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Influence of primary structure on thermal oxidative degradation of polypropylene impact copolymer

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Summary

Thermal oxidative degradation was carried out using four kinds of polypropylene impact copolymers, and the relationship between primary structure and degradation behavior was investigated by the results of ^{13}C-NMR, TEM, GPC and the determination of hydroperoxide value (HPO) and number of chain scission (NCS). The degradation behavior mainly depended on the ethylene content and on the tacticity. The thermal degradation was found to be controllable by the primary structure.

Introduction

Polypropylene impact copolymer (ImPP) is widely applicable polymer material [1-4]. ImPP is mainly produced by multi-stage homo and co-polymerizations of propylene and ethylene. The advantage of ImPP is tailored mechanical properties, which are obtained by changing the reactor conditions and the quantities of comonomer used [5]. As application characteristics of polymer materials, the degradation is one of the important factors. In particularly, PP homopolymer is known to be very vulnerable to oxidative degradation under the influence of elevated temperature and sunlight [6-8]. The degradation has been very extensively studied and has long been recognized as a free-radical chain reaction [9], which leads to polymer chain to scission. Relatively little is known about the degradation of ImPP. Although the degradation chemistry is similar to that of PP homo-polymer, such multiple components make it difficult to get accurate information on the degradation behavior.

In order to get the accurate information, it is necessary to clarify the relationship between degradation behavior and component, namely primary structure such as ethylene content and tacticity. The degradation behavior of PP homopolymer has frequently been estimated by hydroperoxide value (HPO) using infrared (IR) spectroscopy. The measurement of IR, however, is not suitable for the quantitative analysis because of the superposition of absorption band with alcohol and other degradation products [10,11]. In addition, the peak location of hydroperoxide is not fixed in degraded ImPP because of consisting of complicated components such as mixing of PP, polyethylene (PE) and ethylene-propylene rubber (EPR). In the case of ImPP, a titration method is suitable for the determination of HPO. As another accurate evaluation method of the degradation behavior, there is a determination of number of chain scission (NCS), which arises from the hydroperoxide decomposition. The NCS is considered an accurate index indicating the degree of advance of degradation in the initial stage of degradation without volatilization of component since it is calculated from changing in the molecular weight of degraded polymer [12]. The combination of determination of HPO and NCS, thus, will provide with more accurate information on the degradation behavior of ImPP.

In this study, thermal oxidative degradation was carried out using four kinds of ImPP with different primary structure such as ethylene content and tacticity. The relationship between primary structure and degradation behavior was studied by the determination of HPO and NCS.

Experimental

Materials

Four kinds of PP impact copolymer (donated by Sumitomo Wiring Systems Co., Ltd.) were reprecipitated from a boiling xylene solution into ethanol and dried in vacuo at 60 °C for 8h, and then the freeze grindings were carried out with liquid nitrogen. The grinded impact copolymers were sufficiently dried in vacuo and used as samples without antioxidant.

Measurements

Molecular weight of the sample was determined by gel permeation chromatography (GPC) (Senshu, SSC-7100) with polystyrene gel columns (SHODEX, HT-806M) at 140 °C using *o*-dichlorobenzene as a solvent.

The primary structure was determined by ^{13}C-NMR measurement using a Varian Gemini-300 spectrometer at 120 °C on 20% (w/v) solution in hexachloro-1,3-butadiene. 1,1,2,2-tetrachloroethane-d2 was added as an internal lock and used as an internal chemical shift reference.

Morphology of the PP impact copolymer was examined with a JEOL JEM-2010 transmission electron microscope (TEM). The ultrathin films were sectioned into slices with an ultramicrotome at -100 °C. Then, the ultrathin films were stained by ruthenium tetraoxide (RuO_4) for 12h and were put on a copper grid and examined with the TEM device operating at 200 kV.

Thermal Oxidative degradation

Thermal oxidative degradation was carried out at 130 °C in an oven. The sample was put into a small vial and was allowed to stand in the oven in air. In the heater, the vial was covered with a heating jacket to achieve effective heat transfer to the samples. The degraded PP in the small vial was dissolved in 5ml of o-dichlorobenzene containing 2,6-di-t-butyl-p-cresol as an antioxidant, and the obtained PP solution was directly measured by GPC.

Titration method of hydroperoxide

The titration solution denoted “solution A” was prepared by dissolution of sodium iodide in 2-propanol 10ml and then addition of glacial acetic acid 2ml, benzene 30ml. The degraded ImPP (ca. 0.05g) was added into the solution A and refluxed at 70 °C for 10 min.

The hydroperoxide value (HPO) was determined from a potentiometric titration. Sodium thiosulfate standard solution of 0.005N was used as a standard solution. The titration of “solution A“ including the degraded ImPP was performed with this standard solution using a potentiometric titration system (Hiranuma, Inc., COM-1500) equipped with Ag-AgCl and platinum as reference and indicator electrode, respectively [13].

Results and discussion

Characterization of ImPP

The characteristics of ImPP were summarized in Tables I and II. The molecular weights of ImPP1, ImPP2, and ImPP4 are roughly equal.

TEM micrograph has been frequently used to observe the morphology of heterophasic PP systems [14,15]. In order to take a clear micrograph, it is necessary to stain the samples with RuO_4. Dark region in Figure 1 corresponds to the stained ethylene-propylene rubber (EPR) phase, while bright region does to PP matrix. In addition, the

Table I. Number average molecular weight (Mn) and molecular weight distribution (MWD)

Sample	$\overline{M}_n \times 10^{-4}$	MWD
ImPP1	15.1	4.6
ImPP2	11.1	7.1
ImPP3	5.7	6.5
ImPP4	11.2	12.3

Table II. Molecular characteristics of ImPP samples

Sample	mmmm[a] (mol%)	Triad sequence distribution(mol%)[b]						Ethylene content[c] (mol%)
		PPP	PPE	EPE	PEP	PEE	EEE	
ImPP1	86.4	86.5	3.4	1.7	1.7	2.5	4.2	8.4
ImPP2	83.9	86.0	3.7	1.9	1.9	2.8	3.7	8.4
ImPP3	82.9	79.5	3.9	2.4	2.4	4.7	7.1	14.2
ImPP4	87.0	87.5	1.6	1.6	0.8	2.3	6.2	9.3

[a] mmmm ; isotactic pentads. [b] P = propylene unit, E = ethylene unit.
[c] Ethylene content = PEP + PEE + EEE.

bright region in segregated EPR phase corresponds to polyethylene (PE) including linear low density PE [16,17]. As shown in Figure 1, in ImPP3 and ImPP4, the comparatively large domain with the diameter of approximately 1 μm is mainly dispersed within PP matrix, whereas, in the case of ImPP3 and ImPP4, the size of domain is comparatively small. In addition, the black spots (<100nm) are not EPR phases but Ru deposits. It appears that the morphology of ImPP evidently depends on the content of ethylene.

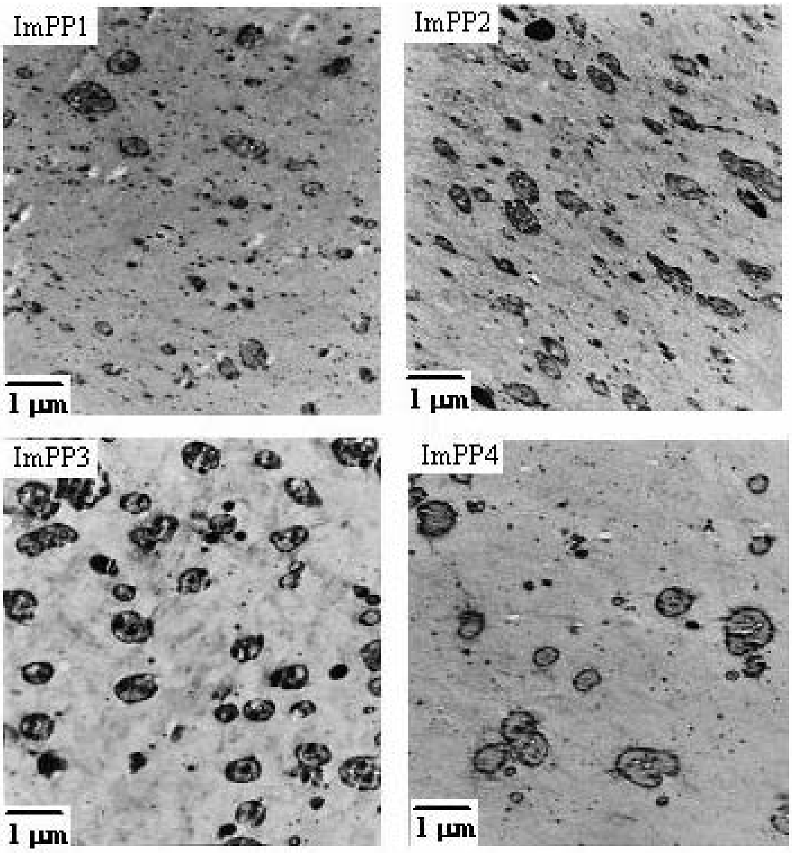

Figure 1. TEM image of ImPP

Behavior of thermal oxidative degradation

Thermal oxidative degradation of ImPP was carried at 130 °C and its degree of advance was estimated by the changes in HPO.

As shown in Figure 2, the HPO of all ImPPs sample displays multi-stages with advance of degradation. The HPO is initially increasing up to about 6 h. The order of increase is the following order; “ImPP1>ImPP2>ImPP4>ImPP3”. This order means instability against the thermal oxidative degradation. Beyond a maximum, the all of HPO decrease with degradation time and finally become negative due to the volatilization of severely degraded PP.

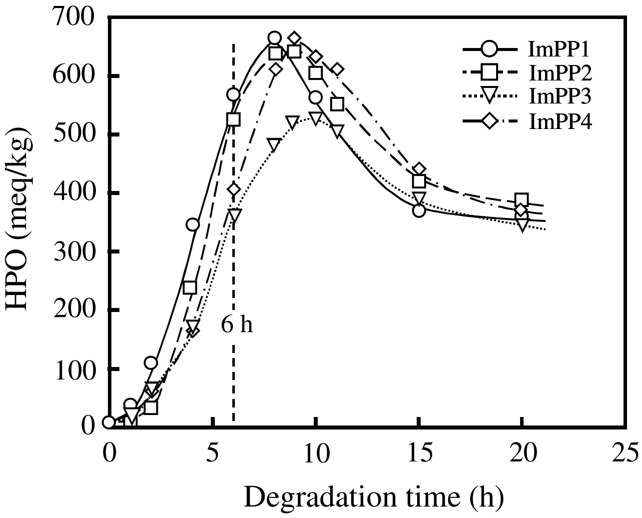

Figure 2. Changes in HPO of ImPP during thermal oxidative degradation

The NCS can be obtained from measurement of the molecular weight by GPC and is given by [12]:

$$NCS = \overline{M}_n^0 / \overline{M}_n^t - 1 - NCL \approx \overline{M}_n^0 / \overline{M}_n^t \tag{1}$$

where $\overline{M}_n^0$ and $\overline{M}_n^t$ are number average molecular weight before and after thermal oxidative degradation, NCL is the number of crosslink. Here the NCL is considered "0" because all of degraded ImPPs are soluble in a hot *o*-dichlorobenzene solvent. Thus, eq. (1) is approximated to eq. (2):

$$NCS \approx \overline{M}_n^0 / \overline{M}_n^t \tag{2}$$

As shown in Figure 3, the initially increasing rate (up to 6h) in NCS is the following order; "ImPP1>ImPP2>ImPP4>ImPP3". This order is in agreement with that of HPO, indicating that the advance rate of degradation has close connection with the primary structure.

The advance rate seems to be the order of lower ethylene content because that with higher ethylene content is slower (see Table II). As mentioned above, the degradation starts by the dissociation of C-H bond.

The dissociation energy of secondary C-H is higher than that of tertiary C-H. Thus, the beginning of oxidative degradation in an ethylene unit is more difficult than that in a propylene one. In our previous work [18], the quantitative analysis using energy dispersive X-ray system directly proved that the degradation resistance of EPR phase was considerably higher than that of the PP matrix, demonstrating that the beginning of oxidative degradation in an ethylene unit was more difficult than that in a propylene one. It will be natural that the advance rate of degradation is dependent on the ethylene content.

The difference between the advance rate of degradation of ImPP1 and ImPP2 having the same ethylene content will be due to the tacticity in PP matrix. The rate of ImPP1 with higher "mmmm" is higher than that of ImPP2, suggesting that the tacticity

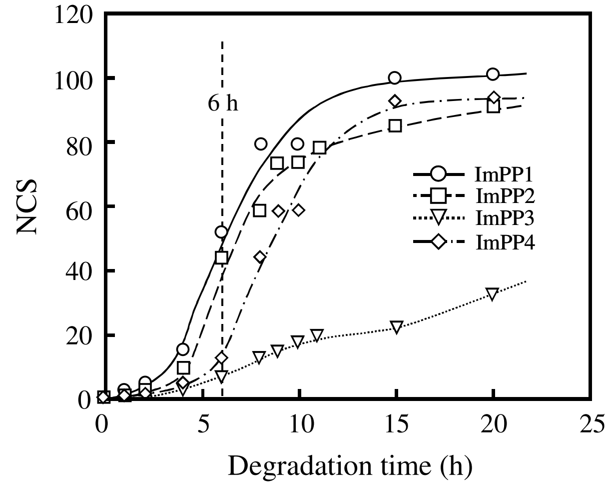

Figure 3. Changes in NCS of ImPP during thermal oxidative degradation: NCS was calculated by eq. (2)

becomes a factor for determining stability of ImPP. The difference of tacticity influences the formation of hydroperoxide. The peroxy radical and tertiary C-H are located on the same side in isotactic unit, and the abstraction of tertiary hydrogen smoothly occurs. In the case of atactic unit, the abstraction reaction is disturbed by the existence of methyl group on the same side [19]. As a consequence, the rate of degradation falls systematically as the tacticity becomes lower, resulting that the ImPP having lower tacticity shows higher stability.

Conclusion

With the aim of clarifying the relationship between primary structure and degradation behavior, the thermal oxidative degradation of ImPP was studied. The degradation behavior was estimated by the HPO and NCS, and the primary structure was determined by ^{13}C-NMR measurement. From these results, it was found that the degradation was depressed by increasing ethylene content and by lowering the tacticity.

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