PACKAGING AND CONVERTING

Adhesives and Sealants

PVdC – Past and Current Barrier Material

Introduction

One of the ongoing challenges for today's consumer goods and products is to provide packaging and protection with enhanced barrier to oxygen, various gasses, water and chemicals. Polyvinylidene di-chloride (PVdC) has been used for decades on paper and plastic films and as extrusion resin. This paper will focus more on the PVdC coatings used in the industry today.

History

Vinylidene chloride was discovered by the French chemist, Regnault in the 1830's and was carefully described. But no further interest was shown until the 1929, when a German chemist, H. Staudinger investigated the material in pursuit of synthetic rubber and determined there was no commercial value. About this time, Dow Chemical scientists felt there was commercial potential and spent six years experimenting and evaluating the new compound. A new line of synthetic resins were created, called VC Plastics. By slightly altering the molecular structure, new resins could be made with many different characteristics. In 1940 this line was trade named as Saran®. Various forms of the solid resins were used from 1942 through 1970, when it was discovered how to create water based latex of this material, as well as solvent based solutions. It now became possible to enhance the barrier properties of paper and films by coatings, in addition to extrusion or lamination. While the chemistry was similar in the two versions, the molecular weight of the latex was consistently higher. This difference resulted in generally higher barrier properties in coatings from latex. In addition, the latex could be manufactured at much higher per cent solids, allowing economies in application.

Chemistry

Vinylidene Chloride monomer, $C_2H_2Cl_2$ is a dangerous and unstable material that must be handled carefully. It will self-polymerize and copolymerize with other monomers. When copolymerized, the resultant polymer is relatively safe and has been approved for various food contact applications.

Pure PVdC is not useful as a coating material. It is far too glassy and brittle to be of much value. Typical comonomers, which might include vinyl chloride, various acrylic and acrylate and nitrile, are used to increase flexibility, specific adhesion and provide other functionality. Other additives are used to stabilize the latex and to serve as emulsifiers, surface tension control, and pH modification and for anti-foam.

Properties

The main advantage of the resultant PVdC coating derived from the latex or solution is the resistance to permeation of gasses and liquids.

Oxygen permeabilities at 23º C range from 0.04 to 1 cc.-mil/100 in^2-day-atm, depending on the comonomer composition. These values are virtually unaffected by the presence of moisture, either humidity or liquid.

Carbon dioxide permeabilities range from 0.1 to 2.4 cc.

Organic solvents also have low permeabilities. N-hexane is 0.0001 to 0.001 g.-mil/100 in^2-day.

Water transmission rates of 0.05 to 0.5 g.-mil/100 in^2-day at 37º C and 90 % relative humidity are routinely achieved.

Barrier Comparisons

An understanding of terms is always useful in discussion and comparisons.

Barrier can be said to be the ability of a material to resist absorption, diffusion, desorption or evaporation of gases or moisture through it.

Chemical resistance is defined as the ability of a material not to be affected by solubilization, softening or changed in any way when exposed to another material, and should no be confused with barrier.

Permeability is the measured behaviour when measuring the ability of liquids, gases or moisture to penetrate through a material.

$$\textbf{Permeability} = \frac{\textbf{(Quantity of Material)} \times \textbf{Thickness}}{\textbf{Time} \times \textbf{Area} \times \textbf{Partial Pressure Drop}}$$

PVdC based materials have been available for decades, being commercially introduced as coatings in the 1970’s. There were two main types: solvent solutions and water based emulsions. Early on in their introduction, the only competing barrier materials were metal foils and exotic film or coating materials. As technology improved, and new materials were invented, alternate barrier materials came available. The creation of alternate barrier technology continues, though sometimes at a cost premium.

PVdC imparts barrier due to the chemical structure. Vinylidene dichloride polymerizes with comonomers to create a backbone that have symmetrical regions. This allows close packing in the dry state, creating crystalline regions. This is the dominant factor controlling barrier. Since the polymer is still considered a thermoplastic, the crystallinity can be lessened or destroyed when temperatures approach the melt point. However, as the polymer cools, the barrier returns as the crystallinity reforms, re-establishing barrier properties.

At room temperature, this crystallinity forms in 10 to 15 days. At 100° C, the process can be accelerated to reach barrier in as little as one to two hours. The better barrier is attained, however, if the crystallization is completed at room temperature (70 – 90° F).

PVdC coatings and adhesives are unique in that they are designed to provide a suitable balance of properties including gas, moisture vapor and grease barrier, heat seal ability, solvent resistance, abrasion resistance, flexibility, and gloss. Other barrier materials typically impart good oxygen or moisture barrier, and/or good flavor/odor barrier, but do not impart the wide balance of properties of PVdC. In addition, many barrier materials are affected by the environment, with temperature or humidity decreasing the barrier properties. PVdC is not affected by these conditions.

PVdC has inherent anti-combustion properties due to the high chlorine content.

Comparison to Other Barrier Technologies

There are many competing technologies to PVdC latex technology. There are advantages and disadvantages to each type of barrier technology. Table 2 below summarizes the various forms of barrier technology used in flexible packaging.

Factors Influencing Barrier Properties

The important factor for any barrier material is that in needs to be a continuous layer with no pinholes or voids. This is also true with PVdC coatings. When coating paper, it is preferable to apply 2 or more thin coats to cover any paper fibers that would act as wicks, from protruding through the coating.

As the coating weight increases, the barrier improves. Depending on the substrate, there will reach a point where adding more PVdC does not significantly improve the barrier. Of course, the PVdC should be fully crystallized before the testing is done. There are some FTIR methods to follow the change in crystallinity.

The type of PVdC used also determines the maximum barrier. Some PVdC crystallize more than others and the high crystalline PVdC have the better barrier properties. There is some influence of the comonomer as well. The temperature and humidity has an impact on the barrier of many materials: the higher the temperature and humidity, the lower the barrier. This is not the case, for the most part, with PVdC. The barrier remains fairly constant under varying test conditions.

Application.

Selection of the appropriate latex or solution is determined by the end use intended and equipment available for application.

In choosing the correct barrier coating or adhesive, the converter should consider:

- What the final structure will be. What are the substrate(s)? Will the substrate(s) be corona treated? Will the substrate(s) be primed? What is the primer?
- What end properties are desired from the structure? Oxygen barrier (low oxygen transmission rate or OTR)? Moisture barrier (low water vapor transmission rate or WVTR)? Odor, flavor, or grease barrier?
- If the application requires a barrier adhesive, what bond strengths are required?
- If the PVdC coating is to be used as a heat seal coating, what heat seal capabilities are required?
- What is the drying capability of the coating or laminating line? PVdC latices are supplied at 45 – 60% solids, so ovens must be capable of removing 40 – 50% water. A web temperature of 185° F must be achievable for optimal barrier performance.
- Location and service of the barrier coating or adhesive supplier? Is technical support readily available?

Uses

1. Coatings on paper or glassine substrates for snack foods, cereal liners, dry cake mixes, and soft drink powders.

2. Coatings on films such as polypropylene, polyester, polyethylene and nylon, for snack foods, meat, cheese, and medical packaging.
3. Heat sealable coatings that impart barrier properties to the package.
4. Barrier laminating adhesives for dissimilar substrates.

Compared to alternative products, films made with PVdC coatings can result in lower environmental impact throughout the packaging life cycle, from lower spoilage of the packaged contents, to less plastic waste to be disposed, to other important environmental considerations.

PVDC films help meet the requirements of European Directive on Packaging and Packaging Waste by enabling less packaging disposal to landfill by reducing the amount of film required to provide the required protection as compared to other plastic films. PVdC containing films satisfy North American and European national requirements regarding direct contact with food, with food migration limits set for additives and monomers.

Handling

PVdC (Polyvinylidene dichloride) latices are water based, with a low pH, These latices are corrosive because of their low pH (1.0 – 4.0), so certain precautions have to be observed to ensure optimum results.

1. PVdC latices will freeze and become unusable if allowed to cool below 32° F. They must always be shipped and stored between 50°- 80° F.
2. The acid nature of the latex will cause corrosion and discoloration if allowed to contact ferrous or polyvalent metals. All storage and handling should be with 316 stainless steel or plastic equipment.
3. Latices, by their nature, contain surfactants that will cause foam when sheared or aggressively agitated. Some of the latices have very low amounts of surfactant and can be described as “non-foaming.” It is better to handle the latex in such a way as to minimize shear and hence reduce generation of foam.

Application

There are a number of different ways to apply Serfene latex satisfactorily, including air knife, Mayer bar, gravure, reverse gravure, smooth roll, and combinations of these. Selection of the most appropriate method depends on the substrate involved, speeds required, coating weight, and available equipment. In general, an excess of latex is applied to the substrate and metered off using either wire wound rods (Mayer bars) or air knife. The air knife offers advantages in line speed and does not physically scrape the coating or damage it. However, it does generate foam and requires more technique in its operation. Wire wound rods are used with slower line speeds and are easier to use. The latex can be applied to the web by gravure or roll coating both with the against the web direction. Direct gravure is generally used in special situations, where problems can be encountered with plugging in the cells and foam. Reverse gravure is a technique that also works well. Coating weight is controlled by reverse roll surface speed. Smooth roll application, either with or against the web direction, is the most commonly used system. Typical handling instructions are as follows:

Coating and Adhesives

Coating a porous substrate such as paper or glassine is generally performed in two or more passes. The first coating acts as a hold out coat and the second or subsequent layers provide most of the barrier. Typically, coating weights of both applications total 6-12 dry lb/ream (where one ream is 3000 ft^2) or 9.5 – 19 gsm and are usually split equally between the two or more applications.

Film coating can be achieved on impervious films with a single application of PVdC, usually between 2 and 4 lb/ream (3.2 – 6.4 gsm). However, only specialty latices will adhere to specific substrates without an adhesion promoter or primer. To obtain good adhesion, especially under humid conditions, of a latex to plastic film, it is necessary to apply select primers. The primer should be applied "in-line" with the PVdC on the first station of a multi-station coater. Special primers can be provided where it is mandatory to prime "out-of-line."

PVdC can also be used as a primer for other coatings, since it provides a very high surface energy surface in the dried state. In very thin coatings, the barrier is low, but provides excellent adhesion for top coats of other materials, including metallization.

Lamination adhesives can be made of PVdC that provide very good balance of optical clarity, adhesion and good barrier properties. Due to the high molecular weight of the latex, the resistance to tunneling of the lamination is very high. With the higher melt point, these types of adhesives do not need further cure or cross linking, and pass most heat seal conditions in the formation of packaging.

PVdC can also be used in spray or dip applications, where irregular parts need to be coated. Because of the low viscosity and fast drying characteristics, superior protective coatings can be applied to metal and plastic parts where high chemical exposure resistance is required.

PVdC has inherent non flammability and ignition resistance. The dried coatings have a UL-94 rating of V-0 (self-extinguishing) and a LOI rating (Limiting Oxygen Index) of 70 and higher. This index determines the minimum volume of oxygen to nitrogen that will support combustion (Air has approximately 21 % volume oxygen). Because of these properties PVdC has been used as a coating and impregnant for textiles, membranes and non woven materials to enhance or provide non flammable properties. Further, flame resistant wall coatings and paints have incorporated PVdC for construction and architectural applications.

Summary

PVdC has been used as a barrier material for decades. Though the use has diminished in favour of alternate barrier technologies, it still maintains the best balance of barrier properties under a variety of use and test conditions. In many cases, it is still the preferred barrier material and some market segments are continuing and actually growing. Due to its versatility and ease of use, many converters can make their own barrier combinations. This leads to reduced inventory of other barrier substrates, reduced lead time to meet orders and is an economical alternative. Additionally, PVdC is used in alternate coating application for flame retardency and three dimensional part coatings. The continued use of PVdC in many applications will continue as a complementary or alternate barrier technology.

Table 1: Typical Barrier Values of Some Materials

Material	OTR	WVTR	CO$_2$	Nitrogen
PVdC	0.04 – 1.0	0.05 – 0.5	0.1 – 2.4	0.01 – 0.2
Polyamide 6	2.6 – 3.2	20 - 25	4.7 – 8.0	0.2 – 0.9
Oriented Polyamide 6	1.2 – 3.3	10	6 - 8	0.7
PVdC – Polyamide 6	0.2	0.2	1.4	0.1
Metallized Polyamide	0.05 - 0.2	0.2		
BOPP	50 - 80	0.5	6 - 10	15 - 30
Oriented PET	0.4 – 1.0	1.8 – 3.0	15 - 25	0.46 - 1
Metallized PET	0.08 - 0.140	0.05		
PVDC Coated PET	0.4	0.3		
LDPE	250 - 350	1.0 – 1.5	1000 - 2000	180
HDPE	150 - 300	0.3 – 0.4	280 - 600	18 - 48
Polystyrene	300 - 400	2 - 11	1000 - 1500	40 - 50
EVOH 0 % RH	0.01 – 0.1	-	0.01 – 0.5	0.01 - 0.02
EVOH 100 % RH	0.65 – 1.15	1.4 - 8	8	-
PVC 1 mil	4-5	8-20		
polychlorotrifluoroethylene (PCTFE)	7	0.035		
Acrylonitrile 1 mil	0.7	4.5		
Polycarbonate 1 mil	160	9		
48ga PET-met/1.2 HDPE 2.5 OD	0.60	0.007	Real world adhesive laminations	
48ga PET-met/1.2 HDPE 1.8 OD	0.96	0.014		

OTR:	cc·mil/100 in^2/24 hours at 73ºF at 75 % RH (ASTM D-1434)
WVTR:	g·mil/100 in^2/24 hours at 100ºF at 90 % RH (ASTM D-96)
CO$_2$:	cc·mil/100 in^2/24 hours /atm. at RT
Nitrogen:	cc·mil/100 in^2/24 hours /atm. at RT

Conversion factor:
cc·mil/100 in^2/24 hours X 2.54 = cc·mm/m^2 /24 hours/atm.
g·mil/100 in^2/24 hours X 164 = g·mm/ m^2 /24 hours

Table 2 – Various Barrier Technologies

Type	Advantages	Disadvantages	Typical Uses
Aluminum foil	Highest barrier – comparable to can or jar	Cost, opaque, can flex crack, pinholes	Multi layer pouches, retort containers, lidding
Metallized films	High durability- second to aluminum foil, good barrier properties	Opaque, cannot be thermoformed or shaped, can scratch during handling	Snacks and confectionery, coffee, light barrier and gas barrier containers
PVdC	Balance of oxygen and moisture barrier, transparent, flexible, retortable and heat sealable	Difficulty in application, limited extrusion temperatures, chlorine containing, disposal	Barrier packaging, bakery, chemically resistant applications
EVOH	Best non-metallic oxygen barrier when dry	Extruded only, poor moisture barrier, oxygen barrier drops when wet	Multi-layer extrusions, formed containers, meat and cheese
SiOx (silicon dioxide) and AlOx (aluminum oxide)	Transparent and environmentally friendly	Expensive, can crack or mar when handled, sometimes adhesion issues	Clear retort pouches, medical and pharmaceutical
Nylon	Multi purpose, formable, retortable, transparent, high puncture resistance	Lower oxygen barrier, some moisture sensitivity	Meat and cheese, cook in bag, retort containers

References

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