

SHORT COMMUNICATIONS

**Glass Transition Temperature of Glassy Polymers
Plasticized by CO₂ Gas**

Hisao HACHISUKA, Takanori SATO, Tohru IMAI,
Yoshiharu TSUJITA,* Akira TAKIZAWA,
and Takatoshi KINOSHITA

*Department of Materials Science and Engineering, Polymeric Materials Course,
Nagoya Institute of Technology, Gokiso-cho,
Showa-ku, Nagoya 466, Japan*

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It is well-known that sorption of vapors and liquids in polymers can cause significant plasticization resulting in substantial decrease in the glass transition temperature (T_g).¹⁻⁴ Such effect is slight in the sorption of gases in polymers since the solubility level is quite low. However condensable gases like CO₂ with high critical temperature are, in general, considerably soluble, particularly in glassy polymers. Correspondingly, it has been reported that glassy polymers are plasticized by sorbed CO₂ at high pressure. Physical properties such as gas sorption and permeation are markedly influenced by the plasticization of glassy polymer by sorbed CO₂.⁵⁻¹² Investigations on the plasticization of glassy polymer at high CO₂ pressure have been carried out.¹³⁻¹⁷ It is of interest as to how much T_g may be reduced by sorbed CO₂. However, it is difficult to determine T_g of glassy polymers at CO₂ high pressure and only a few studies have been reported by Wonders *et al.* They showed that T_g of polycarbonate sorbed at 6.8 atm was 8—9°C lower than that in the absence of CO₂ using a special differential thermal analyzer.¹⁴ Wang *et al.* have also reported that the re-

duction of T_g of polystyrene in the presence of CO₂ was estimated by the change in mechanical relaxation behavior.¹⁵ Chiou *et al.* have furthermore reported in detail that the variation of T_g of various glassy polymers caused by sorbed CO₂ at the pressure range up to 25 atm was determined using a differential scanning calorimeter (DSC).¹⁶ However there are few investigations on the variation of T_g of glassy polymers having relatively high T_g at higher CO₂ pressure.

Here we report on the variation of T_g of various engineering plastics having relative high T_g by CO₂ sorbed under 60 atm at 25°C and a skillful method to determine T_g of glassy polymers using DSC in the range up to 60 atm.

The determination of T_g of various glassy polymers using DSC (SSC-560, Seiko Electronics Co., Ltd.) was carried out as follows. A glassy polymer film and dry ice (CO₂) were placed in a pressure-sealable aluminium pan which was sealed completely by an aluminium lid. The CO₂ pressure in the pan was controlled by the amount of dry ice. To evaluate the CO₂ pressure in the pan, the van der Waals equation, which can express satisfactory real

* To whom all correspondence should be addressed.

gas state, was applied.

$$p = \frac{nRT}{V-nb} - \frac{an^2}{V^2}$$

In this study, V is the volume in the pan subtracting volume of polymer, n is the moles of dry ice (CO_2) in the pan, T is the temperature, a and b are the van der Waals constant ($a = 3.61 \text{ atm}^2 \text{ mol}^{-2}$ and $b = 0.0431 \text{ mol}^{-1}$) for CO_2 , and R is the gas constant. The pressure of *ca.* 60 atm is in the gas-liquid equilibrium state at 25°C . The film was exposed to CO_2 at various pressures in the sealed pan for 24 h to attain sorption equilibrium. Then the sealed pan was quenched to -60°C to maintain the equilibrium sorption amount of CO_2 in polymer at various CO_2 pressures. After that, DSC measurement was performed rapidly at a heating rate of $15^\circ\text{C min}^{-1}$ from -50°C . In this study, we examined various glassy polymers which have relatively high solubility for CO_2 ; poly(2,6-dimethyl phenylene oxide) [PPO] (GE Plastics Japan), two imidized polyamic acids [PAA-0 and PAA-41, the number representing imide content]

(Nissan Chemical Industry Co., Ltd.), and polycarbonate [PC] (Idemitsu R & D Lab.).

Figure 1 shows the DSC thermograms of PPO at atmospheric pressure (A) and PPO sorbed under *ca.* 60 atm of CO_2 prepared by the procedure mentioned above (B). T_g of PPO was reduced from 219°C to *ca.* -7°C by exposure to CO_2 of 60 atm. Scattered fluctuation of DSC thermogram above T_g may be caused by desorption of CO_2 from PPO. It was found that reduction of T_g was caused by plasticization by sorbed CO_2 . ΔC_p , the difference of heat capacity between glassy and rubbery states, for PPO at 60 atm of CO_2 and atmospheric pressure was 0.50 and $0.39 \text{ Jg}^{-1} \cdot \text{deg}^{-1}$, respectively and reasonable values.

Next we examined the variation of T_g of PPO at various pressures of CO_2 . Figure 2 shows T_g of PPO as a function of CO_2 exposure pressure. T_g of PPO was reduced linearly with increase in exposure pressure. This suggests that the plasticization of PPO occurs markedly by sorbed CO_2 and the miscibility between PPO and CO_2 is good. As the results, the physical properties of PPO vary at high CO_2 pressure.

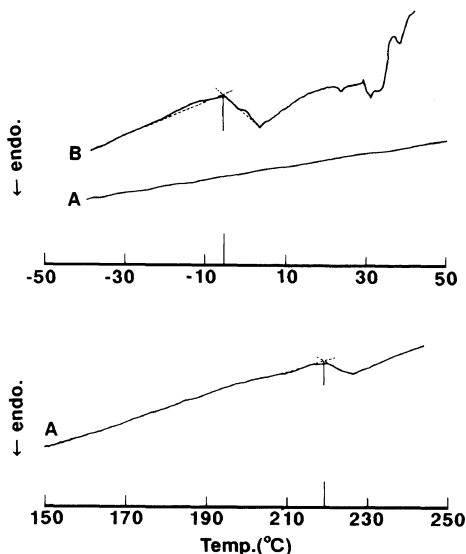


Figure 1. DSC thermograms for PPO at atmospheric pressure (A) and PPO sorbed under *ca.* 60 atm of CO_2 (B).

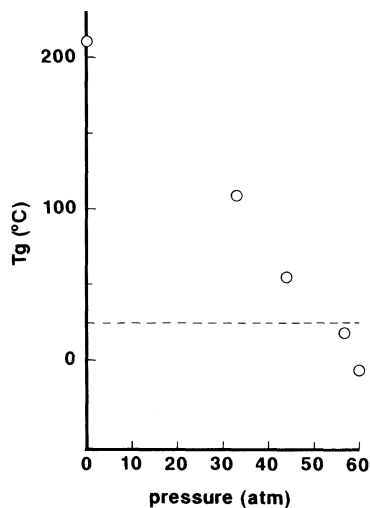


Figure 2. Variation of T_g for PPO as a function of CO_2 exposure pressure.

Table I. Variation in T_g of glassy polymers with sorbed by high CO₂ pressure

Sample	$T_{g0}/^{\circ}\text{C}$	Press/atm	$T_{g1}/^{\circ}\text{C}$	References
PPO	219	33	109	This work
		44	55	This work
		57	19	This work
		60	-7	This work
PC	148	20	97	16
		60	55	This work
PAA-0	156	60	-8	This work
PAA-41	227	60	0	This work
PVC	75	20	57	16
PS	100	20	78	16
PET	74	20	52	16

^a T_{g0} , at atmospheric pressure; T_{g1} , at CO₂ pressure.

Table I shows T_g at both 60 atm of CO₂ and atmospheric pressure for various engineering plastics including some reference values. T_g was reduced markedly by plasticization caused by sorbed CO₂ under 60 atm. It was found that the sorbed CO₂ molecules interestingly played the role of a plasticizer. The degree of reduction of T_g may be attributed to the difference of solubility of CO₂ in each glassy polymer.

The DSC technique under high CO₂ pressure described here provides an easy method to estimate the reduction of T_g of glassy polymer caused by sorbed CO₂ at various pressures. CO₂ at high pressure can cause significant reduction of T_g of glassy polymers which have high CO₂ solubility. This behavior may be quite important in certain applications such as improvement of permeability of glassy polymer films. Some interesting facts in relation to CO₂ plasticization will be reported in the near future.

REFERENCES

1. G. A. Bernier and R. P. Kambour, *Macromolecules*, **5**, 393 (1968).

2. R. P. Kambour, E. E. Romagosa, and C. L. Gruner, *Macromolecules*, **5**, 335 (1972).
3. R. P. Kambour, C. L. Gruner, and E. E. Romagosa, *Macromolecules*, **7**, 248 (1974).
4. R. P. Kambour and C. L. Gruner, *J. Polym. Sci., Polym. Phys. Ed.*, **16**, 703 (1978).
5. Y. Kamiya, K. Mizoguchi, Y. Naito, and T. Hirose, *J. Polym. Sci., Polym. Phys. Ed.*, **24**, 535 (1986).
6. Y. Kamiya, K. Mizoguchi, Y. Naito, and T. Hirose, *J. Polym. Sci., Polym. Phys. Ed.*, **24**, 1525 (1986).
7. K. Mizoguchi, T. Hirose, Y. Naito, and Y. Kamiya, *Polymer*, **28**, 1298 (1987).
8. Y. Kamiya, T. Hirose, Y. Naito, and K. Mizoguchi, *J. Polym. Sci., Polym. Phys. Ed.*, **26**, 159 (1988).
9. J. S. Chiou, Y. Maeda, and D. R. Paul, *J. Appl. Polym. Sci.*, **30**, 4019 (1985).
10. J. S. Chiou and D. R. Paul, *J. Appl. Polym. Sci.*, **32**, 2897 (1986).
11. S. Zhou and S. A. Stern, *J. Polym. Sci., Polym. Phys. Ed.*, **27**, 205 (1989).
12. H. Hachisuka, Y. Tsujita, A. Takizawa, and T. Kinoshita, *Polym. J.*, **21**, 1019 (1989).
13. R. A. Assink, *J. Polym. Sci., Polym. Phys. Ed.*, **12**, 2281 (1974).
14. A. G. Wonders and D. R. Paul, *J. Membr. Sci.*, **5**, 63 (1979).
15. W. V. Wang, E. J. Kramer, and W. H. Sachse, *J. Polym. Sci., Polym. Phys. Ed.*, **20**, 1371 (1982).
16. J. S. Chiou, J. W. Barlow, and D. R. Paul, *J. Appl. Polym. Sci.*, **30**, 2633 (1985).
17. Y. Kamiya, K. Mizoguchi, and Y. Naito, *Polym. Prepr. Jpn.*, **37**, 2187 (1988).