polymer communications

Oxygen enrichment on polymer surfaces measured by heavy ion elastic recoil detection

Alex Zounek, Jörg Kressler*, Eichi Arai and Takashi Inoue*†
*Nuclear Reactor Research Laboratory and *Department of Organic and Polymeric Materials, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152, Japan*
(Received 26 April 1993; revised 1 June 1993)

Using ^{35}Cl elastic recoil detection (ERD) analysis, oxygen enrichment was found on the surfaces of polystyrene and a random copolymer of styrene and acrylonitrile containing 38.7 wt% acrylonitrile. The samples were prepared in a hot press at 200°C between two silicon wafers in an air environment. The oxygen-rich layer on top of the samples was less than 20 nm thick. Heavy ion ERD seems to be a promising method to study the chemical composition of polymer surfaces and concentration profiles up to a depth of several hundred nanometres.

(Keywords: elastic recoil detection; surface; oxygen enrichment)

Introduction

There are basically two types of interesting information on polymeric surfaces: (i) the surface structure or roughness and (ii) the chemical composition. Several methods have been developed for the study of both[1]. A number of methods have been used to study the surface structure or roughness, such as light microscopy (phase measurement interference microscopy), electron microscopy (SEM) and contact angle measurements. To analyse the chemical composition of surfaces, such methods as secondary ion mass spectroscopy (s.i.m.s.), X-ray photoelectron spectroscopy (XPS) and infra-red attenuated total reflection (i.r.-a.t.r.) have been applied widely. These methods have a different lateral and depth resolution, respectively, therefore the chemical composition of the surfaces determined by different methods might differ significantly and should reflect the sample volume probed (lateral and depth). ^{4}He elastic recoil detection (ERD) has frequently been used to study the hydrogen and deuterium distribution in multilayer polymer specimens[2]. In this study ^{35}Cl ERD, which is frequently used to study inorganic materials[3], is applied to study the chemical composition on the surface of polystyrene (PS) and a random copolymer of styrene and acrylonitrile containing 38.7 wt% acrylonitrile (SAN-38.7). The samples were prepared in an air environment at 200°C. Heavy ion ERD has the great advantage that the distribution of such elements as nitrogen or oxygen can be studied very well up to a depth of about 300 nm.

Experimental

Materials. The PS (Denka-Styrol GP-1) had $M_w = 180\,000\ g\ mol^{-1}$ and a polydispersity of 2.0. The M_w value of SAN-38.7 (Mitsubishi Monsanto) was $74\,000\ g\ mol^{-1}$ and the polydispersity was 2.2.

Sample preparation. A polymer plate with a thickness of about 0.5 mm was prepared in a hot press at 200°C between two silicon wafers in an air environment. The polymers were molten for 10 min without pressure and were then annealed for 3 min with a pressure of $50\ kg\ cm^{-2}$.

Elastic recoil detection. $^{35}Cl^{7+}$ ions were accelerated by the Tokyo Institute of Technology 5 SDH-2 Tandem with an accelerating voltage of 1.7 MeV[4]. Thus the final energy of the ions was 13.6 MeV. The monoenergetic ion beam was collimated to a size of about $2\ mm^2$. The incident angle to the surface and the detection angle were both 11°. The atomic species were identified using a time-of-flight (TOF) detector and a surface barrier detector[4]. The concentration profile of oxygen was obtained using a program developed by Bachman[5]. The sample was divided into virtual slabs, each corresponding to a certain energy interval of the different recoils. The atomic concentration was then calculated directly from recoil yields.

Results and discussion

Figure 1 shows the contour plot for the SAN-38.7 sample. Six ridges can be clearly distinguished: ^{1}H, ^{12}C, ^{13}C, ^{14}N, ^{16}O and ^{35}Cl. The ^{35}Cl ridge is caused by scattered primary ions and does not belong to the sample. The recoiled species with the highest energy originate from the surface of the sample and the species with lower energy come from deeper regions. Thus the chemical composition of the sample can be obtained as a function of depth. Oxygen is distributed over the whole sample, i.e. from the surface down to approximately 300 nm (the limit of accurate measurements under the conditions applied). The oxygen in the bulk phase might be due to a number of substances present as impurities, initiator fragments or stabilizers. But there is a clear enrichment of oxygen on the surface, as shown in *Figure 2*. The

† To whom correspondence should be addressed

0032-3861/93/183948-03

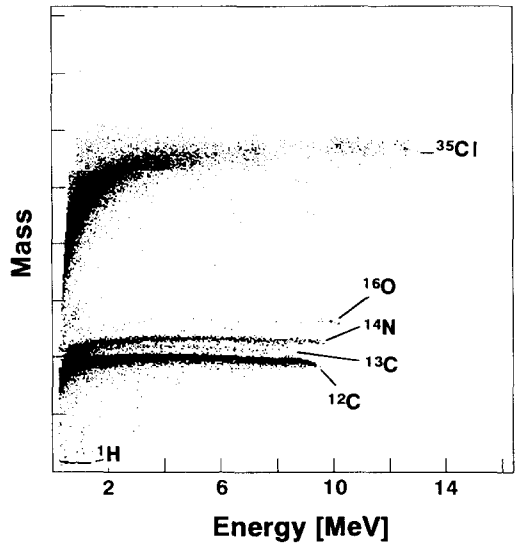

Figure 1 Contour plot obtained by ^{35}Cl ERD for the SAN-38.7 sample

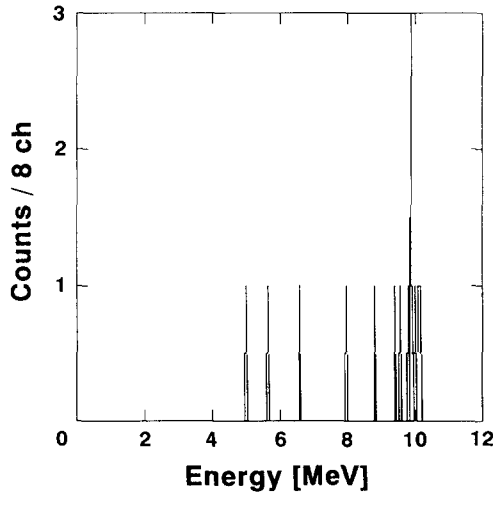

Figure 2 Energy spectrum of oxygen recoils from the SAN-38.7 sample (the counts of eight adjacent channels were summed)

spectrum was analysed in the range from about 4 to 10 MeV. In deeper regions the resolution is not accurate enough for quantitative evaluation due to chance coincidences in the experimental set-up[6]. This oxygen spectrum can be converted into a concentration profile[5]. The concentration profile of oxygen, shown in *Figure 3*, indicates an oxygen peak at the surface with a full width at half maximum (*FWHM*) of approximately 20 nm.

This value is an upper limit for the thickness of the oxygen-rich layer. Several factors must be taken into account for estimation of the true thickness. This ERD measurement has a depth resolution of approximately 10 nm at the surface[7], which leads to an apparent broadening of the real surface. Furthermore, the statistics must be improved for an exact evaluation of the layer thickness. Therefore, the experimental set-up has to be optimized because the application of heavy ion ERD for polymeric systems is connected with a subtle balance between the goal to achieve good statistics and destruction of the sample by high ion doses[7]. In conclusion, it cannot be excluded that the real thickness of the oxygen layer is much smaller than 20 nm.

Figure 4 shows a contour plot of the PS sample. Five ridges can be identified, belonging to the isotopes ^{1}H, ^{12}C, ^{13}C, ^{16}O and ^{35}Cl. Again, oxygen enrichment at the surface can be observed. The concentration profile of oxygen (cf. *Figure 5*) gives approximately the same *FWHM*.

Oxygen enrichment on polymeric surfaces has been detected by various methods. For example, Rånby[8] observed surface oxidation of acrylonitrile–butadiene–styrene plastics after ageing in an air environment by i.r. spectroscopy. The oxidation led to the formation of –OH, –CHO, >C=O, –C–O–O and –COOH groups. Partial oxidation of polymers or strongly adsorbed water might also be reasons for the surface oxygen detected by ERD in this study. Furthermore, it is known that low-molecular weight stabilizers or processing aids, which may contain oxygen, are frequently found enriched on polymeric surfaces[9].

Heavy ion ERD is a new method for detecting chemical changes at surfaces, and has the great advantage that a depth distribution can be obtained simultaneously. However, further studies are necessary for a quantitative

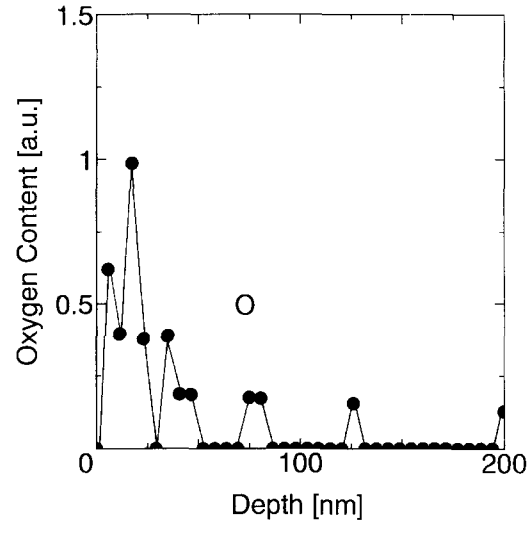

Figure 3 Concentration profile of oxygen in the SAN-38.7 sample calculated up to a depth of 200 nm

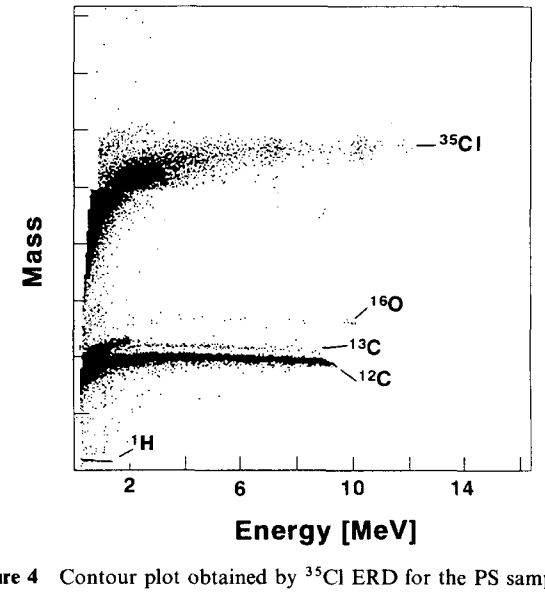

Figure 4 Contour plot obtained by ^{35}Cl ERD for the PS sample

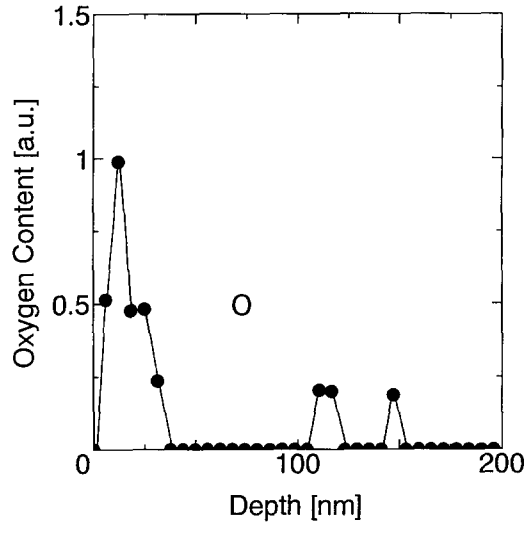

Figure 5 Concentration profile of oxygen in the PS sample calculated up to a depth of 200 nm

evaluation of the results, because the depth resolution at the surface and the detection efficiency have a very sensitive influence on the results, especially in the case of thin films less than 10 nm, and small proportions of elements (< 1%) present in the sample. Heavy ion ERD is not able to provide any information on the chemical species that might be formed during oxidation at the surfaces or during diffusion of low-molecular weight components towards the surface. Therefore, it would be useful to connect the ERD measurements with other highly sensitive methods that provide information on the chemistry of surfaces, such as TOF-SIMS[10] or i.r.-a.t.r.[11].

Acknowledgements

J. K. thanks the Japan Society for Promotion of Science for supporting his stay at TIT and the Humboldt Foundation for kind help.

References

1 Stamm, M. *Adv. Polym. Sci.* 1992, **100**, 357
2 Sokolov, J., Rafailovich, M. H., Jones, R. A. L. and Kramer, E. *J. Appl. Phys. Lett.* 1989, **54**, 590
3 L'Ecuyer, J., Brassard, C., Cardinal, C., Chabbal, J., Deschenes, L., Labrie, J. P., Terrault, B., Martel, J. G. and St.-Jaques, R. *J. Appl. Phys.* 1976, **47**, 881
4 Arai, F., Funaki, H., Katayama, M., Oguri, Y. and Shimizu, K. *Nucl. Instr. Meth.* 1992, **B64**, 296
5 Bachmann, M. Diploma Thesis, J. W. Goethe Universität, Frankfurt, 1991
6 Arai, E., Funaki, H., Katayama, M. and Shimizu, K. *Nucl. Instr. Meth.* 1992, **B68**, 202
7 Kressler, J., Zounek, A., Arai, E., Higashida, N., Sekino, M. and Inoue, T. *Macromolecules* submitted
8 Rånby, B. 'Polymer Surfaces' (Eds D. T. Clark and J. W. Feast), Wiley, Chichester, 1987, p. 381
9 Menzel, G. 'Plastic Additives' (Eds R. Gächter and H. Müller), Hanser, Munich, 1987, p. 715
10 Niehuis, E., van Velzen, P. N. T., Lub, J., Heller, T. and Benninghoven, A. *Surf. Interface Anal.* 1989, **14**, 135
11 Willis, H. A. and Zichy, V. J. I. 'Polymer Surfaces' (Eds D. T. Clark and J. W. Feast), Wiley, Chichester, 1987, p. 287