

Insights into Thermal Degradation of Hot Melt Pressure-Sensitive Adhesive (PSA) with Atomic Force Microscopy - Infrared Spectroscopy (AFM-IR) Analysis

Hu Duan^{1*}, Brian R. Strohmeier¹ and Yunli Fang¹

¹. Materials Science and Characterization, Avery Dennison Corporation, Mentor, OH, United States.

* Corresponding author: hu.duan@averydennison.com

Pressure-Sensitive Adhesives (PSA) are extensively used in tapes, labels, glue dots, stickers and a wide variety of other important commercial and industrial applications. Depending on the manufacturing processes, common types of PSAs include emulsion, solvent and hot melt [1]. Hot melt PSAs are typically formulated with rubber, such as synthetic block copolymers and natural rubber, along with tackifying resins, oils and antioxidants for optimal properties. During manufacturing, the hot melt PSAs are typically mixed, stored, transported and coated onto a web at temperature above 300°F. If the PSAs are subject to excessive heating during these processes, thermal degradation may significantly change the molecular weight and chemical compositions of the adhesive molecules, which could further cause downstream converting and application problems such as high release, low adhesion, excessive adhesive ooze etc.

Thermal degradation of homopolymer [2], block copolymers [3, 4], and hot melt pressure sensitive adhesives [5, 6] formulated with rubbery polymers were previously studied to understand the degradation mechanism. Modern analytical techniques such as FTIR, NMR, GPC, TGA, pyrolysis GC-MS, and rheology have been applied to characterize changes of chemical compositions, physical properties, and mechanical properties. The mechanism of thermal degradation involves radical initiation, propagation and chain termination via either cross-linking or chain scission. While radical depolymerization is associated with the polystyrene block, rubbery blocks with carbon-carbon double bonds typically degrade through random chain scission. As oxidation continues, a complex mixture of alcohols, aldehydes, ketones, carboxylic acids, and esters is formed.

The above mentioned analytical techniques are all considered as bulk analysis with limited or no capability to resolve chemical composition and spatial distribution simultaneously. An emerging hyphenated analytical technique, AFM-IR has been successfully demonstrated to overcome the above limitation on a variety of biological, chemical and polymeric materials with nanoscale imaging and spectroscopy capabilities [7, 8]. In this study, we report on the spatial distribution and morphological evolution of degraded species in block copolymer based hot melt PSA. We started with examination of thin film made with commercial elastomeric block copolymer blends (SI and SIS) after heat aging at 180°C in air for 100 minutes. The aged film turned into immiscible blends with dispersed phase morphology, which is visible under optical microscopy. In the AFM-IR mapping images in Figure 1, 1380cm⁻¹ was chosen to highlight polyisoprene (PI) domains and 1492cm⁻¹ to highlight the dispersed polystyrene (PS) domains. The data show that after thermal degradation, the block copolymer mainly has chain scission at PS-PI block linkage so that PS rich and PI rich domains can have macro phase separation into immiscible blends. The AFM-IR mapping at 1718cm⁻¹ shows enrichment of carbonyl species at the interface of PS/PI domains, where the broken chain ends could more easily be oxidized into acids and esters. In the case of commercial hot melt PSA formulated with the same block copolymer, it takes longer time (180°C in air, 5 hours) to degrade because of the presence of antioxidants and other more thermally stable ingredients. Figure 2 shows mapping at 1380cm⁻¹, 1492cm⁻¹

and 1730cm^{-1} . It follows the same thermal degradation mechanism. The PS and PI blocks have chain scission and the PS rich domains become immiscible with the rest of hot melt ingredients. On the other hand, the PI rich domains are miscible with tackifier and oil and they form the continuous phase surrounding the PS rich domains. These studies illustrate the degradation mechanism and movement of hot melt PSA molecular segments during thermal degradation by taking advantage of AFM-IR's high resolution chemical mapping capability.

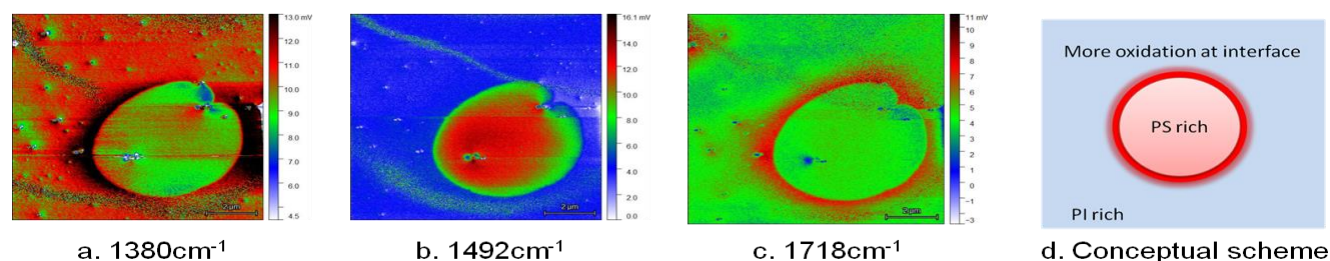


Figure 1. AFM-IR mapping of commercial elastomeric block copolymer blends at 1380cm^{-1} for PI rich domains (a), 1492cm^{-1} for PS rich domains (b) and 1718cm^{-1} (c). Color gradient on the dark red side implies higher concentration. A conceptual scheme of the phase separation is presented in (d). The sample was heat aged at 180°C in air for 100 minutes. Image size: $5\mu\text{m}\times 5\mu\text{m}$.

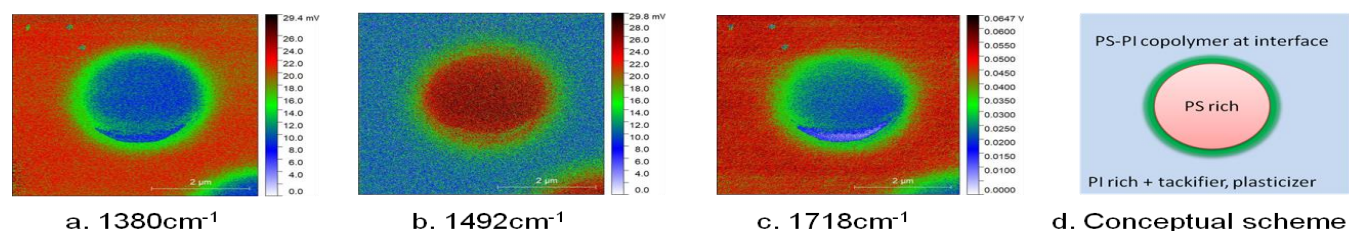


Figure 2. AFM-IR mapping of commercial hot melt PSA at 1380cm^{-1} (left), 1492cm^{-1} (middle) and 1730cm^{-1} (right). A conceptual scheme of the phase separation is presented in (d). The sample was heat aged at 180°C in air for 5 hours. Image size: $5\mu\text{m}\times 5\mu\text{m}$.

References:

- [1] I. Benedek, Pressure-Sensitive Adhesives and Applications, 2nd ed. 2005, (Marcel Dekker, Inc., New York· Basel) p.127.
- [2] S.L. Malhotra, C. Baillet and L.P. Blanchard, Journal of Macromolecular Science: Part A - Chemistry: Pure and Applied Chemistry, 12 (2015), p.1427. DOI:10.1080/00222337808069410
- [3] J. Hacaloglu, M.M. Fares and S. Suzer, European Polymer Journal, 35 (1999), p. 939. DOI:10.1016/S0014-3057(98)00074-3
- [4] S. Fan, T. Kyu, Macromolecules, 33 (2000), p. 9568. DOI:10.1021/ma001200y
- [5] D. Kim, H. Kim and G. Yoon, Journal of applied polymer science, 100 (2006), p.82. doi:10.1002/app.23241
- [6] J. Zhang, Y. Park and H. Kim, Polymer Degradation and Stability, 93 (2008), p. 1008. DOI:10.1016/j.polymdegradstab.2007.12.016
- [7] J. Mathurin et al., Journal of Applied Physics, 131 (2022), p. 010901. DOI:10.1063/5.0063902
- [8] A. Dazzi, C. B. Prater, Chemical Reviews, 117 (2017), p. 5146. DOI:10.1021/acs.chemrev.6b00448