Corrosion-resistant coatings play a crucial role in the process of food preservation. Soft drinks, which are highly acidic, are a specific example of food products that require corrosion resistant coatings. These films must retain their functional integrity when exposed to various physical and chemical stresses. Two important attributes are the mechanical strength and the film adhesion, which are functions of the curing process. This application note discusses how Bruker’s Hysitron TS 77 Select, automated benchtop nanomechanical and nanotribological 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 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 the 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 Bruker’s Hysitron TS 77 Select benchtop nanoindenter equipped with dynamic nanoindentation (Figure 1). Scratch resistance of the coatings was evaluated using Bruker’s two-dimensional capacitive transducer.

<table>
<thead>
<tr>
<th>Beverage</th>
<th>pH</th>
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<tbody>
<tr>
<td>Energy Drink</td>
<td>3.48</td>
</tr>
<tr>
<td>Lime Drink</td>
<td>3.22</td>
</tr>
<tr>
<td>Diet Cola Drink</td>
<td>3.1</td>
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</table>

Table 1. pH values of the beverages used in tested aluminum cans.
Surface Topography and Modulus Variation

Epoxy coatings that were in contact with acidic drinks showed marginal surface degradation. Scanning probe microscopy images showed surface pits on samples exposed to diet cola drink, with a pH of 3.1 (see Table 1). A continuous measurement of hardness and modulus as a function of depth, using Bruker’s dynamic nanoindentation CMX, increases data acquisition throughput. By performing automated constant strain rate CMX indents using Berkovich probe, maps of modulus and hardness covering large areas can be created. Figure 2a-c show variation in modulus as a function of depth at different spatial coordinates, while Figure 2d-f show representative modulus versus contact depth curves for the three epoxy coatings under study.

Coatings used for energy drink storage (Figure 2a) had uniform modulus distribution up to 800 nm into the coating. At higher depths, an increase in storage modulus was observed. However, the coatings for the more acidic drinks, such as lime and the diet cola, (pH 3.22 and 3.1), showed a slightly different trend. The lime drink coating showed a stiff zone at the near surface, with a decrease in stiffness to a relatively uniform region between 200 and 600 nm, followed by stiffening at higher depths. The diet cola coating showed a similar trend with a near surface stiff region, as shown in Figure 2c. This modulus variation, as can be seen in Figure 2, could be a result of either the curing process or induced by reaction to the acidic beverage. Optical microscopy, showed the epoxy regions to appear intact. However, nanoscale topographical measurements showed increased pitting on coatings exposed to the highly acidic diet cola drink (see Figure 3c). 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 degradation mechanism on such coatings are likely physical in nature, as opposed to being the result of chemical reactions, and are likely to be induced by swelling stresses.  

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Figure 2. Modulus map generated from constant strain rate CMX automation, showing distribution at different contact depths for (a) energy drink, (b) lime drink, and (c) diet cola drink coating; and (d-f) representative modulus versus depth curves for energy drink, lime drink, and diet cola drink, respectively.

Figure 3. Scanning probe microscopy images showing variation in surface topography on beverage can coatings.
Scratch Resistance 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. Figure 4a-c shows 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, while the lime drink and energy drink liners showed approximately the same scratch resistance.

Conclusions

Bruker’s Hysitron TS 77 Select benchtop indenter, in combination with dynamic nanoindentation and nanoscratch, proved very useful in characterizing challenging food and beverage can industry coatings. From dynamic nanoindentation constant strain rate mapping, we were able to see curing-induced surface modulus variations. These kinds of studies can have a very large impact upon the lifetime, safety, and product success of food packaging. The methodology presented in this study are generic in nature and can be adopted to study process-induced mechanical property variation on other industry polymer coatings.

References


Authors

Praveena Manimunda, Ph.D. (praveena.manimunda@bruker.com)
and Douglas Stauffer, Ph.D. (douglas.stauffer@bruker.com)