Anal. Chem. 1992, 64, 2797-2803

Mass Spectrometric Analysis of Rubber Vulcanizates by Laser Desorption/Laser Ionization

Keith R. Lykke,[*,†,‡] **Deborah Holmes Parker,**[†,‡,§] **Peter Wurz,**[†,‡] **Jerry E. Hunt,**[‡] **Michael J. Pellin,**[†,‡] **Dieter M. Gruen,**[†,‡] **and John C. Hemminger**[§]

Materials Science and Chemistry Divisions, Argonne National Laboratory, Argonne, Illinois 60439, and Department of Chemistry, University of California, Irvine, California 92717

Robert P. Lattimer

The B. F. Goodrich Co., Research & Development Center, Brecksville, Ohio 44141-3289

Three different vulcanized rubbers have been studied by laser desorption/laser ionization mass spectrometry. Analysis of these vulcanizates by various conventional mass spectrometric methods has been difficult because of the complexity of their mass spectra. The major thrust of the present work is to show that different wavelengths for the postionization step allow selectivity which provides important additional information about the chemical makeup of these complex materials. Near-UV wavelengths selectively ionize aromatic additives, far-UV wavelengths photoionize other nonaromatic species, and VUV wavelengths access all of the desorbed species. The ability to vary these different parameters allows a specificity that rivals other techniques for surface and bulk analysis of polymers and their additives.

INTRODUCTION

Laser desorption (LD) has proven to be a viable means to introduce nonvolatile surface species into the gas phase.[1-13] Other methods, such as thermal desorption and ion bombardment,[14] often tend to thermally decompose the molecules or fragment the molecular species with the incident primary ions. Thus, the fragments are not easily identified with the molecular structure of the original surface which, in very important cases, is polymeric in nature. For laser desorption/laser ablation, the amount of fragmentation depends on the energy absorbed by the surface, the wavelength of the laser beam, and the pulse length of the laser.[15-17] However, by optimizing the laser parameters for a particular analysis system such as a polymer, conditions are achieved that induce very little fragmentation of the polymer itself or its additives. The most widely utilized technique for monitoring the laser desorbed species is prompt-ion mass spectrometry, that is, detection of ions produced directly by the laser desorption process.[1,18,19] This technique has proven to be quite useful in many instances, but it does suffer from severe matrix effects due to the strong dependence of surface ionization and surface neutralization on both substrate chemistry and the nature of the desorbate. These matrix effects arise from the two physical processes involved: laser desorption and ionization of the desorbed species. The first effect depends mainly on the absorbed energy and volatility of the sample while the second effect depends principally on the ionization potential of the desorbed species. In this paper, we report on a method to alleviate some of the inherent matrix effects by analyzing the *neutrals* that are contained in the laser-desorbed plume.[6,8,9,12] This is accomplished with a second laser beam of variable wavelength and intensity. We show that the ability to vary these different parameters allows specificity and detection sensitivity that rivals other techniques for surface and bulk analysis of polymers and their additives. The samples employed to demonstrate these capabilities are three different vulcanized rubbers that have been previously studied mass spectrometrically.[20-23]

Raw rubbers are usually mixed with various additives which produce certain characteristics in the polymer. These additives include vulcanizing agents, fillers, pigments, plasticizers, antioxidants, and antiozonants. Vulcanization cross links the rubbers to impart strength and elasticity and restricts viscous flow. Carbon black acts as a filler in the rubbers studied here, and there are no other pigments in them. A few antioxidants and antiozonants are present in the vulcanizates at the parts per hundred level. These constitute some of the more important species for analysis and are the focus in the

---

[†] Materials Science Division, Argonne National Laboratory.

[‡] Chemistry Division, Argonne National Laboratory.

[§] Department of Chemistry, University of California.

(1) Furstenau, N.; Hillenkamp, F.; Nitsche, R. *Int. J. Mass Spectrom. Ion Processes* 1979, *31*, 85-91.

(2) Asamoto, B.; Young, J. R.; Citerin, R. J. *Anal. Chem.* 1990, *62*, 61-70.

(3) Asamoto, B.; Bryan, S. R.; Judy, C. L.; Linton, R. W.; Hagenhoff, B.; Deimal, M.; Benninghoven, A. *SIMS VII*, 1990.

(4) Becker, C. H.; Jusinski, L. E.; Moro, L. *Int. J. Mass Spectrom. Ion Processes* 1990, 495, R1-R4.

(5) von der Linde, D.; Danielzik, B. *IEEE J. Quantum Electron.* 1989, *25*, 2540.

(6) Pallix, J. B.; Schühle, U.; Becker, C. H.; Huestis, D. L. *Anal. Chem.* 1989, *61*, 805-811.

(7) Meijer, G.; de Vries, M. S.; Hunziker, H. E.; Wendt, H. R. *J. Chem. Phys.* 1990, *92*, 7625.

(8) Nogar, N. S.; Estler, R. C.; Miller, C. M. *Anal. Chem.* 1985, *57*, 2441-2444.

(9) Otis, C. E. *Appl. Phys.* 1989, *B49*, 455.

(10) Lubman, D. M.; *Lasers and Mass Spectrometry*; Oxford University Press: New York, 1990.

(11) Li, Y.; McIver, R. T.; Hemminger, J. C. *J. Chem. Phys.* 1990, *93*, 4719.

(12) Hunt, J. E.; Lykke, K. R.; Pellin, M. J. *Methods and Mechanisms for Producing Ions from Large Molecules*; Plenum Press: Minaki, Canad, 1990.

(13) Engelke, F.; Hahn, J. H.; Henke, W.; Zare, R. N. *Anal. Chem.* 1987, *59*, 909-912.

(14) Gardella, J. A.; Pireaux, J.-J. *Anal. Chem.* 1990, *62*, 645A-660A.

(15) Lazare, S.; Granier, V. *Laser Chem.* 1989, *10*, 25.

(16) Feldmann, D.; Kutzner, J.; Laukemper, J.; MacRobert, S.; Welge, K. H. *Appl. Phys.* 1987, *B44*, 81-85.

(17) Srinivasan, R.; Braren, B. *Chem. Rev.* 1989, *89*, 1303.

(18) Johlman, C. L.; Wilkins, C. L.; Hogan, J. D.; Donovan, T. L.; Laude, D. A.; Youssefi, M.-J. *Anal. Chem.* 1990, *62*, 1167-1172.

(19) Huang, L. Q.; Conzemius, R. J.; Junk, G. A.; Houk, R. S. *Anal. Chem.* 1988, *60*, 1490-1494.

(20) Lattimer, R. P.; Harris, R. E. *Mass Spectrom.* 1985, *Rev. 4*, 369-390.

(21) Lattimer, R. P.; Harris, R. E.; Rhee, C. K. *Anal. Chem.* 1986, *58*, 3188.

(22) Lattimer, R. P. *Rubber Chem. Technol.* 1988, *61*, 658.

(23) Lattimer, R. P.; Harris, R. E. *Rubber Chem. Technol.* 1989, *62*, 548.

0003-2700/92/0364-2797$03.00/0

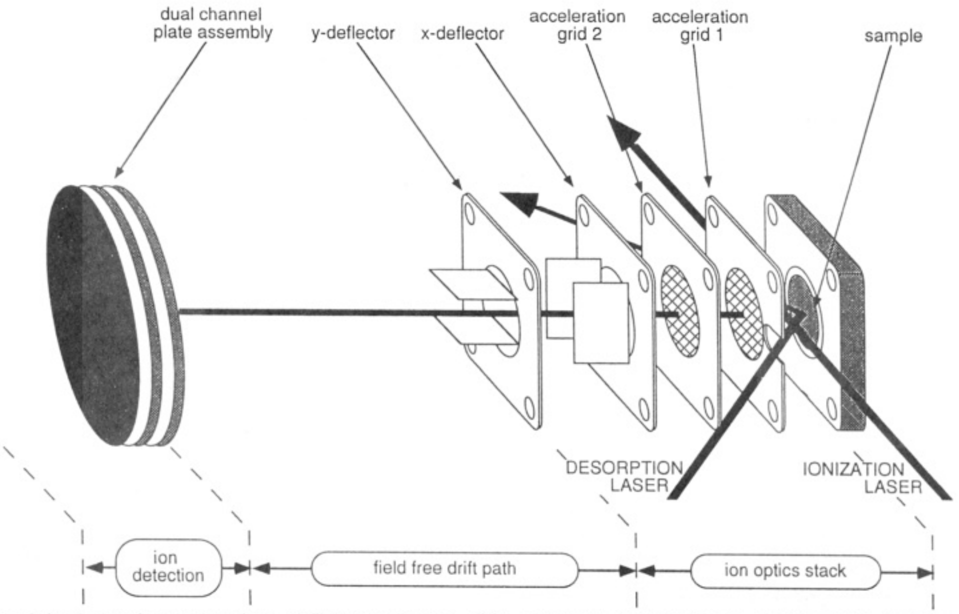


Figure 1. Schematic of the laser desorption time-of-flight apparatus. The sample is mounted on a rapid sample transfer rod and loaded into the system and then the rod is retracted. The sample is typically at 8 kV and grid 1 is at 7.6 kV for postionization or 0 kV for prompt-ion detection. The laser beams enter and exit the apparatus through fused silica windows.

present study. Antioxidants and antiozonants are added to polymers to prevent deterioration due to oxidative degradation of polymer bonds. Other species present in some polymers include flame retardants, mostly halogen-containing compounds that chemically deprive the flame of oxygen; plasticizers that soften brittle polymers and lower processing temperatures; UV stabilizers that protect the polymer from harmful effects of the near UV; mold releases that coat mold surfaces to prevent sticking and to ease removal of the part from the mold; mildicides and fungicides that control microbial attack at the surface of polymers; dyes and pigments that impart color to the polymer; and lubricants that act to reduce friction between polymer molecules (internal) and to reduce friction at interfaces (external).

Few methods exist that can detect and characterize such a wide diversity of molecular species at surfaces, especially when the species are present in only minor concentrations. One currently used method is prompt ion detection following laser desorption. A more elegant method is laser desorption to volatilize the surface molecular species into a neutral plume, followed by laser (species-sensitive) ionization. This method decouples the desorption and the ionization step, allowing each process to be independently optimized. In this paper, we compare these two approaches using well-characterized vulcanizate samples. (We will not discuss in detail the various physical and chemical aspects of the vulcanizates. The interested reader is encouraged to consult ref 21 for details.) Special emphasis is placed on the various possibilities of postionization of the neutral plume. Analysis with the proper choice of laser wavelength and intensity provides information about the polymer that cannot be obtained by other means. This is especially true if the postionization process is combined with high-resolution mass spectrometry. First, we discuss the experimental aspects of this work including the mass spectrometer, the lasers utilized for desorption and ionization, and the details of data capture and manipulation. Then, the results are presented and discussed. Finally, the implications of this new technique are summarized, and future directions for this research are proposed.

EXPERIMENTAL SECTION

The laser desorption/time-of-flight (LD–TOF) apparatus has been discussed in detail previously.[12,24] The mass spectrometer consists of a sample surface, an acceleration field, and a field-free region with an ion detector at the end of the flight path (see Figure 1). The TOF mass spectrometer can be operated in two different modes. First, for measuring the mass spectrum of direct laser desorbed ions (ions produced by the desorption laser alone), the sample is held at 8 kV and the grids are held at ground. Second, for postionization experiments, a two-step acceleration is used with the sample at 8 kV, the first grid at 7.6 kV, and the second grid at ground. In practice, the extraction potentials in the ion source are adjusted to optimize the mass resolution of the ions formed by photoionization of desorbed neutral molecules. The overall flight path length is 120 cm with acceleration distances of 4 mm in each of the two acceleration regions. The accelerated ions are detected using a dual-channel-plate detector with a modest postacceleration potential. Data are recorded in a transient recorder with a maximum time resolution of 5 ns. Further processing of the data is accomplished in a PC-based software system. The typical operating vacuum is $\sim 2 \times 10^{-9}$ Torr. The mass resolution ($m/\Delta m$) of the apparatus is approximately 1000 (fwhm at $m/z \sim 700$ amu) using a 5-ns laser pulse, while a ≤ 70-ps, 266-nm laser pulse yields a resolution exceeding 1500 with the same apparatus.

The vulcanizate samples were prepared in two distinct ways for the analysis described in this paper. For *direct analysis*, a piece of the 2-mm-thick polymer was cut into a 1-cm^2 piece, and the front side was scraped in air with a razor blade to expose a fresh surface and placed immediately (within less than 1 min) into the TOF mass spectrometer via a rapid sample transfer system. These samples were held in place on the sample stub with a press-fit ring holding a copper foil with a 4-mm-diameter hole cut out of the center. For the *extract analysis*, the vulcanizate was allowed to dissolve in the particular solvent for a number of days, and the extract was pipetted (~ 100 μL) onto a polished-stainless-steel stub, evaporated to dryness, and inserted into the TOF mass spectrometer for later analysis. We varied the number of days of sample extraction and noticed no difference in the mass spectra although the solutions became more concentrated for longer extraction periods. A motor-driven micrometer mirror mount permitted the desorption laser beam to be rastered over the entire surface. This capability allows

---

(24) Lykke, K. R.; Pellin, M. J.; Wurz, P.; Gruen, D. M.; Hunt, J. E.; Wasielewski, M. R. *Mater. Res. Soc. Symp. Proc.* **1991**, *206*, 679.

control over the measurement position and provides fresh surface exposure from shot to shot, an important consideration for reliable surface analysis.

Various lasers are used for desorption and ionization. Typically, the 532-nm-focused output (or 266-nm-doubled output) of a Q-switched, mode-locked Nd^{3+}:YAG laser (<100-ps pulse duration) is the desorption beam, followed by one of a number of frequencies generated with a Q-switched Nd^{3+}:YAG laser (~5-ns pulse duration). These wavelengths (and energies) include 1064 nm (the fundamental, 1.16 eV), 532 nm (2nd harmonic, 2.33 eV), 355 nm (3rd harmonic, 3.49 eV), 266 nm (4th harmonic, 4.66 eV), and 212 nm (5th harmonic, 5.83 eV). In addition to these easily generated laser wavelengths, we have available a 3rd harmonic frequency-tripling cell to produce 118-nm radiation (9th harmonic, 10.5 eV). This is described in more detail below. We also use a XeCl excimer laser (308 nm, 4 eV) for desorption or for postionization. The lasers are independently triggered, allowing their relative timing to be adjusted. An iris is used to pick out the central portion of the desorption laser beam, and a series of neutral density filters, or a polarizer in a rotation stage, is used to regulate the beam intensity. The desorption laser is obliquely incident on the sample as shown in Figure 1. The energy of the desorption laser is typically less than 0.01 mJ/pulse with an irradiated area of $<10^{-3}$ cm^2. The ionization laser intensity can be continuously varied using a set of mirror-image beam splitters (one high reflector at a specified wavelength, one uncoated) rotated in opposite senses to keep the beam from deviating in position and direction.

The 118-nm radiation is produced by frequency tripling the third harmonic of a Nd^{3+}:YAG laser in a Xe/Ar mixture. This mixture is optimized by photoionizing acetone with the 118-nm radiation and maximizing the $m/z = 58$ signal in the TOF mass spectrometer. We estimate the intensity of the generated VUV radiation to be ~100 nJ (~10^{11} photons/pulse). The 118-nm beam is separated from the 355-nm laser beam using the dispersion of a MgF_2 lens.[25-28] The two beams are separated by ~2 mm at the sample position. By translating the desorption laser spot ~2 mm on the sample, either 118-nm positionization or 355-nm postionization is obtained. The position of the desorption laser spot is monitored in real time with a video camera. This allows a simple method for quickly acquiring both the 355-nm data and the 118-nm data. Recently, we have installed a translatable 355-nm-high reflector inside of the vacuum system before the TOF ion optics. This allows for total rejection of the 355-nm beam.

RESULTS AND DISCUSSION

The three different types of analysis presented in this paper are laser desorption, laser desorption/laser ionization, and laser ionization alone. Each particular type of analysis has its own merits, and there have been numerous discussions of each (see Introduction for references). Prompt ions, produced by laser desorption, can be detected with high sensitivity and, in many cases, can give a broad overall understanding of the composition of the surface. However, detection of prompt ions from laser desorption suffers from extreme matrix effects. Thus, the measured ion abundances have little or no relation to the quantitative composition of the surface. The ions with the lowest ionization potential (for positive ion desorption) or the highest electron affinity (for negative ion desorption) are usually the ions detected with low laser fluence. However, at higher laser fluences, many of the species present at the surface are detected. At these fluxes, however, fragmentation of desorbing molecules often becomes a dominant channel. For most investigations performed in our laboratory, prompt ions are detected first (both positive and negative ions) to determine the overall makeup of the surface. Many times this will suffice to detect an unknown additive in a polymer. However, after this initial examination, a postionization analysis is usually performed to obtain a more comprehensive characterization of the sample.

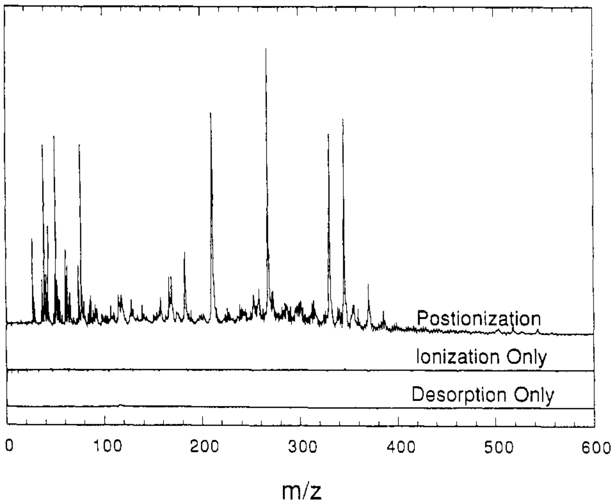


Figure 2. Direct analysis of vulcanizate B. The spectra taken with desorption only (postionization laser blocked) and ionization only (desorption laser blocked) yield a very weak signal and are shown as dashed and dotted lines near the zero signal level. The large peaks in the postionization spectrum 355 nm are indicative of certain additives in this vulcanizate (see text for details). The spectra are offset for clarity.

Postionization Experiments. Figure 2 displays a typical LD-TOF spectrum for vulcanizate B (direct analysis). This spectrum was acquired using the 308-nm excimer laser for desorption, followed by 355-nm light for ionization. Detection via resonantly enhanced multiphoton ionization (REMPI)[29] allows a few of the additives present in the polymer to be preferentially detected over the ubiquitous hydrocarbons in the polymer. A detailed discussion of the vulcanizates and the additives is presented in ref 21. Also included in Figure 2 are spectra obtained with the desorption laser blocked (ionization only) or with the ionization laser blocked (desorption only), showing that this surface analysis method is a probe of the desorbed *neutral* species only. The analysis is much less matrix-dependent than prompt-ion mass spectrometry because the desorption laser provides the energy for neutral particle removal only, without the extra energy needed for direct ionization. In addition to diminishing the matrix effect introduced by the surface, less laser fluence is required for the removal of particles, thus reducing the chance for fragmentation.

Figure 3 is an expansion of a postionization spectrum, accentuating the additive-rich portion of the mass spectrum for vulcanizate B. The higher ionization laser fluence utilized in this spectrum yields more fragmentation than shown in Figure 2 (see later). The molecular weight is labeled for each of the large peaks. Mass 268 is the parent peak for the antiozonant HPPD (see Table I), and $m/z = 211$ is characteristic of the fragment for HPPD. Poly-TMDQ (antioxidant) yields the mass peaks at $m/z = 346$ (parent) and 331 (methyl loss). Some of the other ions present are tentatively assigned to $m/z = 167$ (mercaptobenzothiazole $M^{\bullet+}$), $m/z = 169$ (PhNH-Ph$^{\bullet+}$), and $m/z = 183$ (Ph-NH-Ph-NH$^+$).

We will not discuss the laser desorption process itself in detail in this paper since numerous reviews in the literature

---

(25) VonDrasek, W. A.; Okajima, S.; Hessler, J. P. *Appl. Opt.* **1988**, *27*, 4057–4061.

(26) Van Bremer, S. E.; Johnston, M. V. *J. Am. Soc. Mass Spectrom.* **1990**, *1*, 419–426.

(27) Laporte, P.; Subtil, J. L.; Courbon, M.; Bon, M.; Vincent, L. *J. Opt. Soc. Am.* **1983**, *73*, 1062–1069.

(28) Steenvoorden, R. J. J. M.; Kistemaker, P. G.; de Vries, A. E.; Michalak, L.; Nibbering, N. M. M. *Int. J. Mass Spectrom. Ion Processes* **1991**, *107*, 475–489.

(29) Lustig, D. A.; Lubman, D. M. *Int. J. Mass Spectrom. Ion Processes* 1991, 107, 265–280.

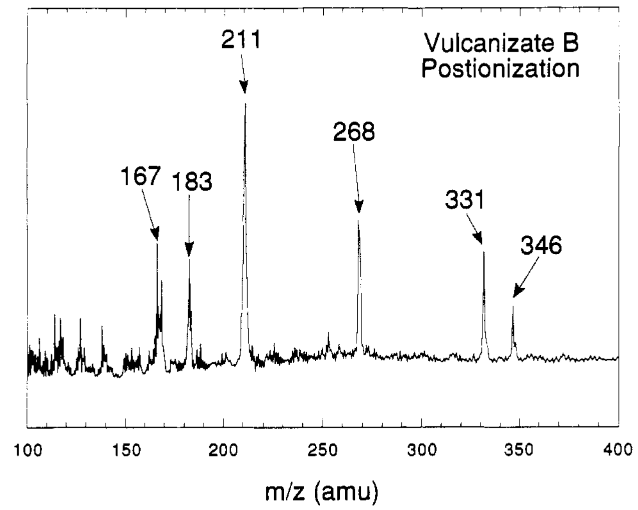
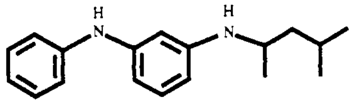
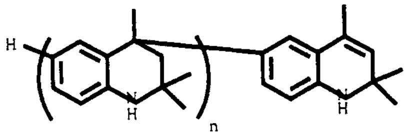


Figure 3. Expansion of the middle mass range for 355-nm postionization of vulcanizate B (direct analysis). The mass range emphasizes the two different additives, HPPD and poly-TMDQ. (See text for details.)

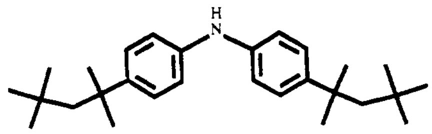
Table I. List of Molecular Additives Detected[a]



HPPD
MW=268)



Poly-TMDQ
MW=173 + 173n



DODPA

molecular additive	molecular weight	vulcanizate
DOPPD *N,N'*-bis(1-methylheptyl)-*p*-phenylenediamine	332	A
DODPA di-*tert*-octyldiphenylamine	393, (322)	A
poly-TMDQ poly(2,2,4-trimethyl-1,2-dihydroquinoline)	346, 331	B
HPPD *N*-(1,3-dimethylbutyl)-*N'*-phenyl-*p*-phenylenediamine	268, (211), (183), (169)	B, C

[a] Vulcanizate A is based on natural rubber, vulcanizate B is a styrene–butadiene rubber, and vulcanizate C is a *cis*-polybutadiene rubber. Fragments observed in mass spectra are listed in parentheses.

already exist.[17,30,31] Two different schools of thought have evolved concerning laser desorption/laser ablation of polymeric species and each seems to be valid under specific conditions. Particle removal results from either desorption due to electronic excitation to an antibonding state of the polymer, followed by bond breaking, or from thermal desorption caused by local heating of the laser-irradiated area. In terms of *surface* species, the thermally activated desorption model can be applicable. However, species in the near-surface region are only accessable via laser ablation/bond breaking (electronic excitation) since the thermal desorption process would tend to decompose some of the higher-molecular-weight additives present.

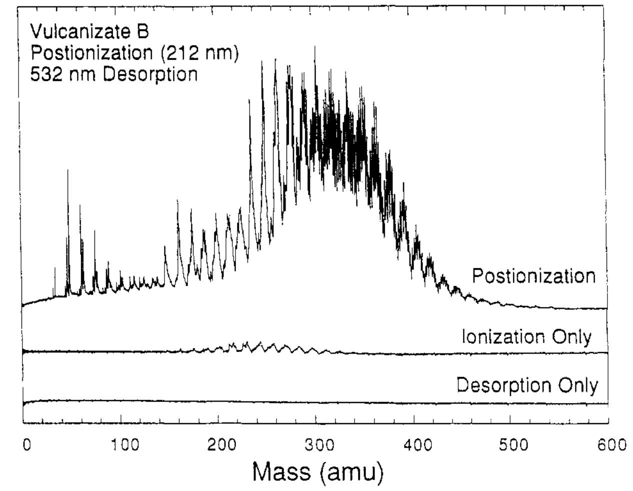


Figure 4. Postionization of vulcanizate B utilizating 212-nm radiation for the ionization laser. Also shown are ionization only (desorption laser-blocked) and desorption only (ionization laser-blocked). Compared with the 355-nm postionization data, the 212-nm radiation yields molecular ions characteristic of the bulk of the polymer and not just additives.

We have explored many different wavelengths for laser desorption and have not observed any differences in the product distribution. Furthermore, we operate the desorption laser at very low fluences. For direct-ion desorption, the laser fluence is adjusted to slightly above the desorption threshold for ion production. The laser fluence can be lowered below this ion-product threshold but still above the lower threshold for neutral particle production. This indicates that the polymer is probably ablated by a thermal desorption mechanism. However, the heating rates are much faster than in a typical thermal programmed desorption (TPD) experiment. In TPD, the heating rates are typically ~1–10 K/s, and the surface (and near-surface) species may either react with other species, dissociate on the surface, or diffuse from the bulk. In laser desorption, the heating rates may approach 10^9 K/s and the desorption channel may dominate other effects due to the desorption preexponential factor. That is, a higher energy pathway may be available simply due to a higher rate of the process.

Since thermal desorption is relatively matrix-independent, most of the observed matrix dependence arises from surface ionization processes. The ionization process can be accomplished in a controlled manner by choosing the proper wavelength (and energy density, vide infra) of the postionization laser in a laser desorption/positionization experiment. To illustrate this point, another set of mass spectra utilizing 212-nm light for ionization is displayed in Figure 4. The desorption-only and ionization-only scans are also shown for consistency. Background gas (pump oil) in the vacuum system is more efficiently ionized by 212-nm radiation than by 355-nm radiation, and ions appear at *m/z* ~150–300 amu in the ionization-only spectrum. However, a comparison of the ionization only and the postionization scans show that the signals from the rubber vulcanizate and additives dominate

---

(30) Avouris, P.; Walkup, R. E. *Annu. Rev. Phys. Chem.* **1989**, *40*, 173–206.

(31) King, D. S.; Cavanagh, R. R. *Adv. Chem. Phys.* **1989**, 45.

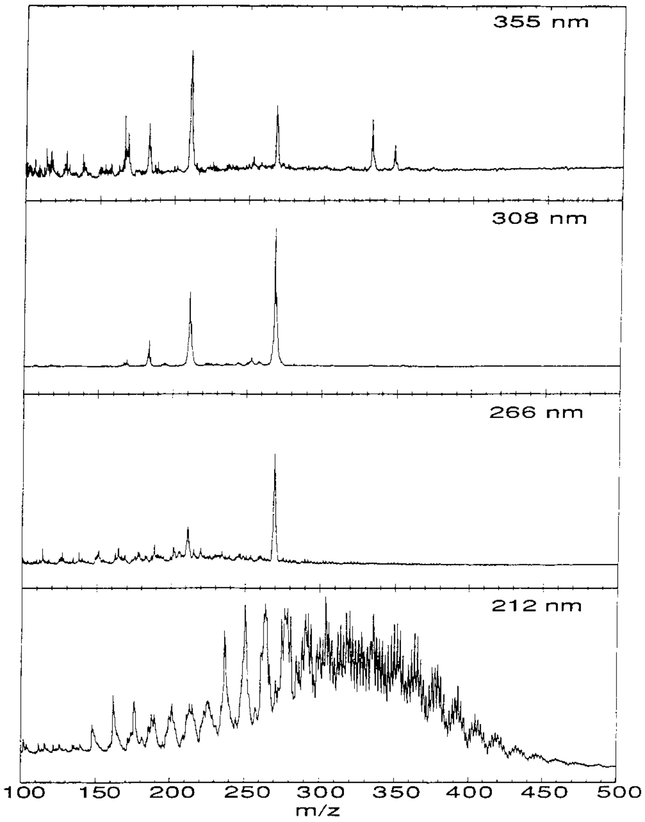


Figure 5. These four panels display postionization data at four different wavelengths for direct analysis of vulcanizate B. Each of the wavelengths accentuates different characteristic species in the vulcanizate.

the background signals. Much more ionization of the processing oils and paraffin wax and less selectivity of the additives occurs for 212-nm photoionization. The 212-nm radiation is absorbed by most of the species, and the ~11.7 eV available for (1 + 1) ionization will ionize most of the species that absorb at 212 nm. Therefore, the selectivity of the 355-, 308-, and 266-nm light (caused by π-π^* transitions in the additives) is absent in the 212-nm case.

Figure 5 displays a panel of the direct analysis experiments of vulcanizate B for wavelengths ranging from 355 to 212 nm. This figure demonstrates that different ionization laser wavelengths access different polymer additives, although there is some overlap between wavelengths. Radiation at 355 nm selectively ionizes the additives that contain aromatic groups, and the 212-nm radiation tends to ionize almost everything except for the small ablation fragments from the polymer. Figure 6 is a spectrum of the same sample utilizing 118-nm ionization, 308-nm desorption, again by direct analysis. The low-mass species are considerably enhanced relative to the high-mass species observed with the longer wavelengths. This is because of the difference in the optical absorption strength for the different species. That is, the small molecular weight fragments from the SBR (styrene–butadiene rubber) surface do not have large oscillator strengths for one photon absorption for $\lambda > 200$ nm. The larger additives observed have large oscillator strengths for one photon absorption (π-π^* transitions), and thus (1 + 1) REMPI is allowed. In summary, the 355-nm light preferentially accentuates the additives in the polymer (selective), the 212-nm light ionizes most of the other large species, while the 118-nm light can be utilized to characterize the majority of the desorbed material (nonselective ionization). This makes the combination of using 118-, 212-, and 355-nm radiation for positionization an extremely powerful technique.

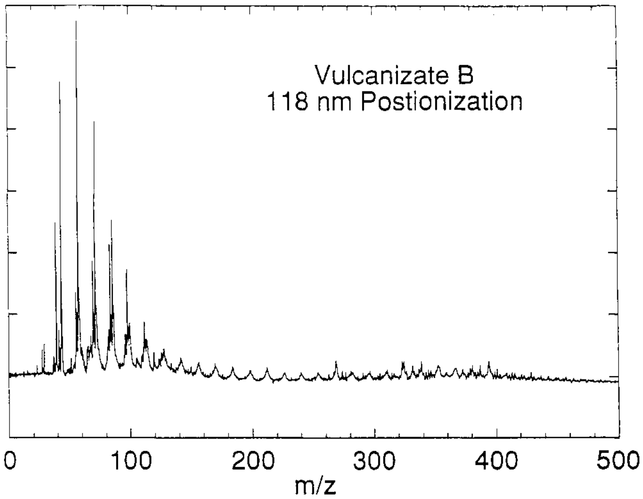


Figure 6. Postionization of vulcanizate B using 118-nm (10.5 eV) radiation. The low-mass region is probably caused by the rubber backbone and is present in higher abundance than the additives that were accentuated with the longer postionization wavelengths.

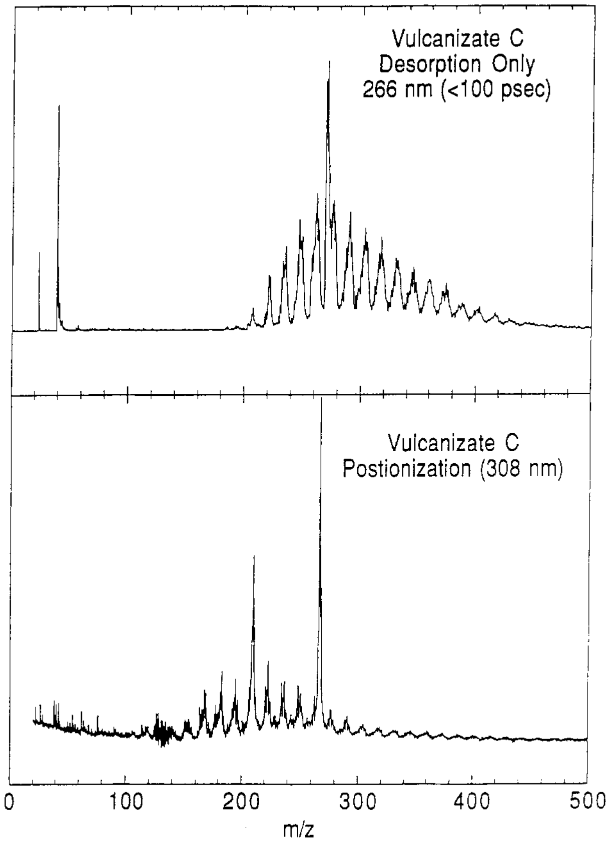


Figure 7. Comparison of postionization with 308-nm (bottom panel) and 266-nm prompt-ion desorption (positive ions, top panel) of vulcanizate C. The 308-nm postionization data were obtained utilizing 266-nm desorption (macropulse from the Q-switched mode-locked Nd:YAG laser). The 266-nm desorption laser pulse for prompt-ion detection is <100 ps in duration. The additives present in the vulcanizate are emphasized in the postionization scan. However, the prompt-ion spectrum does display many mass peaks characteristic to this polymer. The two peaks at low mass in the prompt-ion spectrum are sodium (m/z = 23) and potassium (m/z = 39 and 41).

Prompt Ions. A widely used procedure for analyzing polymers is direct laser ablation and monitoring the prompt ions produced. Figure 7 displays an analysis of vulcanizate C employing this scheme compared with postionization. The desorption pulse (266 nm, <70 ps) produces positive and negative ions directly, given enough laser fluence. The top panel in the figure is the positive-ion spectrum, and the 308-

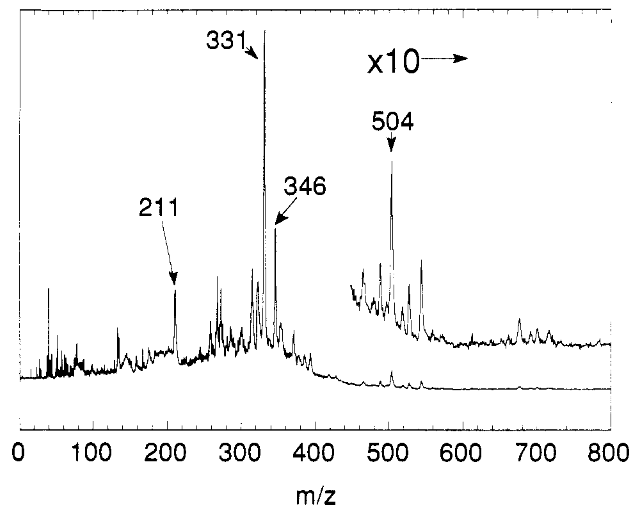


Figure 8. Postionization spectrum of an acetonitrile extract of vulcanizate B. The desorption pulse is the frequency-quadrupled (266 nm) macropulse from the Q-switched mode-locked Nd:YAG laser, and the postionization wavelength is 118 nm. The major peaks visible at high mass are attributable to poly-TMDQ.

nm postionization spectrum is displayed in the bottom panel for comparison. The two peaks at low mass in the desorption-only spectrum (m/z = 23, 39) correspond to Na and K ions, respectively. These two positive ions appear in most direct desorption experiments since the ionization potential for each species is so low (5.1 eV for Na and 4.3 eV for K). In fact, these low-mass alkali-metal prompt ions tend to overwhelm the higher-mass species in direct desorption experiments. However, the higher-mass ions between 200 and 400 amu are caused by ionization of the various surface species, such as processing oils and some of the additives.

Extract Analysis. An additional method for polymer analysis is the use of extract pretreatment of the polymer. In this case, we utilize two different solvent pretreatments—acetone and acetonitrile. The first sample investigated is vulcanizate B extracted in acetonitrile. The TOF mass spectrum is shown in Figure 8. The desorption wavelength is 266 nm (picosecond desorption) and postionization is achieved utilizing 118 nm (one-photon ionization). As is clearly evident, higher-molecular-weight species are detected and are attributable to some of the various additives present in the vulcanizate. Most of the ($m/z > 400$) ions are ascribed to poly-TMDQ additives present at the < 3% level in the bulk vulcanizate. As already pointed out in ref 21, higher-mass species can be observed in extracts that cannot be seen by direct analysis. The low-mass alkyl fragment ions are not observed to any degree in this spectrum in spite of the detectability by one-photon ionization. This is because acetonitrile extracts organic stabilizers in preference to processing oils.[32] Similar mass spectra were recorded following acetone extraction.

Since poly-TMDQ is observed as an additive in most of the vulcanizate B spectra, the laser desorption process was studied in more detail using pure poly-TMDQ as a desorption surface. The pure poly-TMDQ was dissolved in dichloromethane and evaporated on the stainless-steel sample probe. Figure 9 shows the signal obtained from desorption only, ionization only, and positionization. A few points need to be made concerning these spectra. The lack of signal from the ionization-only experiment is indicative of the low volatility of this hindered amine stabilizer. The main peaks in the desorption + postionization spectrum at m/z = 865, 692, 519, 346 are caused by the molecular ion of this oligomeric additive

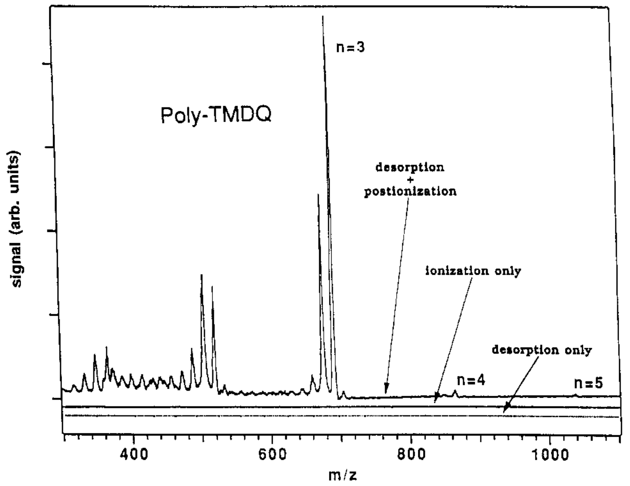


Figure 9. Mass spectra of pure poly-TMDQ acquired utilizing postionization (308-nm desorption, 248-nm postionization, top spectrum), ionization with 248 nm only (middle spectrum), and desorption with 308 nm only (bottom spectrum).

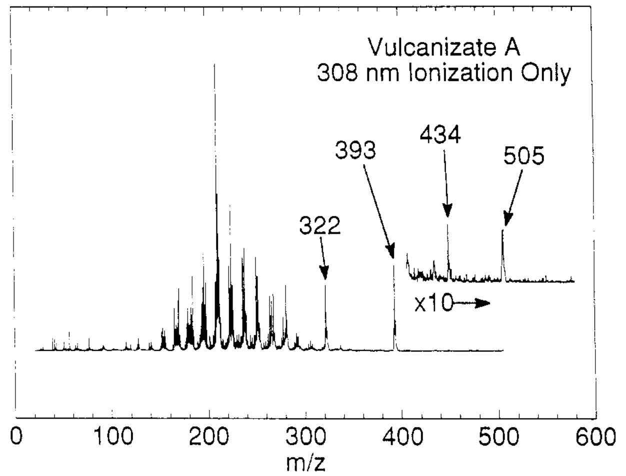


Figure 10. Mass spectrum obtained with 308-nm ionization-only of vulcanizate A (direct analysis). The gas-phase species detected are provided by evaporation from the near-surface region of the polymer and the strongest signals disappear within ~5 min after inserting the sample into the vacuum system.

(see Table I). The mass peaks ~16 units below these main peaks originate from demethylation of the parent peak in the ionization process. The peaks ~16 amu above the parent peaks are attributed to oxidation products. In our earlier work,[12] velocity distributions for laser-desorbed neutrals of these samples were obtained and helped to define the pulse delay between desorption and ionization. In practice, this delay is optimized empirically by varying the time delay and observing the signal on a fast oscilloscope.

Ionization Only. If a polymer additive is volatile enough, its presence can be ascertained via ionization-only spectra. That is, the additive evaporates from the near-surface region for a certain amount of time, and the ionization laser alone will yield a reasonable amount of signal to obtain an analysis of the additive present. Figure 10 is a representative 308-nm ionization-only spectrum from vulcanizate A (direct analysis). The major high-mass peaks are from DODPA (see Table I). DODPA is an antioxidant and forms two dominant photoions, m/z = 393 ($M^{\bullet +}$) and 322 ($(M - C_5H_{11})^+$). A DODPA impurity, originally seen in vulcanizate A by Lattimer et al.,[21] was also seen in the postionization spectrum. This impurity (tri-*tert*-octyldiphenylamine) yields the ions observed at m/z = 505 ($M^{\bullet +}$) and 434 ($(M - C_5H_{11})^+$). By postionization (266-nm desorption, 308-nm postionization, Figure 11), the DODPA peaks are accentuated relative to the rest of the species.

---

[32] Carlson, D. W.; Hayes, M. W.; Ransaw, H. C.; McFadden, R. S.; Altenau, A. G. *Anal. Chem.* 1971, *43*, 1874–1876.

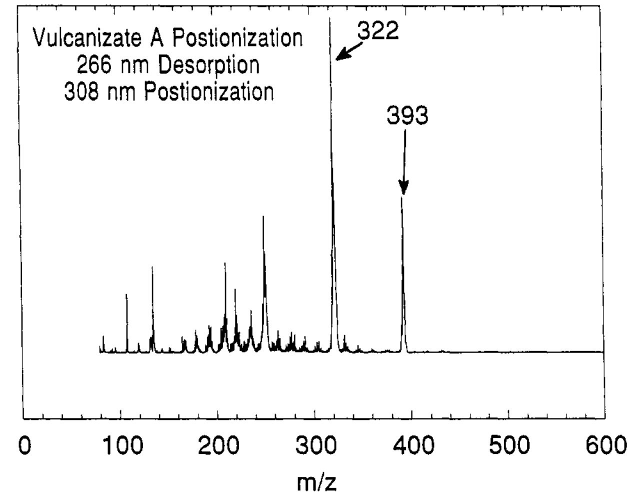


Figure 11. Postionization spectrum of vulcanizate A after the intense ionization-only signals have disappeared. The strongest peaks are characteristic of DODPA.

A unique approach for characterizing a polymeric additive is through multiphoton dissociation/ionization. In this type of experiment, the molecular ion and the associated fragments are detected following intense photon fluxes. Ionization spectra of gas-phase species from vulcanize B are shown in Figure 12. The most intense peaks in the spectrum for low laser fluence are indicative of the polymeric additive HPPD (see Table I for the molecular weights and proper chemical names for the given additives). These species are probably ionized via (1 + 1) ionization at 308 nm (4 eV) and are thus more efficiently ionized than the other species present. This type of ionization scheme (utilizing 250–350 nm) accentuates the aromatic species. Many more fragment peaks are evident in the lower portion of the figure (high fluence). These fragment peaks are due both to fragmentation of the HPPD additive and to fragments from other species present in the gas phase from the ablation of the vulcanizate.

CONCLUSIONS

We have demonstrated that LD–TOF can provide important analytical information about industrially important materials, such as vulcanizate rubbers. The selectivity of the technique allows for a determination of many of the additives present in the vulcanizates. Although not demonstrated in the present experiments, this technique is an extremely sensitive method for detecting surface and near-surface species. In fact, the laser desorption/laser ionization experiments reported in this work left no visible damage on the sample surface. These techniques should be directly applicable to the industrial workplace. A systematic study of the quantification of the detection of additives in polymers is needed. If the detection for direct analysis is shown to be quantifiable, then an "on-line" laser desorption apparatus could be adapted to test for the amount of incorporation of polymeric additives. In addition, segregation phenomena can be probed with this apparatus and will allow a careful examination of various processes involved in the mixing of polymers and additives. Closely related to this is the investigation of diffusion-related phenomena. Diffusion to the surface (blooming) of polymers is an important process, both technologically and scientifically. A future direction of the research reported here is the detailed study of these diffusion processes in model systems. Once these model systems are understood on microscopic and macroscopic levels, the possibility exists to transfer this knowledge into real-world problems.

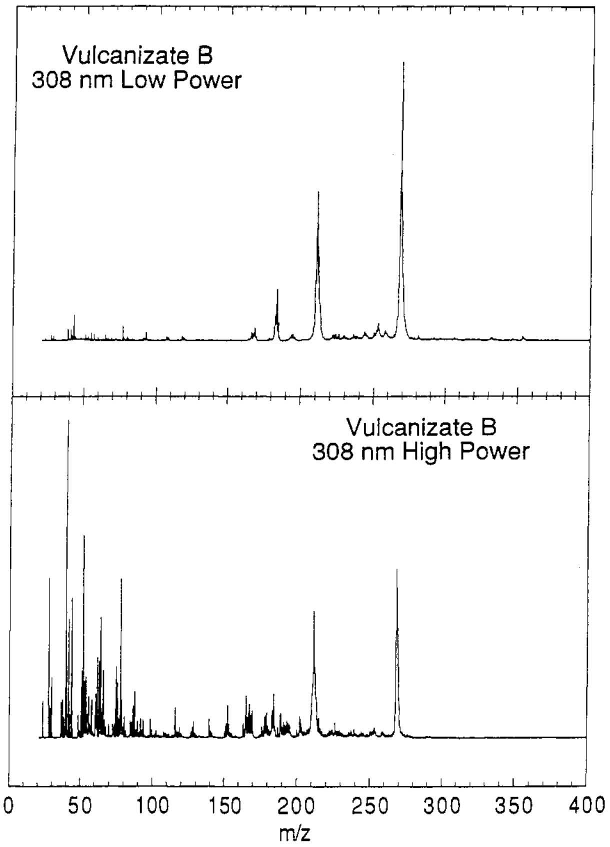


Figure 12. Illustration of the effect of intense laser radiation on the mass spectra of postionization of vulcanizate B (308 nm, direct analysis). The "low-power" spectrum (top panel) displays the peaks characteristic of the HPPD additive and very little else. The "high-power" spectrum (bottom panel) shows peaks characteristic of the HPPD additive along with mass peaks from cracking of the polymer backbone.

ACKNOWLEDGMENT

This work was supported by the U.S. Department of Energy, BES-Materials Sciences and Chemical Sciences, under Contract W-31-109-ENG-38.

Received for review April 7, 1992. Accepted August 20, 1992.

Registry No. DOPPD, 103-96-8; DODPA, 15721-78-5; TMDQ (homopolymer), 26780-96-1; HPPD, 793-24-8.