

Formulating for Extruding Rigid PVC Fenestration Products By Kenneth Abate, Ph.D., FAIC, CPC

In a single short paper, one cannot provide all the detailed information on the formulating of rigid polyvinyl chloride, PVC, or vinyl, as it is commonly called, for its many industrial uses or even for a specialty segment of the market like the window and door industry. Also, the author assumes that the reader understands the basics of the thermoplastic extrusion process, twin screw, both conical and parallel, and single screw.

In the last couple of years vinyl windows have become the number one selling product type sold in the residential market, around 31million annually, surpassing both wood and aluminum based products. (1) Because they are designed to conserve energy and serve a variety of structural requirements, vinyl window and door products will continue to increase their market share. Vinyl fenestration products are durable, not effected by rot, corrosion, cracking, flaking, or insect infestation, are recyclable, and are easy to maintain. They are resistant to fungus and mildew growth. Vinyl windows have excellent fire resistance properties, meeting most building codes for ignitability, flammability, heat released, burning rate, flame spread and smoke generated. Minor scratches do not require painting or repair, and the aesthetics are maintained by simply washing with a mild soap and water. When properly installed and maintained, vinyl window and door products will provide long lasting aesthetics, reliable performance, and continuing energy savings.

Being a good thermal insulator, not only does a vinyl window save money by conserving energy once installed, it is energy efficient in its manufacture. Salt and natural gas, petroleum, or coal are the main starting materials for PVC. PVC accounts for less than 0.3percent of the world's annual gas and oil consumption and about 10 percent of the annual salt consumption. One study indicates that vinyl windows require about one-third as much energy to manufacture as comparable aluminum windows. (2)

Background:

PVC has been around since the late 19th century but did not come into general use until the 20th century when its commercial polymerization processes and the various post-polymerization processing techniques matured. Because of its basic properties (3) and the ability to be readily blended with other materials into "thermoplastic" systems or formulations that produce products ranging from rigid to very flexible, PVC has become commonplace. Its uses span from rigid materials like pipe to the various building products, where high strength to weight ratio, aesthetics, durability, and the ability to be recycled are important, to flexible products ranging from garden hoses, films for laminating, to medical tubing and bags.

The majority of PVC resins are produced commercially by the polymerization of vinyl chloride monomer, VCM. VCM can be produced via ethylene, processing natural gas or the cracking of oil/petroleum, or acetylene, the carbide process. The carbide process is based on the gasification of coal, has a different set of potential impurities than those of the ethylene route, and is used primarily in Asia (China).

Bulk PVC is produced at a number of different molecular weights by solution, suspension, or emulsion polymerization. The final product typically is "graded" by inherent viscosity differences and the number of gel particles allowed. Although suspension and emulsion polymerization at first glance appear to be the same, they are not and have a couple of important differences. In suspension polymerization the bulk phase is aqueous and the initiator is dissolved in the monomer phase. The kinetics of the reaction is the same as that of bulk polymerization. In emulsion polymerization, the initiator is in the aqueous phase, where the polymer particles produced are smaller than those produced in suspension polymerization, are highly dependent on the level and type of surfactant blend used, and higher molecular weights can be produced at a higher rate than with suspension polymerization. Among the various commercial producers of PVC resin, each may use a different surfactant stabilizer "package" during manufacture and

because of differences in the drying technique once polymerization is complete, spray vs. coagulation/precipitation, the residuals differ. There are commercially available co-polymers of vinyl chloride with "acrylic" monomers and/or other vinyl monomers. These are either specialty resins or not readily available in the US unless imported.

PVC is chemically inert, resistant to water and environmental corrosion, is a good electrical and thermal insulator, and maintains its properties over a reasonably large temperature range. Because it is about 57% chlorine, it does not support combustion. It has a low degree of crystallinity, typically quoted around 7-8 % but literature values range from 5 to 12%, and is translucent. By adding other inorganic and organic ingredients, it can be formulated to yield a large variety of final properties and can be processed by all the typical thermoplastic processes commercially used today, extrusion, injection and blow molding, etc. It is also used in the paint and coatings industry to produce plastisols and organosols.

Recently, PVC has come under scrutiny because of potential health and safety concerns but many of these claims are misdirected because in actuality it is the various other materials which have been added to PVC formulations to be able to process for a particular use that are the problem. A good example would be that certain phthalate plasticizers commonly added to PVC to provide flexible materials have been shown to have adverse health effects. The plasticizers leaching out of the PVC are actually the cause of concern rather than the PVC itself. When other plasticizers are used, the concerns are eliminated. (4,5)

Another concern has been the use of Pb stabilizers, especially in products produced in Europe and Asia. As you will see later in this paper, there are other stabilizer options which totally eliminate the use of Pb.

Residual VCM remaining from the polymerization processes is a known carcinogen. With today's highly controlled manufacturing procedures, the residual VCM in commercially purchased PVC resins is extremely low, single digit or less parts per billion. After further processing into consumer goods, residual VCM is almost non-existent.

"Dioxins", which can be generated as a byproduct from PVC manufacture and/or the incineration of PVC materials, is a known health hazard because they persist in the environment, can travel long distances, and have been linked to a variety of health concerns. Dioxins are never produced intentionally but can be produced when anything containing chlorine is burnt. Forest fires, lightning, volcanoes, and activities such as burning wood and trash, diesel vehicle emissions and other manufacturing practices all can generate dioxins. The majority of dioxins generated today come from consumer incineration of garbage and scrap PVC materials, i.e., backyard burning. Global recycling would eliminate much of the dioxins being generated.(6)

Although more than a billion pounds of PVC materials were recycled in 1997(1), more extensive post consumer recycling of PVC is not done primarily due to the concomitant costs and inconvenience of waste PVC collection and reuse. Strong efforts are being made to encourage the collection and reuse of PVC materials rather than burning or simple throwing away but it is up to the consumer to decide the extent of recycling. Each and every one of us needs to make the commitment to recycle and become advocates of environmentally friendly practices.

Formulating:

Formulating blends of PVC resin with other ingredients or "compounding", as it is called in the industry, to produce rigid PVC building products has been going on for decades. A great deal of information is known about the effects of various ingredients and it is up to the formulator to decide what properties are most important and which ones are secondary. Rigid PVC or u-PVC, as it is sometimes referred to in Europe and other parts of the world, needs to be able to be extruded and then perform a specific task. Normally in the fenestration industry, the PVC formulator is concerned about a certain set of properties for ease of handling and extrusion, then

another set of properties once the compound has been extruded into profiled product and will be further processed into complete windows or doors, and finally another once exposed to the environment as a window or door. All of these are important and as is the case with most things, not all of the desired properties are attainable without compromises. For example, one can increase strength but may lose the ability to extrude consistently, or perhaps increase brittleness to the point where the profile readily breaks or is very sensitive to impact temperature, or will pass all the required physical specifications but will badly discolor once exposed to the environment. It is not my intent to provide all the information required to enable the reader to become an expert formulator of PVC blends for the fenestration industry but to give you a general feel for the essential ingredients and what is possible. There is a lot of very good information available on the internet, from the various raw material suppliers, and in print today which the reader can refer to on their own. I have listed some in the bibliography.

It is interesting to note that with most rigid compound formulations the ingredients are listed as “phr”, parts per hundred parts of PVC resin, and then as percentages. One formulator talking with another will talk about usage levels as “parts”. They are talking about phr.

PVC Resin (7):

In any formulation the largest ingredient by weight is PVC. The designation of the PVC used is a general purpose, homopolymer made by either suspension or bulk polymerization. (Emulsion resins are typically used in the manufacture of various paints, plastisols or organosols.) One needs to choose the grade of PVC that offers the best possible set of properties for the economics of the final product. The first choice is molecular weight.

Molecular weight is designated in different parts of the world differently. Here in the USA molecular weight is reported as Inherent Viscosity, IV, or K-value. The higher the IV or K- value the higher the molecular weight. In Europe and Asia, K-value is quoted more than IV and is calculated from relative viscosity. Because there are several different methods of calculating K-value yielding different results, one needs to be careful when using K-value globally. In general, the higher the PVC molecular weight the better the impact strength can be, and the more difficult it can be to get fusion and achieve polymer flow without excessive heat or shear. Typically, resins in the K-value range of 65-67 are used for rigid profile but somewhat lower molecular weights are not uncommon especially for foaming or capping formulations.

Other important properties are the number of allowed gel particles, called “fisheyes”, residual VCM content, % moisture, bulk density, particle size distribution usually classified by sieve analysis, flow analysis, porosity, and resin heat stability. If one uses resin from different suppliers, comparing raw resin properties and base compound properties are a must. Not all resins supposedly the same IV but from different suppliers are the same and one can get very different extrusion and final product properties from the “same” molecular weight range resin from two different suppliers.

Exposure to temperatures above 70°C and/or to ultraviolet light will degrade PVC. In air at elevated temperatures one will see a color change from translucent, almost colorless to yellow, then proceed to orange, brown, and, finally, black with a concomitant general decrease in the mechanical and electrical properties. Even if stored in the dark and in a cold environment, PVC can undergo degradation so the typical conditions for storing color standards cannot be relied upon for colored PVC formulations.

PVC is typically 70 to 80% of any formulation.

Processing Aids (8):

Processing aids function by promoting fusion of the PVC powdered blend into a molten mass that can be appropriately processed and by altering the melt rheology during extrusion. They assist

with faster fusion, better mixing of the components as melting occurs, improving the strength of the melted PVC blend, controlling the die swell, reducing plateout, and achieving a smoother surface and higher production rates. Die swell is the term used to describe the volume increase or swelling that occurs immediately after the melted polymer blend leaves the die opening. Most processing aids today are “acrylic” polymers, i.e., containing acrylate and/or methacrylate monomers, with a variety of different compositions and molecular weights. They are always higher in molecular weight than is the PVC resin and because they are very compatible with the PVC resin, they assist with the interparticle mixing of the PVC particles at the beginning stages of fusion. Other high molecular weight polymer types, styrene derivatives and polyesters, have been promoted and evaluated commercially but they are not in common use today.

In general, the higher the molecular weight of the acrylic processing aid, the higher the die swell expected. Higher die swell can be a good thing if one is trying to make a foamed PVC material but is not good if one is making a solid profile and needs to carefully control dimensions. Acrylic process aids are usually used as a combination of different molecular weights and the polymers can have different monomer content. They also assist with impact strength improvement, weatherability, and there is some evidence that they reduce the crystallinity of the PVC. Acrylic processing aids are used at a 1 to 5 phr level depending on desired properties of the final product.

There is some evidence that fine particle size CaCO_3 , less than 1 micron, can act as a process aid by increasing the friction during melting in the extruder. Other benefits are better heat transfer and increased productivity. Even though a fine particle CaCO_3 may act as a processing aid, it is usually considered a filler.

Impact Modifiers (8):

Impact modifiers are designed to improve the final product's toughness and the ability to not crack and shatter during subsequent manufacturing operations such as cutting with a saw, or punching or routing holes in the profile. They function by absorbing energy and/or dissipating the energy of a propagating crack and can increase the yield of the extruded PVC formulation by acting somewhat like a lubricant. Impact modifiers fall into three very broad categories: “core-shell particulate” polymers, semi-compatible polymers, and fine particulate inorganics.

Core-Shell:

The “core-shell particle” type of technology is where the mechanism of improved impact resistance or toughening is the dispersion of a very small particle with an incompatible, rubbery core and a more compatible outer shell throughout the PVC compound. This technology is used to toughen many other polymeric matrixes across different industries. Chemically, the impact modifiers are based on co-polymers such as methacrylate/butadiene/styrene (MBS), all “acrylics”, acrylate/butadiene/methacrylate, and acrylonitrile/butadiene/styrene (ABS). All have a highly crosslinked, incompatible, rubbery inner core with a grafted, compatible, outer polymeric shell or shells. Obviously, the ability to uniformly disperse the particle within the melted mass is very important for this approach to work. In this approach it is also important to have a small particle size, so as to provide numerous sites for stress/crack control, to be able to readily disperse the particles throughout the bulk matrix, to have compatibility of the outer shell with the PVC, and to minimally influence the overall system's other physical and weathering properties. With a blunt impact, the decrease in brittleness allows the PVC to flex and not break.

Once a crack does initiate, the tip of the crack with its high concentration of shear energy running through the matrix will encounter a rubbery particle that will absorb and dissipate the crack propagation energy and minimize or stop crack propagation. It is important that the outer shell favorably interacts with the PVC so that effective energy transfer occurs between the rubber particle and the surrounding matrix. In general, there is an increase in fusion rate when particulate impact modifiers are used.

Semi-compatible Polymers:

In the semi-compatible polymer approach, the polymer at lower but elevated temperatures is compatible and is dispersed readily as a melt between the PVC primary particles. Polymers of chlorinated polyethylene (CPE) and ethylene- vinyl acetate (EVA) fall into this general category. With CPE as fusion continues, and the temperature increases, the CPE becomes less soluble and forms a discrete particulate phase. Once the mix is cooled after extrusion, the PVC product now has finely dispersed particles of the lower T_g CPE dispersed within the PVC matrix. (9, 10) CPE is manufactured by chlorinating high- density polyethylene. Typical grades of CPE contain 25 or 36 % chlorine so as to be compatible with PVC. CPE with less than 25% chlorination are incompatible with PVC and provide no impact enhancement. Theoretically, the dispersed particles of CPE after PVC extrusion should be spherical but in actuality become flattened and somewhat distorted in the direction of extrusion flow. Because it melts at a low temperature, initially coating the PVC and inorganic particles, and acts like a lubricant as the remainder of the PVC compound is being fused, fusion is delayed with the use of CPE impact modifiers and their use may require adjustments in the lubrication portion of the formulation. Depending on the total formulation,

CPE based materials are not as light stable as the acrylic based impact modifiers and tend to yellow a bit more. CPE is typically used in the 3- 5phr level.

EVA polymers with vinyl acetate content of around 40% are used primarily in Europe as impact modifiers. They are used at quite high levels, 5-15 %, and although impact, and thermal stability is improved, modulus, strength, and heat deflection temperature decrease. The mechanism of impact improvement is the formation of an elastomeric honeycomb network within the PVC matrix. EVA impact modifiers are supplied primarily as pellets as their powders tend to agglomerate. This causes blending and handling difficulties. EVA modified formulations weather close to those modified with the acrylics.

Other polymers have been tried as impact modifiers. Among them are terpolymers of ethylene / vinyl acetate / carbon monoxide, ethylene/propylene/carbon monoxide, polymers of olefins with acrylates, various copolymers of butadiene with acrylonitrile, methacrylates or other rubbers, and even polysiloxane enhanced materials. Although they improve impact resistance, most are not in common usage for a variety of reasons.

Inorganic particles:

The mechanism of improving impact resistance by the use of a hard, very small particle sized inorganic material has been called the cavitation mechanism. It has been described as one in which once the hard particles are very well dispersed throughout the polymer matrix, they will dissipate the impact energy striking them over the total surface of the hard particle such that in any direction the energy transmitted is less than necessary to initiate cracking or to continue crack propagation.

Ultrafine, coated, precipitated CaCO_3 has been found to improve low temperature impact resistance and increase UV stability in rigid PVC products. (11) A variety of organic surface treatments are available but stearic acid or its derivatives are most common. Careful control of the very fine particle size, less than 1 micron, and complete dispersion within the PVC blend are critical. Use levels of from 5 to 20 phr are recommended depending on the application.

More recently, the incorporation of synthetic amorphous silica has been described as improving impact resistance. (12) The particle size, about 150 nm, and surface area are carefully controlled. These materials are used in the 4-8 phr level and may require adjustments in the lubrication to get proper fusion. One of the cautions is that the particles need to be very well dispersed and this may require additional processing steps to do effectively. Silica is also used to

provide improved flow with certain PVC formulations and to reduce the surface gloss. The use level is very low and even very low levels of silica in a formulation can contribute to wear to both the compound blending and the extrusion equipment.

Fillers:

Solid fillers are incorporated into the formulation primarily to reduce cost. Although one can get very involved with providing the proper definition of what a filler is, the author will simply state that it is a solid material which does not change its state during extrusion and maintains, for the most part, its shape during extrusion. To correctly use a filler, one should understand its effect on the overall properties of formulation. One needs to balance cost reduction, use level, and processing changes that may occur with the use of a specific filler versus final product properties desired. PVC fillers can be classified as extender or functional.

Extender fillers are low in cost, have the appropriate size and shape to pack well, are chemically inert within the formulation, compatible with the process, and have an acceptable color, refractive index, and specific gravity. Functional fillers provide some processing or final product advantage. Since it is not always easy to determine which is which, the following are commonly used as fillers:

Limestone, CaCO_3 , is a natural occurring mineral. If mined, it can contain small impurities of Mg, Si, Al, and Fe. Mined and then ground to a specific particle size range, it is inexpensive and you get whatever was in the ground. One should evaluate carefully the use of any naturally occurring material to make sure that it fits one's needs. Limestone from the same company but from different mines may differ significantly in impurities.

CaCO_3 also can be manmade, precipitated, and the impurities and particle size can be more controlled. Precipitated cost more than mined material and is considered to be a functional filler by many. Commonly, CaCO_3 is surface treated with a stearate to improve its hydrophobicity, and the flow properties. When CaCO_3 is treated with stearic acid the surface of the particle chemically reacts to form a monolayer of calcium stearate. This surface treatment also can be beneficial by reducing the lubricant level required, and improving impact.

Kaolin clay is a mineral with the approximate chemical formula $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$. It is a mined mineral with several different plate-like structures. Because of the platy structure aligning with the direction of extrusion, one can obtain an increase in stiffness.

Talc is hydrated magnesium silicate with an idealized formula of $3\text{MgO} \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$. The actual composition varies somewhat in the Mg to Si ratio. It is mined across the country and is associated with a variety of other minerals. It is very soft and is plate-like in its structure. The surface of talc is active so it is commonly surface treated with an organic material. With talc's platy structure, one typically can achieve improved strength with its incorporation into a formulation. Because of impurities, one needs to be careful of the source of talc to avoid discoloration and inconsistencies during processing.

Mica is potassium/aluminum silicate, is platy, and very similar to talc. It is harder than talc and softer than CaCO_3 . It can be used in PVC formulations to improve flexural strength, increase heat deflection temperature, and dimensional stability.

Wollastonite, calcium metasilicate, is typically used as a high aspect ratio mineral for improved stiffness and deflection temperature. It can be abrasive to equipment.

Lubricants:

Lubricants are used in small amounts. They are to function by reducing the resistance to flow of the polymer chains and other ingredients in the formulation, and should not dramatically effect the

other bulk properties of the formulation once it has been extruded. Essentially lubricants act as processing aids but processing aids do not act as lubricants. With PVC formulations lubricants are described as being external or internal lubricants. Although this distinction is made, the difference between materials is not as clean as the names imply. Some materials act as both depending on the use level and extrusion conditions.

If a material provides improved flow of the hot compound through the equipment and is found after extrusion primarily on the outer surface, it is classified as an external lubricant or a metal release aid. During discussions about lubrication, one will hear the phrases, "metal release" and "slip agent". These mean that the lubricant tends to go to the surface and allow the hot plastic extrudate to flow through the metal, vacuum calibrators without sticking and causing chattering.

If after extrusion the lubricant can be found throughout the part, it is classified as an internal lubricant. Internal lubricants provide a reduced melt viscosity. When used at too high a level, they can start to act as an external lubricant, which can cause other problems, typically referred to as "plate out". Plate out is when the lubricants required for processing are squeezed out of the hot bulk plastic as the extrudate is leaving the die and/or going through the vacuum calibrators and either plugs the calibrator's vacuum slots preventing good surface contact between the hot extrudate and the calibrators or collects at the exit of the die and drips. Neither of these is good. In the first instance the surface of the part deteriorates, dimensions may be hard to control, and one will need to shut the line down and clean the vacuum calibrator section. In the latter case, in addition to plugging the calibrators the hot, dripping lubricants make a mess and are safety hazards.

On the surface lubricants and plasticizers might appear to serve the same purpose. The major difference is that plasticizers are used in very much higher use levels than are lubricants. Rigid PVC formulations typically do not contain plasticizers.

There are several chemically different types of lubricants. Each needs to be carefully balanced to maximize the processing improvements and minimize adverse formulation effects. Almost always a combination of lubricant types is used rather than a single material.

Hydrocarbons called paraffin waxes are the most commonly used external lubricant, and are used in very low use levels, less than 1%, with good metal release properties. When these waxes are oxidized under carefully controlled conditions, they are called oxidized polyethylene, OPE. Because of the carboxylic acid groups, OPE has increased solubility, is used at very low levels, and can have a dramatic effect on fusion.

Various long chained carboxylic acids, their esters, amides, and salts are used to assist with lubrication of PVC systems. They are not used alone but as internal lubricants in conjunction with waxes. Stearic acid derivatives are most common but other long chain, saturated, aliphatic acids are used. Derivatives based on montanic acid, octacosanoic acid, can and have been used.⁽¹³⁾ Calcium stearate is commonly used as an internal lubricant as not only will it act as an internal lubricant but also the calcium portion can act as a secondary heat stabilizer. In large amounts calcium stearate starts to act as an external lubricant and can quickly lead to plate out issues.

Esters typically can have both internal and external lubricant properties. Glycerol monostearate (GMS) is frequently used and is relatively inexpensive. Esters based on other multifunctional alcohols are also available and are many times blended with GMS to get improved properties. In general, esters have better heat stability than the corresponding amides. Amides are and can be used as lubricants but because they can discolor more readily than esters, their use is limited.

At times long aliphatic chain alcohols have been used as lubricants. They are inexpensive but do not lubricate as well as acids or esters. In some instances esters and alcohols have been used to increase surface gloss. The use level would be low. The above-described lubricants can be used from less than 1 to 5 % depending on formulation. Lower levels and blends are most common.

Stabilizers:

Two kinds of stabilizers are used by the rigid PVC industry. The first and probably the most important are heat stabilizers and the second are UV stabilizers. PVC resin when exposed to elevated temperatures degrades by the elimination of HCl and the formation of conjugated unsaturation along the PVC chain. The liberated HCl will accelerate further degradation. The unsaturation formed within the PVC chain leads to colored moieties. As a very general rule of thumb, from 1 to 5 conjugated double bonds, the colors are in the UV and therefore not readily noticeable. From 5 to 10 the colors imparted are yellow to orange, and from 10 upward the colors proceed to go through red-brown to purple. The conjugation seems to stop on its own at about 19. Although there is some speculation about the exact mechanism of degradation, in order to thermally process PVC and retard degradation as much as possible, heat stabilizers are required. (14, 15)

Depending on global location and extruded product end use, the commonly used heat stabilizer systems are Pb based, or dialkyltin compounds, or mixed metal stabilizers, or all organic systems. In Europe, an extruder may use several different systems depending on the end market. This can present production contamination concerns so switching back and forth may not be as easy as simply cleaning the equipment.

Commonly used for a long time, Pb based stabilizers offer several extrusion advantages but are very toxic and are sensitive to other chemicals, i.e., the formation of PbS in the presence of sulfur containing environments, etc. Because of its toxicity, Pb based materials are being eliminated globally.

Organo-tin stabilizers are commonly used in the USA. Most are dimethyl, dibutyl, dioctyl Sn based with organic ligands, i.e., carboxylates such as laurates or maleates, which can assist with either preventing or destroying conjugation in the PVC chain. In addition to carboxylic acid ester based dialkyltin stabilizers, dialkyltin mercaptides and reverse esters based on fatty acid esters of mercaptoethanol are used today. These are considered to be a better stabilizer as the mercaptide ligand is a better nucleophile than the carboxylate for replacing labile chlorines along the PVC chain and the reverse esters are less expensive to manufacture. (16) Of importance with Sn stabilizers are the percentage of Sn, the alkyl ligand(s), and whether or not the material is a mixture of dialkyl moieties or the same alkyl groups. Tin stabilizers are used in the 1-2phr range.

Other materials evaluated as PVC stabilizers have been the antimony analogs of the tin mercaptides, cadmium in conjunction with barium and/or zinc, and all organic materials. The antimony materials do not have as good a stabilization effect as does Sn. Both Cd and Sb are toxic, which limits their use. The all-organic materials are not strong enough to be used in light colored profile but are being used in pipe formulations.

A lot of work is going into the development of a Ca/Zn stabilizer system for weatherable profiles today. In addition to closely controlling the ratio of Ca to Zn, a blend of other ingredients such as epoxies, phosphites, polyols, antioxidants, beta- diketones, and uracil derivatives as well as lubricants are typically formulated as a system. Some of these materials are liquids and are easier to handle as a premixed system by the compounder rather than as separate ingredients. These systems are being used in Europe today where the weathering demands might be less severe than in the southern US.

In some cases organic epoxies have been used effectively as HCl scavengers to assist with PVC stabilization. One must watch the chemical type and the overall use levels with epoxies so as to not plasticize the rigid formulation or get migration of the material as objectionable plateout, or exudate.

With mixed metal stabilizers and epoxies, organic phosphites are sometimes used. It is assumed

that they act as both chelators of the mixed metal to improve compatibility and possibly act as ligands in the labile chlorine displacement reaction.

UV stabilizers typically do not assist with heat stabilization. Various "classical" UV stabilizers, hindered amines, phenols, etc., have been incorporated into weatherable PVC formulations to retard degradation due to sunlight. The ability to withstand the high processing temperatures, the potential chemical reactivity, and cost of these materials limits their use. In addition, since only the surface weathers and the UV stabilizer is throughout the total PVC layer, most of the protection afforded by a UV stabilizer goes to waste as it is not on the surface where degradation occurs. My experience is that a good UV stabilizer can prolong initial degradation but once "used up" fast discoloration occurs.

Pigments:

Pigments are used to provide color. In general, ceramic pigments are required for exterior durability with rigid PVC formulations. Because of this, the color range attainable is limited. The most commonly used example is titanium dioxide for white colors but various metallic oxides are used to provide the color ranges seen today. All need to be high temperature, anhydrous HCl, and environmentally stable. For non-weathering or less weathering applications, certain organic pigments can be used but, again, they need to be high temperature and HCl stable.

The pigmentation of any PVC formulation strongly contributes to Heat Build Up values (HBU) of the final product. Simply stated, HBU is the temperature difference between ambient temperature and that of a sample exposed to "sunlight" and allowed to equilibrate at the upper temperature. Because of this, IR reflective pigments are commonly used to keep the HBU as low as possible. HBU is a major contributor to the exterior durability of any rigid PVC for every time the temperature of the profile is elevated, additional degradation occurs, and the higher the temperature, the more the degradation.

TiO₂ is the most commonly used pigment with PVC. TiO₂ provides a very white color and also assists with mitigation of UV light degradation by both blocking the penetration and reflecting the light. With TiO₂, the surface treatment and UV driven reactivity are important. Pure TiO₂ can and does act as a photo/redox-catalyst for the degradation of organic materials, which leads to chalking if not controlled. To control this catalytic activity, TiO₂ can be surface treated with a variety of things but commonly silica or alumina surface treatments are used. (17) As a general rule, the more the inorganic surface treatment and better its uniformity, the less photo-active is the TiO₂ particle and therefore the less chalking that will occur. For this reason you will hear discussions in the industry about chalking and non-chalking grades of TiO₂. For colored compounds, a non-chalking grade should be used. For a white colored profile, controlled chalking may assist with color retention.

Pigments containing Fe should be avoided with PVC. Fe has a large affinity for chloride ions and Fe containing materials catalyze the degradation of PVC materials especially at elevated temperatures.

Comments:

Examples of starting formulations can be obtained from most suppliers of PVC resin, processing aids, impact modifiers, stabilizers, and the various additives. In addition, there are several detailed books or series of books available that give much more detail about the materials discussed and their properties. (18, 19) For the novice and for the skilled formulator, these can be a ready reference source but the technology is changing daily so one should establish a good relationship with the various suppliers in order to take advantage of the latest technologies.

Recently an extensive technical assessment by the U.S. Green Building Council has been made

addressing the overall performance of PVC based building materials and how PVC based materials should be included in its Leadership in Energy and Environmental Design (LEED) rating system. (20) After all the data had been gathered and reviewed by all the technical and environmental personnel, and finally by the public, it was concluded that the evidence comparing the life-cycle assessment and the environmental risk assessment of rigid PVC building products were at least comparable to the alternate materials. This assessment indicates that based on its properties and overall performance, rigid PVC is a good material to use as a “green” building product material.

Formulating rigid PVC is not difficult, but it is not simple. The need to balance blending, storage, and handling of the compound with the need for a robust processing window for extrusion against the overall cost and performance of the profile once extruded and fabricated into commercial products and finally in the environment, is a series of compromises. Sometimes not all the desired requirements can be attained but formulation with PVC is a good candidate with which to start one’s evaluation. Globally, PVC is a very useful and beneficial plastic. Because of its durability and ability to be recycled, its contribution to the fenestration industry should continue to evolve and grow.

Bibliography:

1. “A Clear View, Vinyl Windows and the Environment”, The Vinyl Institute, VIB-0205, www.vinylinfo.org.
2. Fencepost, Sept./Oct. 2006, p. 24.
3. Polymer Handbook, 4th Edition, edited by J. Brandrup, E. H. Immergut, and E. A. Grulke, John Wiley & Sons, ISBN: 0-471016628-6, 1999, pp. V/67 to V/76.
4. “Phthalates Linked to Men’s Health Effects”, C & EN, March 19, 2007, p. 45.
5. “European Phthalates Study: More Regulation Not Needed”, Plastic News, May 8, 2006, p. 5.
6. “Fire Properties of Polyvinyl Chloride”, The Vinyl Institute, March 1990.
7. Possible suppliers: Formosa Plastics, Georgia Gulf chemicals and Vinyls, Oxy Vinyls, Shintech Inc., and others.
8. Possible suppliers: Arkema, Kaneka Texas, Rohm & Haas, and others.
9. “Rigid PVC Formulation Fundamentals Using Tyrin®”, DuPont Dow Elastomers Technical Bulletin H-82081, 2/99.
10. “Improved Ductility in Rigid PVC with Tryin® Impact Modifiers”, DuPont Dow Elastomers Technical Bulletin H-82114, 11/99.
11. Industrial Minerals, July 2001, pp. 35-37.
12. “Inorganic Impact Modifiers and Processing Aid for PVC”, M. Gilbert, et. al., Plastics, Rubber, and Composites, Vol. 34, No. 3, 2005, pp. 111-116.
13. “Impact of Lubricants onto the Processing Behavior of U-PVC”, Beate Treffler, Clariant GmbH Technical Brochure 23.02.2005, pa.clariant.com.
14. “Mechanism of Poly (Vinyl Chloride) Stabilization”, M. H. Fish and R. Bacaloglu, Plastics, Rubber, and Composites, Vol. 28, No. 3, 1999, pp. 119 – 127.
15. Handbook of Environmental Degradation of Materials, edited by Myer Kutz, William Andrew Publishing, Norwich, NY, ISBN: 0- 8155-1500-6, 2005, pp. 155 –156.
16. “Mechanism of Organotin Stabilization of Poly (Vinyl Chloride) 1: The Structure and Equilibria of Alkyltin Thioglycolates and Their Compatibility with PVC”, M. H. Fish, R. Bacaloglu, K. Biesiada, and L. Brecker, Jour. of Vinyl & Additive Tech., Vol. 5, No. 1, March 1999.
17. “A Comprehensive Understanding of TiO₂ Pigment”, Michael P. Diebold, Paint and Coatings Industry, July 2005, pp. 90 – 94.
18. Encyclopedia of PVC, 2nd Edition, Volumes 1-3, edited by Leonard I. Ness and Charles A Heiberger, Marcel Dekker, NY, ISBN: 0- 8247-7427-2 (Vol.1), 1986.
19. Handbook of PVC Formulating, edited by Edward J. Wickson, John Wiley & Sons, ISBN: 0-471-60182-9, 1993.

20. Assessment of the Technical Basis for a PVC-Related Materials Credit for LEED, U. S. Green Building Council, Technical & Scientific Advisory Committee, Feb., 2007, www.usgbc.org.

ABOUT THE AUTHOR

Kenneth Abate, Ph.D., FAIC, CPC is currently Director of Research and Development at Veka Inc. He has authored refereed publications and given numerous presentations at universities and professional society meetings. Dr. Abate has international experience in business and R & D in a broad range of technologies. These include PVC and other polymer formulations for extrusion, polymers and formulating for paints and coatings, insulating foam systems, corrosion identification and prevention, galvanizing, silicone chemistry, photochemical etching and forming, sealants and adhesives, liposomes, and surfactants. In addition to keeping up with science in general, he enjoys music, gardening, and is an avid hunter and fisherman.