The 6th International Symposium on East Asian Resources Recycling Technology
October 23 - 25, 2001, Gyeongju (慶州), Korea
ISBN: 89-952527-0-7 93530

Direct Observation on Pyrolysis of Some Plastics

Tomio Takasu[1], Hideyuki Itou[1], Etsuro Shibata[2], Eiki Kasai[2] and Takashi Nakamura[2]

[1] Department of Materials Science and Engineering, Kyushu Institute of Technology, Japan
[2] Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Japan

Plastics are one of difficult materials for recycling due to their characteristics in use. Recycling ratio of waste plastics was around 40% in last year in Japan, which includes energy recovery. Feed stock recycling and mechanical recycling are not easy because of additives in commercial plastics. Then, pyrolysis treatments have been done to recovery energy. Although plastics are easy to fire, complete combustion of them is not easy if anti-firing agents are added especially. Therefore, researches on pyrolysis or combustion behaviors of plastics containing additives are important from a view point recycling of plastics. Direct observation of popular plastics like polystyrene (PS), polycarbonate (PC), polyphenyle ether (PPE) and polyvinyl chloride (PVC) to investigate their pyrolysis behaviors in the present study. In case of PS, melting and gas evolution started at 90°C and 390°C respectively. And combustion finished at 445°C. On the other hand, more than 600°C and sufficient oxygen are required for complete combustion of PC and PPE.
Keywords: plastics, pyrolysis, hot thermocouple method

Introduction

It is necessary to process plastics inclusions to enable the recovery of non-iron resources from various metal scraps as well as materials such as shredder dust, which were conventionally disposed as waste. Certainly, it is desirable to sort plastics and to send them through separate recycling process, but 100% separation is extremely difficult with the current collecting and sorting technology. Therefore, the waste plastics are used as fuel for energy recovery at time of collection of metal resource, although production of DXN is expected in incinerating plastics containing PVC [1]. For combustion of plastics, much researches have been done from the practical aspect of increased anti-firing property [2], yet there have been no sufficient studies on complete combustion at high temperature. Particularly, commercial plastics contain additives such as extenders and anti-firing agents, so that their pyrolysis and combustion behaviors are complex [3][4].

On the other hand, waste plastics including PVC tend to take up space in landfill, and transportation is a problem. Therefore, if their volume can be reduced by melting and softening at low temperature and then compressed, transportation would become easier, and it would be possible to process them safely in appropriately equipped plants. Also, softening and melting phenomenon becomes important in the RCF (refuse-derived fuel) processing of waste material including plastics.

Therefore, in this study, hot thermocouple method was applied in basic research for thermal recycling of plastics, and phenomena of heat melting and softening as well as pyrolysis and combustion of various plastics were directly observed, and it was shown that hot thermocouple method can be used effectively in this area of research.

Experiment

Samples

The difficulty of plastics as materials is the fact that their composition is not uniform. For example, degree of polymerization for polyethylene differs according to the manufacturers, and their properties may differ slightly. Also, commercial materials tend to contain some kind of additives. For this study, plastics without additives were used. Table 1 shows the plastic samples used in this study.

Procedure

The plastics used as samples were commercially available reagents. DTA/TG was used to study the ba pyrolitic process, and pyrolysis was conducted in air and Ar atmosphere.

Direct observation was done using the hot thermocouple method [5]. The schematic diagram of the apparatus is shown in Figure 1. Heating and temperature measurements were done using the Pt-Pt·Rh thermocouple, the scenes of softening and melting and oxidation pyrolysis by heating was observed on the monitor through the CCD camera, and video recording was made of the process.

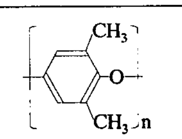
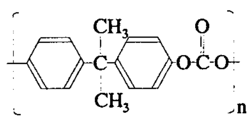
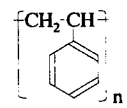
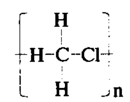
Results and Discussion

Heat analysis

The TG curve of PS is shown as an example of heat analysis result in Figure 2. From this, it was found that in Ar atmosphere, volatilization occurred around 320℃ and volatilization was mostly completed in 470℃. In air, oxidation occurred simultaneously to volatilization, so rapid mass reduction started at 280℃, and was completed at 432℃. Since melting, vaporization, and oxidat occurred simultaneously, clear peak did not appear in DTA.

The DTA/TG measurement results for PVC at temperature increase rate of 10℃/min in Ar atmosphere and air, are shown in Figures 3 and 4. In Ar atmosphere, rapid weight reduction was observed at about 250℃, stopped temporarily at 400℃, and then weight reduction continued to 500℃. In DTA, only one peak which corresponded to the phase-one weight phenomenon in 290℃ area was observed. In general, it is reported that

Table 1 Structural formula and properties of plastics used in this study.

Plastics	Structural formula	Property
Polyphenyle ether **PPE**		・Engineering plastic ・Good workability and high strength ・Glass transition: 211℃ ・Resistance for water, oil and alcohol
Polycarbonate **PC**		・Engineering plastic ・High strength and good weather resistance ・Glass transition: 104 ~150℃ ・Resistance for water and alcohol
Polystyrene **PS**		・General-purpose plastic ・Regeneration by recycling ・Glass transition: 100℃ ・Resistance for water
Polyvinyl chloride **PVC**		・General-purpose plastic ・Flexibility of mechanical property according to additives and polymerization ・Generation of dioxins through combustion

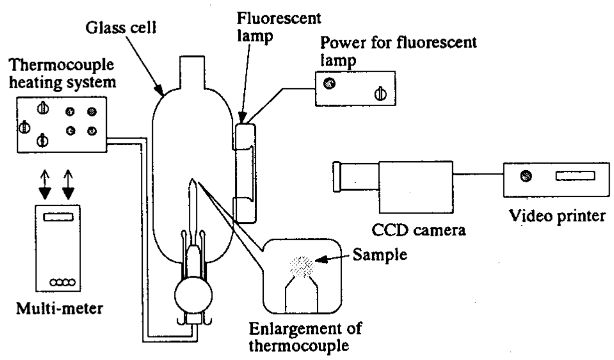


Fig.1 Schematic diagram of hot thermocouple apparatus.

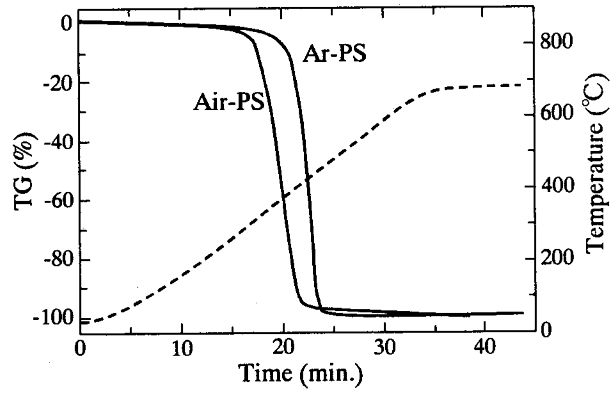


Fig.2 TG curves of PS in Ar atmosphere and air.

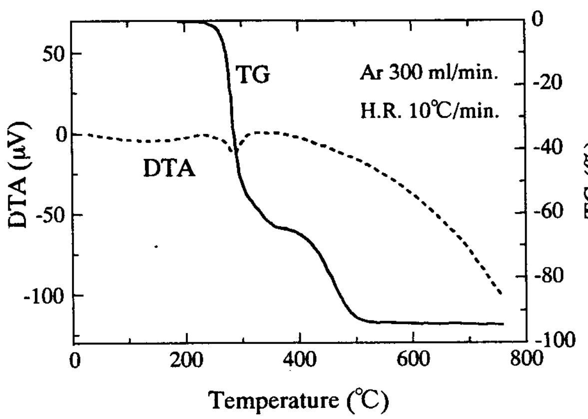


Fig.3 TG curves of PVC in Ar atmosphere.

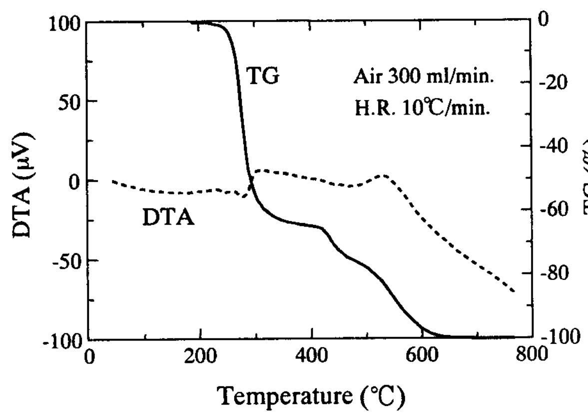


Fig.4 TG curves of PVC in air.

the pyrolysis of PVC occurs in two phases [6], and no difference was observed from the conventional results.

Also, the final volatility ratio was bout 95%, and some ash residue was observed. In air, weight reduction started at 200℃, halted at 400℃, and after two-phase weight reduction to 600℃, volatilization was completed. Heating peak which was thought to be oxidation was observed at 550℃. Although it could not be determined whether this was pyrolysis or oxidation reaction from DTA/TG data only, it is thought that first weight reduction was pyrolysis, and pyrolysis was promoted by oxidation in the air. Also, the pyrolitic reaction at higher than 400℃ decreased due to oxidation.

Direct observation by hot thermocouple method

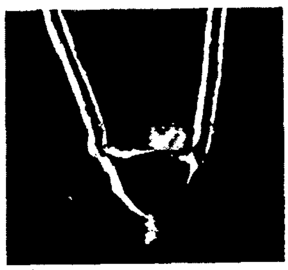
Oxidation behavior of each plastic samples while heating at 10℃/min was directly observed using the hot thermocouple. All samples did not combust, and the progression from melting, oxidation, to volatilization was observed, and production of bubbles was observed for PC and PS. As an example, observation results when PC and PS were heated in air are shown in Photographs 1 and 2, respectively. The starts of melting of PC and PS were about 110℃ and 90℃ which were close to glass transition temperatures, respectively. In the case of PC, after melting, oxidation progressed as charring occurred on the surface, carbon was left over, and it was necessary to raise the temperature to over 900℃ to oxidize this carbon. In the case of PS, the sample melted, and although there was no significant change in appearance, mass reduction was observed due to oxidation, and bubbles were produced as the reaction progressed severely. Above 450℃, carbonization of PS progressed and complete oxidative combustion occurred at 680℃. In Ar atmosphere, there was no large difference in such basic behavior, and it was found that all behaviors shifted slightly to higher temperature side.

Oxidation behavior of PPE was also observed. Temperatures at which melting started, at which bubbles appeared, and at which oxidation finished completely for PS, PPE, and PC are shown in Table 2.

In case of PVC heated in static air, transparency appeared at around 200℃, and the surface started to melt and the corners dissolved. At about 230℃, the sample reddened, the softening progressed, and shape continued to round out. It turned black at 250℃, gas was produced at around 280℃, bubbles were produced and began to foam. This is thought to correspond to the first-phase weight reduction of TG. After then, the process settled down, a the sample seemed to adhere thinly to the Pt disk. It started to react vigorously again at around 560℃, finally became carbon, and complete volatilized at around 800℃.

There were almost no differences in the melting and dissolving behaviors in Ar atmosphere, compared to the result in air. Transparency appeared around 200℃, and the surface started to melt. It turned black at 250℃, gas was produced around 280℃, bubbles were produced, and foaming started. Foaming halted temporarily and the sample spread thinly on Pt disk. It is thought that the wetting between the pyrolitic formation and platinum was good. After that, severe reaction occurred at around 560℃, dissolution occurred in the form of sudden boiling, and volatilization was complete.

Before melting



120℃

440℃

510℃

Photo.1 Observation of PC heated in Air.

Before melting

100℃

260℃

360℃

Photo.2 Observation of PS heated in Air.

Table 2 Transition temperatures of plastic samples (℃).

Atmosphere and plastic samples	Start of melting	Generation of bubbles	Finish of carbonization	Finish of oxidation
Air-PPE	237	--	360	719
O_2-PPE	250	--	385	707
Air-PC	107	439	504	682
O_2-PC	133	488	578	707
Air-PS	93	385	--	444
O_2-PS	70	344	--	435

The difference between air and Ar atmospheres is that after 1st stage decomposition, the sample in Ar atmosphere melted and then wetted and spread out on the Pt disk.

Conclusion

As result of observing the oxidative behavior of plastics using the hot thermocouple method, it was found that PS oxidized readily and oxidation was completely finished at 500℃ or less, and charring occurred from pyrolysis during oxidation of PPE and PC, so that oxidation rate decreased, and temperature of 600℃ and sufficient oxygen was necessary for complete oxidation.

On the other hand, pyrolysis took place in two stages for PVC, and it was found that softening occurred in the process of dissolving to hydrochloric acid in the first stage. Also, PVC was stable compared to other plastics used in this study, and temperature of over 700℃ was necessary for complete oxidative pyrolysis.

Softening, dissolution, and combustion behaviors of plastics could be observed readily by using the hot thermocouple method. Useful information was obtained for combustion behavior and formation of carbon layer, it was shown that this is an useful apparatus for the study of pyrolysis and combustion mechanisms of plastics.

References

[1] Wagner, J.C., and Green, A.E.S. 1992. *Chemosphere* 26: 2039-2054.

[2] Kambour, R.P. 1981. *J. Applied Polymer Science* 26: 861-877.

[3] Modorsky, S.L. 1964. Thermal Degradation of Organic Polymer. *Interscience*, New York.

[4] Knumann, R., and Bockhorn, H. 1994. *Combust. Sci. and Tech.*. 101: 285-299.

[5] Morinaga, K., Yanagase, T., Ohta, Y., and Ueda, Y. 1979. *TMS Paper Selection*: A-79-18.

[6] Matlack, J.D., and Metzger A.P. 1968. *J. Applied Polymer Science* 12: 1745-1750.