

Application Note #1536

Mechanical Characterization of Corrosion-Resistant Coatings

Corrosion-resistant coatings play a crucial role in the process of food preservation.¹ They must retain functional integrity when exposed to various physical and chemical stresses. For example, soft drinks require corrosion-resistant coatings to protect their containers from how acidic they are.² Two important attributes of such coatings are the mechanical strength and the adhesion, which are both a function of the curing process. This application note discusses how Bruker's Hysitron® TS 77 Select automated benchtop nanomechanical test instrument can be used to characterize food and beverage can liner coatings.

Experimental

Three corrosion-resistant polymers from soft drinks of varying pH (10 mm x 10 mm), from different manufacturers, were attached (using Loctite 420) to metal discs, while maintaining the original can curvature. The liner coatings on these samples were in contact with highly acidic beverages for over one year. The pH values of the drinks are shown in Table 1. Surface topographical variations, as well as modulus changes, were mapped using the Hysitron TS 77 nanoindenter equipped with nanoDMA® III (Figure 1). Scratch resistance of the coatings was evaluated using Bruker's two-dimensional capacitive transducer.



Figure 1. (a) Representative food and beverage can liner images; and (b) Bruker's Hysitron TS 77 Select benchtop indenter.

Beverage	pH
Diet Cola Drink	3.1
Lime Drink	3.22
Energy Drink	3.48

Table 1. pH values of the beverages used in tested aluminum cans.

Surface Topography and Modulus Variation

Epoxy coatings that were in contact with the acidic drinks showed marginal surface degradation. Scanning probe microscopy images showed surface pits on the sample exposed to diet cola drink, with a pH of 3.1 (Figure 2). A continuous measurement of hardness and modulus as a function of depth, using Bruker’s CMX, increases data acquisition throughput. By doing automated constant strain rate CMX, indents using a Berkovich probe, large area modulus maps were created. Figures 3a-c show variation in modulus as a function of depth at different spatial coordinates. While Figures 3d-f show representative modulus versus contact depth curves for three epoxy coatings.

Coatings used for energy drink storage (Figure 3a) had uniform modulus distribution up to 800 nm into the coating. At higher depths, an increase in modulus was observed. Modulus variation recorded from coatings exposed to higher acidic drinks, such as lime and diet cola (pH 3.22 and 3.1), showed a slightly different trend. The lime drink coating showed stiffened zone at the surface (top 200 nm). Between 200 and 600 nm, uniform modulus distribution was observed, while the diet cola drink coating showed local stiffened region (Figure 3c). Modulus

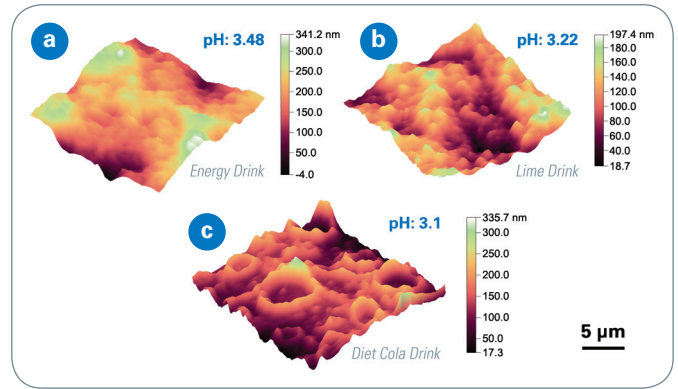


Figure 2. Scanning probe microscopy images showing variation in surface topography on beverage can coatings.

variation seen in Figure 3 could be due to the curing process or induced by acidic beverage drink. At the macro scale, epoxy coatings looked intact. However, nanoscale topographical measurements (Figure 2c) showed nano pits on the coatings exposed to the highly acidic diet cola drink. Coatings used in soft drink storage are known to withstand acidic environments, and it is highly unlikely that chemical reaction resulted in nano pits. Studies indicate the degradation mechanism on such coatings is physical in nature and induced by swelling stresses.³

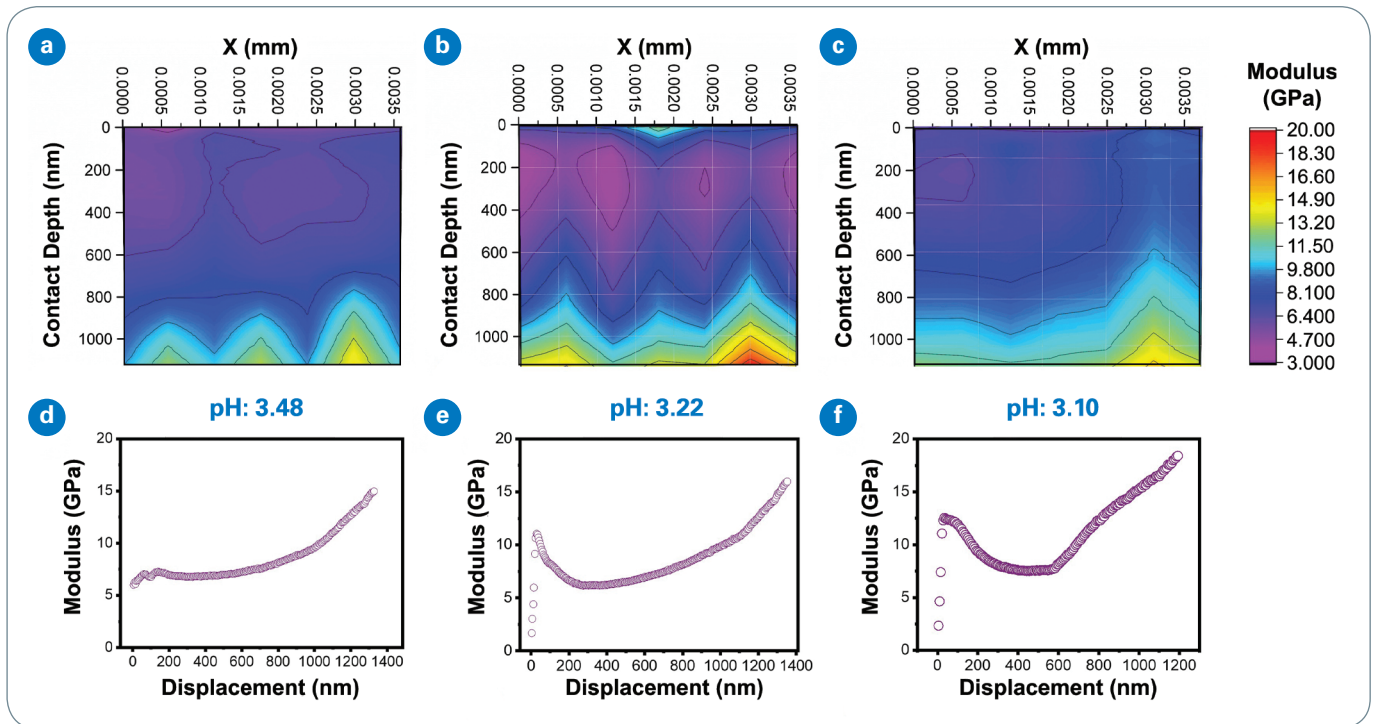


Figure 3. Modulus maps generated from constant strain rate CMX automation, showing distribution at different contact depths for (a) energy drink; (b) lime; (c) diet cola coating; and (d-f) representative modulus vs depth curves.

Scratch Resistance of Can Liner Coatings

Adhesion and scratch resistance of the epoxy coating determines the longevity of can liner coatings. Scratches induced during production may act as a defect and lead to beverage contamination. Nanoscratch tests were performed using Bruker's two-dimensional capacitive transducer at a fixed load of 50 μN on three can liner samples. Figures 4a-c show scanning probe microscopy images recorded post scratch test. Figure 4d compares frictional force recorded from three beverage can samples, while Figure 4e shows scratch groove depth. The liner coating used to store the highly acidic diet cola drink showed higher scratch resistance.

Conclusions

Bruker's Hysitron TS 77, in combination with nanoDMA III and nanoscratch, proved very useful in characterizing challenging beverage can coatings. From nanoDMA constant strain rate mapping, we were able to see curing-induced surface modulus variations. The methodology presented in this study are generic in nature and can be adopted readily to study process-induced mechanical property variations on other industry polymer coatings.

References

1. Geueke, B., "Dossier - Can Coatings," *Food Packag. Forum* pp. 1–10 (2016), doi:10.4067/S0250-71612013000200001.
2. Oldring, P.K., "Packaging Materials 7. Metal Packaging for Foodstuffs," *Intl. Life Sci. Inst.*, p. 44 (2007), doi:D/2007/10.996/7.
3. Lim, J.S.K., Gan, C.L., and Hu, X.M., "Unraveling the Mechanistic Origins of Epoxy Degradation in Acids," *ACS Omega* **4**, pp. 10799–808 (2019).

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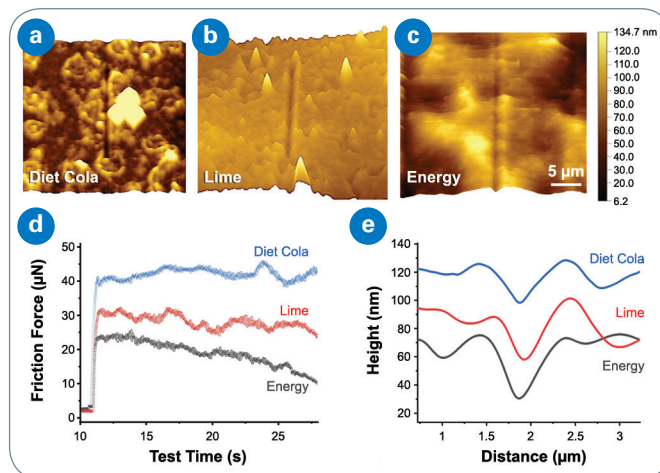


Figure 4. (a-c) Scanning probe microscopy images recorded after the scratch test on beverage can samples; (d) friction force; and (e) line profiles recorded across scratch groove.