The Massachusetts Toxics Use Reduction Institute
University of Massachusetts Lowell

ENVIRONMENTALLY BENIGN RESINS AND ADDITIVES, FOR USE IN THE WIRE AND CABLE INDUSTRY

*****DRAFT*****

TOXICS USE REDUCTION INSTITUTE UNIVERSITY RESEARCH IN SUSTAINABLE TECHNOLOGIES PROGRAM

Technical Report No. 54 **2003**

University of Massachusetts Lowell

Environmentally Benign Resins and Additives, For Use in the Wire and Cable Industry

*****Draft*****

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The Toxics Use Reduction Institute
University Research in Sustainable Technologies Program

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The Toxics Use Reduction Institute is a multi-disciplinary research, education, and policy center established by the Massachusetts Toxics Use Reduction Act of 1989. The Institute sponsors and conducts research, organizes education and training programs, and provides technical support to promote the reduction in the use of toxic chemicals or the generation of toxic chemical byproducts in industry and commerce. Further information can be obtained by writing the Toxics Use Reduction Institute, University of Massachusetts Lowell, One University Avenue, Lowell, Massachusetts 01854.

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University Research in Sustainable Technologies

The University Research in Sustainable Technologies program is a joint project of the Toxics Use Reduction Institute (TURI) and the Center for Environmentally Appropriate Materials (CEAM) at the University of Massachusetts Lowell, with support from the Commonwealth's Strategic Envirotechnology Partnership (STEP).

The program taps the research capabilities of the University of Massachusetts to advance the investigation, development and evaluation of sustainable technologies that are environmentally, occupationally and economically sound. The program provides research funding to UMass faculty from all campuses, annually, on a competitive basis and encourages faculty/industry partnerships and cross-campus collaboration. Industry partners provide guidance, propose applications for new technologies and, in some cases, evaluate and/or adopt processes and technologies resulting from research.

Notice

Introduction

The explosion of the information age has led to a scramble to increase the infrastructure of data carrying capacity. The building industry has seen a large increase in the demand for new housing. The electronic market continues to grow at an astounding pace. All of these industries require insulating wire for use in there products. Shipments of insulated wire increased from $12 billion in 1996, to $18 billion in 1999.

As the amount of wire products increase special attention must be paid to the impact which these products make on the environment. Lately attention has been focused on polyvinyl chloride or PVC. PVC was first created in 1872 by German chemist Eugen Baumann. In 1926 it was plasticized by B.F. Goodrich into the form many of us are familiar with today. In 1999 it was estimated that 592 million pounds of plasticized PVC was used in the wire and cable industry alone.

New legislation in places such as California and Europe have begun to regulate the use of substances that are common additives to PVC. This project proposes to research the technical, economic and environmental feasibility of using alternative resins to PVC in the wire and cable industry.

Resin Manufacture

Typically PVC is commercially produced by a suspension polymer process, where monomer droplets are suspended in an aqueous medium. Suspension polymerization of vinyl chloride is typically carried out in a batch reactor (see Figure 1).

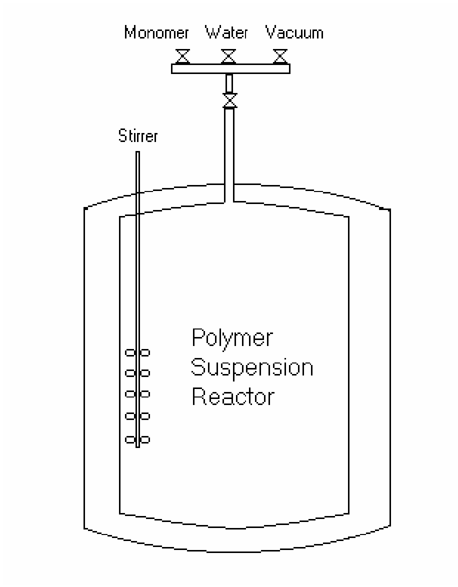


Figure 1 – PVC Suspension Reactor (Simplified)

A typical recipe for PVC includes 180 parts water and 100 parts vinyl chloride plus a small amount of dispersants (<1 part). Typically the average molecular weights for commercial PVC are in the range of 30,000-80,000.

Polyvinyl chloride has very low crystallinity but achieves strength because of the bulky polymer chains. This leads to high process temperatures needed to process PVC. PVC is unstable in light and heat resulting in the evolution of hydrogen chloride. This instability requires the use of stabilizers, such as lead to prevent degradation of the polymer chain. Lead stabilizes PVC by slowing down the dehydrochlorination reaction and absorption of hydrogen chloride as shown in Figure 2.

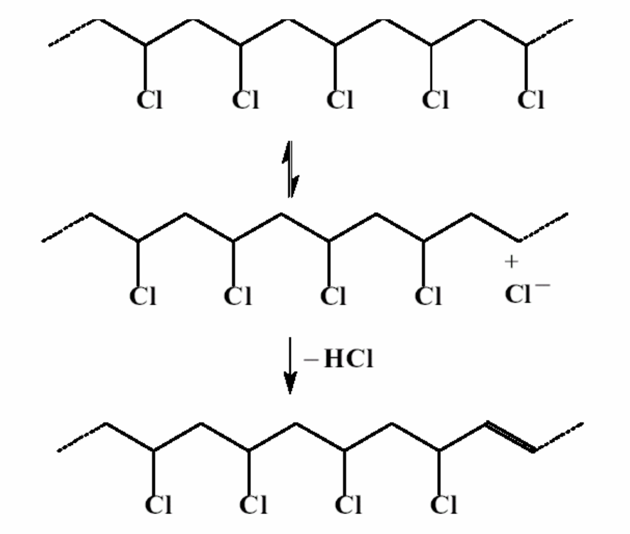


Figure 2 – De-chlorination of PVC

PVC Additives

Lately PVC has come under increasing pressure to remove the toxic chemicals used in its production and product modification. The chlorine in PVC has been known to breakdown and react with its environment to produce a variety of toxic substances. Plasticizers such as di (2-ethylhexyl) phthalate (DEHP) in PVC have been linked to cancer, organ damage, and reproductive toxicity effects. Lead stabilizers in PVC can leach into ground water and adversely effect the environment. Halogenated flame retardants used in PVC building wire have been shown to have detrimental environmental and health effects.

Stabilizers

The degradation of PVC at the elevated temperatures required for thermoplastic processing is an intrinsic characteristic of the polymer, and consists of dehydrochlorination, auto-oxidation, mechano-chemical chain scission, crosslinking, and condensation reactions. To avoid failure of pieces manufactured with PVC this degradation must be controlled, typically by the addition of stabilizers. The heat stabilizer must prevent the dehydrochlorination reaction that is the primary process in degradation. Once the degradation starts, it is very fast and can be stopped only if the stabilizer is already associated with the chlorine atom that becomes allylic.

There are two ways the stabilizer can act:

- By reacting with allylic chlorides, the intermediates in the zipper degradation chain. This process should be faster than the chain propagation itself, requiring a very active nucleophile. However the reactivity of the nucleophile should not be so high as to react with the secondary chlorine of the PVC chain, a process that rapidly exhausts the stabilizer.
- Scavenging the hydrogen chloride generated by degradation is another way to stop the process as the HCl is a catalyst for the chain propagation reaction and the initiation step. However, the diffusion of HCl is quite slow because HCl is associated with the double bond where it was generated. When HCl diffuses away from the reaction center, the zipper degradation reaction stops. The stabilizer should scavenge HCl with high effectiveness to avoid its catalytic effect in chain initiation that starts another zipper dehydrochlorination chain.

PVC is the primarily stabilized today with lead compounds such as tribasic lead sulfate and lead phosphate. Lead is commonly known to cause neural damage as well as kidney damage. Research is also being done to evaluate the effectiveness of organic and organotin compounds as PVC heat stabilizers. Organotin compounds are classified as R_4Sn, R_3SnX, R_2SnX_2, and $RSnX_3$. In compounds of industrial importance, R is usually a butyl, octyl, or phenyl group and X, a chloride, fluoride, oxide, hydroxide, carboxylate, or thiloate. So far, monosubstituted organotin compounds ($RSnX_3$) have had a very limited application, but they are used as stabilizers in PVC films.

Organotin mercaptides (Figure 3) are able to complex with PVC (Figure 4), as well as react with hydrogen chloride as well as prevent autoxidation. Organic compounds are the cutting edge of new stabilizers, significant research is going on to find a non-lead stabilizer.

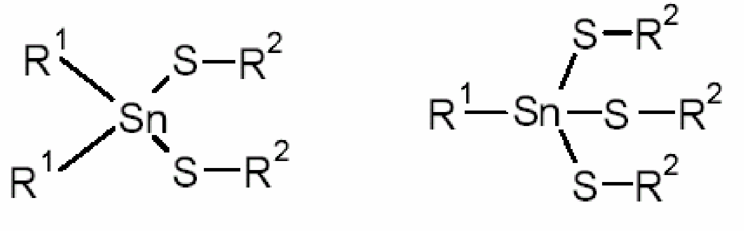


Figure 3 – Organotin Mercaptides

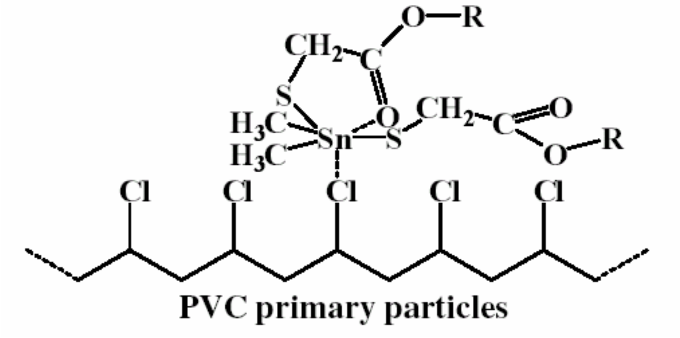


Figure 4 – Complexation of Organotin with PVC

Plasticizers

In its bulk form the polyvinyl chloride is a rigid plastic. To achieve wider usefulness and marketability, PVC is plasticized, typically with phthalates to create flexible PVC. The phthalate imparts flexibility by acting as an "internal lubricant" between PVC chains.

The annual production of polyvinyl chloride is around 9 billion pounds annually. This amount is about evenly distributed between rigid and flexible grades. Rigid pipe for home and other construction uses, accounts for 40% of the total PVC market. Vinyl siding, window frames, rain gutters, and downspouts account for another 10-15%. Packaging applications (*e.g.,* bottles, box lids, blister packaging) account for about 8%. 10% PVC is used in flooring. The remaining 30% is in wire and cable, and surgical products.

PVC is widely manufactured from many companies such as Dow Chemical, Monsanto, and Bordon under trade names such as, Carina, Corvic, Darvic, Exon, etc.

Flame Retarders

PVC has been long used for its excellent performance for price ratio. However developments in the 1970's and 1980's with Ziegler-Natta initiators have led to high performance polyolefin polymers. These high performance polymers meet or exceed the properties of many PVC blends. PVC has remained a strong leader in the wire and cable industry for its inherent fire retardence due to the chlorine attached to the vinyl.

Halogenated compounds have been shown to be effective flame retarders. The inherent flame retardence in PVC means you can use less of an expensive flame retardency additive. However due to the toxicity of these flame retardant compounds ongoing research in this area has led to several alternatives. Inorganic compounds (*e.g.,* antimony compounds, magnesium compounds, zinc borate compounds, aluminum hydroxide) have all been used as flame retarders, with various degrees of success. The most commonly used inorganic flame retardants are the metal hydroxides: aluminum trihydroxide, antimony trioxide and magnesium hydroxide. Both aluminum trihydroxide and magnesium hydroxide are used in halogen-free formulations substituting for brominated flame retardants.

Inorganic phosphor compounds, red phosphor and ammonium polyphosphate, are also widely used as substitutes for bromine.

Of the zinc compounds zinc borate is used in some halogen-free formulations, but other zinc compounds like zinc stannate (ZN) and zinc hydrostannate (ZHN) may be used as synergists together with other flame retardants.

Zinc borate is the most widely used of the zinc flame retardants and is particularly used as substitute for antimony trioxide. Compounds having varying amounts of zinc, boron and water of hydration are available. Zinc borate has a synergistic effect with aluminum trihydroxide and is often used in combination with other flame retardants. In its mode of action zinc borate behaves like aluminum trihydroxide by endothermic release of water.

Currently aluminum hydroxide (or also called alumina trihydrate ATH) is the most widely used inorganic flame retardant; it is low cost and easy to incorporate into plastics. Aluminum trihydroxide functions as a flame retardant in both the condensed and vapor phase. When heated it decomposes and releases water that forms an envelope around the flame, which tends to exclude air and dilute the flammable gases. In addition the decomposition is endothermic, lowering the ambient temperature. Aluminum hydroxide has a tendency of suppressing smoke evolution. The disadvantage of the compound is that very high loading is necessary (up to 50%) affecting the physical properties of the plastic.

Magnesium hydroxide is basically the same as that of aluminum trihydroxide. Magnesium decomposes at 330*C; about 100*C higher than aluminum trihydroxide, and can be used in polymers that are processed at higher temperatures. Magnesium hydroxide forms char and produces less smoke than aluminum trihydroxide.

Wire and Cable Manufacturing

Wire and cable is made to thousands of different specifications, however the basic manufacturing process is the same. A metal core is coated with one or many polymer layers, see Figure 5.

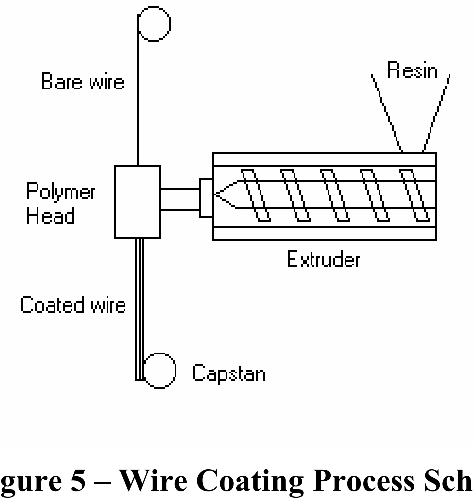


Figure 5 – Wire Coating Process Schematic

Resin, in pellet form, is melted and pressurized in an extruder. The polymer melt flows into a polymer head, where polymer flows over a mandrel and onto a wire at high pressure, see Figure 6.

To form a smooth wire both the pressure and the temperature of the polymer melt must be carefully controlled. The polymer exits the polymer head via a polymer die. This die is optimized to create a smooth surface, and to control die swell, which is dependent on the land length of the die (see Figure 6). Die swell is the amount of swell the polymer experiences outside the die. Depending on the application, the process could be complicated by many extruders, cross-linking resin and multiple layers. The type and dimensions of the resin used will depend on the application. Voltage cable requires a cross-linked resin of high thickness, to prevent electric leakage. In many cases a secondary jacketing step is needed as a protective barrier.

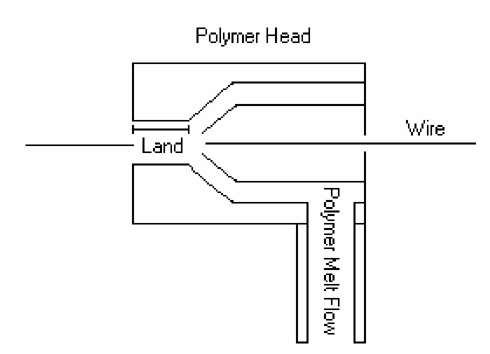


Figure 6 – Polymer Head

Research Plan

The focus of the present research has been to develop an alternative to the lead based stabilizers and the halogenated flame retardence in polyvinyl chloride. Ideally the elimination of PVC, in favor of a polyolefin, is the goal.

To achieve this goal the resin must meet or exceed PVC's physical and chemical properties. To further this goal a test wire and cable line was set up. This cable line will allow many different formulations of resin to be examined, and tested for physical property performance.

A common wire construction of 20 gauge was chosen for the line. A cable head was made up to extrude a .016 inch insulation thickness. A small ¾ inch extruder was more than sufficient to achieve the resin input needed to supply the head. The extruder is fitted with a common low compression screw. A wire straightener was fitted on the line to stabilize the wire in the head, to achieve a consistent product (see Figure 7). A belted take-up was used to draw the wire through the head and an 8 foot cooling bath was used to cool the wire and prevent irregular coating. A motorized pay-off was used to create tension in the line (see Figure 8).

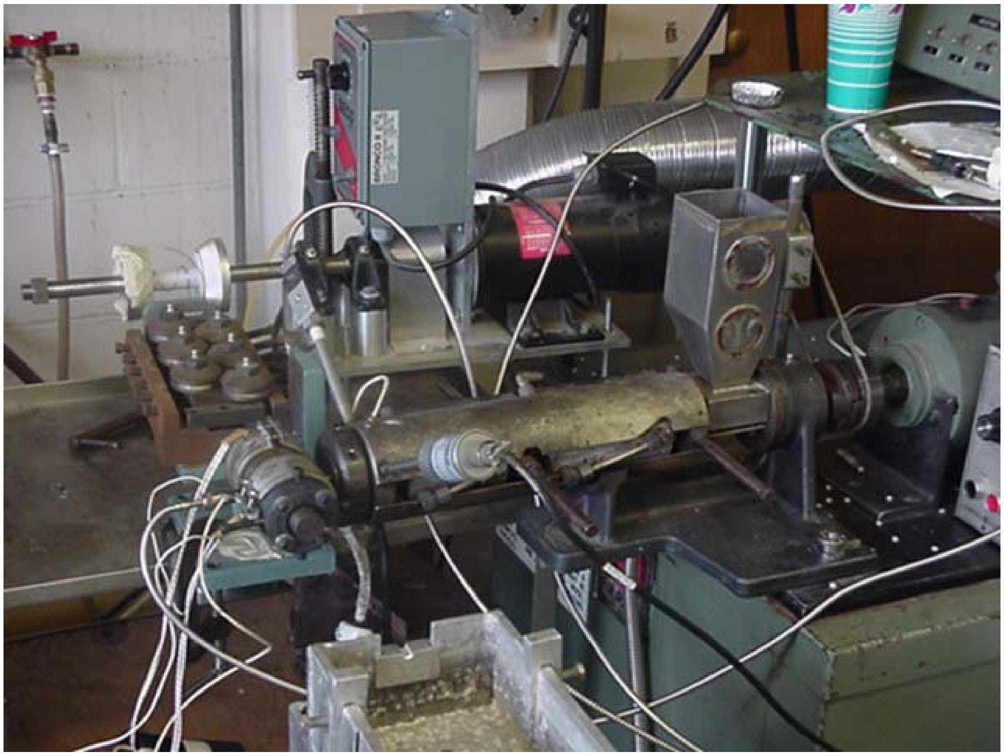


Figure 7 – ¾ Extruder, Wire Head, and Wire Strainer

Figure 8 – Cooling Bath and Take-up

Resins

Currently there are many alternative stabilizers as well as alternative resins to PVC. Over the past year we have explored two such formulations, both from AlphaGary Corporation: Sentra 8030 HF, a polyethylene base resin with a zinc flame retardant; and GW 2038-A-VW1, a PVC based resin that has a barium and antimony stabilizer with a zinc flame retardant.

The resins were both extruded onto wire, using the test line. The processing conditions can be found in Tables 1 and 2.

Table 1 – Polyethylene Resin (Sentra 8030 HF)

Zone 1	Zone 2	Head
340 °F	390 °F	410 °F

Melt Temperature: 350 °F Head Pressure: 600 PSI

Table 2 – PVC Resin (GW 2038-A-VW1)

Zone 1	Zone 2	Head
330 °F	380 °F	400 °F

Melt Temperature: 340 °F Head Pressure: 700 PSI

The results of the processing showed, both polymers extruded smooth, there was no evidence of discoloration, and there was very little shrinkage (see Figure 9).

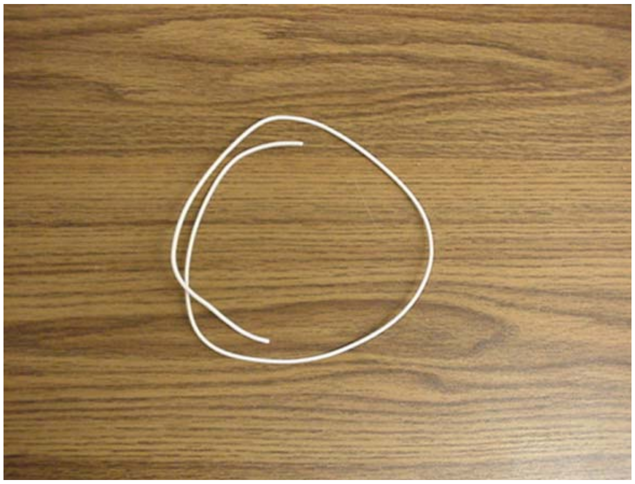


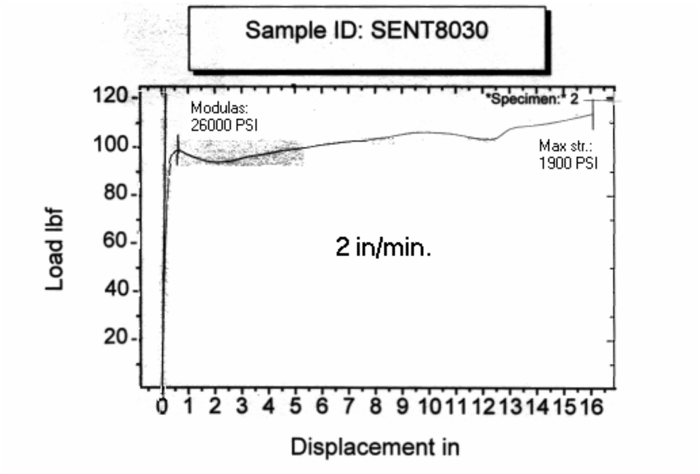
Figure 9 – Extruded Polymer

Test Results

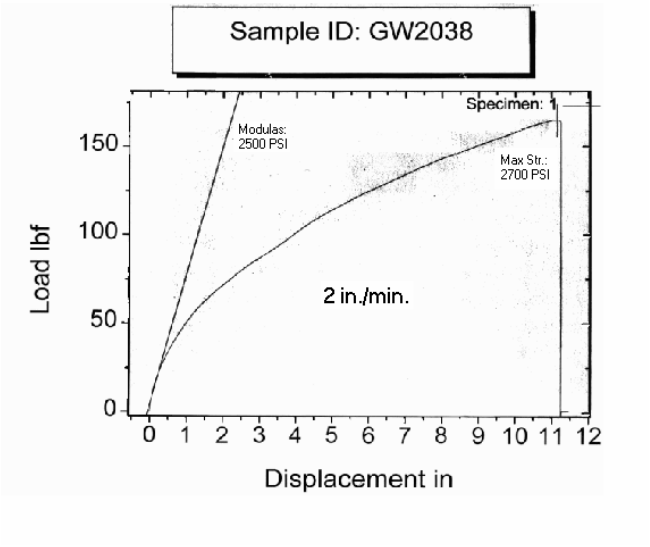
To find a practical solution to PVC additives in wire and cable, we must find substitutes that fulfill its physical, chemical, and processing needs. Tests were performed on the new resins to determine these characteristics.

Tensile Testing

Tensile testing is one of the most commonly used method of determining physical strength. An apparatus pulls on a bar made from the resin and records the force required. In this way hardness and ultimate strength are determined. The Graphs, 1 and 2 shows these results.



Graph 1



Graph 2

As you can see by the graphs, the polyethylene (PE)-based resin (Sentra) exhibited slightly lower ultimate tensile strength, but is harder.

Heat Resistance

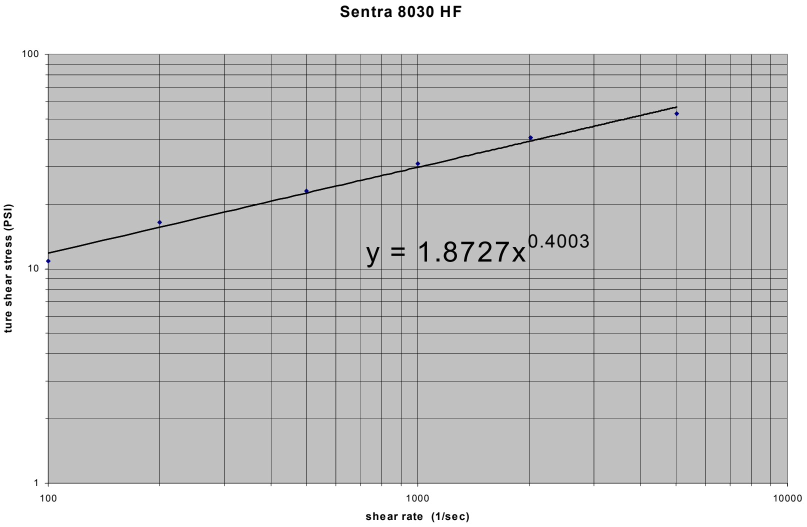
Heat resistance, is a key property of any cable used in a building application. The following chart shows the resins against the typical PVC.

Resin	Maximum Operational Temperature
Sentra 8030 HF	90 °C
GW 2038 A VW1	80 °C
Typical PVC with Pb stabilizer	80-105 °C

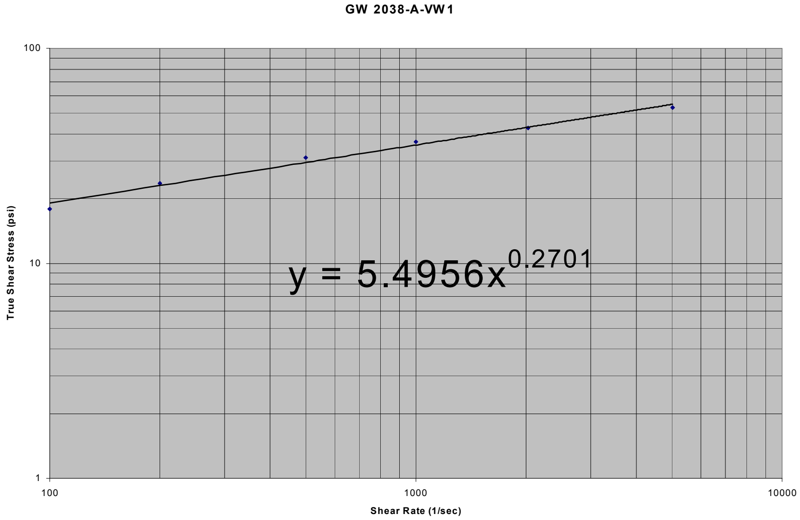
The operational temperature of the new resins falls into the same range as typical PVC.

Rheology

Rheology is the study of flow. In any processing application, optimizing the process requires that the rheology of the polymer is known. The most common rheology test is called capillary rheometry. The capillary rheometry test measures the viscosity of a polymer forced through a die at varying speeds. These results are shown in graph form. Both resins were tested in this manner and the results are shown in Graphs 3 and 4.



Graph 3 – Polyethylene resin



Graph 4 – PVC Resin with non-lead heat stabilizer

The two graphs show typical PVC and PE behavior. The power law index (the number that x is raised to) shows the elastic vs. liquid behavior; the closer to 1 the more liquid, the closer to zero the more elastic. The PVC has more of an elastic behavior, where PE shows more of a liquid behavior at these temperatures.

Price

Any discussion on practical substitutes of PVC would be remiss if it did not talk about price. The PVC blend with the non-halogenated flame retardant is slightly more expensive (by approximately 10-20%) than the traditional halogenated, lead-stabilized PVC formulation. The PE blend is twice as expensive. It must be kept in mind that these are new resin blends and the price may drop with increased demand.

Future Work

Over the last year only two formulations of halogenated PVC substitutes were explored. Over the next year more resins and formulations will be investigated. In this way we can determine the most suitable substitutes for halogenated PVC.

The testing of wire over the past year was done on a small wire line. This line allowed us to test processability of the wire on a short time scale. Industrial lines run for days. Running a line for days require that process issues that occur on a long time scale be explored. Long time scale issues include, time to change over, temperature stability, etc.

In order to test the long term processability, tests on a production line are necessary. Over the next year, with the help of a wire and cable company, tests will be run on a production line.