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## A COMPARISON OF PYROLYTICAL AND OXIDATIVE DEGRADATION OF POLY(METHYL METHACRYLATE) AND METHYL METHACRYLATE-STYRENE COPOLYMER USING THE CAPILLARY GC AND GC-MS METHODS

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The thermal degradation of poly(methyl methacrylate) (PMMA) and of a methyl methacrylate copolymer with styrene (MMA-ST) were studied in an inert atmosphere and in the air, under conditions simulating a fire. Tubular furnace and high-frequency pyrolyzers were compared. The combustion products were analyzed using the capillary GC and GC-MS methods.

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Plastics based on poly(methyl methacrylate) and its copolymers, especially with styrene, are used as building and interior materials and thus it is important to study their thermal degradation (e.g. refs<sup>1-7</sup>). The decomposition of PMMA can be divided into two stages: *a*) Rapid depolymerization (unzipping) at temperatures below 270°C, with initiation centres at the terminal unsaturated groups. *b*) A slower reaction at temperatures above 270°C that proceeds until the polymer is completely decomposed. The rate of monomer formation depends on the PMMA tacticity and molecular weight. It has been demonstrated<sup>6</sup> that random scission is the initiation step for both the thermal and oxidative degradation, where the activation energy for degradation of PMMA in the air is approximately 4 times lower than that for the degradation under nitrogen. In addition to the monomer that amounts to c. 99% in pyrolysis under nitrogen, isobutyrate has also been identified<sup>3</sup> in the combustion products, as well as the low-molecular substances CO, CO<sub>2</sub> and the C<sub>1</sub> to C<sub>4</sub> hydrocarbons that are produced by the decomposition of the unstable six-membered anhydride ring.

The present work compares the results of pyrolysis of PMMA and MMA-ST copolymer in a tubular furnace and a high-frequency pyrolyzer with thermooxidation under conditions simulating a fire.

## EXPERIMENTAL

PMMA Vedril and MMA-ST copolymer Umacryl, produced in Czechoslovakia, were studied. The other chemicals were obtained from Lachema, Czechoslovakia and were of p.a. purity.

### Apparatus and Methods

In pyrolysis capillary GC, a tubular furnace pyrolyzer<sup>8</sup> and a high-frequency pyrolyzer<sup>9</sup> were employed. Thermooxidation was carried out in a combustion chamber<sup>10</sup>. The combustion products were either directly injected into a gas chromatograph, were frozen out for GC-MS analysis, or were collected in a solution of 2,4-dinitrophenylhydrazine in 2M-HCl for analysis of carbonyl compounds. The thermooxidation temperature was 800°C, equal to that used for pyrolysis.

The degradation products were analyzed on a stainless steel capillary column (50 m × 0.2 mm) coated with squalane, at 70°C, or on a packed column (130 cm × 3 mm i.d.) with 5% OV-101 on silanized Chromosorb W (60–80 mesh) at 232°C, with a gas chromatograph CHROM IV (Laboratorní přístroje, Czechoslovakia). The nitrogen flow rates were 0.3 and 30 ml min<sup>-1</sup> for the capillary and packed column, respectively.

A Finnigan 400 GC/MS instrument (Finnigan MAT, U.S.A.) in the EI mode was employed for the GC-MS analysis under the following conditions: a CP Sil 5 CB fused silica column (50 m × 0.33 mm i.d.) was directly inserted into the ion source, a temperature program included 5 min at 70°C, then 5°C min<sup>-1</sup> up to 200°C, then isothermal; helium carrier gas flow rate, 21 ml . min<sup>-1</sup>, split ratio, 1 : 100 (splitter temperature, 200°C); injected volume, 1 µl (injector temperature, 220°C); electron energy, 70 eV; electron current, 0.30 mA; ion source temperature, 250°C; interface furnace temperature, 200°C.

## RESULTS AND DISCUSSION

In pyrolysis of PMMA in the high-frequency pyrolyzer, only small amounts of the C<sub>1</sub> and C<sub>2</sub> hydrocarbons and methyl isobutyrate are formed in addition to the monomer, in agreement with the theory (Fig. 1a). The high amount of degradation products identified when the furnace pyrolyzer was used (Fig. 1b) indicates the presence of secondary reactions. The compounds were identified on the basis of comparison of accurately measured retention indices with the literature values<sup>11</sup>.

Similar results have been obtained in pyrolysis of the MMA-ST copolymer. Whereas only a small amount of toluene is found in addition to MMA and styrene in a high-frequency pyrolyzer (Fig. 2a), the furnace pyrolyzer yields not only products typical for pure PMMA (Fig. 1b), but also many substances characteristic of the thermal degradation of styrene (benzene, toluene, ethylbenzene (see Fig. 2b)).

The products of the thermooxidation in the combustion chamber (for the combustion conditions for plastics and the sampling procedure, see ref.<sup>10</sup>) are analogous to those obtained from pyrolysis in the furnace pyrolyzer. The capillary GC of the gaseous sample collected from the chamber indicated the presence of MMA and also methane, ethene, ethane, propene, 1-butene and the methyl esters of formic, acetic, acrylic and isobutyric acids.

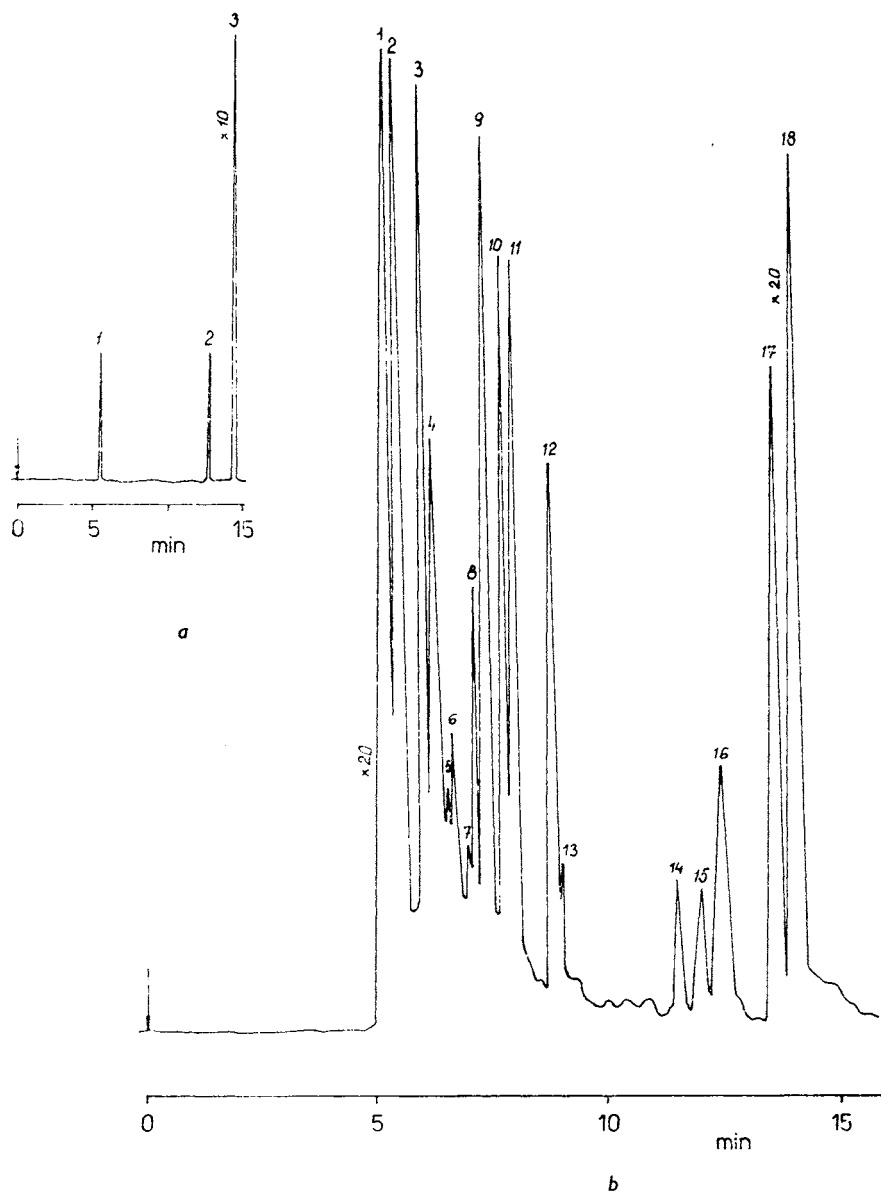


FIG. 1

Comparison of the pyrolysis degradation products of PMMA Vedril obtained with *a* high-frequency and *b* tubular furnace pyrolyzer. *a* 1 Hydrocarbons  $C_1$  and  $C_2$ , 2 methyl isobutyrate, 3 methyl methacrylate; *b* 1 hydrocarbons  $C_1$  and  $C_2$ , 2 propene, propane, 3 butane, 4 methanol, 5, 6 not identified, 7 1-pentene, 8 ethanol, 9 pentane, 10 1-*trans*-3-pentadiene, 11 1,2-pentadiene, 12 methyl acrylate, 13 methyl propionate, 14 1-*trans*-3-hexadiene, 15 not identified, 16 methyl isobutyrate, 17 benzene, 18 methyl methacrylate

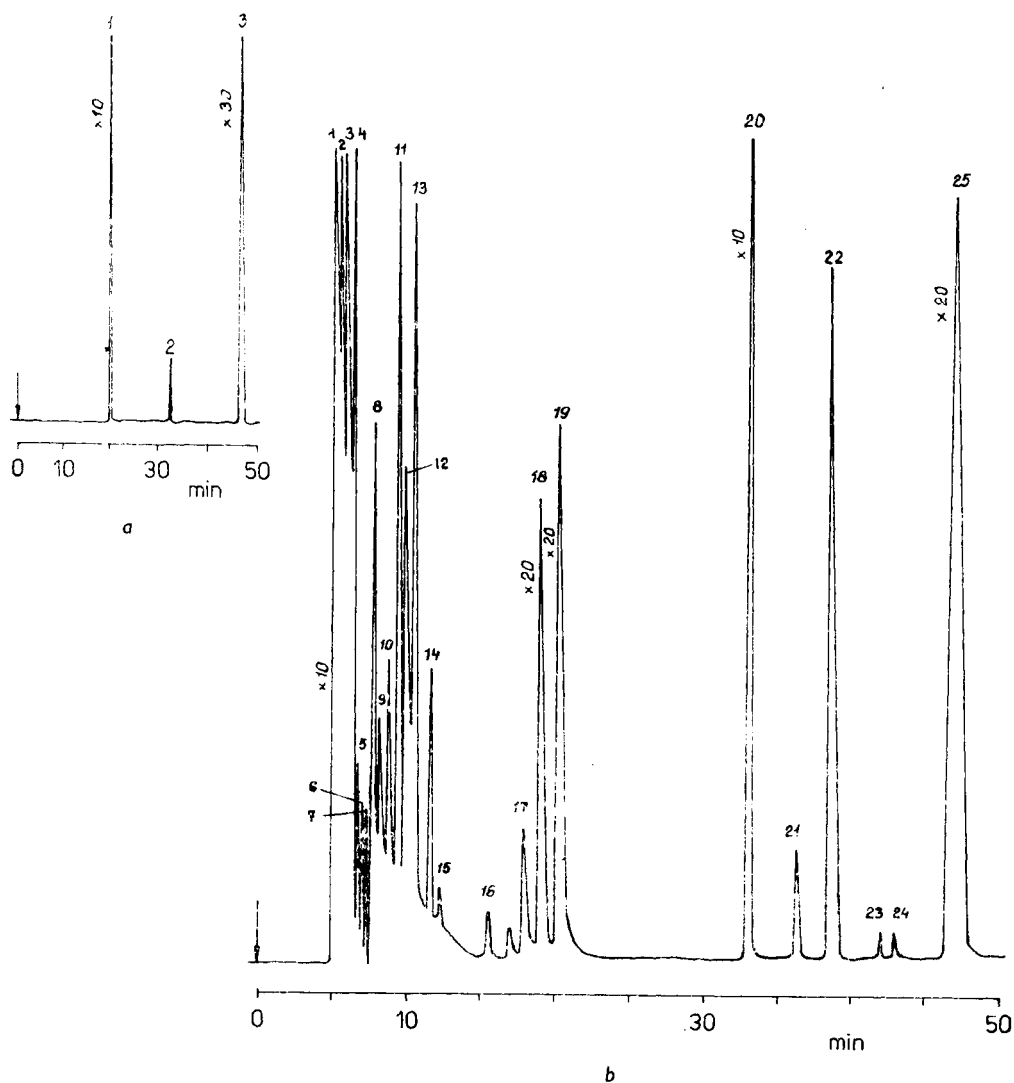


FIG. 2

Comparison of the pyrolysis degradation products of MMA-ST copolymer Umacrlyl obtained with *a* high-frequency and *b* tubular furnace pyrolyzer. *a* 1 Methyl methacrylate, 2 toluene, 3 styrene; *b* 1 hydrocarbons  $C_1$  and  $C_2$ , 2 propene, propane, 3 acetaldehyde, 4 not identified, 5 1-butene, 6 butane, 7 not identified, 8 methanol, 9 methyl acetate, 10 1-pentene, 11 ethanol, 12 1-*trans*-3-pentadiene, 13 1,2-pentadiene, 14 methyl acrylate, 15 methyl propionate, 16 1-*trans*-3-hexadiene, 17 methyl isobutyrate, 18 benzene, 19 methyl methacrylate, 20 toluene, 21 phenylacetylene, 22 ethylbenzene, 23 *p*-xylene, 24 *m*-xylene, 25 styrene

The Umacryl sample was frozen out after thermooxidation and analyzed by GC-MS (Fig. 3). The complex spectrum of the products involves the monomers,

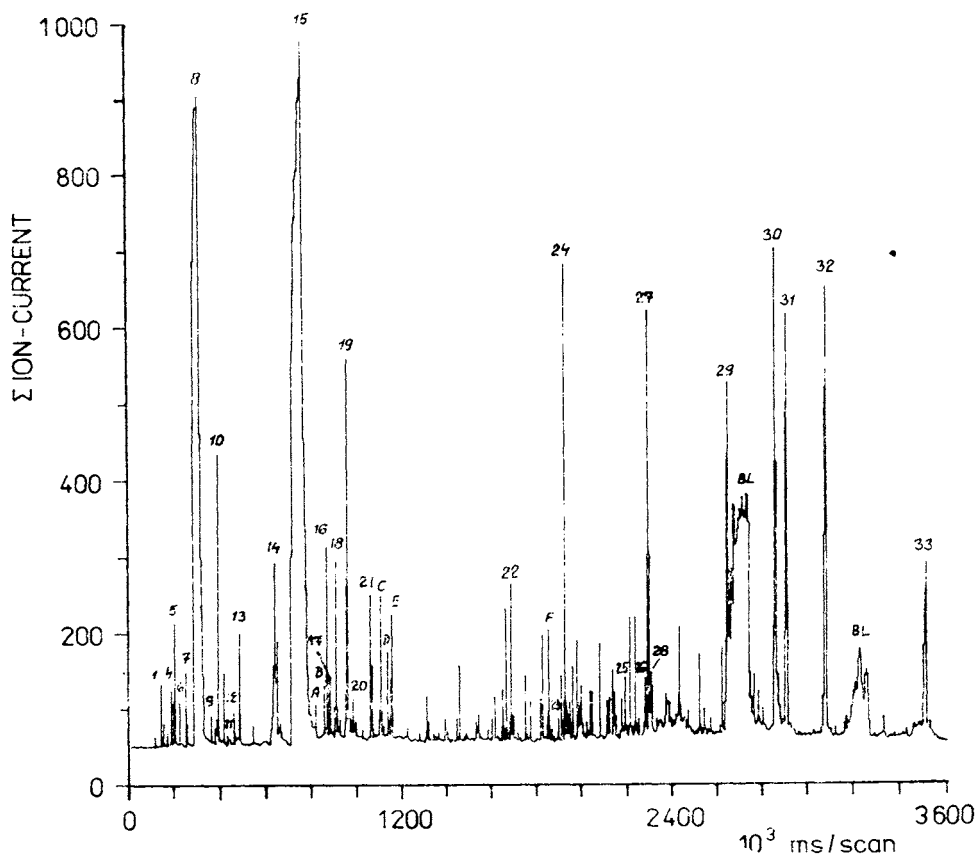


FIG. 3

Thermooxidation products of copolymer Umacryl determined by GC-MS. 1 Acetone, 2 methyl acetate, 3 2-methyl-2-propenal, 4 methyl acrylate, 5 methyl propionate, 6 benzene, 7 methyl isobutyrate, 8 methyl methacrylate, 9 ethenyl methacrylate, 10 toluene, 11 ethyl methacrylate, 12 methyl ester of 2-butenecarboxylic acid, 13 methyl ester of 1-methylenepropanecarboxylic acid, 14 ethylbenzene, 15 styrene, 16 3-phenylpropene, 17 phenylpropane, 18 benzaldehyde, 19  $\alpha$ -methylstyrene, 20 2,3-dihydro-1*H*-indene, 21  $\beta$ -methylstyrene, 22 methyl ester of 1-methylene-2-phenylacetic acid, 23 1,2-diphenylpropane, 24 dimer of MMA-ST, 25 1,3-diphenylpropane, 26 1,2-diphenylethene, 27 2,4-diphenyl-1-butene, 28 1,2-diphenyl-1-propene, 29 diphenylpentane, 30 diphenylhexene, 31 diphenylhexene, 32 1-(2-phenyl-2-propenyl)pentanedioic acid dimethyl ester, 33 triphenylhexene. Uncertain: A 1-phenylethanone, B methyl ester of 3,3-dimethyl-1-butenecarboxylic acid, C 3-butenylbenzene, D 2-methyl-1-propenylbenzene, E phenylacetaldehyde, F 4-phenyl-1-butenecarboxylic acid methylester, BL column bleeding

dimers and trimers, and also unsaturated and saturated esters of carboxylic acids and styrene degradation products.

Aldehydes are difficult to detect among the combustion chamber products because of their instability. The degradation products were, therefore, trapped in a 2,4-dinitrophenylhydrazine solution, converted into the corresponding 2,4-dinitrophenylhydrazones and analyzed by GC (ref.<sup>10</sup>). The pure PMMA Vedril combustion products were found to contain traces of methanal (less than 0.001%), ethanal (0.011%), propanal (0.002%) and acetone (0.006%). The Umacryl copolymer yielded traces of methanal, ethanal (0.012%), propanal (0.004%), acetone (0.010%) and 2-butanone (less than 0.001%).

It further follows from the above results that a large number of volatile products is formed during the combustion of PMMA and MMA-ST copolymer, many of which are toxic for living organisms. Their detection is thus important from the point of view of the dangerous effects of combustion products.

The above results indicate that the high-frequency pyrolyzer is more suitable for characterization of polymers. The results obtained with the furnace pyrolyzer are distorted by secondary reactions and are similar to those obtained by degradation in the air.

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