Topic Area: **CMMSP**

Modification of Surface and Barrier Properties of Polyethylene Terepthalate and Polycarbonate Plastics by Ion Implantation

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Introduction

PET is used to produce a wide range of packaging for foods and beverages. Because oxygen can diffuse through it[1, 2, 3], PET is not suitable for fabrication of bottles for the storage of beer and red wine which are both degraded by oxygen. To store oxygen degradable foods for extended periods of time in PET packaging, oxygen diffusion through the PET must be prevented by incorporating a barrier layer or barrier polymer[1] into the PET matrix. We have begun a study of diffusion of light gases through samples of PET film that have been ion-implanted with aluminium and silicon ions to determine how dose level of these ions affects diffusion rate of helium and other gases through PET film.

Polycarbonate (PC) is used to produce plastic products that have high toughness, high optical clarity and good resistance to UV degradation. However, PC sheet scratches easily because it is relatively soft. If PC sheet can be surface hardened to achieve scratch resistance similar to that of Perspex, it could be used to replace products, such as aircraft windows, currently fabricated from Perspex with tougher products fabricated from PC. Ion-implantation is one method that can be used to increase surface hardness and decrease surface wear rate [4].

Experimental Work

30mm x 30mm square samples were cut from PET (SKYPET-BB resin from SK Chemical Co.), that had been injection-blow moulded into 0.32±0.02 mm thick film by Australian Consolidated Industries (ACI), and from PC (Lexan from GE Plastics) sheet of 8mm thickness. Various samples were implanted with aluminium & silicon ions using a Metal Vapour Vacuum Ion Source (MEVVA) with an accelerating voltage of 20kV to doses of 10^{16} – 5×10^{16} ions/cm^2 and with hydrogen and nitrogen ions in the Plasma Immersion Facility within the Division of Materials and Engineering Science at ANSTO to doses of 10^{17} – 10^{18} ions/cm^2.

The diffusion rate of He gas through each PET sample was determined by placing each sample in turn into a specially constructed vacuum/pressure cell (designated by C in figure 1) which was connected to the vacuum/pressure system of figure 1. O-rings formed the required vacuum/pressure seals with the PET film. A 1 torr MKS Instruments Baratron pressure head was connected to one side of the vacuum/pressure cell via a short section of vacuum line; the other side was connected to a cylinder of helium that was used to supply a constant He gas pressure during measurements.

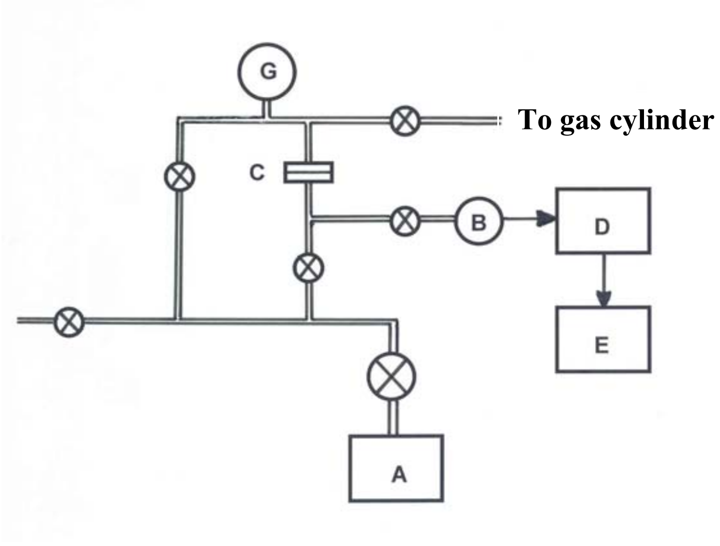

Figure 1. Schematic diagram of the vacuum system used for diffusion measurements.
A rotary pump, **B** Baratron head, **C** Plastic film cell, **D** Pressure gauge
E chart recorder, **G** pressure/vacuum gauge

The output voltage from the Baratron head was recorded on a chart recorder to give direct measurement of pressure rise on the low pressure side of the PET film as a function of time. After each sample was loaded into the sample cell the system was evacuated on both sides of the sample for one hour. All vacuum valves, except the one connected to the Baratron gauge head, were then closed and the initial leak/outgasing rate of the system was determined from the rate of rise of pressure measured by the Baratron gauge. The system was then evacuated and again all vacuum valves except the one connected to the Baratron head were closed. The He gas pressure in the line from the sample cell to the gas cylinder was adjusted to 0.5 atm pressure and maintained at this value. The rate of pressure rise on the low pressure side of the sample in the small volume of the system connected to the Baratron head was then recorded as a function of time. Initially the rate of pressure rise was the same as the leak/outgasing rate but after a period of 2 minutes there was a significant increase in rate of pressure rise as the He gas flowed through the PET film. After about 4 minutes the rate of pressure rise became linear. Rate of rise of He pressure was then determined from this equilibrium rate of pressure rise after 5 minutes from the start of the measurement period by subtracting the background leak/outgasing rate. These measurements were repeated consecutively at several pressures of He, in the order of increasing pressure, for each sample and then another determination of the background leak/outgasing rate was carried out.

The samples of Lexan were attached individually to the rotating circular table of a CSEM Pin-on-disc Tribometer using double sided adhesive tape. Wear testing was carried out on each Lexan sample for 1600 revolutions using a 6mm diameter ruby sphere with a 1N load and wear track speed of 0.10 m/s.

Results & discussion

Diffusion of He through PET

Results obtained at 292K for the unimplanted PET as well as samples implanted with aluminium and silicon are given in figure 2.

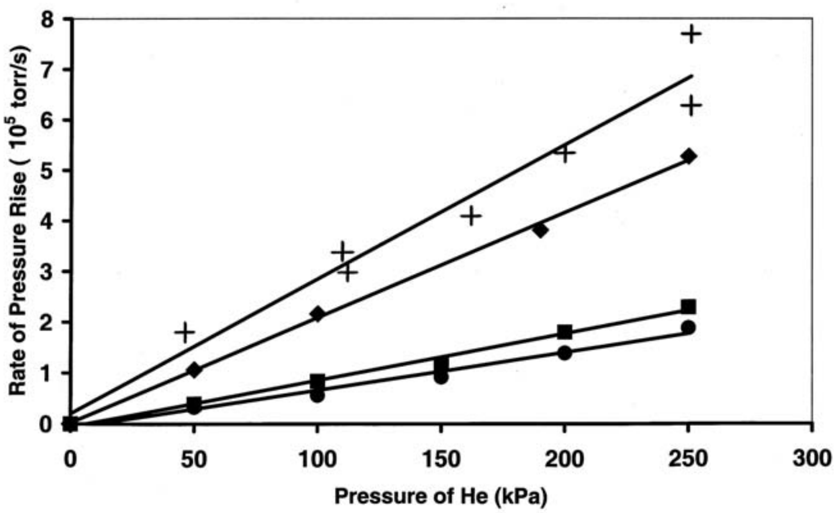

Figure 2: Rates of pressure rise vs He pressure for PET samples
+ unimplanted, ♦ 3x10^{16} Si ions/cm^2 , ■ 5x10^{16} Si ions/cm^2 ,
● 5x10^{16} aluminium ions/cm^2.

Some results obtained for rates of pressure rise and diffusion rates through unimplanted PET and samples of PET implanted with silicon and aluminium are given in Table 1. Diffusion rates at the pressures specified in Table 1 were calculated from the rates of increase of helium pressure using the ideal gas law. The cross sectional area of PET film through which diffusion could occur was a circle of diameter 15 ± 1 mm and therefore area $(1.77 \pm 0.12) \times 10^{-4}$ m^3. The volume of the section of vacuum line + Baratron Head into which helium was diffusing was estimated to be $(2.5 \pm 0.2) \times 10^{-6}$ m^3. Using $PV = nRT$ the number of atoms diffusing through unit area of the PET film per unit time, N_t , is given by

$$N_t \;=\; N_A \frac{V}{R\,T\,A} \frac{dP}{dt}$$

where N_A is Avogadro's number, R is the gas constant, T is the absolute temperature (292 K), A is the cross sectional area of PET film through which diffusion is occurring and V is the volume of the section of vacuum system into which helium is diffusing. dP/dt is the rate of helium pressure rise and is specified by each of the various points plotted in Figure 2.

Clearly, the results of figure 2 and Table 1 show that the diffusion rate of He through the implanted samples is considerably reduced from the diffusion rate through the unimplanted PET at the same differential pressure of He across the PET film. The PET samples changed from being completely transparent before implantation to pale brown after implantation indicating that deposition of Si & Aℓ ions was causing chemical bonding changes as well as filling up voids in the surface layers to reduce helium diffusion rates.

Table 1: Number of He atoms diffusing through 0.32mm thick PET sheet per m^2 per second (N_t) for various pressures of He & for various unimplanted and implanted samples.

PET SAMPLE	**Pressure of He** (± 2 kPa)	**Rate of Pressure Rise of He** (10^5 torr/s)	**N_t** 10^{-16} Atoms s^{-1}.m^{-2}
Unimplanted PET	112	2.99 ± 0.06	1.40 ± 0.24
Unimplanted PET	251	7.70 ± 0.12	3.61 ± 0.60
3x10^{16} Si ions cm^{-2}	100	2.16 ± 0.06	1.01 ± 0.18
3x10^{16} Si ions cm^{-2}	250	5.28 ± 0.11	2.47 ± 0.42
5x10^{16} Si ions cm^{-2}	100	0.84 ± 0.03	0.39 ± 0.07
5x10^{16} Si ions cm^{-2}	250	2.29 ± 0.05	1.07 ± 0.18
5x10^{16} Aℓ ions cm^{-2}	250	1.88 ± 0.04	0.88 ± 0.15

Wear testing of Lexan

The wear tracks produced in samples of Lexan implanted with silicon and aluminium (width at surface 300μm, depth 6μm) were similar to the wear tracks formed in unimplanted Lexan (width 200μm, depth 6μm). Much larger wear tracks with surface width 700μm and depth 10-15μm were formed in all nitrogen implanted samples. The wear tracks in the hydrogen implanted samples were much smaller than for the unimplanted samples. At lower hydrogen dose level (10^{17} ions/cm^2) the wear track was about 100μm in width at the surface with depth 3μm while the higher dose (10^{18} ions/cm^2) hydrogen implanted sample tested produced insignificant wear. For the H implanted samples the coefficient of dynamic friction, μ_k, dropped sharply from 0.27 at the beginning of wear testing to 0.20 and thereafter remained constant. For all other samples μ_k, rose steadily from 0.27 throughout the wear test.

Conclusions

Diffusion rates of helium gas through unimplanted PET film and through samples of PET film implanted with aluminium and silicon have been determined. The diffusion rates of helium through the ion implanted samples are significantly lower than the diffusion rates through the as supplied PET. Ion-implantation of hydrogen into Lexan sheet has been found to significantly reduce coefficient of dynamic friction and the surface wear rate of the Lexan in a standard Pin-on-disc wear test using a 6mm diameter ruby ball.

Acknowledgments

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