

## EFFECT OF COMBINATION OF IRRADIATION AND ZEOLITE ON PYROLYSIS OF POLYMER MATERIALS



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### Abstract

For recycling of waste polymers, degradation behavior of polypropylene (PP) and polyoxymethylene (POM) was studied by a combination of radiolysis and thermolysis methods. The results revealed that thermal degradation temperature of PP was significantly reduced when PP was irradiated in the presence of zeolite. Irradiation induced temperature reduction depended on zeolite structure, composition as well as on the morphology of the mixture. In the presence of zeolite, a series of oxidized products were formed. Initial temperature for the pyrolysis of POM was depressed by irradiation and the irradiated POM had lower final temperature of pyrolysis in the presence of zeolite.

### 1 INTRODUCTION

The major problem in the pyrolysis of waste polymers for chemical recycling, is the degradation of macromolecules occurs at quite high temperature and thus requires considerable amount of energy. It is of practical importance to reduce the degradation temperature and to promote the degradation efficiency. One way to achieve this purpose is to use degradation catalyst. We have found that, for example, proper kind of zeolite is effective to reduce the degradation temperature of PP<sup>[1]</sup>. High energy irradiation is another way which has a significant effect on the thermal stability of polymers<sup>[2]</sup>. Radiation induced chain scission has the function to render polymers more susceptible to thermal degradation<sup>[3-6]</sup>, which is expected to make contribution to the conversion of polymers to small molecules. Furthermore, the addition of a certain kind of additive, typically a halogen-containing compound, greatly accelerates the irradiation induced degradation<sup>[7-10]</sup>. How the presence of a thermal degradation catalyst influences the effect of irradiation and consequently, the behavior of thermal degradation is the topic of the present work.

### 2 EXPERIMENTAL

PP (P8000) and POM materials were used for pyrolysis test by irradiation. Y, L and mordenite types zeolites were purchased from Toso Co. Ltd. The characteristics of the these zeolites are given in Table 1. The zeolite before use were first heated at 550°C for 4 h for degassing. PP and zeolite were mixed either after the two components were irradiated

Table 1 Characteristics of the zeolites used

Trade name	Structure type	Composition(wt-%)				Counter-ions	SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> mole ratio	BET* (m <sup>2</sup> /l)
		SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	K <sub>2</sub> O			
320HOA	HY	73.4	22.2	4.3	-	H <sup>+</sup>	5.6	570
320NAA	NaY	67.4	20.6	12.4	-	Na <sup>+</sup>	5.6	700
500KOA	L	64.9	17.8	0.29	17.0	K <sup>+</sup> , Na <sup>+</sup>	6.2	300
620HOA	H-Mordenite	89.4	10.6	0.55	-	H <sup>+</sup>	15.2	400
640NAA	Na-Mordenite	87.5	7.7	4.9	-	Na <sup>+</sup>	19.2	360

\* Specific surface area

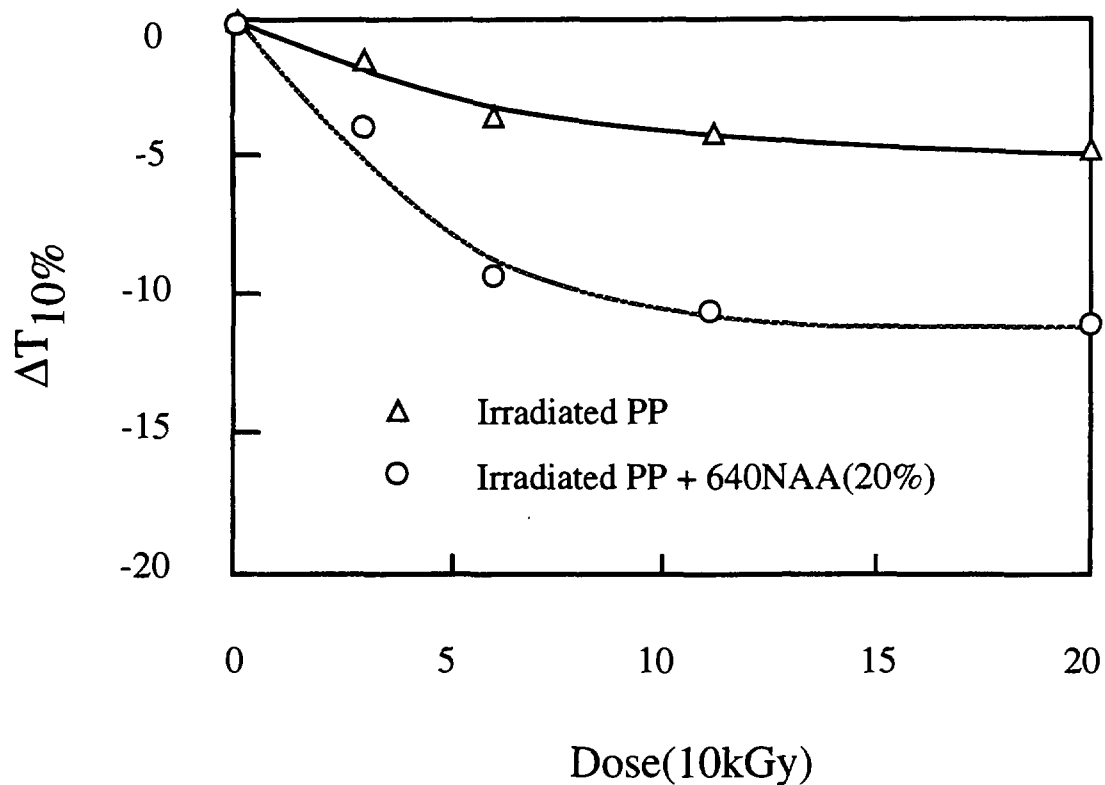


FIG. 1. Irradiation induced reduction of the thermal degradation temperature of PP.

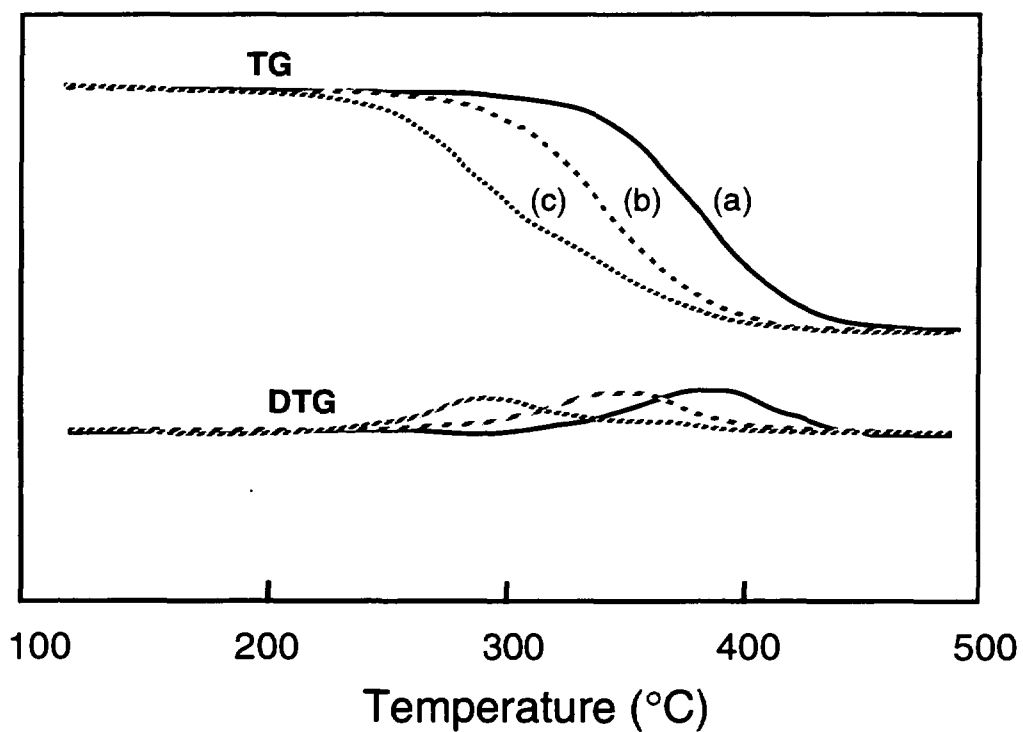


FIG. 2. TG and DTG curves for PP-zeolite mixture molten blend containing 20% 640NAA, (a) without irradiation, (b) irradiated to 60kGy and (c) irradiated to 220kGy.

separately or before irradiation was performed. Mixtures of PP and zeolite were prepared by the following three methods: (1) Powder mixture: zeolite powder and PP powder were mixed by simple stirring; (2) Molten blend: zeolite was added to molten PP at 200°C and mixed by using a Labo Plastomill (Toyoseiki Co. Ltd.); (3) Casting film : zeolite was added to a 1% PP decahydronaphthalene solution, followed by stirring, casting and drying under vacuum at 50°C.

For pyrolysis of POM, irradiated POM was mixed with zeolite for thermal analysis. after irradiation.

Thermogravimetric analyses were performed on a TGA-50 thermogravimetric analyzer (Shimadzu Co. Ltd.). Flow gas (nitrogen) and heating rate used were 50 ml/min and 10°C /min, respectively. Pyrolysis products were identified by using a pyrolyzer-GC-MS-computer on-line instrument (Shimadzu Co. Ltd.) containing a PYZ-4A pyrolyzer, 17A gas chromatograph with a DB-1 column (diameter 0.25mm x 30m) and a QP-5000 mass spectrometer. The temperature programme of the GC column used was as follows; temperature constant at 40°C for the first 4 min and increased to 100°C with a heating rate of 40°C for another 4 min, then increased to 200°C using the same heating rate and kept at this temperature until the end of the experiment.

Irradiation was carried out at room temperature in air with  $\gamma$ -rays from a Co-60 at a dose rate of 10kGy/hr.

## RESULTS AND DISCUSSION

### 3.1 Pyrolysis of irradiated PP in the presence of zeolite

When PP is subjected to high-energy irradiation, whether crosslinking or degradation occurs depends on the radiation conditions. Oxidative degradation occurs predominantly if PP is irradiated in air, and accordingly its thermal stability is reduced.<sup>4-9</sup> In Figure 1, irradiated PP was mixed with zeolite (640NAA) for thermogravimetric measurements. The irradiation induced reduction of degradation temperature ( $\Delta T_{10\%} = (T_{10\%})_{\text{irradiated PP}} - (T_{10\%})_{\text{unirradiated PP}}$ ,  $T_{10\%}$  is the temperature at which weight loss of PP achieved 10% during heating). According to Figure 1, the temperature decrease in the presence of zeolite is about 2.5 times greater when compared with that in the absence of zeolite. It was confirmed that zeolite is effective for degradation temperature reduction of irradiated PP in pyrolysis.

### 3.2 Degradation of irradiated PP-zeolite mixture

The experiment in which PP and zeolite were first mixed and then irradiated was termed in situ irradiation. Typical TG curves of the in-situ irradiated samples can be seen in Figure 2. In this case, significant temperature reduction, with a maximum of about 60°C, was observed.

### 3.3 Effect of various zeolites on pyrolysis of irradiated PP-zeolite

PP-zeolite blends with various kinds of zeolites were irradiated by  $\gamma$ -rays and then subjected to pyrolysis thereafter. Figure 3 shows the variation of  $T_{10\%}$  against dose. The results revealed that different zeolites resulted in different effects. In systems containing 320NAA and 640NAA, both possessing Na<sup>+</sup> cation, irradiation could reduce the degradation temperature; while in systems related to 500KOA and 720KOA, both containing K<sup>+</sup> cation, degradation temperature kept almost constant before and after irradiation. For 320HOA, which was proved to be the most effective catalyst before irradiation[1], showed an unusual

character that  $\Delta T_{10\%}$  increased with increasing dose. The reason why different zeolites resulted in different trends in influence on the thermal degradation behavior of PP is not clear. Nevertheless, it can be seen that counter-ion is one important factor, which might influence the interaction between PP and zeolite during irradiation.

### 3.4 Effect of morphology

From the results discussed above, it could be concluded that in-situ irradiation induced thermal degradation temperature decrease is not only contributed by the additive effects of pre-irradiated PP and pre-irradiated zeolite. There must be other reasons, of which, one possibility is the interaction between these two components during irradiation. In the present experiment, irradiation was performed in the solid state and PP macromolecule could not access the inner surface of the zeolite during irradiation. Therefore, the contact of PP with the outer surface of zeolite, which could be characterized by morphology, is expected to play an important role.

To elucidate the effect of morphology on pyrolysis, PP-zeolite mixtures were prepared by three methods, e.g. powder stirring, molten blending and solution casting. Morphologies of these three kinds of mixtures were observed by scanning electron microscope (SEM), as shown in Figure 4. The PP powder was quite big (about  $100\mu\text{m}$  in diameter) in comparing with zeolite powder (about  $1\mu\text{m}$  in diameter). The zeolite powders deposited on the surface of PP powders in powder mixture (Figure 3 (a) and (d)). In contrast, zeolite could be better dispersed in molten blending mixture (Figure 3 (b) and (e)), because the big PP powder were destroyed under melt condition. However, zeolite powders were not separated completely

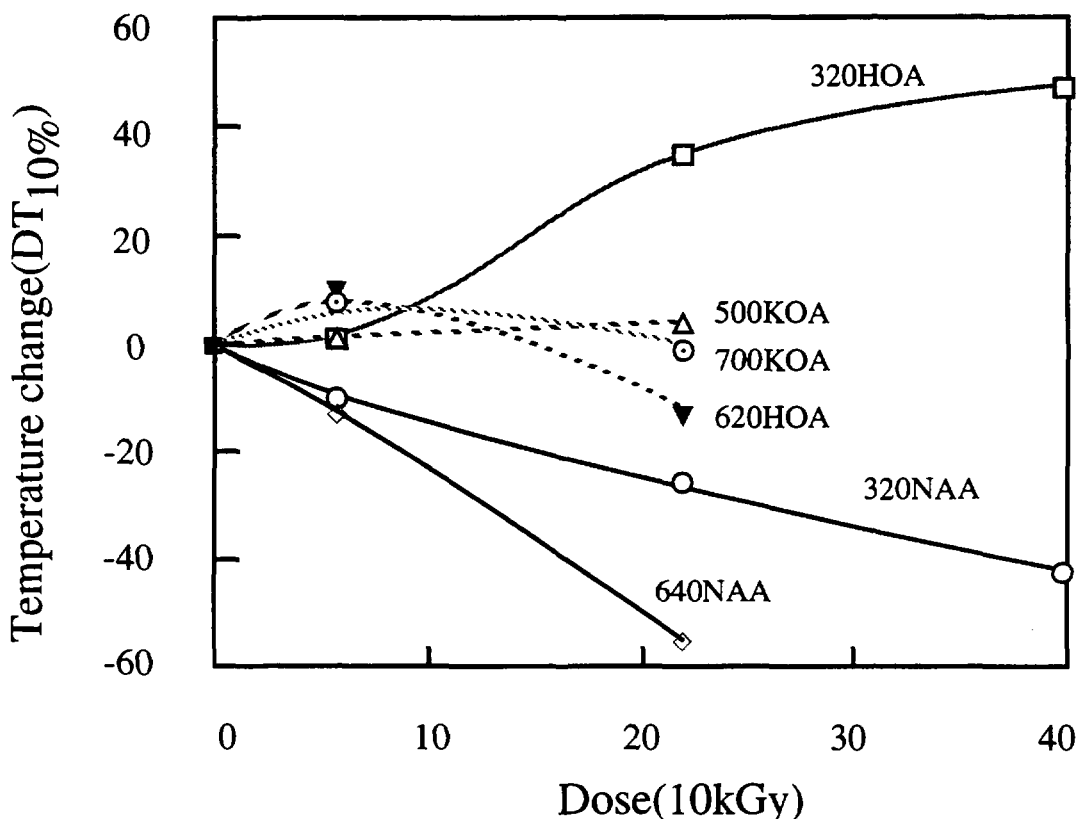
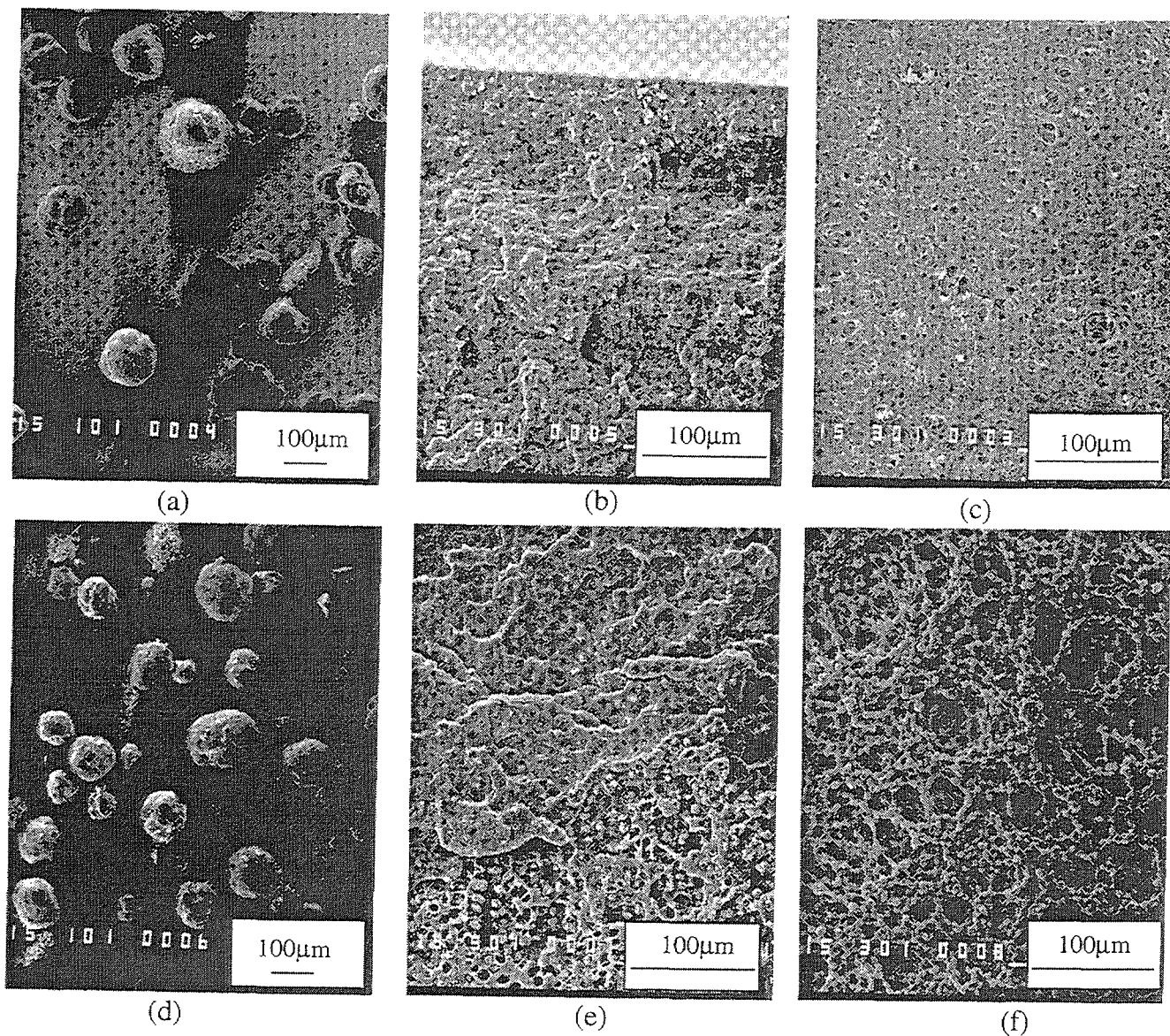


FIG. 3. Effect of zeolites on the change of thermal degradation temperature induced by the irradiation of PP-zeolite mixtures (molten blends containing 20% zeolite).



*FIG. 4. SEM photos for PP-zeolite mixtures  
 (a) powder mixture containing 640NAA 20%;  
 (b) molten blend containing 640NAA 20%;  
 (c) casting film containing 640NAA 20%;  
 (d) powder mixture containing 320NAA 20%;  
 (e) molten blend containing 320NAA 20%;  
 (f) casting film mixtures containing 320NAA 20%.*

under the blending condition and there were still some zeolite aggregates. The most homogenous mixture was the casting film, in which, zeolite powder were dispersed very well (Figure 3 (c) and (f)). Radiation induced effect on the thermal degradation temperature of these three kinds of mixtures are summarized in Tables 2 and 3. For powder mixture of PP-640NAA, notable effect was observed only when as much as 50% zeolite was used and no notable effect was observed when 20% zeolite was used. In solution dispersed mixture, however, even only 5% zeolite loaded, the effect was remarkable. As seen in Table 2, casting method was also more effective to reduce degradation temperature than molten blending in

the case of 320NAA zeolite. It was confirmed that irradiation induced effect was closely related to the extent of zeolite dispersion in the mixture. The more homogeneously dispersed zeolite in the mixture will give greater temperature reduction by irradiation.

### 3.5 Pyrolyzed products identification

Pyrolyzed products of irradiated PP with and without zeolite were identified. Identification was carried out by the same method as describe in the previous paper[1]. Figure 5 shows gas chromatographs of the products in the pyrolysis of unirradiated and irradiated PP. The spectrum of irradiated sample was very similar with that of the unirradiated one. The compounds structures determined by mass spectrometer indicated that the products of irradiated PP were same as that of unirradiated PP and no new product was formed due to the preceding irradiation treatment. However, a quantitative measurement showed that the relative concentration of the hydrocarbon with a certain molecular weight was influenced by irradiation. As a result, the products distribution was shifted to the region of lower molecular weight products, as shown in Figure 6. Hydrocarbons less than 12 carbons slightly increased with increasing dose while those more than 12 carbons remarkably reduced. This effect can be attributed to the contribution of irradiation induced degradation.

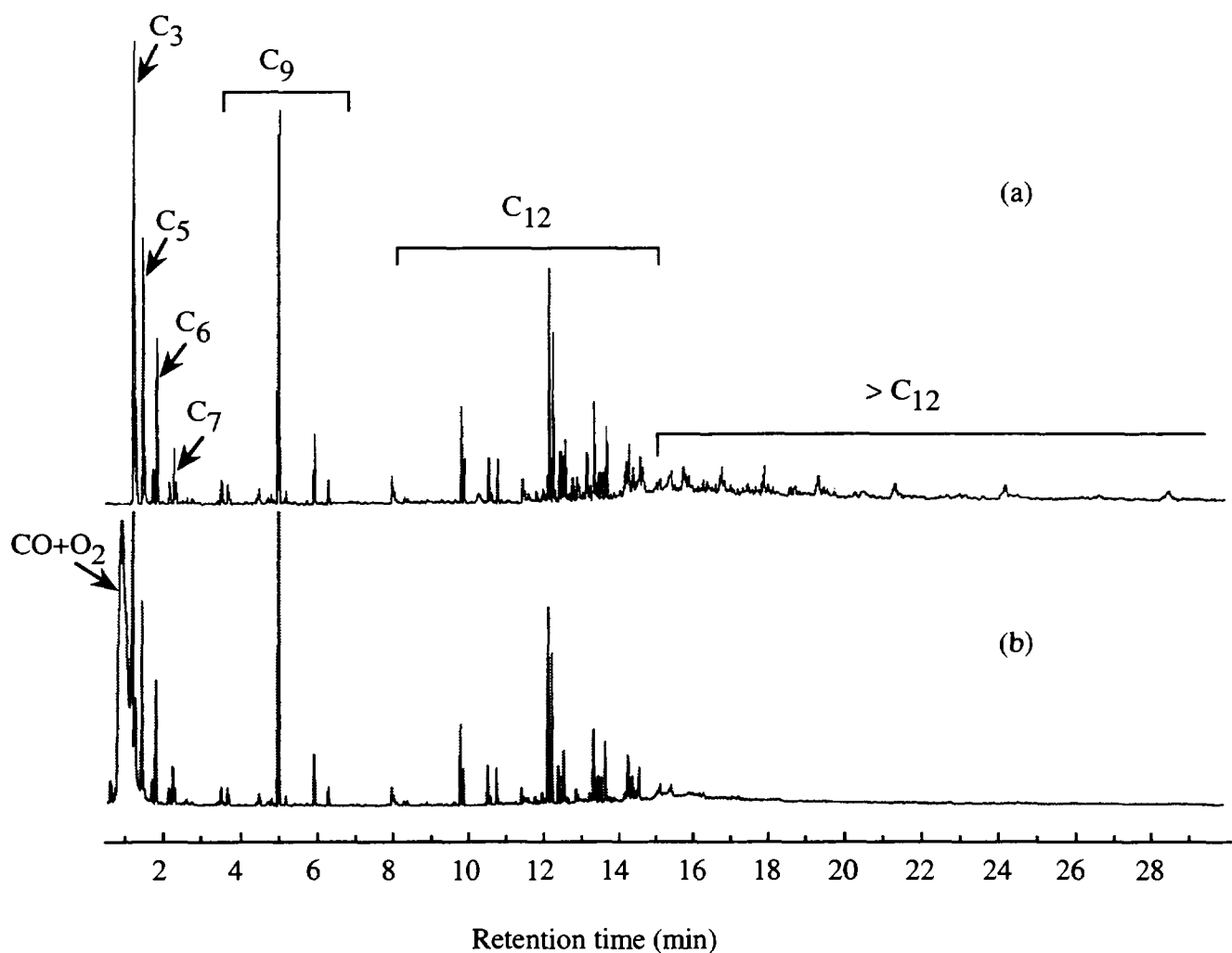


FIG. 5. Pyrolysis-gas-chromatograms for PP  
(a) before irradiation and (b) irradiated to 220kGy.

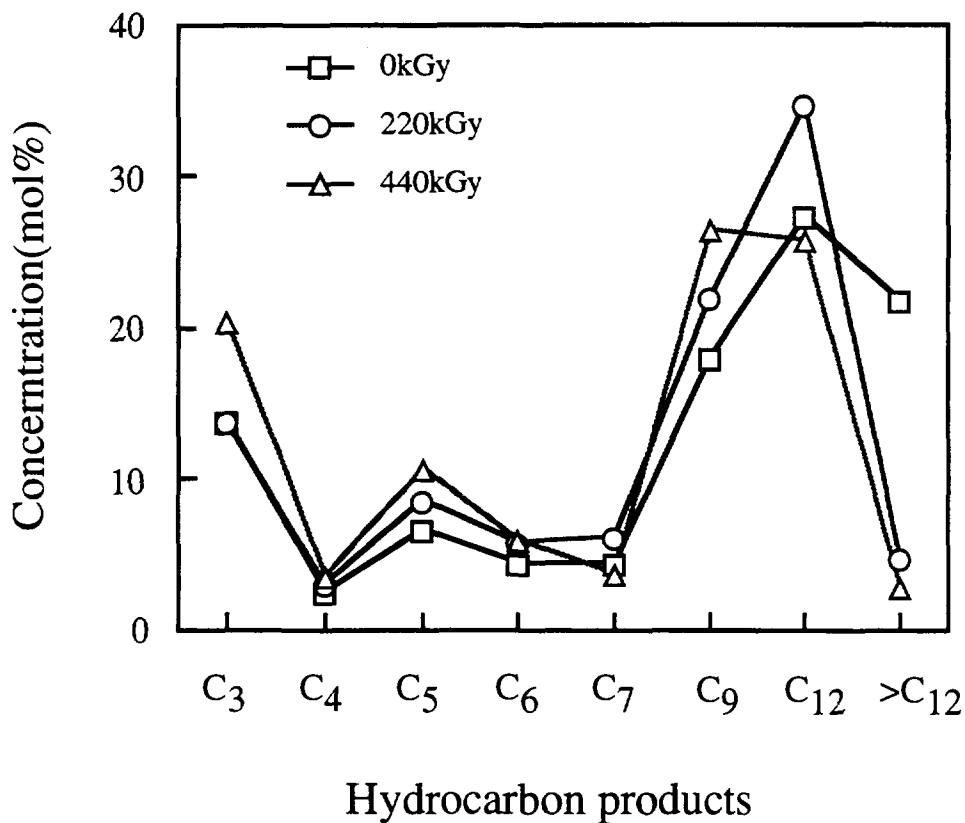


FIG. 6. Effect of irradiation on products distribution in pyrolysis of PP.

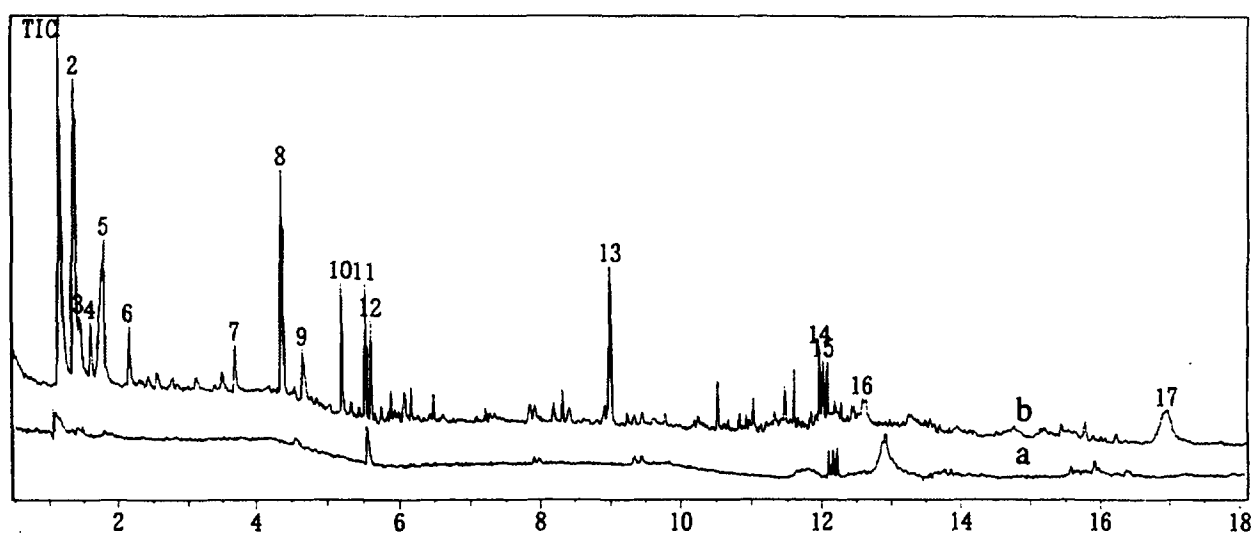


FIG. 7. Comparison of pyrolysis-gas-chromatograms (a) before and (b) after irradiated to 340kGy (casting film containing 640NAA 15%).



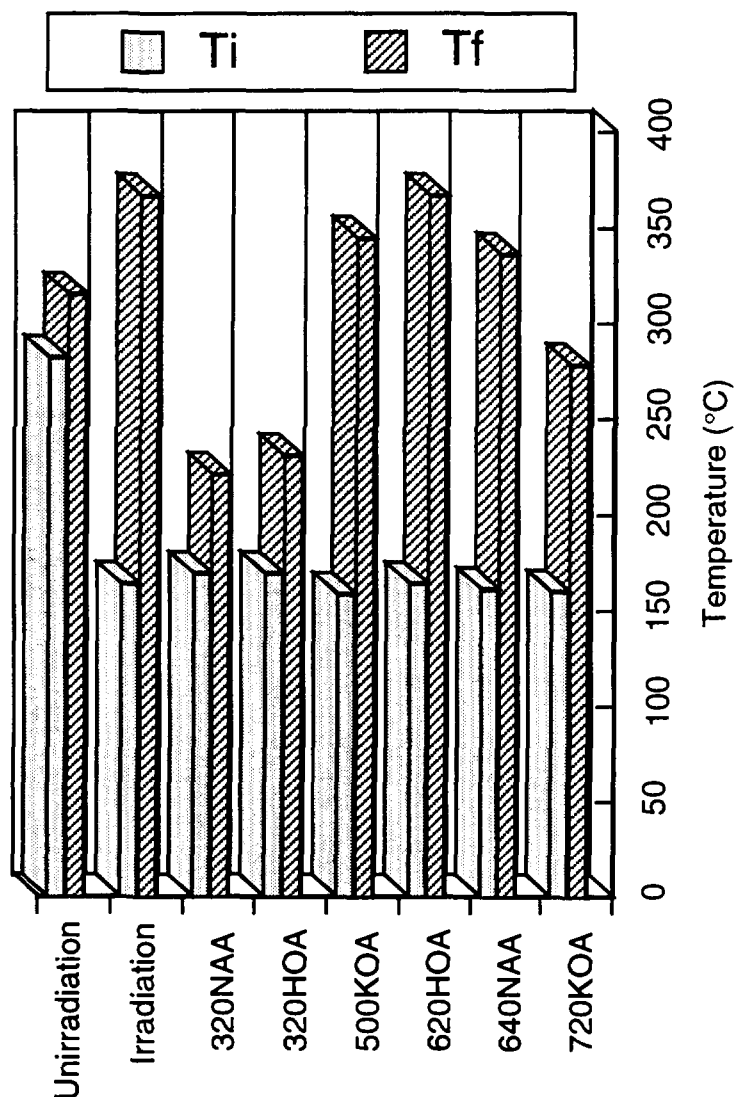


FIG. 8. Effect of zeolite on pyrolysis of irradiated POM (220 kGy).

The foregoing discussion demonstrated that, in the presence of zeolite, irradiation dramatically reduced the thermal degradation temperature. Consequently, the effect of irradiation could be clarified by carrying out the pyrolysis at much lower temperature. Figure 7 is a comparison of the GC spectra obtained for the samples pyrolyzed at 350°C before and after irradiation. No product was elucidated for the sample before irradiation because this temperature was too low to crack down the macromolecules. In contrast, a series of chemicals were observed for the irradiated sample. Structures of these products were identified and are listed in Table 4. Besides hydrocarbons, oxidized products containing carbonyl and hydroxyl groups were also identified. Oxygen containing compound was not observed in the case of without the presence of zeolite. Oxidation occurred possibly only during the process of irradiation but not during pyrolysis because pyrolysis was carried out by using Helium as a carrier gas. In the irradiation of individual PP in air, oxidation unavoidably happens, as indicated by infrared spectra<sup>[7, 14]</sup>. No formation of oxidized product in pyrolysis of irradiated PP was probably due to that the concentration of oxidized chemicals were too small to be identified. Formation of oxidized products for in-situ irradiated sample inferred that radiation induced oxidation was much more pronounced because of the attendance of zeolite during irradiation. Therefore, we may conclude that irradiation induced oxidation is accelerated by

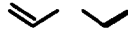







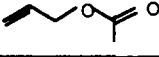
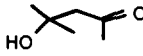


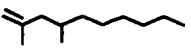

Table 2 The reduction of thermal degradation temperature( $\Delta T$ ) of PP by *in-situ* irradiation in the presence of 640NAA

Dose (10kGy) \ $\Delta T$	powder mixture (zeolite 50%)	powder mixture (zeolite 20%)	molten blend (zeolite 20%)	casting film (zeolite 15%)	casting film (zeolite 5%)
6	-36.1	-11.9	-12.4	-21.1	-17.3
22	-99.4	+6.8	-55.5	-40.0	-16.3
34	-	-	-	-75.6	-45.7
60	-	-	-	-141.5	-101.9

Table 3 The reduction of thermal degradation temperature( $\Delta T$ ) of PP by *in-situ* irradiation in the presence of 320NAA

Dose(10kGy) \ $\Delta T$	molten blend (320 NAA 20%)	casting film (320NAA 15%)
6	-10.1	-18.9
22	-26.0	-34.0

Table 4 Products identified in pyrolysis of irradiated PP-zeolite mixture (Film containing 5% 640NAA irradiated in air to 340kGy at a dose rate of 10Mrad/h, pyrolyzed at 350°C)

Peak number	Retention time(min)	Composition	Possible structure	Yield (mol%)
1	1.139	C <sub>3</sub> H <sub>6</sub> , C <sub>3</sub> H <sub>8</sub>		19.49
2	1.364	C <sub>3</sub> H <sub>6</sub> O		17.65
3	1.438	C <sub>3</sub> H <sub>6</sub> O		4.02
4	1.606	C <sub>4</sub> H <sub>6</sub> O		3.21
5	1.792	C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>		10.85
6	2.164	C <sub>4</sub> H <sub>8</sub> O		2.57
7	3.680	C <sub>6</sub> H <sub>12</sub>		2.29
8	4.438	C <sub>5</sub> H <sub>8</sub> O <sub>2</sub>		8.52
9	4.647	C <sub>5</sub> H <sub>8</sub> O <sub>2</sub>		2.40
10	5.190	C <sub>6</sub> H <sub>12</sub> O <sub>2</sub>		3.30
11	5.515	C <sub>9</sub> H <sub>18</sub>		2.90
12	5.592	C <sub>9</sub> H <sub>20</sub>		2.21
13	8.992	C <sub>9</sub> H <sub>19</sub> O	not identified	6.90
14	11.958	C <sub>12</sub> H <sub>24</sub>		2.88
15	12.022	C <sub>12</sub> H <sub>26</sub>		2.35
16	12.580	not identified	not identified	3.29
17	16.954	C <sub>15</sub> H <sub>30</sub>	not identified	5.19

the addition of zeolite. This conclusion was confirmed by the following observation. Irradiation of the same PP-zeolite mixture under vacuum gave no notable reduction in the thermal degradation temperature.

### 3.6 Pyrolysis of irradiated POM

Effect of zeolite on pyrolysis of irradiated POM is shown in Figure 8. Initial temperature (Ti) and final temperature (Tf) of pyrolysis were estimated from TGA curves. Ti

and  $T_f$  of unirradiated POM were 280°C and 312°C, respectively. The  $T_i$  of pyrolysis of irradiated POM was depressed to 180°C, while  $T_f$  was rather increased. Furthermore, addition of 320NAA or 320HOA zeolite, achieved significantly lower  $T_f$ s compared to the case without zeolite. It means that pyrolysis of irradiated POM is accelerated by catalytic function of zeolite. Both 320NAA and 320HOA zeolite are classified as Ytype, and the others as different types such as L, Mordenite and so on. Thus, it is suggested that structure of zeolite is an important factor to reduce the  $T_f$  in pyrolysis of irradiated POM.

#### 4 CONCLUSIONS

Irradiation is able to render PP much more susceptible to thermal degradation when irradiation was carried out in the presence of zeolite. However this effect was closely related to the types of zeolites, mixing methods and irradiation conditions. In the pyrolysis of properly irradiated PP-zeolite mixtures, new chemicals such as acetone, acetic acid, and etc., could possibly be obtained in addition to the traditional hydrocarbons. Furthermore, it was confirmed that zeolite is more effective to reduce the pyrolysis temperature of irradiated POM.

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