AD-A114 012 AIR FORCE WRIGHT AERONAUTICAL LABS WRIGHT-PATTERSON AFB OH F/G 20/7
ION BEAM METHODS FOR THE SURFACE CHARACTERIZATION OF POLYMERS.(U)
FEB 82 W L BAUN
UNCLASSIFIED AFWAL-TR-81-4169 NL

1 OF 1
AD A
114012

END
DATE
FILMED
05-82
DTIC

AD A114012

AFWAL-TR-81-4169

ION BEAM METHODS FOR THE SURFACE CHARACTERIZATION OF POLYMERS

WILLIAM L. BAUN

MECHANICS AND SURFACE INTERACTIONS BRANCH
NONMETALLIC MATERIALS DIVISION

February 1982

Final Report for period January 1981 to July 1981

Approved for public release; distribution unlimited.

DTIC FILE COPY

MATERIALS LABORATORY
AIR FORCE WRIGHT AERONAUTICAL LABORATORIES
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433

DTIC
ELECTE
APR 30 1982
S D
D

82 04 30 019

NOTICE

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

This report has been reviewed by the Office of Public Affairs (ASD/PA) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.

WILLIAM L. BAUN, Project Engineer
Mechanics & Surface Interactions Branch
Nonmetallic Materials Division

S. W. TSAI, Chief
Mechanics & Surface Interactions Branch
Nonmetallic Materials Division

FOR THE COMMANDER

F. D. CHERRY, Chief
Nonmetallic Materials Division

"If your address has changed, if you wish to be removed from our mailing list, or if the addressee is no longer employed by your organization please notify AFWAL/MLBM, W-PAFB, Ohio 45433 to help us maintain a current mailing list.

Copies of this report should not be returned unless return is required by security considerations, contractual obligations, or notice on a specific document.

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER AFWAL-TR-81-4169	2. GOVT ACCESSION NO. AD-A114 012	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) ION BEAM METHODS FOR THE SURFACE CHARACTERIZATION OF POLYMERS		5. TYPE OF REPORT & PERIOD COVERED Internal Jan 1981 to July 1981
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) William L. Baun		8. CONTRACT OR GRANT NUMBER(s) In-House Report
9. PERFORMING ORGANIZATION NAME AND ADDRESS Materials Laboratory Air Force Systems Command Wright-Patterson AFB, OH 45433		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS Project 2303 Task 2303Q108 WUD #50
11. CONTROLLING OFFICE NAME AND ADDRESS Materials Laboratory (AFWAL/MLBM) Air Force Wright Aeronautical Laboratories Wright-Patterson AFB, OH 45433		12. REPORT DATE February 1982
		13. NUMBER OF PAGES 44
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public distribution; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Polymers, Surface Characterization, Ion Beam Methods, Ion Scattering Spectrometry (ISS), Secondary Ion Mass Spectrometry (SIMS).

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Ion beam methods of surface characterization have not been applied extensively to polymers and other organic materials, but would appear to be very useful for these materials. Applications of high energy ion beam methods would seem to be limited except for specific cases but low energy methods such as ion scattering spectrometry (ISS) and secondary ion mass spectrometry (SIMS) should have numerous uses with polymeric materials. ISS is a true surface method which determines elemental composition at the first monolayer, but tells little about how the elements are combined. SIMS has high sensitivity for many elements, and

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

has the capability of determining something of the molecular structure near the surface. Both ISS and SIMS, as well as high energy methods, give elemental composition with depth. These surface spectroscopies are useful in many areas of polymer technology including synthesis, extrusion and forming, and long time durability and stability under thermal and electromagnetic radiation.

FOREWARD

This technical report was prepared by W. L. Baun of the Mechanics and Surface Interactions Branch, Nonmetallic Materials Division, Materials Laboratory, AFWAL. The work was initiated under Project 2303 "Surface Phenomena" and WUD #50 "Surface and Interface Properties" monitored by Dr. T. W. Haas.

This report covers work done in-house during the period Jan 1981 and July 1981. It covers, in part, invited material presented at the International Union of Pure and Applied Chemistry Meeting on Polymer Degradation held at Durham University, Durham, England, in July 1981.

The author thanks Dr. W. J. Feast and D. Clark, Chemistry Department, Durham University, for providing the opportunity to discuss developments in polymer characterization using ion beam methods.

Accession For
NTIS GRA&I ☒
DTIC TAB ☐
Unannounced ☐
Justification
By
Distribution/
Availability Codes
Dist | Avail and/or Special
A

DTIC COPY INSPECTED 2

BLANK PAGE

TABLE OF CONTENTS

SECTION		PAGE
I	INTRODUCTION	1
II	PRINCIPLES AND PROCEDURES	3
III	INFORMATION OBTAINED BY THESE TECHNIQUES	9
IV	SPECIMEN CHARGING	12
V	APPLICATIONS	14
VI	SUMMARY	19
	REFERENCES	36

LIST OF ILLUSTRATIONS

FIGURE		PAGE
1	Experimental Set-Up for Ion Scattering Spectrometry	20
2	Ion Scattering Spectrum Using $^3He^+$ for Teflon	21
3	Diagram Showing Interactions of a Low Energy Ion in a Solid (Ref. 10)	22
4	Simple Block Diagram Showing Components of a SIMS System	23
5	Diagram of Equipment for SIMS (Ref. 13)	24
6	Charge Compensation in a SIMS Instrument (Ref. 19)	25
7	SIMS Data in Mass Range 160-330 from Teflon Using Charge Neutralization (Ref. 19)	26
8	(a) ISS/SIMS Data for Polypropylene Using $^3He^+$ at 2500 eV. (b) ISS/SIMS Data for Polypropylene Exposed to Low Pressure Mercury Discharge Lamp, Same Conditions as in (a)	27
9	ISS/SIMS Data for Polyethylene, Using $^3He^+$ at 2500 eV	28
10	ISS/SIMS Data for Graphite Using $^3He^+$ at 2500 eV	29
11	Low Energy Ion Scattering Spectrum (2000eV) from PVC (Ref. 6)	30
12	Secondary Ion Mass Spectra from Commercial Two-Part Epoxy Cured at Room Temperature and at 250 °F	31
13	ISS/SIMS Data from Adhesive Side of Failure Surface from Adhesive Bonded Test Specimen	32
14	Positive and Negative SIMS Data for Phenylalanylglycine on Ag Using Argon Primary Ion at 2.25 KeV	33
15	Positive and Negative SIMS Data for Ascorbic Acid (Vitamin C) on Ag (Ref. 31)	34
16	Positive SIMS Data for (a) Polyphenyl Methacrylate and (b) Poly(cyclohexyl) Methacrylate (Ref. 4)	35

LIST OF TABLES

TABLE		PAGE
1	Effect of Ion Impact on a Solid Surface Including Emission Processes and Changes in the Surface Zone (Ref. 9)	5
2	Main Features of SIMS as a Surface Analysis Method (Ref. 9)	7
3	Comparison of Ion Spectroscopies	9
4	Types of Interferences and Typical Examples (Ref. 17)	11
5	Work Function of Polymers (Ref. 18)	12
6	Methods of Change Neutralization (Ref. 17)	12
7	Polymers Studied by Ion Scattering (Ref. 6)	16
8	Potential Materials Application of Surface Analysis Methods	18

BLANK PAGE

SECTION I

INTRODUCTION

Surface molecular structure and elemental composition of polymers have been largely ignored, even though the number of surface sensitive techniques has increased rapidly during the past few years. There are probably two main reasons that surface analysis methods have been applied extensively to metals and alloys but only to a limited degree to polymers and other organic materials. Most surface analysis methods are carried out in very clean ultrahigh vacuum systems which may be contaminated by organic materials. Even just the possibility of contamination usually keeps the organic material outside the vacuum system. The other main obstacle to surface characterization of organic materials is that they are usually very good insulators. When these materials are bombarded with ions, electrons or x-rays, the usual surface probes, they build up a charge which can confuse the interpretation of data or even make it impossible to obtain spectra. There are various compensation methods which will be described, but charging still remains a problem.

Previously surface analysis of polymers have been limited essentially to the use of x-ray photoelectron spectrometry (XPS) (Ref. 1,2). Such an example is the study of the effect of an oxygen plasma treatment on the adhesion of metal films on polymers (Ref. 3). These studies provide elemental and chemical combination data obtained from core level photoemission spectra. However, as pointed out by Gardella and Hercules (Ref. 4), "The technique is not readily exploited for most polymers since the chemical states of carbon, oxygen and silicon, typical of most polymer systems, chemical shifts". Further, they suggest that photoelectron escape depth is sufficient to cause averaging from several atom layers, approaching bulk results. For these reasons it is of interest

to explore alternative methods of surface analysis for polymers. One such method is secondary ion mass spectrometry (SIMS), which has been shown to provide analysis predominantly from the outer one or two atomic layers, but which has been applied only sparingly to polymer surfaces (Ref. 4, 5). Ion Scattering Spectrometry (ISS) probes only the outermost surface layer and has been applied to polymers only once to date insofar as is known (Ref. 6).

SECTION II

PRINCIPLES AND PROCEDURES

a. Ion Scattering Spectrometry (ISS)

Use of low energy backscattered ions to characterize a surface is a relatively recent development. The method has been reviewed by Buck (Ref. 7). High energy ions had been used in the past to analyze surfaces but it was not until Smith (Ref. 8) used low energy (1 KeV) noble gas ions to probe the surface of a variety of materials that the technique came into popular use. It was found from this work and others that when the energy of ions was lowered the scattered ion spectra became simpler and sharper and event from a single surface atom. Therefore, the energy E_1 retained by an ion of mass, M_{ion} with an incident energy E_0 after scattering from an atom of mass M_{atom} through an angle θ is given by Equation 1 which is based on the conservation of kinetic energy and momentum (here M_{ion} is smaller than M_{atom}).

$$\frac{E_1}{E_0} = \frac{M_{ion}^2}{(M_{ion} + M_{atom})^2} \left\{ \cos\theta + \left[\frac{M_{atom}^2}{M_{ion}^2} - \sin^2\theta \right]^{\frac{1}{2}} \right\}^2 \qquad (1)$$

For 90° scattering which is frequently used this reduces to a very simple relationship:

$$E_1/E_0 = (M_{atom} - M_{ion})/(M_{atom} + M_{ion}).$$

The experimental setup for 90° scattering instruments is shown in Figure 1A and is representative of original commercial instrumentation (3M Company, St. Paul, Minnesota) which used a 127° electrostatic analyzer. A great improvement in sensitivity was gained by the development of a cylindrical mirror analyzer (CMA) substituted for the original electrostatic sector as shown in Fig. 1B.

The geometry of the CMA results in a scattering angle near 138°. The major advantage of low energy ion scattering is the extremely fine surface selectivity when low energy ions collide with the surface atom. The probability for neutralization is very high because of the long residence time (10^{-14} to 10^{-16} sec.). Only about one in 10^3 of the scattered particles retain a positive charge even after one collision. Therefore, the probability that an ion is still in the charged state after two or more collisions is very small. Since the detector responds only to charged particles, contributions from particles which scatter more than once are almost certainly neutral and not counted by an ion detector. These facts suggest that an instrument using time-of-flight methods to detect either ions or neutrals would be extremely useful. An inherent feature of ion scattering which may be considered an advantage is the simultaneous sputtering of the surface as energy is transferred to the surface atoms from the ion beam. It is an advantage in that the concentration of the various atomic species may be followed with depth. On the other hand it is a disadvantage because damage is being produced by the sputtering. Once the atom sputters from the surface the sample is changed, and an exact experiment on that spot may not be repeated. However, ion current density may be kept very low by rastering the beam over a large area, thus minimizing surface damage. One positive feature of ion scattering compared to most other spectroscopies is the simplicity of the spectra. Binary ion scattering results in one peak for each isotope of an element present. For instance the scattering of helium from teflon in Fig. 2 results in the appearance of only two peaks in the spectrum, one for carbon and one for fluorine. Each peak is very sensitive to the amount present but absolute quantitative analyses can be difficult since the scattered yield depends on scattering cross section and neutralization efficiency, neither of which is well known for most elements. During the ion scattering experiment atoms are sputtered from the surface,

allowing depth profiling analysis from the removal of the surface layers by the probe ion. Use of helium ions gives a very slow rate of surface removal. Neon and argon provide much higher sputtering rates or the ion beam may be focused and rastered on the surface to reduce sputtering while the signal is gated from the center of the crater to minimize crater edge effects. The signal may be collected and imaged from the surface using the rastered beam to give a lateral analysis of the surface. Therefore ion scattering provides a combination of indepth analyses and lateral analyses to give a three-dimensional picture of the chemical makeup of the surface.

b. Secondary Ion Mass Spectrometry (SIMS)

When a low energy ion strikes the solid surface it undergoes a number of interactions which are outlined in Table 1 (Ref. 9) and illustrated in Fig. 3 (Ref. 10).

TABLE 1.

EFFECT OF ION IMPACT ON A SOLID SURFACE INCLUDING EMISSION PROCESSES AND CHANGES IN THE SURFACE ZONE (Ref. 9)

EMISSION PROCESSES	CHANGES IN THE SURFACE OF THE TARGET
Atomic and molecular particles	Loss of surface particles
Neutrals	Sputtering
Positive ions	Recoil implantation
Negative ions	
Excited particles	Implantation
Electrons	Primary ions
	Surface atoms (recoil)
Surface processes (Auger de-excitations, e.g.)	Lattice destruction
Bulk processes (ionization, e.g.)	
	Imperfections
Photons	Amorphization
Gas phase processes	Chemical effects
Surface processes	
Bulk processes	Breaking of bonds
	Bond formation

The process under consideration here is process #5 as seen in Figure 3 (the reflected ion giving energy to the surface atom which is sputtered). The sputtered species which are removed from the surface are made up of both positive and negative ions as well as neutral particles. Neutral particles have much more abundance than ionic species and have also been used for surface analysis. Surface analysis by SIMS falls into two categories, low current density sputtering and high current density sputtering. Categories are determined by the characteristics of the primary ion beam. A low current density sputtering analysis results in a very small fraction of the surface being disturbed, a result that approaches a basic requirement of a true surface analysis method. This is generally known as the Static SIMS (SSIMS) method. High current density sputtering removes more material and is required for preparing elemental depth profiles. In the high current density method, changes are seen in the surface and near surface regions. Table 2 shows the main features of SIMS as a surface analysis method (Ref. 9). Of the positive attributes listed probably the extremely high sensitivity for many elements is the greatest advantage of SIMS. On the other hand, the large differences in sensitivity for different surface structures and chemical combination is the largest negative factor involved in SIMS analyses. Isotopic identification and the sensitivity to hydrogen are two other important uses of the SIMS method. These advantages and disadvantages are reviewed by Werner (Ref. 11) and quantitative aspects are discussed by the same author (Ref. 12).

TABLE 2.

MAIN FEATURES OF SIMS AS A SURFACE ANALYSIS METHOD (REF. 9)

Positive	- Information depth in the "monolayer range"
	- Detection of all elements including hydrogen
	- Detection of chemical compounds
	- "Lateral resolution" in the range of atomic distances
	- Isotope separation
	- Extremely high sensitivity for many elements and compounds ($<10^{-6}$ monolayers)
	- Quantitative analysis after calibration
	- Negligible destruction of the surface (SSIMS)
	- Elemental profiling (Dynamic SIMS)
Negative	- Large differences in sensitivity for different "surface structures" (factor 1000)
	- Problems in quantitative interpretation of molecular spectra
	- Ion induced surface reactions

Equipment for SIMS may be as simple as that shown in Fig. 4 or as complex as the ion microprobe. In a simple system a SIMS experiment required a vacuum chamber to house the experiment, a sample holder, an ion source, an energy analyzer and a mass analyzer. In such simple systems the noble or reactive gas fills the system and the entire chamber including the ion gun and sample area are at approximately 1-5 x 10^{-5} torr.

A more complicated type of instrument seen in Fig. 5 is one in which the performance is improved through the use of a differentially pumped vacuum system to produce ultra high vacuum in the vicinity of the sample.

This also allows the entry of a reactive gas in the sample chamber area while sputtering with a noble ion for studying chemical changes or reactions of the surface. Still another improvement and added complexity may be made to the SIMS instrument by the mass analysis of the primary beam. The energy filter is generally made up of several elements whose function is to optimize collection of the secondary ions and to filter and focus the ions at the entrance to the mass analyzer. The mass analyzer in simple systems is usually a quadrupole filter. Colton and coworkers (Ref. 14) show equipment using a quadrupole filter capable of detecting mass species at more than 5000 amu. It is recognized that SIMS has been used successfully as a stand-alone technique to solve and to perform surface physics research (see review by Colton, Ref. 15). However, it appears that the area of greatest use of SIMS thus far is as a complement to other surface characterization methods. The extremely high sensitivity for some elements can be taken advantage of by using SIMS with other techniques in which these elements do not show high sensitivity. The SIMS technique is also ideal to use with fundamentally low resolution methods such as ion scattering, and to separate and identify the adjacent masses which may be present at the sample surface. The most popular combination of instruments used thus far has been ISS-SIMS and AES-SIMS. SIMS has also been used on scanning electron microscopes, allowing high quality imaging along with lateral and depth analysis of the sample.

SECTION III

INFORMATION OBTAINED BY THESE TECHNIQUES

The two ion beam techniques most popularly used for true surface analysis are Ion Scattering Spectrometry and Secondary Ion Mass Spectrometry. Both of these techniques have certain capabilities and limitations. These features are summarized in Table 3 (Ref. 16).

TABLE 3.

COMPARISON OF ION SPECTROSCOPIES

Parameter	Ion Scattering Spectrometry (ISS)	Secondary Ion Mass Spectrometry (SIMS)
Principle	elastic binary collision with surface ion	sputtering of surface atoms by ion beam
Probe	~1 to 3 keV ions	~1 to 3 keV ions
Signal	ion current versus energy	ion current versus mass
Applicable elements	$Z \geq 3$	all (if possible and negative SIMS)
Surface sensitivity	high	variable
Elemental profiling	yes	yes
Image-spatial analysis	yes	yes
Spectral shift	possible, but generally no	no
Information of chemical combinations	yes, in fine features but generally no, especially polymers	in some cases (fingerprint spectra)
Quantitative analysis	yes	maybe with similar standards
Influence of operating conditions and matrix	no	yes
Isotopic analysis	yes, in principle but generally no because of resolution limits	yes
Beam induced surface changes	yes, sputtering damage (minimal with low fluence)	yes, sputtering damage (minimal in "static" mode)

These two techniques may be applied in a gentle manner as described earlier using a near static ion beam to produce little change in the surface and also in a mode in which chemical profiling with depth is possible. ISS can detect all of the elements heavier than helium in the periodic table. The sensitivity variation across the periodic table is probably less than one order of magnitude. SIMS provides a distinct advantage of being able to analyze, in principle, all of the elements in the periodic table. Being able to identify isotopes is a definite advantage. The sensitivity of the SIMS technique can vary several orders of magnitude (perhaps up to 10^4) due to a rapidly changing secondary ion yield caused by matrix and chemical effects. The ability of ion scattering to resolve different elements in a complete unknown is at times somewhat limited. There are few intrinsic limitations or spectral interferences but the technique is fundamentally a low resolution technique in which there may be some uncertainty as to the exact identity of a given line. Specificity may be improved by going to a scattering ion closer to the mass of the unknown element, that is, we would use helium for the light elements usually found in polymers, neon for intermediate mass elements, and argon for the heavy elements.

Ion scattering gives very little information on the chemical combination of the element detected in the sample, however, recently discovered yield variations and the use of other fine features in the spectrum give some possibility of using ion scattering to determine chemical species at the surface but probably not in polymers. The appearance of cluster ions in the secondary ion mass spectrum gives a good possibility of using SIMS to determine chemical combinations and deduce molecular structure in polymers. The interpretation of such spectra is extremely complicated and has to be treated with a great deal of care. Molecular ions can be dislodged from

the surface and give some idea of the chemical combination, but molecular complexes may also be synthesized at the sample surface in the gas phase above the sample surface. The presence of such ions in the mass spectrum does not unequivically prove the presence of such species in or on the sample itself. Sufficient resolution in the mass spectrum is often required to separate species occurring at the same nominal mass number. Some of these interferring species are shown in Table 4 (Ref. 17 from unpublished data of Evans).

TABLE 4.

TYPES OF INTERFERENCES AND TYPICAL EXAMPLES (REF. 17)

Interference type	Interfering ion	Analyt. ion	Required resolution
Multiply charged	$^{28}Si^{2+}$	$^{14}N^{+}$	950
Matrix ion	$^{62}Ni^{2+}$	$^{31}P^{+}$	3200
Matrix selfpolymers	$^{16}O_2^{+}$	$^{32}S^{+}$	1800
ions	$^{28}Si_2^{+}$	$^{56}Fe^{+}$	2950
Prim. ion-matrix	Cu_3O^{+}	$^{207}Pb^{+}$	1050
molecular ions	Si_2O^{+}	$^{75}As^{+}$	3250
	AlO_2^{+}	$^{59}Co^{+}$	1500
Hydride ions	$^{30}SiH^{+}$	$^{31}P^{+}$	4000
	FeH^{+}	$^{55}Mn^{+}$	3300
	SnH^{+}	$^{121}Sb^{+}$	19500
Hydrocarbon ions	$C_2H_3^{+}$	$^{27}Al^{+}$	650
	C_2H_3	$^{63}Cu^{+}$	650
	C_2H_2	CN	2000

SECTION IV

SPECIMEN CHARGING

A serious problem encountered in ion beam methods of analysis is that of specimen charging. Impact of energetic positive ions causes development of a positive charge on the surface of an insulator. This effect is especially prevalent in polymers, because they are usually excellent insulators. Table 5 lists work functions for some typical polymers. Is is questionable whether the term work function should be used for polymers, but the high value of these numbers shows the reason for the charging exhibited by polymers.

TABLE 5.

WORK FUNCTION OF POLYMERS (REF. 18)

Polymer	Work Function, ϕ
Teflon	5.75
Chlortrifluoroethylene	5.30
Vinyl Choroide	5.13
Sulfone	4.95
Styrene	4.90
Methyl Methacrylate	4.68
Nylon 6.6	4.30

This charge will influence or even prevent the emission of secondary ions. To overcome this charging of insulators there have been numerous methods used, as seen in Table 6.

TABLE 6.

METHODS OF CHANGE NEUTRALIZATION (REF. 17)

(1) Deposition of a conducting thin film or of a grid.

(2) Use of Cs^+ as primary ions, in this way a conducting layer is continuously formed.

(3) Compensation of the charging by means of an extra electron beam.

(4) Use of neutral beams: the charging is reduced from the case of positive primary ions.

TABLE 6. (Cont'd)

(5) Application of special electrodes for draining excessive negative charge.

(6) Shift of target holder potential V_H by ΔV in a direction opposite to the previous charging of the insulator.

Some of these have significant limitations or contaminate the surface by coating a conductor on the surface of the insulator. In the mechanism of the charging of the insulator surface the impact of the positive ions cause secondary electron emission and consequently positive charge buildup. The obvious way of removing this charge is then to flood the surface with a beam of low energy electrons restoring charge neutrality. This method of charge compensation by electron bombardment is shown from work of Muller (Ref. 19) in Fig. 6. Muller's method has the advantage that deflecting the electron beam means that the surface of the sample cannot see the hot electron source and therefore cannot be contaminated by material boiled from the electron source. Since there is no direct line of sight, there is little heating caused by electrons from the filament. An example of SIMS spectra in the high mass range when using the charge compensation method of Muller, is seen in Fig. 7. Here strong, sharp symmetrical peaks are observed well out into the mass 300 range from the polymer Teflon, which has a very high work function as shown in Table 5. Muller's method uses very low energy thermal electrons ($\sim$5eV). Wittmaack (Ref. 20) used a focussed beam of intermediate energy electrons (100-500eV), while Magee and Harrington (Ref. 21) used well defined electrons in the energy range 500-2000eV for charge compensation. Whatever the exact method used, charge neutralization is necessary for most polymers to obtain either SIMS or ISS data. The effects which may be caused by neutralization include contamination due to heating of the specimen causing diffusion or transport of the mobile ions such as Na^+ and K^+ to the surface.

SECTION V

APPLICATIONS

As mentioned earlier, ion beam methods have not been applied extensively to organic materials and polymers. Ion scattering has been applied to adhesive bonding materials to determine the locus of failure (Ref. 22) and contamination effects (Ref. 23). DiBennedetto and Scola (Ref. 24) have used both ISS and SIMS to characterize surfaces of treated glass fibers and fiber/polymer interfaces. The results show how SIMS can be used to study the chemical surface and chemical changes on the surface and at interfaces. By working at low power levels with insulator surfaces, the SIMS analysis showed changes in the structure of a polymerized silane coating as a function of depth of penetration into the interface. The concentration of nitrogen and hydrogen generated from the surface maintained a relatively constant level as the distance from the air-silane interface increased; then within 160 A into the surface, a dramatic increase in the nitrogen level was noted, to a depth of 240A. In this region, the simplicity of the SIMS spectra, with major peaks corresponding to the atomic constituents of y-aminopropyltriethoxysilane, namely, H, C, N, O, and Si, suggested that low-molecular-weight oligomer was present in this region. This means that the silane coating was not sufficiently cured to provide a mechanically stable interface. Finally, from 240 A to the silane-glass interface, the nitrogen and hydrogen generated from the surface reached a lower constant level but about three times higher than that generated from the air-silane domain. This suggests that the silane polymer coating adjacent to the glass interface is different from the silane polymer at the air interface. Thus, it is clear that the ISS/SIMS technique can be used to define the interface and interphase regions and also to follow changes at the interface due to a chemical reaction.

Gardella and Hercules (Ref. 14) have shown SIMS data for poly (alkyl methacrylates) and also ISS data for Teflon. They found changes in molecular fragmentation patterns with only very slight changes in polymer processing. Careful examination of core level XPS data shows no identifiable changes in core level binding energies or intensity ratios. Side chain structure in the ester portion of the poly (alkyl methacrylates) dramatically influenced static SIMS data.

There have been no papers published concerned only with ISS of polymers except for Thomas, et al (Ref. 6) and for abstracts of meeting presentations by Sparrow and Mishmash in 1977 (Ref. 25) and Gardella and Hercules in 1979 (Ref. 26). Both ISS and SIMS data appear in papers in which the emphasis is in another area, such as the cleaning of surfaces by ultraviolet light (Ref. 27). Figure 8 shows ISS/SIMS data from that work for polypropylene and polypropylene exposed to UV light. Although the spectral changes are subtle they are typical of changes seen during long time aging and weathering. Usually, following UV exposure, slightly more oxygen is observed in the ISS data. SIMS data show some changes in the fragmentation pattern and larger fragments are observed. Perhaps further study of such changes may be attributed to bond breakage and cross linking effects.

Even on similar linear polymers, SIMS shows a different fragmentation pattern as can be seen in Fig. 9, ISS/SIMS data for polyethylene.

On the other hand, the ion scattering spectrum is very non individualistic. In fact, the ISS data for graphite in Fig. 10, is so similar to spectra obtained from straight chain polymers, that they probably could not be distinguished from each other.

Thomas, et al (Ref. 6) also found ion scattering data to be somewhat non individualistic, but theyalso determined that it was very useful for determining segregation at the surface of a polymer. Table 7 from Thomas, et al (Ref. 6) shows the variation in the oxygen to carbon ratio at the surface compared to the bulk values.

TABLE 7.

POLYMERS STUDIED BY ION SCATTERING (REF. 6)

The C, H and O-containing polymers studied, with the theoretical O:C ratios derived from the formula of the repeating chemical unit. Also listed are the measured O:C ratios obtained by comparing the LEIS peak areas (2750 eV He^+) and the ratios after correction for the difference in sensitivities of the two elements based on the sensitivity ratio O:C = 18.1:1.

Polymer	Formula	O:C bulk	O:C measured	Corrected
PC	$C_{16}H_{14}O_3$	0.19	1.9	0.10
PI	$C_{22}H_{10}O_5N_2$	0.23	0.76	0.04
PMMA-218	$C_5H_8O_2$	0.4	0.34	0.02
PMMA-XT	$C_5H_8O_2$	0.4	0.27	0.01
PBDDA	$C_{10}H_{14}O_4$	0.4	0.32	0.02
PET	$C_{10}H_8O_4$	0.4	1.1	0.06
PVA	C_2H_4O	0.5	0.77	0.04
POM	CH_2O	1.0	2.8	0.15

Thomas, et al (Ref. 6) found that ISS data were very reproducible, but that because of low scattering cross sections for carbon and oxygen and because common impurities such as alkali elements segregate to the surface, the

scattering intensities were low and frequently surface impurities overpowered the scattering from the polymer. An example of this is seen in Fig. 11, ISS data for He^+ scattering from polyvinyl/chloride at 2000eV.

SIMS is very sensitive to surface molecular structure, showing fragmentation pattern changes even on the same material but given different treatment. Figure 12 shows SIMS data for a commercial two-part epoxy mixed under the same conditions and then divided into two portions, one cured 24 hours at room temperature and the other cured one hour at 250°F.

As can be seen, some larger fragments are seen in the sample held at elevated temperature, and sodium has segregated to the surface. Such segregation is very common in high temperature cured specimens, where sodium is often found at the failure surface in an adhesive failure mode. ISS/SIMS data from the adhesive side of a titanium-epoxy failure interface from a tensile test specimen are shown in Fig. 13.

The fragmentation pattern is different from this temperature sensitive tape epoxy and sodium is seen at the failure interface. Sodium was also observed on the matching titanium side of the specimen.

Although little data for polymers has yet made its way to the literature, SIMS has been applied to other solid organic materials. Karasek (Ref. 28) in 1974 showed that parent masses and predictable fragments were observed in the + SIMS data for organic materials such as benzoic acid and chlorobenzoic acid, even when extremely energetic 8KeV argon ions were used to obtain spectra. Benninghoven and his associates have applied near static conditions to obtain spectra from a wide variety of materials ranging from amino acids, nucleic acids, peptides, drugs and vitamins (Refs. 29-31). An example of both positive and negative SIMS data from a peptide (Ref. 30) is seen in Fig. 14 (Ref. 30) and for vitamin C in Fig. 15 (Ref. 31). Note the $(M+1)^+$ and $(M-1)^-$ ions present in the spectra.

a. Potential Applications

There are many possible areas of polymer technology in which ion beam methods of analysis could be used. In the synthesis of polymers, solid monomers, catalysts and co-catalysts could be analyzed by secondary ion mass spectrometry. In the extrusion or other forming process, the distribution of processing aids such as lubricants could be determined. During use or accelerated testing the polymer could be analyzed to determine stability to electromagnetic radiation. Some specific areas and potential materials in which surface analysis might prove beneficial are listed in Table 8.

TABLE 8.

POTENTIAL MATERIALS APPLICATIONS OF SURFACE ANALYSIS METHODS

A. Adhesives - epoxy-phenolic, polymide, etc.

B. Coatings - polyimides, Teflon, etc.

C. Composite structure - polybenzimidizoles, polyimides, etc. with figerglas

D. Fibers - aromatic polyamides, etc.

E. Films - polyimide (Kapton), polyester (Mylar), metallized polymers, etc.

SIMS appears to be ideal for looking at materials such as these listed in Table 8. Gardella and Hercules (Ref. 4) have shown that SIMS shows differences in spectra due to very gentle process variables. These processing differences did not show measurable effects on XPS data. These authors also determined that SIMS was very sensitive to small structural changes in polymers and differences in functional groups. Figure 16 shows spectra from polyphenyl methacrylate and polycyclohexyl methacrylate.

SECTION VI

SUMMARY

Although low energy ion beam methods of analysis have not been applied extensively to polymer surface characterization, it appears that these methods should have wide applicability for polymers. Limitations such as vacuum uncompatibility and specimen charging do cause problems, but in many cases may be overcome to allow analysis.

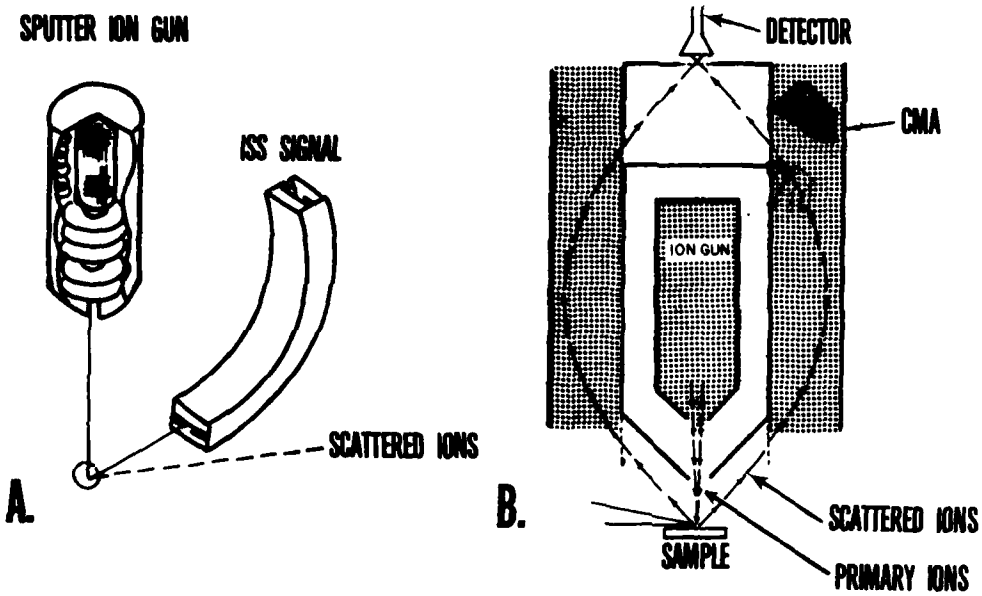

Figure 1. Experimental Set-Up for Ion Scattering Spectrometry

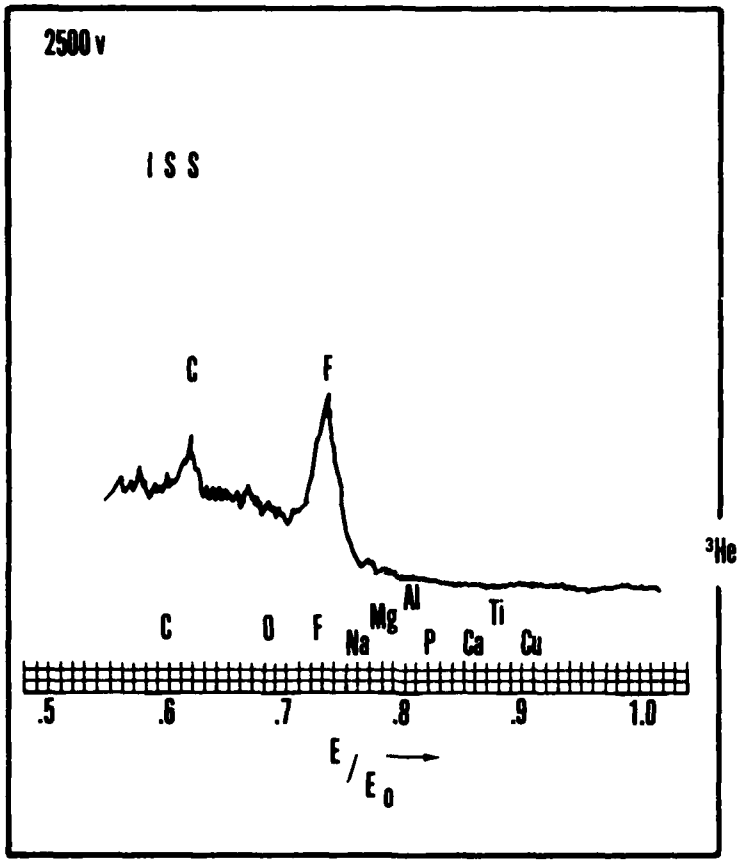

Figure 2. Ion Scattering Spectrum Using $^3He^+$ for Teflon

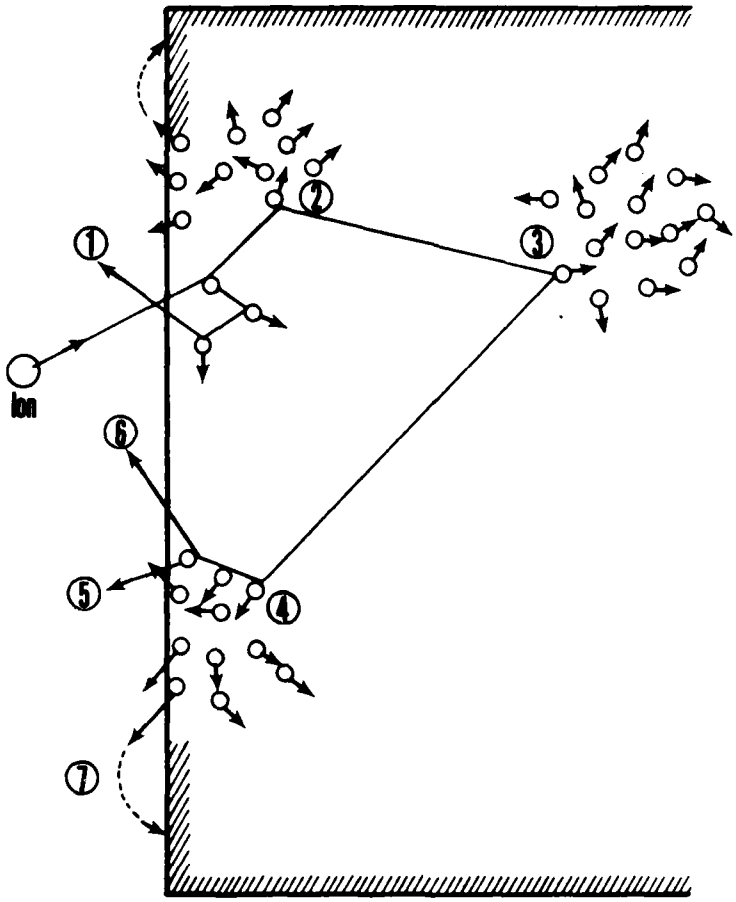

Figure 3. Diagram Showing Interactions of a Low Energy Ion in a Solid (Ref. 10)

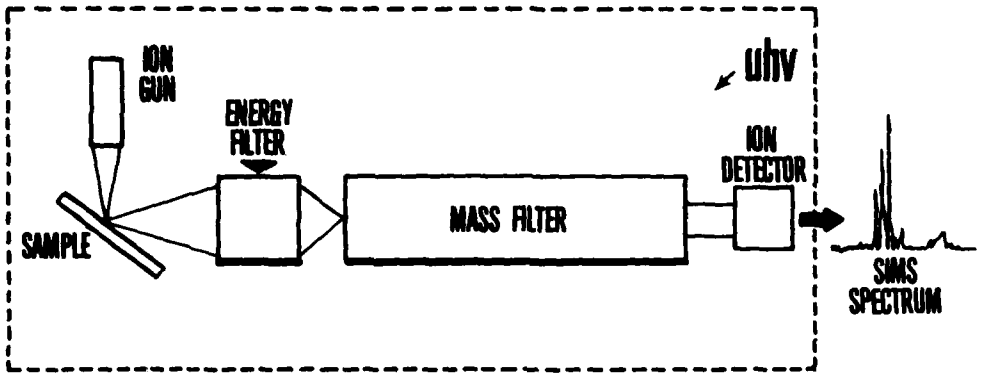

Figure 4. Simple Block Diagram Showing Components of a SIMS System

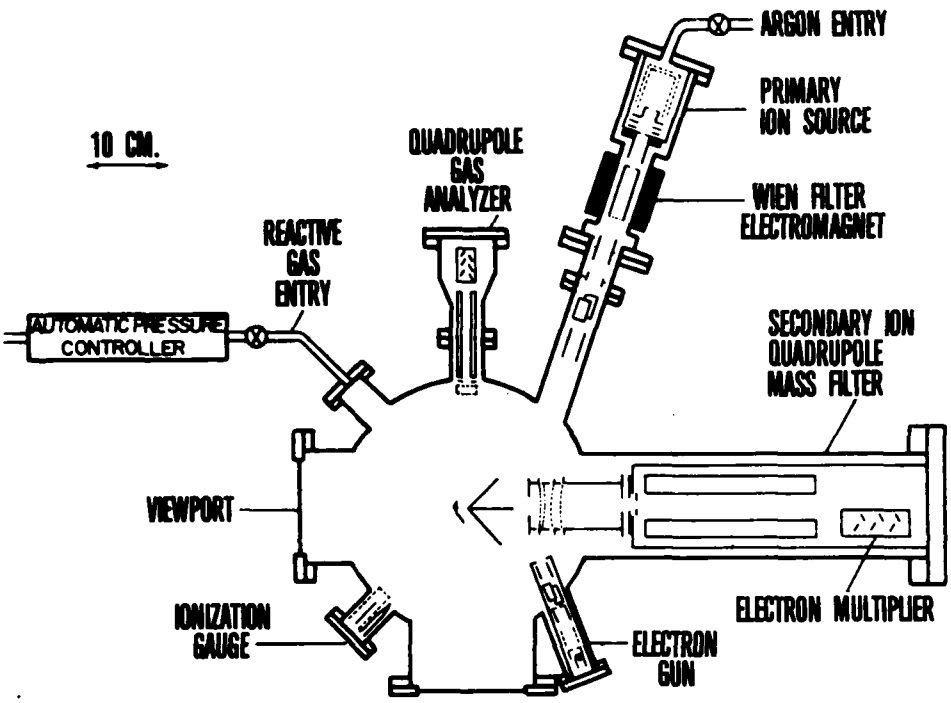

Figure 5. Diagram of Equipment for SIMS (Ref. 13)

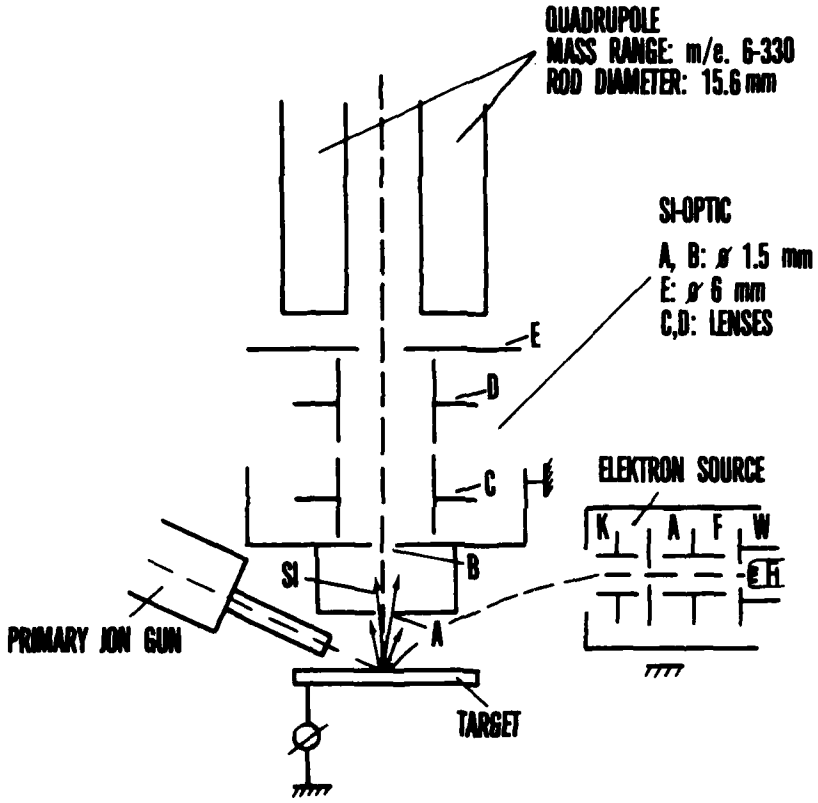

Figure 6. Charge Compensation in a SIMS Instrument (Ref. 19)

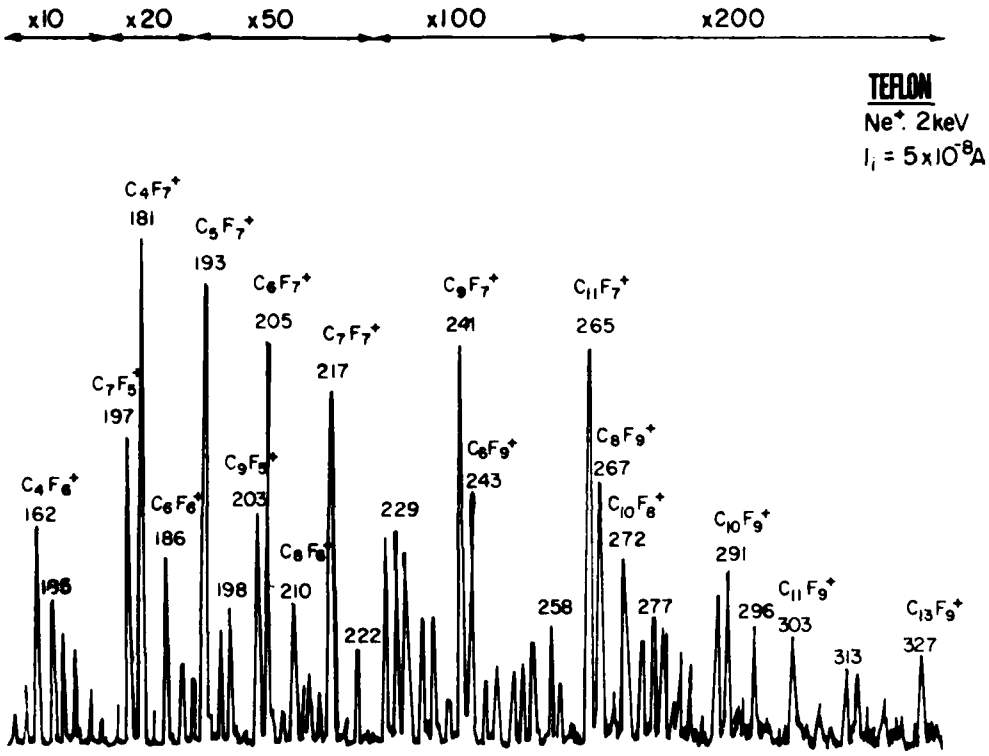

Figure 7. SIMS Data in Mass Range 160-330 from Teflon Using Charge Neutralization (Ref. 19)

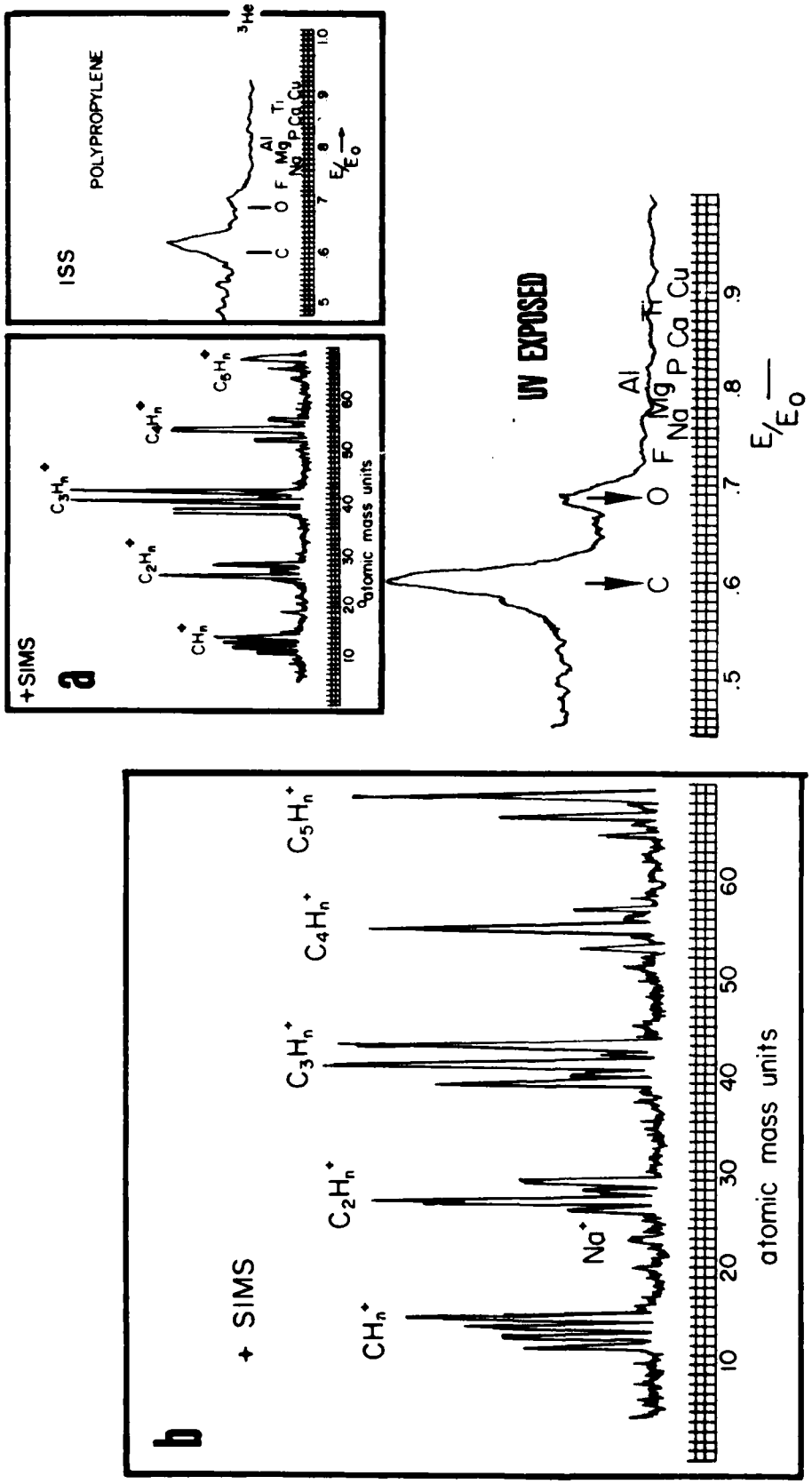

Figure 8. (a) ISS/SIMS Data for Polypropylene Using $^3He^+$ at 2500 eV. (b) ISS/SIMS Data for Polypropylene Exposed to Low Pressure Mercury Discharge Lamp, Same Conditions as in (a)

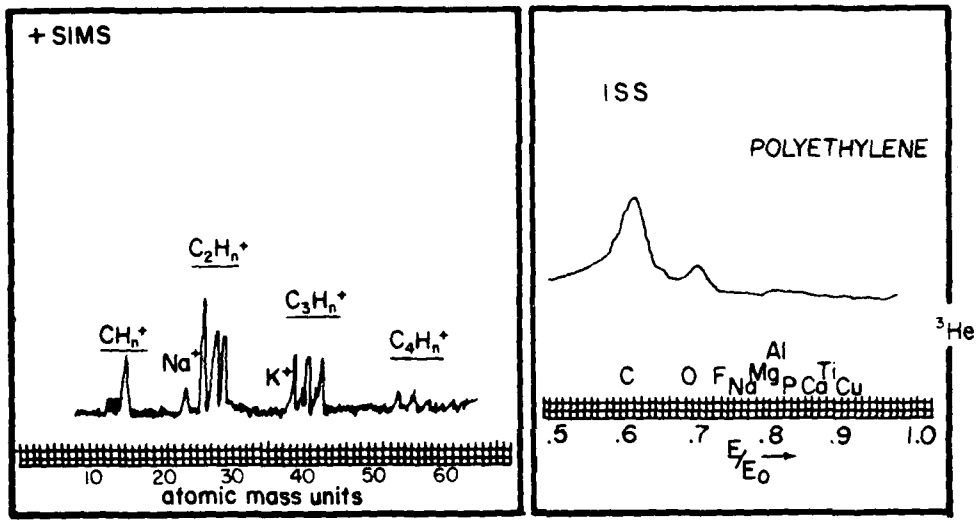

Figure 9. ISS/SIMS Data for Polyethylene, Using $^3He^+$ at 2500 eV

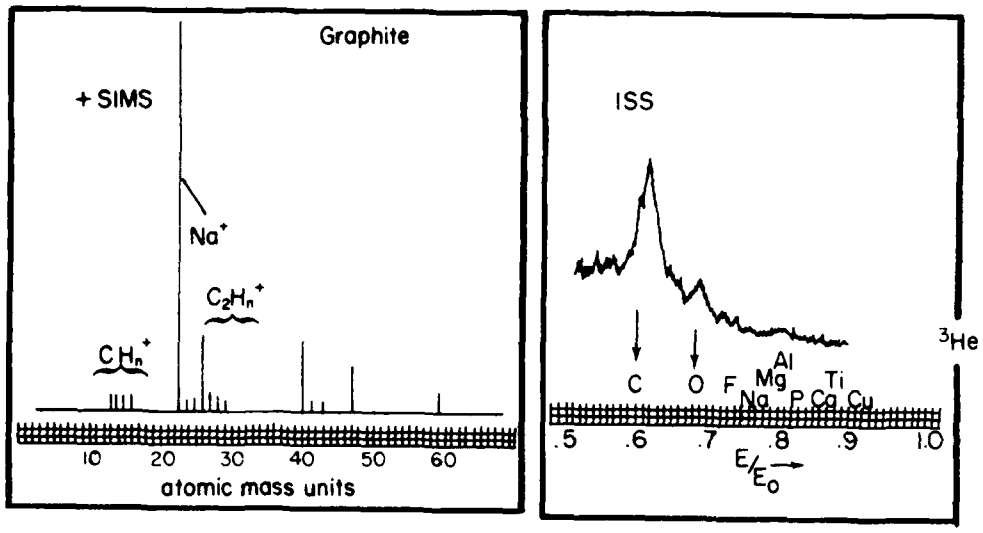

Figure 10. ISS/SIMS Data for Graphite Using $^{3}He^{+}$ at 2500 eV

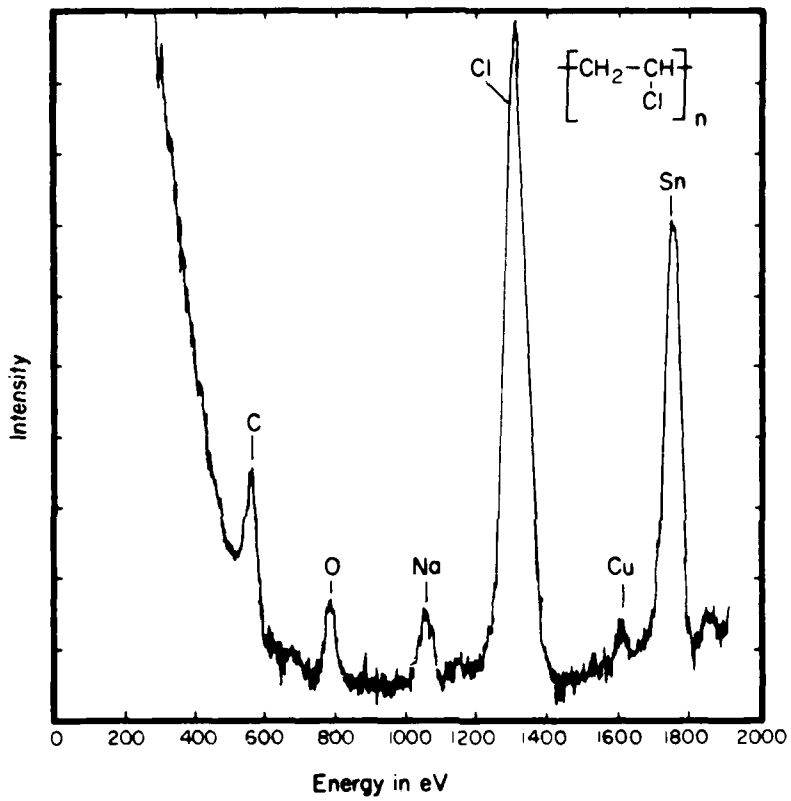

Figure 11. Low Energy Ion Scattering Spectrum (2000eV) from PVC (Ref. 6)

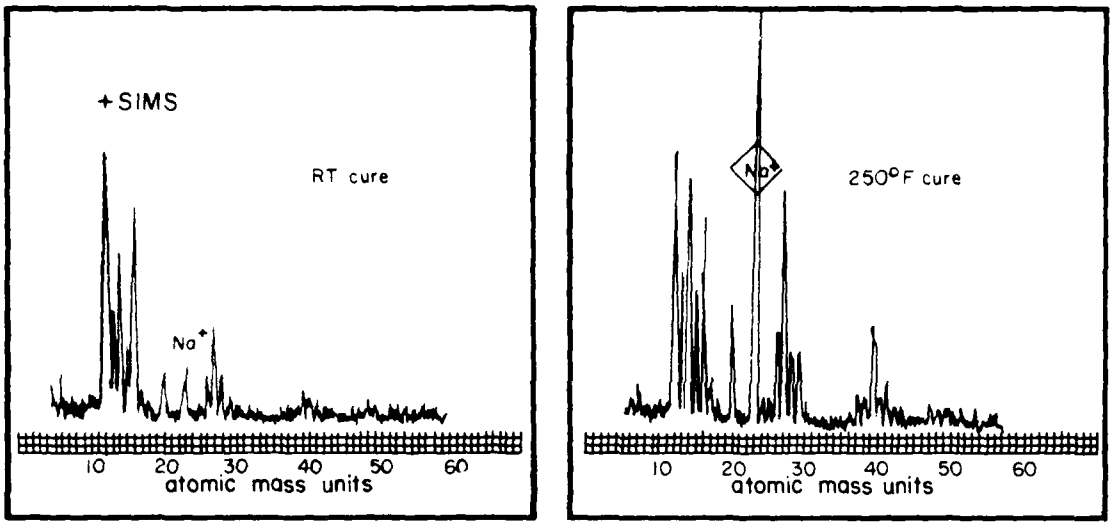

Figure 12. Secondary Ion Mass Spectra from Commercial Two-Part Epoxy Cured at Room Temperature and at 250°F

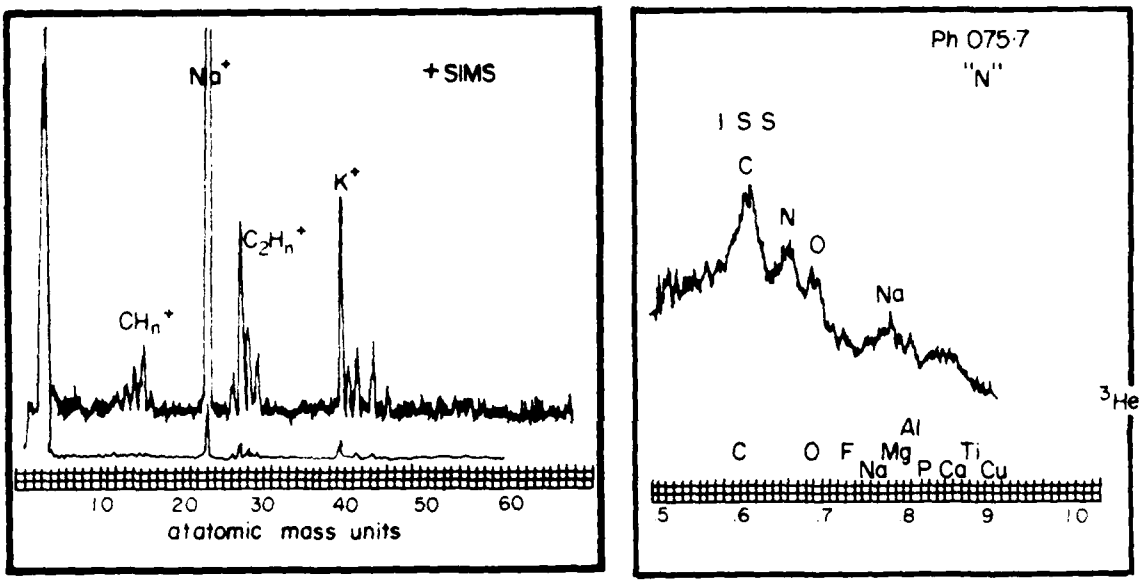

Figure 13. ISS/SIMS Data from Adhesive Side of Failure Surface from Adhesive Bonded Test Specimen

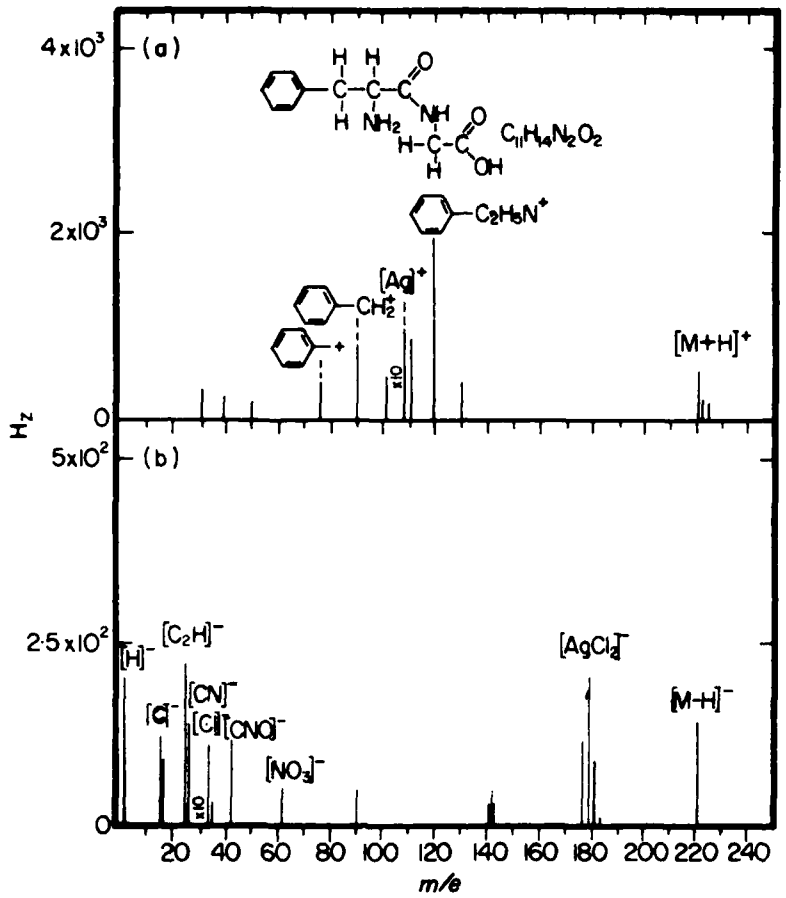

Figure 14. Positive and Negative SIMS Data for Phenylalanylglycine on Ag Using Argon Primary Ion at 2.25 KeV

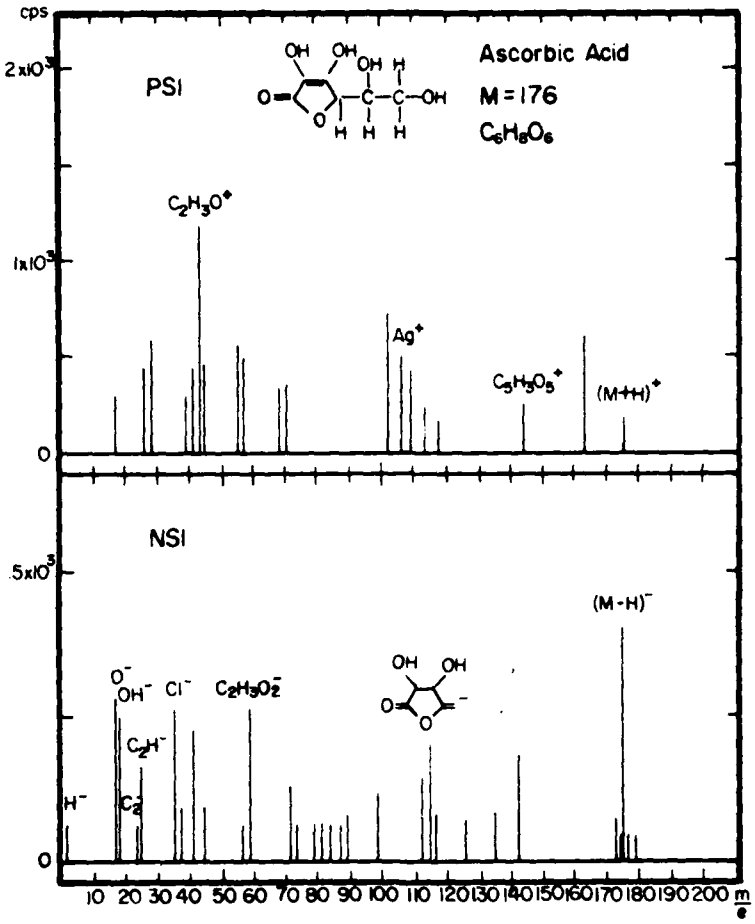

Figure 15. Positive and Negative SIMS Data for Ascorbic Acid (Vitamin C) on Ag (Ref. 31)

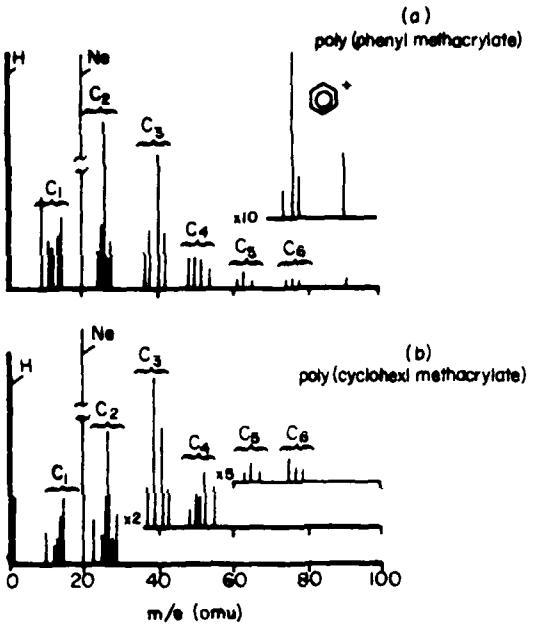

Figure 16. Positive SIMS Data for (a) Polyphenyl Methacrylate and (b) Poly(cyclohexyl) Methacrylate (Ref. 4)

REFERENCES

1. R. Holm and S. Storp, Surface and Interface Analysis 2, (1980).

2. D. T. Clark, Crit. Rev. Solid State Material Sci. 8, 1 (1978)., and also this volume, Pergamon Press.

3. J. M. Burkstrand, J. Vac. Sci. Technol. 15 223 (1978).

4. J. A. Gardella and D. M. Hercules, Anal. Chem. 52, 226 (1980).

5. H. W. Werner, Microchem. Acta, Supplement VII, p. 63 (1977).

6. G. E. Thomas, G. C. J. van der Ligt, G. J. M. Lippits, and G. M. M. van de Hei, Appl Surf. Sci, 6, 204 (1980).

7. T. M. Buck, in Methods of Surface Analysis, A. W. Czanderna, Ed. Elsevier Amsterdam, pp. 75-102 (1975).

8. D. P. Smith, J. Appl. Phys. 38, 340 (1967).

9. A. Benninghoven, Surf. Sci. 53, 596 (1975).

10. H. Winters, Advances in Chem. Sci. 158, M. Kaminsky, ed., ACS, 1976.

11. H. W. Werner, in Electron and Ion Spectroscopy of Solids, L. Piermans, ed. Plenum Publishing, N.Y. pp 324-441, 1978.

12. H. W. Werner, Surf. and Interface Anal. 2, 56 (1980).

13. P. H. Dawson and P. A. Redhead, Rev. Sci. Instru. 48, 159 (1977).

14. R. J. Colton, J. E. Campana, T. M. Barlak, J. J. Decorpo and J. R. Wyatt, Rev. Sci Instrum. 51, 1685 (1980).

15. R. J. Colton, J. Vac. Sci. Technol. 18, 737 (1981).

16. W. L. Baun, in Adhesion Measurement of Thin Films, Thick Films, and Bulk Coatings, K. Mittal, Ed., ASTM, Philadelphia pp. 41-53 (1978).

17. H.W. Werner Vacuum 10, 493 (1974).

18. D. A. Seanor, Electrical Properties of Polymers, K. C. Frisch and A. V. Patsis, Eds., Technomic, Westport, Conn. pp. 37-58 (1972).

19. G. Muller, Appl Phys. 10, 317 (1976).

20. K. Wittmaack, J. Appl. Phys. 50, 493 (1979).

21. C. W. Magee and W. L. Harrington, Appl. Phys. Lett. 33, 193 (1978).

REFERENCES (Cont'd)

22. W. L. Baun, J. Adhesion 7, 261 (1976).

23. J. Solomon and W. L. Baun, Surface Contamination, Vol II, K. Mittal, Ed. Plenum Press, N.Y. 609, (1979).

24. A. T. DiBennedetto and D. A. Scola, J. Coll. Inter Sci. 64, 480, (1978).

25. G. R. Sparrow and H. Mishmash, Abstracts, 28th Pittsburgh Conf. Cleveland, Ohio (1977).

26. J. A. Gardella, Jr. and D. M. Hercules, Abstracts, 30th Pittsburgh Conf. Cleveland, Ohio (1979).

27. W. L. Baun, Applic. of Surf. Sci. 6, 39 (1980).

28. F. W. Karasek, Res./Dev. 25, 42 (1974).

29. A. Benninghoven, D. Jaspers and W. Sichtermann, Appl. Phys. 11, 35 (1976).

30. A. Benninghoven and W. Sichtermann, Org. Mass Spec. 12, 595 (1977).

31. A. Benninghoven and W. Sichtermann, Anal. Chem. 50, 1180 (1978).