

CFFA October 2011

PVC Resins

William David Peebles

Sr. Customer Technical Service Specialist
Formosa Plastics Corporation
Baton Rouge, Louisiana

October 2011



Fermosa Plastics®

1

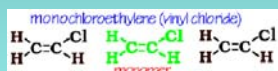
Topics

- Introduction
 - + Definitions and Chemical Structures
- Public Concerns
- Manufacturing Process
 - + Types of Processes
 - + Typical Flow Diagram and General Recipes
- Key Resin Property
- Summary and Questions

2

What Is a Mono-mer?

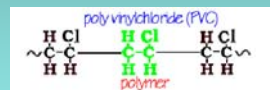
- A single compound from which a polymer is made
- Ethylene, propylene, styrene, and vinyl chloride are examples of monomers



3

What Is a Poly-mer?

- A large molecule composed of a finite number of repeating units (monomers)
 - + Poly- = many
 - + -Mer = part

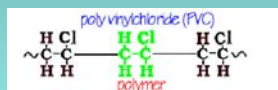


DNA, PE, PP, PS, and PVC are examples of Polymers

4

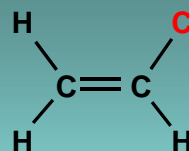
What Is Polymerization?

1. The bonding of two or more monomers to form a polymer.
2. A chemical process that effects this bonding.



5

Vinyl Chloride Monomer



Odorless, Colorless, Gas

Liquid under Pressure

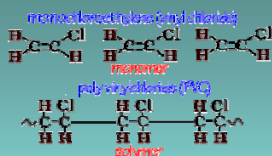
Boiling Point -14° C (Freon 134A
boils at -28.5 ° C)

Very Low Solubility in Water

Molecular Weight = 62.5

6

Polyvinyl Chloride



White powder

Good insulator

PVC is NOT soluble in VCM or water

7

Public Concerns

1. Angiosarcoma
2. Brain Tumors
3. Dioxin

Allegation

The industry covered up the facts about angiosarcoma of the liver.

Fact

The chemical industry played a major role in discovering the link between exposure to vinyl chloride and angiosarcoma of the liver. After the discovery, the industry responded swiftly to make its workplace safe. B. F. Goodrich Company first observed the appearance of angiosarcoma in its Louisville plant and promptly advised the government of a potentially serious health problem. Marcus M. Key, M.D., then assistant Surgeon General and Director of the National Institute of Occupational Safety and Health (NIOSH), congratulated B. F. Goodrich Company in a letter dated January 31, 1974. Key stated: "Had not the Company taken the initiative it did in following up on suspicions aroused by the occurrence of the rare type of liver cancer (i.e., angiosarcoma) discovered in several of its employees at autopsy, it is entirely possible that the significance presently attached to the appearance of those tumors would not have been realized for several more years."

9

Allegation

Vinyl chloride causes brain cancer.

Fact

A significant amount of epidemiological research has been done to determine whether a causal link exists between exposure to vinyl chloride and brain cancer. The results of this research have been reviewed by some of the world's leading authorities, including British epidemiologist Sir Richard Doll, who identified the link between smoking and cancer; Dr. Aaron Blair, director of the Occupational Epidemiology Division of the National Cancer Institute; and the International Agency for Research on Cancer (IARC), which studied the health records of more than 12,000 vinyl chloride workers in Europe. Their conclusion has been that the accumulated evidence does not support a causal link between exposure to vinyl chloride and brain cancer.

10

Allegation

Vinyl manufacturing is a major source of dioxin.

Fact

Dioxin is a byproduct of several end human activities, including incineration, forest fires, metal smelting, and certain industrial processes involving chlorine and other organic compounds. Vinyl production accounts for an extremely small amount of dioxin - only grams per year. Fireplaces and vehicle exhaust each produce more dioxin than vinyl manufacturing. The good news is that dioxin levels in the environment are declining, and this has happened even as vinyl production has soared. Here is what EPA and other federal agencies say:

§ "Dioxin levels in the environment have declined significantly since the 1970s, following EPA regulatory controls and industry actions. EPA's best estimates of emissions from sources that can be reasonably quantified indicate that dioxin emissions in the United States decreased by about 80 percent between 1987 and 1995, primarily due to reductions in air emissions from municipal and medical waste incinerators, and substantial further declines continue to be documented." ("Dioxin: Summary of the Dioxin Reassessment Science," Information Sheet 1, U.S. EPA, June 12, 2000)

§ "As a result of EPA's efforts, along with efforts by state government and private industry, known industrial emissions in the United States will be reduced by more than 90 percent from 1980 levels within the next year or so." ("Questions and Answers about Dioxin," Interagency Working Group on Dioxin, July 2000)

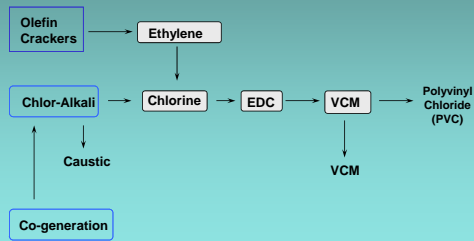
11

Dioxin (cont)

This analysis (EPA Report) indicates that between reference years 1987 and 2000, there was a significant reduction in the releases of dioxin-like compounds to the circulating environment of the United States from regulated industrial sources. In 1987 and 1995, the leading source of dioxin emissions to the U.S. environment was municipal waste combustion; however, because of reductions in dioxin emissions from municipal waste combustors, it dropped to the 4th ranked source in 2000. Burning of domestic refuse in backyard burn barrels remained fairly constant over the years, but in 2000, it emerged as the largest source of dioxin emissions to the U.S. environment that could be reliably quantified. Other potentially large sources were identified, but were not included in the inventory due to uncertainties in available data. These included forest fires and landfill fires.

12

Process Breakdown



13

How Is PVC Made?

There are 4 major types of polymerization:

- Suspension
- Dispersion
- Mass
- Solution

14

Major Resin Processes

- Suspension resin (S-PVC) particle size is determined by agglomeration in the reactor and is 75 - 200 μm in size.
- Dispersion resin (D-PVC) has no large agglomeration and particle size is determined by surfactants and level for emulsion or external shear for microsuspension. Particle size is 0.2 - 2 μm .

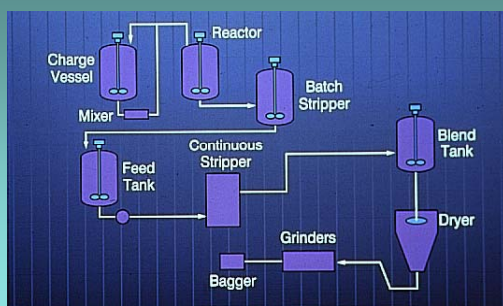
15

Two Major Types of Dispersion Resin

- Emulsion
 - + Water soluble initiator; Particle size independent of agitation.
- Microsuspension
 - + Monomer soluble initiator; High shear mixing determines the particle size distribution (PSD)

16

Dispersion PVC Process



17

Emulsion Polymerization

- Micellar : Soap forms 50 Å micelles that swell with VCM. Water soluble initiator is absorbed causing the monomer to react to polymer. Large VCM droplets feed the growing micelles.
- Nucleation : Polymerization occurs in the water phase and grow till they precipitate. Surfactant is absorbed on the surface, stabilizing the particle.
- Most likely both methods occur to produce the latex.

18

Typical Emulsion Formulation

- Water 120 PHR
- VCM 100
- Surfactant 1
- Initiator 0.05
- Buffers 0.1
- Reaction Temperature 45-55 ° C
- Reaction Time 8-18 hours
- K Value 60-80

19

Blending Resins

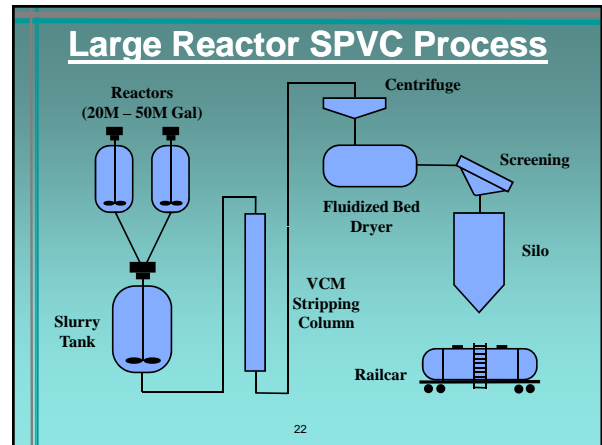
- Made by the suspension process
- Low residual suspension agent level
- Non-absorptive particles
- Particle size between dispersion and suspension particles (30 microns)
- Advantages
 - Lower costs
 - Lower viscosity at low and high shear
 - Improved air release
 - lower gloss
- Disadvantages
 - Lower physical properties
 - Higher gelation temperatures
 - Possible settling
 - Lower gloss

20

Summary

- For Dispersion/Emulsion resin the critical properties are:
 - Surfactant type and level
 - Degree of agglomeration
 - Particle size distribution
 - molecular weight
- These four properties affect
 - Rheology
 - Gelation
 - Gloss
 - Clarity
 - Air release
 - Foam quality
 - Fusion

21



Polymerization Recipe

- Water
- VCM
- Suspending Agent(s)
- Initiator(s)
- Optional Ingredients
 - Molecular Weight regulators (X-linking or CTA)
 - Buffers
 - Termination Chemicals
 - Antioxidants/Antifoams

23

PVC Reactor

- 20M – 50M gal capacity (50M – 150M lb/batch)
- Often bottom mounted agitation

24

**Stripping Column
(Residual VCM)**

- Removes (strips) un-polymerized VCM, to be recovered and reused



25

PVC Dryers

Many types of dryers are used to dry PVC:

- Fluid Bed
- Flash-Fluid
- Flash Cyclone
- Rotary
- Spray



- CONTACT FLUIDIZER™
- 63 m2 for s-PVC

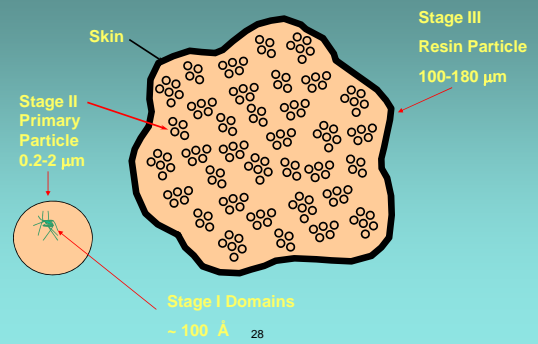
26

Why PVC Particles?

- PVC is the only major polymer that is processed into end products in the same physical form that it was produced in the reactors.
- All other major polymers are compounded and sold as pellets.
- The formation and morphology of the PVC particles in the reactor is the key to its processing and its many uses.

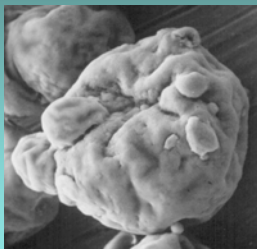
27

PVC Particle (Cross Section)



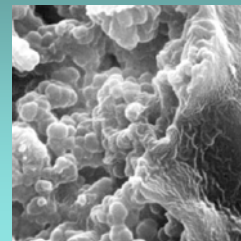
28

**S-PVC Resin Particle
300X**



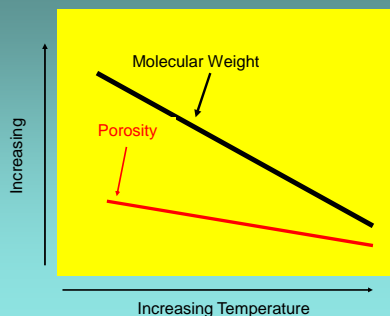
29

**Interior S-PVC Particle
90% Conversion 3000X**



30

S-PVC Effect of Temperature



31

Key Resin Properties

- I. Molecular Weight (MW)
- II. Porosity
- III. Bulk Density (BD)
- IV. Particle Size Distribution (PSD)
- V. Color & Heat Stability
- VI. Contamination
- VI. Gels
 - A. Hard
 - B. Soft
- VII. Residuals
 - A. Vinyl Chloride Monomer (RVCM)
 - B. Volatiles
 - C. Methanol Extractables

32

Molecular Weight

- Length of polymer—increases with increasing MW
- Physical properties—increase with increasing MW
- Flexibility — increases with increasing MW
- Processing temp — increases with increasing MW



Analytical Test
Typically Reported
Values (Unitless)

Dilute Solution Viscometry
Inherent Viscosity (IV)
Relative Viscosity (RV)

33

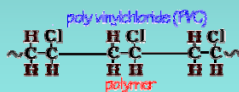
What is Molecular Weight?

- The sum of the atomic weights of all of the atoms in a molecule
- In normal molecules, such as ammonia, water, and methanol, MW's are easy to determine:
 - + $\text{NH}_3 = 14 + (3) \cdot 1 = 17$
 - + $\text{H}_2\text{O} = (2) \cdot 1 + 16 = 18$
 - + $\text{CH}_3\text{OH} = 12 + (3) \cdot 1 + 16 + 1 = 32$

34

What Is a Polymer Molecular Weight?

- In macromolecules (polymers), the MW is more difficult to characterize.
- A large molecule composed of a finite number (n) of repeating units (monomers).
- In PVC, the molecular weight is: $(62.5) \cdot n$ where $n > 1000$

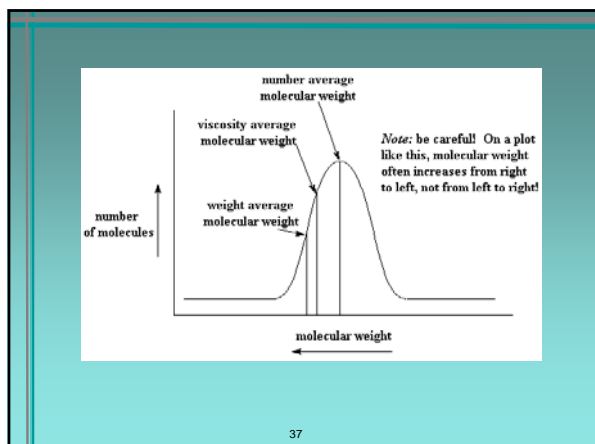


35

What Is a Average Molecular Weight?

- The average MW of a single polymeric chain in a bulk polymer, reflecting a distribution of chain lengths present in all polymers.
- This average MW is reported in several ways and is dependent on the measurement procedure used in its determination.

36



Reporting Average Molecular Weight

- Commercially, Viscosity Average MW is used to characterize PVC.
 - Relative Viscosity is the fundamental measurement of solution viscosity.
 - K Value is a mathematical relationship based on relative viscosity and concentration by mass of PVC in a dilute solution.
- 38

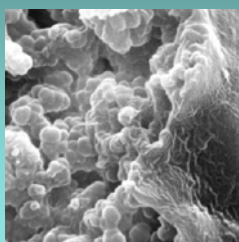
Factors Influencing Average Molecular Weight Measurements

- Solvent
 - Temperature
 - Concentration
- 39

Properties Influenced by Molecular Weight

- Processing Rate (fusion)
 - Physical Properties (impact, stability, shear strength, etc.)
 - IV, RV, K-Value
 - BD
 - Porosity
 - Moisture
 - RVCN
- 40

Interior S-PVC Particle 90% Conversion 3000X



Types of PVC Resins

- Rigid – Typically K-66 (IV = 0.92) and lower; little if any plasticizer (tensile modulus > 689 MPa at std conditions)
 - Flexible - Typically K-67 (IV = 0.93) and higher; miscellaneous plasticizers (< 20.7 MPa at std conditions)
- 42

Types of PVC Resin

- **Semi-Rigid**
 - + Typically K-61 (IV-0.80) to K-67 (IV-0.93)
 - + These resins are used in both plasticized and unplasticized applications
 - + One definition = tensile modulus between 20.7 and 689 Mpa at std conditions

43

Summary

- Polyvinyl chloride (PVC) resin is a polymer.
- There are several different types of PVC resins, with diverse properties and uses.
- A resin's molecular weight determines its initial physical properties and processing characteristics.
- The wide variety of compounds that can be made from PVC make it a versatile resin, suitable for many applications.

44

Resins And Selection

- **Thank you!**
- **Acknowledgements**

Formosa Plastics Corporation
Steve Rice

- **Questions?**

William David Peoples
Formosa Plastics Corporation
Baton Rouge, LA 70805-4929
225-354-8237
wpeoples@fibr.fpcusa.com
www.fpcusa.com



Formosa Plastics®

45

Appendix

Process description

46

Description – Suspension PVC (s-PVC) Process

Polyvinyl chloride (PVC) is most frequently produced via the batch, suspension polymerization process, using large (20,000 – 50,000 gal) stainless steel reactors. The reactors are arranged in separate, fixed, production lines. Prior to each batch a reactor coating is applied to the reactor walls and cured. (These coatings are typically proprietary compounds such as formabenzyl, polymer with 1-naphthol copolymer and caustic in a water solution). This reactor coating helps prevent PVC build-up on the reactor walls, baffles, nozzles, etc. Each reactor batch produces 50,000 – 150,000 lbs of PVC.

PVC is produced from the monomer, vinyl chloride (CH₂-CHCl). During this free radical, exothermic reaction the double bond is broken and the monomer units continue to add to each other forming a PVC molecule (CH₂-CHCl)_n where n is in the range of 1000 or more. Since the polymerization temperature determines the molecular weight of the PVC, large amounts of heat must be removed during the polymerization reaction in order to keep the polymerization temperature constant. Reflux condensers, as well as cooling baffles and jackets, are used to remove this heat.

A reactor batch consists of at least: VCM monomer, water (the heat transfer medium), suspending agent(s) (stabilize the particle formation), and initiator ("catalyst" used to start the polymerization). Other additives such as buffers, antioxidants, and chain transfer agents, etc. can be used to make particular products.

The components are all added to the reaction vessel and steam or hot water is used to heat the contents to reaction temperature. Chilled water in the jackets, agitators, and baffles and/or reflux condensers are used to maintain the reaction temperature in the vessel. As the polymerization continues, more and more of the VCM is converted to PVC and the free VCM disappears at about 75% conversion. Polymerization continues until the desired conversion point (85% to 95%) is reached and then the reaction is normally terminated with a free radical scavenger.

The reactor contents are then transferred to another, larger vessel (blow down tank). During this transfer and while in this new tank, the unreacted monomer is continually being removed from the slurry. From the blow down tank the slurry is fed into a stripper feed tank or directly into the stripper itself. The stripper is a multiple-tray, countercurrent, continuous, steam-stripping column used to remove most of the remaining unreacted monomer from the slurry. The concentration of residual vinyl chloride monomer (RVCM) in the PVC, after the stripper, is normally less than 10 ppm and most often much lower.

After the continuous slurry stripper, the slurry is sent to a larger tank (blend tank, dryer feed tank), which is used to feed continuous centrifuges. These centrifuges feed dryers (fluid bed, flash-fluid bed, flash-cyclone, etc. dryers). From the dryers the resin is sent to silos and then loaded into railcars or trucks for delivery to customers.

Customers then compound the resin into powder compound or pellets and produce the myriad of vinyl products that we see everyday – pipe, siding, credit cards, wire, wall coverings, etc.

47