis

Primary molecular products of mechanical fracture were determined for polymers of different structure. For the first time the velocities of the products translation were measured, and kinetic energies and translation temperatures (2000–5400 K) were calculated.

## INTRODUCTION

Macroscopic fracture of any solid material is preceded by the accumulation of a large quantity of microcracks. The formation of such a microcrack is of explosive character. The clarification of reasons for superhigh rates of microcrack formation requires the knowledge of the mechanism of their development at the molecular level. During the fracture of a real polymeric material the occurrence of microcracks takes place in the sites of the largest stress concentration. The elastic energy, stored in stretched macromolecules, at their fracture dissipates in the following way:

—It transforms into heat, inducing the rise in temperature in the fracture zone, infrared radiation,<sup>1-3</sup> thermal destruction, and flow.

—It is spent on the fragmentation of free ends of the broken chain and is carried away by the primary molecular products of mechanical destruction in the form of vibratory, rotatory, and translational energy.

—It leads to electronic excitation and ionization and is carried away by photons,<sup>4,5</sup> electrons,<sup>6,7</sup> and ions.<sup>8</sup>

Much attention has been given to the study of different radiations and emissions.<sup>1-8</sup> At the same time the literature, dealing with the study of primary molecular products of mechanical destruction has not been available, though the data on the composition and energy characteristics of these products could allow us to understand the explosive mechanism of microcrack formation. This fact is due to the existence of a number of methodical difficulties. The main reason lies in the necessity of synchronizing the system of high-speed registration of molecular products with the moment of the specimen fracture. To solve the problem, one should use a time-of-flight mass spectrometer. The triggering of such a spectrometer is realized at the moment of quick cutting a specimen by a main crack. This was earlier done with piezoelement fixed on the tractor axle of a stretcher.<sup>9</sup> However, the present study shows that the electrical signal of piezoelement appears only in 7000–12000  $\mu\text{s}$  after the leading edge of the infrared (IR) radiation pulse, accompanying the stage of the fast growth of the main crack in poly-

mers,<sup>1-3</sup> while the time of flight, e.g., for the molecules of methyl methacrylate (MMA), at room temperature from the crack to the ionic source of the mass spectrometer is only 420  $\mu$ s. Thus, one could registrate the molecular products repeatedly reflected from the walls of the vacuum camera, but not those flying directly from the crack.

The discovery of primary molecular products of fracture as such became possible only after we created the installation whose triggering was realized with a IR-radiation pulse.

## EXPERIMENTAL

The following materials were investigated: an amorphous polymer of linear structure, poly(methyl methacrylate) (PMMA), a network polymer based on diglycidyl ether of resorcinol (DGER) and methaphenylene diamine (MPhDA), and composite material, ebonite. At room temperature all the materials undergo brittle fracture. The specimens were turned in the shape of dumbbells with the length of the working section 10 mm. To localize the fracture, a notch was preliminarily made in the middle of the working section. The experiments were performed at room temperature in vacuum  $5-9 \times 10^{-4}$  Pa.

## RESULTS AND DISCUSSION

The main molecular products of PMMA mechanical fracture are MMA (mol mass = 10 amu) and water (mol mass = 18 amu).<sup>10</sup> In Figure 1 are given the kinetics of IR radiation, accompanying the formation of fresh surfaces of PMMA fracture (curve 1) and the variation in the local concen-

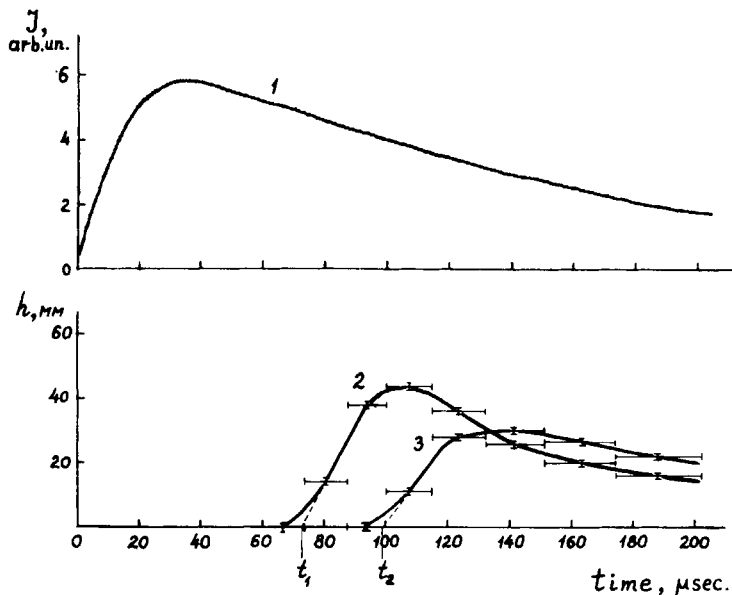


Fig. 1. IR-radiation pulse (curve 1) during PMMA mechanical fracture (breaking).  $I$  is the radiation intensity;  $h$  is the height of the mass-spectrum peak of the product. For water,  $m/e = 18$  (curve 2); for MMA,  $m/e = 41$  (curve 3).

tration of the molecular products of the fracture (water and MMA) in the ionic source (curves 2,3).

The so-called "induction period"  $t_i$  of the  $i$ th product kinetics (curves 2,3) is due to the time during which the  $i$ th molecules fly over the distance  $L$  from the specimen to the ionic source. The values of time-of-flight  $t_i$  obtained from the kinetic curves allow us to calculate the velocities  $V_i = L/t_i$  and kinetic energies  $E_i = M_i V_i^2/2$  of the molecule translation. If we assume that the escape of molecular products from the crack is similar to the process of effusion, we can calculate the translation temperature of gaseous products in the fast-moving crack according to the following formula<sup>11</sup>:

$$T_i = \frac{M_i V_i^2}{3R} \text{ (K)}$$

where  $M_i$  is the molecular mass of the  $i$ th product (amu);  $V_i$  is the most probable velocity of  $i$ th molecules in the beam (cm/s);  $R = 8.314 \times 10^{-7}$  erg/mol K is universal gas constant.

For network polymer DGER-MPhDA the main molecular products of mechanical fracture are acetaldehyde (mol mass = 44 amu) and water (mol mass = 18 amu).<sup>9</sup> In Figure 2 are given the kinetics of IR radiation, accompanying the formation of fresh fracture surfaces of network polymer DGER-MPhDA (curve 1) and the variation in the local concentration of the molecular products of fracture (acetaldehyde and water) in the ionic source (curves 2,3).

The main product of mechanical fracture of ebonite is water. In Figure 3 are given the kinetics of IR radiation (curve 1) and the variation in the water concentration in the ionic source (curve 2).

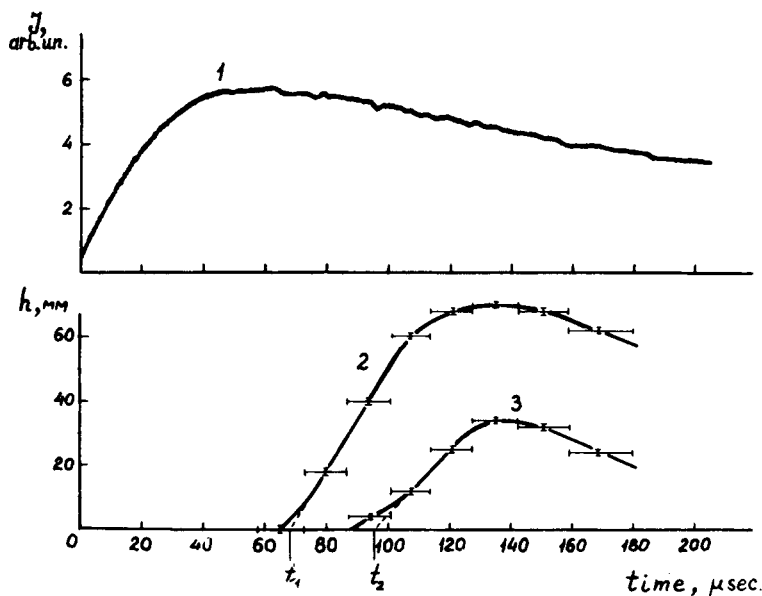


Fig. 2. IR-radiation pulse (curve 1) during the breaking of network polymer DGER-MPhDA.  $I$  is the intensity of the radiation;  $h$  is the height of the mass-spectrum peak of the product. For water,  $m/e = 17$  (curve 2); for acetaldehyde,  $m/e = 43$  (curve 3).

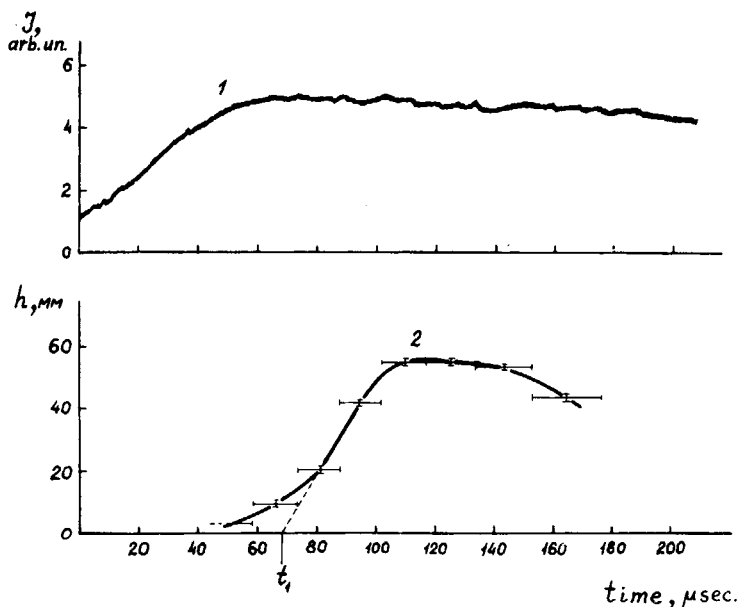


Fig. 3. IR-radiation pulse (curve 1) during ebonite breaking.  $I$  is the radiation intensity;  $h$  is the height of the mass-spectrum peak of the product. For water,  $m/e = 17$  (curve 2).

The results of the calculation of velocities, kinetic energies, and translation temperatures of primary molecular products of mechanical fracture for all the polymers under consideration are given in Table I.

The results obtained allowed us to establish three main facts:

1. Translation temperatures of all the primary products of mechanical fracture for the polymers under consideration are extremely high. For PMMA the values of the temperatures exceed those calculated in Ref. 2 from IR radiations.

2. Values of velocities and, correspondingly, of translation temperature for water for all the polymers are close.

3. For PMMA the temperature of MMA is approximately twice as much as that of water.

TABLE I  
Velocities, Kinetic Energies, and Translation Temperatures of Primary Molecular Products of Mechanical Fracture of the Polymers Under Consideration<sup>a</sup>

Polymer	Molecular products	Velocity (m s <sup>-1</sup> )	Kinetic energy (eV)	Translation temperature (K)
PMMA	MMA	1160 <sup>+160</sup>	0.70 <sup>+0.21</sup>	5410 <sup>+1530</sup>
	Water	1580 <sup>+335</sup>	0.23 <sup>+0.11</sup>	2190 <sup>+460</sup>
DGER-MPhDa	Acetaldehyde	1210 <sup>+100</sup>	0.33 <sup>+0.06</sup>	2570 <sup>+450</sup>
	Water	1680 <sup>+305</sup>	0.26 <sup>+0.11</sup>	2040 <sup>+310</sup>
EBONITE	Water	1690	0.27	2065

<sup>a</sup> The values of velocities and temperatures as well as the mentioned scatter of values, given in the table, are due to the experimental error in Figures 1-3 while determining the value of time of flight,  $t_i$ , which can be found from crossing the inflectional tangent to the kinetic curve at the growth stage  $h(t)$  with the abscissa (time).

Such high values of MMA and acetaldehyde temperatures are probably explained by the fact that, during the polymer chain breaking, a considerable part of the accumulated elastic energy transforms into the kinetic energy of the translation of MMA and acetaldehyde detachable fragments.

The closeness of  $V$  values for water for all the polymeric materials indicates to its similar origin, that is, the sorptive one.

The difference in the temperatures of MMA and water shows that, apparently, Maxwell velocity distribution has not yet been reached in the mixture of gaseous products in the crack. The lower temperature of water is probably due to the fact that during polymer chain breaking a considerably smaller part of the elastic energy is transferred to its molecules, since occluded water is connected with the polymer chain only by "weak" hydrogen bonds.

### CONCLUSION

"Superhot" molecular products occurring in each act of polymer chain breaking, are able to initiate the breaking of several adjacent polymer chains at once. The development of such a branched chain reaction may determine the explosive character of microcrack formation during the mechanical fracture of polymers.

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