



**IDENTIFICATION AND CHEMICAL MODIFICATION OF PYROLYSIS
PRODUCTS DERIVED FROM HALOGEN- AND NITROGEN-CONTAINING
SYNTHETIC POLYMERS**

Ph.D. Thesis

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1. INTRODUCTION AND AIMS

Thermal decomposition in an inert atmosphere (pyrolysis) is one of the most intensively studied recycling methods of polymers. It makes possible obtaining valuable compounds and energy recovery. There are industrial processes for the pyrolytic recycling of municipal waste plastics, however the pyrolysis process of plastic waste derived from electrical and electronic equipments and automotive shredder residue is difficult to accomplish or lead to the formation of corrosive and harmful compounds (originated from halogen and nitrogen-containing polymers and additives).

The modification, diminution, or complete elimination of the undesirable pyrolysis products may be carried out with the help of adequate catalysts. Therefore it is necessary to search and study catalysts that can be successfully used for the pyrolytic recycling of those polymers the direct pyrolysis of which is not favorable from environmental and economic points of view.

Analytical pyrolysis focuses on the qualitative and quantitative identification of products formed during thermal decomposition of macromolecules under inert atmosphere. From the obtained information we can deduce the composition and structure of the sample, the decomposition reactions and their kinetics. The analytical pyrolysis studies of polymers provide valuable information about their thermal properties and thermal decomposition characteristics. Therefore it has an important role in the development of environmentally acceptable recycling technologies.

The main goal of this PhD work was the chemical transformation of the thermal decomposition products of nitrogen- and halogen-containing polymers over zeolites. Accordingly, the analysis and catalytic conversion of the volatile thermal decomposition products of halogen-containing and of nitrogen-containing polymers have been studied by analytical pyrolysis. Moreover, the regeneration of the applied zeolite catalysts by heat treatment in air has been examined.

2. EXPERIMENTAL

Polymers

- polyamides: polyamide-6 (PA-6), polyamide-6,6 (PA-6,6), polyamide-12 (PA-12)
- polyacrylonitrile (PAN) and its *co*-polymers: poly(acrylonitrile-butadiene-styrene) (ABS), poly(styrene-acrylonitrile) (SAN)
- polyurethanes: polyester based polyurethane (PUR_{est}) and polyether based polyurethane (PUR_{eth})
- polychloroprene (PCP)
- poly(vinylbenzyl-chloride) (PVBC)
- poly(4-chlorostyrene) (PCS), poly(4-bromostyrene) (PBS)

Zeolite catalysts

- *Y zeolites (FAU)*: NaY, NH₄NaY, calcined NH₄NaY, ultra stabilized HY (HUSY)
- *Beta zeolites (BEA)*: Na-beta (Na-β), NH₄-beta (NH₄-β), H-beta (H-β),
- *A4 (LTA)*
- *13X (FAU)*

Methods

Thermal decomposition of nitrogen- and halogen-containing polymers and catalytic conversion of their pyrolysis products were studied by pyrolysis-gas chromatography/mass spectrometry (Pyrolysis-GC/MS) and thermogravimetry-mass spectrometry (TG-MS).

The possibility of catalysts' repeated utilization was studied by pyrolysis experiments in a horizontal furnace. X-ray diffraction, elemental analysis and BET surface area measurements were carried out to examine the original, deactivated and regenerated zeolites.

3. NEW SCIENTIFIC RESULTS

1. Over sodium Y zeolite (NaY) the heavy oil fraction of pyrolysis oils derived from nitrogen-containing polymers (polyamide-6,6, polyamide-6, polyamide-12, polyacrylonitrile, styrene-acrylonitrile and acrylonitrile-butadiene-styrene *co*-polymers, polyester and polyether based polyurethanes) is cracked to gases and to compounds of gasoline volatility. Low molecular mass N-containing thermal decomposition products of polymers are still present invariably in the converted pyrolysate, while long chain amides, amines, nitriles and diisocyanate are converted into N-containing aromatic, alkylaromatic and cyclic compounds. The composition of the converted pyrolysis oil considerably depends on the primary oil composition (C1, C2).
2. The effect of sodium zeolites (13X, NaY, Na β) on the pyrolysis products of halogen-containing polymers varies depending on the carbon-halogen bonds (C3).
 - a. Chlorine-containing thermal decomposition products of poly(vinylbenzyl chloride) are hardly or not detectable in the modified pyrolysis oil. On the other hand the formation of benzene and alkylbenzenes (toluene, ethyltoluene, dimethylbenzene, ethylbenzene), methylstyrene, naphthalene, and methylnaphthalene is promoted.
 - b. Chlorine is completely eliminated from vinyl chloride group of chloroprene and chloroprene cyclic dimer. The second chlorine atom of the chloroprene cyclic dimer is eliminated partially (20-40%) over sodium zeolites, since the ring aromatization stabilizes the C-Cl bond.
 - c. Splitting of halogens from aromatic rings is limited; dehalogenation can reach 40-60% in the pyrolysis oils of poly(4-chlorostyrene) and poly(4-bromostyrene).
3. Protonic Y zeolites (ultrastabilized HY (HUSY), NH₄NaY)
 - a. These zeolites are suitable to eliminate completely or diminish considerably the nitrogen content of pyrolysis oils of nitrogen-containing polymers. Low molecular weight nitriles may still be present and enriched in the most volatile fraction of the oil (except that of polyurethanes) (C2).
 - b. These zeolites advance the cracking and aromatization of hydrocarbon chain segments of oligomers, consequently aromatic and alkylaromatic hydrocarbons (benzene,

naphthalene, indane, indene and their alkyl compounds) become the main components of the modified pyrolysis oils (except that of PAN). Besides, the amount of low molecular mass olefins (C3-C6) is considerably increased among the products. (C2).

4. Y and beta zeolites (NaY, HUSY, NH₄NaY, Naβ, Hβ, NH₄β) mixed with polyamide-6,6 (PA-6,6) influence the thermal decomposition reactions of the polymer (*cis*-elimination, C-N bond cleavage), that is to say the composition of the pyrolysate. The effect of zeolites mainly depends on the quality of cations, however the differences between Y and β zeolites with identical cation content are not negligible either. The presence of NaY and Naβ hardly changes the pyrolysis oil composition of PA-6,6. The cracking effect of ammonium and hydrogen form Y zeolites is more evident, moreover these catalysts promote the *cis*-elimination of amid groups to a larger extent than the same form of β zeolites.
5. In the presence of Y zeolites the thermal decomposition of PA-6,6 and ABS shifts to 20 and 10 °C higher temperature, respectively. This retarding effect of Y zeolites is not due to heat transfer limitation but to the interaction of the surface of Y zeolites and the polymers (C1).
 - a. The delay of thermal decomposition of PA-6,6 may be caused by the interaction of the surface of Y zeolites and the polar amide groups hindering their *cis*-elimination and intramolecular rearrangement in the initial stage of thermal decomposition.
 - b. The retarding effect of Y zeolites in the thermal decomposition of ABS indicates that the surface of Y zeolites promotes the chain termination of the polymers' free radical thermal decomposition.
6. The amount of solid residue derived from the thermal decomposition of PA-6,6 and ABS increases as a consequence of carbonaceous deposit formed on the surface of the zeolites. The process of oxidative removal of deposit is different that refers to differences in physical and chemical properties of the coke deposited on protonic and NaY zeolites (C1, C2).

4. CONCLUSIONS

Sodium zeolites transform the thermal decomposition products of polymers into low molecular weight alkenes, nitrogen- and halogen-containing aromatic and alkylaromatic molecules. That is to say, these zeolites are unsuitable for the effective removal of the halogen and nitrogen content of the pyrolysis oils.

Protonic zeolites promote the transformation of the polymers' thermal decomposition products into aromatic hydrocarbon compounds. The main compounds of modified pyrolysate are aromatics, dominantly alkylbenzenes and alkyl-naphthalenes. Nitrogen-containing compounds are not or only hardly detectable in the modified pyrolysis oils.

X-ray diffraction and BET surface area measurements revealed that the framework structure of zeolites is not damaged at the operation temperature of pyrolysate conversion (at 500-600 °C) moreover the catalytic activity decreased due to coke deposit can be recovered by thermal treatment in air at 600 °C. Repeated regenerations do not evoke significant decrease in activity either.

5. PUBLICATIONS AND PRESENTATIONS

Publications

1. J. Bozi, Zs. Czégény, M. Blazsó, *Conversion of the volatile thermal decomposition products of polyamide-6,6 and ABS over Y zeolites*, *Thermochimica Acta* 472 1-2 (2008) 84-94. (IF: 1,659)
2. J. Bozi, M. Blazsó, *Catalytic modification of pyrolysis products of nitrogen-containing polymers over Y zeolites*, *Green Chemistry* 11 10 (2009) 1638-1645. (IF: 4,542)
3. M. Blazsó, J. Bozi, *Catalytic Conversion of Thermal Decomposition Products of Halogen Containing Polymers Studied by Pyrolysis-GC-MS*, *Current Analytical Chemistry* 7 2(2011) 110-116. (IF: 2,143)

Proceedings

1. Bozi J., Czégény Zs., Blaszó M., *Nitrogéntartalmú polimerek pirolízisoldajának módosítása, zeolitok katalitikus hatásának vizsgálata*, Tavaszi Szél Proceedings 189-194., Tavaszi Szél 2007, Zrínyi Miklós National Defense University, Budapest, May 17-20, 2007.

Presentations and posters

1. Bozi J., Czégény Zs., Blaszó M., *Hulladék műanyagok pirolízisoldajának módosítása, katalizátorok hatásának analitikai vizsgálata (Upgrading pyrolysis oil of waste plastics; analytical studies on the activity of catalysts)*, Conference of Chemical Engineering '2007, Veszprém, April 25-27, 2007.
2. Bozi J., Czégény Zs., Blaszó M., *Nitrogéntartalmú polimerek pirolízisoldajának módosítása, zeolitok katalitikus hatásának vizsgálata*, X. Forum of Doctoral Candidates, Mátraháza, May 7-9, 2007.
3. Bozi J., Czégény Zs., Blaszó M., *Nitrogéntartalmú polimerek pirolízisoldajának módosítása, zeolitok katalitikus hatásának vizsgálata*, Tavaszi Szél 2007, Zrínyi Miklós National Defense University, Budapest, May 17-20. 2007.
4. Bozi J., Czégény Zs., Blaszó M., *Nylon-6,6 pirolízisoldaj komponenseinek átalakulása zeolitokon*, HAS Chemical Research Center, Scientific Days, Budapest, May 22-24, 2007.
5. Bozi J., Czégény Zs., Blaszó M., *Poliamid-6,6 hőbomlástermékeinek átalakulása mikro- és mezopórusos katalizátorok hatására (poster)*, Centenary Chemist Conference, Sopron, May 29 - June 1, 2007.
6. Bozi J., Czégény Zs., Blaszó M., *Poliamid-6,6 hőbomlástermékeinek szilárd fázisú mikro- és mezopórusos katalizátorok hatására történő átalakulása*, Seminar of the Institute of Materials and Environmental Chemistry, HAS Chemical Research Center, Budapest, June 12, 2007.
7. Bozi J., *Nitrogéntartalmú polimerek pirolízisoldajának módosítása, zeolitok katalitikus hatásának vizsgálata*, Report of II. grade doctoral candidates, ELTE, Budapest, November 17, 2007.

8. Bozi J., Czégény Zs., Blaszó M., *Nitrogéntartalmú polimerek pirolízisoldaja*, Forum of Doctoral Candidates, Debrecen, November 28, 2007.
9. Bozi J., *Nitrogéntartalmú polimerek hőbomlástermékeinek átalakítása mikro- és mezopórusos katalizátorokon*, XI. Forum of Doctoral Candidates, Mátrafüred, April 21-22, 2008.
10. Bozi J., Blaszó M., *Nitrogéntartalmú műanyag hulladékok hőbomlástermékeinek vizsgálata a környezetbarát hasznosíthatóság szempontjából*, Meeting of the working committee of HAS Polymers and Natural polymers, Budapest, April 24, 2008.
11. M. Blaszó, J. Bozi, Zs. Czégény, *Py-GC/MS Study on the Conversion of Pyrolysis Oil of Waste Plastics for Obtaining Halogen and Nitrogen Free Product*, 18th International Symposium on Analytical and Applied Pyrolysis, Lanzarote, Spain, May 18-23, 2008.
12. Bozi J., *Nitrogéntartalmú polimerek hőbomlástermékeinek átalakítása mikro- és mezopórusos katalizátorokon*, Audience of Junior Research Fellows, Chemical Research Center, Hungarian Academy of Sciences, Budapest, June 5, 2008.
13. J. Bozi, M. Blaszó, *Thermal decomposition of nitrogen and halogen containing polymers*, (**poster**), Austrian - Croatian - Hungarian Combustion Meeting - ACH2008, Sopron, October 3, 2008.
14. Bozi J., *Polimerek pirolízisoldajának módosítására használt zeolitok regenerálhatóságának vizsgálata*, „DOKISULI” – XII. Forum of Doctoral Candidates, Mátraháza, April 20-21, 2009.
15. Bozi J., Blaszó M., *Polimerek pirolízisoldajának módosítására használt zeolitok regenerálhatóságának vizsgálata*, Conference of Chemical Engineering '2009, Veszprém, April 21-23, 2009.
16. J. Bozi, M. Blaszó, *Thermal analysis studies on the regeneration of zeolites used for upgrading polymer pyrolysis oil*, 10th Conference on Calorimetry and Thermal Analysis (CCTA) of the Polish Society of Calorimetry and Thermal Analysis (PTKAT) and 2nd Joint Czech - Hungarian - Polish - Slovakian Thermoanalytical Conference, Zakopane, Poland, August 30 - September 3, 2009.
17. Bozi J., Blaszó M., *Polimerek pirolízisoldajának módosítására használt zeolitok regenerálhatóságának vizsgálata*, Seminar of the Institute of Materials and Environmental Chemistry, HAS Chemical Research Center, Budapest, October 6, 2009.
18. Bozi J., Blaszó M., *Pirolízis GC/MS és TG-MS alkalmazási lehetőségei a polimerek pirolízisoldaj-módosításának vizsgálatában* Meeting of junior analysts, Budapest, February 25, 2010.

19. Bozi J., *Halogén- és Nitrogéntartalmú Szintetikus Polimerek Környezetre Ártalmas Hőbomlástermékei. Műanyag-hulladékok Veszélyes Pirolizistermékeinek Kémiai Átalakítása*, Anyag- és Környezetkémiai Intézet szemináriuma, (MTA KK), Ph.D. házivédés, 2011. január 21., Budapest

Other publications

1. Zs. Czégény, J. Bozi, M. Blaszó, *Effect of flame retardants on the thermal decomposition of typical polymer components of electronic waste*, Proceedings 43-47., Centenary Chemist Conference and 1st joint Czech - Hungarian - Polish – Slovakian Thermoanalytical Conference, Sopron, May 29 - June 1, 2007.
2. J. Bozi, Zs. Czégény, E. Mészáros, M. Blaszó, *Thermal decomposition of flame retarded polycarbonates*, J. Anal. Appl. Pyrolysis 79 (2007) 337-345
3. M. Blaszó, J. Bozi, *Application of pyrolysis for treatment and utilization of difficult waste*, CD Proceeding ID 240, 5th Dubrovnik Conference on Sustainable Development of Energy Water and Environment Systems, Dubrovnik, Croatia, September 29 – October 3, 2009.
4. J. Bozi, M. Blaszó, *Thermal decomposition of PP and ABS mixed with halogen containing polymers*, Proceeding CD, 6th International Conference on Modification, Degradation and Stabilization of Polymers, Athens, Greece, September 5-9, 2010.
5. Gy. Mink, P. Szabó, É. Fekete, B. Lengyel, J. Bozi, S. Fejes, M. Volkai, E. Török, Z. Lázár, J. Papp, G. Orbán, *Kinetic Study of Dehalogenation of Chlorinated Aromatics by Limestone*, International Congress Energy and Environment 2010, Opatija, Croatia, October 18-22, 2010. Energy and Environment, 2010, 1, 465-475 (ISBN 978-953)