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SHORT COMMUNICATIONS

Glass Transition Temperature of Glassy Polymers Plasticized by CO_2 Gas

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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 CO_2 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 CO_2 at high pressure. Physical properties such as gas sorption and permeation are markedly influenced by the plasticization of glassy polymer by sorbed CO_2.[5-12] Investigations on the plasticization of glassy polymer at high CO_2 pressure have been carried out.[13-17] It is of interest as to how much T_g may be reduced by sorbed CO_2. However, it is difficult to determine T_g of glassy polymers at CO_2 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 CO_2 using a special differential thermal analyzer.[14] Wang *et al.* have also reported that the reduction of T_g of polystyrene in the presence of CO_2 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 CO_2 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 CO_2 pressure.

Here we report on the variation of T_g of various engineering plastics having relative high T_g by CO_2 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 (CO_2) were placed in a pressure-sealable aluminium pan which was sealed completely by an aluminium lid. The CO_2 pressure in the pan was controlled by the amount of dry ice. To evaluate the CO_2 pressure in the pan, the van der Waals equation, which can express satisfactory real

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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 ($a=3.61\,\text{atm}\,l^2\,\text{mol}^{-2}$ 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 $15\,^{\circ}\text{C}\,\text{min}^{-1}$ 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 $0.39\,\text{J}\,\text{g}^{-1}\cdot\text{deg}^{-1}$, 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.

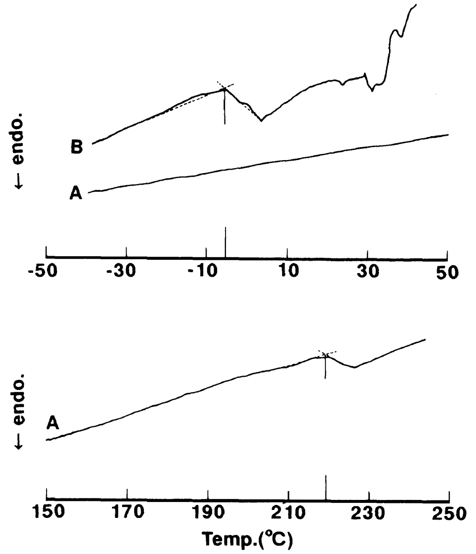

Figure 1. DSC thermograms for PPO at atmospheric pressure (A) and PPO sorbed under *ca.* 60 atm of CO_2 (B).

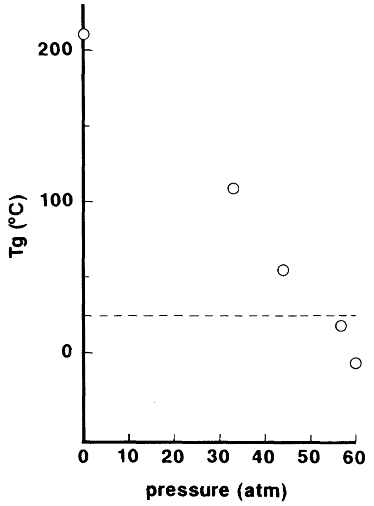

Figure 2. Variation of T_g for PPO as a function of CO_2 exposure pressure.

Table I. Variation in T_g of glassy polymers with sorbed by high CO_2 pressure

Sample	T_{g_0}/°C	Press/atm	T_{g_1}/°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_{g_0}, at atomospheric pressure; T_{g_1}, at CO_2 pressure.

Table I shows T_g at both 60 atm of CO_2 and atmospheric pressure for various engineering plastics including some reference values. T_g was reduced markedly by plasticization caused by sorbed CO_2 under 60 atm. It was found that the sorbed CO_2 molecules interestingly played the role of a plasticizer. The degree of reduction of T_g may be attributed to the difference of solubility of CO_2 in each glassy polymer.

The DSC technique under high CO_2 pressure described here provides an easy method to estimate the reduction of T_g of glassy polymer caused by sorbed CO_2 at various pressures. CO_2 at high pressure can cause significant reduction of T_g of glassy polymers which have high CO_2 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 CO_2 plasticization will be reported in the near future.

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