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Mechanical properties of polycyclo-olefins in the vicinity of the glass transition temperature

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Summary

Mechanical properties of polycyclo-olefins (PCOs) were investigated in the vicinity of the glass transition temperature (T_g). According to tensile tests, the fracture modes of PCOs such as brittle, ductile, and impact processes were largely dependent on the elongation speeds below T_g. In addition, the stress–strain curves were found to be superimposed by the shift factors on transverse and longitudinal axes, giving a typical master curve for tensile fracture behavior.

Introduction

Transparent glassy polymers such as polycarbonate (PC), polymethyl methacrylate (PMMA), and polyethylene terephthalate (PET) have been used for many optical applications in electronic media, such as television sets, portable telephones, optical lenses, and optical discs. Recently, much attention has been paid to the polyolefinic glassy polymers such as polycyclo-olefins (PCOs) as a novel type of transparent material because they are environmental friendly and have outstanding heat and chemical resistances. The mechanical and optical data of PCOs have been examined. Shin et al. [1] analyzed the chemical structure of several types of cyclic olefin copolymer (COC), and investigated the surface characteristics such as surface energy and peel strength. Seydewitz et al. [2] investigated morphology and micromechanical behavior of different types of COC. In particular, they studied the influence of the type and content of cyclic monomers on the micromechanical deformation behavior using electron microscopy. Chien et al. [3] investigated the effect of molding process conditions on the tensile strength of COC parts. Oh et al. [4] simultaneously measured dynamic birefringence and viscoelasticity of several types of COC over a wide frequency region from the rubbery to the glassy zone. Kim et al. [5] investigated the stress–optical coefficients and elastic modulus data of COCs with different compositions across the glass transition temperature T_g. The mechanical characteristics of the transparent glassy polymers in the vicinity of T_g is very important for optimizing molding conditions for preparing transparent sheets and films. A great deal of attention has been given to the yielding behavior of the glassy polymers to investigate their mechanical properties for temperature and the strain rate. Bauwnes et al. [6] investigated tensile yield stress behavior of PC and polyvinyl chloride (PVC) in the glass transition region. Foot et al. [7] measured yield stress on amorphous PET film covering a wide range of strain rates and temperature. They described the data from tests using an extension of the Eyring approach including two processes. G'Sell and Souahi [8] investigated the tensile mechanical properties of PMMA near T_g. They analyzed the tensile data in terms of an entropy-based statistical model based on the stress−strain response of a chain network. Gauthier et al. [9] investigated the tensile data of PC, PMMA, PET, and polystyrene (PS) below and through T_g on the basis of a molecular theory of nonelastic deformation proposed by Perez and coworkers. Drozdov [10] derived the stress−strain relations of PMMA concerned with constitutive equations for the viscoelastic and viscoplastic behavior at uniaxial loading in the range of the strain rate and temperature. These equations described the experimental response in tests with constant strain rates and accounted for changes in relaxation spectra in the vicinity of the yield point. Swallowe et al. [11] investigated the stress−strain behavior of PMMA and PS over a wide range of strain rate and temperature. The relationship between strain rate and activation properties such as energy or volume is investigated by applying the Eyring theory to the PMMA stress−strain curves at their yield points. However, there are few systematic studies on the tensile properties of PCOs over the wide range of the strain rate at around T_g. The purpose of this study is to provide the tensile properties of PCO sheets and to identify the existence of mechanical transition in the vicinity of T_g.

Experiments

Materials

The skeletal structure of the PCO used in this study is shown in Figure 1. The sample sheets with 2 mm thickness were provided by the ZEON Co. under the trade name of ZEONOR®1600, which were molded by injection with a cylinder temperature of 548−573K, input pressure 106 MPa, and output pressure 75 MPa.

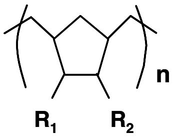


Figure 1. Skeletal structure of PCO

Dynamic mechanical analysis

Dynamic mechanical properties were investigated using a dynamic mechanical analyzer (Rheology Co. Ltd, DVE-V4) on sample specimens of length 30 mm and width 4 mm. The temperature dependences of the dynamic tensile moduli, storage tensile modulus E' and loss modulus E'' were measured between 323 and 503 K at a constant frequency of 10 Hz and a heating rate of 2 K min^{-1}.

Tensile tests

The uniaxial tensile behavior was investigated using a Shimadzu AGS-5kN. Notch-shaped specimens with gauge length 1 mm and width 2 mm were used. The tensile strain λ and elongation rate $\dot{\lambda}$ were calculated from the ratio of the increment of the length between clamps to the initial gauge length. The tensile stress was determined by dividing the tensile load by the initial cross section.

Results and discussion

Figure 2 exemplifies the dynamic mechanical spectra measured at 10 Hz. As shown in Figure 2, a sharp relaxation peak in E'' curve, ascribed to the glass transition T_g, is located at 444K and the storage modulus E' sharply reduces around the temperature. To estimate the activation energy for the relaxation process, we examined the frequency dependence of the E'' peak in the temperature range from 373 to 493 K. The semi-logarithmic plot of the frequency against the inverse of temperature yields the apparent activation energy ΔH^*, giving 680 kJ/mol, which is typical of glassy polymeric materials.

Figure 3(a) shows stress−strain curves measured at 411 K. The strain axis was transferred to the elongation times in Figure 3(b). It is interesting to note that the shape of stress−strain curves can be divided into three types: in the lower elongation

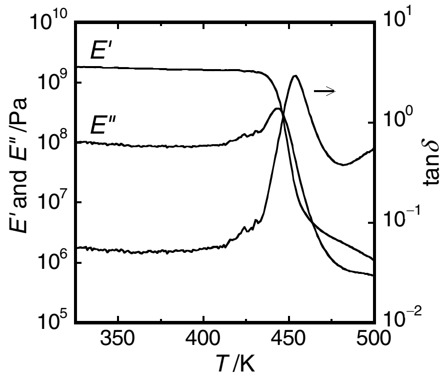


Figure 2. Dynamic mechanical spectra of PCO measured at 10 Hz

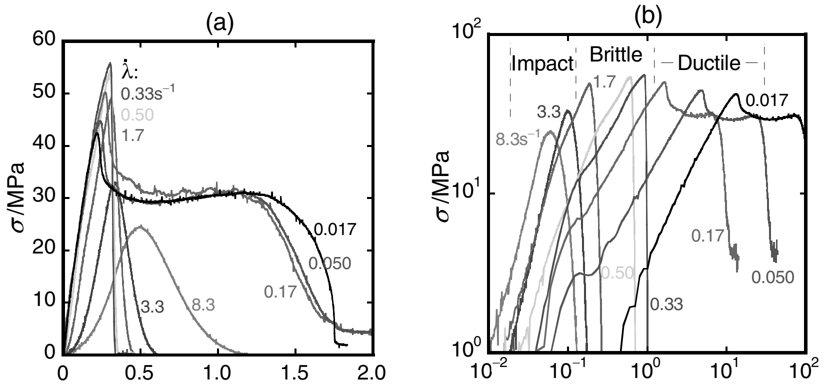


Figure 3. (a) Stress−strain curves measured at 411K and (b) the corresponding stress−elongation time curves

rates ($\dot{\lambda}$ < 0.17 s^{-1}) the stress–strain curves show a clear yield point, which is in the ductile fashion; in the middle deformation rates ($\dot{\lambda}$ = 0.33–1.7 s^{-1}), the samples broke at around the yield point, showing a brittle manner; and in the higher deformation rates ($\dot{\lambda}$ > 3.3 s^{-1}), the shape of stress–strain curves is much different from those of other stress–strain curves, which is symmetrical like a distribution curve. The symmetric curve thus obtained is very similar to the force-time curves measured by usual instrumented impact tests [12]. This implies that the deformation mechanism at high elongation rates involves the impact fracture process. These results led us to conclude that there exists a distinguished mechanical transition at $\dot{\lambda}$=3.3 s^{-1} in the temperature range of $T < T_g$.

At 436K, the ductile-like tensile feature appears in the middle deformation rate ($\dot{\lambda}$ = 0.50–1.7 s^{-1}), which seems to be intermediate between brittle and ductile and may be referred to as pseudo-ductile mode (see Figure 4). In addition, the tensile behavior measured beyond T_g (Figure 5) was essentially different from that measured at less than T_g. The overall stress level was considerably low and drawablity was relatively high, which may be denoted as visco-elastic mode. Thus, this indicates the existence of a clear mechanical transition above a temperature in the region from 436K to 448K.

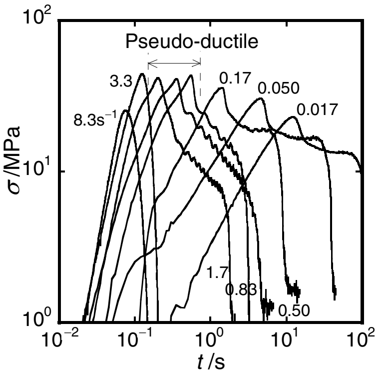


Figure 4. Stress–elongation time curves at 436K

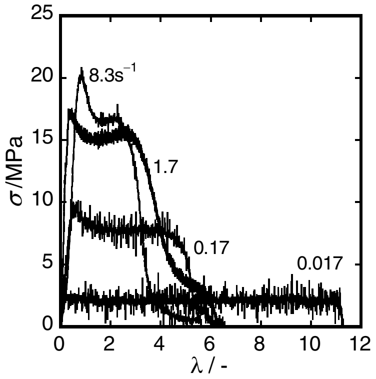


Figure 5. Stress–strain curves at 448K

Using the tensile data measured over a wide range of temperatures and elongation rates, we constructed the phase diagram of the PCO fracture mode. In Figure 6, the deformation modes characterized from stress–strain tests are indicated as a function of temperature and deformation rate on the mechanical map. Foot et al. [7] also showed a similar deformation map for PET. The map in Figure 6 makes it possible to predict the PCO fracture mode from the values of $\dot{\lambda}$ and temperature. Above T_g, the fracture mode is found to be independent of $\dot{\lambda}$ and is essentially different from the modes in the temperatures lower than T_g. In this region, the deformation behavior seems not to be accompanied by the plastic deformation that causes the ductile and brittle modes. This indicates that T_g is one of the most important mechanical transition points. At temperatures lower than T_g, the ductile fracture mode is dominated in the lower elongation rates ($\dot{\lambda}$ < 0.3 s^{-1}). The brittle mode region evolves in the middle elongation rates ($\dot{\lambda}$ = 0.3–2 s^{-1}), and at higher temperature above 425K the pseudo-ductile mode appears instead of brittle and impact modes. In the higher elongation rates ($\dot{\lambda}$ > 2 s^{-1}) the impact mode region appears independent of temperature. It is

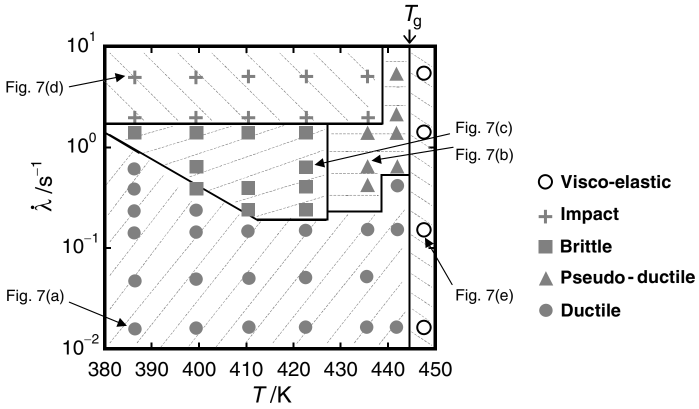
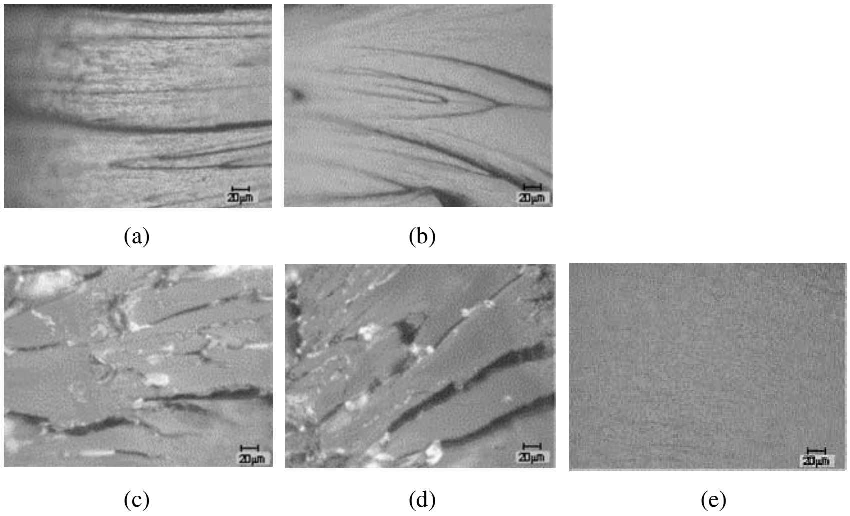


Figure 6. Phase diagram of PCO fracture mode against elongation rates and temperature

interesting to note that the brittle region narrows with decreasing temperature in which the brittle mode appears to change to the ductile one at temperatures of less than 410K.

The fractured surfaces of PCOs at breaking are shown in Figures 7(a)–(e). These represent the ductile, pseudo-ductile, brittle, impact, and visco-elastic modes of deformation, respectively. It was confirmed from these figures that the features of these pictures correspond to the fracture modes characterized by the stress–strain curves.

In this work, we investigated the yield stress on the stress–strain curves in the ductile region, which is the most important for practical processes. Yielding behavior in glassy polymers can be analyzed as a mechanically activated rate process as suggested by Eyring [11, 13]. According to the rate theory, the yield process of glassy polymers



(a) (b)

(c) (d) (e)

Figure 7. The fractured surface of PCO at breaking. (a) Ductile; (b) pseudo-ductile; (c) brittle; (d) impact; (e) visco-elastic modes shown in Figure 6

at high temperatures can be considered to be caused by the jump of polymer segments from one equilibrium position to another. The applied stress σ_y induces molecular flow along the deformation direction, and the flow rate in the forward direction is given by eq. (1)

$$\dot{\lambda} = \dot{\lambda}_0 \exp(-\Delta H/RT)\exp(V^* \sigma_y/RT) \tag{1}$$

where ΔH is the potential barrier of flow in the stress direction and V^* is the activation volume of flow units. Equation (1) can be rewritten as eq. (2)

$$\sigma_y/T = R/V^* \ln\dot{\lambda} + (-R/V^* \ln\dot{\lambda}_0 + \Delta H/V^* T) \tag{2}$$

In Figure 8, the yield stresses σ_y are plotted against the elongation rate in the ductile plastic deformation region. According to eq. (2), σ_y/T is proportional to log $\dot{\lambda}$ and the activation volume V^*, and the activation energy ΔH of the yield process can be obtained from the slopes and intercepts of the lines in Figure 8. Figure 9 shows temperature dependence of the values of V^* in the ductile deformation region from 387 to 442K. There are two distinct regions. In first region from 387 to 423K, V^* values slightly increase and ΔH was estimated to be 190 kJ/mol. In second region from 423 to 442K, V^* dropped and ΔH became 880 kJ/mol. It is interesting to note that this value is relatively close to the activation energy ΔH^* for the molecular mobility around T_g. Therefore, the temperature from 423 to 442K is a mechanical transition region in the deformation mechanism of PCOs.

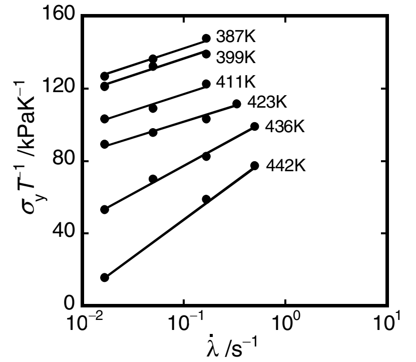


Figure 8. Elongation rate dependence of the yield stress in the ductile deformation region

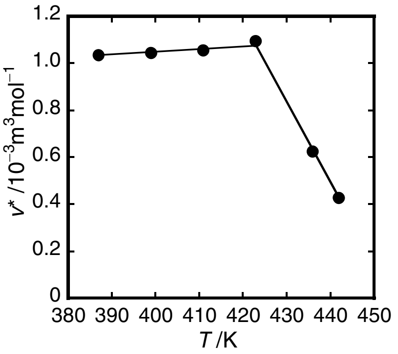


Figure 9. The temperature dependence of the activation volume

The stress–elongation time curves in the brittle and the ductile regions were found to be superposed by shifting the transverse after adjustment of the maximum yield stress. Figure 10(a) shows the superposed master curves measured in the brittle region at 411K, which can be obtained by shifting the transverse to the curve at $\dot{\lambda}$ = 0.33 s^{-1} as the reference curve. Figure 10(b) also shows the master curves in the ductile region at 411K, where the curve at 0.017 s^{-1} is taken as the reference. The transverse shift is elongation rate shift, which simply means shortening elongation time.

The transverse shift factors a_t are plotted against the elongation rate (see Figure 11). We can find the straight relation between a_t and $\log\dot{\lambda}$, giving −1 slope. This means that a_t is proportional to the inverse of $\dot{\lambda}$ and the deformation rate dependence of the

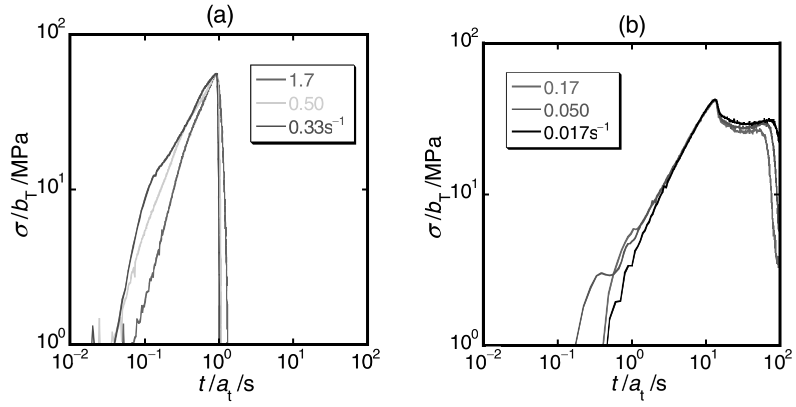


Figure 10. (a) The superposed master curves in the brittle region at the reference elongation rate of 0.33 s^{-1} and at 411K and (b) the superposed master curves in the ductile region at the reference elongation rate of 0.017 s^{-1} and at 411K

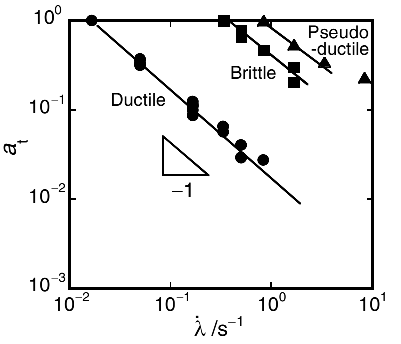


Figure 11. Shift factors a_t plotted against the elongation rate

stress–strain curves can be expressed by considering that the deformation time of PCOs becomes shorter with increasing elongation rate. Consequently, we can predict the stress–strain curves over a wide range of elongation conditions using this relation.

Conclusions

Mechanical properties of PCOs were investigated in the vicinity of the glass transition temperature, T_g. According to tensile tests in the vicinity of T_g over a wide range of deformation rates, the following results have been obtained: the tensile behavior of PCOs in the vicinity of T_g are divided into ductile, brittle, and impact fracture modes depending on elongation rate and temperature. The yield behavior in the ductile region takes place according to the Eyring rate theory. The activation volume of flow units dropped just below T_g. According to comparison of activation energies between the rate theory and the relaxation process, a temperature just below T_g is considered a mechanical transition region in the deformation mechanism. The stress–strain curves for tensile behavior can be superimposed by the shift factors of elongation time and stress axes. The shift factors of the elongation time axis are simply expressed by elongation rate. The master curves make it possible to predict the fracture mode of PCOs.

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