

Application of SIMS in Polymers and Lignocellulosic Materials

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SYNOPSIS

Secondary Ion Mass Spectrometry (SIMS), a new surface analysis technique, has begun to be applied to the studies of organic macromolecule surfaces either for chemical imaging and functional group analysis or for the determination of molecular weight distribution. The instrumental conditions that are critical for obtaining a meaningful spectrum are discussed for polymers which have properties similar to lignocellulosic materials, i.e., they are thermally fragile and electrically insulating. Examples are given for qualitative and quantitative analyses. Possible uses of SIMS for characterization of lignocellulosic materials are suggested. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Secondary ion mass spectrometry (SIMS) is a technique for surface analysis, in which a beam of high-energy primary ionic or neutral particles impinges a sample surface and leads to sputter of secondary ions, the relative currents of which can be measured by mass spectrometry, giving a SIMS spectrum. SIMS can be divided into several types depending on the nature of primary particles and mass analyzer used. When using neutral atoms as the primary particles, it is called fast atom bombardment SIMS (FAB); when using laser as primary beam, it is designated as laser microprobe (LAMMS); and when using a time-of-flight mass analyzer, it is called TOF SIMS. The development of SIMS has been reviewed by Honig et al. from its roots in the 1930s.¹

PRINCIPLE

When a beam of primary ions impinges the sample surface, the surface particles sputter and ionize. The sputtering process can be described by Sigmund's treatment of a collision cascade^{2,3} (see Fig. 1). The momentum of primary ions is transferred to the lattice atoms, and collision sequences, i.e., the collision

casades, among atoms in the near-surface region are initiated. Some energy is dissipated into the bulk of the sample, while some collision cascades return to the surface during the process. If a surface atom or molecule receives energy greater than its surface binding energy, and the imparted momentum has a component perpendicular to the surface, sputtering may take place. The sputtered particles may be atoms, clusters of atoms, fragments of molecules, and intact molecular species, either neutral or ionized. It is, of course, the ionized particles that can be measured by mass spectrometry.

Clearly, the signal intensity is dependent on the sputtering yield S and the ionization probability R^+ . The sputtering yield (number of secondary particles emitted per primary particle impact) is a function of primary ion atomic number, and inert gas ions appear to give a higher sputtering yield.⁴ This is one reason why the inert gases are commonly used as ionic source in SIMS. A reactive ionic beam can also be used. A compound different from the original will be formed on the sample surface, which influences the sputtering yield—increasing it if forming a volatile compound or decreasing it if forming a more stable solid compound. Reactive primary ions, such as oxygen and cesium, have been used for enhancing the yield of certain secondary ions.⁵ The ionization probability is dependent on the chemistry of the surface and the sputtered species.

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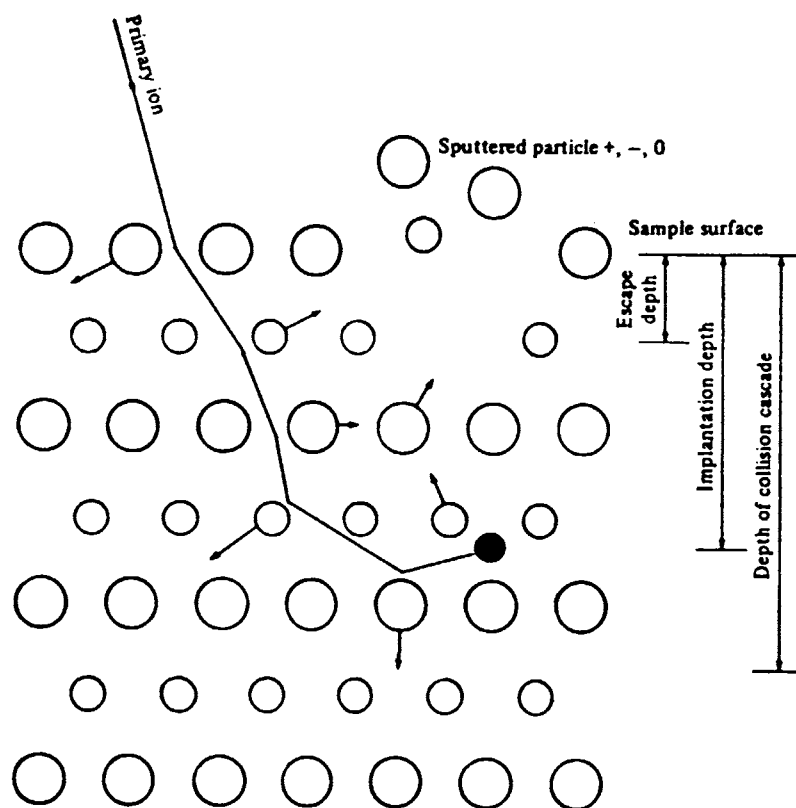


Figure 1 Schematic diagram of the sputtering process (reproduced from Ref. 73, with permission).

Although S and R^+ have not yet been explained precisely, their relation to some operation conditions of SIMS have been established by experimentation. It has been shown that the secondary ion yield increases with primary beam energy, beam flux, and primary particle mass. For organic samples, however, the primary beam energy and beam flux should be controlled within a certain limit, or the sample will be damaged. If lower primary beam currents are used, not exceeding 5 nA/cm^2 , the technique is called static SIMS; it is designated dynamic SIMS if much higher primary beam currents (typically $> 1 \times 10^{-6} \text{ A/cm}^2$) are used. In dynamic SIMS, the sensitivity increases greatly, up to the parts per billion level, because of the high primary beam current.⁶ Because of its etching effects, information on depth profiles can be obtained that is specifically useful in the semiconductor industry. However, dynamic SIMS is not suitable for plant fiber samples due to its damaging organic materials. Therefore, only static SIMS will be discussed in this paper.

Although many theoretical models have been proposed to describe the mechanism of the secondary ions emission, normally they are valid only for subsets of data and in qualitative terms and are derived from metals or simple inorganic compounds.

Thus, they are not suitable for polymers with high molecular weight. The incompleteness of the theories makes quantitative analysis difficult; only indirect methods can be used to reach semiquantitative analysis.

Colton et al.⁷ discussed this emission from surfaces that contain various organic compounds including polymers. The formation of polyatomic, molecular or cluster, ions has been described as direct emission from the surface and recombination of sputtered species above the surface by particle bombardment. The recombination results in fragment ions different from the sample structure.⁷ However, under static SIMS conditions, it was shown that the recombination or reaction between ions or neutrals above the surface does not occur to a measurable level, since the density of particles leaving the surface is extremely low.⁸

INSTRUMENTATION

Instrumentation for SIMS consists of four basic components: namely, a primary beam source, a sample holder, a mass spectrometer, and an ultra-high vacuum system.

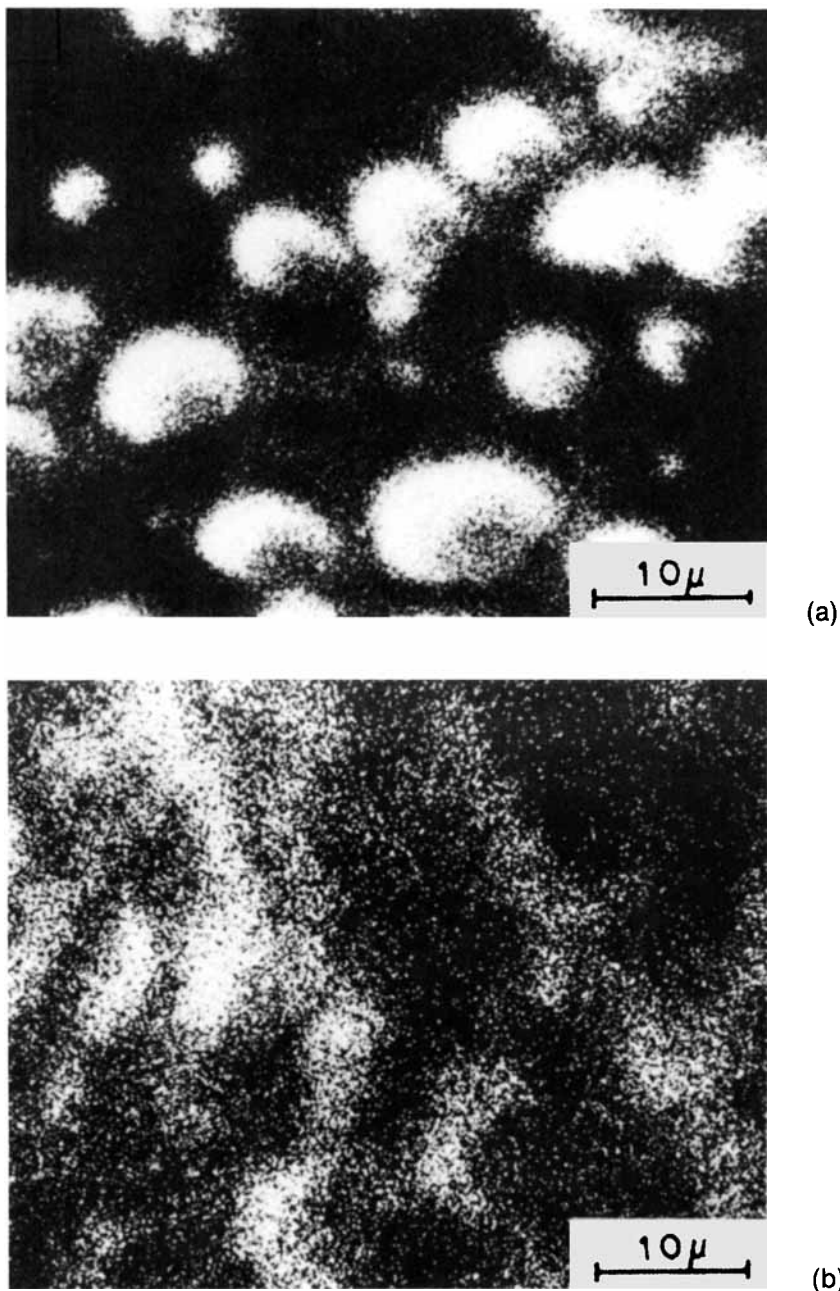


Figure 2 Chemical imaging of CN^- induced by 10 keV Ga^+ primary ion for the samples: (A) simple binary blend of PP and nylon 6; (B) the same blend as A but with acrylic polymer as compatibilizer (reproduced from Ref. 9, with permission).

The inert gases are usually used to produce primary beams. The primary beam can be an ion or atom beam; the latter is required by FAB/SIMS. For static SIMS, the primary beam current is required to be controllable. The beam flux is from 10 pA to 5 nA with low energy (< 10 keV). To keep the primary beam free of impurity, it has to pass through a mass filter.

Liquid metal sources yield a primary beam that can be focused into small spots on the sample surface (down to 500 Å in diameter). With the liquid metal sources, chemical imaging with submicron resolution is possible, and one may obtain chemical information at small points of interest on the sample surface. Chemical imaging is performed by scanning the sample surface while the mass analyzer records only

a given ion. Figure 2 is the chemical image of a binary blend of polypropylene/nylon 6. A negative fragment ion CN^- , representative of nylon 6 in this case, was recorded for imaging. It is clear that the compatibilizer makes the blend more miscible due to increased affinity among component polymers.⁹

The unique power of SIMS on chemical imaging and microanalysis has also been used in studying silicon contaminant on LDPE and print ink on packaging film,¹⁰ PMMA/PS blend,¹¹ and polymer extrudate of poly(ether sulfone) containing 6% of dimethylsiloxane.¹²

LAMMS, where a laser beam is used as the primary beam, has advantages of fast speed and high spatial resolution.^{13,14} The main drawback of the technique is a lack of reproducibility at present. The fragmentation behavior of polymers under laser bombardment is still not well understood.¹⁵ The quantification of spectra has not been developed yet. Since there still are many problems with the practical application of this technique, it will not be discussed here.

The quadrupole analyzer is normally used for mass analysis because of its compactness, facilitating fixing in the UHV system. It has, however, a lower transmission, especially at a high mass range and a lower resolution compared with magnetic sector mass analyzers.

The magnetic sector mass analyzer may offer many advantages, especially its higher transmission and resolution. It has found applications in high-performance dedicated dynamic SIMS systems. However, due to its large size, complexity, and difficulty in being combined with other surface analytical systems, it is generally less commonly applied in static SIMS.

It is obvious that the sensitivity of SIMS is controlled by the transmission of the mass analyzer. The time-of-flight (TOF) mass spectrometer appears to be a promising one, whose transmission can be greater than 30%, which increases its sensitivity to 100–1000 times that of the quadrupole analyzer. Moreover, it has a nearly unlimited mass range, which is very useful for the analysis of organic compounds and polymers with high molecular weight. It needs, however, a pulsed primary ion beam, resulting in a more complex primary beam system.

The TOF/SIMS has been applied successfully to the characterization of most classes of polymers, including polyurethanes, polymethacrylates, polyamides, polysiloxanes, polyglycols, perfluorinated polyethers, and Teflon brand fluorocarbon resin.^{16–18} There are some unique applications, such as determination of repeat units and endgroups, structure analysis of complex polymers, or calculation of molecular weight distribution for oligomers.^{16,18–21}

Figure 3 is the SIMS spectrum of polystyrene obtained using a TOF mass analyzer.¹⁶ The peaks in the right half of the spectrum (2200–6000 D) originate from the intact oligomers. Therefore, the intensity distribution of these peaks reflects the molecular weight distribution of the sample. Below this region, the fragments come from a single C—C bond cleavage in the polymer backbone, combined with the loss of one hydrogen. The mass difference between consecutive peaks of the same series refers to the repeat unit, while the mass of the terminal group can be determined from the difference between the parent peaks and repeat unit series.

The high transmission of TOF makes it possible to obtain a polymer spectrum of a very small area with high spatial resolution using a primary beam

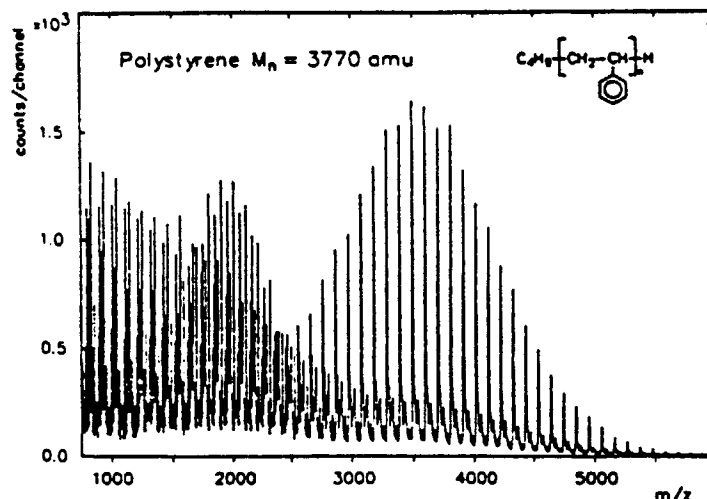


Figure 3 Positive secondary ion spectrum of PS with $M_n = 3770$ au prepared on a silver substrate (reproduced from Ref. 16, with permission).

source like liquid metal sources. In the case of a quadrupole analyzer, the ion dose has to reach the damage range in order to obtain sufficient signal intensity due to its low sensitivity. The high sensitivity of TOF has shown its ability in the analysis of surface contaminants and additives in polymers.^{22,23}

PRACTICAL APPLICATIONS

The literature shows that SIMS has rarely been considered in paper science. However, in the past decade, especially in the recent few years, many polymer SIMS studies have been reported. It is believed that their results should be of great value to the plant fibrous materials that also have macromolecular structure. Therefore, this paper will first review the application of SIMS to polymer surfaces and then discuss the possibilities of SIMS analysis on lignocellulosic materials.

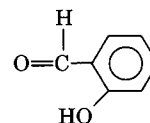
The lignocellulosic materials have some properties similar to those of conventional polymers, i.e., thermal fragility, being easily damaged by the primary beam bombardment. In addition, they are electrical insulators, which results in a buildup of charge during ion impact. The analytical conditions are therefore critical in order to obtain any useful surface information from SIMS spectra for such materials.

1. Analytical Conditions

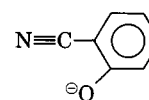
1.1. Sample Preparation

The method of sample preparation can influence profoundly the secondary ion formation and emission processes. In earlier polymer SIMS studies, the sample was prepared by dissolving the polymer in organic solution and dropping it on a clean metal foil to form a layer or thin film. The metal substrate usually enhances the secondary ion yield because of a matrix effect.²⁴ The metal foil is usually an acid-etched silver foil,⁷ but copper, nickel, aluminum, and other metals have also been reported.^{8,25,26} Glass disks and silicon wafers^{27,28} can also be used. Even more simply, the polymer solution can be directly evaporated on the polished sample stub.²⁹ Nevertheless, this method is not suitable for plant fibrous samples, and the dissolution of a sample may change its original surface composition. Also, some signal from the substrate will interfere with the sample spectrum.²⁹ Lastly, many studies directly using the sample as received were reported, such as thick films and compressed powder.^{30,31} In the case of a thick film, the sample is attached to the sample holder by means of double-sided adhesive tape.

The derivatization technique can be used for sample preparation, which is helpful for studying some functional groups.³² An example of applying this technique is the investigation of the structure of plasma-treated polymers. Lub³³ used the aldehyde



as a derivatization compound to identify primary amino groups on a polystyrene (PS) surface contacted with ammonia or nitrogen plasma. Thereby, it was discovered that only the polymer treated with ammonia plasma has primary amino groups since the peak at 118 D



which reflects the presence of primary amino groups, was formed only after treatment in ammonia plasma.

1.2. Damage Effects

As mentioned above, the primary beam current in static SIMS should be less than 5 nA/cm². Even under such a low current, the exposure time of the sample to the primary beam still has to be limited or the sample may be damaged.

It was found that damage appears on PS around $1-5 \times 10^{13}$ ion/cm² impinging on the sample under the bombardment of 4 keV Ar⁺ at flux 1 nA/cm². The lower limit corresponds to an exposure time of about 27 min.³⁴ For different samples and different primary ion energies, the dose upon which the sample starts being damaged is different.^{8,35-37} It is, however, generally accepted that the spectrum of undamaged polymers with good signal-to-noise ratio can be obtained by using a 1 nA/cm² primary ion beam at 2-4 keV for a total dose of about 10¹² ion/cm².²³

1.3. Charge Problem

For electrically insulating samples, positive charge on the sample surface will build up with the bombardment of positive primary ions. The charge buildup on the sample surface changes its surface potential, which directly influences the signal intensity of secondary ions, consequently causing signal instability, peak broadening, and signal reduction, distorting the SIMS spectrum. It has been reported that the charge can build up and cause a complete loss of signal in a few seconds.³⁸⁻⁴⁰

The use of an electron flooding gun is a normal approach to overcome this problem. It has been reported that the impact area of electrons should be larger than that of primary ions and the flux ratio of electron beam to ion beam, I_e/I_i , should be higher than 1 if effective neutralization is required.³⁴ Low-energy ion beams tend to give more effective neutralization.⁴¹ At normal doses of the electron beam, i.e., several nA/cm² at 700 eV during normal acquisition time, the flooding gun does not cause damage on the polymer surface. One has, however, to take care because electron-stimulated ion emission (ESIE) may occur, though in most cases it can be negligible.^{8,29,42}

Besides the electron gun, the charge can also be compensated by placing a conducting grid on the sample surface or evaporating a conducting layer on the surface to make the sample surface grounded.³⁸

Since the accumulation of the positive potential on the sample surface is related to the impact of the primary ions, the charge problem will be largely alleviated when using neutral atoms as primary particles. The effect of FAB on stability of the surface

potential can be seen from Figure 4. It is clear that the charge is more controllable when using atomic argon bombardment instead of Ar ions (in this example, the decay may partially originate from surface damage).⁶ Campana and Rose reported that FAB/SIMS has been used for surface analysis of thick polymer films to reduce the charge effects.⁴³

The spectra produced by atomic beam sources are essentially the same as those by ions.⁴¹ Brown and Vickerman showed that almost identical spectra were obtained from polyethylene oxide by ion and atom primary beams.³⁷ Therefore, it appears that the pattern of SIMS spectrum is independent of primary particle charge state under suitable conditions. A series of polymers from PS and polyethylene (PE) to polyethylene-terephthalate (PET),^{6,37,43,44} polymer colloid,⁴⁵ plasma-treated polymers,⁴⁶ and rubbers⁴⁷ have been analyzed with FAB/SIMS.

1.4. Primary Ion Mass and Energy

It was discovered that the energy and nature of the primary ions would affect the yield of the secondary ions. Briggs and Hearn studied systematically the effects of the primary ion mass and energy.³⁰ The various primary ions they used included He⁺, Ne⁺, Ar⁺, Xe⁺, and Ga⁺. The energy range is from 1 to 10 keV. Their results show that by increasing the primary ion mass and energy the total secondary ion yield increases, especially in the high mass range. Therefore, one may obtain meaningful SIMS spectra with high intensity at high mass range by using heavy primary ions with high energy. But the damage on the sample due to severe operating conditions must be controlled.⁴¹ From the trade-off reached between the positive and negative effects of the primary ion energy and mass, it was suggested that an optimum condition is probably the use of 2 keV Xe⁺ ions with a flux in the order of 1 nA.

Though the energy and mass of the primary ions influence the signal intensity, the fragmentation pattern in static SIMS is determined predominantly by the sample molecular structure, rather than by the type of primary ion used.⁴⁸

1.5. Sampling Depth

It is quite clear that SIMS is more surface-sensitive than is ESCA according to many direct comparisons of ESCA and SIMS.²³ Under static conditions, Surman and Vickerman demonstrated that the sampling depth is only 1–2 atomic layers for nonvolatile organic compounds.⁴⁹

It has been established from some studies on polymers that the sampling depth of static SIMS is

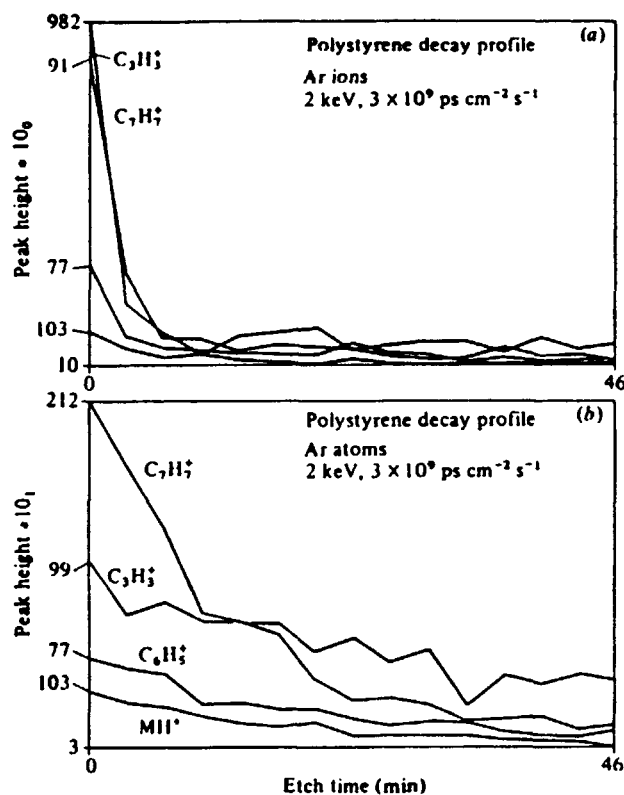


Figure 4 The decay of secondary ion yield from PS as a function of time argon ion (with electron neutralization) and argon atom bombardment (reproduced from Ref. 6, with permission).

about 10 Å.^{23,50} Obviously, any surface contaminant might influence the SIMS result due to the high surface sensitivity of static SIMS. Therefore, maximum care has to be taken to keep the sample from contamination during sample preparation.

2. Qualitative Analysis

It is accepted that vapor-phase conventional mass spectrometry rules are generally valid in polymer SIMS as well, because the secondary ions pattern directly reflects the original structure without recombination during emission.^{6,8} Many qualitative analyses of spectra from polymer surfaces have been reported, from simple linear carbon chain polymers, such as polyethylene (PE) (either high density or low density),^{8,29} polypropylene (PP),⁴¹ polyisobutylene,⁸ and polystyrene (PS),^{29,30} to a series of poly(alkyl methacrylate),^{25,27,35,41,51} nylons,^{41,52} unsaturated polymers *cis*-polybutadiene and *cis*-polyisoprene,²⁸ and various complicated rubber products.^{10,28,47,53,54}

An example of qualitative analysis is the interpretation of the spectrum from PS (Fig. 5). The peaks at 77, 91, 103, and 115 D are characteristic peaks that originate from the fragment ions $C_6H_5^+$, $C_7H_7^+$ /cyclic tropyllium cation, $C_6H_5-C_2H_2^+$, and $C_6H_5-C_3H_2^+$, respectively. In general, an even-numbered fragment ion with an intensity observed here (the peak at 128 D) is very rare in static SIMS of hydrocarbons. This ion is explained as a naphthalene structure with one electron removed from the π -system without hydrogen loss or addition. It comes from unsaturated or aromatic polymers.²⁸ Other peaks in the PS spectrum, such as 39 D $\rightarrow C_3H_3^+$, 51 D $\rightarrow C_4H_3^+$, 65 D $\rightarrow C_5H_3^+$, are the normal peaks for aromatic hydrocarbons in conventional mass spectrometry, which means that the fragmentation pattern of static SIMS is similar to the conventional one.²⁹

The example given above is simple. In some circumstances, there may be two possible explanations for the same peak. For example, the peak at 69 D for poly(methyl methacrylate) (PMMA) originates from two possible fragments: $C_5H_9^+$ and $C_4H_5O^+$. These two ions have the same mass-to-charge ratio due to the limited spectrometer resolution. To make correct assignment of this peak, Brinkhuis and van Ooij employed the isotopic labeling technique. After deuteration of PMMA, it was found that the peak at 69 shifted to 74 D ($C_4D_5O^+$), whereas only a very weak peak was observed at 78 D ($C_5D_9^+$). Consequently, the ion at 69 D was assigned to $C_4H_5O^+$.²⁵

A compilation of standard SIMS spectra has been

published,⁷² which helps the qualitative interpretation of unknown polymer spectra.

3. Quantitative Analysis

Although the SIMS technique normally produces only qualitative information, since the fragmentation mechanism of the polymers is not understood quantitatively, there have been some reports dealing with the relative quantitative analysis of a given component in copolymer based on the relative intensities of characteristic peaks. An example is the determination of the monomer content in a copolymer system of nylon 6 and nylon 66.⁵⁵ The peak at 114 D (MH^+) is a characteristic peak of nylon 6, because 114 D is virtually absent in nylon 66, while the peak at 55 D originates from the polyamide backbone that exists in both monomers. Consequently, the intensity ratio of 114/55 reflects the content of monomer nylon 6 (Fig. 6). Furthermore, a peak at 213 D, which is only a very weak peak in the spectra from the homopolymers, can be ascribed to an ion involving both monomer units. It is easily understandable that this peak becomes prominent as the contents of both monomers reach equivalence.

Utilizing a similar method, the copolymer of ethyl methacrylate/hydroxyethyl methacrylate (EMA/HEMA)^{27,56} and other copolymers have been studied quantitatively.^{57,58}

In a study of rubber cross-linking, van Ooij et al.⁴⁷ found that there are linear relationships between normalized intensities of S_1^- ions and total cross-link densities and between intensities of S_4^- clusters and percentages of polysulfidic cross-links (the normalization was done using total negative ions yield of the sample from S_1^- to S_6^-). It was suggested that SIMS can allow one to quantify the total cross-link density and the amount of polysulfides using a calibration curve based on a conventional method.

In addition, it was reported that the CH^-/O^- ratio in negative ion spectra correlates with the atomic C/O ratio in many polymers.^{27,41} This suggests that the quantitative analysis for certain elements might be accomplished by SIMS.

4. Negative Ion Spectra

It was reported that the negative ion spectra from polymers such as PE, PP, PS, PMA, and PET normally contain little structural information, as they are confined mainly to $C_nH_n^-$, O^- , OH^- , and $C_2H_m^-$ depending on the type of polymer.⁴¹ It is considered that the reason is that the positive charge

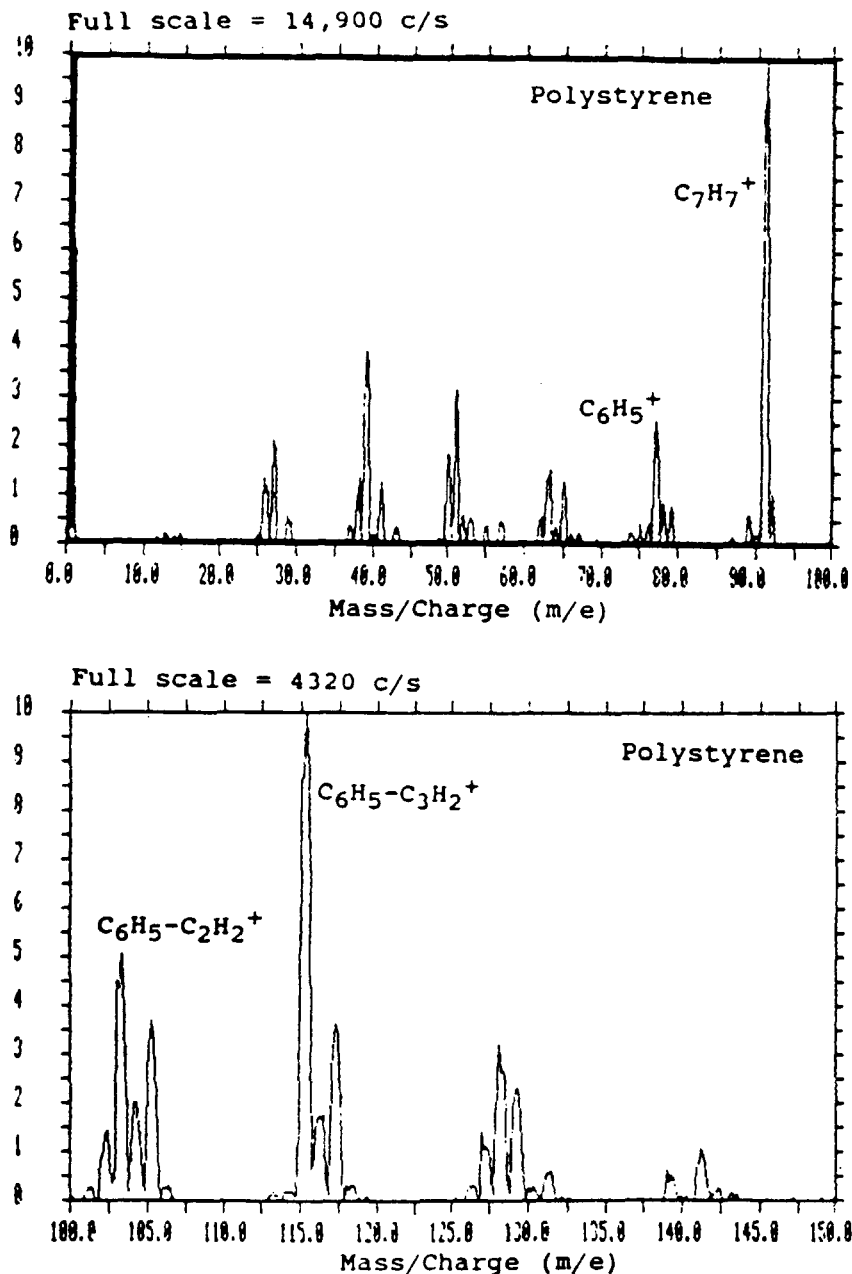


Figure 5 SIMS spectrum of pure PS (4.5 keV Xe^+ , neutralized with a 500 eV defocused electron source) (reproduced from Ref. 28, with permission).

accumulated on the sample surface prevents production of negative ions with structural information and their escape from the surface. In recent years, some investigators were successful in obtaining negative ion spectra by means of making the sample surface electrically neutral or slightly negative. Normally, an electron gun, which might be combined with setting a negative target bias, was used to overcome the positive charge.⁴⁴ It was also reported that

similar neutralization can be achieved by focusing the electron beam only onto the nearest piece of metalwork instead of over the sample surface, so the ESIE can be avoided.²³ Subsequently, the negative ion spectra of poly(ethylene oxide) (PEO) and polycarbonate have been obtained under normal conditions. It is believed that the electronegative elements such as oxygen stabilize the negative ion clusters like RO^- and ROO^- .^{30,51}

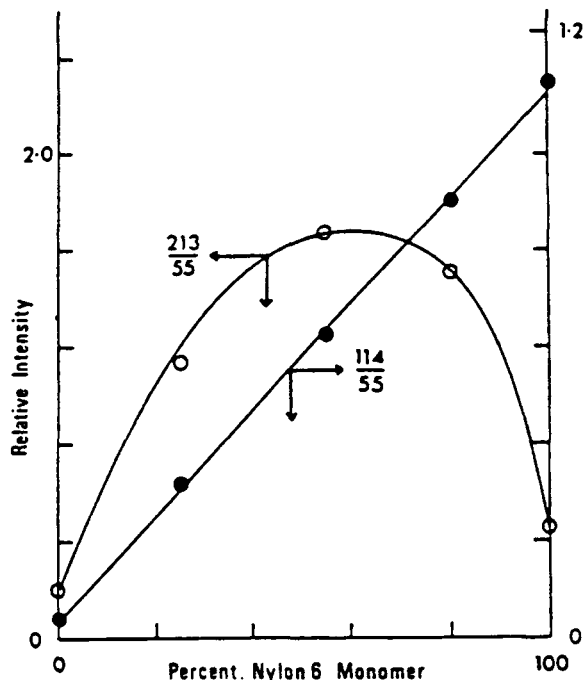


Figure 6 Correlation of SIMS relative peak intensities with nylon 6/66 copolymer composition (wt %). 114 D is almost entirely due to nylon 6 monomer, 213 D represents a 6-66 linkage, and 55 D is a nonspecific intense fragment seen in all the spectra useful for normalization (reproduced from Ref. 41, with permission).

The negative ion spectra can be viewed as a complement to positive ion spectra. They provide detailed structural information on a polymer's side chain and backbone.^{51,57} This additional information has been shown to have some benefits in studies on oxygen plasma-treated methacrylate polymers.⁴⁴

5. Some Practical Applications

Besides the chemical imaging and qualitative and quantitative analyses mentioned above, other practical applications could be studies of trace inorganic components⁵⁹ and surface segregations.^{28,41,60} The following is an example of the analysis of the polymer surface segregation effect.⁶¹ Poly(ether urethanes) containing fluorinated chain extenders are segregated into soft segment (SS) and hard segment (HS). The SS is polytetramethylene glycol (PTMG), and the HS contains 4,4'-methylene-bis(phenyl isocyanate) (MDI) units and fluorinated diol chain extender. After analysis of model polymers of each segment, it was found that the peaks at 106 and 127 D represent the two segments, respectively and that the I_{106}/I_{127} ratio is a measurement of the HS : SS mol ratio, which was confirmed by ESCA

analysis. From the variation in the I_{106}/I_{127} ratio of other poly(ether urethanes) based on PTMG/MDI/ethylene diamine, it was demonstrated that increasing the SS molecular weight leads to an increase of SS segregation to the surface.⁵³

Poly(vinyl chloride) (PVC) sheets made from two different sources of polymer gave acceptable and unacceptable levels of ink adhesion. Being analyzed by SIMS, it was found that there was a higher surface concentration of EBS ($\text{CH}_2\text{NHCOC}_{17}\text{H}_{35}$)₂ for the "bad" sample. This means that the surface concentration of EBS affects the ink adhesion.²³

The chemical changes of polymer surfaces by plasma^{23,33,46,62,63} and flame⁶⁴ treatments can also be monitored by SIMS. It was reported that the spectrum of PP after treatment in SF_4 plasma showed a partial incorporation of fluorine on the surface, which was transformed into a surface resembling a fluoropolymer, while in an air plasma, oxygen is incorporated into the surface, making the surface similar to an oxygen-containing polymer.⁶⁴

Moreover, SIMS has been shown to be sensitive to the orientation of molecules and segments at the surface.²⁸ By recording a depth profile of secondary ions from carbon, hydrogen, and deuterium in annealed styrene/methyl methacrylate copolymers, the orientation of the copolymers to the surface was revealed.⁶⁵ It should be noticed here, however, that the investigation was performed under dynamic conditions.

6. Lignocellulosic Materials

As mentioned before, only a few SIMS studies of lignocellulosic materials have been published. Most of them were not aimed at surface analysis, such as the study of the distribution of inorganic wood preservatives in the wood cell wall based on LAMMS,⁶⁶⁻⁶⁸ the LAMMS study on indigo-dyed cotton fibers,⁶⁹ and the study of photographic paper,⁷⁰ in which the information obtained was from deep layers under the surface because of the perforation effect by the primary beam.

A surface analysis of cellulose nitrates with FAB/SIMS has been initiated by Fowler and Munro.⁷¹ The exposure of cellulose nitrates to heat and light can cause deleterious changes in their chemical and physical properties. The thermal and photo-degradation of cellulose nitrates is clearly indicated in their positive spectra (see Fig. 7). The intensity difference of the peaks at 29, 30, 41, and 46 D are taken to reflect the degradation (their assignment is shown in Table I). The relative intensities of 30 and 46 D (representatives of NO^+ and NO_2^+ , re-

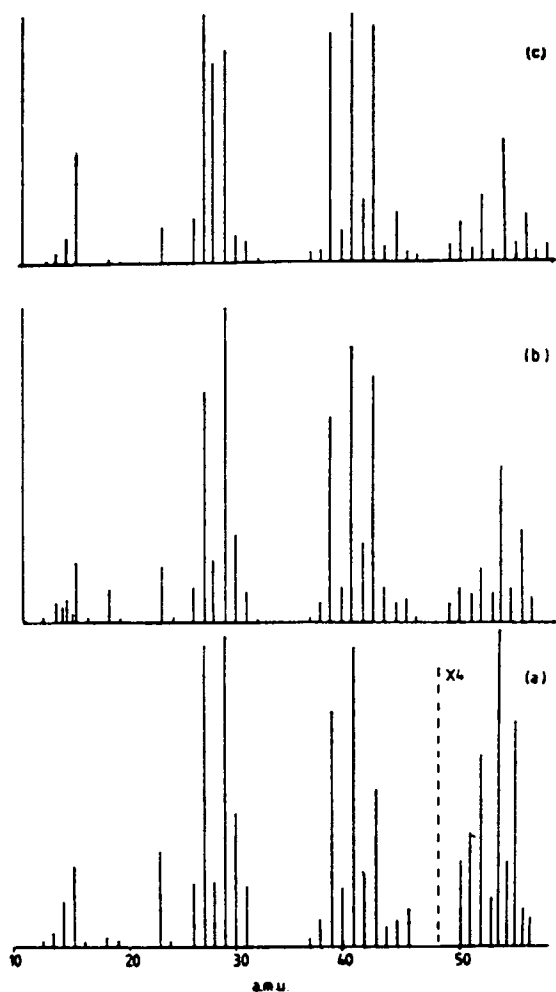


Figure 7 FAB SIMS spectra for (a) pristine 2.2 DOS cellulose nitrate, (b) thermally degraded material (17 h at 130°C), and (c) X-ray degraded material (12 h, $Ti_{K\alpha}$) (reproduced from Ref. 71, with permission).

spectively) are decreased after thermal degradation, which indicates a small loss of NO_2 from the nitrate groups. Very low intensities of peaks 30 and 46 D in Figure 7(c) show a major loss of nitrate functionality on the surface of cellulose nitrate after X-ray degradation.

In 1988, Davies et al.²⁶ claimed that SIMS spectra of cellulose ether had been obtained for the first time by their group. Three samples were employed, i.e., 2-hydroxypropyl cellulose (HPC), 2-hydroxypropyl methyl cellulose (HPMC), and methyl cellulose (MC). The results showed that the change of methyl and hydroxypropyl degree of substitution (DOS) in HPMC can be followed by the intensity ratio of 45/59 D.

Unfortunately, the spectra in the reports mentioned above have not been given full assignments and the range of detected mass was not so high as

to reflect the macromolecular structure of cellulose. Basically, what were analyzed are the substituent groups on cellulose. Therefore, it is quite clear that fundamental investigations have to be carried out before the macromolecular structures of polysaccharides and lignin can be analyzed by SIMS. The undamaging primary particle dose and optimum conditions have to be set up for this type of polymer. The pure cellulose and other polysaccharide lignin model compounds should be studied to find characteristic peaks for each component, which could help in the interpretation of spectra from real lignocellulosic material. Indeed, there are no vapor-phase conventional mass spectrometry rules that can be followed for these types of samples due to their nonvolatility. Some assignments from other polymers should be useful, e.g., peaks at 77, 91, 105, 115, 128, and 141 are believed to originate from the aromatic structure²⁸ that exists in lignin to a large extent. The peaks at 85, 97, 99, 101, 111, 115, 127, 155, 171, and 173 are considered as fragments from the cellulose backbone.²⁶

As mentioned above, the intensities ratio CH^-/O^- correlates with the atomic ratio C/O in the polymer,^{27,41} which directly reflects the relative contents of lignin and polysaccharides since polysaccharides have much more oxygen according to their molecular formulas. Furthermore, the derivatization technique⁶⁹ could be used in these materials. Thereby, the hydroxyl groups, which are very important in the interpretation of paper formation, might be routinely determined by derivatization with acetyl chloride. It is also possible to determine various functional groups directly and to discriminate the basic structural units of lignin with SIMS. Moreover, trace inorganic component analysis and chemical imaging might also be useful in the pulp and paper science.

In short, SIMS should be a very promising technique for surface analysis of lignocellulosic materials. Although much fundamental work has to be

Table I Assignments for FAB Spectra of Cellulose Nitrates (reproduced from Ref. 71, with permission)

Peak (au)	Possible Assignment
29	$C_2H_5^+$, CHO^+
30	NO^+ , CH_2O^+
31	CH_2OH^+
41	$C_3H_3^+$, $CH_2C=N^+$
43	$C_3H_7^+$, $CH_3C=O^+$
46	NO_2^+

done, more informative spectra would be obtained compared with ESCA. In the latter, the spectra often overlap due to small chemical shifts. In addition, there is no requirement of volatility in SIMS, which is necessary in the vapor-phase conventional mass spectrometry. As the SIMS technique develops, leading to the improvement of resolution and increase of mass range, it is believed that the application of SIMS will be wider and deeper.

CONCLUDING REMARKS

SIMS has increasingly been used for applications on polymer surfaces in the last decade and continues to develop at an accelerating rate. During the review of the literature for this report, it was found that more than half of the articles about SIMS of polymers were published in the last 3 years. Either positive or negative ion spectra with meaningful information can be routinely obtained without destroying the polymer surface structure. Qualitative analysis can be completed by following the rules of conventional EI mass spectrometry or by running standard compounds. Spectral quantitation has been started, especially on copolymers in which a monomer content can be measured by the intensity of its characteristic fragments. Many practical uses from chemical imaging and functional groups analysis to molecular weight distribution have been found in various polymers.

To the authors' knowledge, only a few SIMS studies have been performed on wood fibers and other lignocellulosic materials. SIMS, however, seems to be a promising technique for this type of application, since it provides, e.g., more structural information than does ESCA, though the latter has received more attention in this field.

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