THE EFFECTS OF RETORT CONDITIONS ON CLEAR HIGH BARRIER LAMINATED STRUCTURES

Thomas R. Mueller
Rohm and Haas Company

ABSTRACT

Retort packaging is rapidly developing as a flexible alternative to cans. The ability to offer packaging with see through qualities has spurred the growth of high barrier laminate films. The clear retort package also offers the advantage of microwaveability right in the pouch, offering consumers extra convenience. This paper will examine the barrier and interlaminate bond qualities before and after retort of several different clear, high barrier film laminates, as compared to conventional foil structures.

INTRODUCTION

The retort pouch was originally developed in the United States for the US Government and utilized mainly for the NASA space program. This structure was then adopted as the Department of Defense combat ration in 1975 (MRE). MRE pouches were tested and designed to standards much stricter than for usual commercial distribution and handling. Retort pouches are now in use in every part of the world, especially where refrigeration is limited. These pouches dramatically improve shipping and warehouse efficiency, as well as delivering fresher tasting food with less water and requiring less cooking time.

Food laws and retort packaging are very specific. The basic tenet of these laws is the assumption of a functional barrier. There is a list of approved materials, otherwise defined by extraction testing under conditions of use. The three regulations that are sited for retort packaging are 21CFR177.1390, 177.1395, and 175.105. 21CFR177.1390 covers laminate structures for use at temperatures of 250°F and above. Aluminum Foil is the only functional barrier stated in the regulation. Regulations are very specific and complex.

Chemistry of Adhesives Used in Retort Pouches

The adhesive systems utilized for retort packaging are either solvent based or solventless. The approved chemistry listed in the regulation for retort is aliphatic isocyanate based with an aromatic isocyanate based adhesive utilized on the outer layers where barrier is present. Solventless adhesives are constrained in their use in retort packaging by the coating weights that can be achieved in the solventless laminating process. Typical coat weights achievable in solventless laminating are about 1.5 pound per ream (2.4 g/m²), whereas for solvent borne adhesives, coat weights of about 3 pounds per ream (4.8 g/m²) can easily be achieved. Therefore, for some very extreme processing conditions, solventless adhesives may not be the adhesive of choice.

Adhesives used in retort packaging are specially synthesized and formulated polyester or polyurethane adhesives. These adhesives are used with coreactants that allow further polymerization of the pre-polymer adhesive components (build larger chain molecules from smaller components). The coreactants are either isocyanate (containing pre-polymers or adducts that react with hydroxyl functionality in the adhesive) or hydroxyl functional materials that react with an isocyanate terminated adhesive. In both cases, the resultant polymer is a polyurethane polymer.

A urethane is formed by the reaction of a hydroxyl functional polyester and isocyanate:

```
                                        O
                                        |
C-O-H        +      N=C=O    ------▶   O=C-N-H
hydroxyl             isocyanate         urethane
functional
```

A diisocyanate will react with a diol to form a polyurethane:

```
                                                   O            O
                                                   ||           ||
O=C=N - R - N=C=O + HO – R’ - OH --> -[- C - N - R - N - C - O – R’ - O -]-

diisocyanate   diol              polyurethane
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It is very important to properly mix the components of a retort adhesive. Improper mix ratios of the two components used in retort adhesives will lead to reduced performance of the polyurethane adhesive. If excess hydroxyl component is used, the adhesive will not cure properly, and it will remain tacky. The adhesive will exhibit reduced heat and chemical resistance, and it will have poorer product resistance. The resultant bond strengths will be lower. If excess isocyanate component is used, the cure will take longer to achieve and will be dependent on moisture entering the laminate to complete the cure. The adhesive will remain tacky until enough moisture has entered the laminate to react with the isocyanate and complete the cure. The resultant cure may be more hard or brittle than expected, leading to lower package performance.

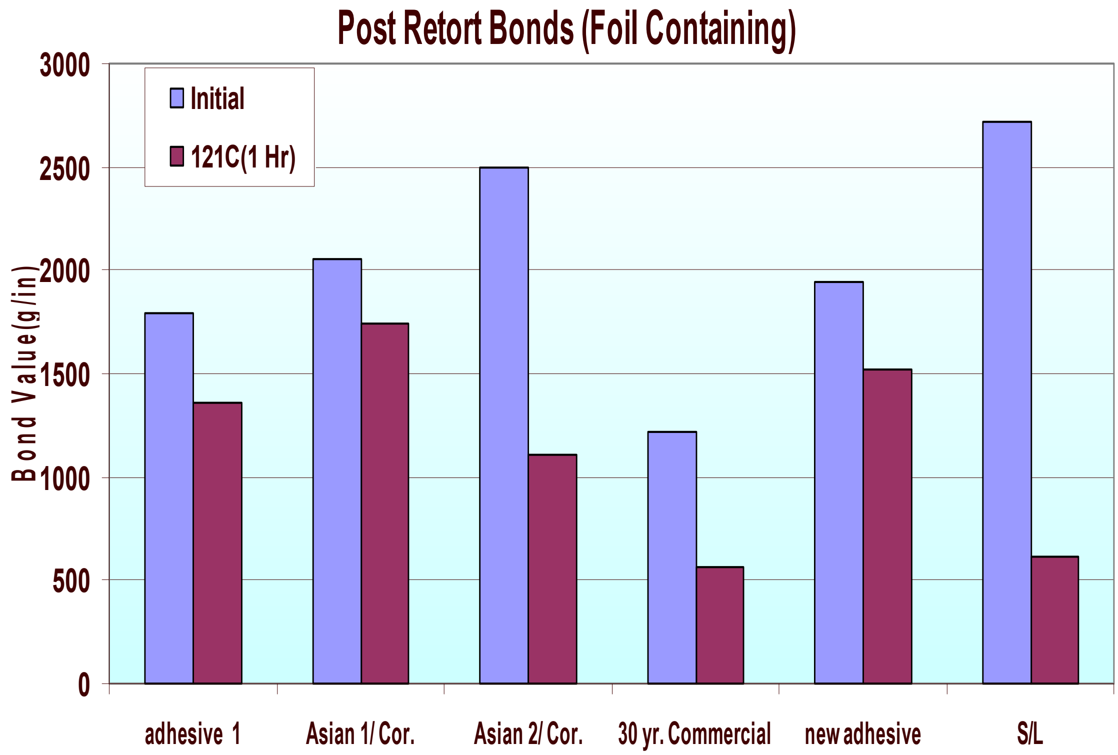
All polyurethane adhesives require time after application for the reactions to complete (for curing to take place), and retort adhesives often require time and elevated temperature to finish the curing. Full curing is necessary for use of the laminate in food packaging, because all isocyanate must be reacted before the laminate can be used. The FDA rules cover extractive limitations – these limitations are determined on fully cured adhesives. Bond strengths are not the measure of full cure; an adhesive can have high enough bond strengths to allow further processing of the laminate (slitting, etc.), but the adhesive may not be fully cured. Cure recommendations of the adhesive supplier must be followed. Depending on the adhesive, times of between three and ten days at 120°F may be required to fully cure the adhesive for retort packaging. Some adhesives may be cured at ambient temperatures, but the curing times will be longer (as long as 10 to 14 days at ambient temperature).

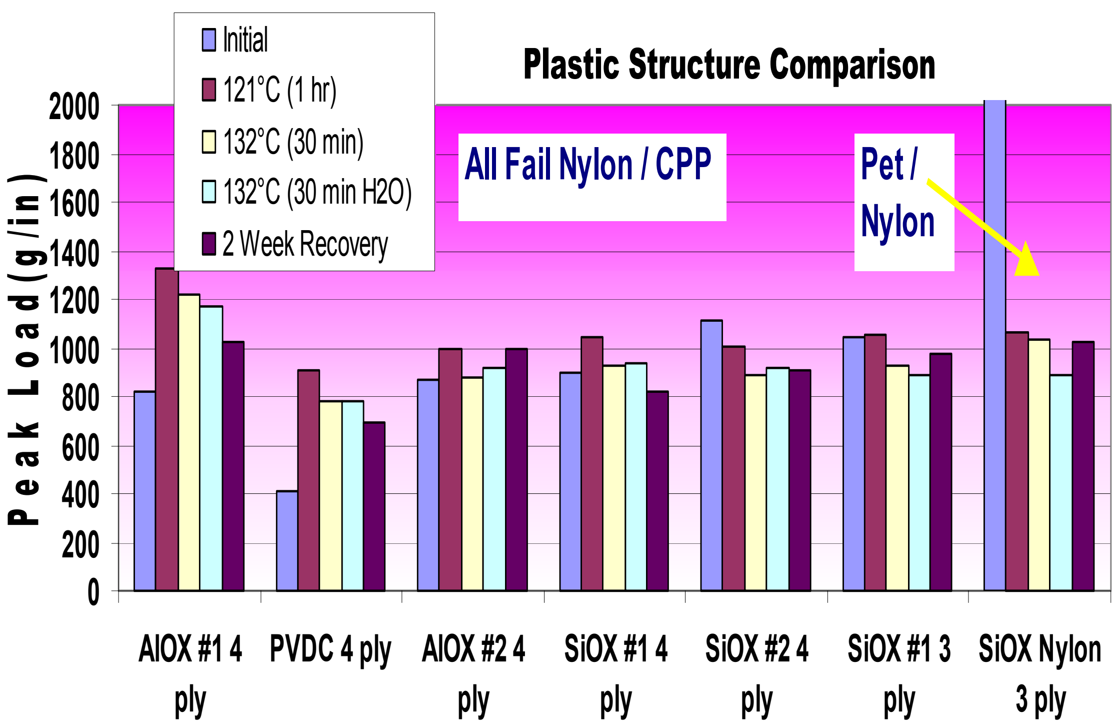
Performance of Adhesives in Retort Structures

Adhesive strength:

Four ply laminations were made with and without foil.
The foil containing structures were as follows: PET/adhesive/Al foil/adhesive/nylon/adhesive/CPP. The all plastic (clear) structures were: PET/adhesive/barrier PET/adhesive/nylon/adhesive/CPP. Solvent based adhesive weights in all structures were 2.75 +/- 0.25 pounds per ream, and solventless adhesive weights were 1.35 +/- 0.1 pounds per ream. Various commercially available barrier polyesters were used in these experiments. The laminations were cured in a hot room at 120°F for a minimum of seven days and were pouched on commercial pouching equipment. The pouches were filled with water and were retorted at 121°C for one hour, 132°C for 30 minutes, or 132°C for 30 minutes and water quenched. Bonds were tested on the inner ply of the pouch immediately after retort and after two weeks of recovery time. Bonds were measured on one inch wide strips in a T- peel configuration pulled at 10 inches per minute.

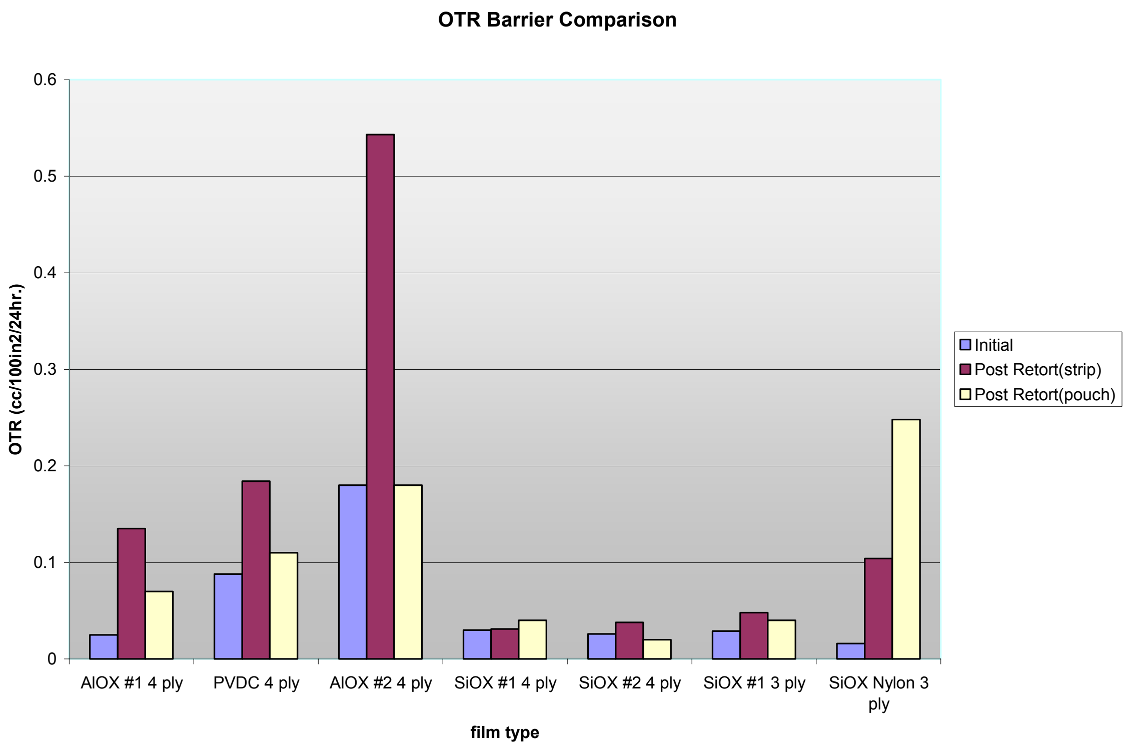
The following graphs show that the post retort bonds depend on the adhesive that is used and the retort conditions. Post retort recovery bonds are not consistently higher than immediately after retort.

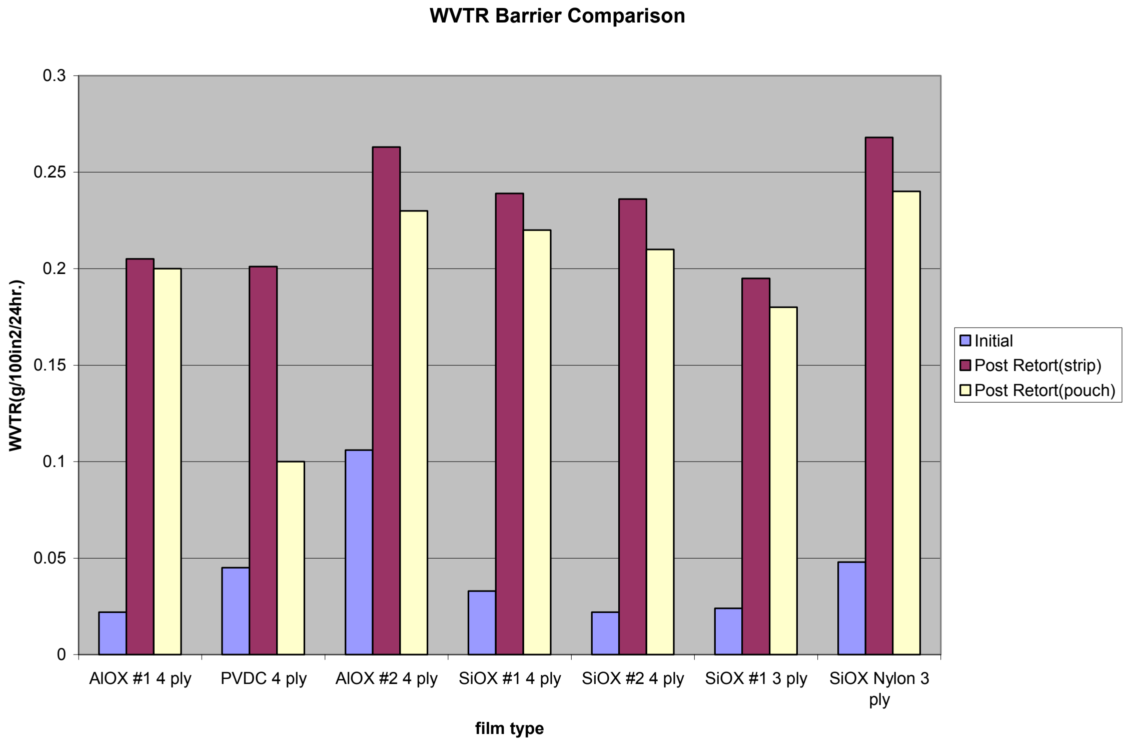

Post Retort Bonds (Foil Containing)
Initial
121C(1 Hr)
Bond Value(g/in)
3000
2500
2000
1500
1000
500
0
adhesive 1
Asian 1/ Cor.
Asian 2/ Cor.
30 yr. Commercial
new adhesive
S/L


Plastic Structure Comparison
Initial
121°C (1 hr)
132°C (30 min)
132°C (30 min H2O)
2 Week Recovery
All Fail Nylon / CPP
Pet / Nylon
Peak Load (g/in)
2000
1800
1600
1400
1200
1000
800
600
400
200
0
AlOX #1 4 ply
PVDC 4 ply
AlOX #2 4 ply
SiOX #1 4 ply
SiOX #2 4 ply
SiOX #1 3 ply
SiOX Nylon 3 ply

Barrier Properties of Pouches post retort:

Barrier (OTR and WVTR) performance of laminations were tested both in sheets of laminate and pouched laminate that were exposed to the 121ºC for one hour retort condition. Pouches were filled with water before retorting. Laminates and pouches were allowed to recover for 24 hours after retorting before barrier properties were tested. Barrier performance was the most consistent with the SiOx barrier films. The results are shown below:





Conclusions:

Different retort conditions produce different results, with the 132 ºC water quench processing condition being the most severe. Bonds do recover post retort, especially when there is foil in the structure. Barrier properties degrade post retort using any type of clear barrier film, however, the SiOx coated polyester films have shown more consistent barrier performance than the other clear barrier options. There is no universal adhesive for all retort conditions and substrate combinations.

Acknowledgments:

I would like to thank the personnel of the Rohm & Haas Midwest Pilot Coating Center for their support in the fabrication of the various laminates and the Laboratory Technical Service personnel for the physical and barrier testing performed. I would also like to acknowledge the various film suppliers who contributed to this study including Celplast, Pliant Corp., and Honeywell.

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The Effects of Retort Conditions on Clear High Barrier Laminated Structures

Presented by:
Thomas R. Mueller
Technical Service Manager
Rohm and Haas Company

Agenda

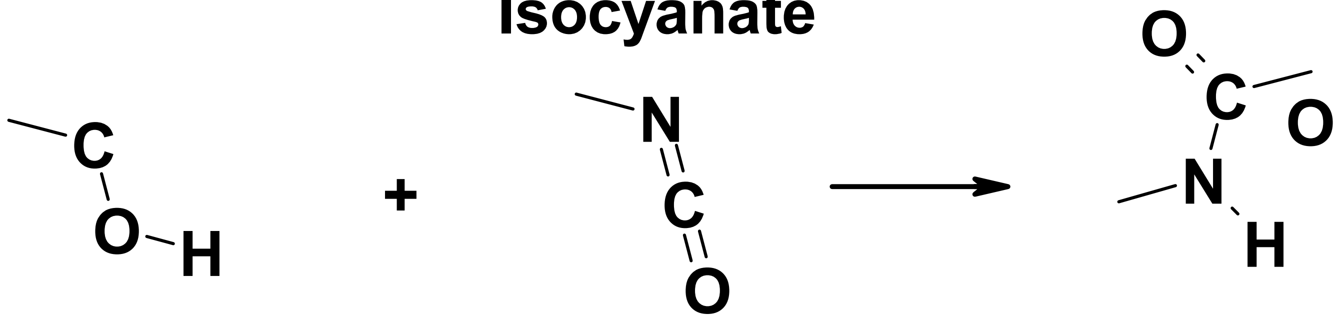
- Brief chemistry review of adhesives
- FDA regulations for retortable flexible packaging
- Performance parameters for retortable laminates
- Laminate structures tested
- Results
- Conclusions

Urethane Chemistry

Definition

- The reaction between an “isocyanate” group and “hydroxyl” group creates a “urethane”.

Isocyanate



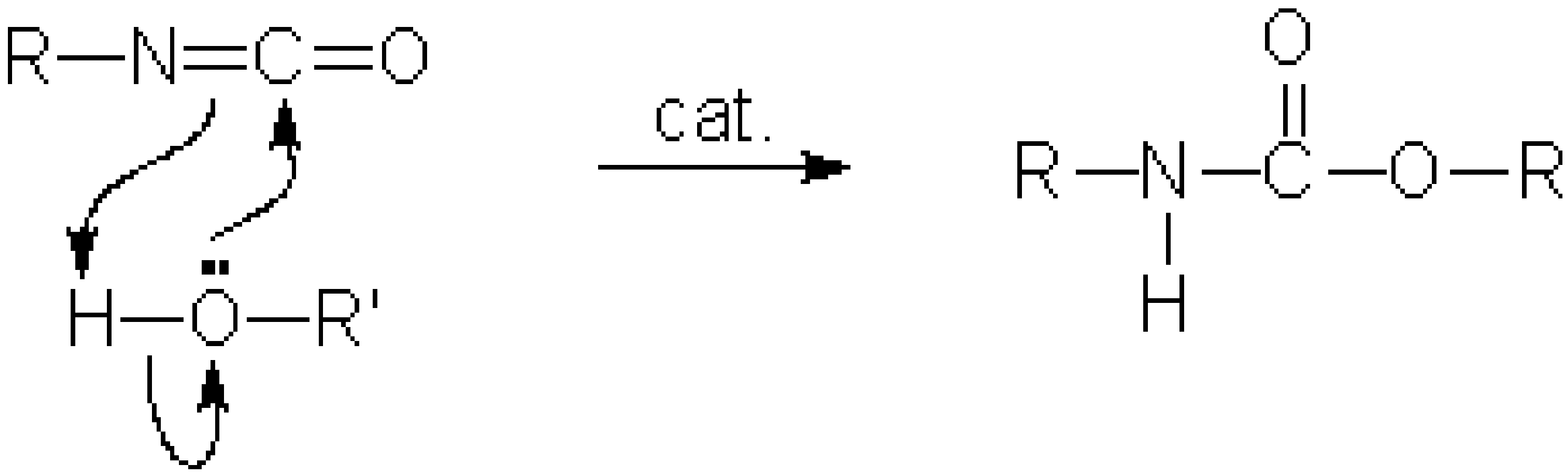
Hydroxyl (-OH) -containing molecule

Urethane

Polyurethane Reaction:

Isocyanate

Urethane unit



Reaction with -OH

Key Regulations
Adhesive Lamination Food Packaging

21 CFR 175.105

- Substances for use only as components of adhesives.

21 CFR 177.1390

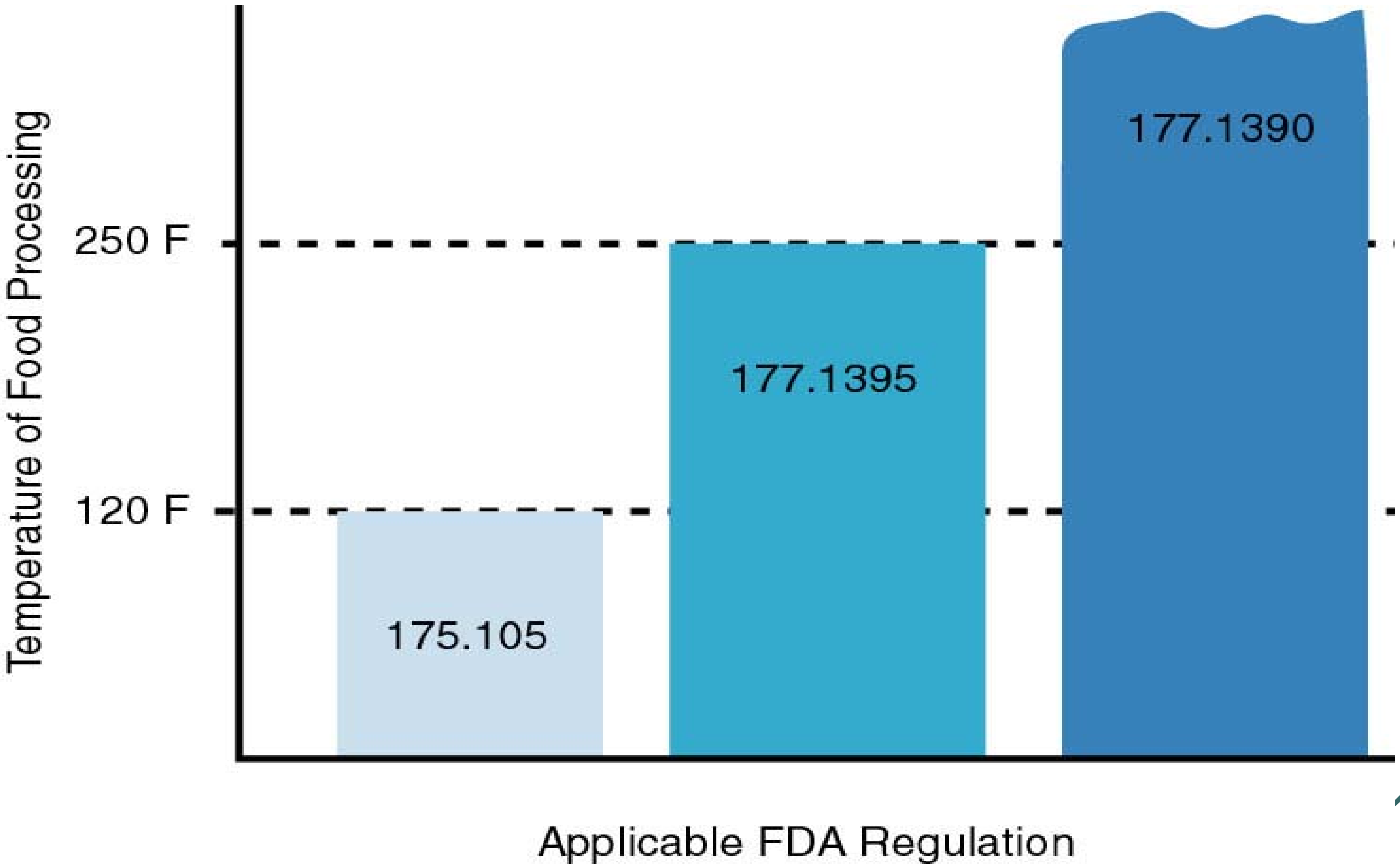
- Laminate structures for use at temperatures of 250°F and above (as retortable laminates).

Key Regulations
Adhesive Lamination Food Packaging

21 CFR 177.1395

- Laminate structures for use at temperatures between 120°F and 250°F (as boilable, hot-fill laminates).

FDA Regulations and Temperatures



Lamination Structures

- PET/adhesive/Al foil /adhesive/nylon/adhesive/CPP
- PET/adhesive/barrier PET /adhesive/nylon/adhesive/CPP

Adhesives

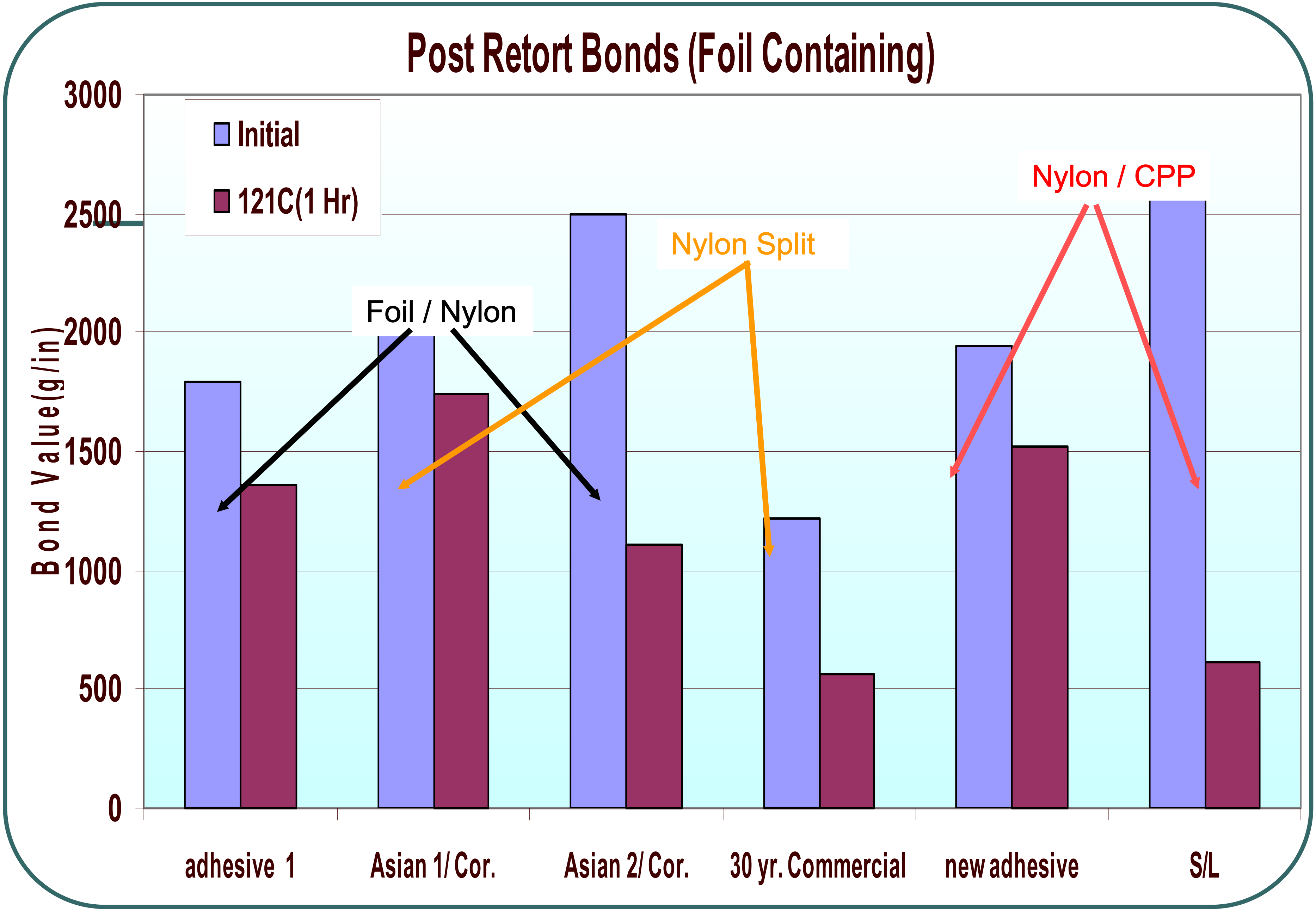
- Solvent based 2.75 ± 0.25 pounds per ream
- Solventless 1.35 ± 0.1 pounds per ream
- Hot room cure (120°F) 7 days
- Pouched on commercial equipment

Retort Conditions

- 121°C for one hour
- 132°C for 30 minutes
- 132°C for 30 minutes water quench

Testing Conditions

- Inner ply immediately after retort
- Inner ply 2 weeks after retort
- One inch T-peel at 10 inches per minute
- Barrier testing: OTR (cc/100 in^2/ 24hrs) WVTR (g/100 in^2/ 24 hrs)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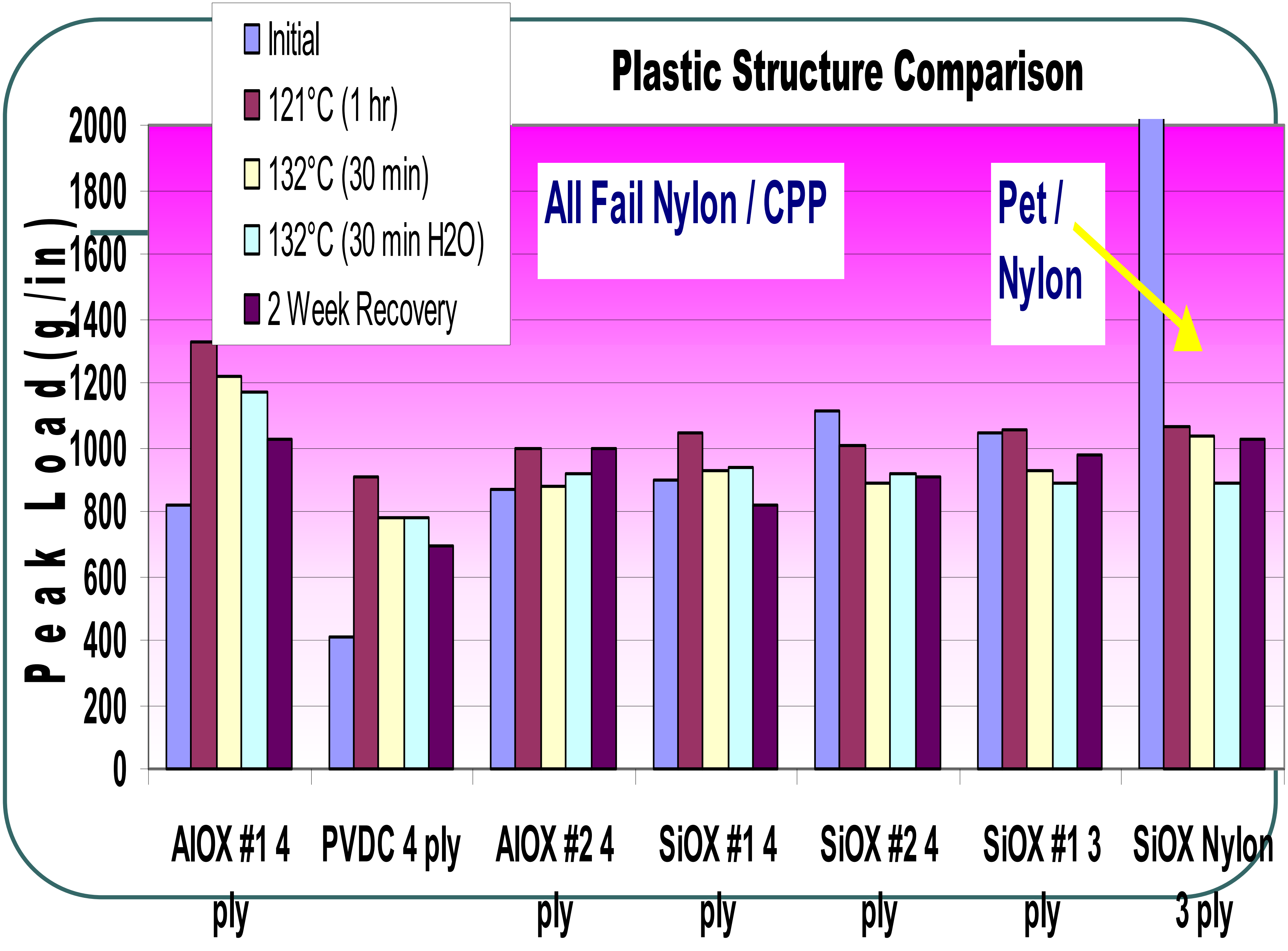
Nylon / CPP
Nylon Split
Foil / Nylon
adhesive 1
Asian 1/ Cor.
Asian 2/ Cor.
30 yr. Commercial
new adhesive
S/L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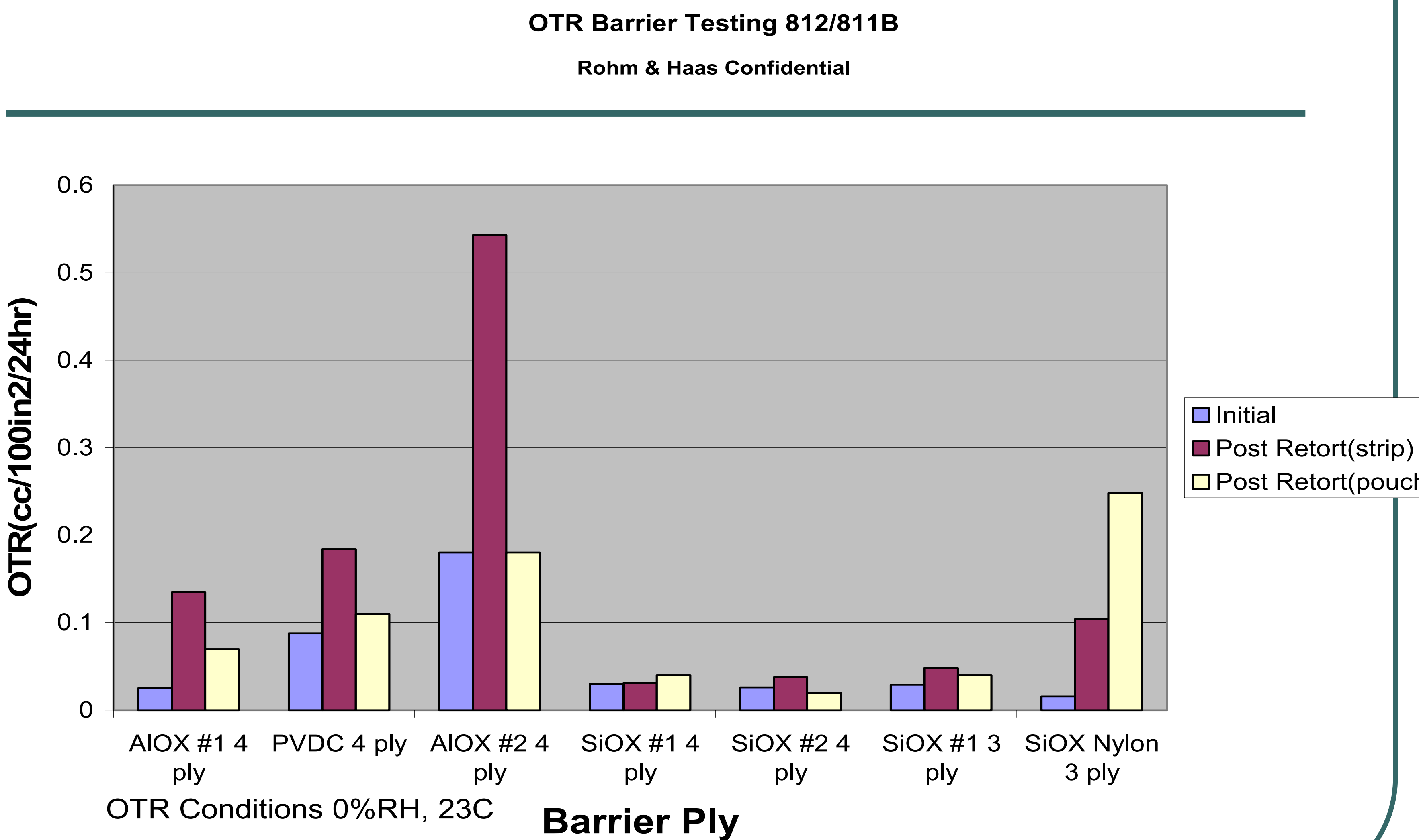
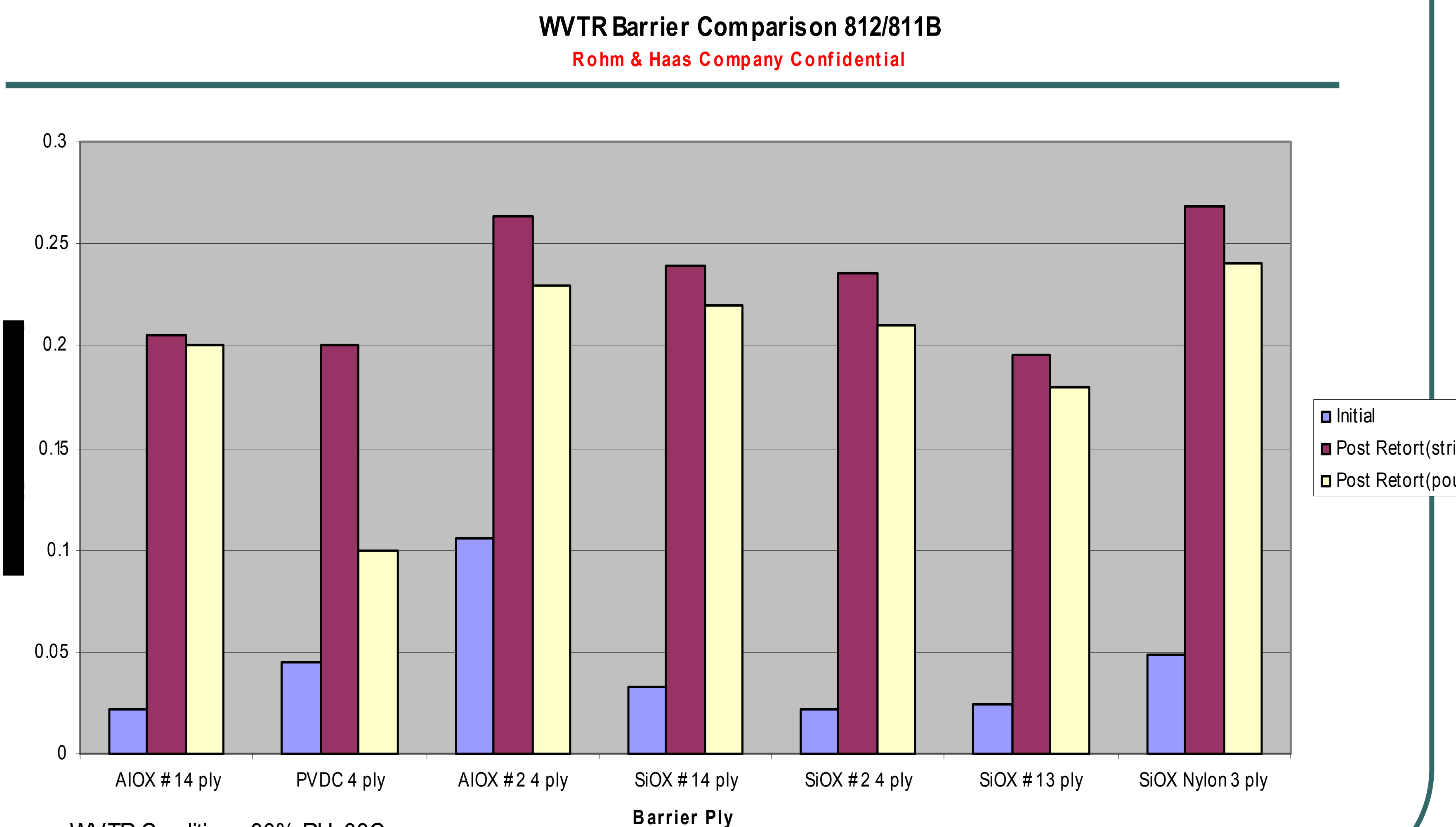
Peak Load (g/in)
0
200
400
600
800
1000
1200
1400
1600
1800
2000
AlOX #1 4 ply
PVDC 4 ply
AlOX #2 4 ply
SiOX #1 4 ply
SiOX #2 4 ply
SiOX #1 3 ply
SiOX Nylon 3 ply

OTR Barrier Comparison



WVTR Barrier Comparison



WVTR Conditions 90% RH, 38C

Conclusions

- Different retort conditions give different results – 132°C water quench most severe
- Bonds do recover post retort – especially foil structures
- Clear barrier film properties do degrade post retort – SiOx films are most consistent
- There is no universal adhesive for all retort conditions and substrate combinations

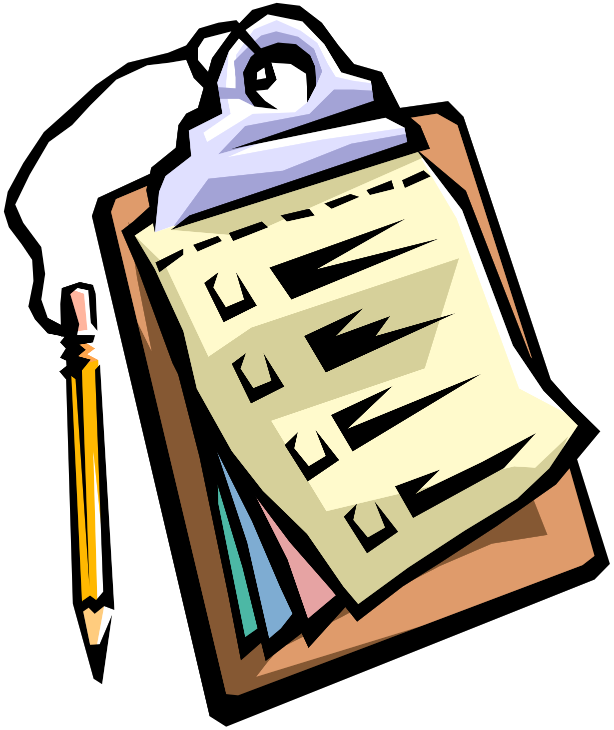
Thank You

PRESENTED BY

Thomas R. Mueller

Technical Service Manager

Rohm and Haas Company



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