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THE PYROLYSIS OF POLYMERS AND IDENTIFICATION OF THE SOOT ADSORBED COMPONENTS

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Various polymers like polyethylene, polyvinyl chloride, polyamide 6 and polypropylene were burnt in an open flame furnace according to DIN 4102. The generated soot particles were collected on glass fiber filters followed by elution with tolouene. A great part of the soot extract adsorbed compounds could be identified by means of gaschromatographic and mass spectrometric analysis. For polyvinyl chloride and polystyrene mainly aromatic combustion products like naphthalene, phenanthrene, pyrene and chrysene were detected in contrast to polyethylene and polypropylene which form aliphatic and olefinic products. In the chromatograms these components are often interfered by superimposition of the aromatics. The extractions of the sample receiver with nitromethane lead to the separation of the aromatic - from the aliphatic compounds. Monomeric and dimeric ϵ-caprolactam were mainly formed by burning polyamide 6.

Introduction

The investigation of combustion gases of polymers, single compounds and new developed polymer products is gaining more and more importance. From the great number of nontoxic natural- and complete harmless for health synthetic products it is known that they may form harmful compounds undergoing a thermal treatment. In the field of the analysis of combustion gases extensive investigations have been carried out in the last years [1-16].

Until now only some authors describe the formation of soot and the higher molecular compounds especially the polycyclic aromatic compounds (PAH) during the combustion processes in a vertically arranged quartz tube [1-3,9].

We have taken up these results and are performing combustion experiments under nearly real conditions in an open flame furnace according to DIN 4102 [23,26].

Experimental

Materials

The following materials have been burned in the open flame furnace according to DIN 4102: Polystyrene (PS), impact resistant polystyrene (IPS), polyvinyl chloride (PVC), polyethylene (PE), polypropylen (PP) and polyamide 6 (PA).

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Basing on the small burner test (DIN 4102) the polymer samples have been burned in the furnace according to the testing specifications [23,26]. The soot which is formed during the temperature controlled combustion is collected by use of a membrane pump on glass fibre filters installed above the sample. The air flow rate has been adjusted to 6 l/min.

Analytical equipment and conditions

Gas chromatograph: Perkin-Elmer Sigma 2b; Detector: flame ionization detector; Column: SE 54 fused silica capillary column 50 m; Initial temperature: 100°C; Final temperature: 310°C;
Heating rate: 4°C/min; Prepressure of the carrier gas helium 2 bar
Additional experiments carried out by use of a Finnigan MAT 8200 and a Finnigan MAT CH 5 gas chromatography/mass spectrometry system (GC/MS). Some of the PAH identified by comparing their retention times with those of reference standards of Machery and Nagel Co.

Sample pretreatment

After collecting the soot the impacted filters were weighed and 4 hours extracted with toluene in a soxhlet extractor. The solution was concentrated nearly to dryness in an rotation evaporator and treated with 1 ml toluene followed by filtration through a glass fibre filter.

Results and discussion

Impact resistant Polystyrene (PS)

In contrast to PE and PP during the combustion of IPS great amounts of soot are generated. The glass fibre filter has to be changed after 5 min sampling due to a decrease of the air flow rate effected by the filter cake. The following listed compounds could be identified:

tetrahydronaphthalene, naphthalene, (1-)2-methylnaththalene, biphenyl, acenaphthylene, diphenylethane, fluorene, (1,1-)1,2-diphenylethene, dihydrophenanthrene, dimeric styrene, phenanthrene, anthracene, 9-methylphenanthrene, 2-phenylphenanthrene, 4,5-dihydropyrene, fluoranthene, diphenylacetylene, pyrene, benzofluorene, terphenyl, 11H-benzo(a)fluorene, benzo(c)phenanthrene, trimeric styrene, benzo(a)anthracene, chrysene, isomeric binaphthalenes, benzo(j)-fluoranthene, benzo(e)pyrene, quaterphenyl

The main part of the soot adsorbed compounds are of aromatic nature. On the one hand they are direct degradation components of the polymers (dimeric and trimeric PS) and on the other hand they are formed by condensation or recombination reactions of decomposition products in the gas phase. The chromatograms of IPS and PS are quite similar showing only differences in the concentrations of dimeric and trimeric styrene which is higher in the case of PS.

Polyvinyl chloride (PCV)

Especially with respect to the thermal decomposition and the HCl evolution PVC is has been extensively investigated. Hydrogen chloride is the main degradation component. PCV is not easily inflammable and goes out after removal of the flame. In our experiments regarding the analytical determinations only sufficient soot could be collected from the burning of three samples. A typical chromatogram of the toluene extracted and separated compounds is shown in Fig. 1. The indicated numbers are referring to the compounds as listed below the Figure.

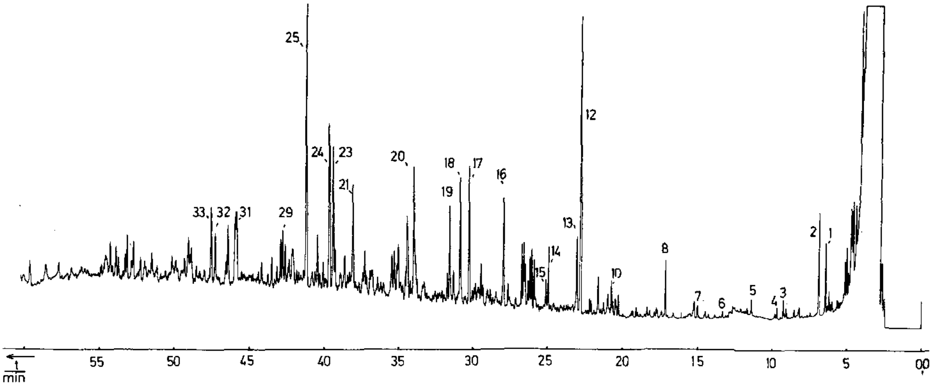

Fig. 1 Chromatogram of the PVC-soot adsorbed compounds

Compounds which have been adsorbed on PVC soot:

B. 1-ethyl-2-methylbenzene, C. 1,3,5-trimethylbenzene, D. 1-methyl-3-propylbenzene, E. 2-methyl-1,4-diethylbenzene, F. tetramethylbenzene

1. tetrahydronaphthalene, 2. naphthalene, 3. 2-methylnaphthalene, 4. 1-methylnaphthalene, 5. biphenyl, 6. acenaphthylene, 7. diphenylethane, 8. fluorene, 9. 1,1- or 1,2-diphenylethene, 10. 9,10 dihydrophenanthrene, 11. not identified, 12. phenanthrene, 13 anthracene, 14. not identified, 15. 9-methylphenanthrene, 16. 2-phenylphenanthrene, 17. fluoranthene, 18. diphenylacetylene, 19. pyrene, 20. benzofluorene, 20a. not identified, 21. benzo(c)phenanthrene, 22. not identified, 23. benzo(a)anthracene, 24. chrysene, 25.-28. not identified, 29. and 30, binaphthalene, 31. benzo(j)fluoranthene, 32. benzo(e)pyrene), 33. benzo(a)pyrene.

The compounds indicated as A-F are not marked on the chromatogram. Their peaks are superimposed by the solvent peaks. But they could be separated by applying a lower column temperature of 60°C and identified by GC/MS. The composition of the soot adsorbed compound of PVC shows great similarities comparing these results with those taken from the IPS experiments.

Polyamide 6 (PA)

The PA material is not easily inflammable but it burns continuously accompanied by dropping. The identified compounds are mentioned below:

ε-caprolactam, dimeric ε-caprolactam, tetrahydronaphthalene, biphenyle, diphenylethane, phenanthrene, fluoranthene, diphenylacetylene

This is in agreement with the results reported previously [21].

Polypropylene (PP)

The pure PP is easily inflammable and burns accompanied by dropping. The formation of soot is more intensive than in the case of PA, PVC and PE. Mainly aliphatic and olefinic components could be detected by means of the GC and GC/MS (see also Ref. 4,5,11). But special interest has been focussed on the detection of the PAH. For the analysis of the PAH a modification of the sample pretreatment is required because the PAH peaks are overlapped by the olefinic and aliphatic compounds peaks.

After the extraction and concentrating the extract 1 ml cyclohexane was added followed by dosage of 1 ml nitromethane and shaking for 1 hour on a mechanical shaker. An amount of 70-80% of the PAH components are enriched in the nitromethane phase. The below listed substances could be identified:

naphthalene, 2-methylnaphthalene, biphenyl, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)pyrene

Polyethylene (PE)

The burning properties of PE are similar to those of PP.
From thermal decomposition studies it is known that mainly longchained, unbranched saturated as well as unsaturated (at the end of the molecules) degradation products are formed during the combustion of PE. The samples had to be treated in the same way as described for the PP material. The decomposition products which have been identified are:

naphtalene, (1-)2-methylnaphthalene, biphenyl, phenanthrene, fluoranthene, pyrene

A quantitative determination of the degradation products is impossible because only a small portion of the soot formed can be collected on the glass fibre filter. The greatest part remains in the combustion apparatus. Due to the dropping of the polymers a quantification of the sample material is impossible too. The application of an evaluation method in which the quantification refers to the amount of the collected soot leads to unreliable results.

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Zusammenfassung - Verschiedene Kunststoffe wie zum Beispiel Polyethylen, Polyvinylchlorid, Polyamid 6 und Polypropylen wurden in offener Flamme in 'Anlehnung an DIN 4102 verbrannt. Die dabei entstehenden Russpartikel wurden auf Glasfaserfiltern gesammelt und mit Toluol extrahiert. Durch gaschromatographische und massenspektrometrische Untersuchungen konnten die Hauptbestandteile des Russextraktes analysiert werden. Bei Polyvinylchlorid und Polystyrol handelt es sich vorwiegend um aromatische Verbindungen, wie zum Beispiel Naphthalin, Phenanthren, Pyren und Chrysen. Die Hauptkomponenten des extrahierten Russes von Polyethylen und Polypropylen bestanden aus aliphatischen und olefinischen Produkten, die im Chromatogramm die aromatischen überdeckten. Durch Ausschütteln der Probenvorlage mit Nitromethan konnte eine Trennung der aromatischen von den aliphatischen erreicht werden. Bei der thermischen Zersetzung von Polyamid 6 wurden als Hauptabbauprodukte das Mono und Dimere des ϵ-Caprolactams gebildet.

Резюме - В открытой пламенной печи, согласно ДИН 4102, сжигались полиэтилен, полипропилен, поливинилхлорид и полиамид 6. Образующаяся сажа была собрана на стекловолокнистых фильтрах с последующим элюированием ее толуолом. Большая часть экстракта адсорбированных соединений может быть идентифицирована с помощью газ-хроматографического и масс-спектрометрического анализа. При сгорании поливинилхлорида и полистирола главным образом образуются такие ароматические соединения, как нафталин, фенантрен, пирен и хризен, тогда как в случае полиэтилена и полипропилена - образуются алифатические и олефиновые соединения. На хроматограммы этих компонент часто накладываются ароматические соединения. Экстракция полученного образца нитрометаном позволила разделить ароматические и алифатические компоненты. Главными продуктами сгорания полиамида 6 были мономерный и димерный ϵ-капролактам.