

PLASTICIZERS USE AND SELECTION FOR SPECIFIC POLYMERS

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This chapter will provide information on:

- types of plasticizers used
- concentration range in practical applications
- reasons for their selection
- specific mechanisms of plasticizers action
- potential effects on other additives used on the polymer properties
- typical generic formulations

This scheme of data presentation is followed as much as the available literature permits.

11.1 ACRYLONITRILE-BUTADIENE-STYRENE, ABS

11.1.1 FREQUENTLY USED PLASTICIZERS

Several types of plasticizers are used in ABS. These include: hydrocarbon processing oil,¹ phosphate esters (e.g., triphenyl phosphate,¹ resorcinol bis(diphenyl phosphate),² or oligomeric phosphate),¹ long chain fatty acid esters,^{3,4} and aromatic sulfonamide.⁵

11.1.2 PRACTICAL CONCENTRATIONS

- hydrocarbon processing oils: 1-3 phr
- phosphate esters: 2 phr (flow improvement) 10-15 (flame retardation)
- long chain fatty acid esters: 0.2-0.5 wt%
- aromatic sulfonamide: 2-10 phr

11.1.3 MAIN FUNCTIONS PERFORMED BY PLASTICIZERS

Plasticizers play secondary roles in ABS, such as:

- reduction of melt viscosity and processing temperature
- improved mold release
- flame retardation and smoke reduction

Aromatic sulfonamide plasticizer is designed to produce non-fogging parts for automotive industry from ABS, its blends, and other polymers.

11.1.4 MECHANISM OF PLASTICIZER ACTION

No studies are thus far available that propose the mechanism of action of plasticizers in any of the functions listed in Section 11.1.3.

11.1.5 EFFECT OF PLASTICIZERS ON POLYMER AND OTHER ADDITIVES

Even small additions (1-2 wt%), such as may be required to increase flowability, will affect the mechanical properties of ABS. This influence is complex. For example, the addition of process oil reduces both tensile strength and elongation whereas phosphate plasticizers have only a small effect on tensile strength but increase elongation. On the other hand, mineral oil increased impact strength substantially (by about 50%). Phosphate plasticizers reduce impact strength when their concentration increases.¹ Flexural strength and modulus are not affected by additions of small amount of plasticizers (up to 4 wt%).

Melt flow rate depends on the type and the concentration of plasticizer selected. Resorcinol bis(diphenyl phosphate) at a concentration of 4 wt% almost doubled the melt flow rate being substantially more effective than triphenyl phosphate. Mineral oil did not affect the melt flow when added at 2 wt% but reduced it when the concentration was doubled. This, and the effects on mechanical properties, indicate that phosphate compounds interact with polymer chains (as typical of plasticizers) whereas mineral oil acts as an external lubricating oil that is incompatible with the polymer.

Even small amounts of phosphate plasticizers improve flame retarding properties but at least 8 phr are needed to meet typical flame resistance requirements. The concentration may be varied depending on the formulation, which may include other flame retarding components.

When ABS is contacted with other materials that contain plasticizers (e.g., PVC) stress cracking may occur. Time to break and the force required have been drastically reduced when ABS was contacted with nineteen samples of PVC each containing different plasticizers.⁶ This shows that the performance of ABS will depend on the type and amount of other materials in the formulation.

11.1.6 TYPICAL FORMULATIONS

Flame retarding formulation:⁷

PC/ABS (5:1)	91.9 wt%
Fyrolflex RDP	8.0 wt%
PTFE	0.1 wt%
UL94 1.6/3.2 mm	V0/V0

Flow modification:⁷

ABS	98 wt%
Fyrolflex RDP	2 wt%
42% increase in melt flow index over control (no plasticizer).	

11.2 ACRYLICS

11.2.1 FREQUENTLY USED PLASTICIZERS

Acrylic copolymers may be internally plasticized by the selection of an appropriate composition of monomers which give the copolymer the required glass transition temperature.

This process, although known and possible may not be practical in the production of commercial materials.

Acrylic binders in water-based paints must have film-forming properties at the temperatures of paint drying. If the paint was to contain a polymer with a low glass transition temperature, T_g , so it could form a film at room temperature then the film formed would be soft and would not perform its protective functions. This requires that the polymer should have a low glass transition temperature, T_g , during its cure cycle and a higher T_g in its operating lifetime. Different methods can be used to achieve this but the use of coalescing solvents is the most popular method. Coalescing solvents can be used to plasticize an acrylic copolymer, which lowers the T_g below ambient and helps in film formation. This mechanism is discussed in Section 11.2.4.⁷ Typical coalescing solvents include ethylene and propylene glycols and their esters, butyl cellosolve, butyl carbitol, and many other. More information on various types of coalescing solvents can be found elsewhere.⁸

Controlled drug release properties are achieved through the application of coating to the surface of the capsule. A surface coating is applied in a microencapsulation process that frequently uses a plasticized acrylic copolymer.⁹ The type and concentration of plasticizer determines the rate of drug release. Triethyl citrate is a typical plasticizer used in such microencapsulation.

Acrylic sealants, adhesives and coatings use m,p-cresol propoxylate (Macol 85) and alkyl benzyl phthalate (Santicizer 160) as permanent coalescing plasticizers. Acrylic based floor polishes use alkyl benzyl phthalate (Santicizer 160) and dialkyl adipate (Santicizer 141). These plasticizers are also permanent coalescing agents.

Many other applications of plasticizers are reported in the literature. These include dioctyl phthalate in ink for jet printers,¹⁰ dibutyl phthalate or phosphate in dentures,¹¹ a variety of types in pressure sensitive adhesives,¹² diesters of phthalic and benzoic acids in surface coatings for polymers,¹³ and plasticizers and coalescing agents in nail varnishes.¹⁴

11.2.2 PRACTICAL CONCENTRATIONS

- water-based coatings: 0-15% (coalescing solvents)⁷
- polymer surface coating: 1-25% (plasticizers/coalescents)¹³
- controlled-release drugs: up to 15%
- concrete sealer: 1-3% (coalescent)
- sealants: 2-10% (plasticizer/coalescent)
- ink for jet printer: 1.5%¹⁰
- nail varnish: 6.6% (plasticizers 4.8%, coalescing solvents 1.8%)¹⁴

11.2.3 MAIN FUNCTIONS PERFORMED BY PLASTICIZERS

The following functions are performed by plasticizers and coalescing agents in acrylic resins:

- coalescing (film forming properties, mechanical properties improvement)
- decrease of glass transition temperature (improved elongation, elasticity, low temperature curing)
- control migration rate of drug (controlled-release properties)
- adhesion promotion (softening surface of polymer coated by surface layers)

11.2.4 MECHANISM OF PLASTICIZER ACTION

Figure 11.1 shows macroscopic stages of film formation. Four stages are pictured here:⁸

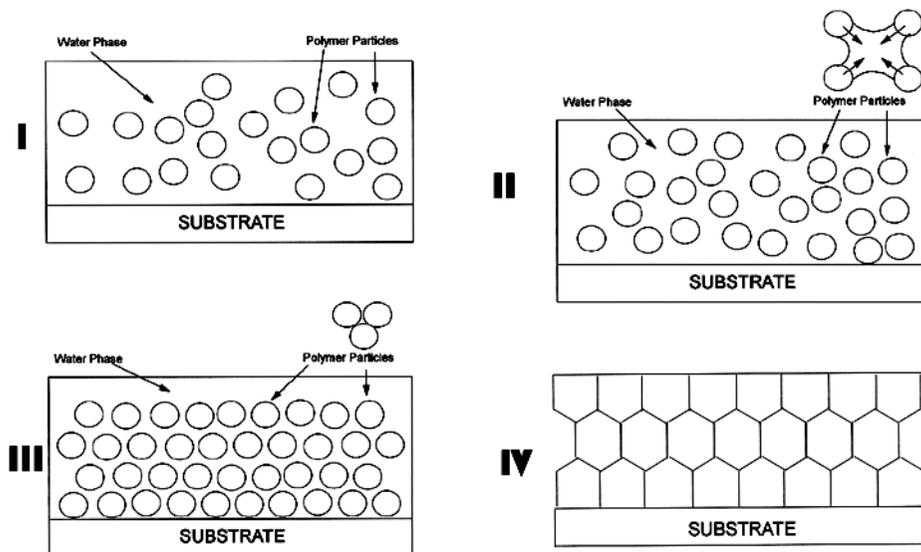


Figure 11.1. Macroscopic stages of film formation from water-borne coating. [Adapted, by permission from Randall D in *Handbook of Solvents*, Wypych G, Ed., *ChemTec Publishing*, Toronto, 2001.]

- application of wet film (I)
- initial evaporation of water (II)
- close packing of latex particles on further evaporation of liquid phase (III)
- formation of film.

In order to understand this mechanism further we have to consider the thermodynamic and chemical mechanisms of film formation, specifically:

- the kinetics of evaporation of water and solvent/plasticizer
- the effect of trace solvent
- the effect of micellar structure of latex (surfactants)
- the coalescence of particles.

An understanding of these fundamental principles is needed to explain the mechanism.

After the coating has been applied to the surface of the substrate, water begins to evaporate but this is also accompanied by the loss of the coalescing solvent, although it is usually less volatile than water.

The latex particles come closer together as the liquids evaporate but they are kept apart by the repulsion forces of the surface coating composed of surfactants used in polymerization. It has not yet been determined when and why these repulsion forces are finally overcome and what role solvent concentration and its dissolving characteristics play in this process.

It is currently understood⁷ that the solvent promotes the diffusion of polymer chains from one particle to another. As they cross boundaries they help in the formation of a uniformly built film. Temperature also plays role here as does the polymer structure. The mobility of polymer chains increases rapidly above the glass transition temperature. It is therefore, a combination of the ambient temperature, the glass transition temperature of

polymer, and the effective reduction of the glass transition temperature by the coalescing solvent that determine the rates of diffusion of the polymer chains. In selecting the solvent, the formulator must take into account the factors that will affect its rate of loss. If, for example, it is very volatile, it will be removed from the applied coating quickly and film properties may not become fully developed. If it is too slow the curing rate may also be too slow. In addition, slow evaporating solvents increase concentration and time of removal of trace solvents and thus increase the dangers of indoor pollution. The presence of slowly evaporating coalescent solvent or the retention of permanent coalescents also affect the hardness of the coating, make it more likely to pick up dirt, and increase the cost of maintenance.

11.2.5 TYPICAL FORMULATIONS

Drug release coating:⁹

Acrylic resin (Eudragit RS30D)	12
Triethyl citrate	1.5
Magnesium stearate (antitackiness agent)	1.0
Water	60.0

This composition processed at 38°C (film forming temperature) was suitable for the controlled release of salbutamol.

Concrete sealer:

Acrylic copolymer	100
Water	150
Butyl cellosolve	8

This composition, after spraying and drying at ambient temperature, substantially reduces the water uptake by concrete.

11.3 BROMOBUTYL RUBBER

11.3.1 FREQUENTLY USED PLASTICIZERS

Poly(ethylene vinyl alcohol) and cellulose acetate are used in tire innerliner¹⁵. High molecular weight polyisobutylene plasticizer (molecular weight 2,300 daltons) is used in pressure sensitive tape for roofing applications.¹⁶

11.3.2 PRACTICAL CONCENTRATIONS

- tire innerliner:¹⁵ amount sufficient to lower the softening point of a starch plasticizer mixture to the range 110-170°C (without plasticizer it is over 200°C)
- pressure sensitive adhesive¹⁶35-55%

11.3.3 MAIN FUNCTIONS PERFORMED BY PLASTICIZERS

Bromobutyl rubber is relatively impermeable to air and moisture and it is often a major portion of the tire innerliner composition. The addition of the starch/plasticizer dispersion composite further reduces the already low air permeability of the butyl rubber-based composition. Starches with high softening points are difficult to incorporate it into rubber composition without plasticizer.¹⁵

In pressure sensitive roofing tape, the plasticizer imparts a resiliency and gives a permanent tack.¹⁶ It is essential to select an appropriate concentration of plasticizer in relation to the type and concentration of the tackifying resin.

11.3.4 EFFECT OF PLASTICIZERS ON POLYMER AND OTHER ADDITIVES

From the studies performed on roofing tape,¹⁶ it is known that lowering the molecular weight of plasticizer to 1,290 daltons results in extensive bleeding at elevated temperatures (116°C). Tekni-plex¹⁷ developed a technology using dry reinforcing ingredients, which allows the production of plasticizer-free products from several resins including bromobutyl rubber.

11.4 BUTYL TERPOLYMER

11.4.1 FREQUENTLY USED PLASTICIZERS

Polybutene¹⁸ and polyisobutylene^{19,20} are the most frequently used plasticizers. Paraffinic, naphthenic, and aromatic process oils are also used.^{19,20} Esters of fatty acids and phosphates are also used but are less common.²⁰

11.4.2 PRACTICAL CONCENTRATIONS

- polyisobutylene:^{19,20} 5-9%
- process oil:²⁰ 26-28%

11.5 CELLULOSE ACETATE

11.5.1 FREQUENTLY USED PLASTICIZERS

Large body of information is available on the plasticization of cellulose acetate because of the long history of the polymers and the wide spread applications for plasticized cellulose acetate.²¹⁻⁴⁹ The following plasticizers and plasticizing compounds are frequently used:

- acetyl triethyl citrate (biodegradable film³² and cigarette filter⁴⁴)
- tributyl citrate (osmotic membrane⁴⁶)
- triethyl citrate (biodegradable film,³² food wraps,³⁸ cigarette filters,^{39,44} and osmotic membrane⁴⁶)
- tri-(2-ethylhexyl) phosphate (flame retarding plasticizer)
- triphenyl phosphate (photographic film base,^{2,28} flame retardant in sheeting, moldings and coatings,² magnetic tape produced between 1935 and 1960, and conductive composite⁴²)
- dimethyl phthalate ((film, varnishes, rocket propellants, lacquers, safety glass)³⁴ conductive composite⁴²)
- diethyl phthalate (eyewear frames,²¹ biodegradable film,³⁰ fast-fusing plasticizer,³⁶ scotch tape, mulch film,⁴⁰ conductive composite,⁴² film,⁴⁷ biodegradable, and compostable plastics⁴⁹)
- di-(2-ethylhexyl) phthalate (coatings)³⁵
- dimethyl sebacate
- dioctyl sebacate (membranes²⁶)
- polyalkylene glycol (biodegradable foam⁴³)
- polyethylene glycol (fibers²⁷ and osmotic membrane⁴⁶)
- polypropylene glycol (film³³)

- sulfolane (2,3,4,5-tetrahydrothiophene-1,1-dioxane)³⁷
- toluenesulfonamide derivatives (paper laminate⁴⁵)
- triacetin – glyceryl triacetate (cigarette filter,^{44,48} microspheres,⁴¹ and paper laminate⁴⁵)
- internal plasticization (reaction with maleic anhydride, glycerol, and citrate esters during melt processing²²)
- liquids and vapor in contact with the polymer (water²¹ and methanol²⁴)

11.5.2 PRACTICAL CONCENTRATIONS

The following are the most typical ranges of plasticizer concentrations in different products:

- acetyl triethyl citrate (biodegradable film³² – 20-50%, cigarette filter⁴⁴ – 1-40 wt%)
- tributyl citrate (osmotic membrane⁴⁶ – 21-23 wt%)
- triethyl citrate (biodegradable film³² – 20-50%, osmotic membrane⁴⁶ – 5-8 wt%)
- triphenyl phosphate (photographic film base² – 13-17 phr²⁸, flame retardant in sheeting² – 15 phr, moldings² – 20 phr, conductive composite⁴² – 30-60 phr)
- dimethyl phthalate (conductive composite⁴² – 30-60 phr)
- diethyl phthalate (biodegradable film³⁰ – 10%, mulch film⁴⁰ – 17 wt%, conductive composite⁴² – 30-60 phr, biodegradable, compostable plastic⁴⁹ – 25 wt%)
- dioctyl sebacate (membranes²⁶ – 34 wt%)
- polyalkylene glycol (biodegradable foam⁴³ – 20-40 phr)
- polyethylene glycol (fibers²⁷ – 10-40 wt%)
- polypropylene glycol (film³³ – 19 wt%)
- triacetin (cigarette filter⁴⁸ – 9 wt%, microspheres⁴¹ – 6-10 wt%, paper laminate⁴⁵)

11.5.3 MAIN FUNCTIONS PERFORMED BY PLASTICIZERS

The following functions are performed by plasticizers:

- reducing material hardness and other mechanical properties such as tensile strength, tensile modulus, flexural strength, flexural modulus²¹
- reducing glass transition temperature³²
- influencing diffusion coefficient of liquids and gases permeating through membranes^{24,26}
- imparting flame retarding properties² (phosphates)
- permanent coalescing agent and solvent
- fiber-to-fiber bonding agent
- shortening the drying process in solvent-containing processes by reducing the amount of solvent required

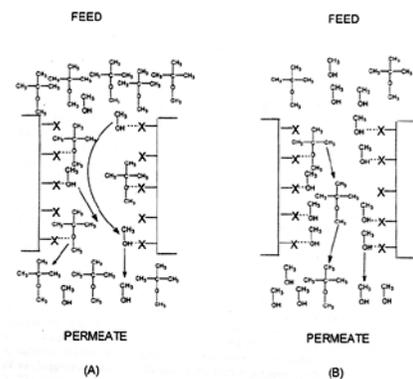


Figure 11.2. Schematic transport model of MeOH and MTBE. A. Low MeOH concentration. B. High MeOH concentration. X - hydrophilic groups. [Adapted, by permission, from Shuguang Cao, Yanqiao Shi, Guanwen Chen, *Polym. Intl.*, **49**, No.2, Feb.2000, p.209-15.]

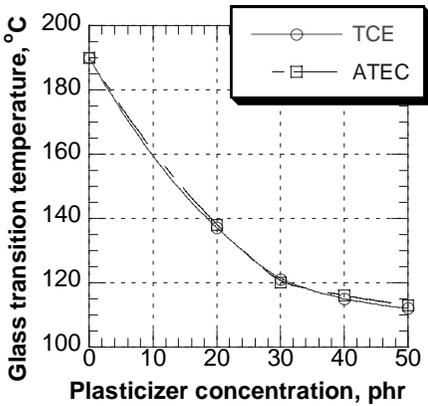


Figure 11.3. Glass transition temperatures of cellulose acetate samples plasticized with variable quantities of triethyl citrate, TCE, and acetyl triethyl citrate, ATEC. [Data from Ghiya V P; Dave V; Gross R A; McCarthy S P, *J. Macromol. Sci. A*, **A33**, No.5, 1996, p.627-38.]

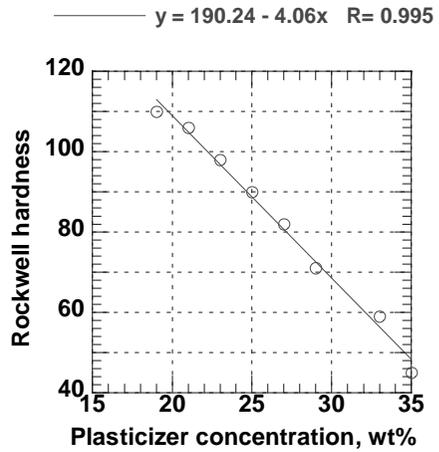


Figure 11.4. Rockwell hardness of cellulose acetate samples plasticized with variable quantities of diethyl phthalate. [Data from Garner D P; DiSano M T, *Polym. Mater. Sci. Eng.*, **75**, 2, 301-2, 1996.]

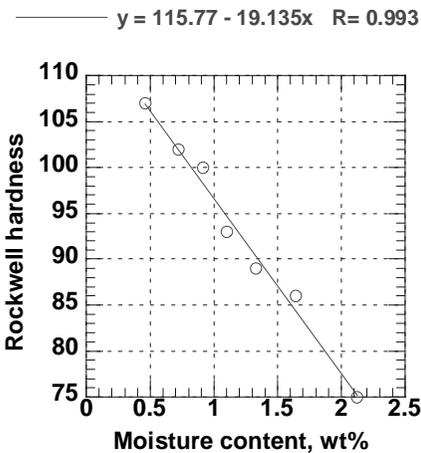


Figure 11.5. Rockwell hardness of cellulose acetate samples plasticized with 24.9 wt% of diethyl phthalate at different moisture levels. [Data from Garner D P; DiSano M T, *Polym. Mater. Sci. Eng.*, **75**, 2, 301-2, 1996.]

11.5.4 MECHANISM OF PLASTICIZER ACTION

In many instances polymers are in contact with liquids that penetrate their structure. This process is usually accelerated when the liquid has a plasticizing effect on polymer. The permeation of a solvent through a pervaporation membrane is a special case of such a situation. Figure 11.2 shows a schematic transport model of a mixture of methanol, MeOH, and methyl tert-butyl ether, MTBE, through cellulose triacetate pervaporation membrane.²⁴

In this composition of solvents, MeOH has a much greater plasticizing effect than MTBE. Experimental data show that when methanol concentration in its feed is low, the permeation of MTBE is very low but it drastically increases when

the concentration of MeOH in the feed goes above 15 wt%. The permeation of MeOH is quite independent of its concentration in the feed.

At low concentration of MeOH in the feed, a large number of both MeOH and MTBE molecules are dissolved in the membrane but only the smaller molecules of methanol permeate (Figure 11.2.A). As the degree of plasticization increases (as the MeOH con-

centration increases), more hydrophilic groups are blocked by MeOH and MTBE passes through the membrane unabsorbed. This causes an increase in MTBE pervaporation flux (Figure 11.2.B).

11.5.5 EFFECT OF PLASTICIZERS ON POLYMER AND OTHER ADDITIVES

Figure 11.3 shows that the addition of citrate plasticizer decreases the glass transition temperature of the polymer as a result of the plasticizing effect. There is very little difference between the plasticizers – most likely because the plasticizers used in the study had very similar chemical structures.³²

Figure 11.4 shows that an increased concentration of plasticizer reduces the hardness of cellulose acetate parts. Figure 11.5 shows that the potential moisture absorption must be accounted for to predict real properties of products in their normal performance conditions.²¹ Water acts as co-plasticizer and changes properties of the product depending on the amount of equilibrium moisture absorbed.

Because of its origin, cellulose acetate is considered an environmentally-friendly polymer. It is therefore important that additives used for its processing do not change its toxicity or decrease its biodegradability. Figure 11.6 shows that the addition of triethyl citrate increases the degradation rate of polymer. The higher the concentration of the plasticizer the faster the decomposition of polymer during composting.³²

Cellulose acetate plasticized by 10 wt% of diethyl phthalate had the same biodegradation rate, measured by conversion of carbon to CO₂, as unplasticized polymer.³⁰ At the same time, the plasticizer decomposed very rapidly to harmless degradation products. After 10 weeks more than 80% plasticizer was converted compared to about 20% polymer conversion.

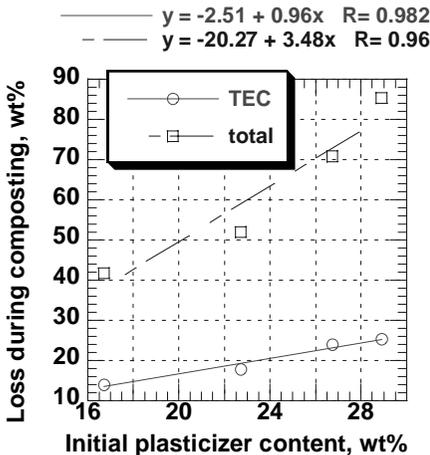


Figure 11.6. Loss of triethyl citrate, TEC, and total composition (cellulose acetate + TEC) during composting for 30 days. [Data from Ghiya V P; Dave V; Gross R A; McCarthy S P, *J. Macromol. Sci. A*, **A33**, No.5, 1996, p.627-38.]

Cellulose acetate produces acetic acid when degraded. This process is of considerable importance in preservation of magnetic tapes and laminated documents. Magnetic recording tape backing was manufactured from cellulose acetate from its invention in 1935 in Germany until 1960. Polymer deterioration caused a loss of plasticizer (triphenyl phosphate) causing rapid deterioration of the tape. Similar problems existed in films where plasticized cellulose acetate was used until 1985. The degradation process faster at higher temperatures and humidities.

In the middle of the 20th century some museum quality documents have been displayed by laminating them between sheets of cellulose acetate. The Declaration of Independence written by Thomas Jefferson in 1776 is one such document. In 1947, this document was laminated between two

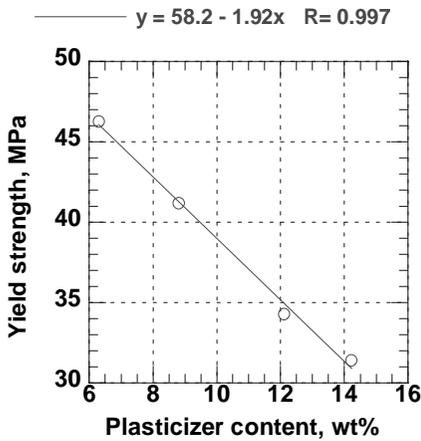


Figure 11.7. yield strength of cellulose acetate propionate vs. dioctyl adipate concentration. [Data from Moskala E J; Pecorini T J, *Polym. Eng. Sci.*, **34**, No.18, Sept.1994, p.1387-92.]

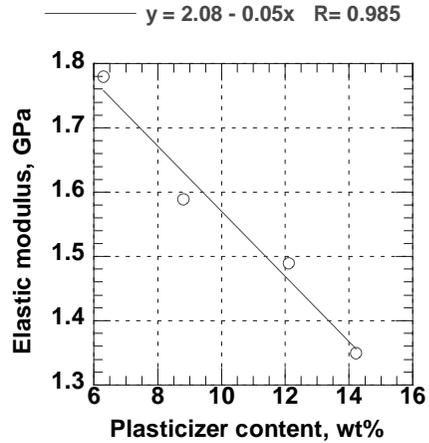


Figure 11.8. elastic modulus of cellulose acetate propionate vs. dioctyl adipate concentration. [Data from Moskala E J; Pecorini T J, *Polym. Eng. Sci.*, **34**, No.18, Sept.1994, p.1387-92.]

sheets of cellulose acetate. It is feared that this treatment may ultimately lead to complete deterioration of the document.⁵⁰

11.6 CELLULOSE BUTYRATES AND PROPIONATES

11.6.1 FREQUENTLY USED PLASTICIZERS

The use of the following plasticizers has been documented:^{23,51-58}

- cellulose butyrate: dioctyl adipate,⁵⁸ o-phenylphenol ethylene oxide adduct,⁵⁹ and N-toluene sulfonamide⁵⁹
- cellulose propionate: poly(1,3-butylene glycol adipate) (Drapex 429),²³ polyester sebacate (Paraplex G-25),²³ and dioctyl adipate⁵⁸

11.6.2 PRACTICAL CONCENTRATIONS

Dioctyl adipate was used in a concentration range from 6 to 14 wt%.⁵⁸ Polyester sebacate was used in a concentration of 7.7 wt%, and polyglycol adipate at concentration of 11.9 wt%.²³

11.6.3 MAIN FUNCTIONS PERFORMED BY PLASTICIZERS

Plasticizers has been used to lower the glass transition temperature of polymers^{23,58} and to improve polymer moldability.⁵⁸

11.6.4 EFFECT OF PLASTICIZERS ON POLYMER AND OTHER ADDITIVES

Figures 11.7 and 11.8 show that both yield strength and elastic modulus of cellulose acetate propionate decreases linearly when the concentration of plasticizer increases.

11.7 CELLULOSE NITRATE

11.7.1 FREQUENTLY USED PLASTICIZERS

The following plasticizers are/were used in the plasticization of cellulose nitrate:⁶⁰⁻⁷⁴

- acetyl tributyl citrate⁶³
- acrylic resin (Acronal 700 L)⁶⁴ in UV resistant lacquers and coatings on paper, plastic film, and aluminium foil
- aliphatic polyurethane as polymeric plasticizer in paints⁷¹
- butyl benzyl phthalate in nail enamel⁶² and jet ink composition⁷²
- camphor in nail enamel,⁶⁰ celluloid⁷⁰ (two parts of cellulose nitrate and one part of camphor), horn-like material (credited as the first application of plastics beginning in 1870)⁷⁰
- castor oil (the first use of plasticizer *circa* 1860)⁷⁰
- dibutyl phthalate^{63,70} in nail enamel,⁶⁰ films,⁷⁰ and preparation stimulating nail growth⁷⁴
- dimethyl phthalate⁶⁶ – auxiliary plasticizer for surface coatings
- diisooctyl phthalate in lacquers⁷⁰
- epoxidized soybean oil⁶³
- 2-ethylhexyl diphenyl phosphate
- glyceryl triacetate⁶³
- glyceryl tribenzoate in nail enamel⁶²
- N-ethyl (o,p)-toluenesulfonamide⁷³ as plasticizer in alcohol-resistant jet ink
- octyl diphenyl phosphate⁶⁷ in flame retarding, low smoke formulations
- sucrose acetate isobutyrate⁶³ in nail enamel⁶²
- tricresyl phosphate⁶⁵ for flame retarded products and coatings and in films⁷⁰
- triethylene glycol⁶⁹
- urea resin (Plastigen G)⁶⁸ in flexible coatings having reduced yellowing, high gloss retention, and resistance to aging

11.7.2 PRACTICAL CONCENTRATIONS

- nail enamel: camphor – 5 phr + dibutyl phthalate 27.7 phr,⁶⁰ combination of three plasticizers – 10 wt%⁶²
- lacquer: cellulose nitrate/urea resin = 1/1.5⁶⁸
- film:⁷⁰ camphor – 33 wt% or phthalate plasticizer – 20 wt%
- jet ink composition: butyl benzyl phthalate – 25 phr⁷² or N-ethyl (o,p)-toluenesulfonamide – 20 phr⁷³
- nail growth stimulating formulation: dibutyl phthalate – 20 phr⁷⁴

11.7.3 MAIN FUNCTIONS PERFORMED BY PLASTICIZERS

The following are the main functions played by plasticizers in cellulose nitrate:

- softening and imparting flexibility to polymeric film (e.g., nail enamel⁶⁰ or jet ink⁷²)
- promoting heat-sealability and adhesion of coating⁶²
- flame retarding properties (phosphate plasticizers)
- improvement of outdoor performance⁶⁸
- improvement of processability⁷⁰

- improvement of solvent resistance⁷³

11.7.4 EFFECT OF PLASTICIZERS ON POLYMER AND OTHER ADDITIVES

Measurements of the saturated vapor pressures of plasticizers over plasticized cellulose nitrate were used for calculation of chemical potentials of plasticizers and partial enthalpies and entropies of mixing.⁶¹

Phthalate plasticizers were found to be stable in cellulose nitrate film, which, tested after 41 years of storage, retained all initial amount of 20 wt% of plasticizers.⁷⁰ Camphor is known to be slowly lost from celluloid. After 30-40 years it reaches a concentration of 15 wt% (initial concentration 33 wt%) and this remains quite stable.⁷⁰

The loss of plasticizer may be accelerated by the decomposition of cellulose nitrate which produces nitrous oxides that then combine with water to form nitrous and nitric acids. Acids affect the stability of plasticizers and their interaction with the polymer.

11.7.5 TYPICAL FORMULATIONS

Fast-drying, non-bubbling pigmented nail enamel:⁶⁰

Ethyl acetate	30.5 wt%
Butyl acetate	25.0
Isopropyl alcohol	5.0
Nitrocellulose	18.0
Polyester film-forming resin	9.0
Camphor	1.0
Dibutyl phthalate	5.0
Benzophenone-1	0.5
Vinyl silicone fast drying copolymer VS-80	0.8
Stearalkonium hectorite	2.0
Pigments	3.0
Dow Corning 200/350 antifoam agent	0.2

Jet ink composition:⁷²

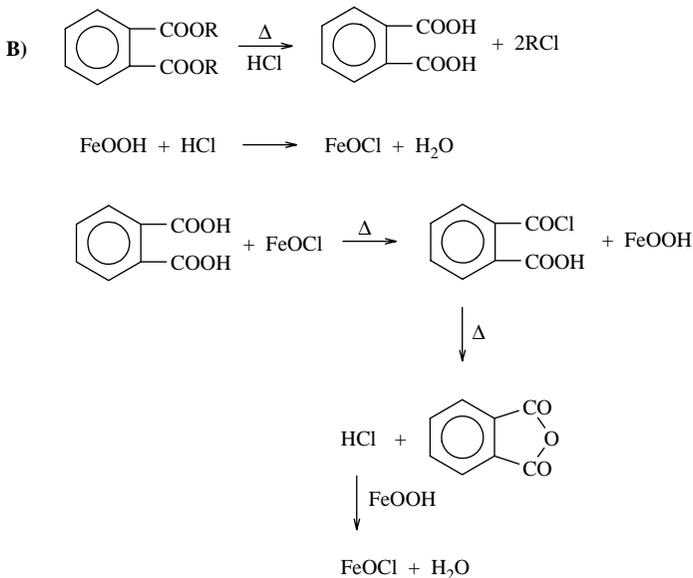
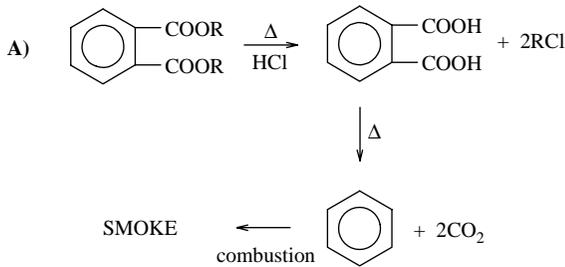
Acetone	50.0 wt%
Ethanol, anhydrous	20.0
Cellulose nitrate (35%, isopropanol 15%, acetone 50%)	18
Super ester A-75 (Arakawa)	3.0
Benzyl butyl phthalate	1.5
Primary amyl acetate	3.0
Orasol Black RLI (Ciba)	4.0
Silwet L-7622 (Crompton)	0.5

11.8 CHLORINATED POLYVINYLCHLORIDE

Chlorination of polyvinylchloride increases its tensile, compression and flexural strengths by about 30%. Impact strength more than doubles and even elongation doubles. Considering this, plasticization will most likely act in the opposite direction and reverse these changes important in some applications.^{71,72} In addition, plasticization lowers the heat distortion temperature that in many applications of chlorinated polyvinylchloride, CPVC, is a critical performance characteristic.⁷¹

In one application⁷³ plasticizer was used to improve processability and to take advantage of antiplasticization to improve specific properties of finished product. CPVC was plasticized with 1,4-cyclohexane dimethanol dibenzoate (Benzoflex R 352). When this plasticizer was used at 7 phr, the viscosity of the blend was reduced through the replacement of polymer-polymer hydrogen bonding by polymer-plasticizer hydrogen bonding.⁷³ Lowering the plasticizer level to 4 phr resulted not only in lowering the viscosity and increasing the thermal stability but also tensile strength, flexural strength and modulus were increased. At the same time, oven sag resistance and impact strength were decreased. These changes were explained by the effect of antiplasticization.⁷³

In the cable industry, plasticization of CPVC by phthalates and phosphates improves the flexibility and processability of CPVC. However, the addition of plasticizer lowers the limiting oxygen index and increases smoke production. The schematic diagram below illustrates the mechanism of degradation in the absence (**A**) and the presence (**B**) of the smoke-suppressing compound – basic iron oxide, FeOOH.⁷⁴



When exposed to heat CPVC produces substantial quantities of HCl, which is a volatile product of degradation. When FeOOH is not present (**A**), the phthalic acid that is produced is then decarboxylized to benzene. Under high temperature conditions benzene is further degraded and produces smoke. Only traces of phthalic anhydride are detected under these conditions.

When a small amount of FeOOH (0.25 phr) is present, smoke production is suppressed by 40%. This is attributed to the formation of phthalic anhydride as shown by reactions in scheme (**B**). Only small quantities of FeOOH are needed because it is active in a cyclical process which keeps both required forms in equilibrium. Phthalic acid produces four times as much smoke as phthalic anhydride, which sublimates out of the system.

11.9 CHLOROSULFONATED POLYETHYLENE

Chlorosulfonated polyethylene, CSP, was developed by Dupont to be used in vulcanized and non-vulcanized products. Unplasticized it is very flexible material and as such it is found in many applications where it competes with plasticized PVC. Although plasticizers are not normally used, there are some exceptions.

Antitack rubber suitable for manufacturing pneumatic tires is produced from combination of CSP and natural rubber.⁷⁵ This composition used 3 wt% of an undisclosed plasticizer (process oil). A paper transport belt made from a blend of CSP and EPDM rubber used 3 phr of polyethylene glycol and 25 phr of dioctyl sebacate.⁷⁶ A membrane obtained from blending CSP and chlorinated polyethylene contained 6 phr of tri-(2-ethylhexyl) phosphate.⁷⁸

These cases suggest that the plasticizer may function as a compatibilizer of the polymer blend. In one case,⁷⁸ a phosphate plasticizer was selected because it reduced mildew growth in conjunction with a common fungicide (Busan 11).

Process oil, possibly dioctyl adipate or dioctyl sebacate, has been used in a transmission belt compound.⁷⁷ It also produces a softening effect. In application of fluoroplastic additives, Dupont research gave formulation of vulcanized CSP which contained 20 phr of dioctyl sebacate.⁷⁹ It is probable that some quantities of plasticizers can be found in CSP formulations, particularly in vulcanized products.

11.10 COPOLYMERS

The information given here for copolymers is much less material specific than it is for homopolymers because copolymers have a wide variety of chemical compositions and structures.⁸⁰⁻⁹³ The information is intended to show the importance of plasticizers in copolymers. Examples given also include some novel polymeric plasticizers that are copolymers themselves.

11.10.1 FREQUENTLY USED PLASTICIZERS

The following applications of plasticizers have been reported:

- citrate esters were used to prepare plastic compositions for medical containers to store red blood cells. A polyolefin based copolymer was used as a matrix.⁸⁴
- naphthenic oil and dioctyl phthalate were used to plasticize styrene-ethylene-butylene-styrene, SEBS, copolymer (Kraton G type). The plasticized copolymer

was used to modify asphalt in roofing, sealing, paving, and waterproofing applications.⁸⁵

- high levels of plasticizer (white oil) were used to produce crystal gels from linear SEBS copolymers⁸⁷
- nonfugitive polyoxyethylene aryl ether plasticizer was found to improve film-forming properties of a coating based on an urethane acrylic copolymer⁸⁶
- a hydroxyl group-containing monomer was used in a copolymerization with vinyl chloride alone or in the mixture with other monomers. The presence of hydroxyl groups in the polymer increase the plasticizer (dioctyl or dihexyl phthalate) uptake in a water-based system⁸⁹
- lauric, sebacic, and citric acids esters were used as plasticizers in large concentrations to form biodegradable copolymer products in aqueous dispersions⁹⁰
- polystyrene oligomer and dioctyl phthalate were used to selectively plasticize styrene blocks in a ϵ -caprolactone-styrene diblock copolymers⁹²
- a variety of plasticizers, including most of the common groups, were proposed for use in interpolymers of an α -olefin/vinylidene aromatic copolymer for applications in films, adhesives, sealants and molded parts⁹¹
- photopolymerizable unsaturated liquid plasticizer based on bisphenol-diacrylate or ethoxylated trimethylenol propane triacrylate was used in preparation of photo-resists and solder masks⁸¹
- a copolymer of ethylene and carbon monoxide with grafted benzotriazole UV absorber was developed for use in PVC formulations⁸⁰
- large quantities of water are absorbed by acrylic based latex but only a small part of this water plasticizes the copolymer with the remaining part being separated from polymer⁸⁸
- sorbitol was used as a water soluble plasticizer for ion sensitive polymeric materials⁸³

11.10.2 PRACTICAL CONCENTRATIONS

Concentration of plasticizer used in various applications varies over a wide range:

- 2 phr polyoxyethylene aryl ether plasticizer improved film-forming properties of coating based on urethane acrylic copolymer⁸⁶
- 11 wt% of copolymeric plasticizer with grafted UV absorber was used in PVC formulation⁸⁰
- 5-20 wt% of citrate plasticizer was used in formation of a red blood cell container made from polyolefin based copolymer⁸⁴
- 25 to 40 wt% of naphthenic oil alone or in a mixture with dioctyl phthalate was used to plasticize SEBS for asphalt modification⁸⁵
- 40 phr dihexyl phthalate and 5 phr of epoxidized soybean oil were incorporated into a water-based coating based on hydroxyl bearing copolymer⁸⁹
- 10-50 phr of plasticizer was incorporated in a biodegradable copolymer product⁹⁰
- 250 phr of white mineral oil was used to form novel crystal gels from linear SEBS copolymers⁸⁷

11.10.3 MAIN FUNCTIONS PERFORMED BY PLASTICIZERS

The following functions were performed by plasticizers in copolymers:

- providing reactive sites for grafting UV absorber⁸⁰
- facilitating processing with an ingredient that is photopolymerizable⁸¹
- lowering viscosity without affecting adhesive strength⁸²
- suppressing hemolysis (premature breakdown) of red blood cells⁸⁴
- non-fugitive coalescing agent which assists in film formation and contributes to flexibility of coating⁸⁶
- improving crack propagation, tear and fatigue resistance⁸⁷
- increasing plasticizer take-up by interacting with hydroxyl groups of binder in water based system⁸⁹
- helping in biological degradation of material⁹⁰
- lowering the glass transition temperature by affecting a selected block⁹²

11.10.4 MECHANISM OF PLASTICIZER ACTION

A diblock copolymer was synthesized, which contained ϵ -caprolactone, PCL, and polystyrene, PS, blocks.⁹² This copolymer did not crystallize at any temperature when quenched. PCL the crystallizing block, has a melting point of 50°C. The PS block has a glass transition temperature of 95°C. Because the PS block solidifies before the PCL may begin crystallizing, the crystallization of the copolymer cannot occur. To remediate the situation it is necessary to increase the mobility of the PS block by selective plasticization. Two plasticizers were used for this purpose: oligomeric polystyrene and dioctyl phthalate, DOP. Both plasticizers were intended to plasticize the PS blocks without affecting the PCL blocks.

Figure 11.9 shows that the intention was fulfilled. Regardless of the concentration of plasticizer, the melting point of the PCL blocks remained unchanged at about 50°C. The higher the plasticizer concentration (the lower the ϕ_{PS}) the lower the glass transition temperature. DOP plasticizes the PS blocks without affecting the PCL blocks. It has been established that the plasticizer is fully miscible with the PS blocks.

Crystallinity studies⁹² show that there is a dramatic change in PCL crystallinity when the concentration of plasticizer is sufficient to reduce the glass transition temperature of the PS block to about 40°C which occurs at $\phi_{PS} \sim 0.4$. The suggested reason for the lack of crystallization has been now confirmed by these results.

These results illustrate important practical principles that will help in developing systems having suitable properties for certain applications by simply choosing the right concentration of a suitable plasticizer for block copolymers or possibly polymer blends as well.

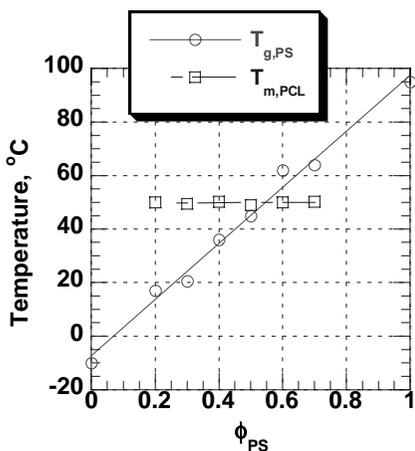


Figure 11.9. Glass transition temperatures of polystyrene block, $T_{g,PS}$, and melting temperatures of ϵ -caprolactone block, $T_{m,PCL}$, for ϵ -caprolactone-styrene diblock copolymer plasticized with variable amounts of DOP ($\phi_{PS} = (\text{weight of PS})/(\text{total weight of PS and DOP})$). [Data from Nojima S; Tanaka H; Rohadi A; Sasaki S, *Polymer*, **39**, Nos.8-9, 1998, p.1727-34.]

11.11 CYANOACRYLATES

Most commercial glues such as the popular Crazy Glue do not use plasticizers. These glues are based on ethyl and butyl derivatives of cyanoacrylate. A new development involves the use of octyl-2-cyanoacrylate in medical and veterinary applications. These new adhesives usually require plasticizers.

11.11.1 FREQUENTLY USED PLASTICIZERS

For medical purposes acetyl tributyl citrate is most commonly used.^{94,100} Older inventions suggested also dioctyl phthalate, a useful plasticizer for use in contact with human skin.^{104,105} In veterinary applications, dioctyl phthalate^{95,96,97,98,99,102} and acetyl tributyl citrate^{96,98,102} are likely to be used. It should be underlined that this difference between medical and veterinary application is more of precautionary nature than formulation based on previous results of studies or regulations which may limit dioctyl phthalate use for this applications.

Polydimethylsiloxane, hexadimethylsilazane, and polymethylmethacrylate are also added to increase the flexibility and elasticity of polymer.¹⁰¹ The adhesive can be made plasticizer-free by using a composition of polymers containing a mixture of alkyl groups from C₁ to C₈.¹⁰³ The use of suitable proportions of different monomers gives the required properties.

11.11.2 PRACTICAL CONCENTRATIONS

acetyl tributyl citrate has been used in concentration ranges as below:

5-7 wt%⁹⁴

10-30 wt%⁹⁷

18-25 wt%^{98,100}

dioctyl phthalate has been used in concentration ranges as below:

20 wt%^{95,96}

10-30 wt%⁹⁷

18-25 wt%^{98,100,104,105}

10-15 wt%⁹⁹

The above shows that concentrations of plasticizer are fairly consistent.

11.11.3 MAIN FUNCTIONS PERFORMED BY PLASTICIZERS

The main reason for the use of plasticizers in formulations is to increase flexibility. More extensive study has been conducted with dioctyl phthalate, DOP, where appearance, curing time, film formation, flexibility and durability have been evaluated for n-butyl cyanoacrylates containing from 15 to 50 wt% plasticizer. When DOP was at a 35 wt% or above, no film was formed. With the plasticizer at 15 wt%, flexibility and durability suffered. A 20-25 wt% range has produced the best overall performance.

11.12 ETHYLENE-PROPYLENE-DIENE COPOLYMER, EPDM

11.12.1 FREQUENTLY USED PLASTICIZERS

EPDM is an elastic polymer that is usually processed without plasticizers and it is generally offered as plasticizer-free alternative product but there are some specific applications in which following plasticizers are used:

- polyisobutylene (the most frequently used non-migrating plasticizer of EPDM compositions)^{106,112,113,117}
- paraffin oil^{107,110,115}
- dibutyl phthalate¹⁰⁷
- dioctyl phthalate¹¹¹
- vulcanized vegetable oil¹¹⁶

11.12.2 PRACTICAL CONCENTRATIONS

These concentrations of plasticizers are used in various products:

- pressure sensitive tapes used to join rubber membranes
 - 40-50 wt% of polyisobutylene^{106,117}
 - 5-9 wt% polyisobutylene¹¹²
 - 60 phr¹¹³
- hose formulation – 16.8 wt% dioctyl phthalate¹¹¹
- cold shrinkable cable joint protection – 20 wt% paraffinic oil¹¹⁵
- weatherstripping composition – 15 wt% of vulcanized vegetable oil¹¹⁶

11.12.3 MAIN FUNCTIONS PERFORMED BY PLASTICIZERS

In pressure sensitive tapes plasticizer participates in the development of surface tack. Older versions of pressure sensitive tapes suffered from poor heat resistance, creep failure, reduced tack at lower temperatures, poor resistance to UV and extensive bleeding. These drawbacks can be corrected by the proper selection of the plasticizer.

11.12.4 EFFECT OF PLASTICIZERS ON POLYMER AND OTHER ADDITIVES

Surface tack was optimized by the careful selection of matrix materials and tackifiers as well as of plasticizers. The selections and concentrations of other components helps to determine the concentration of plasticizer which is variable as seen in Section 11.12.2.

11.13 EPOXY RESIN

11.13.1 FREQUENTLY USED PLASTICIZERS

Many conventional plasticizers such as phosphates and phthalates are not compatible with the majority of epoxy resins, especially at higher concentrations. They are easily lost from the system and if retained they do not affect flexibility.¹¹⁸

Several groups of flexibilizers are used in epoxy resins to modify their mechanical properties. These include:

- monofunctional epoxy compounds (e.g., epoxidized oils) which influence molecular weight of the cured resin¹²⁰
- low molecular weight polyamide resins (e.g., condensation products of trimerized or dimerized vegetable oils and polyamines). These are curing agents that, when added at certain proportions to other curatives in the system, may help to modify properties
- mercaptan terminated materials (e.g., polysulfides)¹²¹
- reactive diluents (e.g., derivatives of glycidyl ether). These are added on the resin side to reduce its viscosity but are reactive with the curative. They are similar to monofunctional epoxy compounds and they affect the molecular weight of poly-

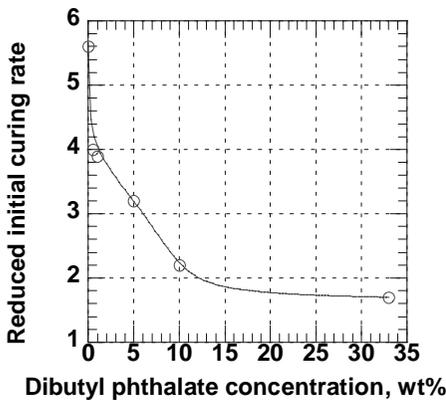


Figure 11.10. Reduced initial curing rate of epoxy resin vs. concentration of dibutyl phthalate. [Data from Smirnov Yu N; Dzhavadyan E A; Golodkova F M, *Polym. Sci. Ser. B*, **40**, Nos.5-6, May-June 1998, p.190-3.]

- a variety¹³¹ of phthalates,¹³⁵ phosphates, adipates, and sebacates
- cyclohexyl pyrrolidone¹³³
- polyoxypropylene diols and triols and hydroxyl-terminated polybutadiene¹³⁷

11.13.2 PRACTICAL CONCENTRATIONS

The following concentrations of plasticizers have been used:

- dibutyl phthalate – 0-30 wt%,¹²⁴ 0-40 phr,¹²⁷ and 30 wt%¹³²
- dioctyl phthalate – 2 wt%¹²⁸
- di-n-decyl phthalate – 0.2-2 wt%¹³⁶
- cyclohexyl pyrrolidone – 1 wt%¹³³
- poly(propylene glycol alkylphenyl ether) – 4.3 wt%¹³⁰
- polysulfide (Thiocol LP3) – 0-60 phr¹²¹
- copolymer of adipic acid and ethylene and diethylene glycols – 5 wt%¹²⁵

11.13.3 MAIN FUNCTIONS PERFORMED BY PLASTICIZERS

A short list of the functions of plasticizers in epoxy resins includes:

- viscosity reduction^{120,131,133,135,137}
- decrease of apparent activation energy of curing reaction¹²¹
- reduction of hardness¹³²

It is apparent that plasticizers are mostly used in epoxy resins to reduce viscosity. At the same time they increase the mobility of reacting components and help in dissipation of thermal energy formed from exothermic curing reactions.

11.13.4 EFFECT OF PLASTICIZERS ON POLYMER AND OTHER ADDITIVES

Figure 11.10 shows that the initial curing rate of epoxy resin decreases when the concentration of dibutyl phthalate increases. The plasticizer acts as an inhibitor because its molecules form complexes with proton donors. Even small amounts of dibutyl phthalate may

mer and thus influence its mechanical properties.¹²²

For these reasons plasticizers are not used to modify mechanical properties of the final product but are still quite useful, especially in the modification of processing characteristics (viscosity) of epoxy resins.

The following compounds are found in various formulations:

- dibutyl phthalate^{124,128,132}
- di-n-decyl phthalate¹³⁶
- low molecular weight (~2,000 daltons), condensation product of adipic acid and ethylene and diethylene glycols¹²⁵
- isodecyl pelargonate (high migration in epoxy systems)¹²⁹
- poly(propylene glycol alkylphenyl ether) (Plastilit 3060) a hydrophobic plasticizer¹³⁰

substantially decrease the concentrations of free ~NH and HO~ groups involved in epoxide ring opening because the ester group of the plasticizer is a much stronger donor than the ether group of the oxirane ring.

11.14 ETHYLENE-VINYL ACETATE COPOLYMER, EVA

EVA is an internally plasticized copolymer used to plasticize or to reduce the amount of plasticizer in polyvinylchloride. A graft copolymer of EVA and PVC is produced (Vinnolit VK 801) containing equal amounts of both polymers.¹³⁸ The graft copolymer is either used alone to give an unplasticized article or as a PVC additive.

The addition of EVA to PVC may be considered either as a modification by a solid plasticizer or as polymer blending. To eliminate plasticizer from certain articles (e.g., medical products and toys) this technology is applied frequently. Membranes are formulated by using combination of PVC and EVA in order to limit amount of a low molecular weight plasticizer such as dioctyl phthalate or dioctyl sebacate.¹⁴¹

Low odor hose was formulated using a combination of PVC, EVA and a low molecular weight plasticizer, such as DOP. The formulation shows that only a small amount of DOP was added most likely to accommodate pigments and fillers:¹³⁹

PVC resin	46.35 wt%
BaZn stabilizer	1.16
Calcium carbonate	11.59
EVA polymer	32.45
DOP plasticizer	6.95
Stearic acid lubricant	0.12
Titanium dioxide	1.38
Pigment	<i>quantum satis</i>

Sometimes plasticizer is deliberately added to a product to make it less sensitive to external plasticizer. This laminating adhesive is used in conjunction with PVC.¹⁴⁰

Polyurethane dispersion	17.5 wt%
EVA dispersions	69.0
Acrylate dispersions	7.5
Plasticizer	5.0
Stabilizers, coloring	1.0

To perform as an adhesive the formulation does not require plasticizer but it is known from prior art that the migration of plasticizer from PVC will affect adhesion. Properties can be modified if plasticizer is added during compounding and its addition at this stage will limit its migration from PVC.

EVA has also been compounded in combination with polylactic acid in a formulation of a biodegradable shrink film.¹⁴² Here, di-(2-ethylhexyl) azelate was used as plasticizer.

11.15 IONOMERS

11.15.1 FREQUENTLY USED PLASTICIZERS

Two groups of plasticizers are reported as being used in ionomers – regular and ionic plasticizers:

- dioctyl phthalate in the plasticization of polymethylmethacrylate ionomer,^{144,147,150} polyphenylene oxide ionomer,¹⁴⁵ sulfonated polystyrene ionomer,¹⁴⁸ and sodium and zinc neutralized ethylene-methacrylic acid copolymer based ionomers¹⁵¹
- 4-decyylaniline in plasticization of polymethylmethacrylate ionomer^{144,150}
- glycerol in the plasticization of polymethylmethacrylate ionomer^{144,147,150} and sulfonated polystyrene ionomer¹⁴⁸
- salts of 2-ethylhexyl-p-dimethylaminobenzoate in the plasticization of poly(styrene-b-isobutylene-b-styrene)¹⁴³
- sodium salts of benzenesulfonic and dodecylbenzenesulfonic acids in the plasticization of sulfonated syndiotactic polystyrene ionomers¹⁴⁶
- zinc stearate in the plasticization of poly(styrene-b-isobutylene-b-styrene)¹⁴³

11.15.2 PRACTICAL CONCENTRATIONS

The following concentrations of plasticizers have been used in ionomers:

- dioctyl phthalate – 13 and 26 wt%,¹⁴⁴ 4 to 31 wt%,¹⁴⁵ 22.4 and 40.2 wt%,¹⁴⁷ and 10 wt%^{148,151}
- glycerol – 13 and 27 wt%,¹⁴⁴ 9.2 and 19.4 wt%,¹⁴⁷ and 10 wt%¹⁴⁸
- 4-decyylaniline – 14 and 26 wt%¹⁴⁴
- sodium salts of benzenesulfonic and dodecylbenzenesulfonic acids – molar ratios of plasticizer to sodium sulfonate groups: 0.5, 1, and 2¹⁴⁶
- salts of 2-ethylhexyl-p-dimethylaminobenzoate – 4.8-8.5 wt%¹⁴³

11.15.3 MAIN FUNCTIONS PERFORMED BY PLASTICIZERS

- modification of the nature and strength of electrostatic interactions¹⁴⁹
- lowering processing temperature¹⁴³
- modification of morphological properties^{144,147}
- modification of viscoelastic properties^{147,148}
- influencing cluster formation^{145,150}
- influencing crystallization¹⁴⁶

11.15.4 MECHANISM OF PLASTICIZER ACTION

In addition to the more conventional plasticizers, ionic plasticizers are also used. This is specific case of plasticization which acts on different segments of ionomers. Ionomers are composed of polymeric chains which have certain number of ionic groups. The ionic groups that are distinct from the nonpolar polymer chain form aggregates known as multiplets. The multiplets are ionic crosslinks surrounded by matrix of polymer chains. At a certain ionic content, the restricted mobility of ionic crosslinks becomes the significant factor in determining the glass transition temperature of the ionomer.

This analysis suggests that two different kinds of plasticizers may be needed to plasticize ionomers:

- conventional plasticizers that plasticize the polymeric chains but that may also affect the ionic crosslinks
- ionic (polar) plasticizers that act preferentially on ionic crosslinks.

These ionomers may be selectively modified by the type and concentration of plasticizer chosen.

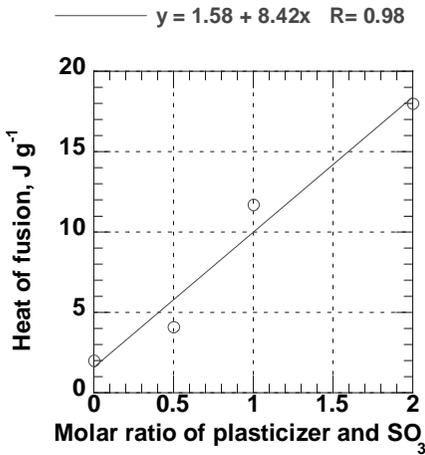


Figure 11.11. Heat of fusion of isothermally crystallized Na⁺ sulfonated syndiotactic polystyrene ionomer vs. molar ratio of sodium salt of dodecylbenzene-sulfonic acid. [Data from Orlor E B; Gummaraju R V; Calhoun B H; Moore R B, *Macromolecules*, **32**, No.4, 23rd Feb.1999, p.1180-8.]

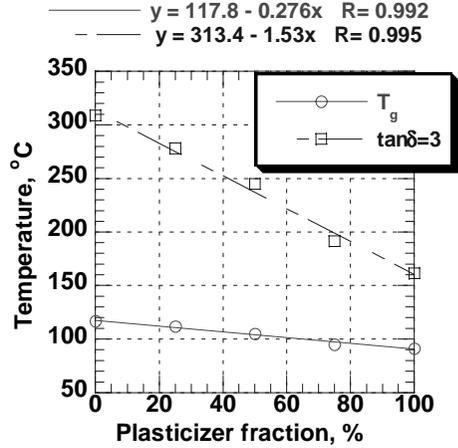


Figure 11.12. Effect of fraction of stoichiometric concentration of 2-ethylhexyl-p-dimethylaminobenzoate used for ionic plasticization of poly(styrene-b-isobutylene-b-styrene), having 4.7% sulfonated phenyl units, on glass transition temperature, T_g, and temperature at which tanδ=3. [Data from Storey R F; Baugh D W, *Polym. Eng. Sci.*, **39**, No.7, July 1999, p.1328-34.]

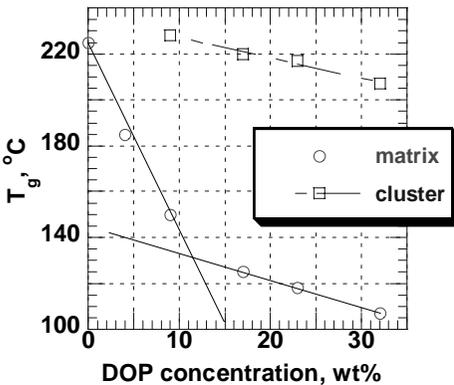


Figure 11.13. Glass transition temperatures of matrix and clusters of polyphenylene oxide ionomer plasticized with variable quantities of dioctyl phthalate. [Adapted, by permission, from Hee-Seok Kim; Joon-Seop Kim; Jin-Wook Shin; Young-Kwan Lee, *Polym. J. (Japan)*, **31**, No.3, 1999, p.306-8.]

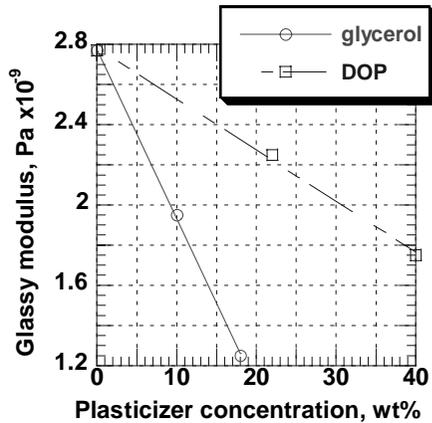


Figure 11.14. Effect of plasticizer type and content used for plasticization of PMMA ionomer on glassy modulus. [Adapted, by permission, from Ma X; Sauer J A; Hara M, *Polymer*, **38**, No.17, 1997, p.4425-31.]

11.15.5 EFFECT OF PLASTICIZERS ON POLYMER AND OTHER ADDITIVES

There is a strong electrostatic interaction between the ionic groups of sulfonated syndiotactic polystyrene ionomer. This strong interaction prevents crystallization from the melt.

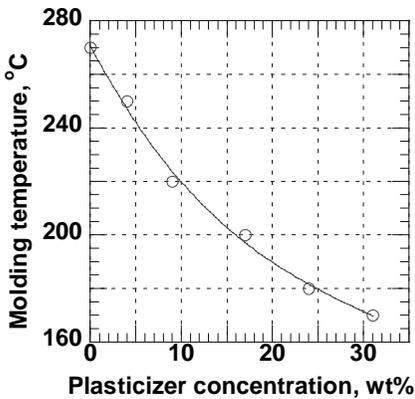


Figure 11.15. Molding temperature of polyphenylene oxide ionomer plasticized with variable quantities of dioctyl phthalate. [Data from Hee-Seok Kim; Joon-Seop Kim; Jin-Wook Shin; Young-Kwan Lee, *Polym. J. (Japan)*, **31**, No.3, 1999, p.306-8.]

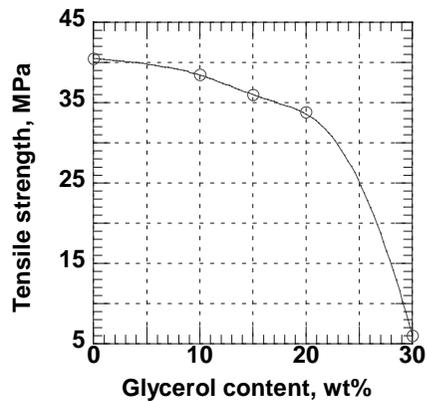


Figure 11.16. Tensile strength of sulfonated polystyrene ionomer plasticized with variable amounts of glycerol. [Adapted, by permission, from Ma X; Sauer J A; Hara M, *J. Polym. Sci.: Polym. Phys. Ed.*, **35**, No.8, June 1997, p.1291-4.]

The addition of ionic plasticizer such as sodium salt of dodecylbenzenesulfonic dramatically increases the ability of the ionomer to crystallize. Figure 11.11 shows that the heat of fusion of an isothermally crystallized ionomer increases with the addition of a plasticizer. This behavior is attributable to the separation of ionic domains, which enhances the molecular mobility of the crystallizable chains and also increases the crystallization rate as the amount of plasticizer increases.¹⁴⁶

Plasticization of poly(styrene-*b*-isobutylene-*b*-styrene) ionomer by 2-ethylhexyl-*p*-dimethylaminobenzoate causes a decrease in the glass transition temperature, T_g , as the amount of plasticizer increases (Figure 11.12). This lowering of the T_g indicates that there is a slight plasticization of the non-ionic polystyrene phase. A much larger shift is observed in temperature at which $\tan\delta = 3$. This indicates a preferential plasticization of the ionic clusters.¹⁴³

Figure 11.13 illustrates the effect of dioctyl phthalate on the clusters and matrix of polyphenylene oxide ionomer. As stated in Section 11.15.4, dioctyl phthalate, DOP, influences both the matrix polymer and ionic clusters. But the intensities of these effects are different. Up to about 10 wt% DOP, the matrix T_g rapidly decreases (DOP preferentially plasticizes polymer chains). Above 10 wt%, the T_g of both matrix and clusters decreases at similar rates.¹⁴⁵

Comparing Figures 11.12 and 11.13, it is possible to conclude that regular plasticizers have a preferential effect on polymer matrix whereas ionic plasticizers affect ionic clusters. This clarifies the distinction between the mechanisms of their action as indicated in Section 11.15.4.

Figure 11.14 compares effect of polar glycerol and non-polar DOP on PMMA ionomers. A polar plasticizer decreases the modulus at a rate three times greater than does non-polar DOP. Glycerol acts as a dual plasticizer on clusters and on the matrix polymer

whereas DOP preferentially plasticizes the matrix polymer.¹⁴⁷ By selecting the plasticizer type and controlling its concentration, it is possible to improve the processability of ionomers. Figure 11.15 shows that the molding temperature of polyphenylene oxide ionomer decreases quite rapidly as the concentration of dioctyl phthalate increases.¹⁴⁵

Two rates of the tensile strength decrease are seen from Figure 11.16. The slow initial decrease is caused by gradual plasticization and the sudden decrease occurs when some critical concentration of plasticizer is attained. Above the critical plasticizer concentration, the clusters become sufficiently separated to destroy the reinforcing ionic structure.

11.16 NITRILE RUBBER

11.16.1 FREQUENTLY USED PLASTICIZERS

Aromatic mineral oil plasticizers are highly compatible with nitrile rubber, NBR, naphthenic oils are only partially compatible, and paraffinic mineral oil plasticizers are incompatible with nitrile rubber.¹⁵² Dibenzyl ether, phthalates, and polyglycol ether are the most frequently used plasticizers in NBR.¹⁵² Also, synthetic or fatty acid esters,¹⁵³ vulcanized vegetable oils (factice),¹⁵⁴ chloroparaffins,¹⁵⁵ and phosphate plasticizers¹⁵⁶ are in frequent use.

The following plasticizers have been used in formulations of various nitrile rubber products:

- dioctyl phthalate in the production of materials for automotive applications with low permanent compression set,¹⁵⁷ artificial leather,¹⁵⁸ plastisol containing mixture of PVC and NBR,¹⁵⁹ seal,^{160,166} rubber laminate,¹⁶² slush molding compositions^{163,165}
- fatty acid ester (Struktol WB 222) in the production of a sealing strip¹⁶¹ and a molded part¹⁶⁴

Although numerous plasticizers can be used in nitrile rubber applications, DOP is the most frequent choice.

11.16.2 PRACTICAL CONCENTRATIONS

- 2 phr fatty acid ester in a NBR sealing strip¹⁶¹
- 5 phr DOP in a NBR sealing member^{160,166}
- 5-20 phr DOP in a NBR compound for automotive parts having low compression set¹⁶⁷
- 15 phr DOP in a NBR laminate¹⁶²
- 25-45 wt% DOP in an artificial leather strip based on PVC/NBR blend¹⁵⁸
- 30 phr fatty acid ester in an article molded from NBR/PVC=80/20¹⁶⁴
- 50 wt% of DOP in a plastisol based on a PVC/NBR blend¹⁵⁹
- 45-85 phr in slush molding compound based on a PVC/NBR plastisol¹⁶³
- 70-100 phr in a slush molding compound based on a PVC/NBR plastisol¹⁶⁵

These data show that low to moderate concentrations are used in articles composed of NBR or having high NBR content whereas blends with PVC utilize higher concentrations of plasticizers.

11.16.3 MAIN FUNCTIONS PERFORMED BY PLASTICIZERS

- viscosity reduction in plastisols¹⁵⁹

- dispersion aid for solid additives¹⁶¹
- modification of rheological properties to make plastisols useful in slush molding process^{163,165}
- lowering sliding resistance¹⁶⁴
- modification of viscoelastic properties (“cheesecutter” effect)¹⁵⁸

11.16.4 TYPICAL FORMULATIONS

Typical formulation for processing nitrile rubbers:

Nitrile rubber	100 parts
Carbon black	65
DOP	15
Zinc oxide	5
Stearic acid	1
Trimethyldihydroquinoline	1
Decimal peroxide	5
Coagent	0-20

11.17 POLYACRYLONITRILE

Plasticizers have been very important in the development of new technologies based on polyacrylonitrile, PAN, but the types selected, and the reason for their use differ significantly from that in other polymers.

In plastic Li-ion batteries, 20 wt% of dibutyl phthalate is added to the electrode composition to be molded and later to be extracted with diethyl ether. This results in the desired microporous electrode.^{168,169}

PAN-based lithium-salt electrolytes are obtained by plasticizing the electrolytes with propylene carbonate, ethylene carbonate, dimethylformamide, dimethylsulfoxide, etc. These compounds are considered solvents in other applications but in these electrolytes they are used to lower the glass transition temperature, dissolve salt, and make the polymer amorphous. Some of these functions are typical of plasticizers.^{170,171,175} An improved version of the electrolyte is based on ternary mixtures of plasticizers consisting ethylene, propylene and butylene carbonates.¹⁷⁶ This mixture improves low temperature conductivity.

A variety of plasticizers have been used to make absorbent hydrogel particles for wound dressing from PAN.¹⁷² These include glycerin, polyethylene glycol, polypropylene glycol, and vegetable and mineral oils.

Tributyl phosphate has been used to plasticize a polyacrylonitrile-based material for barcode printing. In this application the polymer absorbs the infrared light that is radiated or reflected from a pattern.¹⁷³

The decomposition temperature of PAN is below its melting point.¹⁷⁷ Its melt processing requires use of fugitive plasticizers (in other words solvents that have a plasticizing action) for processing. Ethylene carbonate is used as a fugitive plasticizer in a process by which films, fibers or shaped products can be extruded from pellets.^{174,178,179}

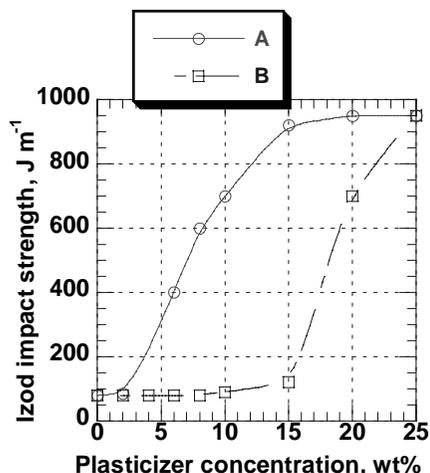


Figure 11.17. Izod impact strength of polyamide-11 plasticized with variable quantities of p-methylbenzenesulfonamide, A, and p-butyl hydroxybenzoate, B. [Data from Li Q F; Tian M; Kim D G; Wu D Z; Jin R G, *J. Appl. Polym. Sci.*, **83**, No.7, 14th Feb. 2002, p.1600-7.]

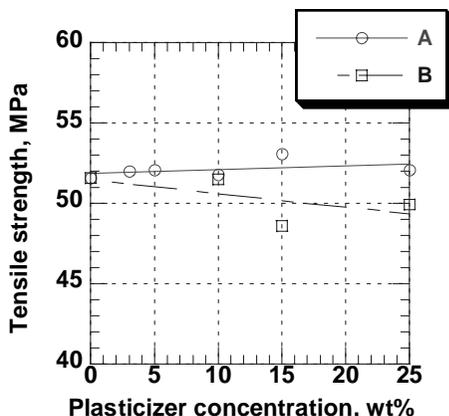


Figure 11.18. Tensile strength of polyamide-11 plasticized with variable quantities of p-methylbenzenesulfonamide, A, and p-butyl hydroxybenzoate, B. [Data from Li Q F; Tian M; Kim D G; Wu D Z; Jin R G, *J. Appl. Polym. Sci.*, **83**, No.7, 14th Feb. 2002, p.1600-7.]

11.18 POLYAMIDE

11.18.1 FREQUENTLY USED PLASTICIZERS

The following plasticizers have been found to be useful in modifying the properties of polyamides:

- N-butylbenzenesulfonamide, BBSA,^{180,182,187,191,192,193,194,196,198,199}
- N-ethylbenzenesulfonamide, EBSA,^{182,194,195}
- N-propylbenzenesulfonamide, PBSA,¹⁹⁴
- N-butyl-N-dodecylbenzenesulfonamide, BDBSA,¹⁸²
- N,N-dimethylbenzenesulfonamide, DMBSA,¹⁸²
- p-methylbenzenesulfonamide¹⁸¹
- o,p-toluene sulfonamide¹⁸⁷
- p-toluene sulfonamide¹⁸⁷
- 2-ethylhexyl-4-hydroxybenzoate^{180,191,192,196}
- hexadecyl-4-hydroxybenzoate¹⁹⁶
- 1-butyl-4-hydroxybenzoate¹⁸¹
- dioctyl phthalate^{195,196}
- diisodecyl phthalate¹⁹⁶
- di-(2-ethylhexyl) adipate¹⁹⁶
- tri-(2-ethylhexyl) phosphate¹⁹⁶

In this long list of different compounds used in plasticization of polyamide, the great majority is used for either experimental or specific purposes. N-butylbenzenesulfonamide and 2-ethylhexyl-4-hydroxybenzoate are the two plasticizers of various polyamides in most commercial applications. Due to the nature of the polymers, plasticizers are most usually polar compounds.

11.18.2 PRACTICAL CONCENTRATIONS

- N-butylbenzenesulfonamide – from zero up to stoichiometric equivalent of amide units,¹⁸² 1 to 5 wt% in adhesive composition,¹⁸⁷ 3 to 8 wt% in polyamide thermoplastic composition,¹⁹¹ 15 wt% in molded articles,¹⁹² 3 to 13.7 wt% in monofilaments,^{193,194} and 10 to 25 wt% in combination with one of the phthalate, adipate or phosphate plasticizer listed in Section 11.18.1¹⁹⁶
- N-ethylbenzenesulfonamide – from zero up to the stoichiometric equivalent of amide units¹⁸² and 20 wt% in hotmelt adhesive¹⁹⁵
- 2-ethylhexyl-4-hydroxybenzoate – 3 to 8 wt% in a polyamide thermoplastic composition¹⁹¹ and 15 wt% in molded articles¹⁹²
- dioctyl phthalate – 5 wt% in the hotmelt adhesive¹⁹⁵

11.18.3 MAIN FUNCTIONS PERFORMED BY PLASTICIZERS

- improvement of impact strength,¹⁸¹ especially at low temperatures^{192,196}
- improvement of toughness¹⁸⁵
- increase of fatigue life¹⁹³
- decrease of the glass transition temperature¹⁸²
- improvement of open time of hotmelt adhesives^{187,195}

11.18.4 EFFECT OF PLASTICIZERS ON POLYMER AND OTHER ADDITIVES

Figure 11.17 shows the effect of two plasticizers on the Izod impact strength of polyamide-11. The p-methylbenzene sulfonamide has a dramatic effect on impact strength.¹⁸¹ As little as a few percent of plasticizer rapidly improves impact strength. Larger additions of p-butyl hydroxybenzoate are required to obtain similar effects. Figure 11.18 shows that both plasticizers have little or no influence on the tensile strength of polyamide-11. Both graphs illustrate that the use of plasticizers brings substantial improvements to the performance of the polymer.

Figure 11.19 shows that even small additions of plasticizer improve the fatigue life of monofilaments of polyamide-6,6. The minimum fatigue life required of the commercial product is 50 minutes, so at least 3 wt% plasticizer is needed to make the product useful in practical applications.¹⁹³

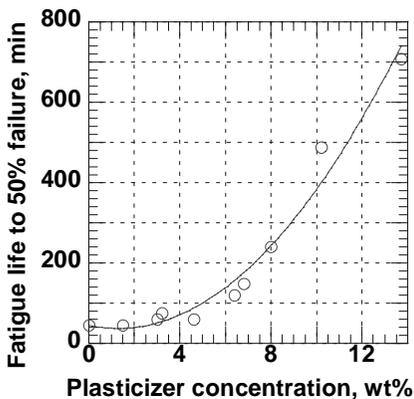


Figure 11.19. Effect of N-methylbenzene sulfonamide on fatigue life of polyamide-6,6. [Data from US Patent 6,249,928.]

11.19 POLYAMINE

Polyamines are mainly used as curing agents for polyurethane or epoxy systems.²⁰¹⁻²⁰³ These are usually two-components systems used as adhesives, coatings or electrocoatings. The role of plasticizers in these systems is to make it possible for the two parts to have similar weights, to reduce the rate of cure (increase pot life), and to improve such rheological properties as flowability and self-leveling.

The type of plasticizer used here is less critical, although it should have good compatibility both with the polyamine and the cured polymer. Good compatibility with polyamine reduces the amount of plasticizer required and good compatibility with the cured material reduces the physical loss of plasticizer from the product.

Suitable plasticizers include phthalates, phosphates, partially hydrogenated terpenes, adipates, chloroparaffins, castor oil, etc. It is best that the plasticizer does not contain water since it will interfere with the cure of polyurethanes.

The amounts used are determined by the properties required in the final product. For example in the case of a cold curable two-component polyurethane used in waterproofing,²⁰¹ additions of plasticizer lower than 20 wt% did not extend the potlife as required. Additions over 130 wt% caused plasticizer bleedout. This gives a very broad range of concentrations to adjust properties of product.

11.20 POLYANILINE

The process of making polyaniline, PANI, conductive is called doping. This involves protonation, partial oxidation, or partial reduction. Doped polyanilines have low solubilities in solvents which complicates their processing.²⁰⁴ Two processing methods are generally used: melt processing (e.g., extrusion or injection molding) or solution processing (e.g., casting or spraying). In order to conduct these processes PANI or deprotonated PANI (emeraldine base) are processed followed by a post-doping process. Once the conductive properties of PANI are activated it is usually incorporated in a carrier polymer (e.g., polymethylmethacrylate, cellulose acetate, etc.). This process requires that a certain temperature regime be followed that is dictated by the properties of both the polyaniline derivative and the matrix polymer. Although PANI derivatives are normally quite thermally stable they may not withstand some of the required processing temperatures.

The above explanations show two potential reasons for the use of plasticizers: the decrease of processing temperature for either the matrix polymer or for PANI or for its derivative. Simple substances such as hydroquinone, resorcinol, tert-butyl hydroquinone, 4-hexyl resorcinol, and bisphenol-A have been used as plasticizers in conjunction with polymethylmethacrylate as the matrix polymer.²⁰⁴ In addition to improved processability, plasticizers have been helpful in organization of polymer chains (hydrogen bonding and phenyl stacking), which results in better charge transfer between the PANI chains.²⁰⁴

Diesters of phosphoric acid are the best protonating agents for PANI and they are also good plasticizers.²⁰⁵ An oligoester of phosphoric acid was synthesized and used as plasticizer/doping agent in PANI. It was found to improve the thermostability of the plasticized polymer.²⁰⁵

Three groups of plasticizing/protonating agents have been used in the preparation of a conductive composite of PANI and cellulose acetate: sulfonic acids, phosphonic acids (phenyl phosphonic acid), and aliphatic diesters of phosphoric acid (diphenyl, dioctyl and dibutyl).^{206,207} These plasticizers improved the flexibility of the film but also significantly lowered the percolation threshold. The addition of plasticizer improves the dispersion of PANI in cellulose acetate.²⁰⁷ In this and other inventions²⁰⁸ based on the composite polymer it has been found to be important that the plasticizer not only helps to dissolve or soften PANI but also plasticizes the matrix polymer. In some inventions,²⁰⁹ a combination of plasticizers has been used. For example dodecylbenzenesulfonic acid acted as a doping

agent and a plasticizer of PANI. Many other compounds including alcohols, ethers, phenols, amines, etc. have been used to plasticize the matrix polymer and help in processing.²⁰⁹

11.21 POLYBUTADIENE

11.21.1 FREQUENTLY USED PLASTICIZERS

Plasticizers used in polybutadiene include:

- dioctyl sebacate in a power transmission belt²¹⁰
- chlorinated paraffins in a power transmission belt²¹⁰
- dibutyl phthalate in an adhesive composition²¹¹
- dioctyl phthalate in the compatibilization of polystyrene/polybutadiene immiscible blends²¹⁷
- paraffinic, aromatic, or naphthenic mineral oils in pressure-sensitive adhesives²¹² and in a tire tread^{213,214}
- 1,2-dinitratodecane and 2-ethylhexyl nitrate in a solid propellant binder²¹⁵
- polyisobutylene²¹⁶

11.21.2 PRACTICAL CONCENTRATIONS

- 1-100 phr in a power transmission belt²¹⁰
- 10-30 phr in a pressure sensitive adhesive²¹²
- 10-40 phr in tire compounds²¹⁴
- 30 wt% in an adhesive²¹¹
- 40-75 wt% in a propellant binder²¹⁵

11.21.3 MAIN FUNCTIONS PERFORMED BY PLASTICIZERS

Plasticizers in polybutadiene compounds carry out these functions:

- enhancing tackifying action^{211,212}
- increasing elasticity of product^{213,214}
- lowering temperature of processing²¹⁵
- supplying energy from burning and fuel oxidizing²¹⁵
- compatibilization of blend components²¹⁷

11.22 POLYBUTYLENE

11.22.1 FREQUENTLY USED PLASTICIZERS

Low molecular polybutylene is used to plasticize some polymers (e.g., polyethylene and polystyrene). It is approved by the EPA for use in the manufacture of articles for food contact applications.²¹⁸ Its use in combination with aliphatic lactate ester has been proposed as a plasticizer blend for many resins.²²³ It is also plasticized by:

- mineral oil in a hot melt adhesive^{219,220,221}
- polybutene in a hot melt adhesive^{219,220,221}
- dioctyl adipate, phthalate, maleate, dibutyl phthalate, isodecyl perlargonate, and oleyl nitrile in propellants²²²

11.22.2 PRACTICAL CONCENTRATIONS

- 5-15 wt% in hot melt adhesive^{219,220,221}

11.22.3 MAIN FUNCTIONS PERFORMED BY PLASTICIZERS

- providing viscosity control^{219,220,221}
- improving propellant processing²²²
- improving brushability of plasticized resin compound²²³

11.23 POLY(BUTYL METHACRYLATE)

11.23.1 FREQUENTLY USED PLASTICIZERS

- Texanol was used in a poly(butyl methacrylate) latex to demonstrate the effect of the plasticizer on interparticle chain diffusion of the polymer in a waterborne system²²⁴
- phthalates, adipates, citrates, epoxy and polymeric plasticizers in rubber eraser composition²²⁵
- ionic oligomer in coatings²²⁶

11.23.2 PRACTICAL CONCENTRATIONS

- 3-9 wt% in coating²²⁶
- 30-50 wt% in rubber composition²²⁵

11.23.3 MAIN FUNCTIONS PERFORMED BY PLASTICIZERS

- influencing polymer diffusion rate in waterborne systems²²⁶
- increasing film formation rate²²⁶
- improving film properties²²⁶

11.24 POLYCARBONATE

11.24.1 FREQUENTLY USED PLASTICIZERS

The following plasticizers have been used:

- tritoyl phosphate, pentaerythritol tetraborate, and trimellitic acid tridecyloctyl ester to increase the crystallization rate
- tetraethylene glycol dimethyl ether to increase the crystallization rate²³³
- tri-(2-ethylhexyl) phosphate^{227,228}
- dicyclohexyl phthalate to promote thermal transfer of image²³⁰
- dibutyl phthalate in electrolyte for lithium batteries²³²
- dioctyl phthalate in photoconductive element²³⁶
- phthalate plasticizers in impact resistant laminate²³⁴
- mineral oil in cover tapes²³⁵
- resorcinol diphenyl phosphate in flame retarded blends with polyphenylene oxide²³⁸

11.24.2 PRACTICAL CONCENTRATIONS

- 300 ppm to 1 phr to improve crystallization²³³
- 1-2 phr to improve melt flow²³⁸
- 10-15 to provide flame retarding²³⁸
- up to 5 wt% in molding composition²³¹
- 10 wt% trimellitic acid tridecyloctyl ester to increase crystallization rate
- up to 100 phr in electrolyte to obtain porous membrane²³²

Polycarbonates are one of a class of polymers in which small additions of plasticizer cause substantial changes in properties.

11.24.3 MAIN FUNCTIONS PERFORMED BY PLASTICIZERS

The use of plasticizers in polycarbonate causes many typical and some unusual changes such as:

- an increased rate of crystallization²³³
- a lowering of the glass transition temperature²²⁷
- affecting γ -relaxation (spacial arrangement of phenyl rings)²²⁷
- causing antiplasticization²²⁷
- plasticizer interacting with another molecule of plasticizer has increased mobility in the system as compared with a single molecule of plasticizer surrounded by polymer molecules²²⁸
- increased transfer rate of dye²³⁰
- extraction of plasticizer allows for formation of porous membrane²³²
- increased flexibility and toughness^{235,237}
- increased resistance to stress corrosion²³⁶
- lowered viscosity and improved melt flow²³⁸
- flame retarding properties²³⁸

11.25 POLYESTER

11.25.1 FREQUENTLY USED PLASTICIZERS

Various low molecular weight polyesters are polymeric plasticizers. These are likely to be compatible with polyester resins.²⁴⁷ Other groups of plasticizers are also used in plasticization of aliphatic and aromatic polyesters and copolyesters, as follows:

- polyalkylene ethers (e.g., polyethylene glycol, polytetramethylene glycol, polypropylene glycol or their mixtures) having molecular weight in the range from 400 to 1500 daltons^{239,243}
- glyceryl monostearate in shrink film applications²⁴¹
- octyl epoxy soyate, epoxidized soybean oil, epoxy tallate, epoxidized linseed oil in shrink film applications^{244,245}
- polyhydroxyalkanoate in biodegradable compositions²⁴⁶
- glycols (e.g., ethylene glycol, pentamethylene glycol, hexamethylene glycol, etc.) in biodegradable fiber²⁴⁹
- anionic and cationic plasticizers (e.g., dioctyl sulfosuccinate, alkane sulfonate, or sulfonated fatty acid) in sulfonated polyesters in hotmelt applications²⁵⁰
- phthalate and trimellitate plasticizers in hotmelt traffic marking composition²⁵¹
- polyethylene glycol di-(2-ethylhexoate) in flame resistant compositions (additional brominated flame retardant used)²⁵²

11.25.2 PRACTICAL CONCENTRATIONS

- 1-4 wt% of glyceryl monostearate²¹⁴
- 1-5 wt% of phthalate or trimellitate²⁵¹
- 3-4 wt% of polyethylene glycol di-(2-ethylhexoate)²⁵²
- 1-10 wt% of octyl epoxy soyate^{244,245}
- 10 phr of polyester sebacate²⁴⁷

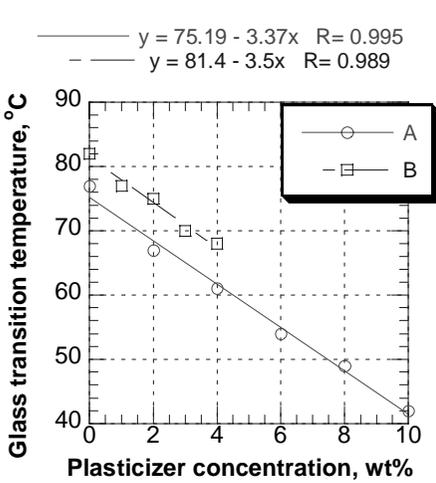


Figure 11.20. Glass transition temperature of polyester shrink film containing variable amounts of plasticizers. A - octyl epoxy soyate, B - glyceryl monostearate. [Data from US Patents 5,824,398, and 5,589,126.]

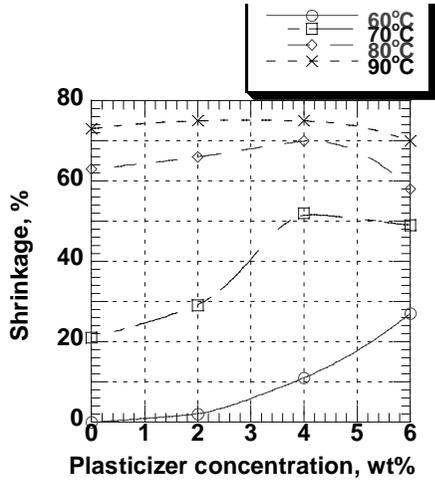


Figure 11.21. Shrinkage of polyester film plasticized with variable amounts of octyl epoxy soyate at different shrinking temperatures. [Data from US Patent 5,589,126.]

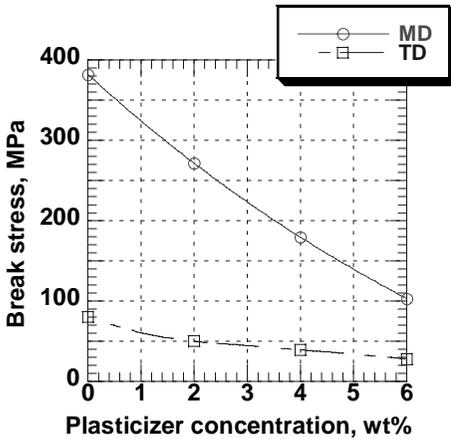


Figure 11.22. Break stress of polyester film plasticized with variable amounts of octyl epoxy soyate. MD - machine direction, TD - transverse direction. [Data from US Patent 5,589,126.]

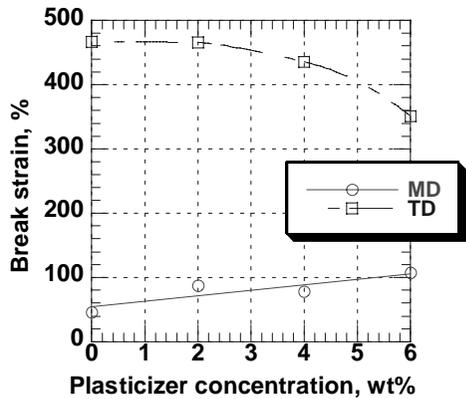


Figure 11.23. Break strain of polyester film plasticized with variable amounts of octyl epoxy soyate. MD - machine direction, TD - transverse direction. [Data from US Patent 5,589,126.]

- up to 15 wt% of glycol²⁴⁹
- 0.5-25 wt% of polyalkylene ethers^{239,243}
- up to 30 wt% of ionic plasticizer²⁵⁰

Low to moderate concentrations of plasticizers are used in polyester. The majority of products made from polyesters are produced without plasticizers. Mylar film is an example of a polyester product that does not contain plasticizer as are numerous formulations for plastic bottles.

11.25.3 MAIN FUNCTIONS PERFORMED BY PLASTICIZERS

- melt viscosity adjustment²³⁹ and gel viscosity reduction²⁴⁸
- lowering the glass transition temperature^{239,241}
- lowering the softening point²⁴⁸
- regulation of a shrink rate²⁴¹
- lowering on-set temperature of shrinking²⁴¹
- increase of the fracture toughness²⁴²
- reduction of crystallinity²⁴⁶

11.25.4 EFFECT OF PLASTICIZERS ON POLYMER AND OTHER ADDITIVES

Figure 11.20 shows that glass transition temperature decreases linearly with a very similar slope for two different plasticizers. Figure 11.21 shows that the effect of plasticizer concentration on the film shrinkage is a complex phenomenon. The influence of the glass transition temperature on the process of shrinking is clearly visible when shrinkage occurs at 60°C. The more the plasticizer present in the formulation the higher the shrinkage of a film. At the higher shrinking temperatures both the glass transition temperature and the shrinking process temperature work together to produce results. During the shrinking process the material is able to change its structure but the material should adjust to the shape of article being wrapped. At the higher temperatures and the higher concentrations of plasticizers the shape memory is not retained and the material does not shrink as expected.

One of the reasons for the changes in the mechanical properties can be attributed to the changes in crystallinity. It has been reported²⁴⁶ that the addition of 10 wt% of polyhydroxyalkanoate reduced the crystallinity of a polycarbonate polymer from a 50-90% range down to 30%.

Figure 11.22 shows that two different rates of break stress occur in the oriented (MD) and the unoriented (TD) directions in the film. The break stress changes more rapidly in the oriented direction because the plasticizer affects crystallinity and orientation. In Figure 11.23 break strain and its changes are seen to be very different in the two directions. The addition of plasticizer affects the integrity of the amorphous phase and that allows the strain to decrease in the unoriented direction. The plasticization of the crystalline phase causes increase in strain in the oriented direction.²⁴⁴

11.25.5 TYPICAL FORMULATIONS

Shrink film:²⁴⁵

Polyester	96 wt%
Octyl epoxy soyate	4

Shrink film:²⁴¹

Polyester	97 wt%
Glyceryl monostearate	3

Flame resistant composition:²⁵²

PET	21 parts
PET/PEO copolymer	18
Bromine flame retardant	16
Polyethylene glycol di(2-ethylhexoate)	4
Nucleating agent	4

11.26 POLYETHERIMIDE

Pentaerythritotetrabenzoate ester (Benzoflex S-552) was used to plasticize poly(arylene ether)/polyetherimide blends.²⁵⁴ A microporous membrane was manufactured from plasticized polyetherimide. Plasticizer was then removed by leaching into a suitable solvent.²⁵⁵

11.27 POLYETHYLACRYLATE

Dipropylene glycol dibenzoate, isodecyl diphenyl phosphate, dibutyl phthalate, and 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate have been used in a stripable film coating composition.²⁵⁷

The effect of dibutyl, dihexyl, and dioctyl phthalates on the rubbery modulus of polyethylacrylate has been evaluated.²⁵⁶ It was found that the rubbery modulus was independent of the plasticizer type at all concentrations studied.

11.28 POLYETHYLENE

It is somewhat surprising that many plasticizers are used for various purposes in polyethylene technologies as discussed below.

11.28.1 FREQUENTLY USED PLASTICIZERS

- dioctyl phthalate, DOP, in low density polyethylene,²⁵⁸ in the production of microporous film,²⁶³ in a composite based on chlorinated polyethylene,^{266,271} and the hotmelt adhesive for the pavement marking²⁷²
- glyceryl tribenzoate in adhesives²⁶⁹
- polyethylene glycol having molecular weight of 8,000 daltons in a polyethylene foam²⁵⁹ and in a biodegradable composition²⁶⁷
- sunflower oil in biodegradable formulations containing starch²⁶⁰
- paraffin wax having molecular weight from 400 to 1,000 daltons in preparation of surface modified film^{261,268} and porous film²⁷⁰
- paraffin oil in the production of microporous film²⁶³
- mineral oil in fusion process of fishing line²⁶²
- glycerin in binder formulation for metal and ceramic powder injection molding²⁶⁴ and in a biodegradable plastic composition²⁶⁷
- EPDM as a high molecular weight plasticizer in the extruded polyethylene pipe²⁶⁵
- EVA as a high molecular weight plasticizer in the extruded polyethylene pipe²⁶⁵

11.28.2 PRACTICAL CONCENTRATIONS

- 0.1 wt% of sunflower oil as biodegradable plasticizer²⁶⁰
- 0.1-3 wt% of polyethylene glycol in compatibilizing foam components²⁵⁹
- 1.5 wt% of glycerin in sintering process²⁶⁴
- 1-3 wt% of dioctyl phthalate, DOP, in hotmelt adhesive²⁷²
- 3-10 wt% of EDPM to plasticize pipe²⁶⁵
- 5 wt% of glyceryl tribenzoate in adhesive²⁶⁹
- 30 phr of DOP in plasticized low density polyethylene²⁵⁸
- 20-75 phr of DOP to plasticize chlorinated polyethylene²⁶⁶

- 60-80 parts of paraffin wax to prepare surface modified film by plasticizer extraction^{261,268}
- 50-70 wt% of DOP in production of microporous film^{263,270}
- immersion in mineral oil fusion of fishing line²⁶²

11.28.3 MAIN FUNCTIONS PERFORMED BY PLASTICIZERS

There many reasons to add plasticizers to the polyethylene formulations. Smaller amounts are added for conventional reasons, such as to make material more flexible. This includes applications in hotmelt adhesives^{269,272} and plasticization of pipe material.²⁶⁵ It is shown that up to 30 phr of plasticizer can be added to polyethylene.²⁵⁸ Small amounts of plasticizer are also needed to compatibilize different polymers²⁶⁴ or formulation components²⁵⁹ as well as to facilitate the biodegradative properties.²⁶⁰

Chlorinated polyethylene requires larger additions of plasticizers. Amounts of plasticizers and types used in chlorinated polyethylene are very similar to plasticizers used in polyvinylchloride.

Very large concentrations of plasticizers are used to produce permeable films and films with surface modification. In these cases,^{261,263,268,270} plasticizer may consist up 70% of initial composition. This mixture is then extruded, plasticizer is removed by extraction and film is stretched to improve mechanical properties of microporous or surface modified film.

11.28.4 MECHANISM OF PLASTICIZER ACTION

It is suggested that the plasticization of a low density polyethylene, LDPE, occurs inside the spherulitic crystallite in the interlamellar and interfibrillar regions. DOP-plasticized LDPE melts at lower temperatures as a result of plasticization.²⁵⁸

11.28.5 TYPICAL FORMULATIONS

Composition for metal sintering process:²⁶⁴

Stainless steel powder	91.35 wt%
Polyvinyl alcohol	5.25
Glycerin	1.46
Water	0.366
Release aid	0.551
High density polyethylene	1.023

Extruded polyethylene pipe:²⁶⁵

High density polyethylene	92.40 wt%
Additives	2.60
EPDM molecular weight 6,500	5.00

Pavement marking compound:²⁷²

Hydrocarbon resin	12 parts
Polyethylene	5
DOP	3
Glass beads	20
Titanium dioxide	8
Calcium carbonate	52

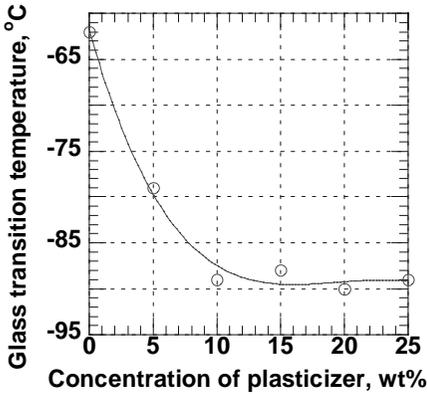


Figure 11.24. Glass transition temperature of plasticized poly(ethylene oxide) vs. concentration of dioctyl phthalate. [Data from Queiroz S M; Machado J C; Porto A O; Silva G G, *Polymer*, **42**, No.7, 2001, p.3095-101.]

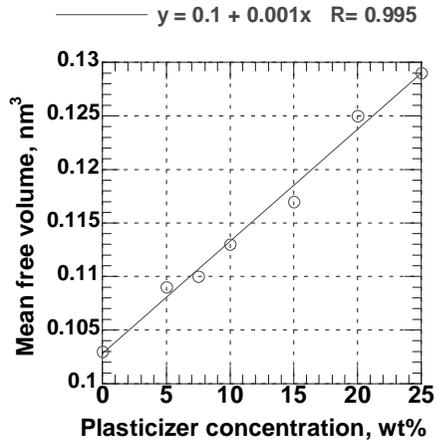


Figure 11.25. Mean free volume of plasticized poly(ethylene oxide) vs. concentration of dioctyl phthalate. [Data from Queiroz S M; Machado J C; Porto A O; Silva G G, *Polymer*, **42**, No.7, 2001, p.3095-101.]

11.29 POLY(ETHYLENE OXIDE)

11.29.1 FREQUENTLY USED PLASTICIZERS

- dioctyl phthalate²⁷³
- ethylene carbonate^{273,277}
- propylene carbonate²⁷⁴
- polyethylene and polypropylene glycols in a pressure sensitive adhesives^{275,276}
- tetraethylene glycol and tetraglyme in polymer electrolytes²⁷⁷
- polyoxyethylene-sorbitane monolaureate (Tween 20) in polymer-modifier compositions²⁷⁹
- polyethylene glycol and glycerin in transdermal drug delivery systems²⁸⁰
- a broad range of plasticizers in a denture stabilizing composition²⁸¹

11.29.2 PRACTICAL CONCENTRATIONS

- 22 wt% of polyoxyethylene-sorbitane monolaureate (Tween 20)²⁷⁹
- up to 25 wt% DOP in a polymer gel²⁷³
- up to 30 wt% of plasticizer in a denture stabilizing composition²⁸¹
- 32.3 wt% of polyethylene glycol and 32.3 wt% of glycerin in a transdermal drug delivery system²⁸⁰
- up to 70 wt% of ethylene or propylene glycol in a pressure sensitive adhesive^{275,276}

11.29.3 MAIN FUNCTIONS PERFORMED BY PLASTICIZERS

- improvement of processability²⁷³
- increased flexibility²⁷³
- weakening of the interchain interaction²⁷³
- increasing space between molecules²⁷³

- increasing free volume^{273,277}
- decreasing of glass transition temperature^{273,277}
- increasing ionic conductivity in Li-based batteries^{277,278}
- creating ionically-conducting pathways in amorphous phase²⁷⁷

11.29.4 EFFECT OF PLASTICIZERS ON POLYMER AND OTHER ADDITIVES

Figure 11.24 shows that rapid changes in glass transition temperature occur only for lower concentrations of plasticizer (up to 10 wt%). It is known that compatibility limit of dioctyl phthalate with poly(ethylene oxide) is 15 wt%.²⁷³ Free volume increases linearly with the amount of plasticizer increasing but crystallinity of polymer changes only little. This shows that plasticizer modifies mostly amorphous phase.

11.30 POLYISOBUTYLENE

Depending on molecular weight, polyisobutylene, PIB, can be liquid or solid. Liquid grades of PIB are frequently used as plasticizers. Solid grades are chemically inert elastomers which have resistance to the oxidative and thermal degradation and a low gas permeability. Because of these properties they find many applications. Some of these applications require plasticizers.

A low molecular weight PIB is used in many adhesive compositions. It plays role of a plasticizer and/or a tackifier. Adhesive composition based on EPDM rubber, useful in water-tight joints of roofing membranes, contains 5-9 wt% PIB.^{282,283} A pressure sensitive roofing tape is also based on EPDM plasticized with PIB.²⁸⁴

In the sporting goods, EPDM plasticized with PIB is used for grips of golf clubs, tennis rackets, bicycles, and tools. Grips provide good non-slipping properties.²⁸⁵ PIB plays a role of tackifier in adhesive compositions used as wound dressing.²⁸⁶

The formulations based on EPDM and brominated butyl rubber are plasticized with PIB to obtain water tight joints of rubber membranes.²⁸⁷ Peroxide curing causes some degradation of brominated butyl rubber which tackifies product.

An antioxidant was chemically attached to a low molecular weight PIB and used in natural rubber.²⁸⁹ Improved aging and ozone resistance resulted from a better retention of antioxidant.

Solid PIBs are used in plasticized formulations. In the drug containing adhesive of transdermal patch, 10-40 wt% plasticizer (mineral oil, silicone oil, octyl palmitate, etc.) is added to plasticize material and impart hydrophobic properties.²⁸⁸ Petrolatum or mineral oil was used in adhesive skin barrier which is a pressure sensitive adhesive based on PIB.²⁹²

Self-fusing tape is based on a composition containing halogenated PIB and medium molecular weight PIB.²⁹⁰ A composition also contains 2 to 18 wt% of polybutene which is a nonextractable plasticizer.²⁹⁰

Water-stop composition because of its expansion and controlled swelling on the water immersion. The following is the composition:²⁹¹

Crosslinked butyl rubber	10-12 wt%
Polyisobutylene	6-8
Non-swelling clay (ball clay)	14-19
Talc	1-2

Carbon black	1-2
Cellulose fiber	3-4
Plasticizer (process oil - Kendex 0842)	26-28
Tall oil fatty acid	5-2
Water swellable sodium and calcium bentonites	13-16.5 each

11.31 POLYISOPRENE

11.31.1 FREQUENTLY USED PLASTICIZERS

- a broad range of esters of phthalic acid and other dicarboxylic acids, aliphatic, aromatic and naphthenic oils, a low molecular weight polybutenes in sealants and adhesives²⁹³
- polybutene as a non-extractable plasticizer in a self-fusing tape²⁹⁴
- aromatic or paraffinic oil, esters of phthalic, adipic, and sebacic acids in rubber composition for tires and belts²⁹⁵

11.31.2 PRACTICAL CONCENTRATIONS

- 5 wt% of naphthenic oil and 15 wt% of polyisobutylene²⁹³
- 2-18 wt% of polybutene²⁹⁴
- 5 wt% of aromatic oil²⁹⁵

11.31.3 MAIN FUNCTIONS PERFORMED BY PLASTICIZERS

- change of rheological properties of uncured mixture²⁹³
- effect on vibration damping²⁹³
- effect on elastic properties of cured rubber²⁹⁵

11.31.4 TYPICAL FORMULATIONS

Sealant with damping properties:²⁹³

3,4-polyisoprene	10 wt%
Chalk	32
Precipitated calcium carbonate	25
Terpene phenolic resin	10
Naphthenic oil	5
Polyisobutylene	15
Antioxidant	1
Calcium oxide	1
Zinc oxide	1

11.32 POLYIMIDE

11.32.1 FREQUENTLY USED PLASTICIZERS

- diethylene glycol dibenzoate and dimethyl phthalate in membranes²⁹⁶
- reactive plasticizer having two four-membered rings²⁹⁷
- triallyl phosphate²⁹⁷
- diethynyldiphenyl methane and phenylethynyldiphenyl methane as reactive plasticizers in resin-transfer molding
- 4-hydroxybenzophenone²⁹⁸

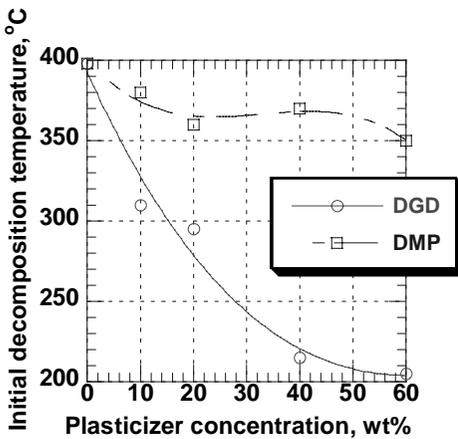


Figure 11.26. Initial decomposition temperature of polyimide membrane of different types and amounts of plasticizers. DGD – diethylene glycol dibenzoate, DMP – dimethyl phthalate. [Data from Totu E; Segal E; Covington A K, *J. Thermal Analysis Calorimetry*, 52, No.2, 1998, p.383-91.]

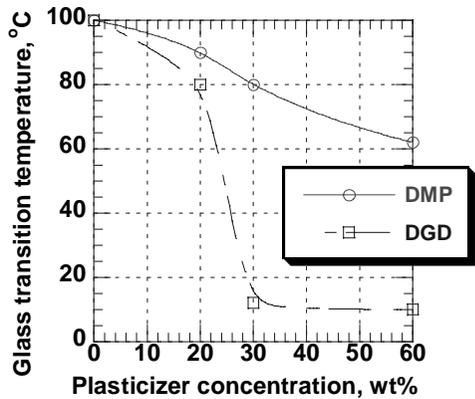


Figure 11.27. Glass transition temperature of polyimide membrane for different types and amounts of plasticizers. DGD – diethylene glycol dibenzoate, DMP – dimethyl phthalate. [Adapted, by permission, from Totu E; Segal E; Covington A K, *J. Thermal Analysis Calorimetry*, 52, No.2, 1998, p.383-91.]

11.32.2 PRACTICAL CONCENTRATIONS

- 10-60 wt% diethylene glycol dibenzoate and dimethyl phthalate²⁹⁶
- 12-17 wt% of reactive plasticizer²⁹⁷
- 0.25-5 wt% triallyl phosphate²⁹⁷
- 10 wt% 4-hydroxybenzophenone²⁹⁸

11.32.3 MAIN FUNCTIONS PERFORMED BY PLASTICIZERS

- lowering the glass transition temperature^{296,297}
- increasing membrane flexibility²⁹⁶
- affecting optical properties of membrane (transparent with diethylene glycol dibenzoate and opaque with dimethyl phthalate)²⁹⁶
- enhancing processability²⁹⁷
- increasing dimensional and thermooxidative stability²⁹⁷
- facilitating crystallinity and increasing crystallization window by 50°C²⁹⁸
- lowering viscosity

11.32.4 EFFECT OF PLASTICIZERS ON POLYMER AND OTHER ADDITIVES

Figures 11.26 and 11.27 show the initial decomposition and the glass transition temperatures for two plasticizers. Plasticizer, which rapidly decreases the glass transition temperature, forms less thermally stable material. It was proven within the course of this research that combination of both plasticizers permits to optimize properties.²⁹⁶

A combination of reactive and non-reactive plasticizers was found to offer advantages. A reactive plasticizer reduces the amount of potential volatiles in the final product and helps in the reduction of viscosity and thus improves processability. On the other

hand, a reactive plasticizer crosslinks material which thus needs a non-reactive plasticizer to increase its flexibility.²⁹⁷

The crystallization rate and the range of temperatures at which crystallization may occur depend on the glass transition temperature. It was found that a small addition of plasticizer (10 wt%) enhanced crystallizing abilities of polyimide.²⁹⁸

11.33 POLYLACTIDE

11.33.1 FREQUENTLY USED PLASTICIZERS

Poly lactide is a very popular, environmentally-friendly polymer, which needs plasticizers in its various applications. The following plasticizers have been used:

- polypropylene glycol and epoxy-functionalized polypropylene glycol (molecular weights 720 and 640, respectively) have been studied as biodegradable plasticizers²⁹⁹
- polyethylene glycol having molecular weight in the range from 600 to 8,000 in film applications,³⁰⁰ injection molded parts,³⁰¹ in polymer scaffolds,³⁰⁹ in biodegradable compositions,³¹⁷ and in nanocomposites³¹⁸
- partial fatty acid ester (Loxiol GMS 95) and glucose monoester (Dehydrat VPA 1726) in injection molded parts³⁰¹
- a range of biologically-degradable plasticizers including citrate or adipate esters, epoxidized soybean oil, acetylated coconut oil, and linseed oil in impact modified products^{303,304,316}
- acetyl tributyl citrate, glycerol triacetate, and glycerol tripropionate in molded product and film,³⁰⁵ and acetyl tributyl citrate in surface coatings³¹⁰
- di-(2-ethylhexyl) azelate or di-(2-ethylhexyl) adipate in biodegradable shrink films³⁰⁶
- citrate plasticizers³¹⁶ (triethyl citrate, tributyl citrate, acetyl triethyl citrate, and acetyl tributyl citrate) in films,³⁰⁷ coated papers,³¹⁴ and moldings³¹¹
- lactide monomer, oligomeric lactic acid³⁰⁸ or lactic acid³¹⁵
- epoxidized soybean oil or epoxidized linseed oil³¹³

The above list shows that a wide range of plasticizers can be used. One common expectation from the plasticizer is that it will be biologically degradable and it will increase biodegradation rate of composition.

11.33.2 PRACTICAL CONCENTRATIONS

- polyethylene glycol: 2.5-10 wt%,³⁰¹ 10-20 wt%,³⁰⁰ 20 wt%,³¹⁸ and up to 25 wt%³¹⁷
- 10-40 wt% of polypropylene glycols²⁹⁹
- partial fatty acid ester: 2.5-10 wt%³⁰¹
- glucose monoester: 2.5-10 wt%³⁰¹
- adipate esters: 8-15 wt%,³⁰³ 5-20 wt%,³⁰⁴ and 5-20 phr³⁰⁶
- azelate ester: 5-20 phr³⁰⁶
- citrate esters: 1-10 wt%,³¹⁴ 6-12 wt%,³¹⁰ 8-15 wt%,³⁰³ 9-15 wt%,³⁰⁵ 5-20 wt%,³⁰⁴ 10-30 wt%,³⁰⁷ and 20-30 wt%³¹¹
- epoxidized soybean oil: 5-20 wt%³⁰⁴
- acetylated coconut oil: 5-20 wt%³⁰⁴

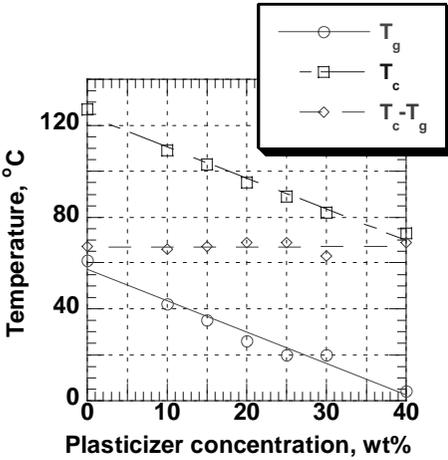


Figure 11.28. Glass transition temperature, T_g , and crystallization temperature, T_c , of polylactide plasticized with variable amounts of epoxidized polypropylene glycol having molecular weight of 640 daltons. [Data from McCarthy S; Song X, Antec 2001. Conference proceedings, Dallas, Texas, 6th-10th May, 2001, paper 363.]

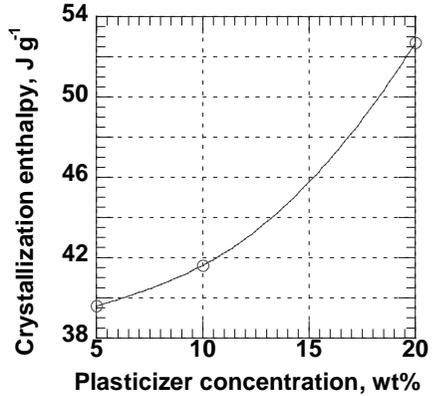


Figure 11.29. Crystallization enthalpy of polylactide plasticized with variable amounts of polypropylene glycol having molecular weight of 1000. [Data from Paul M-A; Alexandre M; Degee P; Pluta M; Gleski A; Dubois P, New Nanocomposite Materials Based on Plasticized Poly(l-lactide) and Organo-modified Montmorillonites, Belgian Polymer Group Meeting 2002, Mons, Belgium.]

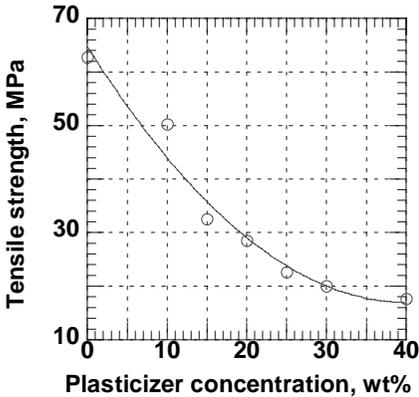


Figure 11.30. Tensile strength of polylactide plasticized with variable amounts of epoxidized polypropylene glycol having molecular weight of 640 daltons. [Data from McCarthy S; Song X, Antec 2001. Conference proceedings, Dallas, Texas, 6th-10th May, 2001, paper 363.]

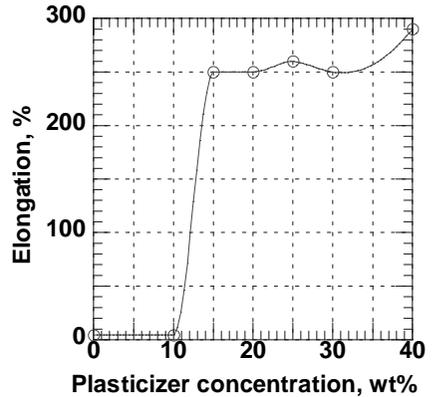


Figure 11.31. Elongation of polylactide plasticized with variable amounts of epoxidized polypropylene glycol having molecular weight of 640 daltons. [Data from McCarthy S; Song X, Antec 2001. Conference proceedings, Dallas, Texas, 6th-10th May, 2001, paper 363.]

- lactide: 15-25 wt%³⁰⁸
- oligomeric lactic acid: 30-60 wt%³⁰⁸

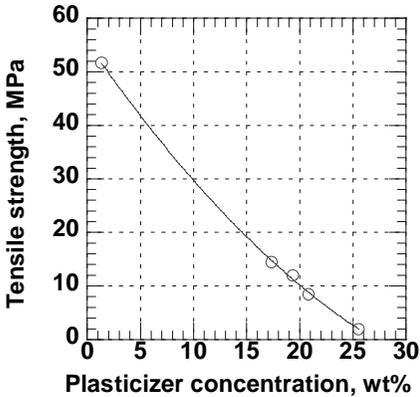


Figure 11.32. Tensile strength of lactide plasticized poly lactide. [Adapted, by permission, from Sinclair R G, *J. Macromol. Sci. A*, **A33**, No.5, 1996, p.585-97.]

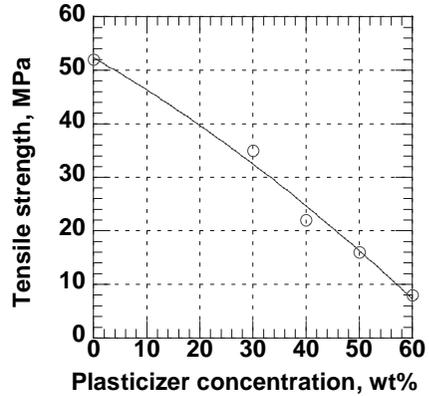


Figure 11.33. Tensile strength of oligomeric lactic acid plasticized poly lactide. [Adapted, by permission, from Sinclair R G, *J. Macromol. Sci. A*, **A33**, No.5, 1996, p.585-97.]

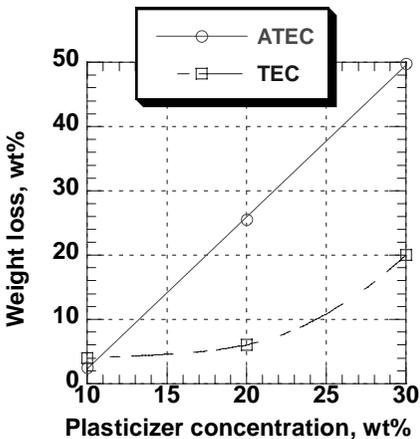


Figure 11.34. Weight loss of poly lactide subjected to 28 days of hydrolytic degradation vs. concentration and type of plasticizer (ATEC – acetyl triethyl citrate, TEC – triethyl citrate). [Data from Labrecque L V; Kumar R A; Dave V; Gross R A; McCarthy S P, *J. Appl. Polym. Sci.*, **66**, No.8, 21st Nov.1997, p.1507-13.]

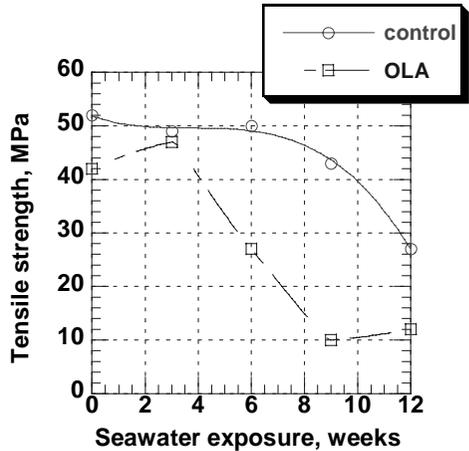


Figure 11.35. Tensile strength of poly lactide unplasticized and plasticized with 10 wt% of oligomeric lactic acid vs. exposure time to seawater. [Data from Sinclair R G, *J. Macromol. Sci. A*, **A33**, No.5, 1996, p.585-97.]

11.33.3 MAIN FUNCTIONS PERFORMED BY PLASTICIZERS

- increasing ductility of this normally quite brittle polymer^{299,301}
- increasing a very low elongation of unplasticized polymer (typically 3-5%)²⁹⁹
- increasing the elastic properties without affecting the anti-blocking properties³⁰⁵
- improvement of an impact strength³⁰⁶

- improvement of the tear resistance³¹¹
- decreasing the glass transition temperature^{307,313,316}
- reducing the melt viscosity³¹⁰
- reducing the die pressure³¹³
- retaining or increasing the biodegradation rate^{303,304,311,312,313,314}
- improvement of coating quality³¹⁶
- reducing tendency of coating to crack³¹⁶

11.33.4 EFFECT OF PLASTICIZERS ON POLYMER AND OTHER ADDITIVES

Figure 11.28 shows that polypropylene glycol acts as a plasticizer because it capable to decrease the glass transition temperature. Epoxy group was grafted on plasticizer in order to prevent its loss from product. Crystallization temperature decreases parallel to the glass transition temperature. In fact, the difference between crystallization, T_c , and glass transition, T_g , temperatures is constant in the whole range of plasticizer concentration.²⁹⁹ Lowering the glass transition temperature increases chain mobility and this, in turn, increases crystallization rate. In other study,³¹⁸ the same conclusion comes from determination of crystallization enthalpy which increases when plasticizer concentration increases.

Figure 11.30 shows that the tensile strength of a polylactide plasticized with epoxy-modified polypropylene glycol decreases monotonically with increased addition of plasticizer. Figure 11.31 shows that unplasticized polylactide has very small elongation. Addition a small amounts of polypropylene glycol rapidly increases elongation, which remains almost constant when more plasticizer is added. This is due to the fact that a brittle behavior is replaced by a ductile behavior when some critical amount of plasticizer is present.²⁹⁹

Comparison of Figures 11.32 and 11.33 with Figure 11.30 shows that each plasticizer has different behavior. Polylactide can be plasticized with its own monomer (Figure 11.32) but results are poor because tensile strength is rapidly lost. This is improved by the use of lactic acid oligomer (Figure 11.33) but the tensile strength change is still substantially less favorable than with polypropylene glycol (Figure 11.30). This shows that a selection of a type and a concentration of plasticizer is essential for building properties of products designed with polylactate. It should be added that lactide migrates to the surface and changes its properties. It may also cause premature degradation of polylactide.³⁰³

Figure 11.34 shows that the plasticizer structure and its amount determine biodegradation rate of the plasticized polylactate. Figure 11.35 shows that plasticizer increases the degradation rate on exposure to seawater. This is important for products in packaging applications developed to reduce threat to the marine life.³⁰⁸ It is estimated that about 100,000 marine animals and about 1-2 million sea birds are killed yearly by the toxic residues of a plastic litter.

11.34 POLYMETHYLMETHACRYLATE

11.34.1 FREQUENTLY USED PLASTICIZERS

- di-(2-ethylhexyl) phthalate in erasers³²⁷
- 2-hydroxyethyl methacrylate in bone cements³²⁰
- 4-cyanophenyl 4-heptylbenzoate in photorefractive materials³¹⁹
- plasticizers used in PMMA ionomers are discussed in Section 11.15

Plasticizers are used in polymethylmethacrylate in very specific cases only. PMMA ionomers are the most likely users of the ionic plasticizers.

11.34.2 PRACTICAL CONCENTRATIONS

- 37 wt% of di-(2-ethylhexyl) phthalate³²⁷
- 10 and 20 wt% of 4-cyanophenyl 4-heptylbenzoate³¹⁹

11.34.3 MAIN FUNCTIONS PERFORMED BY PLASTICIZERS

- reduction of the glass transition temperature³¹⁹
- improvement of the diffraction efficiency of the photorefractive materials³¹⁹
- increased rotational mobility³¹⁹
- improvement of ability to absorb water by a hydrophilic additive³²⁰
- improvement of impact resistance³²⁰
- improvement of crack growth inhibition³²⁰
- improvement of elongation³²⁰

11.34.4 MECHANISM OF PLASTICIZER ACTION

In bone connective prosthesis it is important to modify polymethylmethacrylate to improve elongation, adhesion to bone, inhibition of crack growth in connecting cements, and impact resistance. All these requirements can be addressed by plasticization which usually improves all these parameters. Considering the type of application, it is also essential that plasticization has permanent nature because of difficulties in replacement and potential hazards from migrating chemicals. The method selected was to add hydrophilic monomer which cannot migrate because it is attached to the copolymer backbone but by its presence it can help in absorption and retention of certain amounts of moisture. Water is a known plasticizer of many polymers, including polymethylmethacrylate. A constant presence of water modifies the polymer to requirements.³²⁰

11.34.5 TYPICAL FORMULATIONS

Rubber eraser:³²⁷

Polymethylmethacrylate	25 wt%
Di-(2-ethylhexyl) phthalate	37
Calcium carbonate	38

11.35 POLYPROPYLENE

11.35.1 FREQUENTLY USED PLASTICIZERS

Atactic (amorphous) polypropylene is a popular plasticizer in many applications, such as modified bitumen roofing, paper lamination, adhesives and sealants, asphalt pavement modification, wire and cable, carpet, tiles, films, and automotive products.²⁷² In some applications, plasticizers are used in polypropylene processing:

- polybutenes in flexible film applications, such as shelf-liners, tablecloth, shower curtains, and wallpaper³³⁰
- dioctyl sebacate³³³
- paraffinic oil³³³
- isooctyl tallate³³³
- plasticizing oil (Drakeol 34)³³⁴

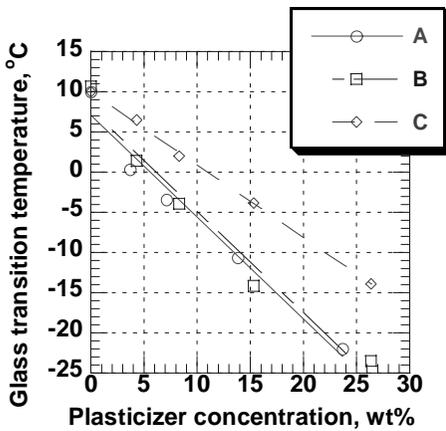


Figure 11.36. Glass transition temperature of polypropylene plasticized with variable quantities of different plasticizers. A – dioctyl sebacate, B – isooctyl tallate, C – paraffinic oil. [Data from Ellul M D, *Rubber Chem. Technol.*, **71**, No.2, May/June 1998, p.244-76.]

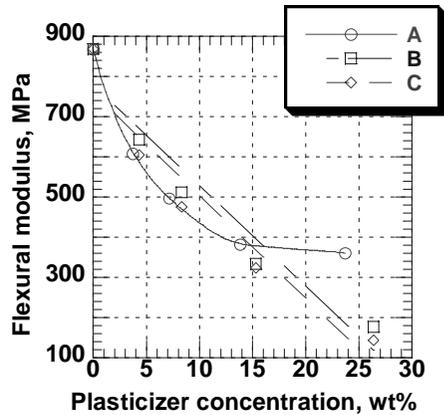


Figure 11.37. Flexural modulus of polypropylene plasticized with variable quantities of different plasticizers. A – dioctyl sebacate, B – isooctyl tallate, C – paraffinic oil. [Data from Ellul M D, *Rubber Chem. Technol.*, **71**, No.2, May/June 1998, p.244-76.]

- paraffinic, naphthenic, and aromatic processing oils in automotive weatherseals³³⁵
- glycerin in ceramic and metal powder injection molding³³⁶
- polyol as compatibilizer of mixtures of several polymers³³⁷

11.35.2 PRACTICAL CONCENTRATIONS

- 5-10 wt% of polybutene (5 wt% polybutene reduces modulus by 40%)³³⁰
- 3.7-23.7 wt% of dioctyl sebacate³³³
- 4.5-36 phr of isooctyl tallate³³³
- 4.5-72 phr of paraffinic oil³³³
- 1.3-1.6 wt% of glycerin³³⁶

11.35.3 MAIN FUNCTIONS PERFORMED BY PLASTICIZERS

- improvement of film flexibility³³⁰
- reduction of secant modulus³³⁰
- improvement of clarity and gloss³³⁰
- increase in tear strength³³⁰
- improvement of izod impact strength³³³
- depression of the glass transition temperature³³³
- facilitation of molding³³⁶
- compatibilization of polymers³³⁷

11.35.4 EFFECT OF PLASTICIZERS ON POLYMER AND OTHER ADDITIVES

Figure 11.36 shows that the glass transition depression is a linear function of plasticizer concentration. Two ester plasticizers depress the glass transition temperature more extensively than paraffinic oil.³³³ Dioctyl sebacate decrease the flexural modulus more rapidly with smaller concentrations of plasticizer (up 10 wt%) then the flexural modulus levels

off. In the case of paraffinic oil and isoocetyl tallate the flexural modulus decreases linearly with plasticizer concentration increase.³³³

11.36 POLY(N-VINYL CARBAZOLE)

Poly(N-vinyl carbazole), PVK, is a glassy polymer which easily fails by a cracking fracture. Plasticizers are needed to improve mechanical properties, reduce viscosity, and lower processing temperature.³³⁸ PVK is employed in photorefractive systems and as such it must possess photoconductivity and electro-optic effects. These are related to the crystallization and the glass transition temperature.³³⁹

Numerous photoconductive plasticizers are used to lower the glass transition temperature to below 20°C and act as hole transporting plasticizers.^{339,341} These include N-methylcarbazole, N-ethylcarbazole, N-butylcarbazole, N-hexylcarbazole, N-phenylcarbazole, 1,3-biscarbazolylpropane, o-nitroanisole, m-nitroanisole, p-nitroanisole, and triphenylamine.^{339,341}

Individual plasticizers may be used but frequently a good balance of properties is achieved by using plasticizers' mixtures.³³⁹ A combination of 1,3-biscarbazolylpropane and N-ethylcarbazole gave required a low glass transition temperature (-6.3°C) and high stability.³³⁹ Plasticizers are added in concentrations needed to achieve required properties. Practical concentrations are in the range of 6 to 50 wt%, most frequently about 30%.^{339,341}

11.37 POLY(N-VINYL PYRROLIDONE)

11.37.1 FREQUENTLY USED PLASTICIZERS

- glycerin^{342,343,345}
- polyethylene glycol having molecular weight in the range from 200 to 600 daltons³⁴²
- dioctyl adipate³⁴⁴
- triethyl citrate, acetyl triethyl citrate, or tributyl citrate³⁴⁵
- dipropylene glycol dibenzoate³⁴⁶

11.37.2 PRACTICAL CONCENTRATIONS

- glycerin in biomedical electrodes from 50 to 75 wt%³⁴³ and 5 to 35 wt% in pressure-sensitive adhesives³⁴⁵
- 15 wt% of dioctyl adipate in a thermoplastic composition compatibilized by poly(N-vinyl pyrrolidone), PVP³⁴⁴
- from 2 to 10 wt% of dipropylene glycol dibenzoate in a photosensitive polymer composition for the flexographic printing plates³⁴⁶

11.37.3 MAIN FUNCTIONS PERFORMED BY PLASTICIZERS

- improvement of processing characteristics³⁴³
- reduction of swelling in hot oil³⁴⁴
- improvement of flexibility³⁴⁴

11.37.4 MECHANISM OF PLASTICIZER ACTION

The glass transition temperature, T_g , corresponds directly to polymer cohesive energy and its packing density. T_g depression can be used to predict influence of plasticizer on the T_g

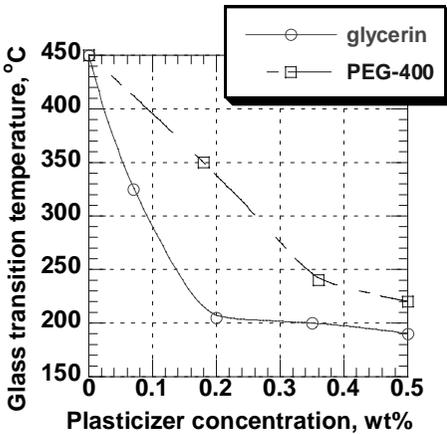


Figure 11.38. Glass transition temperature of poly(N-vinyl pyrrolidone) plasticized with different amounts of PEG having molecular weight of 400 daltons and glycerin. [Data from Feldstein M M; Shandryuk G A; Plate N A, *Polymer*, **42**, No.3, 2001, p.971-9.]

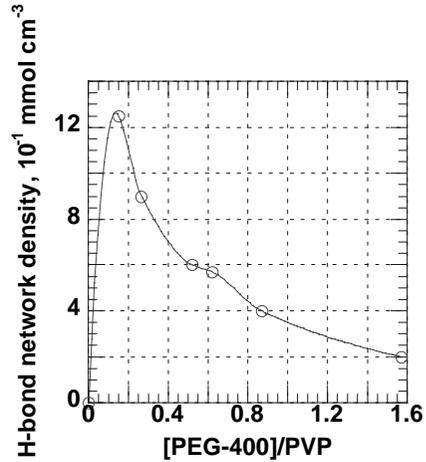


Figure 11.39. Density of hydrogen bond network formed between poly(N-vinyl pyrrolidone) plasticized with different amounts of PEG having molecular weight of 400 daltons. [Data from Feldstein M M; Shandryuk G A; Plate N A, *Polymer*, **42**, No.3, 2001, p.971-9.]

of a system.³⁴² Fox equation is used to estimate the effect of water and plasticizer, as follows:

$$\frac{1}{T_g} = \frac{W_{PVP}}{T_{gPVP}} + \frac{W_{H_2O}}{T_{gH_2O}} + \frac{W_p}{T_{gp}} \quad [11.1]$$

where:

- T_g the glass transition temperature of system
- T_{gi} the glass transition temperatures of mixture components (poly(N-vinyl pyrrolidone), water, and plasticizer, respectively)
- w_i the weight fractions of mixture components (poly(N-vinyl pyrrolidone), water, and plasticizer, respectively)

Equation 11.1 describes influence of plasticizers, which have one hydroxyl group per molecule. When more hydroxyl groups are present in a plasticizer (e.g., glycerin or polyethylene glycol, PEG), a negative deviation results. This may be corrected by adjusting parameter that is a weight fraction of plasticizer that interacts using two or more hydroxyl groups with polymer.³⁴²

Figure 11.38 shows that plasticizers may substantially decrease the T_g . At the same time, experimental values are lower than the values predicted by equation [11.1]. This means that more than one hydroxyl group in the plasticizer interacts with the polymer forming the hydrogen bonds.³⁴²

Figure 11.39 shows that the network density of the hydrogen bonds passes through a maximum when [PEG]/[PVP] is around 0.15 or [OH]/[PVP] = 0.3.³⁴² Further increase in the plasticizer concentration causes network to swell, and this results in the decrease of

network density. At the same time hydrogen bonds remain unaffected even at large excess of plasticizer.

11.37.5 TYPICAL FORMULATIONS

Thermoplastic composition compatibilized by PVC and plasticizer:³⁴⁴

Poly(vinylidene fluoride)	40 parts
Nitrile rubber	60
Poly(N-vinyl pyrrolidone)	3.2
Dioctyl adipate	15
Phenolic curative	4.8

11.36 POLYPHENYLENE ETHER

11.36.1 FREQUENTLY USED PLASTICIZERS

- diphenyl phthalate, triphenyl trimellitate, or pentaerythritol tetrabenzoate in flame retarded composition containing boron compound^{347,350}
- triphenyl phosphates and diphenyl phthalates in blends with polycarbonate, PC,³⁴⁸ and in a secondary battery container³⁵¹
- triphenyl and other aromatic phosphates in the flame retarded compositions^{349,355}
- polyethylene glycol, polyamide oligomers, ethylene-bis-stearoamide, and polyethylene oligomers in blends with polystyrene^{352,353}
- triphenyl phosphate or phthalic acid ester in thermoplastic resin compositions³⁵⁶
- polybutene in formulations having improved environmental stress cracking resistance³⁵⁷

11.36.2 PRACTICAL CONCENTRATIONS

- phosphates: 15-35 wt% in blends with PC,³⁴⁸ 40 phr in flame retarded compositions,³⁴⁹ 15 wt% in a flame retarded composition containing boron compound,³⁵⁰ 11 to 17 wt% in flamed retarded blends with polystyrene,³⁵¹ and 65 to 100 phr in a flame retarded composition³⁵⁵
- phthalates: 15-35 wt%³⁴⁸

The above examples show that it is still unclear what is the minimum concentration of phosphate plasticizer required to obtain flame retarded composition.

11.36.3 MAIN FUNCTIONS PERFORMED BY PLASTICIZERS

- to impart flame retarding properties^{347,349,350,355}
- to increase flexural modulus of blend with PC³⁴⁸
- to increase flexibility of molded part³⁴⁹
- to improve environmental stress cracking resistance³⁵⁷

11.37 POLYSTYRENE

11.37.1 FREQUENTLY USED PLASTICIZERS

- polybutenes³⁵⁸
- liquid paraffin and zinc stearate as internal plasticizers added during styrene polymerization³⁵⁸

- dimethyl, diethyl, dipropyl, dibutyl, diheptyl, dioctyl, and diisodecyl phthalates in optical sensing films³⁶¹ and in decoy flare compositions³⁶⁸
- di- and tri-isopropylbiphenyls^{363,372}
- dioctyl phthalate^{364,366,374}
- benzyl butyl phthalate³⁶⁹
- tricresyl phosphate in plastisols³⁶⁵
- dioctyl sebacate³⁶⁶
- mineral oil³⁶⁷
- paraffinic mineral oil³⁷³
- adipates and glutarates in expanded polystyrene³⁷⁰
- polyol as a compatibilizer³⁷¹

11.37.2 PRACTICAL CONCENTRATIONS

- liquid paraffin – up to 7 wt% and zinc stearate – 0.1 wt% (addition during polymerization)³⁵⁸
- dimethyl phthalate – 7 wt% in decoy flare compositions³⁶⁸
- dibutyl phthalate – 25 to 100 phr in sensing films³⁶¹
- dioctyl phthalate – 5 to 25 wt%³⁶⁶ or 3 wt%³⁷⁴
- dioctyl sebacate – 5 to 25 wt%³⁶⁶
- tricresyl phosphate – 18 wt% in plastisol³⁶⁵
- mineral oil – up to 10 wt%³⁶⁷ and 5 to 10 wt% in oriented polystyrene compositions³⁷³

11.37.3 MAIN FUNCTIONS PERFORMED BY PLASTICIZERS

- improvement of processability³⁵⁸
- improvement of impact resistance³⁵⁸
- improvement of heat resistance (polybutenes)³⁵⁸
- improvement of the environmental stress cracking (polybutenes)³⁵⁸
- increase in sensitivity of optical sensing films (phthalates)³⁶¹
- formation of chlorine-free plastisols³⁶⁵
- antiplasticization³⁶⁷
- lowering melting point³⁶⁸
- compatibilization of various polymers³⁷¹
- improvement of product clarity (small amounts)³⁷³
- improvement of impact strength³⁷³
- enlargement of orientation and thermoforming window³⁷³

11.38 POLYSULFONE

A production of transparent articles from polysulfone required addition of plasticizer to polysulfone that was specially purified to remove certain reaction impurities.³⁷⁵ Plasticizer is added to improve film flexibility. Plasticizers having high compatibility with polysulfone include diethyl phthalate, benzyl butyl phthalate, tricresyl phosphate, and methyl phthalyl ethyl glycolate. Up to 30 wt% of plasticizer can be used but usually 10 wt% of plasticizer is added.³⁷⁶

Compressed CO₂ and N₂O plasticize polysulfone. N₂O is more polar than CO₂ and it is slightly more effective in plasticization of polysulfone.³⁷⁷

11.39 POLYSULFIDE

11.39.1 FREQUENTLY USED PLASTICIZERS

- isooctyl benzyl phthalate (Santicizer 261) in caulks, sealants,^{378,379} and a bridge joint construction³⁸³
- benzyl butyl phthalate in the recycling of hardened adhesives and sealants³⁸⁰
- chlorinated paraffins in sealants^{379,384}
- alkyl sulfonic acid esters of phenol and/or cresol in the recycling of hardened adhesives and sealants³⁸⁰
- hydrogenated perphenyl (HB-40) in corrosion-inhibiting sealants^{381,384}
- 2,2,4-trimethyl-1,3-pentanediol and 1-isobutyrate benzyl phthalate (Texanol benzyl phthalate or Santicizer 278) in fuel resistant cables³⁸²

11.39.2 PRACTICAL CONCENTRATIONS

- isooctyl benzyl phthalate – 15-30 wt%,³⁷⁹ 5-45 wt%³⁸³
- chlorinated paraffins – 15-30 wt%³⁷⁹
- benzyl butyl phthalate – 40-60 wt% (solution recycling of sealants)³⁸⁰
- texanol benzyl phthalate – 23.5 wt%³⁸²

11.39.3 MAIN FUNCTIONS PERFORMED BY PLASTICIZERS

- viscosity control³⁷⁸
- increased filler loading³⁷⁸
- improved mixing of two-component sealants³⁸¹
- carrier liquid for depolymerization reaction³⁸⁰
- carrier liquid for curative³⁸¹
- masterbatch liquid improving dispersion of minor components^{382,384}
- additive increasing modulus of sealants³⁸¹

11.40 POLY(PHENYLENE SULFIDE)

A microporous membrane was made from poly(phenylene sulfide) containing plasticizer.³⁸⁵ The membrane is produced from a mixture of components. The mixture is extruded or cast to form a membrane, followed by controlled cooling (quenching) or coagulation. The membrane is then passed through a section in which the plasticizer (and optionally the second polymer) are leached out of the system into a solvent which does not affect poly(phenylene sulfide). Before, during, or after leaching operation, the membrane is stretched. There is a criterion set for plasticizer, which should be capable to dissolve at least 10 wt% of poly(phenylene sulfide) at extrusion or casting temperatures. Some plasticizers are capable to dissolve even more than 50% poly(phenylene sulfide). These include diphenyl methyl phosphate, triphenyl phosphate, diphenyl phthalate, tetraethylene glycol dimethyl ester, hydrogenated terphenyl, etc. Diphenyl phthalate and hydrogenated terphenyl have been selected for the membranes according to the invention.³⁸⁵ Concentrations of plasticizers have been in the range of 40 to 47 wt% and methylene chloride was used as a leaching solvent. The concentration and type of plasticizer and the conditions of stretching and leaching determine the pore sizes and density of pores.³⁸⁵

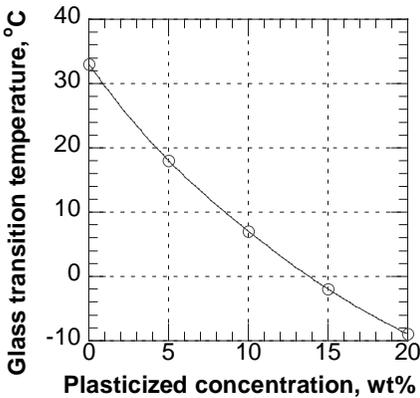


Figure 11.40. Glass transition temperature of polyvinylacetate plasticized with dibutyl phthalate vs. plasticizer concentration. [Data from Averco-Antonovich I U; Gotlib D M; Chakirov R R; Sokolova Y A, *Macromol. Symp.*, **176**, Nov. 2001, p.181-7.]

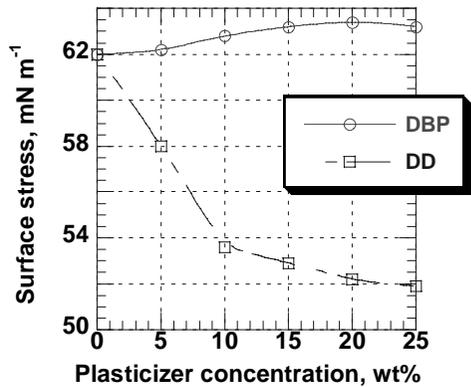


Figure 11.41. Surface stress of water dispersion of polyvinylacetate in presence of variable amounts of dibutyl phthalate, DBP, and mixture of dioxane derivatives, DD. [Adapted, by permission, from Averco-Antonovich I U; Gotlib D M; Chakirov R R; Sokolova Y A, *Macromol. Symp.*, **176**, Nov. 2001, p.181-7.]

11.41 POLYVINYLACETATE

11.41.1 FREQUENTLY USED PLASTICIZERS

Polyvinylacetate in a partially saponified form may perform function of its own plasticizer.³⁸⁹ In some other applications, it is plasticized by the following plasticizers:

- dibutyl phthalate³⁸⁶
- benzyl butyl phthalate in a paper adhesive³⁹⁵
- dipropylene glycol dibenzoate (Benzoflex 9-88)³⁹¹ and in textile inks³⁹²
- castor oil in cosmetics³⁸⁸
- glycerin, ethylene and propylene³⁹¹ glycols and their derivatives, and polyols in biodegradable compositions³⁹⁰
- polar compounds having high solubility parameters (glycerin, triethanolamine, ethylene glycol, propylene glycol, diethylene glycol, dipropylene glycol, etc.) in fragrance containing products³⁹⁶
- propylene glycol and glycerin in edible food coatings³⁹³
- ethylene glycol in paper adhesives³⁹⁵
- triacetin, triethyl citrate, acetyl triethyl citrate, tributyl citrate, and epoxidized soybean oil in a surface stabilization of sand and soil³⁹⁴

11.41.2 PRACTICAL CONCENTRATIONS

- dibutyl phthalate – 5 to 25 wt%³⁸⁶
- benzyl butyl phthalate (5.53 wt%) in addition to ethylene glycol (1.86 wt%)³⁹⁵
- dipropylene glycol dibenzoate (1 wt%) in addition to polypropylene glycol (1.2 wt%)³⁹¹
- polar plasticizer – 2 to 13 wt%³⁹⁶

- dipropylene glycol dibenzoate – 10 to 15 phr³⁹²
- propylene glycol – 3 to 5 wt%³⁹³
- triacetin, triethyl citrate, acetyl triethyl citrate, tributyl citrate, or epoxidized soy-bean oil – either at 5 wt% is suitable for the sand/soil stabilization³⁹⁴

This polymer requires only small additions of plasticizers. Plasticizers in most instances must be compatible with water-based systems and environment-friendly.

11.41.3 MAIN FUNCTIONS PERFORMED BY PLASTICIZERS

- lowering the glass transition temperature³⁸⁶
- increasing viscosity of water based system³⁸⁶
- imparting flexibility^{388,389,392}
- increasing the water vapor permeability³⁹³
- increasing cohesion in a particulate material³⁹⁴

11.41.4 EFFECT OF PLASTICIZERS ON POLYMER AND OTHER ADDITIVES

Figure 11.40 shows gradual decrease of the glass transition temperature of polyvinylacetate composition when the amount of plasticizer increases.³⁸⁶

Effect of two plasticizers (DBP – dibutyl phthalate and DD – a mixture of dioxane derivatives) on surface stress has been compared (Figure 11.41). Surface stress is useful in understanding the effect of plasticizer on the critical concentration of micelle formation and the potential stability of water dispersion of stabilizer.

The critical concentration of micelle formation, G_{∞} , is a limiting value of absorption, G_m , calculated from equation:

$$G_m = \left(-\frac{1}{RT} \right) \left[\frac{d\sigma}{d(\ln c)} \right] \quad [11.2]$$

where:

- R gas constant
- T absolute temperature
- σ surface stress
- c critical concentration of micelle formation.

Knowledge of the critical concentration of the micelle formation is useful in calculation of the surface area occupied by one plasticizer molecule:

$$S_o = \frac{1}{G_{\infty} N_A} \quad [11.3]$$

where:

- N_A Avogadro's number

Figure 11.41 shows two different behaviors of plasticizers. A plasticizer based on a mixture of dioxane derivatives, DD, decreases surface stress, which means it has the surface activity similar to non-ionogenic surfactants and the ability of micelle formation. Dibutyl phthalate, DBP, does not have this surface activity, and this may cause problems with the stability of its water dispersions.³⁸⁶

11.42 POLYVINYLALCOHOL

11.42.1 FREQUENTLY USED PLASTICIZERS

- polyethylene glycol in a blend with methylcellulose,³⁹⁷ in pharmaceutical tablets coating composition,⁴⁰⁶ in production of sintered products from ferrite,⁴⁰⁸ in moldable and extrudable compositions,^{412,427} in light sensitive materials,⁴¹⁴ in hydrogels,⁴¹⁵ in coating of enzyme-containing granules,⁴¹⁷ and in hydrogel used in wound-dressings⁴¹⁹
- ethylene glycols in removable coatings,³⁹⁸ in masking automotive coating,⁴⁰² in adhesive gel,⁴⁰⁵ in tire sidewall coating,⁴⁰⁷ in hydrogels,⁴¹⁵ in blends with polyamide,⁴¹⁶ in coating of enzyme-containing granules,⁴¹⁷ and in extruded fragrances⁴³⁰
- propylene glycol in adhesive gel,⁴⁰⁵ in coating of enzyme-containing granules,⁴¹⁷ in controlled-release bleach activators,⁴²² and in extruded fragrances⁴³⁰
- polypropylene glycol in light sensitive materials,⁴¹⁴ in hydrogels,⁴¹⁵ in coating of enzyme-containing granules,⁴¹⁷ in hydrogel used in wound-dressings⁴¹⁹
- glycerin (1,2,3-propanetriol) in masking automotive coating used to prevent paint overspray,⁴⁰² in a high performance compounds,³⁹⁹ in blends with pectin,^{403,404} in adhesive gels,⁴⁰⁵ in pharmaceutical tablets coating compositions,⁴⁰⁶ tire sidewalls coatings,⁴⁰⁷ in water soluble films,⁴⁰⁹ in preventive coatings for fresh produce,⁴¹⁰ in moldable and extrudable compositions,^{412,424,427} in top soil for gardens and lawns,⁴¹³ in light sensitive materials,⁴¹⁴ in hydrogels,⁴¹⁵ in coatings of enzyme-containing granules,⁴¹⁷ in hydrogels used in wound-dressing,⁴¹⁹ in moldable polymeric compounds,⁴²⁰ in controlled-release bleach activators,⁴²² in biodegradable composite articles,⁴²³ in mop heads,⁴²⁶ in orthopedic casting gloves,⁴²⁸ and in extruded fragrances⁴³⁰
- monostearyl citrate in preventive coatings for fresh produce⁴¹⁰
- triacetin in the soil erosion prevention⁴¹¹
- soy lecithin acts as a plasticizer by attracting moisture without compromising barrier properties of coating⁴¹⁸
- benzyl butyl phthalate in adhesive for bonding paper to a particle board⁴²¹
- dipropylene glycol dibenzoate in strippable coating⁴²⁹
- lactone-modified polyvinylalcohol, PVOH, is used as a plasticizer⁴²⁵

Water-soluble plasticizers are used in most cases unless improved water protection is required. In these cases water insoluble plasticizers are used. In many applications, biodegradable plasticizers are used. It is recognized that plasticizers in PVOH coatings increase tackiness and reduce barrier properties of such coatings. This is typical of polyethylene glycol.⁴⁰⁶ Glycerin is known to migrate to surface which makes product sticky. Glycerol facilitates crystallization of PVOH which may cause product inhomogeneity and deformation.⁴²⁰

11.42.2 PRACTICAL CONCENTRATIONS

- polyethylene glycol: 10 to 25 wt%,⁴⁰⁶ 5 to 50 wt%,⁴⁰⁸ and 1 to 10 wt%⁴¹²
- ethylene glycol: 2 wt%,⁴⁰² 0.5 to 3 wt%,⁴⁰⁵ 1 to 3 wt%,⁴⁰⁷ and 10 wt%⁴¹⁶
- propylene glycol: 0.5 to 3 wt%⁴⁰⁵ and 5 wt%⁴²²

- glycerin: 1 wt%,⁴⁰² 0.5 to 3 wt%,⁴⁰⁵ 1 to 3 wt%,⁴⁰⁷ 20 wt%,⁴⁰⁹ 0.1 to 5 wt%,⁴¹⁰ 0.5 to 5 wt%,⁴¹³ 5 wt%,⁴²² 12 to 19 wt%,⁴²⁴ and 5 to 9 wt%⁴²⁸
- soy lecithin: 0.3 to 0.5 wt%⁴¹⁸
- benzyl butyl phthalate: 8.6 wt%⁴²¹
- dipropylene glycol dibenzoate: 0.7 to 4 wt%⁴²⁹

In the majority of applications, plasticizers are added in modest quantities most likely because larger additions affect surface properties of products and cause problems related to the hydrophilic nature of plasticizers used. Larger quantities of plasticizers have been added to products such as controlled-release of pharmaceutical tablets, sintered materials produced from ferrites, and water soluble films.

11.42.3 MAIN FUNCTIONS PERFORMED BY PLASTICIZERS

- improvement of thermooxidative stability³⁹⁹
- reduction of processing temperature³⁹⁹
- improvement of oil and chemical resistance³⁹⁹
- improvement of film flexibility^{403,407,410,419,420,421,428}
- increased molecular mobility,⁴¹⁰ which permits to attain a better packing efficiency through a molecular rearrangement⁴⁰⁴
- reduction of the glass transition temperature^{406,417,424}
- improvement of gas permeability⁴¹⁰
- improvement of biodegradability⁴¹¹
- improvement of adhesion and agglomeration in particulate materials⁴¹³
- improvement of processing of highly viscous materials^{416,421}

11.42.4 TYPICAL FORMULATIONS

Film coating of tablets (pharmaceutical, nutritional supplements, food, etc.):⁴⁰⁶

Polyvinylalcohol	38 to 46 wt%
Polyethylene glycol	10 to 25
Talc	9 to 20
Pigment/opacifier	20 to 30
Lecithin	0 to 4

Top dressing soil for gardens and lawns:⁴¹³

Sand	50-70 wt%
Polyvinylalcohol	0.4-5
Glycerol	0.5-5
Water	5-20
Clay (hydrated aluminum silicate)	10-40
Coloring pigment	1-5
Urea	1-2
Peat moss	5-20

Moisture barrier coating:⁴¹⁸

Polyvinylalcohol	7 to 12 wt%
Flow aid	3 to 5
Colorant	4.8 to 8

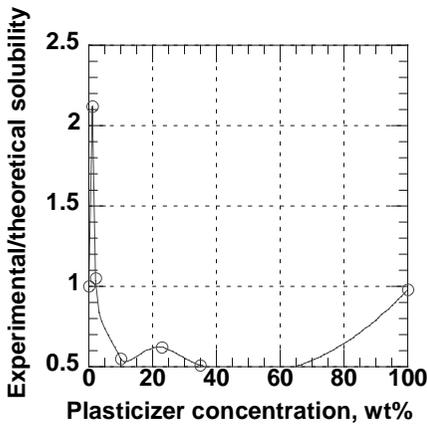


Figure 11.42. Effect of dihexyl adipate on solubility of 4-[3,5-bis(tert-butyl)-4-hydroxyphenyl]butane-2,2-diol in plasticized PVB vs. concentration of plasticizer. [Adapted, by permission, from Mar'in A P; Tatarenko L A; Shlyapnikov Y A, *Polym. Deg. Stab.*, **62**, No.3, 1998, p.507-11.]

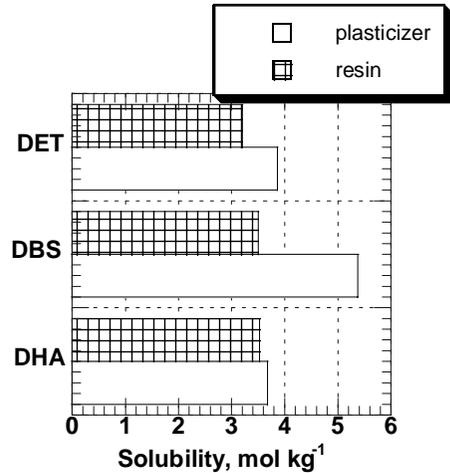


Figure 11.43. Solubility of 4-[3,5-bis(tert-butyl)-4-hydroxyphenyl]butane-2,2-diol in plasticizer and resin containing 26 wt% plasticizer. DET – triethylene glycol, DBS – dibutyl sebacate, DET – dihexyl adipate. [Data from Mar'in A P; Tatarenko L A; Shlyapnikov Y A, *Polym. Deg. Stab.*, **62**, No.3, 1998, p.507-11.]

Soy lecithin	0.3 to 0.5
Suspending agent	0.07 to 0.12
Water	75 to 85

11.43 POLYVINYL BUTYRAL

11.43.1 FREQUENTLY USED PLASTICIZERS

- tetraethylene glycol di-n-heptanoate in laminated glass applications^{431,440}
- triethylene glycol di-(2-ethylhexanoate) in laminated glass applications⁴⁴²
- triethylene glycol diheptanoate in laminated glass⁴⁴³
- dihexyl adipate in laminated glass^{432,433,434,436,442,443,445,446,447,449,451,454}
- hexyl cyclohexyl adipate in laminated glass⁴⁴³
- dibutyl sebacate in laminated glass⁴³²
- polyethylene glycol in cathodes for fuel cells⁴⁴⁴
- biphenyl or its derivatives in electrographic photoconductor⁴⁴⁸
- diglycidyl ether of bisphenol A as resins plasticizer in aqueous emulsions⁴⁵³

11.43.2 PRACTICAL CONCENTRATIONS

- tetraethylene glycol di-n-heptanoate: 37.4 phr,⁴³¹ and 35 to 45 phr⁴⁴⁰
- triethylene glycol di-(2-ethylhexanoate): 25 to 45 phr⁴⁴²
- triethylene glycol diheptanoate: 25 to 45 phr⁴⁴³
- dihexyl adipate: 33 phr^{433,436,447,449} and 25 to 45 phr^{442,443,445,446,451,454}
- hexyl cyclohexyl adipate: 25 to 45 phr⁴⁴³

11.43.3 MAIN FUNCTIONS PERFORMED BY PLASTICIZERS

- effect on solubility, migration, and diffusivity of other additives⁴³²

- reduce stiffness of polymer⁴⁴²
- increase absorption of impact forces by the laminated glass⁴⁴²
- control adhesion to glass⁴⁴³
- reduce residual stress in the photoconductive layer⁴⁴⁸
- affect maximum processing temperature above which undesirable bubbles are formed⁴⁵²
- improve film-forming properties⁴⁵³

11.43.4 EFFECT OF PLASTICIZERS ON POLYMER AND OTHER ADDITIVES

In high extrusion throughput processes involving polyvinylbutyral, PVB, the resin is partially melted before plasticizer addition. Location of plasticizer injection is important. If the plasticizer is injected too far downstream, high yellowness and discharge melt temperature surging occurs.⁴³¹ If the plasticizer is injected too close, it can back up into the primary feed barrel inlet and cause plugging.⁴³¹

In addition to plasticizer and the resin, other additives are included in composition, such as for example antioxidants⁴³² or UV stabilizers.⁴⁴⁶ Figure 11.42 shows that with small additions of a plasticizer an antioxidant dissolves better than predicted by a sum of its solubilities in polymer and plasticizer. Larger additions of the plasticizer cause a strong polymer plasticizer interaction which decreases the antioxidant dissolution.⁴³² Figure 11.43 shows that the solubility of antioxidant in dihexyl adipate and triethylene glycol is lower than its solubility in dibutyl sebacate but the type of plasticizer has influence on plasticized resin.⁴³²

11.44 POLYVINYLCHLORIDE

11.44.1 FREQUENTLY USED PLASTICIZERS

The majority of plasticizer types discussed in Chapter 2 have been either designed for or used with polyvinylchloride, PVC. But the list of the most common plasticizers changes due to the various circumstances such as the cost of their production, the environmental and safety concerns,^{462,474} the development of a new group of materials, etc. For example, di-(2-ethylhexyl) phthalate dominated plasticizer use for many decades until recent findings, which questioned its health safety and its readiness to leach out of medical products. The problems with use of the most prominent representative of the phthalate group suddenly changes the structure of supply and demand.

The list below characterizes the most current applications:

Phthalates

- di-n-hexyl phthalate^{479,483}
- diisohexyl phthalate^{479,483}
- diisooheptyl phthalate^{479,483} in sheet flooring⁴⁸⁸
- di-(2-ethylhexyl) phthalate^{479,543} in PVC reinforced with cellulose whiskers,⁴⁶³ in flexible hose for toilet systems,⁴⁶⁷ in studies of interaction with blood,⁴⁷² as a coplasticizer in flame retarded compositions,⁴⁷⁶ in sheet flooring,^{488,546} in plastisol compositions containing nitrile rubber,^{493,545,554} in studies on use of newsprint as a filler,⁴⁹⁹ in studies on gelation and fusion properties,^{502-504,522} in photolytic studies,⁵⁰⁶ in glass transition temperature studies,⁵⁰⁹ in compatibilized blend,⁵³² in recycling carpet waste,⁵³⁷ and in acoustical control earpieces⁵⁴⁰

- diisononyl phthalate⁴⁵⁵ in creep resistant plastisol⁴⁷⁷ and in antimicrobial gloves manufacture⁵⁴⁹
- diisodecyl phthalate in electrical insulation,⁴⁸⁷ in compression set studies,⁴⁹⁶ and in photolytic studies⁵⁰⁶
- diisoundecyl phthalate in photolytic studies⁵⁰⁶
- diundecyl phthalate in light stable retroreflective highways signs,⁵²⁹ in oil resistant applications,⁵³⁸ in flame retardant compositions,⁵⁵¹ and in medical containers⁵⁵⁸
- benzyl butyl phthalate in sheet flooring⁴⁸⁸ and in masonry bondable membrane⁵⁵²
- di-(2-ethylhexyl) tetrabromophthalate in flame retarding applications,^{490,531,535,541,550}
- di-(2-ethylhexyl) tetrachlorophthalate in the synergistic flame retarding system^{535,541}

Low temperature and other general plasticizers:

- a mixture (1:1) of diethylene glycol dibenzoate and dipropylene glycol dibenzoate⁴⁸⁹ and blends with triethylene glycol dibenzoate and di-(2-ethylhexyl) adipate⁴⁹²
- dihexyl adipate in interlayer of laminated glass⁵³⁹ and in glazing compounds⁵⁴⁷
- di-(2-ethylhexyl) adipate,⁴⁵⁶ in food contact and medical applications,⁵³⁶ in interlayer of laminated glass,⁵³⁹ in acoustical control earpieces,⁵⁴⁰ in glazing compounds,⁵⁴⁷ and in biocompatible materials⁵⁴⁸
- diisodecyl adipate in the glass transition temperature studies⁵⁰⁹
- dihexyl azelate in interlayer of laminated glass⁵³⁹ and in glazing compounds⁵⁴⁷
- di-(2-ethylhexyl) sebacate in ion-selective membranes⁴⁶⁶ and in NO diffusion studies⁴⁷⁵
- n-butyryl tri-n-hexyl citrate in composition for medical containers⁵³⁰
- di-(2-ethylhexyl) trimellitate⁵³⁵ as medically acceptable plasticizer in flexible medical products⁴⁶⁸ and in the studies of interaction with blood⁴⁷²
- tri-(2-ethylhexyl) trimellitate in composition for medical containers,⁵³⁰ in a flame retarded composition for wire and cable,⁵⁴¹ and in biocompatible materials⁵⁴⁸
- pyromellitates in studies on potential candidates for plasticizers^{480,481}

Flame retardant plasticizers:

- isopropylphenyl diphenyl phosphate in flame retarded applications^{495,497,501}
- 2-ethylhexyl diphenyl phosphate in glass transition temperature studies⁵⁰⁹ and in a semiconducting floor covering⁵³³
- alkyl aryl phosphate (Santicizer 2148) in smoke suppression⁵⁰⁷ and in a flame retarded composition⁵⁵⁰
- chloroparaffin in a flame retarded composition⁴⁷⁶

Other monomeric plasticizers:

- epoxidized soybean oil^{455,456,476,477,507,536,546,547,551}
- 2-nitrophenyl octyl ether in ion-selective membranes⁴⁶⁶ and in NO diffusion studies⁴⁷⁵
- triallyl cyanurate as a reactive plasticizer which promotes high temperature creep resistance⁴⁵⁵
- pentaerythritol ester plasticizer in flame retarded composition⁵⁵⁰

- lower alkyl biphenyls⁵⁵³
- polyol in plasticizing/compatibilizing a blend with starch⁵⁶⁰

Polymeric plasticizers and blends:

- ethylene interpolymers (Evaloy) low smoke flexibilizers^{457,458} and as an aid in the melt compounding⁵⁰⁰
- polyester-type, propanediol-based polymeric plasticizers⁴⁵⁹
- polyester adipate in a paintable PVC sheet⁵⁵⁷
- polyester glutarate (Plasthall P-550) in a light stable retroreflective highways signs⁵²⁹
- polymeric plasticize, which withstands fats (e.g., Plaxter P20 or P80), in multi-layer hose for transporting hot fluids⁵³⁴
- polymer blending with various polymers, such as acrylonitrile butadiene rubber,⁴⁶⁴ ethylene vinyl acetate⁴⁶⁴ (in flexible hose for toilet systems⁴⁶⁷), ethylene acrylic copolymer,^{464,556} and nitrile rubber^{493,538,545,554}

In addition to the chemical structure of a plasticizer, special requirements are common, such as food grade, electrical grade, etc. Electrical and food grade plasticizers are commonly available. Electrical grade plasticizers differ from general grades by a tight control of ionic impurities.⁴⁸⁷

The above analysis of the most recent applications of plasticizers shows that phthalates and di-(2-ethylhexyl) phthalate are still the main PVC plasticizers. It may be noted that diundecyl phthalate receives a growing interest in applications in which leaching, evaporation, and migration are serious drawbacks.

Other types of plasticizers are used according to the requirements related to properties (e.g., low temperature properties, flame retarding properties, etc.). Epoxidized soybean oil continues to be an important plasticizer of many formulations because it plays a dual role of a secondary plasticizer and a secondary stabilizer. Trimellitates seem to gain more applications due to their biocompatibility and environmentally friendly nature.

It appears that polymeric plasticizers are not gaining many new applications but instead blending with other polymers is used for low fogging/low odor formulations.

11.44.2 PRACTICAL CONCENTRATIONS

- di-(2-ethylhexyl) phthalate: 85 to 100 phr in the slush molding composition containing up to 30 phr of highly crosslinked nitrile rubber,⁴⁹³ 50 phr when used as a single plasticizer in a smoke suppressed formulation using inorganic additives,⁵⁰⁷ 80 phr in a polymer blend,⁵³² 80 phr in a compatibilized blend containing PVC, polyolefin and/or styrenic polymer,⁵⁴³ 5 to 35 phr in the calendered flooring sheet,⁵⁴⁶ and 85 phr in slush molding composition⁵⁵⁴
- diisononyl phthalate: 48 wt% (100 phr) in a cold dip molding of antimicrobial gloves⁵⁴⁹
- diisodecyl phthalate: 55 phr in wire and cable applications⁴⁸⁷
- diundecyl phthalate: 137.29 phr per 100 phr of PVC and 107.14 phr of crosslinked nitrile rubber⁵³⁸ and 50 phr in composition flame retarded by Sb_2O_3 ⁵⁵¹
- benzyl butyl phthalate: 100 phr in a masonry bondable membrane⁵⁵²
- di-(2-ethylhexyl) adipate: 16 phr in addition to 10 phr of epoxidized soybean oil in food contact/medical grade PVC,⁵³⁶ 50 phr in a laminating layer of safety

- glass,⁵³⁹ 65 wt% in an earplug formulation,⁵⁴⁰ and 31 wt% (48 phr) in medical applications⁵⁴⁸
- di-(2-ethylhexyl) azelate: 55 phr in a laminated glazing unit⁵⁴⁷
 - tri-(2-ethylhexyl) trimellitate: 120 phr (53% wt) in the plasticization of an ultra high molecular weight PVC having high absorption limit of plasticizer (57 wt% as compared with 41 wt% for general PVC resins),⁴⁶⁸ 37 to 40.5 weight percent in medical tubing,⁴⁷² and ~50% of total plasticizers (n-butyryl tri-n-hexyl citrate – 20% and epoxidized soybean oil – 30%) in medical containers which have 30 wt% total plasticizer⁵³⁰
 - isopropylphenyl diphenyl phosphate: up to 50 phr when used as a single plasticizer in the flame retarded composition⁴⁹⁵
 - 2-ethylhexyl diphenyl phosphate: minimum 30 phr with general plasticizer in the range of 0 to 50 phr, depending on the amount of filler and polymer type⁵³³
 - di-(2-ethylhexyl) tetrabromophthalate: 10 phr (in addition to 20 phr of DOP) in flame retardant composition⁵³¹ and 40 phr with addition of 10 phr of di-(2-ethylhexyl) tetrachlorophthalate and 34.3 phr of tri-(2-ethylhexyl) trimellitate in flame resistant, low smoke wire and cable^{535,541}
 - pentaerythritol ester plasticizer: 33 phr in addition to 10 phr di-(2-ethylhexyl) tetrabromophthalate and 5 phr of isodecyl diphenyl phosphate in flame retarding composition⁵⁵⁰
 - epoxidized soybean oil: 3 to 10 phr^{507,532}
 - polymeric plasticizer: 70 phr (propanediol derivative polyester),⁴⁵⁹ 25 to 45% of polyester glutarate of total plasticizer composition for fluorescent highway retroreflective signs (total plasticizer is 30 to 35 phr),⁵²⁹ and 40-60 phr in cable and wire system⁵⁴²
 - ethylene vinyl acetate copolymer: 30-40 wt% (in addition to 30 wt% of a low molecular weight plasticizer)⁴⁶⁷

As expected from the requirements of numerous processing technologies used in PVC, the concentrations of plasticizers vary in a broad range. Other polymers discussed in this chapter are usually processed by one or two different methods of processing and thus plasticizer concentration reflects more precisely the requirements of a particular polymer. Plasticizer concentration in PVC must be reviewed in the context of the processing method and the expected rigidity of articles produced.

11.44.3 MAIN FUNCTIONS PERFORMED BY PLASTICIZERS

- make products more flexible⁴⁵⁹
- lower the glass transition temperature^{505,509}
- affect packing density and free volume^{508,516}
- affect chain mobility and crystallization⁵⁰⁸
- improve compatibility with other polymers^{505,532,544,560}
- lower processing viscosity⁴⁵⁹
- determine rheological characteristics of plastisols and melts^{484,499,523,545}
- determine viscoelastic properties of materials^{490,508}
- determine impact resistance of material^{500,564} and impact dispersing properties⁵⁵⁵
- determine scratch, wear, and slip resistance of material⁵⁴⁶
- lower processing temperature⁴⁵⁹

- affect fusion temperature^{484,502-504,522}
- affect gelation temperature^{484,502-504,522,561}
- affect discoloration of PVC^{510,521}
- absorb radiation between 300 and 340 nm in a laminated glass⁵⁴⁷
- affect thermal degradation of PVC^{512,515,517,518,539}
- affect an outdoor performance of products^{526,527,519,529,548}
- affect plasticizer take up rate (or dry-blending time)⁴⁷⁸
- make products of varying rigidity⁴⁶⁴
- affect creep resistance at elevated temperatures by reactive plasticizers⁴⁷⁷ or blending⁵⁶⁵
- improve flammability of product^{490,531,535,541,550,551}
- improve limiting oxygen index⁴⁹⁰
- improve heat release rate⁴⁹⁷
- reduction of smoke (high molecular weight flexibilizers)^{457,458}
- increase of a low temperature flexibility^{457,458}
- affect foaming rate and microcellular structure^{513,561}
- increase chemical and oil resistance (high molecular weight flexibilizers)^{457,458,534}
- increase filler loading^{476,499}
- affect water uptake^{466,557}
- improve water-based coating receptivity⁵⁵⁷
- determine permeability to different gasses⁴⁷⁵
- reduction of odor by limiting carbon disulfide solubility⁴⁶⁷
- affect fogging^{486,556}
- affect shrinkage of product due to plasticizer loss⁵¹⁴
- determine surface tack of product^{498,524} or improve sliding resistance⁵⁵⁹
- affect acoustical properties of materials^{540,562,563}
- determine biological stability of a product⁵⁰⁰ and antimicrobial properties⁵⁴⁹
- affect the concentration of ionic impurities^{487,542}
- affect stain resistance of material⁴⁸⁸
- affect retroreflective properties of materials⁵²⁹
- affect blood compatibility^{472,530,558}
- affect environmental compatibility of product⁴⁷³
- determine health hazards, especially in medical and food applications^{473,536,558}
- affect performance of other additives⁵⁰⁷
- determine cost of product⁴⁸⁴
- help in material recycling⁵³⁷

The above list created on the basis of experimental findings and products development shows importance of plasticizers for the properties of materials manufactured from PVC. These effects are discussed in many parts of this book and their importance for some groups of products are discussed in Chapter 13. The above list may be frequently consulted to evaluate potential changes in material caused by plasticizer addition (also in the case of other polymers).

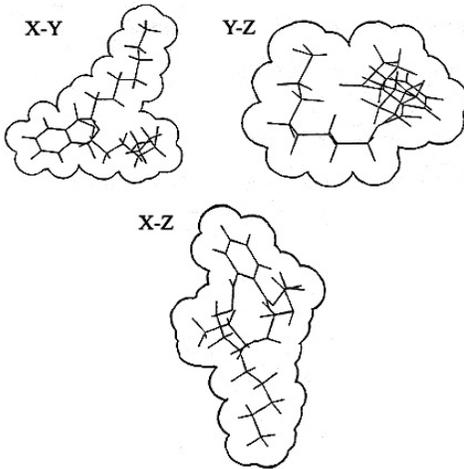


Figure 11.44. Projections of di-n-octyl phthalate molecule on different planes as labelled. Minimum energy conformation was calculated. [Adapted, by permission, from Coughlin C S, Mauritz K A, Storey R F, *Macromolecules*, **23**, 3187-31-92, 1990.]

$$y = 0.25717 + 0.0023476x \quad R = 0.996$$

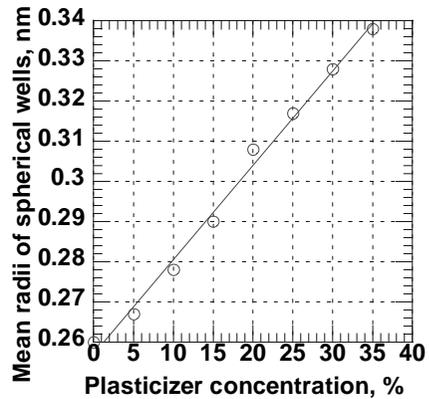


Figure 11.45. Mean radii of spherical wells for PVC plasticized with dioctyl phthalate vs. plasticizer concentration. [Data from Borek J; Osoba W, *J. Polym. Sci.: Polym. Phys. Ed.*, **34**, No.11, Aug.1996, p. 1903-6.]

11.44.4 MECHANISM OF PLASTICIZER ACTION

Incorporation of plasticizer in PVC system is expected to lead to an increased free volume. Experimental determination of free volume is very difficult as is to obtain temperature of absolute zero. Early developments searched for the reasons of free volume change and relationship between free volume and changes of chain mobility which parallel free volume changes. These findings suggest that free volume can be increased by:

- increase in temperature
- decrease in molecular weight (either low molecular polymer or additives (e.g., plasticizers))
- increase in chain mobility (more end groups, lower interaction between chains (e.g., low polarity, decreased hydrogen bonding))
- increase in hydrodynamic volume (e.g., numerous, long side chains)

Combination of these properties affects free volume.

The space occupied by a plasticizer depends on its molecular shape. The size of the plasticizer molecule affects free volume but also affects plasticizing efficiency, processing and permanence characteristics of materials through diffusion. Free volume increase brought about by plasticization is quantified in terms of the glass transition temperature, T_g , of polymer/plasticizer blend according to the following equation:

$$V_f = V[0.025 + \alpha_f(T - T_g)] \quad [11.4]$$

where:

- V_f average free volume in polymer
- V total volume of sample
- α_f thermal expansion coefficient
- T sample temperature
- T_g glass transition temperature.

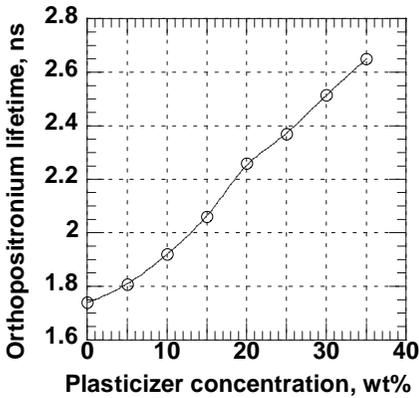


Figure 11.46. Orthopositronium lifetime for PVC plasticized with dioctyl phthalate vs. plasticizer concentration. [Data from Borek J; Osoba W, *J. Polym. Sci.: Polym. Phys. Ed.*, **34**, No.11, Aug.1996, p. 1903-6.]

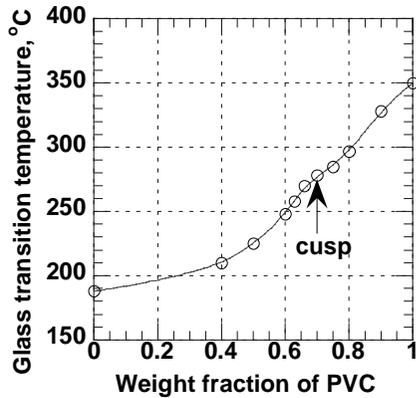


Figure 11.47. Glass transition temperature of PVC-di-(2-ethylhexyl) phthalate vs. weight fraction of PVC. [Data from Vilics T; Schneider H A; Manovicu V; Manovicu I, *Polymer*, **38**, No.8, 1997, p.1865-70.]

Glass transition temperature can be predicted from equation:

$$T_g = T_{g2} - kw_1 \quad [11.5]$$

where:

- T_g glass transition temperature of polymer-plasticizer(s) mixture
- T_{g2} glass transition temperature of unplasticized polymer
- k plasticizer efficiency parameter
- w_1 weight fraction of plasticizer.

Free volume depends on the size and the conformation of the plasticizer molecule. This can be analyzed by assuming a regular geometry and using the radius of the sphere occupied by a molecule of the plasticizer but this leads to substantial errors as can be seen from Figure 11.44.⁵⁶⁶ Real molecules are far from having a regular shape (each projection gives different total and free volumes).

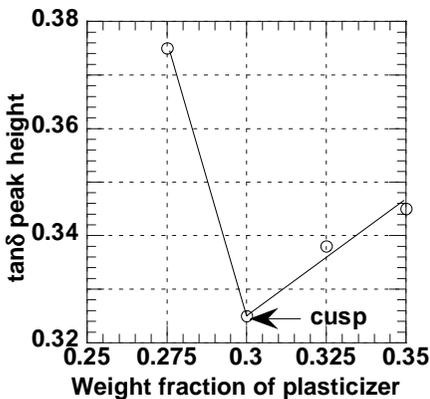


Figure 11.48. $\tan\delta$ of PVC-di-(2-ethylhexyl) phthalate vs. weight fraction of plasticizer. [Data from Vilics T; Schneider H A; Manovicu V; Manovicu I, *Polymer*, **38**, No.8, 1997, p.1865-70.]

Increased concentration of the plasticizer increases free volume as seen in Figure 11.45. The mean radius of the spherical well correlates with the free volume which has a linear correlation with the plasticizer concentration.⁵⁶⁷

Positron annihilation spectroscopy was employed to study the effect of plasticizer addition on free volume. The positronium atoms may form in amorphous regions of the polymer. In these regions, free volume exists if orthopositronium may live for several nanoseconds.⁵⁶⁷ The lifetime of the longest lived component, τ_3 , is attributed to the pick-

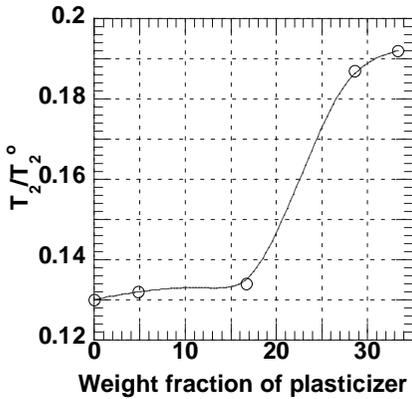


Figure 11.49. Spin-spin relaxation times of di-(2-ethylhexyl) phthalate in mixture with PVC, T_2 , and pure state, T_2^0 , vs. plasticizer concentration. [Adapted, by permission from Garnaik B; Sivaram S, *Macromolecules*, **29**, No.1, 1st Jan.1996, p.185-90.]

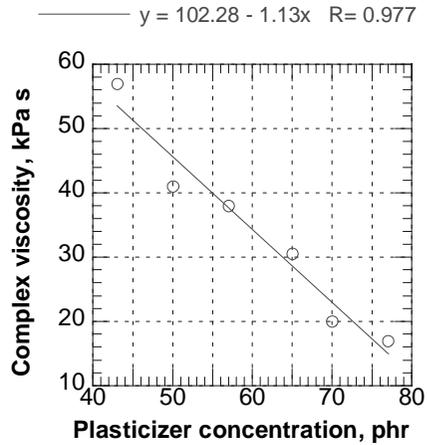


Figure 11.50. Complex viscosity of PVC plastisol at 140°C vs. concentration of di-(2-ethylhexyl) phthalate. [Data from Marcilla A; Garcia J C, *Eur. Polym. J.*, **33**, No.3, March 1997, p.357-63.]

off annihilation of orthopositronium. Figure 11.46 shows that the lifetime of the longest lived component, τ_3 , increases when the concentration of the plasticizer increases. The lifetime also approached several nanoseconds, thus free volume is increased.⁵⁶⁷

The glass transition temperature, T_g , is the other fundamental quantity related to plasticization. Equation 11.4 shows that T_g and free volume are related. Equation 11.5 assumes that there is a simple linear relationship between properties of a plasticizer, described by its efficiency parameter, k , and T_g . In reality, these functions are complex and non-linear.

Any equation based on additivity fails to correctly predict T_g of plasticizer-polymer mixtures because it neglects specific PVC-plasticizer interactions. Figure 11.47 shows that T_g versus plasticizer concentration curve appears discontinuous as if composed of two different curves: below and above a certain critical composition. The point of discontinuity is called “cusp”. Cusp was theoretically predicted⁵⁶⁸ by assuming that below the glass transition temperature of the critical blend the plasticizer does not contribute further to free volume changes of the mixture.⁵⁰⁹ Dynamic mechanical analysis also confirms the critical concentration of the plasticizer. On approaching the critical concentration, $\tan\delta$ curve peaks begun to flatten and broaden with increasing plasticizer content to sharpen again on further concentration increase. Figure 11.48 shows that the $\tan\delta$ peak has minimum value at cusp (30 wt% for di-(2-ethylhexyl) phthalate). It is suggested that the concentration at the cusp point corresponds to the maximum homogeneity of PVC-plasticizer blend.⁵⁰⁹

NMR studies bring still another contribution to the understanding of the plasticization mechanism of polyvinylchloride. The spin-spin relaxation time, T_2 , is sensitive to the low-frequency motions. It is useful in monitoring interactions between hydrogens in PVC chain and carbonyl groups of plasticizer. Figure 11.49 shows the relationship between the dimensionless values of T_2/T_2^0 and the plasticizer weight fraction.⁵²⁰ T_2 is the spin-spin

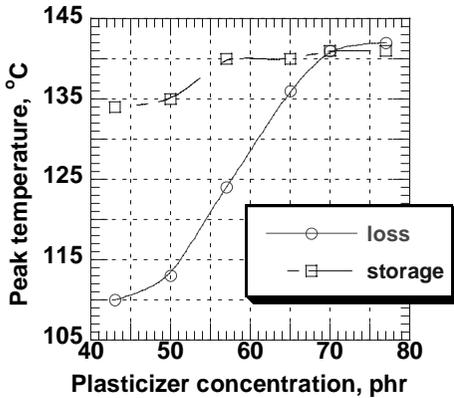


Figure 11.51. Peak temperatures of loss and storage moduli for various concentrations of di-(2-ethylhexyl) phthalate. [Data from Marcilla A; Garcia J C, *Eur. Polym. J.*, 33, No.3, March 1997, p.357-63.]

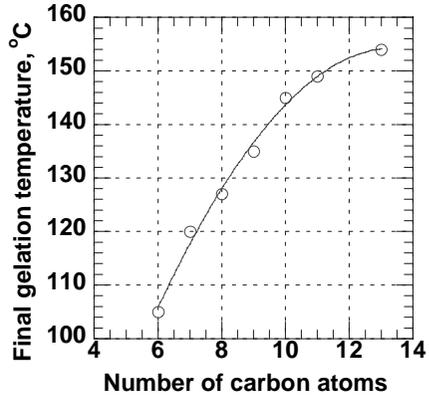


Figure 11.52. Final gelation temperatures of plastisols containing phthalates of alcohols having different lengths of hydrocarbon chains. [Data from Krauskopf L G; Godwin A D, *J. Vinyl Additive Technol.*, 5, No.2, June 1999, p.107-12.]

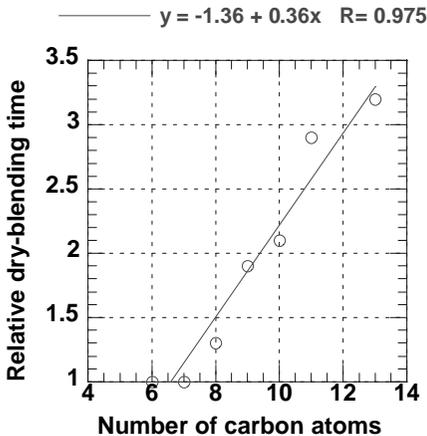


Figure 11.53. Relative dry-blending time for plastisols containing phthalates of alcohols having different lengths of hydrocarbon chains. [Data from Krauskopf L G; Godwin A D, *J. Vinyl Additive Technol.*, 5, No.2, June 1999, p.107-12.]

relaxation time of plasticizer in PVC/di-(2-ethylhexyl) phthalate (the same plasticizer as used in studies reported in Figures 11.47 and 11.48) mixture and T_2^0 is the spin-spin relaxation time for a pure plasticizer. Smaller additions of the plasticizer do not cause any change in ratio. Apparently the plasticizer is utilized for interaction with PVC and thus the mobility of plasticizer is reduced. Once a certain critical point is passed, the plasticizer mobility (and value of ratio) suddenly increases and it ultimately attains a constant value again after which further addition of the plasticizer may lead to an inhomogenous mixture of PVC and the plasticizer. These data seem to point to the same direction as the data discussed above.

11.44.5 EFFECT OF PLASTICIZERS ON POLYMER AND OTHER ADDITIVES

Chapter 9 contains a broad discussion of steps of plasticization with special attention to PVC. For this reason we only show a few examples of plasticizer influence. Figure 11.50 shows that increased concentration of the plasticizer reduces viscosity during the gelation process.

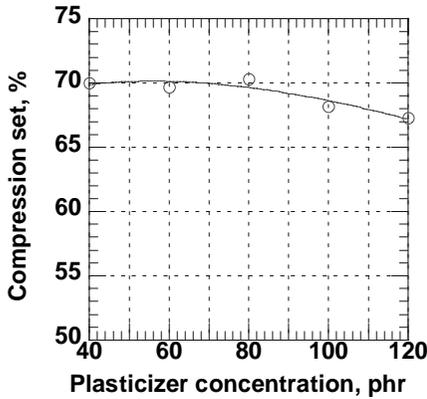


Figure 11.54. Compression set of PVC plasticized with variable amounts of didodecyl phthalate. [Data from Rehm T, *J. Vinyl Additive Technol.*, **3**, No.4, Dec.1997, p.286-91.]

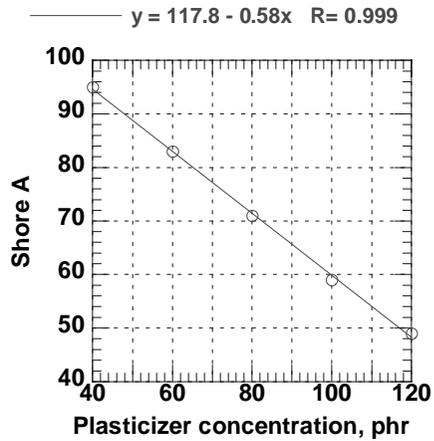


Figure 11.55. Shore A of PVC plasticized with variable amounts of didodecyl phthalate. [Data from Rehm T, *J. Vinyl Additive Technol.*, **3**, No.4, Dec.1997, p.286-91.]

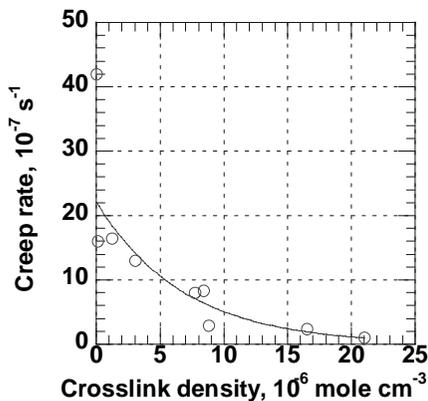


Figure 11.56. Creep rate of PVC plasticized with triallyl cyanurate vs. crosslink density. [Data from Horng-Jer Tai, *Polym. Eng. Sci.*, **41**, No.6, June 2001, p.998-1006.]

Figure 11.51 shows that there is a considerable difference in the peak temperatures of storage and loss moduli at different plasticizer concentrations.⁵⁰³ Both curves show that there is an increase in temperature of gelation when plasticizer concentration increases. This is because more plasticizer needs to be absorbed.

The temperature peak of loss modulus is mainly affected by fusion of PVC crystallites whereas storage modulus is affected by both fusion and gelation processes and thus temperature maxima are most likely to be different.⁵⁰³

Figure 11.52 shows that the higher the alcohol in the plasticizer the higher the temperature of gelation. It is not only the temperature increase but also dry-blending time (Figure 11.53), which is an important component of processing time and cost.⁴⁷⁸

During cooling, plasticized PVC regains its microcrystalline structure that is responsible for its high degree of elasticity.⁴⁹⁶ Figure 11.54 shows that plasticizer concentration has little effect on compression set of plasticized PVC. The higher melting fractions of the microcrystalline structure are responsible for excellent retention of shape by plasticized PVC.⁴⁹⁶ Mechanical properties change with concentration of the plasticizer. Figure 11.55 shows that Shore A linearly decreases with plasticizer concentration increasing.⁴⁹⁶ The effect of plasticizer on tensile strength is similar. At the same time the material becomes

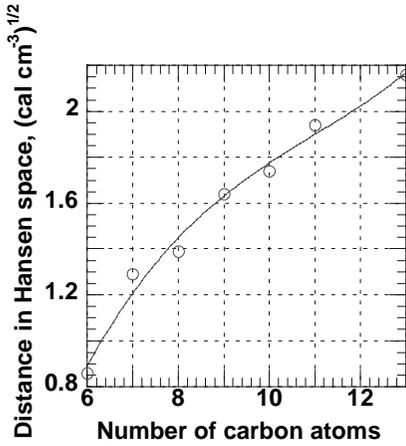


Figure 11.57. Distance in Hansen space for plasticizers containing phthalates having alcohols of different lengths of hydrocarbon chains. [Data from Krauskopf L G; Godwin A D, *J. Vinyl Additive Technol.*, 5, No.2, June 1999, p.107-12.]

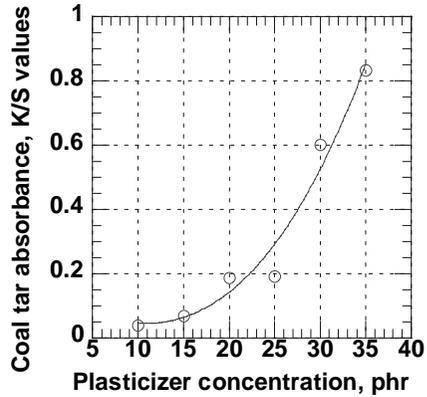


Figure 11.58. Absorbance of coal tar stainant versus concentration of di-(2-ethylhexyl) phthalate. [Data from Colletti T A; Renshaw J T; Schaefer R E, *J. Vinyl Additive Technol.*, 4, No.4, Dec.1998, p.233-9.]

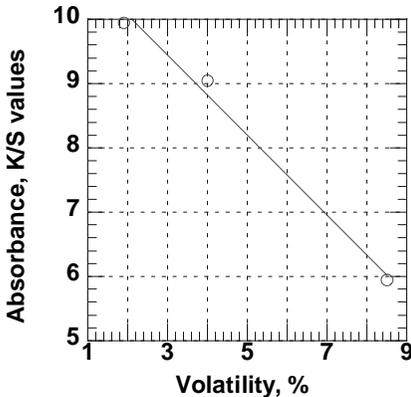


Figure 11.59. Absorbance of yellow dye stainant versus volatility of different plasticizers (diisononyl, di-(2-ethylhexyl), and diisooheptyl phthalates). [Data from Colletti T A; Renshaw J T; Schaefer R E, *J. Vinyl Additive Technol.*, 4, No.4, Dec.1998, p.233-9.]

more elastic and elongation adequately increases with an increased concentration of the plasticizer.

Microcrystalline properties of the plasticized PVC depend on the PVC type, plasticizer type and conditions of processing (heating and cooling temperatures and rates). These compositions and conditions may be varied to obtain required properties but there is a limit of how far creep and high temperature properties can be adjusted by formulation and processing characteristics. If lesser creep or stability of shape at elevated temperatures are required, then the polymer must be modified by the use of reactive plasticization. Figure 11.56 shows that the creep rate decreases with increased crosslink density caused by reactive plasticizer (triallyl cyanurate). The crosslinking increases the gel content and decreases the swell ratio.⁴⁵⁵ Similar results have been

obtained when trimethylpropane trimethacrylate was used as the reactive plasticizer.⁴⁷⁷ Due to formation of crosslinked network the material also withstands higher temperatures (lower creep at elevated temperatures).⁴⁷⁷

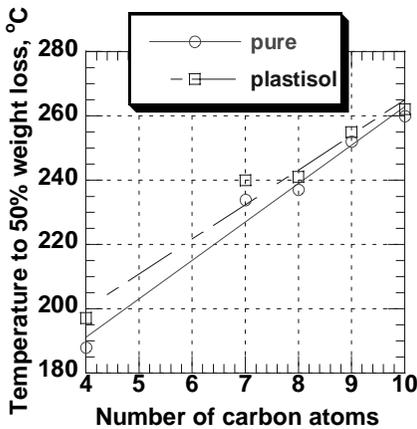


Figure 11.60. Temperature to 50% weight loss of pure and plastisol plasticizers having different number of atoms in alcohol part. [Data from Marcilla A; Beltran M, *Polym. Deg. Stab.*, **53**, No.2, 1996, p.261-8.]

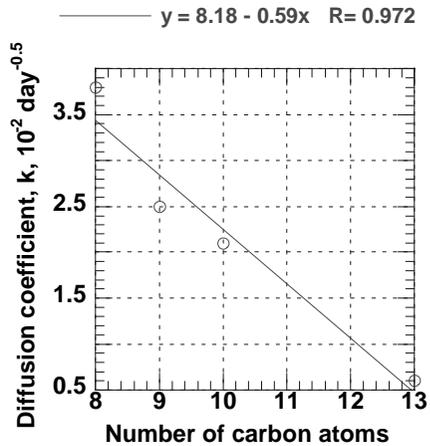


Figure 11.61. Diffusion coefficient for phthalates having different number of carbon atoms in alcohol part. [Data from Dedov A V; Bablyuk E B; Nazarov V G, *Polym. Sci. Ser. B*, **42**, Nos.5-6, May-June 2000, p.138-9.]

Introduction of a plasticizer causes separation of PVC chains relative to the concentration of the plasticizer (see Section 11.44.4 on discussion of the effect of plasticizer on free volume). Also the plasticizer type plays a role in this process. Figure 11.57 shows that the interaction radius of different plasticizers, expressed here by distance in Hansen space, increases with the size of the plasticizer molecule.⁴⁷⁸ Plasticizer concentration has similar effect on separation of chains and mobility of different molecules within the system. This modification of structure has implications on some properties discussed below.

Figure 11.58 shows that the plasticized PVC is stained more readily when the concentration of the plasticizer increases. It is interesting to note that only the amount of the plasticizer actually present in formulation affects staining. More volatile plasticizers escape more readily from plasticate and thus real concentration of the plasticizer in formulation is lower than if a less volatile plasticizer was used in spite of the fact that the same concentration of the plasticizer was initially added. Figure 11.59 shows absorbance of oil soluble dye for plasticizers having different volatility. The more volatile the plasticizer the higher its loss from the product during processing and the lower the staining.⁴⁸⁸ Figure 10.61 shows that staining characteristics of materials are a function of Small's solubility parameters of different plasticizers.

Volatility of pure plasticizers and the volatility of plasticizers in plasticized PVC differ (Figure 11.60).⁵¹⁵ Temperature of loss of a pure plasticizer is consistently lower than the temperature of plasticizer loss from plastisol. This is due to interaction between plasticizer and PVC chain. In order to remove the plasticizer from plastisol, additional energy is required to overcome the energy of hydrogen bonding. Compatibility between the plasticizer and the polymer also plays a role since small differences are recorded for higher molecular weight (less compatible) plasticizers.⁵¹⁵

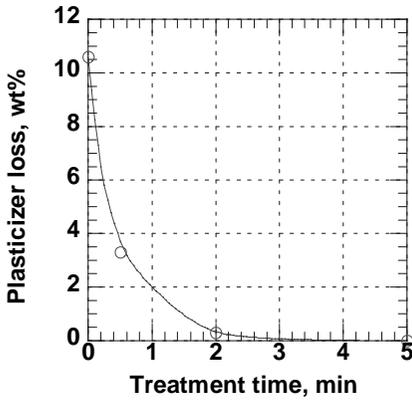


Figure 11.62. Plasticizer loss from PVC plasticized with 10 phr of epoxidized soybean oil and 40 phr of di-(2-ethylhexyl) phthalate and 40 phr of poly(ethylene-co-vinyl acetate-co-carbon monoxide). [Data from Audic J-L; Poncin-Epaillard F; Reyx D; Brosse J-C, *J. Appl. Polym. Sci.*, **79**, No.8, 22nd Feb.2001, p.1384-93.]

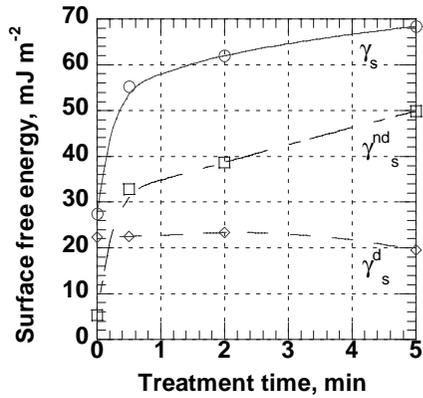


Figure 11.63. The effect of treatment time on surface free energy of PVC plasticized with 10 phr of epoxidized soybean oil and 40 phr of di-(2-ethylhexyl) phthalate and 40 phr of poly(ethylene-co-vinyl acetate-co-carbon monoxide). [Data from Audic J-L; Poncin-Epaillard F; Reyx D; Brosse J-C, *J. Appl. Polym. Sci.*, **79**, No.8, 22nd Feb.2001, p.1384-93.]

Figure 11.61 shows principles of diffusivity of plasticizers. Diffusion coefficient, k , comes from the following equation:

$$\frac{M_\tau}{M_0} = k\tau^d \quad [11.6]$$

where:

- M_τ amount of plasticizer which outdiffused from material in time τ ,
- M_0 initial concentration of plasticizer
- k, d coefficients (in data in Figure 11.61 $d=0.5$)

Several mathematical models have been proposed to quantify diffusion. The following relationship relates diffusion coefficient, k , with molecular weight of plasticizer, M :

$$\log k = 1 - 0.0062 M \quad [11.7]$$

The equation is only approximate but it shows, together with data in Figure 11.61, that diffusion of the plasticizer decreases with its molecular weight increase.

Plasticizer migration creates numerous problems in use of PVC articles. Plasticizers are known to migrate to food, blood, and pharmaceuticals.^{456,524} Production of multilayer materials from PVC having different compositions of layers also create problems because of plasticizer migration. It was found that 27 to 30% of initial contents of plasticizers in formulations containing 48 to 100 phr migrates to the rigid PVC.⁵²⁴ This precludes feasibility of design based on required performance (e.g., surface layers of floor covering benefit from low concentration of plasticizers which will reduce staining and mechanical wear whereas core layers benefit from larger concentrations of plasticizers which improve flexibility and damping characteristics).

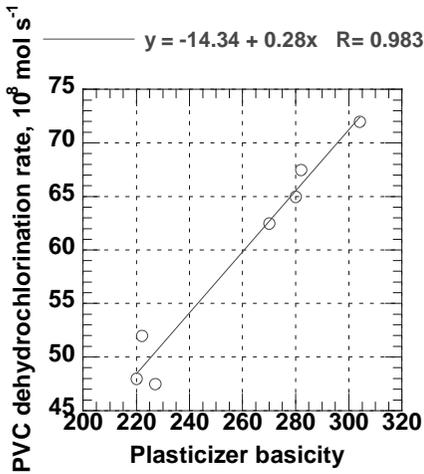


Figure 11.64. PVC dehydrochlorination rate vs. plasticizer basicity. [Data from Minsker K S, *Intl. J. Polym. Mater.*, 33, Nos.3-4, 1996, p.189-97.]

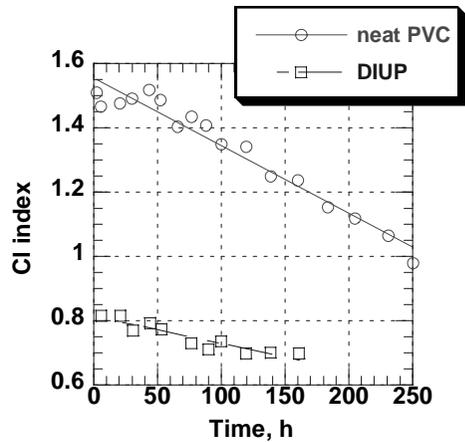


Figure 11.65. Cl index of neat PVC and PVC plasticized with diisoundecyl phthalate vs. time of exposure to 290 nm in the presence of air. [Data from Balabanovich A I; Denizligil S; Schnabel W, *J. Vinyl Additive Technol.*, 3, No.1, March 1997, p.42-52.]

Plasma treatment is currently exploited as a potential solution to migration problem. The action of plasma changes surface functional groups, surface wettability, and causes formation of crosslinks in surface layers. Several cold plasma treatments have been applied to PVC plasticized by di-(2-ethylhexyl) phthalate.⁴⁵⁶ The best results have been obtained with argon plasma treatment. Figure 11.62 shows that the plasticizer does not migrate when treatment is sufficiently long. The effect observed was explained by the changes in wettability (Figure 11.63) and the effect of elastomeric copolymer – both suppressing plasticizer migration. The surface free energy, γ_s , and its non-disperse term, γ_s^{nd} , increase along with the duration of treatment whereas the disperse energy, γ_s^{d} , remains practically constant.

It may not be frequently appreciated that the loss of plasticizer by either migration or evaporation leads to shrinkage. The approximate shrinkage (or change of dimensions can be calculated from equations):⁵¹⁴

$$\frac{\Delta L_{\text{GM}}}{L_{\text{GM}0}} \approx \frac{P_L}{7} \quad [11.8]$$

$$P_L = \frac{C_{P0} - C_p}{C_{P0}(1 - C_p)} \quad [11.9]$$

where:

ΔL_{GM}	change in dimension [m]
$L_{\text{GM}0}$	dimension before plasticizer loss [m]
P_L	plasticizer loss ratio [dimensionless]
C_{P0}	plasticizer fraction before shrinkage [dimensionless]
C_p	plasticizer fraction after shrinkage [dimensionless]

Equation [11.8] shows that shrinkage depends on the initial plasticizer content and its loss. The relationship is based on some simplifications such as uniform distribution of plasticizer during its loss (in reality there is a gradient of plasticizer concentration; less plasticizer on the surface) and isotropy of material (in reality materials have different properties along with their length and thickness, such as orientation, crystallinity, and many related properties). On the other hand these simplifications do not change the general character of a relationship between a plasticizer loss and shrinkage.

Basicity of plasticizer impacts thermal dehydrochlorination rate of PVC degradation (Figure 11.64). Studies on PVC cables from laboratory samples and materials collected from field applications after 34 years of service show that there is very little change in properties and plasticizer concentrations. Cables plasticized with chloroparaffin and DOP lost only 4% of initial plasticizer after 4 weeks of aging at 100°C.⁴⁶⁹ This shows that thermal degradation of PVC is likely to affect product performance during the production stage but not during its use.

Plasticizers may protect PVC from UV degradation. Figure 11.65 shows that addition of diisoundecyl phthalate protects C-Cl bond from dissociation.⁵⁰⁶ Also, carbonyl group formation is reduced in the presence of plasticizers.

11.44.6 TYPICAL FORMULATIONS

Electrical grade PVC:⁴⁸⁷

PVC	100 parts
Diisodecyl phthalate	55
Stearic acid	0.5
Calcium carbonate	20
Clay (Glomax LL)	10
Barium stearate	3
Zinc stearate	0.5
BTH antioxidant	1
Diphenyl isodecyl phosphite	1
Titanium dioxide	2
Barium oxide	0.5

All raw materials must be of electrical grade quality (low ionic content)

Low odor permeability hose:⁴⁶⁷

PVC	100 parts
BaZn stabilizer	2.5
Calcium carbonate	25
EVA polymer	70
DOP	15
Stearic acid	0.25
Titanium dioxide	3

Formulation has low solubility of carbon disulfide

Composition for medical containers:⁵³⁰

PVC	59 wt%
Vitamin E	12

n-butyryl tri-n-hexyl citrate	6
Tri-(2-ethylhexyl) trimellitate	13.8
Epoxol 9-5	9
Calcium zinc stabilizer (CZ-11)	0.1
Acrawax	0.1
The presence of vitamin E and selected plasticizers suppresses hemolysis of red blood cells	

Food contact and medical applications:⁵³⁶

PVC	100 parts
Di-(2-ethylhexyl adipate)	16
Epoxidized soybean oil	10
Ethoxylated nonylphenol (antifogging agent)	4
Wax E	0.2
Dilauryl 3,3'-thiodipropionate	0.7
Zn stearate	0.2
BHT	0.1

Biocompatible material for blood lines with irradiation resistance:⁵⁴⁸

PVC	65 wt%
Diocetyl adipate	31
Epoxidized soybean oil	2.9
CaZn stabilizer	1
Lubricant	0.1
Product can be subjected to radiation sterilization	

Flame retardant composition:⁵³¹

PVC	100 parts
DOP	20
Di-2-ethylhexyl tetrabromophthalate	10
Sb ₂ O ₃	5
Tin stabilizer	3
The formulation has LOI=33.5	

Flame retarded composition of high performance:⁵³⁵

PVC	100 parts
Sb ₂ O ₃	15
Triocetyl trimellitate	34.3
Lead stabilizer	5
Diocetyl tetrabromophthalate	30
Diocetyl tetrachlorophthalate	10
Formulation for cable and wire has LOI=37, low smoke (276) and good low temperature properties	

Compatibilized blend of polymers of high thermal stability:⁵³²

PVC	100 parts
DOP	80
BaZn heat stabilizer	5.91
Epoxidized soybean oil	9.84
Stearic acid	0.39
Zinc stearate	0.39
Antioxidant	0.28
Chlorinated polyethylene	55.96
Ethylene 1-octene copolymer	28.12

Composition containing nitrile rubber:⁵³⁸

PVC	100 parts
Diundecyl phthalate	137.29
Crosslinked nitrile rubber	107.14
Heat stabilizer	7.91
Antioxidant (Irganox 1010)	0.56
Co-stabilizer (Irgafos 168)	0.56
Stearic acid	0.28
Processing aid (K-175)	3.39

The formulation has oil resistance, good low temperature, smoke suppressing and char forming properties

Formulation for lamination of safety glass:⁵³⁹

PVC	100 parts
Dioctyl adipate	50
Epoxidized soybean oil	5
BaZn stabilizer (UZB 793)	3
Perchlorate stabilizer (CPL 46)	0.2
Antioxidant (Irganox 1010)	1
UV absorber (Tinuvin 328)	0.2

Formulation provides impact energy dissipation properties, and long-term service use stability

Laminated glazing unit interlayer:⁵⁴⁷

PVC	100 parts
Dihexyl azelate	55
Perchlorate stabilizer (#5377)	0.1
UV absorber (Tinuvin 328)	0.5
BaZn stabilizer (L-1960)	1.5
BaZn stabilizer (KP-11)	0.5

The formulation is capable to eliminate UV radiation between 300 and 340 nm

Sound attenuation composite:⁵⁶³

PVC (Geon 178)	12.19 wt%
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PVC (Formolon 40)	2.44
Barium sulfate	61.57
Microspheres (K-1)	1.27
Hydrated alumina (ATH 204)	1.47
Mineral spirits	2.68
Plasticizer (H-150)	9.6
Heat stabilizer (Thermchek 1776)	0.47
Heat stabilizer (Thermchek 904)	0.15
Pigment paste	0.99
Flammability additive (Thermoguard CPA)	0.73
Flame retardant (Frysol CEF)	1.49
Surfactant (Triton 114)	1.07
Compatibilizer (Desical)	0.44
Froth stabilizer (Silicone DC 1250)	3.47

Impact resistant coating:⁵⁶⁴

PVC	20-30 wt%
VC-VA copolymer	10-20
Calcium carbonate	15-20
Hollow plastic spheres	0.3-0.4
Phthalic ester of C ₉ or higher alcohol	30-40

11.45 POLYVINYLIDENEFLUORIDE

11.45.1 FREQUENTLY USED PLASTICIZERS

- dibutyl sebacate in the inner sheath of a flexible oil pipe⁵⁶⁹
- adipic polyester in a porous membrane⁵⁷⁰
- glyceryl tributyrate⁵⁷¹
- tricresyl phosphate⁵⁷²
- dibutyl phthalate^{574,575}

11.45.2 PRACTICAL CONCENTRATIONS

- 5 to 10 wt% of tricresyl phosphate⁵⁷²
- 10 wt% dibutyl sebacate⁵⁶⁹
- 15 phr of dibutyl phthalate⁵⁷⁵
- up to 46 wt% of dibutyl phthalate⁵⁷⁴
- 50 to 117 phr of adipic polyester⁵⁷⁰

11.45.3 MAIN FUNCTIONS PERFORMED BY PLASTICIZERS

- creation of the porous structure by extraction of plasticizer from a membrane⁵⁷⁰
- formation of gels^{571,574}
- enhancing piezoelectric activity⁵⁷²
- helping in a crystal perfection⁵⁷²
- assisting in obtaining the most polar polymorph^{572,574}
- improvement in the ferroelectric switching⁵⁷²
- formation of the polymer electrolytes⁵⁷⁵

11.46 POLYVINYLIDENECHLORIDE

Packaging films with controlled transmission of CO₂ and O₂ are produced from plasticized polyvinylidenechloride, PVCD. This film is very suitable for packaging of gassing cheese.⁵⁷⁶ The film contains 8 to 10 wt% plasticizer selected from the following group: polymeric condensation product of azelaic acid and 1,3-butanediol, polymeric plasticizer of adipic acid and propylene glycol, epoxidized soybean oil, or acetyl tri-*n*-butyl citrate. The film formulations are so designed that CO₂ permeability increases and O₂ permeability possibly remains the same.^{576,579}

Packaging film from plasticized PVCD has improved thermal stability and reduced stickiness to metal surfaces when only 2 wt% of epoxidized soybean oil is added as a plasticizer. In addition, the metal soaps of ricinoleic acid are added. They also act as plasticizers.⁵⁷⁷ The addition of 1 to 4 wt% tetraethylene glycol di-(2-ethylhexoate) is expected to reduce oxygen transmission rates and to improve extrudability of film.⁵⁷⁸

11.47 POLYURETHANES

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Plasticizers are blended with polyurethanes, PU, to regulate their rheological, thermal, and mechanical properties.⁵⁸⁰⁻⁵⁸⁴ Plasticizers are used in PU synthesis to lower viscosity of reaction medium and to dissolve reaction components (e.g., aromatic diamines).⁵⁸⁵⁻⁵⁸⁷

This section includes the following: mechanism of the specific actions of plasticizers on the PU, the analysis of material properties affected by plasticizers, description of chemically inert liquids applied as PU plasticizers, and discussion of selection principles of plasticizers for the segmented polyurethanes.

The special attention is given to the mechanism of plasticizers action in segmented polyurethanes and perspectives of plasticizers application for regulating properties of polyurethane compositions.

11.47.1 THE MECHANISM OF THE SPECIFIC ACTION OF PLASTICIZERS AND ITS EFFECT ON POLYURETHANES PROPERTIES

The common structural feature of PUs is their block structure. These PUs are called segmented polyurethanes, SPU.⁵⁸⁸ The SPU polymer chains consist of alternating hard and soft blocks (segments) of different polarity. The hard blocks form as a result of diisocyanate reaction with a low molecular mass diols, diamines, and other low molecular mass bifunctional substances.⁵⁸² The molecular structure of soft segment is determined by the chemical structure of oligomers used in the SPU synthesis.

Many properties of such materials have been related to their microheterogeneous structure caused by microphase separation of hard and soft blocks in SPU as discovered by Cooper and Tobolsky. The distribution of hydrogen bonds of different types in domains and outside of the domains of hard blocks (in the soft phase)⁵⁸³ and van der Waals forces play an important role in formation of SPU properties. The extent to which these factors

affect SPU properties (including the microphase separation) depends on their chemical structure and also on a ratio of hard to soft blocks in a material.

The change of PU properties as a result of the plasticization process does not always correspond to the well-known views on the plasticization pattern, which were developed based on investigations of plasticized polymers having a uniform chemical structure of soft and hard phases (for example, PVC and esters of cellulose). In fact, the traditional views on plasticization of polymers are not suitable for explanation of many effects observed by blending different plasticizers in polyurethane material. This behavior can be demonstrated on an example of segmented polyether-urethane-ureas. Their initial structure and properties (without plasticizers) are widely investigated.

We used SPU synthesized on the base of prepolymer of tetramethylene oxide diol (molecular mass $M=1300$) obtained by interaction of appropriate diol ($M=1000$) with a double excess of 2,4-toluylene diisocyanate. This prepolymer was cured by melted methylene-bis-(*ortho*-chloraniline) (MOCA). The plasticizers have been so chosen that they are compounds capable to completely destroy the domains of hard blocks. Tributyl phosphate, TBP,⁵⁸⁴ is such a plasticizer. Also, plasticizer poorly influencing the self-association of urethane-urea hard blocks in SPU, such as di-(2-ethylhexyl) phthalate, DOP, was used.

Considering existing reference data, such as the glass transition temperatures of SPU samples and plasticizers, and the experimental results on an equilibrium swelling, Q , of initial (non-plasticized) SPU samples, the following compounds have been taken as SPU plasticizers: TBP, tricresyl phosphate, TCP, dibutylcarbitolformal, DBCF, DOP, and dioctyl adipate, DOA.

The procedure of PU synthesis included the preliminary mixing of melted MOCA with plasticizer. All selected plasticizers having properties of proton acceptors dissolve MOCA. The solution was mixed with prepolymer for 5 minutes at 55°C and residual pressure 3-5 kPa. The reaction mixture was cured in metal forms for 4 days at 80±1°C. The samples have been kept at room temperature for not less than 15 days before testing.

The mechanical characteristics of SPU – tensile strength, σ_k , (the maximum stress calculated on the initial cross-section area) and the relative critical deformation, ϵ_c , (relative deformation at the stress σ_k) have been evaluated for the strain rate, $v = 0.28 \text{ s}^{-1}$. The mechanical modulus, E_0 , was evaluated from the initial, linear part of the strain diagrams.

The glass transition temperature of plasticized SPUs was measured by the differential scanning calorimetry method, DSC, using differential scanning microcalorimeter DSM-2 at the scanning rate 1°C per min.

Molecular structure of initial and plasticized materials was studied by the IR-spectroscopy using an IFS66/S Fourier-transform spectrometer (Brüker Corporation). SPU films have been prepared without use of volatile solvents. The reaction mixture was cured at 80±1°C between glasses preliminary covered with 2x10⁻⁵ m thick Teflon-4 films. As it was shown earlier, this anti-adhesive film does not affect the spectral regions under study. The band of amide-I, characteristic for carbonyl group vibrations was used as an analytical band (the wavenumber range was $\nu = 1620 - 1750 \text{ cm}^{-1}$). The plasticizer densities have been evaluated with the densitometer VIP-2 (precision 1 kg/m³).

It follows from the data given in Table 11.1 that TBP shows the lowest value of the glass transition temperature (-131°C) among plasticizers under examination, and TCP shows the highest temperature (-63°C). The glass transition temperature of the soft phase

of initial non-plasticized SPU samples is -54°C . The data also show that a set of plasticizers used in the experiment permit to vary their glass transition temperature over a wide range: beginning from -63°C , close to the glass transition temperature of the soft phase of a non-plasticized SPU (-54°C), up to -131°C a value that is 77 degrees lower than the glass transition temperature of a soft phase of polymer.

Values of the glass transition temperature of plasticizers obtained by the DSC method at a low heating rate differ a little (approximately 2-4 degrees) from the reference data that have been obtained at heating rates 10 times faster than used in our experiments. This is also true for the SPU glass transition temperature. Under the heating rate of about 0.17°C per sec., the glass transition temperature of SPU of the same structure (as it was in our experiments) is as much as -52°C . The small difference in value, estimated under various conditions, is due to the relaxation character of the glass transition processes.

Results of swelling experiments conducted with SPU samples (Tables 11.1 and 11.2) show that the increase of a plasticizer concentration, C_0 , in samples during synthesis results in the increase of equilibrium swelling in this plasticizer and increase in the equilibrium concentration of a plasticizer, C_e , in the swollen samples. The data give a ground to supposition that in the investigated range of concentrations C_e , the plasticizer is distributed in SPU on the molecular level.

Table 11.1 Properties of plasticizers and equilibrium swelling of plasticized SPU samples at $25 \pm 0.20^{\circ}\text{C}$

Plasticizer	Chemical structure	ρ , kg m^{-3}	V_1 , $\text{m}^3 \text{kmol}^{-1}$	T_g , $^{\circ}\text{C}$	Q
TCP	$\text{OP}(\text{OC}_6\text{H}_4\text{CH}_3)_3$	1170	0.315	-62	0.39
TBP	$\text{OP}(\text{OC}_4\text{H}_9)_3$	973	0.273	-131	4.30
DOP	$\text{C}_6\text{H}_4(\text{COOC}_8\text{H}_{17})_2$	974	0.400	-91	0.10
DOA	$\text{C}_4\text{H}_8(\text{COOC}_8\text{H}_{17})_2$	922	0.400	-106	0.15
DBCF	$\text{CH}_2(\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OC}_4\text{H}_9)_2$	976	0.344	-107	0.28

Table 11.2 Equilibrium swelling, Q, and plasticizer concentration, C_e , in SPU samples made with different initial plasticizer concentrations and swollen at 25°C

C_0 , %	DOP		DOA		DBCF		TCP		TBP	
	Q	C_e , %								
0	0.1	9	0.15	13	0.28	22	0.39	28	4.30	81
7	0.16	14			0.32	24			4.49	82
8	0.16	14	0.17	15					4.67	82
12			0.20	17			0.47	32		
14	0.22	18			0.39	38			5.26	84
16			0.25	20						
22	0.34	25					0.67	40	6.15	86
25			0.37	27						
30	0.47	32			0.55	35	0.87	47	7.32	88

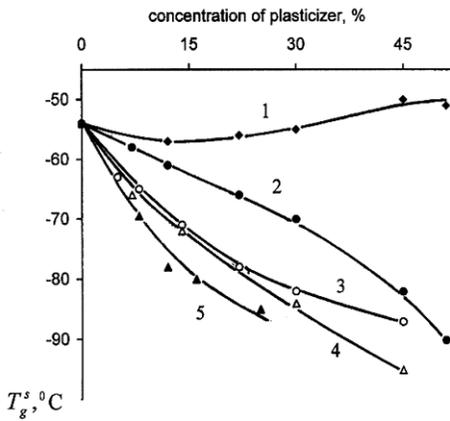


Figure 11.66. Dependence of the glass transition temperature of the soft phase of SPU on the concentration of TCP (1), TBP (2), DOP (3), DBCF (4), and DOA (5).

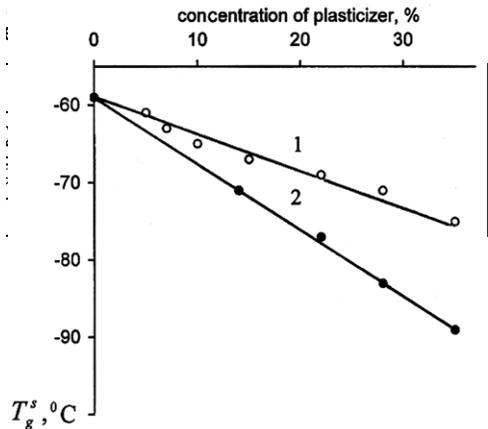


Figure 11.67. Dependence of the glass transition temperature of the homopolyurethane flexible chains on the concentration of DOP (1) and TBP (2).

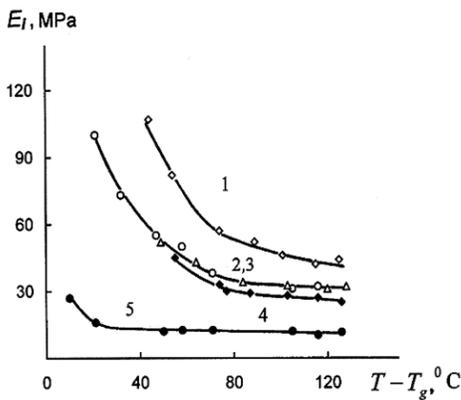


Figure 11.68. Dependence of the initial modulus, E_i , on the $(T - T_g^s)$ value for the SPU initial samples (1) and for samples with 30% plasticizer: DOP (2), DBCF (3), TCP (4) and TBP (5).

Figure 11.66 shows the dependence of the glass transition temperature, T_g^s , of the SPU soft phase on the plasticizer concentration. It follows from the comparison of the experimental data that the lowest T_g^s value is typical of SPU samples plasticized by DOA (the glass transition temperature equals -106°C). The glass transition temperature of TBP is 40 degrees lower than that of DOP (Table 11.1), but T_g^s value of samples plasticized by DOP is significantly lower than that of the samples plasticized by TBP (a concentration of both plasticizers in SPU was the same). Consequently there must be additional factors influencing the T_g^s value of the soft SPU phase.

Different data have been found for the homopolyurethane samples when tetramethylene oxide diol having $M = 1,000$ was used as the curative instead of aromatic diamine MOCA. As a result of such replacement, the elastomer lacks of the microdispersed hard phase. The glass transition temperature, T_g , of the homopolyurethane samples, plasticized with TBP, is significantly lower than T_g of the samples plasticized by DOP (Figure 11.67). This agrees with the traditional concept of the polymer plasticization. Decrease in the glass transition temperature of plasticizer and increase in its thermodynamic compatibility with polymer should, indeed, result in lowering the glass transition temperature of soft segments of plasticized material.

The traditional views on plasticization of polymers are based on results of studying the single phase polymer systems and microheterogeneous polymers which have the same chemical structures of hard and soft phases.

With respect to the classical theory of plasticization the thermal behavior of the segmented polymers is anomalous. A vivid example of this is not only the major difference between the degree of influence of DOP and TBP on T_g^s value of the SPU soft phase and on T_g^s value of homopolyurethane. At the larger concentration of TCP in SPU, T_g^s of the soft phase of the plasticized samples is higher than that of the soft phase of initial samples (Figure 11.66), even though the glass transition temperature of TCP is 9 degrees lower than T_g^s of the plasticized elastomer (Table 11.1). Within the framework of traditional view of the mechanism of polymers plasticization this observation does not have any reasonable explanation.

The "anomalies" in the mechanical behavior of plasticized SPU samples reveal the dependence of the mechanical modulus, E_i , calculated from the initial linear part of the strain curve (Figure 11.68) on the difference between the temperature of experiment, T , and T_g^s of the polymer soft phase ($T - T_g^s$). For example, the higher the glass transition temperature of a sample (the sample with TBP) the smaller the E_i value. On the contrary, the SPU samples plasticized by DOP or DBCF having lower glass transition temperatures show greater values of modulus E_i . The dependences of E_i and ($T - T_g$) for samples containing 30% DOP or DBCF are practically the same in a wide temperature interval. But when the differences ($T - T_g$) are equal, the modulus of the samples plasticized by TBP is several times less than that of samples plasticized by DOP or DBCF.

Thus, the value of decrease in the glass transition temperature of the elastomer's soft phase is not a unique criterion for efficiency of polyurethane block-copolymers plasticization. Similar results have been derived from the study of properties of SPU synthesized on the base of propylene oxide diol.

The observed anomalies in the character of change in the glass transition temperature of a soft phase of polyurethane block copolymers during plasticization and mechanical behavior of such materials can be explained if it is considered that the chemical structure of soft phase and hydrogen bonds distribution may significantly change.

The changes in SPU soft phase during plasticization can be observed by IR analysis of samples with different plasticizers. IR spectra of SPU samples plasticized by TBP, TCP, and DBCF in the wavenumber range from 1620 to 1750 cm^{-1} (amide I) are shown in Figure 11.69. For the convenience of comprehensive analysis these spectra are presented so that every SPU film (the spectrum of which is given in the Figure 11.69) contains the same quantity of carbonyl groups of urethane and urea groups per unit of a gel volume without a plasticizer. MOCA concentration in the reaction mixture without considering a plasticizer for samples differs by no more than 2% of the MOCA mass. This permits the use of the band $\nu=1577 \text{ cm}^{-1}$ as an internal standard. This band is characteristic for vibrations of CH groups of MOCA aromatic ring after its reaction with isocyanate group of prepolymer.

The absorption band at $\nu=1639 \text{ cm}^{-1}$ is known to correspond to the most ordered structures – self-associates of urea groups in urethane-urea domains of hard blocks. From comparison of spectra of the initial and plasticized samples it becomes evident that the intensity of this band practically does not change in a wide range of DBCF concentrations in SPU. Consequently, DBCF does not essentially affect the formation of the ordered asso-

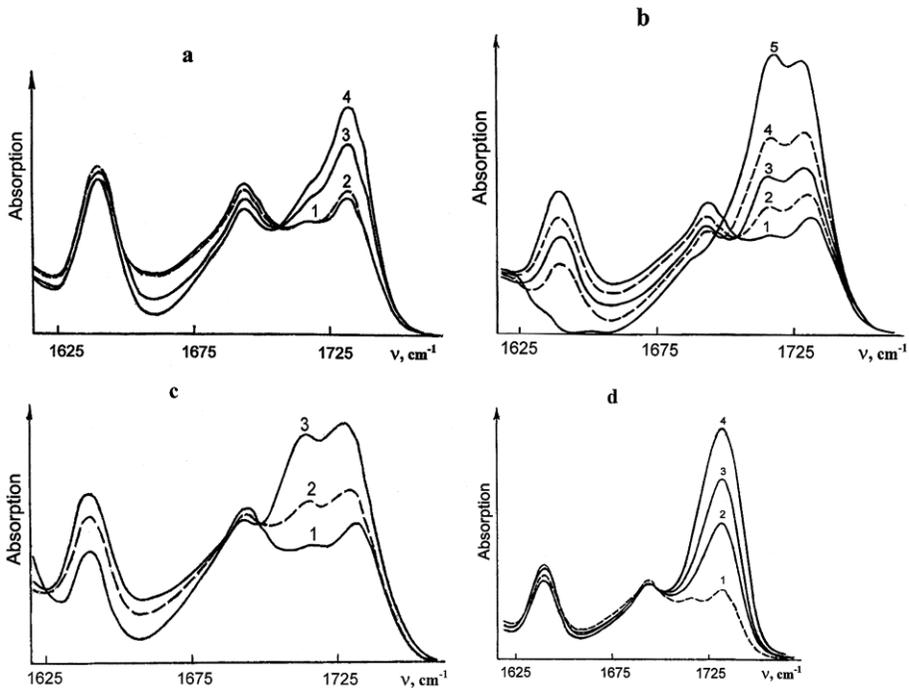


Figure 11.69. IR-spectra of the initial SPU samples (1) and of the plasticized samples: a - DBCF (2 - 7, 3 - 30, 4 - 45%); b - TBP (2 - 12, 3 - 22, 4 - 30, 5 - 45%); c - TCP (2 - 30, 3 - 51%); d - DOP (2 - 14, 3 - 22, 4 - 30, 5 - 45%).

ciates of the urethane-urea hard blocks that are the basis of hard domains forming a microdispersion hard phase in polymer. The experiments showed the same for DOP and DOA (Figure 11.69). Plasticization by TBP reduces the intensity of this band even at small plasticizer concentrations. At the plasticizer content of about 45% this band disappears. This suggests the absence of hard block aggregates and, hence, the absence of the microdispersion hard phase in polymer. The increase in the TBP content in SPU causes the reduction of the amount of the microdispersion hard phase. All plasticized polymer system is a single soft phase already at 45% TBP in the material.

TCP holds an intermediate place in respect of its influence on the formation of microdispersion hard phase in SPU. At 30% of TCP in a material the slight decrease in intensity of $\nu=1639\text{ cm}^{-1}$ band becomes noticeable. At 55% of TCP, the intensity of this band reduces approximately 2 times (it is possible to determine it more precisely by separation of the amide 1 band into its components). Decreased content of the microdispersion hard phase in the material is a result of the plasticizer influence on the hard blocks solubility in the plasticized soft phase.

Thus, there are two essentially distinguished variants of plasticization of polyurethane block-copolymers: the first one – when the chemical structure of polymer chains of the soft phase practically does not change, and the second one, when the solubility of hard blocks of the soft phase increases and its chemical structure changes.

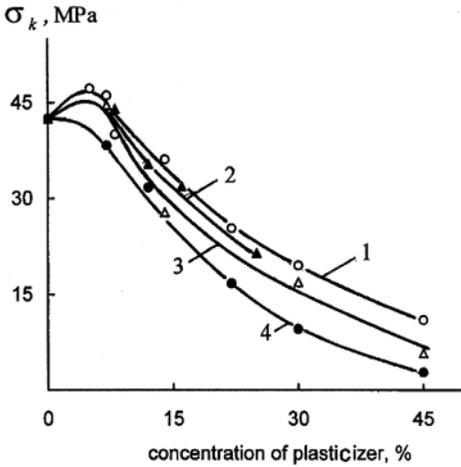


Figure 11.70. Dependence of tensile strength of SPU on the concentration of DOP (1), DOA (2), DBCF (3), and TBP (4).

the SPU soft phase when plasticized by TBP, if compared with SPU plasticized by DBCF, DOP, or DOA. This anomaly disappears with plasticization of homopolyurethane, in which there are no conditions for formation of microdispersion hard phase.

Depending on the temperatures difference ($T - T_g$) and the modulus E_i of plasticized block copolymer samples, the anomalies are related to the dissimilar influence of plasticizers on formation of a microheterogeneous structure. This becomes distinctly evident from IR-spectra (Figure 11.69). An essential decrease in the amount of microdispersion filler in SPU, even at 30% of TBP ($\nu = 1639 \text{ cm}^{-1}$ band intensity decreases approximately 2 times) results in a sharp decrease of E_i (compared with that of samples containing 30% DBCF or DOP). The change in the structure of soft polymer matrix on plasticization by TBP (an increase in amount of hard blocks and hydrogen bonds) is one more factor promoting the occurrence of different E_i values for samples plasticized by DBCF (or DOP) at the equal differences between the experiment temperature, T , and the glass transition temperature, T_g , of the soft phase. Specific effect of plasticizers on the thermal and elastic properties of polyurethanes is related to the dissimilar influence of plasticizers of different chemical structure on the hard blocks solubility. As the amount of the dissolved hard blocks in the soft phase increases, the volume fraction of a hard component and the amount of the proton acceptor groups capable to form H-bonds in this system rises, as well. The action of the mentioned factors on the thermal properties of material is in contradiction to the action of the plasticization effect of a soft phase when chemical structure is constant. The decrease in the amount of a filler – a microdispersion hard phase, causes reduction in the initial modulus of polymer. As a result, the material of a greater glass transition temperature of the soft phase has a lower modulus value. The glass transition temperature of polyurethane block copolymers, which is plasticized by various liquids, is not the unique criterion of efficiency of segmented polyurethanes plasticization.

An influence of plasticizers on the strength of polyurethane block-copolymers depends on some factors such as an influence of plasticizers on the microphase separation

A partial or complete dissolution of the urethane-urea hard blocks of a high glass transition temperature ($T_g \sim 200^\circ\text{C}$) in the SPU soft phase promotes increase in the glass transition temperature of the soft phase of a material. The presence of urethane and urea groups capable of forming H-bonds affects this temperature in a similar way. The amount of these groups in a soft phase rises with increase in the mixability of soft and hard segments of a block-copolymer.

The existence of the cited structural factors inducing an increase in the glass transition temperature of a soft polymeric matrix is the reason for an abnormal change in value of the material plasticized by TCP and the reason for a lesser decrease in T_g^s of

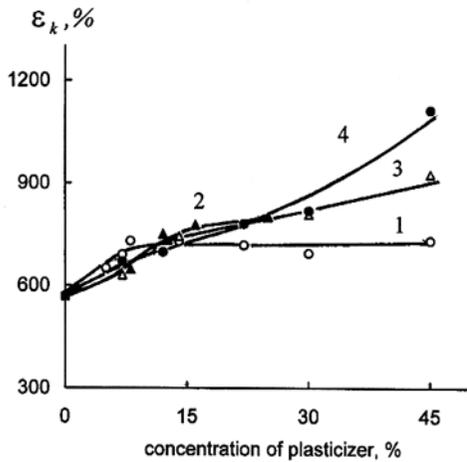


Figure 11.71. Dependence of relative critical elongation of samples on the concentration of DOP (1), DOA (2), DBCF (3), and TBP (4).

the amount of these bonds decreases as a result of specific interactions of plasticizer – a proton-acceptor, with the groups of proton donors in polymer chains. For instance, an increase in the intensity of $\nu=1717$ and $\nu=1732$ cm^{-1} bands in spectra of SPU plasticized by DBCF and esters: TBP and TCP. These bands are referred to as absorption by carbonyl moiety of urethane groups hydrogen bonded with the ether oxygen.^{598,599} As the plasticizer content rises, the relative critical deformation, ϵ_k , of SPU samples (the relative deformation at $\sigma=\sigma_k$) regularly increases. It is strongly demonstrated by TBP plasticization (Figure 11.71).

The ϵ_k values of SPU samples over the wide range of plasticizer's concentrations are not lower than these of the initial non-plasticized samples. Calculations of a rupture stress, f_p , on stretching of the plasticized samples (the stress calculated on the true cross-section area of a sample; $f_p = \sigma_k(\epsilon_k + 100)/100$) shows that at 30% plasticizer content the f_p value is appreciably lower than that at stretching of the non-plasticized SPU samples ($f_p=300$ MPa). Usually, for the practical purposes, the content of plasticizers blended into polyurethanes does not exceed 20%.

11.47.2 PRINCIPLES OF A PLASTICIZER SELECTION

The selection of plasticizers for polyurethane compositions depends on satisfying various tasks such as lowering viscosity, increase in potlife, lowering modulus and hardness of polyurethane, an increase in the low temperature resistance (lowering the glass transition temperature of soft chains), or dissolution of components in reaction mixture.

The general requirements for plasticizers for SPU (as well for other polymers) are the low volatility, a high boiling and decomposition points, a low glass transition temperature and melting point (in the case of pronounced plasticizer ability to crystallize).^{581,584} Plasticizer should be chemically inert.

It follows from the mechanism of a specific influence of plasticizers on the SPU properties that for solving a problem of polyurethane low temperature resistance it is worthwhile to use plasticizers in the presence of which the hard blocks solubility in the

material, a volume “dissolution” of a polymer gel by a low molecular mass liquid, weakening of physical interaction, and a decrease in the amount of hydrogen bonds between the polymer chains.

It is clear from curves (Figure 11.70) that the greatest decrease in strength, σ_k , is observed for samples plasticized with TBP because it increases a hard block solubility in a soft matrix. At 45% of TBP, there is no microdispersion hard phase in material and its strength becomes 20 times lower than that of the non-plasticized SPU. The strength of a polyurethane block-copolymer decreases not only because of the diminishing microdispersion phase, but also as a result of decrease in amount of the interchain H-bonds in the material. The

soft phase of a material does not increase. The same plasticizers are useful in lowering viscosity of reaction mass with retention of high strength.

To lower hardness of polyurethane requires plasticizer capable to dissolve hard blocks of polymer. This causes the decrease in the content of a hard microdispersion phase in SPU and, as a result, the decrease in a mechanic modulus and hardness of material.

The equilibrium swelling of polyurethane samples in plasticizers is an useful method of initial screening. The plasticizers in which polyurethane swells well are suitable for decrease in hardness.

11.47.3 PLASTICIZERS IN USE

The mechanism of influence of plasticizers of different chemical structure on the SPU properties is not complete and experimentally proven. The plasticizers are still selected as a result of trial and error.^{584-586,600-616} The great number of compounds have been tried as SPU plasticizers. These include chloralurethanes,^{584,606} halogenated ethers,⁵⁸⁴ phenolxy-alkyl ethers,^{584,612} esters of carboxylic acids,^{584-586,590,592,600,616-618} esters of phosphoric acid,^{585,601} amines,^{602,603} amides^{584,604,605,619} esters of chlorocarboxylic acids and alcohols.^{606,607}

11.48 PROTEINS

11.48.1 FREQUENTLY USED PLASTICIZERS

- glycerin in a foamed packaging container,⁶²⁵ in soy plastics,^{626,628} in chewable pet toys,⁶³⁰ in medical purpose sealants,^{631,632} in thermoplastic articles,⁶³³ in protein coated medical substrates for local delivery of genes,⁶³⁵ in solubilized protein,⁶³⁷ in biodegradable articles,⁶³⁸ and in edible barrier coatings⁶³⁹
- propylene glycol in foamed packaging container⁶²⁵ and in soy plastics⁶²⁹
- triethylene and ethylene glycols in foamed packaging containers⁶²⁵ and in soy plastics⁶²⁹
- polyethylene glycol (molecular weight of 200 and 400) in soy plastics,⁶²⁹ in sustained-release of bioactive proteins,⁶³⁴ and in edible barrier coatings⁶³⁹
- sorbitol in medical purpose sealants^{631,632} and in edible barrier coatings⁶³⁹
- triacetin in sustained-release of bioactive proteins⁶³⁴

11.48.2 PRACTICAL CONCENTRATIONS

- glycerin: 8 phr,⁶³⁰ 5-20 wt%,⁶³⁷ 10-25 phr,⁶²⁸ 17-25 phr,⁶³⁸
- propylene glycol: 10-25 phr⁶²⁵
- polyethylene glycol: 360 phr (liquid suspension)⁶³⁴
- triacetin: 360 phr (liquid suspension)⁶³⁴

Water acts as a plasticizer affecting practical concentration of organic plasticizer added to achieve required effect.

11.48.3 MAIN FUNCTIONS PERFORMED BY PLASTICIZERS

- improvement of processability^{625,628,630}
- improvement of material flexibility^{625,628,630,635,639}
- modification of fracture behavior⁶²⁶

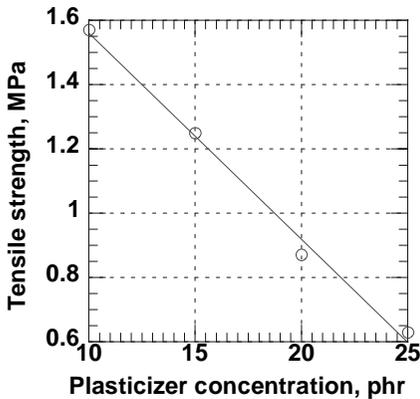


Figure 11.72. Tensile strength of soy protein plasticized with variable amounts of propylene glycol. [Data from Jane Jaay-lin and Su She Zhang, **US Patent 5,710,190.**]

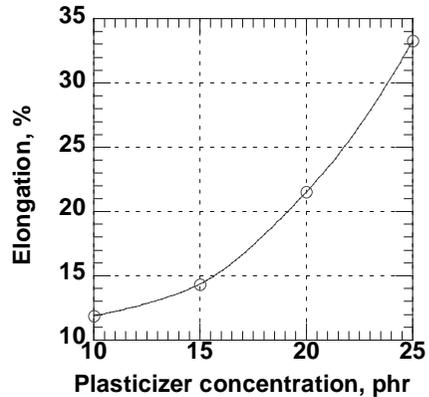


Figure 11.73. Elongation of soy protein plasticized with variable amounts of propylene glycol. [Data from Jane Jaay-lin and Su She Zhang, **US Patent 5,710,190.**]

11.48.4 EFFECT OF PLASTICIZERS ON POLYMER AND OTHER ADDITIVES

Addition of water to process mixture reduces processing viscosity but does not affect the glass transition temperature which is the same as for dry soy protein (150°C).⁶²⁶ Addition of 25 wt% of glycerin drastically decreases glass transition temperature to -50°C. Normally brittle polymer loses mechanical strength but gains flexibility.

Figures 11.72 and 11.73 show effect of propylene glycol on tensile strength and elongation of plasticized soy protein.

11.48 RUBBER, NATURAL

11.48.1 FREQUENTLY USED PLASTICIZERS

Natural rubber is compatible with paraffinic, naphthenic, and aromatic oil plasticizers. Only butyl rubber has similar compatibility. All other synthetic rubbers are compatible with a limited spectrum of mineral oils.¹⁵² These are recent applications:

- aromatic mineral oil in tires having high abrasion resistance,⁶⁴⁰ in tire treads having low rolling resistance and improved ABS braking,⁶⁴⁸ and in a rail support⁶⁵⁰
- paraffin oil in antimicrobial articles⁶⁴⁴ and in vehicle vibration damping devices⁶⁵¹
- process oil in anti-tack bladder⁶⁴⁵ and in tire side wall composition⁶⁵²
- mineral oil (paraffinic, aromatic or naphthenic) in sealing composition which swells on contact with water,⁶⁴⁶ in rubber parts suitable for dampening vibration,⁶⁴⁷ in engine mount,⁶⁴⁹ and in grips of articles⁶⁵³
- ester plasticizers (adipates, sebacates, phthalates, or phosphates) in sealing composition which swells on contact with water.⁶⁴⁶
- polyethylene glycol in antimicrobial articles⁶⁴⁴

11.48.2 PRACTICAL CONCENTRATIONS

- aromatic mineral oil: 8 wt%,⁶⁵⁰ 20-25 phr,⁶⁴⁸ 37.5 phr,⁶⁴⁰
- paraffinic oil: 1.5 phr,⁶⁵¹ 10-12 phr,⁶⁵² 20 phr (in addition to 5 phr of polyethylene glycol),⁶⁴⁴
- naphthenic oil: 10-20 phr⁶⁵³
- processing oil: 3 phr⁶⁴⁵
- mineral oil: 1-10 wt%^{647,649}

11.48.3 MAIN FUNCTIONS PERFORMED BY PLASTICIZERS

- increasing softness of rubber (mineral oils are frequently called softeners)^{643,651}
- improvement of dispersion of minor components and fillers⁶⁴⁰
- dissolving other rubber components⁶⁴⁰
- aid in the breakdown of elastomer^{644,651}

11.48.4 TYPICAL FORMULATIONS

Antimicrobial articles:⁶⁴⁴

Natural rubber	100 parts
Processing aid (pentaerythritol tetrastearate)	2
Polyethylene glycol	5
Silica	40
Calcium oxide (desiccant)	10
Titanium dioxide	5
Zinc oxide	3
Calcium carbonate	20
Paraffinic oil	20
Ethylene glycol dimethacrylate	2.5
Di-(tert-butyl-peroxy-isopropyl)benzene	1
Di-(tert-butyl-peroxy-trimethyl)-cyclohexane	1
Antimicrobial	<i>quantum satis</i>

Anti-tack bladder:⁶⁴⁵

Natural rubber	43 parts
Chlorosulfonated polyethylene	57
Carbon black (N660)	5
Calcium carbonate	32.2
Processing oil	3
Zinc oxide	5
Stearic acid	1
n-phenyl-p-phenylenediamine	1
Wax	3
Titanium dioxide	5
Magnesium oxide	13.3
Sulfur	0.96
Benzothiazyl disulfide	1

Rail support rubber mixture:⁶⁵⁰

Natural rubber	40.0 wt%
Styrene-butadiene rubber	20.0
Soot N 550	25.0
Aromatic plasticizer	8.0
Stearic acid	1.6
Dihydroquinoline derivative	0.3
p-phenylene-diamine derivative	0.5
Sulfonamide accelerator	0.7
Zinc oxide	2.4
Sulphur	1.5

Vehicle vibration damping devices:⁶⁵¹

Natural rubber SMR20	100 parts
Paraffinic oil (Flexon 815)	1.5
Carbon black N550	27
Process aid (Struktol WB 212)	3
Zinc oxide	5
Antioxidant (Flectol H)	0.4
Stearic acid	1
Antioxidant ZMTI	0.6
Coagent (Sartomer 350)	3
Sulfur	1
Peroxide (Vulkup 40)	6

11.49 SILICONE**11.49.1 FREQUENTLY USED PLASTICIZERS**

- hydroxyl endblocked polysiloxane⁶⁵⁸ in a silicone rubber sponge,^{666,669} in a silicone sealant,⁶⁶⁸ in a room temperature vulcanizing composition,⁶⁷³ and in a pressure sensitive adhesive⁶⁸²
- dimethylsiloxane oligomer endblocked with silanol in silicone composition,⁶⁷¹ in RTV silicone,⁶⁷² in provisional dental reconstructive materials,⁶⁷⁵ in sealant compositions,⁶⁷⁶ in an alkoxy-crosslinking RTV silicone rubber,⁶⁷⁹ in continuously manufactured silicone rubber compositions,^{680,684} in silicone sealants,^{681,683} in heat curable compositions,⁶⁸⁵ in liquid compositions,⁶⁸⁶ and in compositions for injection molding⁶⁸⁸
- hydroxy-terminated polydimethylsiloxane in fire-resistant silicone vulcanizates⁶⁶⁰ and in filler containing compositions⁶⁶⁷
- silicone oil of molecular weight lower than 7,000 daltons,⁶⁶³ in slip control films,⁶⁶⁴ and in compatibilized blends with polyamide (polyamide is further plasticized with either phthalates or trimellitates)⁶⁶⁵
- phthalates (alkyl or alkyl-aromatic) in room temperature vulcanizing compositions⁶⁷³
- polyisobutylene in room temperature vulcanizing compositions⁶⁷³
- low viscosity silicone oil in cosmetics⁶⁸⁷

- tripropylene glycol monoethyl ether in cosmetic compositions⁶⁶¹
- ethylene or propylene glycol in hair styling compositions^{674,677}
- glycerin in hair styling compositions^{674,677}
- dioctyl sebacate⁶⁵⁵
- di-(2-ethylhexyl) phthalate⁶⁵⁷
- di-(2-ethylhexyl) adipate⁶⁵⁷ in hair styling compositions⁶⁷⁰ and in custom-fitting articles⁶⁸⁹
- tricresyl phosphate⁶⁵⁷
- diethylene glycol dibenzoate⁶⁵⁷
- acetyl triethyl citrate in hair styling compositions⁶⁷⁰
- trialkyl citrates in hair styling compositions⁶⁷⁸
- epoxidized soybean oil in custom-fitting articles⁶⁸⁹

Cured silicone rubber contains a low molecular weight polysiloxanes as plasticizers. These may have different names as for example the first four materials on the above list but similar properties of the non-reactive, low viscosity liquids. Viscosity of some silicone plasticizers is as low as 10-30 cps (or mPas).

In cosmetics, either esters type plasticizers are used, or plasticizers that have hydrophilic properties (so-called humectants) that bring moisture to formulation.

Many common organic plasticizers can also be used in rubber formulation as listed above.

11.49.2 PRACTICAL CONCENTRATIONS

- hydroxyl endblocked polysiloxane: 2.6 phr⁶⁵⁸ and 10 phr⁶⁷¹
- hydroxyl-terminated polydimethylsiloxane: 5 wt%⁶⁶⁰
- silanol endblocked polysiloxane: 5-50 parts per 100 parts of silica filler,⁶⁶⁵ up to 15 wt%,⁶⁶⁸ 3-30 wt%,⁶⁷³ 15-30 wt%,⁶⁷⁵ up to 25 wt%,⁶⁷⁶ up to 20 wt%,⁶⁷⁸ up to 25 wt%,⁶⁷⁹ up to 40 wt% per 100 parts of reinforcing silica,⁶⁸⁰ 10 wt%,⁶⁸¹ 7 wt% (silica filler was silane treated),⁶⁸³ 10 wt%,⁶⁸⁴ 3 phr,⁶⁸⁵ and 30 phr⁶⁸⁶
- dioctyl sebacate: 8 wt%⁶⁵⁵
- di(2-ethylhexyl) adipate: 4-6 phr⁶⁵⁷
- di-(2-ethylhexyl) phthalate: up to 50 phr⁶⁵⁷ and 15 phr⁶⁸⁹
- tricresyl phosphate: 30 phr⁶⁵⁷
- diethylene glycol dibenzoate: 30 phr⁶⁵⁷
- tripropylene glycol monomethyl ether: 10 phr⁶⁶¹
- acetyl triethyl citrate: 0.05-1 wt%⁶⁷⁰

The amount of polysiloxane-based plasticizer depends on a combination of factors including the required modulus of rubber, the amount of silica filler, and the type of silica filler (treated or untreated with silane).

11.49.3 MAIN FUNCTIONS PERFORMED BY PLASTICIZERS

- reduction of viscosity^{658,672,673}
- improvement of flow properties^{663,673,678}
- reduction of creep hardening⁶⁸⁰
- increase level of dispersion⁶⁸¹
- reduction of modulus⁶⁵⁸
- reduction of rubber hardness⁶⁷³

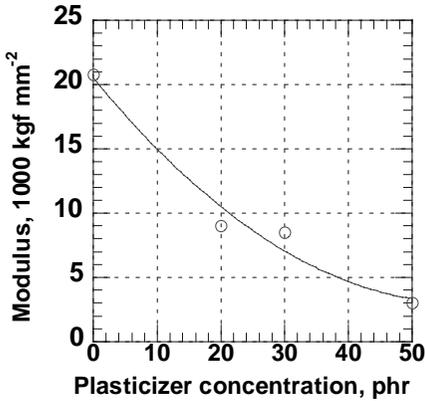


Figure 11.74. Effect of the amount of di-(2-ethylhexyl) phthalate on modulus of plasticized silicone rubber. [Data from Hayashida A, Mori S, Tabei E, US Patent 5,804,257.]

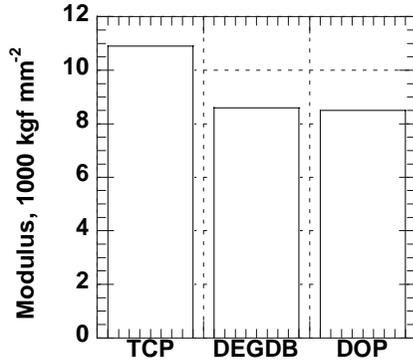


Figure 11.75. Effect of plasticizer type on modulus of plasticized silicone rubber. TCP – tricresyl phosphate, DEGDB – diethylene glycol dibenzoate, DOP – di-(2-ethylhexyl) phthalate. [Data from Hayashida A, Mori S, Tabei E, US Patent 5,804,257.]

- dilution and expansion of rubber network⁶⁷⁵
- densification of filler⁶⁶³
- improvement of silica filler compatibility^{666,669}
- make material heat meltable⁶⁸²
- improvement of storage stability of sealants⁶⁷⁸
- reduction of cost⁶⁷⁵
- hair style retention and restyling capability⁶⁷⁴

11.49.4 EFFECT OF PLASTICIZERS ON POLYMER AND OTHER ADDITIVES

Figure 11.74 shows that silicone rubber responds to plasticization in a similar manner as other polymers. Modulus and elongation increase with the amount of plasticizer increase. The tensile strength is decreased with increased addition of plasticizer. Plasticizer type plays some role but all tested plasticizers have similar compatibility with polymer. Addition of ester type plasticizers to silicone formulation increased UV absorption and UV degradation rate of rubber.⁶⁵⁷

11.49.5 TYPICAL FORMULATIONS

Skin cleaning agent:⁶⁶²

Myristic acid	15 wt%
Palmitic acid	5
Stearic acid	3
Bees wax	3
Polyethylene glycol 6000	2
Ethylene glycol distearate	2
Coconut oil fatty acid diethanolamide	3
Glycerin	15

Potassium hydroxide	5
Purified water	35
Sodium N-lauroylsarcosine	10
Tabular powder of organic silicone resin	2

Face powder (the so-called Pan-Cake):⁶⁶²

Titanium oxide	5 wt%
Kaolin	5
Talc	52
Zinc myristate	5
Iron oxide red	0.7
Iron oxide yellow	2.1
Iron oxide black	0.2
Tabular powder of organic silicone resin	15
Porous globular silica	10
Squalane	3
Glyceryl trioctanoate	2
Antiseptic	proper
Perfume	proper

Hair spray:⁶⁷⁰

Non-silicone polymer	1 wt%
Silicone grafted polymer	2.5
Isododecane	2
Triethyl citrate	0.21
Propylene glycol	0.02
Potassium hydroxide	0.32
Perfume	0.10
Water	8
Ethanol	62.85
Propellant (isobutane)	7.02
Propellant (hydrofluorocarbon 152)	15.98

Silicone sealant with increased work time:⁶⁸¹

Base polymer	58 parts
CaCO ₃	15
SiO ₂	10
Crosslinker (ethyltriacetoxysilane)	4.80
Catalyst	0.0257
Plasticizer	10.00
Adhesion promoter	1.17
Pigment	1.00
Tooling time – 180 s.	

Silicone sealant with improved high temperature adhesion.⁶⁸³

Polydimethylsiloxane having a viscosity of 50,000 cps	55 parts
Calcium carbonate treated with stearic acid	15
Fumed silica reinforcing filler treated with cyclic polydimethylsiloxane	15
Ethyltriacetoxysilane crosslinking component	5.2
Dibutyl tin dilaureate tin condensation cure catalyst	0.033
Iron carboxylate salt	0.5
Polydimethylsiloxane linear plasticizing fluid	7
Di-t-butoxydiacetoxysilane adhesion promoter	1.27
Carbon black pigment	1

11.50 STYRENE-BUTADIENE RUBBER**11.50.1 FREQUENTLY USED PLASTICIZERS**

Styrene-butadiene rubber, SBR, is compatible with the majority of mineral oils but has a limited compatibility with paraffinic oils.¹⁵²

- elastomer plasticizers, such as rosin esters in chewing gum^{690,693,694}
- terpene resins derived from α -pinene, β -pinene, or d-limonene in chewing gum^{690,693,696}
- aromatic mineral oil (Renopal 450) in vulcanizable rubber compounds⁹⁶¹ and in rubber mixture for rail support⁶⁹⁵
- paraffinic mineral oil (Flexon 395) in a rubber composition containing waste polymers⁶⁹⁶
- process oil (PW380 manufactured by Idemitsu Kosan Ltd.) in outsoles⁶⁹²

11.50.2 PRACTICAL CONCENTRATIONS

- 10 to 30 phr in chewing gum^{690,693,694}
- mineral oils: aromatic – 8 phr^{691,695}; paraffinic – 2-10 phr⁶⁹⁶

11.50.3 TYPICAL FORMULATIONS**Outsoles of shoes.**⁶⁹²

SBR	100 parts
Filler	50
Silane coupling agent (Si69)	5
Plasticizer (process oil)	5
Zinc oxide	3
Stearic acid	1
Stabilizer (Nocrac 200)	2
Sulfur	2
Accelerator (Nocceler NS)	1

Rubber compound for rail support.⁶⁹⁵

Natural rubber	40 wt%
SBR	20
Soot N 550	25
Aromatic plasticizer	8
Stearic acid	1.6

Dihydroquinoline derivative	0.3
p-phenylene-diamine derivative	0.5
Sulfonamide accelerator	0.7
Zinc oxide	2.4
Sulfur	1.5

11.51 STYRENE-BUTADIENE-STYRENE

11.51.1 FREQUENTLY USED PLASTICIZERS

- white mineral oil in hot melt adhesive^{697,699}
- aromatic-free oils in sealants⁷⁰⁰
- asphalt in low cost sealant and paving applications⁷⁰⁰
- dibutyl or dioctyl phthalate in shrink film⁶⁹⁸

11.51.2 PRACTICAL CONCENTRATIONS

A simple swelling test can be used to check the amount of oil which plasticizes formulation but would not likely bleed out. Resin samples are allowed to swell to equilibrium and half of the amount of absorbed oil is used in application.⁷⁰⁰

- white mineral oil: 18-20 wt%^{697,699} and 20 phr⁷⁰⁰
- phthalates: 8 wt%⁶⁹⁸

11.51.3 MAIN FUNCTIONS PERFORMED BY PLASTICIZERS

- increasing tack together with tackifying resin^{697,699}
- effect on temperature at which films begins to shrink⁶⁹⁸
- decrease hardness and modulus⁷⁰⁰
- reduce melt and solution viscosity⁷⁰⁰
- improve compounding⁷⁰⁰
- decrease cohesive strength or increase plasticity⁷⁰⁰

11.52 STARCH

Starch is used today in a large number of products with very diverse properties. The roles played by starch include: load bearing polymeric material, a component of biodegradable blends, a filler in biodegradable materials, and even a role of plasticizer. Its popularity stems from a low price, being derived from a renewable source, being familiar component found in the natural environment and as such easily convertible by natural means, chemically reactive, and compatible with many materials.

11.52.1 FREQUENTLY USED PLASTICIZERS

- glycerin^{704,713} in polymer blend with polyurethane,⁷⁰¹ in a blend with polyvinylalcohol,⁷⁰⁶ in blends with polyethylene or polypropylene,⁷⁰⁸ in extruded film,⁷⁰⁹ in plastic sheets,⁷¹¹ in pet chew,⁷¹⁸ in gel capsules,^{721,723,726} in thermoplastic composition,⁷²² in biodegradable plastics,^{724,736} in biodegradable fibers,⁷²⁴ in wood fiber reinforced starch,^{727,728} in protective coatings for fresh produce,⁷²⁹ in biodegradable cigarette filters,⁷³² in biodegradable non-woven fabrics,⁷³³ in food and beverage containers,^{735,739} in cellular plastics for containers,⁷³⁷ in a foamed starch,⁷⁴² in a shortening substitute,⁷⁴⁵ and in materials which stimulate plant growth⁷⁴⁶

- glycerol ester in a biodegradable material⁷²⁰
- sunflower oil in a blend with polyethylene⁷⁰⁷
- vegetable oil in a film forming composition that promotes seed germination⁷⁴⁴
- soybean oil in pharmaceutically active agent⁷¹⁹
- sorbitol in extruded film,⁷⁰⁹ in biodegradable material,⁷²⁰ in gel capsules,^{721,723} in biodegradable fibers,⁷²⁵ and in food and beverage containers^{735,739}
- sorbitol acetate in biodegradable plastics^{724,736}
- polyethylene glycol⁷⁰² in food and beverage containers^{735,739}
- propylene glycol⁷¹⁶ in film forming composition that promotes seed germination⁷⁴⁴
- tributyl acetyl citrate in biodegradable hunting and shooting cartridges⁷³⁰
- triacetin in materials having cellular matrix for beverage containers⁷⁴¹
- diethylene glycol dibenzoate and dipropylene glycol dibenzoate 50/50 weight blend (Benzoflex 50) in adhesives for non-woven fabrics⁷⁴⁷
- succinate polyester in moisture barrier coatings⁷⁰³
- polyester of polyethylene glycol and adipic or succinic acid in moisture barrier coatings⁷³¹ and in release coatings⁷³⁴

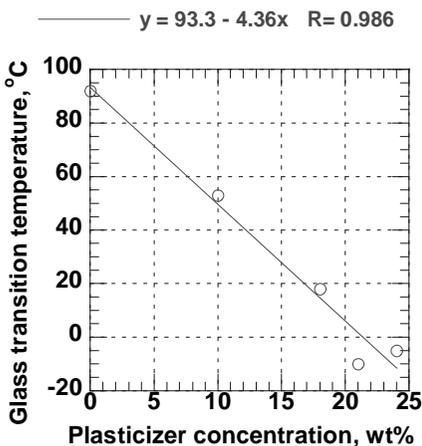


Figure 11.76. Glass transition temperature of starch films plasticized with variable amounts of glycerin. [Data from Lourdin D; Bizot H; Colonna P, *J. Appl. Polym. Sci.*, **63**, No.8, 22nd Feb.1997, p.1047-53.]

- polyol in compatibilization of starch with various polymers⁷⁴³
- polyvinylalcohol in starch foams for absorbent articles⁷⁴⁹
- starch as a plasticizer in manufacture of building panels⁷⁴⁸

Plasticizer selection depends on material application with special attention given to its water resistance. In biodegradable and other similar materials water must be permitted to penetrate material structure and thus help in biological digestion of material. In these applications, glycerin and other similar compounds, capable to attract moisture, are used. This provides products with a benefit of water acting as co-plasticizer effectively reducing the amount of organic stabilizer.

If water barrier or water resistance properties are required hydrophobic materials are needed and these are listed towards the end of the list. Still, care is taken that plasticizers are environmentally friendly to make entire product compatible with environment.

11.52.2 PRACTICAL CONCENTRATIONS

- glycerin: 0.1-5 wt%,⁷²⁹ 0.5 wt%,⁷⁴⁵ 2 wt%,⁷³³ 3-7 wt%,⁷²² 10-40 wt%,⁷²⁶ 16.9 wt%,⁷¹⁸ 15-30 wt%,⁷⁴⁶ 33 wt%,⁷⁰⁹ and 25-75 wt%⁷²¹
- vegetable oils: 0.1 wt%,⁷⁰⁷ 0.5%,⁷¹⁹ and 6.25 wt%⁷⁴⁴
- sorbitol: 35 wt%⁷⁴²
- tributyl acetyl citrate: 3 wt%⁷³⁰

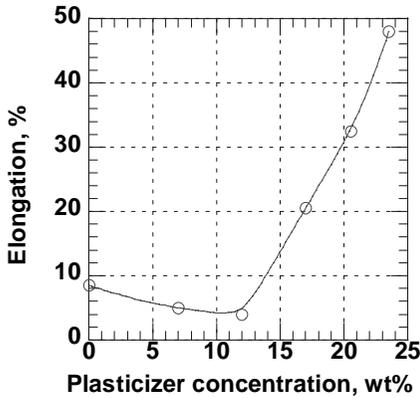


Figure 11.77. Elongation of starch films plasticized with variable amounts of glycerin. [Data from Lourdin D; Bizot H; Colonna P, *J. Appl. Polym. Sci.*, **63**, No.8, 22nd Feb.1997, p.1047-53.]

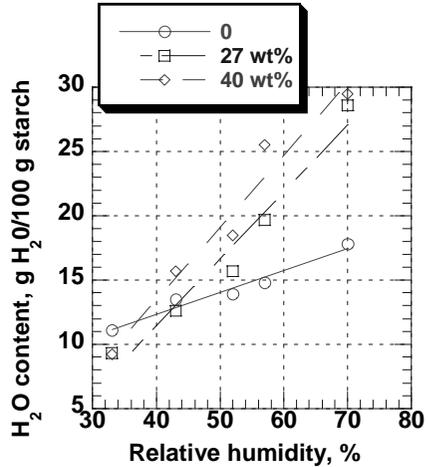


Figure 11.78. Water content in starch plasticized by glycerin at different relative humidities and concentrations of plasticizer. [Data from Lourdin D; Coignard L; Bizot H; Colonna P, *Polymer*, **38**, No.21, 1997, p.5401-6.]

- triacetin: 5-25 wt%⁷⁴⁰
- diethylene glycol dibenzoate and dipropylene glycol dibenzoate 50/50 weight blend: 2-30 wt%⁷⁴⁷
- polyethylene glycol: 30-40 wt%⁷⁰²
- polyester plasticizer: 5-25 wt%,^{703,731,734} 33 phr,⁷⁰³ and 57 phr⁷⁰¹

11.52.3 MAIN FUNCTIONS PERFORMED BY PLASTICIZERS

- decrease in the glass transition temperature of starch⁷¹⁰
- increase in the flexibility and decrease in brittleness of plasticized materials⁷²⁷
- influencing moisture absorption rate and equilibrium⁷¹⁰
- at smaller concentrations plasticizer may cause antiplasticization (glycerin)⁷¹³
- influence on the thermal degradation properties (effect of both type and concentration).⁷¹⁵ In some controlled processes the thermal degradation of starch in the presence of plasticizer is called as the thermomechanical digestion.⁷⁴⁶
- strong interaction with starch (glycerol molecules are immobilized as determined by NMR)⁷⁰⁴
- increase in biodegradation rate caused by environmental exposure (e.g., vegetable oil, tributyl acetyl citrate, etc.)^{707,716,730,732,733}
- some plasticizers (e.g., glycerin) play role of humectants^{728,741}
- some plasticizers help to form moisture barrier (e.g., polyethylene glycol, polyester plasticizers, etc.)⁷³¹ or prevent redispersibility of water in adhesive⁷⁴⁷
- starch acts as plasticizer in cement-containing formulations. It retards reaction of setting by removing majority of moisture. Starch also helps to create small air bubbles which increase insulation value of building panels⁷⁴⁸

11.52.4 EFFECT OF PLASTICIZERS ON POLYMER AND OTHER ADDITIVES

Figure 11.76 shows that the glass transition temperature of starch films plasticized with glycerin is a linear function of plasticizer concentration. Glass transition temperature starch plasticized by glycerin is around room temperature at the plasticizer concentration of about 15 wt%. Figure 11.77 shows relationship between elongation of starch films plasticized with glycerin versus concentration of plasticizer. Figure 11.77 shows antiplasticization-like behavior. At lower concentrations of plasticizer the elongation decreases up to 12 to 17 wt% of glycerin to increase rapidly. Interpretation of data from Figures 11.76 and 11.77 seems to offer explanation.⁷¹³ At room temperature material is in a brittle state if concentration of plasticizer is below $\sim 15^{\circ}\text{C}$. A small decrease in elongation noted up to 12 wt% of plasticizer is most likely due to the gradually increased crystallization facilitated by the increased chain mobility and the interactions in the presence of plasticizer. After passing through a minimum, the elongation rapidly increases because polymer (starch) changes behavior from brittle to ductile.

Addition of increased amounts of glycerin increases moisture absorption (Figure 11.78). The equilibrium moisture depends on both the plasticizer concentration and the relative humidity of surrounding atmosphere.⁷¹⁰ It is also noticeable that starch without plasticizer behaves differently (lower rate of moisture increase at different relative humidities). This indicates that glycerin controls moisture absorption in plasticized samples. The presence of glycerin seems more important than its concentration.

11.52.5 TYPICAL FORMULATIONS

Edible pet chew:⁷¹⁸

Soy protein	15.55 parts
Wheat gluten	15.55
Gelatin	8.5
Corn starch	25.4
Garlic powder	1.1
Onion powder	1.1
Lecithin	0.6
Turkey powder	2.8
Chicken powder	2.8
CaCO ₃	0.6
Tricalcium phosphate	0.6
Water	8.47
Glycerol	16.9

Film forming composition for soft capsules:⁷²³

Iota-carrageenan	6-12 wt% in wet film
Modified starch	12-30
Plasticizer	5-30
Buffer	0.5-2
Preservative	0-0.2

Biodegradable polymeric composition:⁷²⁴

Starch with 12 wt% water	40.5
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Poly(ethylene vinyl alcohol)	30.4
Poly(ethylene acrylic acid)	4.3
Erucamide	0.25
Plasticizer*	21.5
Fluidizer**	3.1
*sorbitol acetate 65.5 wt% + water 14 wt% + glycerine 0.5 wt%	
**sorbitol ethoxylate trioctadecanoate	

Biodegradable fiber:⁷²⁵

Starch	38.2 weight parts
Sorbitol	12.8
Glycerol	8.5
Thermoplastic starch	54.5
Water	<0.1
Polyamide	40.5

Non-toxic, biodegradable projectiles for shotgun cartridges:⁷³⁰

Polyester urethane (Bionolle 3001)	87.5 wt%
Corn starch	8.0
Tributylacetyl citrate	3.0
TiO ₂ (anatase)	0.5
Calcium carbonate	0.5
Calcium stearate	0.5

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