Sorption of CO_2 in the Photocrosslinked PVCA Film

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Sorption behavior of CO_2 in the photocrosslinked poly(vinyl cinnamate) film was examined. The amount of sorbed CO_2 was enhanced with the degree of crosslinking, while the amount decreased beyond *ca.*95 % crosslinking.

One of the most important factors, which affects the gas sorption ability of a polymer, is the primary structure, *i.e.*, chemical structure. In addition, other factors must be considered, for example, those which relate to molecular packing. In the case of a glassy polymer which has no strong adsorption site, the sorption site of a gas seems to be the free volume in the polymer[1,2]. With respect to the molecular packing, it is expected that the crosslinking structure affects the gas sorption behavior of polymers. However, there has been few reports on this subject. Only a few reports on the water sorption behavior have been presented[3-7]. Recently, we found that the sorption of polar molecules, such as water and some alcohols, depend on the degree of crosslinking of the photocrosslinked PVCA film[8,9].

The CO_2 sorption behavior on various polymer films is currently being investigated due to their theoretical and practical significance[10-13]. Consequently, revealing the factors which affect the CO_2 sorption of the polymer is worth examining. In this study, the effect of the degree of crosslinking of the photocrosslinked poly(vinyl cinnamate) (PVCA) film on CO_2 sorption was examined. Recently, the quartz microbalance has been widely used for measuring the mass change and is useful for observing the sorption change *in situ* in a thin film state. The technique is particularly reliable for a crosslinked polymer[14].

Poly(vinyl cinnamte) was purchased from Aldrich Co., Ltd. and used without further purification. It is well known that the PVCA undergoes an intermolecular photodimerization of the cinnamate moiety in the solid state resulting in a highly crosslinked structure[15]. This is the reason why PVCA was chosen for this study. PVCA was dissolved in toluene. The sensitizer was not used in order to avoid the bad effect on the sorption behavior as an impurity. The solution was spin-coated on an AT-cut quartz crystal oscillating element (4MHz). After drying by heating at 150 °C in N_2, the film was photoirradiated in N_2 at 290 nm using a 500-W high pressure mercury lamp. The degree of crosslinking was controlled by changing the photoirradiation time. The sample was then post-heated at 150 °C for 1 h in a N_2 atmosphere. The thickness of all films was held at *ca.* 3.0 μm. The degree of crosslinking was determined from an FT-IR analysis based on the variation in the absorbance at 1630 cm^{-1} which is assigned to the C=C stretching vibration[9]. The precision of the estimated degree of crosslinking was suffice for the qualitative analysis.

An oscillator was placed in a thermostated small vessel and its output was monitored with a frequency counter. Various CO_2 concentrations were prepared under atmospheric pressure by mixing high purity CO_2 and N_2 which were supplied from gas cylinders and introduced into the vessel.

The amount of sorbed CO_2 (M) was determined as a function of the partial pressure of CO_2 (p) at 30 °C. M is the weight of sorbed CO_2 per 1 gram of the photocrosslinked PVCA film. The sorption isotherms for the photocrosslinked PVCA with different degrees of crosslinking are shown in Figure 1. It is well known that the sorption of CO_2 in a glassy polymer is successfully described by the dual-mode sorption model[10,11]. All isotherms shown in Figure 1 are similar in form to the model obtained in the region of low CO_2 pressure. This result suggests that the sorption behavior of photocrosslinked PVCA is also governed by the Langmuir-type adsorption. In other words, the free volume in the crosslinked polymer act as an important adsorption site.

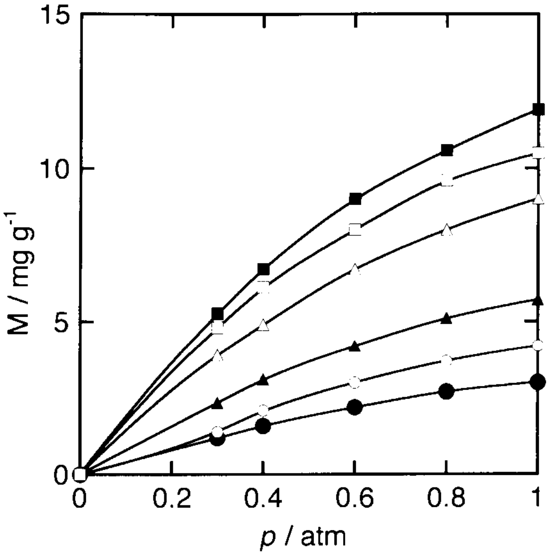

Figure 1. Sorption isotherms of CO_2 in the PVCA films with different degrees of crosslinking measured at 30 °C; ●) the degree of crosslinking = 0 %, ○) 34%, ▲) 52 %, △) 86 %, ■) 95 %, and □) 99%.

Shown in Figure 2 is the M vs the degree of crosslinking at p = 1.0 atm depicted by using the values of M from Figure 1. M clearly depends on the degree of crosslinking. It is noteworthy that the maximum amount of sorbed CO_2 occurred at high degree of crosslinking. A similar behavior was observed for water and some alcohol sorption in these films before[9]. As the origin of this behavior, the decomposition of the polymer by exposure to UV light was then ruled out from IR analysis. The effect of CO_2 plasticization does not seem to be large because of the low pressure and the crosslinked structure of the polymer. Consequently, the morphology change of the polymer should be taken into consideration. As mentioned above, the adsorption site is the free volume in the polymer and the free volume might be called microvoids because the free volume is frozen by the crosslinked structure. It is easily expected that there exists a distribution of microvoids in the crosslinked polymer and the mean size of the microvoids becomes smaller with the degree of crosslinking. This is because the microvoids are divided into small microvoids as the crosslinking reaction proceeds. The increment of the sorption amount is explained by the increment of the effective microvoids for CO_2 adsorption. If the size of the CO_2 is larger than the size of the microvoids for a high degree of crosslinking (*ca.*95%), the sorption amount decrease as shown in this study. The pore diameter seems to be of the order of nanometer. Other data supporting this interpretation is under investigation.

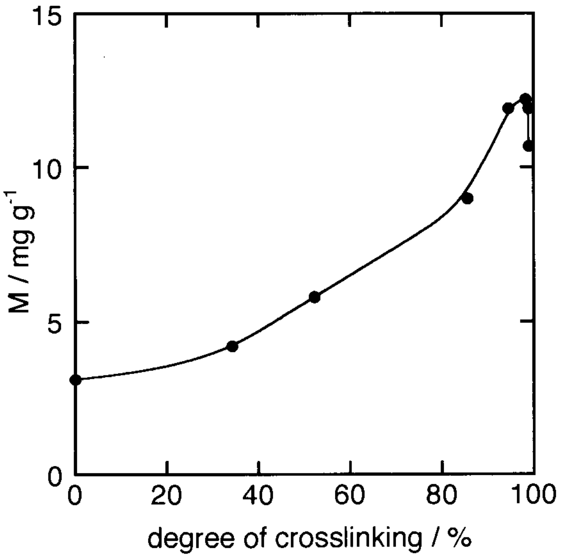

Figure 2. Effects of the degree of crosslinking on the CO_2 sorption ability of the photocrosslinked PVCA measured at p = 1.0 and 30 °C.

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