

Title	一次構造を制御したプロピレン-エチレンコポリマーの熱安定性に関する検討
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Effects of ethylene comonomer on the thermal stability of propylene-ethylene copolymer

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Introduction

Polypropylene (PP) is one of the most important commercial polyolefins.

Due to its advantages, such as, environment low load, ease of processability, low cost, high melt index and light weight, Nowadays, 40 million tons PP are produced in a year in the world, which is the maximum production among various plastic materials. The weakest point of PP is ease of degradation by thermal and photo stimulations, and catalyst residues, because radical is easily and steady generated on tertiary carbon atoms a material is achieved by adding stabilizer, but stability of PP it self is required from a viewpoint of long-term use, recycling and reuse.

Auto oxidative degradation mechanism of PP explained radicals may then quickly react with O₂ by the auto oxidation scheme¹⁾.

In a previous research, the thermo-oxidative degradation of PP was examined in terms of stereoregularity of the primary chain, where syndiotactic PP was reported as being more stable than isotactic PP(iPP) against thermo-oxidative degradation.²⁾ Suzuki et al. examined the effect of the stereoregularity of PP on the thermo-oxidative reaction. They prepared four PPs with different tacticity characterized in Table 1, and their degradation behaviors at 145°C were evaluated by Thermogravimetry(TG). They found that the stereoirregularity of mmmm under 80 mol% significantly delayed the start and progress of the degradation (Figure 1).³⁾

Table 1 Characterization of fractioned PPs

Sample	Mn	MWD	mmmm (mol%)
PP1	74000	8.5	91
PP2	25000	3.2	87
PP3	18000	5.1	76
PP4	11000	4.6	52

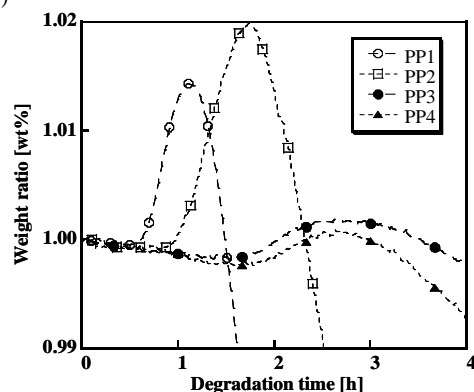


Figure 1 Degradation behavior of fractionated PPs

The photo-oxidative stability of ethylene-propylene random copolymer with a low ethylene content was also investigated, resulting in the improvement of the photo-stability from that of iPP. The effect of the ethylene comonomer was prominent for a long irradiation time.⁴⁾

Manabe et al. knowledge obtained by thermal oxidative degradation of a polypropylene impact copolymer was examined using transmission electron microscope equipped with an energy dispersive X-ray system, the oxidation resistance of the ethylene-propylene rubber phase was found to be higher than that of the PP matrix.⁵⁾ The content of the ethylene of polypropylene impact copolymer at this time was 5.6 and 12.8 mol% ethylene content.

On the contrary to the effect of tacticity of PP on the thermal oxidative degradation, the effect of the ethylene content is not understood in details, in spite of the previous reports. Therefore, in this study, I synthesized propylene-ethylene copolymer(rPP) with different ethylene contents as irregularity within primary structures, and examined the detailed effect of the ethylene comonomer. It was found that ethylene content over 5.3 mol% was significantly stabilize rPP.

Experiments

Materials

rPPs having different contents of ethylene were synthesized using TiCl_4 /dibutyl phthalate/ MgCl_2 , triethylaluminum (TEA) was used as the co-catalyst, diluted by toluene, Ziegler-Natta catalyst. cyclohexyl dimethoxy silane (CMDMS) was added as an external donor. Toluene was purified by passing through the molecular sieves 13X column. N_2 (Uno Sanso Corp.), propylene and TEA were used without further purification.

Polymerization

The contents of ethylene were controlled by flow rate ratio of propylene and ethylene at 1 atm. Polymerizations were performed with 100 of Al/Ti molar ratio at 60°C in 30 minutes, using toluene as a solvent. In order to remove catalyst residues, the synthesized rPPs were reprecipitated from a boiling xylene solution into excess amounts of methanol.

Characterization of propylene-ethylene copolymers

The number average molecular weight (M_n) and molecular weight distribution (MWD) of the obtained rPP samples were determined by Gel Permeation Chromatography (GPC: Senshu, SSC-7100) with styrene-divinylbenzene gel columns (SHODEX, HT-806M) at 140°C, where the samples were dissolved in o-dichlorobenzene containing 2,6-di-t-butyl-p-cresol as an antioxidant. The primary structure was determined by ^{13}C -NMR measurement using a Varian Gemini-300 spectrometer at 120°C, where hexachloro-1,3-butadiene was used as a solution (sample/solvent ratio was 20% (w/v)). 1,1,2,2-tetrachloroethane- d_2 was added as an internal chemical shift reference.

Thermal degradation Analysis

The weight ratios of the rPP samples during thermal oxidative degradation at 145°C was measured by a thermo gravimetric (TG, METTER TG50) under 50 ml/min of air flow. The thermal analyzer was calibrated using the 'Curie point' of nickel as a reference.

Results and Discussion

The synthesized PP and rPP samples are characterized in Table 2. The ethylene contents were successfully controlled to 3.3, 5.3, 16.6, and 18.6 mol%, where the increases of the ethylene contents accompany the decrease of mmmm.

Moreover, the n_E values, 1-2, mean that the ethylene monomer was randomly distributed even with 18.6 mol% of E.C. Figure 1 showed the results of TG at 145°C. The changes in the weight ratios of the PP and rPPs display a multi-stage behavior in

progress of degradation,^{6), 7)} a period of constant weight, namely induction period, is initially seen, and then the weight ratio sharply increase, so called auto-acceleration period, where the fast incorporation of oxygen into the polymer chains causes the mass gain. Once the curve arrives at the maximum, the weight ratio begins to decrease steadily, where evaporation of volatile species, as a result of chain scission, exceeds the mass gain by the O₂ incorporation into the polymer. ⁸⁾ And finally the weight ratio becomes negative. As was previously stated, the duration of the induction period, after which the auto-accelerated degradation starts, strongly depends on the tacticity of PP. Seen in Figure 2, the contents of ethylene had little influence on the duration of the induction periods. The increasing speeds of the weight ratios, which correspond to the speed of the spread of the oxidized region, are similar between the PP and rPP with 3.3 mol% of ethylene content, but significantly suppressed over 5.3 mol% of E.C. The weight-decrease speeds after the maximum also followed the same tendency, namely, significant stabilization over 5.3 mol%. From Table 2, it is found that the E.C. over 5.3 mol% corresponds to mmmm under 80 mol%. The 80 mol% of mmmm is the very value, from which the disarray of the stereoregularity largely suppressed the degradation. Thus, we found that 80 mol% of mmmm is the critical value to achieve significant stabilization for both E.C. and disarray of the stereoregularity.

Table 2 Characterization of the PP and rPP samples					
Sample	Mn	MWD	mmmm (mol%)	E.C. (mol%)	η_E (mol%)
PP	36000	6.5	96.6	0.0	0.0
rPP1	32000	5.6	90.7	3.3	1.4
rPP2	25000	7.3	79.8	5.3	1.2
rPP3	13000	11.3	61.9	16.6	1.6
rPP4	14000	5.5	55.4	18.6	1.6

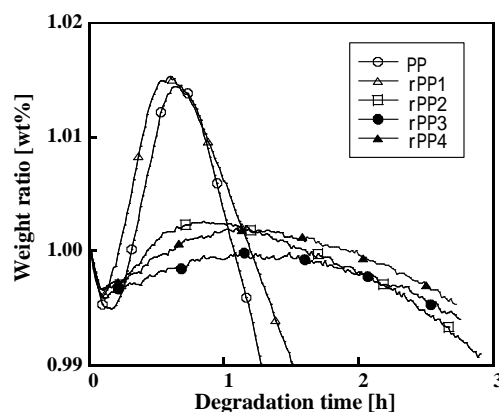


Figure 2 Degradation behavior of the PP and rPP samples

Conclusion

The effect of ethylene comonomer on the stability of rPP against thermal oxidative degradation was examined by varying ethylene content of rPPs from 3.3 mol% to 18.6 mol%. I found that the ethylene content, which led to less than 80 mol% of mmmm significantly suppressed the progress of degradation.

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