Electron Beam Gas and Aroma Barrier Technology

By Im Rangwalla

A new organofunctional silane-based electron beam curable gas and aroma barrier technology has been developed. This technology can be used as a coating or an adhesive to laminate various similar or dissimilar substrates used in flexible packaging. A detailed description of the chemistry, manufacturing process and typical oxygen barrier values in comparison with other commonly available gas barrier materials will be discussed.

Background

The global packaging market is estimated at approximately $450 billion. North America and Europe represent about 29% and 27%, estimated at $130 and $120 billion respectively. In America, flexible packaging is approximately $20 billion.[1]

Flexible packaging developed as a significant industry after the development of plastic technology. Since then, it has been a growth industry. While rigid, paperboard, glass and metal containers have seen low to negative growth in the last decade, flexible packaging has experienced a 3.5-4.0% growth. See Figure 1.

Flexible packaging is very versatile in combining the appropriate properties of plastic, paper and aluminum foil to provide the required protection to the packaged product, thus offering the least expensive option for packaging when compared to the other packaging segments. There are several reasons for the sustained growth of flexible packaging.

- Utilizing the least amount of material (source reduction).
- Energy efficiency.
- Cost effectiveness.

If one were to break down the market segments where flexible packaging is being used in the U.S., 55% is used for food packaging and 7% used in medical packaging. See Figure 2.[2]

FIGURE 1

Packaging segments growth comparison 1996-2003

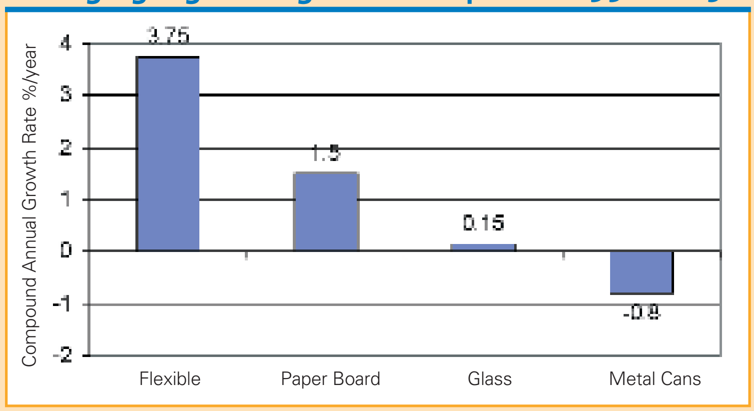
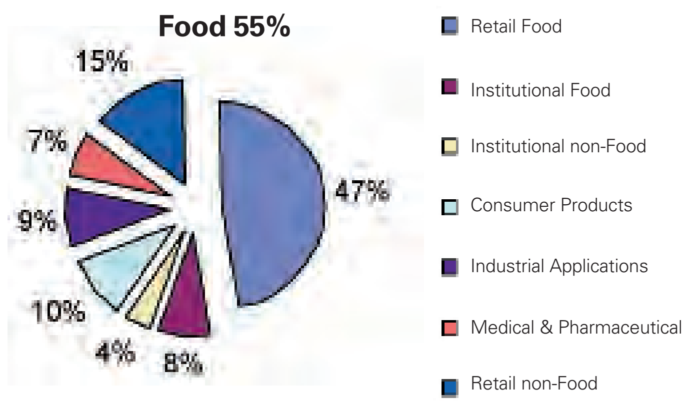


FIGURE 2

U.S. packaging sales breakdown by end-use segment, totaling $21.3 billion



A total of 62% or $13 billion of flexible-packaging material is supplied for food and medical packaging. The packaging for these markets was previously supplied in glass or metal cans, which provided absolute protection to food in terms of water vapor, gas (oxygen) and aroma.

Therefore, over the years development of water vapor, gas and aroma barrier technology was a key factor for achieving growth in flexible packaging, providing adequate shelf life for the packaged products. Table 1 describes commonly available barrier materials used in flexible packaging.[3]

Usually in flexible packaging, various types of polymeric films would be laminated to a high-barrier component such as aluminum foil to provide the required protection and shelf life.

For example, processed meats require a high-oxygen barrier to avoid going rancid. Usually the packaging material for these meats would be prepared using PVDC (poly vinylidine di chloride) coated PET (polyester) adhesive laminated to a PE sealant layer, or a PET would be adhesive laminated to an EVOH (ethylvinyl alcohol) co-extruded sealant layer. Both these materials would provide the required oxygen barrier to the meat. The moisture barrier obtained by the polyolefin is sufficient in this case. The adhesive normally used in these processes is a time-cured, 2-part solventless adhesive.

To simplify the process, the adhesive would have oxygen barrier properties. This combined with the instantly cured laminating adhesive properties as offered by a EB-cured

TABLE 1

Commonly available barrier materials used in flexible-packaging applications

Material	Barrier Provided	Food Segment Commonly Used
BOPP, PE	Medium Moisture Barrier	Snacks, processed, meats/cheese
Metallized BOPP	High Moisture Barrier, Light barrier	Chips, Other Salty Snacks
Metallized PET	High Moisture, Oxygen and Aroma Barrier	Coffee, Tea, Ketchup, other Bag-in-Box, Wine
PVDC coated PET, & BOPP	High Oxygen Barrier, Medium Moisture Barrier	Processed Meats/Cheese
PET	Low Oxygen Barrier, Aroma Barrier	Low-Shelf Life Food Product, High Aroma Products like Wet Wipes
Nylon	Low Oxygen Barrier, Aroma Barrier	Some Meats, Non-Foods
PVDC extruded	High Moisture, Oxygen and Aroma Barrier	Meats
EVOH Coex as a sealant Layer	High Oxygen Barrier, Aroma Barrier	Meats, Fruit Juices
Aluminum Foil, SiOx, AlOx	Absolute Oxygen, Aroma and Water Barrier	Fruit Juices, Wines, Stand Up Pouches, Bag-in-Box

laminating adhesive[4] would make the entire manufacturing process very simple and cost effective. This process would further allow one to use commonly available PET and sealant layers. This proposed barrier adhesive structure is shown in Figure 3.

A barrier adhesive that can also be used as a coating has been developed. The chemistry, properties, etc., are described below.

Barrier Adhesive or Coating Chemistry

Dow Corning and ESI researchers set out to improve the adhesion of metallized aluminum on BOPP and PET. They worked with organofunctional silanes type Z-6032 (vinyl benzyl amine alkoxysilane). See in Figure 4.

The researchers hypothesized that by coating and metallizing these silanes on polyolefin films at very low coat weights (<0.5gsm) and EB treating, the vinyl group would graft to the polyolefin. The formation of the Si-O-AL bonds would provide the required adhesion to the aluminum.

The aluminum adhesion to the polyolefin was substantially increased. It also substantially improved the barrier property of the metallized OPP structure. More importantly, the barrier property of the unmetallized OPP also improved.

This discovery led to the development of an entire class of organofunctional silanes and ethylenically unsaturated carboxylic acids, providing a gas barrier property as well as adhesive property upon EB treatment.[5,6,7,8,9,10,11,12]

The oxygen barrier property comes from the high polarity of the salt created by the unsaturated carboxylic acid and the amino organofunctional silane. Si-O-Si crosslinking and EB curing of the unsaturated carboxylic acid maintains the oxygen barrier at

Figure 3

Currently available meat and cheese pouch vs. proposed structure

Current Structure

PET (12 micron) PVDC coating (3 micron) PU Adhesive (2 micron) PE Sealant (50 microns)	**OR**	PET (12 micron) PU Adhesive (2 micron) EVOH Sealant (50 micron)

Proposed Structure

PET (12 micron)
EB Cured Barrier Adhesive (3 Microns)
PE Sealant (50 microns)

Figure 4

Chemical structure of Z-6032 silane

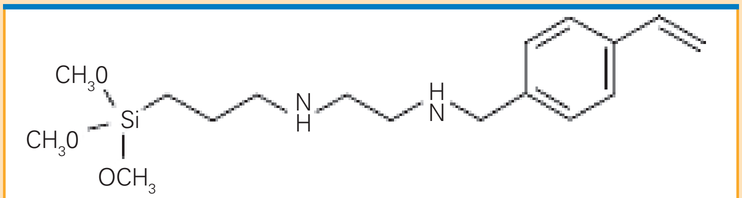


Figure 5

Silane condensation upon exposure to moisture

$$RSi(OMe)_3 + HOH \longrightarrow RSi(OMe)_2OH + MeOH$$
$$RSi(OMe)_2OH + HOH \longrightarrow RSi(OMe)(OH)_2 + MeOH$$
$$RSi(OMe)(OH)_2 + HOH \longrightarrow RSi(OH)_3 + MeOH$$
$$RSi(OMe)_3 \longrightarrow RSiO_{1'5} + 1.5\ HOH$$

Figure 6

Polymerization of itaconic acid upon exposure to electron beam (R = COOH)

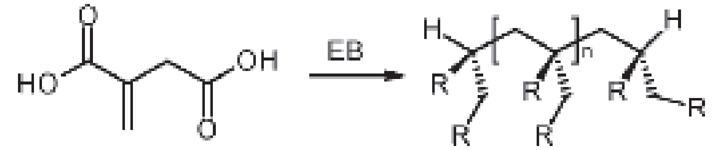


Figure 7

EB-cured barrier adhesive process

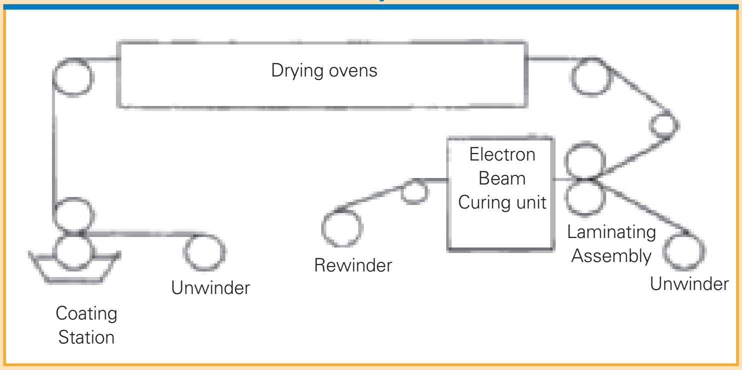


Figure 8

OTR of different barrier materials for PET\LDPE laminate T=23˚C

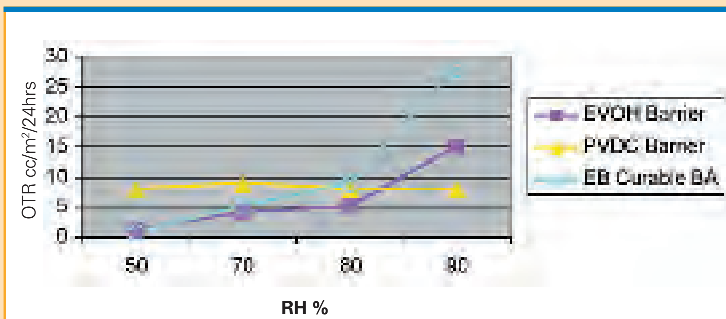
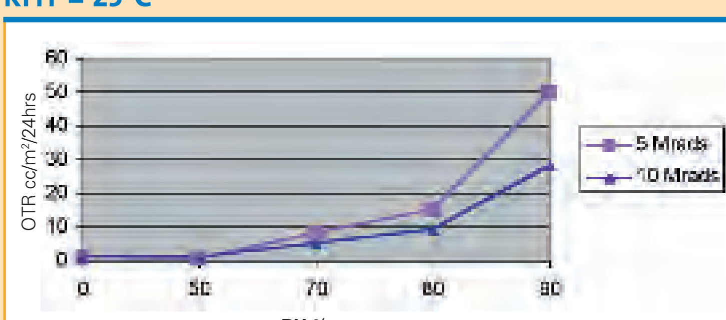


Figure 9

OTR of PET/BA/LDPE BA thickness as a function of RHT = 23˚C



high humidity and provides the adhesion. See Figures 5 and 6.

The formulation most preferred for a multitude of commonly used flexible-packaging products is shown in Table 2.

Process

The formulation is prepared in isopropylalcohol (IPA) water mixture as 60% solids. One can use ethoxy silanes to avoid methanol. Since there are solvents involved in the process, an EB-thermal hybrid cure is required and is shown in Figure 7. In-line corona treatment is preferred for both films.

The application method is reverse roll on a corona-treated film. The adhesive is then dried to evaporate the solvent and water. The second corona-treated film is laminated to it. The whole structure is then EB treated at 125kV and 10 Mrads.

Results

The oxygen barrier, aroma barrier and adhesion obtained for various polymeric films using this process are shown in Table 3.

One of the challenges of flexible-packaging containing all organic or plastic materials is to protect the product packaged from outside aromas that may contaminate it. And, at the same time, keep the packaged product's aroma protected so that it is not depleted over time. Aroma measurements were taken using Aromatran, from the Mocon Company, St. Paul, Minn., which offers standard equipment to measure aroma transmission rates. In addition, companies can devise their own methods to measure aroma transmission such as gas chromatography.

The results clearly indicate that the oxygen barrier is coming from the 3 micrometer of the coating and is independent of the polymeric films used. Remarkable results are seen using metallized OPP. The OTR (oxygen transmission rate) of metallized OPP improves greatly, providing foil-like performance.

Comparison of EB-cured barrier adhesive with commonly available barrier materials like PVDC coating and EVOH for PET/LDPE laminate is shown in Figure 8.

The OTR of the EB-barrier adhesive is comparable with commonly available barrier materials. However, just like EVOH, the EB-barrier adhesive is humidity sensitive.

The OTR at high humidity is very dose sensitive. Figure 9 shows where the OTR of the PET/BA/LDPE laminate cured at two different dose levels, 5 and 10 Mrads. The OTR at 70% RH is comparable for both the cure levels. However, the barrier adhesive cured at 5 Mrads after 70% just takes off and is non-existent at 90% RH. The barrier adhesive cured at 10 Mrads is still humidity sensitive, but to a lesser degree. This result confirms the polymerization and crosslinking of itaconic acid, requiring a high EB dose to maintain barrier at high humidity.

The high EB dose of 10 Mrads to cure has some ramifications. For example, it limits the processing speed and is harmful to the underlying polymeric substrates.

A priming process was developed to maintain the EB dose to 3 Mrads while maintaining the oxygen barrier at high humidity. This process is described in Table 4.

A primer and barrier adhesive maintains the low OTR at high humidity and drops the EB dose down to 3 Mrads. This laminate maintains the barrier after flexing approximately 20 times, indicating that the laminate is resistant to flex cracking—an important property in flexible packaging. Gelbo flexing is a standard test used to determine the ability of the package to withstand flex cracking that is induced by normal wear-and-tear of the flexible package. In this test, the package is mechanically put through several twists (20 being the industry standard) and the oxygen barrier measured before and after twisting (Table 5). Usually materials that are glass-like will crack upon twisting thus the OTR will increase after gelbo flexing.

Conclusion

The results indicate that an entire new family of EB-curable barrier materials—mostly oxygen and aroma—have been developed. This chemistry provides a gas and aroma barrier when used as a coating or an adhesive with a broad range of films commonly used in flexible packaging. These materials

Table 2

Formulation of barrier adhesive and coating

	Wt%
Dow Corning 6601 (Silane grafted PEI)	19
Itaconic Acid	71
Bis-Gamma-Triethoxysilyl Propylamine	10

Formulation is applied as 60% solids in IPA:H_2O 50:50.

Table 3

Oxygen barrier, aroma barrier and adhesion of various polymeric materials prepared by the EB-cured barrier adhesive

Material	O_2 Barrier at RH 50% and T= 23˚C cc/m²/24hrs	O_2 Barrier at RH 80% and T= 23˚C cc/m²/24hrs	Aroma Barrier	Adhesion
Pet12M / BA 3M / LLDPE50M	1.0	9.6	Excellent	Substrate Tear
OPP18M / BA3M/ OPP18M	1.0	7.8	Excellent	Substrate Tear
OPPmet18M / BA3M / OPP18M	0.8	0.8	Excellent	Substrate Tear
LDPE50M / BA 3M / LDPE50M	1.5	9.0	Excellent	600gms/inch
OPP 30M / BC 3M	2.0	10.0	Excellent	NA

Note: Oxygen barrier measured by Mocon Oxtran 2/20 series. Aroma barrier measured by in-house developed testing method for both polar and non-polar constituents.

have also been tried on several different types of inks mostly solvent-based flexography. No adhesion issues were experienced. FDA approval is mandatory for the commercial success of these newly developed barrier materials for food-packaging applications. However, limited studies with 95% ethanol through a 50 micron LDPE film as a functional barrier resulted in < 50 ppb migration. This result is consistent with the nature of the materials used. The final product after EB treatment results in a highly crosslinked structure, providing no chance of migration.

Future work in the development of these materials includes:

- Making the coating or adhesive water-based or nearly 100% solids. Currently, it is made in IPA and water.
- Reducing the dose to cure the barrier adhesive without the use of a primer.
- Making the barrier adhesive humidity less sensitive without the use of a primer or high EB dose to cure.
- Detailing food law migration work.

TABLE 4

PET/LDPE laminate using a barrier primer and a barrier adhesive process

PET Prime with A1170 Bis-Gamma-Triethoxysilyl Propylamine
Coat Weight 0.5 M (Dry)
Laminate 50 M LDPE with 3 M of EB Barrier Adhesive (Dry)
EB Cure at 125kV and 3 Mrads

The results of this laminate are shown in Table 5 as a function of gelbo flexing measured at 50% and 90% RH and 23°C.

TABLE 5

OTR of PET/LDPE laminate prepared with EB-barrier adhesive with a barrier primer as a function of gelbo flexing

Gelbo Flex Cycles	OTR cc/m²/24hrs at 50% RH	OTR cc/m²/24hrs at 90% RH
0	1.8	1.2
10	5.0	4.0
20	4.5	3.0

OTR Measured at 23°C with Mocon Oxtran 2/20 series. EB dose to cure 125kV, 3 Mrads.

Acknowledgements

This paper was originally presented at the TAPPI PLACE Conference 2006.

References

1. "Economic Advantages of In-line Printing Coating and Laminating Using Low Voltage EB Equipment," Im Rangwalla & Urs Laeuppi, Tappi Euro PLACE 2005, Vienna, Austria.
2. Flexible Packaging Association-USA SOI 2003.
3. "Controlled / Modified Atmosphere Vacuum Packaging of Foods," Aaron L. Brody Phd. Food and Nutrition Press USA, 1989.
4. "Performance Properties of Electron Beam Curable Laminating Adhesives for Flexible Packaging Applications," Stephen C. Lapin, & Chuck Wasserman, TAPPI PLACE 2004, Indianapolis, Indiana USA.
5. "Barrier Coatings," U.S. Patent 6,6794,042.
6. "Silicone/Multifunctional Acrylate Barrier Coatings," U.S. Patent 6,686,008.
7. "Alkylenimine/Organic Barrier Coatings Having Bis-Silanes Additives," U.S. Patent 6,6541,088.
8. "Silicone Containing Laminating Adhesives," U.S. Patent 6,514,584.
9. "Reactive Silicone/Alkylenimine Barrier Laminating Adhesives Having Bis-Silanes Additives," U.S. Patent 6,436,498.
10. "Barrier Coatings Having Bis-Silanes," U.S. Patent 6,416,817.
11. "Reactive Silicones/Alkylenimines Barrier Laminating Adhesives and Applications Thereof," U.S. Patent 6,399,171.
12. "Silicone/Multifunctional Acrylate Barrier Coatings," U.S. Patent 6,686,008.

—Im Rangwalla is senior process development engineer, Energy Sciences Inc., Wilmington, Mass.