LCMS/MS and TOF-SIMS Identification of the Color Bodies on the Surface of a Polymer

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The source of discoloration on a polymer surface can often be identified by washing the surface of the discolored polymer to collect the color bodies, then analyzing the washings using liquid chromatography-mass spectrometry (LCMS), with an in-line ultraviolet (UV) detector set at the optimum wavelength for the particular color bodies. A reference sample having no discoloration is also analyzed in the same way. In this paper, results from this methodology are compared with direct time of flight-secondary ion mass spectrometry (TOF-SIMS) analysis of a discolored polymer. The benefits and shortcomings of each methodology are discussed. (J Am Soc Mass Spectrom 2005, 16, 295–301) © 2004 American Society for Mass Spectrometry

Surface discoloration of a polymer can result from a number of different phenomena, e.g., contamination, component migration, oxidation, and other chemical reactions. Components rising to the surface can give rise to bloom [1], e.g., protective waxes are beneficial, but thiazoles (Mercaptobenzothiazole) are undesirable. Oxidation of antioxidants can form color bodies, e.g., phenolic antioxidants can form quinone methides [2]. The first step in identifying a color body is to separate it from the polymer, and this can often be achieved by washing the surface with a suitable solvent. The washings will be a complex mixture of the color bodies, additives, and other surface contaminants. Identification of the colored components requires further separation of the mixture, analysis of the separated components, and the ability to ascertain which of the components are colored. The combination of LCMS(/MS) with an in line diode array detector (DAD) is able to do the complete analysis in a single experiment.

The introduction of atmospheric pressure ionization sources has transformed LCMS from a difficult and unreliable technique into a routine analytical tool [3]. Color bodies are often polar molecules, which means that they are easy to ionize in an electrospray (ESI) ion source. However, the electrospray spectrum contains few (if any) fragment ions and therefore the identifica-

tion of unknowns requires that either an LCMS/MS spectrum is acquired and/or exact mass measurements [4] are performed to get the elemental formula of the pseudo molecular ion. An in line UV detector (preferably a DAD) is employed to determine which of the components separated by the HPLC column absorb at the appropriate wavelength to give the observed discoloration. Structure elucidation is made much easier if the analyst has a thorough knowledge of the sample chemistry and its history.

Imaging mass spectrometry [5] is a powerful technique for mapping the concentration of a compound on the surface of a matrix and has applications in many fields, including the analysis of inorganic materials, polymers, and biological materials. If the mass spectrometer is a time of flight (TOF) system, and is used to mass analyze secondary ions produced by bombarding a surface with high-energy particles, the technique is known as TOF-SIMS [6]. TOF-SIMS has been used to detect light stabilizers [7] and antioxidants [8] on the surface of a polymer, as well as for the characterization of the bulk polymer [9].

The polymer formulations in this study all contain mixtures of benzothiazole and thiuram disulfide accelerators, which are known to be synergistic combinations [10, 11].

Experimental

The outermost layer of normal and discolored polymer samples were washed with acetonitrile and the washings

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Table 1. Compounds of interest in the 3 polymer layers

Component	Amount (%)		
	Bottom Layer	Middle Layer	Top Layer
EPDM	38	33	33
N650 – Thermal process Carbon Black	33	-	-
N990 – Thermal process Carbon Black	11	-	-
Sunpar 2280 – high viscosity, low volatility paraffinic oil	12	6	6
CMBT – Copper 2-Mercaptobenzothiazolate	<1	-	-
Clay	-	38	38
Hisil 532 – Precipitated Silica inorganic filler	-	10	10
CaCO ₃	-	5	5
TBTD – Tetrabutyl thiuram disulfide	1	<1	<1
Black masterbatch containing ODPA – Octylated diphenylamine	-	<1	<1

evaporated to low volume. It was noted that after washing, the discolored sample lost its color, and its washings were a pale yellow/green in color, whereas the washings from the control sample were colorless.

LCMS and LCMS/MS

Spectra were acquired on a Hewlett-Packard (Palo Alto, CA) 1090 series II liquid chromatograph with a diode array detector, coupled to a Micromass (Beverly, MA) Q-TOF2 mass spectrometer. Chromatography was performed on a 2.1 mm diameter by 150 mm Luna RP column (Phenomenex, Torrance, CA) eluted with a mobile phase consisting of water (A) and acetonitrile (B). A gradient elution at 300 μ L/min starting from 70% A to 5% A in 10 min, with a 10 min hold at 5% A was used to separate the compounds of interest prior to mass spectral analysis. DAD/UV spectra were collected at 2 nm resolution. The Q-TOF was operated in positive ion electrospray mode with 3.0 kV applied to the inlet capillary. The LM and HM resolutions on the quadrupole filter were set to 5, resulting in a bandwidth of $\sim$ 1.5 Da. and the inlet cone was set at 100 V. Two product ion experiments of 471⁺ were performed, one at 80 V collision energy, and a second at 40 V, using argon as the collision gas. Prior to the analysis, the TOF analyzer was calibrated with NaI/RbI to 10 ppm accuracy.

TOF-SIMS

Spectra were acquired using a Physical Electronics model TFS-2000 TOF-SIMS (Eden Prairie, MN). The primary ion source was gallium. The liquid metal source was operated at a beam energy of 18 kV, a repetition rate of $\sim$ 10kHz and a pulse width of $\sim$ 1 ns. The beam was rastered over a 256 $\times$ 256 pixel area (150 μ m $\times$ 150 μ m area). The gun was fired at each pixel and a full mass spectrum was recorded. The beam position was recorded with each spectrum allowing for chemical maps to be extracted from the

data set. A low-energy (<30 eV) electron source was utilized (pulsed alternately with the primary ion source) to minimize static charge build-up on the electrically insulating samples. Positive secondary ions were extracted from the surface after each primary ion pulse. These secondary ions were accelerated into a triple focusing time-of-flight mass analyzer. The secondary ions were detected using a micro-channel plate detector and a 256 stop time-to-digital converter (156 ps time resolution). The flight time for each ion packet was recorded and the spectrum converted to a mass scale using a time to mass algorithm built into the instrument software.

Results and Discussion

The polymer samples were three component experimental E/P formulations. Each layer was a compounded ethylene/propylene/diene monomer (EPDM) rubber containing filler, carbon black, plasticizer, and antioxidants (Table 1); on aging the top layer of the polymer became discolored.

Figure 1 contains the HPLC results from the diode array detector for the analysis of the acetonitrile washings of the colored and control polymers. The UV chromatograms show that the extract from the discolored sample contains one component (retention time 13.28 minutes) that absorbs strongly over the range 380 to 450 nm, and is not present in the reference sample. The complete UV spectrum and electrospray mass spectrum of this component are in Figure 2.

The molecular weight and isotopic distribution of the molecular ion are consistent with it being tetrabutyl thiuram disulfide (TBTD) plus copper (Figure 3). Smith et al. [12], reported that copper ions could form two different types of complexes with thiuram disulfides. An ML⁺ complex, which is water-soluble and has a λ_{max} near 380 nm and a neutral ML₂ complex with λ_{max} around 430 nm. The UV spectrum of the complex detected in the acetonitrile washings is consistent with it having the ML₂ structure.

Figure 1. DAD traces from the LCMS analysis of the acetonitrile extracts: (a) Extract from control polymer, 220 to 500 nm; (b) extract from control polymer, 380 to 450 nm; (c) extract from Green polymer, 380 to 450 nm; (d) extract from Green polymer, 220 to 500 nm.

This neutral complex will only be detected if it becomes charged in the electrospray source. Positive ion electrospray mass spectra usually contain $(M + X)^+$ ions, where X is, e.g., H , Na , or NH_4 . Metal complexation has been used to improved the sensitivity of LCMS, e.g., Brodbelt et al. [13] report that when flavanoids are complexed with a metal and

neutral auxiliary ligand (L) they form cationized species that are two orders of magnitude more abundant than the protonated species, but the resulting ion is $[M^{II}(\text{flavonoid-H})L]^+$.

Traeger has reported [14] that the neutral metal carbonyl compound $cis\text{-Cr}(\text{CO})_2(\text{dpe})_2$ ($\text{dpe} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$); gives an ESI spectrum containing

Figure 2. LCMS spectrum and UV spectrum of the component in the discolored polymer extract that elutes from the HPLC column at 13.28 min.

Figure 3. Isotope distributions: (a) Theoretical distribution for $C_{18}H_{36}N_2S_4Cu$; (b) acquired data for the color body.

the 17-electron $trans-[Cr(CO)_2(dpe)_2]^+$ cation, i.e., Cr(0) has been oxidized to Cr(I). Dithiocarbamate ligands are known to stabilize high oxidation states [15], i.e., Cu(III) in

Scheme 1

Scheme 2

$[Cu(R_2dtc)_2]^+$. They are able to do this because they have a resonance form **1**, that has a positive charge on the nitrogen and the π -electron flow from nitrogen to the sulfur atoms gives a ligand with very strong σ -donor properties.

We conclude, therefore, that the color body is the neutral ML_2 complex, and that in the electrospray source copper (II) is being oxidized to copper (III). The resulting cation is stable because L is a dithiocarbamate. Reduction of Cu(II) complexes during electrospray has been reported by Gianelli et al. [16].

The electrospray LCMS spectrum contains few fragment ions and therefore an LCMS/MS spectrum was obtained as shown in Figure 4, and the fragment ions in the LCMS/MS spectrum are consistent with the suggested structure. When the mass calibration of the MS/MS spectrum was corrected to give the expected mass for the m/z 116 fragment ion, then the results listed in Table 2 were obtained. These fragment ion masses are in good agreement with the

Table 2. Masses and most likely elemental compositions of the fragment ions in the ms/ms spectrum (Figure 4)

Measured mass (Da)	Relative abundance (%)	Calculated mass (Da)	Measured–calculated mass (mDa)	Formula
116.0354	36.13	116.0354	0	$C_8H_{10}NS$
128.1436	10.46	128.1439	–0.3	$C_8H_{18}N$
172.1165	100	172.1160	0.5	$C_9H_{18}NS$
190.0668	1.68	190.0657	1.1	$C_8H_{17}NCu$
268.0255	20.36	268.0255	0	$C_9H_{19}NS_2Cu$
286.0357	3.57	286.0361	–0.4	$C_9H_{21}ONS_2Cu$
395.1639	1.08	395.1649	–1	$C_{20}H_{31}N_2S_3$
471.1102	63.13	471.1057	4.5	$C_{18}H_{36}N_2S_4Cu$

Figure 4. LCMS/MS spectrum of the pseudo molecular ion m/z 471. The exact masses and most likely elemental compositions for these ions are in Table 2.

calculated masses for the expected fragment ions. The only anomalous result is that for the fragment ion at m/z 286, because the exact mass gives an elemental formula containing oxygen.

The strong affinity between metals and dithiocarbamates is well documented in the scientific literature, and forms the basis of a number of analytical methods for the quantitative determination of metals. Sedlak et al. [17] report that for complexes of metals and Diethyldithiocarbamates the complexing strength follows the order: Cu(II) > Ni(II) > Pb(II) > Cd(II) > Zn(II).

A similar relationship is not unexpected for the dibutyldithiocarbamate, which may explain why copper from the copper 2-mercaptobenzothiazolate (CMBT) in the bottom layer migrates through the upper two lay-

ers, and forms the green complex with the tetrabutyl thiuram disulfide (TBTD) in the top layer. More details of the diffusion of curatives in elastomers can be found in studies by Gardiner [18, 19].

Having identified the source of discoloration using extraction plus LCMS/MS, we wondered whether similar data could be obtained by direct analysis of the polymer surface. Survey spectra were obtained from both the outside surface of the polymer and by slicing the polymer and looking at the freshly exposed polymer surface. TOF-SIMS of the surface of the discolored sample yielded spectra (Figure 5a and c) that contained the m/z 471 pseudo molecular ion and m/z 172 fragment ion that were seen in the electrospray LCMS/MS spectra (Figure 4), and these ions were absent in the spectra

Figure 5. TOF-SIMS spectra of the polymer surface: (a) Discolored polymer; (b) the control sample; (c) expansion of discolored polymer spectrum to show the isotopic distribution of the m/z 471 pseudo molecular ion; (d) expansion of control polymer to show the absence of the m/z 471 pseudo molecular ion.

Figure 6. (a) Spectrum of the control polymer; (b) spectrum of the discolored sample when both spectra were acquired from freshly exposed polymer; (c) Spectrum a subtracted from Spectrum b.

trum of the control sample (Figure 5b and d). The spectra of both samples contain many ions from silicones, e.g., m/z 207, 281, and 325 which are common surface contaminants, that make it difficult to see the ions of interest. The relative abundance of these ions was reduced when spectra were obtained from a freshly exposed polymer surface (Figure 6a and b), and because

the color body was distributed throughout the upper polymer layer. The same conclusions were reached from the two methods of sample preparation. By subtracting the averaged spectrum of the control sample from that of the discolored sample (Figure 6c), more fragment ions indicative of the presence of the copper dithiocarbamate were detected, i.e., m/z 412 and 268. If

Figure 7. Negative ion TOF-SIMS spectrum of the control polymer subtracted from the spectrum of the discolored sample.

one compares Figures 6 and 5 with Figure 4, then it is apparent that the copper dithiocarbamate is only detected in the colored sample, and that direct TOF-SIMS analysis is giving the same results as the more complex extraction followed by LCMS/MS methodology.

Close examination of the spectra of the surface showed the presence of ions from oxidation of the thiuram (m/z 487 Figure 5c) that are not present in the LCMS spectra. The m/z 394 ion in the spectrum of the control sample is protonated octylated diphenylamine (ODPA) antioxidant (also detected by GCMS analysis of the extracts) and the amine gives the expected MH^+ ion [20]. The background subtracted negative ion SIMS spectra (Figure 7) were interesting because they contained benzothiazole ions from the CMBT (m/z 166) and fragment ions from the thiuram (m/z 204). One can also see evidence for stearate (m/z 283), palmitate (m/z 255), and myristate (m/z 227) ions coming from stearic acid in the polymer.

Conclusions

The method of choice for the analysis of color bodies on the surface of a polymer is obviously extraction followed by LCMS/MS with an in-line DAD, because this gives unequivocal identification of the colored components. However, the method is time consuming and labor intensive. This study shows that TOF-SIMS can quickly provide clues as to the identity of color bodies, which for the analysis of known formulations may provide enough information to allow reformulation of the polymer so as to avoid the discoloration problem. For unknown formulations, the data analysis can be more complicated, as current TOF-SIMS databases are limited compared to the more extensive electron impact ionization MS databases available. However, the high mass resolution data provided by TOF-SIMS can be used to create a short list of possible fragments that can be useful for spectral interpretation. TOF-SIMS can also provide information about oxidation of compounds on the surface, which is not readily detected when samples are analyzed using the extraction LCMS methodology. Finally, these results suggest that once a color body has been identified, TOF-SIMS can be used to quickly confirm that the same color body causes surface discoloration of new samples.

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