Thermal degradation of nitrogen-containing polymers, acrylonitrile-butadiene-styrene and styrene-acrylonitrile

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Abstract–Thermal degradation of nitrogen (N)-containing recycled plastics (styrene-acrylonitrile (SAN), acrylonitrile-butadiene-styrene (ABS)) was carried out in a stirred-batch reactor at 300-400 °C under nitrogen stream. The degradation oil began to be generated over 300 °C. Recycled SAN plastic was converted to oil with 91.3 wt% yield at 380 °C, while only 70.9 wt% of recycled ABS plastics was converted to oil at the same temperature and both oils contained about the same 3.7 wt% nitrogen as an elemental basis. Rate of oil formation from the thermal degradation of SAN was much higher than that of ABS, but showed a similar degradation pattern in terms of chemical composition. In oil products, aromatic contents obtained at 360 °C were 70 wt% for SAN and 79 wt% for ABS, respectively, and decreased to 59 wt% and 57 wt% at 380 °C with increasing degradation temperature. Dominant product of both degradation oils was styrene, and the following was ethylbenzene for ABS, but none in case of SAN. Both oils contained the N-containing plastic additives that give rise to a confusion for the identification of authentic N-containing degradation products.

Key words: Thermal Degradation, N-containing Recycled Plastics (ABS & SAN), Degradation Temperature, Characteristics of Liquid Product

INTRODUCTION

The majority of thermoplastic wastes such as high-density polyethylene (HDPE), low-density polyethylene (LDPE), polypropylene (PP), polystyrene (PS) and polyvinylchloride (PVC) comprise up to 70-80 percent of all waste plastics, and the conversion of these waste plastics to useful materials has been extensively studied [Lee et al., 2002; van Grieken et al., 2001; Miskolczi et al., 2004]. Scale-up pyrolysis processes are now being developed in several countries, in order to produce massive fuel oil from waste plastics. The prospects of their recycling present a tremendous opportunity for reducing landfill usage and cost of disposal as well as an opportunity to reuse natural resources [Ciliz et al., 2004; Williams and Williams 1999; Oh et al., 1999].

N-containing copolymers consisting of acrylonitrile monomer such as ABS and SAN, among engineering thermoplastics, are greatly increasing in usage of many practical aspects [Dong et al., 2001]. Those plastics are degraded in a several steps differently from hydrocarbon-type plastics and generate a large portion of N-containing degraded products, which are undesirable to reuse as fuel oil [Brebu et al., 2002]. Feasible studies are needed to determine which method is more desirable--either a recycling of feed stock or a recovery of energy, and thereafter to find a proper technology for recycling second-usage of N-containing waste polymers which is counted as about 20 wt% of all plastic wastes. Detailed chemical composition and the content of degraded products obtained by a practical experiment condition will be helpful to make such decision.

According to TGA/FTIR study of Suzuki [Suzuki and Wilkie, 1995], major degradation products of ABS terpolymer consisted of

the constituents of ABS polymer itself, and Brebu [Brebu et al., 2002] and Day [Day et al., 2002] improved the quality of ABS degradation oil by using combined catalysts such as silica and alumina, or iron oxide with reducing the contents of N-containing compounds. Since N-containing degraded products are more polar than the major oil products, these appear as an adverse effect on the physicochemical characteristic of oil as well as the emission during combustion if the degraded oil is wanted as a fuel.

Various additives including antioxidants, developers, fillers, absorbers or inhibiters of UV are employed in order to stabilize and improve the chemical and physical properties of plastics during the plastic manufacturing process. In particular, many additives containing nitrogen are widely used as antioxidants and color developers [Swasey, 1992]. Such chemicals seem to evolve into the degradation oil during the thermal degradation process of N-containing plastics because they have a similar polarity to that of N-containing degradation products, and may cause difficulties in identifying authentic degraded N-containing products. Such chemicals are rarely mixed with non-polar degradation oil generated from the degradation of majority plastics such as polyethylene (PE), so that they are rather left over in residue.

This paper presents the yields of oil, residue and gas, and the degradation rates of N-containing recycled plastic into liquid product, and the quantitative results on the chemical composition of N-containing degraded products obtained by large-scale thermal degradation experiments at various reaction temperatures.

EXPERIMENTAL

1. Materials and Experiments

Two hundred grams of N-containing recycled plastics obtained from a local recycling company (Daeshin Recycling Co.) was used

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as a raw material for the degradation experiments. Thermal degradation experiments were carried out at various temperatures between 300 °C and 400 °C under atmospheric pressure, in a stirred batch type reactor (volume 1.1 liter), which was schematically shown in a previous paper [Lee et al., 2004]. Reaction temperature was raised with a heating rate of 9 °C/min to the desired temperature under nitrogen stream, and mechanical stirring was maintained at 200 rpm.

At the beginning of the experiment, the sample was weighed and charged into the reactor. The reactor was sealed, purged with a nitrogen stream to remove the oxygen from the reactor, and then heated at a determined temperature program. When the temperatures of reactants, 320 °C, 340 °C, 360 °C and 380 °C were conducted, respectively, oil product was collected with a constant interval of reaction time until no more oil product was collected with maintaining the temperature. Weight of oil products collected at constant intervals during the reaction was measured with a microbalance and was cumulated in a collection bottle. Gas products were vented after cooling by condenser to 7 °C. Oil reaction products were analyzed by a GC/MS.

2. Analysis

Elemental analysis, thermal gravimetric analysis and GC/MS analysis of degradation oils were performed on a CHN-2000 elemental analyzer (LECO. Co., USA), TGA-501 thermal gravimetric analyzer (LECO. Co., USA), and HP5980/HP5972 Gas Chromatograph/Mass Spectrometry (Hewlett Packard, USA), respectively. Elemental analysis data on the degradation oils for SAN and ABS are shown in Table 1. GC/MS analyses were performed on a DB-

5ms and a DB-1701 capillary column (30 m, 0.25 mm id, 0.25 μm film) with a polar liquid phase, since the degradation products consisted of polar nitrogen compounds heavily [Suzuki and Wilkie, 1995; Tiganis et al., 2002]. Aniline-d_7 for the semi-quantitative analyses of N-containing hydrocarbons, toluene-d_8, ethylbenzene-d_{10}, styrene-d_8 and other standard chemicals were used as internal standards, and three point calibration curves were used. The analytical procedure of detailed hydrocarbon group type was described in a previous paper [Seo and Shin, 2002].
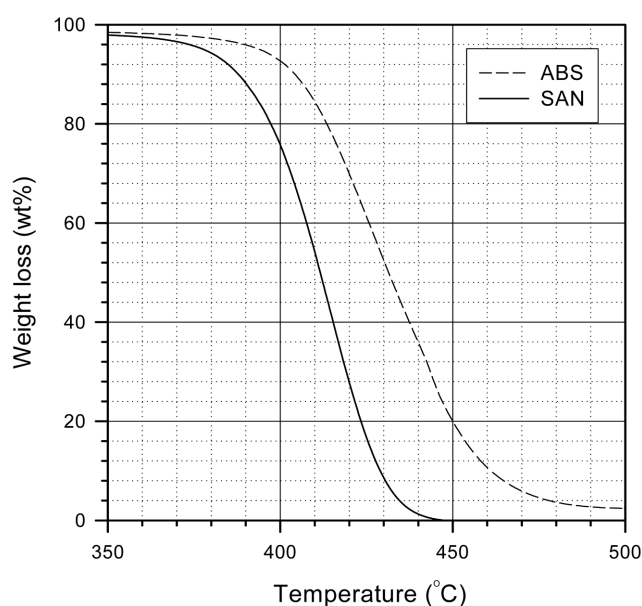
RESULTS AND DISCUSSION

1. Yields of Products

TGA curves of recycled SAN and ABS depicted in Fig. 1 show that these polymers degrade in a single step degradation trend and ABS needs a little higher degradation temperature than SAN. According to the TGA study [Suzuki and Wilkie, 1995], ABS copolymer degrades in several steps with increasing temperature, namely evolution of butadienes followed by styrene and then acrylonitrile. Yang et al [Yang et al., 2004] have also reported two step degradation of ABS, in which the second degradation occurred even at a higher temperature. However, we could observe a single step degradation pattern till 800 °C, and a much longer time was needed to diminish the remaining 10 wt% of ABS. These results mean that TGA curves of commercial ABS samples in the region of high temperature can appear different, due to including filler with inorganic materials in the commercial sample or not. Thermal degradation of N-containing recycled plastics yielded less oil and more residues, and the degradation oil contained much more nitrogen content as an elemental analysis, when compared with the thermal degradation products of plastics composed of solely carbon and hydrogen [Lee et al., 2002; Brebu et al., 2002].

Thermal degradation products over N-containing recycled plastics were classified in three groups: oil, gas, and residue that remains at the bottom of the reactor after reaction. Table 2 shows the yields of oil, residue, and gas and the calorific values of oil product. Yields of oil product over both recycled ABS and SAN were 79.9 wt% and 91.3 wt% at 380 °C, respectively, which showed higher yields than those obtained at 360 °C. These volatile components were increased with increasing temperature, whereas the yield of residue decreased as a reverse relation in each type of polymer. This means that the C-C bonds were more cracked at a higher temperature than at a lower temperature and this resulted in higher yield of oil products. Also, both SAN and ABS with different chemical structure, which had different curves of degradation temperature as indicated by TGA analysis, showed a great difference in yield of oil and res-

Table 1. Results of elemental analyses of liquid products

	Elemental analysis (wt%)			
	Carbon	Hydrogen	Nitrogen	Oxygen
SAN	86.57	7.66	3.68	-
ABS	84.54	8.41	3.69	0.72

Fig. 1. TGA curves for recycled SAN and ABS.

Table 2. Weight % yields of liquid, gas and residue produced from the thermal degradation of recycled ABS and SAN at 360 °C and 380 °C

Yield (wt%)	SAN		ABS	
	360 °C	380 °C	360 °C	380 °C
Oil	81.4	91.3	73.4	79.9
Residue	15.5	6.6	23.7	17.3
Gas	3.1	2.1	2.9	2.8

idue at each constant temperature. On the other hand, the gas yield ranged from 2 wt% to 3 wt% did not appear to be a big difference at both 360 °C and 380 °C and also both SAN and ABS. Calorific values of ABS and SAN degradation oils with relatively low nitrogen contents of 3-4 wt% in oil product, as presented in Table 1, are about 9,700 kcal/kg, which was obtained from the oil product at a degradation temperature of 380 °C. This value showed about 90%, based on those of commercialized gasoline and diesel oil.

2. Degradation Rate into Oil Product

The cumulative amounts of liquid product obtained from the thermal degradation of recycled SAN and ABS using different tem-
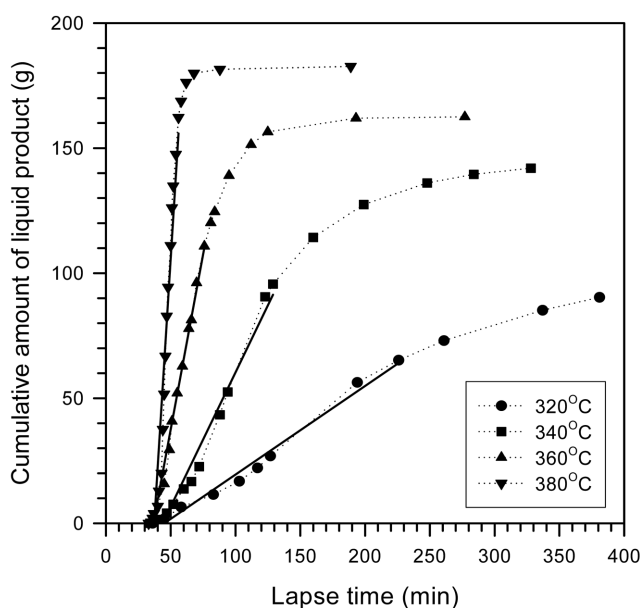
peratures, respectively, are presented in Figs. 2 and 3. Liquid product started to accumulate in the reservoir after about 40 min corresponding to a degradation temperature of plastics. It was not above 300 °C until the oil products began to be formed by degradation of N-containing plastics. Degradation rates were determined by the ratios of increased cumulative amounts of degradation oil to the increased time at each temperature, which was obtained in the range of initial reaction time as shown by solid line in Figs. 2 and 3.

Fig. 2 shows the degree of conversion into oil product by the thermal degradation of SAN at various temperatures. The curves of cumulative amount of liquid product by thermal degradation at various temperatures show a similar behavior in a single step, but a different degradation rate and yield of liquid product. The thermal degradation of SAN took place at above 300 °C of degradation temperature. Yields of oil product were sharply increased from about 70 wt% to about 90 wt% with increasing degradation temperatures from 340 °C to 380 °C. To elucidate the relationship between the degradation rates as a slope appearing by a solid line in Fig. 2 and degradation temperature, the degradation rate as a function of degradation temperature was presented in Fig. 4. The degradation rate into liquid product was sharply increased with increasing degradation temperature and, moreover, for degradation temperature of above 360 °C was exponentially increased with increasing degradation temperature. This result is due to more cracking of the polymer into lower molecule weight products at a higher temperature. Also, at the lapse time that the oil was no longer generated the case of SAN plastics showed 15.5 wt% and 6.6 wt% residues at the degradation temperatures of 360 °C and 380 °C, respectively, as shown in Table 2. It implies that at a higher temperature the residue consisting of heavy molecular weight is more cracked into lower molecule weight products. This is contrasted with Suzuki and Wilkie's [Suzuki and Wilkie, 1995] report, in which no residue was left at the ending point of 530 °C in their TGA experiment. It is believed that this difference is due to an experimental size and the purity of SAN. Two hundred

Fig. 2. Cumulative amount of liquid product from the thermal degradation of recycled SAN at different temperatures.

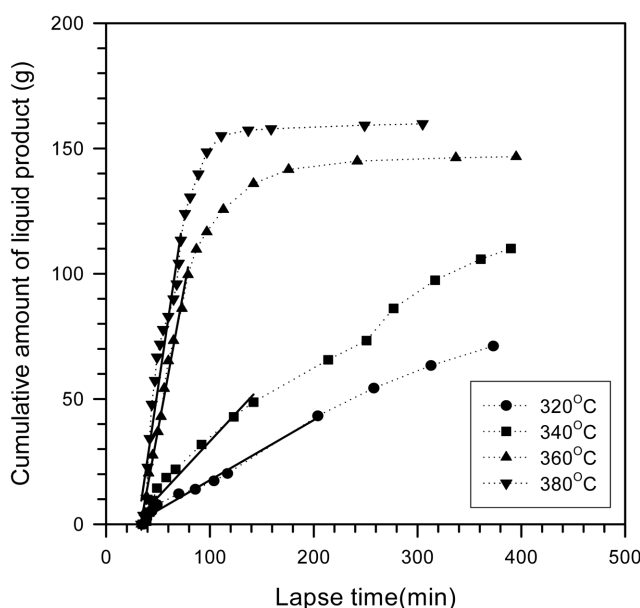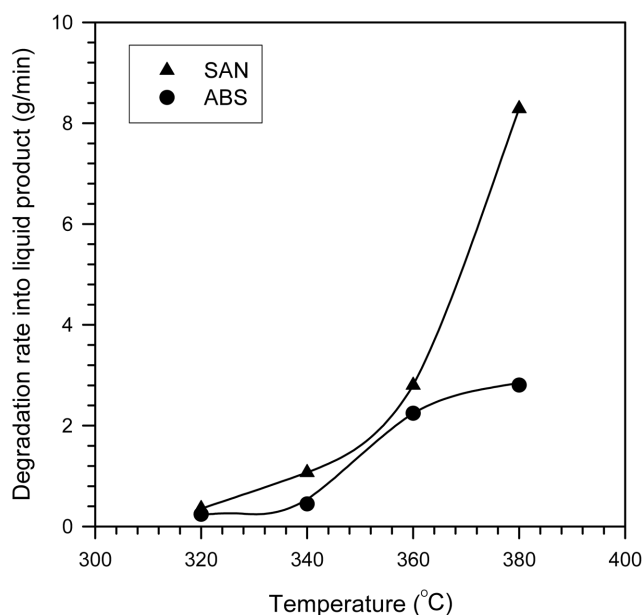**Fig. 3. Cumulative amount of liquid product from the thermal degradation of recycled ABS at different temperatures.**

Fig. 4. Degradation rates as a function of temperature on degradation of recycled SAN and ABS into oil product.

grams of recycled plastics with pellet type of 1/8 inch size was employed in the experiment instead of milligram of pure plastics.

Thermal degradation of ABS, as shown in Fig. 3, occurred much differently from that of SAN at the same reaction temperature. The cumulative amount of liquid product by thermal degradation of ABS as a function of lapse time of reaction was relatively small, compared to that of SAN. Thus, yields and formation rate of oil from ABS were far inferior to those of SAN, as shown in Table 2. Oil yield did not even reach to about 80 wt% at 380 °C, compared with the 90 wt% oil yield obtained by thermal degradation of SAN. The lower the degradation temperature, the more residues remained in the reactor. In Fig. 4, degradation rate over ABS was dramatically increased from 0.4 g/min to 2.2 g/min between 340 °C and 360 °C, but it slowly increased over 360 °C. This result clearly differed from that of SAN, in which the degradation rate of SAN was sharply increased with degradation temperature.

3. Chemical Characterization of Degradation Oil

Identification and weight fraction of thermal degradation products of recycled SAN and ABS are summarized in Tables 3 and 4. For commercial SAN and ABS, many different chemicals including antioxidants, developers and fillers are added into plastics in order to protect from the oxidation, UV, and also to improve the

Table 3. Weight % fraction of each hydrocarbon groups in liquid products

Wt%	SAN		ABS	
	360 °C	380 °C	360 °C	380 °C
Paraffin	0	0	0	0.46
Olefin	0	0	0	0.73
Naphthene	0	0	0	0
Aromatics	69.85	58.70	78.79	56.78
N-containing HC	30.15	41.30	21.21	42.03

Table 4. Weight % fraction of major compounds in liquid products by thermal degradation of recycled ABS and SAN

Wt%	SAN		ABS	
	360 °C	380 °C	360 °C	380 °C
Toluene	2.78	1.08	8.30	5.70
Ethylbenzene	3.20	1.03	16.10	10.60
Styrene	49.53	44.64	35.49	30.60
Alkyl-benzenes	0.65	0.15	3.70	2.00
Alkyl-styrenes	6.12	2.73	6.70	4.88
Styrene dimers	7.57	9.47	8.50	3.00
Total aromatics	69.85	59.10	78.79	56.78
2-Butenenitrile			0.80	2.30
Benzenebutyronitrile	6.67	2.03	9.50	15.50
2-Naphthalenenitrile	2.17	1.35	2.81	0.05
Benzene-alkylnitrile	10.50	15.50		
Quinolinamines	4.13	10.50		
Imidazoles	4.04	8.14		
Other N-hydrocarbons	4.81	5.13	8.09	24.10
Total N-hydrocarbons	30.15	41.30	21.21	42.03

physical and chemical properties of plastics. Hindered phenols such as butylhydroxy-anisole and butylhydroxy-toluene, and hindered amine light stabilizers (HALS) such as quinolinamines, benzotriazoles and imidazoles are widely used for this purpose. These chemicals will also take part in the thermal degradation reaction, and their carbon chains of high-molecular weight may be cleaved into lower-molecular weight compounds. However, as most HALS compounds among these chemicals have high melting points around 250 °C [Swasey, 1992], it is suggested that some of these additive chemicals will remain in the degradation oil as melted phase themselves, some labile chemicals will be completely decomposed and some will react with other decomposed chemicals. Benzotriazoles and imidazoles identified by GC/MS analysis are supposed to be included in those chemicals.

Hydrocarbon compositions of oil product from commercial polymers were dependent on the chemical structure of monomer and chemical additives such as antioxidant, developers and fillers. As seen in Table 3, for liquid paraffin, olefin, naphthene, aromatic and N-containing hydrocarbon products distribution both SAN and ABS plastics having styrene monomer showed a similar composition over aromatics and N-containing hydrocarbons only produced, in which there was a greater amount of pure aromatics and a less amount of N-containing hydrocarbons. With the increase of degradation temperature from 360 °C to 380 °C, the fraction of aromatics was decreased, whereas N-containing hydrocarbons were more produced. The increase of degradation temperature resulted in an increase of N-substituted non-aromatics, rather than pure aromatics. It is expected that N-substituted non-aromatics would be more generated due to an increase in carbon-carbon breakages with raising degradation temperature as well as an increase in the reaction of nitriles with degraded hydrocarbons containing active radicals. It means that the increase of degradation temperature results in more reactivity of polar components. In the study of Barman [Barman, 2002], the polar compounds obtained during thermo-oxidative degradation of the oil were increased with heating time and at a higher heating temperature. The degradation oil over SAN and ABS at 380 °C showed a high portion of about 40 wt% nitrogen containing hydrocarbons such as benzenebutyronitrile and 2-naphthenenitrile among oil components. It would be undesirable to use the degradation oil of ABS and SAN as fuel oil because the nitrogen content in the oil is too high. However, it would be more feasible that pure aromatic products such as styrene and ethylbenzene are selectively recovered in terms of chemical recycling, due to its high fraction of around 60 wt% at 380 °C and around 70 wt% at 360 °C in oil products.

Table 4 shows the distribution of major compounds in oil product obtained by degradation of recycled SAN and ABS. Styrene as a main product was more produced on SAN (40-50 wt%) than ABS (30-40 wt%) and also was decreased with increasing degradation temperature. The degradation oil over ABS contained less styrene and more toluene, ethylbenzene and alkylbenzenes such as trimethylbenzens, butylbenzenes when compared with that of SAN.

For nitrogen containing hydrocarbons, as benzotriazoles and imidazoles are highly polar compounds, these additive chemicals are rarely mixed with the degradation oil formed by the thermal degradation of recycled plastics such as PE or PP, but are rather present in the bottom or residue. However, degradation oil from N-containing plastics such as ABS and SAN contains a large fraction of

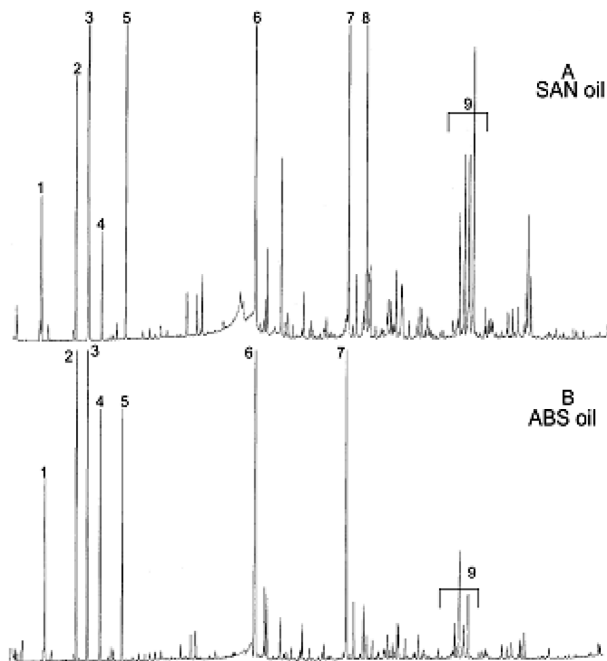**Fig. 5. G. C. peaks of oil product obtained from degradation oils of recycled SAN and ABS at 380 °C.**

1. Toluene	6. Phenylbutyronitrile
2. Ethylbenzene	7. 1,3-Diphenylpropane
3. Styrene	8. Styrene dimers
4. Alkylbenzene	9. N-containing additives
5. Alkylstyrene	

polar materials degraded from polyacrylonitrile. This large polar fraction is composed of benzenebutyronitrile, phenylacetonitrile and other various nitrogen containing hydrocarbons. These degradation products are evolved with nitrogen containing plastic additives simultaneously during thermal degradation because of similar polarities and then are co-present with additive chemicals as composition of degradation oil. These additive chemicals caused a great confusion in identifying the authentic degradation products. Group peaks pointed out as number 9 at the chromatogram of Fig. 5 are imidazole and others, but those are hardly possible to be formed in such thermal degradation conditions, in spite of the fact that there are many possibilities for acrylonitrile monomers to react with each other, or with other radicals. Most of them are separated from non-polar products such as paraffin and aromatic hydrocarbons but some exist as miscible with non-polar hydrocarbons, so that the degradation oil looks cloudy and is seen as two different separated layers.

CONCLUSIONS

1. It was not until above 300 °C that the oil started to be formed from thermal degradation of N-containing recycled SAN and ABS. Thermal degradation of these recycled plastics yielded less oil, and more residues, compared to that of non-N-containing recycled plastics, and also the content of nitrogen in the oil obtained was about 3.7 wt%.

2. The degradation rate of the plastics and the yields of oil increased with increasing the degradation temperature. In case of SAN degradation the yields of oil and residue increased in about 80 wt%

to about 90 wt%, and decreased in 15.5 wt% to 6.6 wt% with increasing the temperature from 360 °C to 380 °C, respectively. Oil yields and degradation rate of ABS were inferior to those from SAN. The degradation rate of ABS increased sharply up to 360 °C and then increased slowly at a higher temperature.

3. Degradation oils of recycled SAN and ABS were mainly consisting of aromatics and N-containing hydrocarbons, without paraffins, olefins and naphthenes, in each hydrocarbons group of liquid products. Its proportion showed much higher contents of aromatics including styrene and comparatively lower contents of N-containing hydrocarbons. However, the increase of degradation temperature from 360 °C to 380 °C was decreased for aromatic products, whereas N-containing hydrocarbons increased.

4. Cyanoalkylbenzene such as 4-phenylbutyronitrile, quinoline and imidazole compounds were found in the degradation oils for recycled SAN and ABS, but quinoline and imidazole compounds such as aminoquinoline are also the kinds of chemical additives which are usually added in the plastic. Since polarity of N-containing degradation products is similar to that of chemical additives of plastics such as HALS, these degradation products become co-present with chemical additives in the oil. Thus, they cause a confusion in identifying the authentic degradation products.

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