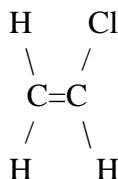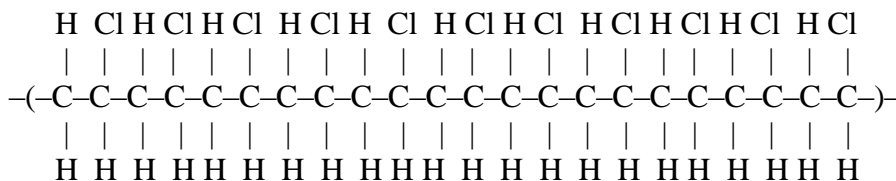# PVC

PVC, otherwise known as poly(vinyl chloride), is a polymer (from the Greek term "poly" meaning many, and "mer" meaning unit – many units) of vinyl chloride, $H_2C=CHCl$, where C is a carbon atom, H is a hydrogen atom, and Cl is a chlorine atom.

```
       H     Cl
        \   /
         C=C
        /   \
       H     H
```
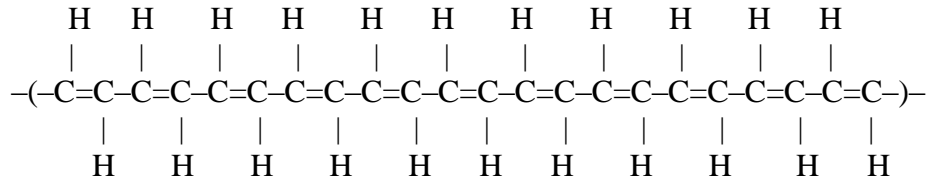
Vinyl Chloride Monomer

With the proper initiator, the carbon-carbon double bond can be opened to permit the addition of more monomer units to the molecule, like links to a chain, to form the vinyl chloride polymer:

```
    H  Cl H Cl H Cl  H Cl H  Cl  H Cl H Cl  H Cl H Cl H Cl  H Cl
    |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
 –(–C–C–C–C–C–C–C–C–C–C–C–C–C–C–C–C–C–C–C–C–C–C–)–
    |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
    H  H  H  H H  H  H  H  H H H H  H  H  H  H  H  H H H  H  H H  H
```

Poly(vinyl chloride)

The longer the chain (measured as molecular weight), the more improved the properties of the polymer become. The long chains become entangled and are not easily pulled out of the polymer mass, thereby enhancing the strength of the material. The downside of high molecular weight is that the material becomes harder to process – the melt viscosity increases with molecular weight.

Because of the proximity of the hydrogen atom to the chlorine atom, PVC is highly susceptible to thermal degradation, evolving HCl, hydrochloric acid, and regenerating a carbon-carbon double bond on alternating carbon groups.

```
        H   H   H   H   H   H   H   H   H   H   H
        |   |   |   |   |   |   |   |   |   |   |
  –(–C=C–C=C–C=C–C=C–C=C–C=C–C=C–C=C–C=C–C=C–C=C–)–
        |   |   |   |   |   |   |   |   |   |   |
        H   H   H   H   H   H   H   H   H   H   H
```

Degraded PVC with Conjugated Double Bond Structure

The alternating carbon-carbon double bonds creates a chromophore which adds color to the otherwise water-clear polymer with increasing levels of degradation, beginning with yellowing, turning to red and then to brown, and finally producing a black mass with extensive degradation.

Until the advent of modern stabilization techniques, PVC could not be melt processed without plasticizers to reduce the temperature at which the polymer could be processed. Today, however, stabilizer systems exist which prevent, postpone, and interfere with the degradation process and allow sufficient time for the polymer to be processed into rigid products like pipe, siding, fencing, and outdoor furniture without the effects of degradation.

POLYMERIZATION

Vinyl chloride monomer is easily polymerized with initiators, however, the heat of the polymerization reaction must be removed and controlled during the reaction to avoid excessive degradation of the polymer. The most common method of manufacturing pipe resins is through suspension polymerization. Vinyl chloride monomer does not appreciably dissolve in water and forms a two-phase, oil-in-water, system. With the inclusion of a suspending agent and vigorous stirring, very small droplets of monomer can be suspended in the water. As the temperature of the bath is allowed to rise in temperature, the polymerization reaction begins in the small droplets, and the excess heat of polymerization is transferred to the water where it can be controlled. If the polymerization temperature is controlled to a low temperature, very few initiation sites are developed within the suspension droplet and very long polymer chains are formed before all of the monomer is consumed; however, the reaction is slow and takes time. On the other hand if the reaction temperature is less controlled, the temperature of the bath rises, more initiation sites are evolved at the elevated temperature and the monomer is rapidly consumed producing more chains of low molecular weight polymer, with the likelihood of slight degradation and off-color product. The reaction takes place faster but produces low-molecular-weight polymer with lower properties.

Inside the droplet, as polymerization proceeds and molecular weight increases, the polymer begins to drop out of solution but continues to polymerize as long as there is monomer available. These polymer droplets (called primary particles) coalesce within the monomer droplet to create the particle structure of the grains of PVC powder. Once the polymerization is completed, the primary particles have coalesced to form a porous structure, similar to a bunch of grapes, or a raspberry, within the grain of PVC powder.

The water is removed from the polymer and the PVC powder is allowed to dry before being bagged, or placed in a shipping container for transportation to the point of use.

DRY BLENDING

The PVC resin arrives in a granular form, like sugar, but requires the inclusion of additives like stabilizers, lubricants, processing aids, fillers, and colorants before it can be processed. The PVC powder is added to a large intensive mixer, similar to a home blender. The intensive mixing action creates heat by friction of the resin particles rubbing against each other. As the resin heats, the liquid ingredients are added to the formulation, which are absorbed into the porous resin particles. Next the low-melting ingredients and waxes are added, followed by the higher-melting waxes and polymeric additives which get dispersed and adsorbed onto the surfaces of the PVC resin particles. Finally the solid additives are added and dispersed into the dry blend. The hot mixture is then transferred to a less intensive blender where the formulation is cooled and transferred to a silo or large holding container prior to processing.

PROCESSING

When processing PVC, whether molding or extrusion, it is essential to thoroughly melt and mix the molten mass into a homogeneous melt prior to forming into a product. Unmelted particles act as non-uniformities, or stress risers, where defects can initiate within the part or test specimen, ultimately reducing the properties of the material and the service life of the product. Processing PVC too hot and/or too fast can result in the grains of powder melting on the outside surface and sticking together, such that the part appears to be a solid mass, but rather has a porous structure of sintered powder. When immersed in a weak solvent like anhydrous acetone or methylene chloride, the remaining porous particle structure swells and appears as flaking on the surface, especially in the midwall of the product. For optimum properties, it is essential to thoroughly melt the PVC powder so that no evidence of the particle exists – the last part to melt is the primary particles. If any of the powder structure remains, the unmelted portions become sites for defect initiation and failure during testing or when used in-service.

Modern stabilization systems can provide substantial processing time for rigid PVC without loss of properties or appearance. Properly stabilized material can be processed into product, reground, and reprocessed to make product. In fact, properly stabilized PVC can improve its properties with additional heat history. Each time a PVC compound is melted, molded or otherwise heat processed it will increase its molecular weight (inherent viscosity), until such time that the stabilization system cannot adequately protect it – then the degradative process controls molecular weight and physical properties. Therefore, each time a properly stabilized PVC compound is milled and/or molded, or extruded, one can expect to see an increase in molecular weight with a corresponding increase in properties, until the degradative processes overcome the stabilization system and the material begins to degrade, and discolor, with the accompanying loss of performance.

MILLING & MOLDING

Extrusion or injection molding provides adequate processing energy to completely melt the powder blend and homogenize the molten mass, but they require an appreciable amount of material to process – a minimum of fifty to several hundreds of pounds. For small batches of resin for testing – about a half pound – the powder blend is processed on an instrument called a two-roll mill. It consists of two counter-rotating heated steel drums in an arrangement similar to the wringer of an old washer. The gap between the two rolls can be closely controlled, and the temperature of the rolls is controlled with steam or oil heaters. The powder blend is placed in the nip between the two rolls and sticks to one roll as it gets heated and squeezed through the gap and forms a thin sheet. The sheet can be cut and folded during milling to ensure adequate dispersion of all the ingredients, while the shearing action at the gap between the rolls ensures sufficient melting, or fluxing of the PVC powder. Once milling is completed, the fluxed PVC sheet can be removed for rapid cooling on a cold surface.

The cooled sheet can be cut into strips, weighed and charged into an aluminum picture-frame mold for preparation of test specimens. There is very little shearing action in compression molding so that test plaques cannot be adequately prepared directly from the powder blend, but from milled sheet or molded or extruded product. The charged mold is placed between two temperature-controlled platens in a compression press and held under contact pressure for the prescribed preheating period. Then the mold is compressed to the desired compression load for the prescribed molding duration. A slight excess of material is squeezed out of the mold as flash, thus ensuring a completely-filled mold cavity. After suitable molding time, the heats are turned off and cooling water is allowed to circulate through the platens and cool the mold, which remains under pressure until adequate cooling of the molding is attained. The cooled molded plaque is removed from the mold and can be cut or machined into the appropriately-shaped specimens for the desired tests.

TENSILE TESTING

Longitudinal tensile testing of the pipe is used to test the product to ensure that the PVC powder has been adequately fluxed during processing and has reached its prescribed tensile strength. Specimens must be prepared directly from the wall of the pipe and not remolded. Molding the material after extrusion would only ensure adequate fusion of the PVC powder and would not provide useful information on the extrusion.

There should be no significant difference between the tensile properties of a well-fused extruded pipe and a compression-molded plaque of the same material. If, however, the extrusion cannot pass the acetone immersion test, i.e., the extrusion evidenced flaking when immersed in anhydrous acetone, the result of the test cannot be directly used to assess the material properties – rather the test result is an indication of adequacy of the extrusion of the PVC.

If there is some question about the material's initial properties due to insufficient fluxing of the PVC during extrusion, one can cut sections of the pipe and compression mold a plaque. While there is little shearing action in compression molding, there is enough to

eliminate the unmelted portions of a previously extruded product. The properties of the initial compound can thusly be assessed. The inherent viscosity of the pipe compound should be compared to that of the molded plaque to ensure that any improvement that has apparently occurred is due to improved homogeneity and not to enhanced molecular weight. Every heat history applied to a properly-stabilized compound has the tendency to increase molecular weight of the PVC with concurrent improvement in properties.

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