

FILLERS IN COMMERCIAL POLYMERS

Several aspects of this discussion are common to all polymers. These include the major applications of polymers, the most common methods of polymer processing, the most frequently used fillers and their typical concentrations, additives used to incorporate fillers, special methods of filler incorporation, fillers pre-treatment, and special considerations affecting the selection of a filler. These data found in the most recent literature are recorded in a tabular form for clarity and ease of comparison. This is followed by some examples of current use of fillers in particular polymers. The examples can be used to develop numerous new applications for fillers in material improvement. They elaborate on the most recent developments in filler and filled material improvements.

The application of polymer affects choice of filler. For example, to prepare conductive materials, special fillers must be used to obtain the required properties. Also, the method of processing imposes certain constraints on the choice and treatment of the filler before its use. For example, polymers processed at high temperature require fillers which do not contain moisture. This affects both the choice of the filler and/or its pretreatment. The choice of additives used to improve the incorporation of the filler depends on the application and the properties required from a product but it is also determined by the processing method. For example, the viscosity of a melt is reduced by special lubricating agents whereas the viscosity of filler dispersions is controlled by the surface treatment of filler. In some cases, the order of addition is important or a special filler pretreatment is used to achieve the desired results. These methods are discussed in special section in the table. Some fillers simply cannot be used with some polymers. In other cases, special care must be taken to ensure polymer stability or filler may interact with some vital components of the formulation. This subject is discussed in special considerations of filler choice.

15.1 ACRYLICS¹⁻²

| | |
|---|--|
| Major polymer applications | paints, coatings, roofing, sealants, elastomers, fibers, industrial filters, battery separators, carbon and graphite fibers, ceramics |
| Important processing methods | mixing/compounding, extrusion, calendering, Banbury mixer, vulcanization, wet and dry spinning |
| Typical fillers | calcium carbonate, titanium dioxide, fumed silica, zinc oxide, carbon black, aluminum silicate, graphite, ceramic microspheres |
| Typical concentration range | 20-70 wt% |
| Auxiliary agents | silane, mostly amine-functional |
| Special methods of incorporation | in ceramics manufacture, the presence of sodium ions on the alumina surface could inhibit the formation of covalent bonding with acrylate polymers, the surface adsorption can be regulated by adjusting pH ¹ |
| Methods of filler pretreatment | neutralization in ceramic applications |
| Special considerations | titanium dioxide accelerates UV degradation; copper compounds catalyze thermal and UV degradation; neutral and basic fillers are recommended because acidic fillers and pigments retard cure |

Acrylic polymers also include water emulsions of acrylic resins, acrylate resins used in ceramic applications, and the precursor of carbon fiber, namely acrylonitrile. The table includes also some information on acrylic elastomers. Polymethylmethacrylate is discussed under a separate subsection.

Water emulsions used in paints, coatings, and sealants contain substantial amounts of fillers which are incorporated by the conventional methods of dispersion. Frequently, grinding is used in the paint industry. In sealants, fillers are used for reinforcement, rheology, and crosslinking. The rheology of a sealant may be controlled by the incorporation of fumed silica in quantities around 3 wt%. The non-sag properties of sealant are partially due to fumed silica but are also regulated by pH adjustment in the presence of other additives such as special acrylic resins and polyurethane thickeners. The combination of both effects gives the sealant its final properties. The reinforcement of the sealant is produced through a combination of two processes: the interaction of silica particles and crosslinking through zinc oxide.

Fillers in a sealant are added in limited quantities because high loadings affect the elastomeric properties of acrylic resin. In coatings, larger quantities of fillers and pigments can be used because the coating is not required, in most cases, to tolerate large elongations. Exterior coatings, which require crack bridging capabilities, are an exception. In this case, elongation in excess of 1000 % is required. Here, the filler load is substantially reduced. Some exterior textured coatings or stuccos, require unusual fillers such as silica flours, glass beads, and ceramic microspheres. These fillers are used to obtain different decorative effects. Silica flour added in large quantities plays the role of the classical filler added to reduce price. It often is

added in large quantities, sometimes as high as 80 wt%. Silica flour of various particle size is mixed to achieve increased packing density and imitates the effect of the old cementitious stucco. In some finishes, ceramic microspheres of large sizes (several millimeters in diameter) are added to produce surface imperfections. During tooling they form grooves and holes of different sizes which imitate the handmade finishes used throughout the world but, most notably, in Italy. Solid, colored glass beads 1 mm in diameter and larger are used at maximum packing density to obtain a type of finish which has a color similar to the color of the glass beads (or their mixtures). The acrylic resin in this application acts as a binder. Several different colors can be mixed together to obtain its required effect which is usually named after some traditional well-known name, e.g., *pefefer and saltz* (pepper and salt).

Work on ceramics shows the effects of polymer adsorption on the filler surface (Figure 15.1). The adsorption is a reversible phenomenon controlled by the pH of an alumina slurry. Coiled chains are formed at low pH and, due to ionization, stretched out chains form at a higher pH.

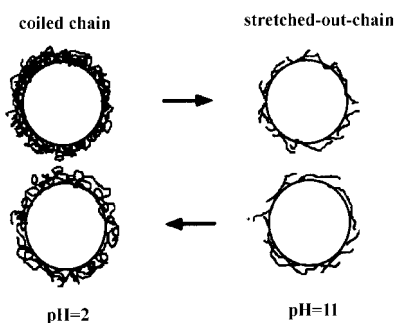


Figure 15.1. Configuration of polyacrylate adsorbed at different pH. [Adapted, by permission, from Lee D H, Condrate R A, Reed J S, *J. Mater. Sci.*, **32**, 1997, 471-8.]

15.2 ACRYLONITRILE-BUTADIENE-STYRENE COPOLYMER (ABS)³⁻⁶

| | |
|----------------------------------|---|
| Major polymer applications | appliance (refrigerator liners, kitchen appliance housings, vacuum cleaners, power tools), automotive (instrument panels, consoles, door parts, knobs, trim, wheel covers, mirror and headlight housing, front radiator grilles), business machines (computers, discs, phones), packaging, pipes and fittings, recreation (snowmobiles, boats, vehicles), toys, luggage, lunch and tool boxes, medical applications, lawn and garden equipment, furniture, hot tubs, military |
| Important processing methods | injection molding, extrusion, film lamination, calendering, blow molding, thermoforming |
| Typical fillers | talc, magnesium hydroxide, antimony oxide, carbon black, nickel or copper coated carbon fibers, glass beads |
| Typical concentration range | carbon black for color and UV protection - 0.5-3 wt%, general and flame retarding fillers - 30-60 wt%; nickel coated fibers for EMI shielding - 10 wt% (about half compared with the required concentration of carbon fiber), stainless steel fiber - 0.5-3 wt% |
| Auxiliary agents | premixing of nickel coated fibers in polymer prior to injection molding increased the shielding efficiency of fibers ⁵ |
| Special methods of incorporation | color concentrate of carbon black gave 3 times better jetness compared with mixed-in powdered carbon black ³ |
| Methods of filler pretreatment | drying |
| Special considerations | moisture in excess of 0.1% will cause bubbling; iron, copper, manganese, cobalt impurities catalyze oxidation |

Filler mixing technology is important in ABS processing. Carbon black must be well dispersed to obtain good jetness and impact strength. High jetness is relatively easy to obtain by the use of high surface area carbon black and by adjusting its concentration to requirements. As the carbon black content is increased, high impact strength becomes more difficult to maintain because impact strength decreases as undispersed surface area increases. The best impact retention is achieved when a lower concentration of carbon black was subjected to two stage mixing. First carbon black is dispersed in ABS and then the granulate obtained after solvent evaporation is used as a color concentrate.³ The impact retention of carbon black containing ABS dispersed in this way is independent of the surface area of carbon black but decreases as the concentration of carbon black increases.

Dispersion of conductive fillers is even more critical. Here,⁵ two methods have been used. In one, the nickel coated carbon fibers were added directly to the ABS. in the other, the coated fibers were pre-dispersed with a solvent in ABS, then the solvent was evaporated to form a granulate. Figure 15.2 shows the results. A two stage dispersion is clearly critical for obtaining good shielding effectiveness. Figure 15.3 shows the effect of nickel coating on carbon fiber performance. A coating

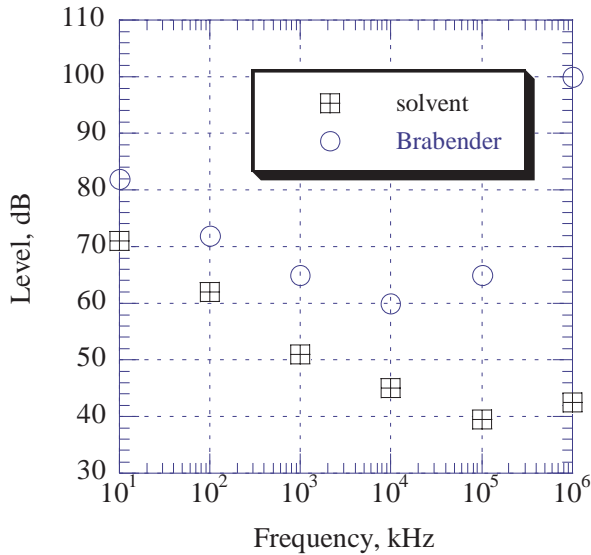


Figure 15.2. Shielding effectiveness of nickel-coated carbon fiber in ABS depending on method of mixing. [Adapted, by permission, from Guanghong Lu, Xiaotian Li, Hancheng Jiang, *Composites Sci. & Technol.*, **56**, No.2, 1996, 193-200.]

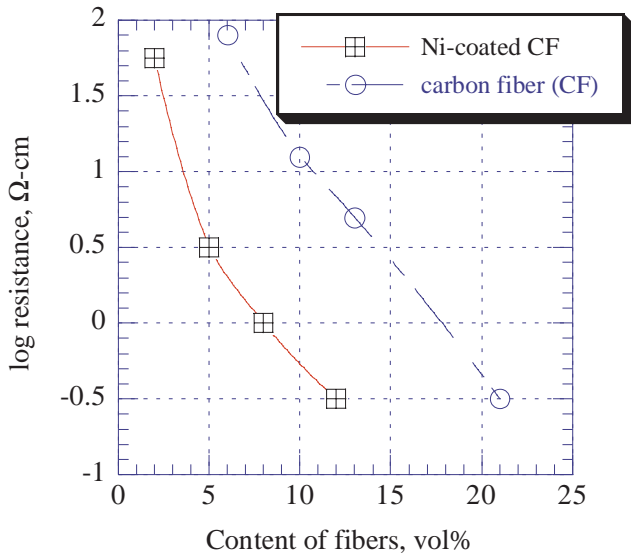


Figure 15.3. Resistivity of ABS composite vs. content of fibers. [Adapted, by permission, from Guanghong Lu, Xiaotian Li, Hancheng Jiang, *Composites Sci. & Technol.*, **56**, No.2, 1996, 193-200.]

with an optimal thickness of 0.2-0.5 μm allows for a substantial reduction in carbon fiber (as much as by one half) needed to obtain the conductance required. Nickel coating makes the fiber more conductive and gives better mechanical properties to the fiber which helps it to withstand processing conditions.

15.3 ACRYLONITRILE-STYRENE-ACRYLATE (ASA)⁷

| | |
|----------------------------------|---|
| Major polymer applications | mirrors for personal watercraft, recreational vehicle antennas, pool accessories, exterior cable enclosures, large screen displays, sheet outdoor furnishings, profiles, spas, marine applications, skylights, ski bindings |
| Important processing methods | injection molding, extrusion, thermoforming |
| Typical fillers | carbon black, glass beads |
| Typical concentration range | 5-20 wt% |
| Auxiliary agents | silane for treatment of glass beads |
| Special methods of incorporation | not reported |
| Methods of filler pretreatment | silane coupling agent |
| Special considerations | none reported |

The addition of glass beads to ASA resulted in the decrease of tensile and flexural yield strength, notched and unnotched impact strength, and resistance to steady crack propagation. Flexural modulus was the only parameter which was improved.⁷

15.4 ALIPHATIC POLYKETONE⁸

| | |
|----------------------------------|---|
| Major polymer applications | automotive (fuel lines and connectors, fuel pump components, fuel tanks, filters, injection rails, air inlet, manifolds, gears, wheel covers), gears for business machines, liners for flexible fuel hoses, automotive fuel system components, industrial molded parts, film fibers |
| Important processing methods | injection molding, blow molding, extrusion, powder coating, spinning |
| Typical fillers | glass fiber, mica, wollastonite, calcium carbonate |
| Typical concentration range | 15-30 wt% |
| Auxiliary agents | not reported |
| Special methods of incorporation | not reported |
| Methods of filler pretreatment | not reported |
| Special considerations | not reported |

Several fillers (glass fiber, mica, wollastonite, and calcium carbonate) were compared in this study.⁸ Flexural modulus increased as the concentration of filler increased, but the highest rate of increase was obtained first with glass fiber then next with mica. Calcium carbonate and wollastonite caused a much lower change in flexural modulus. Flexural strength was substantially improved by glass fiber but all of the other fillers had practically no effect on flexural strength. The deflection temperature under load was increased by all fillers but the gains obtained with glass fiber were spectacular. Only 5 wt% glass fiber was needed to double the heat deflection temperature. A further increase in glass fiber concentration did not produce any further improvement. Izod impact strength is increased by glass fiber. All other fillers decrease impact strength. This study shows that although all of the fillers tested can be used with polyketone but only one – glass fiber improves all of its mechanical properties.

15.5 ALKYD RESINS⁹

| | |
|----------------------------------|---|
| Major polymer applications | coatings, paints, varnishes, electrical applications, pavement marking, artist’s paints, putties, printing inks |
| Important processing methods | compounding/mixing, molding |
| Typical fillers | calcium carbonate, titanium dioxide, glass fiber, silica, iron oxides, clay, mica, zinc oxide, lithopone |
| Typical concentration range | 30-60 wt% |
| Auxiliary agents | flow control additives, wetting and dispersing additives, antifoaming additives |
| Special methods of incorporation | grinding, sand milling |
| Methods of filler pretreatment | typically no treatment |
| Special considerations | filler porosity is important consideration in silica matting agents; some silica matting agents affect thixotropy of alkyd paints |

Alkyd resins are used in many traditional applications which have a well established technology. New studies are infrequently reported. The inherent high gloss of alkyd paints requires special materials which can produce matt surfaces finish. Several products (different grades of Gasil) have been developed recently for this purpose. Rheological studies have shown that some types of silica disrupt the rheological networks of paints. Silica which did this had pore size of 100 to 400 Å. Special types of alkyd resins are required to take advantage of these rheological modifiers. If the pore size of silica is large enough to capture the structure forming components of the alkyd resin, silica affects the performance of alkyd resin. Wax coating does not affect this process of rheological interference. The matting effect depends on the number of particles and the number of which protrude from the surface. These properties, combined with smaller pore sizes, make some silica good matting agents. An added advantage is that they can be stirred into the paint.⁹

15.6 ELASTOMERS, TPO

| | |
|----------------------------------|--|
| Major polymer applications | automotive, car bumper, wire insulation, hose tube, sheet |
| Important processing methods | injection molding, blow molding, extrusion |
| Typical fillers | calcium carbonate, talc, carbon black, wollastonite |
| Typical concentration range | carbon black - 1-2 wt%, general filler - 10-30 wt%; proprietary formulations |
| Auxiliary agents | not reported |
| Special methods of incorporation | not reported |
| Methods of filler pretreatment | components must be dry before processing |
| Special considerations | talc reduces mold shrinkage |

15.7 EPOXY RESINS¹⁰⁻⁵⁷

| | |
|----------------------------------|--|
| Major polymer applications | surface protective coatings (protective and decorative - automotive, metal cans, industrial flooring, anticorrosive paints), electrical/electronics (printed circuit panels, conductive adhesives), composites (building/construction, marine, electrical/electronics, aircraft, communication satellites, automotive, pipes, consumer products), bonding and adhesives, flooring, tooling and casting, biosensors |
| Important processing methods | casting, lamination, molding, compounding |
| Typical fillers | calcium carbonate, barium sulfate, talc, kaolin, mica, quartz, sand, glass spheres, silica, titanium dioxide, aluminum hydroxide, carbon fiber, glass fiber, aramid fiber, aluminum, copper, silver, iron, graphite, molybdenum disulfide, zirconium silicate, lithium aluminum silicate, vermiculite, slate powder, titanium boride, ground rubber, iron oxide, microvoids |
| Typical concentration range | up to 90 wt% (sand); in situ formed silica - 2-43 wt%, alumina - 5-20 wt%, fractal approach to the critical filler volume fraction in conductive composites determines the required concentration of filler ⁴⁵ |
| Auxiliary agents | aminopropyltriethoxy silane, ^{18,43} epoxy silane, ²⁸ modified polyethyleneimide, ¹⁸ epoxy resin ^{12,46} |
| Special methods of incorporation | <i>in situ</i> polymerization of metal alkoxides; ¹¹ nanocomposite synthesis ^{49, 50} |
| Methods of filler pretreatment | Kevlar fibers for applications in composites were treated by coating with epoxy resin (1% epoxy resin on the fiber surface) or microwave plasma in an atmosphere of ammonia which grafts amine groups on the fiber surface. Fiber coating with epoxy reduced water absorption of composite whereas ammonia treated fiber behave in a manner similar to untreated fiber; rubber-epoxy interface was modified by carbonyl terminated copolymers of butadiene-acrylonitrile; ^{12,43} plasma modification of carbon fiber; ²¹ glass beads were encapsulated by grafted polybutyl acrylate and polystyrene; ³⁰ admicellar polymerization of styrene monomer on the surface of glass fiber improved properties of composite; ³⁶ epoxy sizing of carbon fibers; ⁴⁶ plasma treatment of carbon fibers was found to produce graphitic, phenolic, carbonyl, and carboxyl groups; ⁴⁶ vapor-grown carbon fibers are produced by decomposing of gas-phase hydrocarbon in the presence of ultrafine iron catalyst; ⁴⁷ |
| Special considerations | fillers absorb part of the heat generated during the curing; ¹⁵ additions of silica (35-52 wt%) to UV-curable epoxy did not have a significant effect on cure rate; ¹⁷ the use of microvoids (see Figure 8.35) for epoxy toughening gives the same results as rubber toughening; ²⁴ glass A beads filled epoxy degrades rapidly in a marine environment when glass concentration increases above 12 wt%; ²⁷ Fe ₂ O ₃ catalyzes the curing reactions of epoxy resins ²⁹ |

Epoxy mortars for patching applications are the most highly filled materials. With the proper selection of silica sand mixture as the filler, the filler concentration can be as high as 95 wt%. This, and similar materials produced from a reactive polyure-

thane systems are probably the most highly filled plastics. Another example of highly filled epoxies can be found in the liquid metal compounds which are epoxies highly filled with metals such as steel, aluminum, titanium, bronze, and copper. The loading of metal powder in these materials can reach 70 wt%. This level of iron powder was used in pipeline sealants.¹⁹ The inclusion of metal powders has a bearing on the corrosion protection of epoxy coating.⁴⁴ The addition of iron powder improves corrosion protection whereas addition of copper or nickel reduces the protective capabilities of epoxy coatings.⁴⁴ Barrier properties of epoxy coatings containing adhesion promoter and glass flakes have been evaluated by electrochemical impedance spectroscopy.⁴⁸

Titanium boride was used in an epoxy system to induce electrical conductivity.¹² A high filler loading of 46 vol% was selected to study the effect of thermal expansion and contraction on electric conductivity. The filler chosen was composed of rigid particles which cannot form particle-particle connections other than through direct contact. Figure 15.4 shows the relationships of relative thermal expansion and specific electric resistivity. The resistivity increases slowly with temperature until the contacts between particles of filler are broken which results in a rapid increase in resistance.¹²

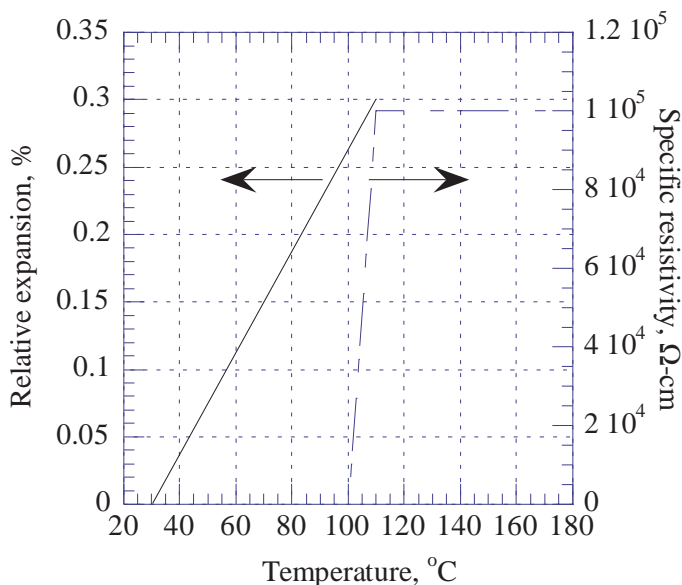


Figure 15.4. Thermal expansion and electric conductivity vs. temperature for epoxy filled with 46 vol% titanium boride. [Data from Strumpler R, Maidorn G, Garbin A, Ritzer L, Greuter F, *Polym. & Polym. Composites*, 4, No.5, 1996, 299-304.]

The resistivity of epoxy resins depends on the loading of fillers and on their chemical composition (Figure 15.5). When good filler dispersion was the criterion for determining maximum filler loading there was a considerable difference in the

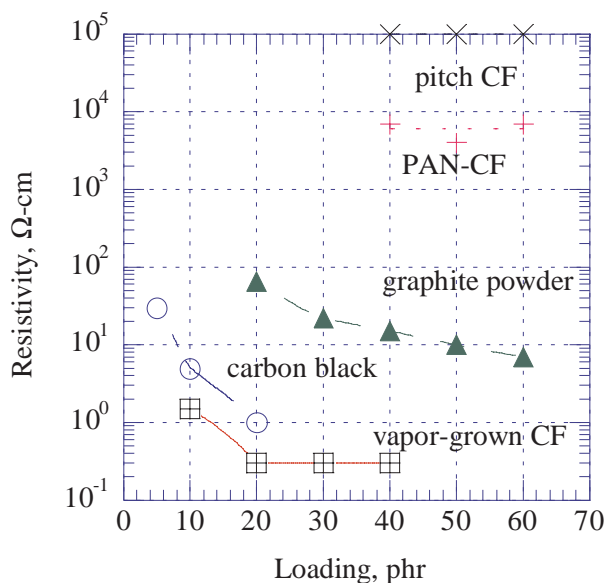


Figure 15.5. Resistivity of epoxy resin vs. filler load. [Adapted, by permission, from Katsumata M, Endo M, Ushijima H, Yamanishi H, *J. Mat. Res.*, **9**, No.4, 1994, 841-3.]

loading achieved by various types of fillers. Only 20 phr of carbon black could be incorporated. Graphite fiber, pitch and PAN carbon fibers could be used up to a concentration of 60 phr. The vapor-grown carbon fiber could be used up to only 40 phr but it was the one which gave the best performance in reduction of resistivity.⁴⁷

Thermal conductivity and expansion are important properties of adhesives used in electronics. Both properties influence the performance of computer chips. Generally, the chip has a protective cover which is attached by an adhesive. The adhesive bond must be maintained during thermally induced movement in the chip. The chip is bonded to its base with an adhesive which must also take thermal movement and, in addition, transfer heat from the chip. Two epoxy adhesives were used in the study: silica filled epoxy (65 and 75 wt% SiO₂ epoxy) and epoxy containing 70 wt% Ag.²⁶ Figure 15.6 shows their thermal conductivities. The behavior of both adhesives is completely different. The silver filled adhesive had a maximum conductivity at about 60°C whereas the maximum for SiO₂ filled adhesive was 120°C. The T_g of both adhesives was 50 and 160°C, respectively. Below its T_g, the thermal conductivity of the adhesive increases at the expense of increased segmental motions in the chain molecules. Above the T_g the velocity of photons rapidly decreases with increasing temperature and the thermal conductivity also decreases rapidly.

Microwave propagation in carbon black/epoxy resin composites shows that for small particle size inclusions, magnetic wave propagation increases with filler concentration but for large particles the propagation of magnetic waves does not depend on the concentration of the inclusions.²⁵

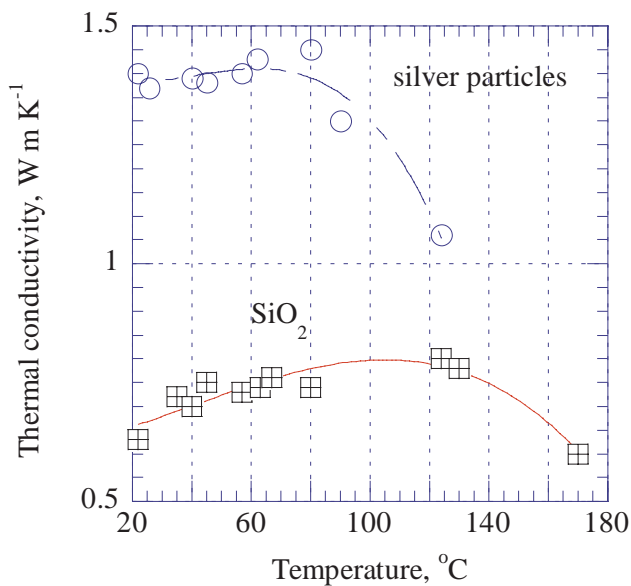


Figure 15.6. Thermal conductivity of filled epoxies vs. temperature. [Data from Nyilas A, Rehme R, Wyrwich C, Springer H, Hinrichsen G, *J. Mat. Sci. Lett.*, **15**, No.16, 1996, 1457-9.]

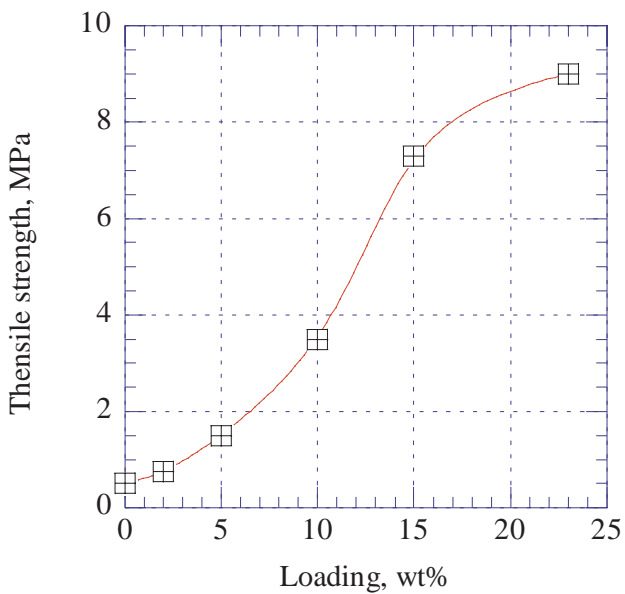


Figure 15.7. Tensile strength of epoxy/montmorillonite nanocomposite vs. filler concentration. [Adapted, by permission, from Lan T, Pinnavaia T J, *Chem. of Mat.*, **6**, No.12, 1994, 2216-9.]

Treatment of glass beads with epoxy silane improved the adhesion of glass beads/epoxy composite which resulted in a substantially lower water uptake and

better retention of properties after water immersion.²⁸ A similar improvement in composite properties was obtained in a jute/epoxy system.⁵⁴ Glass beads mixed with rubber particles improved the fatigue resistance of an epoxy composite reducing the localized stress at the crack tip.³² The methods of improvement of adhesion between the carbon fiber and the matrix are reviewed elsewhere.⁵³ The compressive strength of an epoxy composite can be improved by glass beads, quartz, and calcium carbonate (see Figure 8.25).³⁴ The shape of the particle has an effect on fracture behavior of filled epoxy composite.³⁵ The best properties are obtained with spherical silica particles. Fracture behavior of glass fabric/epoxy laminates can be improved by the addition of alumina.³⁷ Mechanical properties can be dramatically increased (tensile strength is increased 9 times) when the clay used as a filler is in the nanocomposite form (Figure 15.7).

Filled epoxy resins wastes can be ground and used as a filler for various materials.^{39,40} Recycled rubber particles are sometimes used for toughening of epoxy resins.⁵²

15.8 ETHYLENE VINYL ACETATE COPOLYMER, EVA⁵⁸⁻⁶²

| | |
|----------------------------------|--|
| Major polymer applications | hot-melt coatings, hot-melt adhesives, wall covering adhesives, paints, tubing, sporting goods, footwear, baby products, controlled release devices, wire and cable (semiconductor shields, automotive wire, automotive ignition, low-smoke cable), asphalt modification, slow burning candles, cap liners |
| Important processing methods | mixing/compounding, injection molding, extrusion, Banbury mixer, two-roll mills, cold feed extruders, reaction injection molding |
| Typical fillers | calcium carbonate, clay, aluminum hydroxide, magnesium hydroxide, zinc oxide, silica, quartz, red phosphorus |
| Typical concentration range | up to 45 wt% (magnesium hydroxide up to 60 wt%) ⁶² aluminum hydroxide up to 80 wt% |
| Auxiliary agents | siloxane, ⁵⁸ silanes, fatty acids, unsaturated polymeric acids |
| Special methods of incorporation | stearic acid is used to avoid sticking during the mixing; red phosphorus is usually added in the form of a masterbatch containing 50 wt% red phosphorus |
| Methods of filler pretreatment | thermal treatment, ⁵⁸ trimethylchlorosiloxane treatment ⁵⁸ |
| Special considerations | red phosphorus is an excellent flame retardant for EVA, used up to 8 wt% it gives V-0 rating |

The dynamic viscosity and shear modulus of silica filled EVA were related to the work of adhesion of filler particles.⁵⁸ The work of adhesion depends on the particle size distribution and load of filler. The increase in particle size of filler causes an increase in work of adhesion.

15.9 ETHYLENE-ETHYL ACETATE COPOLYMER, EEA⁶³⁻⁶⁶

| | |
|----------------------------------|---|
| Major polymer applications | hose, tubing, additive to other polymers |
| Important processing methods | extrusion/compounding, Banbury mixer, extrusion, calendering |
| Typical fillers | calcium carbonate, titanium dioxide, zinc oxide, carbon black, aluminum silicate, graphite, magnesium hydroxide, aluminum hydroxide |
| Typical concentration range | carbon black 5-20 wt%, calcium carbonate and many other fillers up to 50 wt% |
| Auxiliary agents | silane, mostly amine-functional |
| Special methods of incorporation | roll milling |
| Methods of filler pretreatment | none reported |
| Special considerations | metal hydroxides catalyze the oxidation of char to convert carboxyl groups to carbon dioxide ⁶⁵ |

Calcium carbonate stabilizes EEA at elevated temperatures. The stabilizing effect depends on particle size, type of calcium carbonate and coating. Calcite gives better stabilization than whiting or precipitated calcium carbonate. Also, a stearate coated grade improves thermal stability. The filler prevents formation of acetic and propanoic acids by interacting with carboxyl groups. Metal hydroxides (Mg and Al) also stabilize EEA as they decompose endothermally. For this mechanism to work, the metal hydroxide must decompose at a much lower temperature than the degradation temperature of the copolymer. Otherwise, the hydroxide will interact with the reactive groups of the copolymer and change the mechanism of the degradation of the polymer.^{64,65}

15.10 ETHYLENE-PROPYLENE COPOLYMERS, EPR & EPDM⁶⁷⁻⁸⁴

| | |
|---|--|
| Major polymer applications | automotive radiator hose, garden hose, wire and cable, tires, roofing, gaskets, conveyor belts |
| Important processing methods | extrusion, molding, calendering, coating |
| Typical fillers | calcium carbonate, calcinated clay, aluminum hydroxide, magnesium carbonate, magnesium hydroxide, antimony trioxide, calcium borate, huntite, hydromagnesite, zinc oxide, talc, silica |
| Typical concentration range | carbon black 20-40 wt%, most others 30-65 wt% |
| Auxiliary agents | organic silane, ⁷¹ aliphatic alcohols ⁸⁰ |
| Special methods of incorporation | processing history has an essential effect on conductivity; shear imposed during mixing causes a fracture of secondary carbon aggregates; increased temperature during mixing may preferentially form rubber-carbon bonds rather than the carbon-carbon bonds required for conductivity; vulcanization temperature may affect recovery of broken connections between carbon-carbon bonds; talc reduces melt viscosity which results in a smooth surface of extruded and calendered products as well as reduced wear of equipment ⁷¹ |
| Methods of filler pretreatment | silane treated talc increases modulus and reduces compression set; ⁷⁷ maleated or sulfonated EPDM interacts with zinc oxide; ^{75,76} esterification of precipitated silica with methanol, propanol, and hexadecanol; ⁸⁰ modification of precipitated silica with methacrylic and vinyl silane; ⁸⁰ calcium carbonate was modified with monoallyl and monodecyl maleate ⁸¹ |
| Special considerations | in conductive applications special conductive carbon blacks must be employed; fire resistant cables have good balance of properties when 180/20 phr alumina/magnesium carbonate is used; for high LOI 400 phr alumina is used; zinc oxide is used as an ionic crosslinker; ^{72,74,75} carbon black was found to be a very efficient UV stabilizer for a system having a high electrical conductivity; ⁶⁹ there is an interaction between ionic crosslinks with zinc oxide and hydroxyl groups of carbon black through hydrogen bonding ⁷³ |

In EPR formulations, calcium borate was found to be a good replacement for the combination of antimony trioxide with an organic flame retardant.⁶⁷ Calcium borate, in addition to affecting flame retardation, also reinforces the polymer. Another alternative is based on huntite/hydromagnesite filler. Here, some antimony trioxide and organic flame retardant combination must be added. The huntite/magnesite filler combination cannot, by itself, halt flame spread.^{68,70}

In carbon black filled EPDM, the production of foamed materials is affected by filler.⁷⁸ Cell density decreases with the amount of carbon black but increases with the amount of blowing agent. The size of cells decreases in the presence of carbon black because of the alkaline surface of carbon black.⁷⁸

15.11 IONOMERS

| | |
|----------------------------------|---|
| Major polymer applications | membranes, adhesives, elastomeric applications |
| Important processing methods | injection molding, extrusion, vulcanization, molding, calendering, coating |
| Typical fillers | calcium carbonate, aluminum hydroxide, magnesium carbonate, magnesium hydroxide, zinc oxide, talc, silica |
| Typical concentration range | 20-40 wt% |
| Auxiliary agents | silanes |
| Special methods of incorporation | not reported |
| Methods of filler pretreatment | not reported |
| Special considerations | not reported |

15.12 LIQUID CRYSTALLINE POLYMERS, LCP⁸⁵⁻⁸⁹

| | |
|----------------------------------|--|
| Major polymer applications | microwave cookware, fiber optic connectors, capsules for electronic devices, watches, cameras, audiovisual equipment, under-bonnet automotive components, aerospace structures |
| Important processing methods | injection molding, fiber spinning, extrusion |
| Typical fillers | glass fiber, wollastonite, carbon black, magnesium carbonate |
| Typical concentration range | 30-70 wt% |
| Auxiliary agents | not reported |
| Special methods of incorporation | materials have skin/core morphology in which the relative amounts of skin and core vary with processing parameters as does the distribution of reinforcement ⁸⁸ |
| Methods of filler pretreatment | drying is very important to prevent hydrolysis ⁸⁹ |
| Special considerations | processing result strongly depends on previous thermal and pre-shear treatment which may cause thermal instability; ⁸⁵ glass and mineral fibers are known to have weak adhesion to LCP therefore decrease its toughness; ⁸⁷ small additions of carbon black (1%) reduce melt viscosity ⁸⁹ |

Thermotropic liquid crystalline polymers can be formulated with high concentration of glass fiber to withstand working temperatures in excess of 300°C. In processing LCP, one problem arises. LCP orients itself in the direction of shear or flow – the process which benefits many materials but makes products from pure LCP excessively anisotropic. To balance mechanical properties it has been suggested⁸⁷ that some quantities of short glass or mineral fibers be added to LCP.

Figure 9.13 shows the effect of filler concentration on torque. The smallest increase was due to magnesium carbonate and the largest due to the presence of glass fibers.⁸⁹ The mechanical properties of filled composites are substantially improved by additions of magnesium carbonate, wollastonite and glass fiber. The most important improvement is in creep resistance (Figures 6.68 and 8.69).

15.13 PERFLUOROALKOXY RESIN, PFA⁹⁰

| | |
|----------------------------------|---|
| Major polymer applications | silicon wafer carriers, pump, pipes, fittings, filtration, tubing, column packing, marine coatings, wear resistant products, coating for hostile environments, automotive weather seals for doors and windows |
| Important processing methods | injection molding, extrusion, coating |
| Typical fillers | magnesium oxide, calcium hydroxide, PTFE, graphite, molybdenum disulfide, carbon black, metal particles |
| Typical concentration range | 3-30 wt% |
| Auxiliary agents | not reported |
| Special methods of incorporation | not reported |
| Methods of filler pretreatment | not reported |
| Special considerations | metal oxides play the role of acid acceptors |

15.14 PHENOLIC RESINS^{55,57,91-98}

| | |
|----------------------------------|---|
| Major polymer applications | aircraft interiors, automotive (pump housings, transmission reactors, timing pulleys), marine, construction, coatings, adhesives, carbonless copy paper, abrasives, friction materials, laminates, foundry resins, battery separators, wood bonding, composites, foam, hollow spheres |
| Important processing methods | lamination, molding, coating, compounding |
| Typical fillers | wood flour, glass fiber, carbon fiber, mica, wollastonite, mineral wool, talc, magnesium hydroxide, graphite, molybdenum sulfide, carbon black, cashew shell particles, alumina, chromium oxide, brass and copper powder, iron particles, steel fiber, ceramic powder, rubber particles, aramid, wollastonite, cellulosic fiber, lignin |
| Typical concentration range | 30-60 wt% |
| Auxiliary agents | stearates, fluoropolymers, carboxylic groups-containing copolymers which reduce viscosity of filled polyester (BYK-W 995) ⁹² |
| Special methods of incorporation | not reported |
| Methods of filler pretreatment | lignin treated by methylation decreases the rate of cure of phenolic adhesives; ⁹⁴ carbon fiber was anodically oxidized and subjected to various treatments with coupling agents ⁹⁷ to improve interfacial interaction with phenolic resins and oxidative stability of carbon fibers; titanate coupling of oxidized fibers resulted in improved adhesion to matrix and enhanced thermal stability of fibers ⁹⁸ |
| Special considerations | cobalt salts reduce UV and thermal stability; steel fiber and acrylic fiber give the best wear retention to brake pads; ⁵⁵ composites containing graphite have much better flame retarding properties than composites containing aramid or glass fiber; ⁵⁷ glass fiber slows down the cure rates of novolac resins ⁹⁶ |

Figure 15.8 shows the effect of aramid fibers on the friction coefficient and the specific wear rate of brake pads. Additions of up to 15 vol% aramid fiber are economical to reduce the coefficient of friction decrease which remains constant up to 40 vol%. At the same time, the specific wear rate decreases steadily as fiber concentration increases. This suggests that wear rate is improved by the material reinforcement.⁵⁵

Fire resistance is an important property of phenolic resins. The combination of phenolic resin with Expancel™ expandable microspheres leads to many useful products. Composites for high speed train interiors take advantage of the light weight, excellent fire rating, and very low thermal conductivity.⁹¹ Polyester filled with aluminum hydroxide is an alternative solution for train interior materials. The resin and filler can be easily processed when viscosity regulating additives are added.⁹²

The properties of novolac laminates can be improved by the addition of fillers.⁹³ Corrosion protective materials suffered from delamination because of varia-

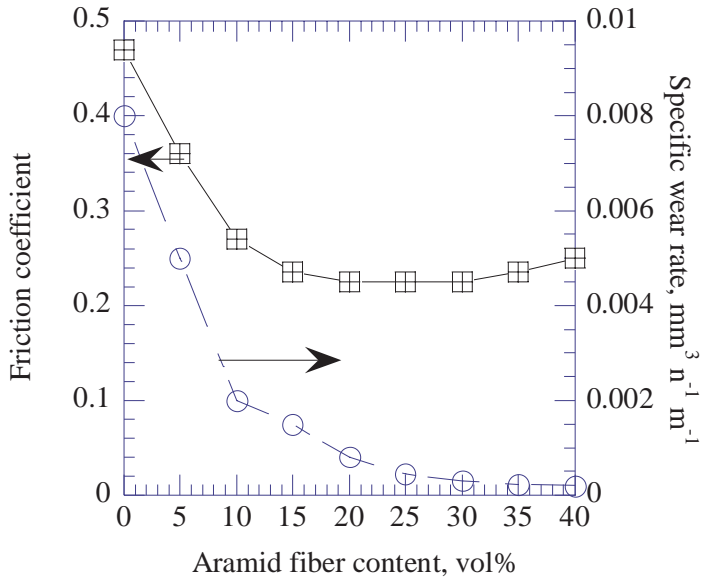


Figure 15.8. Friction coefficient and specific wear rate of phenolic brake pads containing varying concentrations of aramid fiber. [Adapted, by permission, from Bijwe J, *Polym. Composites*, **18**, No.3, 1997, 378-96.]

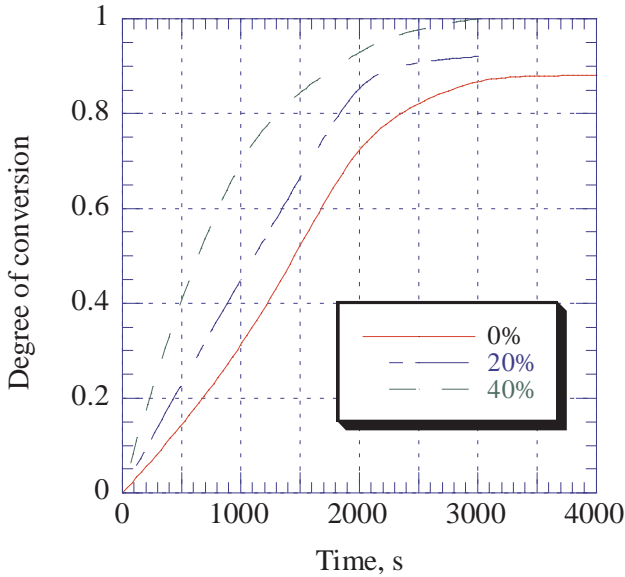


Figure 15.9. Degree of conversion vs. cure time of novolac resin. [Adapted, by permission, from Murayama H, Min K, Antec '97. Conference proceedings, Toronto, April 1997, 759-65.]

tions in thermal expansion rates. When the laminate was made from two layers – one containing carbon fiber and the other filled with 15-20% graphite powder, the

heat flow and temperature distribution across the laminate was improved and delamination was eliminated.⁹³

Figure 15.9 shows the effect of glass fiber on the rate of conversion of novolac resin.⁹⁶ The addition of glass fiber decreases rate of curing and degree of conversion. The chemical mechanism of this process is not discussed.

15.15 POLY(ACRYLIC ACID), PAA⁹⁹

| | |
|----------------------------------|---|
| Major polymer applications | dispersants for pigments and fillers, thickeners, toothpaste, hydraulic fluids, ion exchange resins, binder for ceramic, dental cements, polyelectrolytes |
| Important processing methods | compounding |
| Typical fillers | metal oxide, kaolin, clay |
| Typical concentration range | as required for application |
| Auxiliary agents | not applicable |
| Special methods of incorporation | none reported |
| Methods of filler pretreatment | none reported |
| Special considerations | poly(acrylic acid) has acid properties therefore it will interact readily with basic fillers such as for example alumina or magnesium hydroxide ⁹⁹ |

15.16 POLYAMIDES, PA^{4,100-126}

| | |
|---|---|
| Major polymer applications | automotive industry (radiator end tanks, inlet manifolds, rocker covers), electrical components (connectors, switches, motor frames), bearing cages, mechanical handling components, fibers, carpets, tire reinforcement, many other applications |
| Important processing methods | melt spinning, injection molding, extrusion |
| Typical fillers | glass fiber, carbon fiber, aramid, antimony trioxide, zinc borate, stainless steel fiber, graphite, nickel coated graphite, aluminum flakes, metallized glass |
| Typical concentration range | stainless steel fiber - 1-7 wt%, 30 wt% or more graphite, 15-50 wt% carbon black for conductive materials, glass spheres and fibers up to 70 wt%, carbon fiber - 20 wt%, silicon oxide and silicates up to 40 wt%, LCP up to 30 wt%, wollastonite - 40 wt% (can be used in conjunction with glass fiber, ¹⁰³ copper/polyamide-11 composite was made with 90 wt% spherical copper powder ¹⁰⁹) |
| Auxiliary agents | silanes, ¹²⁵ waterborne silanes, ¹¹⁹ compatibilizers in polymer blends |
| Special methods of incorporation | for delustering, titanium dioxide is added to polymer at 210°C to avoid excessive agglomeration; the order of addition of glass fiber to PP/PA-6 blend affects blend mechanical performance, glass fiber must be added to already compatibilized blend to avoid filler encapsulation; ¹⁰⁷ the use of vacuum hopper and premixing of polymer with copper spheres causes a reduction in porosity of highly filled polyamide ¹⁰⁹ |
| Methods of filler pretreatment | silane treatment of wollastonite; ¹⁰³ polyamide has ability to wet carbon fiber, polyamide behaves like a melt at 180°C even though its melting temperature is 225°C ¹¹⁵ |
| Special considerations | copper compounds catalyze thermal and UV degradation; titanium dioxide lowers UV stability, titanium dioxide is used as agent; red phosphorus in combination with zinc borate gives V-0 or V-1 rating with halogen-free system and inhibits corrosion because it can trap trace amounts of phosphine produced from red phosphorus |

In applications which require electric conductivity, polyamides are processed either with carbon fiber or with graphite. These applications include business machines (copying machines, computer printers), electronic packaging, carpet fiber, and EMI shielding. Other fillers, such as nickel coated graphite, stainless steel fiber, aluminum flakes and metallized glass are used less often. Polyamide is one of the best EMI shielding materials. When compounded with only 15% nickel coated glass fiber, it gives an attenuation of 50 db. By comparison, polyamide compounded with 30% graphite fiber gives an attenuation of only 30 db. Figure 15.10 illustrates the affect of particle size on resistivity.¹¹⁰ The general rule for filled materials is that the lower the particle size of the conductive particle the higher the conductivity of the resultant material. In conductive materials filled with fibers, this relationship is more complex and more dependent on filler type.

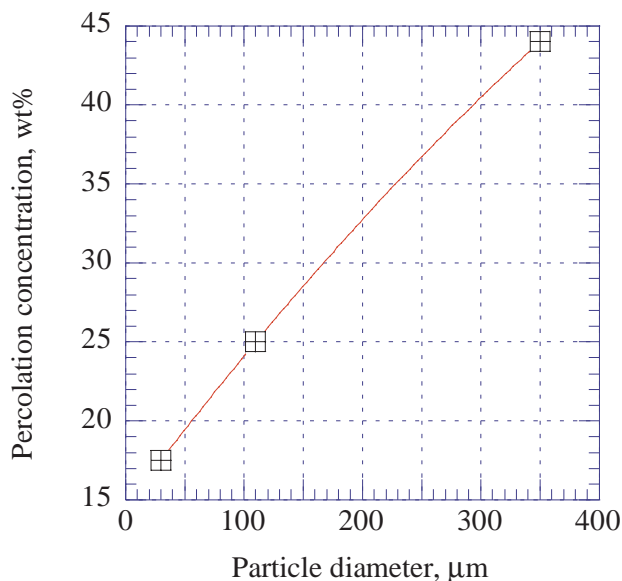


Figure 15.10. Weight fraction of copper for lower percolation concentration vs. particle diameter of copper particles in polyamide. [Adapted, by permission, from Larena A, Pinto G, *Polym. Composites*, **16**, No.6, 1995, 536-41.]

Less than 10% of the polyamide produced is made in a flame retardant version. The best system is composed of a combination of red phosphorus and zinc borate (see table above). The only drawback of this system is its color which is restricted to brick red or black. If other colors are required, ammonium polyphosphate is used either in combination with organic flame retardants or with antimony trioxide. It is possible to manufacture a very wide range of colors in the halogen free system. Some systems make use of the addition of novolac or melamine resins. For intumescent applications, ammonium polyphosphate, in combination with other components, is the most frequently used additive. Figure 13.6 shows that fillers such as calcium carbonate and talc (at certain range of concentrations) improve the effectiveness of ammonium polyphosphate. This is both unusual and important.¹⁰⁰ It is unusual because, in most polymers, the addition of fillers has an opposite influence on the efficiency of ammonium polyphosphate and it is important because ammonium polyphosphate must be used in large concentrations (minimum 20%, typical 30%) in order to perform as a flame retardant.

The use of magnesium hydroxide in polyamides is restricted by the low degradation temperature and the low hydrolytic stability of polyamides. Polyamide 6 and 6.6 begin to degrade at around 350°C whereas magnesium hydroxide releases water between 320 and 440°C. *In situ* production of water lowers the thermal stability of polyamides.¹⁰¹ The addition of 60 wt% magnesium hydroxide produced a flame

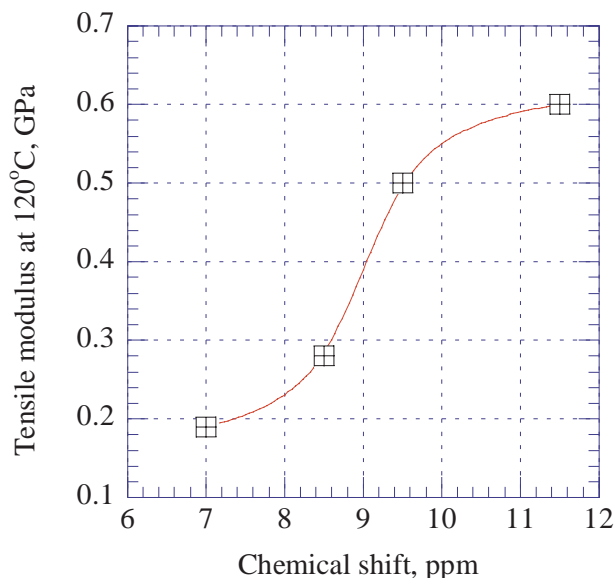


Figure 15.11. Tensile modulus of composites made from nylon and different fillers (montmorillonite, saponite, hectorite and mica) vs. ^{15}N -NMR chemical shifts of model compounds of fillers. [Adapted, by permission, from Usuki A, Koiwai A, Kojima Y, Kawasumi M, Okada A, Kurauchi T, Kamigaito O, *J. Appl. Polym. Sci.*, **55**, No.1, 1995, 119-23.]

retardant polyamide 6 with its degradation temperature overlapping with that of the filler.¹¹¹ A similar method was not successful with polyamide 6.6.

Fillers play an important role in powder coating of polyamide to form articles with a metal-like look (e.g., handles, mountings for radiators and pipes). For a material to be powder coated, it must withstand the stoving temperatures (170°C or more). It must also be electrically conductive, be chargeable and its reactive groups must be able to link with the coating system.¹⁰⁴ Fillers such as metal and metal coated ceramic spheres and carbon fibers are added to polyamide for its strength and paintability.

When aluminum borate whiskers were incorporated in SAN/PA-6 blends, the whisker, due to acid/based interaction had a better affinity to PA-6 than to SAN and for this reason they ended up in residence in the polyamide phase.¹⁰⁵ A similar principle was used to obtain a conductive blend by compounding PA, PP and carbon black.¹⁰⁶ Carbon black has a better affinity to polyamide and thus it prefers to reside in the polyamide phase or in the interphase formed between two immiscible polymers. Even when carbon black is added initially to polypropylene, it still transfers to the polyamide phase. This migration and preferential location of carbon black is not only an interesting scientific principle but it also has important practical implications. For the purpose of conductivity, a certain threshold concentration of carbon black is required to enable percolation and this threshold concentration is substantially lower if the carbon black settles in only one phase. This phase be-

comes richer in carbon black than the average concentration in blend. This principle allows materials to be formulated in more efficient manner.

Fiber reinforcement plays important role in polyamide processing. The orientation of fibers is not only influenced by the method of processing but also by external strain. Figures 14.9 and 9.29 show the effect of small strains on glass fiber orientation in polyamide 6.¹¹⁴ The reinforcement also depends on interaction between the filler and the matrix polymer. Figure 15.11 shows the relation between NMR chemical shifts of model compounds based on five different fillers and their tensile moduli. The compounds with a higher positive charge density on the nitrogen atoms in the polyamide molecule form stronger composites because the interaction between filler and matrix has an ionic character.¹²⁴

15.17 POLYAMIDEIMIDE, PAI

| | |
|----------------------------------|--|
| Major polymer applications | metal compressors in aerospace applications, pump housings, compressor valve plates, bushings, bearings, wear pads, piston rings and seals, gears, fasteners, plastic engine |
| Important processing methods | injection molding, extrusion, compression molding |
| Typical fillers | carbon fiber, glass fiber, graphite, fluorocarbon, PTFE |
| Typical concentration range | carbon fiber up to 30 wt%, glass fiber 30-40 wt%, graphite up to 20 wt%, PTFE fiber 1-2 wt% |
| Auxiliary agents | not reported |
| Special methods of incorporation | drying (polyamideimide may blister if it contains moisture and its temperature is increased rapidly) |
| Methods of filler pretreatment | drying to prevent degradation and blistering |
| Special considerations | post cure which takes several days to obtain peak mechanical properties |

15.18 POLYAMINES

| | |
|----------------------------------|--|
| Major polymer applications | flocculation of particulate matter, pigment retention aids in paper (e.g. TiO ₂), filtration aids, cosmetics |
| Important processing methods | compounding |
| Typical fillers | titanium dioxide |
| Typical concentration range | as required by application |
| Auxiliary agents | not reported |
| Special methods of incorporation | not reported |
| Methods of filler pretreatment | not reported |
| Special considerations | not reported |

15.19 POLYANILINE, PANI¹²⁷

| | |
|----------------------------------|---|
| Major polymer applications | materials having electric conductivity, protection against static electricity, EMI shielding, corrosion protection |
| Important processing methods | compounding |
| Typical fillers | silica |
| Typical concentration range | up to 40 wt% |
| Auxiliary agents | silica can be used in combination with colloid forming polymers such as PVAI or PVP |
| Special methods of incorporation | polymerization in the presence of filler ¹²⁷ |
| Methods of filler pretreatment | none reported but the type of filler plays essential role in obtaining stable polyaniline dispersion |
| Special considerations | a certain level of fillers is required to obtain stable dispersion; the dispersed polymer or filler must be chosen such that it does not interfere with the conductivity of polyaniline |

15.20 POLYARYLEETHERKETONE, PAEK¹²⁸

| | |
|----------------------------------|---|
| Major polymer applications | valve seats, pump impellers, valve linings, oil well data logging tools, bearing cages, aerospace, cryogenic propellant tank for supersonic air-crafts, nuclear power plants, satellites, fuel valves, bolts and nuts, heat-resistant gears, vacuum pump blades, butterfly valve seatings, piston rings, chemically resistant bearings and cams, machine tools, horizontal stabilizers for helicopters, ducting, semiconductor wafer carriers, belts, tennis racket strings, surgical instruments, sterilization equipment for medical and dental applications, bone screws, implants, fracture fixation plates, high performance conveyors, hot melt adhesives |
| Important processing methods | injection molding, extrusion, wire coating, mixing, melt spinning |
| Typical fillers | glass fiber, carbon fiber, graphite, PTFE |
| Typical concentration range | 20-30 wt% |
| Auxiliary agents | not reported |
| Special methods of incorporation | not reported |
| Methods of filler pretreatment | heat treatment of carbon fibers increases their resistance to oxidation but their adhesion decreases |
| Special considerations | carbon fiber requires treatment to increase adhesion by, for example, oxidation of its surface |

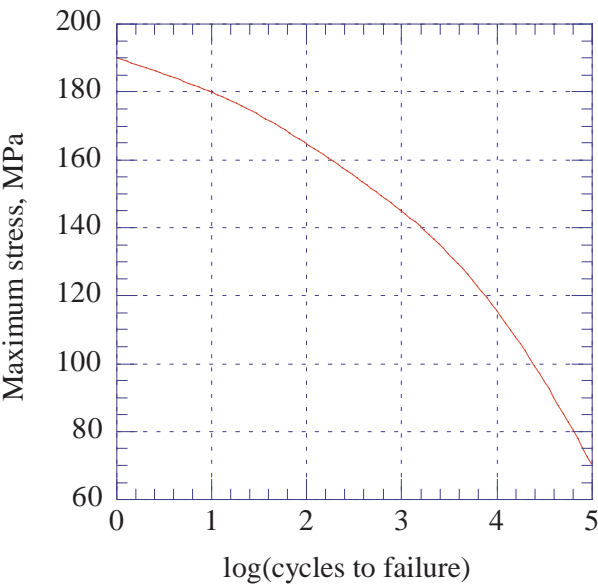


Figure 15.12. Maximum stress vs. cycles to failure for composites based poly(phenylene ether ketone). [Data from Zhou J, Li G, Li B, He T, *J. Appl. Polym. Sci.*, **65**, 1997, 1857-64.]

Figure 15.12 shows the fatigue resistance of carbon and glass fiber filled poly(phenylene ether ketone).¹²⁸ The flexural fatigue depends on tensile properties of the composite. The yield strength of the matrix and the quality of the interface affect the fatigue properties of composites.

15.21 POLY(BUTYLENE TEREPHTHALATE), PBT^{102,103,116,129}

| | |
|----------------------------------|---|
| Major polymer applications | composites, textiles, brush bristles, tire cords, electrical and electronics (connectors, circuit breakers, capacitor housings), automotive (distributor caps, mirror housings, door knobs), housewares, lighting, power tools, sporting goods, plumbing |
| Important processing methods | injection molding, extrusion, monofilament extrusion |
| Typical fillers | carbon fiber, glass fiber, aramid, mica, talc, calcinated kaolin, antimony trioxide, carbon black, zinc borate, glass spheres |
| Typical concentration range | 20-40 wt% |
| Auxiliary agents | coupling agents used in composites |
| Special methods of incorporation | the process design should account for the much faster crystallization rates of filled materials |
| Methods of filler pretreatment | drying, silane coupling |
| Special considerations | material must be completely dry before processing to avoid hydrolysis; the concentration of moisture in material ready for processing should be below 0.05% possibly below 0.025%; carbon black is the most effective UV stabilizer followed by TiO ₂ ; ferrocene and cobalt salts accelerate UV degradation; zinc borate improves laser marking of glass filled composite; addition of glass spheres to glass fiber filled PBT improves melt flow, shrinkage and warpage; ¹⁰² these same improvements cannot be achieved by using talc/glass fiber mixtures; ¹⁰² mica controls warpage and increases flexural modulus and strength, heat distortion temperature, and dielectric strength; ^{103,116} increase in particulate filler content decreases the ductility of weld (the residual strength 50% of the strength of the matrix without filler) but addition of glass fiber only slightly reduces weld strength (10% for 30 wt% glass filled composite) ¹²⁹ |

15.22 POLYCARBONATE, PC^{106,108,130-135}

| | |
|---|--|
| Major polymer applications | compact disks, optical lenses, camera components, goggles, safety glasses, windows, laminated walls, skylights, copying machines, computer printers, gear, bearings, guide pins, rollers, speedometer needles, windscreens, instrument panels, head lamp covers and housings, tool boxes, dental applications, blood collector containers, disposable syringes, medical tubing, pacemaker components, dinnerware, drinking cups, toys |
| Important processing methods | extrusion, calendering, blow molding, injection molding, gas-assisted injection molding, thermoforming, solution casting |
| Typical fillers | glass fiber, wollastonite, titanium dioxide, boric oxide, carbon black and graphite fibers for EMI shielding, molybdenum sulfide, graphite, PTFE |
| Typical concentration range | 10-40 wt%; carbon black 5-20 wt% (tear strength maximum at 5 wt%, tensile strength maximum at 15 wt%) |
| Auxiliary agents | poly(methyl siloxane) and glycidoxo-propyltrimethoxy silane ¹³⁴ |
| Special methods of incorporation | none reported |
| Methods of filler pretreatment | moisture content of composite should be below 0.02% to avoid hydrolytic changes as well as blistering |
| Special considerations | some inorganic pigments accelerate UV degradation; in PP/PC blend carbon black has higher affinity to PC and it is preferentially located in PC phase (compare with polyamide above); ¹⁰⁶ glass fiber reinforced PC has very good retention of mechanical properties on exposure to γ -radiation (see Figure 11.6); ¹⁰⁸ thermal stability of PC/carbon fiber composite is also good (see Figure 11.15) ¹³⁰ |

Flame retardant materials are produced from polycarbonate. Several options are available to produce such materials. A combination of PTFE fibers (2 wt%) and boric oxide (1 wt%) gives V-1 rating. Good results are also obtained by using a combination of alumina and silica or a blend of magnesium carbonate, calcium carbonate with zinc borate. Halogen-free flame retardant grades are readily produced. The addition of zinc borate to polycarbonate substantially reduces the heat release and smoke generation from the compound.¹³²

The thermal properties of polycarbonate are not outstanding and the opportunities to improve it are remote. Addition of 30 wt% of carbon or glass fibers increases deflection temperature under load only by about 20°C to the maximum attainable value of 150°C but coefficient of the thermal expansion is drastically reduced which makes it suitable for many of its potential applications.

Polycarbonate is used in applications which require EMI shielding and static control. EMI shielding requires large quantities of conductive fillers. For example, 40 wt% aluminum flake gives an attenuation of 32 dB, 30 wt% graphite fibers gives 42 dB, and 15 wt% nickel coated glass fiber gives 45 dB.¹³⁵

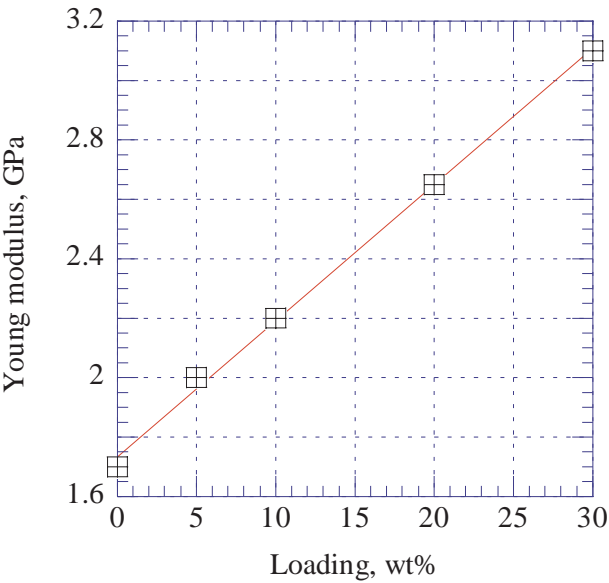


Figure 15.13. Young modulus of polycarbonate vs. amount of carbon fiber. [Adapted, by permission, from Zihlif A M, Di Liello V, Martuscelli E, Ragosta G, *Int. J. Polym. Mat.*, **29**, Nos.3-4, 1995, 211-20.]

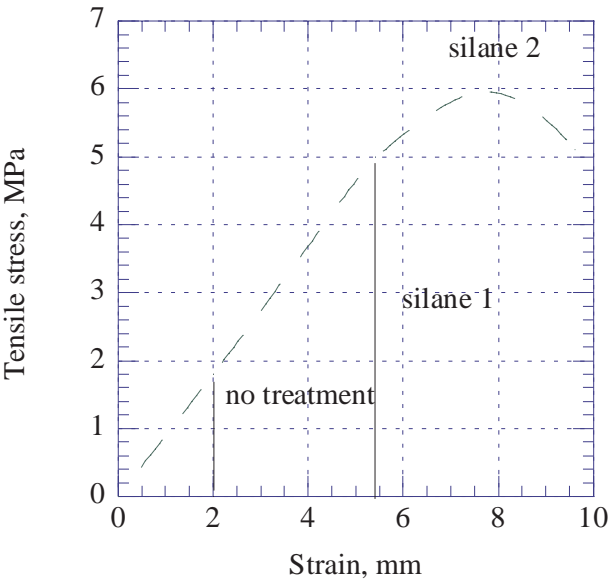


Figure 15.14. Strain-stress curve of 10% zinc oxide filled polycarbonate. [Adapted, by permission, from Tanaka T, Waki Y, Hamamoto A, Nogami N, Antec '97. Conference proceedings, Toronto, April 1997, 3054-8.]

Fiber reinforcement improves mechanical properties by amounts relative to the amount of fiber used. Figure 15.13 gives the relationship between Young modu-

lus and the load of carbon fibers.¹³³ The effect of carbon fibers on tensile yield stress can be determined from Figure 8.7. Morphological observations indicate that there is good interfacial bonding. Figure 15.14 vividly illustrates the gains in improved mechanical properties that a coupling agent can provide. Two to six percent of coupling agent was used to treat ZnO for a 3-fold improvement in tensile stress.¹³⁴

15.23 POLYETHERETHERKETONE, PEEK^{85,136-139}

| | |
|----------------------------------|--|
| Major polymer applications | valve seats, pump impellers, valve linings, oil well data logging tools, bearing cages, aerospace, cryogenic propellant tank for supersonic aircrafts, nuclear power plants, satellites, fuel valves, bolts and nuts, heat-resistant gears, vacuum pump blades, butterfly valve seatings, piston rings, chemically resistant bearings and cams, machine tools, horizontal stabilizers for helicopters, ducting, semiconductor wafer carriers, belts, tennis racket strings, surgical instruments, sterilization equipment for medical and dental applications, bone screws, implants, fracture fixation plates, high performance conveyors, hot melt adhesives |
| Important processing methods | injection molding, extrusion, wire coating, mixing |
| Typical fillers | glass fiber, carbon fiber, graphite, PTFE |
| Typical concentration range | typically 30 wt% but high glass loading can go up to 75 wt% ⁸⁵ |
| Auxiliary agents | binders are needed in prepregging step (polyimide is an example of such binder) ¹³⁷ |
| Special methods of incorporation | drying is only necessary to prevent molding defects because the polymer has very high resistance to hydrolysis |
| Methods of filler pretreatment | heat treatment of carbon fibers increases their resistance to oxidation but their adhesion decreases |
| Special considerations | high temperature treated carbon fiber requires treatment to increase adhesion by, for example, oxidation; wear and friction grades usually contain combination of graphite, carbon fiber, and PTFE |

The introduction of fillers to PEEK creates a higher nucleation rate. The surface of carbon fibers and nuclei within the PEEK matrix compete for crystallization growth. Epitaxial transcrystalline growth was frequently observed on the fiber surface in carbon fiber reinforced PEEK composites.

Reinforcement with glass fiber or carbon fiber doubles the tensile strength and modulus and, at the same time, the impact strength is also increased. Carbon fibers improve properties by at least 50% over PEEK filled with glass fibers. Thermal properties are also improved in this reinforcement, again especially by carbon fiber. Heat deflection temperature more than doubles due to reinforcement to values over 300°C. Solvent resistance is usually determined by the degree of fiber reinforcement and by the adhesion between fiber and matrix. PEEK/carbon fiber composite has an excellent resistance to water (Figure 15.15)¹³⁹ and to high temperature.

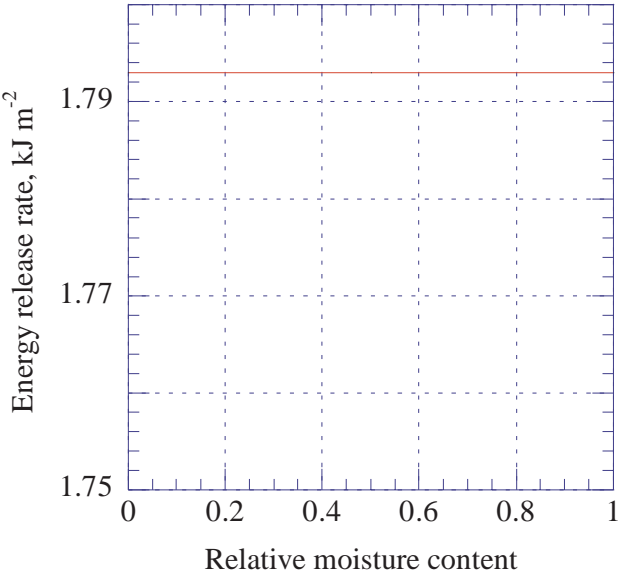


Figure 15.15. Energy release rate, G_{Ic} , vs. moisture content. [Data from Selzer R, Friedrich K, *Composites, Part A*, **28A**, 1997, 595-604.]

15.24 POLYETHERIMIDE, PEI

| | |
|----------------------------------|--|
| Major polymer applications | microwaveable cookware, electronic connectors, automotive engine sensors, bulb sockets, vacuum pump vanes, aircraft interiors, steam sterilizable surgical components |
| Important processing methods | injection molding, blow molding, extrusion |
| Typical fillers | glass fiber, carbon fiber |
| Typical concentration range | 20-40 wt% |
| Auxiliary agents | not reported |
| Special methods of incorporation | not reported |
| Methods of filler pretreatment | not reported |
| Special considerations | PEI has very good fire resistance (LOI 47%) compounding with 30 wt% glass fiber reduces LOI to 32; compounding of PEI with glass fiber does not affect heat deflection temperature |

15.25 POLYETHER SULFONE, PES

| | |
|----------------------------------|---|
| Major polymer applications | aircraft interiors, multipin connectors, coil bobbins, integrated circuits sockets, fiber optics connectors, dip switches, automotive fuses, printed circuit boards, transformer wire coatings, microwave cook-ware, sight glasses, membranes, medical applications (due to the resistance to different methods of sterilization), coatings |
| Important processing methods | injection molding, extrusion, blow molding, compression molding, thermoforming, casting |
| Typical fillers | glass fiber, carbon fiber |
| Typical concentration range | 30 wt% |
| Auxiliary agents | not reported |
| Special methods of incorporation | not reported |
| Methods of filler pretreatment | drying to below 0.05 wt% |
| Special considerations | moisture causes bubbles, streaking, and splay marks; compounding with glass fiber has very little effect on PES heat deflection temperature and marginally increases LOI but tensile strength is improved in a broad spectrum of temperatures |

15.26 POLYETHYLENE, PE^{38,45,59,64,83,103,140-195}

| | |
|---|---|
| Major polymer applications | packaging and film are the major applications, many others |
| Important processing methods | blow film extrusion, molding, cast film extrusion, extrusion, injection molding, rotational molding |
| Typical fillers | barium sulfate, calcium carbonate, carbon black, calcium sulfate whiskers, diatomaceous earth, glass fiber, glass spheres, hollow silicates, kaolin, mica, talc, wollastonite, silica, magnesium hydroxide, hydrotalcite, red mud, ground tire rubber, ferromagnetic powder, nickel fibers, wood flour, zirconium silicate, starch, soot, marble, aluminum, lignin, sand |
| Typical concentration range | generally ≥ 40 wt%; calcium carbonate, calcinated kaolin, talc - 20-40 wt%; carbon fiber 5-30% (depending on aspect ratio); ¹⁴¹ titanium dioxide - 1 wt% (occasionally concentrations of 10 wt% are found in thin sections); ¹⁴³ ferromagnetic powder - up to 90 wt%; ¹⁵³ stainless steel fiber - 2-3 wt%; ¹⁵⁴ nickel fibers for magnetic properties - 10-30%; ¹⁵⁵ starch in biodegradable products - 4-8 wt% ¹⁶⁵ |
| Auxiliary agents | polymer grafting by maleic anhydride or unsaturated diacid anhydride, silanes, titanates, acryloamide was grafted on the surface of calcium carbonate to contain 0.2-1.8% amide groups which were then used for interaction with compatibilizer containing carboxyl groups; ¹⁴⁰ aminosilane treatment of kaolin; ¹⁴² phosphate treatment of calcium carbonate increases adhesion of mechanical properties of material; ¹⁴⁶ low molecular weight polyethylene wax was used as dispersing agent for carbon black ¹⁸⁹ |
| Special methods of incorporation | usually surface modification of filler is performed prior to filler incorporation into the polymer; high concentration of calcium carbonate (40 wt%) provides a film which has properties similar to paper but surpasses paper in resistance to moisture; chlorinated PE containing carboxyl groups was used as compatibilizer with calcium carbonate; ¹⁴⁰ masterbatches of titanium dioxide contain 40-50 wt% pigment; ¹⁴³ rubber modification to incorporate zirconium silicate without a loss of mechanical strength ¹⁵⁹ |
| Methods of filler pretreatment | moisture removal by drying, preparation of masterbatches; moisture pickup by titanium dioxide and its concentrates was found to cause lacing which causes film defects, drying of the filler is a simple remedy ¹⁵⁰ |
| Special considerations | hydrotalcite is used as acid neutralizer with various stabilizing packages; anatase titanium dioxide decreases UV stability; presence of transition metals (Ni, Zn, Fe, Co) affects thermal and UV stability; addition of 15 wt% calcium carbonate increases coating-to-substrate adhesion of polyethylene materials; ¹⁴⁹ carbon black in concentration above 2 wt% in conjunction with crosslinking improves UV stability of polyethylene films; ¹⁵⁸ carbon black is better antioxidant than many commercial antioxidants; ¹⁶⁴ improved thermal conductivity, more stable bubble with calcium carbonate improves output of blown film; ¹⁶⁷ talc was used to prevent melt sag in blow molding process; ^{180,184,186} talc can also be used to reduce gas permeability in film for food packaging industry; ^{183,188} sand was found to reduce photodegradation of PE; ¹⁹¹ small additions (1-2 wt%) of some metal oxides also give some UV protection whereas other metal oxides increase degradation rate; ¹⁹² HALS was immobilized on the surface of silica incorporated into PE which reduced its activity as UV stabilizer ¹⁹⁵ |

Infrared studies give us information on filler distribution in PE matrix. Figure 10.12 shows the schematic diagram of the perceived distribution of talc particles in relationship to crystalline formations in PE. The diagram shows that talc is in association with crystallites. This is due to the fact that talc particles affect nucleation through intimate contact and chain alignments on the surface of the filler. The addition of a small amount of titanium dioxide has a strong nucleating action which results in smaller spherulites formed due to the competition of the increased number of growing sites.¹⁴³ Nucleation of LDPE was also increased by particulate silica. Adsorption of polymer chains by the filler affects crystallization.^{147,148}

Mechanical properties depend on filler-matrix interaction but there are some characteristics of fillers which influence the mechanical behavior of composite. Most fillers increase tensile strength but calcinated kaolin increases tensile strength about 3 times more than calcium carbonate or talc. Impact strength is improved by calcinated kaolin. It is lowered by the addition of either talc or calcium carbonate.¹⁰³ This effects can be changed by tailoring the interface between the matrix and the filler. In one example, chlorinated PE containing carboxyl groups was used as compatibilizer.¹⁴⁰ Also, calcium carbonate was modified by grafting acryloamide with 0.2-1.8% amide groups onto its surface. This increased its degree of interaction. The tensile strength of this composite was increased by over 50% and its impact strength by about 120% compared with neat resin (when calcium carbonate was added without compatibilizer, the impact strength of the composite dropped to below 25% of that of neat resin).¹⁴⁰ Similarly, the effect of kaolin was improved by coating it with maleic grafted polyethylene which increased the impact energy of the filled PE by a factor of 4 compared with neat resin.¹⁴² In blown films, calcium carbonate, in the concentration range of 5-20 wt%, was found to increase dart impact strength. But, the tensile strength and elongation decreased as the concentration increased. Additions of talc in the same concentration range decreased all mechanical properties.¹⁵²

The most common method to make PE fire retardant is through the use of phosphoric esters of polyols. An alternate method uses magnesium hydroxide. Figure 15.16 shows the effect of varying amounts of aluminum hydroxide and magnesium hydroxide on the limiting oxygen index (LOI).¹⁹⁰ Magnesium oxide gives a marginally better performance but in both cases a large amount of metal oxide is needed. If such large quantities are used, the impact resistance of the material is substantially reduced. The impact resistance can be improved in these compositions by additions of silane-crosslinkable polyethylene.

The electric conductivity of polyethylene can be improved by addition of many fillers. Figure 15.17 shows the effect of aspect ratio of the fiber on the electric conductivity of polyethylene filled with carbon fiber.¹⁴¹ Depending on the aspect ratio, different levels of carbon fiber are needed to obtain the same effect. When a very high aspect ratio is used, 2 vol% carbon fiber gives the same effect as can be obtained with 30 vol% of carbon fiber having aspect ratio of 1. Compared with

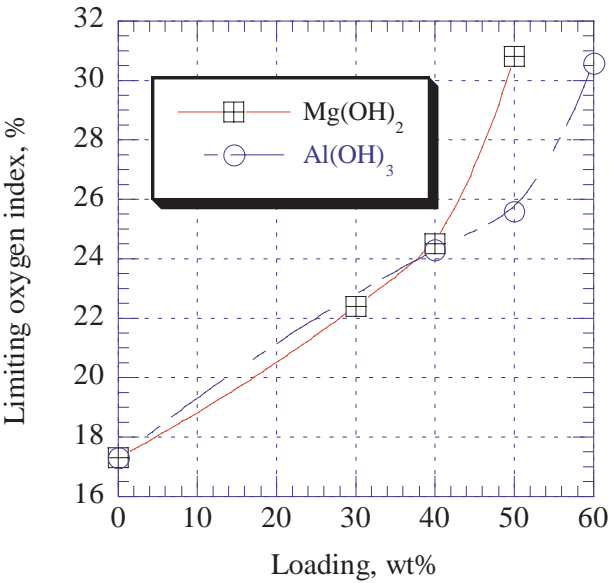


Figure 15.16. Limiting oxygen index of polyethylene vs. concentration of filler. [Adapted, by permission, from Yeh J T, Yang H M, Huang S S, *Polym. Degradat. Stabil.*, **50**, No.2, 1995, 229-34.]

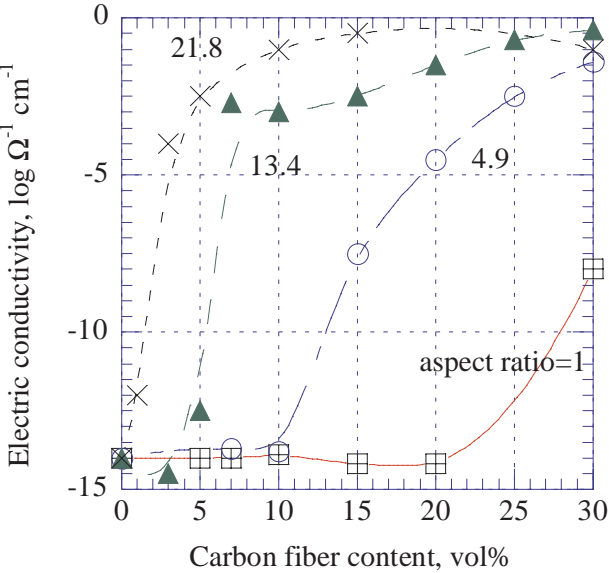


Figure 15.17. Electric conductivity of polyethylene filled with carbon fibers of different aspect ratio vs. volume content. [Adapted, by permission, from Agari Y, Ueda A, Nagai S, *J. Appl. Polym. Sci.*, **52**, No.9, 1994, 1223-31.]

polypropylene, polyethylene required about 50% more carbon black to develop the same conductivity.¹⁴⁵ A better wetting of the filler in polyethylene results in higher

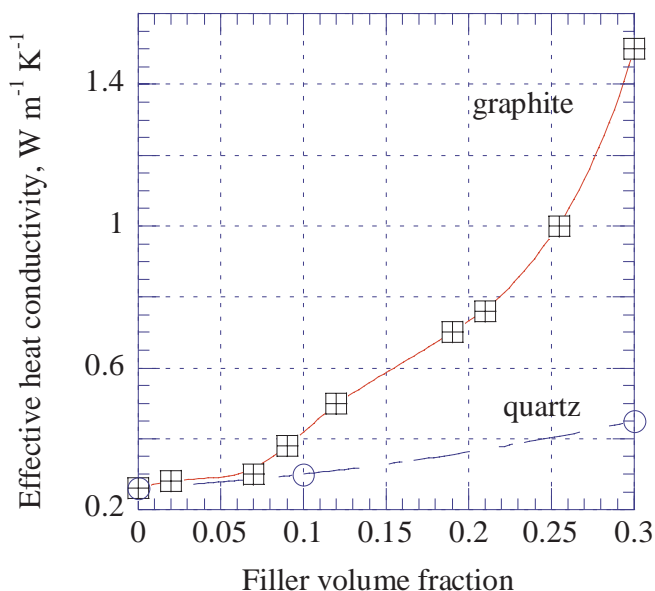


Figure 15.18. Effective heat conductivity of polyethylene vs. filler volume fraction. [Data from Privalko V P, Novikov V V, *Adv. Polym. Sci.*, **119**, 1995, 31-77.]

colloidal stability but also in a higher percolation threshold. This affects the amount of carbon black needed to obtain a certain level of conductivity. For polyethylene to be conductive it must be filled above a certain threshold concentration with conductive filler. Below this threshold level, conductivity remains quite constant and it is largely independent of filler concentration. In this range, conductive filler particles are not in proper contact. When a certain threshold value is reached, the conductivity increases very rapidly as more carbon black is added. Eventually, a plateau of ultimate conductivity is reached which depends on the matrix and on the type of carbon black used.¹⁴⁵ Large concentrations (80-90 wt%) of ferromagnetic materials are required to reach threshold concentration (see Figure 14.15).¹⁵³ Conductivity changes rapidly when 3 wt% stainless steel fiber is added to polyethylene.¹⁵⁴ Similarly, magnetic properties can be changed with additions from 10 to 30 wt% of nickel fibers. The fibers must be in the proper orientation to develop optimum magnetic properties.¹⁵⁵ One study¹⁷⁴ sought to obtain a material with low resistivity at room temperature and high resistivity at elevated temperatures. It also attempted to obtain material in which such change occurs within a few degrees Celsius. The composites which were developed can switch rapidly from a low to a high resistivity. These composites are used in devices which can limit electric fault currents. The materials were developed by selecting an appropriate process of incorporation (quality of mixing) and by the choice of carbon black. A composition which combined coarse and fine carbon blacks gave the required performance.

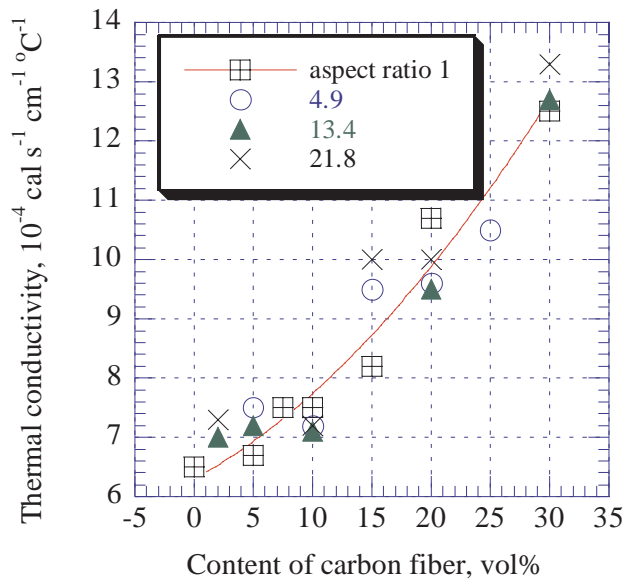


Figure 15.19. Thermal conductivity of polyethylene vs. volume content of carbon fiber. [Adapted, by permission, from Agari Y, Ueda A, Nagai S, *J. Appl. Polym. Sci.*, **52**, No.9, 1994, 1223-31.]

Heat conductivity of composite materials are severely and adversely affected by structural defects in the material. These defects are due to voids, uneven distribution of filler, agglomerates of some materials, unwetted particles, etc. Figure 15.18 shows the effect of filler concentration on thermal conductivity of polyethylene. Graphite, which is a heat conductive material, increases conductivity at a substantially lower concentration than does quartz. These data agree with the theoretical predictions of model.³⁸ Figure 15.19 shows the effect of volume content and aspect ratio of carbon fiber on thermal conductivity.¹⁴¹ This figure should be compared with Figure 15.17 to see that, unlike electric conductivity which does depend on the aspect ratio of the carbon fiber, the thermal conductivity is only dependent on fiber concentration and increases as it increases.

15.27 POLYETHYLENE, CHLORINATED, CPE^{82,196-199}

| | |
|----------------------------------|--|
| Major polymer applications | wire and cable, autoignition wire, roofing membranes, technical hoses, power steering hose, transmission oil cooler hose, car axle boots, automotive air ducts and hoses, impact modification for PVC in pipe, vinyl siding, window profiles and FR ABS |
| Important processing methods | peroxide vulcanization, molding, mixing, extrusion |
| Typical fillers | clay, carbon black 3-10 wt%, titanium dioxide 1-2 wt%, magnesium oxide is used as thermal stabilizer (typically 5-10 phr) |
| Typical concentration range | 20-40 wt% |
| Auxiliary agents | not reported |
| Special methods of incorporation | CPE was used as PVC modifier to increase filler concentration ¹⁹⁹ |
| Methods of filler pretreatment | aluminum filler was prepared from the reaction of aluminum chloride and carboxylic acid such as hydroxybenzoic, aminobenzoic, anthranilic acids to form an active filler which improves the mechanical properties of CPE ¹⁹⁸ |
| Special considerations | presence of zinc, copper, iron and nickel compounds accelerated dehydrochlorination; combination of basic magnesium carbonate and aluminum hydroxide is used as flame retardant and smoke suppressant; ⁸² chlorinated polyethylene adsorbs on the surface of titanium dioxide forming a layer 1-20 nm thick depending on the acid/base interaction parameter of titanium dioxide ¹⁹⁷ |

15.28 POLYETHYLENE, CHLOROSULFONATED, CSM^{82,196,200}

| | |
|----------------------------------|---|
| Major polymer applications | coated fabrics, inflatable boats, roofing, pool liners, industrial effluent pit liners, radiator and heater hoses, wire and cable, adhesives, automotive components (high-temperature timing belts, power steering pressure hose, gaskets, spark plugs), boots, industrial products (hose, rolls, seals, gaskets, diaphragms), and lining for chemical processing equipment |
| Important processing methods | vulcanization, coating, extrusion, compounding, injection molding |
| Typical fillers | silica, calcium carbonate, carbon black, magnesium hydroxide, basic magnesium carbonate, metal oxides (typically MgO) are used as curing agents |
| Typical concentration range | 20-30 wt% |
| Auxiliary agents | none reported |
| Special methods of incorporation | none reported |
| Methods of filler pretreatment | thermal treatment at 800°C and hexadecanol treatment were performed to study the effect that hydroxyl groups have on silica reinforcement ²⁰⁰ |
| Special considerations | magnesium hydroxide and basic magnesium carbonate are used as flame and smoke retarding additives ⁸² |

15.29 POLY(ETHYLENE OXIDE), PEO & PEG²⁰¹⁻²⁰⁵

| | |
|----------------------------------|---|
| Major polymer applications | pharmaceutical applications, controlled release drugs, , polyester fibers, unsaturated polyester resins, oil exploration, polyols, surfactants, haircare, switching elements, polymer electrolytes, lithium batteries, nanocomposites |
| Important processing methods | compounding, reacting with other chemicals |
| Typical fillers | graphite, fumed silica, molybdenum disulfide, vanadium oxide |
| Typical concentration range | graphite - 10-40 wt%; fumed silica - 10 wt% |
| Auxiliary agents | not reported |
| Special methods of incorporation | not reported |
| Methods of filler pretreatment | not reported |
| Special considerations | fumed silica used as rheological additive ²⁰⁴ addition of salts decreases solubility of resin in water |

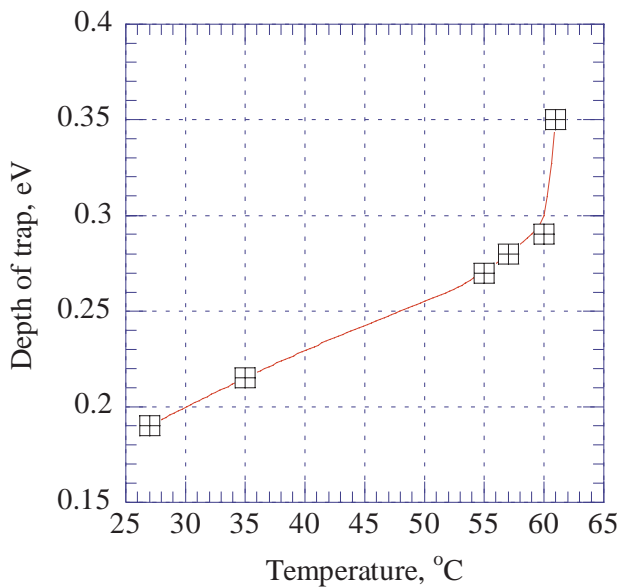


Figure 15.20. The depth of trap vs. temperature. [Adapted, by permission, from Kimura T, Asano Y, Yasuda S, *Polymer*, **37**, No.14, 1996, 2981-7.]

The poly(ethylene glycol)/graphite system acts as a switching element. A switching element is a polymer composite with dispersed conductive particles such as carbon black, graphite or metal particles. The switching element has a low resistance at low temperature (switch-on) and a high resistance at high temperature (switch-off). The

principle of action of such system is explained by Figure 15.20. A small difference in temperature causes a rapid change in resistance. The explanations of this phenomenon are two: the classical explanation is based on the premises that with temperature increasing conductive particles are too distant to transfer electrons; the more recent explanation attributes the sudden change in resistivity to the change of dielectric constant of poly(ethylene glycol).²⁰¹ A similar system was developed based on polyethylene.

Poly(ethylene oxide) is also used in nanocomposites which contain molybdenum disulfide or vanadium oxide. The inorganic filler and the organic matrix interact at a molecular level forming xerogels, which are nanocomposites with controlled ion mobility.^{202,203,205}

15.30 POLY(ETHYLENE TEREPHTHALATE), PET^{103,206-209}

| | |
|----------------------------------|--|
| Major polymer applications | packaging, bottles, film, fiber, textiles, brush bristles, composites, electrical, automotive, housewares, lighting, power tools, sporting goods, plumbing |
| Important processing methods | injection blow molding, extrusion, blow molding, injection molding, monofilament extrusion |
| Typical fillers | carbon fiber, glass fiber, aramid, mica, glass spheres, talc, clays, wollastonite, fly ash |
| Typical concentration range | glass fiber composites - 30-55 wt%, general purpose fillers - 20-40 wt% |
| Auxiliary agents | coupling agents used in composites; γ-aminopropyltrimethoxy silane; ²⁰⁶ maleic anhydride modification ²⁰⁸ |
| Special methods of incorporation | filler and interfacial modifier were premixed before extrusion ²⁰⁶ |
| Methods of filler pretreatment | drying |
| Special considerations | material must be dry before processing to avoid hydrolysis; warping can be reduced by the use of mixed fillers (e.g., glass beads and mica) also, talc and clays; ferrocene and cobalt salts accelerate UV degradation |

The treatment of glass beads with silane improves their adhesion. This benefits most properties of the composite but its tensile strength is slightly lower than that of neat resin. The crystallization rate of PET is higher in the presence of filler. Glass beads cause a heterogeneous nucleating effect. Introduction of a modifier lowers the nucleation rate and acts as a compatibilizer. The combination of glass beads and the modifier increases tensile properties and the impact strength of the composite.²⁰⁶ Figure 10.7 shows the effect of mica on the crystallization rate of PET.²⁰⁹

15.31 POLYIMIDE, PI^{137,210-212}

| | |
|----------------------------------|--|
| Major polymer applications | aerospace, electronics (mostly films and coatings), photosensitive materials for positive imaging, solar cells, hollow fiber membranes, composites, nuclear power plants, space shuttle, microprocessor chip carriers, structural adhesives |
| Important processing methods | vapor phase deposition, spin coating, injection molding, casting, extrusion, drawing of oriented films, compression molding, sintering |
| Typical fillers | carbon fiber, glass fiber, graphite lubricant for wear resistant applications; molybdenum sulfide, PTFE, antimony trioxide, barium titanate, clay, silica, aluminum nitride, smectite |
| Typical concentration range | in general 2-40 wt%, graphite - 15-40 wt%, PTFE - 10 wt%; clay - 5-15 wt% |
| Auxiliary agents | aminosilane, methylpyrrolidone (deagglomeration and stabilization of filler suspension) ²¹⁰ |
| Special methods of incorporation | moisture increases decomposition rate therefore processed materials must be dry; polymerization of PI in the presence of deagglomerated suspension of aluminum nitride ²¹⁰ |
| Methods of filler pretreatment | drying, deagglomeration ²¹⁰ |
| Special considerations | trace metals such as Co, Cu, Ni radically reduce thermal stability; some carbon fibers cause degradation due to the surface impurities; some types of glass reduce stability of polyimide; polyimide is used as modifier of PEEK/carbon fiber composite ¹³⁷ |

Polyimide was used as a model material in studies of polymer metal interfaces where metal layers were formed by metallization, plasma deposition, chemical vapor deposition, electrochemical deposition, etc.²¹¹ In most of the cases studied, the interpenetration of metal was so good that the metal layer could not be removed by any other means but abrasion. An investigation of interface, determined that the metal particles were found in the surface layers in diminishing quantities perpendicular to the surface and not, as expected, in the form of a sharp borderline between the metal and polymer. Some difficulties exist when metallized polyimides are used for chip production. These diffuse layers of metals complicate design and performance due to the gradients of conductivity which they produce.

Figure 15.21 shows the effect of the method of composite preparation on basal spacing of $\text{CH}_3(\text{CH}_2)_n\text{NH}_3^+$ montmorillonites and the number of carbon atoms.²¹² The processing at 300°C produces more rigid polyimide with a smaller basal spacing. The material prepared by high temperature curing gives the CO_2 permeability shown in Figure 15.22. Gas permeability is reduced which is attributed to the layered structure (~10 Å spacing), high aspect ratio, and staircase-like arrangement of layers which all increase the effect of filler. In the simple mixtures of filler and polymer, permeability has the linear relationship with the filler concentration.

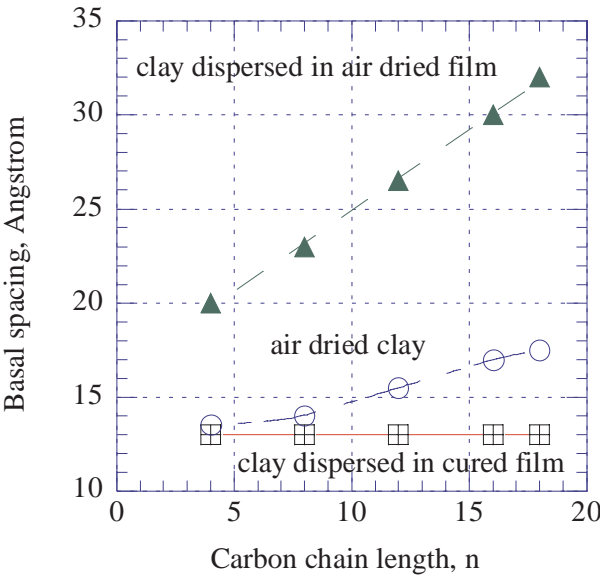


Figure 15.21. Basal spacing of $\text{CH}_3(\text{CH}_2)_{n-1}\text{NH}_3^+$ montmorillonites vs. the number of carbon atoms. [Adapted, by permission, from Lan T, Kaviratna D, Pinnavaia T J, *Chem. of Mat.*, **6**, No.5, 1994, 573-5.]

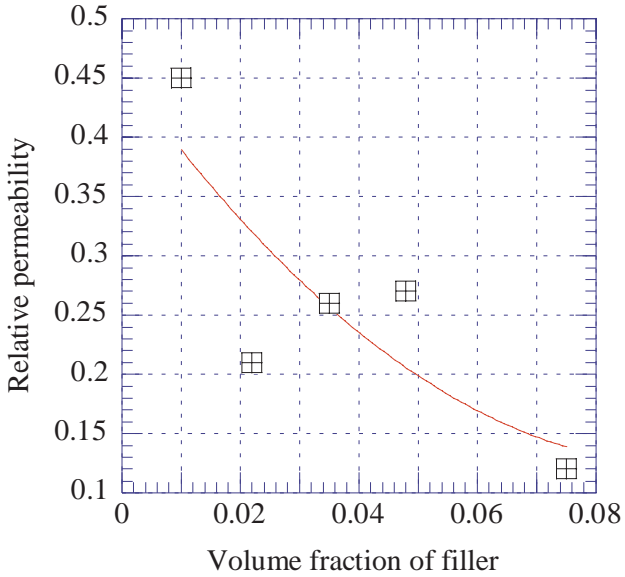


Figure 15.22. CO_2 permeability of cured polyimide films containing $\text{CH}_3(\text{CH}_2)_{17}\text{NH}_3^+$ montmorillonite vs. volume fraction of filler. [Data from Lan T, Kaviratna D, Pinnavaia T J, *Chem. of Mat.*, **6**, No.5, 1994, 573-5.]

15.32 POLYMETHYLMETHACRYLATE, PMMA^{99,197,213-223}

| | |
|----------------------------------|---|
| Major polymer applications | optical fibers, dials, optical components, household items, car rear lights, artificial stones (filled products) for injection molded bath sinks, and kitchen worktops, bone cement, composites, medical applications (e.g. bone cement) |
| Important processing methods | casting, injection molding, compression molding |
| Typical fillers | aluminum hydroxide, silica, titanium dioxide, glass fiber, mica, barium sulfate, titanium fiber, nickel, aluminum |
| Typical concentration range | generally - 20-30 wt%; carbon black - 5-30 wt%; glass powder in bone cement - 30-80 wt%; titanium fiber - 1.5%, aluminum or nickel for conductive applications - 20 vol% |
| Auxiliary agents | silanes ²²¹ |
| Special methods of incorporation | fillers are most frequently dispersed in monomer in the presence of catalyst and monomer is then polymerized |
| Methods of filler pretreatment | carbon black was oxidized prior to incorporation ²¹³ |
| Special considerations | according to inverse gas chromatography, PMMA is considered acidic, it therefore interacts better with fillers which have basic character; ⁹⁹ PMMA was found to form thick layers adsorbed on the surface of glass, titanium dioxide, silica and mica (1400, 51-70, 17, and 110 nm thick, respectively); ¹⁹⁷ very strong interaction between polymer and titanium dioxide caused formation of brittle coatings which failed prematurely; ²²⁰ formation of clay/K ₂ S ₂ O ₈ complex is a reason for catalytic effect on polymerization, the composites formed have better thermal stability, hardness, and compression strength ²²² |

NMR studies indicate that hydroxyl groups on the surface of silica are consumed during polymerization of PMMA. These groups are utilized in a reaction with polymer.²¹⁵ Polymer adsorbed on the surface of alumina changes conformation.²²³

Glass powder was used to fill bone cement. Figure 15.23 shows that the affinity index of bone cement increases as glass powder concentration increases. Synthetic material is more readily accepted by the body when more inorganic filler is present.²¹⁶ The fact that calcium and silicate ions are consumed from the cement indicates that silane coupling, although advantageous for adhesion improvement, would detract from the bioactive qualities of the cement. The addition of a small amount of titanium fiber (1.5 wt%) to another formulation of bone cement substantially increased its resistance of crack propagation.²¹⁷

Phosphorus-containing PMMA is frequently used for flame resistant applications.

Figure 14.7 shows resistivity of aluminum filled PMMA. The resistance rapidly drops when the concentration of aluminum exceeds 20 vol%. Slightly less (about 18-20 vol%) nickel is needed to obtain the same resistance.²¹⁸

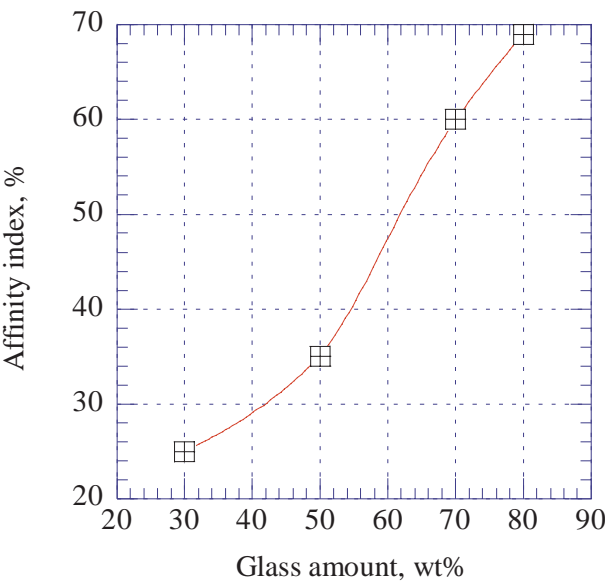


Figure 15.23. Affinity index of bone cement based on PMMA vs. concentration of glass powder. [Adapted, by permission, from Tamura J, Kawanabe K, Yamamuro T, Nakamura T, Kokubo T, Yoshihara S, Shibuya T, *J. Biomed. Mat. Res.*, **29**, No.5, 1995, 551-9.]

15.33 POLYOXYMETHYLENE, POM^{108,224,225}

| | |
|----------------------------------|--|
| Major polymer applications | appliances, automotive (door handles, window winders, tank filler necks and caps, carburetor, screw caps for cooling system expansion tanks, fuel pumps) phones (dialing units and slider guideways), pneumatic components, parts of textile machines, shower parts, home electronics and hardware, bearings, cams, containers, pump impellers, rollers, springs, clips, and many other applications |
| Important processing methods | injection molding, blow molding, rotational molding, extrusion, foam molding, compression molding, transfer molding |
| Typical fillers | glass fiber, glass beads, carbon fiber, aramid fiber, carbon black, metal flakes, zinc whisker, talc, calcium carbonate, PTFE fiber |
| Typical concentration range | generally - 20-40 wt%; PTFE, aramid fiber - 2-10 wt%, glass fiber 20-30 wt%, glass microspheres - 10-30 wt% |
| Auxiliary agents | not reported |
| Special methods of incorporation | not reported |
| Methods of filler pretreatment | drying |
| Special considerations | carbon black is the best UV stabilizer; printability of POM is obtained by addition of talc or calcium carbonate; 0.2-0.3% moisture may reduce thermal stability by 20-30°C; (γ-sterilization degrades POM rapidly) |

The addition of glass beads reduced tensile strength, fracture toughness, and strain energy release rate but improved flexural modulus.²²⁴ The tensile strength is inversely proportional to the square root of the glass sphere diameter. Reinforcing POM with glass fiber improved all its mechanical properties.²²⁵

15.34 POLY(PHENYLENE ETHER), PPO^{135,226}

| | |
|----------------------------------|--|
| Major polymer applications | electronics (computer and television housings, keyboard frames, interface boxes), automotive (instrument panels, interior and exterior trim, glove compartments, wheel covers, electric connectors, fuse boxes), air conditioner housings, hospital and office furniture, production of blends |
| Important processing methods | injection molding, blow molding, extrusion, thermoforming |
| Typical fillers | calcium carbonate, glass fiber, carbon fiber, zinc borate, PTFE, aluminum flake, graphite fiber, nickel coated graphite fiber |
| Typical concentration range | glass fiber - 10-40 wt%, carbon fiber - 10-20 wt%, also filled with a combination of mineral filler and glass fiber - 40 wt%, PTFE - 2-3 wt% |
| Auxiliary agents | silicone powder ²²⁶ |
| Special methods of incorporation | PPO is processed with PS which acts as plasticizer |
| Methods of filler pretreatment | not reported |
| Special considerations | zinc borate, especially in combination with red phosphorus or organic compounds of phosphorus, gives good fire retarding and smoke depressing system; the following are the effects on EMI shielding on addition of conductive fillers: aluminum flake, 40 wt% - 30 dB, graphite fiber, 30 wt% - 40 dB, nickel coated graphite fiber - 42 dB |

15.35 POLY(PHENYLENE SULFIDE), PPS^{181,227,228}

| | |
|----------------------------------|---|
| Major polymer applications | automotive lighting, ignition and braking systems, carburetor parts, fuel components, chip carriers, phone jacks, IC card connectors, transistor encapsulation, tape recorder head mounts, relay components, motor fans, coil bobbins, sockets, relay units, food choppers, steam hair drier parts, lamp sockets, microwave oven components, pump housings, impeller diffusers, oil well valves, halogen lamp sockets |
| Important processing methods | coating, injection molding, blending, compression molding, lamination, thermoforming |
| Typical fillers | calcium carbonate, talc, glass fiber, carbon fiber, PTFE, aramid fiber |
| Typical concentration range | glass fiber - 20-60 wt%, carbon fiber - 20-30 wt%, PTFE - 10-20 wt%, aramid fiber - 10-15 wt%, general fillers (talc, calcium carbonate) up to 65 wt% |
| Auxiliary agents | none reported |
| Special methods of incorporation | not reported |
| Methods of filler pretreatment | not reported |
| Special considerations | glass composites have very high LOI= 47%; glass fiber reinforcement increases heat deflection temperature by more than 150°C to over 260°C at 40 wt% glass fiber |

15.36 POLYPROPYLENE, PP^{4,21,67,77,103,106,118,136,143,145,157,162,177,180-1,184-6,229-308}

| | |
|----------------------------------|--|
| Major polymer applications | automotive, packaging, furniture, electrical components, fibers, tapes, many others |
| Important processing methods | extrusion, blow molding, injection molding, thermoforming |
| Typical fillers | calcium carbonate, talc, glass fiber, glass beads, glass flakes, silica flour, wollastonite, mica, sepiolite, magnesium hydroxide, carbon black, clay, metal powders (aluminum, iron, nickel), steel fiber, silicon carbide, phenolic microspheres, wood fiber and flour, antimony trioxide, hydrotalcite, zinc borate, bismuth carbonate, red phosphorus, potassium-magnesium aluminosilicate, fly ash, hydromagnesite-huntite |
| Typical concentration range | general range - 20-50 wt%; with some fillers mechanical properties decrease even at low loadings (10%); calcium carbonate - 10-60 wt%, kaolin - 20-40 wt%; ^{103,270} talc - 20-40 wt%; ^{184,270} glass beads - 20-50 vol%; ¹¹⁸ carbon black - 10-30 wt%; ⁷⁷ glass fiber - 1-60 vol%; ^{157,230} magnesium hydroxide - 60-65 wt% (for V-0 classification); antimony trioxide - 10 wt% (for V-0 classification) |
| Auxiliary agents | silanes, ^{103,107,247,281} titanates, ²⁸¹ fatty acids; ²⁸¹ polymer grafting with maleic anhydride to increase interaction, ^{107,242,243,244,246,247,269} stearic acid, nucleating agents; octamethylcyclotetrasiloxane; ¹⁷⁷ amino silane; ²³¹ dimeric aluminates ²³⁹ acrylic acid ²⁶⁰ |
| Special methods of incorporation | slurry process in which polymer powder and fibers are suspended in water followed by dewatering and wet sheet formation similar to paper manufacture technology; melt impregnation of fiber bundles in equipment containing fluidized bed zone and heating zone followed by extrusion through die; filler encapsulation is faster than blend compatibilization therefore filler must be added to compatibilized blend; ¹⁰⁷ compatibilizers were used with glass beads to improve mechanical properties of composite ²⁴¹ |
| Methods of filler pretreatment | if coupling agent is required, filler is usually pretreated before incorporation; fluidized bed glass fiber impregnation in sheet forming; surface modification of chalk and carbon fiber by acetylene gas plasma; ²¹ stearic and oleic acids; ²⁶⁴ phosphate coating for talc ²⁷⁹ |
| Special considerations | chemical composition of filler surface affects nucleation of filler; traces of heavy metals decrease thermal stability and cause discoloration; surface free energy of fillers determines interaction; large difference in thermal properties of fillers and polymer may cause stress; hydrotalcite is used as acid neutralizer with stabilizing packages; anatase titanium dioxide decreases UV stability; presence of transition metals (Ni, Zn, Fe, Co) affects thermal and UV stability; calcium carbonate and talc were found to immobilize HALS stabilizers in PP; ²⁶⁸ with organic masterbatches such as ethylene diamine phosphate V-0 classification can be obtained with 20-25 wt%, at the same time tensile strength and impact strength are substantially reduced |

Fillers affect the nucleation rate as polypropylene crystalizes. The addition of 2.5 wt% titanium dioxide reduces the size of spherulite by a factor of 3 due to an in-

creased number of sites which create competition between growing spherulites.¹⁴³ Spherulites did not grow in the surface skin. Even an addition of 40 wt% titanium dioxide did not cause spherulites to grow in the skin. An increased addition of titanium dioxide affected dispersion. On average 2.5 crystals per cluster were found at 10 wt% titanium dioxide and 5 crystals per cluster were detected at 40 wt% addition. Transcrystallinity is the other phenomenon observed in polypropylene. Transcrystallinity develops either on the surface of air bubbles or on the surface of fibers such as glass fibers. Transcrystalline structures are more effectively developed when there is any degree of mechanical stress created around the fiber.¹³⁶ The effect of several fibers, such as carbon fiber, E-glass fiber, and Twaron were evaluated using polarizing light microscopy.²³⁴ Both the shear gradient at the interface and the temperature gradient were found to influence transcrystallinity. Figures 7.18 and 10.13 show transcrystallinity on the surface of bamboo fibers.²³⁵ Filler particles oriented during material flow affect the orientation of polymer chains and crystallites because they grow on the surface of the filler particles. A similar orientation of talc particles and polymer chains was found in thermoformed and blow molded polypropylene.^{180,181,184,186} The orientation of short glass fibers and related molecular orientation of the matrix can be regulated by process parameters of injection molding.²⁵⁹ Electron spin resonance studies of calcium carbonate and talc filled polypropylene indicate that filler orientation during injection molding depended on the filler load.²⁶⁷ The best orientation was obtained at 15 vol% filler.

Mechanical properties of filled polypropylene depend on several factors which are discussed below. The Izod impact strength of carbon black filled polypropylene decreases marginally as the concentration of carbon black decreases.⁷⁷ The addition of 20 wt% carbon black to polypropylene produced a substantial (400%) increase in flexural modulus and a 40% increase in flexural strength. Tensile yield strength is a more complex property. Small additions of carbon black (up to 10 wt%) increase tensile yield strength but increasingly higher concentrations eventually decreases tensile yield strength until it drops below that of neat resin. Talc and kaolin in concentrations up to 30 wt% did not change the tensile strength of polypropylene, but improved the flexural modulus by a factor of 2. Talc alone substantially reduced impact strength.¹⁰³ Calcium carbonate filled polypropylene had poorer mechanical properties and was more difficult to process than the neat polymer.²⁵⁵ However, when calcium carbonate was surface coated by stearates, elongation and impact strength were maintained and whiteness and processing characteristics were improved.²⁵⁵ The addition of glass beads containing rubbery inclusions brought improved toughness to polypropylene.²²⁹ The particles changed the crack growth mechanism by cavitation, shear yielding, and particle matrix debonding. Failure by debonding from the surface of glass beads treated with amine silane occurred at strain of 0.7%.²³¹ Figures 8.51 and 8.52 show the effect of temperature on the influence of yielding, cavitation, and debonding which are the major mechanisms of composite failure.²³² Figure 15.24 compares the tensile

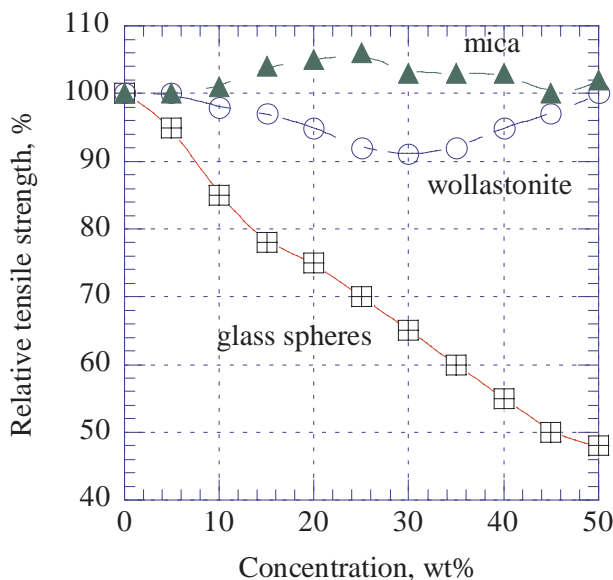


Figure 15.24. Tensile strength of polypropylene vs. concentration of three fillers. [Adapted, by permission, from Jarvela P A, Jarvela P K, *J. Mat. Sci.*, **31**, No.14, 1996, 3853-60.]

strength of polypropylene compounded with selected fillers.²⁸³ Mica and wollastonite do not affect properties of neat resin whereas glass beads decrease tensile strength. The technology of production of microporous propylene sheets took advantage of filler debonding.²³⁷ A sheet of polypropylene which contains 65.8 wt% calcium carbonate is extruded. The base sheets are stretched biaxially in a stretching machine to 500 to 1500%. This causes debonding of the filler which results in a soft microporous membrane with controlled gas and water vapor permeability.^{237,278} Microporous polypropylene hollow fibers were prepared with a similar process.^{238,276} Glass fibers affect the mechanical properties of polypropylene depending on the concentration, their length and their adhesion to the matrix. Figure 15.25 shows the effect of fiber length on tensile modulus, strength, and Charpy impact.²³⁰ All characteristics of mechanical performance increase when a fiber length increases. Filler mixtures can be selected to optimize the properties of composite. Calcium carbonate and mica, when combined with maleic anhydride, enable the product to meet required properties.^{242,251} The proportions of glass fiber and mica may be varied to regulate properties. For example, tensile and flexural strength depend on glass fiber content, and warpage and shrinkage can be regulated by mica.²⁵⁸ Combinations of fillers with different shapes (platelet, spherical, elongated) give a better performance than would be obtained from a single filler.²⁸³ A novel product hydrated potassium-magnesium aluminosilicate improves several properties of a polypropylene composite, including tensile strength and modulus, weld strength, UV stability, fire retardation and smoke suppression. It has no effect

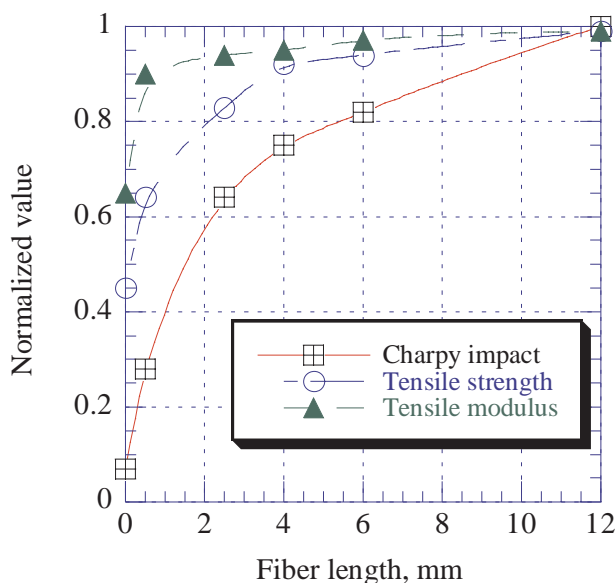


Figure 15.25. Normalized composite properties vs. fiber length. [Adapted, by permission, from Thomason J L, Vlug M A, *Composites, Part A*, **28A**, 1997, 277-88.]

on rheological properties.²⁴⁹ Smectite was used to prepare nanocomposite with an average interlayer distance of 2.3 nm.^{284,285}

Figures 12.3, 12.4, 12.8 and 14.14 contain data comparing the effect of talc and magnesium hydroxide on the burning behavior of polypropylene.⁴ Ignition time, ignition temperature, rate of combustion, and limiting oxygen index are substantially improved by the addition of magnesium hydroxide compared to the addition of talc. A substantial improvement is obtained when a large quantity (60 wt%) of magnesium hydroxide is used. The effect of magnesium hydroxide is illustrated by data from cone calorimetry (Figure 15.26).⁶² Glass beads reduce heat release by dilution (but heat released is still greater than theoretical calculations). Magnesium hydroxide substantially reduces heat release due to its endothermic degradation which releases water.⁶² Magnesium hydroxide is a suitable additive for polypropylene because polypropylene is typically processed at 200°C which is below the temperature at which magnesium hydroxide degrades. Magnesium hydroxide also reduces smoke release.⁶² The major drawback is the large amount which must be used to produce these results. Several factors contribute to the performance obtained from magnesium hydroxide including endothermic decomposition, release of water into a vapor phase, dilution of burning components, insulating effect of the oxide char residue. Different grades of magnesium hydroxide produce different results. The reason why is not yet known.²⁵⁶ A substantial decrease of mechanical properties is observed when magnesium hydroxide is used in the quantity required to obtain fire rating (~60 wt%).²⁷² Coating the filler and an addition of rubbery par-

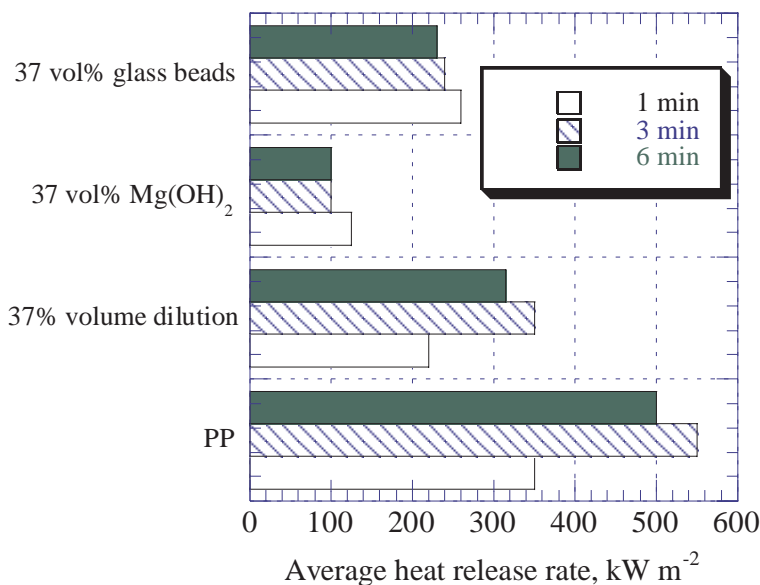


Figure 15.26. The effect of magnesium hydroxide on heat release from polypropylene. [Data from Rothon R N; Hornsby P R, *Polym. Degradat. Stabil.*, **54**, Nos 2-3, 1996, 383-5.]

tics improves the mechanical performance of the material. Magnesium hydroxide coating materials were evaluated in an extensive study.²⁸¹ The objective was to improve the mechanical properties of polypropylene. Of the materials studied, fatty acid derivatives made the best coating.²⁸¹ The amount of coating was also very important. For the type of magnesium hydroxide used, the monolayer coverage required a coating of 7 wt% fatty acid derivative.²⁸¹

A carbon black addition above a percolation threshold of 5 vol% increases the conductivity until a plateau is reached at 20 vol%.¹⁴⁵ As the level increases above 10 vol%, the viscosity of the filled polypropylene increases rapidly (see Figure 9.9). As with polyethylene, carbon black is preferentially contained in one phase of a two phase blend.¹⁰⁶ This phenomenon is used in practice to lower the concentration of carbon black required for a certain level of conductivity. Here, again, carbon black is concentrated in the preferred location. Carbon black and copper powder were used to improve connectivity of YBaCuO in ceramic superconductors.²⁴⁰ Dispersion of copper particles and the related changes in conductivity were enhanced by the presence of acrylic acid modifier.²⁶⁰

15.37 POLYPYRROLE^{127,308-310}

| | |
|----------------------------------|--|
| Major polymer applications | nonmetallic conductors, EMI shielding, battery electrodes, sensors, electronic displays, optoelectronic systems, capacitors, controlled release agents for other components |
| Important processing methods | Langmuir-Blodgen technique of monolayer production, solution polymerization over the substrate, electrochemical anodic polymerization, chemical oxidation of pyrrole in carbon black suspension |
| Typical fillers | silica, tin oxide, carbon black |
| Typical concentration range | carbon black - 10-85 wt%, silica - 1-3wt% |
| Auxiliary agents | support materials such as PMMA; chemical oxidant determines the size of particles in polypyrrole/silica nanocomposites ³⁰⁹ |
| Special methods of incorporation | polymerization is conducted in a dispersion of filler in monomer ³⁰⁸ |
| Methods of filler pretreatment | preparation of a very uniform colloidal suspension of filler especially for chemical synthesis of nanocomposites; the quality of the suspension determines the particle size of primary particles, the thickness of the coating and the uniformity of the material |
| Special considerations | EMI shielding without fillers is 45 dB; fillers are added to form stable gels ¹²⁷ |

In suspensions of carbon black in pyrrole, anodic polymerization takes advantage of the fact that carbon black particles are negatively charged on their surface which makes it possible for them to migrate to a positively charged anode where they become embedded within a growing polypyrrole matrix.³⁰⁸ This production method is suitable for production of materials for sensors, supercapacitors, fuel cells, etc. The effect of carbon black on the chemical oxidation of pyrrole in carbon black suspensions is shown in Figure 6.26.³⁰⁸

15.38 POLYSTYRENE & HIGH IMPACT, PS & HIPS^{30,226,311-323}

| | |
|----------------------------------|--|
| Major polymer applications | packaging, electrotechnical components, insulating film, household items, toys, blending with other polymers, and numerous other applications |
| Important processing methods | injection molding, extrusion, blow molding, thermoforming |
| Typical fillers | calcium carbonate, glass beads, barium sulfate, mica, kaolin, talc, glass fibers, silica, montmorillonite, zeolites; PTFE, zinc borate, titanium dioxide, red phosphorus, copper |
| Typical concentration range | generally - 10-30 wt%; PTFE - 5-15 wt%; zinc borate - 4-6 wt%; red phosphorus - 7-15 wt% |
| Auxiliary agents | silanes (most frequently epoxy and methacryloxy), dispersing agents such as alkanes and stearic acid; silicone powder with methacrylic functional groups for flame retardant applications with magnesium hydroxide ²²⁶ |
| Special methods of incorporation | for high impact polystyrene, the filler is dispersed in rubber and then incorporated into the matrix polymer; encapsulation of glass beads by grafted polybutylacrylate and polystyrene; ³⁰ free radical grafting of polystyrene onto montmorillonite interlayers; ³¹² in pan-milling of titanium dioxide with polystyrene, the improvement of impact strength results from the mutual influence on particle size reduction and the creation of new interacting surfaces; ³¹⁵ melt grafting of glass beads can be conducted by modifying the bead surface with epoxy silane and reaction of epoxy groups with poly(styrene-co-maleic anhydride) through diamine spacer ³¹⁹ |
| Methods of filler pretreatment | drying, especially for extrusion applications |
| Special considerations | dewetting angles can be calculated which represent filler-matrix adhesion; ³²⁰ carbon black is a compatibilizer of PVDF/PS blends; ³²¹ the thickness of a silane layer coating was estimated to be ~16 nm ³²² |

Filler/matrix adhesion determines the rate of particle debonding (Figure 15.27). The debonding of glass beads either treated and untreated with silane begins at the same low strain but the rates and the extent of debonding are different.^{311,318} The material properties depend on filler distribution throughout the sample. Figure 15.28 shows that distribution of glass beads in an injection molded article depends on the particle size of the beads. The large and small beads formed a similar core/shell structure but larger particles tended to be located more in the core (about 70%) than smaller particles (about 50%).³¹⁶ Also, the distance from gate affects particle distribution. Particles tend to accumulate close to a free surface causing almost double the concentration of beads at the free surface compared with their concentration in the feed. Orientation of talc particles parallel to the wall of the mold or the dies was determined for polystyrene filled with talc.³¹⁷ The addition of small amounts (<1 wt%) of rigid particles (barium sulfate and crosslinked polystyrene beads were used in the experiment) dramatically improves the impact strength of

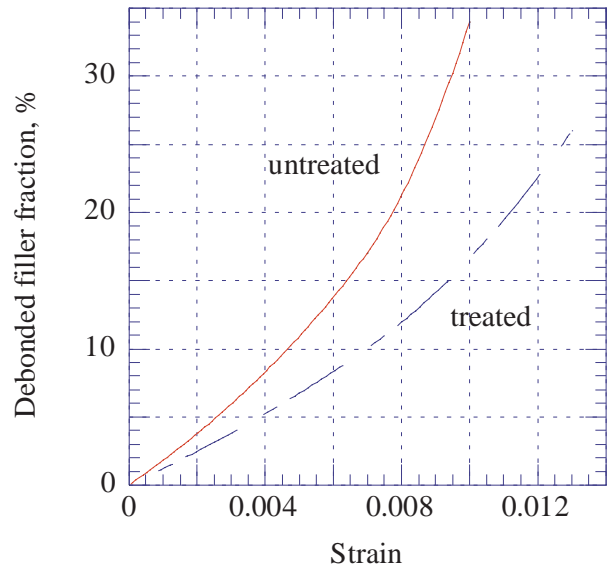


Figure 15.27. Debonded glass bead fraction, ϕ_d , vs. strain for polystyrene composites. [Adapted, by permission, from Meddad A, Fisa B, *Macromol. Symp.*, **108**, 1996, 173-82.]

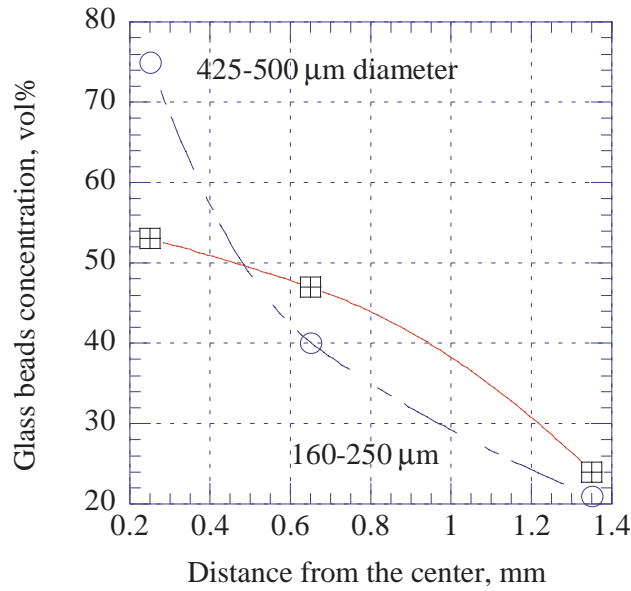


Figure 15.28. Glass concentration across the thickness of the sample. [Data from Ogadho S O, Papathanasiou T D, *Composites Part A: Applied Science and Manufacturing*, **27A**, No.1, 1996, 57-63.]

polystyrene. A specific particle diameter must be determined and selected to get the optimum improvement (see Figure 8.19).³¹⁴ The mechanism of action is related to the formation of voids and extension of crazes from these voids.

In fire retardant applications, a combination of zinc borate with ammonium polyphosphate gives V-0 rating. The use of zinc borate permits a reduction in the amount of ammonium polyphosphate. Red phosphorus alone or in combination with ammonium polyphosphate or melamine phosphate also produced a V-0 rating. The heat release rate can be effectively improved by small additions (1-2 wt%) of silicone powder in combination with other flame retarding additives or at higher concentration (15 wt%) when used by itself.²²⁶

15.39 POLYSULFIDES

| | |
|----------------------------------|---|
| Major polymer applications | sealants, rocket propellant binders, electrical potting compounds, additives to epoxy, fuel hoses and tubing, insulating glass, fuel-contact sealants |
| Important processing methods | vulcanization, moisture or chemical curing of premixed compounds |
| Typical fillers | calcium carbonate, carbon black, zinc oxide, calcium oxide and hydroxide |
| Typical concentration range | 30-50 wt% |
| Auxiliary agents | not reported |
| Special methods of incorporation | not reported |
| Methods of filler pretreatment | drying for moisture cured systems |
| Special considerations | calcium oxide is used as acid scavenger and desiccant; zinc oxide is a curing agent in vulcanization processes; calcium oxide and hydroxide are used as acid scavengers |

15.40 POLYSULFONE, PSO

| | |
|----------------------------------|---|
| Major polymer applications | tubing, in medical applications which require resistance to hot water and sterilization, microwave cookware, printed circuit boards |
| Important processing methods | injection molding, blow molding, extrusion, thermoforming |
| Typical fillers | glass fiber, carbon fiber, aramid fiber, PTFE |
| Typical concentration range | glass fiber - 20-30 wt%, PTFE - 8-15 wt% |
| Auxiliary agents | not reported |
| Special methods of incorporation | not reported |
| Methods of filler pretreatment | drying |
| Special considerations | material should have a moisture content below 0.05% to prevent bubbling, surface streaks, etc. |

15.41 POLYTETRAFLUOROETHYLENE, PTFE³²⁴⁻³²⁷

| | |
|----------------------------------|---|
| Major polymer applications | wear reduction, friction reduction, film, tubes, gaskets, valve and pump parts, tank lining, laboratory equipment, filtration membranes, bearings, piston rings, seals, non stick coating, electric insulation applications, Gore-Tex™ membranes |
| Important processing methods | solid phase forming, sintering, ram extrusion, compression molding, paste extrusion (mixed with lubricants and forced through cold die followed by lubricant evaporation and sintering), spraying, flow coating, dip, coating, film coating, fiber spinning |
| Typical fillers | glass fiber, carbon fiber, graphite, metal powders (bronze), molybdenum sulfide, boron nitride, carbon black, Ni-Zn ferrite |
| Typical concentration range | glass fiber - 15-25 wt%; graphite - 20-30 wt% |
| Auxiliary agents | not reported |
| Special methods of incorporation | fillers are premixed with powdered resins and then molded |
| Methods of filler pretreatment | not reported |
| Special considerations | high temperature deflection decreases with glass fiber loading and after heating to 200°C the effect of reinforcement disappears |

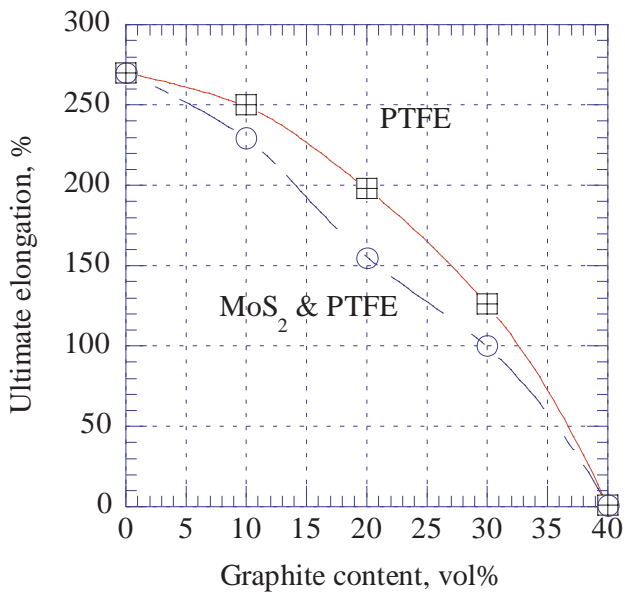


Figure 15.29. Elongation vs. filler content. [Data from Fengyuan Yan, Qunji Xue, Shengrong Yang, *J. Appl. Polym. Sci.*, **61**, No.7, 1996, 1223-9.]

Neat PTFE has several properties which eliminate its need for additives. A very high limiting oxygen index ($>95\%$) means that resin is nonflammable. Its thermal and electric insulation properties and its low friction coefficient means that further improvements are rarely needed. An improvement in mechanical properties may sometimes be needed but this is usually obtained at the expense of chemical resistance because most fillers detract from the chemical resistance of neat PTFE. The addition of NiZn ferrite powder is used to impart ferromagnetic properties to the polymer for the electronic industry.³²⁴ The addition of graphite, molybdenum disulfide, boron nitride, metal powders, and glass fiber increases wear resistance and thermal conductivity. The addition of graphite above 40 wt% increases the porosity of the composite because it generates a change in morphology.³²⁵ Figure 8.37 shows that the wear rate of graphite/PTFE and molybdenum sulfide/PTFE composites changes above 40 wt% of filler.³²⁶ Addition of particulate fillers usually results in deterioration of mechanical properties as Figure 15.29 shows. The principles of operation under high wear conditions with lubrication were studied.³²⁷

15.42 POLYURETHANES, PU & TPU³²⁸⁻³⁵⁰

| | |
|----------------------------------|---|
| Major polymer applications | TPU: coatings, footwear, automotive, wire and cable, hose and tubes, film and sheet PU: coatings, sealants, adhesives, foams, primers, mortars, and numerous other products |
| Important processing methods | TPU: injection molding, extrusion, blow molding, solution coating of fabrics and calendering coating PU: compounding, mixing, chemical or moisture cure |
| Typical fillers | calcium carbonate, calcium sulfate, silica, organic fibers, graphite, mica, bentonites, sand, aluminum hydroxide, sepiolite, rubber particles |
| Typical concentration range | calcium carbonate - 30-60 wt%; calcium sulfate - 5-10 wt%; sand up to 95 wt%; glass beads - 30-40 wt%; sepiolite - 40 wt% |
| Auxiliary agents | drying agents, process oils, surfactant for silica modified foam with good insulation properties ³³⁷ |
| Special methods of incorporation | fillers are frequently pre-dispersed in polyol (for better mechanical properties) or plasticizers (to dry while dispersing); hydroxyapatite was modified by reaction with hexamethylene diisocyanate ³⁴² |
| Methods of filler pretreatment | TPU: Total moisture of the system should not exceed 0.1% to prevent hydrolysis and blistering PU: depends on application but typically moisture below 0.05% is required to prevent reaction with water leading to property loss and bubbling |
| Special considerations | sepiolite treatment below 550°C does not alter the properties which modify the rheological properties of adhesives; ³³² filler presence may affect adhesion (see Figure 8.54); ³³⁸ rubber particles are hygroscopic and can absorb 1.4% moisture with the rate of 0.01% per minute (similar to carbon black) ³⁴⁰ |

Polyurethane filled with glass beads was studied to determine the effect of concentration, particle size, and coupling (Figures 15.30, 15.31, and 15.32). The value of strain at failure decreases as concentration increases. The mode of failure also changes as the concentration of glass beads increases. At lower concentrations (12 and 24 vol%), the material shows stress softening before the failure. At the highest concentration, simple brittle failure occurs. The material with smaller particles has a higher modulus and withstands higher strain before it fails but the characters of both strain-stress curves are similar. The stress-strain relationship of polyurethane filled with treated glass beads is linear and failure occurs at a higher stress than with untreated beads. The material containing untreated beads has lower tensile properties but higher elongation.³³⁰

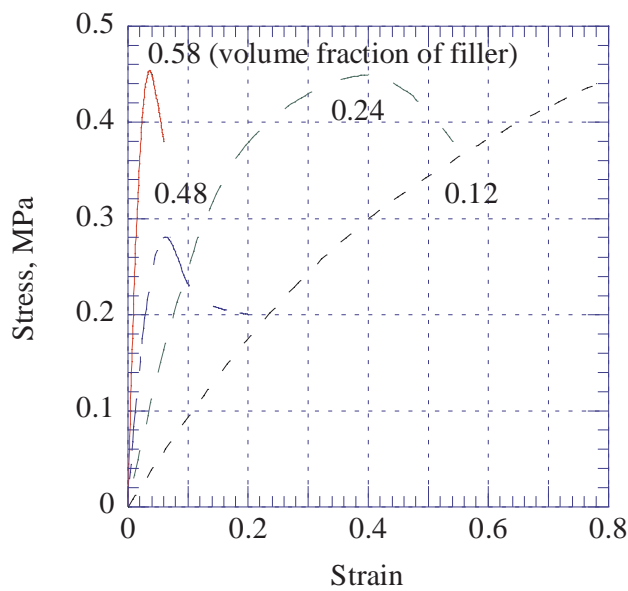


Figure 15.30. Stress-strain curves for glass bead filled polyurethane with different concentrations of glass beads. [Data from Vratsanos L A, Farris R J, *Polym. Engng. Sci.*, **33**, No.22, 1993, 1458-65.]

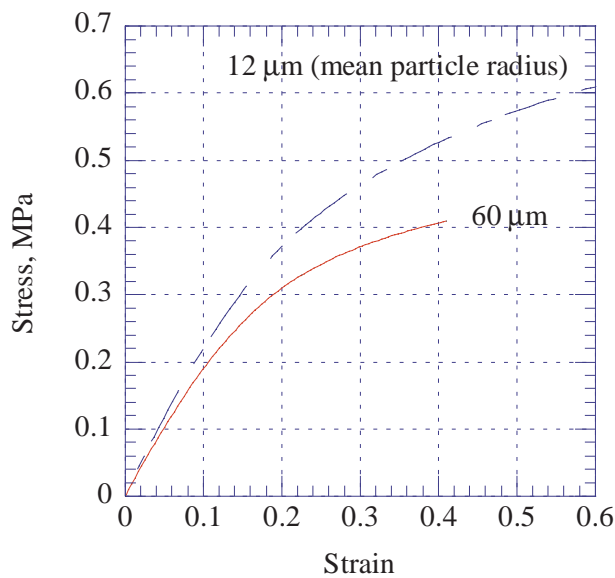


Figure 15.31. Stress-strain curves for glass bead filled polyurethane with different diameter of glass beads. [Data from Vratsanos L A, Farris R J, *Polym. Engng. Sci.*, **33**, No.22, 1993, 1458-65.]

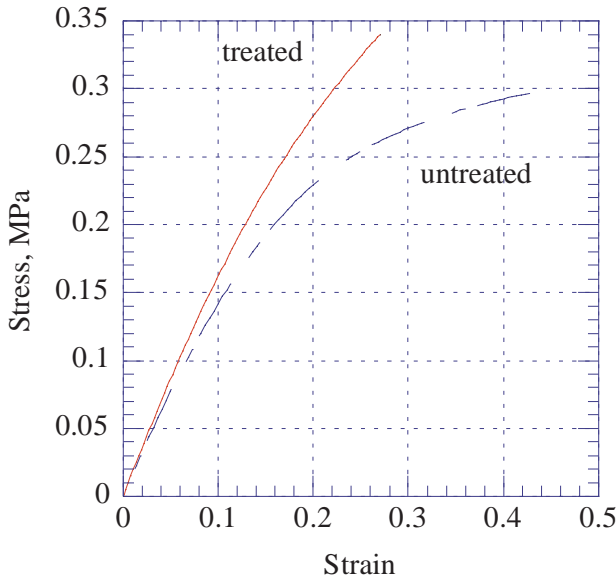


Figure 15.32. Stress-strain curves for glass bead filled polyurethane with coated and uncoated glass beads. [Data from Vratsanos L A, Farris R J, *Polym. Engng. Sci.*, **33**, No.22, 1993, 1458-65.]

Flame retardant polyurethanes are mostly manufactured with compounds of phosphorus, such as ammonium phosphate or polyphosphate.³²⁹ Aluminum hydroxide alone or in combination with melamine is an alternate approach. In intumescent applications, graphite is frequently used. Calcium carbonate is useful as a flame retarding additive, in combination with other flame retarding materials, because of its large endothermic peak found in DTA curves.³³¹

15.43 POLY(VINYL ACETATE), PVAc³⁵¹⁻³⁵⁶

| | |
|----------------------------------|--|
| Major polymer applications | production of poly(vinyl alcohol), adhesives, paints |
| Important processing methods | mixing/compounding |
| Typical fillers | calcium carbonate, clay, mica, talc, aluminosilicate |
| Typical concentration range | 20-30 wt% |
| Auxiliary agents | thickeners |
| Special methods of incorporation | silanes were polymerized in the presence of PVAc to form reinforced composite ^{354,365} |
| Methods of filler pretreatment | not reported |
| Special considerations | calcium carbonate (10-20 wt%) enhances rheology; stearate treated calcium carbonate does not interact with polymer and gives composite with a lower mechanical performance; ³⁵¹ fillers used in adhesives should have limited interaction with matrix otherwise they decrease elasticity of the adhesive joint ³⁵⁵ |

15.44 POLY(VINYL ALCOHOL), PVA³⁵⁷

| | |
|----------------------------------|---|
| Major polymer applications | sizing agents, binders, protective colloids, photographic papers, toners, film, water-soluble laundry bags, seed tapes, sanitary pads, belts, printing rolls, controlled drug delivery, membranes |
| Important processing methods | casting, extrusion |
| Typical fillers | carbon black, silica, calcium carbonate, clay, zinc oxide, titanium dioxide, sand, aluminum oxide, magnesium oxide, zirconia, ferrite, graphite |
| Typical concentration range | 20-30 wt%; in some applications up to 98 wt% |
| Auxiliary agents | calcium stearate |
| Special methods of incorporation | <i>in situ</i> precipitation of filler ³⁵⁷ |
| Methods of filler pretreatment | not reported |
| Special considerations | not reported |

15.45 POLY(VINYL BUTYRAL), PVB³⁵⁸

| | |
|----------------------------------|--|
| Major polymer applications | safety glass interlayer (automotive windshields), control of light, heat and sound in construction glass, bulletproof glass, adhesives and sealants, binders for rocket propellant, photoconductive papers, magnetic tapes, powder coating, wood sealers and primers, inks, ceramic binders, dry toners, wash primers, composite fiber binders |
| Important processing methods | compounding, powder coating, extrusion |
| Typical fillers | calcium carbonate, aluminum hydroxide, zinc oxide, rust protective fillers |
| Typical concentration range | 20-30 wt% |
| Auxiliary agents | not reported |
| Special methods of incorporation | not reported |
| Methods of filler pretreatment | not reported |
| Special considerations | not reported |

15.46 POLY(VINYL CHLORIDE), PVC^{82,199,358-372}

| | |
|---|--|
| Major polymer applications | profiles, cables, siding, windows, pipes, fittings, flooring, footwear, film and sheet, coated fabrics, tubing, gutters, drain pipes, packaging, furniture trim, bottles, gloves, wallpaper, foam backings of carpets, domestic appliances, office equipment, toys, protective clothing, metal protection in automotive and many more |
| Important processing methods | extrusion, plastisol coating, thermoforming, calendering, blow molding, rotational molding, injection molding |
| Typical fillers | calcium carbonate, clay, talc, silica, antimony trioxide, aluminum hydroxide, magnesium hydroxide, carbon fiber, aluminum fiber, titanium dioxide, carbon black, sand, wood fiber |
| Typical concentration range | calcium carbonate - 20-30 wt% (rigid) 30-40 wt% (flexible), talc 5-25 wt%, antimony trioxide - 3-6 wt%, aluminum hydroxide, magnesium hydroxide - 20-40 wt%, sand 40-60 wt% |
| Auxiliary agents | lubricants, dispersing agents, compatibilizers (chlorinated polyethylene), ¹⁹⁹ acrylic impact modifier to improve impact with talc ³⁶⁰ |
| Special methods of incorporation | dry blending including preparation of initial premix, compounding and pelletization |
| Methods of filler pretreatment | seldom used |
| Special considerations | zinc oxide decreases thermal stability; combination of zinc oxide with carbon black reduces UV stability; high concentrations of TiO ₂ or carbon black are needed to improve UV stability, at lower concentrations these fillers will reduce UV stability; copper-containing compounds, iron salts, cadmium, cobalt, manganese, lead salts reduce thermal stability of PVC (also fillers containing these metals); sand was found to protect PVC from UV degradation; ³⁵⁹ calcium carbonate interferes with radiation crosslinking of PVC ^{363,366,370} |

Addition of fillers impacts mechanical properties of PVC. For example, calcium carbonate decreases yield stress and talc decreases impact strength. The aim of research on PVC is to obtain compositions with balanced properties. Ultrafine talc is used in application where impact and stiffness must be simultaneously improved.³⁶⁰ Flexural modulus is improved by addition of ultrafine and general purpose talcs. But addition of either type of talc rapidly decreases impact strength. If ultrafine talc is incorporated with an acrylic modifier both stiffness and impact are improved (depending on the amounts of both talc and modifier, the flexural modulus can be improved by up to 60% and the impact strength by 1500%).³⁶⁰ The surface of fillers plays a critical role. Although surface modification of filler can bring advantages, the inherent properties of the untreated filler are equally important. The extensive use of calcium carbonate in PVC is, among other factors (mostly economic), related to its basicity which causes it to interact well with PVC (which is acidic). If surface modification changes this interaction, the performance of the composite may be affected. Fillers are added to PVC to provide thermal and UV

stabilization. For example, calcium stearate may play the role of an associate thermal stabilizer when used in a system with calcium salts of fatty acids. These stabilizers use combinations of two or more metals – one of which (e.g. zinc) produces metal chlorides which accelerate PVC degradation. The presence of large amount of calcium salts helps to convert this chloride to calcium chloride which does not increase the degradation rate of PVC. Also, calcium carbonate can react with hydrogen chloride which is produced as PVC degrades. On the other hand, inclusion of fillers which contain admixtures of metals such as iron, nickel, copper, etc. reduces PVC thermal stability. Fillers also affect UV stabilization by adsorption of HALS stabilizers which immobilizes them and prevents them from performing as radical scavengers.

Antimony trioxide is a suitable flame retardant for PVC considering that it requires chlorine to perform. Small additions (3-6 wt%) are sufficient for rigid and semi-rigid compositions. Making plasticized PVC flame retardant requires higher concentrations (15-20 wt%). Antimony trioxide is a white pigment it influences the color. Therefore, small particle size antimony pentoxide from a spray drying process is used to give dark colors as well as the transparent materials. Aluminum hydroxide is another additive used, although, its wide spread application is hampered by a need for larger concentrations at which mechanical properties are affected. Magnesium hydroxide has been used as a fire retardant with an aim to limiting interference with stabilizers.⁸² Magnesium hydroxide is marginally better than aluminum hydroxide for smoke suppression.³⁶⁴ Combinations of aluminum hydroxide and magnesium hydroxide with zinc borate were also studied as a potential replacement for antimony oxide.³⁶⁷ These combinations provided improvement over antimony oxide in the flame retarding properties of heat release, specific extinction area, smoke, and CO emission. The best performing formulations required higher concentration of inorganic flame retardants (concentration increased by ~250%) but even at the same level of loading, formulations containing zinc borate in combination with aluminum hydroxide gave better performance than combinations of aluminum hydroxide with antimony oxide.³⁶⁷ Figure 13.8 shows that the performance of aluminum and magnesium hydroxides can be enhanced by coating the powders with zinc hydroxystannate.³⁷² Smoke reduction can be obtained by various iron, copper, nickel and vanadium compounds which, although reduce the smoke but do affect thermal stability and, frequently, the UV stability of PVC. Other materials used include molybdenum and boron compounds.

In the area of conductive plastics, PVC is used in static control applications and EMI shielding. Static control, involving tiling and sheeting in industrial applications, is achieved by addition of carbon black. EMI shielding is a relatively new application for PVC in which metal and carbon fibers are used.

15.47 RUBBERS^{71,341,345,346,373-397}

| | |
|----------------------------------|---|
| Major polymer applications | applications are given for specific rubbers in the tables which follow |
| Important processing methods | see under individual materials |
| Typical fillers | carbon black, talc, in EMI shielding field: silver plated aluminum, silver plated nickel, silver coated glass spheres, silver plated copper, silver, nickel and carbon black |
| Typical concentration range | general guidelines: carbon black - 10-40 wt%, clay, talc - 5-60 wt%, calcium silicate - 1-8 wt%, aluminum silicate - 5-40 wt%, magnesium aluminum silicate - 5-30 wt% |
| Auxiliary agents | product specific |
| Special methods of incorporation | processing history has an essential effect on conductivity; amount of shear imposed and mixing causes the fracture of secondary carbon aggregates; increased temperature during mixing may preferentially form rubber-carbon bonds rather than the carbon-carbon bonds required for conductivity; vulcanization temperature may affect recovery of broken connections between carbon-carbon bonds |
| Methods of filler pretreatment | silanes including amino- and mercaptosilanes; treatment is more common with silica and clays |
| Special considerations | in conductive applications, special conductive blacks must be employed; in silver containing gaskets, galvanic corrosion is a problem, attention should be given to material with which shield is connected (potential difference), with zinc or aluminum casing nickel filled materials are preferred |

In addition to the general information included here, the specific information is discussed below for different rubber types. Dispersion of fillers is an important part of rubber processing technology. A test was developed to measure dispersion based on viscosity increase.³⁷⁴ Atomic force microscopy combined with image analysis was used to quantify a dispersion of carbon black.³⁷⁸ Aggregate size distribution and interaggregate distances can be measured by this method. Good dispersion of filler increases tensile strength, elongation and cut growth and decreases abrasion loss.³⁸¹ Rubber mixing with additives including fillers was analyzed elsewhere.³⁸⁴ The effect of carbon black dispersion on rheological properties of rubber compounds and their morphology can be found in the literature.^{385,386} A model of chemical and physical crosslinks was developed³⁸⁸ and particles debonding conditions were analyzed.³⁸⁹

15.47.1 NATURAL RUBBER, NR⁸⁴, 398

| | |
|---|---|
| Major polymer applications | pumps, valves, piping, hoses, machined components, tubes, boots, waterproof clothing, and bathing apparel, wire and cables, instrument panels, electrician's gloves, tires, heels and soles, conveyor belts, vibration dampers, shock absorbers, latex foams, tire cord impregnation, switchboard panels, plugs, sockets, telephone receivers, storage-battery cases, toys, gloves, pumps, pipes, valves |
| Important processing methods | vulcanization, coating, Banbury mixer, Gordon plasticator, skim coating, sheeting, calendering, tubing |
| Typical fillers | carbon black, calcium carbonate, dolomite, clays, calcinated clays, talc, soapstone, zinc oxide, fumed silica, borates, iron oxide, zinc oxide, magnesium carbonate, pulverized polyurethane foam, barium and strontium ferrites, magnesium aluminum silicate, nylon fibers, quartz; in EMI shielding field: silver plated aluminum, silver plated nickel, silver coated glass spheres, silver plated copper, silver, nickel and carbon black |
| Typical concentration range | carbon black - 20-30 wt%, calcium carbonate, quartz, talc - 15-25 wt%, silica - 15-30 wt%, titanium dioxide - 5 wt%, zinc oxide - 3-5 wt%, magnesium aluminum silicate - 20-40 wt%, barium or strontium ferrite (magnetic fillers) - 15-35 wt%, pulverized polyurethane foam - 15-30 wt% |
| Auxiliary agents | fatty acids, amines, silanes, multipurpose additive |
| Special methods of incorporation | processing history has an essential effect on conductivity; amount of shear imposed and mixing causes the fracture of secondary carbon aggregates; increased temperature during mixing may preferentially form rubber-carbon bonds rather than carbon-carbon bonds required for conductivity; vulcanization temperature may affect recovery of broken connections between carbon-carbon bonds |
| Methods of filler pretreatment | not reported |
| Special considerations | in conductive applications special conductive blacks must be employed; in silver containing, gaskets galvanic corrosion is a problem, attention should be given to material with which shield is connected (potential difference), with zinc or aluminum casing nickel filled materials are preferred |

Flexible magnets were prepared by incorporation of barium and strontium ferrites.³⁷⁷ The permittivity and dielectric loss were reduced by use of calcium carbonate, talc, kaolin, and quartz.³⁹⁰ Quartz gave the best dielectric properties.

Figure 15.33 shows benzene uptake by natural rubber samples.³⁹⁸ Filled samples absorb less solvent (lower swelling). The carbon black containing sample had a lower benzene uptake than the silica filled sample. The lower swelling of the carbon black containing sample is due to high bound rubber content, the crosslink density of the black filled vulcanizate, and a strong rubber-filler interaction.

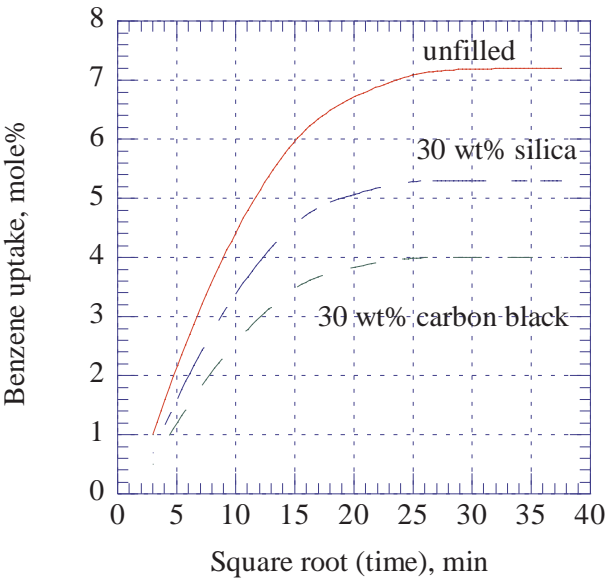


Figure 15.33. Benzene uptake for natural rubber. [Adapted, by permission, from Unnikrishnan G, Thomas S, Varghese S, *Polymer*, **37**, No.13, 1996, 2687-93.]

15.47.2 NITRILE RUBBER, NBR^{362,399-405}

| | |
|----------------------------------|--|
| Major polymer applications | gaskets, packing, automotive hoses, seals, industrial hoses, printing rolls, belt covers, footwear, hose jackets, polymer modification, tires |
| Important processing methods | vulcanization, coating, molding |
| Typical fillers | calcium carbonate, kaolin, carbon black, talc, zinc oxide, cellulose fibers |
| Typical concentration range | carbon black - 25-50 wt%, calcium carbonate - 20-50 wt%, kaolin - 2-40 wt%, talc 30-40 wt%, cellulose fiber 5-15 wt%, zinc oxide - 2-6 wt% |
| Auxiliary agents | stearic acid, aminopropylsilane |
| Special methods of incorporation | processing history has an essential effect on conductivity; amount of shear imposed and mixing causes the fracture of secondary carbon aggregates; increased temperature during mixing may preferentially form rubber-carbon bonds rather than the carbon-carbon bonds required for conductivity; vulcanization temperature may affect recovery of broken connections between carbon-carbon bonds; reaction between carboxyl groups of rubber and hydroxyl groups of carbon black occurs during molding at high temperature (190°C), in the case of sulfur-vulcanized systems, low molding temperature (150°C) favors weak physical bonds between rubber and filler ³⁹² |
| Methods of filler pretreatment | silane treatment of carbon black during mixing with rubber; ⁴⁰² co-precipitation of cellulose xanthate and NBR latex ⁴⁰⁵ |
| Special considerations | in conductive applications special conductive blacks must be employed; in silver containing gaskets galvanic corrosion is a problem, attention should be given to material with which shield is connected (potential difference), with zinc or aluminum casing nickel filled materials are preferred |

Figure 15.34 shows the relationship between bound rubber and oxygen content in carbon black. Figure 15.35 gives the relationship between the oxygen content and storage modulus. Figure 15.36 compares oxygen content with interaction parameter. Oxygen containing groups on the carbon black surface can react with NBR carboxyl groups. This reaction controls the concentration of bound rubber. The interaction parameter ($I = \sigma / \eta$) is a ratio of the slope of the stress-strain curve, σ , to the carbon-carbon networking factor, η , calculated from the storage modulus. Interaction parameter increases linearly with the concentration of functional groups on the filler surface. The storage modulus depends on reinforcement and chemical bonding between filler and rubber.

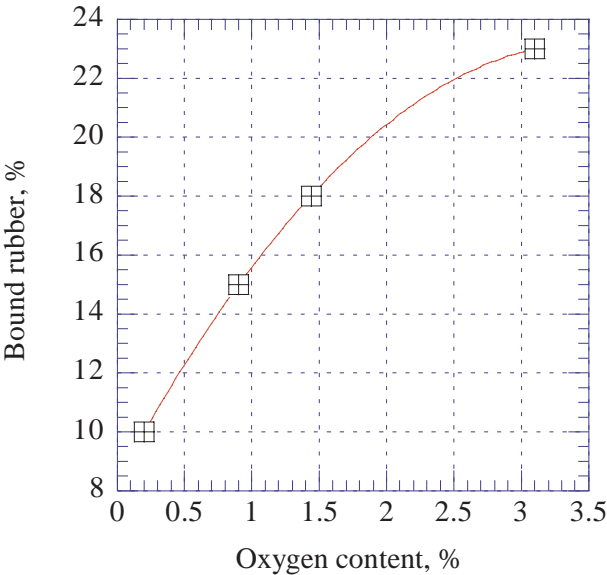


Figure 15.34. Bound rubber vs. oxygen content in carbon black determined for NBR compositions. [Data from Bandyopadhyay S, De P P, Tripathy D K, De S K, *J. Appl. Polym. Sci.*, **58**, No.4, 1995, 719-27.]

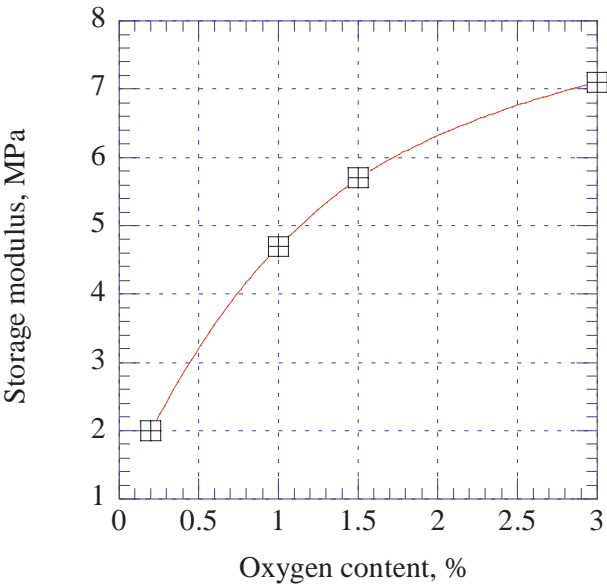


Figure 15.35. Storage modulus vs. oxygen content in carbon black determined for NBR compositions. [Data from Bandyopadhyay S, De P P, Tripathy D K, De S K, *J. Appl. Polym. Sci.*, **58**, No.4, 1995, 719-27.]

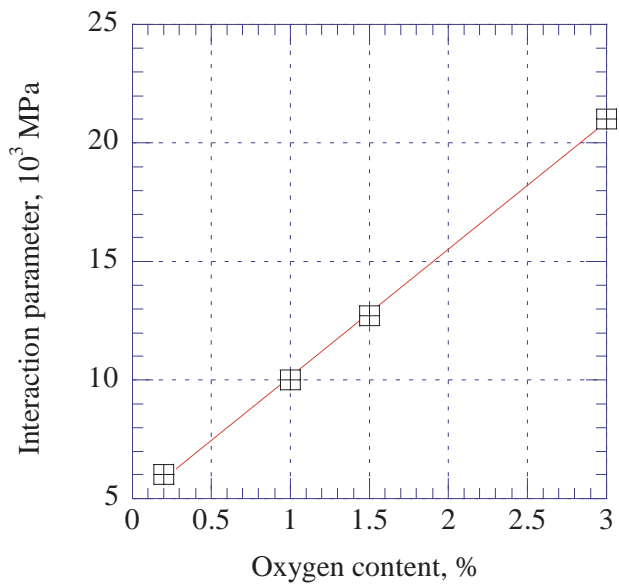


Figure 15.36. Interaction parameter vs. oxygen content in carbon black determined for NBR compositions. [Adapted, by permission, from Bandyopadhyay S, De P P, Tripathy D K, De S K, *J. Appl. Polym. Sci.*, **58**, No.4, 1995, 719-27.]

15.47.3 POLYBUTADIENE RUBBER, BR^{84,406-408}

| | |
|----------------------------------|--|
| Major polymer applications | modification of other polymers (e.g., HIPS and ABS), golf balls, tires, conveyor belts, hoses, seals and gaskets, rubberized cloth |
| Important processing methods | mixing, vulcanization, molding, extrusion, blow molding, injection molding |
| Typical fillers | carbon black, zinc oxide |
| Typical concentration range | carbon black - 30 wt%, zinc oxide - 3 wt % |
| Auxiliary agents | not reported |
| Special methods of incorporation | not reported |
| Methods of filler pretreatment | not reported |
| Special considerations | not reported |

15.47.4 POLYBUTYL RUBBER, HR

| | |
|----------------------------------|---|
| Major polymer applications | belting, steam hose, curing bladders, O-rings, shock and vibration products, structural caulks and sealants, water-barrier applications, roof coatings, and gas-metering diaphragms |
| Important processing methods | mixing, vulcanization, molding |
| Typical fillers | carbon black, zinc oxide, clay; barium titanate, in EMI shielding field: silver plated aluminum, silver plated nickel, silver coated glass spheres, silver plated copper, silver, nickel and carbon black |
| Typical concentration range | carbon black - 20-50 wt%, zinc oxide - 2 wt% |
| Auxiliary agents | process oil, fatty acids |
| Special methods of incorporation | processing history has an essential effect on conductivity; amount of shear imposed and mixing causes the fracture of secondary carbon aggregates; increased temperature during mixing may preferentially form rubber-carbon bonds rather than the carbon-carbon bonds required for conductivity; vulcanization temperature may affect recovery of broken connections between carbon-carbon bonds |
| Methods of filler pretreatment | not reported |
| Special considerations | in silver containing gaskets galvanic corrosion is a problem, the attention should be given to material with which shield is connected (potential difference), with zinc or aluminum casing nickel filled materials are preferred |

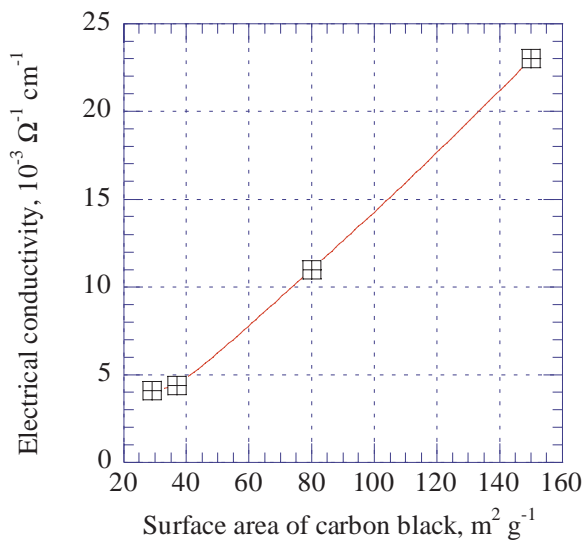


Figure 15.37. Electric conductivity vs. surface area of carbon black incorporated into butyl rubber. [Adapted, by permission, from Nasr G M, Badawy M M, Gwaily S E, Shash N M, Hassan H H, *Polym. Degradat. Stabil.*, **48**, No.2, 1995, 237-41.]

Figure 15.37 shows that conductivity of butyl rubber increases with surface area of carbon black increasing.⁴⁰⁹

15.47.5 POLYCHLOROPRENE, CR^{198,410-412}

| | |
|----------------------------------|---|
| Major polymer applications | wire and cable jacketing, hose, tubes and covers (auto and industrial), automotive gaskets, seals, CVJ boots and air springs, power transmission belts, molded and extruded goods, cellular products, adhesives, sealants, and protective coatings, foamed wet suits, latex dipped goods (gloves, weather balloons, automotive), paper, and industrial binders (shoe board), construction applications (bridge pads/seals, soil pipe gaskets, waterproof membranes, asphalt modification) |
| Important processing methods | vulcanization, dip coating, coating, sheeting, calendering, extrusion |
| Typical fillers | carbon black, zinc oxide, magnesium oxide; in EMI shielding field: silver plated aluminum, silver plated nickel, silver coated glass spheres, silver plated copper, silver, nickel and carbon black |
| Typical concentration range | carbon black - 20-40 wt%, zinc oxide - 3-4 wt%, magnesium oxide - 2-3 wt%, calcium carbonate, clay silica - 10-70 wt% |
| Auxiliary agents | lubricants, surfactants, waxes, oils |
| Special methods of incorporation | processing history has an essential effect on conductivity; amount of shear imposed and mixing causes the fracture of secondary carbon aggregates; increased temperature during mixing may preferentially form rubber-carbon bonds rather than the carbon-carbon bonds required for conductivity; vulcanization temperature may affect recovery of broken connections between carbon-carbon bonds |
| Methods of filler pretreatment | not reported |
| Special considerations | in conductive applications special conductive blacks must be employed; in silver containing gaskets galvanic corrosion is a problem, the attention should be given to material with which shield is connected (potential difference), with zinc or aluminum casing nickel filled materials are preferred; aluminum chloride is an important initiator of degradation; metal oxides are curing agents; carbon black is efficient CR stabilizer ⁴¹¹ |

Fast extrusion furnace black with a particle size of 360 Å, was used to verify different theoretical concepts of percolation which by definition predicts a rapid change in conductance when volume fraction of conductive particles attains a critical value. Figure 15.38 shows the effect of a carbon black addition to polychloroprene. Up to 30 phr carbon black, the conductivity of polychloroprene is almost constant and then it increases linearly as concentration of carbon black increases. The following equation applies: $\sigma = \sigma_0 (P - P_c)^\beta$ where: σ_0 is constant, P is concentration of conducting particles, P_c is percolation threshold, and β is exponent which accounts for cluster size.⁴¹⁰ When data from the Figure 15.38 are replotted as in Figure 15.39 it is evident that the percolation law is valid.

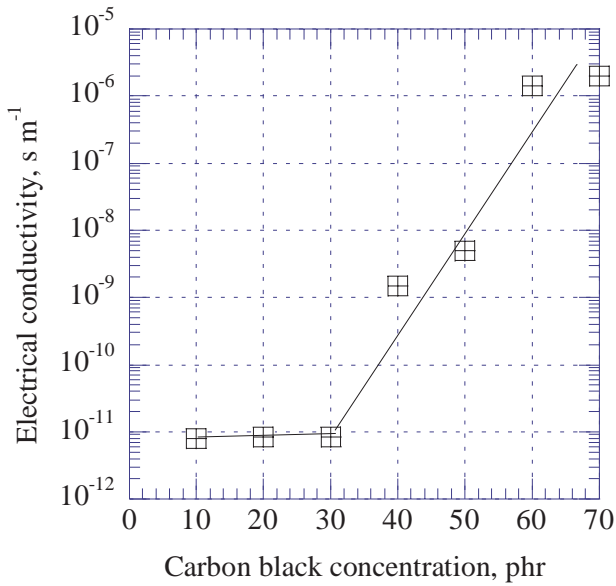


Figure 15.38. Electric conductivity of polychloroprene vs. concentration of carbon black. [Adapted, by permission, from Ali M H, Abo-Hashem A, *Plast. Rubb. Comp. Process. Appln.*, **24**, No.1, 1995, 47-51.]

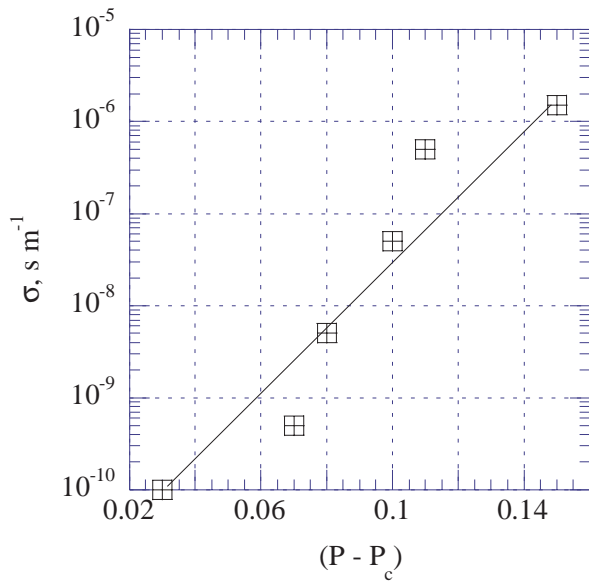


Figure 15.39. Plot of σ vs. $(P - P_c)$ in a logarithmic scale. [Adapted, by permission, from Ali M H, Abo-Hashem A, *Plast. Rubb. Comp. Process. Appln.*, **24**, No.1, 1995, 47-51.]

15.47.6 POLYISOBUTYLENE, PIB^{399,413}

| | |
|----------------------------------|---|
| Major polymer applications | sealants, roofing membranes |
| Important processing methods | compounding, vulcanization, coating, sheeting |
| Typical fillers | carbon black, calcium carbonate, kaolin, zinc oxide, clay |
| Typical concentration range | carbon black - 20-30 wt%, calcium carbonate - 30-50 wt%, zinc oxide 2-3 wt% |
| Auxiliary agents | not reported |
| Special methods of incorporation | not reported |
| Methods of filler pretreatment | not reported |
| Special considerations | not reported |

15.47.7 POLYISOPRENE, IR^{84,414-416}

| | |
|----------------------------------|--|
| Major polymer applications | pressure-sensitive adhesives, ablatives |
| Important processing methods | mixing, vulcanization, extrusion, calendering, molding |
| Typical fillers | carbon black, zinc oxide, kaolin, calcium carbonate, silicates, titanium dioxide |
| Typical concentration range | carbon black - 20-40 wt% |
| Auxiliary agents | stearic acid |
| Special methods of incorporation | not reported |
| Methods of filler pretreatment | not reported |
| Special considerations | zinc oxide is a curing agent |

15.47.8 STYRENE-BUTADIENE RUBBER, SBR^{207,417-435}

| | |
|----------------------------------|--|
| Major polymer applications | tires, flooring, conveyor belts, shoe products, sheet, tubing, tank and caterpillar tracks, sporting goods, toys, coated fabrics, automotive mechanical goods |
| Important processing methods | mixing, compression molding, calendering, vulcanization, coating |
| Typical fillers | carbon black, silica, lead oxide (γ-radiation shields), sodium aluminum silicate, clay, mica, kaolin, carbon fiber; crosslinked PS beads |
| Typical concentration range | carbon black - 20-50 wt%, precipitated silica - 25-60 wt%, calcium carbonate - 40-70 wt%, lead oxide - 88 wt%, zinc oxide - 1-2 wt%, clay - 20-80 wt%, mica - 20-30 wt%, kaolin - 20-35 wt%, carbon fiber - 15-30 wt% |
| Auxiliary agents | silane modification of silica, ⁴²⁰ process oils, lubricants |
| Special methods of incorporation | carbon fiber was added at the end of mixing to limit breakage; ⁴²⁷ silane addition stage was varied to improve properties of silica-filled composite ⁴³⁰ |
| Methods of filler pretreatment | thermal treatment of carbon black to increase adhesion and amount of bound rubber ⁴²⁰ |
| Special considerations | zinc oxide is crosslinking agent; ³⁷⁴ carbon black is a more efficient UV stabilizer in sulfur-cured SBR than in radiation or peroxide cured; ⁴¹⁷ vulcanization conditions affects electric conductivity of carbon black filled SBR; ⁴³² solvent diffusion and swelling rate decrease as concentration of carbon black increases ⁴³³ |

Carbon black loading and its surface area are the factors which determine mechanical properties of the filled rubber. Figure 15.40 shows the effect of nitrogen surface area and carbon black loading on the tensile strength of a tire compound. An increased surface area of carbon black contributes to an increase in tensile strength. There is a maximum performance which is attainable with each type of carbon black with the general tendency being that maximum performance is obtained at higher concentrations as the surface area decreases.³⁷⁹ Figure 15.41 shows the effect of the surface area of carbon black on the essential parameters of tire performance.³⁷⁹ The tensile and tear strength increases as the surface area of carbon black increases but the fatigue life and cut growth decreases when the surface area of carbon black increases.

The addition of kaolin increased the tensile strength of SBR by a factor of up to 4, modulus by a factor of up to 5 and swelling was reduced by 60%.⁴²⁴ Crosslinked polystyrene beads increase the tensile strength, modulus, and elongation of SBR.⁴³⁵

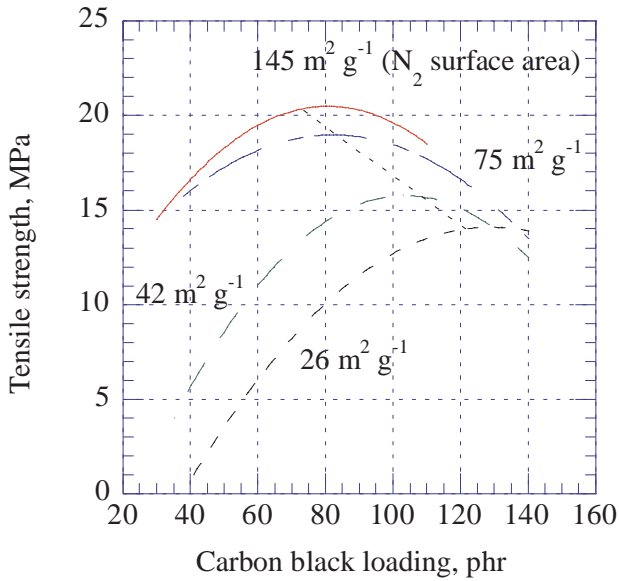


Figure 15.40. Tensile strength of SBR vs. carbon black loading. [Adapted, by permission, from Byers J T, Meeting of the Rubber Division, ACS, Cleveland, October 17-20, 1995, paper B.]

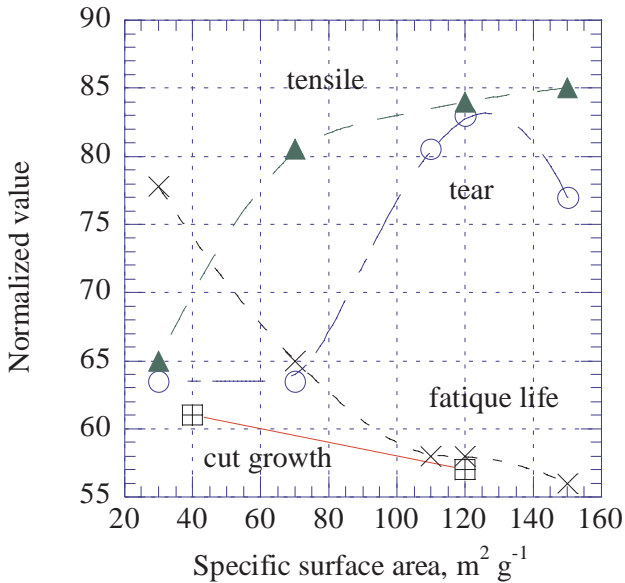


Figure 15.41. Properties of SBR vs. specific surface area of carbon black. [Adapted, by permission, from Byers J T, Meeting of the Rubber Division, ACS, Cleveland, October 17-20, 1995, paper B.]

15.48 SILICONES, SI^{90,436-452}

| | |
|----------------------------------|--|
| Major polymer applications | automotive (shaft sealing rings, spark plug caps, o-rings, gaskets, ignition cables, coolant and heater hose), general tubing, transfusion and dialysis tubing, door and windows seal, caulking and sealants |
| Important processing methods | injection molding, extrusion, room temperature, moisture or chemical cure of premixed compounds, vulcanization, casting |
| Typical fillers | fumed silica, calcium carbonate, carbon black, silver, glass beads, metal powders, precipitated silica, aluminum oxide, montmorillonite, mica, zinc oxide |
| Typical concentration range | fumed silica - 3-5 wt%, calcium carbonate - 20-50 wt%, glass beads - 5-20 wt%, aluminum oxide - 30-50 wt%, zinc oxide - up to 60% |
| Auxiliary agents | silanes |
| Special methods of incorporation | alkyl peroxide bridging to vinyl containing siloxane polymers used for conductive applications improved curing characteristics decreased by the presence of carbon black; crosslinking based on platinum catalyzed polyvinylmethyl siloxane and polymethyl hydrogen siloxane is not inhibited by carbon black; <i>in situ</i> silica formation; ⁴³⁷ in formation of PDMS nanocomposite, montmorillonite was delaminated in polymer prior to crosslinking ⁴⁴⁰ |
| Methods of filler pretreatment | choice of carbon black for conductive applications is crucial because impurities on carbon black may have an adverse effect on mechanical properties; aluminum oxide and calcium carbonate were coated by a hydrophobic layer of PDMS; ⁴⁴³ heat treatment of fumed silica reduces its ability to reinforce polymer, especially in temperatures above 200°C ⁴⁴⁴ |
| Special considerations | in conductive applications, special conductive blacks must be employed; fillers influence chemical degradation reactions in siloxanes; ^{438,447,451,452} zinc oxide was found to increase thermal resistance of PDMS ^{451,452} |

Silicone mechanical properties are inherently poor therefore reinforcement is an essential part of the product development process. A fumed silica addition is one method of silicone improvement by compounding in conjunction with other fillers. The example below shows the results obtained during the development of a nanocomposite material with a low degree of solvent uptake (Figure 15.42). Montmorillonite was delaminated prior to the silicone being cured. The results are compared with the effect of carbon black in SBR. The solvent uptake is inversely proportional to the filler reinforcing strength. Carbon black has strong reinforcing effect on SBR due to molecular interactions but the reinforcement of carbon black still does not match the effect of montmorillonite in the silicone nanocomposite. The advantage of the nanocomposite comes from the differences in surface areas of the fillers. Carbon black has typical surface area in a range from 20 to 100 m²/g whereas delaminated silicate has a surface area of 750 m²/g. The larger surface area

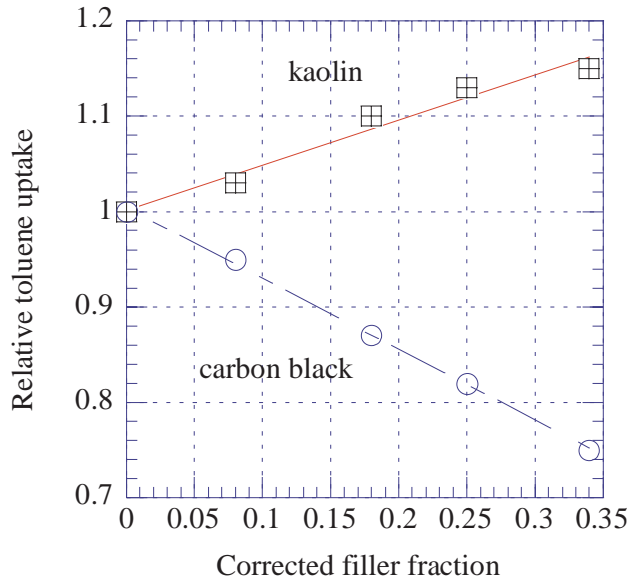


Figure 15.42. Toluene uptake vs. filler concentration. [Data from Burnside S D, Giannelis E P, *Chem. of Mat.*, 7, No.9, 1995, 1597-600.]

increases the probability of interaction and thus results in the reinforcement and lower solvent uptake shown in Figure 15.42.⁴⁴⁰ In another method, small particle sized filler can be incorporated by an *in situ* synthesis.⁴⁴² The results obtained show that degradation temperature can be substantially increased by the selection of composition of metal oxide particles which were formed *in situ*.

15.49 STYRENE-ACRYLONITRILE COPOLYMER, SAN¹⁰⁵

| | |
|----------------------------------|--|
| Major polymer applications | housings for electronic and electrical applications, instrument lenses packaging for high barrier properties, bottles, appliances (housings, air conditioner parts, refrigerator shelves, blenders, lenses), house- wares (eating utensils, beverage/food containers, display boxes), auto- motive (dashboard, battery cases) |
| Important processing methods | injection molding, extrusion, blow molding, thermoforming, casting |
| Typical fillers | glass fiber, PTFE, aluminum borate whiskers |
| Typical concentration range | glass fiber - 10-40 wt%, PTFE - 10-15 wt% |
| Auxiliary agents | not reported |
| Special methods of incorporation | not reported |
| Methods of filler pretreatment | drying especially for extrusion; the surface of the injection molded part is affected by moisture |
| Special considerations | reprocessing affects color and melt flow index |

15.50 TETRAFLUOROETHYLENE-PERFLUOROPROPYLENE, FEP⁹⁰

| | |
|----------------------------------|---|
| Major polymer applications | wire coating, data transmission cable, lined pipes, components for valves and pumps |
| Important processing methods | injection molding, wire coating, extrusion |
| Typical fillers | graphite, glass fiber, bronze |
| Typical concentration range | 10-30 wt% |
| Auxiliary agents | not reported |
| Special methods of incorporation | not reported |
| Methods of filler pretreatment | not reported |
| Special considerations | creep and wear resistance are minimized by addition of fillers |

15.51 UNSATURATED POLYESTERS⁴⁵³⁻⁴⁵⁶

| | |
|----------------------------------|--|
| Major polymer applications | composites, corrosion protection, surfboards, cultured stones, composites, bathroom sinks and vanity tops, countertops |
| Important processing methods | injection molding, compression molding, resin transfer molding, pultrusion, casting, encapsulation |
| Typical fillers | calcium carbonate, aluminum hydroxide, glass fiber, crashed marble, glass fiber, antimony trioxide, carbon black, quartz, saw dust |
| Typical concentration range | aluminum hydroxide - 30-80 wt%, quartz - up to 90 wt%, saw dust - 20-50 wt%, calcium carbonate - 50-74 wt%; glass fibers - 20 wt% |
| Auxiliary agents | silane; ⁴⁵³ maleic anhydride treatment of saw dust ⁴⁵⁴ |
| Special methods of incorporation | degassing of mold after filling ⁴⁵⁴ |
| Methods of filler pretreatment | coating with thermoplastic polymer; zinc hydroxystannate coating of fire retardant fillers increases their performance |
| Special considerations | coated aluminum hydroxide enhances esthetics of coatings |

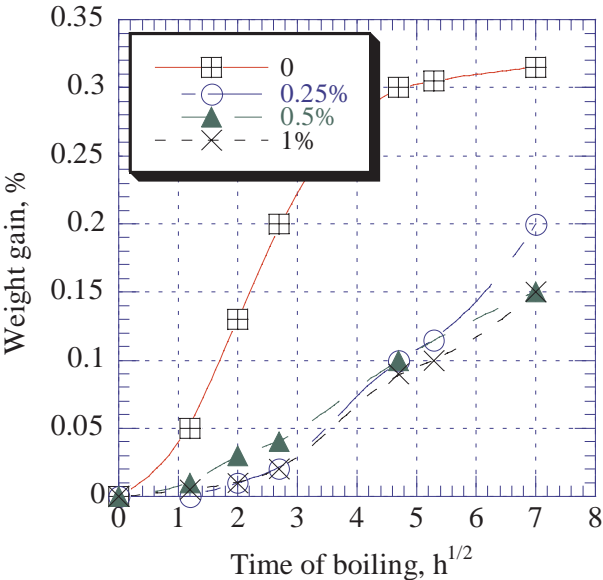


Figure 15.43. Weight gain by unsaturated polyester filled with quartz vs. time in boiling water. [Adapted, by permission, from Kominar V, Narkis M, Siegmann A, Breuer O, *Sci. & Engng. Composite Materials*, 3, No.1, 1994, 61-6.]

Figure 15.43 shows the effect of boiling in water on weight gain by unsaturated polyester/quartz composite.⁴⁵³ The addition of 0.5% silane was sufficient to reduce water uptake. A further increase in silane did not contribute to improvement. A sim-

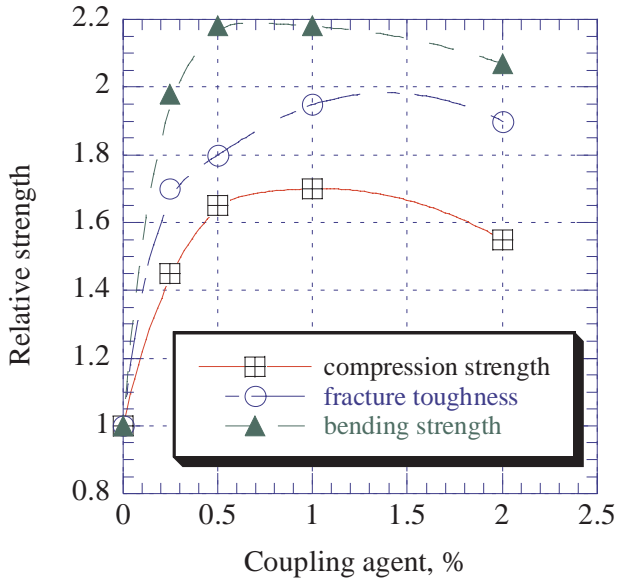


Figure 15.44. Coupling agent effect on mechanical performance of unsaturated polyester filled with quartz. [Adapted, by permission, from Kominar V, Narkis M, Siegmann A, Breuer O, *Sci. & Engng. Composite Materials*, 3, No.1, 1994, 61-6.]

ilar amount of silane is sufficient to improve bending and compression strength and toughness (Figure 15.44). An inexpensive composite of unsaturated polyester was made with saw dust.⁴⁵⁴

15.52 VINYLIDENE-FLUORIDE TERPOLYMERS, PVDF^{321,457-460}

| | |
|----------------------------------|---|
| Major polymer applications | membranes, cables, valves, acid storage tanks, tubing, filtration |
| Important processing methods | extrusion, molding |
| Typical fillers | carbon black, silica, barium titanate, lead zirconium titanate, zeolite, copper powder |
| Typical concentration range | carbon black - 5-15 wt%, ceramic filler up to 40 wt%, silica - 20-50 wt%, zeolite - 0.1-1 wt%, copper 10-30 wt% |
| Auxiliary agents | tetraethoxysilane ⁴⁵⁸ |
| Special methods of incorporation | pre-dispersion of filler in PVDF solution followed by removal of solvent; ⁴⁵⁷ <i>in situ</i> formation of silica ⁴⁵⁸ |
| Methods of filler pretreatment | not reported |
| Special considerations | filling with carbon black can lead to the development of material with switching properties (10 fold increase in resistance at certain temperature) ⁴⁵⁹ crystallization history has effect on performance of switching material ⁴⁵⁹ |

REFERENCES

- 1 Lee D H, Condrate R A, Reed J S, *J. Mater. Sci.*, **32**, 1997, 471-8.
- 2 Magrupov M A, Umarov A V, Saidkhodzhaeva K S, Kasimov G A, *Int. Polym. Sci. Technol.*, **23**, No.1, 1996, T/77-9.
- 3 Yu M C, Bissell M A, Whitehouse R S, Antec '95. Volume III. Conference proceedings, Boston, Ma., 7th-11th May 1995, 3246-50.
- 4 Costa L, Camino G, Bertelli G, Borsini G, *Fire & Mat.*, **19**, No.3, 1995, 133-42.
- 5 Guanghong Lu, Xiaotian Li, Hancheng Jiang, *Composites Sci. & Technol.*, **56**, No.2, 1996, 193-200.
- 6 Tsukuda R, Sumimoto S, Ozawa T, *J. Appl. Polym. Sci.*, **59**, No.6, 1996, 1043-6.
- 7 Nabi Z U, Hashemi S, *J. Mat. Sci.*, **31**, No.21, 1996, 5593-601.
- 8 Gingrich R P, Machado J M, Londa M, Proctor M G, Antec '95. Vol. II. Conference Proceedings, Boston, Ma., 7th-11th May 1995, 2345-50.
- 9 Aldcroft D, *Polym. Paint Col. J.*, **184**, No.4366, 1994, 423-5.
- 10 Ketrup A A, Lenoir D, Thumm W, Kampke-Thiel K, Beck B, *Polym. Degradat. Stabil.*, **54**, Nos 2-3, 1996, 175-80.
- 11 Da-Wei Liu, Jackson C L, Barnes J D, *Polym. Adv. Technol.*, **7**, No.4, 1996, 333-9.
- 12 Strumpler R, Maidorn G, Garbin A, Ritzer L, Greuter F, *Polym. & Polym. Composites*, **4**, No.5, 1996, 299-304.
- 13 Yang Q, Pritchard G, Phipps M A, Rose R G, *Polym. & Polym. Composites*, **4**, No.4, 1996, 239-46.
- 14 Srivastava V K, Pathak J P, *Polym. & Polym. Composites*, **3**, No.6, 1995, 411-4.
- 15 Rebouillat S, Escoubes M, Gauthier R, *J. Adhesion Sci. Technol.*, **10**, No.7, 1996, 635-50.
- 16 Pearson R A, Azimi H R, Bagheri R, Qian J Y, Antec '95. Vol. II. Conference Proceedings, Boston, Ma., 7th-11th May 1995, 2656-61.
- 17 Bittmann E, Ehrenstein G W, Antec '96. Volume II. Conference proceedings, Indianapolis, 5th-10th May 1996, 1465-70.
- 18 Pritykin L M, Razumova O V, Sokolova Y A, Antonov S M, Bolshakov V I, *Int. Polym. Sci. Technol.*, **23**, No.3, 1996, T/80-1.
- 19 Kushchevskaya N F, Shvets T M, *Int. Polym. Sci. Technol.*, **22**, No.12, 1995, T/21-2.
- 20 Shin Jen Shiao, Te Zei Wang, *Composites*, **27B**, No.5, 1996, 459-65.
- 21 Akovali G, Dilsiz N, *Polym. Engng. Sci.*, **36**, No.8, 1996, 1081-6.
- 22 Wu S-L, Tung I-C, *Polym. Composites*, **16**, No.3, 1995, 233-9.
- 23 Lambert C, Chauvet H, Larroque M, *Polymer*, **37**, No.15, 1996, 3441-5.
- 24 Bagheri R, Pearson R A, *Polymer*, **36**, No.25, 1995, 4883-5.
- 25 Achour M E, Miane J L, Lahjomri F, El Malhi M, Carmona F, *J. Mat. Sci. Lett.*, **14**, No.20, 1995, 1425-9.
- 26 Nyilas A, Rehme R, Wyrwich C, Springer H, Hinrichsen G, *J. Mat. Sci. Lett.*, **15**, No.16, 1996, 1457-9.
- 27 Lekatou A, Faïdi S E, Lyon S B, Newman R C, *J. Mat. Res.*, **11**, No.5, 1996, 1293-304.
- 28 Wang J Y, Ploehn H J, *J. Appl. Polym. Sci.*, **59**, No.2, 1996, 345-57.
- 29 Hong S G, Lin J J, Yuan Ze, *J. Appl. Polym. Sci.*, **59**, No.10, 1996, 1597-605.
- 30 Luzinov I, Voronov A, Minko S, Kraus R, Wilke W, Zhuk A, *J. Appl. Polym. Sci.*, **61**, No.7, 1996, 1101-9.
- 31 Achour M E, El Malhi M, Miane J L, Carmona F, *J. Appl. Polym. Sci.*, **61**, No.11, 1996, 2009-13.
- 32 Azimi H R, Pearson R A, Hertzberg R W, *J. Appl. Polym. Sci.*, **58**, No.2, 1995, 449-63.
- 33 Palumbo M, Donzella G, Tempesti E, Ferruti P, *J. Appl. Polym. Sci.*, **60**, No.1, 1996, 47-53.
- 34 Yang Q, Pritchard G, *Polym. & Polym. Composites*, **2**, No.4, 1994, 233-9.
- 35 Ohta M, Nakamura Y, Hamada H, Maekawa Z, *Polym. & Polym. Composites*, **2**, No.4, 1994, 215-21.
- 36 Grady B P, Antec '97. Conference proceedings, Toronto, April 1997, 2490-3.
- 37 Kumar P, Gawahale A R, Rai B, *Adv. Composite Materials*, **4**, No.4, 1995, 279-85.
- 38 Privalko V P, Novikov V V, *Adv. Polym. Sci.*, **119**, 1995, 31-77.
- 39 Whalen J P, Poston D D, Antec '94. Conference Proceedings, San Francisco, Ca., 1st-5th May 1994, Vol. I, 924-8.
- 40 Dzeskiewicz L A, Ralston J D, Antec '94. Conference Proceedings, San Francisco, Ca., 1st-5th May 1994, Vol. I, 931-4.
- 41 Mamunya E P, Davidenko V V, Lebedev E V, *Polym. Composites*, **16**, No.4, 1995, 319-24.
- 42 Meijerink J I, Eguchi S, Ogata M, Ishii T, Amagi S, Numata S, Sashima H, *Polymer*, **35**, No.1, 1994, 179-86.
- 43 Dufresne A, Lacabanne C, *Polymer*, **34**, No. 15, 1993, 3173-8.

- 44 Kouloumbi N, Tsangaris G M, Kyvelidis S T, *J. Coatings Technol.*, **66**, No.839, 1994, 83-8.
- 45 Ming Qiu Zhang, Jia Rui Xu, Han Ming Zeng, Qun Huo, Zhi Yi Zhang, Feng Chun Yun, Friedrich K, *J. Mat. Sci.*, **30**, No.17, 1995, 4226-32.
- 46 Bogoeva-Gaceva G, Burevski D, Dekanski A, Janevski A, *J. Mat. Sci.*, **30**, No.13, 1995, 3543-6.
- 47 Katsumata M, Endo M, Ushijima H, Yamanishi H, *J. Mat. Res.*, **9**, No.4, 1994, 841-3.
- 48 Miszczyk A, Szalinska H, *Prog. Org. Coatings*, **25**, No.4, 1995, 357-63.
- 49 Messersmith P B, Giannelis E P, *Chem. of Mat.*, **6**, No.10, 1994, 1719-25.
- 50 Lan T, Pinnavaia T J, *Chem. of Mat.*, **6**, No.12, 1994, 2216-9.
- 51 Konstantellos B, Sideridis E, *Coll. Polym. Sci.*, **273**, No.4, 1995, 307-16.
- 52 Bagheri R, Williams M A, Pearson R A, *Polym. Eng. Sci.*, **37**, No.2, 1997, 245-51.
- 53 Tang L-G, Kardos J L, *Polym. Composites*, **18**, No.1, 1997, 100-13.
- 54 Gassan J, Bledzki A K, *Polym. Composites*, **18**, No.2, 1997, 179-84.
- 55 Bijwe J, *Polym. Composites*, **18**, No.3, 1997, 378-96.
- 56 Akay M, Mun S K A, Stanley A, *Composites Sci. Technol*, **57**, 1997, 565-71.
- 57 Hsieh F Y, Beson H D, *Fire Mater.*, **21**, 1997, 41-9.
- 58 Shang S W, Williams J W, Soderholm K J M, *J. Mat. Sci.*, **30**, No.17, 1995, 4323-34.
- 59 Singhal A, Fina L J, *Polymer*, **37**, No.12, 1996, 2335-43.
- 60 Kerber M L, Ponomarev I N, Lapshova O A, Grinenko E S, Sabsai O Y, Dubinskii M B, Burtseva I V, *Polym. Sci. Ser. A*, **38**, No.8, 1996, 867-74.
- 61 Haagh G A A V, Peters G W M, Meijer H E H, *Polym. Engng. Sci.*, **36**, No.20, 1996, 2579-88.
- 62 Rothon R N; Hornsby P R, *Polym. Degradat. Stabil.*, **54**, Nos 2-3, 1996, 383-5.
- 63 Tang H, Chen X, Luo Y, *Eur. Polym. J.*, **32**, No.8, 1996, 963-6.
- 64 McNeill I C, Mohammed M H, *Polym. Degradat. Stabil.*, **49**, No.2, 1995, 263-73.
- 65 McNeill I C, Mohammed M H, *Polym. Degradat. Stabil.*, **48**, No.1, 1995, 189-95.
- 66 Dole P, Chauchard J, *Polym. Degradat. Stabil.*, **47**, No.3, 1995, 441-8.
- 67 Toure B, Lopez Cuesta J-M, Longerey M, Crespy A, *Polym. Degradat. Stabil.*, **54**, Nos 2-3, 1996, 345-52.
- 68 Toure B, Lopez Cuesta J M, Gaudon P, Benhassaine A, Crespy A, *Polym. Degradat. Stabil.*, **53**, No.3, 1996, 371-9.
- 69 Younan A F, Choneim A M, Tawfik A A A, Abd-El-Nour K N, *Polym. Degradat. Stabil.*, **49**, No.2, 1995, 215-22.
- 70 Toure B, Lopez-Cuesta J, Benhassaine A, Crespy A, *Int. J. Polym. Analysis and Characterization*, **2**, No.3, 1996, 193-202.
- 71 *Int. Polym. Sci. Technol.*, **23**, No.7, 1996, T/1-3.
- 72 Kurian T, Khatgir D, De P P, Tripathy D K, De S K, Peiffer D G, *Polymer*, **37**, No.25, 1996, 5597-605.
- 73 Datta S, De S K, Kontos E G, Wefer J M, Wagner P, Vidal A, *Polymer*, **37**, No.15, 1996, 3431-5.
- 74 Datta S, Bhattacharya A K, De S K, Kontos E G, Wefer J M, *Polymer*, **37**, No.12, 1996, 2581-5.
- 75 Kurian T, De P P, Khatgir D, Tripathy D K, De S K, Peiffer D G, *Polymer*, **36**, No.20, 1995, 3875-84.
- 76 Datta S, De S K, Kontos E G, Wefer J M, *J. Appl. Polym. Sci.*, **61**, No.1, 1996, 177-86.
- 77 Chiu H-T, Chiu W-M, *J. Appl. Polym. Sci.*, **61**, No.4, 1996, 607-12.
- 78 Guriya K C, Tripathy D K, *J. Appl. Polym. Sci.*, **62**, No.1, 1996, 117-27.
- 79 Kurian T, De P P, Tripathy D K, De S K, Peiffer D G, *J. Appl. Polym. Sci.*, **62**, No.10, 1996, 1729-34.
- 80 Zaborski M, Slusarski L, Vidal A, *Polim. Tworz. Wielk.*, **38**, No.6, 1993, 263-8.
- 81 Zaborski M, Slusarski L, *Composite Interfaces*, **3**, No.1, 1995, 9-22.
- 82 Levesque J L, Fraval J T, Antec '93. Conference Proceedings, New Orleans, La., 9th-13th May 1993, Vol. II, 1957-64.
- 83 Zhu J, Ou Y-C, Feng Y-P, *Polym. Int.*, **37**, No.2, 1995, 105-11.
- 84 Coran A Y, Ignatz-Hoover F, Smakula P C, *Rubb. Chem. Technol.*, **67**, No.2, 1994, 237-51.
- 85 Otaigbe J U, Quinn C J, Beall G H, Antec '97. Conference proceedings, Toronto, April 1997, 1826-30.
- 86 Zyuzina G F, Vinogradova N K, Gribova I A, Krasnov A P, *Polym. Sci.*, **36**, No.9, 1994, 1205-8.
- 87 Plummer C J G, Wu Y, Gola M M, Kausch H H, *Polym. Bull.*, **30**, No.5, 1993, 587-94.
- 88 Liu C, Manzione L T, *Polym. Engng. Sci.*, **36**, No.1, 1996, 10-4.
- 89 Scaffaro R, Pedretti U, La Mantia F P, *Eur. Polym. J.*, **32**, No.7, 1996, 869-75.
- 90 Knowles J, *Polym. Paint Col. J.*, **185**, No.4366, 1995, 26-7.
- 91 Elfving K, Soderberg B, *Reinf. Plast.*, **40**, No.6, 1996, 64-5.
- 92 Brown N, Linnert E, *Reinf. Plast.*, **39**, No.11, 1995, 34-7.
- 93 *Reinf. Plast.*, **40**, No.10, 1996, 66-70.
- 94 Peng W, Riedl B, *Polymer*, **35**, No.6, 1994, 1280-6.

- 95 Balchandani N, *Pop. Plast. Packag.*, **40**, No.2, 1995, 41-2.
- 96 Murayama H, Min K, *Antec '97*. Conference proceedings, Toronto, April 1997, 759-65.
- 97 Wang T, Sherwood P M A, *Chem. of Mat.*, **6**, No.6, 1994, 788-95.
- 98 Tiejun Wang, Sherwood P M A, *Chem. of Mat.*, **7**, No.5, 1995, 1031-40.
- 99 Hegedus C R, Kamel I L, *J. Coatings Technol.*, **65**, No.820, 1993, 31-43
- 100 Levchik G F, Levchik S V, Lesnikovich A I, *Polym. Degradat. Stabil.*, **54**, Nos 2-3, 1996, 361-3.
- 101 Hornsby P R, Wang J, Rothon R, Jackson G, Wilkinson G, Cossick K, *Polym. Degradat. Stabil.*, **51**, No.3, 1996, 235-49.
- 102 Schleifstein R A, Property Enhancement with Modifiers and Additives. Retec proceedings, New Brunswick, N.J., 18th-19th Oct.1994, 89-101.
- 103 Turner J D, Property Enhancement with Modifiers and Additives. Retec proceedings, New Brunswick, N.J., 18th-19th Oct.1994, 65-87.
- 104 Baque T, *Kunststoffe Plast Europe*, **86**, No.8, 1996, 22-3.
- 105 Persson A L, Bertilsson H, *Composite Interfaces*, **3**, No.4, 1996, 321-32.
- 106 Narkis M, Tchoudakov R, Breuer O, Siegmann A, *Antec '95*. Vol. II. Conference Proceedings, Boston, Ma., 7th-11th May 1995, p.1343-6.
- 107 Benderly D, Siegmann A, Narkis M, *Antec '95*. Vol. II. Conference Proceedings, Boston, Ma., 7th-11th May 1995, 3168-71.
- 108 McIlvaine J, *Antec '95*. Volume III. Conference proceedings, Boston, Ma., 7th-11th May 1995, 3346-9.
- 109 Belanger B, Sanschagrin B, Fisa B, *Antec '96*. Volume II. Conference proceedings, Indianapolis, 5th-10th May 1996, 1762-7.
- 110 Larena A, Pinto G, *Polym. Composites*, **16**, No.6, 1995, 536-41.
- 111 Hornsby P R, Wang J, Cosstick K, Rothon R, Jackson G, Wilkinson G, *Flame Retardants '94*. Conference proceedings, London, 27th-28th January 1994, 93-108.
- 112 Hamada H, Hiragushi M, Takahashi K, Machida K, *Antec '97*. Conference proceedings, Toronto, April 1997, 3326-30.
- 113 Jia N, Kagan V A, *Antec '97*. Conference proceedings, Toronto, April 1997, 1844-8.
- 114 Wagner A H, Kalyon D M, Yazici R, Fiske T J, *Antec '97*. Conference proceedings, Toronto, April 1997, 996-1000.
- 115 Rammoorthy M, Muzzy J, *Antec '97*. Conference proceedings, Toronto, April 1997, 2500-4.
- 116 Canova L A, *Antec '93*. Conference Proceedings, New Orleans, La., 9th-13th May 1993, Vol. II, 1943-9.
- 117 Turcovsky G, *Antec '94*. Conference Proceedings, San Francisco, Ca., 1st-5th May 1994, Vol. I, 796-800.
- 118 Meddad A, Fellahi S, Pinard M, Fisa B, *Antec '94*. Conference Proceedings, San Francisco, Ca., 1st-5th May 1994, Vol. II, 2284-8.
- 119 Zolotnitsky M, Steinmetz J R, *Antec '94*. Conference Proceedings, San Francisco, Ca., 1st-5th May 1994, Vol. III, 2756-60.
- 120 Hornsby P R, Wang J, Jackson G, Rothon R N, Wilkinson G, Cosstick K, *Antec '94*. Conference Proceedings, San Francisco, Ca., 1st-5th May 1994, Vol. III, 2834-9.
- 121 Ou Y-C, Yu Z-Z, *Polym. Int.*, **37**, No.2, 1995, 113-7.
- 122 Quintanilla L, Pastor J M, *Polymer*, **35**, No.24, 1994, 5241-6.
- 123 Messersmith P B, Giannelis E P, *Chem. of Mat.*, **5**, No.8, 1993, 1064-6.
- 124 Usuki A, Koiwai A, Kojima Y, Kawasumi M, Okada A, Kurauchi T, Kamigaito O, *J. Appl. Polym. Sci.*, **55**, No.1, 1995, 119-23.
- 125 Ou Y, Yang F, Chen J, *J. Appl. Polym. Sci.*, **64**, 1997, 2317-22.
- 126 Horst J J, Spoormaker J L, *J. Mater. Sci.*, **32**, 1997, 3541-51.
- 127 Steskal J, Kratochvil P, Armes S P, Lascelles S F, Riede A, Helmstedt M, Prokes J, Krivka I, *Macromolecules*, **29**, No.21, 1996, 6814-9.
- 128 Zhou J, Li G, Li B, He T, *J. Appl. Polym. Sci.*, **65**, 1997, 1857-64.
- 129 Stokes V K, *Antec '93*. Conference Proceedings, New Orleans, La., 9th-13th May 1993, Vol. II, 2067-74.
- 130 Nofal M M, Zihlif A M, Ragosta G, Martuscelli E, *Polym. Composites*, **17**, No.5, 1996, 705-9.
- 131 Joo Y L, Lee Y D, Kwack T H, Min T I, *Antec '96*. Vol. I. Conference Proceedings, Indianapolis, 5th-10th May 1996, 64-8.
- 132 Benrashid R, Nelson G L, *J. Fire Sci.*, **11**, No.5, 1993, 371-93.
- 133 Zihlif A M, Di Liello V, Martuscelli E, Ragosta G, *Int. J. Polym. Mat.*, **29**, Nos.3-4, 1995, 211-20.
- 134 Tanaka T, Waki Y, Hamamoto A, Nogami N, *Antec '97*. Conference proceedings, Toronto, April 1997,

- 3054-8.
- 135 Rowberry P J, Conductive Polymers, Conference papers, Bristol, UK, 1992, paper 13.
- 136 Xavier S F, *Pop. Plast. Packag.*, **41**, No.4, 1996, 61-64.
- 137 Davis R M, Gardner S H, Marand E, Laot C, Reifsnider K, DeSmidt H, McGrath J, Tan B, Antec '97. Conference proceedings, Toronto, April 1997, 2494-9.
- 138 Cantwell W J, Zulkifli R, *J. Mater. Sci. Lett.*, **16**, 1997, 509-11.
- 139 Selzer R, Friedrich K, *Composites, Part A*, **28A**, 1997, 595-604.
- 140 Wang Y, Lu J, Wang G, *J. Appl. Polym. Sci.*, **64**, 1997, 1275-81.
- 141 Agari Y, Ueda A, Nagai S, *J. Appl. Polym. Sci.*, **52**, No.9, 1994, 1223-31.
- 142 Hindryckx F, Dubois P, Patin M, Jerome R, Teyssie P, Garcia Marti M, *J. Appl. Polym. Sci.*, **56**, No.9, 1995, 1093-105.
- 143 Burke M, Young R J, Stanford J L, *Plast. Rubb. Comp. Process. Appln.*, **20**, No.3, 1993, 121-35.
- 144 Hashmi S A R, Chand N, *J. Mat. Sci. Lett.*, **14**, No.5, 1995, 377-9.
- 145 Mamunya E P, Shumskii V F, Lebedev E V, *Polym. Sci.*, **36**, No.6, 1994, 835-8.
- 146 Fu Q, Wang G, Liu C, *Polymer*, **36**, No.12, 1995, 2397-401.
- 147 Janigova I, Chodak I, *Eur. Polym. J.*, **30**, No.10, 1994, 1105-10.
- 148 Janigova I, Chodak I, *Eur. Polym. J.*, **31**, No.3, 1995, 271-4.
- 149 Ruiz F A, Polymers, Laminations & Coatings Conference, 1995, 647-51.
- 150 Hansen H, Polymers, Laminations & Coatings Conference, 1995, 653-8.
- 151 Mayadunne A, Bhattacharya S N, Kosior E, Boontanjai C, Antec 95. Volume I. Conference proceedings, Boston, Ma., 7th-11th May 1995, 1178-82.
- 152 Ruiz F A, Antec '94. Conference Proceedings, San Francisco, Ca., 1st-5th May 1994, Vol. III, 2766-9.
- 153 Fiske T J, Gokturk H S, Kalyon D M, Antec '93. Conference Proceedings, New Orleans, La., 9th-13th May 1993, Vol. I, 614-7.
- 154 Gokturk H S, Fiske T J, Kalyon D M, Antec '93. Conference Proceedings, New Orleans, La., 9th-13th May 1993, Vol. I, 605-8.
- 155 Fiske T, Gokturk H S, Yazici R, Kalyon D M, Antec '97. Conference proceedings, Toronto, April 1997, 1482-6.
- 156 Berenbrok P A, Liles B E, Antec '97. Conference proceedings, Toronto, April 1997, 2931-2.
- 157 Bush S F, Tonkin J D, Antec '97. Conference proceedings, Toronto, April 1997, 3081-85.
- 158 Turley R S, Strong A B, *J. Adv. Materials*, **25**, No.3, 1994, 53-9.
- 159 Levering A W, Te Nijenhuis K, *J. Adhesion*, **45**, No.1-4, 1994, 137-48.
- 160 Albertsson A-C, Barenstedt C, Karlsson S, *J. Environmental Polym. Degradat.*, **1**, No.4, 1993, 241-5.
- 161 Mateev M M, Totev D L, *Kaut. u. Gummi Kunst.*, **49**, No.6, 1996, 427-31.
- 162 Jacobson K E, Eller R, Polyolefins VIII. Conference Proceedings, Houston, Tx., 21st-24th Feb.1993, 494-509.
- 163 Minkova L, Magagnini P L, *Polym. Degradat. Stabil.*, **42**, No.1, 1993, 107-15.
- 164 Mwila J, Miraftab M, Horrocks A R, *Polym. Degradat. Stabil.*, **44**, No.3, 1994, 351-6.
- 165 Albertsson A C, Griffin G J L, Karlson S, Nishimoto K, Watanabe Y, *Polym. Degradat. Stabil.*, **45**, No.2, 1994, 173-8.
- 166 Griffin G J L, *Polym. Degradat. Stabil.*, **45**, No.2, 1994, 241-7.
- 167 Callari J J, *Plast. World*, **52**, No.3, 1994, 22-6.
- 168 Svorcik V, Micek I, Jankovskij O, Rybka V, Hnatowicz V, Wang L, Angert N, *Polym. Degradat. Stabil.*, **55**, 1997, 115-21.
- 169 Le Bras M, Bourbigot, Le Tallec Y, Laureys J., *Polym. Degradat. Stabil.*, **56**, 1997, 11-21.
- 170 Tavman I H, *J. Appl. Polym. Sci.*, **62**, No.12, 1996, 2161-7.
- 171 Hao Tang, Xinfang Chen, Aoqing Tang, Yunxia Luo, *J. Appl. Polym. Sci.*, **59**, No.3, 1996, 383-7.
- 172 Ou Y C, Zhu J, Feng Y P, *J. Appl. Polym. Sci.*, **59**, No.2, 1996, 287-94.
- 173 Savadori A, Scapin M, Walter R, *Macromol. Symp.*, **108**, 1996, 183-202.
- 174 Modine F A, Duggal A R, Robinson D N, Churnetski E L, Bartkowiak M, Mahan G D, Levinson L M, *J. Mat. Res.*, **11**, No.11, 1996, 2889-94.
- 175 Svorcik V, Rybka V, Hnatowicz V, Bacakova L, *J. Mat. Sci. Lett.*, **14**, No.24, 1995, 1723-4.
- 176 Sinien L, Xiaoguang Z, Zhongneng Q, Huan X, *J. Mat. Sci. Lett.*, **14**, No.20, 1995, 1458-60.
- 177 Dubnikova I L, Gorokhova E V, Gorenberg A Y, Topolkaraev V A, *Polym. Sci., Ser. A*, **37**, No.9, 1995, 951-8.
- 178 Bomal Y, Godard P, *Polym. Engng. Sci.*, **36**, No.2, 1996, 237-43.
- 179 Kobayashi M, Takahashi T, Takimoto J, Koyama K, *Polymer*, **37**, No.16, 1996, 3745-7.
- 180 Chang Ho Suh, White J L, *Polym. Engng. Sci.*, **36**, No.11, 1996, 1521-30.

- 181 Suh C H, White J L, *Polym. Engng. Sci.*, **36**, No.17, 1996 2188-97.
- 182 Fiske T J, Gokturk H, Kalyon D M, Antec '96. Volume II. Conference proceedings, Indianapolis, 5th-10th May 1996, 1768-72.
- 183 Gill T S, Xanthos M, Wirsbo Co., Antec '96. Volume II. Conference proceedings, Indianapolis, 5th-10th May 1996, 1757-61.
- 184 Suh C H, White J L, Antec '96. Vol.I. Conference Proceedings, Indianapolis, 5th-10th May 1996, p.958-62.
- 185 Casenave S, Ait-Kadi A, Brahimi B, Riedl B, Antec '95. Vol. II. Conference Proceedings, Boston, Ma., 7th-11th May 1995, 1438-42.
- 186 Chang Ho Suh, White J L, *J. Non-Newtonian Fluid Mechanics*, **62**, Nos.2/3, 1996, 175-206.
- 187 Kretzschmar B, *Kunststoffe Plast Europe*, **86**, No.4, 1996, 20-2.
- 188 Gill T S, Xanthos M, *J. Vinyl and Additive Technol.*, **2**, No.3, 1996, 248-52.
- 189 Hollis R D, Hyche K W, Color and Appearance Retec: Effects in Plastics. Conference proceedings, Oak Brook, Il., 20th-22nd Sept. 1994, 94-105.
- 190 Yeh J T, Yang H M, Huang S S, *Polym. Degradat. Stabil.*, **50**, No.2, 1995, 229-34.
- 191 Sanchez-Solis A, Estrada M R, *Polym. Degradat. Stabil.*, **52**, No.3, 1996, 305-9.
- 192 Gordienko V P, Dmitriev Y A, *Polym. Degradat. Stabil.*, **53**, No.1, 1996, 79-87.
- 193 Gordienko V P, Dmitriev Y A, *Polym. Sci., Ser. B*, **37**, Nos.5-6, 1995, 249-50.
- 194 Beloshenko V A, Kozlov G V, Slobodina V G, Prut E V, Grinev V G, *Polym. Sci., Ser. B*, **37**, Nos.5-6, 1995, 316-8.
- 195 Tino J, Mach P, Hlouskova Z, Chodak I, *J. Macromol. Sci. A*, **A31**, No.10, 1994, 1481-7.
- 196 Nichols M E, Pett R A, *Rubb. Chem. Technol.*, **67**, No.4, 1994, 619-28.
- 197 Hedgus C R, Kamel I L, *J. Coatings Technol.*, **65**, No.821, June 1993, 49-61
- 198 Yamada H, Inagaki S, Okamoto H, Furukawa J, *Int. Polym. Sci. Technol.*, **21**, No.6, 1994, T/29-35.
- 199 Ventresca D A, Berard M T, Antec '97. Conference proceedings, Toronto, April 1997, 3574-9.
- 200 Roychoudhury A, De P P, Roychoudhury N, Vidal A, *Rubb. Chem. Technol.*, **68**, No.5, 1995, 815-23.
- 201 Kimura T, Asano Y, Yasuda S, *Polymer*, **37**, No.14, 1996, 2981-7.
- 202 Liu Y J, Schindler J L, DeGroot D C, Kannewurf C R, Hirpo W, Kanatzidis M G, *Chem. of Mat.*, **8**, No.2, 1996, 525-34.
- 203 Ruiz-Hitzky E, Aranda P, Casal B, Galvan J C, *Adv. Mat.*, **7**, No.2, 1995, 180-4.
- 204 Khan S A, Baker G L, Colson S, *Chem. of Mat.*, **6**, No.12, 1994, 2359-63.
- 205 Lemmon J P, Lerner M M, *Chem. of Mat.*, **6**, No.2, 1994, 207-10.
- 206 Ou Y, Yu Z, Zhu J, Li G, Zhu S, *Chinese J. Polym. Sci.*, **14**, No.2, 1996, 172-82.
- 207 Casoli A, Charneau J Y, Holl Y, d'Allest J F, *J. Adhesion*, **57**, Nos.1-4, 1996, 133-51.
- 208 Rebeiz K S, Rosett J W, Nesbit S M, Craft A P, *J. Mat. Sci. Lett.*, **15**, No.14, 1996, 1273-5.
- 209 Gerspacher M, O'Farrell C P, Nikiel L, Yang H H, *Rubb. Plast. News*, **26**, No.2, 1996, 39-40.
- 210 Chen X, Gonsalves K E, Chow G M, Xiao T D, *Adv. Mat.*, **6**, No.6, 1994, 481-4.
- 211 Wool R P, Long J M, *Macromolecules*, **26**, No.19, 1993, 5227-39.
- 212 Lan T, Kaviratna D, Pinnavaia T J, *Chem. of Mat.*, **6**, No.5, 1994, 573-5.
- 213 Asai S, Sumita M, *J. Macromol. Sci. B*, **34**, No.3, 1995, 283-94.
- 214 Molino L N, Topoleski L D T, *J. Biomed. Mat. Res.*, **31**, No.1, 1996, 131-7.
- 215 Joseph R, Zhang S, Ford W T, *Macromolecules*, **29**, No.4, 1996, 1305-12.
- 216 Tamura J, Kawanabe K, Yamamuro T, Nakamura T, Kokubo T, Yoshihara S, Shibuya T, *J. Biomed. Mat. Res.*, **29**, No.5, 1995, 551-9.
- 217 Topoleski L D T, Ducheyne P, Cuckler J M, *J. Biomed. Mat. Res.*, **29**, No.3, 1995, 299-307.
- 218 Lei Yang, Schruben D L, *Polym. Engng. Sci.*, **34**, No.14, 1994, 1109-14.
- 219 Liqing Sun, Aklonis J J, Salovey R, *Polym. Engng. Sci.*, **33**, No.20, 1993, 1308-19.
- 220 Hegedus C R, Kamel I L, *J. Coatings Technol.*, **65**, No.822, July 1993, 37-43.
- 221 Sunkara H B, Jethmalani J M, Ford W T, *Chem. of Mat.*, **6**, No.4, 1994, 362-4.
- 222 Visser S A, *J. Appl. Polym. Sci.*, **63**, 1997, 1805-20.
- 223 Grohens Y, Schultz J, *Int. J. Adhesion Adhesives*, **17**, 1997, 163-7.
- 224 Hashemi S, Din K J, Low P, *Polym. Engng. Sci.*, **36**, No.13, 1996, 1807-20.
- 225 Hashemi S, Gilbride J T, Hodgkinson J, *J. Mat. Sci.*, **31**, No.19, 1996, 5017-25.
- 226 Pape P G, Romenesco D J, Antec '97. Conference proceedings, Toronto, April 1997, 2941-52.
- 227 Okiyokota M, Hamada H, Hiragushi M, Hasegawa T, Antec '97. Conference proceedings, Toronto, April 1997, 3319-21.
- 228 Dreibelbis G L, Antec 95. Volume III. Conference proceedings, Boston, Ma., 7th-11th May 1995, 4374-6.

- 229 Hornsby P R, Premphet K, *J. Mater. Sci.*, **32**, 1997, 4767-75.
- 230 Thomason J L, Vlug M A, *Composites, Part A*, **28A**, 1997, 277-88.
- 231 Sjogren B A, Berglund L A, *Polym. Composites*, **18**, No.1, 1997, 1-8.
- 232 Asp L E, Sjogren B A, Berglund L A, *Polym. Composites*, **18**, No.1, 1997, 9-15.
- 233 Averous L, Quantin J C, Crespy A, *Polym. Eng. Sci.*, **37**, No.2, 1997, 329-37.
- 234 Cai Y, Petermann J, Wittich H, *J. Appl. Polym. Sci.*, **65**, 1997, 67-75.
- 235 Mi Y, Chen X, Guo Q, *J. Appl. Polym. Sci.*, **64**, 1997, 1267-73.
- 236 Gahleitner M, Bernreitner K, Neissl W, *J. Appl. Polym. Sci.*, **53**, No.3, 1994, 283-9.
- 237 Nakamura S, Kaneko S, Mizutani Y, *J. Appl. Polym. Sci.*, **49**, No.1, 1993, 143-50.
- 238 Nago S, Mizutani Y, *J. Appl. Polym. Sci.*, **53**, No.12, 1994, 1579-87.
- 239 Liao K, Chen X, Zheng C, *J. Appl. Polym. Sci.*, **57**, No.10, 1995, 1245-50.
- 240 Acosta J L, Jurado J R, *J. Appl. Polym. Sci.*, **57**, No.4, 1995, 431-7.
- 241 Roesch J, Barghoorn P, Muelhaupt R, *Makromol. Chem. Rapid Commun.*, **15**, No.9, 1994, 691-6.
- 242 Jancar J, DiBenedetto A T, *Sci. & Eng. Composite Materials*, **3**, No. 4, 1994, 217-26.
- 243 Jancar J, DiBenedetto A T, *J. Mat. Sci.*, **30**, No.6, 1995, 1601-8.
- 244 Jancar J, DiBenedetto A T, *J. Mat. Sci.*, **30**, No.9, 1995, 2438-45.
- 245 Baranovskii V M, Tarara A M, Khomik A A, *Int. Polym. Sci. Technol.*, **20**, No.1, 1993, T/98-9.
- 246 Jancar J, DiBenedetto A T, Dianselmo A, *Polym. Engng. Sci.*, **33**, No.9, 1993, 559-63.
- 247 Chiang W Y, Yang W D, Pukanszky B, *Polym. Engng. Sci.*, **34**, No.6, 1994, 485-92.
- 248 Baranovskii V M, Bondarenko S I, Kachanovskaya L D, Zelenev Y V, Makarov V G, Ovcharenko F D, *Int. Polym. Sci. Technol.*, **22**, No.1, 1995, T/91-3.
- 249 Schott N R, Rahman M, Perez M A, Antec '94. Conference Proceedings, San Francisco, Ca., 1st-5th May 1994, Vol. III, 2846-50.
- 250 Borden K A, Weil R C, Manganaro C R, Antec '94. Conference Proceedings, San Francisco, Ca., 1st-5th May 1994, Vol. III, 2761-5.
- 251 Jancar J, DiBenedetto A T, Antec '94. Conference Proceedings, San Francisco, Ca., 1st-5th May 1994, Vol. II, 1710-2.
- 252 Gendron R, Daigneault L E, Tatibouet J, Dumoulin M M, Antec '94. Conference Proceedings, San Francisco, Ca., 1st-5th May 1994, Vol. I, 167-71.
- 253 Wong K W Y, Truss R W, *Composites Sci. & Technol.*, **52**, No.3, 1994, 361-8.
- 254 Borden K A, Weil R C, Manganaro C R, Antec '93. Conference Proceedings, New Orleans, La., 9th-13th May 1993, Vol. II, 2167-70.
- 255 Skelhorn D A, Antec '93. Conference Proceedings, New Orleans, La., 9th-13th May 1993, Vol. II, 1965-70.
- 256 Hornsby P R, Mthupha A, Antec '93. Conference Proceedings, New Orleans, La., 9th-13th May 1993, Vol. II, 1954-6.
- 257 Sain M M, Kokta B V, Antec '93. Conference Proceedings, New Orleans, La., 9th-13th May 1993, Vol. I, 320-4.
- 258 Canova L A, Fergusson L W, Parrinello L M, Subramanian R, Giles H F, Antec '97. Conference proceedings, Toronto, April 1997, 2112-6.
- 259 Gerard P, Raine J, Pabiot J, Antec '97. Conference proceedings, Toronto, April 1997, 526-31.
- 260 Suri A, Min K, Antec '97. Conference proceedings, Toronto, April 1997, 1487-91.
- 261 Barbosa S E, Kenny J M, Antec '97. Conference proceedings, Toronto, April 1997, 1855-9.
- 262 Ewing F, Leatherman M, Antec '97. Conference proceedings, Toronto, April 1997, 2924-7.
- 263 Rabello M S, White J R, Antec '97. Conference proceedings, Toronto, April 1997, 2991-5.
- 264 Clemens M L, Doyle M D, Lees G C, Briggs C C, Day R C, Flame Retardants '94. Conference proceedings, London, 27th-28th January 1994, 193-202.
- 265 Schott N R, Rahman M, Perez M A, *J. Vinyl and Additive Technol.*, **1**, No.1, 1995, 36-40.
- 266 Schneider J P, Myers G E, Clemons C M, English B W, *J. Vinyl and Additive Technol.*, **1**, No.2, 1995, 103-8.
- 267 Rockenbauer A, Korecz L, Pukanszky B, *Polym. Bull.*, **33**, No.5, 1994, 585-9.
- 268 Hu X, Xu H, Zhang X, *Polym. Degradat. Stabil.*, **43**, No.2, 1994, 225-8.
- 269 Borden K A, Wei R C, Manganaro C R, *Plast. Compounding*, **16**, No.5, 1993, 51-5.
- 270 Desai S C, *Pop. Plast. Packag.*, **39**, No.7, 1994, 53-60.
- 271 Kim G M, Michler G H, Gahleitner M, Fiebig J, *J. Appl. Polym. Sci.*, **60**, No.9, 1996, 1391-403.
- 272 Wang J, Tung J F, Fuad M Y A, Hornsby P R, *J. Appl. Polym. Sci.*, **60**, No.9, 1996, 1425-37.
- 273 Chunmin Ye, Jingjiang Liu, Zhishen Mo, Gongben Tang, Xiabin Jing, *J. Appl. Polym. Sci.*, **60**, No.11, 1996, 1877-81.

- 274 Wang Z, *J. Appl. Polym. Sci.*, **60**, No.12, 1996, 2239-43.
- 275 Long Y, Shanks R A, *J. Appl. Polym. Sci.*, **62**, No.4, 1996, 639-46.
- 276 Nago S, Mizutani Y, *J. Appl. Polym. Sci.*, **61**, No.13, 1996, 2355-9.
- 277 Yu Long, Shanks R A, Melbourne, *J. Appl. Polym. Sci.*, **61**, No.11, 1996, 1877-85.
- 278 Nago S, Mizutani Y, Tokuyama Corp., *J. Appl. Polym. Sci.*, **61**, No.1, 1996, 31-5.
- 279 Liu Z, Gilbert M, *J. Appl. Polym. Sci.*, **59**, No.7, 1996, 1087-98.
- 280 Alonso M, Gonzalez A, de Saja J A, *Plast. Rubb. Comp. Process. Appln.*, **24**, No.3, 1995, 131-7.
- 281 Hornsby P R, Watson C L, *J. Mat. Sci.*, **30**, No.21, 1995, 5347-55.
- 282 Khare A, Mitra A, Radhakrishnan S, *J. Mat. Sci.*, **31**, No.21, 1996, 5691-5.
- 283 Jarvela P A, Jarvela P K, *J. Mat. Sci.*, **31**, No.14, 1996, 3853-60.
- 284 Furuichi N, Kurokawa Y, Fujita K, Oya A, Yasuda H, Kiso M, *J. Mat. Sci.*, **31**, No.16, 1996, 4307-10.
- 285 Kurokawa Y, Yasuda H, Oya A, *J. Mat. Sci. Lett.*, **15**, No.17, 1996, 1481-3.
- 286 Benderly D, Siegmann A, Narkis M, *J. Mat. Sci. Lett.*, **15**, No.15, 1996, 1349-52.
- 287 Greso A J, Phillips P J, *Polymer*, **37**, No.14, 1996, 3165-70.
- 288 Rabello M S, White J R, *Polym. Composites*, **17**, No.5, 1996, 691-704.
- 289 Eggers H, Schummer P, *Rubb. Chem. Technol.*, **69**, No.2, 1996, 253-65.
- 290 Pukanszky B, Maurer F H J, Boode J W, *Polym. Engng. Sci.*, **35**, No.24, 1995, 1962-71.
- 291 Zaini M J, Fuad M Y A, Ismail Z, Mansor M S, Mustafah J, *Polym. Int.*, **40**, No.1, 1996, 51-5.
- 292 Stricker F, Muelhaupt R, *High Perform. Polym.*, **8**, No.1, 1996, 97-108.
- 293 Le Bras M, Bourbigot S, *Fire & Mat.*, **20**, No.1, 1996, 39-49.
- 294 Johnson K C, Antec '96. Volume III. Conference proceedings, Indianapolis, 5th-10th May 1996, 3545-9.
- 295 Montsinger L V, Antec '96. Volume II. Conference proceedings, Indianapolis, 5th-10th May 1996, 2546-9.
- 296 Cheung T, Tjong S C, Li R K Y, Antec '96. Volume II. Conference proceedings, Indianapolis, 5th-10th May 1996, 2256-9.
- 297 Tiganis B E, Shanks R A, Long Y, Antec '96. Volume II. Conference proceedings, Indianapolis, 5th-10th May 1996, 1744-9.
- 298 Stockblower D, Antec '96. Volume II. Conference proceedings, Indianapolis, 5th-10th May 1996, 1690-4.
- 299 Ishibashi J, Kobayashi A, Yoshikawa T, Shinozaki K, Antec '96. Vol. I. Conference Proceedings, Indianapolis, 5th-10th May 1996, 386-90.
- 300 Hojabr S, Boock J R B, Antec 95. Volume III. Conference proceedings, Boston, Ma., 7th-11th May 1995, 3620-7.
- 301 Curtis B J, Malloy R, Jones J, Antec 95. Volume III. Conference proceedings, Boston, Ma., 7th-11th May 1995, 3594-8.
- 302 Averous L, Quantin J C, Lafon D, Crespy A, *Int. J. Polym. Analysis and Characterization*, **1**, No.4, 1995, 339-47.
- 303 Hattori K, Morford S, Delany D T, *J. Vinyl and Additive Technol.*, **1**, No.3, 1995, 170-3.
- 304 Driscoll S B, Nanavaty P, Stockbower D W, Polymer Additives for Injection Moulding and Extrusion Applications. Retec proceedings, White Haven, Pa., 18th-19th Oct.1995, p.161-85.
- 305 Kikkawa K, *Polym. Degradat. Stabil.*, **49**, No.1, 1995, 135-43.
- 306 Guerra-Echevarria G, Eguiazabal J I, Nazabal J, *Polym. Degradat. Stabil.*, **53**, No.1, 1996, 1-8.
- 307 Zhao W, Hasegawa S, Fujita J, Yoshii F, Sasaki T, Makuuchi K, Sun J, Nishimoto S, *Polym. Degradat. Stabil.*, **53**, No.2, 1996, 199-206.
- 308 Wampler W A, Rajeshwar K, Pethe R G, Hyer R C, Sharma S C, *J. Mat. Res.*, **10**, No.7, 1995, 1811-22.
- 309 Maeda S, Armes S P, *J. Mat. Chem.*, **4**, No.6, 1994, 935-42.
- 310 Faguy P W, Ma W, Lowe J A, Pan W P, Brown T, *J. Mat. Chem.*, **4**, No.5, 1994, 771-2.
- 311 Meddad A, Fisa B, *Macromol. Symp.*, **108**, 1996, 173-82.
- 312 Akelah A, Moet A, *J. Mat. Sci.*, **31**, No.13, 1996, 3589-96.
- 313 Kobayashi M, Takahashi T, Takimoto J, Koyama K, *Polymer*, **36**, No.20, 1995, 3927-33.
- 314 Mitsui S, Kihara H, Yoshimi S, Okamoto Y, *Polym. Engng. Sci.*, **36**, No.17, 1996, 2241-6.
- 315 Qi Wang, Jizhuang Cao, Guangjin Li, Xi Xu, *Polym. Int.*, **41**, No. 3, 1996, 245-9.
- 316 Ogadhoh S O, Papatthanasou T D, *Composites Part A: Applied Science and Manufacturing*, **27A**, No.1, 1996, 57-63.
- 317 Kim K J, White J L, *J. of Non-Newtonian Fluid Mechanics*, **66**, Nos.2/3, 1996, 257-70.
- 318 Meddad A, Fisa B, *J. Mater. Sci.*, **32**, 1997, 1177-85.

- 319 Friedrich C, Scheuchenpflug W, Neuhaeusler S, Roesch J, *J. Appl. Polym. Sci.*, **57**, No.4, 1995, 499-508.
- 320 Godard P, Bomal Y, Biebuyck J J, *J. Mat. Sci.*, **28**, No.24, 1993, 6605-10.
- 321 del Rio C, Acosta J L, *Polymer*, **35**, No.17, 1994, 3752-7.
- 322 Alberola N, Bergeret A, S, *Polym. Composites*, **15**, No.6, 1994, 442-52.
- 323 Li Shucai, Peng Weijang, Lu Xiuping, *Int. J. Polym. Mat.*, **29**, Nos.1-2, 1995, 37-42.
- 324 Baranovskii V M, Bondarenko V V, Zadorina E N, Cherenkov A V, Zelenev Y V, *Int. Polym. Sci. Technol.*, **23**, No.6, 1996, T/87-9.
- 325 Fengyuan Yan, Wenhua Wang, Qunji Xue, Long Wei, *J. Appl. Polym. Sci.*, **61**, No.7, 1996, 1231-6.
- 326 Fengyuan Yan, Qunji Xue, Shengrong Yang, *J. Appl. Polym. Sci.*, **61**, No.7, 1996, 1223-9.
- 327 Zhang C-Z, Liu W-M, Xue Q-J, Shen W-C, *J. Appl. Polym. Sci.*, **66**, 1997, 85-93.
- 328 Tabor R L, Polyurethanes '94. Conference proceedings, Boston, Ma., 9th-12th Oct.1994, 288-94.
- 329 Modesti M, Simioni F, Albertin P, *Cell. Polym.*, **13**, No.2, 1994, 113-24.
- 330 Vratsanos L A, Farris R J, *Polym. Engng. Sci.*, **33**, No.22, 1993, 1458-65.
- 331 Dolui S K, *J. Appl. Polym. Sci.*, **53**, No.4, 1994, 463-5.
- 332 Torro-Palau A, Fernandez-Garcia J C, Orgiles-Barcelo A C, Pastor-Blas M M, Martin-Martinez J M, *Int. J. Adhesion Adhesives*, **17**, 1997, 111-9.
- 333 Sergeeva L M, Slinchenko E A, Brovko A A, Fainleib A M, Nedashkovskaya N S, *Polym. Sci., Ser. B*, **38**, Nos.5/6, 1996, 225-30.
- 334 Smock D, *Plast. World*, **54**, No.12, 1996, 35-9.
- 335 Porter J R, Groseth C K, Little D W, Polyurethanes '95. Conference Proceedings, Chicago, Il., 26th-29th Sept.1995, 532-7.
- 336 Sendjarevic A, Sendjarevic V, Wang X, Haidar A, Dutta U, Klempner D, Frisch K C, Polyurethanes '95. Conference Proceedings, Chicago, Il., 26th-29th Sept.1995, 418-26.
- 337 Okoroafor M O, Wang A, Bhattacharjee D, Cikut L, Haworth G J, Polyurethanes '95. Conference Proceedings, Chicago, Il., 26th-29th Sept.1995, 303-9.
- 338 Oien H T, Polyurethanes '95. Conference Proceedings, Chicago, Il., 26th-29th Sept.1995, 137-41.
- 339 Chen L, Liu K, Yang C Z, *Polym. Bull.*, **37**, No.3, 1996, 377-83.
- 340 Bauman B D, Plastics Finishing: Responding to Tomorrow's Global Requirements. Retec proceedings, Detroit, Mi, 21st-22nd March 1995, 62-73.
- 341 Eisenbach C D, Ribbe A, Goeldel A, *Kaut. u. Gummi Kunst.*, **49**, No.6, 1996, 406-10.
- 342 Bos M, Van Dam G W, Jongsma T, Bruin P, Pennings A J, *Composite Interfaces*, **3**, No.2, 1995, 169-76.
- 343 Wang K J, Sue H J, Antec '95. Vol. II. Conference Proceedings, Boston, Ma., 7th-11th May 1995, 1758-64.
- 344 Urabe N, Takatsugi H, Ito M, Toko H, Fukui M, *Int. Polym. Sci. Technol.*, **22**, No.5, 1995, T/68-72.
- 345 Sombatsompop N, Sims G L A, *Cell. Polym.*, **15**, No.5, 1996, 317-34.
- 346 Sims G L A, Sombatsompop N, *Cell. Polym.*, **15**, No.2, 1996, 90-104.
- 347 Brovko O O, Sergeeva L M, Slinchenko O A, Fainleib O M, *Polym. Int.*, **40**, No.4, 1996, 299-305.
- 348 Caillaud J L, Deguillaume S, Vincent M, Giannotta J C, Widmaier J M, *Polym. Int.*, **40**, No.1, 1996, 1-7.
- 349 Sergeeva L M, Skiba S I, Karabanova L V, *Polym. Int.*, **39**, No.4, April 1996, 317-25.
- 350 Martin-Martinez J M, Macia-Agullo T G, Fernandez-Garcia J C, Orgiles-Barcelo A C, Torro-Palau A, *Macromol. Symp.*, **108**, 1996, 269-78.
- 351 Kovacevic V, Lucic S, Hace D, Cerovecki Z, *J. Adhesion Sci. Technol.*, **10**, No.12, 1996, 1273-85.
- 352 Kovacevic V, Lucic S, Hace D, Glasnovic A, *Polym. Engng. Sci.*, **36**, No.8, 1996, 1134-9.
- 353 Gerard J F, Chabert B, *Macromol. Symp.*, **108**, 1996, 137-46.
- 354 Landry C J T, Coltrain B K, *J. Macromol. Sci. A*, **31**, No.12, 1994, 1965-73.
- 355 Kovacevic V, Lucic S, Hace D, Glasnovic A, Smit I, Bravar M, *J. Adhesion*, **47**, No.1-3, 1994, 201-15.
- 356 Landry C J T, Coltrain B K, Landry M R, Fitzgerald J J, Long V K, *Macromolecules*, **26**, No.14, 5th July 1993, 3702-12.
- 357 Suzuki F, Nakane K, Piao J-S, *J. Mat. Sci.*, **31**, No.5, 1996, 1335-40.
- 358 Mukha B I, Kolupaev B S, Mukha Y B, *Int. Polym. Sci. Technol.*, **23**, No.6, 1996, T/57-9.
- 359 Sanchez-Solis A, Padilla A, *Polym. Bull.*, **36**, No.6, 1996, 753-58.
- 360 Wiebking H E, *J. Vinyl and Additive Technol.*, **2**, No.3, 1996, 187-9.
- 361 Malanda L M, Park C B, Balatinez J J, Antec '96. Volume II. Conference proceedings, Indianapolis, 5th-10th May 1996, p.1900-7.
- 362 Karpukhin A, Ledeneva I N, Aleksandrov V I, *Int. Polym. Sci. Technol.*, **23**, No.4, 1996, T/29-31.

- 363 Ulkem I, Bataille P, Schreiber H P, *J. Macromol. Sci. A*, **31**, No.3, 1994, 291-303.
- 364 Molesky F, Schultz R, Midgett S, Green D, *J. Vinyl Additive Technol.*, **1**, No.3, 1995, 159-61.
- 365 Zolotnitsky M, Steinmetz J R, *J. Vinyl and Additive Technol.*, **1**, No.2, 1995, 109-13.
- 366 Bataille P, Schreiber H P, Mahlous M, Antec '93. Conference Proceedings, New Orleans, La., 9th-13th May 1993, Vol. II, 1757-9.
- 367 Ferm D J, Shen K K, Antec '94. Conference Proceedings, San Francisco, Ca., 1st-5th May 1994, Vol.III, 3522-6.
- 368 Chudinova V V, Guzeev V V, Mozzhukhin V B, Pomerantseva E G, Nozrina F D, Zhil'tsov V V, Zubov V P, *Int. Polym. Sci. Technol.*, **21**, No.10, 1994, T/102-4.
- 369 Liptak P, *Int. Polym. Sci. Technol.*, **21**, No.8, 1994, T/50-3.
- 370 Bataille P, Mahlous M, Schreiber H P, *Polym. Engng. Sci.*, **34**, No.12, 1994, 981-5.
- 371 Liptak P, Zelenak P, *Int. Polym. Sci. Technol.*, **20**, No.9, 1993, T/57-9.
- 372 Baggaley R G, Hornsby P R, Yahya R, Cussak P A, Monk A W, *Fire Mater.*, **21**, 1997, 179-85.
- 373 Abdel-Aziz M M, Gwaily S E, *Polym. Degradat. Stabil.*, **55**, 1997, 269-74.
- 374 Cochet P, Barnuel P, Barriquand L, Grobert J, Bomal Y, Prat E, IRC '93/144th Meeting, Fall 1993. Conference Proceedings, Orlando, Fl., 26th-29th Oct.1993, Paper 162.
- 375 Monthey S, Duddleston B, Podobnik J, *Rubb. World*, **210**, No.3, 1994, 17-9.
- 376 Pehlergard P, *Rubb. S. Africa*, **10**, No.5, 1995, 8-12.
- 377 Anantharaman M R, Kurian P, Banerjee B, Mohamed E M, George M, *Kaut. u. Gummi Kunst.*, **49**, No.6, 1996, 424-6.
- 378 Maas S, Gronski W, *Kaut. u. Gummi Kunst.*, **47**, No.6, 1994, 409-15.
- 379 Byers J T, Meeting of the Rubber Division, ACS, Cleveland, October 17-20, 1995, paper B.
- 380 Evans L R, Meeting of the Rubber Division, ACS, Montreal, May 5-8, 1996, paper D.
- 381 Bomo F, Meeting of the Rubber Division, ACS, Montreal, May 5-8, 1996, paper E.
- 382 Estrin R I, Pesin O Y, *Int. Polym. Sci. Technol.*, **22**, No.1, 1995, T/12-6.
- 383 Karsek L, *Int. Polym. Sci. Technol.*, **21**, No.10, 1994, T/35-40.
- 384 Yoshida T, *Int. Polym. Sci. Technol.*, **20**, No.6, 1993, T/29-39.
- 385 Dick J S, Pawlowski H A, *J. Elastomers Plast.*, **27**, No.1, 1995, 11-38.
- 386 Leblanc J L, *Prog. Rubb. Plast. Technol.*, **10**, No.2, 1994, 112-29.
- 387 Li Y, Wang M J, Zhang T, Zhang F, Fu X, *Rubb. Chem. Technol.*, **67**, No.4, 1994, 693-9.
- 388 Furukawa J, Yamada E, *J. Appl. Polym. Sci.*, **52**, No.11, 1994, 1587-93.
- 389 Babich V F, Lipatov Yu S, Todosijchuk T T, *J. Adhesion*, **55**, Nos.3-4, 1996, 317-27.
- 390 Saad A L G, Younan A F, *Polym. Degradat. Stabil.*, **50**, No.2, 1995, 133-40.
- 391 Heuert U, Knorgen M, Menge H, Scheler G, Schneider H, *Polym.Bull.*, **37**, No.4, Oct.1996, 489-96.
- 392 Bandyopadhyay S, De P P, Tripathy D K, De S K, *Kaut. u. Gummi Kunst.*, **49**, No.2, 1996, 115-9.
- 393 de Candia F, Carotenuto M, Gargani L, Guadagno L, Lauretti E, Renzulli A, *Kaut. u. Gummi Kunst.*, **49**, No.2, 1996, 99-101.
- 394 Nakajima N, *Int. Polym. Processing*, **11**, No.1, 1996, 3-13.
- 395 Gownder M, Letton A, Hogan H, Antec '95. Vol. II. Conference Proceedings, Boston, Ma., 7th-11th May 1995, 1983-6.
- 396 Donnet J B, Wang T K, *Prog. Rubb. Plast. Technol.*, **11**, No.4, 1995, 261-7.
- 397 Lin C R, Lee Y D, *Macromol. Theory & Simulations*, **5**, No.6, 1996, 1075-104.
- 398 Unnikrishnan G, Thomas S, Varghese S, *Polymer*, **37**, No.13, 1996, 2687-93.
- 399 Kiselev V Y, Vnukova V G, *Int. Polym. Sci. Technol.*, **23**, No.5, 1996, T/88-92.
- 400 Nunes R C R, Mano E B, *Polym. Composites*, **16**, No.5, 1995, 421-3.
- 401 Bandyopadhyay S, De P P, Tripathy D K, De S K, *J. Appl. Polym. Sci.*, **58**, No.4, 1995, 719-27.
- 402 Bandyopadhyay S, De P P, Tripathy D K, De S K, *J. Appl. Polym. Sci.*, **61**, No.10, 1996, 1813-20.
- 403 Bandyopadhyay S, De P P, Tripathy D K, De S K, *Polymer*, **37**, No.2, 1996, 353-7.
- 404 Mandal U K, Tripathy D K, De S K, *Plast. Rubb. Comp. Process. Appln.*, **24**, No.1, 1995, 19-25.
- 405 de Sena Affonso J E, Nunes R C R, *Polym. Bull.*, **34**, No.5/6, 1995, 669-75.
- 406 Cheng J, Bigio D I, Briber R M, Antec '96. Vol. I. Conference Proceedings, Indianapolis, 5th-10th May 1996, 365-9.
- 407 Addad J P C, Frebourg P, *Polymer*, **37**, No.19, 1996, 4235-42.
- 408 Garbow J R, Asrar J, Hardiman C J, *Chem. of Mat.*, **5**, No.6, 1993, 869-75.
- 409 Nasr G M, Badawy M M, Gwaily S E, Shash N M, Hassan H H, *Polym. Degradat. Stabil.*, **48**, No.2, 1995, 237-41.
- 410 Ali M H, Abo-Hashem A, *Plast. Rubb. Comp. Process. Appln.*, **24**, No.1, 1995, 47-51.
- 411 Delor F, Lacoste J, Lemaire J, Barrois-Oudin N, Cardinet C, *Polym. Degradat. Stabil.*, **53**, No.3,

- 1996, 361-9.
- 412 Lawandy S N, Botros S H, Darwish N A, Mounir A, *Polym. Plast. Technol. Engng.*, **34**, No.6, 1995, 861-74.
- 413 El-Shall M S, Slack W, *Macromolecules*, **28**, No.24, 1995, 8456-8.
- 414 Khromov M K, Niazashvili G A, Sakhnovskii N L, Koroleva T A, *Int. Polym. Sci. Technol.*, **23**, No.5, 1996, T/82-4.
- 415 Khromov M K, Niazashvili G A, *Int. Polym. Sci. Technol.*, **23**, No.5, 1996, T/24-6.
- 416 Kida N, Ito M, Yatsuyanagi F, Kaido H, *J. Appl. Polym. Sci.*, **61**, No.8, 1996, 1345-50.
- 417 Basfar A A, Silverman J, *Polym. Degradat. Stabil.*, **46**, No.1, 1994, 1-8.
- 418 Furtado C R G, Nunes R C R, de Siqueira Filho A S, *Polym. Bull.*, **34**, No.5/6, 1995, 627-33.
- 419 Fuelber C, Bluemich B, Unseld K, Herrmann V, *Kaut. u. Gummi Kunst.*, **48**, No.4, 1995, 254-9.
- 420 Wolff S, Wang M J, Tan E H, *Kaut. u. Gummi Kunst.*, **47**, No.12, 1994, 873-84.
- 421 Zaborski M, Slusarski L, Donnet J B, Papirer E, *Kaut. u. Gummi Kunst.*, **47**, No.10, 1994, 730-8.
- 422 Donnet J B, Wang W, Vidal A, Wang M J, *Kaut. u. Gummi Kunst.*, **46**, No.11, Nov.1993, 866-71.
- 423 Dutta N K, Choudhury N R, Haidar B, Vidal A, Donnet J B, Delmotte L, Chezeau J M, *Polymer*, **35**, No.20, 1994, 4293-9.
- 424 Helaly F M, El-Sawy S M, Abd El-Ghaffar M A, *J. Elastomers Plast.*, **26**, No.4, 1994, 335-46.
- 425 Wolff S, Wang M-J, Tan E-H, *Rubb. Chem. Technol.*, **66**, No.2, 1993, 163-77.
- 426 Clarke J, Freakley P K, *Rubb. Chem. Technol.*, **67**, No.4, 1994, 700-15.
- 427 Abdel-Aziz M M, Youssef H A, El Miligy A A, Yoshii F, Makuuchi K, *Polym. & Polym. Composites*, **4**, No.4, 1996, 259-68.
- 428 Karasek L, Meissner B, Asai S, Sumita M, *Polym. J. (Jap.)*, **28**, No.2, 1996, 121-6.
- 429 Sendjarevic A, Sendjarevic V, Wang X, Haidar A, Dutta U, Klemperer D, Frisch K C, Polyurethanes '95. Conference Proceedings, Chicago, IL, 26th-29th Sept.1995, 418-26.
- 430 Gorl U, Rausch R, Esch H, Kuhlmann R, *Int. Polym. Sci. Technol.*, **23**, No.7, 1996, T/81-7.
- 431 Nasr G M, Badawy M M, Gwaily S E, Attia G, *Polym. Int.*, **38**, No.3, 1995, 249-55.
- 432 Nasr G M, *Polym. Test.*, **15**, No.6, 1996, 585-91.
- 433 Nasr G M, Badawy M M, *Polym. Test.*, **15**, No.5, 1996, 477-84.
- 434 Kovacevic V, Lucic S, Hace D, Glasnovic A, *Polym. Engng. Sci.*, **36**, No.8, 1996, 1134-9.
- 435 Cha Y J, Choe S, *J. Appl. Polym. Sci.*, **58**, No.1, 1995, 147-57.
- 436 Chen C-H, Cheng C-H, *J. Composite Mat.*, **30**, No.1, 1996, 69-83.
- 437 Sharaf M A, Kloczkowski A, Mark J E, *Rubb. Chem. Technol.*, **68**, No.4, 1995, 601-8.
- 438 Visser S A, Hewitt C E, Binga T D, *J. Polym. Sci., Polym. Phys.*, **34**, No.9, 1996, 1679-89.
- 439 Yuan Q W, Kloczkowski A, Mark J E, Sharaf M A, *J. Polym. Sci., Polym. Phys.*, **34**, No.9, 1996, 1647-57.
- 440 Burnside S D, Giannelis E P, *Chem. of Mat.*, **7**, No.9, 1995, 1597-600.
- 441 Leezenberg P B, Frank C W, *Chem. of Mat.*, **7**, No.10, 1995, 1784-92.
- 442 Wen J, Mark J E, *J. Appl. Polym. Sci.*, **58**, No.7, 1995, 1135-45.
- 443 Soares R F, Leite C A P, Botter W, Galembek F, *J. Appl. Polym. Sci.*, **60**, No.11, 1996, 2001-6.
- 444 Zumbrum M A, *J. Adhesion*, **46**, Nos.1-4, 1994, 181--96.
- 445 Kaewpanya R, Meinecke E A, 149th ACS Rubber Division Meeting, Spring 1996. Conference preprints, Montreal, 5th-8th May 1996, paper 32.
- 446 Wang S Q, Inn Y W, *Polym. Int.*, **37**, No.3, 1995, 153-5.
- 447 Yang A C M, *Polymer*, **35**, No.15, 1994, 3206-11.
- 448 Ebengou R H, Cohen-Addad J P, *Polymer*, **35**, No.14, 1994, 2962-9.
- 449 Cochrane H, Lin C S, *Rubb. Chem. Technol.*, **66**, No.1, 1993, 48-60.
- 450 Okel T A, Waddell W H, *Rubb. Chem. Technol.*, **68**, No.1, 1995, 59-76.
- 451 Visser S A, *J. Appl. Polym. Sci.*, **63**, 1997, 1805-20.
- 452 Visser S A, *J. Appl. Polym. Sci.*, **64**, 1997, 1499-1509.
- 453 Kominar V, Narkis M, Siegmman A, Breuer O, *Sci. & Engng. Composite Materials*, **3**, No.1, 1994, 61-6.
- 454 Marcovich N E, Reboredo M M, Aranguren M L, *J. Appl. Polym. Sci.*, **61**, No.1, 1996, 119-24.
- 455 Kenny J M, Opalicki M, *Composites Part A: Applied Science and Manufacturing*, **27A**, No.3, 1996, 229-40.
- 456 Kenny J M, Opalicki M, Molina G, Antec '95. Vol. II. Conference Proceedings, Boston, Ma., 7th-11th May 1995, 2782-9.
- 457 Gregorio R, Cestari M, Bernardino F E, *J. Mat. Sci.*, **31**, No.11, 1996, 2925-30.
- 458 Yano S, Okubo N, Takahashi K, *Macromol. Symp.*, **108**, 1996, 279-89.

- 459 Zhang M, Jia W, Chen X, *J. Appl. Polym. Sci.*, **62**, No.5, 1996, 743-7.
- 460 Abramova N A, Diikova E U, Lyakhovskii Yu Z, *Polym. Sci.*, **36**, No.9, 1994, 1308-9.