

# ***Review of Phenolic Resins for use in Contact Cements***

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# Abstract

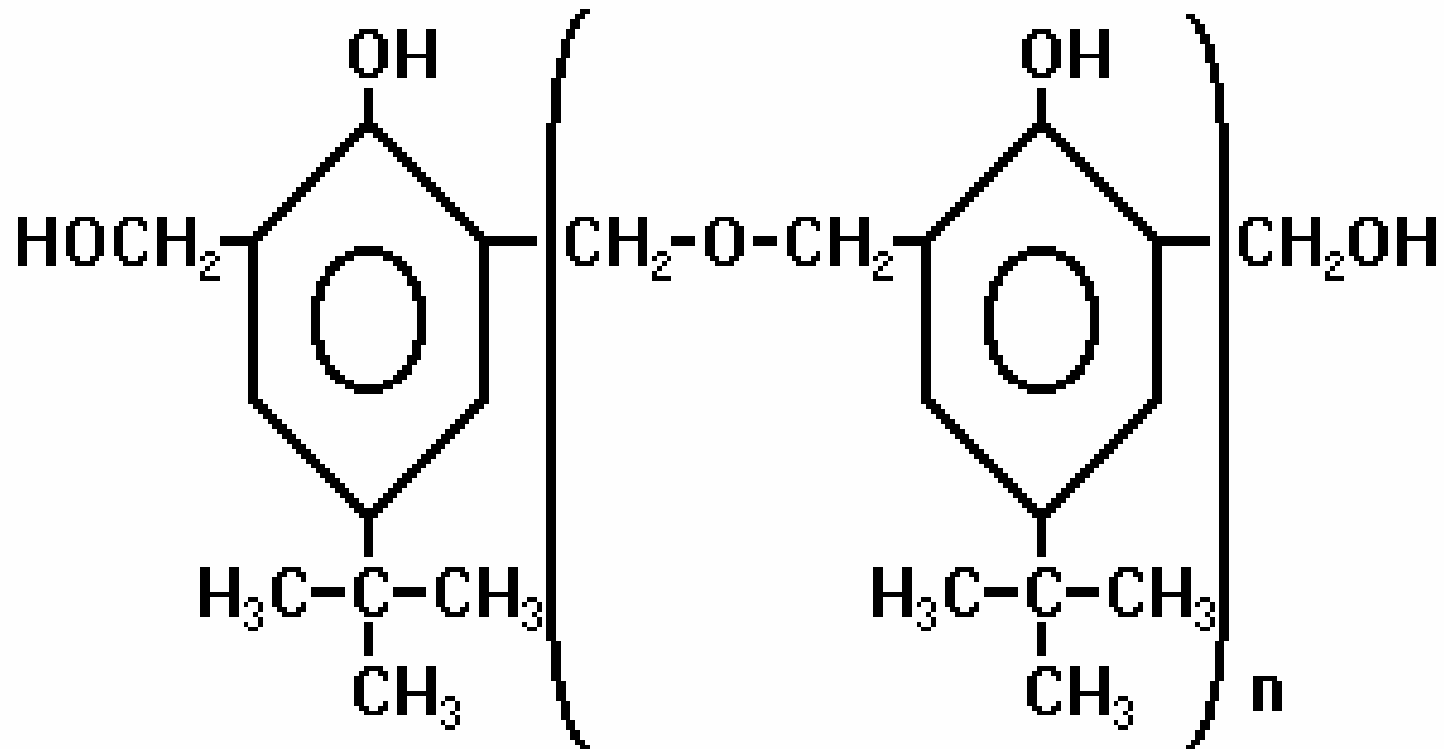
Phenolic resins have been used as a major component of solvent borne contact cements for many years. This paper will address performance advantages that phenolic resins impart, and will highlight the impact on adhesives that are made by modifying the structure of the phenolic resin. The discussion will include commonly described physical properties of phenolic resins, and what these different properties mean to the adhesive manufacturer. Performance details will include open time, shear adhesion, T-peel values, and adhesive failure temperatures.

# Basic Resin Chemistry

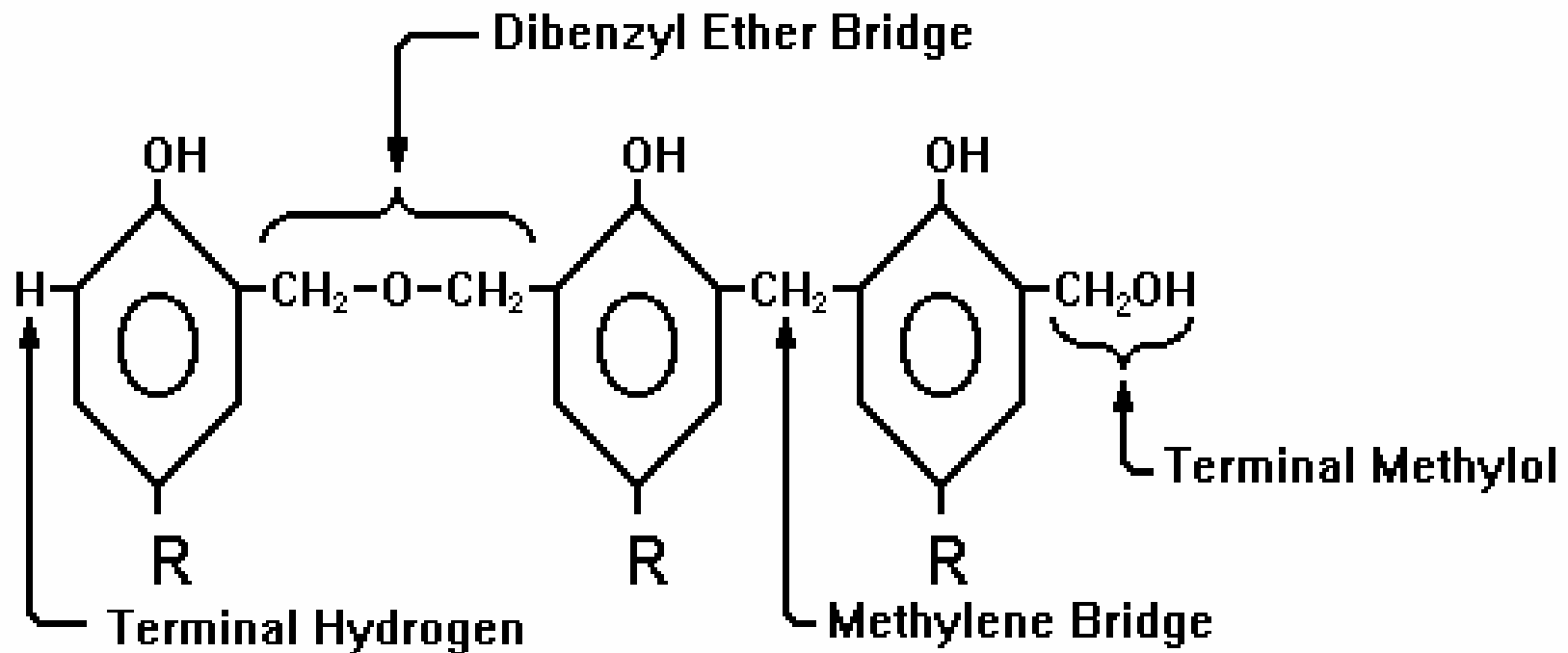
## Heat Reactive Phenolic Resins

- Reaction product of alkylphenol with formaldehyde under basic conditions
- Variations in Phenolic Resins
  - Molecular weight
  - Physical Properties
  - Monomers
  - Modifications by other materials

# Heat Reactive Resin Structure



# Functional Groups



# Monomers used in Resins

- para-tertiary Butylphenol (PTBP)
- Bisphenol A (BPA)
  - Functions as crosslinker
- para-tertiary Amylphenol (PTAP)
- para-tertiary Octylphenol (PTOP)
- Resorcinol

# Physical Properties

- Molecular Weight
- Melting Points
- Methylol Content
- Color

# Molecular Weight

- Distribution can be controlled by processing parameters
- Molecular weight can be controlled by degree of reaction
- Addition of crosslinking monomers can greatly increase molecular weight

# Melting Points

- Ball & Ring Softening Point
  - Function of inherent melt viscosity
  - Generally a function of molecular weight
- Capillary Melting Point
  - Function of crystallinity of polymer
  - Generally a function of polydispersity

# Methylol Content

- Indirectly determined by water driven off by complete condensation of polymer
- Includes two components of resin
  - ortho hydroxymethyl groups
  - Dibenzyl ether bridges that further react
- Function of reactivity towards MgO

# Color

- Function of heat history of resin
- Function of age of resin
- Function of contamination by metals
- Reports of effect on performance
- Develops over time

# Test Formulation

## Pre-reaction

- Resin 45.0 grams
- Elastomag 170S 4.5 grams
- Water 2.0 grams
- Solvent System\* 47.5 grams

# Test Formulation

## Rubber Base

- Neoprene AD 100
- Elastomag 170S 4
- Zinc Oxide 5
- Antioxidant 2246 2
- Solvent System 593

# DuPont Solvent System

- Toluene 33.3 Parts by Weight
- MEK 33.3 Parts by Weight
- Hexane 33.3 Parts by Weight

# Test Protocols

## Dynamic Peel

- 180 degree T-Peel test
  - based on ASTM D 1876
  - Measures strength of adhesive bond between flexible substrates
  - Substrate used is Canvas Duck
  - Determined at different temperatures
  - Direction of pull is perpendicular to bond
  - Samples pulled apart by tensile tester

# Test Protocols

## Shear Adhesion

- Indication of optimal open time
  - Canvas strips are bonded to metal panels
  - Direction of pull is in-line
  - Assembly made at different time intervals following coating of adhesive
  - Samples pulled apart by tensile tester

# Test Protocols

## CRT Failure Temperature

- Indication of heat resistance
  - Samples are bonded like T-peel specimens
  - Standard weight is applied to one end
  - Temperature is raised continuously at constant rate
  - Measurement of separation made at different temperatures
  - Failure is when separation of bond is complete

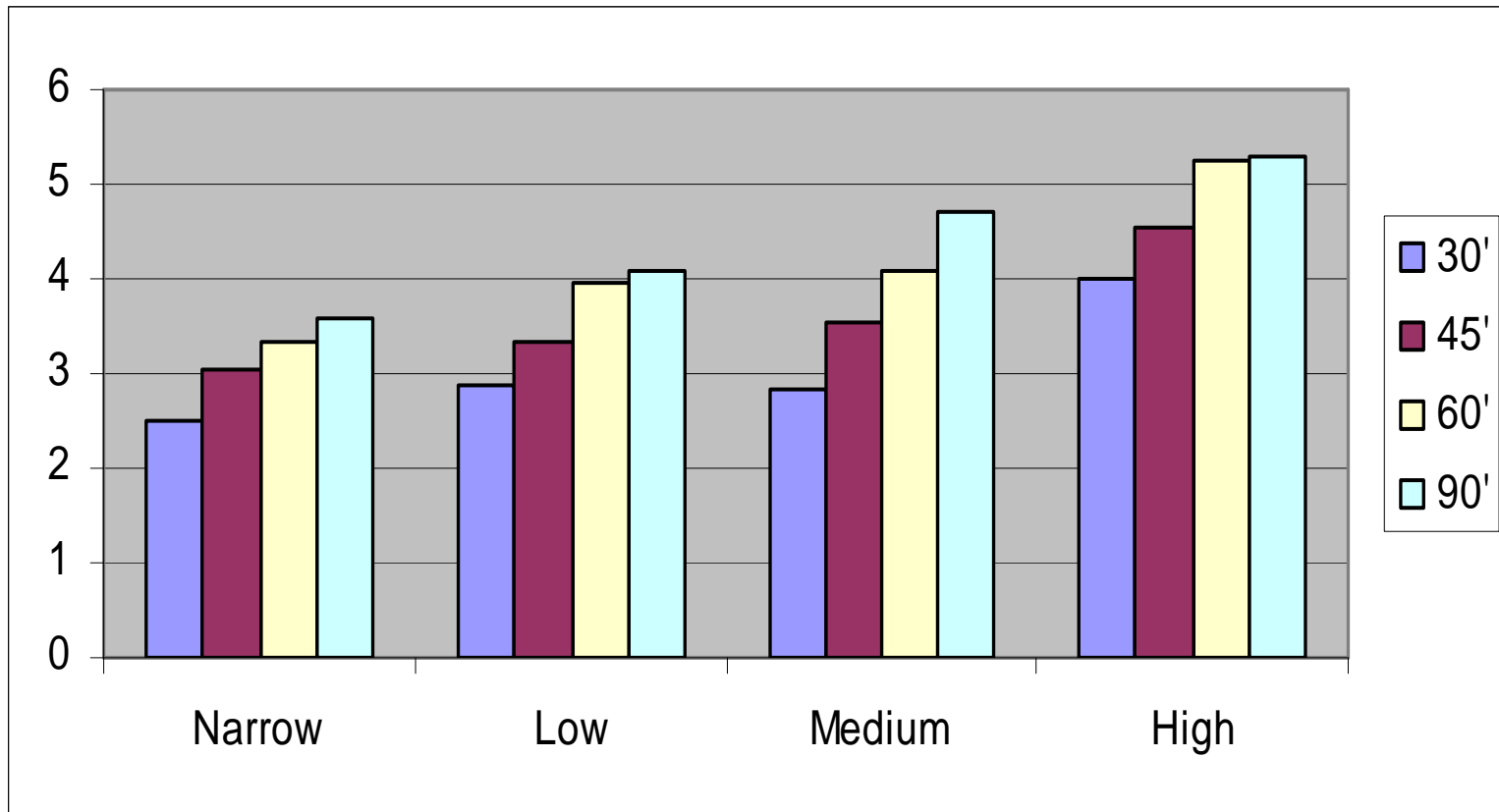
# Molecular Weight Study

- Four different commercial resins studied that use the same monomer (PTBP)
  - Narrow Molecular weight
  - Low Molecular Weight
  - Medium Molecular Weight
  - High Molecular Weight

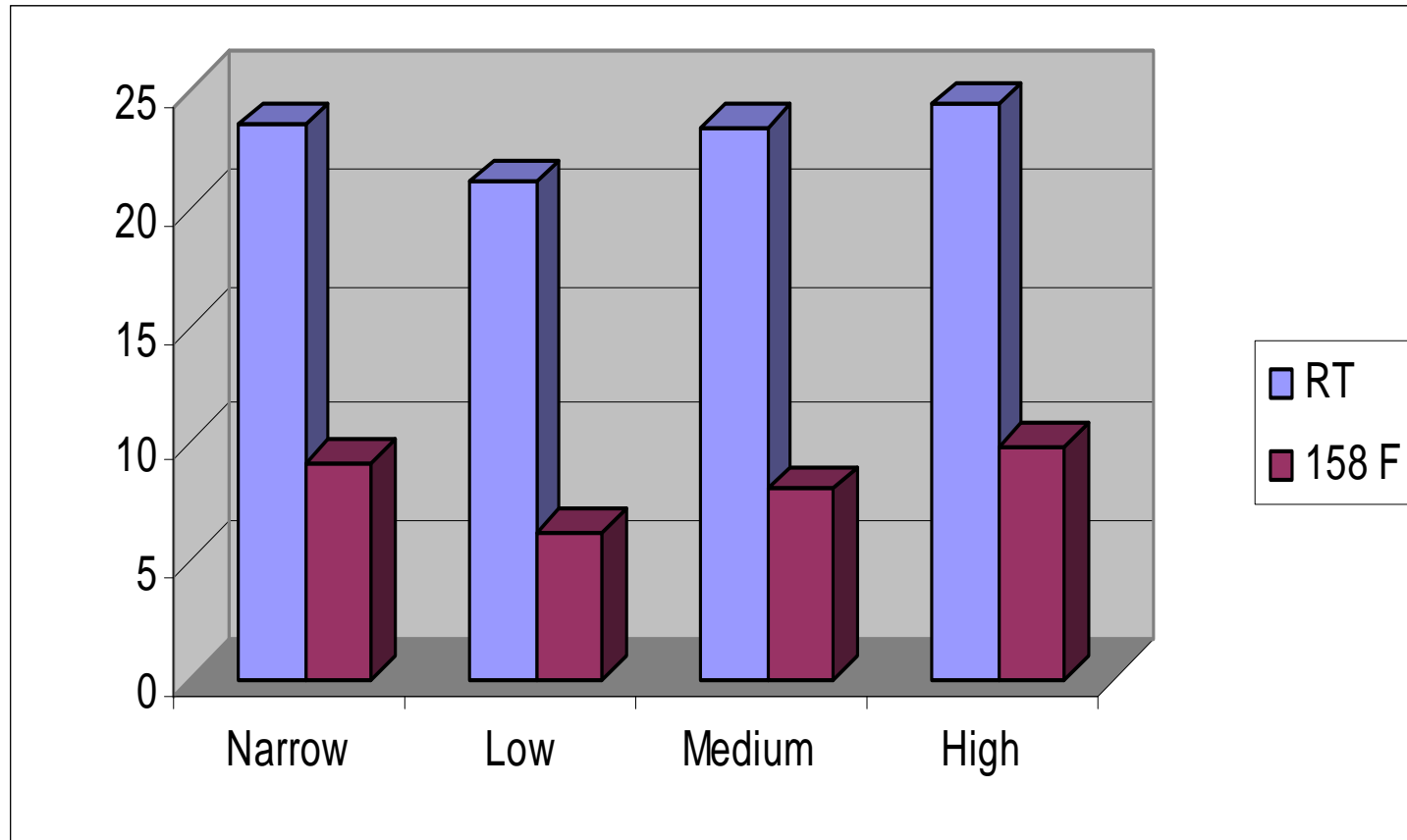
# Molecular Weight of Resins

	Mw	Mn	Mz	PDI
Narrow	1800	575	2600	2.8
Low	2000	500	3800	3.8
Medium	3500	900	7000	3.5
High	5000	1075	12000	4.8

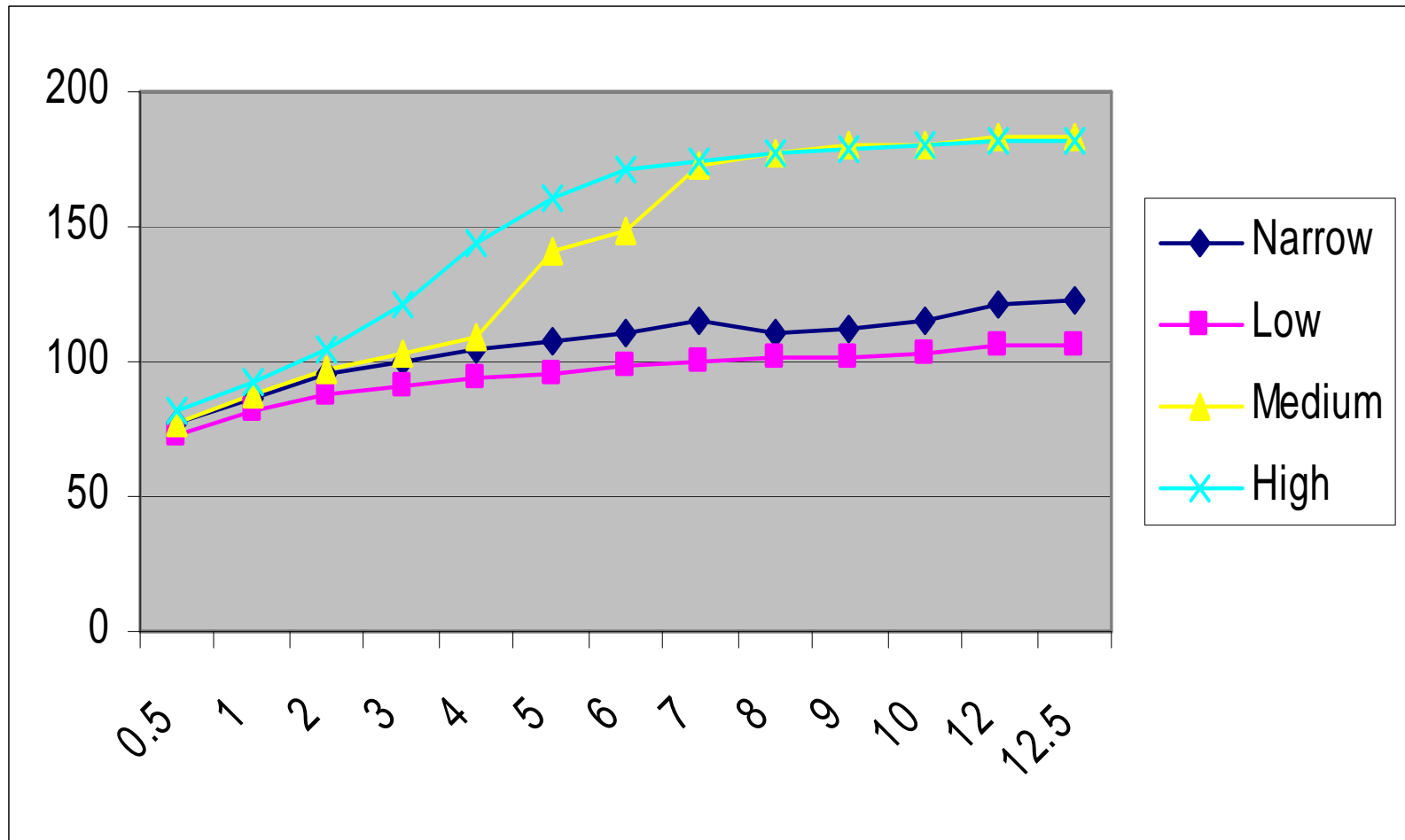
# Molecular Weight vs. Open Time (Shear Adhesion)



# Molecular Weight vs. Dynamic Peel



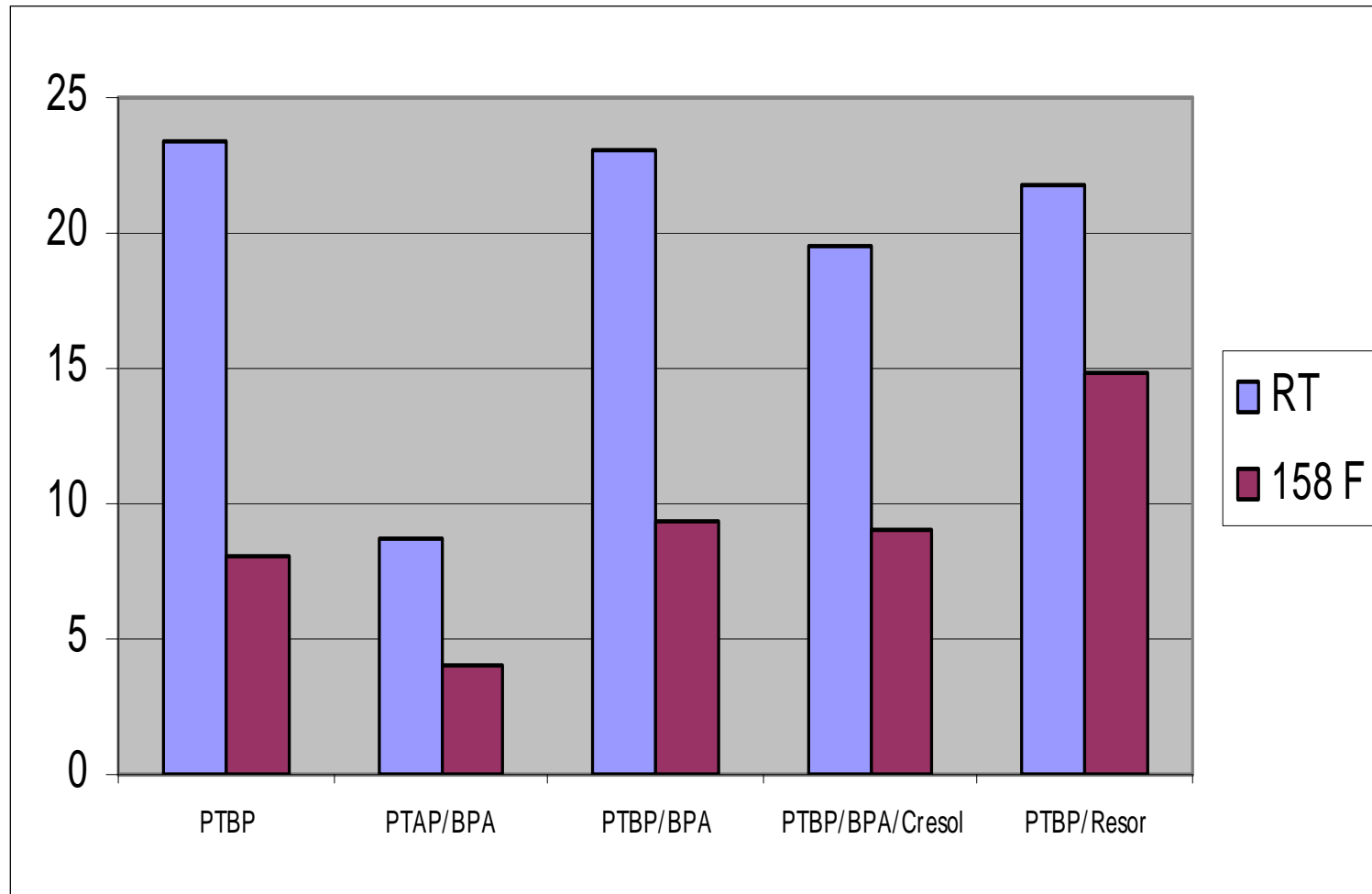
# Molecular Weight vs. CRT Failure



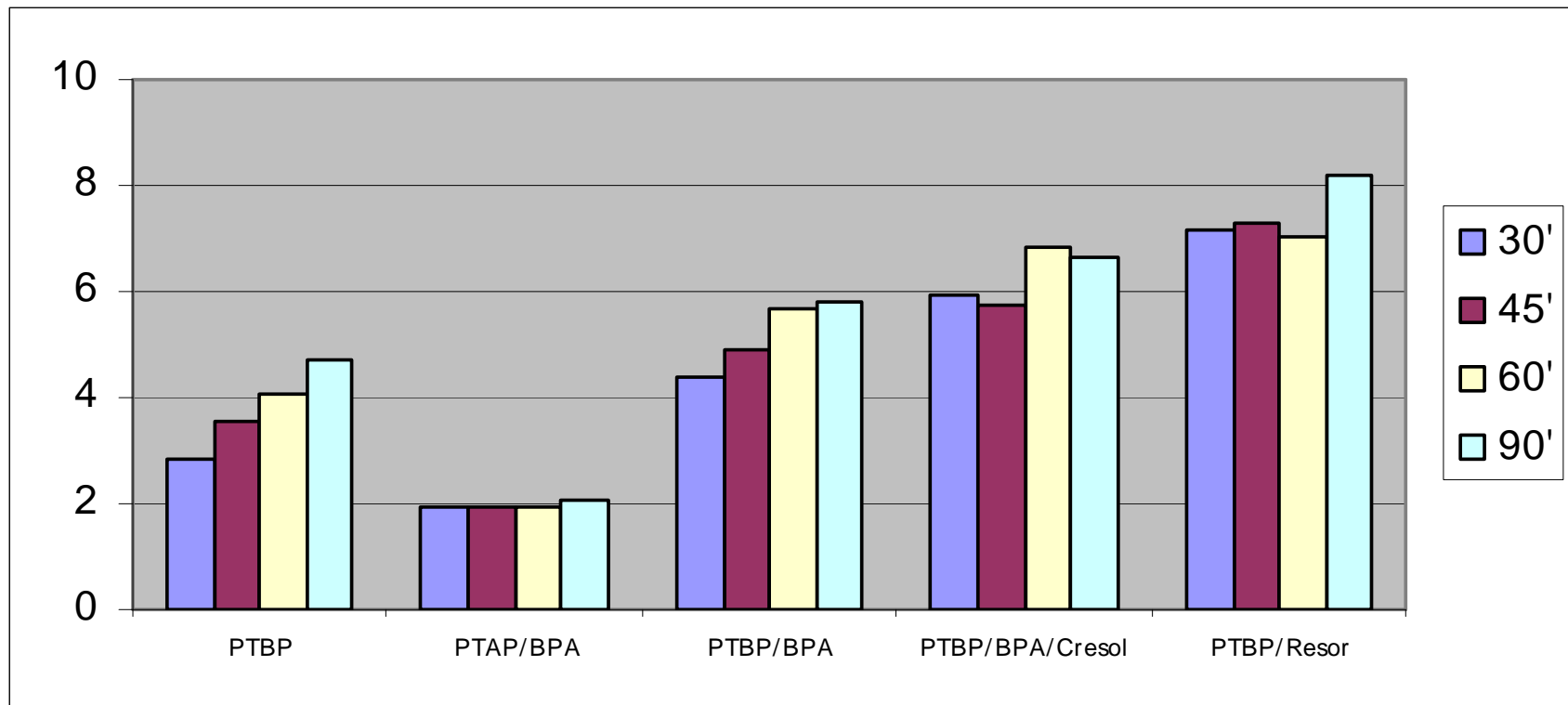
# Monomer Study

- Commercial Resins made from varying monomers tested against each other
  - PTBP
  - PTBP plus Bisphenol A
  - PTBP plus Bisphenol A plus Cresol
  - PTAP plus Bisphenol A
  - PTBP plus resorcinol

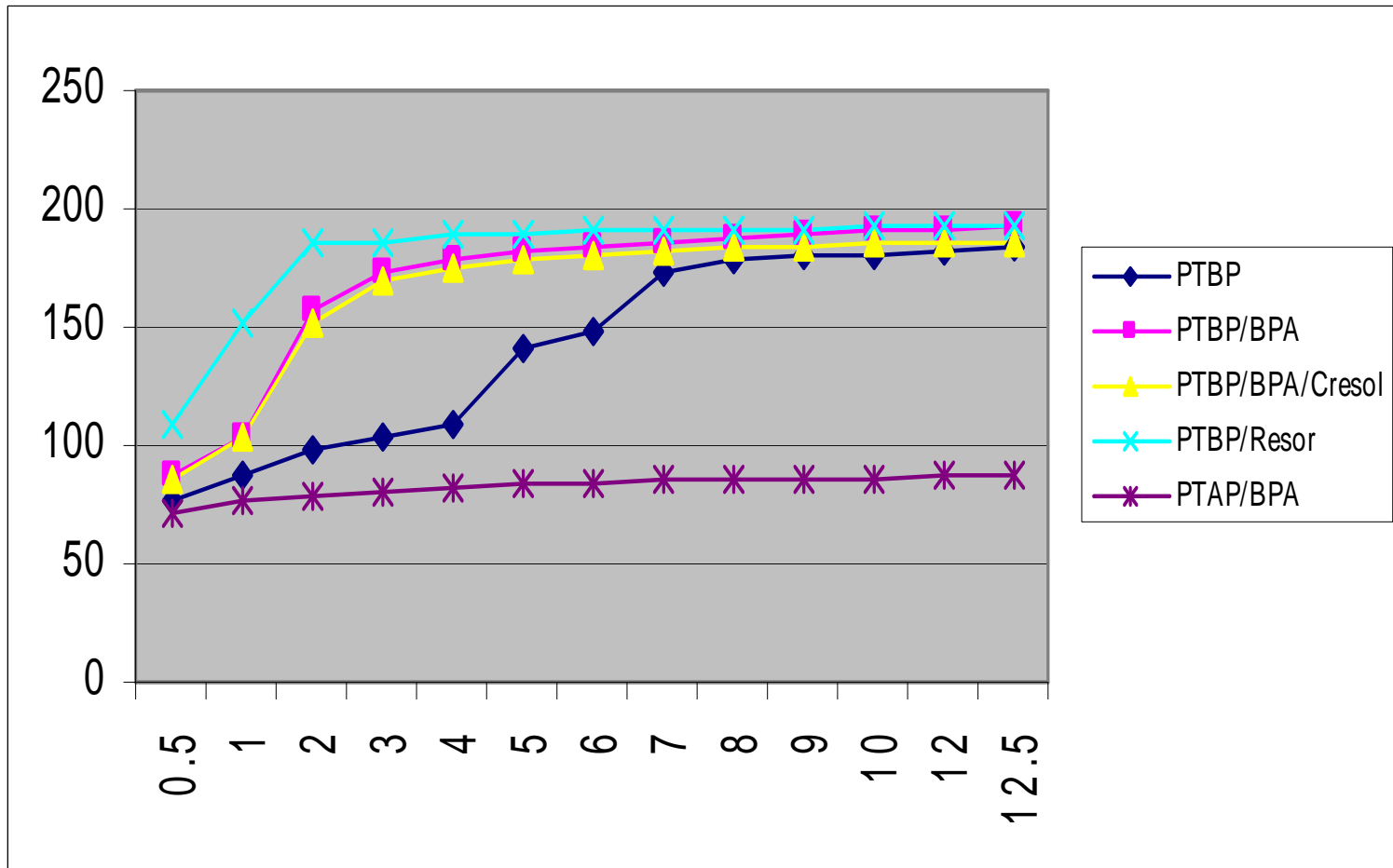
# Monomer vs. Dynamic Peel



# Monomer versus Open Time



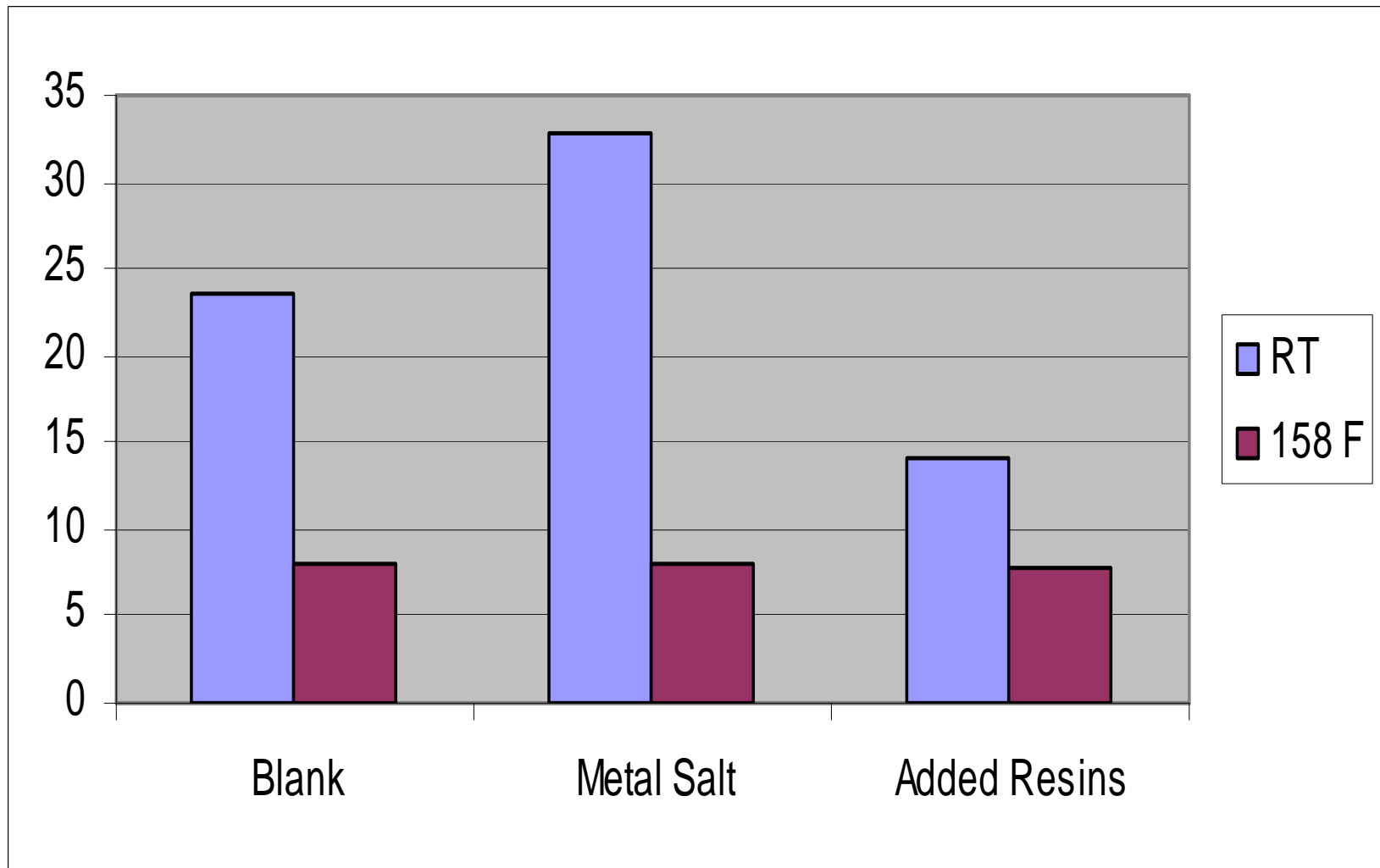
# Monomer vs. CRT



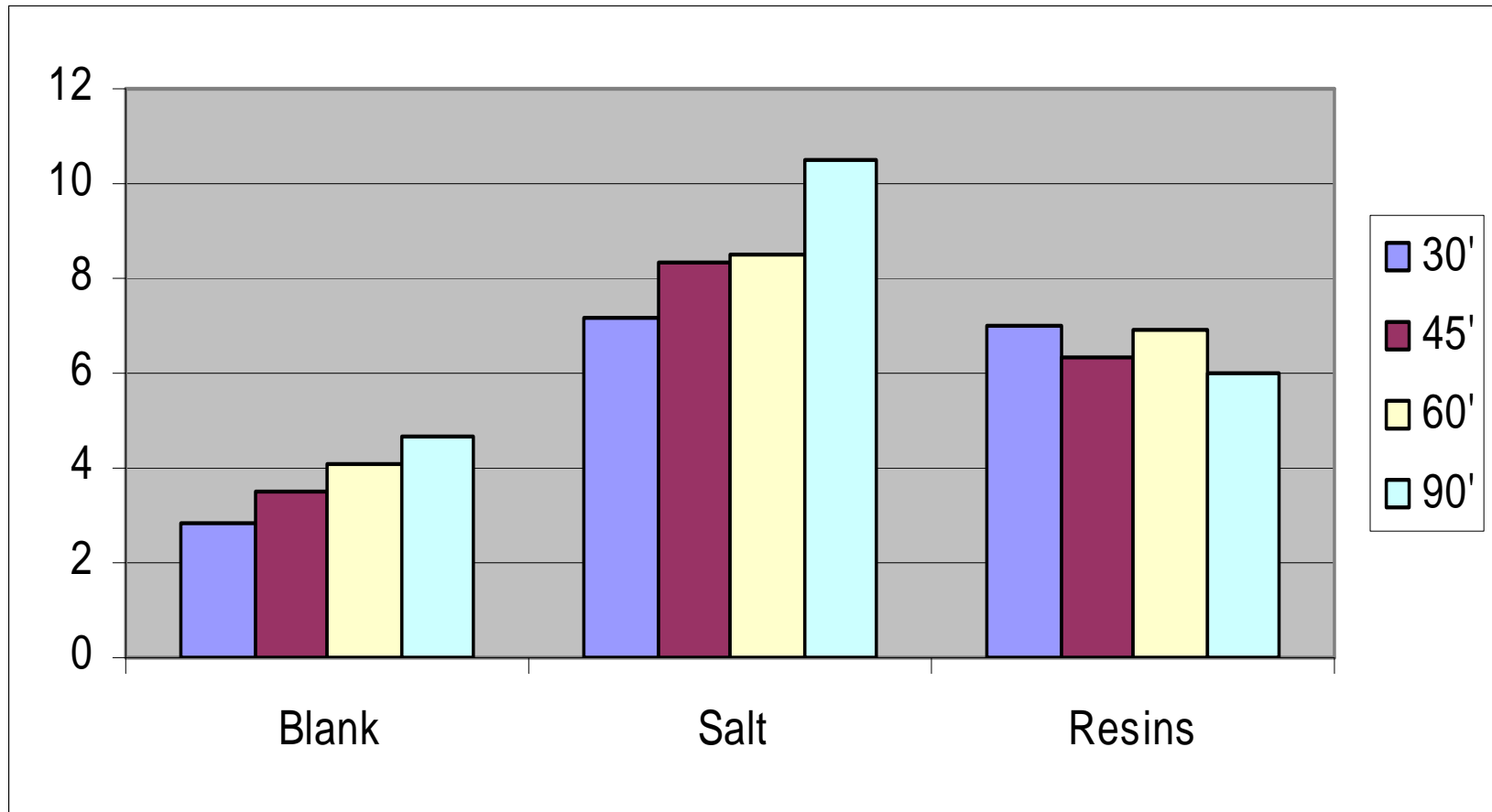
# Use of Additives

- Resins made to which additives were added were compared to each other
  - Metal Salt which caused dark color
  - Zincated resin plus natural tackifier Resin
  - Blank with no additives

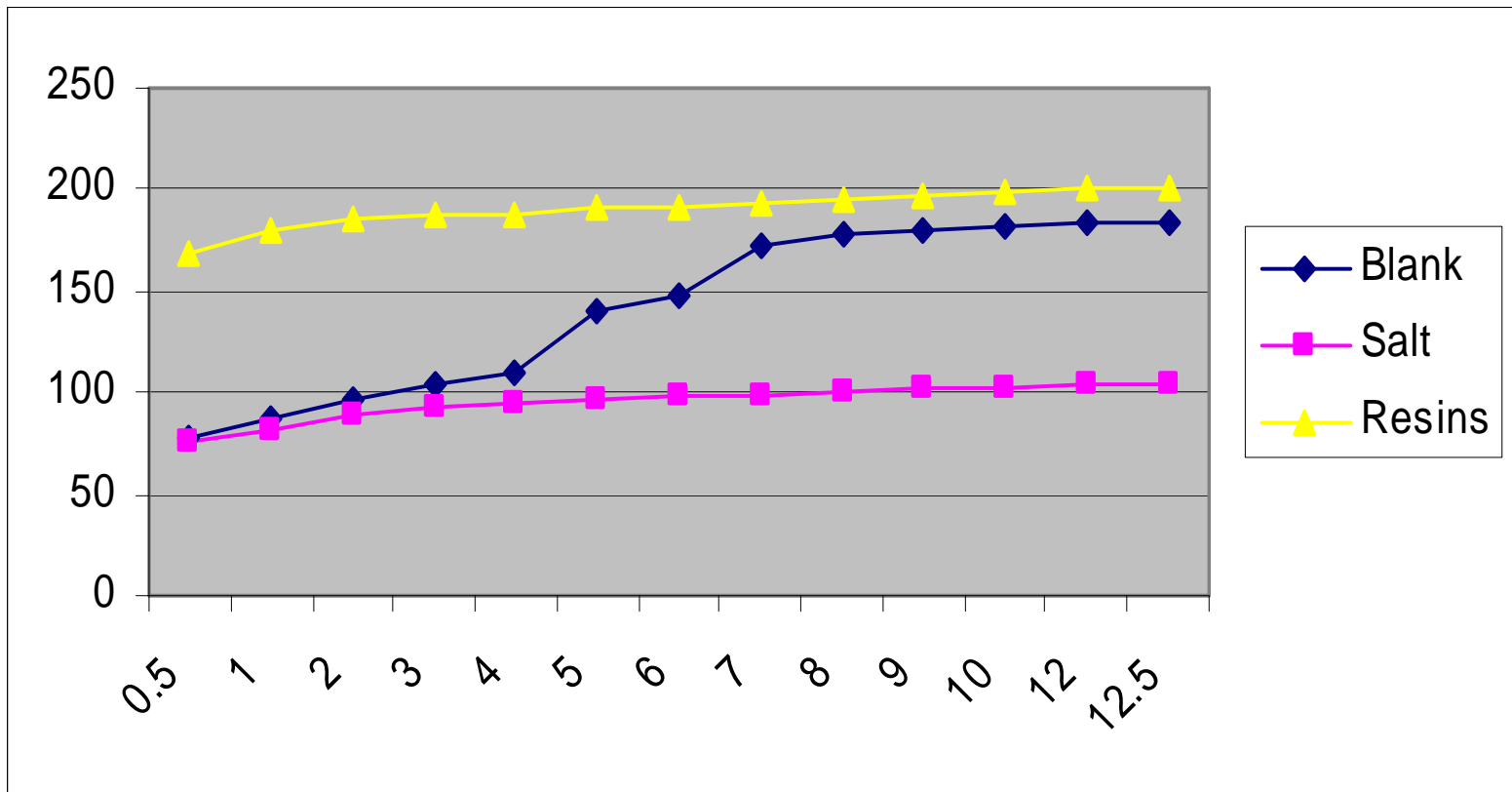
# Effect of additives on bond strength



# Effect of additives on Open Time



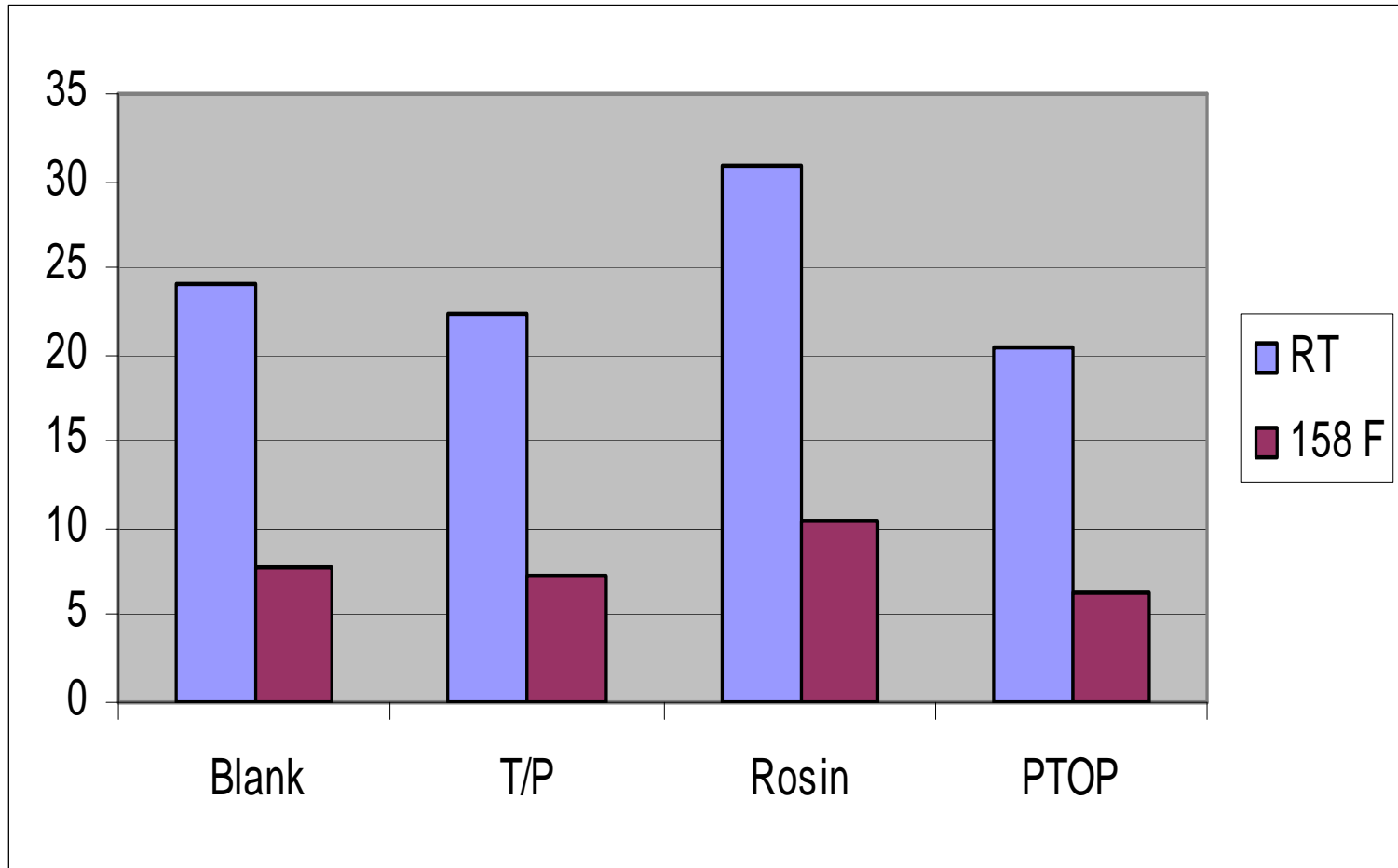
# Additive effect on CRT Failure Temperature



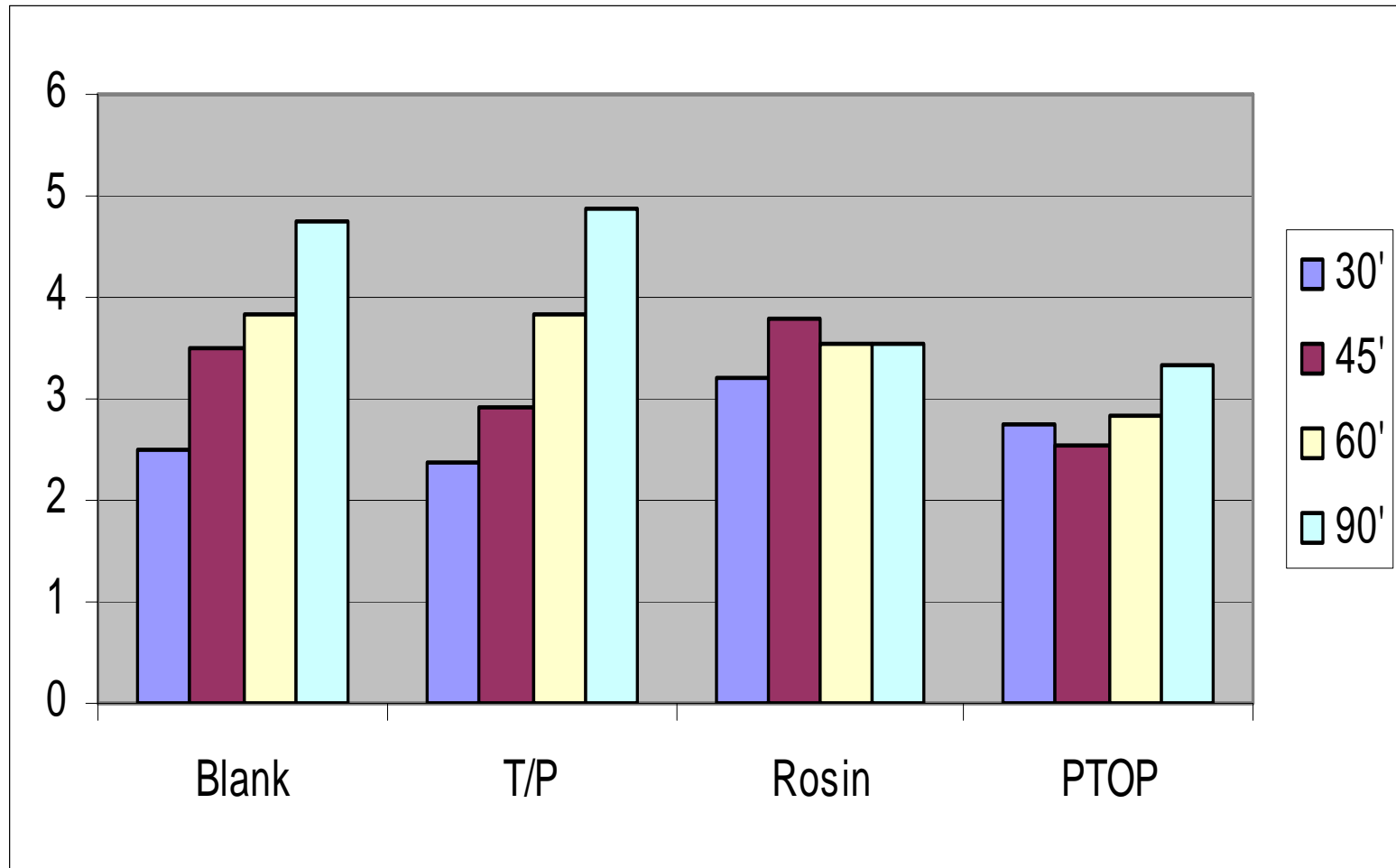
# Effects of Tackifier Resins

- Use of thermoplastic tackifier resins
  - Terpene phenolic resin
    - B&R Softening Point 110-120 C
  - Rosin based tackifier resin
    - B&R Softening Point 150-160 C
  - Octylphenol novolak resin
    - B&R Softening Point 85 – 95 C

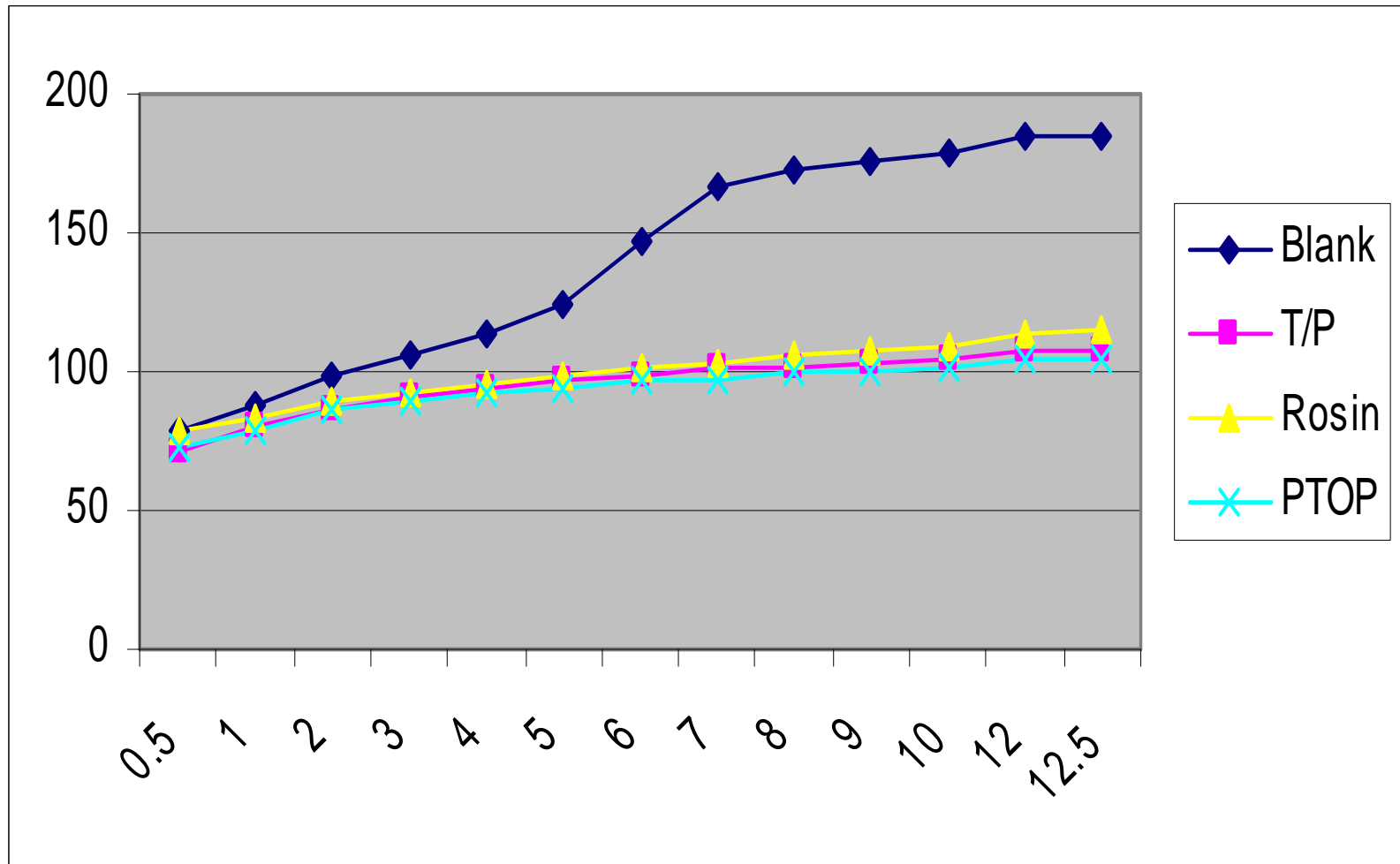
# Effect on Bond Strength



# Effect on Open Time



# Effect of Tackifiers on Failure Temp



# Conclusions

- Changing molecular weight can have a large impact on adhesive performance
- Use of different monomers can have large impact on adhesive properties
- Additives can be added to resins to enhance performance
- Choice of tackifier resin can help to optimize performance

# Resins Used in this Study

# Narrow MW Resin

- Commercial Name HRJ-1367
  - Ball & Ring Softening Point 90 – 100 C
  - Methylol Content 14 – 18 %
  - Typical Color 2-3

# Low MW Resin

- Commercial Name SP-103
  - Ball & Ring Softening Point 87 – 95 C
  - Capillary Melting Point 63 – 70 C
  - Methylol Content 8 – 11 %
  - Typical Color 2-3

# Medium MW Resin

- Commercial Name FRJ-551
  - Ball & Ring Softening Point 100 – 110 C
  - Capillary Melting Point 77 – 91 C
  - Methylol Content 12 – 16 %
  - Typical Color 2-3

# High MW Resin

- Commercial Name HRJ-11331
  - Ball & Ring Softening Point 110 – 120 C
  - Capillary Melting Point 93 – 104 C
  - Methylol Content 10 – 14 %
  - Typical Color 2-3

# PTBP/Bisphenol A Resin

- Commercial Name SP-134
  - Capillary Melting Point 60 – 75 C
  - Methylol Content 13 – 18 %
  - Typical Color 2-3

# PTBP/Bisphenol A/Cresol Resin

- Commercial Name SP-154
  - Capillary Melting Point 74 – 88 C
  - Methylol Content 8 – 12 %
  - Typical Color 2-3

# PTAP/Bisphenol A Resin

- Commercial Name SP-12
  - Capillary Melting Point 57 – 66 C
  - Methylol Content 7 – 10 %
  - Typical Color 2-3

# PTBP/Resorcinol Resin

- Commercial Name SP-126
  - Capillary Melting Point 63 – 77 C
  - Methylol Content 10 – 15 %
  - Color 12-16

# Resin modified with other resins

- Commercial Name SP-184
  - Ball & Ring Softening Point 143 – 160 C

# Terpene Phenolic Resin

- Commercial Name SP-553
  - Ball & Ring Softening Point 110 – 120 C
  - No methylol content
  - Typical color 6-8

# Rosin derived Resin

- Commercial Name SP-560
  - Ball & Ring Softening Point 146 – 160 C
  - No methylol content
  - Acid number 60-70
  - Typical color 4 - 7

# PTOP Tackifier Resin

- Commercial Name SP-1068
  - Ball & Ring Softening Point 85 – 95 C
  - No methylol content
  - Acid number 25 - 42
  - Typical color 1-3

# Acknowledgements

- Thank you for your kind attention.
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  - World Adhesive Conference
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