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Study of local oxidative degradation in polypropylene impact copolymer by energy dispersive X-ray system

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Summary

In this study, the thermal oxidative degradation of a polypropylene (PP) impact copolymer was examined using a transmission electron microscope equipped with an energy dispersive X-ray system (TEM/EDX). The oxidative behavior was visually captured by oxygen line analysis. The oxidation resistance of the ethylene-propylene rubber (EPR) phase was considerably higher than that of the PP matrix, indicating that the degradation behavior of the PP impact copolymer was heterogeneous. It was found that the higher resistance of the EPR phase originated from its primary structure by ^{13}C-NMR measurement.

Introduction

Polypropylene (PP) impact copolymer is a heterophasic PP system improved by rubber modification [1-4]. Since the impact copolymer shows superior mechanical properties, it has rapidly captured a big segment of the thermoplastic market. In contrast to PP homopolymers, the impact copolymer is produced mainly by the multi-stage copolymerization of propylene with ethylene. The advantage of this polymerization process is that the mechanical properties can be tailored to create a wide range of specific end-use application characteristics by changing the reactor conditions and the quantities of comonomer used [4].

The impact copolymer exhibits bi- or multi-phase morphology depending on its EPR and PE contents. The superior mechanical properties originate in this complicated morphology. Thus, retaining the morphology is very important with respect to the material life.

PP is easily degraded by a stimulus such as elevated temperature or sunlight [5-13], which causes the PP to become brittle. PP degradation chemistry has been recognized as a free-radical chain reaction, which leads to polymer chain scission [14]. It is generally accepted that this chain scission is responsible for the brittleness. In the case of an impact copolymer, the degradation chemistry will be similar to that of PP. However the degradation behavior is complicated due to its multiple components and morphology. For example, the change of morphology by degradation surely has a great influence on the mechanical properties and also changes the appearance.

Investigations of the degradation of impact copolymers are insufficient due to its multiple components and morphology. From the viewpoint of its primary structure, PP has tertiary carbon atoms and is known to be very vulnerable to oxidative degradation under the influence of elevated temperature and sunlight [5-15]. PE and EPR have relatively more oxidative stability because of their primary structures with less tertiary carbon atoms. The oxidative degradation, however, is affected by the morphology in the solid state. The oxidation of semi-crystalline polymer is initially confined to the amorphous phase [9]. Thus, it is thought that degradation occurs in the EPR phase, which mainly forms an amorphous phase. Considering these contradictory tendencies, it is necessary to investigate the degree of degradation in each phase-separated PP and EPR phase.

Direct observation of phase-separation in rubber-modified PP is possible by transmission electron microscopy (TEM) [16,17]. TEM can directly reveal the aggregation of the rubber phase on microtomed surfaces. In order to carry out qualitative measurements simultaneously, TEM, combined with energy dispersive X-ray (EDX) analysis, was used to identify unique observation points. It appears, thus, that TEM observation with EDX analysis is suitable for clarifying the complicated degradation behavior of impact copolymers.

In this study, the localization of oxidative degradation in an impact copolymer was directly observed by TEM/EDX measurement in order to discuss the degradation behavior of the copolymer.

Experimental

Materials

Weight-average molecular weight ($\overline{M}_w$), molecular weight distribution, and ethylene content of PP impact copolymer were 4.5×10^5, 5.6 and 12.8 mol%, respectively.

Measurements

Morphology and elementary analysis of the impact copolymer were examined with a JEOL JEM-2010 transmission electron microscope with the energy dispersive X-ray system (TEM/EDX). The PP pellet was cut with an ultramicrotome at -100 °C. The thin slice was put on a copper grid and examined with the TEM device operating at 200 kV. As the measurement condition of EDX analysis was performed simultaneously, the sample was irradiated with the electron beam of 10 nm ϕ for 30 seconds per one spot.

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 1,2,4-trichlorobenzene. Benzene-d^6 was added as an internal lock, and hexamethyldisiloxane was used as internal chemical shift reference.

Results and discussion

TEM has frequently been used to observe the morphology in heterophasic PP systems [3, 16]. In order to gain a clear micrograph, it is necessary to stain the samples with RuO_4. Staining is not suitable when investigating the localization of oxidative degradation in this study, since it is accompanied by oxidation. Therefore, the TEM observation was attempted without the staining. Figure 1 schematically shows the preparation method of TEM sample.

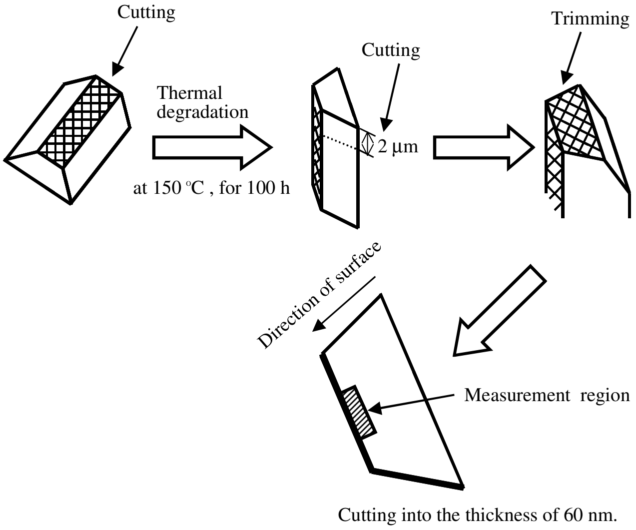

Figure 1. Preparation scheme of a sample for TEM observation

The longitudinal side of the pellet was trimmed and then tightly fixed to a planar plate using epoxy resin. The thermal oxidative degradation of this fixed sample was performed using an oven in air at 150 °C for 100 h. After the degraded sample was cut from the top in the position of 2 µm and trimmed, it was cut into a thickness of 60 nm. As shown in the figure, the degraded sample could be measured by TEM/EDX system in the range of the surface to an inner region using this preparation method.

Figure 2 shows the TEM image of a degraded PP impact copolymer. The arrow indicates the EPR phase (see Figure 2(a)). Although the interface of the EPR phase on the PP matrix is not very clear, the EPR phase seems to disperse in a form like the branch of a river. This EPR fraction was extracted by xylene solvent at 30 °C, and its thermal properties were examined with a differential scanning calorimeter (DSC) (METTLER DSC 820), suggesting that the EPR phase is amorphous.

The oxygen line analysis was simultaneously carried out with the EDX analyzer. Here the scan was performed toward the surface, passing through the areas marked with Roman numerals in Figure 2(b). The result of the analysis is shown in Figure 3.

The degree of oxidation is increasing toward the surface at a depth of less than 0.5 µm (between the X and XI spots). Considering the oxygen diffusion, this tendency is reasonable. It appears, however, that the degree of oxidation is nearly independent of depth over 0.5 µm. The degree of oxidation declines extremely at the II and IX spots, corresponding to the EPR phases. This phenomenon can not account for the oxygen

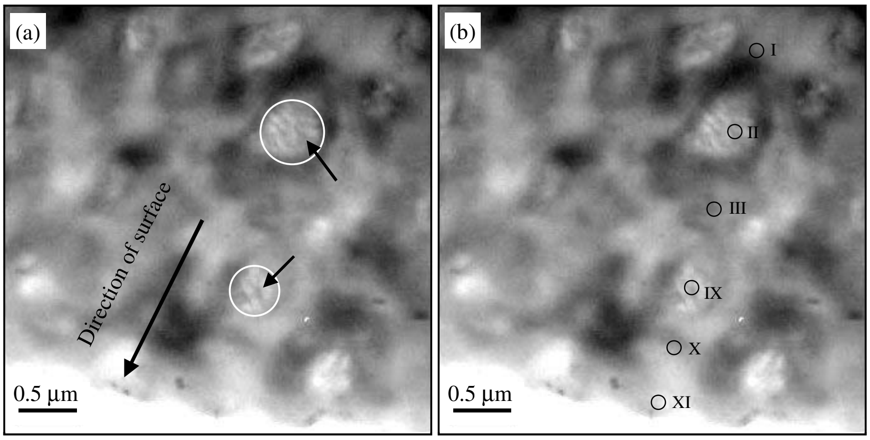

Figure 2. TEM image of degraded PP impact copolymer

diffusibility, since the EPR phase consists of an amorphous polymer whose diffusibility is superior to that of the semi crystalline PP matrix [17]. Therefore, the higher oxidation resistance of the EPR phase must be ascribed to a unique primary structure.

As shown in Table I, the EPR fraction is mainly composed of ethylene-propylene sequences, and its length of pure propylene sequence is found to be very short.

The degradation of the PP is believed to propagate by a free radical chain reaction [14]. The formation of an alkyl radical by the dissociation of the C-H bond occurs first, and the reaction of this alkyl radical with oxygen leads to the scission of the polymer chain. It is well known that 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. The smaller degree of oxidation in the EPR phase is ascribed to the lower propylene content, regardless of the higher oxygen diffusibility.

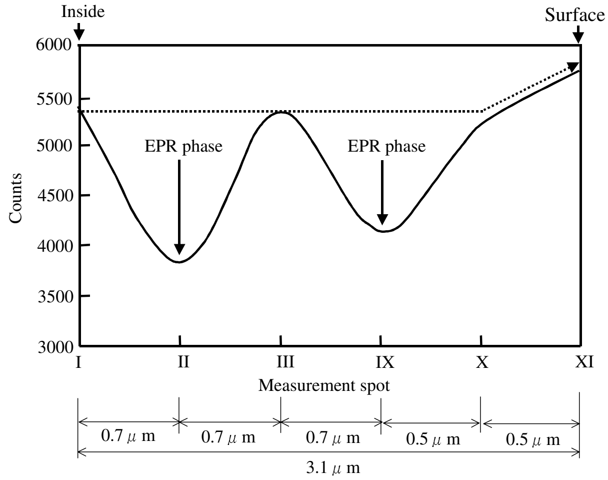

Figure 3. Oxygen line analysis of degraded PP impact copolymer by EDX

Table 1. Sequence distribution of EPR fraction

Triad sequece /mol% *					
EEE	EEP	PEP	EPE	PPE	PPP
17.3	23.0	9.4	12.7	22.4	15.2

*Determined by ^{13}C-NMR. E : Ethylene unit. P : Propylene unit.

Conclusions

The thermal oxidative degradation behavior of a PP impact copolymer has been studied by direct observation using TEM/EDX. Oxygen line analysis was successfully used to find that the degradation behavior of the PP impact copolymer was heterogeneous. The oxidation resistance of the EPR phase was found to be higher than that of the PP matrix.

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