doi: 10.56761/EFRE2022.S4-P-021901

Non-equilibrium plasma of pulsed corona discharge for the purpose of air purification from typical ventilation exhausts of polymer production

*I. Filatov**, *V. Uvarin, D. Kuznetsov*

Institute of Electrophysics UB RAS, Yekaterinburg, Russia
**fil@iep.uran.ru*

Abstract. The paper presents the results of a study of the impact of pulsed corona discharge plasma on air containing volatile products of polymer pyrolysis. The following materials were chosen as objects of study: rubber, polypropylene and ABS plastic. Polymeric materials were subjected to pyrolysis at a temperature of 550–650 °C. Analysis of the products was carried out by GC/MS method. These are aliphatic and aromatic unsaturated compounds of various structures, including monomers. Components with increased volatility (b.p. < 160 °C) can pollute the air, so they were studied in detail. For the research, a pulsed corona discharge was used with the following parameters: pulse duration 40 ns, pulse repetition rate 10 Hz, voltage 100 kV, current – up to 100 A. The relative reactivity of the components was estimated using the method of competing reactions. It is shown that the method more effectively removes unsaturated and saturated aliphatic compounds whereas aromatic compounds eliminate less effectively. It is shown that high reactivity of unsaturated compounds is due to their interaction with ozone. The found dependencies will be useful in the development of new energy-efficient air purification technologies for the tasks of primary and secondary processing of plastics.

Keywords: Plastics manufacturing, plastics recycling, air purification, non-equilibrium plasma, corona discharge.

1. Introduction

The production and recycling of polymeric materials are the one of most important sources of air pollution with volatile organic compounds (VOCs) [1]. Technologies using non-equilibrium plasma (NP) of electric discharges of various types are promising for air purification from VOCs vapors. A significant part of them is monomeric compounds used for the production of polymers: butadiene, styrene, acrylonitrile, methyl methacrylate (MMA), acrylic esters and many other compounds. As a rule, these are highly toxic compounds. The air can be polluted by them during production, processing and molding of plastics, recycling. A large amount of VOCs is formed during the heat treatment of plastics and during their recycling through pyrolysis in order to obtain chemical raw materials [2].

The work presents the results of a study of the impact of pulsed corona discharge plasma on air containing volatile products of pyrolysis of polymers of wide application: rubber, polypropylene, ABS plastic. To create test mixtures, objects from the above materials were subjected to pyrolysis then subjected to distillation with the separation of the volatile fraction (b.p. up to 160 °C), because it is the fraction that is more responsible for air pollution. These are the model mixtures based on these fractions in the gaseous state that were exposed to the pulsed discharge plasma. The initial and processed mixtures were analyzed using the gas chromatography mass spectrometry GC/MS method. The patterns found were analyzed using the method of competing reactions developed by us [3, 4].

2. Procedures and methods

2.1. Objects of study

Objects were selected as materials for the study are shown on Fig.1. Rubber gloves (*a*) made of natural latex. Disposable medical masks made of polypropylene (*b*) and a filament of ABS plastic for 3D printing (*c*). A sample of 10 g of the material was subjected to pyrolysis in a stainless steel tube at temperature of 550–650 °C, volatile products were collected in a cooled receiver, then subjected to distillation with the selection of a volatile fraction with b.p. less than 170 °C. This fraction was introduced into the air mixture and subjected to pulsed corona plasma treatment.

a *b* *c*

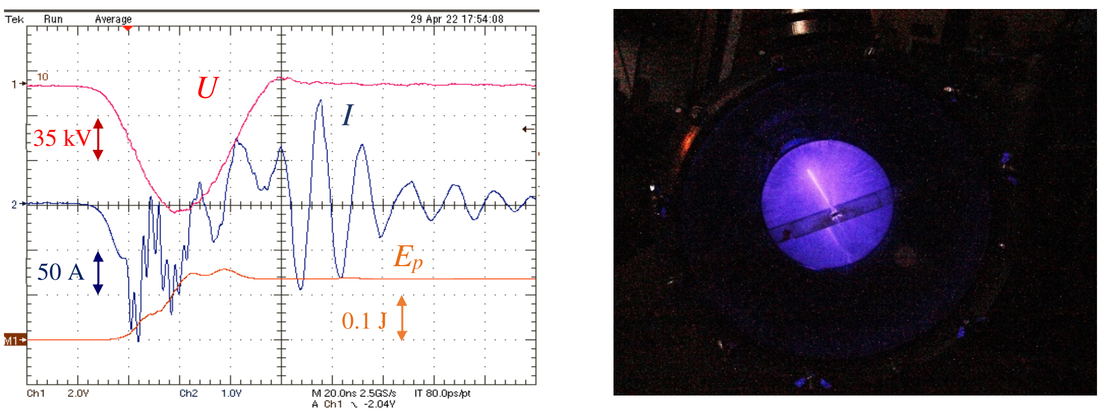
Fig.1. Objects of research: (*a*) – rubber gloves made of natural latex (cross-linked isoprene); (*b*) – disposable medical masks (polypropylene); (i) – a filament for 3D printing (ABS plastic).

2.2. Experimental setup

The experimental setup is described in detail in [3]. A high-voltage pulse generator was built according to the scheme using SOS switches [5]. Installation parameters are shown in Table 1.

Table1. Experimental setup parameters

Parameter	Value
Voltage (amplitude)	100 kV
Current (amplitude)	150 A
Pulse half-height duration	40 ns
Pulse energy	120–140 mJ
Pulse repetition frequency	10 Hz
Discharge chamber length	560 mm
Internal diameter of the discharge chamber	110 mm
Electrode diameter	0.24 mm
Gas system volume	26 dm^3



a *b*

Fig.2. (a) – oscillograms of the typical pulse; (b) – external view of the corona discharge during operation.

A typical pulse oscillograms is shown in Fig.2a, the discharge gap during operation is shown in Fig.2b. The pulse energy E_p was calculated from the waveforms $U(t)$ and $I(t)$, for each series according to the formula: $E_p = \int U(t)\mathrm{I}(t)dt$. The specific energy E was calculated by the formula $E = E_\mathrm{p}\, ft/V$, where V is the volume of the gas system of the installation, $V = 26$ dm^3. As a mixture simulating air, a commercial gas mixture "Synthetic air" with the composition N_2:O_2 = 80:20 (vol.) was used. The test fraction in liquid form in the amount of 50 μl was introduced into the volume of the gas system and in the gaseous state was evenly distributed over the volume of the system. The gas mixture was processed by a series of pulses with a duration of t = 2–6 minutes. The initial gas mixture and the mixture after processing by a series of pulses were analyzed by the GC/MS method, the ozone content was determined by the spectrometric method at a wavelength of 255 nm according to a procedure similar to [6].

2.3. Analysis method

The analysis was carried out on a Varian Saturn 2100T GC/MS complex equipped with a Varian VF-5MS capillary column with an inner diameter of 0.25 mm, a phase film thickness of 0.25 μ, and a length of 30 m. Analysis conditions: evaporator temperature – 250 °C, without flow splitting, amount of gaseous sample injected with a syringe – 0.5 ml, carrier gas (helium) velocity – 1 ml/min. The temperature of the transition part is 175 °C, the ion trap T is 150 °C. The temperature regime of the columns is specified in each case especially. The binding of chromatographic peaks to specific compounds from the NIST mass spectra database was carried out using the software supplied with the Varian Saturn complex. For convenience, each of the compounds discussed is accompanied by a CAS number, which can be used to obtain comprehensive data of the mentioned compound using the website [7], NIST [8] or National Center for Biotechnology Information [9].

3. Results

3.3. Rubber pyrolysis products

Natural rubber (see Fig.1a) is a polymerized, cross-linked isoprene. During pyrolysis at temperatures up to 650 °C, it forms a liquid mixture of organic compounds of aromatic and aliphatic structure with a good yield (up to 80 %). The volatile fraction was separated at a temperature < 70 °C and served as the object of study. Conditions for GC/MS analysis: column temperature – 50 °C. Fig.3 shows typical chromatograms of air with the addition of a fraction (top) and chromatograms with increasing specific energy (top to bottom). It can be seen that the main component of the fraction is isoprene ***1a*** with an estimated initial concentration of 430 ppm, which is effectively removed by pulsed discharge plasma. Measurement of the ozone concentration shows that it is formed only after the complete removal of the impurity. In the course of plasma treatment, it is possible to determine the formation of a certain amount of oxidation product ***1b***. Unsaturated compounds, as shown earlier [6, 10, 11] are effectively removed by ozone generated by non-equilibrium plasma in air mixtures.

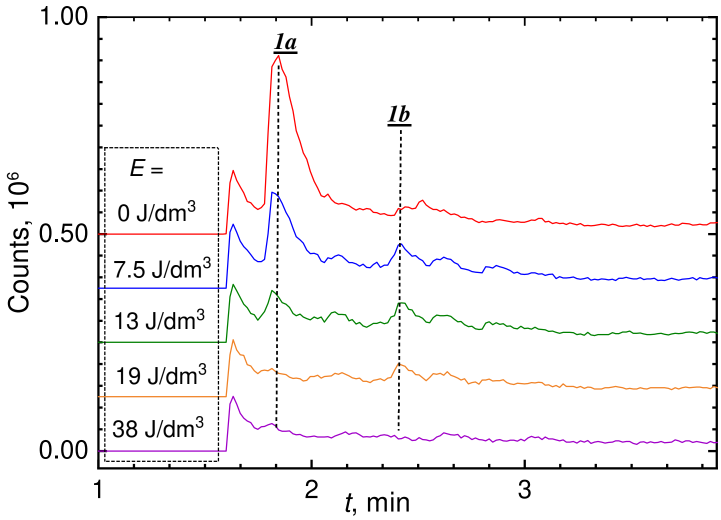


Fig.3. Chromatograms of the volatile fraction of the rubber pyrolysis product at different E. The numbers indicate the chromatographic peaks of the compounds: ***1a*** – Isoprene (CAS # 78-79-5); ***1b*** – Isoprene oxide (CAS # 1838-94-4).

3.3. Polypropylene pyrolysis products

Polypropylene is a very widely used plastic. In particular, disposable medical masks are made from it (Fig.1b). During pyrolysis at temperatures up to 600 °C, it forms a liquid complex multicomponent mixture of aliphatic compounds with a good yield (up to 90 %). The light fraction was separated at a temperature < 120 °C and served as the object of study. Additional conditions for GC/MS analysis: column temperature – 50 °C, exposure for 10 minutes, then temperature is increased to 200 °C at a rate of 20 °C/min. Fig.4 shows typical chromatograms of air with an admixture of a fraction (top) and chromatograms with increasing specific energy (from top to bottom). The main component of the fraction is 2,4-dimethyl-1-heptene ***2e*** with an estimated initial concentration of 486 ppm, which is effectively removed by treatment with pulsed discharge plasma. The fraction contains a number of unsaturated hydrocarbons (***2a***, ***2b***, ***2e***, ***2f***, ***2k***) and saturated (***2d***, ***2e***). It is interesting to note that unsaturated hydrocarbons are removed clearly better than saturated hydrocarbons, which is associated with the presence of a reaction center with ozone in them – a double bond [6, 10, 11]. Measurement of ozone concentration shows that it is formed only after complete removal of impurities. During processing, it is possible to identify a number of intermediate oxidation products – (***2h***, ***2i***, ***2j***, ***2l***), which are also removed during further processing.

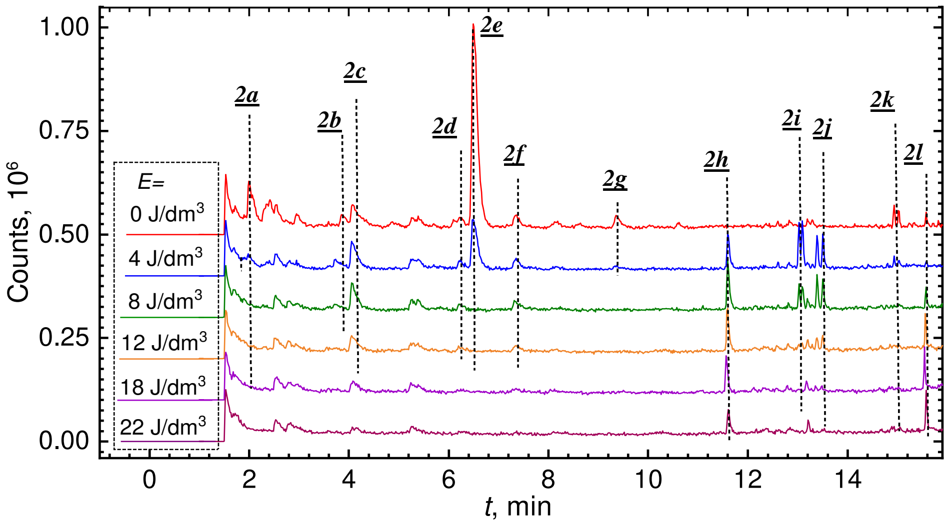


Fig.4. Chromatograms of the volatile fraction of the polypropylene pyrolysis product at different *E*. The numbers indicate the chromatographic peaks of the compounds: ***2a*** – 2-Methyl-1-pentene (CAS # 763-29-1); ***2b*** – 3-Methyl-2-hexene - (NIST C17618778); ***2c*** – 3-Methyl-2-hexane (CAS # 589-34-4); ***2d*** – Cyclohexane, 1,3,5-trimethyl- (NIST C1839630); ***2e*** – 2,4- Dimethyl-1-heptene (CAS # 19549-87-2); ***2f*** – Cyclohexane, 1,3,5-trimethyl-, (1α,3α,5α)- (NIST C1795273); ***2f*** – 2-sec-Butil-3-methyl-pentene (CID 549943); ***2h*** – 2-Heptanone-4-methyl (CAS # 6137-06-0); ***2i*** – Oxirane, (2-methylpropyl)-(CAS # 23850-78-4); ***2j*** –2 -Heptanone, 4,6-dimethyl (19549-80-5); ***2k*** – 3-Undecene, (E) (CAS # 1002-68-2); ***2l*** – 2-Nonene-1-ol (CAS # 22104-79-6).

3.3. ABS pyrolysis products

ABS plastic is widely used for the manufacture of office equipment cases and 3D printing (Fig.1c). It is a product of copolymerization of styrene, acrylonitrile and butadiene. During pyrolysis at temperatures up to 550 °C, it forms a liquid mixture of aromatic and aliphatic organic compounds with good progress (up to 85 %). The light fraction was separated at a temperature < 170 °C and served as the object of study. Additional conditions for GC/MS analysis: column temperature – 70 °C, exposure for 7 minutes, then temperature is increased to 200 °C at a rate of 20 °C/min. Fig.5 shows typical chromatograms of air with an admixture of a fraction (top) and chromatograms with increasing specific energy (top to bottom). The main components are clearly identified and it was possible to measure the initial concentrations of the components, using standard references: number, name, starting concentration (ppm), respectively: ***3a***, toluele, 72; ***3b***, ethylbenzene, 52; ***3c*** – styrene, 204; ***3d*** – benzene-(1-methylethyl), 20; ***3f*** – α-Methylstyrene, 24. It can be seen that unsaturated compounds are removed more efficiently and it is possible to see the intermediate product of styrene oxidation ***3e*** – (benzaldehyde). As was shown before, unsaturated compounds are removed by the discharge plasma more efficiently than aromatic ones, which is in good agreement with [10, 11]. Aromatic hydrocarbons have increased stability, however, if the aliphatic tail contains more hydrogen, they are removed better, which is consistent with [12].

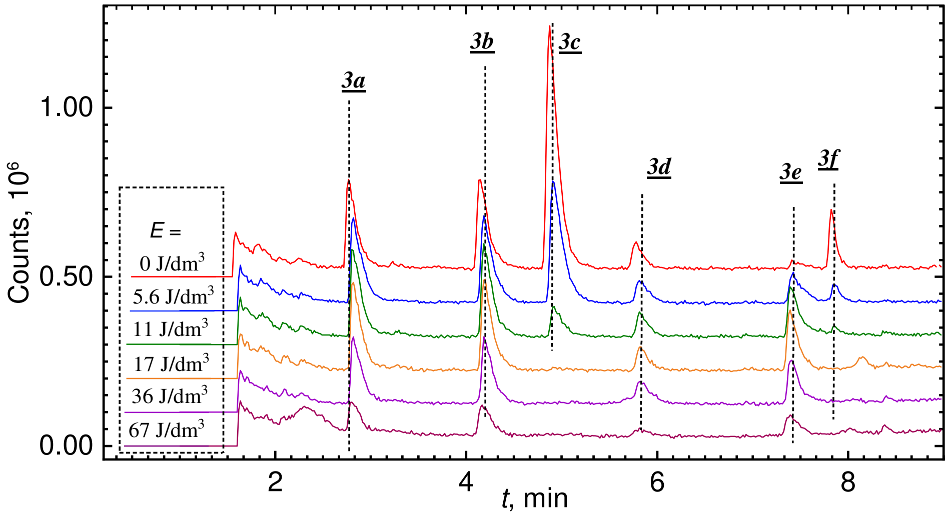


Fig.5. Chromatograms of the volatile fraction of the ABS pyrolysis product at different *E*. The numbers indicate the chromatographic peaks of the compounds: ***3a*** – Toluele (CAS # 108-88-3); ***3b*** – Ethylbenzene (CAS # 100-41-4); ***3c*** – Styrene (CAS # 100-42-5); ***3d*** – Cumene (CAS # 98-82-8); ***3e*** – Benzaldehyde (CAS #100-52-7); ***3f***– α-Methylstyrene (CAS # 98 -83-9).

4. Conclusion

With the help of the GC/MS method, on the example of complex mixtures of volatile products of plastic pyrolysis, it is shown that the plasma of a pulsed corona discharge effectively removes unsaturated volatile compounds. This effect can be explained by their reaction of components with ozone generated by non-equilibrium plasma. The regularities found will be useful for the development of technologies for air purification by plasma-chemical methods at different stages of production and processing of plastics. Research on the evaluation of the energy parameters of processes continues.

Funding

The work was financially supported in part by the RFBR Grant No. 20-08-00882 and RFBR & Sverdlovsk region, Grant No. 20-48-660062 r_a.

Acknowledgement

The work was carried out with the involvement of equipment: 'GC/MS complex Varian Saturn 2100T' from the Centre of collective usage, IEP UB of the RAS.

5. References

[1] Schnelle Jr K.B., Dunn R.F., Ternes M.E., *Air Pollution Control Technology Handbook.* (CRC press, 2016.); doi: 10.1595/205651318X696657

[2] Wampler T.P., *Applied pyrolysis handbook*. (CRC press, 2006.)

[3] Filatov I.E., Uvarin V.V., Kuznetsov D.L., *Tech. Phys.*, **63**(5), 680, 2018; doi: 10.1134/S1063784218050079

[4] Filatov I.E., Uvarin V.V., Kuznetsov D.L., *J. Phys.: Conf. Ser.*, **1147,** 012122, 2019; doi: 10.1088/1742-6596/1147/1/012122

[5] Rukin S.N., *Sci. Instrum.*, **91**, 011501, 2020; doi: 10.1063/1.5128297

[6] Filatov I.E., Uvarin V.V., Kuznetsov D.L., *Tech. Phys. Lett.*, 46(1), 94; 2020; doi: 10.1134/S1063785020010216

[7] CAS Common Chemistry [online], https://commonchemistry.cas.org

[8] NIST Chemistry WebBook [online], https://webbook.nist.gov

[9] National Center for Biotechnology Information [online], https://pubchem.ncbi.nlm.nih.gov

[10] Filatov I.E., Uvarin V.V., Kuznetsov D.L., *Proc. IEEE 2020 7th International Congress on Energy Fluxes and Radiation Effects (EFRE)*, Tomsk, Russia, 317, 2020; doi: 10.1109/EFRE47760.2020.9242056

[11] Filatov I.E., Uvarin V.V., Kuznetsov D.L., Proc. *IEEE 2020 7th International Congress on Energy Fluxes and Radiation Effects (EFRE)*, Tomsk, Russia, 322, 2020; doi: 10.1109/EFRE47760.2020.9242070

[12] Filatov I.E., Uvarin V.V., Nikiforova E.V., Kuznetsov D.L., *J. Phys.: Conf. Ser.*, 2064, 012094, 2021; doi: 10.1088/1742-6596/2064/1/012094