

Crystallization and Molecular Relaxation of Poly(Ethylene Terephthalate) Annealed in Supercritical Carbon Dioxide

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Abstract: Poly(ethylene terephthalate) was annealed at different temperature and pressure of supercritical carbon dioxide (CO₂) using samples quenched from the melt. Crystallization and molecular relaxation behavior due to CO₂-annealing of samples were investigated using differential scanning calorimetric and dynamic mechanical measurements. The glass transition and crystallization temperatures significantly decreased with increasing temperature and pressure of CO₂. The dynamic mechanical measurement of samples annealed at 150 °C in supercritical CO₂ showed three relaxation peaks, corresponding to existence of different amorphous regimes such as rigid, intermediate, and mobile domains. As a result, the mobile chains were likely to facilitate crystallization in supercritical state. It also led to the decreased modulus of CO₂-annealed samples with increasing pressure.

Keywords: Polyester, Crystallization, Supercritical carbon dioxide, Dynamic mechanical properties

Introduction

Supercritical fluids have recently received much attention because of their peculiar characteristics such as liquid-like density, high diffusivity, low viscosity, tunable solvent power and zero surface tension. Especially, supercritical carbon dioxide (SCCO₂) is more attractive solvent in being non-toxic, non-flammable, inexpensive, recyclable, and environmentally-friendly [1-4]. In relation to polymer, its use continues to increase in the field of polymer synthesis, modification and processing [5-10]. Recently many studies have been devoted to understanding changes of morphology and properties of polymers due to SCCO₂ treatment such as morphology, swelling, glass transition, and crystallization rate.

Poly(ethylene terephthalate) (PET) is an important polymer in textile end-uses and industrial applications with some crystallinity dependent on thermal history. SCCO₂-induced modification may provide changes in physical properties of PET. Many investigators have reported the results on CO₂-induced changes in structure and properties of polymers such as morphology, glass transition behavior, crystallinity, and mechanical properties using vibration spectroscopy, and thermal analysis [11-17]. The glass transition temperature of polymers is lowered by the use of gaseous and liquid CO₂, and supercritical CO₂ has a strong plasticizing effect on polymers. The plasticization by SCCO₂ can increase the mobility of the polymer chains, and thus allows the chains to result in CO₂-induced crystallization. Kamiya *et al.* [18] reported the CO₂-induced crystallinity of approximately 29 % for PET crystallized at 60 atm and 65 °C. Grant *et al.* [19] have shown that a dramatic change in the PET molecular structure and motion follows SCCO₂ treatment. They demonstrated

three-region model for the existence of three motional regimes of crystalline, rigid amorphous, and mobile amorphous using NMR relaxation measurements. However in our knowledge, no experimental result using dynamic mechanical measurements was shown in the literature about molecular relaxation behavior in amorphous regime of SCCO₂-treated PET.

In this study, crystallization and molecular relaxation using thermal analysis and dynamic mechanical measurements were investigated for CO₂-annealed PET with different temperature and pressure.

Experimental

Materials

PET used in this investigation was a commercial sample in the form of chips with an intrinsic viscosity of 0.8 g/ml. Quenched PET films were prepared by melt-pressing the polymer at 250 °C in the melt-presser and then immediately quenched in ice-water bath. Finally films of thickness of 0.131 mm were obtained, and carbon dioxide (purity: 99.9 %) was used after drying by passing over molecular sieves.

Annealing was carried out at 50, 100, 150, and 200 °C for 1 hour in high-pressure CO₂ chamber with temperature-controller equipment. Different CO₂ pressures of 1, 50, 100, and 200 atm were also used for annealing. Pressure and temperature of CO₂ were monitored by pressure transducer and thermocouple, respectively.

Measurements

FT-IR spectroscopic spectra of samples were obtained using Jasco FT-IR 300E with an attenuated total reflectance method. Wide angle x-ray diffraction (WAXD) measurements were carried out with Rigaku Rint 2100 series, using CuK_α radiation at a scan rate of 5 °/min. The PET samples were

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heated to 250 °C at a rate of 10 °C/min in differential scanning calorimeter (DSC2010, Du Pont). A cooling scan was also recorded to find crystallization behavior by cooling from 250 °C to room temperature at a rate of 10 °C/min. Tensile test was carried out using an Instron tensile tester, and the gauge length and crosshead speed were 25 mm and 10 mm/min, respectively. Dynamic mechanical properties were measured by a dynamic mechanical analyzer (Du Pont, DMA983). Loss tangent was scanned between room temperature and 150 °C at 1 Hz and at a heating rate of 2 °C/min.

Results and Discussion

Figure 1 shows DSC thermograms of quenched and SCCO₂-annealed samples obtained during the first heating at a rate of 10 °C/min. Quenched sample has a glass transition temperature (T_g) near 75 °C, and crystallization peak and melting temperature appear near 150 °C and 260 °C, respectively. Annealing at 50 °C and 1 atm does not show any change in glass transition, crystallization, and melting temperatures except somewhat increased heat of crystallization and fusion. However, in case of sample CO₂-annealed at 50 atm and 50 °C, significant shifts toward lower temperature are detected in the glass transition and crystallization temperatures. The sample annealed at 50 atm shows an intermediate behavior in crystallization between quenched and annealed samples at 100 atm. That is, there appeared two crystallization temperatures. On further increasing CO₂ pressure to 100 atm, a sharp crystallization peak near 60 °C is shown with decreased T_g . The decrease in T_g is known to be due to a role of CO₂ as a plasticizer [1,20]. Thus it is considered that this plasticization of CO₂ may appear even below supercritical state, and may be completely acted above a critical condition. As a result, CO₂-induced crystallization appears at lower temperature compared to the sample by conventional thermal crystallization. Figure 2 shows DSC thermograms of SCCO₂-annealed samples. No

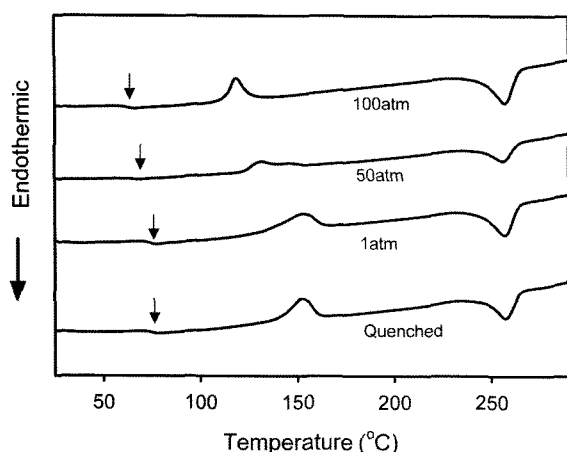


Figure 1. DSC thermograms of quenched and annealed samples at 50 °C and at different CO₂ pressure.

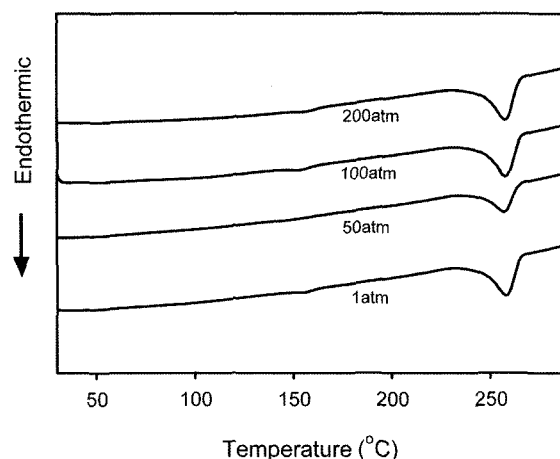


Figure 2. DSC thermograms of samples annealed at 150 °C and at different CO₂ pressure.

Table 1. Melting temperature and heat of fusion of CO₂-annealed samples at 150 °C

Pressure (atm)	Melting temperature (°C)	Heat of fusion (J/g)
1	257.7	42.2
50	257.2	44.2
100	257.9	44.4
200	257.7	45.4

glass transition temperature and crystallization were seen except melting peak near 257 °C. Table 1 represents that the existence of CO₂ leads to significantly increased crystallinity of sample.

According to WAXS measurements as shown in Figure 3, sample annealed at 50 °C and 100 atm shows a slight crystalline peak near $2\theta = 18^\circ$, 23° and 28° , whereas no clear diffracted crystalline pattern is seen in the sample annealed at 1 and 50 atm [1,13]. It indicates that the SCCO₂-annealing results in

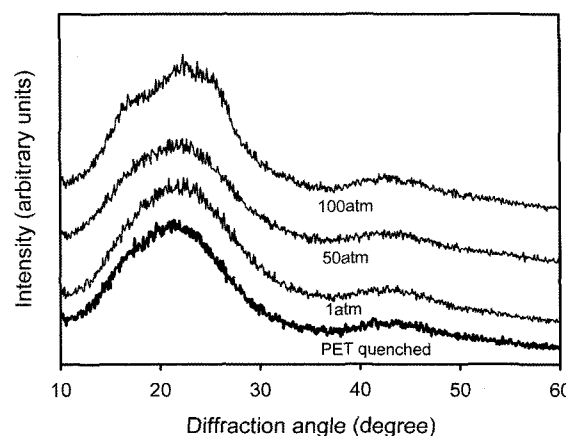


Figure 3. X-ray diffraction curves of quenched and annealed samples at 50 °C and at different CO₂ pressure.

inducing the higher crystallinity due to the activated plasticization effect of CO₂ as described in previous DSC measurements. Figure 4 shows the dominantly increased crystallinity for the samples annealed at 150 °C, however, further analysis for quantitative crystallinity was not carried out in this study.

To clearly understand the crystallization behavior of PET in SCCO₂ condition, the dynamic mechanical measurements were performed. Figure 5 shows loss tangent of samples annealed at 50 °C with different CO₂ pressure. The molecular relaxation behavior of samples is dominantly dependent on the pressure of CO₂, and thus complex morphology may be formed in CO₂-annealed sample. Quenched sample exhibits a sharp relaxation peak at 105 °C, which may be due to glass transition temperature [21]. As the CO₂ pressure increases, the maximum loss tangent peak decreases and the relaxation peak temperature is shifted toward the lower temperature except the sample annealed at 50 atm. The sample annealed at 50 atm showed the somewhat decreased loss tangent peak with a slight increase in T_g. For the sample annealed at 50 atm, a new broad peak also appeared near 80 °C. Moreover, the

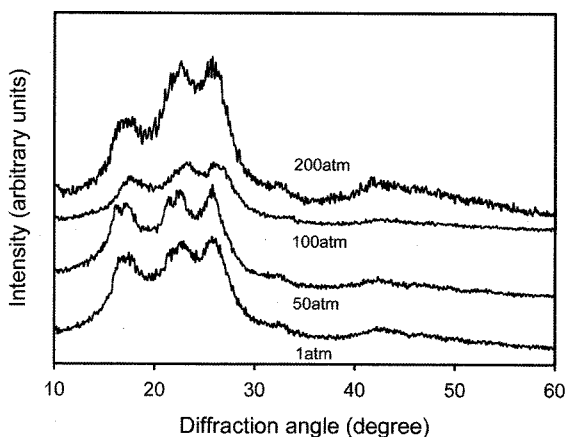


Figure 4. X-ray diffraction curves of quenched and annealed samples at 150 °C and at CO₂ different pressure.

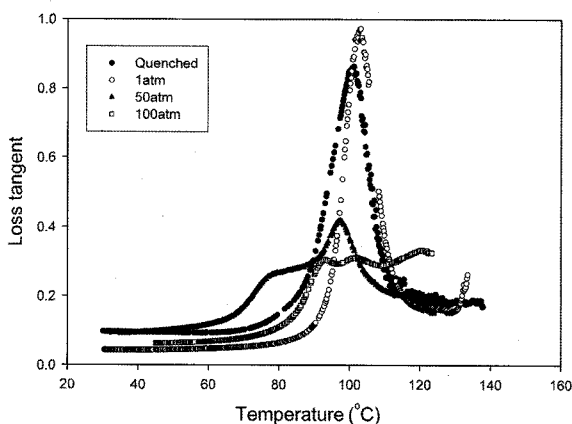


Figure 5. Temperature dependence of loss tangent of quenched and annealed samples at 50 °C and at different CO₂ pressure.

sample annealed in supercritical state exhibited three relaxation peaks near 90 °C, 100 °C, and 120 °C. This behavior indicates strong dependence of relaxation pattern on CO₂ pressure. Since the relaxation behavior is generally governed by the molecular mobility, the dynamic mechanical results may be helpful to understand some relationship between crystallization and molecular relaxation behavior under CO₂ condition. Recalling the DSC results, it can be noted that annealing at 50 atm results in the decrease of glass transition temperature and presence of two crystallization temperatures, and the sample annealed at 100 atm causes the decrease in glass transition temperature with the lowered crystallization temperature. Therefore it can be regarded that the lower relaxation peak of SCCO₂-annealed sample at 50 atm is due to the glass transition of more mobile chains in amorphous domains due to the increased plasticization of CO₂. However, in case of SCCO₂ condition, the morphology of amorphous regime may be more complex because the dominantly activated CO₂ can facilitate the crystallization of sample and thus it may result in creating the rigid amorphous chains on lamellar surfaces. Based on this, three molecular relaxation shown in the sample SCCO₂-annealed at 100 atm may be explained in terms of existence of mobile, normal, and rigid amorphous chains. This result may be compared with three-regime model reported by Grant *et al.* [19]. They suggested that PET treated with supercritical CO₂ had three motional regimes of mobile amorphous, rigid amorphous, and crystalline according to solid NMR studies. However in our dynamic measurements, there appeared no evidence which can be seen as crystalline regime since the samples SCCO₂-annealed at 150 °C with high crystallinity showed only one relaxation peak near 125 °C as shown in Figure 6, indicating that the relaxation peak near 120 °C of SCCO₂-annealed sample is due to glass transition of rigid amorphous regime, not due to crystalline relaxation.

The stress-strain curves (Figure 7) were obtained for quenched sample and CO₂-annealed samples at 150 °C. The quenched sample exhibited a clear yield phenomenon near 70 % elonga-

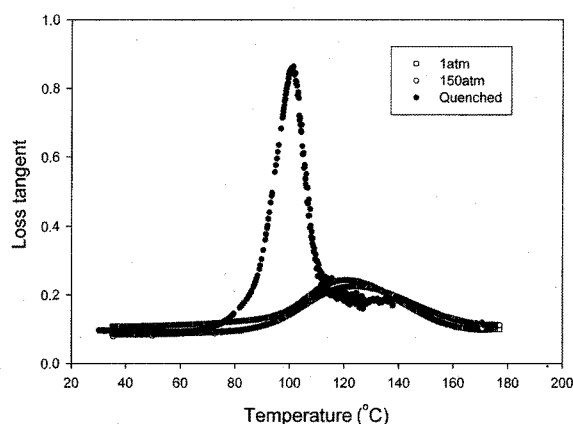


Figure 6. Temperature dependence of loss tangent of quenched and annealed samples at 150 °C and at different CO₂ pressure.

tion, however, the annealed samples did not so. Breaking stress and modulus versus CO₂ pressure are shown in Figure 8 and 9. Breaking stress does not show any constant dependence with increasing CO₂ pressure, however, modulus tends to

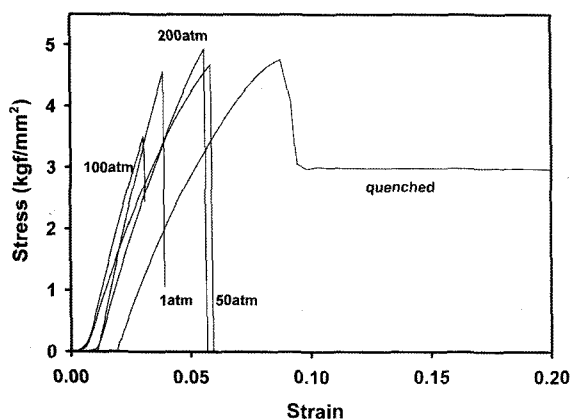


Figure 7. Stress-strain curves of annealed samples at 150 °C and different CO₂ pressure.

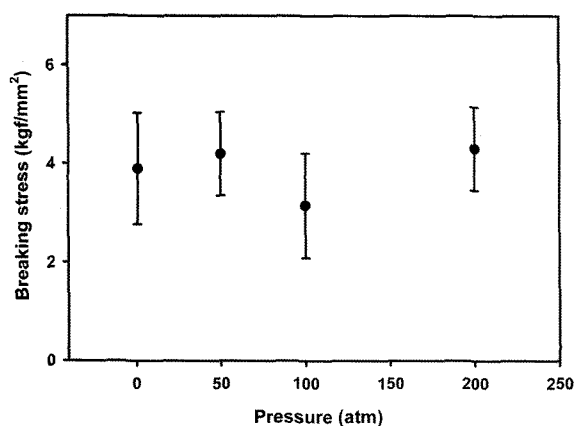


Figure 8. Breaking stress of annealed samples at 150 °C versus SCCO₂ pressure.

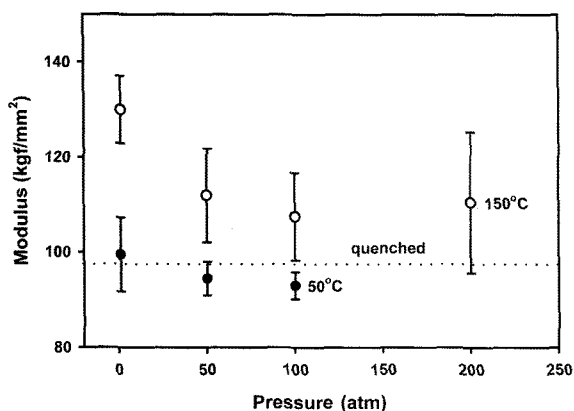


Figure 9. Tensile modulus of annealed samples at 50 °C and 150 °C versus SCCO₂ pressure.

decrease gradually for annealing temperatures of 150 °C and 50 °C. The decrease of modulus may be attributed to the increased mobile region in CO₂-annealed samples as described in previous dynamic mechanical properties. That is, it is because the decrease of modulus due to increased mobile amorphous region is more dominant compared to the increase of modulus resulting from the increased crystallinity due to CO₂-annealing. Consequently, the mechanical properties of CO₂-annealed PET, especially modulus in low elongation of sample are largely dependent on the mobility of amorphous chains.

Conclusion

From investigating the poly(ethylene terephthalate) annealed at different CO₂ conditions, the following conclusions were derived. The glass transition temperature and crystallization temperature decreased with increasing CO₂ pressure. Three relaxation peaks observed in the dynamic mechanical measurements were ascribed to existence of the different molecular mobility in amorphous domains like mobile, intermediate, and rigid regimes. Modulus of samples annealed in supercritical CO₂ tended to decrease with increasing CO₂ pressure, indicating the dominant effect of molecular mobility on the mechanical properties.

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