

Composition of Nitrogen Containing Compounds in ABS Degradation Oils

M. Brebu^a, Y. Sakata^{a*}, M. A. Uddin^a, A. Muto^a, K. Murata^b, C. Vasile^c

^a Department of Applied Chemistry, Okayama University, Okayama 700-8530, Japan,

^b Mitsui Engineering & Shipbuilding Co. Ltd., Chiba 290-0067, Japan,

^c "P. Poni" Institute of Macromolecular Chemistry, Ro 6600 Iasi, Romania.

E-mail: yssakata@cc.okayama-u.ac.jp Fax: +81-86-251-8081

The influence of temperature and catalysts on the amount and distribution of nitrogen containing compounds in ABS degradation oils was studied. The catalytic experiments were carried out both in liquid and gas phase contact in a polymer/catalyst ratio of 10g/2g. The amount of nitrogen in oils usually increase with the temperature but slowly decrease at 420°C. γ Fe₂O₃ catalyst in liquid phase contact seems to be effective in reduction of nitrogen in oil.

Introduction

Degradation of the waste plastic into fuel oil is a suitable way both for recovery of the material contents of the waste and for saving the petroleum resources¹. When ABS is presented in polymer waste the nitrogen coming from the acrylonitrile units is contained both in the gaseous product (as very toxic NH₃ or HCN) and in the degradation oil², these causing the formation of harmful compounds when the oils are used as fuel. In this study the decomposition of ABS in different thermal and catalytic conditions was performed with the aim to find the condition for a reduction of the nitrogen in degradation oils

Materials and Methods

Acrylonitrile-butadiene-styrene copolymer (ABS) was obtained from Asahi Chemical Industries Co. Ltd. The iron based catalysts, γ Fe₂O₃ (TR99701), α FeOOH and Fe₃O₄ carbon composite (TR990517) were supplied by Toda Kogyo Corporation, Japan.

ABS degradation was performed thermal and catalytic, in a glass reactor, under atmospheric pressure, by semi-batch operation. Experimental conditions and the method for characterization of the degradation products were described in a previous paper³. 10 g of polymer was used in each experiment. In catalytic experiments 2g catalyst were added, mixed with the polymer in the case of catalysis in liquid phase contact (LPC) or deposited on a stainless steel mesh at 12 cm from the bottom of the reactor, in the case of catalysis in gas phase contact (GPC). The experiments were conducted at 360, 380, 400 and 420°C in order to study the influence of the temperature of degradation on the amount and the distribution of the products and especially of the nitrogen containing compounds. In catalytic degradations method the temperature in the oven was maintained at 400°C.

The gaseous products were analyzed by a YANACO: G180 gas chromatograph with a thermal conductivity detector (TCD). The analysis of the amount of carbon and nitrogen containing compounds and the identification of the main degradation products in the liquid oils were performed by gas chromatographic method, using a flame ionized detector (FID – YANACO: G6800) respectively an atomic emission detector (AED: HP G2350A) and a mass selective detector (MSD: HP 5973). The composition of degradation oils was characterized using C-NP-grams (C stands for carbon) and N-NP-gram (N stands for nitrogen) curves, obtained by plotting the weight percent of carbon containing compounds and the nitrogen amount in the degradation oils, versus the carbon number (equivalent to the boiling points) of the normal paraffin.

Results and Discussions

Thermal degradation

The temperature has a significant role both on the rate of the degradation and the amount and quality of the products (Table 1). As it was expected, increasing of temperature clearly favors the formation of gases and oils, the amount of both types of products being more than two times higher when the process is conducted at 400°C in respect with 360°C. In addition the density of oils also increases, indicating an advanced degradation of the polymer.

Table 1. Balance material for 10 g ABS degradation at different temperatures (*: G=100-L-R)

Method	Temp (°C)	Product yield (wt %)			Liquid density (g/ml)	N amount in oil (mg/ml)
		Gas (G)*	Liquid (L)	Residue (R)		
Non catalytic	360	3.4	23.7	72.9	0.8495	39.73
Non catalytic	380	4.2	38.9	56.9	0.8683	40.27
Non catalytic	400	7.2	49.5	43.3	0.8684	49.70
Non catalytic	420	6.5	56.0	37.5	0.8750	41.18

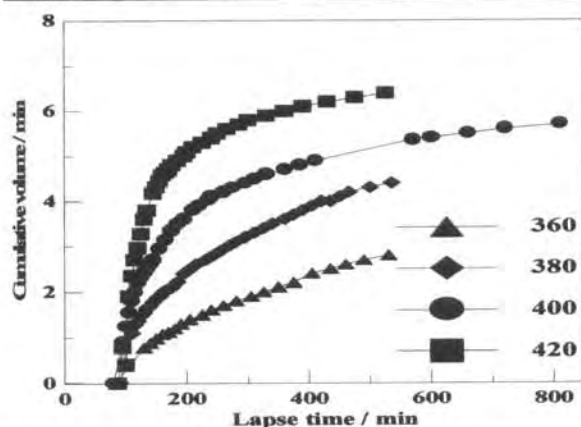


Fig. 1. Cumulative volume of liquid products obtained in thermal degradation of 10g ABS at different temperatures.

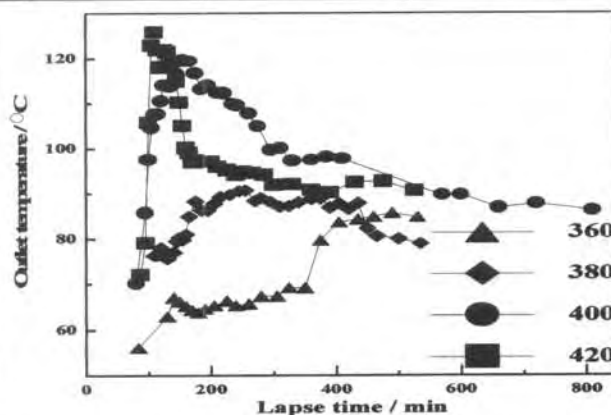


Fig. 2. Variation of the temperature at the outlet of the oven during the degradation process.

The slope of the cumulative curve of oils (Fig. 1) shows the importance of the temperature on the rate and the amount of the oil accumulation. At low temperatures of degradation the formation of oils occurs at almost constant rate in a long lapse time range while at high temperatures the rate is very high in the first moments of the degradation process and then continuously decreases. This fact is also reflected in the variation of the temperature at the outlet of the reactor (Fig. 2) that increases in time when the experiment was running at 360 and 380°C but presents a maximum soon after the accumulation of the oil starts in the case of degradation at 400 and 420°C.

ABS degradation produces oils with compounds distributed in the range of boiling points of n-C₅-n-C₂₅ (b. p.: -0.5-405.1°C), with a main peak at n-C₉ (38-49%) and other peaks at n-C₆ (2-6%) and n-C₁₃ (4-17%) – Fig. 3. According to GC-MS analysis the main compounds are toluene (13-15%), ethylbenzene (14-16%), styrene (23-31%), methylethylbenzene (4-8%) and α -methylstyrene (7-11%), in the n-C₈-n-C₁₀ carbon number range and 4-phenylbutyronitrile (3-16%) for n-C₁₃. Increasing the temperature of degradation, C-NP-gram curves are shifted to high carbon numbers (high boiling points, equivalent to heavier products), confirming the increase in density of the degradation oils.

The amount of nitrogen in oils is of 40-50 mg/ml, corresponding to 17-43% from the initial nitrogen in ABS. This value is really high, considering that only 4.2% from the nitrogen in PAN is founded in degradation oil, a great amount of nitrogen remaining in the residue even at very high temperature (1500°C for degradation in inert atmosphere⁴).

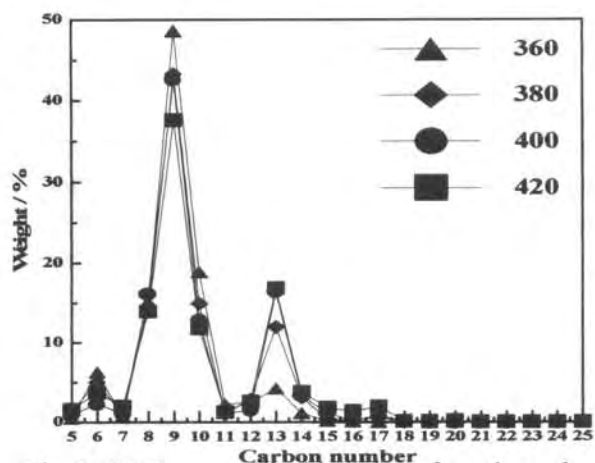


Fig. 3. C-NP-gram of liquid products from thermal degradation of 10g ABS at different temperatures.

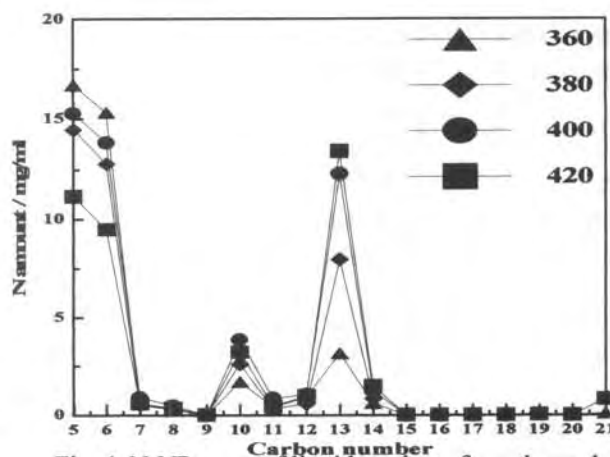


Fig. 4. N-NP-gram of liquid products from thermal degradation of 10g ABS at different temperatures.

From Fig. 4 one can see that nitrogen in degradation oils is distributed mainly in the range of boiling points of $n\text{-C}_5 - n\text{-C}_{14}$ ($-0.5-252.5^\circ\text{C}$), with peaks at $n\text{-C}_6$, $n\text{-C}_{10}$ and $n\text{-C}_{13}$, but small amounts can be detected even at $n\text{-C}_{21}$. Nitrogen containing compounds from the $n\text{-C}_5-n\text{-C}_6$ carbon number range were identified as acetonitrile, propane- and propene- nitrile, 2-methyl propane- and 2-methyl propene- nitrile and 2 butenenitrile, all of them generated by the decomposition only of the acrylonitrile units from ABS macromolecular chain.

Similar with the case of C-NP-gram, the N-NP-gram curves are shifted at higher temperature of degradation to high carbon numbers. The total amount of nitrogen in oils increase, especially due to formation of 4-phenylbutyronitrile ($n\text{-C}_{13}$ peak). Unexpectedly the total amount of nitrogen in oil decreases when the degradation is running at 420°C in respect with 400°C , and this is reflected in the decreasing of the nitrogen containing compounds at $n\text{-C}_5$ and $n\text{-C}_6$.

Catalytic degradation

From the balance material of the degradation (Table 2) one observe that the catalysts causes a increase in the amount of gases in the detriment of oils, in respect with non catalytic procedure but the differences are not so important. When the catalysis occurs in gas phase contact the amount of gases and oils is smaller than in liquid phase contact, the density of oils decreases and all three catalyst give very similar results, both in the amount, density and the N content of oils. The catalysts have different action in liquid phase contact, αFeOOH giving the highest percentage and density of oil but $\gamma\text{Fe}_2\text{O}_3$ produces oil with the lowest amount of nitrogen.

Only αFeOOH in liquid phase contact has a small effect on the rate of the production of oils. This fact is confirmed by the shape of the cumulative volume curve (Fig. 5) and the sudden increase in the temperature measured in the zone of catalysis in gas phase contact, that shows the end of the process after a lapse time of 350 minute.

Table 2. Balance material for 10 g ABS degradation in various catalytic conditions

Catalyst/method	Temp ($^\circ\text{C}$)	Product yield (wt %)			Liquid density (g/ml)	N amount in oil (mg/ml)
		Gas (G)	Liquid (L)	Residue (R)		
$\gamma\text{Fe}_2\text{O}_3$ LPC	400	8.6	44.3	47.1	0.8720	28.25
$\gamma\text{Fe}_2\text{O}_3$ GPC	400	6.9	41.3	51.8	0.8604	32.15
αFeOOH LPC	400	10.4	48.7	40.9	0.8854	39.86
αFeOOH GPC	400	9.5	40.7	49.8	0.8646	31.39
TR990517 LPC	400	10	41.8	48.2	0.8708	41.26
TR990517 GPC	400	6.7	39.6	53.7	0.8609	31.51

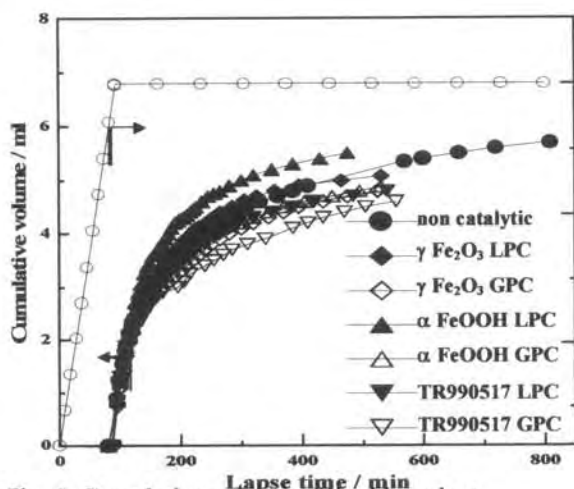


Fig. 5. Cumulative volume of liquid products.

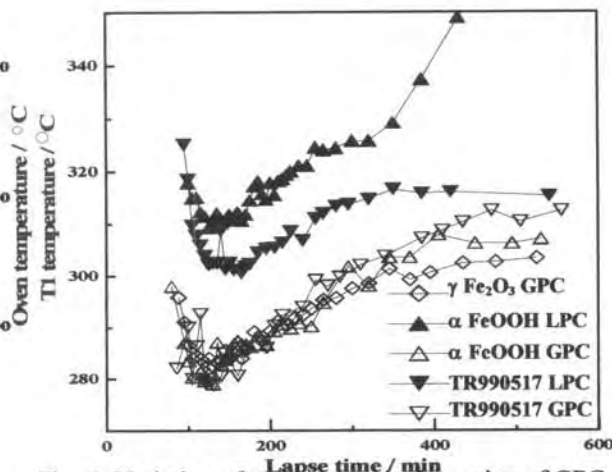


Fig. 6. Variation of temperature in the region of GPC

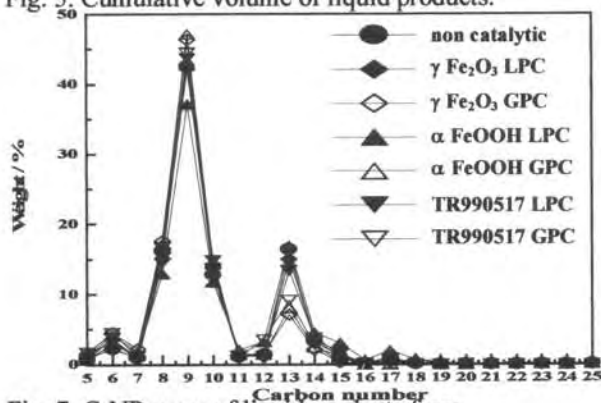


Fig. 7. C-NP-gram of liquid products from

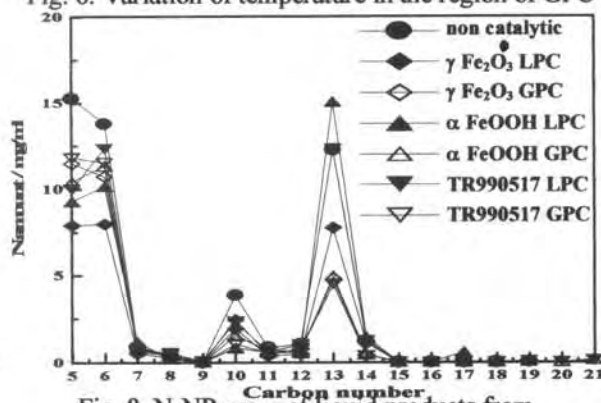


Fig. 8. N-NP-gram of liquid products from

The similarity in the action of the catalysts in gas phase contact is also proved by the overlapping of the curves in Fig. 5-8. The common action of the catalysts is the reduction of the amount of 4-phenylbutyronitrile, proved by the decrease of the maximum corresponding to n-C₁₃. At the beginning of the process the temperature in the region of the catalysts in gas phase contact is lower with 20°C in respect with the case of liquid phase contact that means endothermic cracking reaction on catalysts and explain the low density of the oils.

γ Fe₂O₃ catalyst in liquid phase contact has no influence on the rate of accumulation of oil (the corresponding curve in Fig. 5 is overlapped with that of non catalytic degradation) but strongly decrease the total amount of nitrogen in oil by decreasing the amount of both the compounds obtained from acrylonitrile units (n-C₅ and n-C₆) and the 4-phenylbutyronitrile produced by interaction between acrylonitrile and polystyrene units. So we can supposed that this catalyst act as an inhibitor for acrylonitrile decomposition.

Conclusions

Temperature has a great effect both on the rate of formation, the amount and the quality of degradation oil. Running the degradation at 420°C seems to decrease the total amount of nitrogen in the oils. Even the catalysts has no significant improvement in the recovery of oil, the γ Fe₂O₃ catalyst in liquid phase contact decrease the total amount of nitrogen in oil to less than 60% than the non catalytic procedure.

References

1. R. C. Mordi, R. Field, J. Dwyer, *J. Anal. Appl. Pyrolysis*, 1994, **29**, 45.
2. M. Blazso, *J. Anal. Appl. Pyrolysis*, 1997, **40-41**, .
3. Y. Sakata, M. A. Uddin, K. Koizumi, K. Murata, *Polym. Degrad. Stab.*, 1996, **53**, 111.
4. C. Vasile, *St. Cerc. Chim.*, 1973, **21**, 81.