PHYSICAL ELECTRONICS

CHEMICAL IMAGING
at the Interface of a Bulk Elastomer Laminate

OVERVIEW

Elastomer-based products are often composed of elastomer blends to meet the requirements of a specific application. Particular areas of importance regarding the performance of an elastomer blend include permeability, durability, cure versatility, compatibility and vulcanizability. Of the chemical and physical properties pertaining to an elastomer blend, some of the most germane properties include mix homogeneity, phase distribution and additive diffusion. The relative compatibility of natural rubber and bromobutyl rubber ensures a fine dispersion morphology, typically less than 0.5 µm, a property which has made this blend commercially significant.

Time-of-Flight SIMS (TOF-SIMS) has been applied to probe the interface of a natural rubber (NR) bromobutyl rubber (BrIIR) laminate cross-section. The BrIIR contains 2.0 wt.% bromine. The laminate also contains phases of carbon black, zinc oxide, sulfur and dibenzothiazole disulfide (MBTS) in addition to processing oil and stearic acid. Details of the laminate processing may be found elsewhere [1]. The resulting laminate was block-faced at -130 °C for analysis by TOF-SIMS. The interface of the

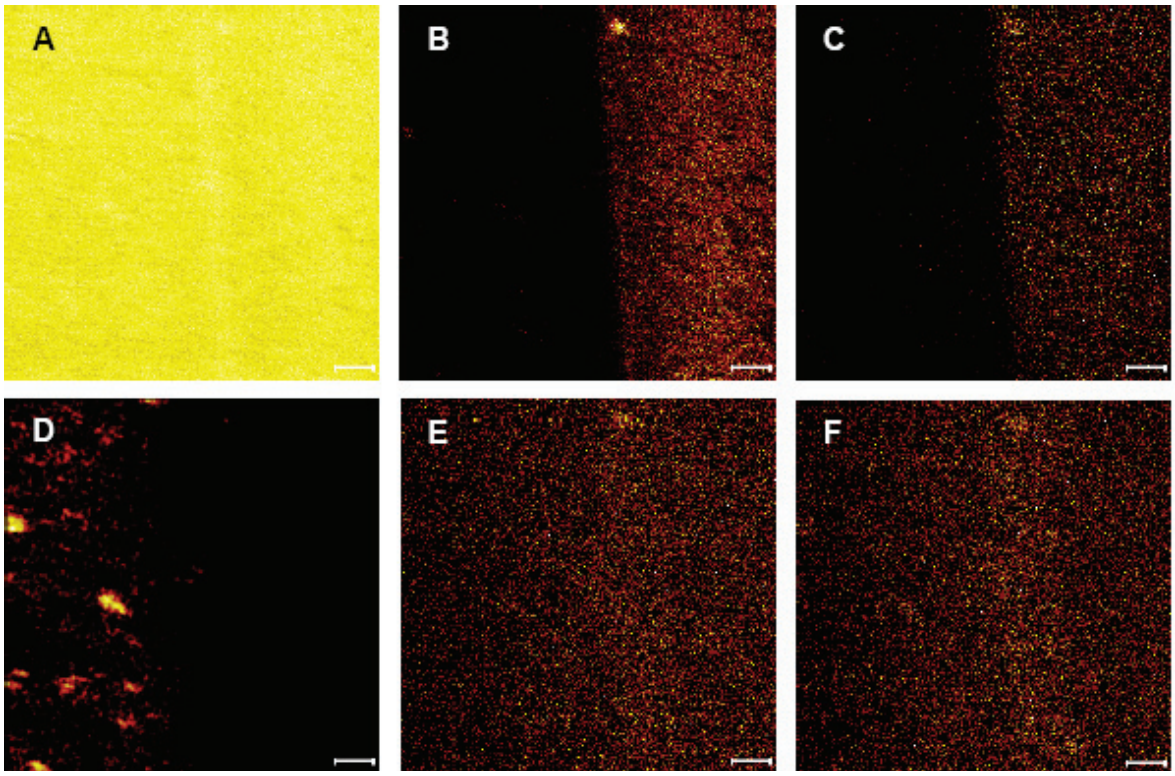

Figure 1: Negative polarity ion images of the NR-BrIIR laminate interface. (A) Total ion. (B) O^- (16 m/z). (C) S^- (32 m/z). (D) $^{79}Br^-$ & $^{81}Br^-$ (79 & 81m/z). (E) SCN^- (58 m/z). (F) $C_7H_4S_2N^-$ (166 m/z). The scale marker is 10 µm.

laminate cross-section was probed to evaluate the segregation of chemical phases, the distribution of particulates, and the diffusion of additives.

EXPERIMENTAL

An unbunched 30 keV Au^+ primary ion beam was used to acquire both positive and negative polarity images at the interface of the NR-BrIIR laminate cross-section. A raw data stream was collected in each polarity to allow further post-acquisition evaluation (i.e. retrospective analysis) of the data. The Au^+ primary ion beam had a DC current of 1.5 nA. A 100 µm x 100 µm area of the laminate interface was imaged in each polarity, at the same location on the sample, allowing direct comparison of the chemical information collected in each polarity. A raw data stream file was collected for 20 minutes in each polarity. Charge compensation was accomplished using 7 eV electrons.

RESULTS

Effective charge compensation enabled resolution of small features at the laminate interface in both secondary ion polarities. Ion imaging allowed the identification of major chemical constituents, phase-segregated chemical domains, particulates within the bulk elastomers, particulates at the laminate interface, and additive diffusion at the interface. Ion images from the negative and positive polarities are given in Figure 1 and Figure 2, respectively. In each of these figures, the NR is to the right side of the images and the BrIIR is to the left side of the images.

The negative polarity (Figure 1) reveals characteristic indicators of the NR, the additive MBTS, and phase-segregated domains of BrIIR. The NR side of the laminate is defined by the O^- and S^- ion signals. Within the NR layer, linescans show an oxygen-depleted zone of approximately 10 µm from the laminate interface while sulfur remains relatively immobile (less than 3 µm interface width). The linescan data is displayed in Figure 3. The Br^- ions, imaged using both isotopes at 79 and 81 *m/z*, clearly identify the BrIIR portion of the laminate. In Figure 1D, the image contrast has been adjusted to reveal phase-segregated bromobutyl domains. The bromobutyl domains range in size from approximately 1 µm to 10 µm. The SCN^- and $C_7H_4S_2N^-$ fragment ion signals arise from the additive MBTS. These images reveal that MBTS is enriched within a 10 µm region of NR at the laminate interface.

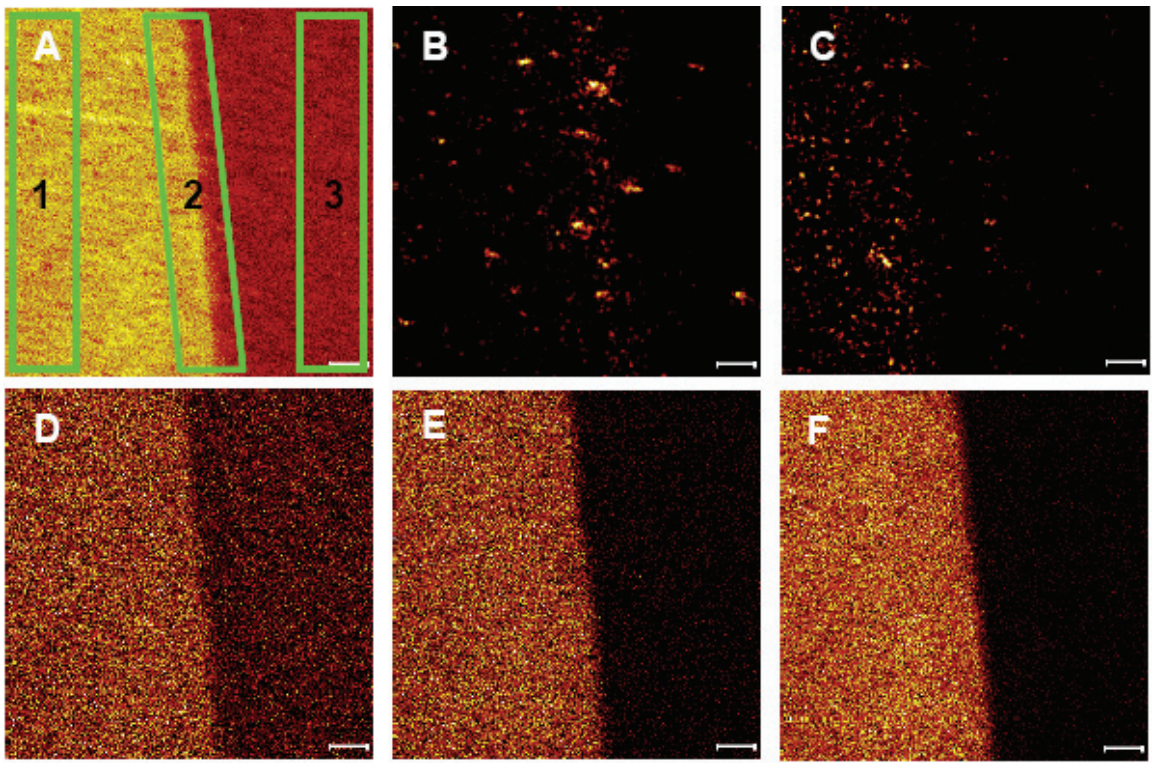

Figure 2: Positive polarity ion images of the NR-BrIIR laminate interface. (A) Total ion. (B) Na^+ (23 m/z).(C) Zn^+ (64 m/z). (D) $C_5H_9^+$ (69 m/z). (E) $C_6H_{11}^+$ (83 m/z). (F) $C_7H_{13}^+$ (97 m/z). The scale marker is 10 µm. The regions-of-interest (ROIs) are indicated on the total ion image.

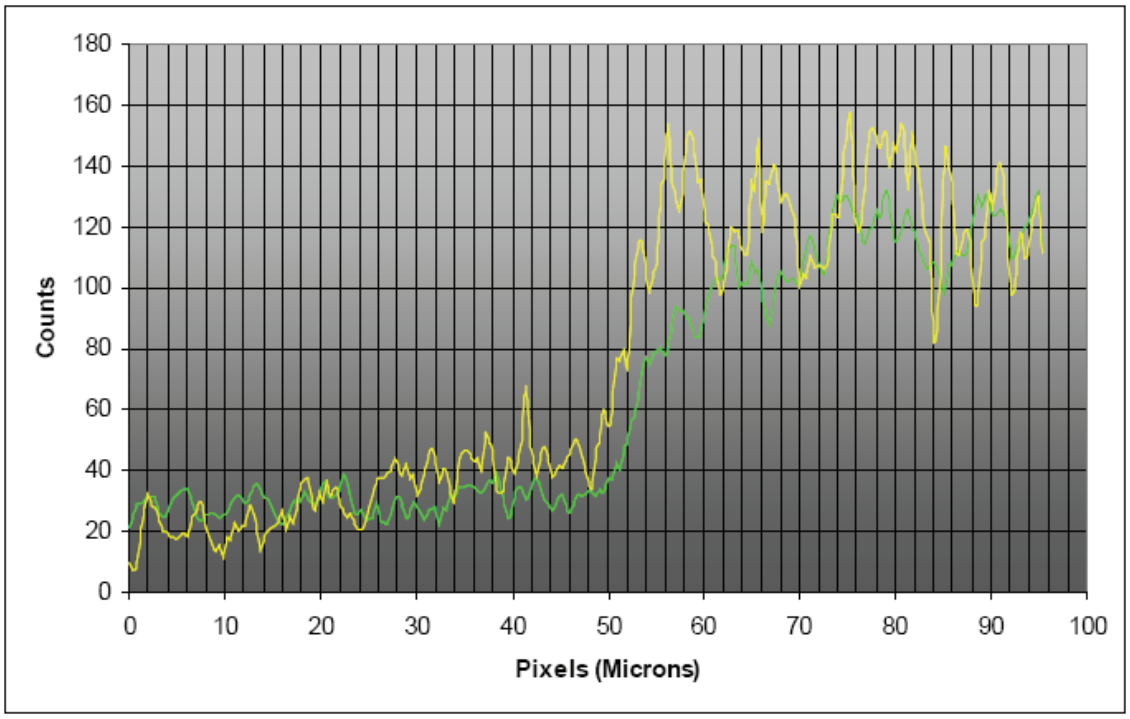

Figure 3: Linescans of O- (green) and S- (yellow) determined from the respective ion images. The linescan of oxygen indicates a depletion zone of approximately 10 µm wide. The interface width of sulfur is approximately 3 µm wide.

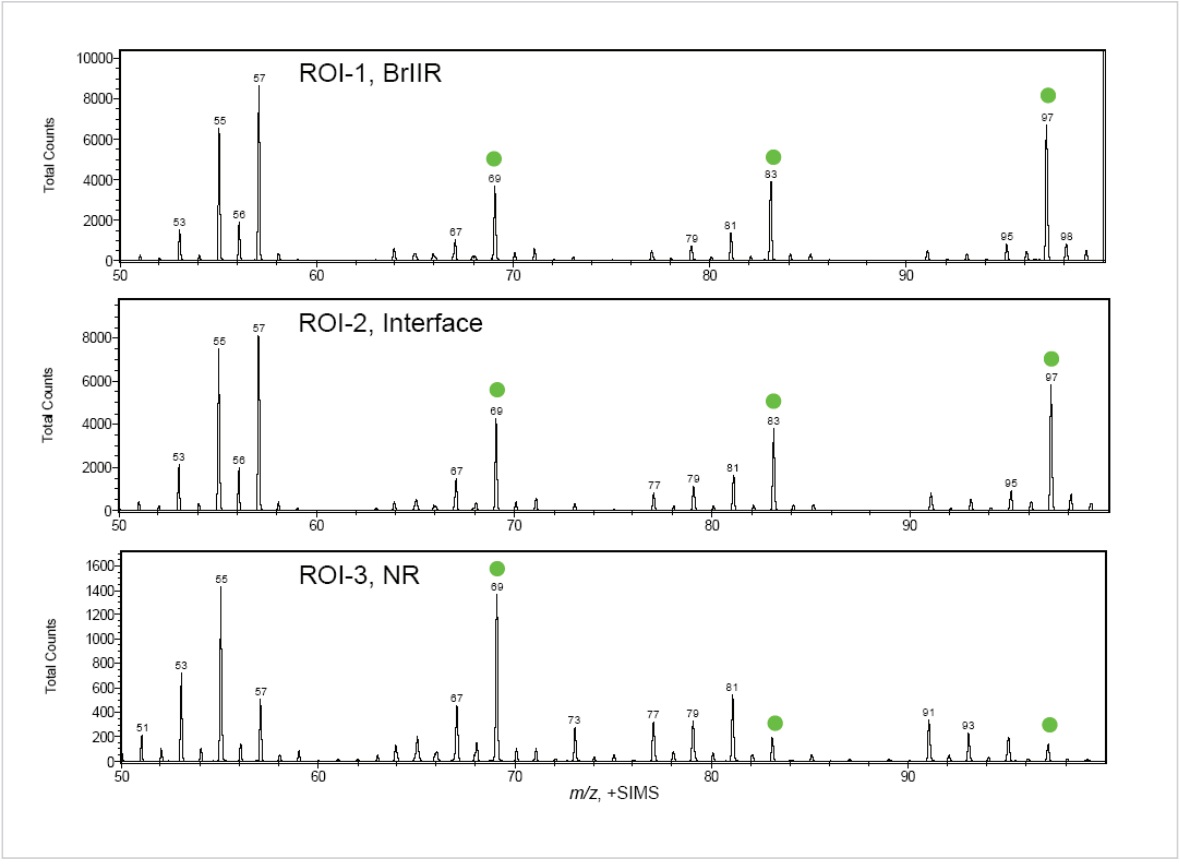

Figure 4: Mass spectra from the positive polarity regions-of-interest (ROIs) indicated in Figure 2A.

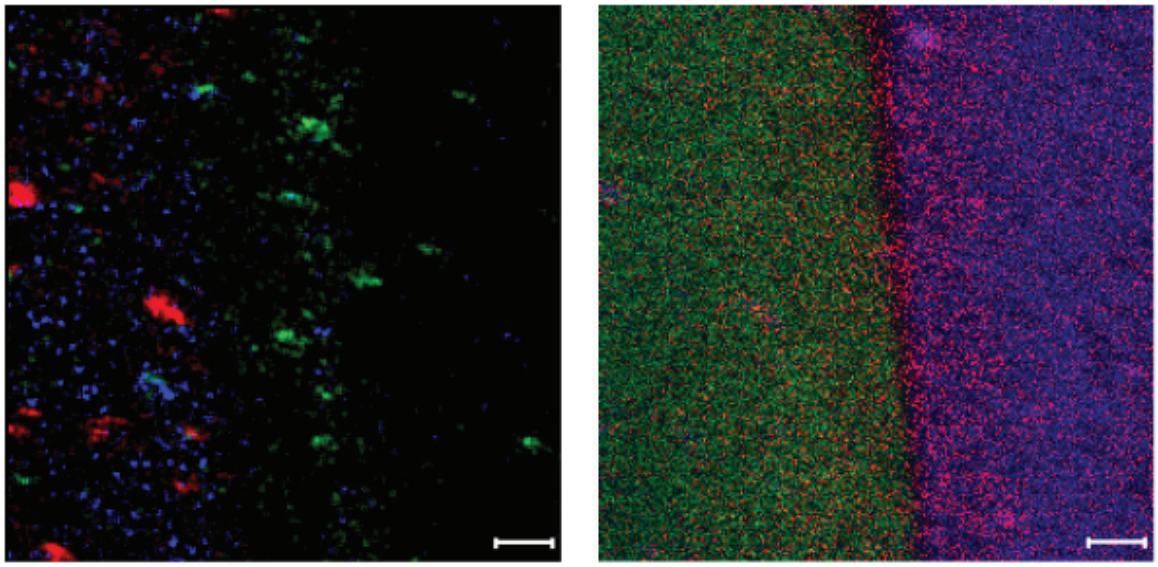

Figure 5: Ion image overlays. LEFT: Red - Br- (79 & 81 m/z); Green - Na^+ (23 m/z); Blue - Zn^+ (64 m/z). RIGHT: Red - $C_7H_4S_2N^-$ (166 m/z); Green - $C_7H_{13}^+$ (97 m/z); Blue - O^- (16 m/z). The scale marker is 10 µm.

The positive polarity images (Figure 2) show a significant accumulation of inorganic particles at the laminate interface as indicated by the Na^+ image. The ZnO domains, identified in the Zn^+ image, appear to be uniformly distributed within the BrIIR, but a depletion zone exists near the laminate interface. The ZnO domains range in size from approximately 0.5 µm to 4 µm. Other inorganic particles range in size from approximately 1 µm to 8 µm. The $C_6H_{11}^+$ and $C_7H_{13}^+$ fragments are unique to BrIIR, a conclusion that is confirmed by the region-of-interest (ROI) spectra displayed in Figure 4. While the $C_5H_9^+$ fragment is strongly correlated with BrIIR, it is not a unique indicator.

Chemical image overlays, containing ion images from both polarities, are rendered in Figure 5. These overlay images show the relative location of particulates and additive diffusion at the laminate interface.

CONCLUSION

TOF-SIMS is a unique tool for evaluating the segregation of chemical phases, the distribution of submicron size particulates, and the diffusion of additives in bulk, insulating specimens. This capability of TOF-SIMS has been demonstrated by evaluating the interface of a laminate cross-section consisting of natural rubber (NR) and 2 wt.% bromobutyl rubber (BrIIR) with several additives

ACKNOWLEDGEMENTS

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REFERENCES

[1] D. A. Winesett, A. H. Tsou, Application of High Resolution Chemical Imaging Techniques for Butyl Rubber Blends, submitted to Proc. of the 172nd Technical Meeting of the Rubber Div. of the Am. Chem. Soc.

Physical Electronics
18725 Lake Drive East,
Chanhassen, MN 55317
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