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Abstract

The first photodegradable plastic cap for a glass beer bottle was developed and tested. The cap's design is the same as the current plastic, screw-on cap for soda bottles. A photodegradable resin was added to the soda cap plastic to make it photodegradable. Caps with 0%, 10%, and 25% photodegradable additive were made. Tests show that the photodegradable cap meets most of the physical properties required for a beer or a soda cap. A photodegradable cap with 10% degradable additive will cost about three times more than current metal crowns, but only about 10% more than current plastic soda caps. The photodegradable caps can be made on a large scale using the same process as for regular soda caps. 10,000 caps were made for testing.

Introduction

There are two major drawbacks with the current twist-off metal crowns used on beer bottles. The crown can become permanent litter because its tin-free steel material does not degrade. The bottle cap is prone to rusting, which binds the crown to the bottle. This increases the removal torque and makes it painful for the customer to twist the cap.

The first photodegradable plastic cap was developed. It has the same design as the screw-on plastic caps for soda bottles. The new cap eliminates the two drawbacks of the metal crown. To make a suitable beer cap, the new cap had to preserve the flavor of beer, be degradable, have a low, uniform, removal torque, have a safe blow-off pressure, be able to obtain FDA approval if required, use the current process equipment, and not be cost prohibitive. We focused on developing a degradable cap for 12 oz glass beer bottles that now have metal caps. This photodegradable cap development can also be used to replace current plastic soda caps that produce lasting litter. In Figure 1, the photodegradable cap is on the left, the regular soda cap is in the middle, and the metal crown for beer is on the right.

We will divide this paper into two parts. First, we discuss the methodology used in developing the photodegradable cap. And second, we discuss the cap's physical properties, degradable characteristics, processing properties, and economics.

Methodology

Degradable solution

We researched the feasibilities of a biodegradable cap and a phodegradable cap. Photodegradable materials break down as a result of ultraviolet (UV) exposure. Biodegradability means that the deterioration is caused by the materials interaction with environmental organisms. A photodegradable cap is the best solution because current biodegradation technology can only degrade thin plastic films, and not the thick plastic needed to make a cap.

Suitable cap material and design

We wanted an inexpensive, easily processed plastic cap that would fit onto a glass bottle, retain the beer's carbonation and prevent oxygen from going into the beer bottle. The soda industry uses such a cap for their 2 liter plastic bottles and 16 ounce glass bottles.

We looked into low permeable plastics for our cap. We selected the polypropylene currently used for soda caps and the design standard for the soda cap industry. By using existing proven design, a failure of the photodegradable cap would be due primarily to the photodegradable material and not the cap's design. Two soda cap companies agreed to work with us.

Photodegradation technology

We researched different photodegradation technologies and only found one company that had the technology applicable to our project. Their current technology can make the cap's material, polypropylene, photodegradable, but not the cap's liner, poly vinyl chloride. Thus, we developed a photodegradable cap and not a degradable liner.

A polymer is made photodegradable by introducing into its molecular chain ultraviolet (UV) light sensitive carbonyl groups e.g. ketones. A plastic containing a sensitizing group, when exposed to UV radiation, will be broken down into smaller components that the environment can degrade. These carbonyl groups have energy absorbances with a maximum of around 280-290 nanometers (nm) and they cut off sharply at about 330 nm.

Criteria	Test	Soda Cap Standard	Result
Blow-off Pressure	Secure Seal Test	No leaks below 100 psig Cannot separate below 175 psig.	Passed
Safe from abuse	Elevated Temperature Cycling Test	Closure must remain on finish after cycling.	Passed
	Ball Impact Abuse Test	Closure must not separate from bottle finish	Passed
Cap has low, uniform removal torque	Refrigerated Removal Torques	No torques above 17 in-lbs.	Average of 12.2 in-lbs Passed.
Cap preserves beer's flavor	Short Term Carbonation Retention Test	Cannot lose more carbonation than control packages.	Passed
	Long Term Refrigerated Carbonation Retention	After 12 weeks, 90% of test bottles have less than 5% carbonation loss, 100% have less than 10% carbonation loss.	average of 3% loss (range of 1 to 4%) passed.
	Oxygen Permeation	0.001 cc/day	.007 cc/day Taste Test required.

Table 1. Physical properties of photodegradable cap with 10% additive

This range of wavelengths is present in the sun's rays, but barely present in fluorescent light and not present in incandescent light. Window glass also screens most of this range of wavelengths. Thus, a plastic modified with this technology should not photodegrade under artificial light or by sunlight through a window glass.

A master batch of photodegradable resin was developed for our use. This resin was then mixed with the regular plastic at two ratios of 10% and 25% by weight to make the photodegradable plastic. Two soda-cap companies molded caps out of the photodegradable polypropylene and did the testing for blow-off pressure, abuse strength, impact strength, and removal torque.

Physical Properties of Photodegradable Caps

The photodegradable cap would make a suitable beer cap if it passed the standards for plastic soda caps. The photodegradable caps were tested to determine their physical properties. The photodegradable cap, at zero UV exposure, had the same physical properties as a regular soda cap. Thus, the photodegradable cap had the necessary physical properties for making a suitable beer cap.

About 800 caps with 10% photodegradable additive were tested. The 25% additive caps had similar physical properties. In this report, the physical property results are described in detail for the 10% caps with no UV exposure, and the degradability results are described in detail for the 25% caps with 0 to 420 hours of exposure.

The photodegradable caps were made without any coloring pigment. The coloring pigment normally used for soda caps inhibits photodegradation. The photodegradable cap was also tested with a regular, nondegradable soda cap liner.

Table 1 summarizes the physical properties of the photodegradable cap with 10% additive.

Blow-Off Pressure

Blow-off pressure is defined as the internal pressure required to separate the cap from the finish of the bottle. The 10% additive degradable cap had a blow-off pressure of 175 psig. This meets the soda cap standard. This value was determined using the Secure Seal Test for soda caps. In this test, the bottle's pressure is increased up to 175 psig at a rate of 5 psig per second. To pass this test, the cap cannot have leaks below 100 psig and must not separate from the bottle below 175 psig.

Abuse Strength

The photodegradable cap had the same ability to withstand abuse as the regular soda cap. This was tested using the Elevated Temperature Cycling Test, which examines the cap's characteristics when exposed to extreme temperture conditions. Twenty-four filled bottles are placed in an oven at 90°F and heated to 140°F for 6 hours. This cycle is repeated three times. The caps are inspected for any deformation, cocked or released caps. To pass this test, the cap must remain on the bottle throughout all test cycles.

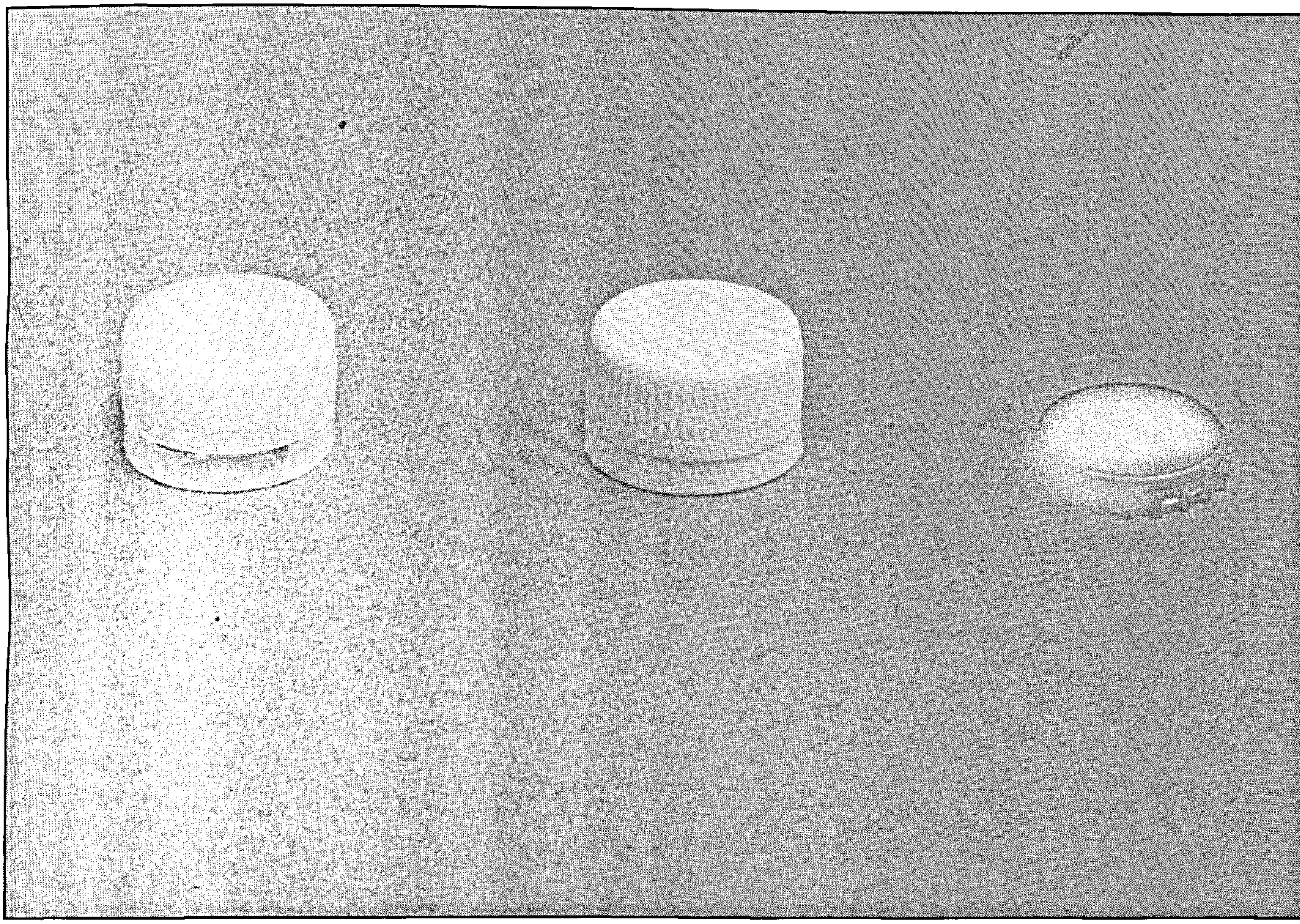

Figure 1. Photodegradable, regular soda, and metal crown caps left to right

Impact Strength

The photodegradable cap had the same impact strength as the regular soda cap. This result was determined with the ball impact test. A 10 ounce steel ball is dropped from a height of 30 inches onto caps fixed on filled bottles. This procedure was done at various temperatures and at various impact angles. Forty impacts are tested on forty closures at four angles in ambient temperatures. The test is repeated on packages held at 40°F. Caps may leak, but cannot separate from the finish.

Both the Elevated Temperature Cycling Test and the Ball Impact Test were repeated for caps which were exposed to 3 days of natural sunlight. The exposed caps passed both tests.

Removal Torque

The photodegradable cap had an average removal torque of 12 inch pounds, and a maximum removal torque of 14.5 inch pounds. This meets the soda cap standard, which requires a maximum removal torque less than 17 inch pounds. The average removal torque for the first batch of photodegradable caps was 20 inch pounds. This was too high and did not meet the soda cap standard. Thus, the degradable additive increased the cap's removal torque, probably by increasing the plastic's coefficient of friction. The removal torque was lowered by using a modified cap design which reduced the contact between the cap and the bottle.

Carbon Dioxide and Oxygen Permeability

The photodegradable cap has the same carbon dioxide and oxygen permeability as the regular soda cap. This is probably acceptable to the beer industry. However, there is no current standard for acceptable rate of carbon dioxide and oxygen loss. Taste tests need to be done to see if the plastic cap's gas permeability is low enough to preserve the beer's flavor. If not, the cap's permeability can be reduced further by a variety of methods, including coating the liner with an impermeable polyvinylidene chloride coating.

The cap has an average of 3% (range of 1 to 4%) carbon dioxide loss in 90 days. This was determined through both short term and long term carbonation retention tests for soda caps.

The photodegradable cap's oxygen permeability is 7 times more than the existing metal crowns for beer (0.007 cc/24 hours vs. 0.001 cc/24 hours). This was determined using the Mocon oxygen permeability test. The Mocon test was done at 70°F with an oxygen pressure gradient of 1 atmosphere. For beer, the storage temperature and the actual oxygen pressure gradient are lower, 40°F and 0.21 atmospheres, respectively. Thus, the actual oxygen permeability for beer will be lower than the Mocon test value. However, even under the actual conditions of the beer, the photodegradable cap should have 7 times more oxygen permeability than the metal crown.

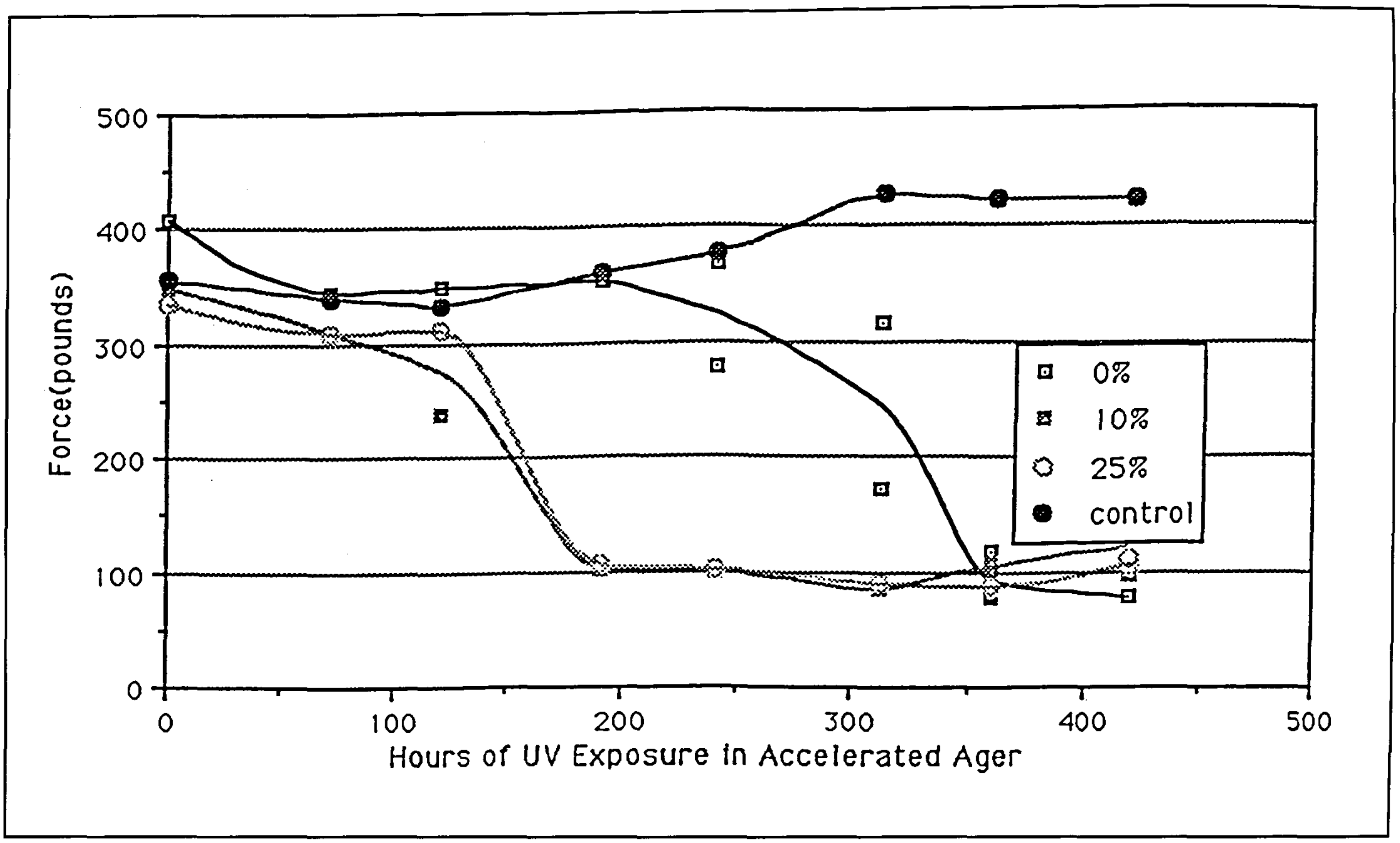

Figure 2. Force vs. UV exposure time for photodegradable cap

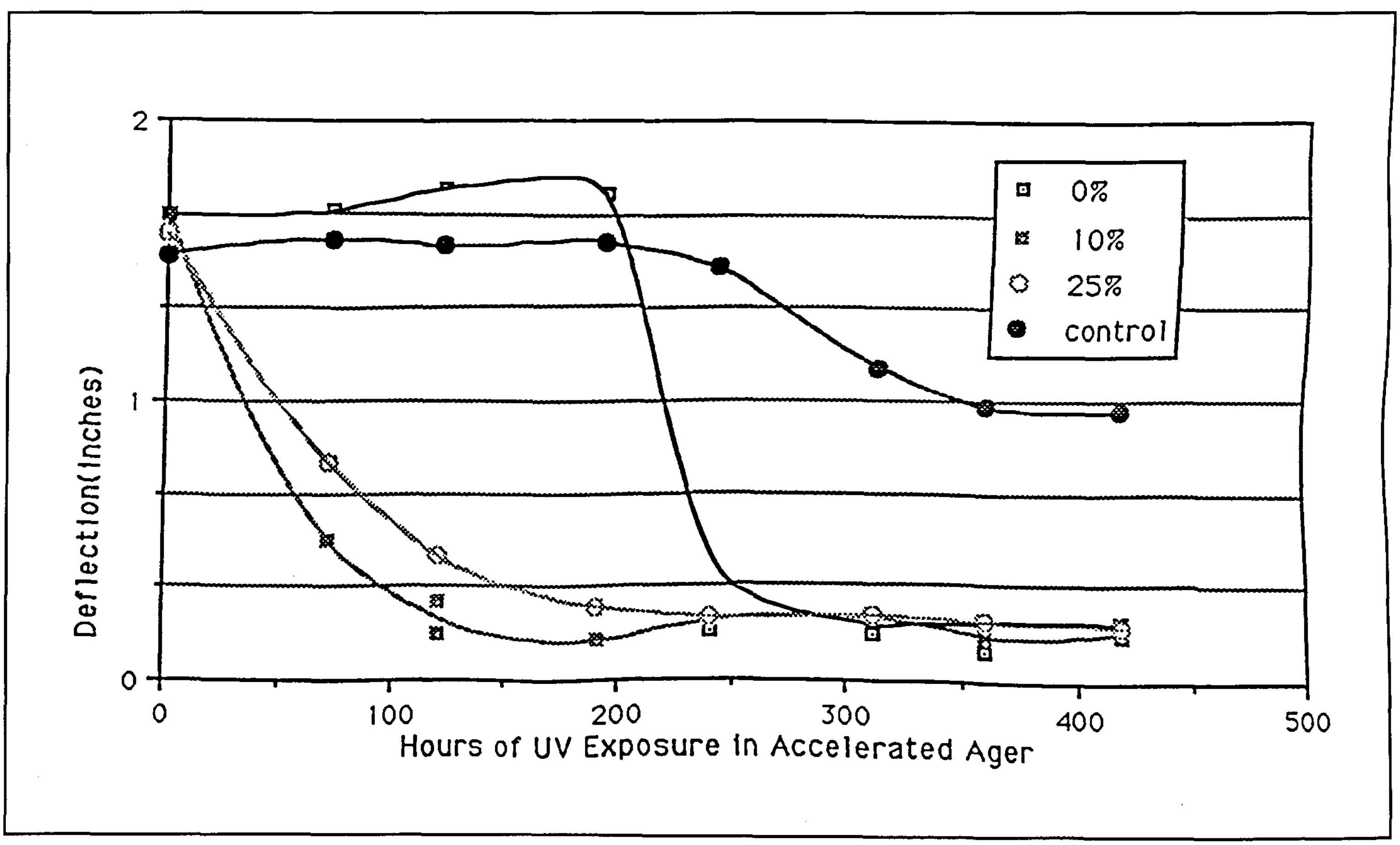

Figure 3. Deflection vs. UV exposure time for photodegradable cap

Photodegradation Measurements

A Q-Panel accelerated UV ager was used to expose the caps. We used a Tinius Oslen compression/tensile tester to check the degradability of the caps. A 1/2 inch punch was used to puncture a hole through the roof of the cap. The force and the deflection needed to puncture the hole was measured. The punctured cap was visually observed for signs of degradation,such as the size of the broken cap pieces.

The maximum force and the deflection needed to puncture the cap as a function of UV exposure are shown in Figures 2 and 3. The control cap is the regular pigmented soda cap. The 0% cap is the cap with no additive and no pigment. The 10% cap has 10% degradable additive by weight and no pigment. The 25% cap has 25% degradable additive by weight and no pigment.

Because of degradation, the maximum force needed to puncture through the cap decreases as a function of UV exposure for the 10% and the 25% caps. The control cap does not photodegrade at all, while the 0% cap photodegrades a lot slower than the 10% and the 25% caps. However, the 0% cap photodegrades faster than the control cap. This is because natural polypropylene, without any UV inhibitors, photodegrades. Cross-linking is probably responsible for the force reaching an asymptote at 100 pounds. As the cap photodegrades, the polypropylene polymer chains break into smaller pieces. At a certain point when the pieces are small enough, they start to cross-link with each other, which increases the force needed to go through the plastic. Hopefully in natural exposure, the weather elements like the wind and the rain will degrade the caps with time and minimize the cross-linking. The asymptote for the force at 100 pounds probably does not indicate an end to photodegradation. The developer of the degradable additive believes that the deflection is a better measure of photodegradation than the force.

The deflection needed to puncture through the hole is shown in Figure 3. Compared to control caps, the 10% and the 25% cap's deflection decreased significantly with UV exposure because of photodegradation. The 0% caps also photodegraded, but more slowly than the caps with degradable additive. The cap on the right in Figure 4 is the 25% cap with no UV exposure, which deflected 1.7 inches before being punctured. The cap on the left in Figure 4 is the 25% cap with 200 hours of UV exposure in the accelerated ager, which deflected only 0.2 inches before being punctured. This shows photodegradation has occurred. The deflection reaches an asymptote at 0.2 inches which is the limit of our test procedure.

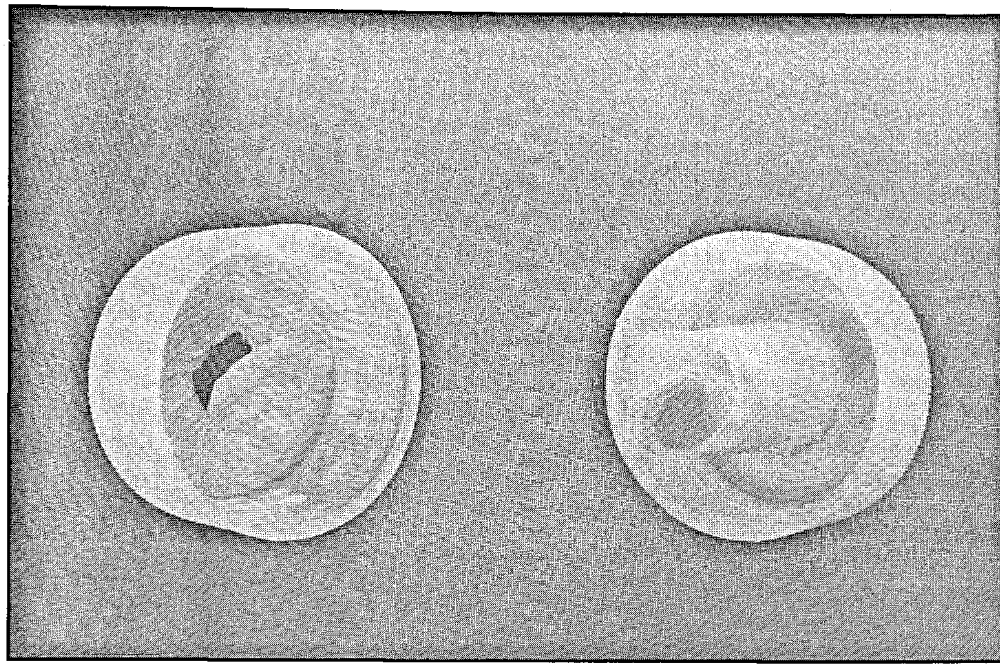

Figure 4. Caps after puncture test

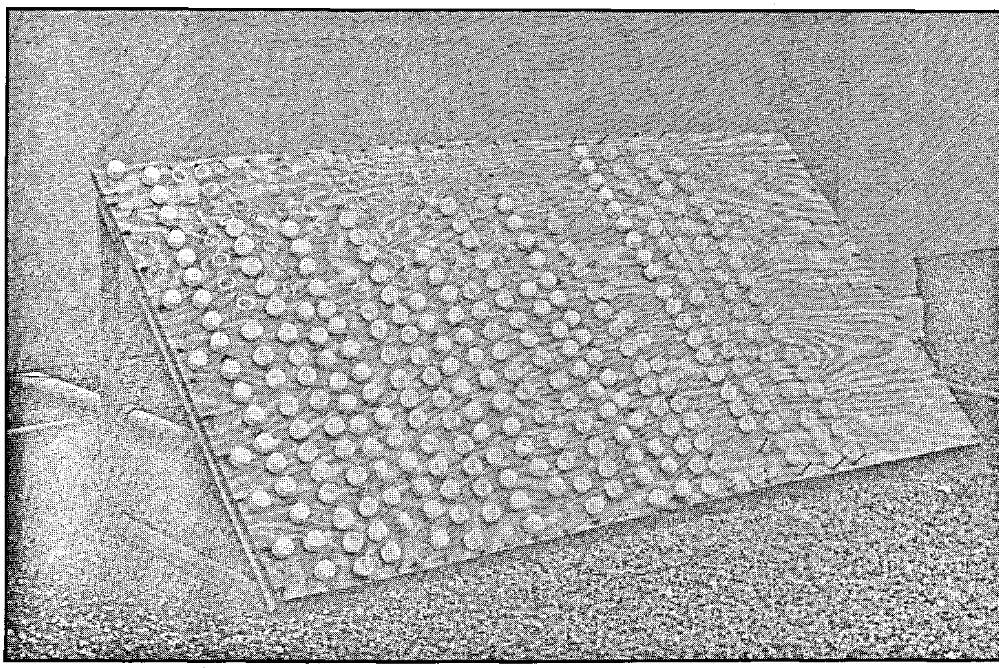

Figure 5. Setup to evaluate exposure of caps

Both Figures 2 and 3 do not show significant difference between the 10% and 25% caps. However, visual observations of the caps after the compression test showed that the 25% cap photodegraded more than the 10% cap. The 25% cap had more degraded "dust," small fine particles of plastic, and was broken into smaller pieces. Thus, the visual observation was a better measure of photodegradation than the compression test. The compression test showed that the 10% and the 25% caps photodegrade, but could not distinguish between the two. The visual observation showed that the 25% cap degraded faster than the 10% cap, the 0% cap did not degrade much, and the control cap did not degrade at all.

In addition to the accelerated UV exposure, the caps were also exposed to natural sunlight. This was done by attaching the caps to a board directed South at 45° angle to the sun. Figure 5 shows the natural exposure setup. The board is located on top of Harvey Mudd's Engineering building. As of now, the caps have been exposed to 7 weeks of natural sunlight. Qualitatively, the 25% cap broke into small pieces when it was stepped on. The 10% also broke into pieces, but more force was required than for the 25% cap. Even after 7 weeks in natural sunlight, the 0% cap and the control cap remained intact when they were stepped on.

Processing Properties

5000 photodegradable caps were made using injection molding, and 5000 using rotary compression molding. Both soda cap companies reported the photodegradable plastic had the same processing characteristics as their regular soda cap plastic. Thus, the photodegradable cap can be made on a large scale using the process for regular soda caps.

FDA Status

It is not clear whether FDA approval is needed for degradable caps used with food or beverages. Even if FDA approval is not necessary, it may be requested for marketing purposes.

Economic Analysis

A photodegradable cap with 10% degradable additive will cost 3 times more than the current metal crown for beer. However, regular plastic soda caps cost about 2.7 times more than the metal crowns. The higher price is mainly due to plastic versus metal rather than the degradable additive. As a rule of thumb, adding 10% degradable additive will increase the plastic's cost by 10%.

To use the photodegradable cap, new capping machines are required. The rest of the current beer bottling equipment can be used. A new capping machine with a capacity of 1000 bottles per minute costs about $80,000. The entire U.S. market consumes 18 billion bottles of beer per year. A company would need 4 new capping machines, which would cost about $320,000, a relatively small expense when prorated over 1 billion bottles of beer per year.

A new finish is also required on glass beer bottles, which should be easy to do. The new finish is the standard 1626 finish found in soda bottles. In fact, most beer companies already sell beer in 32 glass bottles with this finish, which has an aluminum screw-on cap instead of a plastic screw-on cap.

Summary

We have developed and tested the first photodegradable plastic cap which can be used for beer or soda bottles. They cap's design is the same as the screw-on plastic cap for the current 2 liter soda bottles. The photodegradable cap has the same physical properties as the regular soda cap, except for a higher removal torque. The high removal torque problem was solved by using a modified cap design which reduced the surface of contact between the cap and the bottle. Thus, the photodegradable cap had the necessary physical properties to make a beer or a soda cap. To use as a beer cap, taste tests will have to be done to see if oxygen and carbon dioxide permeability are low enough.

Accelerated UV exposure and compression tests showed that the photodegradable caps photodegrade. Visual observation was a better measure of photodegradation than the compression test.

The photodegradable caps have the same processing properties as the regular soda cap plastic. Thus, the caps can be made on a large scale.

The photodegradable cap is economically feasible. It costs 3 times more than the metal cap but only 10% is due to the degradable additive. To use the cap, new capping machines are required.

The degradable additive made the regular, nondegradable soda cap photodegradable, yet did not change the regular plastic's physical or processing properties, except for the removal torque. In summary, a workable photodegradable plastic cap for beer or soda has been developed and tested.

Acknowledgements

We would like to thank the beer company that funded this research project, the two soda cap companies, and the photodegradable resin manufacturer that helped us to successfully complete this project.

We also wish to thank Prof. Banwell at California State University Pomona for training on the use of the compressor/tester and allowing its use on the photodegradable bottle caps.