Present at 238th ACS National Meeting, August 22-26,2009, Washington DC Environ.Divn.

New contamination derived from marine debris plastics

Katsuhiko Saido[1a)],Tadashi Itagaki[1a)], Hideto Sato[1b)],Yoichi Kodera[2)], Osamu Abe[3)], Naoto Ogawa[4)], Seon-Yong Chung[5)] and Kiyotaka Miyashita[6)]

1a) College of Pharmacy, 1b) College of Science & Technology, Nihon University

2) National Institute of Advanced Industrial Science and Technology

3) Seikai National Fisheries Research Institute, Fisheries Research Agency

4) Faculty of Agriculture, Shizuoka University

5) College of Engineering, Chonnam National University

6) National Institute for Agro-Environmental Sciences,

Due to human carelessness, plastics find their way into rivers and then into the sea (3-5). In 1975, the Smith, Bon Laboratory reported plastic debris to be present in large quantities in the Sargasso Sea, with consequent marine pollution (6).

In 2007, Moore et al. confirmed refuse disposal of 1 million tons in the northern Pacific Ocean. (7).To date, no studies have been conducted on plastic decomposition at low temperature in the environment owing to the mistaken conception that plastic does not decompose.

This study was conducted to clarify that drift plastic does indeed decompose to give rise to hazardous chemicals in the ocean.

The authors thus established a method to study plastic decomposition at room temperature, which involves water-soluble heat transfer and use of an extractant. Polystyrene(PS) was found to decompose at 30°C to produce the styrene monomer(SM), 2,4-diphenyl-1-butene(styrene dimer,SD), 2,4,6-triphenyl-1-hexene(styrene trimer,ST) .

Materials and Method

Materials

Unmolded virgin PS pellets were used in this study after being refined by solvent extraction.

Method

The silicone oil bath was placed on stirrer bearing with a heat regulator. The thermal decomposition of plastics was carried out in 4.9g of heating medium (polyethylene glycol) in a round-bottomed flask bearing with Y-tube and stirrer chip on the oil bath. The Y-tube was attached with a thermocouple, an introduction tube of N_2 gas and reflux condenser, respectively. N_2 gas of which was adjusted 50ml/min by the regulator from a N_2 cylinder. When the internal temperature reached the fixed temperature, 0.100g of plastic was added to the medium with mixing by stirring at 500 rpm. The reaction temperature was adjusted and retained ±1 ºC of the fixed temperature by thermocouple and digital thermometer (CUSTOM CT-1310) inserted in the reaction solution directly. After reaction at the fixed

temperature for the fixed time, the reaction mixture dissolved in solvent and recovered was transferred to a separatory funnel was washed with water. Then the mixture was transferred in another solvent and the part of polymer was precipitated. The detail of the method was shown previously.

Result and discussion

New marine contamination due to plastics debris

UNEP has shown 1,000,000 seabirds and 100,000 marine mammals to die yearly owing to the ingestion of and/or entanglement in such debris (1). Each year, as much as 150,000 tons of plastic debris wash up onto the shores of Japan (2).

Analyses have been extensively conducted on the rivers and oceans of the world and the results clearly demonstrate the presence of nonylphenol and phthalic acid ester (PAE), bisphenol-A(BPA) (3-7).

The sources and elution pathways of these chemicals should be clarified in greater detail. The generation of BPA from polycarbonate (PC) or epoxy resine has clearly been shown a possibility. The cause for BPA generation is difficult to specify since this compound, like PAE, is used as a plasticizer of polyethylene, a raw material of PC. Chemicals such as SM, SD and ST may be present in the environment as pollutants. But the styrene oligomer does not occur naturally in the ocean.

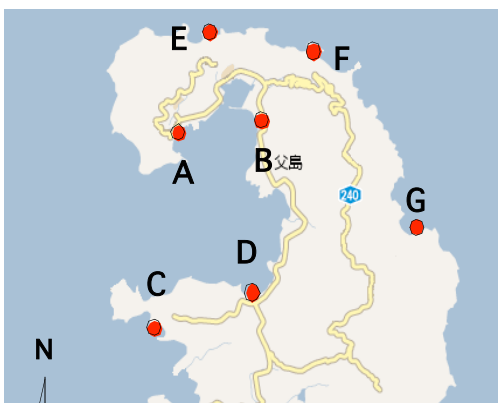
The amount of styrene oligomer has been determined based on that of PS scattered throughout the environment. Plastic debris on the Japanese coast has been found to be 85% PS. Detailed analysis on the Ogasawara/Chichijima island shown in Fig.-1.

The results are enumerated in Fig. -2

Sea sand and water from China that reaches the West Coast of North America, along the northern Pacific Ocean, were thus examined by GC/MS. All samples were found to contain significant amounts of the styrene oligomer.

Fig.-2 shows only the results for the styrene oligomer in a circle. The left side of the circle is for sea sand (unite: ppb) and the right side, for water (unite: ppb). The concentration of contamination is indicated by its height in each case. SM is shown as red, SD as yellow and ST as orange. Fig.-2 indicates ST to be present at 10 ppb to 3,000 ppb as low and high concentrations, respectively. The styrene oligomer in sea water was 1/1000 that in sand.

Thus, in the northern Pacific Ocean, the styrene oligomer appears to be generated by PS decomposition. Large cities such as Shanghai, Busan, Tokyo and Los Angeles, showed greater styrene oligomer values. Such cities are thus greater contributors to the direct discharge of pollutants.



Place	Composition	Sand(ppb) SM	Sand(ppb) SD	Sand(ppb) ST	Water(ppb) SM	Water(ppb) SD	Water(ppb) ST
Ogasawara	A Omura beach	10	30	-	1.16	0.22	3.37
Chichijima	B Ocean center	2,860	490	12,740	2.66	0.17	3.20
Island	C Suzaki	-	-	-	2.94	0.33	9.20
	D Ogiura	50	80	1,110	1.63	1.02	3.90
	D	80	40	550	-	-	-
	E Miyanohama	130	60	820	2.41	0.22	3.56
	F Tsurihama	70	70	470	-	-	-
	G Hatsune	50	30	160	7.22	0.71	6.26
	H East beach	10	10	-	4.25	0.78	4.06
	I Maruberi bay	30	10	90	-	-	-

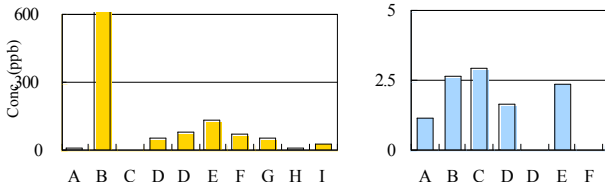


Figure 1. Detailed Analytical Results on Ogasawara Chichijima Island

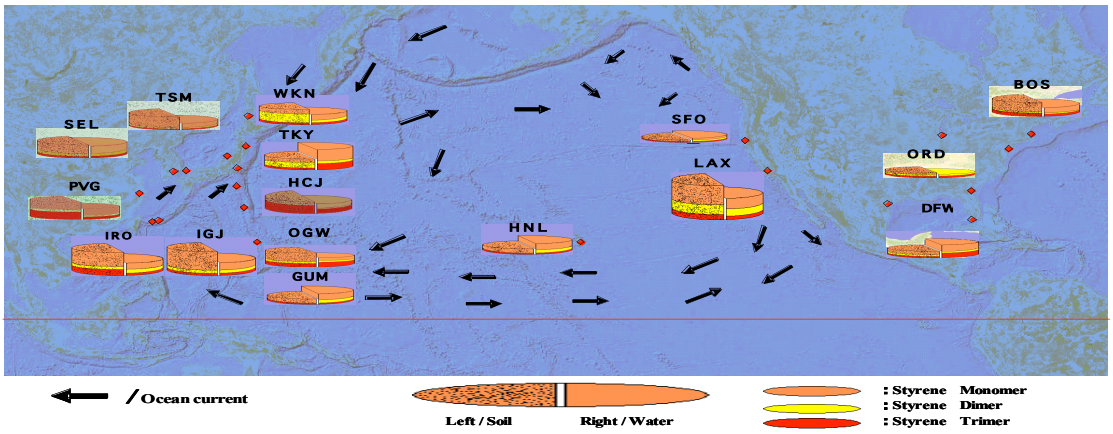


Figure.2 Typical Pacific Ocean Current and Analytical Results on Chemicals Derived from Marine Debris Plastic, China to U.S.A.

Islands with small populations and small-scale industry, as in the case of Iriomotejima, Ishigakijima, Jeju, Tsushima, Sado, Rishirijima, and Rebunjima Islands should thus incur pollution from the considerable plastic debris that reaches their shores. Hachijojima is 300km south, Ogasawara /Chichijima 1,000km south, and Guam 3,000km south from Tokyo and Oahu 6,000km southeast from Tokyo, a solitary island in the northern Pacific Ocean. The authors consider the sources of contamination of these islands to come by way of the ocean waste, as suggested by Moore (8).

Conclusion

The quantities of ST from plastic decomposition were measured and the velocity constants were determined within the temperature range, 30°C to 250°C. Based on kinetic parameters and

quantities of drift plastics found on the coasts of Japan, the generation of ST from PS was computed by simulation. The results were found fully consistent with data from field analysis. Suitable treatment and effective countermeasures to combat uncontrolled wastes such as to be found in marine debris are urgently required for the future. To prevent plastic scattering in the nature including land-filing method, economical feasible recycling method should be developed.

Acknowledgement

This research was supported by grants from "Academic Frontier" Project for Private Universities: matching fund subsides from the Ministry of Education, Culture, Sports, Science and Technology, 2002-2006.

References:

1. J. G. B. Derraik, *Marine Polltn. Bull,* **44**, 842 (2002)
2. A. Kojima, *et al., JEAN*2007 Report, 40 (2008).
3. C. Wahlberg, L. Renberg, U.Wideqvist., *Chemospher,***20,** 179 (1990).
4. T .Urashima, K. Miyashita, J. *Mater Cycles Waste Manag.,* **5,**77(2003).
5. T. Suzuki, *et al.*, *Environ. Sci.Technol.,* **38(8),** 2389(2004).
6 J. Sajiki,J. Yonekubo, *Chemospere*, 51, 55 (2003).
7. C. E. Mackintosh. *et al. Environ. Sci. Technol.,* **38(8)**,2011 (2004).
8. C. J. Moore. *et al. Marine Polltin. Bull,* **42**, 1297(2001).