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A REVIEW OF VINYL TECHNOLOGY FOR NON-SCIENTISTS IN THE VINYL INDUSTRY

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ABSTRACT

PVC has a large sales volume, second only to polyethylene. Its high chlorine content provides it with a very high level of combustion resistance for building products, electrical enclosures, and wire & cable insulation. PVC has a unique ability to be compounded with a wide variety of additives, making it possible to produce materials in a range from flexible elastomers to rigid compounds, materials that are weatherable such as for siding and windows, compounds that have stiff melts and little elastic recovery for outstanding dimensional control useful in profile extrusion, or low viscosity melts which compete effectively with ABS and PC/ABS in thin walled injection molding parts such as computer monitor housings.

Some of PVC's properties are attributed to unique structures. The polymer precipitates from its monomer and grows into primary particles, which are later the melt flow units. Fusion into larger structures and product strength are controlled by break-down of the grains into primary particles, by the choice of additives, by the amount of melting (temperature), and by the number of tie molecules (molecular weight).

The main type of polymerization is the suspension process, with significant polymerization made by the mass process and emulsion process. In the suspension process, the polymerization takes place in droplets of monomer suspended in a water.

PVC is environmentally sound. With over 50% chlorine content, chlorine makes PVC one of the most energy efficient polymers, makes PVC inherently flame retardant, and acts as a marker, enabling automated equipment to sort PVC containers from other plastics in the waste stream. Analysis from 155 large-scale, commercial incinerator facilities, found no relationship between the chlorine content of waste nor the addition of PVC, and dioxin emissions from combustion processes. New requirements from the U.S. EPA make scrubbers mandatory on all incinerators and are necessary whether or not PVC is present in the waste feed.

INTRODUCTION

Poly(vinyl chloride) (PVC) has large and broad uses in commerce. It is second in volume only to polyethylene and had a volume sales in North America in 1995 of 6.2 billion kilograms (13.7 billion pounds) (1). See figure 1 for volumes of several thermoplastics. This large volume of sales can be attributed to several unique properties. Vinyl compounds usually contain close to 50% chlorine. Not only does the chlorine provide no fuel, it acts to inhibit combustion in the gas phase, providing the vinyl with a very high level of combustion resistance, useful in many building applications as well as many electrical housings and electrical insulation applications.

PVC has a unique ability to be compounded with a wide variety of additives, making it possible to produce materials in a range from flexible elastomers to rigid compounds, materials can be made that are virtually unbreakable, materials are made that are weatherable with good property retention for over 30 years, compounds that have stiff melts and little die swell for outstanding dimensional control in profile extrusion, or low viscosity melts for thin walled injection molding such as large monitor housings for the computer industry. Some of the breadth of PVC's applications are seen in table 1.

Figure 1. North American Sales - 1995

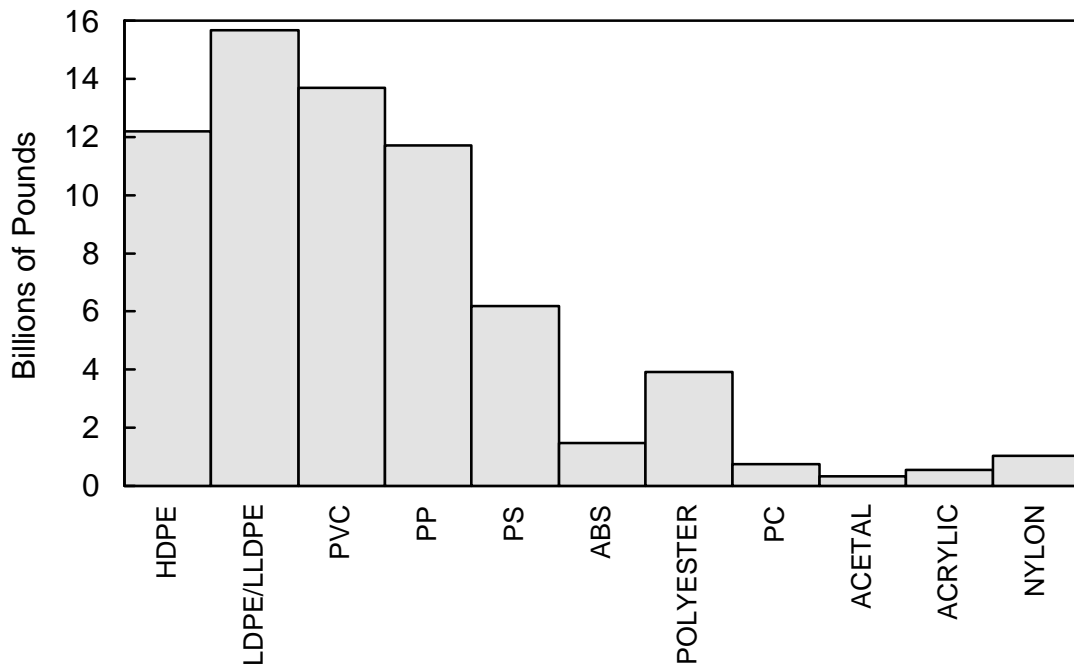
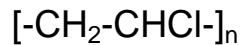


Table 1. PVC Applications.

<i>Rigid PVC Applications</i>	<i>Plasticized PVC Applications</i>
<p><i>Construction</i> water pipe & fittings sewer pipe and fittings drainage pipe bathroom tile siding, soffits, windows gutters & down spouts sprinkler systems electrical boxes, electrical conduit smoke alarms wood-like trim walls and roofing</p>	<p><i>Construction</i> window seals, window screens toilet flappers tile flooring, sheet flooring carpet backing and foam backing toilet seats wire fence coating electrical wire insulation cable sheathing wall-board trim, wall-bumper guards lawn edging</p>
<p><i>Packaging</i> bottles, blister packaging anti-static electronics packages</p>	<p><i>Packaging</i> meat wrap shrink wrap</p>
<p><i>Appliances and machines</i> electrical enclosures on washers, dryers, and dishwashers ice-makers thermostats electrical outlet boxes computer housings, printers satellite dishes</p>	<p><i>Appliances and machines</i> refrigerator door seals electrical wire insulation extension cords telephone cords hoses</p>
<p><i>Medical and safety</i> fittings filters solutions eyewash apparatus</p>	<p><i>Medical and safety</i> blood bags intravenous solutions, tubing oxygen masks and tents goggles, gloves, aprons</p>
<p><i>Automotive</i> glove boxes knobs</p>	<p><i>Automotive</i> dash boards, coated fabrics, handles electrical wire insulation floor mats, side panels steering wheels</p>
<p><i>Miscellaneous</i> desk edging book-binders furniture sea-walls signs light fixtures</p>	<p><i>Miscellaneous</i> artificial fishing worms lawn chairs room dividers briefcases, notebooks shoe soles, rainwear table cloths, shower curtains pond liners</p>

Produced by free radical polymerization, PVC has the following structure:



where the degree of polymerization, n , ranges from 500 to 3500.

The first discovery of PVC was in 1872 when E. Baumann found that exposure of vinyl chloride to sunlight produced a white solid powder and melted with degradation at above 130°C. (2, 3). From 1912 to 1926, German workers at Chemische Fabrik Griesheim-Electron tried but failed to build machinery that could process PVC and overcome its instability; finally they gave up their patents (3). In 1926, Waldo Semon at BFGoodrich, (the BFGoodrich Vinyl Division is now The Geon Company, an independent company), while looking for an adhesive to bond rubber to metal for tank liners, found that boiling PVC in tricresyl phosphate or dibutyl phthalate (now called plasticizers), made it highly elastic (3), thus he invented the first thermoplastic elastomer.

Even to this day, as in the early years of PVC, some tend to build sophisticated equipment to run simple compounds. For example, twin screw extruders process powder compound sized with vacuum calibrators, to make window profiles. And others tend to build sophisticated compounds to run on simple equipment. For example, single screw extruders process cubed compound (where flow units are established and die swell is low) making die design and vacuum sizing less complex, to make window profiles.

DISCUSSION

VINYL CHLORIDE MONOMER

Vinyl chloride is made from two abundant raw materials, ethylene and chlorine, in an oxychlorination process (4). The chemistry goes through an ethylene dichloride (EDC) intermediate step. The ethylene is manufactured from hydrocarbon feedstocks, paraffinic feedstocks, ethane, or gas oils, all coming from oil and gas (5). Less than 0.3% of the world's supply of gas and oil is used to make vinyl chloride (6).

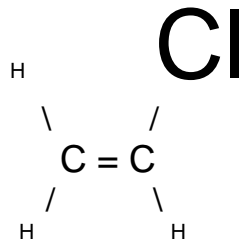
Chlorine is made from sodium chloride (table salt) by electrolysis. Both chlorine and caustic soda are products of this electrolysis reaction. Caustic soda is used in a wide variety of processes including aluminum manufacture, plastics manufacture, paper, petroleum processing, cleaners, and cotton & cellulose processing.

Beside vinyl chloride, chlorine is used in the manufacture of products for cosmetics, coatings, purifying water, making paper, swimming pool disinfectants,

agricultural crop protection, pharmaceuticals, polycarbonate, bullet proof glass, paints, carpet backing, shoe soles, glues, paint and white pigments for paint, sugar, corn syrup, rocket propellant, flame retardants, gasoline additives, and many other applications. About 34% of the world's production of chlorine goes to make vinyl chloride/PVC (7). PVC is a stable, safe place to use the chlorine. Because the use of chlorine and caustic soda must be balanced, it is necessary to make PVC in order to make all the products that use caustic.

Table 2 illustrates the balance of raw materials involved in making PVC and the low environmental impact of PVC.

Vinyl chloride monomer is a gas at standard temperatures and pressures but is normally used at higher pressures where it is a liquid. It has the chemical structure:

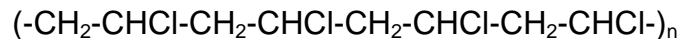


As illustrated, the hydrogen atoms are smaller than carbon atoms and the chlorine atom is larger.

POLYMERIZATION

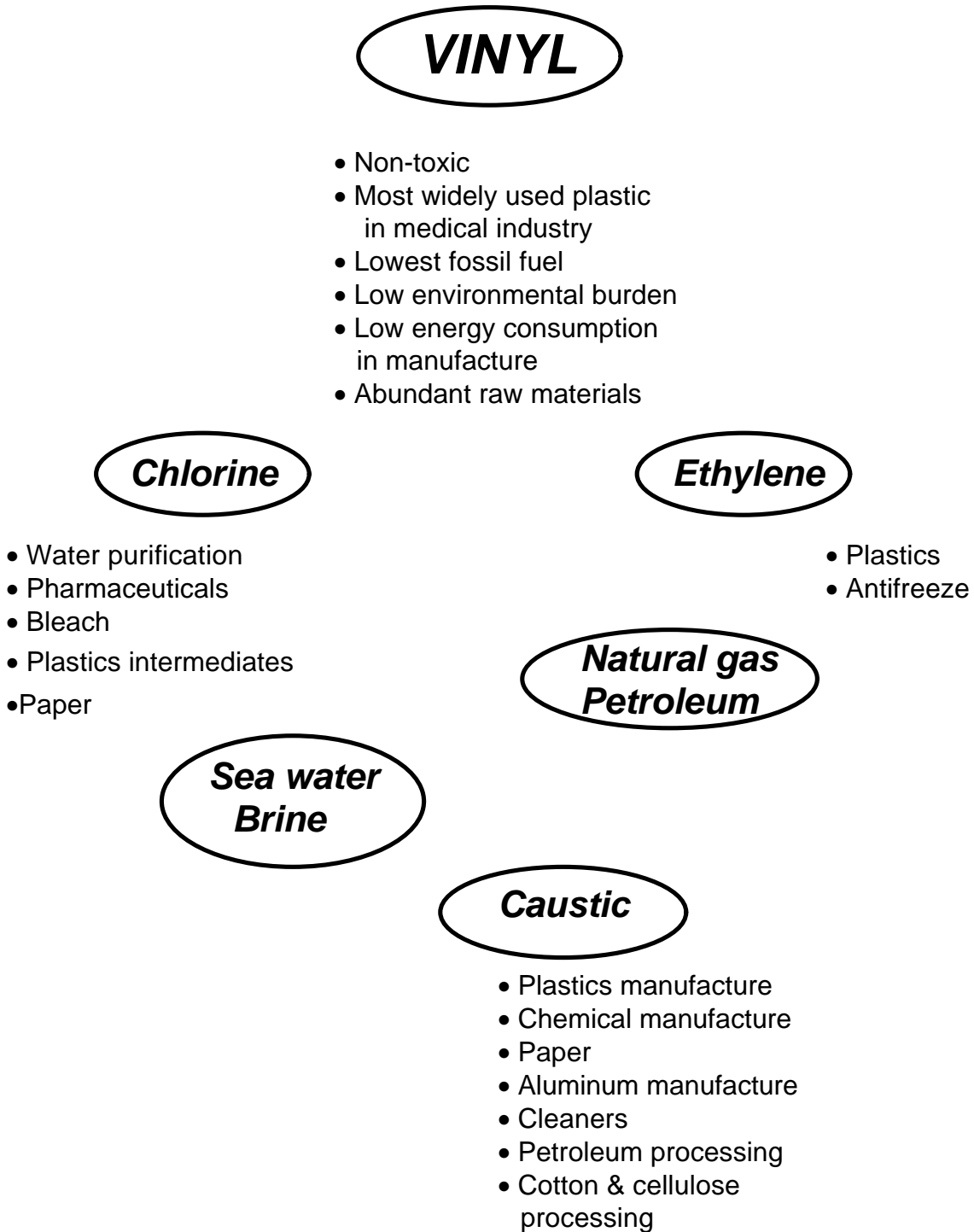
Molecular structure

The addition of vinyl monomer to a growing PVC chain results in a chlorine atom on every other carbon atom (8).



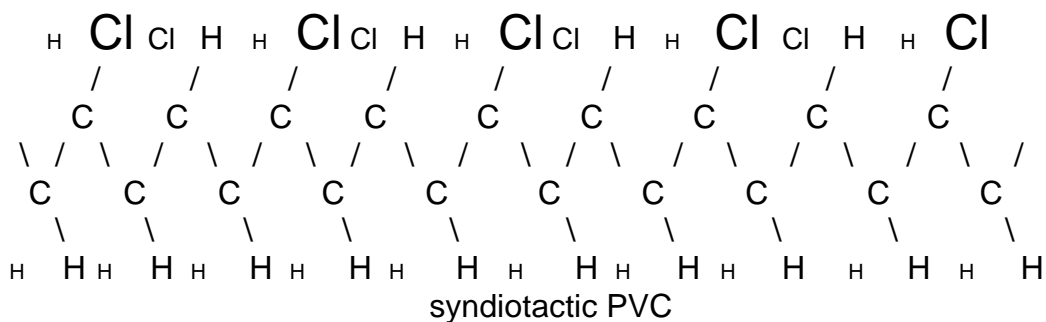
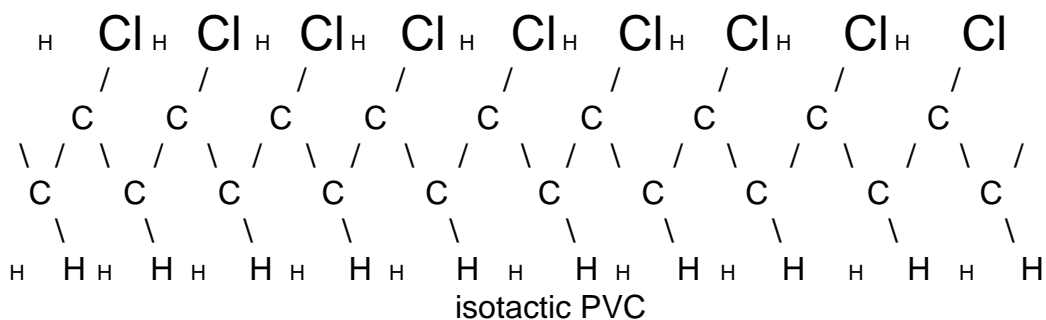
The repeated addition of monomer grows PVC to a long molecule of about 500 to 3500 monomer units (figure 2).

Table 2. Vinyl is an environmentally sound thermoplastic.



Stereoregularity

Stereoregularity refers to positions in space, similar to stereo music. When vinyl chloride monomer adds to a growing PVC chain, it can take two possible positions in space. Isotactic structure has the adjacent chlorine atoms oriented to same side of the carbon-carbon-carbon plane. Syndiotactic structure has the adjacent chlorine atoms oriented to opposite sides of the carbon-carbon-carbon plane. Atactic PVC is a mixture of the two orientations. Because syndiotactic PVC is able to crystallize, that is, pack together nearly perfectly, it is extremely important in understanding the properties of PVC as will be further discussed.



The formation of syndiotactic PVC is nearly random, the orientation nearly a coin toss. The probability of three consecutive monomer units being syndiotactic is about 25%; the probability of the first is 100%, it can be either side; the probability of two consecutive units is 50%; the probability of three consecutive units is 25% = 100% X 50% X 50%. Actually the coin toss is rigged slightly in favor of more syndiotactic structure at lower polymerization temperatures (9 - 12).

Morphology as polymerized

By morphology, we are referring to how all the physical structures of PVC fit together.

The major type of polymerization of PVC is the suspension polymerization route with a minor amount made by emulsion and mass polymerization. The morphology formed during polymerization strongly influences the processability and physical properties.

In the suspension polymerization of PVC, droplets of monomer 30 - 150 μm in diameter are dispersed in water by agitation, see figure 3. (One μm (micrometer) is one-millionth of a meter or 4/100,000 inch. A thin membrane formed at the water/monomer interface by dispersants is 0.01 - 0.02 μm thick and has been found to be a graft copolymer of polyvinyl chloride and the dispersant (13, 14). The membrane stabilizes the monomer droplets from excessive agglomeration to what would be called a solid charge. Early in the polymerization, particles of PVC deposit onto the membrane from both the monomer and the water sides forming a skin 0.5 - 5 μm thick that can be observed on grains sectioned after polymerization (13, 15). Primary particles, 1 μm diameter, deposit onto the membrane from the monomer side and water phase polymer, 0.1 μm diameter, deposits onto the skin from the water side of the membrane (13). These domain sized water phase particles may be one source of the observed domain structure (16).

Figure 3. Droplets of monomer dispersed in water.

For both suspension and mass polymerizations at less than two percent conversion, PVC precipitates from its monomer as stable primary particles, slightly below 1 μm diameter (13, 17 - 19), see figure 4. This insolubility of polymer in its monomer is a rarity in the polymer world and gives PVC some unique properties not possible with other polymers. Above two percent conversion, these primary particles agglomerate somewhat. Sectioning the PVC shows particles at 1 μm diameter, and agglomerates of primary particles at 3 - 10 μm diameter (13, 16, 20, 21), see figure 5.

Figure 4. Droplets of monomer at low conversion, showing precipitated PVC.

These primary particles also contain smaller internal structures. Electron microscopy reveals a domain structure at about 0.1 μm diameter (20, 22, 23). As mentioned earlier, PVC polymerized in the water phase and deposited on the skin, may be the source of some of the domain sized structures.

On an even smaller scale is the microdomain structure at 0.01 μm spacing. X-ray data reveals structure spaced at about 0.01 μm (24 - 26). This data suggests a structure where the crystallites (perfectly packed molecules of PVC) of about 0.01 μm spacing are tied together by molecules in the amorphous regions (randomly packed PVC molecules).

Hierarchical structure of PVC

As we have just discussed and will now review, PVC has structure which is built upon structure which is built upon even more structure. These many layers of structure are all important to performance and are inter-related. A summary of these structures is listed in table 2. Also figure 6 examines a model of these hierarchies on three scales.

Figure 5. A PVC suspension grain showing its formation from monomer droplets and a cross-section showing the skin and primary particles.

Grain
~ 150 μm dia.

Skin
~ 2 - 5 μm thick

Primary particles
~ 1 μm dia.

Cross-section

Table 2. Summary of polyvinyl chloride morphology.

<i>Feature</i>	<i>Size</i>	<i>Description</i>
Droplets	30 - 150 μm diameter	The dispersed monomer during suspension polymerization.
Membranes	0.01 - 0.02 μm thick	The membrane at the monomer-water interface in suspension PVC. It is usually a graft copolymer of PVC and the dispersant such as polyvinyl alcohol.
Grains	100 - 200 μm diameter	After polymerization, the free flowing powder that is usually made up of agglomerated droplets. There is about a billion grains in 10 pounds of PVC resin. A grain is made of about a million primary particles.
Skins	0.5 - 5 μm thick	The shell on grains made up of PVC deposited onto the membrane during suspension polymerization. In mass polymerization it is PVC compacted on the surface of the grain.
Primary particles	1 μm diameter	Formed as a single polymerization site in both suspension and mass polymerization by precipitation of polymer from the monomer. Made up of a billion molecules, it is often the melt flow unit established during melt processing. In emulsion polymerization it is the emulsion particle.
Agglomerates of primary particles	3 - 10 μm diameter	Formed during polymerization by the merging of primary particles.
Domains	0.1 μm diameter	Formed under special conditions such as high temperature melting at 205°C followed by lower temperature mechanical work at 140 - 150°C. Water phase polymerization also produces domain sized structure.
Microdomains	0.01 μm spacing	Crystallite spacing.
Secondary crystallinity	0.01 μm spacing	Crystallinity that is re-formed from the amorphous melt and is responsible for fusion (gelation).

Figure 6. The hierarchical structure of PVC.

Morphology during processing

The first step in processing is usually powder mixing in a high speed, intensive mixer. PVC resin, stabilizers, lubricants, processing aids, fillers, and pigments are added to the powder blend for distributive mixing. For both suspension and mass PVC resins, intensive mixing results in a progressive increase in apparent bulk density with higher mixing temperatures (27). This increase in apparent bulk density is due to the smoothing and rounding of the irregular surface. However the grains of PVC are largely unchanged and are not grossly deformed nor are they broken down to smaller particles (27).

PVC powder compounds are heated, sheared, and deformed during melt processing. Pure shear is work done on a melted PVC compound, in the gap between two metal surfaces, where one of the metal surfaces moves past the other. During this process, the grains of PVC are broken down. First the skin is torn, exposing the PVC grain's internal structures (28). Then the grains are broken down to agglomerates of primary particles, then to primary particles as the melt flow units. The primary particles seem to be persistent and fairly stable structures in the melt (29 - 36). This processing window of stable primary particles exists even with continued melt processing. The primary particle is about a billion molecules of PVC held together by a structure of crystallites and tie molecules (37).

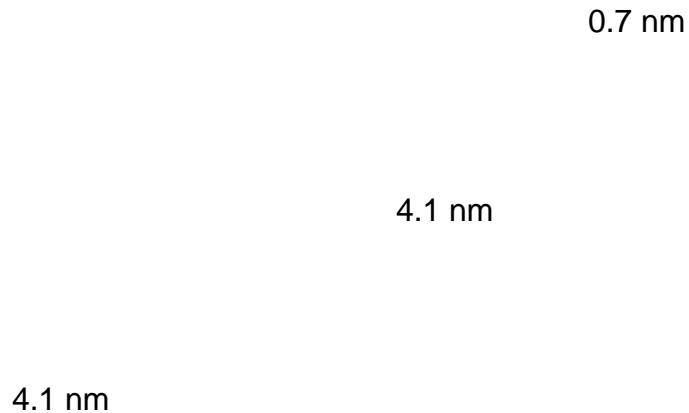
Crystallites are small crystals. A crystalline structure is one where the molecules are shaped so they are packed very tightly, nearly perfectly, like spoons in their tray, as differentiated from spoons, knives, and forks all thrown in a drawer. In polymers, crystals prevent polymer molecules from slipping by each other and act to tightly bind the molecules together. It takes a high level of melting energy to destroy the crystal and allow a PVC molecule to flow.

The PVC crystallites are small (average 0.7 nm = 3 monomer units) in the PVC chain direction, and are packed laterally to a somewhat greater extent (4.1 nm) (37, 38). One nanometer (nm) is one-billionth of a meter or 4/100,000,000 of an inch. A model of the crystallite is drawn in figure 7. The crystalline structure of PVC is made of syndiotactic structures (39 - 42). The crystals are small and imperfect when compared to other polymers, and they have a broad melting range from 120 - 250°C. (250 - 480°F). PVC is processed in a range where some PVC crystallites never melt.

PVC fusion (gelation)

The PVC primary particle flow units (billion molecule bundles) can partially melt, free some molecules of PVC, which can entangle at the flow unit boundary. These entangled molecules can recrystallize upon cooling, forming

Figure 7. The crystallite structure of PVC.



secondary crystallites, and tie the flow units together into a large three dimensional structure (37, 43). This process is known as fusion or gelation.

The strength created by the fusion process is strongly dependent on the previous processing temperature and the molecular weight of the PVC (43 - 49). The strength of this large three dimensional fused (gelled) structure has been shown to be critical in determining Izod impact (see figures 8, 9), creep rupture strength (see figures 10, 11), and even flow in injection molding. Izod impact is the energy required to break a sharply notched PVC bar, held in a clamp and hit with a swinging pendulum weight. Creep rupture strength measures the maximum load that can be carried by a certain sized PVC specimen for a period of time. As with steel and other materials, PVC will eventually stretch and break, unless the part design is thick enough (such as pipe wall thickness) to carry the load for the desired lifetime. In these cases both the melt temperature during processing and the PVC molecular weight play a large role in the Izod and creep rupture (43 - 46). A model accounting for molecular weight effects and processing temperature effects on PVC fusion is presented in figure 12.

Figure 8. Izod (energy to break) dependence on PVC molecular weight.

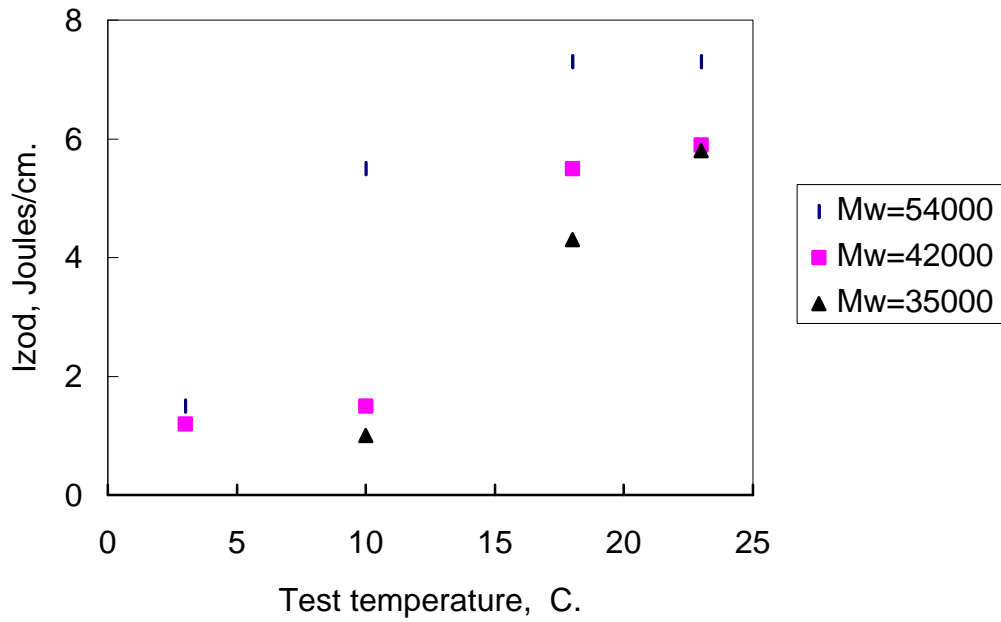


Figure 9. Izod (energy to break) dependence on PVC processing temperature.

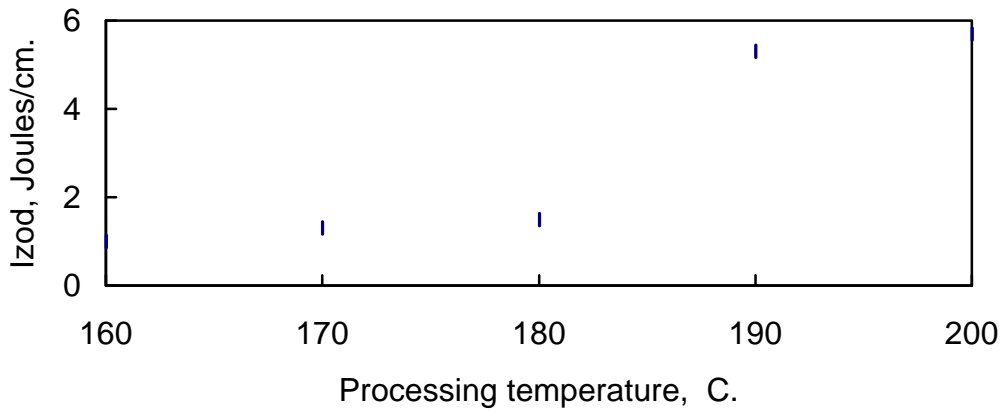


Figure 10. Creep rupture stress (load per area) dependence on PVC molecular weight.

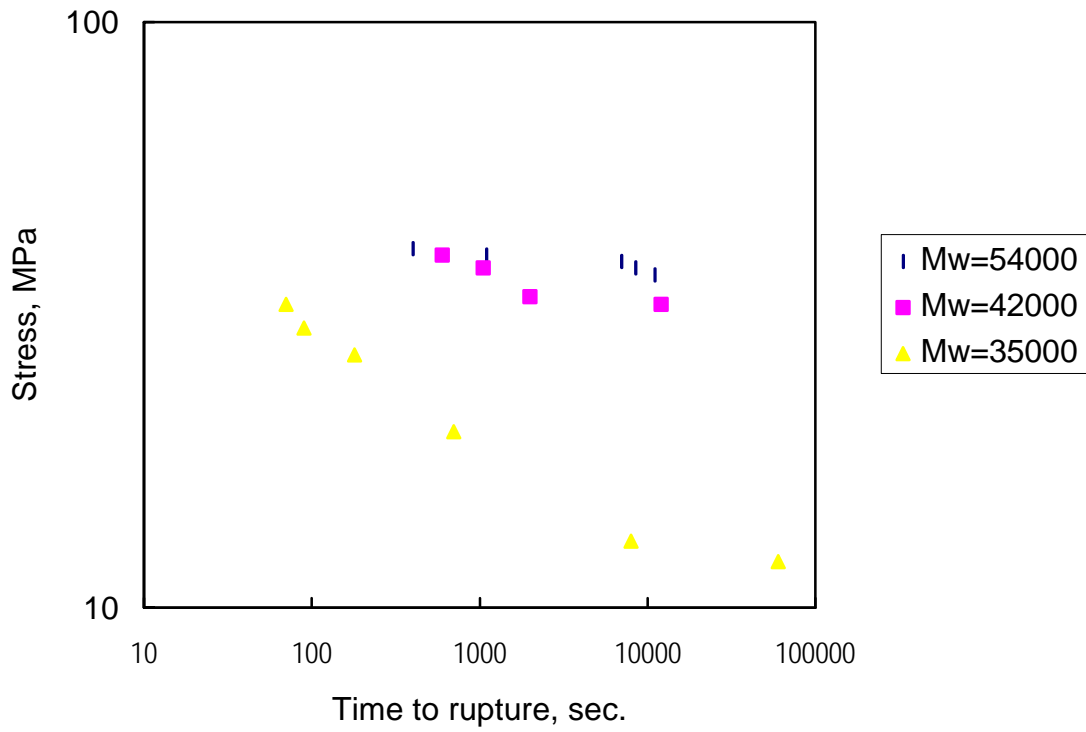


Figure 11. Creep rupture stress (load per area) (at 50°C) dependence on PVC processing temperature (ref. 47).

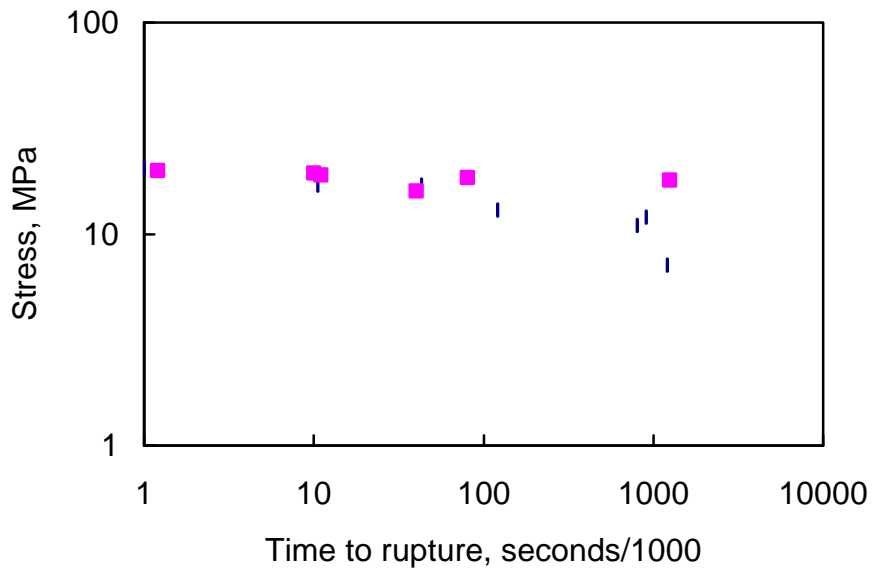


Figure 12. Model for PVC fusion, accounting for molecular weight effects and processing temperature effects.

a) Unfused PVC primary particles.

b) Partially melted PVC primary particles.

c) Partially melted then recrystallized high molecular weight PVC, showing strong three dimensional structure.

d) Partially melted then recrystallized low molecular weight PVC, showing weak three dimensional structure.

Plasticized PVC Morphology

While most of the discussion has been on rigid PVC, plasticized PVC has the same structures as rigid PVC, except that plasticizer enters the amorphous phase of PVC making the tie molecules elastomeric. The grains break down to 1 μm primary particles which become the melt flow units (49). The crystallites are not destroyed by plasticizer (37). Partial melting allows entanglement at the flow unit boundaries, followed by recrystallization upon cooling to form a strong three dimensional structure (43, 50) held together by crystallites and elastomeric tie molecules.

PVC's glass transition temperature, T_g.

Rigid PVC has a glass transition temperature, T_g, of about 80°C (180°F). That means that it softens from a hard, glassy material to a softer, rubbery material at about 80°C. Molecules pack together (not as perfectly as crystals) and are not mobile at room temperature, making the PVC hard or glassy. As the temperature increases, the molecules vibrate more. The vibrations separate the molecules, making them more mobile. At 80°C vibrations are sufficient to separate the molecules enough that they can readily move past each other, thereby making them soft and rubbery.

Plasticizer is soluble in PVC and separates the molecules, it lowers T_g from 80°C to below room temperature, if enough plasticizer is added, thus making a flexible, elastomeric PVC at room temperature.

PVC molecular weight measurements

PVC molecular weights are usually determined in the USA using inherent viscosity (IV) measured according to ASTM D1243, 0.2 grams/100 ml of cyclohexanone at 30°C. Sometimes in scientific literature, "IV" means intrinsic viscosity, an extrapolation of inherent viscosity at several concentrations of PVC to a value at zero concentration. Intrinsic viscosity is seldom used commercially, rather inherent viscosity (IV) measured at a low PVC concentration is used. In Europe, K values are used, measured at 1% in cyclohexanone. The relationship between inherent viscosity, K value, number average molecular weight (M_n), and weight average molecular weight (M_w) for commercial grades of PVC are shown in table 3 (51).

Table 3. Quick reference for commercial PVC molecular weights.

Inherent viscosity ASTM D1234	K value 1% in cyclohexanone	Number average molecular weight M_n ($\times 10^{-3}$)	Weight average molecular weight M_w ($\times 10^{-3}$)
0.42	45	15.0	30.0
0.47	48	18.0	36.0
0.52	50	20.0	40.0
0.57	53	22.5	45.0
0.62	55	25.0	50.0
0.67	57	27.5	55.0
0.73	59	30.5	61.0
0.78	61	33.0	67.0
0.83	63	36.0	72.0
0.88	65	38.5	78.0
0.92	67	41.0	82.5
0.98	69	44.0	89.5
1.03	70	47.0	95.0
1.08	72	50.0	101.0
1.13	74	52.5	107.5
1.21	76	57.0	117.0
1.30	79	62.5	128.5
1.40	82	68.5	141.0
1.60	87	81.0	168.0
1.80	92	93.5	195.0

ENVIRONMENTAL CONSIDERATIONS AND RECYCLING (ref. 52, 53)

Any use of chlorine, including its use in PVC, has been attacked by some environmental groups who would shut down many industries, regardless of their benefits and regardless of whether there was no environmental harm. The usual attack accuses dioxin formation.

Chlorine, the material used to make PVC

Organochlorines (including dioxins and furans) are produced from burning wood and other vegetable matter, and are natural by-products of forest fires (54, 55). Chlorine-based chemicals are everywhere, and have been so since before the existence of man. Both dioxins and furans have been found in lake sediments dating back to 1860 (56) and samples taken from ice cores in Greenland dating back to 1869 show definite chlorine content (57). Given the fact that chlorine compounds are naturally produced in such vast quantities, and so widely distributed in the natural world, banning production of chlorine to keep chlorine compounds out of the environment would be futile, extremely costly,

and would deprive the world of hundreds of products critical to society's health and well-being. And the environment would be worse off.

Over 30% of the chlorine produced on a global basis goes to make PVC. Not only is chlorine essential to the chemical composition of PVC, it provides a number of unique properties that give this versatile plastic a distinct advantage in product applications and the marketplace. It makes PVC inherently flame retardant. PVC is the world's leading electrical insulation material. PVC is over 50% chlorine and as a result, is one of the most energy efficient polymers. In addition, recycling PVC is easier because the chlorine in PVC acts as a marker, enabling automated equipment to sort PVC containers from other plastics in the waste stream (58).

Vinyl Solid Waste and Recycling

Although vinyl is the world's second most widely used plastic, less than one-half percent by weight is found in the municipal solid waste stream because most vinyl applications are long-term uses, such as pipe and house siding, that are not disposed of quickly.

About 6.5 million pounds of post-consumer vinyl were recycled in the U.S. in 1994 and an additional 300 million pounds of vinyl post industrial scrap was diverted from landfills and recycled. Also high technology landfills are often lined with thick-gauge vinyl and use vinyl pipe to handle liquid leachate and methane gas, to protect the environment.

Incinerating PVC Wastes

A recent study sponsored by the American Society of Mechanical Engineers (ASME), involving the analysis of over 1,700 test results from 155 large-scale, commercial incinerator facilities throughout the world, found no relationship between the chlorine content of waste and dioxin emissions from combustion processes. Instead, the study stated, the scientific literature is clear that the operating conditions of combustors are the critical factor in dioxin generation (59). This work includes and confirms a number of other studies, most notably, the work conducted in 1987 by the New York Energy Research and Development Authority. Those tests revealed that the presence or absence of PVC had no effect on the amount of dioxin produced during the incineration process (60).

Incinerator scrubbing systems can remove about 99 percent of the hydrogen chloride generated by incinerating vinyl plastics and other chlorine-containing compounds and materials (61). New requirements from the U.S. Environmental Protection Agency make scrubbers mandatory on all incinerators so that they can neutralize a range of acid gases, including sulfur

dioxide and nitrogen oxide, which are produced by a variety of materials. Since acid generated in incinerators comes from a variety of sources including such things as table salt and paper products, scrubbers are necessary whether or not PVC is present in the waste feed (62).

Municipal incinerators are often targeted as a primary cause of acid rain. In fact, power plants burning fossil fuels, which produce sulfur dioxide and nitrogen oxide, are actually the leading cause of acid rain, along with automotive exhaust (63, 64). In Europe and Japan, studies show that only about 0.02 percent of all acid rain can be traced to incineration of PVC (65).

Some municipalities in Germany have restricted the use of certain vinyl products in municipally funded building projects. Industry is working to change those restrictions with several notable reversals, including Berlin and Bielefeld. Government studies on PVC in Belgium and The Netherlands concluded there should be no bias against the use of PVC (66 - 68).

In a fire, vinyl is not unusually hazardous and damaging

The real hazards in a fire are carbon monoxide and heat; these are especially a problem with other materials that readily burn. Because vinyl products contain chlorine, they are inherently flame-retardant and resist ignition. When it does burn, however, vinyl produces carbon monoxide, carbon dioxide and hydrogen chloride. Virtually all burning materials produce carbon monoxide, which is by far considered the greatest toxic hazard in fires because of the abundant levels produced and the low levels that cause death (69). Hydrogen chloride is an irritant. Research indicates that lethal levels of hydrogen chloride are never reached or even approached in real fires. In a typical fire, hydrogen chloride levels rarely exceed 300 ppm, a fact confirmed by the Boston Fire Department and Harvard University (70). In hundreds of autopsies conducted on fire victims in the U.S., not one death has been linked to the presence of PVC.

Bell Laboratories studied wire and cable compounds made of PVC or other halogen-based compounds vs. halogen-free compounds and found that neither type of material presented a clear-cut advantage in a fire, and that the halogenated compounds sometimes outperformed the nonhalogenated products in terms of creating less corrosion (71).

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REFERENCES

1. *Modern Plastics*, **7**, No. 1, 70 - 78 (1996).
2. E. Baumann, *Ann.*, **163**, 308 (1872).
3. *Chemical & Engineering News*, **62** No. 25, 38 (1984).
4. *Hydrocarbon Processing*, **74**, No.3, 148 (1995).
5. *Hydrocarbon Processing*, **74**, No.3, 116 - 122 (1995).
6. *On Geon, Environmental Newsletter*, The Geon Company, **Issue 18**, December (1994).
7. B. Hileman, J.R. Long, E.M. Kirschner, *Chem. & Engr. News*, **72**, **NO.47**, 12 (1994).
8. C.S. Marvel, J.H. Sample, M.F. Roy, *J. Am. Chem. Soc.*, **61**, 3241 (1939).
9. J.W.L. Fordham, *J. Polym. Sci.*, **39**, 321 (1959).
10. Y.V. Glazkovskii, Y.G. Papulov, *Vysokomol Soedin.*, **A10**, 492 (1968).
11. H. Germar, K.H. Hellwege, K. Johnson, *Makromol. Chem.*, **60**, 106 (1963).
12. O.C. Bockman, *British Plastics*, **June**, 364 (1965).
13. J.A. Davidson, D.E. Witenhafer, *J. Polym. Sci.: Polym. Phys. Ed.*, **18**, 51 (1980).
14. R. Tregan, A. Bonnemayre, *Rev. Plast. Mod.*, **23**, 7 (1970).
15. J.W. Summers, E.B. Rabinovitch, *J. Macromol. Sci. - Phys.*, **B29** No.2, 219 (1981).
16. J.W. Summers, *J. Vinyl Technol.*, **2** No.1, 2 (1980).
17. N.D. Bort, V.G. Marinin, A.Y. Kalinin, V.A. Kargin, *Vysokomol. Soedin.*, **10**, 2574 (1968).
18. G. Palma, G. Talamini, M. Tavan, M. Carezza, *J. Polym. Sci. - Phys.*, **15**, 1537 (1977).
19. M. Carezza, G. Palma, G. Talamini, M. Tavan, *J. Macromol. Sci. - Chem.* **A11**, 1235 (1977).
20. G.R. Johnson, *SPE Technical Papers*, **XXVI**, 379 (1995).
21. F.R. Kulas, N.P. Thorshang, *J. Appl. Polym. Sci.*, **23**, 1781 (1979).
22. P.H. Geil, *J. Macromol. Sci. - Chem.*, **A11**, 1271 (1977).
23. G. Menges, N. Berndtsen, *Kunststoffe*, **66 (1966)** **11**, 9 (1976).
24. C.J. Singleton, T. Stephenson, J. Isner, P.H. Geil, E.A. Collins, *J. Macromol. Sci. - Phys.*, **B14**, 29 (1977).
25. W. Wenig, *J. Polym. Sci. - Phys.*, **16**, 1635 (1978).

26. D.J. Blundell, *Polymer*, **20**, 934 (1979).
27. E.M. Katchy, *J. Appl. Polym. Sci.*, **28**, 1847 (1983).
28. E.B. Rabinovitch, *J. Vinyl Technol.*, **4**, No.2, 62 (1982).
29. F.R. Kulas, N.P. Thorshaug, *J. Appl. Polym. Sci.*, **23**, 1781 (1979).
30. H. Munstedt, *J. Macromol. Sci. - Phys.*, **B14**, 195 (1977).
31. P.G. Faulkner, *J. Macromol. Sci. - Phys.*, **B11**, 251 (1975).
32. A.R. Berens, V.L. Folt, *Polym. Engr. Sci.*, **8**, 5 (1968).
33. A.R. Berens, V.L. Folt, *Trans. Soc. Rheol.*, **11**, No.1, 95 (1967).
34. E.B. Rabinovitch, J.W. Summers, *J. Vinyl Technol.*, **2**, No.3, 165 (1980).
35. G. Menges, N. Berndtsen, *Kunststoffe*, **66**, No.11, 9 (1976).
36. C. Singleton, J. Isner, D.M. Gezovich, P.K.C. Tsou, P.H. Geil, E.A. Collins, *Polym. Engr. Sci.*, **14**, 371 (1974).
37. J.W. Summers, *J. Vinyl Technol.*, **3** No.2, 107 (1981).
38. W. Wenig, *J. Polym. Sci. - Phys.*, **16**, 1635 (1978).
39. G. Natta, P. Corradini, *J. Polym. Sci.*, **20**, 251 (1956).
40. G. Natta, I.W. Gassi, P. Corradini, *Rend. Accad. Naz. Lincei.*, **31** (1.2), 1 (1961).
41. A. Nakajima, S. Hayashi, *Kolloid Z. U. A. Polymere*, **229**, No.1, 12 (1969).
42. C.E. Wilkes, V.L. Folt, S. Krimm, *Macromolecules*, **6**, No.2, 235 (1973).
43. J.W. Summers, E.B. Rabinovitch, *J. Vinyl Technol.*, **13**, No.1, 54 (1991).
44. L.G. Shaw, A.R. DiLuciano, *J. Vinyl Technol.*, **5**, 100 (1983).
45. D.E. Marshall, R.P. Higgs, O.P. Obande, *Plast. & Rubber Process Applications*, **3**, 353 (1983).
46. P.J.F. VanderHeuval, *5th Int. Conf. Plastics Pipes*, Paper 20, (1982).
47. P. Benjamin, *J. Vinyl Technol.*, **2**, 254 (1980).
48. K.V. Gotham, M.J. Hitch, *The British Polym. J.*, **10**, 47 (1978).
49. T.F. Chapman, J.D. Isner, J.W. Summers, *J. Vinyl Technol.*, **1**, No.3, 131 (1979).
50. J.W. Summers, E.B. Rabinovitch, P.C. Booth, *J. Vinyl Technol.*, **8**, No.1, 2 (1986).
51. D.E. Skillicorn, G.A. Perkins, A. Slark, J.V. Dawkins, *J. Vinyl Technol.*, **15**, No.2, 105 (1993).
52. The Vinyl Institute, a Division of The Society of the Plastics Industry, Inc., 65 Madison Avenue, Morristown, NJ 07960.
53. D. Wisner, The Geon Company, One Geon Center, Avon Lake, OH 44012.
54. R. Clement, C. Tashiro, *Abstracts, Dioxin*, '91, S34 (1991).
55. G. Mariani, *Chemosphere*, **24**, No.11, 1545 (1992).
56. R.M. Smith, et. al., *Chemosphere*, **25**, 95 (1992).
57. P.A. Mayewski, *Science*, "... South Greenland Icecore", **May** (1986)
58. J.W. Summers, B.K. Mikofalvy, S. Little, *J. Vinyl Technol.*, **12**, No.3, 161 (1990).
59. *The Relationship Between Chlorine In Waste Streams and Dioxin Emissions From Combustors*, The American Society of Mechanical Engineers, Draft January 6, (1995).

60. *Results of the Combustion and Emissions Research Project at the Vicon Incinerator Facility in Pittsfield, Massachusetts, prepared by Midwest Research Institute for the New York State Energy Research and Development Authority, Final Report*, June (1987).
61. *Air Emission Tests at Commerce Refuse to Energy Facility, May 26 - June 5, 1987, Vol. I, test results*, ESA 20522 449, Energy Systems Associates, Pittsburgh, PA, (July 1987).
62. K.L. Churney, A.E. Ledford, S.S. Bruce and E.S. Domalski, National Bureau of Standards, Gaithersburg, Maryland, *The Chlorine Content of Municipal Solid Waste from Baltimore County, Maryland and Brooklyn, New York*, (NBSIR 85-3213), April (1985).
63. "PVC is a Good Bet to Survive Its Global Environmental Travails", *Modern Plastics*, June (1990).
64. R.S. Magee, "Plastics in Municipal Solid Waste Incineration: A Literature Study", Hazardous Substance Management Research Center, New Jersey Institute of Technology.
65. P. Lightowlers and J.N. Cape, "Does PVC Waste Incineration Contribute to Acid Rain?", *Chemistry and Industry*, June (1987).
66. *Chemical Week*, Europe/Mideast News, December 14 (1994).
67. *Persbericht*, Nederlandse Federatie voor Kunststoffen, page vv, June 25 (1993).
68. *Executive Newsline*, page 2, December 26 (1995).
69. G.L. Nelson, D.V. Canfield, J.B. Larsen, "Carbon Monoxide--Study of Toxicity in Man." *11th Int. Conf. on Fire Safety*, San Francisco, CA, January 13-17, (1986).
70. W.A. Burgess, R.D. Treitman, A. Gold, "Air Contaminants in Structural Firefighting," Harvard School of Public Health, NFPCA Grant 7X008, (1979).
71. P.R. Dickinson, "Evolving Fire Retardant Materials Issues: A Cable Manufacturer's Perspective," *Fire Technology*, November (1992).