3

PVC ADDITIVES

PVC formulations include a large number of additives performing essential functions during their processing and regulating performance properties of final products. In the separate sections of this chapter, various groups of additives are briefly discussed to show their significant types, average concentrations, reasons for addition, most essential properties, and their essential mechanisms of action.

Only the most synthetic description of additives is possible, considering that many groups of additives require an entire book to discuss them in sufficient detail. If such monographic sources are available, they are referenced in the sections below.

3.1 PLASTICIZERS

Plasticizers are the most voluminous additives of semi-rigid and flexible PVC formulations. Their properties, mechanisms of action, and effect on properties of plasticized materials have been extensively discussed in a specialized monographic source,[1] and data on different grades are included in the plasticizer database.[2]

Table 3.1 gives the types of plasticizers most frequently used in PVC, the reasons for addition, their typical range of properties, concentrations employed, and applications in different products.

Table 3.1. PVC main plasticizers.

Types: *Phthalates*: benzyl butyl, di-(2-ethylhexyl), di(2-propylheptyl), di-911, dibutyl, didecyl, diisodecyl, diisohexyl, diisononyl, diisoundecyl, di-n-hexyl, diisotridecyl, diundecyl *Low temperature and other general plasticizers*: di-(2-ethylhexyl) adipate, dihexyl adipate, diisodecyl adipate, dihexyl azelate, acetyltributyl citrate, n-butyryl tri-n-hexyl citrate, 2-ethylhexyl benzoate, diethylene glycol dibenzoate, dipropylene glycol dibenzoate, triethylene glycol dibenzoate, isodecyl benzoate, di-isononyl cyclohexane-1,2-dicarboxylate, di-(2-ethylhexyl) sebacate, di-(2-ethylhexyl) trimellitate, N-aklyl pyrrolidone-based, tri-(2-ethylhexyl) trimellitate, pentadecyl phenol sulfonate (Mesamoll) *Flame retardant*: 2-ethylhexyl diphenyl phosphate, chloroparaffins, di-(2-ethylhexyl) tetrabromophthalate, di-(2-ethylhexyl) tetrachlorophthalate, isopropylphenyl diphenyl phosphate, octyl diphenyl phosphate, tetraphenyl neopentylglycol diphosphate, tricresyl phosphate, tris-2-ethylhexyl phosphate *Polymeric*: ethylene interpolymers (Evaloy), propanediol-based polyesters, nitrile rubber, polyol ester from food-approved sources, and other polymers blended with PVC

Table 3.1. PVC main plasticizers.

Applications: appliances, automotive underbody sealants and upholstery, awnings, blood bags, coated fabrics, films, flexible hoses, floor tiles, food packaging, food wrap, geomembranes, glazing compounds, gloves, inflatable warehouses and sport facilities, ion-selective membranes, laminated glass, laminating films, liners, luggage, medical containers, packaging, rainwear, roofing membranes, sheet flooring, shower curtains, table cloth, tarpaulins, toys, upholstery, wallcoverings, wire & cable		
Reasons for use: improve compatibility with other additives and polymers, improve flame resistance, improve low-temperature performance, increase chain mobility, increase filler loading, increase flexibility and elongation, influence blood compatibility, lower glass transition temperature, lower viscosity, lower processing, gelation and fusion temperatures, modify foaming rate and microcellular structure		
Potential adverse effects: affect color, affect outdoor performance, affect toxicity of products, decrease chemical resistance, decrease flame resistance, decrease fog resistance, decrease stain resistance, increase coefficient of friction, increase gas permeability, increase porosity, increase price, increase smoke generation, increase surface tack, lower scratch resistance, lower tensile strength & modulus, lower wear resistance		
Typical concentrations: 5 to 180 phr		
Molecular weight: 178-13,500	Melting point, °C: –83 to –49	Boiling point, °C: 208-523
Refractive index (20°C): 1.43-1.58	Density (20°C), kg/m^3: 848-1400	Viscosity (20°C), mPas: 1.2-36,000
Volume resistivity, Ω-cm: 3x10^6-1x10^{15}		Surface tension, mN/m: 24-45.2
Maximum exposure concentration, NIOSH-IDLH, ppm: 30-5,000		LD$_{50}$ oral rat, mg/kg: 2330-64,000

The above table shows that a large number of products manufactured from PVC require plasticizers. The table also indicates that there is a large variety of plasticizers (the *Plasticizers Database*[2] contains 1475 plasticizers). The data ranges of properties included at the end of Table 3.1 show that there is a variety of choices to fulfill requirements, but the section "Potential adverse effects" also shows that not very well thought-out plasticizer selection may affect the properties of the end product.

Below, some general rules governing plasticizer properties are discussed.

Using the example of di-alkyl adipates, Figure 3.1 (projection X-Y) shows that their molecular dimensions increase with the chain length of alcohol increasing.[3] Figure 3.2 shows different projections of plasticizer molecule which show that these molecules are not symmetrical. Projection Y-Z shows that the molecular size of plasticizer is actually decreasing with the number of carbon atoms in alcohol increasing. There is not much increase in size for the X-Y projection. It should be noted that the data are for plasticizers made out of linear alcohols. If alcohols have branches, their dimensions are affected. This behavior has implications on some properties of plasticizers. The diffusion coefficient is one of them (Figure 3.3). Diffusion coefficient increases with temperature and decreasing number of carbon atoms. It should be noted that the lower the number of carbon atoms, the more rapid the increase in diffusion coefficient caused by temperature increase. At the process temperatures, low molecular weight plasticizers are lost much faster

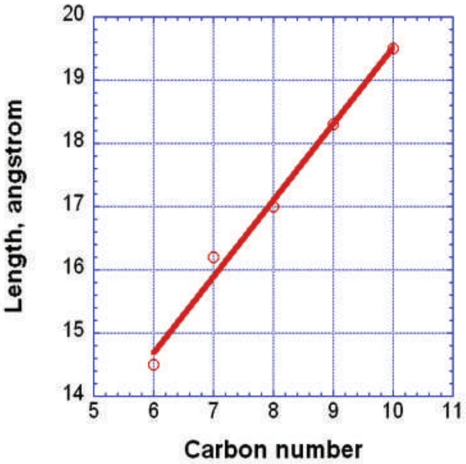

Figure 3.1. Length of dialkyl adipates vs. carbon number of their alcohols. [Data from Coughlin, C. S.; Mauritz, K. A.; Storey, R. F., *Macromolecules*, **24**, 2113-2116, 1991.]

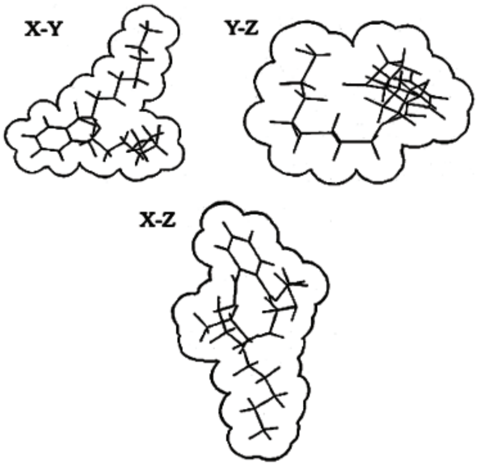

Figure 3.2. Projections of di-n-octyl phthalate molecule on different planes as labelled. Minimum energy conformation was calculated. [Adapted, by permission, from Coughlin, C. S.; Mauritz, K. A.; Storey R. F., *Macromolecules*, **23**, 3187-31-92, 1990.]

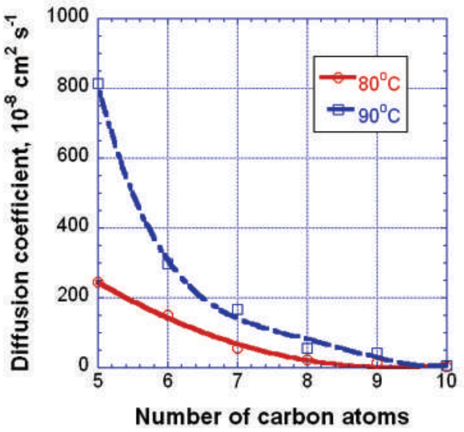

Figure 3.3 Diffusion coefficient of various phthalates having different number of carbon atoms in their alcohol segment. [Data from Storey, R. F.; Mauritz, K. A.; Cox, B. D., *Macromolecules*, **22**, 289-294, 1989.]

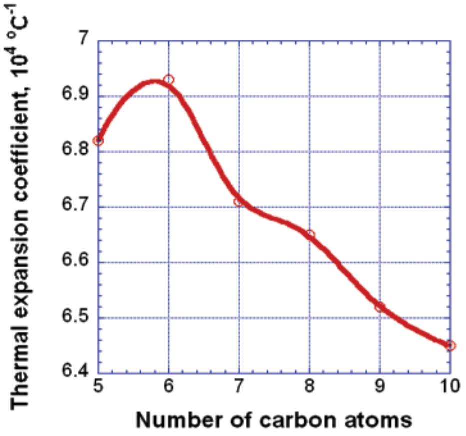

Figure 3.4. Thermal expansion coefficient of various phthalates having different number of carbon atoms in their alcohol segment. [Data from Storey, R. F.; Mauritz, K. A.; Cox, B. D., *Macromolecules*, **22**, 289-294, 1989.]

than their higher molecular weight homologs. It should also be considered that the diffusion coefficient affects two processes: compounding and product use. This means that smaller molecules of plasticizer diffuse faster into PVC grains, and their compounding process is more effective, but during material storage and use, losses of lower molecular weight homologs are more extensive and their fogging

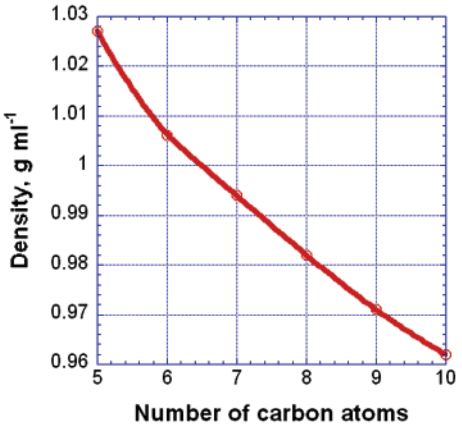

Figure 3.5. Density of various phthalates having different number of carbon atoms in their alcohol segment. [Data from Storey, R. F.; Mauritz, K. A.; Cox, B. D., *Macromolecules*, **22**, 289-294, 1989.]

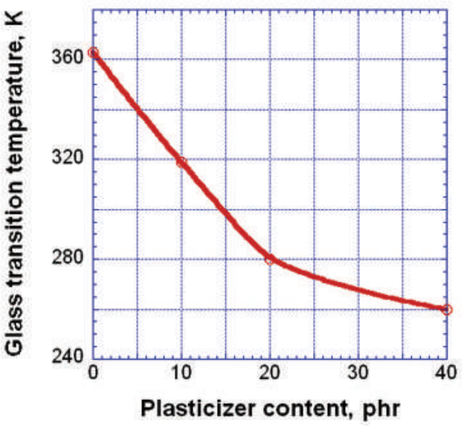

Figure 3.6. Glass transition temperature of PVC containing variable quantities of plasticizer. [Data from Dashora, P.; Gupta, G., *Polymer*, **37**, 2, 231-4, 1996.]

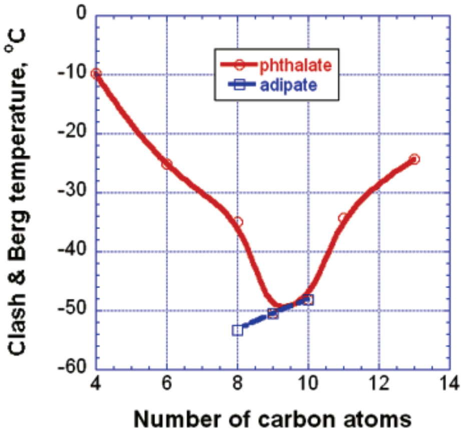

Figure 3.7. Clash & Berg temperature of PVC containing 50 phr plasticizer having variable number of carbon atoms in alcohol part and two different acids. [Data from Wickson, E. J., **Handbook of Polyvinyl Chloride Formulating**, *John Wiley & Sons*, New York, 1993.]

characteristics are worse. Figure 3.4 shows that the length of the carbon chain in alcohol influences the coefficient of thermal expansion as well as plasticizer density (Figure 3.5). The data in Figure 3.5 are for linear alcohols. Branching in alcohol slightly increases density as compared with linear alcohols.[5]

The increase of a free volume by the addition of a plasticizer is the most fundamental principle of plasticizer action which explains theory behind its plasticizing action (see more on this subject in *Handbook of Plasticizers*).[1]

Plasticizers lower glass transition temperature (Figure 3.6), which explains why plasticized PVC can withstand more moderate temperatures. Figure 3.7 shows that there is no straightforward relationship between the length of the carbon chain in alcohol and low-temperature properties of plasticizers. In the case of adipates, increase in their molecular weight causes a decrease in their Clash & Berg temperatures. In the case of phthalates, a minimum of Clash & Berg temperature is observed in the case of nine carbons containing alcohol.

The solvating strength of plasticizer depends on its chemical structure as it relates to its physical properties. The application of Hansen solubility parameters (δ_d = dispersion interactive forces, δ_p = dipole interactive forces, and δ_h = hydrogen bonding forces) is the most successful method of predicting the interaction between plasticizers and PVC. Table 3.2 shows values of these parameters for PVC and selected plasticizers.

Table 3.2. Hansen parameters of selected plasticizers & PVC. [Data from Wypych, A., **Plasticizers Database**, Version 3.0, *ChemTec Publishing*, Toronto, 2012.]

	δ_d	δ_p	δ_h
	$(MPa)^{1/2}$		
PVC	18.4	11.1	1.9
Benzyl butyl phthalate	19.1	11.3	3.1
Dimethyl phthalate	18.6	10.8	4.9
Dibutyl phthalate	17.8	8.6	4.1
Di-(2-ethylhexyl) phthalate	16.6	8.0	3.1
Diisononyl phthalate	16.2	7.31	3.8
Di-(2-ethylhexyl) adipate	16.7	6.2	3.5

Compatibility in the Hansen system increases when values of all three forces of solvent more closely match the values of solute. Table 3.2 shows that benzyl butyl phthalate has the best match of parameters with PVC and it is known to be the most aggressive plasticizer of PVC. In the case of phthalates, the longer the hydrocarbon chain of alcohol involved in the plasticizer, the worse the match of its parameters and the worse a solvating power of plasticizer. Diisononyl phthalate is close in solvating power to di-(2-ethylhexyl) adipate which is considered as a secondary plasticizer. The more extensive use of Hansen solubility parameters in the assessment of solvating power of various plasticizers is hampered by frequently uncertain or lacking values of Hansen solubility parameters.

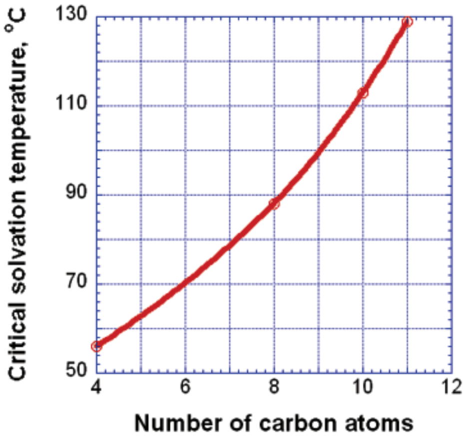

Figure 3.8. Critical solvation temperature of PVC containing phthalates of different length of hydrocarbon chain in alcohol rests. [Data from Goernitz, E.; Zecha, H., *Langmuir*, **3**, 738-741, 1987.]

Figure 3.8 shows that the length of the hydrocarbon chain in alcohol influences critical solvation temperature. In practical terms, less volatile, higher molecular weight plasticizers require increased processing temperature.[8]

PVC is one of the most flame-resistant polymers but only in rigid formulations which do not contain many other additives. Addition of other polymers or additives decreases its flame resistance to the point that it frequently requires the addition of special plasticizers, organic flame retardants, or special fillers. Plasticized PVC must contain at least 20% flame retarding plasticizer to be self-extinguishing.[9]

More than 100 plasticizers have now commercial importance, among which phthalates are the most widely used plasticizers, which is changing because of some findings suggesting their toxicity in animals followed by extrapolation to the potential risk of adverse health effects in humans.[10] Because of this and the pursuit to use renewable resources, research is pointing to many new solutions.[10] One of the common is the use of plasticizers derived from cardanol which were found potentially useful for replacement of di-(2-ethylhexyl) and diisononyl phthalates in semi-rigid formulations.[10]

The use of non-ortho-phthalate plasticizers in PVC packaging and medical devices is of interest due to the worldwide regulatory trends to minimize or eliminate phthalate plasticizers (particularly di-(2-ethylhexyl)phthalate and dioctyl phthalate.[11] The dry-blending cycle time of a suspension grade PVC formulated with various non-DOP plasticizers, such as di-(2-ethylhexyl) terephthalate, tris (2-ethylhexyl) trimellitate, and alkyl sulfonic phenyl ester was compared with the DOP standard.[11] The blending cycle time was related to the plasticizer efficiency. The alkyl sulfonic phenyl ester was slightly more efficient than DOP.[11] The dry-blending cycle time of the di-(2-ethylhexyl) terephthalate plasticized PVC was optimized by increasing the plasticizer pre-heating temperature or decreasing its concentration (the di-(2-ethylhexyl) terephthalate concentration and the PVC temperature at the time of plasticizer addition were significant to determine whether the dry blend will reach peak amperage).[11] The tris (2-ethylhexyl) trimellitate concentration and the PVC temperature at the time of plasticizer addition were significant for the dry blend to reach peak amperage.[11]

PVC plasticizers are composed of epoxidized bioesters of vegetable oil fatty acids obtained by partial transesterification with alcohol and glycerin, and further acetylation and epoxidation.[12] The epoxidized bioesters are composed of mixtures of epoxidized mono, di and triglyceride esters, having oxirane index equal to or less than 8.[12]

3.2 FILLERS

Fillers are the most commonly used additives by weight. The reasons for their use go beyond the limits outlined by their names, which suggest price reduction. Table 3.3 lists the important PVC fillers, their applications, reasons for use, potential adverse effects on product quality, average concentrations, and selected properties.

Table 3.3. PVC fillers.

<table>
<tr><td colspan="3">Types: aluminum fiber, aluminum hydroxide, antimony trioxide, calcium carbonate, carbon black, carbon fiber, hollow glass beads, kaolin, magnesium hydroxide, mica, sand, silica, silica carbide, talc, waste leather particles, wollastonite, wood fiber, wood flour, zeolite</td></tr>
<tr><td colspan="3">Applications: bottles, coated fabrics, domestic appliances, drain pipes, film & sheet, fittings, flooring, foam backing for carpets, footwear, furniture trim, gloves, gutters, metal protection, office equipment, packaging, pipes, profiles, protective clothing, siding, toys, tubing, wallpaper, windows, wire & cable</td></tr>
<tr><td colspan="3">Reasons for use: abrasion resistance, cost reduction, electric conductivity (metal fibers, carbon fibers, carbon black), EMI shielding (metal and carbon fibers), electric resistivity (mica), flame retarding properties (aluminum hydroxide, antimony trioxide, magnesium hydroxide), impact resistance improvement (small particle size calcium carbonate), improvement of radiation stability (zeolite), increase of density, increase of flexural modulus, impact strength, and stiffness (talc), nucleating agent for bubble formation, permeability (mica), smoke suppression (magnesium hydroxide), thermal stabilization (calcium carbonate), wear resistance (aluminum oxide, silica carbide, wollastonite)</td></tr>
<tr><td colspan="3">Potential adverse effects: calcium carbonate interferes with radiation curing, calcium carbonate may react with pollutant (SO_2) to form sulfate, fillers containing cadmium, cobalt, copper, iron, lead, or nickel reduce thermal stability, low concentration of carbon black and titanium dioxide reduces UV stability, zinc oxide decreases thermal stability, zinc oxide in combination with carbon black reduces UV stability</td></tr>
<tr><td colspan="3">Typical concentrations: antimony trioxide: 3-6 wt% in rigid and semi-rigid, 15-20 wt% in flexible; calcium carbonate: 20-30 wt% rigid, 30-40 wt% flexible; magnesium hydroxide: 20-40 wt%; sand: 40-60 wt%; talc: 5-25 wt%</td></tr>
<tr><td>Density (20°C), kg/m^3, 120-10,500</td><td>Moss hardness: 1-7</td><td>Thermal conductivity: W/Km, 0.01-450</td></tr>
<tr><td colspan="2">Thermal expansion coefficient, 1/K: 4.3x10^{-6} to 8.5x10^{-8}</td><td>Refractive index (20°C): 1.48-1.7</td></tr>
<tr><td>Whiteness: 55-98</td><td>Dielectric constant: 1.2-9.1</td><td>Volume resistivity, Ω-cm: 10^{-5}-10^{16}</td></tr>
<tr><td>Particle size, µm: 0.005-90</td><td>Specific surface, m^2/g: 0.15-400</td><td>Oil absorption, g/100 g: 5-175</td></tr>
</table>

The short discussion below includes the most critical effects of fillers on properties of PVC products containing fillers. This brief discussion is designed to highlight the most critical impacts of fillers, but it does not include details of fillers actions which are extensively characterized in a specialized monograph on fillers, entitled *Handbook of Fillers.*[13]

Table 3.3 shows that there are many possible choices of fillers and they offer a wide range of properties which may influence the selection of a particular prod-

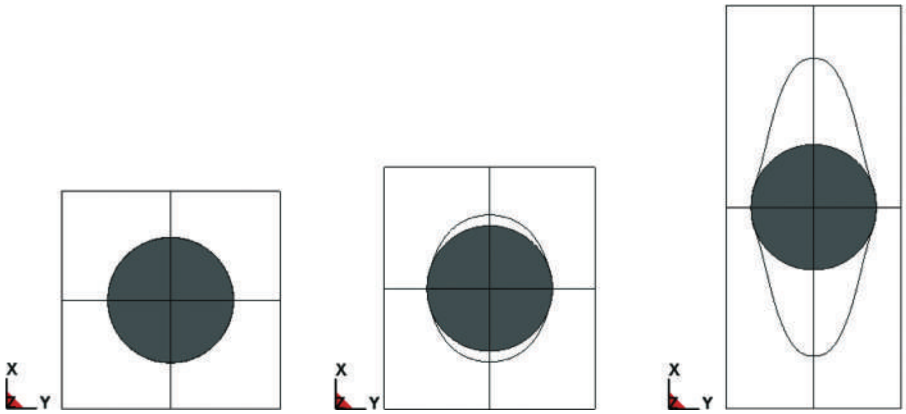

Figure 3.9. Section view of unit cell model displaying void growth around a particle at macroscopic longitudinal strains of (a) 0, (b) 0.1 and (c) 0.6. [Adapted, by permission, from Ognedal, A. S., Clausen, A. H., Berstad, T., Seeling, T., Hopperstad, O. S., *Int. J. Solids Structures*, in press, 2014.]

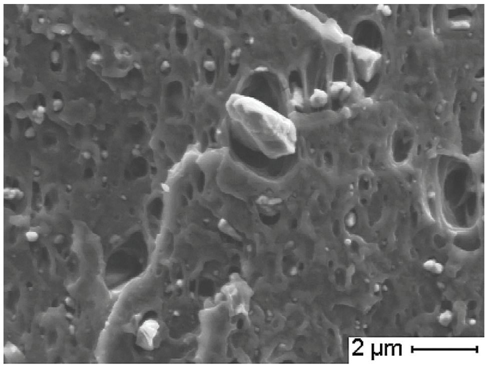

Figure 3.10. Microstructure of deformed test specimens of mineral-filled PVC by 0.4 longitudinal strain. [Adapted, by permission, from Ognedal, A. S., Clausen, A. H., Berstad, T., Seeling, T., Hopperstad, O. S., *Int. J. Solids Structures*, 51, 7-8, 1494-1506, 2014.]

uct. High density is their common feature and drawback. With the exception of hollow glass beads (infrequently used), fillers have a density much higher than PVC alone, which limits their application.

Calcium carbonate is the most widely-used filler in all polymers, including PVC. Three main grades are available: milled, precipitated, and precipitated with a surface coating. The milled grade has a mineral origin, and its quality depends on the mineral composition and the effect of milling in consideration of size distribution of particles and their shape. This is the most frequently-used grade because of its relatively low cost. Its main drawback in the plasticized composition is high plasticizer demand caused by its low packing density. The other essential drawback comes from its chemical structure which does not contain any groups which may interact with PVC; therefore, its application usually results in lowering the mechanical performance of the product. Precipitated grades have smaller particles and their narrow distribution. They can be specially tailored to increase packing density which reduces plasticizer demand. Grades coated with salts of fatty acids are known to interact with PVC and absorb less plasticizer; therefore, their incorporation affects the mechanical properties of PVC products to a lesser extent.

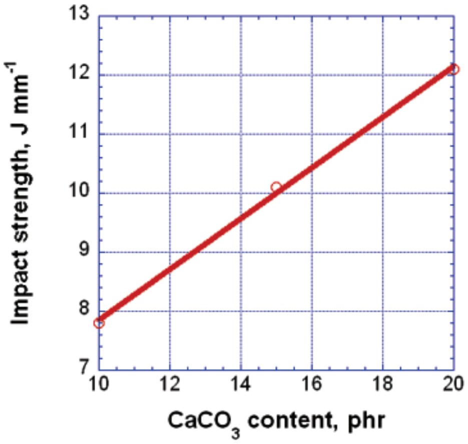

Figure 3.11. Impact strength of PVC containing 5 phr chlorinated polyethylene and variable amounts of calcium carbonate. [Data from Ventresca, D. A.; Berard, M. T., *J. Vinyl Additive Technol.*, **3**, 4, 274-278, 1997.]

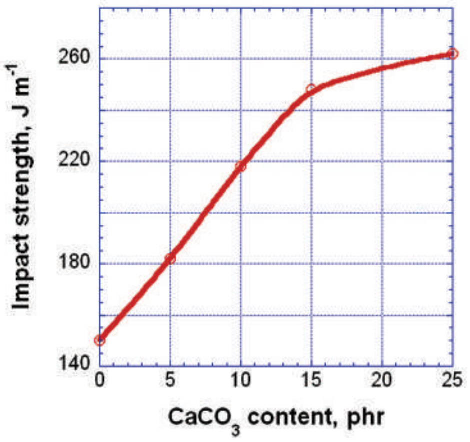

Figure 3.12. Impact strength of PVC containing 5 phr acrylic impact modifier and variable amounts of calcium carbonate. [Data from Wiebking, H. E., *J. Vinyl Additive Technol.*, **2**, 3, 187-189, 1996.]

Figure 3.9 shows a schematic diagram of the effect of increasing stress on particle debonding.[14] Figure 10 shows debonding on SEM micrograph.[14] Debonding not only increases the volume of voids in composites but also causes substantial degradation of mechanical performance.

One method of increased interaction between filler and polymer is to use the third component, which has better interaction with filler. Chlorinated polyethylene is such a component, and in addition, it is an impact modifier of PVC. Calcium carbonate particles become coated with chlorinated polyethylene, CPE, which increases dispersion of CPE domains and the amount of calcium carbonate which can be used without adverse effect on the impact strength of the material (Figure 3.11).[15] A study[16] shows that the use of acrylic impact modifier also permits the improvement of impact resistance with the addition of calcium carbonate (Figure 3.12).

Combination of impact modifier and filler can be used to balance conflicting mechanical properties to the requirements. It was required that impact strength and stiffness will be increased simultaneously.[16] Selection of impact modifier level and content of ultrafine talc permitted the achievement of this set of properties.[16]

Another successful combination which permits increase mechanical performance includes PVC, filler, and coupling agent.[17] Coupling agent increases chemical interaction of aluminum oxide with PVC chains and reduces the mass loss caused by wear (Figure 3.13). A similar goal can be achieved by polymer blending using a polymer which interacts well with both filler and PVC (e.g., silica carbide and ABS).[17]

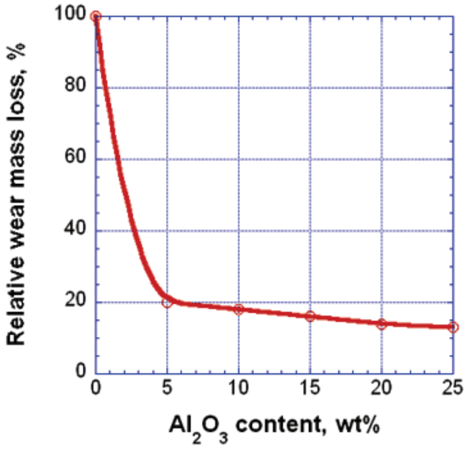

Figure 3.13. Relative wear mass loss vs. filler concentration in the presence of coupling agent. [Data from Yang, F.; Hlavacek, V., *Powder Technol.*, **103**, 2, 182-188, 1999.]

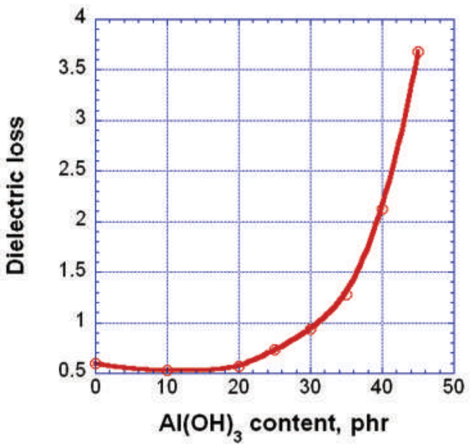

Figure 3.14. Dielectric loss vs. aluminum hydroxide content. [Data from Mansour, S. H.; Iskander, B. A.; Nasrat, L. S., *Polym.-Plastics Technol. Eng.*, **45**, 7, 857-863, 2006.]

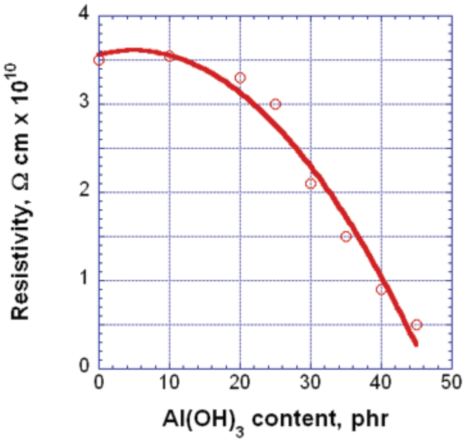

Figure 3.15. Resistivity vs. aluminum hydroxide content. [Data from Mansour, S. H.; Iskander, B. A.; Nasrat, L. S., *Polym.-Plastics Technol. Eng.*, **45**, 7, 857-863, 2006.]

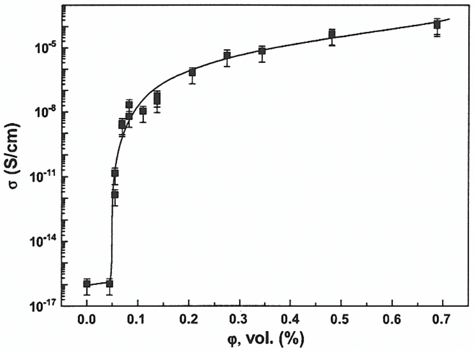

Figure 3.16. Electrical conductivity of PVC versus volume content of carbon nanotubes. [Adapted, by permission, from Mamunya, Y., Boudenne, A., Lebovka, N., Ibos, L., Candau, Y., Lisunova, M., *Compos. Sci. Techn.*, **68**, 1981-88, 2008.]

Some fillers are used to change electrical characteristics of PVC, and most of them influence the electrical properties of PVC. Figure 3.14 shows the effect of aluminum hydroxide on dielectric loss and Figure 3.15 shows its impact on resistivity. In the case of results reported in Figures 3.14 and 3.15, aluminum hydroxide was added to improve the flame resistance of PVC, and it was expected that it would not adversely affect the electrical performance of PVC. The results show that up to 25 phr aluminum hydroxide can safely be used in the formulation.

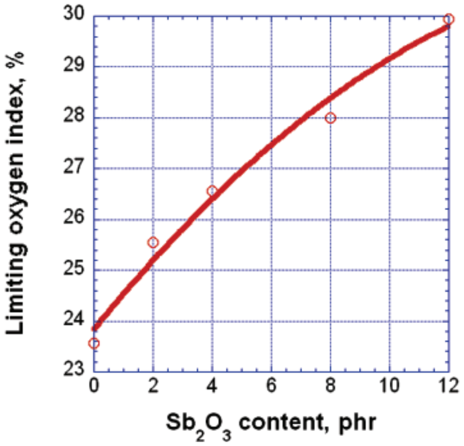

Figure 3.17. Limiting oxygen index of PVC containing variable concentrations of antimony dioxide. [Data from Wang, H.; Wang, H.; Guo, Z.; Qi, S.; Tian, C., *J. Fire Sci*., **24**, 3, 195-210, 2006.]

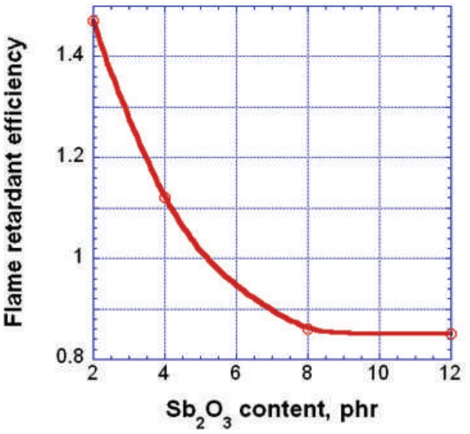

Figure 3.18. Flame retardant efficiency in PVC containing variable concentrations of antimony dioxide. [Data from Wang, H.; Wang, H.; Guo, Z.; Qi, S.; Tian, C., *J. Fire Sci*., **24**, 3, 195-210, 2006.]

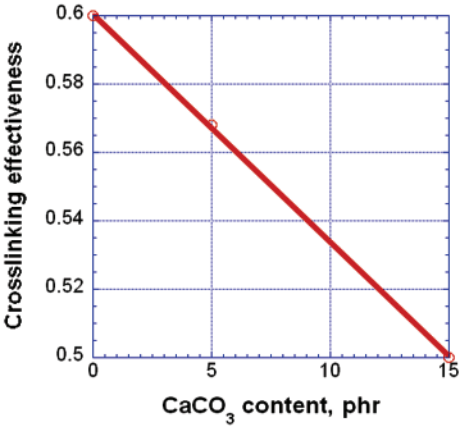

Figure 3.19. Crosslinking effectiveness of γ-rays vs. $CaCO_3$ content. [Data from Bataille, P.; Mahlous, M.; Schreiber, H. P., *Polym. Eng. Sci*., **34**, 12, 981-5, 1994.]

Figure 3.16 shows that electrical conductivity can be dramatically improved by the addition of carbon nanotubes.[19] The electrical conductivity of composites abruptly increases by many orders of magnitude when the filler content exceeds the threshold concentration.[19]

Several fillers are involved in the modification of flame-retarding properties of semi-rigid and flexible PVC. Figure 3.17 shows a typical result of increased addition of flame-retarding filler. The limiting oxygen index increased with increased addition of filler, but Figure 3.18 shows that the efficiency of flame retardant decreased with its concentration increase.[20]

Incorporation of fillers affects PVC transparency to a broad range of radiation wavelength including UV, visible, and infrared. Figure 3.19 shows that even γ-radiation is affected as it penetrates the material.

3.3 PIGMENTS AND DYES

Table 3.4 contains information on the most essential pigments used in PVC.

Table 3.4. PVC pigments and dyes.

<table>
<tr><td colspan="3">Types: antraquinone, azo, carbon black, diarylide yellow, dosazo, fluorescent, metallic flakes, monoazo orange, naphthol red, optical brighteners, pearlescent (usually coated mica), perylene, phthalocyanine, quinacridone, titanium dioxide, zinc oxide, etc.</td></tr>
<tr><td colspan="3">Applications: common to all products</td></tr>
<tr><td colspan="3">Reasons for use: coloring, protection against UV degradation (carbon black and titanium dioxide)</td></tr>
<tr><td colspan="3">Potential adverse effects: crocking (transfer to materials in contact on rubbing), effect on electrical properties (some pigments contain soluble salts), migration (bleeding and blooming), plate-out, reactivity (with other pigments or additives), resistance to alkali, acids, and soaps, shear sensitivity (change of intensity or hue), sulfide staining, thermal instability (should withstand minimum 5 mins of process temperature), toxicity (e.g, cadmium or lead), UV resistance</td></tr>
<tr><td colspan="3">Typical concentrations: titanium dioxide for UV protection – 4-10 wt%, carbon black for UV protection – at least 1 wt%, coloring – quantum satis</td></tr>
<tr><td>Density, kg/m^3: 1,300-5,600</td><td>Particle size, nm: 8-4,000</td><td>Specific surface area, m^2/g: 7-560</td></tr>
<tr><td>Hegman fineness: 2-8</td><td>Oil absorption, g/100 g: 10-55</td><td>Refractive index (20°C): 2.5-2.7</td></tr>
<tr><td colspan="2">Coefficient of linear thermal expansion, $10^{-6}/K$: 8-9.1</td><td>Brightness (TiO_2): 99-100</td></tr>
<tr><td colspan="2">Thermal conductivity, W/Km: 0.065-1</td><td>Dielectric constant: 48-114</td></tr>
</table>

Titanium dioxide is the most crucial pigment for PVC articles manufactured for outdoor use because it gives UV protection. The details of its mechanism of action are omitted here because they were discussed in a monograph on stabilization specially designed to be used together with this book.[22] For practical purposes of selection of titanium dioxide for coloring or UV protection, it is essential to assure that titanium dioxide is in the rutile form and has a surface coating designed to minimize its catalytic effect on PVC degradation. These coatings usually contain zirconium and/or silica and aluminum. Titanium grades are rated according to their photoactivity, which explains why coated rutile should be used (Table 3.5).

Table 3.5 Effect of composition of titanium dioxide on its photocatalytic activity. [Data from Worsley, D. A.; Searle, J. R., *Mater. Sci. Technol.*, **18**, 681-684, 2002.]

Pigment description	Photoactivity index, %
70/30 anatase/rutile (photocatalyst)	100
Anatase	47
Anatase with Al/Si coating	2.2
Rutile with Al coating	3.1
Rutile with Al/Zr coating	1.9
Rutile with Al/Si coating	0.62
Rutile with Al/Si/Zr coating	0.76
Rutile with Al/Si coating (exterior UPVC)	0.38

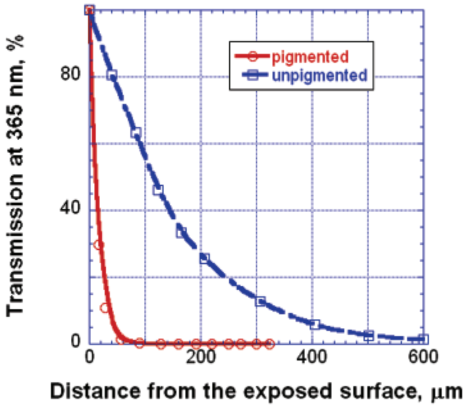

Figure 3.20. Transmission of radiation at 365 nm through rigid PVC without and with 4.1 wt% titanium dioxide. [Adapted, by permission, from Anton-Prinet, C.; Mur, G.; Audouin, L.; Verdu, J.; *Polym. Deg. Stab.*, **61**, 2, 211-6, 1998.]

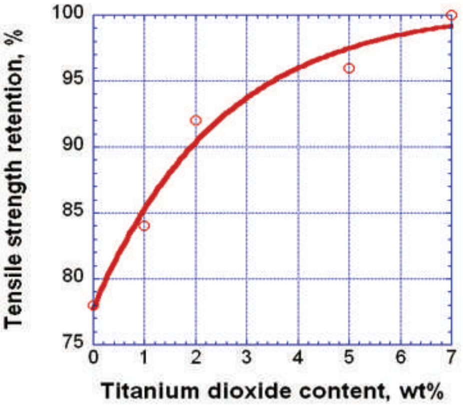

Figure 3.21. Tensile strength of PVC pipe having variable contents of titanium dioxide after UV irradiance of 1100 MJ m^{-2}. [Data from Burn, L. S., *Polym. Deg. Stab.*, **36**, 155-167, 1992.]

Figure 3.20 shows that PVC pigmented with high doses of titanium dioxide is still transparent to UV radiation up to 60 μm from the material surface. This means that the surface of the pigmented article is never protected and has to be protected by the surface replacement mechanism explained in detail elsewhere or other means available (e.g., surface coating or UV stabilizers).[22]

The selection of concentration of titanium dioxide should be considered with a clear understanding of the implications. In studies of PVC pipes it was found that 2 wt% titanium oxide was sufficient to control white color but, as Figure 3.21

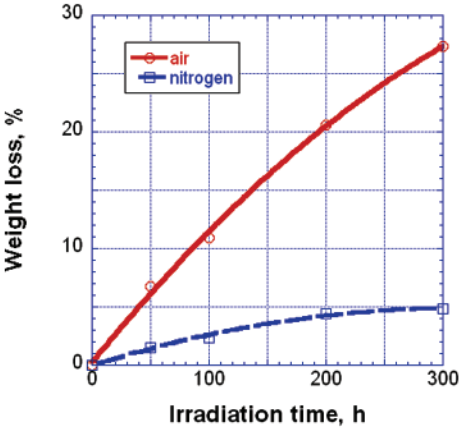

Figure 3.22. Weight loss of PVC containing 1.5 wt% titanium dioxide vs. irradiation time in air and nitrogen atmosphere. [Data from Cho, S.; Choi, W., *J. Photochem. Photobiol., A: Chem.*, **143**, 221-228, 2001.]

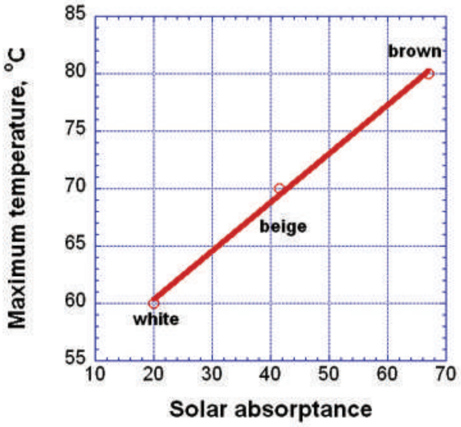

Figure 3.23. Maximum temperature of product vs. its solar absorptance. [Data from Hardcastle, H. K., *J. Vinyl Additive Technol.*, **4**, 3, 169-173, 1998.]

shows, it was not enough to retain tensile strength, which, together with impact strength and burst resistance, is a more critical parameter of performance than color retention.

It should be noted that the conditions of performance also dictate the selection of necessary protection. For example, many pipes are buried underground, and these only require protection for an expected time and conditions of their storage under most extreme conditions. The other case is an atmosphere under which a product performs. Figure 3.22 shows that PVC containing titanium dioxide degrades much slower under an inert atmosphere (nitrogen) than in the presence of air. If then, air is restricted for any reason, this also improves the protection level.

Mixing of titanium dioxide with other pigments may lead to various unexpected effects. For example, anthraquinone pigments combined with high doses of titanium dioxide have undergone a bathochromic shift without even being subjected to light.[27] It is suspected that the bathochromic effect is caused by the crystallization of dye when the concentration of titanium dioxide in the coloring package is higher than 88.5%.[27]

It is also important to consider that the color of a material affects its absorption of infrared radiation when the material is exposed to solar radiation.[28] Figure 3.23 shows that the darker the color, the more extensive the absorption and the higher the temperature.[28] The temperature of products has many further implications on its performance, such as degradation, flexibility, change of shape, mechanical strength, creep, chemical resistance, etc.

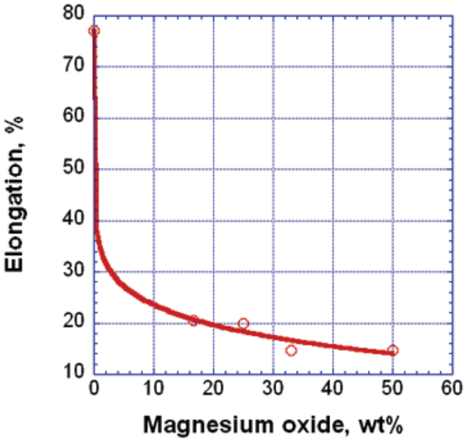

Figure 3.24. Elongation of PVC vs. magnesium oxide content. [Data from Kamisli, F.; Turan, C., *J. Mater. Process. Technol.,* **159**, 1, 40-47, 2005.]

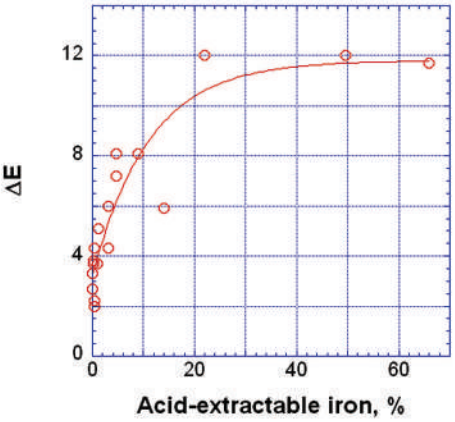

Figure 3.25. Effect of acid-extractable iron on the color of rigid PVC after exposure in Florida for 2 years. [Data from Peake, G. T., *J. Vinyl Additive Technol*., **2**, 3, 184-6, 1996.]

Because of price restrictions, there are attempts to replace titanium dioxide with less expensive pigment. Figure 3.24 shows the results of such an attempt in which magnesium oxide was used as a replacement pigment. It is clear that the effort was not successful because material elongation was drastically decreased even by small additions of magnesium oxide.[29]

Information on pigments other than titanium dioxide is scarce. However, it is quite well established that some iron pigments affect color stability of PVC. Figure 3.25 shows that this is attributable to the concentration of extractable iron in the pigment.[30]

It was found that various contaminants on carbon black surface affect melt stability.[31] The most significant effect was caused by surface oxygen, which can make PVC containing carbon black unprocessable. Also, the presence of iron was found unacceptable because it catalyzed PVC degradation and it was scratching molds.[31]

3.4 THERMAL STABILIZERS

The entire monograph was devoted to PVC degradation and stabilization designed to be used together with this book, and these subjects should be consulted with information included in the monograph.[22] To avoid repetitions, we only have here brief tabular summary information on PVC thermal stabilizers in Table 3.6. The information contained in the table only includes stabilizers which are permitted for their use in North America and the European Union.

Table 3.6. PVC thermal stabilizers.

Types: barium/zinc carboxylates, calcium/zinc carboxylates, magnesium/zinc carboxylate, potassium/zinc carboxylates; butyltin carboxylate, butyltin mercaptide/carboxylate, methyltin mercaptide, butyltin mercaptide, octyltin mercaptide, butyltin maleate, octyltin maleate, butyltin dilaurate; epoxidized linseed oil, epoxidized soybean oil, epoxidized tallate ester, epoxidized octyl stearate, epoxidized propylene glycol dioleate; trinonylphenyl phosphite, phenyl diisodecyl phosphite, diphenyl alkyl phosphite, tris(2,4-butylphenyl) phosphite, distearyl pentaerythritol diphosphite, bis(2,4-dicumylphenyl) pentaerythritol diphosphite; hydroxyphenylpropionate, benzenepropanoic acid, 3-(1,1-dimethyl)-4-hydroxy-5-methyl-1,2-ethanediyl bis(oxy-2,1-ethanediyl) ester, terakismethylene(3,5-di-t-butyl-4-hydroxydrocinnamate)methane, 1,1,3-tris(2'-methyl-4'-hydroxy-5'-t-butylphenyl)butane, 1,3,5-trimethyl-2,4,6-tris (3,5-di-tert-butyl-4-hydroxybenzyl)benzene; β-diketone, β-ketoester, dibenzoylmethane, stearoylbenzoylmethane, dehydroacetic acid, pyrrolidine-2,4-dione; aminocrotonic acid ester, perchlorate (sodium perchlorate), α-phenylindole, dihydropyridine derivative, 6-amino-1,3-dimethyluracil, sodium tetraborate, sodium phenyl phosphinate		
Applications: all PVC formulations require thermal stabilizers		
Reasons for use: to prevent thermal degradation (all stabilizer groups listed in the first cell), to control decomposition rate of foaming agents		
Potential adverse effects: products of reaction with HCl accelerate dehydrochlorination rate, plate-out, influence on taste and odor or products in contact, fogging, staining, low chemical resistance, easy to extract and to be lost by migration		
Typical concentrations: 0.05-5 wt%		
Molecular weight: 337-1178	Melting point, °C: –40-241	Decomposition point, °C: 172-522
Refractive index: 1.45-1.56	Density, 20°C, kg/m^3: 850-1170	Viscosity, 20°C, MPas: 22-9,000
State: solid, paste, liquid	Color: white to yellow	Odor: odorless to mercaptan

The *cis*-1,2-cyclohexanedicarboxylic acid di-mannitol ester-based zinc metal alkoxides were compared with Ca/Zn stearates (1:1).[32] The polyol-based ester stabilizer having molar ratio of *cis*-1,2-cyclohexanedicarboxylic acid di-mannitol ester:$Zn(O_2CCH_3)_2$=1:1 outperformed stearate stabilizer by factor of 3.1 in terms of induction time, 5 in color retention time (color does not change during heating for 50 mins at 180°C).[32] The ester-based stabilizer enhanced the thermal stability of PVC by substituting the labile chlorines in PVC, which led to the improvement in the initial color of the stabilized PVC.[32] It was also capable of complexation of $ZnCl_2$ (known to catalyze rapid PVC degradation suddenly changing color of material to black).[32] The stabilizer has a plasticizing effect on PVC.[32]

3.5 UV STABILIZERS

Similar to the thermal stabilizers, various UV stabilizers are discussed in detail in the companion book,[22] the content of which is not repeated here. Table 3.7 contains general characteristics and chemical composition of UV stabilizers applicable to PVC.

Table 3.7. PVC UV stabilizers.

Types: benzophenone, benzotriazole, bis-benzoxazole, cyanoacrylate, oxanilide; carbon black, titanium dioxide; monomeric sterically hindered amine, oligomeric sterically hindered amine, sterically hindered amine ester; polyphosphates		
Applications: products for outdoor applications		
Reasons for use: protection against UV degradation		
Typical concentrations: 0.025 to 10 phr		
Molecular weight: 12-31,000	Melting point, °C: −56-1825	Boiling point, °C: >350-3000
Density, 20°C, kg/m^3: 950-4,200	Viscosity, 20°C, MPas: 450-6400	Refractive index, 20°C: 1.45-2.6
State: powder and liquid	Color: white to black	Odor: odorless

Polyphosphates were used as inhibitors of poly(vinyl chloride) photodegradation in thin films.[33] They reduced the rate of PVC photodegradation because of direct absorption of UV light, interaction with PVC chain, and acting as radical scavenger.[33]

3.6 IMPACT MODIFIERS

Table 3.8 contains information on the most popular impact modifiers.

Table 3.8. PVC impact modifiers.

Types: calcium carbonate, chlorinated polyethylene (Wellpren), core-shell acrylic (Durastrength, Metablen P, Metablen W, Paraloid KM), ethylene-n-butyl acrylate-carbon monoxide terpolymers (Elvaloy), ethylene-vinyl acetate-carbon monoxide terpolymers (Elvaloy), methacrylate-butadiene-styrene (Clearstrength, Metablen C, Paraloid BTA), silicone-acrylic (Metablen S)
Manufacturers: Arkema (Durastrength 200, 320, 350, 365s, 367, 382, 480, 506, 510, 527, 535, D36X; Clearstrength 140, 223, 303H, 320, 350, 859, E920, E922, E950, E952, W300, XT100); DuPont (Elvaloy 4924); Mitsubishi Rayon (Metablen C-132, 140A, 223A, 323A, 820J, 830J; Metablen P-501A, 531A, 530A, 540A, 551A, 560A, 570A; Metablen S-2001, 2005, 2006, 2030, 2100, SRK200, SX-05, SX-06; Metablen W-300A, 450A); Rohm and Haas (Paraloid BTA-717, 730, 731, 733J, 751, 751U; Paraloid EXL-2315, 2390, 2668, 2690, 2691J, 3691J; Paraloid HIA, HIA-80; Paraloid K-; Paraloid KM-1, 330, 334, 355P, 357P, 370, 376, 377, 390, 606P, 5000, 5450, X-100 PRO; Paraloid TMS, TMS-2670J, and many more), Sundow Polymers (Wellpren 135A, IM 450, 500, 868, 878, 888, 900, 2500);

Table 3.8. PVC impact modifiers.

<table>
<tr><td colspan="3">Applications: automotive, bottles, Christmas tree, conduit, corrugated clear roofing, electrical and electronic appliance housing, exterior trim, fence/deck/rail, glossy surface, injection molded products, packaging film, pipe, ribbed pipe, roofing, siding, sheet, thin-wall parts, window profiles</td></tr>
<tr><td colspan="3">Reasons for use: air mark, chemical resistance, coloring ability, dispersion of fillers, easy thermoforming, impact strength improvement, good dispersion, high output, jetting, low friction, low crease whitening, low melt viscosity, low temperature applications, optical clarity, quick fusion, reduced flow marks, surface finish, uniformity of foamed cell, weather resistance</td></tr>
<tr><td colspan="3">Potential adverse effects: effect on weathering (e.g, MBS), increase of die swell</td></tr>
<tr><td colspan="3">Typical concentrations: 3-14 phr</td></tr>
<tr><td>Density, 20°C, kg/m^3: 960-1250</td><td colspan="2">Molecular weight: 100-5,000,000</td></tr>
<tr><td colspan="2">Glass transition temperature, °C: –54-106</td><td>Volatiles, %: 0.5-1.2</td></tr>
<tr><td>Refractive index: 1.49-1.53</td><td>Particles size, μm: 0.02-300</td><td>Melt index, g/10 min: 3-35</td></tr>
</table>

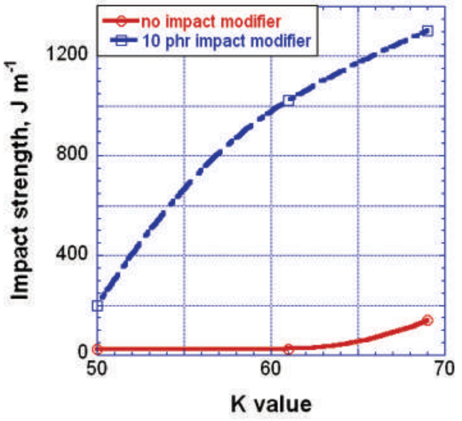

Figure 3.26. Impact strength of PVC, having different molecular weight, with and without acrylic impact modifier (Paraloid KH-334). [Data from Tseng, A. A.; Borrosky, M. A.; O'Connor, S. M.; Knotts, J. J., *Adv. Polym. Technol.*, **10**, 3, 205-218, 1990.]

There are several factors which determine the results of impact modification. They include: PVC molecular weight, condition of material surface, material's thickness, temperature of service, type and structure of impact modifier, its particle size and concentration, UV degradation and stabilization of impact modifier, method of incorporation (dispersion mechanism), shell thickness of core-shell impact modifiers, interaction with other components of formulation (fillers, thermal stabilizers, lubricants). Impact modifiers not only increase impact strength but also affect some other properties. All the above aspects are discussed below, according to the sequence listed above.

Figure 3.26 shows that impact strength of PVC increases with its molecular weight increases, especially at higher molecular weights. For this reason, many products can be manufactured without impact modifier, simply because PVC having a higher molecular weight was selected. Figure 3.26 also shows that the same amount of impact modifier added to different PVC grades increases its impact strength with its rate of change relative to the molecular weight of PVC increase. Figure 3.27 shows that the impact strength of polymers having different molecular weight requires different amounts of the impact modifier.

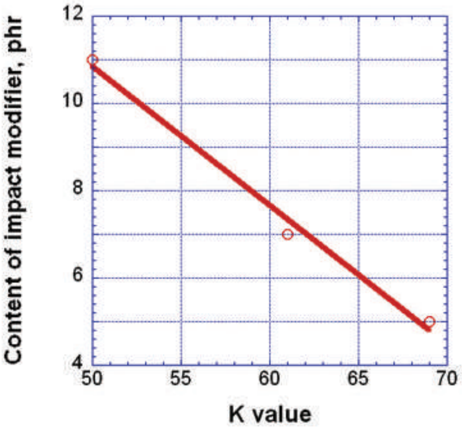

Figure 3.27. The required amount of impact modifier (Paraloid KH-334) to maintain impact strength of 500 J/m for PVC grades having different K number (molecular weight). [Data from Tseng, A. A.; Borrosky, M. A.; O'Connor, S. M.; Knotts, J. J., *Adv. Polym. Technol.*, **10**, 3, 205-218, 1990.]

Rigid PVC is a brittle material. The probability of impact damage increases when surface defects or imperfections are present. Surface defects can be formed by large particles (e.g., fillers), methods of surface finish (e.g., embossing), or degradation (e.g., weathering or environmental stress cracking). A crack initiated from these surface defects propagates until it is stopped, either because impact energy was dissipated (e.g., propagating crack met a cavity and propagating force was applied to a larger surface area; this explains why small particles of, for example, calcium carbonate may increase impact strength), the propagating crack met reinforced material (e.g., craze formation, which changes crystallinity of material and strengthens it), or shear bands have been formed which absorb more energy than crazes. Thinner products usually contain impact modifiers of very small particle size (0.2-0.5 μm), which cause the formation of shear bands. Thicker products are likely protected by craze formation, and this is assisted by impact modifier having a broader particle size distribution (1-3 μm).

Some impact modifiers come with tailored particle size, and others are dispersed during compounding. Chlorinated polyethylene, CPE, can be given as an example of an impact modifier which is dispersed during its compounding. The melt temperature is the dominant factor in controlling the fusion and thus the impact.[35] CPE is dispersed in a complex process.[36] First, CPE is melted, which is easy to achieve because its melting temperature (110-130°C) is much lower than PVC melting temperature.[37] The melted CPE coats PVC particles which remain intact, forming a network. In the next step, PVC melts, and because CPE is added in a small concentration (about 5%) phase inversion occurs, meaning that small inclusions of CPE reside in a large pool of PVC matrix.[36] Depending on thermal properties of PVC and CPE and mixing conditions, a particle size of these inclusions varies. These parameters should be selected to obtain particles of about 1 μm, which produces optimal improvement of impact properties.[36]

Properties of CPE are related to the content of chlorine. Traditionally, CPE containing 36% chlorine was used (and it is still used today) because of its better elasticity and less compatibility with PVC.[36] More recently, CPE containing 25%

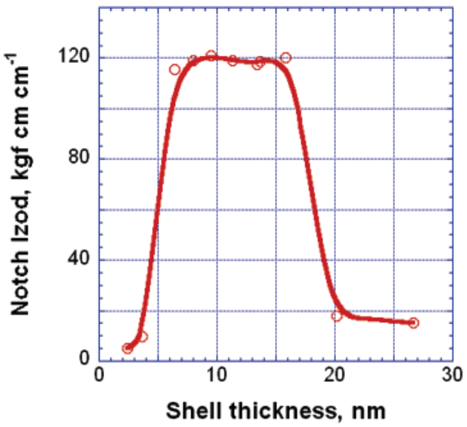

Figure 3.28. Impact strength of PVC containing 8 phr acrylic impact modifier vs. shell thickness of modifier. [Data from Lee, J.-S.; Chang, F.-C., *Polym. Eng. Sci.*, **44**, 10, 1885-1889, 2004.]

chlorine is used because it promotes faster fusion and enhances the melt strength of the formulation.[33] Faster fusion permits the partial or complete elimination of oxidized polyethylene, which is frequently used as fusion promoter.[38] CPE has similar vulnerabilities to PVC; therefore regular PVC thermal stabilizers also stabilize CPE without a need to include special stabilizers.[39]

Chlorinated polyethylene (CPE) is currently the modifier of choice in production of vinyl siding.[40] This modifier, although less efficient than core/shell impact additives, is valued because of its low cost. CPE with a chlorination level of 25 wt% grafted with acrylic monomers can be used as a basis to produce high-performance impact modifier. Grafting acrylic monomers at low levels (7.5%) produced high impact performance.[40]

Predesigned particles of impact modifiers are based on core-shell technology. The core is involved in impact modification, and shell improves adhesion between PVC and impact modifier particles.[41] Three significant combinations are used: methacrylate-butadiene-styrene, MBS, which has a core made out of butadiene-styrene copolymers and shell made out of methylmethacrylate-styrene copolymer, acrylic impact modifiers, AIM, which have a core made out of acrylic and shell from polymethylmethacrylate, and silicone-acrylic have multilayer structures with silicone-acrylic in the core. MBS has excellent compatibility with PVC, similar to ABS,[42] which is used as an impact modifier of PVC, as well. In both cases of ABS and MBS, weather resistance is lacking; therefore they are used for indoor applications only. At the same time, MBS gives translucent to crystal clear products, whereas with AIM, only translucent products are possible. To improve optical properties of AIM, it has to be reformulated. For transparent products, the core is made out of acrylic-styrene copolymers. Comparing silicone and all acrylic impact modifiers, PVC containing silicone-based products has superior low-temperature impact properties.[41] The incorporation of silicone into an acrylic impact modifier provides excellent weatherability, and thermal stability. It has shown improved retention of impact after outdoor weathering in PVC.[41]

The shell thickness of core-shell impact modifier was found to be the most important property, controlling its effectiveness as the impact modifier.[43] Figure 3.28 shows that if the shell thickness is too small (smaller than 4.9 nm) or too large (above the critical value of 15.8 nm), impact strength is rapidly reduced.

Within the range of 4 to 15.8 nm, the thickness of the shell does not seem to matter.

Figure 3.29 shows that selection of the concentration of impact modifier requires careful consideration.[44] The relationship between resultant impact strength and the amount of impact modifier incorporated has an S shape. Selection of too low concentration does not permit one to obtain maximum possible impact strength. Selection of a too high concentration contributes to increased cost without a return on investment because above a specific concentration increase in impact strength is minimal.

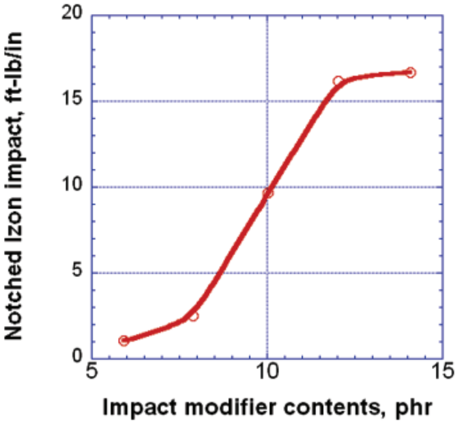

Figure 3.29. Impact strength vs. concentration of impact modifier. [Data from Stevenson, J. C.; Fazey, A. C., *J. Vinyl Additive Technol.*, **3**, 2, 118-125, 1997.]

Addition of impact modifier also frequently affects other properties than impact strength. It was already reported that filler intake can be increased and the rate of flow has been increased, as well. Addition of impact modifier lowers flame resistance of PVC (except when CPE is used) because impact modifiers are more flammable than PVC.[45] Impact modifiers aid in dispersion of additives, modify the elasticity of melt, and enhance the processing window.[46] Some impact modifiers help to improve the surface of the calendered film and preserve the shape of molded and extruded products. At the same time, impact modifiers may increase the die swell (e.g., Metablen P).

Also, other components of the formulation may influence the performance of impact modifiers. Fillers were found to improve impact properties in conjunction with impact modifiers.[15,16] Addition of heat distortion additives increases impact strength.[44] It was also found that lubricants increased the glass transition temperature of impact modifiers by 2 to 8°C.[46]

The bio-based polyhydroxyalkanoates can be used for plasticization, toughening, and processing improvement of unplasticized and plasticized (semi-rigid to flexible) PVC compounds.[48] They also improve the UV stability of PVC by offsetting the yellowing of PVC and not causing additional photodegradation.[48] The ecologically attractive additive can replace several additives, eliminating both undesirable additive interactions and the need to stabilize unstable ingredients.[48]

3.7 ANTIBLOCKING AGENTS

Table 3.9 contains a condensed summary of types and properties of antiblocking agents used in PVC. For a comprehensive review of antiblocking properties, mechanisms of action, and use of the antiblocking agents, see the specialized monographic source.[49]

Table 3.9. PVC antiblocking agents.

Types: silica natural and synthetic, aluminosilicate, ethylene N,N'-bis-stearamide		
Applications: film, extrudable compounds		
Reasons for use: improvement of production rate, reduced coefficient of friction, reduced surface tackiness		
Potential adverse effects: surface roughening, light transmission		
Typical concentrations: 0.3-1.5		
Density, 20°C, kg/m^3: 1,000-3,100	Melting point, °C: 60-1,610	Decomposition, °C: 160-2,230
Thermal conductivity, W/Km: 7.2-13.6		Dielectric constant: 1.9-4
Volume resistivity, Ω-cm: 5.7x10^{11}- 4.5x10^{14}		Oil absorption, g/100 g: 100-300
Specific surface area, m^2/g: 50-750	Mohs hardness: 6	Refractive index, 20°C: 1.4-1.5

Inorganic antiblocking additives are frequently added in concentrations larger than required because they perform other functions, such as surface matting and plasticizer absorption.

Branched, saturated, primary fatty acid amide has been used as a slip and/or antiblocking or mold release agent. It has a formula R–CO–NH$_2$ where R is a saturated, branched hydrocarbon chain having 11 to 23 carbon atoms wherein at least 60 wt% of the R–CO–NH$_2$ molecules have monoalkyl branches, and less than 25 wt% of the R–CO–NH$_2$ molecules have polyalkyl branches.[50]

3.8 RELEASE AGENTS

Table 3.10 contains a condensed summary of types and properties of release agents used in PVC. For a comprehensive review of release properties, mechanisms of action, and use of the release agents, see specialized monographic source.[49]

Table 3.10. PVC release agents.

Types: ethylene N,N'-bis-stearamide, glycerol monostearate, silicone oil
Applications: blow molding, calendering, extrusion, injection molding
Reasons for use: good spreading characteristics, improvement of production rate, reduction of adhesion between the surface of equipment and plastic materials in contact (mostly during their production)

Table 3.10. PVC release agents.

Potential adverse effects: adhesion to the hot metal surface, bubbling, increased mold cleaning frequency, lack of adhesion in joining processes, residue on the product surface, transfer to material in contact, welding impairment		
Typical concentrations: 0.05-1.4		
Density, 20°C, kg/m^3: 870-1,000	Melting point, °C: –84-145	Boiling point, °C: 150-360
Thermal conductivity, W/Km: 0.15-0.17		Surface tension, mN/m: 19.9-21.3
Refractive index, 20°C: 1.37-1.5	Dielectric constant: 2.5-3.1	Iodine value: 0-70

3.9 SLIP AGENTS

Table 3.11 contains a condensed summary of types and properties of slip agents used in PVC.

The modulus of the polymer determines the slope of the stick episode of a stick-slip profile, while the stick-slip frequency and amplitude are more dependent on the polar contribution of the surface energy rather than the cohesive strength of the polymers.[51]

For a comprehensive review of slip properties, mechanisms of action, and use of slip agents see the specialized monographic source.[49]

Table 3.11. PVC slip agents.

Types: ethylene N,N'-bis-oleamide, stearamide, Zn and/or Ca stearate		
Applications: extrudable compounds, transparent sheets		
Reasons for use: compatibility, low transfer to material in contact, low volatility, oxidation and thermal stability, reduced coefficient of friction, reduced surface tack, weather stability		
Potential adverse effects: build up, residue on the product, welding problems		
Typical concentrations: 0.3-1.0		
Density, 20°C, kg/m^3: 880-1,090	Melting point, °C: 60-300	Boiling point, °C: 150-330 (dec)
Refractive index, 20°C: 1.4-1.5	Surface tension, mN/m: 21.3	Molecular weight 199-330

Frequently, proper use of thermal stabilizers is sufficient to improve slip properties to a required level.

3.10 ANTISTATICS

Table 3.12 contains a condensed summary of types and properties of antistatic agents used in PVC. For a comprehensive review of antistatic properties, mechanisms of their action, and the use of antistatic agents see the specialized monographic source.[52]

Table 3.12. PVC antistatics.

Types: carbon black, copper powder, chlorinated polyethylene (blending), dimethylethyl soya ammonium ethosulfate, 1-dodecylpyridinium chloride monohydrate, ethoxylated fatty dimethyl-ethylammoniumethosulfate, ethylene oxide condensate, fluorinated alkyl polyoxyethylene ethanol, glycerol monostearate, graphite, lauric diethanol amide, polyethylene glycol monolaurate, polypyrrole (blending) propanesultone (surface coating), sodium sec-alkane sulfonate		
Applications: films, floor coverings, medical applications, packaging		
Reasons for use: effective in small quantities, elimination of spark discharge, prevention of static build up		
Potential adverse effects: mechanical properties, odor, thermal stability, toxicity		
Typical concentrations: 0.001-35 phr		
Density, 20°C, kg/m^3: 930-8,960	Melting point, °C: –36 to 1,083	Boiling point, °C: 80 to 2,562
Resistivity, Ω-m, 10^8-10^{10} (PVC containing antistatics)		Odor: none to amine-like
Static decay, s: 0.01-10	State: liquid or solid	color: clear to black

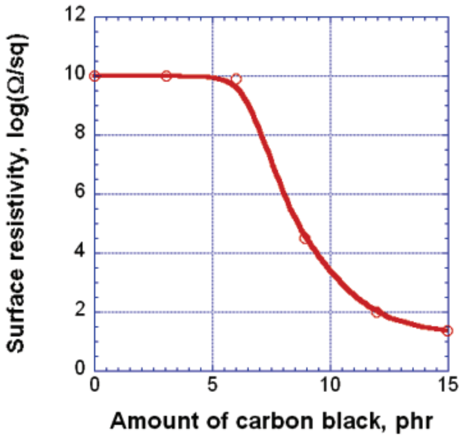

Figure 3.30. Surface resistivity of PVC composites containing variable concentrations of carbon black. [Adapted, by permission, from Chen, C.-H.; Li, H.-C.; Teng, C.-C.; Yang, C.-H., *J. Appl. Polym. Sci*., **99**, 5, 2167-2173, 2006.]

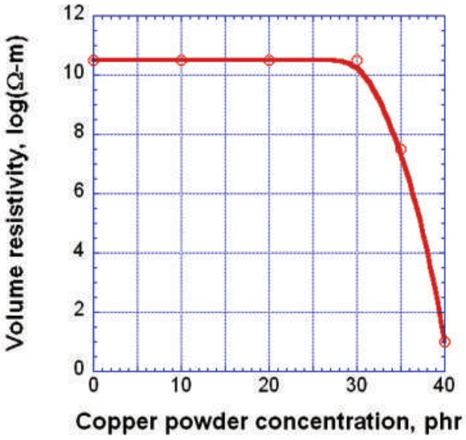

Figure 3.31. Volume resistivity of PVC composites containing variable concentration of copper powder. [Data from Jando, T.; Stelczel, T.; Farkas, F., *J. Electrostatics*, **23**, 117-125, 1989.]

Figure 3.30 shows the effect of the addition of carbon black on surface resistivity of its composite with PVC. Initial addition of up to 6 parts of carbon black has little impact on surface conductivity. When carbon black reaches its threshold percolation concentration, surface conductivity changes rapidly. At the threshold, concentration particles of carbon black are close enough to each other to conduct

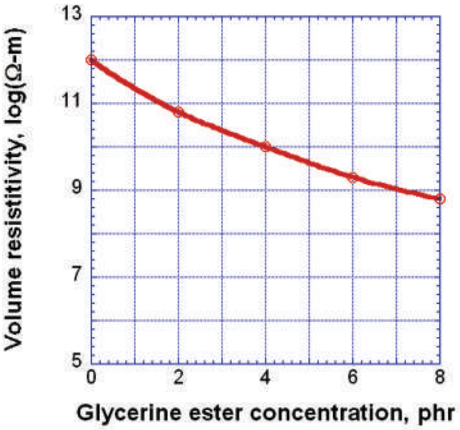

Figure 3.32. Volume resistivity of PVC containing variable concentration of glycerin ester. [Data from Jando, T.; Stelczel, T.; Farkas, F., *J. Electrostatics*, **23**, 117-125, 1989.]

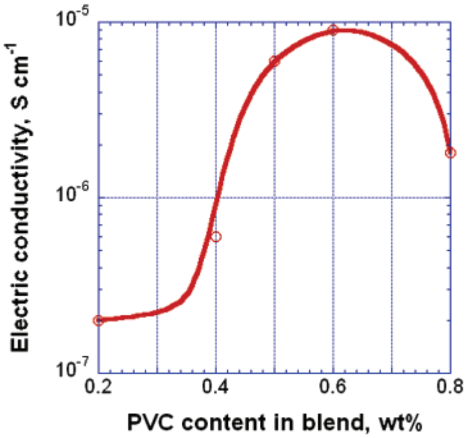

Figure 3.33. Electric conductivity of ternary blend (PEO/PVC/PEDOT-PSS) vs. content of PVC in the blend. [Adapted, by permission, from Rinaldi, A. W.; Matos, R.; Rubira, A. F.; Ferreira, O. P.; Girotto, E. M., *J. Appl. Polym. Sci.*, **96**, 5, 1710-1715, 2005.]

electrons by tunnelling.[53] Once surface resistivity level stabilizes again, further addition of carbon black does very little to alter its change. Figure 3.31 shows that the behavior just described is typical of conductive particulate materials.[54] Addition of organic antistatics has a different influence on the resistivity of PVC compounds. The change of resistivity occurs (Figure 3.32) from the beginning because organic liquids are mobile in composition and they can carry charges even at low levels, but they also have limitations since it is not possible to obtain as low resistivities as in the case of conductive particulates. It is thus not surprising that moderate improvement can be made with organic additives but highly conductive materials, such as required for EMI shielding, can only be obtained with highly conductive particulates, and particularly fibers.

The possibility of obtaining blends of PVC with conductive polymers has also been investigated. Figure 3.33 shows that concentration of conductive polymer is essential for conductivity. Optimal conductivity was obtained at a certain range of PVC concentration. The blends of poly(ethylene oxide), PEO, poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate), PEDOT-PSS, and PVC were designed to maximize thermal stability and conductivity. The thermal stability of the blend is increased by PEO and conductivity was increased by increasing concentration of PEDOT-PSS.[55] Conductivity of PVC-NBR blends can be increased by the addition of polyaniline-DL-camphor sulfonic acid, PANI-CSA. The conductivity of the blend increased linearly with the amount of PANI-CSA.[56]

An antistatic agent was added to isolate fine particles after bulk PVC polymerization.[57] It effectively prevented generation of fine particles and scale (adhering to a reactor wall) during bulk polymerization.[57]

3.11 FLAME RETARDANTS

Table 3.13 contains general information on PVC flame retardants.

Table 3.13. PVC flame retardants.

<table>
<tr><td colspan="3">Types: aluminum hydroxide, antimony trioxide, antimony pentoxide, chlorinated paraffins, cuprous oxide, ferrocene derivatives, magnesium hydroxide, metal chelates (Al, Co, Cu, Fe, Ni, or Zn acetylacetonates), molybdenium oxide, phosphorus-containing plasticizers, sodium antimonate, tin dioxide, zinc borate, zinc hydrostannate, zinc stannate</td></tr>
<tr><td colspan="3">Applications: building materials, carpet backing, conveyor belts, electrical materials, flooring, tiles, roofing, wire and cable, and wall coverings</td></tr>
<tr><td colspan="3">Reasons for use: flame and fire resistance</td></tr>
<tr><td colspan="3">Potential adverse effects: fogging, reduced mechanical properties (e.g., impact strength, tensile strength, and elongation), thermal instability</td></tr>
<tr><td colspan="3">Typical concentrations: 0.1-50 phr</td></tr>
<tr><td>Density, 20°C, kg/m^3: 980-5,590</td><td>Melting point, °C: –90 to 980</td><td>Dielectric constant: 3.83-7.8</td></tr>
<tr><td>Particle size, μm: 0.025-55</td><td>Refractive index, 20°C: 1.44-2.09</td><td>Mohs hardness: 2.5-3.5</td></tr>
<tr><td>Oil absorption, g/100 g:12-44</td><td>Hegman grind: 5.5-6</td><td>Spec. surface area, m^2/g: 0.1-15</td></tr>
</table>

Rigid PVC does not require flame retardants because it does not contribute to fire propagation and passes most flammability tests.[58] The limiting oxygen index of PVC is 45-49, and on this account PVC is only exceeded by chlorinated PVC (60-70) but it is about 3 times higher than that of the other two most common commodity polymers (PE and PP).[49] The heat of combustion of PVC is very low at 16.4 kJ/g, which is again unique among polymers (PE and PP have heat of combustion about 2.6 times higher than that of PVC).[58] These two indicators show that it is difficult to initiate and sustain the fire of PVC, but if it burns, it produces much less energy than other materials which is an essential contributor to control of the spread of fires.[59]

In flexible PVC, the flammability depends on additives, mainly on the type of plasticizers used. Most plasticizers (with the exception of esters of phosphoric acid) are excellent fuels, and they contribute to the rapid decrease of PVC flammability and create demand for use of flame retardants.

PVC owes its inherent flame resistance to the high concentration of chlorine (56.8%). The high presence of chlorine is a drawback for PVC thermal stability, and it requires a proper stabilizing package to delay emission of HCl, but the same emission is also responsible for its flame retarding capabilities. For this reason, some PVC flame retardants (e.g., oxides of various metals and ferrocene derivatives) are used because they can enhance production of HCl when it is needed for flame protection. Multiple aspects of PVC thermal degradation and its mechanisms were discussed in full in a monograph on PVC degradation and stabilization, and this discussion is not repeated here.[22] It is important to note for this discussion that, in addition to HCl, benzene is produced as the principal volatile product. Benzene is an excellent fuel and, therefore, any process which will reduce its formation will increase flame resistance.

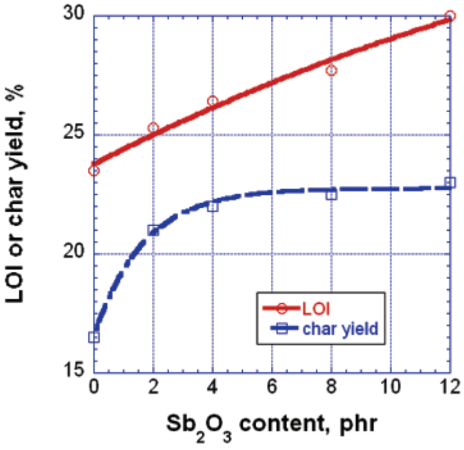

Figure 3.34. Limiting oxygen index and char yield vs. antimony oxide content. [Data from Wang, H.; Wang, H.; Guo, Z.; Qi, S.; Tian, C., *J. Fire Sci.*, **24**, 3, 195-210, 2006.]

PVC can make use of a large number of flame retardants performing their functions according to different mechanisms. Antimony trioxide has a long history of application in PVC. Its mechanism of action is similar to HCl because it produces $SbCl_3$ which has a high boiling point (223°C).[58] Vapors of antimony trichloride participate in fire extinguishing. Figure 3.34 shows that there is almost a linear increase of limiting oxygen index with an increase in flame retardant concentration but char formation is not much affected by increasing concentrations of flame retardant.[60] In thermogravimetric studies, two temperature ranges were selected: first, from 240 to 370°C, is a weight loss caused by HCl emission, and in the second, from 370 to 550°C, cyclization of polyene sequences is the primary process. This means that the first range is related to flammability, and the second to the char formation. The activation energy of the first process decreases from 91.5 to 58.7 kJ/mol, meaning that at this stage production of HCl is intensified by both the presence of HCl and antimony chloride, and this explains why antimony trioxide increases PVC flame resistance. At the second stage, activation energy decreases only slightly from 124.7 to 100.4 kJ/mol, which means that char formation is only marginally influenced by antimony trioxide. In the same studies, it was found that the performance of antimony trioxide can be enhanced by the synergistic effect of the addition of tin dioxide which acts in a condensed phase by which it improves char yield and its morphology.[59]

Hydroxides of magnesium and aluminum produce water at elevated temperatures, which contributes to extinguishing a flame. Also, these two flame retardants promote charring and serve as a barrier to heat and mass transfer.[58] Figure 3.35 shows that much larger quantities of aluminum hydroxide and magnesium hydroxide are needed as compared with antimony trioxide. Magnesium hydroxide

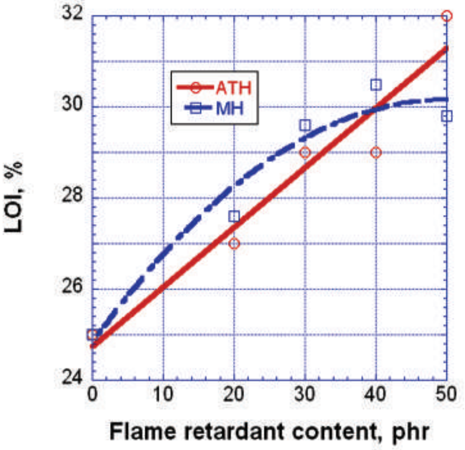

Figure 3.35. Limiting oxygen index of flexible PVC containing variable quantities of aluminum hydroxide, ATH, and magnesium hydroxide, MH. [Data from Cusack, P. A.; Hornsby, P. R., *J. Vinyl Additive Technol.*, **5**, 1, 21-30, 1999.]

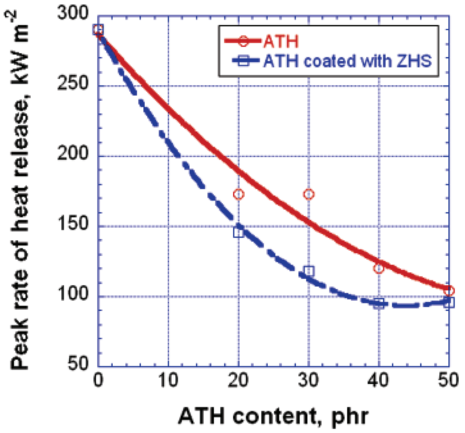

Figure 3.36. Peak rate of heat release from flexible PVC containing variable quantities of uncoated and zinc stannate coated (10%) aluminum hydroxide. [Data from Cusack, P. A.; Hornsby, P. R., *J. Vinyl Additive Technol.*, **5**, 1, 21-30, 1999.]

is slightly more efficient than aluminum hydroxide. These large quantities of mineral additive have implications for formulation. First of all, the viscosity of either melt or paste increases with addition and thus calls for more plasticizer to reduce it. Also, mechanical properties are affected (generally tensile strength and elongation are decreased). The study on aluminum and magnesium hydroxide[60] included evaluation of the potential of zinc hydrostannate and zinc stannate as coating additives which may increase the performance of original fillers. A 10% coating substantially improved performance of flame retardants.[61] Figure 3.36 shows that coating decreases the peak rate of heat release (also, limiting oxygen index is rapidly increased). The peak rate of heat release is used to express the maximum intensity of the fire. Zinc stannate and hydrostannate significantly increase LOI and char yield, and they are very useful flame retardants for flexible PVC.[62] They act by reducing initial decomposition temperature and they stabilize residual char.[62]

Figure 3.37 shows that the addition of aluminum hydroxide decreases the length of a burned sample.[63] The relationship between ATH concentration and burned length is almost linear, as is the relationship between time of burning and amount of ATH.[63] Addition of a small amount of ZnO (1 phr) reduces initial decomposition temperature, and it makes it a very effective synergistic additive to ATH.[64]

Chlorinated paraffins are secondary plasticizers of PVC. If they are used in conjunction with primary plasticizers, which are flammable, they diminish the effect of primary plasticizers on the decrease of flame resistance. Chlorinated paraffins have some drawbacks such as their adverse effect on PVC thermal stability, high viscosity, and toxicity of some grades, and for these reasons, their range of applications diminished.

Phosphorus-based esters have long been used along with flammable plasticizers to diminish their influence on flammability. The rule of thumb is that 20% phosphate plasticizer is required to maintain self-extinguishing properties of PVC.[48] Phosphate ester plasticizers did not work well together with antimony oxide, but the addition of zinc borate produced an excellent flame retarding composition.[65]

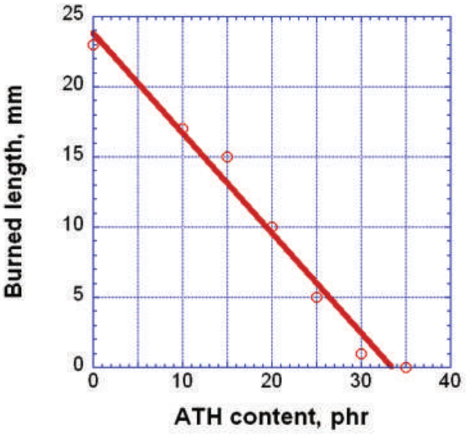

Figure 3.37. Burned length of PVC sample vs. ATH content. [Data from Mansour, S. H.; Iskander, B. A.; Nasrat, L. S., *Polym.-Plastics Technol. Eng.*, **45**, 7, 857-863, 2006.]

Phosphaphenanthrene groups containing castor-oil-based phosphate plasticizer increased decomposition temperature by more than 100°C as compared with DOP.[66] It produced more char and plasticized by it PVC had LOI of 36%.[66] Vegetable oil can be used for the preparation of this flame retarding plasticizer.[66]

The effect of metal oxides and chelates has already been mentioned. The metals involved can react with HCl and their products of the reaction are catalytic to PVC thermal degradation, and thus HCl is produced more rapidly, which contributes to increasing flammability. Zinc borate is a quite popular metal salt used in this application. In addition to zinc chloride, boron chloride reduces flammability.[58] Some studies[67] show that when boron chloride is produced, the B_2O_3 glass layer is destroyed and boron is volatilized, which diminishes its flame stability action.

The synergistic mixture of flame retarding composition comprises from 5 phr metallic alkaline earth borate (calcium borate ($Ca_3(BO_3)_2$) and more than 30 phr of metallic hydroxide (aluminum trihydroxide and/or magnesium dihydroxide) which is suitable for electric and/or optical cables as a layer surrounding one or several conductors.[68]

3.12 SMOKE SUPPRESSANTS

Table 3.14 contains general information on PVC smoke suppressants.

Table 3.14. PVC smoke suppressants.

Types: ammonium octamolybdate, molybdenum trioxide, vanadium oxide, zirconium oxychloride, and inorganic compounds listed as flame retardants		
Applications: the same as for flame retardants		
Reasons for use: decreasing amount of smoke produced during burning		
Potential adverse effects: influence on thermal stability		
Density, 20°C, kg/m^3: 980-5,590	Melting point, °C: –90 to 980	Dielectric constant: 3.83-7.8
Particle size, μm: 0.025-55	Refractive index, 20°C: 1.44-2.09	Mohs hardness: 2.5-3.5
Oil absorption, g/100 g:12-44	Hegman grind: 5.5-6	Spec. surface area, m^2/g: 0.1-15

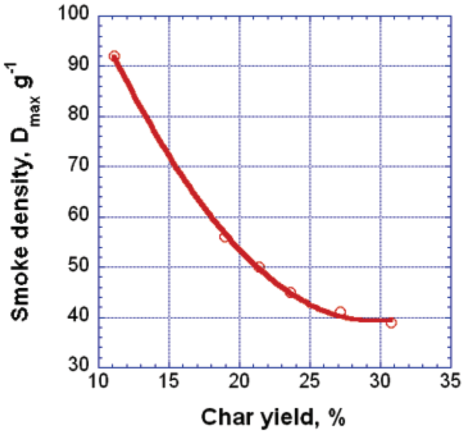

Figure 3.38. Smoke density vs. char yield for PVC/ABS (70/30) blends. [Data from Carty, P.; White, S., *J. Fire Sci.*, **13**, 4, 289-99, 1995.]

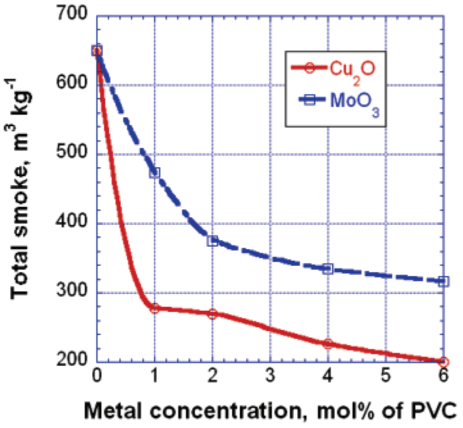

Figure 3.39. Total smoke produced in presence of two smoke suppressants. [Data from Li, B.; Wang, J., *J. Fire Sci.*, **15**, 5, 341-357, 1997.]

Inorganic flame retardants act to some extent as smoke suppressants because they also increase charring, which reduces the formation of volatile aromatic compounds responsible for the production of smoke.[58] It is quite certain that smoke suppressants act in a condensed phase because almost all molybdenum, which is a metal of popular smoke suppressants, is found in char. Figure 3.38 shows data for PVC/ABS blends containing different amounts of smoke suppressant (FeOOH).[69] It is certain from the data that the smoke density decreases when the amount of char increases. This is not surprising since both processes (char formation and smoke formation) compete for the same materials, which can be either converted to char or fuel. Figure 3.39 shows the effect of two smoke suppressants. It was discovered that unlike Cu_2O, MoO_3 delays the production of smoke.[70]

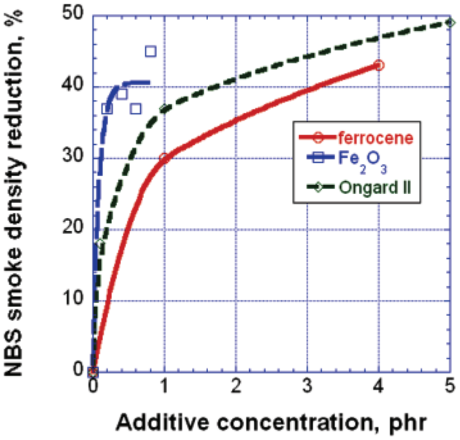

Figure 3.40. Smoke reduction vs. concentration of three smoke suppressants. [Data from Carty, P.; Grant, J.; Metcalfe, E., *Appl. Organometallic Chem*., **10**, 2, 101-11, 1996.]

Cuprous stannate ($Cu_2SnO_3xH_20$) (x is 0, 1, 2 or 3) has been found to act effectively as a smoke suppressant, flame retardant, a thermal stabilizer; and was working against degradation of polymer mechanical properties.[71]

Metal chelates lower decomposition temperature (decrease thermal stability of material), increase char yield and limiting oxygen index, and improve smoke density rating.[72] They are useful synergistic additives for $Al(OH)_3$ and $Mg(OH)_2$. Their two primary functions are catalysts of dehydrochlorination and char formers.

Several smoke suppressants have been tested including ferric oxide, 1,1'-bis(2,4-dichlorobenzoyl) ferrocene, and mixture of magnesium and zinc oxides (Ongard II) which were the most efficient in the reduction of smoke (see Figure 3.40).[73] All additives promoted char formation but there was no simple correlation between smoke suppression and char formation. It was not clear how more effective smoke suppressants function, but, it was thought, in the case of ferrocene it was possible that it was converted to oxychloride, which was known as the effective smoke suppressor.[73]

In the summary of PVC applications of flame retardants and smoke suppressants, it should be pointed out that the number of deaths in Europe and the USA caused by fires has fallen rapidly because of the application of these effective combinations.[74]

3.13 LUBRICANTS

Table 3.15 gives general information on lubricants. The discussion below regards the significant findings regarding lubricants in PVC formulations. For the detailed mechanism of lubricant action, see the specialized monographic source.[22]

Table 3.15. PVC lubricants.

Types: amide wax, butyl stearate, calcium stearate, complex ester, fatty acid esters, oxidized polyethylene wax, paraffin wax, a partial ester of glycerol, phthalate ester, stearic acid
Applications: blow molding, calendering, dip molding, extrusion, injection molding, and rotational molding

Table 3.15. PVC lubricants.

Reasons for use: decrease of adhesion to metal, improved impact resistance, increased thermal stability, lowering viscosity		
Potential adverse effects: affect color and/or gloss, decrease gelation, increase surface tack, lower impact resistance, overlubrication, plate-out, problems with welding, reduce dimensional stability, reduce output		
Typical concentrations: 0.05-3.5		
Density, 20°C, kg/m^3: 850-1,090	State: solid	Color: white to off-white
Odor: odorless to a fatty	Melting point, °C: 46-160	Boiling point, °C: 218-383

In spite of the theoretical models and action mechanisms,[75] lubricants are still divided into external and internal.[75-78] Fish and Bacaloglu[75-77] conducted studies on the effect of lubricants on the glass transition temperature of PVC. Their findings permit us to classify lubricants. Depending on their interaction with PVC, lubricants may or may not be compatible with PVC. Because PVC is a polar material, polar lubricants are compatible and interact with PVC molecules, which increases the mobility of the PVC molecules and decreases its glass transition temperature. The glass transition temperature is less affected by incompatible lubricants, which form separate phases or exude from the polymer. Internal lubricants were found to decrease glass transition temperatures by 13-26°C, external by 0-5°C, and mixed (internal/external) by 6-10°C.[75] Based on these studies, methyl, barium, and calcium stearates are internal lubricants, aluminum and sodium stearate are internal/external, and zinc, lithium, and magnesium stearates and stearic acid are external lubricants.[76-77] External lubricants have a low solubility in PVC and promote good metal release in the PVC melt.[78] They form a thin film between the melt and hot metal, decreasing adhesive forces. Internal lubricants are soluble in PVC. They reduce intermolecular attractions between polymer chains, which decrease elastic rebound and die swell, reduce internal stress, and help to promote flow by intermolecular slippage. The benefits of using internal lubricants include reduced shear burning; improved filling of a die or mold: improved flow, reduced die swell; good clarity, paintability; and good weld line and spider line knitting.[79] Full discussion of these and other findings can be found elsewhere.[22]

Table 3.15 shows potential adverse effects which do not occur when external and internal lubricants and their concentration are properly selected.[80-82] For example, an increase of internal lubrication to lower process temperature may cause surface tackiness and loss of dimensional stability.[80] If excessive amounts of internal lubricants are used in extrusion, reduced heat distortion temperature, plate-out, and reduced impact strength may also occur.[79] On the other hand, increase in external lubrication to lower shear rate may cause plate-out and delay gelation.[80] Too much external lubricant in extrusion may cause several detrimental effects, including poor weld line/spider line knit, partially due to a build-up of external lubricant on spiders that gets dragged off the coating. Excessive amounts may exude to the surface and cause streaking, poor adhesion of laminates or capstocks, the degree of fusion may be affected, and consecutively, product strength may suffer.[79]

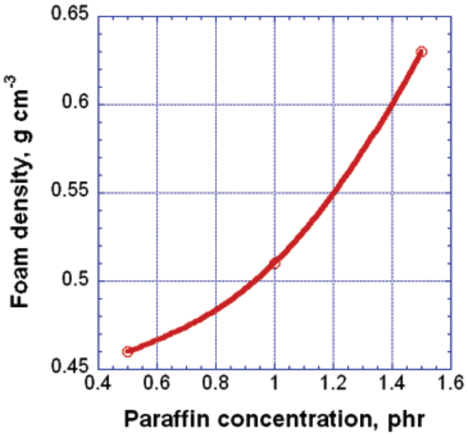

Figure 3.41. Foam density vs. concentration of paraffin lubricant. [Data from Decker, R. W., *J. Vinyl Additive Technol.*, **2**, 2, 121-124, 1996.]

In foams, it was found that lubricant affects the efficiency of foaming. Figure 3.41 shows that when paraffin is used as a lubricant, the density of foam depends on the amount of lubricant.[81] With some ester-based lubricants tested in the same program, the density of foam did not change, even in a broader concentration range.[68] Lubricants control the rate of fusion and, therefore, the rate of heat generation, which affects gas evolution because blowing agents decompose and generate gas at elevated temperatures. These two processes (fusion and gas generation) must be balanced by a proper selection of lubricant, its concentration, and blowing agent type and concentration to achieve specific properties of the foam.[82]

Typically, rigid PVC formulations use about twice as much lubricant as semirigid and flexible formulations.[83] This is because plasticizers act similar to internal lubricants as they interact with PVC, making it more mobile, and flexible.[84] The lubricant was found to affect impact properties because these were controlled by fusion which was influenced by lubricant type and concentration.[85] Lubricant also had a plasticizing effect on the polymer, which had higher tensile strength without lubricant.[86]

3.14 PROCESS AIDS

Table 3.16 contains general data on process aids.

Table 3.16. PVC process aids.

Types: acrylic (Durastrength (also impact modifier), Paraloid K, Plastistrength)
Applications: blow molded bottles, calendered sheet, exterior trim, fence, film, foam, pipe, profile, rigid containers, siding, windows, wood-polymer composites
Reasons for use: clarity, elimination of jetting, elimination of sharkskin, enhanced fusion, high gloss, high output, good weld strength, improved melt strength, metal release properties, reduction of gate blush in injection molding, uniform cellular structure, uniform wall thickness, weather resistance
Potential adverse effects: low melt strength, low output, melt fracture, plate-out

Table 3.16. PVC process aids.

Typical concentrations: 0.2-9.6 phr	
Density, 20°C, kg/m^3: 1,050-1,180	Molecular weight: 300,000-5,000,000
Refractive index, 25°C: 1.49-1.52	Glass transition temperature, °C: 91-106
Particle size, µm, 45-74	

PVC melts have a dry appearance, little strength, and lack of adhesion to a metal surface. Process aids are designed to change all these properties. Almost all rigid formulations and many flexible ones use acrylic process aids.[80] Acrylic process aids are copolymers of methylmethacrylate with ethyl acrylate, butyl acrylate, or butyl methacrylate.[80,88] Selection of monomers is crucial because it affects the glass transition temperature of the copolymer, which should be lower than that of PVC to cause additive to melt below PVC process temperature and thus help to process it.

An acrylic copolymer additive has been found useful as a process aid in highly filled polyvinyl chloride and chlorinated polyvinyl chloride composites. The acrylic additive is especially useful in highly filled PVC flooring tiles, rolled flooring, pipe and siding. The acrylic copolymer additive contains from 50 to 79 wt% of methyl methacrylate monomer units, and has a glass transition temperature of less than 90°C.[89]

High molecular weight of process aid and its high concentration may be the root cause of melt fracture.[80] Considering that this is just contrary to the requirements of process aid performance, the proper compromise must be found.[80] Die swell is also increased by higher concentrations and higher molecular weights of process aids which again calls for optimization.[80]

In foam applications, it is known that it is challenging to obtain foam density below 1 g/m^3 without the use of process aid because of lack of melt elasticity.[82] High melt elasticity permits bubbles to grow without breaking.

3.15 VICAT/HDT MODIFIERS

Table 3.17 contains general information on heat deflection additives

Table 3.17. PVC heat deflection additives.

Types: acrylonitrile-butadiene-styrene copolymer, poly(acrylonitrile-styrene-acrylate), poly(α-methyl-styrene-acrylonitrile)	
Applications: automotive parts, extruded profiles, siding, windows	
Reasons for use: increase of dimensional stability	
Potential adverse effects: embrittlement, weather degradation	
Typical concentrations: 20-60%	
Density, 20°C, kg/m^3: 1,070	Glass transition temperature, °C: 109

Table 3.17. PVC heat deflection additives.

Vicat temperature, °C: 105	Heat deflection temperature, 1.8 MPa, °C: 103
Dielectric constant: 3.9	Coefficient of linear thermal expansion, mm/mm °C: 0.95×10^{-4}

The addition of fillers can be used to increase HDT, but it is rather ineffective because fillers can only raise the HDT to approach the glass transition temperature of PVC.[90] A more effective approach is to blend PVC with another polymer having a higher softening point.[90] The other polymer must have a similar polarity (solubility parameter) to PVC to form a good mixture and mechanical properties.[90] This requirement makes the range of suitable polymers very limited.[90]

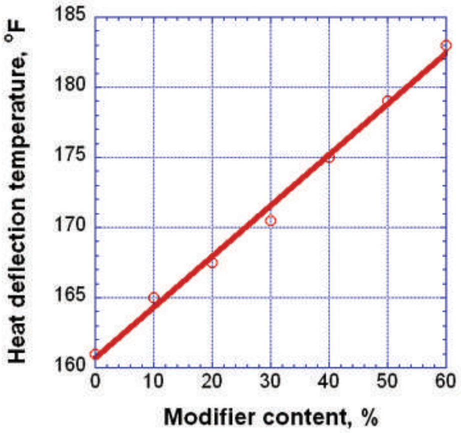

Figure 3.42. Concentration of poly(acrylonitrile-styrene-acrylate) in PVC blend vs. heat deflection temperature. [Data from Zerafati, S., *J. Vinyl Additive Technol.*, **4**, 1, 35-38, 1998.]

Two tests are used to determine dimensional stability: the Vicat test measures penetration of needle and deflection under flexural load determines the temperature of sample deflection.[91] Results of these tests are significant for structural engineers who select plastics for particular applications. There is always the desire to improve the dimensional stability of PVC. Figure 3.42 shows that addition of poly(α-methylstyrene-styrene-acrylo-nitrile), PMSC, causes a linear increase in deflection temperature. For polymers similar to PVC, having low crystallinity, deflection temperature is controlled by their glass transition temperatures.[91] The glass transition temperature of PVC is also controlled by its molecular weight. PMSC is miscible with PVC and it has glass transition temperature much higher than PVC (130°C); therefore, it increases the deflection temperature of the blend.[91]

In the window profile industry, it is essential to increase the temperature of deflection because even in milder climates PVC cannot be used in darker colors and PVC windows cannot be used in hot climate countries. For these applications, weathering is significant, and for these reasons poly(acrylonitrile-styrene-acrylate), ASA, is an excellent choice because it is one of the most UV durable polymers.[92]

3.16 FOAMING AGENTS AND PROMOTERS

Table 3.18 contains general information on PVC foaming agents. The information on foaming promoters (kickers) is omitted here because it is discussed in detail in the complementary book on PVC degradation and stabilization.[22]

Table 3.18. PVC foaming agents.

Types: azodicarbonamide, carbon dioxide, inert gas, sodium bicarbonate	
Applications: coated fabrics, cornices, curtain rails, door frames, guide rails for shutters, furniture profiles, roofing products, plastisol foams, shoe soles, skirting boards, sofit boards, wall and ceiling paneling, wallpaper, window sills, wood-replacement products	
Reasons for use: production of a foamed PVC	
Potential adverse effects: die swell	
Typical concentrations: 1-3 phr	
Density, 20°C, kg/m^3: 1,650-2,160	Gas yield, ml/g: 125-220
Particle size, µm: 3-5	Decomposition temperature, °C: 143-215
Ash, %: 0.1	Gaseous products: CO_2, CO, NH_3, H_2O

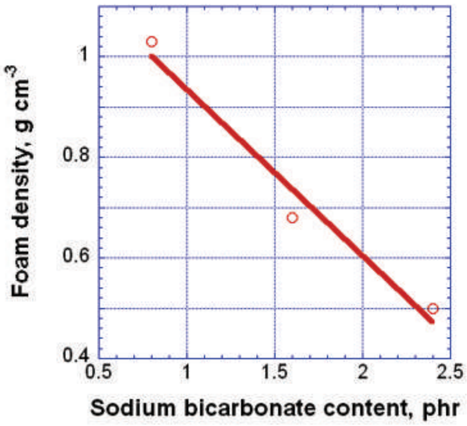

Figure 3.43. Foam density vs. sodium bicarbonate content. [Data from Thomas, N. L.; Harvey, R., *J. Vinyl Additive Technol.*, **5**, 2, 63-70, 1999.]

Two chemical blowing agents are frequently used in PVC foaming: azodicarbonamide (exothermic blowing agent), which gives relatively fast-foaming at a more narrow temperature range (175 to 233°C), and sodium bicarbonate (the endothermic blowing agent), which offers longer foaming times and has a broader range of decomposition temperature (143 to 240°C).[82] Figure 3.43 shows that PVC foam density decreases almost linearly with increased addition of sodium bicarbonate.[94] If too high a quantity of blowing agent is added, cells collapse, producing denser foam.[94] Decomposition of sodium bicarbonate begins at 143°C and continues when the temperature increases. The decomposition temperature of azodicarbonamide is higher than the usual PVC processing temperature; therefore, it has to be lowered by the addition of kickers. The kicker may decrease its temperature to 175°C[95] (and even to 150°C).[96] Degradation temperature of the blowing agent, melt viscosity, and fusion temperature must be synchronized to yield a uniform foam with high efficiency. Studies of the foam extrusion process[97] show that optimal conditions have to be carefully selected in order to obtain the required uniformity and density. The temperature of the melt is critical, considering that below optimum temperature, too high viscosity, and insufficient production of gas produce foamed profiles of high density. If temperature is higher than optimum, too low viscosity of melt, too high pressure drop at the die exit, and too rapid gas expansion cause cells to rupture and collapse.[97,99]

PVC composite foamed board contains 0.8-1.2 parts by weight of composite foaming agent including an inorganic foaming agent (sodium bicarbonate) and an organic foaming agent (azodicarbonamide), 3-5 parts by weight of foam regulator (ZD530).[100] The ratio of the inorganic foaming agent to the organic foaming agent by weight in the composite foaming agent was 1/2-1.[100]

Foam density is not only important because of the weight of material and cost, but it also affects many mechanical parameters such as tensile strength, tensile modulus, flexural strength, impact strength, and deflection temperature, all of which decrease with density decreasing.[98]

Microcellular PVC foams with about 40% reduction of density can be obtained using carbon dioxide blowing.[101] Carbon dioxide can be replaced by argon in the so-called inert-gas blowing process.[102]

PVC foam obtained with supercritical carbon dioxide had a uniform foam structure with a thin bubble wall (less than 5 μm) and bubble density of 10^6 to 10^8 bubbles/cm^3.[103] The bubble diameter was less than 20 μm. The density was reduced from 1.241 to below 0.4 g/cm^3.[103]

3.17 ANTIFOG AGENTS

Table 3.19 gives the general information on antifog agents.

Table 3.19. PVC antifog agents.

Types: polyoxyethylene sorbitan fatty acid ester (Sunthrouzer 100, 700, 720, 810, W-4120; Atmer 100, 103), product of transesterification of native oils with polyethylene glycol (Loxiol A 4), sorbitan monolaurate (Tego), glycerol ester (Atmer 185, 1440)		
Applications: automotive, food wrap films, green houses		
Reasons for use: reduce or eliminate formation of droplets on the surface of transparent material		
Typical concentrations: 2-60 phr		
Density, 20°C, kg/m^3: 959-1,012	Refractive index, 25°C: 1.48-1.52	Dielectric constant: 3.9-4.7
Pour point, °C: –40 to –48	Direct current resistivity, Ω-cm: 0.94x10^{13} to 1.3x10^{13}	

Antifogging is closely associated with the formation of a liquid film on the surface of the glass (particularly a car windshield). It was quite a common phenomenon related to exuding and evaporation of PVC additives, most frequently well-known in the case of plasticizers present in PVC products used by automotive companies for car interior applications. But fogging is applicable to any loss of transparency, for example by PVC wrap film or film for greenhouses. These antifogging additives act as surface active or wetting agents and prevent the formation of discrete water droplets. These antifogging agents can be compounded into the polymer to achieve controlled migration from the bulk to the polymer surface.

Fogging experienced in an automotive interior cannot be solved by adding fogging additives because it is caused by condensation of plasticizer (or other additives vapors on the windshield’s surface). There are only two methods available to reduce or eliminate this effect. One is to use less volatile additives. For example, diisodecyl and 2-propylheptanol esters of phthalic acid pass the fogging test (polymeric plasticizers are even better in this respect).[104] It should be noted that plasticizers are not the only substances causing fogging in automotive applications. Studies of various materials suspected to cause fogging revealed that a popular antioxidant (2,6-di-tert-butyl-4-methylphenol, BHT) was one of the substances causing fogging. Still, tris(chloropropyl) phosphate, flame retarding plasticizer was the primary product condensing on windshields.[105] The second option includes a coating which covers the windshield’s surface and protects it from the formation of droplets due to the changes in the surface tension of glass.

3.18 CROSSLINKING AGENTS

Table 3.20 contains general information on crosslinking agents used in PVC.

Table 3.20. PVC crosslinking agents.

Types: γ-aminopropyltriethoxysilane, bis(γ-trimethoxysilylpropyl)amine, 1,2-ethylenedioxydibutyltin, γ–mercaptopropyltrimethoxysilane, N-(2-aminoethyl)-3-aminopropyltrimethoxysilane, phenylaminopropyltrimethoxysilane, radiative crosslinking		
Reasons for use: improvement of mechanical properties, increase in heat deflection temperature		
Typical concentrations: 2-10 phr		
Density, 20ºC, kg/m^3: 885-1,050	Molecular weight: 164-222	Boiling point, ºC: 92-217
Refractive index, 20ºC, 1.375-1.445		

Aminosilane was found to be more reactive with PVC than mercaptosilane but properties of material crosslinked with mercaptosilane are better.[106] Gel content increases during crosslinking, and elevated-temperature mechanical properties of PVC are improved.[107] Crosslink density was increased with the concentration of crosslinking agent increasing.[108,109] More information on curatives and crosslinkers can be found in a specialized monographic source.[110]

3.19 ADHESION PROMOTERS

Table 3.21 contains general information on PVC adhesion promoters

Table 3.21. PVC adhesion promoters.

Types: blend compatibilizers, degradative surface treatment, ethylene-vinyl acetate copolymer, aromatic polyisocyanurate (Hafvermittler), silanes (e.g., aminosilane), sodium stearate, titanates		
Applications: coated fabrics, filled materials, medical, reinforcing fillers, surface coatings		
Reasons for use: adhesion, compatibility, interaction with fillers		
Potential adverse effects: degradation, stiffness		
Typical concentrations: 0.2-6 phr		
Density, 20°C, kg/m^3: 885-1,140	Molecular weight: 57-222	Boiling point, °C: 39-217
Refractive index, 20°C, 1.375-1.47		

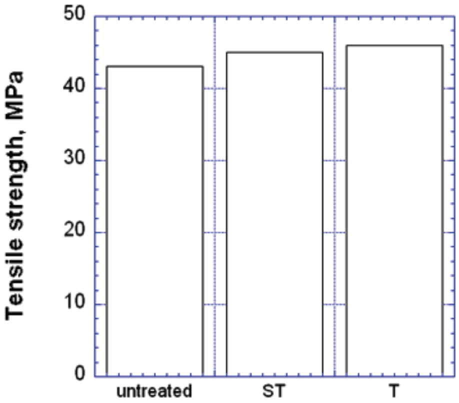

Figure 3.44. Effect of calcium carbonate surface treatment on tensile strength of its composite with PVC containing 25 wt% of calcium carbonate. ST – sodium stearate treated, T – titanate treated. [Data from Sun, S.; Li, C.; Zhang, L.; Du, H. L.; Burnell-Gray, J. S., *Polym. Intern.*, **55**, 2, 158-164, 2006.]

There are many applications for adhesion enhancement in PVC processing and use. The most common involves increased interaction between filler particles and PVC.[113-115] PVC and some fillers, especially the most commonly used calcium carbonate, do not have good interaction because they both lack functional groups which might be useful for this purpose. For this reason, interaction is usually enhanced by various adhesion promoters. Stearate surface coating of calcium carbonate is very common, and it is known to improve polymer-filler adhesion and improve many mechanical properties of composites. Figure 3.44 shows improvement of the tensile strength of PVC containing calcium carbonate with and without treatment. It is quite apparent that treatment improves tensile strength, especially if covalent bonding is involved, as is the case with titanate treatment. Impact strength is much less affected by stearate treatment than by titanate treatment.[113]

Wood-filled PVC has inferior mechanical properties because of lack of interaction. Treatment of wood filler with aminosilane improves acid-base interaction between filler and polymer to the extent that impact strength and tensile properties of the composite are improved over unfilled PVC.[114] Tensile properties of PVC were deteriorated when leather particles were used as a filler. But, after filler particles were treated with ethylene-vinyl acetate copolymer, a coating was produced on the surface of filler particles that promoted adhesion with PVC and improved mechanical properties.[115] These are some recent examples of many applications of filler preparations to enhance its interaction with PVC.

There is extensive literature, not discussed here, on the improvement of adhesion between PVC and another polymer in polymer blends by use of compatibilizers. This is another case of adhesion promotion (out of the scope of this book) used in many practical applications of PVC. There are also physical processes applied to PVC products to increase its compatibility. In one contribution, corona discharge was used to increase the chemical functionality of PVC articles used in biomedical applications.[116] Various silanes were used as primers to increase PVC adhesion to steel, with aminosilanes giving the best results.[117]

Less common in many applications but widespread in coated fabrics is the use of chemical agents to enhance adhesion of the coating to the fabric material, which is especially required in the case of synthetic fabrics such as polyamide and polyester. It is common to add to the base coating aromatic polyisocyanurates which increase adhesion by the formation of covalent bonding with the polymer of fabric.

More information on adhesion promotion and promoters can be found in a specialized monograph.[101]

3.20 BRIGHTENERS

Table 3.22 contains general information on brighteners used in PVC

Table 3.22. PVC brighteners.

Types: bis-benzoxazolyl-stilbene, bis-benzoxazolyl-thiophene, ultramarine blue		
Applications: white products, flexible PVC		
Reasons for use: color appears more brilliant, masking yellow color, whiter-than-white appearance		
Typical concentrations: 5-400 ppm		
Particle size, μm: 15-50	Molecular weight: 430-862	Melting point, °C: 200-359

Ultramarine blue is a historical solution to the elimination of the yellowish appearance of white products. PVC is one of the materials with which ultramarine blue was used for the above purpose in the past. The effect of ultramarine blue is not lasting; therefore optical brighteners are now in use.[119-120] Optical brighteners are able to mask the inherent yellowness of discolored products. Brightened polymer possesses a slightly blue tint.[119] Optical brighteners fluoresce under exposure to ultraviolet light. The two most common brighteners (bis-benzoxazolyl-stilbene and bis-benzoxazolyl-thiophene) have excellent dissolution properties in molten polymers. Bis-benzoxazolyl-stilbene is insoluble in plasticizers, and for this reasons, it is not used in flexible PVC which uses bis-benzoxazolyl-thiophene.[119] Figure 3.45 shows that small quantities of optical brightener dramatically change PVC color from yellow to blue.[119]

3.21 BIOCIDES AND FUNGICIDES

Table 3.23 contains general information on biocides and fungicides used in PVC.

Table 3.23. PVC biocides and fungicides.

Types: 2-n-octyl-isothiazolin-3-one, 2,3,5,6-tetrachloro-4-(methylsulphonyl)pyridine, 4,5-dichloro-2-n-octylisothiazolin-3-one, 10,10-oxybisphenoxarsine, chlorthalonil, n-butyl-1,2-benzisothiazolin-3-one, (N-dichlorofluoromethylthiophthalimide-(trichloromethylthio)phthalimide, zinc bis(2-pyridinethiol-1-oxide)		
Applications: caulks, coated fabrics, construction materials, floor coverings, pool liners, outdoor furniture, sealants		
Reasons for use: protection against biodegradation, protection against staining		
Potential adverse effects: stabilizer may lack weather stability		
Typical concentrations: 500-7000 ppm		
Density, 20°C, kg/m^3: 0.96-1.42	Melting point, °C: 20-183	Molecular weight: 99-502
Glass transition temperature, °C: 50-70		

The 2-n-octyl-isothiazolin-3-one, OIT, 4,5-dichloro-2-n-octylisothiazolin-3-one, DCOIT, and 10,10-oxybisphenoxarsine, OBPA, are the three the most common compounds used to impart biostability.[121-122] OBPA is the most frequently used biostabilizer. OBPA can be used at lower concentrations than the other two biostabilizers. It gives the largest inhibition zone and the best growth prevention. OBPA was also the most durable on exposure to subtropical and Everglades climates.[121]

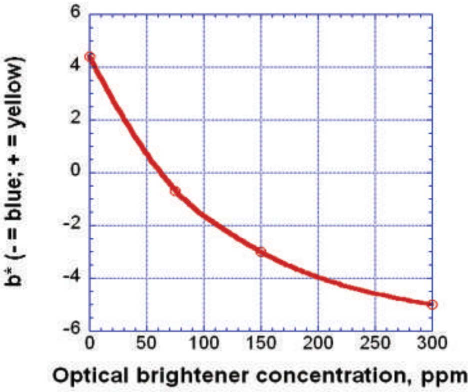

Figure 3.45. Color change from yellow to blue vs. concentration of bis-benzoxazolyl-thiophene in PVC containing 80 phr DOP. [Data from Jervis, D. A., *Plastics Additives Compounding*, **5**, 6, 42-46, 2003.]

Fungi were found to be important colonizers of PVC.[122] Thirty-three fungi species were isolated from PVC buried in grassland soil for 300 days and 15 fungi species were isolated from PVC buried in forest soil. Substantially more fungi were found to use DOA than DOP as their food.[122] OBPA

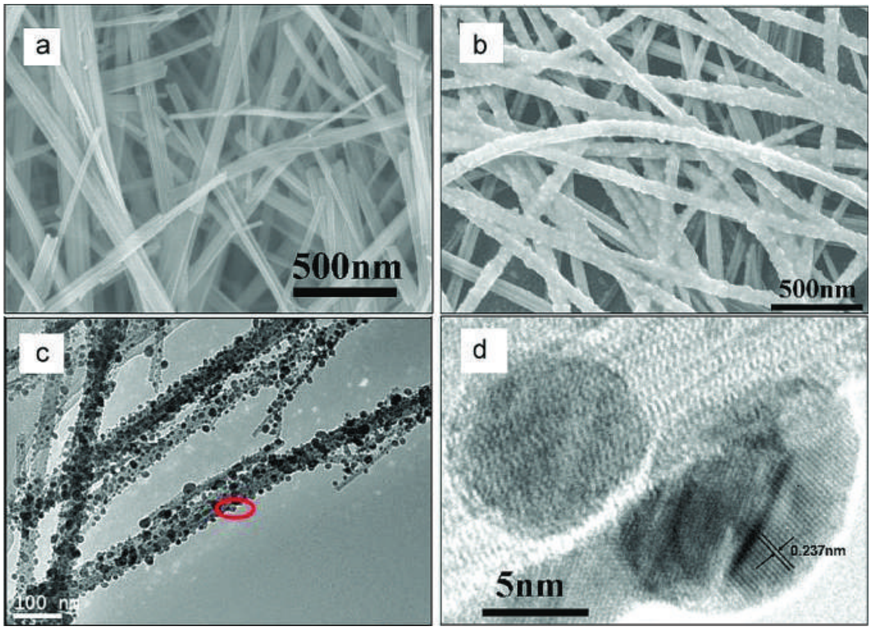

Figure 3.46. The SEM image of TiO_2 nanowire (a), TiO_2/Ag (b); the TEM image of TiO_2/Ag (c); high-resolution TEM image of TiO_2/Ag (d). [Adapted, by permission, from Liu, F., Li, X., Zhao, H., Zhu, D., Zheng, Y., Li, C., *Appl. Surf. Sci*., **258**, 4667-71, 2012.]

was by far the most efficient fungicide of six different types used in the study on grassland soil (2-n-octyl-isothiazolin-3-one, 2,3,5,6-tetrachloro-4-(methylsulphonyl)pyridine, 4,5-dichloro-2-n-octylisothiazolin-3-one, 10,10-oxybisphenoxarsine, n-butyl-1,2-benzisothiazolin-3-one, n-(trichloromethylthio)phthalimide) but n-butyl-1,2-benzisothiazolin-3-one and n-(trichloromethylthio)phthalimide were the most efficient in the case of forest soil exposure.[122]

The broad-spectrum agent oxybisphenoxyarsine was the most used biocide to protect PVC and other plastics.[123] Its withdrawal from sales in the European Union in January 2013 required producers to find substitutes.[123] Commonly used alternatives include 4,5-dichloro-2-n-octyl-3-isothiazolone, butyl-benzyl isothiazolone, zinc pyrithione, and iodopropynyl butyl carbamate.[123] Sanitized has developed Sanitized® PL 14-32 to provide effective and long-lasting antimicrobial protection for flexible polymer applications.[123]

Short term performance of biostabilizer is enhanced when biostabilizer is able to diffuse fast to the surface of product but this fast diffusion may also decrease its long-term performance. The delivery rate of OIT was controlled by its encapsulation in silica and zeolite but no improvement was found in comparison with biostabilizer used without encapsulation.[122]

Bio-based biocide composition contains epoxidized 2-ethylhexyl soyate and a solvent such as epoxidized soybean oil.[124]

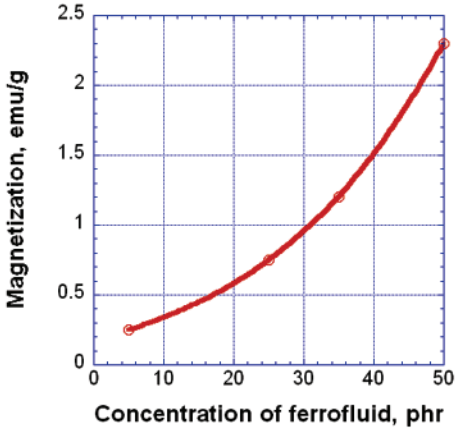

Figure 3.47. Effect of concentration of ferrofluid based on nano-magnetite on magnetization of PVC films. [Data from Yanez-Flores, I. G.; Betancourt-Galindo, R.; Aquino, J. A. Matutes; Rodriguez-Fernandez, O., *J. Non-Crystalline Solids*, **353**, 799-801, 2007.]

Zinc-containing biostabilizers had been restricted to flexible formulations which do not require extensive heat, but the addition of hydrotalcite helps to overcome the catalytic influence of biocide on PVC thermal degradation and permits its use in calendered and extruded formulations.[126]

The antibacterial film was obtained by compounding PVC with TiO_2 nanowire containing gold nanoparticles.[127] Nanowire having 50-60 nm diameter and 0.1 mm length was prepared by hydrothermal method.[127] Figure 3.46 shows SEM and TEM micrographs of nanowires.[127] Gold nanoparticles having a diameter of 5-10 nm were grafted on the surface of nanowire from solution. The film contained 0.63-1.25% nanowire.[127] Antibacterial properties of the film against *Escherichia coli* were dramatically improved.[127]

More information about biostabilizers can be found in a specialized monographic source.[128]

3.22 MAGNETIC ADDITIVES

Table 3.24 contains general information on magnetic additives for PVC

Table 3.24. PVC magnetic additives.

Types: $Co_{80}Ni_{20}$ spherical nanoparticles, ferrofluid, magnetite		
Applications: magnetopolymeric composites		
Reasons for use: to obtain PVC materials having magnetic properties		
Potential adverse effects: deterioration of physical-mechanical properties		
Typical concentrations: 0.4-50 wt%		
Density, 20°C, kg/m^3: 5,100-5,240	Molecular weigh: 159-5,888	Particle size, nm: 5-500

Ferrofluids (FF) consist of colloidal ferromagnetic, single-domain, nanoparticles dispersed in PVC.[131] Ferrofluid was prepared by dispersion of magnetite particles in dioctyl phthalate. Ferrofluid was then used to make films from PVC plastisols.[131] Figure 3.47 shows that magnetization increases with the loading of ferrofluid. The magnetization curve suggests supermagnetic behavior.[131] Spherical nanoparticles based on $Co_{80}Ni_{20}$ were used to obtain magnetopolymeric nanocomposite.[132] The method of incorporation and production of the composite is simple and non-hazardous.[132] Fe_2O_3 and $CoFe_2O_4$ nanoparticles permit production of PVC materials having magnetic properties.[133]

A cooling technique for a photovoltaic cell system was based on using a rotating magnetic field and ferro-nanofluid.[134] Actuation of ferro-fluid by rotating magnetic field enhanced thermal efficiency by 17.8-30%.[134] The generated power increased by 47.5%.[134]

3.23 FLEXIBILIZERS

Table 3.25 contains general information on PVC flexibilizers

Table 3.25. PVC flexibilizers.

Types: ethylene copolymer resins (ECR 732, HP 441)		
Applications: plenum cables		
Reasons for use: flexibility with low smoke and flame resistance		
Typical concentrations: 10-50 phr		
Brittle point, °C: -4 to -30	Melt index, g/100g: 8-35	Total smoke, smk/m^2:169-236

Flame retarding compliant flexibilizers are liquids and solids which are capable of imparting flexibilizing action on PVC but burn less vigorously than conventional plasticizers, such as phthalates, trimellitates, polyester, or benzoate types.[135] Esters of tetrabromophthalic anhydride are used for flame-retarding, low smoke applications. They are frequently used along with solid flexibilizers such as solid ethylene copolymer resin flexibilizers manufactured by DuPont.[135] Other flame retarding compliant flexibilizers include chloroparaffins and alkyl aryl and triaryl phosphate esters which have already been discussed in the section of plasticizers.

The ethylene copolymer resins (ECR and ECR HP) are high-molecular-weight polymers made out of ethylene, acetate or acrylate, and carbon monoxide, all in the polymer backbone.[136] The ethylene is there for strength, the acrylate or acetate for flexibility, and the carbon monoxide for polarity, thus making the polymers miscible with PVC.[136] ECR 741 and 742 are ethylene-vinyl acetate-carbon monoxide copolymers, and ECR HP 441 is a lower melt index copolymer of ethylene, acrylate, and carbon monoxide.[136] Flexibilizers provide PVC with excellent flexibility and impact strength at low temperatures. They are miscible with other plasticizers and PVC, permanent (they do not migrate), increase chemical and oil resistance of product, increase melt strength, and permit the use of higher filler loading.[136]

3.24 NUCLEATING AGENTS

Table 3.26 contains information on PVC nucleating agents

Table 3.26. PVC nucleating agents.

Types: calcium stearate, microcrystals of noble metals, Safoam (proprietary composition of nucleating agent and foaming agent masterbatch in PVC), talc		
Applications: bottles, calendered products, medical, pipes and fittings, siding, windows, wire and cable		
Reasons for use: uniform foaming		
Typical concentrations: 0.1-1 phr		
Density, 20°C, kg/m^3: 1,150-2,850	Melting point, °C: 155 and up	Refractive index: 1.45-1.50
Particle diameter, μm: 1.2-19	Oil absorption, g/100g: 22-57	Mohs hardness: 1-1.5

Polymer nucleation increases crystallinity and many mechanical properties of polymers. It is frequently used in polymers (e.g., polypropylene) but not on a practical scale in PVC, even though it is technically possible.[137] For theoretical purposes, PVC was nucleated by the introduction of the insoluble core from microcrystals of noble metals.[137] It was demonstrated that it is possible to obtain PVC spherulites, which is not the case with commercial polymers.[137]

The major application of nucleation in the case of PVC is not directed towards changes in crystalline and mechanical properties but towards the formation of uniform foams.[138-140] Talc was used as a nucleating agent in the inert-gas extrusion of PVC foam.[139] The application of a nucleating agent (such as Safoam-PT) causes generation of finer cells and density of the product is significantly decreased.[139] In chemically blown materials, calcium stearate was found to be an excellent blowing agent activator which increases dramatically the number of centers of bubble formation and decreases foam density.[140]

More information about the nucleating agents can be found in a specialized monographic source.[141]

REFERENCES

1 Wypych, G., Ed., **Handbook of Plasticizers**, 3rd Edition, *ChemTec Publishing*, Toronto, 2017.
2 Wypych, A., **Plasticizers Database**, Version 3.0, *ChemTec Publishing*, Toronto, 2012.
3 Coughlin, C. S.; Mauritz, K. A.; Storey, R. F., *Macromolecules*, **24**, 2113-2116, 1991.
4 Coughlin C S, Mauritz K A, Storey R F, *Macromolecules*, **23**, 3187-31-92, 1990.
5 Storey, R. F.; Mauritz, K. A.; Cox, B. D., *Macromolecules*, **22**, 289-294, 1989.
6 Dashora, P.; Gupta, G., *Polymer*, **37**, 2, 231-4, 1996.
7 Wickson, E. J., **Handbook of Polyvinyl Chloride Formulating**, *John Wiley & Sons*, New York, 1993.
8 Goernitz, E.; Zecha, H., *Langmuir*, **3**, 738-741, 1987.
9 Levchik, S. V.; Weil, E. D., *Polym. Adv. Technol.*, **16**, 10, 707-716, 2005.
10 Chen, J.; Liu, Z.; Nie, X.; Zhou, Y.; Jian, J.; Murray, R. E., *J. Polym. Res.*, **25**, 128, 2018.

11 Kalkan-Sevinc, Z; Ling, M. T. K., *J. Macromol. Sci., Part B: Phys*., **57**, 1, 44-55, 2018.
12 De Quadros, J. V.; De Carvalho, J. A.; **US9303140B2**, *Nexoleum Bioderivados Ltda*, Apr. 5, 2016.
13 Wypych, G., **Handbook of Fillers**, 4th Edition, *ChemTec Publishing*, Toronto, 2016.
14 Ognedal, A. S., Clausen, A. H., Berstad, T., Seeling, T., Hopperstad, O. S., *Int. J. Solids Structures*, in press 2014.
15 Ventresca, D. A.; Berard, M. T., *J. Vinyl Additive Technol.*, **3**, 4, 274-278, 1997.
16 Wiebking, H. E., *J. Vinyl Additive Technol.*, **2**, 3, 187-189, 1996.
17 Yang, F.; Hlavacek, V., *Powder Technol*., **103**, 2, 182-188, 1999.
18 Mansour, S. H.; Iskander, B. A.; Nasrat, L. S., *Polym.-Plastics Technol. Eng*., **45**, 7, 857-863, 2006.
19 Mamunya, Y., Boudenne, A., Lebovka, N., Ibos, L., Candau, Y., Lisunova, M., *Compos. Sci. Techn*., **68**, 1981-88, 2008.
20 Wang, H.; Wang, H.; Guo, Z.; Qi, S.; Tian, C., *J. Fire Sci*., **24**, 3, 195-210, 2006.
21 Bataille, P.; Mahlous, M.; Schreiber, H. P., *Polym. Eng. Sci*., **34**, 12, 981-5, 1994.
22 Wypych, G., **PVC Degradation & Stabilization**, 4th Edition, *ChemTec Publishing*, Toronto, 2020.
23 Worsley, D. A.; Searle, J. R., *Mater. Sci. Technol.*, **18**, 681-684, 2002.
24 Anton-Prinet, C.; Mur, G.; Audouin, L.; Verdu, J.; *Polym. Deg. Stab*., **61**, 2, 211-6, 1998.
25 Burn, L. S., *Polym. Deg. Stab.*, **36**, 155-167, 1992.
26 Cho, S.; Choi, W., *J. Photochem. Photobiol., A: Chem.*, **143**, 221-228, 2001.
27 Kann, Y., *J. Vinyl Additive Technol*., **5**, 2, 76-80, 1999.
28 Hardcastle, H. K., *J. Vinyl Additive Technol.*, **4**, 3, 169-173, 1998.
29 Kamisli, F.; Turan, C., *J. Mater. Process. Technol.*, **159**, 1, 40-47, 2005.
30 Peake, G. T., *J. Vinyl Additive Technol*., **2**, 3, 184-6, 1996.
31 Nelson, J. R.; Wissing, W. K., *Carbon*, **24**, 2, 123-125, 1986.
32 Dong, T; Li, D; Li, Y; Han, W; Liu, S; *Polym. Deg. Stab.*, **159**, 125-32, 2019.
33 Ahmed, D. S.; El-Hiti, G. A.; Yousif, E., Hameed, A. S., *Molecules*, **225**, 1849, 2017.
34 Tseng, A. A.; Borrosky, M. A.; O'Connor, S. M.; Knotts, J. J., *Adv. Polym. Technol.*, **10**, 3, 205-218, 1990.
35 Berard, M. T.; Ventresca, D. A., *J. Vinyl Additive Technol*., **4**, 3, 174-178, 1998.
36 Berard, M. T.; Williams, S. M., *J. Vinyl Additive Technol.*, **2**, 2, 117-120, 1996.
37 Chen, C. H.; Wesson, R. D.; Collier, J. R.; Lo, Y. W., *J. Appl. Polym. Sci*., **58**, 7, 1107-15, 1995.
38 Effler, L. J.; Berard, M. T., *J. Vinyl Additive Technol*., **9**, 1, 19-25, 2003.
39 Vrandecic, N. S.; Klaric, I.; Kovacic, T., *J. Thermal Anal. Calorimetry*, **74**, 1, 171-180, 2003.
40 Cruz, C. A.; Willis, M. C., **WO2017117077A1**, *Rohm And Haas Company*, Jul. 6, 2017.
41 Yanagase, A.; Ito, M., *J. Polym. Sci., Part A: Polym. Chem.*, **42**, 5, 1112-1119, 2004.
42 Yang, F.; Hlavacek, V., *Powder Technol*., **103**, 2, 182-188, 1999.
43 Lee, J.-S.; Chang, F.-C., *Polym. Eng. Sci*., **44**, 10, 1885-1889, 2004.
44 Stevenson, J. C.; Fazey, A. C., *J. Vinyl Additive Technol*., **3**, 2, 118-125, 1997.
45 Coaker, A. W., *J. Vinyl Additive Technol.*, **9**, 3, 108-115, 2003.
46 Schipper, P. S.; Black, J.; Dymek, T., *J. Vinyl Additive Technol.*, **2**, 4, 304-309, 1996.
47 Bacaloglu, R.; Hegranes, B.; Fisch, M., *J. Vinyl Additive Technol.*, **3**, 2, 112-117, 1997.
48 Kann, Y.; Padwa, A., *J. Vinyl Addit. Technol*., **21**, 259-71, 2015.
49 Wypych, G., **Handbook of Antiblocking, Release, and Slip Additives**, 3rd Edition, *ChemTec Publishing*, Toronto, 2015.
50 Townend, J.D.; Latus, J.; Mccoy, P. J.; Maltby, A. J.; Parker, D. A., **CA2763765C**, *Croda International PLC*, Nov. 3, 2015.
51 Park, J. S.; Lee, S. M.; Soo Joo, B. S.; Jang, H, *Wear*, **378-379**, 11-6, 2017.
52 Pionteck, J.; Wypych, G., Eds., **Handbook of Antistatics**, 2nd Edition, *ChemTec Publishing*, Toronto, 2016.
53 Chen, C.-H.; Li, H.-C.; Teng, C.-C.; Yang, C.-H., *J. Appl. Polym. Sci*., **99**, 5, 2167-2173, 2006.
54 Jando, T.; Stelczel, T.; Farkas, F., *J. Electrostatics*, **23**, 117-125, 1989.
55 Rinaldi, A. W.; Matos, R.; Rubira, A. F.; Ferreira, O. P.; Girotto, E. M., *J. Appl. Polym. Sci*., **96**,

5, 1710-1715, 2005.

56 Samui, A. B.; Manoj, N. R.; Raut, R.; Patankar, A. S., *J. Appl. Polym. Sci.*, **101**, 2, 1217-1222, 2006.

57 Lee, D. K.; Kim, K. H.; Park, B. H.; Lee, S. W.; Ju, J. H., **US9434833B2**, *LG Chem Ltd*, Sep. 6, 2016.

58 Levchik, S. V.; Weil, E. D., *Polym. Adv. Technol.*, **16**, 10, 707-716, 2005.

59 Coaker, A. W., *J. Vinyl Additive Technol.*, **9**, 3, 108-115, 2003.

60 Wang, H.; Wang, H.; Guo, Z.; Qi, S.; Tian, C., *J. Fire Sci.*, 24, 3, 195-210, 2006.

61 Cusack, P. A.; Hornsby, P. R., *J. Vinyl Additive Technol.*, **5**, 1, 21-30, 1999.

62 Xu, J.; Zhang, C.; Qu, H.; Tian, C., *J. Appl. Polym. Sci.*, **98**, 3, 1469-1475, 2005.

63 Mansour, S. H.; Iskander, B. A.; Nasrat, L. S., *Polym.-Plastics Technol. Eng.*, **45**, 7, 857-863, 2006.

64 Qu, H.; Wu, W.; Jiao, Y.; Xu, J., *Polym. Intern.*, **54**, 11, 1469-1473, 2005.

65 Moy, P. Y., *J. Vinyl Additive Technol.*, **4**, 1, 22-25, 1998.

66 Jia, P.; Feng, G.; Bo, C.; Hu, L.; Zhou, Y., *J. Ind. Eng. Chem.*, **60**, 192-205, 2018.

67 Yang, Y.; Shi, X.; Zhao, R., *J. Fire Sci.*, **17**, 5, 355-361, 1999.

68 Lipp, A.; Brix, S., **EP3026679B1**, *Nexans*, June, 28, 2017.

69 Carty, P.; White, S., *J. Fire Sci.*, **13**, 4, 289-99, 1995.

70 Li, B.; Wang, J., *J. Fire Sci.*, **15**, 5, 341-357, 1997.

71 Cassidy, D.; Crossley, D. C.; Bamford, A., **WO2016038359A1**, *William Blythe Limited*, Mar. 17, 2016.

72 Tian, C.; Qu, H.; Wu, W.; Guo, H.; Xu, J., *J. Vinyl Additive Technol.,* **11**, 2, 70-75, 2005.

73 Carty, P.; Grant, J.; Metcalfe, E., *Appl. Organometallic Chem.*, **10**, 2, 101-11, 1996.

74 Carty, P.; Price, D.; Milnes, G. J., *J. Vinyl Additive Technol.*, **8**, 4, 227-237, 2002.

75 Summers, J., *J. Vinyl Additive Technol.*, **11**, 57-62, 2005.

76 Fisch, M. H.; Bacaloglu, R., *J. Vinyl Additive Technol.*, **4**, 1, 4-11, 1998.

77 Bacaloglu, R.; Hegranes, B.; Fisch, M., *J. Vinyl Additive Technol.*, **3**, 2, 112-117, 1997.

78 Chen, C. H.; Wesson, R. D.; Collier, J. R.; Lo, Y. W., *J. Appl. Polym. Sci.*, **58**, 7, 1107-15, 1995.

79 Rapacki, S. R., *J. Vinyl Additive Technol.*, **4**, 1, 39437, 1998.

80 Disson, J.-P; Girois, S., *J. Vinyl Additive Technol.*, **9**, 4, 177-187, 2003.

81 Decker, R. W., *J. Vinyl Additive Technol.*, **2**, 2, 121-124, 1996.

82 Schipper, P. S.; Black, J.; Dymek, T., *J. Vinyl Additive Technol.*, **2**, 4, 304-309, 1996.

83 Chapman, T. F.; Isner, J. D.; Summers, J. W., *J. Vinyl Technol.*, **1**, 3, 131-4, 1979.

84 Daniels, P. H., J. Vinyl Additive Technol., **11**, 2, 76-82, 2005.

85 Berard, M. T.; Ventresca, D. A., *J. Vinyl Additive Technol.*, **4**, 3, 174-178, 1998.

86 Jimenez, A.; Lopez, J.; Iannoni, A.; Kenny, J. M., *J. Appl. Polym. Sci.*, **81**, 8, 1881-1890, 2001.

87 Trupti, D., *Plastics Additives Compounding*, **44-46**, 2004.

88 Hayes, V. O., *J. Vinyl Additive Technol.*, **5**, 2, 71-75, 1999.

89 Lavallee, P. R.; Lavach, M. L.; Hu, R. M., **US9587100B2**, *Arkema Inc*, Mar. 7, 2017.

90 DeArmitt, C., *Plast. Addit. Compounding*, **6**, 4, 32-4, 2004.

91 Zerafati, S., *J. Vinyl Additive Technol.*, **4**, 1, 35-38, 1998.

92 DeArmitt, C., *Plastics Additives Compounding*, **6**, 4, 32-34, 2004.

93 Johnson, R. W.; Oliveri, F. J.; Szamborski, E. C., *J. Vinyl Additive Technol.*, **4**, 2, 94-95, 1998.

94 Thomas, N. L.; Harvey, R., *J. Vinyl Additive Technol.*, **5**, 2, 63-70, 1999.

95 Bateman, F. G.; Masson, J. A.; Raper, E. S., *Thermochim. Acta*, **210**, 243-254, 1992.

96 Hovic, D., *Thermochim. Acta*, **95**, 319-324, 1985.

97 Rabinovitch, E. B.; Isner, J. D.; Sidor, J. A.; Wiedl, D. J., *J. Vinyl Additive Technol.*, **3**, 3, 210-215, 1997.

98 Patterson, J., *J. Vinyl Additive Technol.*, **4**, 1, 26-29, 1998.

99 Dunkelberger, D. L.; Herman, H. R., III., *J. Vinyl Additive Technol.*, **2**, 1, 44-7, 1996.

100 Fang, Q, **EP2998353B1**, *Zhejiang Tianzhen Bamboo & Wood Dev Co Ltd*, May 17, 2017.

101 Juntunen, R. P.; Kumar, V.; Weller, J. E.; Bezubic, W. P., *J. Vinyl Additive Technol.*, **6**, 2, 93-99, 2000.

102 Dey, S. K.; Jacob, C.; Xanthos, M., *J. Vinyl Additive Technol.*, **2**, 1, 48-52, 1996.

103 Chuaponpat, N.; Areerat, S., *Mater. Today: Proc.*, **5**, 11, part 3, 23526-33, 2018.
104 Kozlowski, R. R.; Storzum, U., *J. Vinyl Additive Technol.*, **11**, 4, 155-159, 2005.
105 Loock, F.; Lampe, T.; Bahadir, M., *Fresenius' J. Anal. Chem.*, **347**, 280-5, 1993.
106 Beltran, M. I.; Garcia, J. C.; Marcilla, A.; Hidalgo, M.; Mijangos, C., *Polym. Deg. Stab.*, **65**, 1, 65-73, 1999.
107 Fiaz, M.; Gilbert, M., *Adv. Polym. Technol.*, **17**, 1, 37-51, 1998.
108 Rodriguez-Fernandez, O. S.; Gilbert, M., *J. Appl. Polym. Sci.*, **66**, 11, 2121-2128, 1997.
109 Rodriguez-Fernandez, O. S.; Gilbert, M., *J. Appl. Polym. Sci*., **66**, 11, 2111-2119, 1997.
110 Wypych, G, **Handbook of Curatives and Crosslinkers**, *ChemTec Publishing*, Toronto, 2019.
111 Flores, R.; Perez, J.; Cassagnau, P.; Michel, A.; Cavaille, J. Y., *Polymer*, **35**, 13, 2800-7, 1994.
112 Ferrero, A.; Ferracini, E., *Coll. Polym. Sci*., **265**, 498-505, 1987.
113 Sun, S.; Li, C.; Zhang, L.; Du, H. L.; Burnell-Gray, J. S., *Polym. Intern.*, **55**, 2, 158-164, 2006.
114 Braun, D., *Prog. Polym. Sci.*, **27**, 2171-2195, 2002.
115 Andreopoulos, A. G.; Tarantili, P. A., *J. Macromol. Sci., Pure Appl. Chem*., **A37**, 11, 1353-1362, 2000.
116 Dumitrascu, N.; Borcia, G.; Popa, G., *J. Appl. Polym. Sci*., **81**, 2419-2425, 2001.
117 Boerio, F. J.; Shah, P., *J. Adhesion*, **81**, 6, 645-675, 2005.
118 Wypych, G., **Handbook of Adhesion Promoters**, *ChemTec Publishing*, Toronto, 2018.
119 Jervis, D. A., *Plastics Additives Compounding*, **5**, 6, 42-46, 2003.
120 Hamel, R. G.; McEntee, T. C., *Plastics Additives Compounding*, **2**, 10, 24-27, 2000.
121 Sabev, H. A.; Handley, P. S.; Robson, G. D., *Microbiology*, **152**, 6, 1731-1739, 2006.
122 Coulthwaite, L.; Bayley, K.; Liauw, C.; Craig, G.; Verran, J., *Intern. Biodeterioration Biodeg.*, **56**, 2, 86-93, 2005.
123 *Addit. Polym*., **2016**, 11, 5, 2016.
124 Frenkel, P.; **US9580574B2**, *Galata Chemicals LLC*, Feb., 28, 2017.
125 Mura, C.; Yarwood, J.; Swart, R.; Hodge, D., *Polymer*, **41**, 24, 8659-8671, 2000.
126 Burley, J. W.; Clifford, P. D., *J. Vinyl Additive Technol.*, **10**, 2, 95-98, 2004.
127 Liu, F., Li, X., Zhao, H., Zhu, D., Zheng, Y., Li, C., *Appl. Surf. Sci*., **258**, 4667-71, 2012.
128 Falkiewicz-Dulik, M, Janda, K. Wypych, G., **Handbook of Material Biodegradation, Biodeterioration, and Biostabilization**, 2nd Edition, *ChemTec Publishing*, Toronto, 2015.
129 Kasteleiner, T.; Evans, R.; Yarwood, J.; Hodge, D.; Swart, R., *J. Raman Spectroscopy*, **27**, 9, 695-698, 1996.
130 Webb, J. S.; Nixon, M.; Eastwood, I. M.; Greenhalgh, M.; Robson, G. D.; Handley, P. S., *Appl. Environ. Microbiol*., **66**, 8, 3194-3200, 2000.
131 Yanez-Flores, I. G.; Betancourt-Galindo, R.; Aquino, J. A. Matutes; Rodriguez-Fernandez, O., *J. Non-Crystalline Solids*, **353**, 799-801, 2007.
132 Sanz, R.; Luna, C.; Hernandez-Velez, M.; Vazquez, M.; Lopez, D.; Mijangos, C., *Nanotechnology*, **16**, 5, S278-S281, 2005.
133 Sivalingam, G.; Karthik, R.; Madras, G., *Industrial Eng. Chem. Res*., **42**, 16, 3647-3653, 2003.
134 Heidari, N.; Rahimi, M.; Azimi, N., *Int. Commun. Heat Mass Transfer*, **94**, 32-38, 2018.
135 Coaker, A. W., *J. Vinyl Additive Technol*., **9**, 3, 108-115, 2003.
136 Griffin, E. R., *J. Vinyl Additive Technol.*, 6, 4, 187-191, 2000.
137 Dobreva, A.; Gantcheva, T.; Gutzow, I., *Cryst. Res. Technol*., 27, 6, 743-748, 1992.
138 Thomas, N. L.; Harvey, R., *J. Vinyl Additive Technol.*, 5, 2, 63-70, 1999.
139 Dey, S. K.; Jacob, C.; Xanthos, M., *J. Vinyl Additive Technol*., 2, 1, 48-52, 1996.
140 Schipper, P. S.; Black, J.; Dymek, T., *J. Vinyl Additive Technol*., 2, 4, 304-309, 1996.
141 Wypych, G., **Handbook of Nucleating Agents**, *ChemTec Publishing*, Toronto, 2016.