Interaction of Abrasion and Oil Resistance of Sealant Materials

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Abstract

Packages for holding abrasive and oily food products, such as potato chips, crackers, and dry pet food, often require a combination of sufficient abrasion resistance and oil resistance. In this study, the interaction between abrasion resistance and oil resistance of a series of sealant materials was investigated. To correlate shipping and storage conditions of food products, a Shaker Table Abrasion Test was developed to include both abrasion and oil penetration factors. During the test, a sealant film sample was adhered to the inside wall of a cylindrical shaped container. The container was filled with an abrasive, oily food product and placed on a shaker table at a constant shaker rate, temperature and shaking time, A grading system was developed to quantify both abrasion and oil resistance performances of the tested film samples. Test results show that oil penetration can significantly decrease the abrasion resistance of a sealant material, despite its abrasion resistance performance in a non-oily environment.

Introduction

Protecting the product from abuse is a primary function of packaging. Abuse often arises as the product, package and external environment interact. Examples include puncture from sharp products such bones or noodles from within the packaging, impact puncture from sharp products during filling operations, abrasion from within the package during transportation, and package failure at impact during dropping.

Many test methods and standards have been developed to simulate abuse in the lab or during transportation and handling [1]. An issue with the current laboratory test methods is that they test the film in a standard lab environment and do not correlate with commercial experience.

In an actual package, the product may contain ingredients that change the characteristics of the polymer. For example, oils, found in a variety of products such as snack foods and meat products, may swell the polymer and change its resistance to scratch and abrasion. An example is the packaging of snack foods in composite paperboard canisters. The inside of the canister is abraded as the contents move during shipping and handling, exposing the barrier layer to damage that limits shelf life.

The goal of this work is to: 1) Develop a laboratory test method that better mimics the oily and abrasive environments found in many snack food packages. It should be able to provide quantitative comparisons of different sealant resins for optimizing package design. 2) Investigate the interaction of abrasion resistance and oil resistance of sealant materials.

Standard Test Methods

Several stylus-type scratch tests have been used in the automotive industry to simulate abuse in the lab or during transportation and handling (ISO 1518 and the five-finger scratch test – Ford BN 108-13), and recently researchers at Texas A&M University have developed a scratch test for films (ASTM 7027) that has shown some correlation with commercial experience for flexible packaging [2, 3]. However, there is no standard laboratory test for abrasion resistance of flexible packaging. Blom [4] uses a Taber linear abrasion test to rank abrasion resistance of various plastic films. Many packaging materials, however, are too soft for traditional abrasion tests and gum up the abrasion surface.

There are also tests that simulate shipping and handling, such as ASTM D4169-09, D7386-12, and ISTA methods 3A, 3E, 4AB and 6A. These tests are conducted on the actual package and product and are typically done in the final stages of package development since they are time-consuming and expensive. In addition, they typically do not yield data suitable for material selection needed for optimal design of the package.

Therefore, an economical abrasion test that takes into consideration oily or greasy environments and basic shipping conditions was developed for this research.

Shaker Table Abrasion Test Method

Since standard laboratory abrasion and scratch tests do not correlate with commercial conditions, a Shaker Table Abrasion Test is designed to test abrasion performance of a sealant film, using oily and abrasive food products as the abrasive media.

In the test, a 50-µm (2-mil) monolayer sealant film is adhered to the inside wall of a cylindrical shaped container. Real food products that are abrasive and oily are then put into the container, as shown in **Figure 1**. The specific type of the food product used in the test can vary, depending on the application that is being investigated.

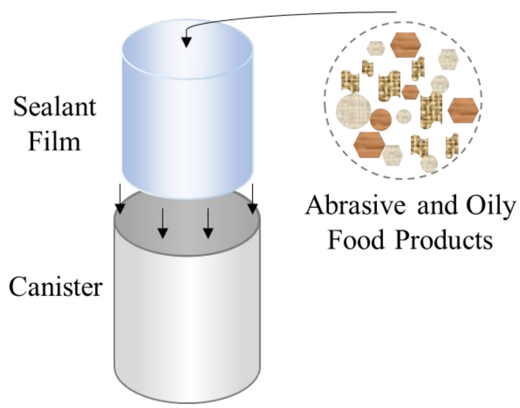

Figure 1. Sample preparation for the Shaker Table Abrasion Test.

Samples are then placed on a shaker/incubator table with controlled temperatures and motion. It is important to recognize that the goal of this test is only to provide quantitative comparison of different sealant materials, not to simulate real shipping and storage conditions, so different types of shaker tables may be used depending on availability.

The shaker table used for this experiment was Eppendorf / New Brunswick Scientific Innova 4000, as shown in **Figure 2**. This model provides a two-dimensional circular motion that ranges from 25 to 500RPM, and uniform controlled temperature from 5°C above ambient to 60°C.

For this experiment, the shaker table was set at 150RPM and 27°C to shake for 24 hours. The shaking time should be sufficient for the films samples to absorb the oil from the food in the container. After shaking, films are detached from the canisters and cleaned for grading.

Figure 2. The shaker used for this experiment [5].

Test Validation

There were two goals for the validation: 1) validate the shaker table test's ability to distinguish the performance of different sealants in abrasive and oily environment, and 2) validate the consistency and repeatability of the test.

Three common sealant materials were selected: 1) LLDPE with poor abrasion and oil resistance, 2) an ionomer grade with good abrasion and oil resistance (Ionomer-M), and 3) an ionomer grade with excellent performance in abrasion and oil resistance (Ionomer-A).

For the first stage of the validation, 50-µm monolayer films of the sealants were tested as described in the previous section. For each sealant sample, 3 to 5 film specimens were tested and the results averaged. The visual difference in the resulting films were significant, as shown in **Figure 3**. After 12 hours of shaking, the LLDPE films already had large areas of deep abrades and scratches. The surfaces of the LLDPE films also became very uneven, which was likely a result of polymer swelling due to oil absorption. The ionomer samples had little to no abrades or scratches. After 24 hours, Ionomer-M films had large areas of minor abrades and scratches, as well as small areas of uneven surface. Ionomer-A films, which was known to have excellent abrasion resistance and oil resistance, only had a few low level abrades or scratches and no uneven surfaces.

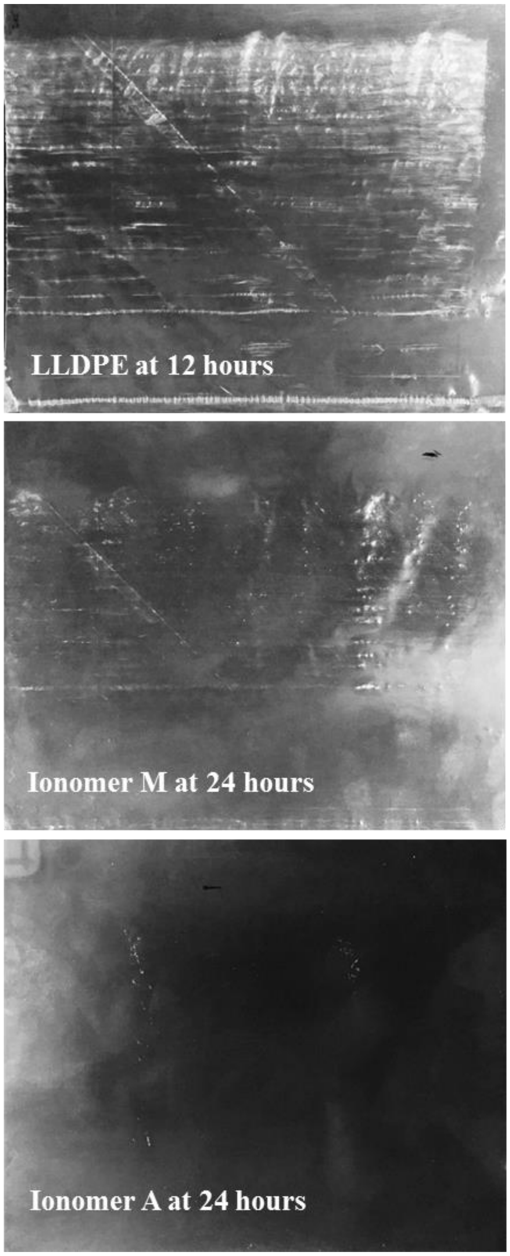

Figure 3. Pictures of the sealant films used for the Shaker Table Abrasion Test validation.

The second stage of validation was to investigate the consistency and repeatability of the test, where Ionomer-A was tested three times and ionomer B was tested twice, each time with a new group of 3 to 5 specimens. The resulting films were graded using a film grading system (will be described in the next section, the higher the score, the better the performance) and are summarized in **Table 1** and in box and whisker diagrams in **Figure 4a** and **Figure 4b**. The standard deviations for the abrasion resistance ratings are around 1, and standard deviations for the oil resistance ratings are within a range of 0-0.5. Considering the inconsistency of the commercial dry food product's orientation in the canisters, this validation experiment suggests that the Shaker Table Abrasion Test is consistent and repeatable.

Table 1. Average (Ave.) and standard deviation (Std. Dev.) of ratings for abrasion resistance and oil resistance.

	Abrasion Resistance Ratings		**Oil Resistance Ratings**	
	Ave.	St. Dev.	Ave	St. Dev.
A1	6	1	9.8	0.4
A2	5	1	10	0
A3	6	2	10	0
M1	2	1	7	0
M2	2.4	0.7	6.6	0.5

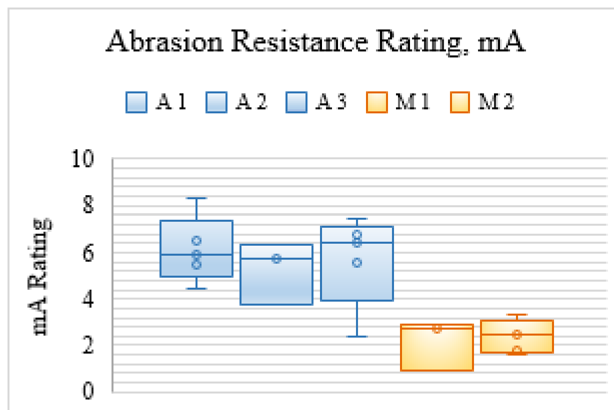

Figure 4a. Abrasion resistant rating, mA.

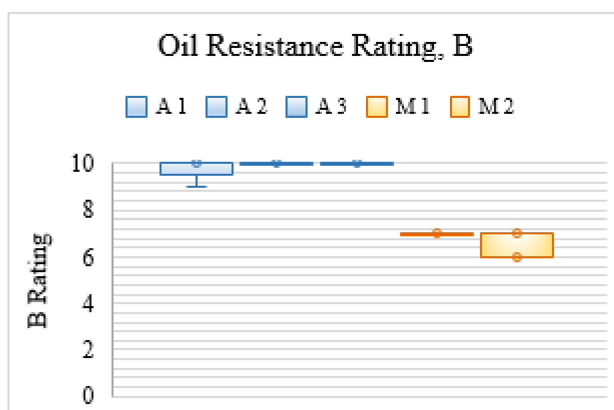

Figure 4b. Oil resistance rating, B.

Film Grading System

Using the film from Ionomer-M as an example, there are two types of impairments on the film, as shown in **Figure 5**: 1) visible abrades and scratches caused by abrasion, marked with dashed lines, and 2) uneven surfaces as a result of softened polymer due to swelling when exposed to oil, marked with boxes with solid borders. Grading systems based on percent areas affected were developed to quantify the performance of abrasion resistance and oil resistance separately.

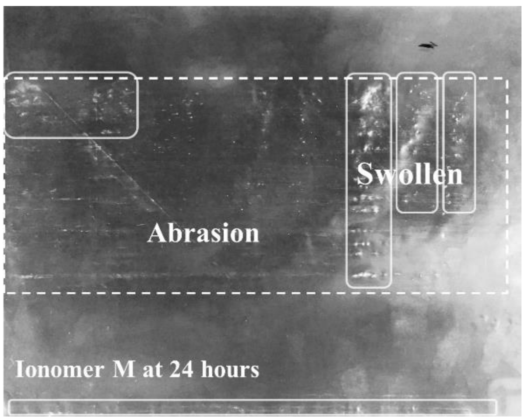

Figure 5. Example of abraded areas and swollen areas on a film after the Shaker Table Abrasion Test.

There are different severity levels of abrades and scratches. For the same grade, films with mostly minor abrades tend to have larger affected areas, and films with more severe abrades tend to have smaller affected areas. This could be a result of different orientations of the dry food products during the test. If the food products are evenly placed in the canister, most areas on the inside wall will have a good chance of getting abraded, which lowers the abuse per area of the wall/ sealant surface. On the other hand, if a piece of abrasive food sticks out near the inside wall of the canister, it might severely abrade certain areas, whereas other smaller pieces might not have a chance to touch the rest of the inside wall. To take this observation into consideration, a multiplier, m, is created as shown in **Table 2**.

Table 2. Multiplier for the abrasion resistance rating.

Severity of Abraded Areas	Very Low	Low	Medium	High	Very High
Multiplier ***m***	0.95	0.75	0.55	0.35	0.15

Based on the percentage of areas with visible signs of abrasion, a rating, A, on a scale of 1 to 10 is summarized in **Table 3**. Overall, the abrasion resistance rating is the product of m and A.

Table 3. Abrasion rating based on areas affected.

	Area Affected (%)							
Abraded Areas	> 80	50 to 80	35 to 50	25 to 35	15 to 25	5 to 15	< 5	< 1
Rating ***A***	1	3	5	6	7	8	9	10
Final Rating	***mA***							

The oil resistance rating is also based on the percentage of areas affected by swollen and uneven surfaces, as shown in **Table 4**. The standard is whether the unevenness is perceptible by the touch of one's finger.

Table 4. Oil resistance rating on a scale of 0-10.

	Area Affected (%)								
Swollen Areas	≥ 50	35 to 50	25 to 35	10 to 25	5 to 10	2 to 5	2 to 1	1 to 0.3	< 0.3
Rating ***B***	0	1	3	5	6	7	8	9	10

Using **Figure 5** as an example again, the abrasion resistance rating is calculated as follows:

$$m = 40\% low + 60\% Medium = 0.63$$
$$A = 3,\ (80 - 50\%)$$
$$mA = 1.9$$

And the oil resistance rating is:

$$B = 5\ (25 - 10\%)$$

Materials

Swelling of the amorphous phase of polyolefins may occur when the polymer is exposed to oil; higher density (crystallinity) polyethylene usually has better oil resistance than lower density grades. Low-density versions of polyethylene (e.g. LDPE, LLDPE, mLLDPE and plastomers) have lower seal initiation temperature and are therefore often used as the sealant layer in flexible packaging. Since the sealant layer is in direct contact with the product, these polymers are not well suited as sealants where oil and abrasion are present.

Another class of sealants, ionomers, has both low seal initiation temperature and outstanding oil resistance. [7] Ionomers are ethylene-acid copolymers partially neutralized with metal salts such as sodium or zinc. The presence of the acid groups and metal salts increases the polarity of the polymer, imparting oil resistance. The ionic linkages between molecular chains provide toughness and scratch/abrasion resistance. The properties of ionomers are primarily determined by the amount of acid, the level of neutralization of these acid groups, and the type of metal salt. While there are many permutations, in general, scratch and oil resistance is found to increase with increasing acid and neutralization.

Combinations of certain ionomers may bring synergistic improvements in abuse resistance [8], which was validated by testing three different blends of ionomers at the same ratio, using the ISO 1518 Scratch Test, as shown in **Figure 6**, where force (N) is the minimum load to leave a scratch on the surface of the sample. The higher the force (N), the better scratch resistance.

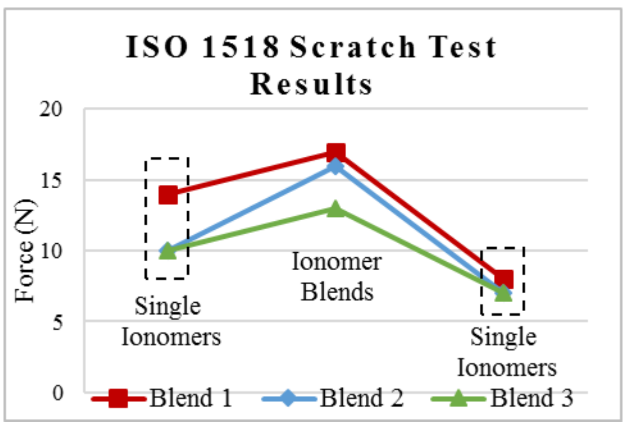

Figure 6. Scratch resistance of three groups of ionomer blends.

The ionomer blends in **Figure 6** had higher scratch resistance than the individual ionomers. However, blending certain ionomers creates higher scratch resistance but not necessarily improves the oil resistance of the sealant polymer. Would the blends keep the improved abrasion resistance in an oily environment? To answer this question, seven ionomer resins were selected to make eight different blends to be tested using the Shaker Table Abrasion Test.

Table 5. Properties of the ionomers selected to make different blends.

	% Acid	**%Neutralization**	**MI (g/10min)**
A	High	Medium	2.5
B	High	Medium	5
C	High	Medium	5.2
D	High	Medium	3.9
E	High	High	1.2
F	High	High	0.7
G	High	High	0.9

Experimental Procedure

The ionomers listed in **Table 5**, were used to make blends (**Table 6**) that might have improved abrasion resistance in an oil-free environment, as suggested in previous studies shown in **Figure 6**.

Table 6. Combinations of blends.

Ionomers		**Blends**	
		Ratio 1	**Ratio 2**
A	B	AB 1	AB 2
A	C	AC 1	AC 2
A	D	AD 1	AD 2
A	E	-	AE 2
F	G	-	F/G 2

50-µm monolayer films of the seven ionomers and eight ionomer blends were made using a cast film process. The films were tested in the Shaker Table Abrasion Test as described in the previous sections of this paper. There were five specimens for each material, and all the samples were tested in the shaker at 27˚C and 150 RPM for 24 hours.

Results and Discussion

The results of this experiment are organized by different blending combinations in the summary box and whisker diagrams in the Appendix section of this paper.

Unlike the scratch test results of ionomer blends in a standard laboratory environment (**Figure 6**), the ionomer blends did not have improved performance using the Shaker Table Abrasion Test in an oily environment. For most blend combinations, both the oil and abrasion resistance ratings fell between the performances of the two component ionomers. This suggests that the improved abrasion resistance might be compromised by the weaker oil resistance in an abrasive and oily environment. This may be the result of the sealant swelling when exposed to oil, which can make the material softer and more prone to abrasion.

Conclusions

In this study, a Shaker Table Abrasion Test was developed to correlate the abrasion resistance of a sealant material to commercial experiences such as the presence of oil or grease in the package. The test was validated to be consistent and repeatable, and was used to investigate the interactions of abrasion and oil resistance of sealants. The results of the experiment suggest that, in an abrasive and oily environment, advanced abrasion resistance of a sealant material can be comprised by weaker oil resistance.

References

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Appendix

Figure 7. Shaker Table Abrasion Test results for ionomers and their blends

Abrasion Resistance Rating, mA
A
AF 1
F
mA Rating
10
8
6
4
2
0
Oil Resistance Rating, B
A
AF 1
F
B Rating
10
8
6
4
2
0
Abrasion Resistance Rating, mA
F
FG 2
G
mA Rating
10
8
6
4
2
0
Oil Resistance Rating, B
F
FG 2
G
B Rating
10
8
6
4
2
0