Abstract
Thermoplastic resin is often used to form molded material without post-curing or aging treatments. Creep and physical aging occur simultaneously in such material, and these effects are dependent on the time and temperature. The effects of physical aging after molding are also dependent on the thermal history of the material, and this has a large influence on the mechanical properties, especially creep. It is therefore necessary to control the progress of physical aging when designing materials. In this study, we examined the creep deformation of polycarbonate to determine the thermal history as the effect of physical aging on the creep behavior. The physical aging effects had a distinct time and temperature dependency that also affected the density of the material. Our findings showed that it was possible to calculate the effect of the thermal history on physical aging using only the relationship between physical aging and density.

Key words: Polycarbonate, Creep, Physical Aging, Density, Thermal History, Thermoplastic

1. Introduction
Creep behavior can be described in terms of viscoelasticity, which greatly influences the reliability of structures, and it is therefore an important factor to control when designing material. Physical aging is a factor that affects creep behavior, and in practice, physical aging occurs in materials that have not been heat treated after molding; such molded materials are used as end products. It is therefore necessary to estimate the creep deformation of molded materials under the influence of physical aging to determine the reliability of structures and improve their design.

When an amorphous polymer is cooled from a rubbery to a glassy state, it ends up in a metastable condition. The process by which the glass contracts to the equilibrium line is known as physical aging [1–3], which results in a stiffening of the solid and is distinct from chemical aging at high temperatures due to molecular degradation. Physical aging occurs in all types of amorphous polymers and their composites [4, 5].

Struik conducted considerable research on the time dependency of physical aging, especially for amorphous polymers and their composites [6]. Cangialosi et al. examined physical aging by measuring the change of the free volume of polycarbonate using a positron annihilation lifetime spectroscopy and
concluded that this change was dependent on the pre-aging time and temperature [7]. Knauss and Emri studied the nonlinear thermo-viscoelastic constitution during physical aging on the basis of the free volume [8] and Miyano et al. examined the effect of physical aging in thermostetting plastics [9]. Other researchers have also studied physical aging behavior [10–16].

Previous studies have investigated the effect of physical aging on creep behavior in PPE composites and suggested that the activation energy in creep tests decreases as the pre-aging treatment time increases [17]. A time–physical aging superposition has been established for the creep behavior of a stainless steel–fiber/PPE composite. The creep behavior during the progress of physical aging can be estimated using this superposition principle based on time–temperature viscoelastic theory [18–19]. However, few attempts have sought to estimate the influence of several factors that are known to affect creep behavior, including the thermal history before the creep test. The purpose of this study was to determine the effect of physical aging on the density and creep behavior of material to permit creep behavior estimates that consider both the time and temperature of the heat treatment when determining the progress of physical aging.

2. Materials and Experimental Procedure

Iupilon S-2000 polycarbonate (PC) manufactured by Mitsubishi Engineering Plastic Company (Tokyo, Japan) was used as test material. The glass transition temperature of the PC was 148°C. To achieve the same physical aging effects, all material was heated to 160°C (i.e., \(T_g + 12°C\)), held at this temperature for 10 min, and then quenched in air [1]. At this point, the material was referred to as “molded.” To determine the effect of physical aging, some heat-treated material was heated further after the quenching. The specimens were rectangular and had a width of 10 mm, a length of 70 mm, and a height of 3 mm.

The creep tests were performed using the three-point bending test method with a creep test machine (Fine Oven DH42; Yamato, Tokyo, Japan) that could control the temperature between room temperature and 300°C in an air atmosphere. The applied loads were 10% of the bending strength (8.3 MPa), the test temperature ranged from 100 to 130°C, and the length of the span was 40 mm. Creep deformation was evaluated according to viscoelastic theory using the creep compliance function \(D(t)\). This value is based on the linear viscoelastic equation for creep strain as follows [20]:

\[
\varepsilon(t) = \int_{-\infty}^{t} D_c(t - \tau, T) \frac{d\sigma}{d\tau} d\tau
\]

A densimetry test was performed using the water substitution method with an AX-120 analytical balance (Shimadzu, Kyoto, Japan) on specimens composed of polycarbonate resin heated under various pre-aging conditions in air. The accuracy of measurement is 0.1mg, precise measurements were obtained.

3. Pre-aging Treatment

For the pre-aging treatment, the molded materials were held at a predetermined temperature for a set period of time and then quenched in air. This treatment ensured a degree of aging before the creep test was performed. The immersion times (pre-aging times \(t_a\)) were 0 (the same as the molded material), 100, 300, and 1,000 min. The predetermined temperatures (pre-aging temperatures \(T_a\)) were 100, 110, 120, and 130°C. The creep tests were conducted immediately after the physical aging treatment at the pre-aging temperature. The pre-aged material
was heated for 15 min at the test temperature to produce a uniform internal temperature before conducting the creep test. Figure 1 shows a schematic representation of the pre-aging treatment and creep test sequence.

4. Effect of Pre-aging Time on Creep Behavior

The effect of the pre-aging time on the creep behavior of PC was examined in a previous paper [18] and O’connell et al. presented that effect from the tests of the stress relaxation response of PC under torsion deformations [15]; however, more details are presented in this report. Data were obtained for all the pre-aging temperatures, but only the results at 130°C are presented here.

Figure 2(a) shows the creep compliance curves for the four pre-aging time intervals at 130°C. As the pre-aging time increased, the creep compliance curve shifted downward and toward longer times. The large shift toward longer times indicates that the physical aging behavior restrained the creep. The downward shift was due to an increase in the bending modulus caused by an increase in density, but this was small and therefore considered negligible. The creep compliance curve of the molded material (i.e., 0 min) was used as the reference, and the other compliance curves were shifted horizontally to create a master curve that included

Fig. 1 Schematic diagram of the (a) heating, (b) holding, (c) quenching, and (d) pre-aging treatment processes, and (e) the creep test

Fig. 2 (a) PC creep compliance curves with various pre-aging times heated to and tested at 130°C; (b) master curve for pre-aging times tested at 130°C (Reference heat treatment time $t_{a0} = 0$ min)
the effect of the pre-aging time on the creep compliance. The master curve for the pre-aging time was obtained by replacing the real time $t$ for each shifted curve by the physical time $t'$ at the reference pre-aging time $0$ min. The master curve for the creep compliance, including the aging effect, is shown in Fig. 2(b). This curve is extremely smooth, implying that the fundamental mechanism of the creep deformation was the same for each pre-aging time. The shift factor obtained by creating the master curve for the aged PC was referred to as the aging time shift factor $\mu_{Tt'}$, and is shown in Fig. 3. This figure plots the aging time shift factor $\mu_{Tt'}$ for all test temperatures versus the pre-aging time on a logarithmic scale. The results confirmed the time–pre-aging superposition principle because the shift factors collapsed onto one line. As the test temperature increased, the slope of the aging time shift factor decreased. Because of this, the progress of physical aging and the creep behavior was proportional to temperature and time. The aging time shift factor relationship with temperature can be described by

$$\mu_{Tt'} = (a - b \times T) \times t_a - (c - d \times T)$$

(2)

where $a$, $b$, $c$, and $d$ are constants and $T$ is the test temperature. The progress of physical aging varied linearly with the pre-aging time. This relationship can be used to calculate the effect of the pre-aging time on the physical aging.

5. Effect of Pre-aging Temperature on Creep Behavior

In the previous section, the effect of the pre-aging time on the creep behavior was analyzed, making it possible to estimate the long-term behavior of PC including the effect of physical aging due to the pre-aging time. We also investigated the effect of the pre-aging temperature using pre-aged PC.

At a predetermined temperature, the material was pre-aged using holding times of 0, 100, 300, and 1,000 min. A creep test was then performed at a predetermined temperature. The results of PC at $130^\circ C$ after pre-aging for 1,000 min at various temperatures are shown in Fig. 4(a). As the pre-aging temperature increased, the creep compliance curve shifted downward and toward longer times. The creep compliance curves for the short time intervals had similar shapes. As in the previous section, the large shift toward longer times indicated that the physical aging behavior restrained the creep behavior, while the negligible
downward shift was due to an increase in the bending modulus caused by the increase in density. The creep compliance curve for pre-aging at 100°C was chosen as the reference, and the other compliance curves were shifted horizontally to create a master curve that included the effect of the pre-aging temperature on the creep compliance. This master curve was obtained by replacing the real time \( t \) for each shifted curve by the physical time \( t' \) at the reference pre-aging temperature of 100°C. The master curve for the pre-aging temperature, shown in Fig. 4(b), was extremely smooth, implying that the fundamental mechanism of the creep deformation was the same for each pre-aging temperature. Comparable results were obtained for other test temperatures and pre-aging times.

The shift factor obtained by creating a master curve for the aged PC was referred to as the aging temperature shift factor \( \mu_{RT} \), and is shown in Fig. 5 for a pre-aging time of 1,000 min. This figure plots the aging temperature shift factor for all test temperatures versus the pre-aging temperature. The shift factors of all test temperatures collapsed onto one line, indicating that the physical aging is influenced by the pre-aging temperature, not the test temperature. Figure 6 shows the aging temperature shift factor \( \mu_{RT} \) for all pre-aging times versus the pre-aging

Fig. 4 (a) PC creep compliance curves with various pre-aging temperatures heated for 1000 min and tested at 130°C; (b) master curve for pre-aging temperature heated for 1000 min and tested at 130°C (Reference pre-aging temperature: \( T_{aR} = 100°C \))

Fig. 5 Effect of the test temperature \( T \) and the pre-aging temperature \( T_a \) on the aging temperature shift factor \( \mu_{RT} \) after heat-treating for 1000 min (reference pre-aging temperature \( T_{aR} = 100°C \))

Fig. 6 Aging temperature shift factor \( \mu_{RT} \) with various heat treatment temperatures \( T_a \) (reference pre-aging temperature: \( T_{aR} = 100°C \))
temperature. The slope of the aging temperature shift factor increased with the pre-aging time. The aging temperature shift factor relationship with pre-aging time can be described by

$$\mu_{RT} = (e + f \times t_a) \times T_a$$

(3)

where $e$ and $f$ are constants. The progress of physical aging varied linearly with the pre-aging temperature. This relationship among time, test temperature, and pre-aging temperature can be used to calculate the effect of the pre-aging temperature on physical aging.

6. Effect of Physical Aging on Creep Behavior and Density

Cangialosi et al. studied physical aging using positron annihilation lifetime spectroscopy, which allows direct determination of the free volume of a system. The progress of physical aging in PC has also been studied by measuring the size and number of cavities in the system [7]. The progress of physical aging decreases the amount of free volume in PC, which leads to an increase in density. Therefore, the progress of physical aging is related to the material density [6]. In the present study, a densimetry test was performed to investigate the progress of physical aging. The effect of the pre-aging temperature and time on the density was also determined. The pre-aging temperatures for PC were 100, 110, 120, 130, and 140°C, and the pre-aging times ranged from zero to 1,000 min. Figure 7 shows the densimetry testing results, which demonstrate the temperature and time dependence of the density. The density increased as the pre-aging temperature and time increased. Thus, physical aging progressed as the pre-aging temperature or time increased. It may be possible to control the state of physical aging by controlling the pre-aging temperature and the duration of the treatment.

It is also necessary to consider the case in which both the pre-aging temperature and pre-aging time affect physical aging. Using the aging time shift factor (see Fig. 3) and the aging temperature shift factor (see Fig. 6), we produced a graph of the combined aging shift factor, as shown in Fig. 8. The reference material and testing conditions corresponded to a pre-aging time of 100 min and a pre-aging temperature of 100°C. The aging shift factor increased with the pre-aging time and temperature, as described by,
where $\mu$ is the aging shift factor. This equation can be used to determine an arbitrary thermal history for PC and to control its creep behavior by changing the conditions of the pre-aging treatment.

A similar tendency was obtained when the results of the aging shift factor and the density measurements were compared. Therefore, the relationship between aging shift factor and the reciprocal density was also examined, as shown in Fig. 9. The aging shift factor was proportional to the reciprocal density according to

$$\frac{1}{\rho} = \alpha + \beta \times \mu$$

where $\rho$ is the density, $\mu$ is the aging shift factor, and $\alpha$ and $\beta$ are constants. This expression can be used to calculate an arbitrary thermal history for PC using only density measurements. Using this relationship, we tried to discuss the applicability of Doolittle equation according to [21]

$$\ln \eta = A - \frac{B}{f_V}$$

where $\eta$ is the viscosity function, $f_V$ is the free volume function and $A$ and $B$ are constants. The aging shift factor is shown the effect of retardation time, and its unit is in logarithmic scale. The progress of physical aging is related to the amount of free volume, and the progress of physical aging is related to the material density. As the density increase, the amount of free volume decreases by lateral chain moving from the unstable state to the stable state. And as the amount of free volume decrease, the mobility of molecular chain decrease. It is, therefore, the creep behavior inhibited by increasing density and physical aging. Therefore, it has been clarified that the relationship between the density and the aging shift factor follows Doolittle equation.

Additional creep tests were performed to confirm whether materials with different heat treatments but the same amount of physical aging have the same creep behavior and density. The materials were heat-treated at 130°C for 100 min, at 125°C for 232 min, and at 120°C for 540 min, conditions that give the same
amount of physical aging according to Eq. (4). The creep tests were performed at 130°C. The material densities were almost the same, and all data collapsed onto one curve, as shown in Fig. 10. In these graphs, the difference in each graph is less than 3%. Therefore, each set of heat treatment conditions produced almost the same creep behavior. The individual pre-aging temperatures and times did not affect the results; instead, the creep behavior was dependent on the aging state.

7. Conclusions

We examined the effect of physical aging on the density of PC. Density measurements demonstrated that the physical aging depended on the pre-aging time and temperature. Moreover, the density of the material increased with the pre-aging time and temperature. The effect of physical aging on the creep behavior was also examined by generating master curves of the pre-aging time and temperature. Aging time and temperature shift factors were obtained from the master curves, along with equations for calculating the shift factors. A graph of the aging shift factor, which included the aging time and temperature shift factors, was produced to confirm the relationship between the pre-aging time and temperature. The aging shift factor was proportional to the reciprocal material density, and the equation describing this relationship was determined, and it has been clarified that the relationship follows the Doolittle equation. Therefore, it was possible to calculate an arbitrary thermal history for PC using only density measurements. The thermal history did not depend on the pre-aging temperature and time; instead, the creep behavior was dependent on the aging state of the material.

References