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Technical Report #5

Ingredients Used in Rigid PVC Compounding

Although PVC is a very versatile polymer, proper compounding and good lubricant balance are critical in obtaining good machine and end product properties.

RESIN

PVC resin is available in a wide range of molecular weights. In the United States, the molecular weight is expressed as inherent viscosity (I.V.); in Europe it is expressed as K value, in Japan it is the degree of polymerization. Commercial PVC resins available range from an I.V. of .50 to 1.15 (K value, 47 to 76). The higher the I.V., the higher the molecular weight and the greater the stiffness. Below is a table showing I.V. vs. equipment and end use.

I.V. Range	Process	End Use
0.05 - 0.65	Injection molding	Very complicated molded end use
0.65 - 0.85	Injection molding and extrusion	Pipe fittings, monofilamenst, sheet, film, profiles, cellular
0.85 - 0.98	Extrusion	Pipe, siding, sheet, film, profiles, flexible window profiles
0.98 - 1.16	Extrusion	Complicated profiles, profiles, flexible, wire and cable

STABILIZERS

Polyvinyl chloride (PVC) is a heat and light sensitive material. It degrades by dehydrochlorination and oxidation. This can be seen by the development of color in PVC. In chemical terms, formation of conjugated double bonds causes the color change. PVC compounds experienced heat history in mixing cycles, extrusion/molding, embossing, thermoforming, laminating and scrap rework. Oxidation products occur by exposure to weathering. The job of the stabilizer is to delay heat degradation so that the compound can be formed into a product before it degrades. The stabilizer does this job by absorption of hydrogen chloride, displacement of active chloride atoms, free radical scavenging, disruption of double bond formation, deactivation of degradation by products, peroxide decomposition and ultraviolet energy absorption.

Stabilizers in pipe extrusion are used mainly to process the PVC through the hot hostile environment of the extruder. They do not significantly affect shelf life or weatherability except in so-called “weatherable” compounds. In these weatherable compounds, the amount of stabilizer is five to seven times the level in pipe, and stabilizers do have a positive effect on weatherability. A given recipe, even with high levels of titanium dioxide, will have less weatherability at half the normal level of stabilizer. Any changes in level or supplier of stabilizers should be checked for weatherability before complete changeover has been made.

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There are several types of stabilizers for PVC resin. Below is a partial list:

Lead Salts–Mainly organic lead compounds like sulfates, silicates, phosphites, stearates, phthalates and maleates. They are inexpensive and provide good heat stability, excellent electrical properties and low water absorption.

Calcium Zinc–Used in food contact applications like blow molded PVC bottles, film and sheet. PVC so stabilized can meet FDA requirements. The stabilization power of calcium-zinc in PVC is weak and, therefore, scrap rework capability is poor. They can provide compounds with crystal clarity and low odor properties.

Barium-Cadmium–Plate-out tendencies, toxicity of cadmium and poor melt viscosity are characteristic of these stabilizers in PVC. They provide good early color, light stability and heat stability.

Tin Mercaptides–Most commonly used to stabilize rigid PVC in the U.S. They give good heat, light and color stability, and promote fusion and reduce melt viscosity. The main type of tin mercaptides in use are methyl tins and butyl tins. These are used in pipe, pipe fittings, siding profiles, cellular vinyl and some bottles. One type of tin mercaptide, di-n-octyltin, and methyl tin are FDA acceptable for food contact applications with PVC. Some of the newer tin mercaptides have external lubrication capability and this must be considered in compounding.

Stabilizer-Lubricant Package

(a) Lead Based Systems–In Europe, these systems have been used in pipe for many years. The advantage is that only two or three ingredients must be mixed with the PVC resin instead of six to nine. The disadvantage is the lack of versatility.

(b) Tin Based Systems–Recently, U.S. tin stabilizer companies have introduced these systems to the U.S. market, but have not penetrated here to the same extent as the lead systems in Europe. However, they offer the same advantages and disadvantages as based lead systems. We may hear more about them in the future.

FILLERS

There are many fillers which can be used with PVC including metal carbonates and silicates, gypsum, clay, alum, barytes and saw dust. The most common are metal carbonates, mainly calcium carbonate (which is usually in the form of ground limestone) and coated with stearic acid. The coating reduces the abrasiveness of the calcium carbonate. It also reduces extruder barrel and screw wear. Calcium carbonate is available in ground and precipitated grades with a range of particle sizes. As a general rule, the finer the calcium carbonate, the better the impact strength of the finished product. If the calcium carbonate is very fine, it can cause titanium dioxide to agglomerate. This will create a TiO2 streak in the part. Normally, increasing calcium carbonate content reduces tensile strength and increases tensile modulus. For pressure pipe, the level should never exceed five parts per hundred resin (phr) because higher levels of calcium carbonate could lower the stress design below 2000 psi which is normally required.

Calcium carbonate can be used in PVC compounds to lower the raw material cost of the finished compound. As the level of calcium carbonate increases, overall material cost decreases, but the weight per foot of product increases. This is because the specific gravity of calcium carbonate is higher than the specific gravity of PVC. This relationship between compound cost reduction and increased weight per foot must be balanced to give an overall economic reduction. Today, this level is between 3 to 4 parts per hundred for pipe. Siding substrate is 8 to 12 phr.

Extruder barrel and screw wear are affected by the amount and the particle size of the calcium carbonate. As amount and coarseness increase, the wear will increase. At levels of 5 parts per hundred and under, wear is considered minimal, but higher levels increase wear drastically. Levels of 40+ phr have been reported. This can cause some barrels and screws to wear out in six weeks. Therefore, this cost must be considered.

Calcium carbonate particles larger than ten microns often cause increased barrel wear and reduced impact strength because they act like holes or stress concentration points. Increased levels can also cause a reduction in tensile modulus (at high part levels). Calcium carbonate serves no useful purpose in PVC except to reduce compound cost and weatherability of compounds.

PIGMENTS

There are three main reasons to use pigments in PVC compounding: to achieve opacity in non-weatherable compounds, for UV protection in weatherable compounds and to achieve a given color. Titanium dioxide is the major pigment used. Other pigments are used in small amounts to achieve the desired color in combination with the titanium dioxide.

In pipe and some profiles, opacity and color are the main purposes of the pigments. For these uses, titanium dioxide levels are normally between o.5 phr to 5.0 phr. At these levels the effect on weathering is minor. Compounds with this level of pigmentation should not be used outdoors. Both color and properties will be drastically affected by long-term exposure to UV radiation. The titanium dioxide used in these compounds is normally controlled chalking rutiles.

In siding, window and other weatherable applications, a high amount of UV screening is needed. The twofold purpose of this screening is to maintain color and properties. The major UV screener used is titanium dioxide. A 10 to 15 phr level is needed to achieve this purpose. In colored PVC compounds a non-chalking rutile titanium dioxide is used along with another pigment to achieve the desired color. Because the titanium dioxide has very limited chalking, the color does not fade on weathering to the extent of semi or chalking titanium dioxide. For white compounds, two titanium materials are sometimes used, in semi-chalking and a freely chalking rutile. The combination is used to achieve the right amount of chalking for maintaining the desired whiteness and cleanliness on exposure to UV radiation. All changes in weatherable ingredients should be tested by outdoor weathering for at least two years before being commercialized.

Some normal problems caused by pigments are staining, plate-out, poor dispersion and pinking. Staining is caused when certain pigments (like lead, cadmium, etc.) react chemically with the atmosphere and the mercaptides of the stabilizer. Colored reaction products are formed. This reaction can occur on processing or on weathering. Therefore, pigments must be carefully chosen in the light of recipe components and the end use.

Pinking is similar in appearance to staining because it forms gray or black streaks on the top three mils of the profile. It seems to come from the action of the compound on the extruder barrel. Changing the melting position in the extruder will often eliminate it. Coated rutile-containing (non-chalking) compounds seldom show pinking. At the present time, we have no clear cut solution to eliminate pinking.

Plate-out is a buildup or deposit on the sizing sleeves, die, embossing roll or screws. Plate-out has often been analyzed to be titanium dioxide and/or calcium stearate, but other materials can cause this problem. The amount of coating on the titanium dioxide can aggravate plate-out, as can exceedingly high stock temperatures. The type and amount of calcium stearate can be another cause. By changing types of lubricant, stabilizer, pigments and processing conditions, the amount of plate-our can be eliminated or controlled.

PROCESSING AIDS

The most common processing aids used with PVC are acrylic polymers. Alpha methylstyrene has also been used. A process aid can reduce or increase melt viscosity, increase frictional heat and reduce uneven die flow. In a compound, it promotes fluxing and acts like an internal lubricant. Increasing levels of processing aid normally allow lower extruder/molding barrel temperatures. Also, it gives the melt hot strength for string-up and draw-down.

Typical levels are between 0 and 5.0 phr depending on the extrusion process. Single screw high shear and multi-screw extrusion require less processing aid, while low shear, single screw extrusion requires more processing aid. It must be remembered that the type of end product made affects the amount of processing aid used. For example, the more complicated the end product, the higher the level of processing aid used.

IMPACT MODIFIERS

Certain applications require higher impact strength than PVC would demonstrate normally. Acrylic, chlorinated polyethylene (CPE), methacrylate-butadiene-styrene (MBS), and acrylonitrile-butadiene-styrene (ABS) polymers are normally used to modify impact strength of PVC. These polymers provide a shock absorber when the PVC is heated to a high enough melt temperature 196(C (385(F) to fuse it. At lower melt temperatures, the impact is lower than it would be without impact modification. At this lower melt temperature, the impact modifier acts like a hole or stress concentrator making the impact lower. Using the proper melt temperature will ensure that the full properties of the impact modifier will be realized.

All impact modifiers reduce the weathering, chemical resistance, tensile strength and stress rupture of PVC compounds. If these properties are desired, the lowest possible level needed to achieve the desired impact should be used. Pipe generally has 0 to 2 phr of impact modifiers, while siding and profile have o to 10 phr. High impact PVC compounds with lower chemical resistance and stress rupture have 6 to 14 phr of impact modifiers.

Weatherability can be affected by both type and level of impact modification. Normally, CPE, EVA and acrylic polymers are used in weatherable compounds. They allow good retention of properties, along with good color retention. Both MBS and ABS impact modifiers are poor in these characteristics, but are good for low temperature properties.

Impact modifiers generally promote flux, with the exception of CPE. As flux promoters, they tend to reduce the temperature of the extruder barrel needed for a given melt temperature. This point needs to be considered when compounding PVC.

LUBRICANTS

Lubricants are materials that control the fluxing (melting) point in the extruder/molder to achieve the best processing characteristics and physical properties. There are three types of lubricants. They are external, internal, and external/internal. They are defined by their effect on the melt in a plasticizing screw, as follows:

External Lubricants–Provide good release from metal surfaces and lubricate between the individual PVC particles and the metal surface. As the level of external lubricant is increased, it moves the melting point of the PVC in the direction of the die.

Internal Lubricants–Provide lubrication at the molecular level, between resin particles, and reduce the melt viscosity. The internal lubricant moves the melting point of the PVC in the direction of the extruder hopper as it is increased in level.

External/Internal Lubricants–These materials provide both external and internal lubrication depending on the combination of chemical groups contained.

EXTERNAL LUBRICANTS

External lubricants are normally non-polar molecules or alkanes. They are usually paraffin waxes, mineral oils or polyethylene. Some stabilizers have oils that carry active ingredients such as external lubricants. External lubricants are normally incompatible with PVC. They help the PVC slip over the hot melt surfaces of the dies, barrels and screws without sticking and contribute to the gloss on the end product surface. Extruder motor amperage is greatly affected by small changes of external lubricants.

Common problems resulting from over-lubrication include: surging of the extruder, lumpiness of the extrudate, incomplete fusing and the necessity of high barrel temperature. In the end product, low impact strength and acetone failure are the common manifestations found.

INTERNAL LUBRICANTS

Internal lubricants are normally polar molecules. They are usually fatty acids, fatty acid esters or metal esters of fatty acids and are very compatible with PVC. They lower melt viscosity, reduce internal friction and promote fusion. Common problems of under-lubrication are rough extrudate, adhesion to metal surfaces, melt fracture, quick fusion and abnormally low barrel temperatures. In the end product, burning, plate-out, matte surfaces and poor impact strength are typical results of under lubrication.

EXTERNAL/INTERNAL LUBRICANTS

These are hard to define because they have chemical groups (polar and non-polar) of both lubricant types. In general, they have long hydrocarbon chains, along with amide, alcohol, acids and ester groups. Common types used in PVC are fatty acid amides and oxidized polyethylenes. Some of these materials will lubricate as an external lubricant before melting and as internal lubricants after melting. Others will do the reverse. Each of these lubricants should be characterized for its type of lubrication in a given compound.

The purpose of lubrication is to achieve the full properties of PVC and a melt that will extrude or mold without problems, at an economical cost. To achieve these goals, experiments must be performed. A bench extruder can be used for gross compounding. But, the final compound will need to be run on commercial size equipment. This is the only proof of the “goodness” of the compound.

Avoid over-compounding for machine problems. After a compound has been developed, tested, and used successfully, usually very little change is necessary. Before any recipe changes are made, equipment should be thoroughly checked.

Temperature controllers and thermocouples should be connected properly and the reading checked. Screw rpm, back pressure instruments and heat bands should be checked. All operating procedures should be compared with previous successful runs with the same compound. Cleanliness and freedom from obstruction of screen packs, nozzles, adapters and dies should also be checked. If all are correct, establish clearly what is wrong with the melt before changing the recipe. An attempt should be made to correct a specific problem in the melt rather than a symptom in the end product which could have many causes. If the problem is still present after all of these points have been checked, the recipe should be changed.