Comparison between Compressive Properties of Polypropylene/Degra-novon Blends after Outdoor Weathering Tests and Accelerated Weathering Tests

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Abstract
The static and dynamic compressive properties of polypropylene/Degra-novon polymer blends after outdoor (natural) weathering and accelerated weathering tests were measured using a universal testing machine and a split Hopkinson pressure bar. Degra-novon in polyolefins, such as polypropylene and polyethylene, accelerates the environmental degradation process by providing a directly digestible component, facilitating oxidation and/or photo-degradation of the polymer chains. The relationship between the mechanical properties, differential scanning calorimetry results, and Fourier transform-infrared spectroscopy data were also examined.

Key words
Weatherability, Biodegradable Polymer, Oxidative Decomposition, Dynamic Properties, Split Hopkinson Pressure Bar Method

1. Introduction
Increasing use of plastic products worldwide has contributed to the ongoing destruction of the global environment. Therefore, investigations have been conducted on biodegradable plastics that can be decomposed by microorganisms into water, carbon dioxide, and biomass [1]. However, compared with many engineering plastics, biodegradable plastics have several problems that prevent their widespread applications, such as brittleness, difficult workability, and high material and processing costs. Lowering material costs is particularly important if biodegradable plastics are replaced by widely used, conventional engineering plastics.

Many attempts have been made to reduce material costs through the addition of granular starch, which is one of the most inexpensive sustainable polymers, to expensive bioplastics such as poly(lactic acid) [2-8]. There have also been attempts to create low-cost biodegradable plastics by adding oxidative decomposition auxiliary agents, i.e., Degra-novon®, to petroleum-derived, inexpensive engineering plastics such as polypropylene [9]. Previously, we examined the effect of the addition of Degra-novon on the mechanical properties of polymers after accelerated weathering and potential usage (useful lifespan) tests [10].

In this study, the compressive properties of polypropylene/Degra-novon polymer blends after outdoor weathering and accelerated weathering tests were compared. The relationships between the compressive properties, differential scanning calorimetry (DSC) results, and Fourier transform-infrared (FT-IR) spectroscopy data are also discussed.

2. Materials
Polypropylene/Degra-novon polymer blends were prepared using polypropylene pellets (Sumitomo Chemical Co., Ltd; Noblen AY564 [11]) and Degra-novon pellets (NOVON JAPAN, Inc.; ECO-3 EPP-N [12]). The recommended mixing ratio for polypropylene and Degra-novon is 80/20 [12]. To examine the changes in the decomposition rate and compressive properties as a function of the mixing rate of Degra-novon, specimens with varying mixing ratios (mass fraction) of polypropylene and Degra-novon (80/20, 60/40, and 0/100) were prepared. The polymer blends were produced using a twin-screw extruder (TECHNOVEL; φ: 20 mm, L/D: 30) at 180°C. The screw speed was 300 rpm, and the feed rate was 100 g/min. After melt mixing, the strands prepared with the twin-screw extruder were cooled rapidly, pelletized, and then dried. Next, 10-mm-thick plates were formed using a hot press at 180°C and 5 MPa for 30 min.

![Fig. 1 Spectral power distribution of the sunshine carbon arc lamp and sunlight [14]](image-url)

3. Test Specimens and Experimental Setup
Dynamic compressive test specimens with a diameter of 12 mm were used. The specimen thickness was 4.8 mm in order to be able to achieve dynamic stress equilibrium within the specimens using our equipment [13]. In the quasi-static tests, which were based on ASTM D695-02a, specimens with a diameter of 8 mm and a thickness of 12 mm were used.

An accelerated weathering test was conducted using a sunshine weather meter (Suga Test Instruments Co., Ltd.; S80, light source: sunshine carbon arc lamp). Fig. 1 shows the spectral power distributions of the sunshine carbon arc...
lamp and sunlight [14]. On the basis of the Japanese Industrial Standard (JIS) B7753, the black panel temperature was 63°C and the duration of the water spray was 18 min per every 120 min. Because the continuous lighting time was 75 h/cycle, specimens were prepared with exposure durations of 275, 300, and 500 h. In addition, specimens were also subjected to outdoor (natural) weathering test on an outdoor balcony or veranda (not accelerated) for 3 or 6 months. Specimens were exposed to the sunlight, as well as the rain. The weight of all the specimens did not change after the weathering tests.

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Quasi-static compressive tests were conducted at a strain rate of $10^{-3}$ s$^{-1}$ (crosshead speed: 1.2 mm/min) using a universal testing machine (A&K Co., Ltd.; RTM-500). At high strain rates of 900–1000 s$^{-1}$, the compressive properties of the specimens were examined using the split Hopkinson pressure bar method, as shown in Fig. 2. The input and output bars were made of an aluminum alloy (2024-T4), and each bar had a diameter of 28 mm and respective lengths of 1900 mm and 1300 mm. The material constants used in the calculations are listed in Table 1. Strain gages were placed on both sides of the input and output bars at distances of 950 mm and 300 mm from the specimens, respectively. The stress and strain on the specimens were calculated from the strain on the bars using Eq. (1) and (2) [15, 16].

$$\sigma(t) = \frac{A_E}{A_S} \varepsilon_f(t)$$

$$\varepsilon(t) = \frac{c_3}{L} \int_0^t \left[ \varepsilon_f(t) - \varepsilon_R(t) - \varepsilon_I(t) \right] dt$$

Brass strikers with a diameter of 20 mm and length of 310 mm were used. The area near the specimens was maintained at a temperature of 23 ± 2°C using silicone rubber heaters (Heatwell®, Kawai Electric Heater Co., Ltd.). Because the strain rate changed slightly during loading, the average value of the strain rate–strain curve was used as the strain rate [17].

4. Results and Discussion

4.1 Static compressive tests

The nominal stress–strain curves of specimens after accelerated weathering tests at a low strain rate are shown in Fig. 3. The effect of exposure duration on the stress–strain curves did not show a clear trend. However, the Young’s moduli of the specimens after the accelerated weathering tests were clearly larger than those before the tests.

The effect of exposure duration on the yield stress and Young’s modulus, including the results of statistical significance tests are shown in Fig. 4. Here, when the peak of stress–strain curves was clearly observed, yield stress was defined as the peak stress immediately after the elastic limit. Instead, when the peak of stress–strain curves was not observed, the yield stress was determined by the intersection of two asymptotic lines of elastic region and plastic region. Student’s t-test was used as the statistical hypothesis test. P<0.05 in the figure means the confidence interval of 95% (statistical significant of 5% significance level) and P<0.01 in the figure means the confidence interval of 99% (statistical significant of 1% significance level). If no statistical significance test results are provided,
no significant difference was obtained. It can be seen in the figure that as the exposure duration increased, the yield stress and Young’s modulus initially increased and then slightly decreased. This behavior is particularly notable for the yield stress of the polypropylene/Degra-novon = 60/40 blend.

The nominal stress–strain curves of the specimens after the outdoor weathering tests at a low strain rate are presented in Fig. 5. No significant effect of the exposure duration on the stress–strain curves was observed. However, the effect of exposure duration on the yield stress and Young’s modulus, including results of statistical significance tests can be seen in Fig. 6. As the exposure duration increased, the yield stress and Young’s modulus increased, except for the yield stress of the polypropylene/Degra-novon = 80/20 blend.

![Fig. 4 Effect of exposure duration on the yield stress and Young’s modulus of specimens after accelerated weathering](image1)

![Fig. 5 Nominal stress–strain curves of specimens after outdoor weathering tests at a low strain rate](image2)

![Fig. 6 Effect of exposure duration on the yield stress and Young’s modulus of specimens after outdoor weathering](image3)
Fig. 7 Nominal stress–strain curves of specimens after accelerated weathering tests at a high strain rate

4.2 Dynamic compressive tests

Nominal stress–strain curves for the specimens after accelerated weathering tests at a high strain rate are presented in Fig. 7. The effect of exposure duration on the yield stress, including results of statistical significance tests are shown in Fig. 8. Here, the yield stresses were determined by the same method as the static compressive tests. Due to the principle of the split Hopkinson pressure bar method, Young’s moduli of dynamic compressive tests were not discussed. For the polypropylene/Degra-novon = 80/20 blend, no clear trend was observed with respect to the effect of exposure duration on the stress–strain curves and yield stress. However, for the polypropylene/Degra-novon = 60/40 blend, the stress–strain curves after 300 h of exposure showed a gradual decline after reaching a maximum, and many cracks on the surfaces of the specimens were eventually observed. For the polypropylene/Degra-novon = 0/100 specimens, the stress–strain curves after 300 and 500 h of exposure showed a steep decline after reaching the maximum stress, and the yield stress of these specimens also clearly decreased. In fact, these specimens broke into small pieces, as shown in Fig. 9.

The nominal stress–nominal strain curves for specimens after outdoor weathering tests at a high strain rate are presented in Fig. 10. Once again, no clear trend was observed in the stress–strain curves for the polypropylene/Degra-novon = 80/20 blend. However, for the polypropylene/Degra-novon = 60/40 blend, the stress–strain curves after 6 months of exposure showed a slight decline once the maximum stress was reached. This tendency is similar to that for the stress–strain curves of the specimens subjected to 300 h of accelerated weathering. For the polypropylene/Degra-novon = 0/100 specimens, the stress–strain curves after 6 months of exposure once again showed a clear decline after reaching a maximum stress, and broke into small pieces (Fig. 9). This tendency is also the same as that seen for the stress–strain curves of the specimens subjected to 300 h of accelerated weathering. Therefore, it can be concluded that 300 h of accelerated weathering was nearly equivalent to 6 months of outdoor weathering on the balcony.

Fig. 8 Effect of exposure duration on the yield stress of specimens after accelerated weathering tests

Fig. 9 Photographs of the polypropylene/Degra-novon = 0/100 specimens after dynamic compressive tests

(a) 300 h  (b) 500 h  (c) 6 months

The effect of exposure duration on the yield stress, including results of statistical significance tests is shown in Fig. 11. No significant difference was observed for the polypropylene/Degra-novon = 60/40 blend and the 0/100 specimens. However, for the polypropylene/Degra-novon = 80/20 blend, a decrease in the yield stress was observed after exposure for 3 months and 6 months.
4.3 Analyses using differential scanning calorimetry and Fourier transform-infrared spectrometry

Because the yield stress and Young’s modulus of the 60/40 blend were changed after exposure at a low strain rate, these specimens were analyzed using DSC (Rigaku Corporation; Thermo Plus2/DSC 8230). The rate of temperature increase was 5°C/min. Figs. 12 and 13 show the heat flow curves, and Table 2 lists the melting points, recrystallization temperatures, and heats of fusion. The melting points and recrystallization temperatures for the 60/40 blend were nearly the same, regardless of the exposure duration. The melting point peaks after accelerated weathering for 275 h and outdoor weathering for 6 months were broad. Based on these results, it appears that the molecular structure was changed during the weathering tests. In addition, the specimens after accelerated weathering for 500 h showed two melting point peaks, suggesting the presence of both a non-eutectic polypropylene and a eutectic composition of polypropylene and Degra-novon. The eutectic composition with Degra-novon decomposed first, after which the peak for non-eutectic polypropylene became prominent, as indicated by the arrow in Fig. 12.

![Fig. 12 DSC results for specimens after accelerated weathering tests (Polypropylene/Degra-novon = 60/40)](image)

![Fig. 13 DSC results for specimens after outdoor weathering tests (Polypropylene/Degra-novon = 60/40)](image)

<table>
<thead>
<tr>
<th>Exposure duration</th>
<th>Melting point</th>
<th>Recrystallization temperature</th>
<th>Heat of fusion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before weathering test</td>
<td>164.9°C</td>
<td>126.3°C</td>
<td>92.2 J/g</td>
</tr>
<tr>
<td>275 h</td>
<td>166.0°C</td>
<td>124.1°C</td>
<td>61.7 J/g</td>
</tr>
<tr>
<td>300 h</td>
<td>163.0°C</td>
<td>123.7°C</td>
<td>69.2 J/g</td>
</tr>
<tr>
<td>500 h</td>
<td>162.1°C (157.9°C)</td>
<td>123.4°C</td>
<td>75.9 J/g</td>
</tr>
<tr>
<td>3 months</td>
<td>165.2°C</td>
<td>123.4°C</td>
<td>72.6 J/g</td>
</tr>
<tr>
<td>6 months</td>
<td>165.1°C</td>
<td>124.3°C</td>
<td>73.3 J/g</td>
</tr>
</tbody>
</table>

**Table 2 Melting points, recrystallization temperatures, and heats of fusion**
Finally, the molecular structure (functional group) of the 60/40 specimens was analyzed using an FT-IR spectrometer (JASCO Corporation; FT/IR-6300). As denoted by the arrows in Fig. 14, exposure slightly affected the peak at 1540–1600 cm$^{-1}$. This peak represents the stretching vibrations of the alkene groups [18, 19]. Based on these results, it can be concluded that the bonds indicated by the arrows in Fig. 15 were broken, and the intermediates reacted with oxygen. Thus, oxidative decomposition occurred.

4. Accelerated weathering for 300 h is equivalent to 6 months of outdoor weathering on a balcony. In the polypropylene/Degra-novon, the degradation of outdoor weathering can be roughly predicted by accelerated weathering using this relationship, even though the conditions of temperature and rain exposure were different.

Further experiments about the effect of each experimental condition (temperature, light exposure, rain exposure and humidity) are required.

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References

5. Conclusions
The compressive properties of polypropylene/Degra-novon polymer blends after outdoor weathering and accelerated weathering tests have been examined.

1. At high strain rates, there was a sudden decrease in the stress after 300 and 500 h of accelerated weathering and 6 months of natural exposure for the polypropylene/Degra-novon = 0/100 specimens and 500 h of natural exposure for the polypropylene/Degra-novon = 60/40 blend. These specimens showed brittle fracture.
2. At low strain rates, the maximum stress and Young’s modulus initially increased with exposure duration and then clearly decreased.
3. From the chemical analyses, it can be concluded that oxidative decomposition of the specimens occurred during the weathering tests.


