

Carberry Reactor による PE, PP, PS の触媒分解 Catalytic degradation of PE, PP and PS by Carberry Reactor

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Catalytic degradation of polyolefins was performed in a continuous flow reactor that allows the study of the degradation processes at steady state. The continuous flow Carberry reactor was operated at atmospheric pressure and at feed rate of 0 - 1.5 kg h⁻¹ polyolefins over two silica-alumina catalysts having different SiO₂/Al₂O₃ mole ratio. Polyethylene (PE), polypropylene (PP) and polystyrene (PS) were degraded at 420, 380 and 360°C respectively. Molar rate of degradation was increased in the presence of catalysts, however the mass rate of degradation was decreased. These interesting results might open new perspectives in understanding the macroscopic mechanism for catalytic degradation of polyolefins.

Key Words: polyethylene, polypropylene, polystyrene, silica-alumina, catalytic degradation, continuous flow reactor

1. Introduction

Since the late of 1970's, a lot of work on catalytic degradation of polymers was carried out by using batch reactor systems to investigate the effectiveness and/or the mechanism during degradation over various catalytic systems. These systems could act as real catalysts or/and as reactants (oxygen donor). In most of the previous studies on the catalytic degradation of polymers, researchers have not distinguished between the two functions of the catalytic systems because this is difficult to be analyzed in a batch reactor. Carberry reactor (a continuous flow operation) is a suitable technique to study the catalytic degradation of polymers because the experimental data are obtained at steady state, that is, at constant temperature, constant pressure and constant amount of reactor content. The author previously reported on the thermal degradation of PE, PP and PS in a continuous flow reactor¹⁾, as well as on the effect of reaction pressure²⁾. In the present study the author carried out the catalytic degradation of PE, PP and PS over two types of silica-alumina catalyst with different SiO₂/Al₂O₃ ratio, in a continuous flow reactor.

2. Experimental

PE (high density), PP and PS were obtained from Mitsui Chemicals, Inc. The catalysts employed in this study were SA-1 and SA-4 commercial silica-alumina from Mizusawa Chemical Industries Co. Ltd. Japan, having SiO₂/Al₂O₃ mole ratio of 5.0 and 0.42 and BET specific surface area of 420 and 240 m² g⁻¹ respectively.

Fig.1 shows a schematic diagram of the experimental set-up used for catalytic degradation of PE, PP and PS under continuous flow operation. The degradation was performed in a stainless steel vessel reactor of 5 l volume in which a rotating cage that contained 100 g of catalyst was installed. The polymers were heated and melted at 200 - 220°C inside an extruder then fed into the reactor at desired feeding rate between 0 and 1.5 kg h⁻¹. Firstly, about 1 kg of polymer was fed into the reactor. Then the reactor was heated up to the final degradation temperature of 420, 380 and 360°C for PE, PP and PS respectively. When volatile products began to be observed, an aliquot amount of raw polymer corresponding to the output (liquid product + gases) was continuously fed into the reactor by the extruder. The rate of feed input was gradually adjusted to that of product output in order to keep constant the amount of

reactor content. The volatile products leaving the reactor were passed through a water-cooled vent condenser. The condensed liquid products (oils) were collected in a receiver having a glass level gauge while the gaseous products passed through a seal pot and a gas meter before collection for analysis. The catalyst/polymer mass ratio was of about 1/10 in our experimental procedure that is much smaller compared to other procedures where higher amounts of catalysts are used (even catalyst/polymer mass ratio of 1/1).

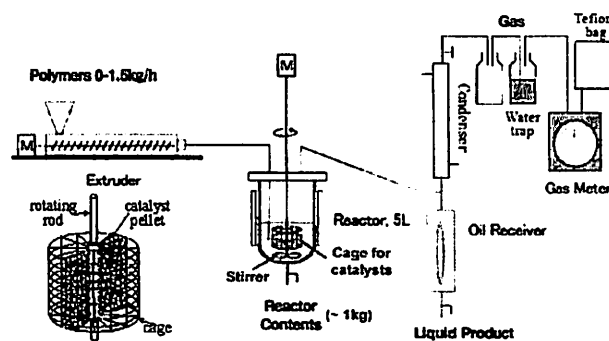


Fig.1 Carberry reactor for catalytic degradation of PE, PP and PS in a continuous flow operation.

3. Results and Discussion

The mass rate of volatilization increased with degradation temperature (Fig. 2a), the variation decreasing in the PS > PP > PE order that might be explained by the opposite trend for thermal stability of these polymers. The catalytic degradation decreased the mass rate of volatilization, the effect being small for PE. The activation energies were calculated from Arrhenius plots drawn based on the mass rate of volatilization (Fig. 2b). They increased for catalytic degradation on SA-1 compared to thermal degradation as following: from 220.9 to 230.5 kJ for PE, from 216.3 to 218.0 kJ for PP and from 207.5 to 221.0 kJ for PS. It is clear that the activation energies of thermal degradation were increasing with the thermal stability of the polymers and were higher for catalytic degradation. Two distinct effects decrease the mass rate of volatilization for catalytic degradation compared to the thermal degradation.

Effect 1:

In the preceding papers[1,2] the author proposed a macroscopic mechanism for thermal degradation of polyolefins by chain reactions involving free radicals.

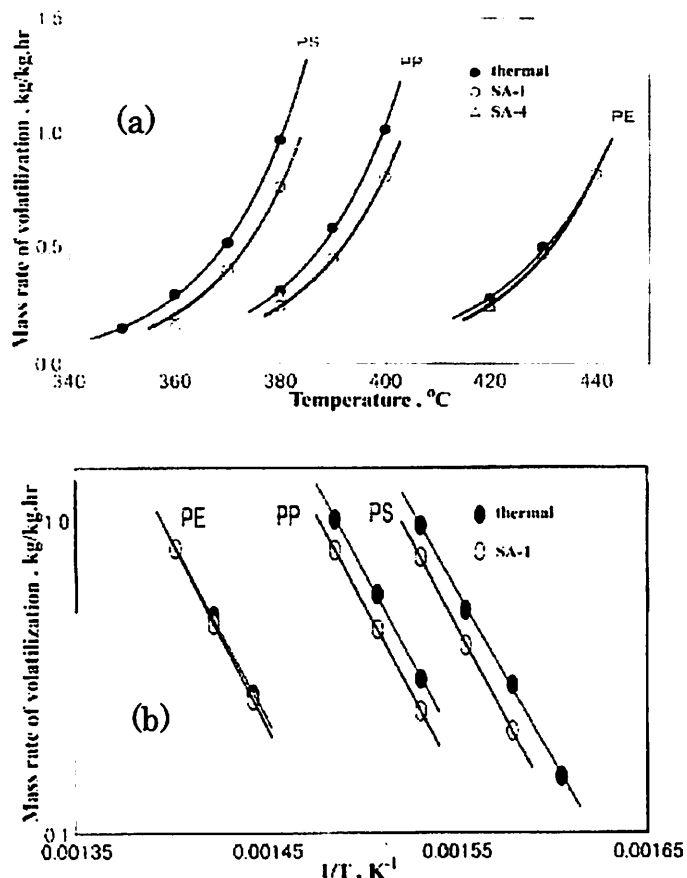


Fig.2 Variation of mass rate of volatilization with temperature and Arrhenius plots for catalytic degradation of PE, PP and PS over silica-alumina.

Two main types of C-C bond scission simultaneously occur during thermal degradation and are responsible for the reduction of the molecular weight of the products. One is a random scission of C-C bonds which causes a molecular weight reduction of raw polymer into smaller oligomers increasing the reactor content. The other one is a chain-end scission of C-C bonds generating volatile products which causes the dissipation of reactor content. The volatile products are not formed directly from the initial macromolecules but they result from the degradation of oligomers in reactor content. The ratio between the two types of C-C bond scissions depends on the polymer type and affects the properties of the reactor content and volatiles, as described above. The chain-end scission takes place at the gas-liquid interface in working reactor. Consequently, the volatilization of products during thermal degradation of polymers is a heterogeneous reaction in which the reactant is in a liquid phase and the product is in a gas phase.

For the catalytic degradation of polymers the reaction system is much more complicated than the above mentioned reaction system for the thermal degradation of polymers, because it involves three phase (gas, liquid and solid), namely, three phase reactor. Silica-alumina catalyst has a remarkable effect on the product distribution, but not on the mass rate of volatilization, as shown in the previous paper [3]. This experimental observation suggests that the catalyst accelerates the chain-end scission, but not the random one. As a result the distribution of reactor content shifts to the higher molecular

weight side. Since the rate of chain-end scission is proportional to the number of molecules, the mass rate of volatilization is influenced.

Effect 2 :

According to the above mentioned macroscopic mechanism the molecules inside the reactor content have a long part of the chain anchored in the liquid phase and a shorter part at the end of the chain that shifts to the vapor phase due to the strong kinetic energy. The vehement movements of the chain-end in the vapor phase cause the scission of the chain at gas-liquid interface. Moreover, the chain-end scission at gas-liquid interface cause a temperature drop between the liquid and vapor phase that usually exceed 50°C.[2] Long-chain molecules could be produced having the boiling point higher than the temperature of the vapor phase. As soon as they jump up into the vapor phase, they condense in liquid droplets (very fine particle like a fog) due to a temperature drop from the liquid to the vapor phase in reactor. The very small liquid droplets are transported out of reactor by the upward high stream of volatile products. This transport phenomenon increases the mass rate of volatilization and explains the presence in liquid products of compounds with high boiling points that normally should not leave the reactor.

For example the vapor phase from degradation of PP at 380°C had a temperature below 330°C that is equivalent to n-C20, however, the NPgram of the liquid product of PP shows the liquid product contains significant amounts of compounds. And the NPgram of the liquid product of PE shows a swelling on the carbon number distribution around n-C20 resulted from the above-mentioned effect.

Meanwhile the supplementary chain-end scissions occurring during catalytic degradation decrease the size and the boiling point of the molecules. The formation of liquid droplets in the vapor phase and their transport out of reactor in the pyrolysis oil is diminished compared to thermal degradation. For PP degradation this is observed by almost total disappearance of compounds above n-C20 in pyrolysis oils. This causes a decrease in the mass rate of volatilization during catalytic degradation comparing with thermal degradation of polymers. The latter effect relates to the dispute concerning the activation energy of degradation calculated from the mass rate of volatilization. At higher temperatures there are less amounts (relative amounts in mass rate) of droplet components for the thermal degradation due to a smaller drop in temperature between liquid and vapor phase.[2] Consequently the increase of mass rate of volatilization due to transport phenomenon of droplets becomes negligible. This explains the lower differences (approaching to zero at 440°C) in mass rate of degradation between thermal and catalytic procedure for PE compared to PP and PS.

References

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