NOTE

Carbon-Dioxide-Induced Plasticization Effects in Solvent-Cast Polyethylene Membranes

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INTRODUCTION

Plasticizers are known to produce in polymers many subtle changes at the macro level, including increased softness and ductility, a lowering of the glass-transition temperature (T_g), and increased chain mobility.[1–10] It has been reported that carbon dioxide (CO_2) induces plasticization in certain glassy polymers due to its condensibility at certain pressures.[2–4] It is assumed that plasticization occurs when the polymer absorbs carbon dioxide to an extent that it increases the free volume of the polymer. The swelling of polymer matrix caused by the absorption of CO_2 enhances the segmental mobility, which in turn, increases the permeability of gases.[10] Sanders[3] studied the CO_2-induced changes in poly(ether sulfone) and observed a significant decrease in the T_g. Most of the reported studies on carbon-dioxide-induced plasticization effects were carried out on polymers with polar groups in either the main chain or a side chain. Based on the results, it was hypothesized that these polar groups interact with CO_2 and give rise to plasticization effects at high pressures.[2–4] The results were supported by the shift in the IR frequency of carbonyl groups as a result of CO_2 exposures and by NMR relaxation studies.[6–11] Also, CO_2 exposed poly-

(methyl methacrylate) showed increased intersegmental spacing by 0.18 Å as measured by wide angle x-ray diffraction (WADX).[7] Similar results were obtained for polycarbonate and cellulose acetate, and the increased segmental spacing resulted in the enhanced permeability of gases.[6–8] No definite trend however was noticed by Bos et al.[10] between the threshold gas pressure, which induces plasticization, and the chemical structure or the physical properties of the polymer. Also, no association was observed with respect to changes in T_g or fractional free volume and the CO_2 gas pressure.[10]

This article deals with the effect of CO_2 on the microhardness of solvent-cast polyethylene (PE) films. Microhardness is one of the important mechanical parameters that can offer direct information about changes in the morphology and microstructure of thermoplastics. These results were substantiated by Young's modulus, which is also sensitive to the segmental chain movement. As far as we are aware, data concerning the effect of CO_2-induced plasticization on microhardness and tensile modulus are still not available. The interaction of CO_2 with a nonpolar polymer resulted in a lowering of microhardness and Young's modulus.

EXPERIMENTAL

Film Preparation

Films (40μ thick) of low-density PE were prepared. We dissolved commercially available PE granules in tolu-
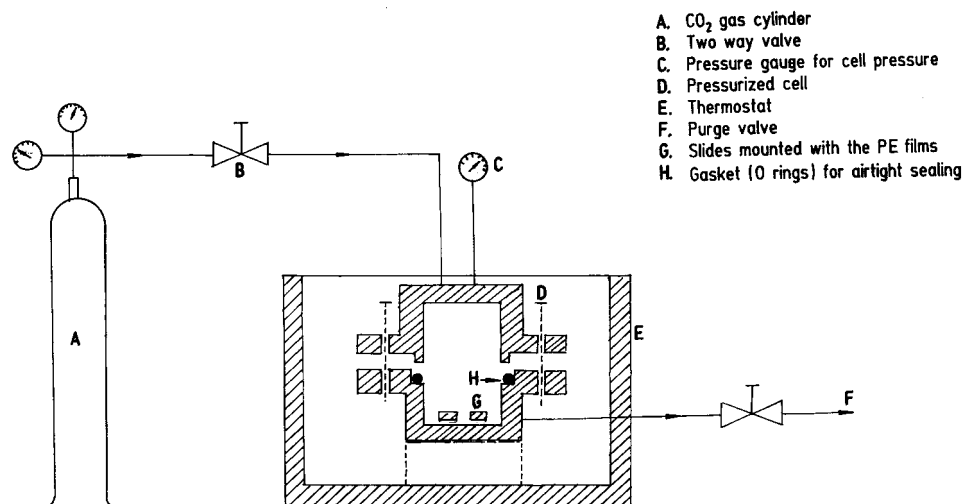
Figure 1   Arrangement for the pressure chamber.

ene at 100°C to prepare a 3% solution, and we cast the membranes by pouring the solution on a 24 × 24-cm glass plate in a vacuum oven at 100°C. The membranes were dried for 3 days at 95°C under vacuum before use. Films were free from any visible defects. The thickness of the films was measured at different places to ensure uniformity and was found to be 40 ± 2 μm.

Optical Microscopy

Films were examined in a polarized optical microscope (Leica DMLP, Germany) for the spherulitic pattern of the crystals and other structural details. The asymmetrical nature of the film was noticed, with one surface being smooth and shiny and the other being rough and dull.

Scanning Electron Microscopy

The surface relief of solvent-cast films was observed on a JSM-840 JEOL (Japan) scanning electron microscope at 5 kV after the surface was coated with a thin layer of gold in a JFC-1100 (Japan) sputter coating unit.

Carbon Dioxide Exposure

PE films were exposed to CO_2 (10 kg/cm^2) in a pressure chamber for 48 h at 27°C. All tests [Fourier transform infrared (FTIR) spectroscopy, microhardness, and tensile Modulus] were conducted within 30 min after the removal of films from the pressure chamber. Figure 1 depicts the arrangement of the pressure chamber. It consisted of a cell (D) that could be pressurized up to 15

kg/cm^2 by a CO_2 gas cylinder (A) with the help of a valve (B). The cell pressure could be monitored by a pressure gauge (C). The cell could be maintained at a fixed temperature by means of a thermostat (E). Specimens for microhardness tests were mounted on glass slides (G) and pressurized. For other tests, specimens were prepared and kept in a free state inside the chamber.

IR Spectra

The IR spectra of control and CO_2-exposed films were taken on a Nicolet-Impact 410 FTIR spectroscope (USA). The continuous line in Figure 2 represents the spectrum of a control PE film, and the dotted line represents that of a CO_2-exposed film.

Microhardness

Microhardness measurements were performed with a Carl–Zeiss Vickers microhardness tester (MPH-10) (Germany). The microhardness (H, kg/mm^2) values were derived from the residual projected impression with the equation $H = kp/d^2$, where d is the mean diagonal length of the indentation, p is the applied force in kg, and k is a geometrical factor equal to 1.854. A load of 1.25 g was used. A total of 10 readings each were taken for the exposed and control films. Load cycles of 15 s were used. Care was taken to mount the films in such a way that the shining surface faced the indentor.
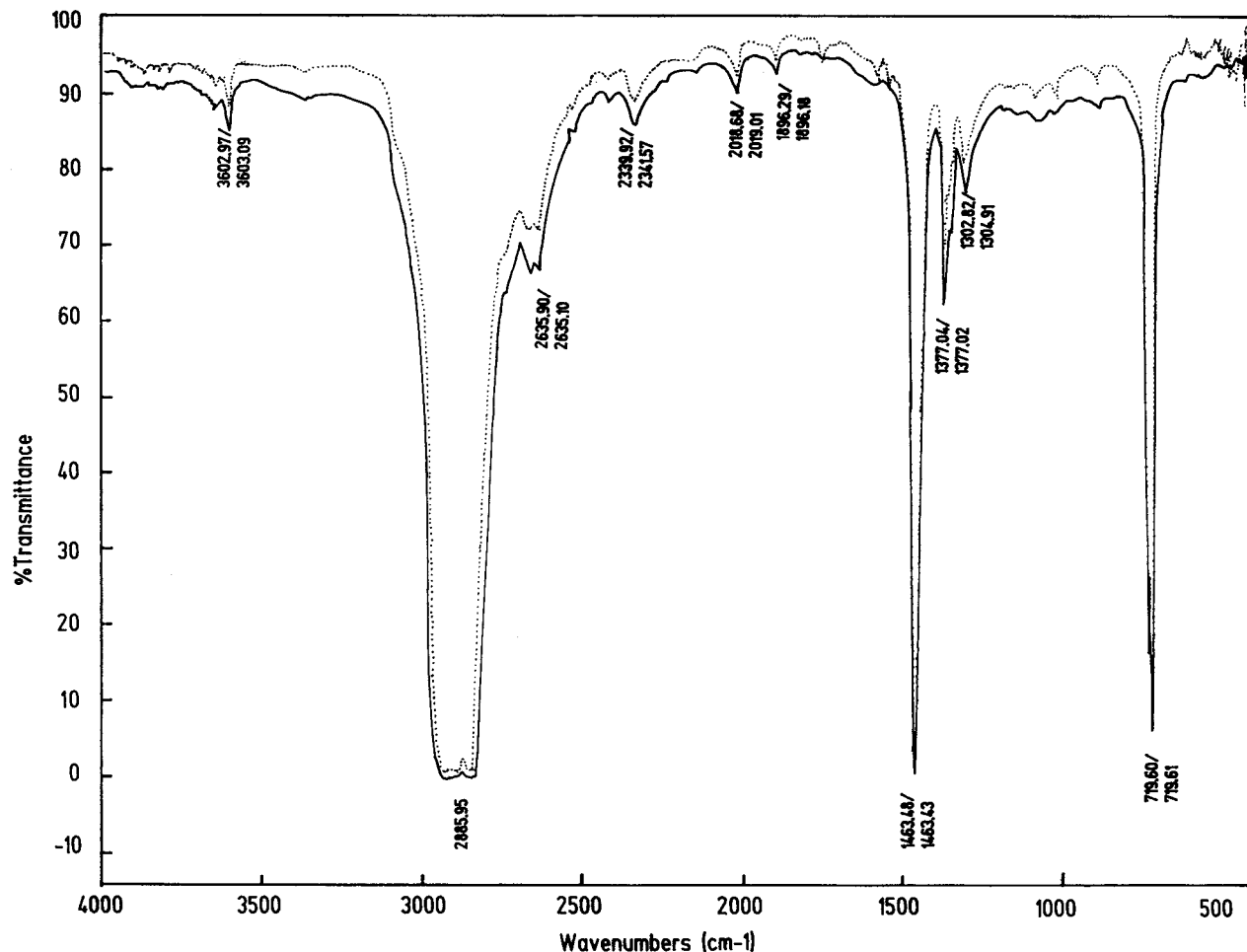
Figure 2 FTIR spectra of control (continuous line) and exposed (dotted line) film.

Tensile Modulus

Test specimens 100 mm in length and 10 mm in width were prepared from the films. The stress–strain curves were recorded with a Good-brand Testometric Micro 350 tensile tester (UK) with a crosshead speed of 150 mm/min.

RESULTS AND DISCUSSION

Table I presents the data on the Vickers microhardness of solvent-cast PE membranes before and after CO_2 exposure. The CO_2 exposed films showed reduced microhardness. The reduction in microhardness was statistically significant at a 95% confidence level from their corresponding control values except for in Experiment 4, where the variable (i.e., SD) in the control specimen was found to be on the higher side. However, the trend was consistent for the six experiments done at different times. The reduction in microhardness af-

ter the CO_2 exposure can be explained on the basis of a plasticization effect induced by carbon dioxide in polymeric membranes.[4–10] It is well known that a plasti-

Table I   Microhardness of Unexposed and CO_2-Exposed PE Films

	H [kg/mm^2 $\times$ 10^{-3} ($M \pm SD$)]	
Experiment Number	Unexposed Films	CO_2-Exposed Films
I	2.93 ± 0.08	1.94 ± 0.13
II	3.19 ± 0.10	2.18 ± 0.16
III	2.87 ± 0.06	1.69 ± 0.19
IV	3.80 ± 1.02	3.20 ± 0.09*
V	4.09 ± 0.92	3.26 ± 0.10
VI	3.94 ± 0.89	3.10 ± 0.12

$n = 10$. Values were significant at the 95% level except for the value marked by an asterisk (*). SD = standard deviation.

Table II   Mechanical Properties of Control and CO_2-Exposed PE Films

Sample	Tensile Strength (N/mm^2)	CV %	Elong at Break (%)	CV (%)	Modulus (N/mm^2)	CV %
Unexposed	0.75	16.0	4.65	17.8	2236	21.1
Exposed	0.50	20.0	5.10	22.0	2161	28.0
Unexposed	0.48	19.0	6.0	18.3	3025	13.3
Exposed	0.34	23.0	8.0	25.0	2614	22.8
Unexposed	0.65	19.5	7.9	18.0	2017	15.4
Exposed	0.42	22.0	10.0	25.6	1629	20.7

$n = 8$. cv = coefficient of variation.

cizer interacts with a glassy polymer in such a way that it increases the segmental chain mobility. Because the microhardness testing is a measure of elastic and plastic deformation caused by dislocation and slip movement as a result of imposed stress, it can be inferred that absorbed CO_2 helps in increasing the deformation as measured by microindentation. Structurally, the plasticizing molecules are physically absorbed at the interfaces of an amorphous structure that exists in the polymer and influence its mechanical properties.[10–14] The enhanced segmental chain motion due to plasticization effects has also been explained on the basis of increased free volume.[1,4–8] The data on microhardness quantified the plasticization effect in terms of reduced hardness of the film.

Table II presents tensile strength, elongation, and initial modulus values for control and CO_2-exposed films. The data show that after the exposure to an easily condensible gas with large molecules with low root mean square velocities, the tensile strength of the film was reduced, and there was a corresponding increase in elongation at break. Because of the solubility of the gas in the polymer matrix, chain mobility was enhanced, which helped the material to dissipate the applied stress in the form of increased extension. The initial modulus, an indication of resistance to change under tensile load, indicated that there was a reduction in the resistance offered by chain molecules to the applied stress. It is hypothesized that the absorbed carbon dioxide influenced the initial modulus. Although the effect was consistent, there appeared to be variation in the values of tensile strength, elongation, and initial modulus as indicated by a fairly large coefficient of variation. This could be due to subtle batch-to-batch variation in the structure during the film preparation. The other reason for the variation could be explained on the basis of the structure revealed by electron micrographs of the cast films. Figure 3 shows the lower smooth surface, whereas Figure 4 shows the upper surface, of the cast film with globular structure. There was a contiguous globular pattern forming a network structure with microholes in between. These structural variations could have influenced the load–elongation behavior, resulting in large variations. It is known that stress concentration increases substantially at discontinuities, microholes, and other structural irregularities under tensile loading.[16] All these will vary the load-distribution pattern of the chain molecules, resulting in a spectrum of tensile properties.

The FTIR spectra of the unexposed and CO_2 exposed membranes were identical and are shown in Figure 2. Before and after exposure to carbon dioxide, there was practically no shift in the absorption frequency for the CH_2 moiety (1463 cm^{-1}) and other characteristic frequencies for PE (CH— stretching at 2885 cm^{-1} and CH_2 rocking at 719 cm^{-1}). In the absence of any polar groups in the polymer chain, it may be inferred that the plasticization effect was physical in nature as the FTIR spectra ruled out the possibility of chemical interaction between the CO_2 moiety and ethylene molecules. The study substantiated that the plasticization was dependent on the physical state of the swollen glassy polymer network caused by absorbed CO_2. It was the number of CO_2 molecules sorbed that was important in causing plasticization and not its polar character.[10] The idea
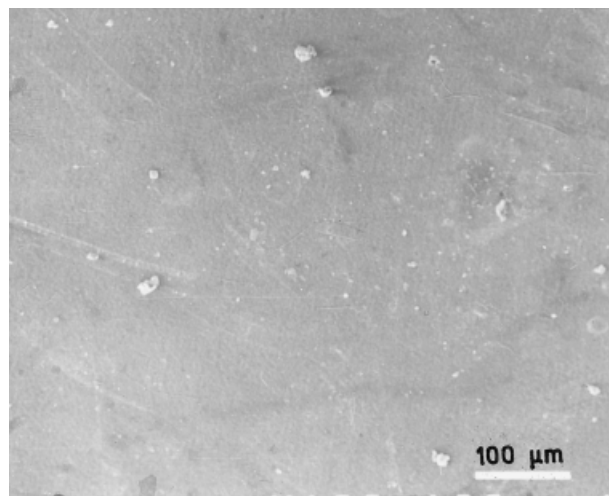

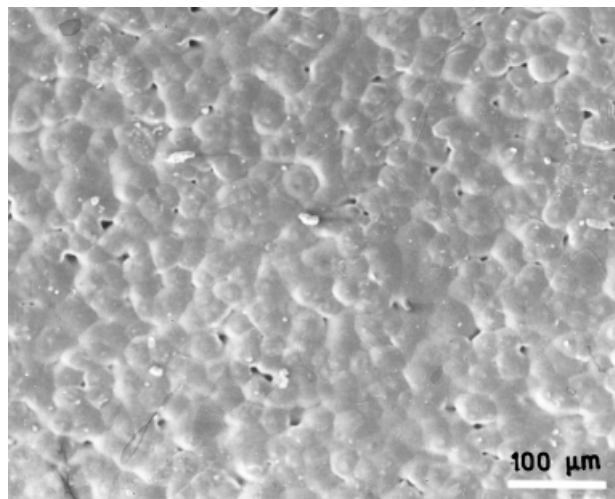**Figure 3** Scanning electron micrograph of smooth (lower) surface of PE film at 100× magnification.

Figure 4 Scanning electron micrograph of rough (upper) surface of PE film at 100× magnification.

was supported by the fact that inert gases such as argon also showed plasticization effects at elevated pressures.[17]

CONCLUSIONS

The study showed that at high pressures, carbon dioxide induces plasticization in PE, a nonpolar polymer. It altered the mechanical properties of the film indicated by reduced microhardness and tensile modulus. In the absence of a shift in the absorption frequency for CH_2, the FTIR results ruled out the possibility of any chemical interaction. Unlike most of the previous studies reported in literature, which have emphasized polar–polar interactions (polymer–gas interactions) for the observed plasticization effects, we hypothesize that the plasticization effect is physical in nature and is caused by the absorption of CO_2, leading to deterioration in mechanical properties, and that the effect may be reversible on a temporal scale.

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