

Polymer Additives and Reinforcements

I. INTRODUCTION

In Chapter 5, we discussed the techniques for the modification of polymer properties based on structural modification of polymers either during or post polymerization. Even though structural modification of polymers often leads to significant property modification, very few polymers are used technologically in their chemically pure form; it is generally necessary to modify their behavior by the incorporation of additives. Additives are usually required to impart stability against the degradative effects of various kinds of aging processes and enhance product quality and performance. Thus many commercial polymers must incorporate thermal and light stabilizers, antioxidants, and flame retardants.¹ In addition to these additives that influence essentially the chemical interaction of polymers with the environment, other additives are usually employed to reduce costs, improve aesthetic qualities, or modify the processing, mechanical, and physical behavior of a polymer. Such additives include plasticizers, lubricants, impact modifiers, antistatic agents, pigments, and dyes. These additives are normally used in relatively small quantities; however, nonreinforcing fillers are employed in large quantities to reduce overall formulation costs provided this does not result in significant or undesirable reduction in product quality or performance. In some cases, a given polymer may still not meet the requirements of a specific application even with the incorporation of additives. In such cases, the desired objective may be achieved through alloy formation or blending of two or more polymers. In this chapter, we discuss the upgrading of the performance of polymers through the use of additives and reinforcements.

II. PLASTICIZERS

Many commercial polymers such as cellulose, acrylics, and vinyls have glass transition temperatures, T_g , above room temperature. They are therefore hard, brittle, glasslike solids at ambient temperatures. To extend the utility of these polymers, it is usually necessary to reduce the T_g to below the anticipated end-use temperature. The principal function of a plasticizer is to reduce the T_g of a polymer so as to enhance its flexibility over expected temperatures of application. For example, unplasticized PVC is a rigid, hard solid used in such applications as credit cards, plastic pipes, and home siding. Addition of plasticizers such as phthalate esters reduces the modulus and converts the polymer into a leathery material used in the manufacture of upholstery, electrical insulation, and similar items.

Plasticizers are usually high boiling organic liquids or low melting solids. They are also sometimes moderate-molecular-weight polymers. Like ordinary solvents, plasticizers act through a varying degree of solvating action on the polymer. The plasticizer molecules are inserted between the polymer molecules thereby pushing them apart. This reduces the intensity of the intermolecular cohesive forces. The plasticizer may also depend on polar intermolecular attraction between the plasticizer and polymer molecules, which effectively nullifies dipole–dipole interactions between polymer molecules. As a result, plasticization is difficult to achieve in nonpolar polymers like polyolefins and highly crystalline polymers.

Polymer plasticization can be achieved either through internal or external incorporation of the plasticizer into the polymer. Internal plasticization involves copolymerization of the monomers of the desired polymer and that of the plasticizer so that the plasticizer is an integral part of the polymer chain. In this case, the plasticizer is usually a polymer with a low T_g . The most widely used internal plasticizer monomers are vinyl acetate and vinylidene chloride. External plasticizers are those incorporated into the resin as an external additive. Typical low-molecular-weight external plasticizers for PVC are esters formed from the reaction of acids or acid anhydrides with alcohols. The acids include ortho- and iso-terephthalic, benzoic, and trimellitic acids, which are cyclic; or adipic, azelaic, sebacic, and phosphoric acids, which are linear. The alcohol may be monohydric such as 2-ethylhexanol, butanol, or isononyl alcohol or polyhydric such as ethylene or propylene glycol. The structures of some plasticizers of PVC are shown in Table 9.1.

Table 9.1 Chemical Structures of Some PVC Plasticizers

Plasticizer Type	Chemical Structure	Example
Phthalate Esters (Dialkylphthalate)		
Phosphate Esters (Trialkyl-phosphate)		
Adepates, azelates, oleates, sebacates (Aliphatic diester)		
Glycol Derivatives		
Trimellitates (Trialkyltrimellitate)		

Phthalate, terephthalate, adipate, and phosphate esters are generally referred to as monomeric plasticizers. Linear polyesters obtained from the reaction of dibasic acids such as adipic, sebacic, and azelaic acids with a polyol constitute the group of polymeric or permanent plasticizers. They have much higher molecular weights than the monomerics and as such are less volatile when exposed to high temperatures either during processing or in end-use situations, less susceptible to migration, and less extractible.

They impart enhanced durability or permanence on PVC products, hence the name permanent plasticizers. Another group of plasticizers known as epoxy plasticizers is derived from vegetable oils. An example is epoxidized soybean. These plasticizers confer heat and light stability on PVC products, which, however, usually have relatively poor low-temperature properties.

The ideal plasticizer must satisfy three principal requirements. These are compatibility, performance, and efficiency. In addition, it should be odorless, tasteless, nontoxic, nonflammable and heat stable. Compatibility of a plasticizer with the host polymer demands the absence of blooming even with long usage of the plasticized material. Incompatibility can also be manifested by poor physical properties, possibly after some period of usage.

Permanence requires low volatility, extractability, nonmigration, and heat and light stability. Lack of permanence involves long-term diffusion into the environment. The consequent loss of plasticizer gradually enhances brittleness as the T_g of the plasticized polymer increases. Volatility is generally a function of molecular weight. Increasing the molecular weight of the plasticizer by using polymeric plasticizers tends to decrease volatility and hence increase permanence. However, this may lead to a decrease in low-temperature flexibility. Internal plasticization precludes plasticizer migration or volatility since the plasticizer molecules are an integral part of the polymer chain.

The level of plasticizer required to achieve the desired changes in properties is a measure of plasticizer efficiency. Plasticizer efficiency may also be measured on the basis of the magnitude of change induced in a number of physical properties of the polymer such as tensile strength, modulus, or hardness. For example, the actual reduction in T_g of the polymer per unit weight of plasticizer added is also known as the plasticizer efficiency.

It must be emphasized, however, that quite frequently no single plasticizer can satisfy all the above requirements or produce all the desired property enhancements. It is generally necessary to blend several plasticizers and compromise some properties, particularly those that are not critical to the specific application. For example, some applications require that DOP-plasticized PVC remains flexible at low temperatures. This requires further addition of DOP to the formulation to achieve the desired flexibility, but the additional DOP would adversely affect the hardness and performance of the product at ambient temperatures. Instead, aliphatic diesters such as DOA and DBS (dibutyl sebacate), which are more effective in enhancing low-temperature flexibility than DOA, are needed to improve low-temperature performance. However, the use of these esters is accompanied by unacceptable levels of volatility and oil extraction. Consequently, in such applications a combination of phthalate and aliphatic esters is required to produce the desired product even though some compromise in product performance will occur.

Plasticizers, particularly for PVC, constitute one of the largest segments of the additives market. The wide range of applications of flexible PVC depends largely on broad plasticizer technology that imparts the desired flexibility. The characteristic properties and typical applications of plasticized PVC are shown in [Table 9.2](#).

III. FILLERS AND REINFORCEMENTS (COMPOSITES)

The need to meet exacting end-use requirements and at the same time reduce costs is stimulating a broad spectrum of product development involving the use of fillers and reinforcements to upgrade product performance rather than the development of new and usually more expensive resins. For example, because of their advantageous light weight, high strength, fatigue life, and corrosion resistance, structural composites have been used successfully and admirably in aircraft and in numerous industrial and consumer applications in place of conventional materials like metals. Fiber-reinforced materials have moved within a short time from being a curiosity to having a central role in engineering materials development. Polymers, thermoplastics, and thermosets can be reinforced to produce quite frequently a completely new kind of structural materials.

Different types of fillers are employed in resin formulations; the most common are calcium carbonate, talc, silica, wollastonite, clay, calcium sulfate, mica, glass structures, and alumina trihydrate. Fillers serve a number of purposes. Inert materials like wood flour, clay, and talc serve to reduce resin costs and, to a certain extent, improve processability and heat dissipation in thermosetting resins. Both alumina trihydrate and talc improve flame retardance. Mica is used to modify the electrical and heat-insulating properties of a polymer. Parts molded from composites containing phlogopite mica as a reinforcement exhibit little or no warpage on demolding or subjection to elevated temperature. A variety of fillers, e.g., particulate fillers like carbon black, aluminum flakes, and metal or metal-coated fibers may be used to reduce mold shrinkage as well as to produce statically conductive polymers, shielding of electromagnetic interference/radio frequency interference (EMI/FMI).⁴ Particulate fillers such as carbon black or silica are used as reinforcing fillers to improve the strength and abrasion resistance of commercial elastomers. Fibers such as asbestos, glass, carbon, cellulose, and aramid are used principally to improve some mechanical property/properties such as modulus, tensile strength, tear strength, abrasion resistance, notched impact strength, and fatigue strength as well as enhance the heat-deflection temperature.

Fibers are available in a variety of forms. For example, carbon fibers are obtained from the pyrolysis of organic materials such as polyacrylonitrile (PAN) and rayon for long fibers and pitch for short fibers.

Table 9.2 *General-Purpose PVC Plasticizers*

Abbreviations	Chemical Designations	Advantages	Limitations	Applications
Low-Molecular-Weight Phthalates				
BBP	Butyl benzyl phthalate	Rapid fusing (high-solvating); low migration into flooring asphaltics	High volatility as compared with the commodity phthalates; costs slightly more than DOP	Flooring: processing aid in calendaring and extrusion; expanded-foam formulations
BOP	Butyl octyl phthalate	Rapid fusing	Same as above	Same as above
DHP	Dihexyl phthalate	Same as above	Same as above	Same as above
DIHP	Diisoheptal phthalate	Same as above	Same as above	Same as above
Commodity Phthalates				
DOP (DEHP)	Di-2-ethylhexyl phthalate	Good property balance; industry standard for general applications; relatively low cost; good weatherability; good compatibility in PVC)	Moderate plasticizer volatility; moderate low-temperature properties (–38°C at 40% concentration in PVC).	General-purpose calendaring and extrusion; plastisols; flooring
DINP	Diisononyl phthalate	Low volatility (less than 2% per ASTM D1203); good electrical properties; similar to DOP in cost	Fair weatherability; fair low-temperature properties (similar to that of DOP)	Competes “head on” with DOP
Linear phthalates	C ₇ ,C ₉ ,C ₁₁ , C ₆ ,C ₈ ,C ₁₀	Low volatility (–2%); better low-temperature properties: 7 to 9°C better than DOP and DIMP (to –47°C at 40% plasticizer concentration); very good weathering	Costs slightly more than DOP; slightly poorer electrical properties	Automotive wire and cable jacketing compounds; outdoor applications; plastisols; automotive interiors (except for crash pads)
DIDP	Diisodecyl phthalate	Very low volatility (–1%); good electrical properties; good viscosity stability	Low-temperature properties (–38°C); fair weatherability	Wire and cable; sealants; plastisols; calendaring applications
High-Molecular-Weight Specialties				
DUP	Diundecyl phthalate	Good electrical properties; volatility less than 1% at 48°C to –50°C at 40% concentration; exceptionally good viscosity stability in a plastisol; very low fogging in interior applications (automotive)	Slow processing characteristics; marginal compatibility with PVC; costs about 20 cents per pound more than DOP; high hydrocarbon extraction	Wire and cable up to 90°C; sealants; automotive interiors (crash pads); roofing membranes
DTOP	Ditridecyl phthalate	Less than 1% volatility; good electrical properties	Slow processor; high viscosity; fair low-temperature properties (–38°C); marginal compatibility with PVC	Wire and cable up to 90°C; automotive interiors; sealants
UDP	Undecyl dodecyl phthalate	Volatility less than 1%	Fair low-temperature properties to –38°C; slow processor; marginal compatibility with PVC	Wire and cable up to 90°C; automotive interiors

Table 9.2 (continued) *General-Purpose PVC Plasticizers*

Abbreviations	Chemical Designations	Advantages	Limitations	Applications
Linear phthalates	C ₉ ,C ₁₀ ,C ₁₁	Volatility less than 1%; low-temperature properties to 50°C; good outdoor weathering; low viscosity; improved compatibility with PVC	Costs more than DOP	Wire and cable to 90°C; automotive interiors; roofing membranes

Note: Plasticizers for PVC also include special-purpose products in applications such as flooring (benzyl phthalates); stain resistance (monobenzoates or benzyl phthalates); food and film wrap (adipate esters with superior low-temperature and oxygen-permeation properties); flame retardance (phosphate esters); wire and cable (trimellitates with exceptionally low volatility); heat stabilizers as well as plasticizers (epoxy); mar resistance of styrene (polymeric, isophthalates, and terephthalates); and polymeric plasticizers for long-term usage. These materials are more expensive than DOP and have specialty niches in the market.

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Glass structures, the most widely used reinforcement, are available as roving, mat, hollow or solid spheres, bubbles, long or short fibers, and continuous fibers.⁵ The form has a significant influence on properties. The impact strength of glass-mat-reinforced polypropylene is approximately four to five times that obtained with short fibers.⁶ The most important form of filler is E-glass, which is used typically to reinforce thermoset polyester and epoxy resins. E-glass is boroaluminosilicate glass having low alkali-metal content and containing small percentages of calcia (CaO) and magnesia (MgO). For special applications such as in the manufacture of aerospace materials, fibers of boron, Kevlar, PBT, and especially carbon are generally preferred.⁷ Typical properties of some fiber reinforcements are shown in Table 9.3. Table 9.4 shows the properties of some fiber-filled engineering thermoplastics composites. The effect of mineral fillers on the properties of nylon 6/6 is shown in Table 9.5.

Table 9.3 *Properties of Some Reinforcing Fibers*

Property	Glass					Steel
	Boron	Kevlar-49	Carbon	E-Glass	S-Glass	
Tensile strength (10 ³ psi)	495–500	525	400	500	700	600
Tensile modulus (10 ⁶ psi)	56	20	32	10.5	12.4	59
Density (lb/in ³)	0.086–0.096	0.052	0.063	0.092	0.090	0.282

The mechanical properties of particulate-filled composites are generally isotropic; that is, they are invariant with direction provided there is a good dispersion of the fillers. On the other hand, fiber-filled composites are typically anisotropic. In general, fibers are usually oriented either uniaxially or randomly in a plane. In this case, the composite has maximum modulus and strength values in the direction of fiber orientation. For uniaxially oriented fibers, Young's modulus, measured in the orientation direction (longitudinal modulus, E_L) is given by Equation 9.1:⁷

$$E_L = E_m (1 - \phi_f) + E_f \phi_f \quad (9.1)$$

where E_f is the tensile modulus of the fiber, E_m is the modulus of the matrix resin, and ϕ_f is the volume fraction of filler.⁷

The performance of composites is influenced by the adhesive strength of the filler–matrix interface. The presence of water absorbed by the filler surface and of thermal stresses generated by the differential thermal coefficients of linear expansion between the filler and matrix materials reduces interfacial adhesive strength. Polymers have relatively higher linear expansion coefficients than filler materials (60 to 80 × 10⁻⁶ per °C for graphite). Therefore, in practice, interfacial adhesive strength is enhanced by the use of coupling agents, which are usually low-molecular-weight organofunctional silanes, stercates, or titanates that act as a bridge between the matrix resin and fiber material (Table 9.6). Coupling

Table 9.4 *Properties of Some Engineering Thermoplastics Composites*

Property	Poly(etheretherketone) (PEEK)			Polyetherimide			Polyethersulfone			Nylon 6/6		
	Unreinforced	30% Glass	30% Graphite	Unreinforced	30% Glass	30% Graphite	30% Carbon Fibers	Unreinforced	30% Glass	30% Carbon Fiber	20% Kevlar-49	
Tensile strength (10 ³ psi)	13.2	20.3	31.2	15.2	24.5	30.0	30.0	11.9	25.0	36.0	18.2	
Flexural modulus (10 ⁵ psi)	5.65	11.6	22.4	4.80	12.0	25.0	25.0	4.8	13.0	27.0	8.8	
Elongation at break (%)	150	3	3	60	3	1.4	1.7	40	2.5	2.0	2.3	
Izod Impact Strength (ft-lb/in)	—	—	—	—	—	1.6	1.6	1.2	2.5	2.2	3.1	
Heat-deflection temperature under load (264 psi) (°F)	298	572	572	392	410	410	420	190	485	490	490	

Table 9.5 *Effect of Mineral Fillers on Nylon 6/6*

Property	Unfilled Resin	Mica	Calcium Carbonate	Wollastonite	Glass Beads	Alumina	Talc
Specific gravity	1.14	1.50	1.48	1.51	1.46	1.45	1.49
Tensile strength (psi)	11,800	15,260	10,480	10,480	9,780	9,200	8,980
Tensile elongation (%)	60	2.7	2.9	3.0	3.2	2.8	2.0
Flexural modulus (10 ³ psi)	410	1,540	660	780	615	645	925
Izod impact(notched) (ft-lb/in.)	0.06	0.6	0.5	0.6	0.4	0.5	0.6
Heat-deflection temperature (°F)	170	460	390	430	410	395	445
Mold shrinkage (in./in.)	0.018	0.003	0.012	0.009	0.011	0.008	0.908

Table 9.6 *Structures of Representative Coupling Agents*

Vinyl silane	$\text{CH}_2=\text{CH}-\text{Si}-(\text{OCH}_3)_2$
Epoxy silane	$\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{CH}_2 \quad \text{CH}-\text{CH}_2-\text{OCH}_2\text{CH}_2\text{CH}_2-\text{Si}(\text{OCH}_3)_3 \end{array}$
Primary amine silane	$\text{H}_2\text{NCH}_2-\text{CH}_2-\text{CH}_2-\text{Si}-(\text{OC}_2\text{H}_5)_3$
Titanate	$\begin{array}{c} \text{CH}_3 \\ \\ (\text{CH}_2=\text{C}-\text{COO})_3-\text{T}_i-\text{OCH}-(\text{CH}_3)_2 \end{array}$

agents generally have two different terminal groups one of which is designed specifically to combine with the matrix resin and the other with the fiber reinforcement. For example, the amino group in γ -aminopropyltriethoxy silane, $(\text{C}_2\text{H}_5\text{O})_3\text{-Si}-(\text{CH}_2)_3\text{-NH}_2$, can react with the epoxy functionality in an epoxy matrix, while the ethoxy groups on hydrolysis during application on the fibers form the silanol group $-\text{Si}-(\text{OH})_3$, which condenses with silanol groups on the glass fiber to form covalent $\text{Si}-\text{O}-\text{Si}$ bonds.

The search for new reinforcements or new applications for older materials is frequently linked to the development of new resins or new grades of the same resin to optimize performance. In broad terms, composites are characterized by two extremes of materials. On one end are the polyester-fiberglass automotive exterior body panels of Fiero or Corvette, representative of the relatively low cost and minimal performance materials. Thermoplastics — including polycarbonate, polypropylene, nylon, ABS, polystyrene, high-density polyethylene, acetal copolymer, SAN, poly(butylene terephthalate), PET, thermoplastic polyurethane, and polysulfone — as well as thermosets such as cross-linkable polyesters, phenolics, and polyurethanes are the matrix resins used in these composites. On the other end of the composite materials spectrum, are the high-cost, high-performance advanced composites typified by the carbon- and boron-fiber-reinforced structural materials used in many aircraft and aerospace applications. Thermosets, notably epoxies, have dominated advanced composite matrix resins. However, thermosetting materials are being challenged because of the increasing interest in high-performance thermoplastic resin matrices. The growing interest in thermoplastic matrix composites stems from their promise of improved durability and toughness and possibilities for increased cost effectiveness in production and maintenance. Thermoplastics have relatively longer shelf-life than thermosets and their reprocessability offers potential for possible repair of design and fabricating faults. Processing of thermoplastics potentially simplifies fabrication and reduces manufacturing cycle times, particularly by eliminating the curing cycles normally required for cross-linking thermoset materials. This also permits access to the wider variety of manufacturing methods for processing thermoplastics. Figure 9.1 shows schematically the simplified requirements for utilizing thermoplastic resin matrices relative to thermosets in composite production.

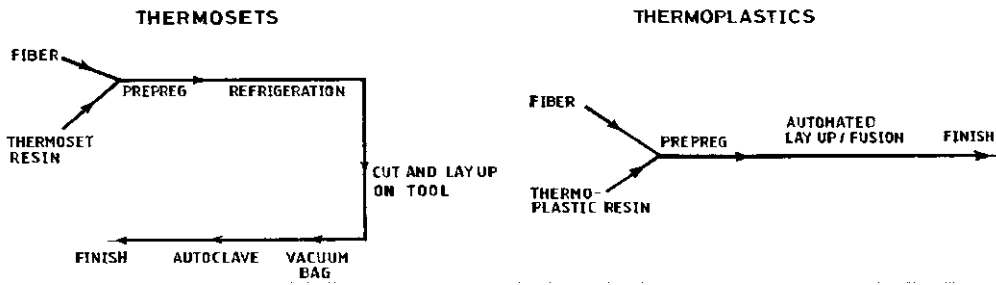


Figure 9.1 Schematic diagram illustrating the simplified requirements for utilizing thermoplastic resin matrices compared with thermoset resin matrices.

Table 9.7 Markets and Typical Applications for Composites

Market	Typical Applications
Aircraft/aerospace/ military	Helicopter blades and shell; control surfaces and floor beams (Boeing 767); F-16s horizontal stabilizer, skin, dorsal access panels and leading edge fairing, and vertical tail fin skins and louver fin leading edge and rudder
Appliances/business equipment	Refrigerator compressor bases, room air conditioner parts, interior dishwasher parts, business machine bases and housings
Construction	Reinforced plastic bathtubs and shower fixtures, dimensionally stable reinforced plastic window lineals and doors, traffic signs, pedestrian shelters, telephone booths, and traffic kiosks
Consumer products	Recreational and sporting goods and recreational-vehicle equipment; microwave dinnerware and office furniture
Corrosion-resistant equipment	Underground gasoline tanks and reinforced plastic pipes and fittings; flooring for chemical processing plants and pulp and paper mills; tank linings for the storage of crude oil; piping and fittings for petroleum refineries; caustic and sulfur dioxide scrubbers; mixing tanks for phosphoric acid fertilizer solutions
Electrical/electronic	Fiber-optic cable; satellite dish and antenna, protective coverboards, light poles, electrical conduit, bus bar insulation, and third-rail insulators and covers
Marine	Sailboat, powerboat, minesweeper, military craft clad with reinforced plastics
Land transportation	Exterior body parts, suspensions, chassis, load floors, bumpers, driveshafts, lead springs, under-hood components, and automotive frames

The market for polymer composites has continued to expand in all forms of transportation (aerospace, aircraft, marine, automotive), in the construction industry and numerous other industrial and consumer applications. The increased use of composites in place of conventional materials is driven by their established advantages such as corrosion resistance, high strength-to-weight ratio, and moderate costs as well as the design flexibility offered by novel resin/reinforcement combinations together with new processing and machinery innovations. Table 9.7 summarizes the markets and typical applications for composites.

IV. ALLOYS AND BLENDS

The traditional method of enhancing properties by adding fillers and reinforcements, while still effective in some applications, has been inadequate for coping with the increasing performance requirements of design problems and the changing material specifications. Development of new resin systems to meet demands for high performance materials would undoubtedly take too long and would certainly be too expensive since it would require huge investments in totally unexplored technologies and new plant facilities. An alternative to the development of new polymers is the development of alloys and blends that are a physical combination of two or more polymers to form a new material. The basic objective

is to combine the best properties of each component in a single functional material that consequently has properties beyond those available with the individual resin components and that is tailored to meet specific requirements. Another goal is to optimize cost/performance index and improve processability of a high-temperature or heat-sensitive polymer.

Although the terms *alloys* and *blends* are used interchangeably, they differ in the levels of inherent thermodynamic compatibilities and in resulting properties. In general, a necessary though not sufficient condition for thermodynamic compatibility (miscibility) is a negative change in the free energy of mixing, ΔG_m , given by Equation 9.2.

$$\Delta G_m = \Delta H_m - T \Delta S_m \quad (9.2)$$

where ΔH_m and ΔS_m are, respectively, the changes in enthalpy and entropy of mixing at temperature T. Generally because of their large size and unfavorable energy requirements, chains from a given polymer prefer to intertwine among themselves than with those of another polymer. Consequently, the magnitude of ΔS_m is usually small. Therefore, for two polymers to be thermodynamically miscible, ΔH_m must be negative, zero, or, at most, slightly positive. If ΔH_m is strongly positive, the components of a physical mixture separate into different phases resulting in a blend. However, some polymers tend to be mutually soluble, at least over a limited concentration range. Such are called alloys. In other words, alloys represent the high end of the compatibility spectrum. Individual polymeric components in alloys are intimately mixed on a molecular level through specific interactions such as donor-acceptor or hydrogen bonding between the polymer chains of the different components.

The composition dependence of a given property, P, of a two-component polymer system may be described by Equation 9.3:¹⁰

$$p = p_1 C_1 + p_2 C_2 + I p_1 p_2 \quad (9.3)$$

where P_1 and P_2 are the values of the property for the isolated components and C_1 , C_2 are, respectively, the concentrations of the components of the system. I is the interaction parameter that measures the magnitude of synergism resulting from combining the two components. If I is positive, then the magnitude of the property for the system exceeds that expected for a simple arithmetic averaging of the two component properties. The system in this case is referred to as synergistic. If I is negative, then the mixture has a property value less than that predicted from the weighted arithmetic average. This is known as nonsynergistic. Polymer systems for which I is either zero or nearly zero are called additive blends. They have properties that are essentially arithmetic averages of the properties of their components (Figure 9.2).

Compatible polymer blends form single-phase systems and have a single property, like the glass transition temperature, the value of which is generally the weighted arithmetic average of the values of the components of the blend. At certain compositions, some compatible polymer blends exhibit strong intermolecular attraction and hence have a high level of thermodynamic compatibility. This results in properties superior to those of the individual components alone. Such blends display synergistic properties (e.g., tensile strength and modulus). Only a few commercially available polymers are truly compatible. Some of these are shown in Table 9.8. Examples of the most significant commercial engineering alloys are polystyrene (PS)-modified poly(phenylene oxide) (PPO) and polystyrene (PS)-modified poly(phenylene ether) (PPE).

Incompatible polymer blends consist of a heterogeneous mixture of components and exhibit discrete polymer phases and multiple glass transition temperatures corresponding to each of the components of the blend. A polymer blend with completely incompatible components has limited material utility because the components separate during processing due to lack of interfacial adhesion, which is required for optimum and reproducible polyblend properties. Improvement in adhesion in such blends can be effected by the addition of compatibilizers. Compatibilizing agents provide permanent miscibility or compatibility between otherwise immiscible or partially immiscible polymers creating homogeneous materials that do not separate into their component parts. The most effective compatibilizing agents are generally block and graft copolymers whose polymer blocks or segments are the same as the components of the polyblend. The inherent compatibility between the segments of the compatibilizer and each component

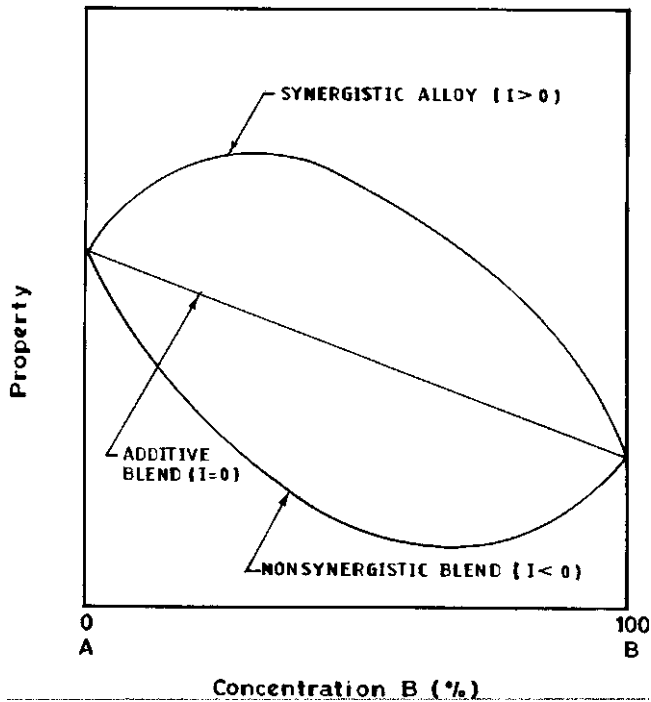


Figure 9.2 Composition dependence of the property of a two-component polymer system: alloy properties better than arithmetic averages; blend properties equal to or less than arithmetic averages.

Table 9.8 Representative Miscible Polymer Blends

Polymer 1	Polymer 2
Polystyrene	Poly(2,6-dimethyl-1,4-phenylene oxide)
	Poly(methyl vinyl ether)
	Tetramethyl BPA polycarbonates
Poly(vinyl chloride)	Polycaprolactone
	Poly(butadiene-co-acrylonitrile)
	Chlorinated polyethylene
	Poly(ethylene-co-vinyl acetate)
Poly(methyl methacrylate)	Poly(vinylidene fluoride)
	Poly(styrene-co-acrylonitrile)
	Poly(vinylidene fluoride)

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of the blend effectively ties the discrete polymer phases together. It is useful to visualize the function of a compatibilizing agent as akin to that of the emulsifier in water–oil emulsified systems.

As we said earlier, the primary objectives in blending are to enhance material processing characteristics and optimize product performance while minimizing costs. A common strategy for achieving these objectives is to combine a crystalline polymer with an amorphous polymer. The aim is to exploit the strengths of each component while deemphasizing their weaknesses. Crystalline materials such as nylon, poly(butylene terephthalate) (PBT), and poly(ethylene terephthalate) (PET) offer excellent chemical resistance, processing ease, and stiffness, but suffer from poor impact strength and limited dimensional stability. On the other hand, amorphous polymers such as polycarbonate (PC) and polysulfone have outstanding impact strength and dimensional stability but poor chemical resistance. Polycarbonate–poly(ethylene terephthalate) blends combine the desirable properties of polycarbonates with the

Table 9.9 Major Properties and Applications of Some Commercially Available Alloy/Blends

Alloy/Blends	Trade Name/ Manufacturer	Major Properties	Applications
PC/SMA	Arloy/Arco Chemical	Toughness and heat resistance, excellent moldability	Switches, power tools, food trays, lighting fixtures, automotive interior trim, connectors
PC/ABS	Bayblend/Mobay	Improve low temperature impact strength, processability and stiffness	Business machine housings and components, industrial and mechanical parts, switches, terminal blocks, food trays
SMA/ABS	Cadon/Monsanto	Improved ductility, and impact and heat resistance	Automotive interior trim, instrument panel, appliance and equipment housings
PC/ABS	Cycoloy/Borg-Warner Chemicals	Improved no-load heat resistance, impact strength	Electroplated parts, grilles, wheel covers, appliances, instrument panels, telecommunications
ABS/Nylon	Elemid/Borg-Warner Chemicals	Chemical resistance, low-load warpage resistance, toughness processing	Power tools, automotive and agricultural components
PPE/Nylon	GTX/General Electric	High heat and chemical resistance, dimensional stability, ductility	Automotive exterior body panels, wheel covers, mirror housings
Polysulfone/ABS	Mindel-A631/Union Carbide	Platability, processability, toughness	FDA- and NSF-recognized for food processing and food service systems
PPE/PS	Noryl/General Electric	Improved processing, combination of heat resistance, excellent dimensional stability and toughness	Computer and business equipment housings, automotive instrument panels, interior trim, connectors, electrical housings, medical components
PC/PBT, PC/PET	Xenoy/General Electric	Balance of chemical resistance, toughness, low-temperature impact strength and high temperature rigidity	Automotive, lawn and garden materials handling, sporting goods, military

From Wigotsky, V., *Plast. Eng.*, 42(7), 19, 1986. With permission.

excellent chemical resistance of PET and have been specified for use in many applications, for instance, as replacements for metal, including automotive, lawn and garden appliances and electrical/electronic, consumer, industrial/mechanical, sporting and recreation, and military equipment.¹¹ A blend of PPO and nylon is used for fenders and rocker panels of some automobiles, applications demanding chemical-resistant performance under high impact and high heat. Table 9.9 lists some alloys and blends, their characteristic properties, and areas of application.

V. ANTIOXIDANTS AND THERMAL AND UV STABILIZERS

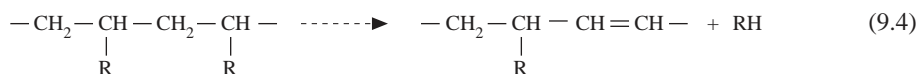
Polymers, during fabrication or storage or in service, may be exposed, sometimes for long periods, to the separate or combined effects of moderate or high temperatures, ultraviolet radiation, and air or other potential oxidants. Under these environmental conditions, polymers are susceptible to thermal, UV, and/or oxidative degradative reactions initiated, in most cases, by the generation of free radicals. Polymer stabilization, therefore, involves incorporation of antioxidants and thermal and UV stabilizers to minimize, if not avoid, such degradative reactions.

A. POLYMER STABILITY

Polymers deteriorate through a complex sequence of chemical reactions resulting from the separate or combined effects of heat, oxygen, and radiation. In addition, polymers may be susceptible to attack and mechanical failure on exposure to water (hydrolysis) or a variety of chemical agents. Molecular weight is changed considerably in most of these reactions by chain scission and/or cross-linking. However, deterioration can also occur without significant change in the size of the polymer molecules.

1. Nonchain-Scission Reactions

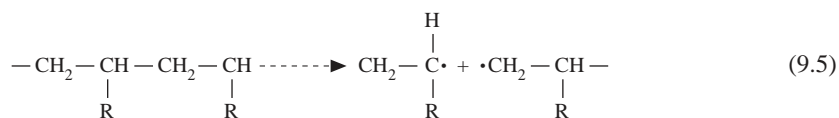
Nonchain-scission reactions resulting, for example, from the application of heat, involve elimination of a small molecule — usually a pendant group — leaving the backbone essentially unchanged (Equation 9.4).



Vinyl polymers are particularly susceptible to thermal degradation. A typical example is rigid PVC, which is impossible to process under commercially acceptable conditions without the use of thermal stabilizers. Unstabilized PVC undergoes dehydrochlorination near the melt processing temperature. This involves liberation of hydrochloric acid and the formation of conjugated double bonds (polyene formation). The intense coloration of the degradation products is due to polyene formation. A second example of a polymer that undergoes nonchain-scission reaction is poly(vinyl acetate) or PVAc. When heated at elevated temperatures, PVAc can liberate acetic acid, which is followed by polyene formation.

2. Chain-Scission Reactions

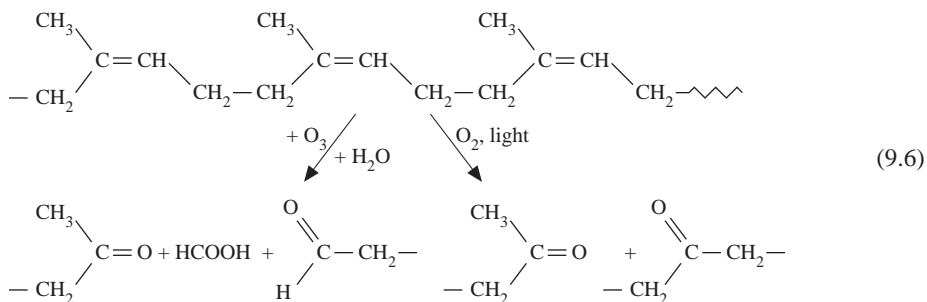
The chemical bonds in a polymer backbone may be broken with the generation of free radicals by heat, ionizing irradiation, mechanical stress, and chemical reactions (Equations 9.5).



In the thermal degradation of polyethylene and polystyrene, for example, chain scission occurs through the homolytic cleavage of weak bonds in the polymer chain. This results in a complex mixture of low-molecular-weight degradation products. In some cases, particularly 1,1-disubstituted vinyl polymers, the long-chain radical formed from initial chain scission undergoes depolymerization resulting in the reduction of molecular weight and formation of monomers. In a few cases, e.g., PMMA, the initial chain scission occurs at one end of the molecule and the subsequent depolymerization results in a gradual decrease in molecular weight. In other cases, e.g., poly(α -methylstyrene), the initial chain scission occurs at random sites and as such there is an initial rapid reduction in molecular weight.

3. Oxidative Degradation

In the presence of oxygen or ozone, as soon as free radicals form, oxygenation of the radicals gives rise to peroxy radicals, which through a complex series of reactions result in polymer degradation. Oxidative degradation may occur at moderate temperature (thermal oxidation) or under the influence of ultraviolet radiation (photooxidation). Unsaturated polyolefins are particularly susceptible to attack by oxygen or ozone (Equation 9.6).



4. Hydrolysis and Chemical Degradation

In addition to the separate or combined effects of heat, oxygen, and radiation, polymers may deteriorate due to exposure to water (hydrolysis) or different types of chemical agents. Condensation polymers like nylons, polyesters, and polycarbonates are susceptible to hydrolysis. Structural alteration of some polymers may occur as a result of exposure to different chemical environments. Most thermoplastics in contact with organic liquids and vapors, which ordinarily may not be considered solvents for the polymers, can undergo environmental stress cracking and crazing. This may result in a loss of lifetime performance or mechanical stability and ultimately contribute to premature mechanical failure of the polymer under stress.

B. POLYMER STABILIZERS

The two main classes of antioxidants are the free-radical scavengers, (primary antioxidants, radical or chain terminators) and peroxide decomposers (secondary antioxidants or synergists). Free-radical scavengers, as the name suggests, inhibit oxidation through reaction with chain-propagating radicals, while peroxide decomposers break down peroxides into nonradical and stable products. Commercial antioxidants include organic compounds like hindered phenols and aromatic amines, which act as free-radical scavengers, as well as organic phosphites and thioesters that serve to suppress homolytic breakdown.

Thermal stabilizers may be based on one or a combination of the following classes of compounds: barium/cadmium (Ba-Cd), calcium/zinc (Ca-Zn), organotin, organo-antimony, phosphite chelates, and epoxy plasticizers. Ba/Cd stabilizer systems, which represent the largest share of the PVC stabilizer market, are available as liquids or powders. The liquids normally employ one or more of the following anions combined with the respective metal: nonyl phenate, octoate, benzoate, naphthenate, and neodecanoate. Conventional Ba/Cd powder stabilizer systems have one or more of the anions of the following acids: stearic, palmitic, and lauric. The powder Ba/Cd stabilizers, which act both as thermal stabilizer and lubricant, are normally employed in rigid and semirigid products. Ca/Zn stabilizers represent a small volume of the stabilizer market. The best known Ca/Zn stabilizer systems are associated with FDA-sanctioned products, including blown films, medical and beverage tubing, blood bags, blister packs, and bottles. The organotin compounds are butyl-, methyl-, and octyltin and are available in liquid and solid forms. Most organotin stabilizers are used in rigid extrusion and injection molding processes for such products as PVC pipes, profiles, and bottles as well as fittings, siding, and clear PVC bottles.

UV radiation in the range 290 to 400 nm has potentially degradative effects on polymers since most polymers contain chemical groups that absorb this radiation and undergo chain scission, forming free radicals that initiate the degradative reactions. UV stabilizers are employed to impede or eliminate the process of degradation and, as such, ensure the long-term stability of polymers, particularly during outdoor exposure. Light stabilizers are typically UV absorbers or quenchers. The former preferentially absorbs UV radiation more readily than the polymer, converting the energy into a harmless form. Quenchers exchange energy with the excited polymer molecules by means of an energy transfer mechanism. Other UV stabilizers deactivate the harmful free radicals and hydroperoxides as soon as they are formed. Pigments offer good protection for polymers by absorbing UV radiation. Carbon black, used widely in tire manufacture, absorbs over the entire range of UV and visible radiation, transforming the absorbed energy into less harmful infrared radiation. Pigments and carbon black cannot be used, unfortunately, in applications where transparency is required. In these applications, stabilizers that contribute minimal color or opacity are used. For example, transparent polymers like polycarbonate can be protected against yellowing and embrittlement from UV light (photolysis) by incorporating compounds like benzophenone derivatives (e.g., 2-hydroxybenzophenone) and 2-hydroxybenzotriazoles. These highly conjugated compounds are able to convert absorbed UV radiation to less harmful heat energy without chemical change by forming a transient rearranged quinoid structure that changes back to the initial form. Other UV stabilizers include acrylic and aryl esters, hindered amines, and metal salts. Unlike conventional UV stabilizers, the metallic complexes interact with photoexcited polymer molecules, deactivating them by dissipating excess energy as infrared radiation.

VI. FLAME RETARDANTS^{13,14}

Most materials, synthetic or natural, burn on exposure to temperatures that are sufficiently high. The response of polymers to high temperatures depends on their formulation and configuration in the end-use situation. The essential goal of flame retardancy is to preserve life and prevent or at least minimize damage to property. Therefore, the function of flame retardants in a resin formulation is ideally the outright inhibition of ignition where possible. Where this is impossible, a flame retardant should slow down ignition significantly and/or inhibit flame propagation as well as reduce smoke evolution and its effects. The presence of flame retardants also tends to cause substantial changes in the processing and ultimate behavior of commercial resins.

The burning characteristics of polymers are modified by certain compounds — including alumina trihydrates; bromine compounds; chlorinated paraffins and cycloaliphatics; phosphorus compounds, notably phosphate esters; and antimony oxides, which are used basically as synergists with bromine and chlorine compounds. The halogens are most effective in the vapor phase; they act in the flame zone by forming a blanket of halogen vapor that interferes with the propagation of the flame by interrupting the generation of highly reactive free radicals, thus tending to quench the flame. Others such as phosphorus or boron operate in the condensed or solid phase, minimizing the availability of fresh fuel. They form a glaze that limits the heat and mass transfer necessary for flame propagation and/or lowers the melt temperature of the polymer causing it to flow away from the flame. Table 9.10 shows the characteristics and end use of various flame retardants.

Flame retardants may be classified as additives, reactives, intumescent, and nonflame-retardant systems based on their method of incorporation in the resin formulation or their mode of action. Additive flame retardant systems can be further classified essentially as fillers, semiplasticizers, or plasticizers depending on their melting points and area of application. Typical additive flame retardants are halogenated additives used alone or in synergistic combinations with antimony oxide (with PS, PP, polyester, and nylons), phosphate esters, mineral hydrates, boric acid, sodium tetraborate, and ammonium bromide. Additive flame retardants are used with both thermoplastics and thermosets. The use of additive flame retardants involves the addition of very high-melting inorganic materials that will reduce combustibility. This is based on the rationale that the fewer the combustibles, the less burning will occur. Alumina trihydrate, which dominates the flame retardant market in terms of sales volume, serves this function. In addition, it liberates water at high temperatures and this further dampens flame energy. Alumina trihydrate is a typical dual function filler additive (like calcium carbonate and clays), which provides noncombustible filling plus gas or moisture release at elevated temperatures. Alumina trihydrate is used as a primary flame-retardant additive in carpet backing, in electrical parts, and in applications employing glass-fiber-reinforced unsaturated polyester. It is also used in sheet and bulk molding compounds for electrical enclosures in business machine and computer housings, and in laminated circuit boards. Alumina trihydrate offers low-cost flame retardance in epoxy systems and for wire and cable insulation, cross-linked PE and ethylene vinyl acetate copolymers and for flexible polyurethane foams.

Flame retardants that melt or flux at or near the polymer processing temperature are known as semiplasticizing additives, while those that truly flux during processing are referred to as plasticizing additives. These types of flame retardants can be tailor-made for a specific polymer. Plasticizing flame retardant filler additives provide beneficial effects in the processing of rigid polymers and quite often improve the physical properties of the polymer. Commercial examples of plasticizing filler additives include phosphate systems in polyphenylene oxides, phosphates or chlorinated paraffins in vinyl chloride and vinyl acetate polymers, and octabromobiphenyl oxide and brominated aromatic compound in ABS.¹³

In reactive flame retardants, retardancy is built into the polymer chain through appropriate polymerization or postpolymerization techniques. For example, the current additive method of producing flame retardant high-impact polystyrene involves blending decabromobiphenyl oxide and antimony oxide to produce a blend with 8 to 10% combined bromine content. Reactive flame retardants with the same bromine content can be obtained either by brominating the resin or copolymerizing styrene and brominated styrene. Reactive flame retardants include halogenated acids such as tetrabromophthalic anhydride and tetrachlorophthalic anhydrides, halogenated or phosphorated alcohols (e.g., dibromoneopentyl glycol, dibromopropanol) and halogenated phenol bisphenol A. These materials are usually incorporated into the polymer molecular structure through copolymerization with other reactive species.

The use of reactive flame retardants has a number of advantages over that of additive flame retardants. With flame retardants as an integral part of the polymer chain rather than incorporated as an additive,

Table 9.10 *Characteristics and Applications of Flame Retardants*

Market/ Characteristics	Alumina Trihydrate		Bromine Compounds		Chlorine Compounds	
	Resin	End Use	Resin	End Use	Resin	End Use
Markets						
Electrical parts	Unsaturated, polyesters, epoxies, phenolics, thermoplastic rubbers	Switch gear, standoff insulation, electrical connections, junctions boxes, circuit boards, insulating sheet, potting compounds	Nylon 6/6, 6, PBT PET, polycarbonate, epoxy, polypropylene	Connectors, terminal strips, bobbins, switches, relays, circuit boards	Nylon 6/6, 6 polypropylene PBT	Same as for bromine compounds
Electronic housing and enclosures	Unsaturated polyester	Portable power tools, business machine housings, computer housings	ABS, HIPS, polycarbonate	Business machines, computers, TV monitors, copiers	—	—
Wire and cable	LDPE, XLPE, PVC, EPDM	Automotive wire, appliance wire, insulation and jacketing compounds	XLPE, LDPE, EPDM, thermoplastic rubber	Power, industrial and marine cable; electronic wire	XLPE, LDPE, EPDM, thermoplastic rubbers	Same as for bromine compounds
Appliances	Unsaturated polyester	Home laundry equipment, air conditioning equipment	HIPS, ABS, polypropylene	TV cabinetry, power tool housings, kitchen appliances	Polypropylene	Power tool housings, electrical sockets
Building and construction	Unsaturated polyester, PVC, acrylic, EPDM, polyurethane, flexible polyurethane	Paneling, bathroom tubs, shower stalls, countertops, wall coverings, flooring, roofing compounds, cushioning, mattresses	Unsaturated polyester, rigid polyurethanes foam, expandable polystyrene foam	Building panels, translucent sheet, corrosion-resistant equipment, thermal insulation	Unsaturated polyester	Same as for bromine compounds
Transportation (automotive)	Epoxies, acrylics, PVC	Adhesives sealants, upholstery fabrics	Flexible polyurethane foam, rigid polyurethane foam, unsaturated polyesters	Seating, crash padding, thermal insulation (trucks), marine usage (shipboard components, coatings)	Unsaturated polyester	Seating, panels, sheathing
Characteristics	Require high loading to achieve modest flame retardance. Low cost. Low smoke advantage. Nontoxic. Multifunctional extender. Flame-retardant mechanism: endothermic (heat-absorption) cooling of flame upon release of water of hydration		Highly efficient and versatile for wide range of applications. Requires uses of antimony oxide. Broad range of high-performance products available, as aromatic, cycloaliphatic, and bromine/chlorine paraffins. Vapor-phase flame-retardant mechanism. Flame-retardant elements interrupt chemical reactions of combustion in flame zone.		Relatively low smoke generation. One high-performance additive and one high-performance reactive formulation used. Paraffins have low heat stability and are plasticizing. Flame retardant mechanism similar to bromine.	

Table 9.10 (continued) *Characteristics and Applications of Flame Retardants*

	Phosphorus Compounds		Antimony Oxide	
	Resin	End Use	Resin	End Use
Markets				
Electrical	Modified polyphenylene oxide (PPO)	Connectors, terminal strips, etc.	Nylon 6/6, 6, PBT, PET	Connectors, switches, circuit boards, terminal strips
Electronic housing and enclosures	Modified PPO	Business machines	ABS, HIPS	Business machines
Wire and cable	PVC	Communications cable	PVC, XLPE, LDPE, EPDM	PVC building wire, similar uses as for bromine and chlorine compounds
Appliances	Modified PPO	Kitchen appliances, TV cabinetry	HIPS, ABS, polypropylene	TV cabinetry, power tools, kitchen appliances
Building and construction	Rigid polyurethane foam, PVC, unsaturated polyesters	Thermal insulation, wall coverings, flooring, sanitary ware, laminates	Unsaturated polyester, rigid PVC, flexible PVC	Building panels, panels, windows, insulation covering
Transportation (automotive)	PVC, flexible polyurethane foam, rigid polyurethane foam	Upholstery, seat cushioning, thermal insulation (trucks)		
Characteristics	Phosphorus promotes char formation to protect substrate, and halogen acts in vapor phase. Good thermal stability. Process with modified PPO up to 550–600°F. Flame-retardant mechanism: condensed phase. Flame retardant induces reactions in host resin that lead to charring and insulation against further burning.		Inert material by itself. Must be used with halogen-type compound. Used in all polymers where halogen compounds are the selected flame-retardant system. As a synergist, enhances efficiency.	

From Wigotsky, V., *Plast. Eng.*, 41(2), 23, 1985. With permission.

the loss of performance of the base polymer due to diluents (other constituents) in the resin formulation is minimized. In addition, migration and/or bloom are completely eliminated while compounding costs are substantially reduced. Leaching of reactive flame retardants by solvents and corrosives is relatively more difficult than leaching additive retardants.

Reactive flame retardants are used mainly with thermoset resins, particularly unsaturated polyesters, both reinforced and unreinforced. A technique for introducing flame retardants into unsaturated polyesters involves the use of compounds with residual unsaturation such as diallyl tetrabromophthalate, which is used as a cross-linking agent alone or with styrene.

Intumescent flame retardance is based on the formation of a char on the surface of the resin on the application of heat, consequently insulating the substrate from further heat and flame. Phosphorous compounds such as inorganic or organic phosphates, nitrogen compounds such as melamine, and polyhydroxy compounds — usually pentaerythritol — are used in intumescent formulations. High loadings, are usually required to achieve the required level of fire retardancy. This tends to degrade the physical properties of the base polymer. Intumescent flame retardant systems are generally limited to polymers with low processing temperature (e.g., PP) because they expand considerably on application of heat.

Nonflame-retardant systems are polymeric systems that inherently have some level of flame retardance and therefore do not require additive or reactive flame retardants. Examples include PVC and its compounds, poly(vinylidene chloride) films and compounds, phenolic foams, amide-imides, polysulfones, and poly(aryl sulfides).

VII. COLORANTS^{15,16}

As we said earlier, very few polymers are used technologically in their chemically pure form; it is generally necessary to incorporate various additives and reinforcements to assist processing and achieve desired properties. Unfortunately, these components also often produce a significant amount of undesirable color and opacity in the resin. Each resin itself has its color that may vary from grade to grade or batch to batch. For example, polystyrene crystal is transparent, whereas high-impact polystyrene has a white, somewhat translucent, appearance while the common grade flame-retardant polystyrene is opaque. The color of general-purpose ABS is off-white and opaque. Glass fibers, the most common reinforcements added to nylons and polyesters, darken the color of these resins.¹⁷ The marketability of a polymer product quite frequently depends on its color; therefore the purpose of adding a colorant to a resin is to overcome or mask its undesirable color characteristics and enhance its aesthetic value without seriously compromising its properties and performance.

Colorants are available either as organic pigments and dyes or inorganic pigments. They may be natural or synthetic. By convention, a dye is a colorant that is either applied by a solution process or is soluble in the medium in which it is used, while pigments are generally insoluble in water or in the medium of use. Dyes are generally stronger, brighter, and more transparent than pigments. As a result of the intrinsic solubility, dyes have poor migration fastness and this restricts their use as polymer colorants. Inorganic pigments are largely mixed metal oxides with generally good-to-excellent light fastness and heat stability but variable chemical resistance. Organic pigments and dyes are generally transparent and possess good brightness. The heat stability and light and migration fastness of organic pigments range from poor to very good. [Table 9.11](#) shows some colorants, their characteristics, and their applications.

Colorants are used in polymers either as raw pigments (and dyes), concentrates (solid and liquid), or precolored compounds. Precolored resins, solid and liquid concentrates, are all offsprings of the basic dry pigments. Colorants are available in a variety of forms, including pellets, cubes, granules, powder and liquid, and paste dispersions. Raw pigments are generally supplied as fine particles, which require dust control measures. To optimize color development when raw pigments are used, the size of pigment particles or agglomerates must be reduced and coated with appropriate resin. Most finished colors use multiple pigments. This requires a homogeneous mixing of all the pigments in the formula in high-shear mixing equipment to produce a uniform color. Precise metering into the processing machine is required to produce consistent colors since some components of the pigment system, though present in relatively small quantities, have strong color characteristics. Raw colorants or pigments generally cost less than other forms of colorants, but they can be more difficult to disperse and may result in inconsistent master batches.

Table 9.11 *Characteristics and Applications of Some Colorants*

Pigment	Characteristics	Applications
Reds		
Quinacridones (medium red-magenta)	Good to excellent heat stability in 500–525°F range, excellent high fastness, expensive, some grades difficult to disperse	Widely used in automotive applications, propylene fibers
Perylenes (scarlet to violet)	Excellent fastness, and heat stability in 325–500°F range, expensive, some grades difficult to disperse	Extensive use in automobile, finishes, synthetic fibers
Diazol (scarlet to medium red)	Very good heat stability, light fastness, easily dispersible, relatively expensive	Widely used in vinyls and polyolefins
Azo (scarlet to bluish reds)	Heat stability in the 450–500°F range, light fastness range from poor to good, economical, limited light fastness in tint	Polyolefin packaging, toys housewares
Permanent red 2B (scarlet to bluish reds)	Economical light red shades, good heat stability and light fastness in mass tone and near mass tone; tendency to plate out, limited light fastness in tints with white	Widely used in vinyls, polyolefins, rubbers
Oranges		
Isoindolinone (medium orange)	Transparent, excellent heat stability and light fastness, relatively expensive	Used for vinyls, polyolefins, and styrenics
Diaryl orange (medium orange)	Heat stability in 450–500°F range, fair light fastness, bright, clear, high tinting strength, moderate price, limited light fastness, some tendency toward bleeding	Used in polyolefins for packaging, toys
Yellows		
Isoindoline (reddish yellow)	Very good to excellent heat stability (500–575°F), good to very good light fastness, transparent or opaque	Used in PVC and polypropylene and some engineering plastics
Quinophthalone (greenish yellow)	Moderate light fastness, good to excellent heat stability; tint light fastness limited	Used in vinyls and polyolefins
Metal complex (greenish yellow)	Heat stable (550–575°F), light fastness good to excellent	Some engineering resins, PVC and polypropylene
Greens		
Phthalocyanine (bluish to yellowish green)	Heat stable to 600°F, light fast, easy to disperse	Very broad use in vinyls, polyethylene styrenics, polypropylene and some engineering resins
Blues		
Indanthrone (reddish blue)	Very good light fastness and heat stable expensive	Light tinting of vinyls, in rigid PVC
Violets		
Carbazole (reddish violet)	Very high tinting strength, expensive limited light fastness	Polyolefins and vinyls
Metal Oxides		
Iron oxides (synthetic), red-maroon	Good heat stability, inexpensive, inert, poor tinting strength, dull	Variety of plastics but not in rigid PVC
Zinc ferrite tan	Good heat stability, inert, light fast, good weatherability, more expensive than other iron oxides	Variety of plastics but not in rigid PVC
Iron oxides (natural), siennas	Inexpensive, color uniformity can contain impurities	Limited use in plastics, polyethylene film bags
Chromium oxide green	Good heat stability and light fastness, excellent weatherability and chemical resistance, inexpensive, dull, poor tinting strength	Can be used in most thermoplastics and thermosets
Mixed metals oxides		
Nickel titanium yellow	Excellent weatherability, inert, easy to disperse, good chemical resistance, poor tinting strength, weak color	Engineering resins, PVC siding

Table 9.11 (continued) *Characteristics and Applications of Some Colorants*

Pigment	Characteristics	Applications
Inorganic browns	Heat and light stable, good chemical resistance, good color uniformity, relatively expensive	Most thermoplastics and thermosets
Cadmiums, cadmium yellow sulfide	Excellent heat stability, good alkali resistance, light fast, sensitive to moisture and acids, poor weatherability, toxicity concerns	Wide use in plastics including engineering resins
Chrome yellow	Bright colors, inexpensive, good hiding power, poor heat stability, poor chemical resistance, possibly toxic	Fairly broad use in thermoplastics and thermosets

From Wigotsky, V., *Plastic. Eng.*, 42(10), 21, 1986. With permission.

Color concentrates are intimately mixed dispersions of pigments in a base carrier resin. The pigment content of concentrate is usually in the 2 to 30% range, but higher loadings are being developed to enhance versatility and cost/performance benefits. The pigments and resin are subjected to high stress during processing to promote thorough dispersion of the colorant. The concentrate is blended with the resin material being colored in a predetermined proportion by weight known as the let-down ratio to produce the desired color and opacity in the master batch or end product. To ensure compatibility between the concentrate and the let-down resin, the color concentrate is generally made from the same generic polymer as the let-down resin but with a higher melt index so as to promote ready and even mixing. A uniform blend of concentrate must be fed either continuously by a metering device or by weight on a batch basis into the processing equipment, which must be able to convert the blend of pellets into a uniform melt. Color variation is produced if the melt is nonuniform or the concentrate is not completely incorporated into the resin.

Concentrates are available in solid or liquid forms. Solid color concentrate, the major form in which colorants are manufactured and sold, comes in pellet, cube, granulated, and powder forms. They usually consist of dry pigments, additive components encapsulated in a base resin carrier. Dispersion and color control are excellent, weighing is less critical, and flowability is good for easy feeding while cleanup is easier because of the need to process color with the carrier resin.¹⁵ It is, however, necessary to ensure that the pigment carrier and other components of the concentrate do not compromise the resistance to heat, light, basic physical properties, and rheological compatibility of the resin. Liquid concentrates possess many of the advantages of solid concentrates but are usually more costly. They allow lower pigment loading and can sometimes be used at slightly lower concentrations because they cover more surface. Liquid concentrates require less material handling and floor space for inventory, and their production does not involve a previous heat history. Some resins, however, are unable to absorb a high percentage of liquid.

There is currently a trend to increase the multifunctional nature of color concentrates so that color as well as other desired properties are added to the resin system. This increases the processor's flexibility in meeting user's needs and simplifies user inventory by reducing the need to stock large quantities of tailored resins.

Precolored compounds provide the processor with a single source of color and resin. This eliminates the need for mixing during processing and provides highly accurate color control, particularly in cases where the base resin is subject to color variations arising from lot-to-lot color differences. In complex part designs where resin flow may not be uniform or where equipment is unable to provide uniform mixing, precolored compounds offer the best method of making a uniformly colored part. However, processors sometimes tend to have preference for dry pigments and concentrates for greater flexibility of inventory and color changeover. For example, from an inventory standpoint, it is much simpler to stock a supply of basic natural resin to satisfy diverse, changing requirements with smaller supplies of dry pigment or color concentrate. A processor who prefers to compound his color from pigment must, of course, have the proper equipment and an in-depth knowledge of the process. One of the growth areas for precolored resin is in specialized engineering applications where not only colorants but a variety of other modifiers must be included in the compound. For example, fiber-reinforced resins that may also contain mold-release agents, flame retardants, and other additives are best made from fully compounded precolored resin.

Certain fundamental criteria must be considered in selecting a colorant for a particular application. These include the ability of the colorant to provide the desired color effect and withstand processing conditions and whether or not the fastness will satisfy end-use requirements. Therefore, the initial step in the selection of a colorant is to determine whether it will provide the coloristic properties desired, alone or in combination with others. The performance properties of a colorant are generally of two types — those related to processing and those related to the ultimate end use. The most important processing-related property is the heat stability of the colorant. It must be able to withstand not only the process temperature encountered during manufacture but also, for possibly prolonged periods, the temperature in the end-use situation.

Migration fastness is related to the solubility of the colorant in the polymer. Color migration is manifested through bleeding, blooming, or plate-out. Bleeding is the migration from a colored polymer film to an adjacent uncolored or differently colored material, while blooming involves colorant migration, recrystallization, and formation of a dustlike coating on the surface of the polymer. Plate-out is characterized by the building of a coating on the metallic surfaces of processing equipment. Inadequate light fastness of a colorant is usually manifested in the form of fading or, in the case of some colorants, darkening. The severity and rapidity of color change depend on the chemical structure of the colorants, its concentration in the part, and part thickness.

The compatibility of a colorant is assessed not only on the basis of the ease with which it can be mixed with the base resin to form a homogeneous mass but also on the requirement that it neither degrades nor is degraded by the resin. In relation to product functional properties, incompatibility of a colorant can affect mechanical properties, flame retardancy, weatherability, chemical and ultraviolet resistance, and heat stability of a resin through interaction of the colorant with the resin and its additives. Flame retardancy, for example, may impinge directly on the performance of a colorant. Pressure to produce materials with lower levels of toxic combustion products can involve organic fire retardant additives that interact with the colorant either to negate the effect of the additives or affect the color.

VIII. ANTISTATIC AGENTS (ANTISTATS)

Most synthetic polymers, unless specially treated, are good electrical insulators. They are therefore capable of generating static electricity, which can be potentially costly and dangerous. Static-induced accumulation of dust reduces the attractiveness and thus saleability of products displayed on store shelves. The attraction of a formed part to the charged surfaces of a processing mold prevents proper ejection of the formed part and consequently slows down production. Electrostatic charges can cause problems when textile, films, or powders join up in automatic machinery. Sparks, and possibility explosions or fires, can occur when static electricity is induced from plastics on nearby conductor. Damage of sensitive semiconductors and similar complex microelectronic devices can also occur from either the direct discharge from the conductive skin of personnel or by exposure of such devices to the close approach of a static-charged polymer material.²⁰

When two surfaces that are in intimate contact are rubbed together or pulled apart, static electricity is generated. This is due to the transfer of electrons from the surface of the donor material, which consequently becomes positively charged, to the surface of the acceptor material, which then becomes negatively charged. For materials that are nonconductive, these static charges do not flow easily along the surfaces and therefore remain fixed or static. Whether a material behaves as a donor or an acceptor depends on its position in the triboelectric series (Table 9.12). For example, if nylon and propylene are rubbed together, nylon is the donor, while polypropylene is the acceptor.

The generation of static charges is not confined strictly to nonconductors only; conductors also generate static charges, but since they dissipate the charge quickly the level of static charges developed by these materials is difficult to measure. When a conductor and nonconductor are separated or rubbed against each other, the nonconductor develops a measure of static charge. The nonconductor will not lose its charge to the ground. Consequently, the charge is removed by employing other techniques. The use of air-ionizing bars and blowers provides an atmosphere of ionized air capable of neutralizing the charged objects or surfaces. However, this does not provide lasting protection since it does not prevent another charge from forming once the object is removed from the ionized air atmosphere. To ensure an extended removal of static charges from the surface, the nonconductor must be made sufficiently conductive to carry charge to the ground. A layer of water, even a few molecules thick, will do this

Table 9.12 *The Triboelectric Series*

Negative [-] end		
1. Teflon	9. Rubber	17. Polyester
2. PVC	10. Brass, stainless steel	18. Aluminum
3. Polypropylene	11. Nickel, copper, silver	19. Wool
4. Polyethylene	12. Acetate fiber	20. Nylon
5. Saran	13. Steel (carbon)	21. Human hair
6. Polyurethane foam	14. Wood	22. Glass
7. Polystyrene foam	15. Cotton	23. Acetate
8. Acrylic	16. Paper	
Positive [+] end		

satisfactorily since high conductivity is not required for the removal of static charges. Antistatic agents (antistats) are therefore hygroscopic chemicals that can generate this layer of water by pulling moisture from the atmosphere.

There are essentially two types of antistats that are commonly used in polymers to get rid of static electricity: those that are applied topically and those that are incorporated internally into the polymer. Both improve the conductance of polymer surfaces by absorbing and holding a thin, invisible layer of moisture from the surrounding air onto the polymer surface. Topical coatings are usually applied using wipe, spray, dip, or roller coating techniques. Topically applied antistats are particularly useful where antistat cost control and performance are essential or when the mechanical performance of a polymer is negatively affected by an internal additive.²⁰ Reapplication of topical antistats may be required, particularly in cases of high-friction end uses. Hence, antistats applied to the surface of parts are used primarily in applications where temporary static protection is desired. The techniques for applying topical antistats necessarily involve wasteful amounts of antistats and leave an undesirable oil-like surface.

Internal antistats are compounded directly into the polymer mix prior to processing. They then migrate slowly and continually through the molecular interstices and the bulk polymer to its surface where they absorb the water necessary to prevent accumulation of static charges. In this case, it is necessary to balance the rate of such migration and the rate of surface removal of the antistat to provide long-term protection for the part.

Major types of organic antistatic agents include quaternary ammonium compounds, amines and their derivatives, phosphate esters, fatty acid polyglycol esters, and polyhydric alcohol derivatives such as glycerine and sorbitol.²⁰ Selection of the appropriate antistat depends on its compatibility with the polymer, the end use of the part, and the desired level of antistatic activity. Other factors that need to be considered include the effect of antistatic agent on color, transparency, and finish of the polymer part; its possible toxicity; stability during processing; and degree of interference with physical properties and ultimately cost effectiveness.

IX. PROBLEMS

9.1. Explain the following observations:

- The magnitude of an electrostatic charge increases with increasing intimacy of contact and the speed of separation of the two materials whose surfaces are in contact with each other.
- Graft copolymers of PVA/EVA are available commercially as flexible films. Applications include outdoor exposed materials such as roofing, pond membranes, and swimming pool covers as well as medical uses such as processing of blood.
- Code specification of PVC wire and cable used in building has been raised from 60 to 90°C. This has caused a reformulation from the use of DOP and/or DINP to phthalates such as DUP, DTDP, and UDP, which are used in combination with trimellitate ester such as trioctyl trimellitate.
- Although phthalate esters less volatile than DOP are used in most automotive interior applications, trialkyl trimellitates are recommended.
- Plasticizers sanctioned for food-contact applications include soya and linseed oil epoxides and various adipates.

- f. Furniture covered with tablecloths and upholstery made with plasticized PVC sometimes get discolored and tacky. Suggest a possible solution to the problem.
- g. Polystyrene is completely immiscible with PVC. Styrene–maleic anhydride (SMA) copolymers, on the other hand, show a degree of miscibility with PVC that assures part integrity and toughness.
- h.

Blend	Properties
PC/PBT	Toughness, chemical resistance
PC/PET	Toughness, chemical resistance, and high temperature rigidity

- i. ABS is more susceptible to oxidation than polystyrene.
- j. PVC requires incorporation of thermal stabilizers and antioxidants but not flame retardants.
- k. Black pigments are not normally used as colorants for rigid PVC used for home siding and window profiles, while pigments containing heavy metals are usually avoided as colorants for polymers used for toys and food wrapping.
- 9.2. The front and rear bumper beams on the 1993 Toyota Corolla were made from polypropylene/fiberglass composite. Estimate the longitudinal modulus of these beams assuming a fiberglass (E-glass) composition of 50%.

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