Chain Entanglement of Polyester Film from Environmental Degradation

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In the present paper we deal with the chain entanglement changing of polymer films by the environmental degradation. Test samples were optical polyester (O-PET) films which substituted 9.9-bis-(4-(2-hydroxyethoy) phenyl)fluorine for an ethylene glycol unit in a conventional PET structure. This amorphous O-PET film was degraded by accelerated exposure test or UV irradiation. It was found that ketone and ether peaks of IR spectra increased and the molecular weight decreased slightly. Tensile tests resulted in an increase in Young's modulus and a decrease in the yield strain. Increasing of the molecular entanglement density was saturated with the accelerated exposure test over 5 hours. It was almost the same saturated value as that of UV irradiation. It was considered that environmental degradation of O-PET film increased the molecular entanglement density as the major effect from UV irradiation. Molecular entanglement density was measured for re-molded O-PET films after the degradation process to cancel out the previous high order structure. The molecular entanglement density of original O-PET film and the degraded O-PET film were almost the same value after the re-molding. Environmental degradations of O-PET are responsible for the damage of chemical structure and the high order structure.

Key words: Entanglement molecular weight, Weather meter, UV irradiation, Mechanical properties, Recycle

1. INTRODUCTION

One of the major problems of polymer recycle process is unavoidable physical and chemical degradations of recycled polymer materials, causing of the lack of the economical value. The lower molecular weight, the oxidation and the other chemical changing were observed in any case. The authors have provided some explanations about the crazing process in various polymers including regenerated polymers. The craze composite films exhibited optical, electrical and gas permeable functional polymers[1-4]. Craze generation in regenerated PET film was different from the original PET film. The mechanical deterioration of a degraded polymer was too high as the result from the chemical degradation. And authors proposed two degradations; one is the degradation of high order structures, and the other is the miscibility that postulats the existence of immiscible molecule which would be generated in the recycle process. We discussed the miscibility of regenerated polyester in our previous report[5, 6]. The present report is concerned with the molecular entanglement of polyester films after environmental degradations.

2. EXPERIMETAL

Amorphous and optical polyester (O-PET) which

consisted of terephthalate and ethylene glycol and 9,9-bis-(4-(2-hydroxyethoxy) phenyl)fluorene (BHEPF) was used[7](Fig. 1). Solvent cast films of O-PET were degraded by accelerated exposure test of weather meter (Suga test instruments WEL-SUN-HC, 63°C. 50% R.H., Rain: 18min/120min, Exposure times: 1～50 hours) or UV irradiation (Iuchi SLUV-8, 20 °C , 65%R.H, Irradiation time: 18 ～ 63 hours). Entanglement molecular weight (M_e) was estimated by an original tension balanced method for dynamic mechanical analysis (TA Instruments DMA2980). Average molecular weight by GPC, mechanical properties by a

Fig. 1. Chemical structure of O-PET (X: 40%, Y: 60%).
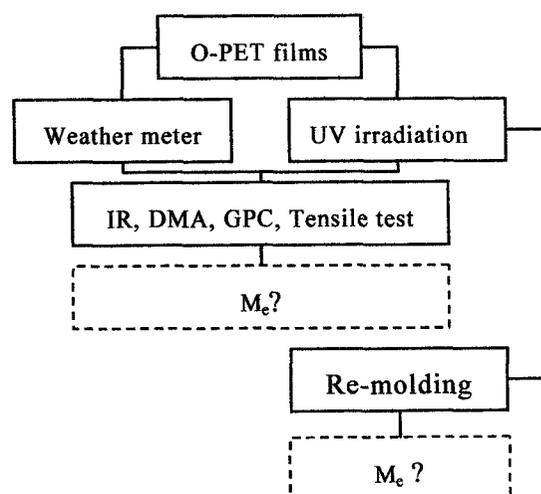
Fig. 2. Diagram of experimental degradation process and molecular entanglement (Me) estimation.

simple tensile test and chemical degradation by IR analysis for O-PET films were evaluated. This experimental diagram was shown in Fig. 2. A re-molding process is discussed later.

3. RESULTS AND DISCUSSION

3.1 Chemical degradation

Figure 3 shows molecular weight of O-PET film after accelerated exposure and UV irradiation tests. Molecular weight decreased with the increasing of degradation times at first and saturated to the constant
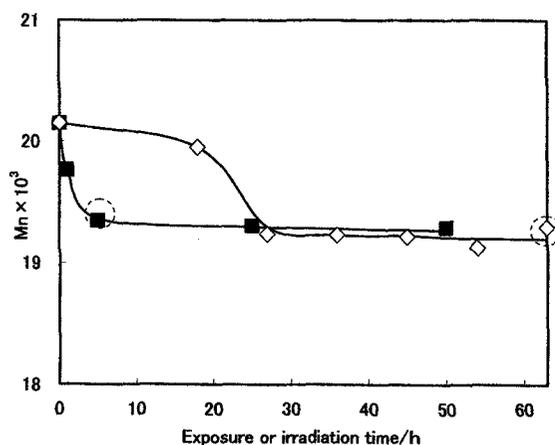
Fig. 3. Number - average molecular weight of degraded O-PET by accelerated exposure test (■) or UV irradiation (◇). The UV irradiation time of 63 hours corresponds to the exposure time of 5 hours for UV irradiation energy.

value for accelerated exposure and UV irradiation tests. However, molecular distribution curve of the O-PET was almost the same as that of the exposed or irradiated O-PET. The UV irradiation time of 63 hours corresponds to the exposure time of 5 hours for UV irradiation energy. Those points were marked by dotted circles. The result of the UV irradiation test is corresponding to the primary process of the accelerated

exposure test. In this case, major driving force of the degradation was the UV irradiation and the degradation area would be limited in the film surface which absorbed UV ray. However, the transition of lower molecular weight would be negligible for the mechanical properties.

Figure 4 shows IR spectra of O-PET films after accelerated exposure or UV irradiation. Differential spectrophotometry was applied to this measurement, because the distinction between the original O-PET and the degraded O-PET was difficult to observe. The absorbencies of ketone and ether were observed at $1720cm^{-1}$, $1250\ cm^{-1}$, $1100\ cm^{-1}$. These were increased with the increase of the exposure or irradiation time. These typical results of the degradation in the air should not affect the mechanical properties except on the film surface.

3.2 Degradation of mechanical properties

Mechanical properties after the degradation are shown in Fig. 5 and 6. Yield strain curve of a degraded O-PET film was similar to the decreasing curve of average molecular weight (Fig. 3). Mechanical properties were ca. 25% reduction in the yield strain and almost constant value in the yield stress. Young's modulus increased with an increasing UV irradiation time at a turning point of 20 hours as well as the yield strain. Characteristic of irradiated O-PET film changed to brittle films. Reductions in the mechanical properties couldn't be ignored and molecular weight and chemical structure changes would not be enough to decrease the mechanical properties. Yield stress should increase with an increasing specific factor (C_∞) corresponding to the molecular rigidity. It might suggest that the mechanical changes were not responsible for the C_∞ as a result of the molecular structure. We speculated that high order structure was changed with UV irradiation.

3.3 Entanglement molecular weight

Molecular entanglement is estimated under the melting state by viscoelastic analysis, conventionally. However, a polymer film will possess the specific molecular entanglement as the result from the history of a thermodynamically process or a molding method.
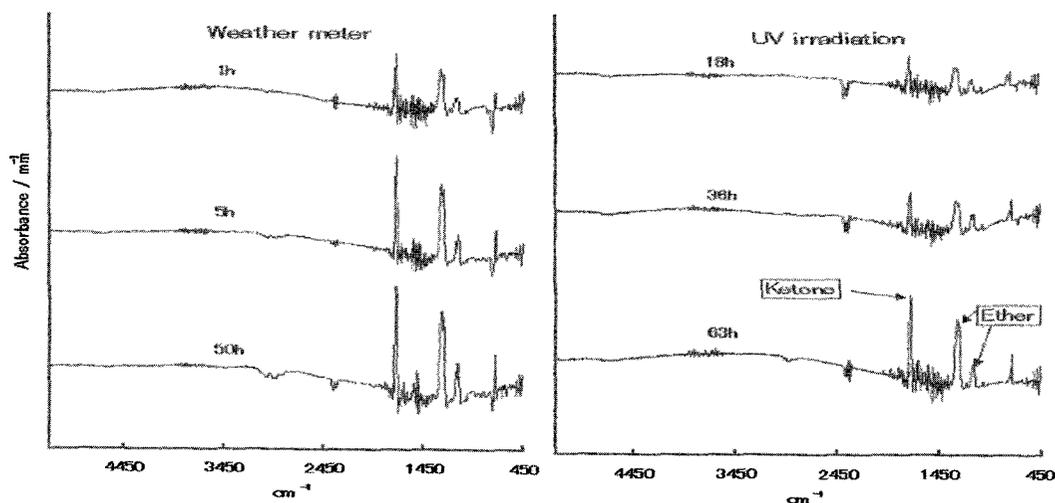
Fig. 4. Accelerated exposure or UV irradiation times dependence of differential infrared spectra of O-PET films.
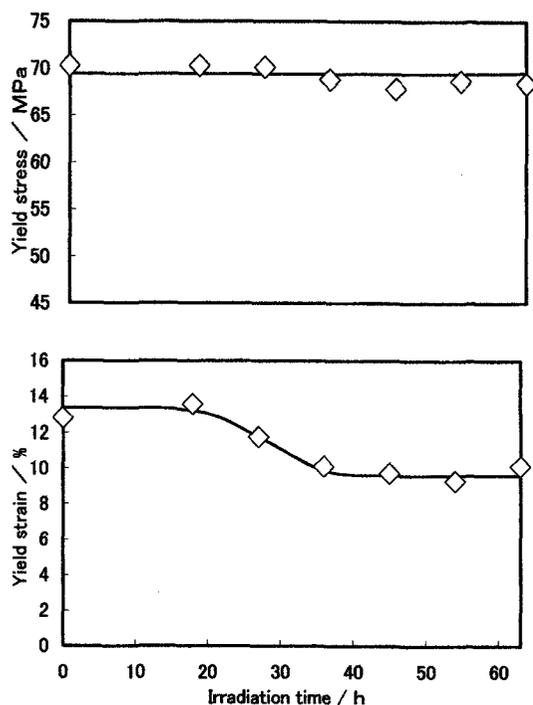
Fig. 5. UV irradiation time dependence of yield stress and strain.
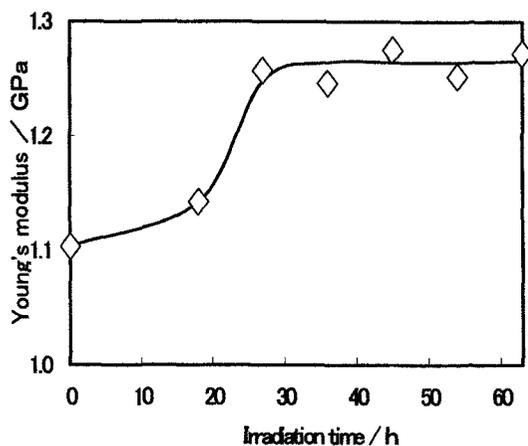
Fig. 6. UV irradiation time dependence of Young's modulus.

It must be measured under the solid state or the melting state which is held the molecular entanglement. In this paper, a molecular entanglement of a solid state is estimated from a plateau modulus which is analyzed under the condition of the gage length holding. The molecular entanglement of the polymer film could be kept at the temperature on the state of the plateau modulus, however, low viscoelastic polymers are not suitable for this method. The entanglement molecular weight (M_e) is given by the following equation (1).

$$M_e = \rho\, RT/G^0_n \qquad (1)$$

where ρ is the density, R is the gas constant, T is the temperature and G^0_n is the plateau modulus. M_e is molecular weight of an entanglement strand between two entanglement junctions in the molecular chain, adjacently. A higher M_e is corresponding to the lower molecular entanglement density.
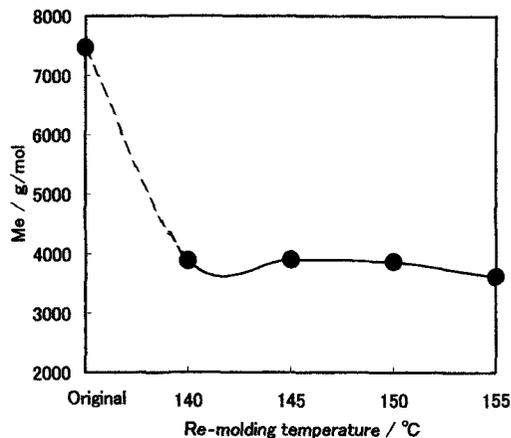
Fig.7. Relationship between entanglement molecular weight (M_e) and re-molding temperature of O-PET films by a rolling press.

Figure 7 shows an annealing temperature dependence of M_e. The sample film was annealed by a rolling process. M_e of the original O-PET film was varied with the increasing processing temperature and it was altered to the constant value of ca. 4000 g/mol at the annealing temperature of 140℃. It would be suggested that the molecular entanglement of the previous high order structure is canceled by the annealing process with a mechanical shearing. M_e of the molded film by a rolling is different from the film by a solvent cast method, because the molecular entanglement depended on the molding process. M_e of the cast film varied with a concentration and temperature in a case of a casting. Molding history should be controlled to estimate M_e of the solid state polymer.

3.4 .Entanglement molecular weight of degraded O-PET films

M_e of degraded O-PET films was shown in Fig. 8. These curves, similar to the curve of average molecular weight, decreased to ca. 4800 g/mol (accelerated exposure test) or ca. 5200 g/mol (UV irradiation) with

Table I

M_e of re-molded O-PET films after the accelerated exposure time of 5 hours.

Re-molding temperature /℃	M_e /g/mol
As exposure	5160
140	4020
150	3970

increasing exposure or irradiation time. This decreasing M_e could be responsible for the high order structure changing by the degradation. Chemical degradation and the decreasing average molecular weight should be minor causes.

Table I shows M_e of re-molded degradation films after the annealing with a cancellation of the history. M_e of re-molded degradation films were the same as that of re-molded original film. It was considered that lower M_e of degraded O-PET film was resulted from the high order structural degradation. We presume that reformed high order structure of O-PET film was localized at the low density region between molecular entanglements, not but at the high density region around molecular
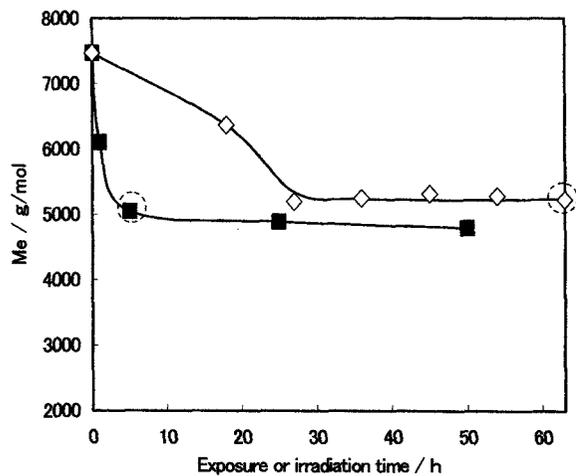
Fig.8. Accelerated exposure (■) and UV irradiation (◇) time dependence of entanglement molecular weight. The UV irradiation time of 63 hours corresponds to the exposure time of 5 hours for the UV irradiation energy.

entanglements. Degradation of M_e is similar to an aging treatment and it is important for the degraded polymer properties.

4. CONCLUSIONS

Accelerated exposure and UV irradiation caused the degradation of high order structure which was the increases in the molecular entanglement. The degradation of M_e was mainly resulted from UV irradiation. Environmental deterioration should be discussed carefully to estimate the degradation of the sample as exposure or the molded sample from the regenerated polymer. The re-molding process in this paper, which was the same as a recycle process except the factor of contaminations, was schematically shown in Fig. 9. The degradation of high order structure will be recovered by re-molding process, however, recycled O-PET should be the blend of O-PET and chemical degraded O-PET.

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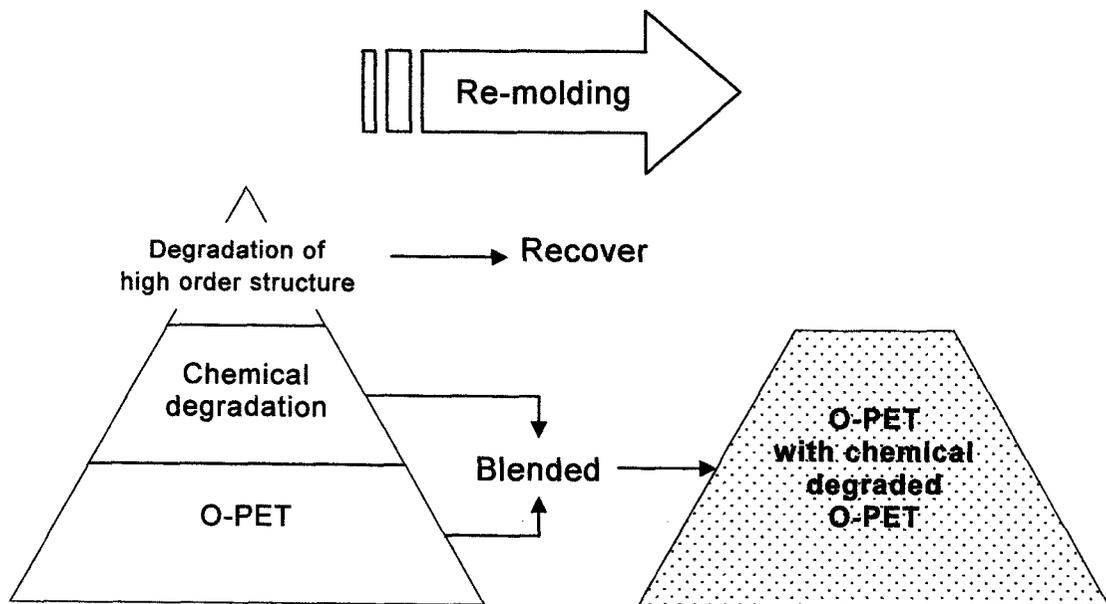
Fig. 9. Schematic diagram of re-molding process for environmental degraded O-PET.